POLYMER-SUPPORTED CATALYSTS

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ABSTRACT

POLYMER-SUPPORTED CATALYSTS

By

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Homogeneous catalysts have been limited from developing into large-scale commercial chemical industry tools by several factors. Two of these factors have been their difficult removal from solution and their tendency to form aggregates of low solubility. It was proposed that the attachment of ligands present in a homogeneous catalyst to an inert polymeric support might provide a means of relieving both of these problems. If the supported ligand could be used to form analogs of a homogeneous catalyst on the polymer, then the filtration of the polymer would make removal of the catalyst from solution simple. If the supporting polymer had a fairly rigid matrix, then metal-metal bond formation or other types of aggregation might be prevented.

Four questions summarize the primary interests of this research:

1. Could a working analog of a homogeneous catalyst be supported within a polymer matrix?

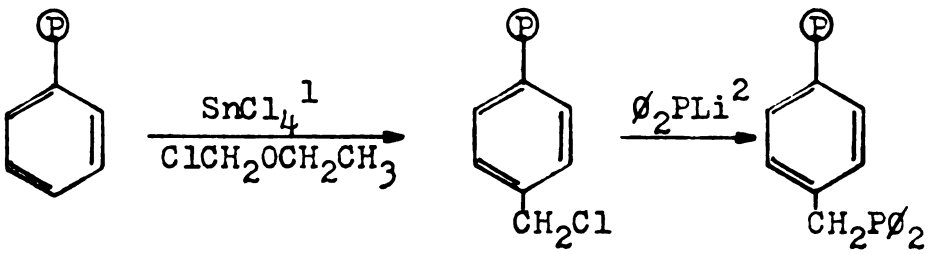
2. Would the support used produce predictable alterations in the selectivity of a supported catalyst?

3. Could new, more active catalysts be synthesized by supporting their precursors on a rigid polymer matrix and then activating them?

4. Could chelation by the polymer-supported ligands be controlled and/or prevented?

Styrene-divinylbenzene copolymer "beads" were chosen as the polymer support. Initial investigations used phosphination of this support via Scheme 1 to create a polymer-supported ligand suitable for the complexation of Wilkinson's Catalyst,[3] $RhCl(P\phi_3)_3$, to the polymer. This complexation was

Scheme 1



successfully achieved by the eqilibration of phosphinated copolymer beads with Wilkinson's Catalyst, giving an active catalytic polymer which could be reused many times without serious loss of activity.[4,5]

Supported Wilkinson's Catalyst catalyzed the hydrogenation of substrates of large size or high polarity (e.g., Δ^2-cholestene or allyl alcohol respectively) at a much slower rate than non-supported Wilkinson's Catalyst. This was attributed to the effects of the polymer support, which was nonpolar and which displayed size selectivity due to its pore-containing structure. The pore structure restricted the diffusion of substrates into the interior of the catalyst beads, where the majority of the catalyst was .

The supported titanocene system developed by C. Gibbons[6] was used to reduce a variety of hydrocarbon substrates, but oxygen-containing compounds were found to be

inactive to hydrogenation with that catalyst.

The supported titanocene system was investigated to determine if titanocene, which is normally a polymeric aggregate in its homogeneous hydrogenation form, was activated by attachment to a polymer support. Comparisons of the catalytic reduction rate per mmol of titanocene present indicated that at least a 25-fold activation had occurred in supporting the catalyst. This was attributed to the ability of the rigid supporting matrix used (20% divinylbenzene) to keep metal atoms apart, preventing aggregation and the accompanying loss in activity.

The failure of supported titanocene to fix nitrogen to ammonia using either van Tamelin[7] or Vol'pin-Shur[8] conditions would also support the belief that metal association was uncommon in the supported system, because dimeric titanocene is necessary for nitrogen fixation to ammonia.[9] Vol'pin and Shur reported that monomeric titanocene was involved in the formation of aniline by titanocene when phenyllithium was reagent used to reduce Ti(IV) to Ti(II) .[8] When a sample of supported titanocene was run through Vol'pin-Shur nitrogen fixation procedures with some homogeneous titanocene present, an unusually large amount of aniline was formed. This seemed to verify the concept that supported titanocene was largely monomeric.

Chelation studies used phosphinated copolymer equilibrated with $[RhCl(COE)_2]_2$ (COE = cyclooctene) or with $RhCl(CO)(P\phi_3)_2$ followed by analysis for free ligand. The

studies tended to confirm the presence of chelation in 2% divinylbenzene copolymer systems while 20% divinylbenzene copolymer supports restricted chelation due to the polymer matrix's rigidity.[10]

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POLYMER-SUPPORTED CATALYSTS

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A THESIS

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To the glory of God

Not because He needs it,

but because the God

Who wants everyone to know Him personally (John 17:3)

is worthy of all glory.

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My sincere thanks and praise go to my preceptor, Dr. Robert H. Grubbs. His thoughts, suggestions, encouragement, and most of all his patience have been prime movers in this work.

The contributions of many of the faculty members at Michigan State, who have been of the utmost importance in the development of my philosophy of science and its practical application, are also gratefully acknowledged.

The character of "the Grubbs Group" or rather the characters in the Grubbs Group, have provided me with unique memories. From our early, pre-grant days of chemical and equipment "grubbing" to our present state of moderate affluence, they have remained as bizarre as ever.

Many other grad students, undergrads, stockroom men, and especially the secretaries (who run this whole place anyway) were sources of much appreciated aid. I'd express my thanks more individually, but there is a paper shortage.

Incredibly great thanks go to those many joint heirs in Christ who have directly helped in the typing of this thesis or who would have if I had needed them. Agape strikes again.

A special smile goes to the lady in white.

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INTRODUCTION

Homogeneous catalysis by transition metal complexes has been a recognized process since the early 1950's,[1] and has recently experienced growing application. Heinemann has estimated that a three-fold increase in the use of homogeneous catalysts in industry has occured in the last ten years.[2] Homogeneous catalysts have several advantages over heterogeneous ones:

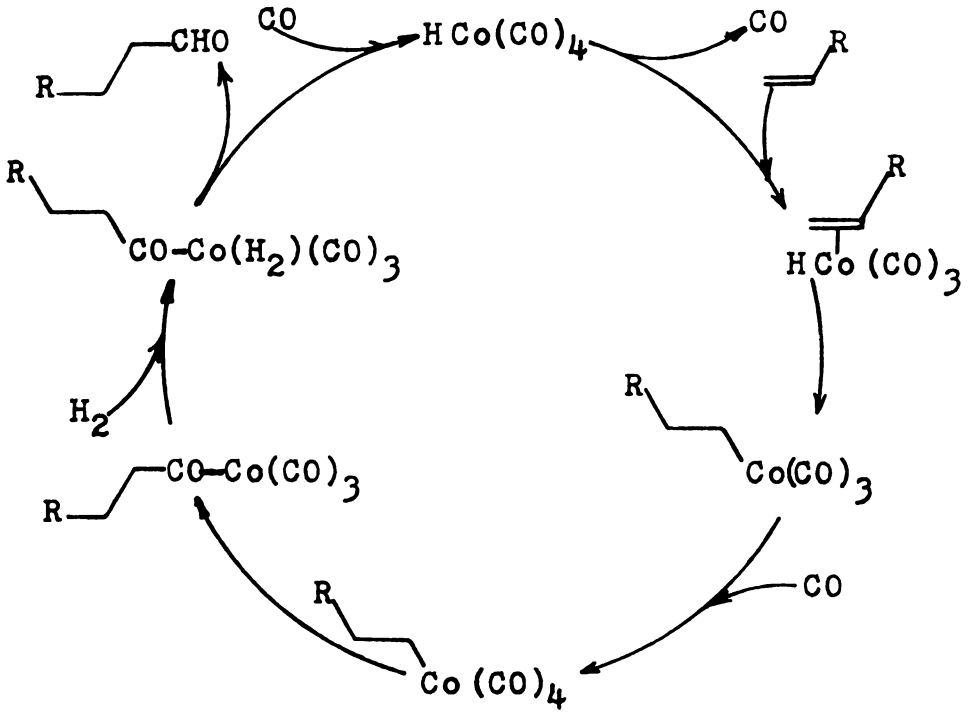
1. simpler mechanistic investigation.
2. greater selectivity.
3. better mass and heat transfer characteristics.

There is one great disadvantage of homogeneous catalysts relative to heterogeneous catalysts, however, as pointed out by Cotton and Wilkinson:[3]

> For separation of the products from reactants and catalyst, heterogeneous systems have great practical advantage over homogeneous ones,...

This problem of the separation of a homogeneous catalyst from the solution in which it has served as a catalyst has been the major hindrance to the greater employment of homogeneous catalysts in commercial processes. Methods which remove the catalyst almost invariably destroy its activity, requiring a separate regeneration step. An

example of this is the Oxo Process, which uses the homogeneous catalyst $HCo(CO)_4$. The Oxo Process is the most widely used homogeneous catalytic process in industry today.[4] This process converts alkenes to aldehydes in high yields as shown in Scheme 1. To remove the catalyst from the process stream, however, it must be precipitated by treatment with alkali, then regenerated by acidification and extraction with an organic solvent.[5] This is an unusually simple process, for most homogeneous catalysts would not survive such harsh treatment, and most could not be so readily regenerated after removal from solution.



The Oxo Process

Scheme 1

New research in the sciences has often been the result of the observation of natural processes. The research reported in this thesis is an example of new work stimulated by the consideration of natural catalytic systems, the enzymes. Active sites on enzymes are protected and isolated from the surrounding medium by the general hydrophobic nature of the supporting protein.[6] Substrates are able to diffuse into the active sites, however, and then diffuse out again after reaction. As is well known, the activity of enzymes as catalysts is very high -- the supporting protein does not seem to hinder the ability of the active site to operate, and may even enhance it to some extent by keeping deactivating substances away.

Support of a homogeneous catalyst within a synthetic matrix might duplicate some of the advantages of an enzyme. The supported catalyst might display its former activity, and yet be modified by the nature of the supporting matrix in such a way that a change in its selectivity would be observed. A hydrophobic matrix, for example, might allow hydrocarbon substrates to reach the catalyst but hinder polar substrates. If the matrix was a material which could be easily filtered, then removal of the supported catalyst would be a very simple process which would cause no deactivation of the catalyst.

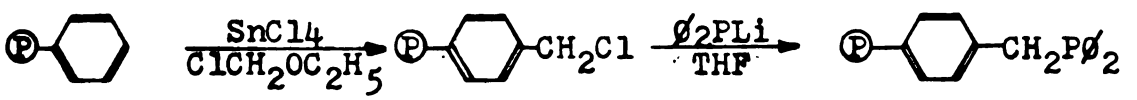
The idea of a supported catalyst is not new, of course, but the concept of supporting a homogeneous

system primarily within the support is quite new. At the time of this work's early stages, a few reports of homogeneous catalysts supported primarily within a matrix were published. Haag and Whitehurst at Mobil Oil Corporation attached $[RhCl(CO)_2]_2$ to a diphenylphosphine-substituted styrene-divinylbenzene copolymer and catalyzed the hydrogenation of 1-hexene with it.[7a] The same workers used a sulfonated ion exchange resin, Amberlyst 15, to support $[Pd(NH_3)_4]^{++}$ in an ionic and a reduced form. The resins were used to reduce alkenes and alkynes in catalytic hydrogenations.[7b] Lazcano and Germain used Amberlyst A27, a strongly basic ion exchange resin, to support a low concentration of $[PdCl_4]^{--}$. This was used to reduce cyclohexene, styrene, and nitrobenzene. Both ketones and aromatic systems were unaffected.[8] They also found that their catalyst could be reused at least eight times without the formation of any metallic palladium.

For the research reported here, it was decided to use styrene-divinylbenzene copolymer beads as the supporting matrix for the preparation of enzyme-like catalysts. Beads ranging in size from 30 to 400 mesh and with a divinylbenzene content of two or twenty percent were used. The divinylbenzene content is a good approximation of the amount of cross-linking in the copolymer. The cross-linking gives the copolymer a pore-containing structure and thereby affects the ability of some

substrates to diffuse into the inner area of the beads.

Since many useful homogeneous catalysts have triphenylphosphine ligands, it was decided to use a similar ligand to functionalize the polymer. The route proposed for the attachment of this ligand is outlined in Scheme 2. The copolymer was first chloromethylated, using the method of Pepper, Paisley, and Young,[9] and then treated with lithiodiphenylphosphide, prepared by the "direct method" of Tamborski, et al.[10]



Scheme 2

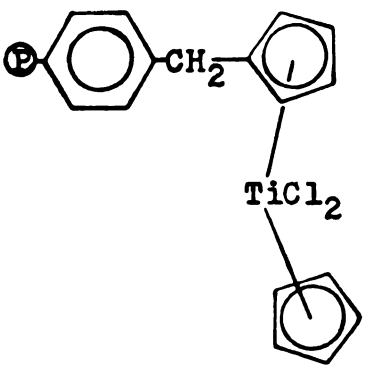
Once phosphine ligands were attached to the copolymer beads, it was felt that the ligands could be used to displace those of a labile metal complex in solution with the polymer, giving a new metal complex attached to the beads. Wilkinson's Catalyst,[11] $RhCl(P\emptyset_3)_3$, was chosen for the first attempts because it is difficult to remove from solutions without deactivating it. Furthermore, the mechanisms of its reactions have been studied in great detail. Not only would the successful support of such a catalyst open the possibility of reusing it many times, but it was expected that if most of the supported catalyst was within the interior of the polymer beads,[12] then its selectivity might also be improved. This effect might be of two types,

size and polarity. Because of the pore structure of the polymer beads, a catalyst supported within the interior of the beads might be inaccessable to large substrates, such as steroids, while others of somewhat smaller size might display differential rates of hydrogenation based on their bulk. Because the copolymer is also nonpolar, substrates which contain polar substituents, such as allyl alcohol, might be reduced more slowly by the supported catalyst than by the homogeneous form. It has already been observed that a similar polymer excludes water quite well because of its nonpolar nature.[13]

A possibility which develops, once one has established the validity of the concept of a matrix supported catalyst, is the creation of new, highly activated catalysts. This is especially true if matrix binding sites are distributed in a controllable manner. Transition metal complexes must have a site of coordinative unsaturation in order to be reactive.[14] The formation of such a site of unsaturation in many homogeneous complex systems leads to dimerization or polymerization of the active species to produce insoluble precipitates. Such aggregates are much less reactive than the original monomeric species might have been. By attachment of the precursor complex to a fairly rigid matrix, it should be possible to form an active catalyst without aggregation because of the mobility restrictions of the matrix-supported ligand to which the metal is bound. Substrates in solution might then diffuse in to

react with the metal and then diffuse out again afterwards, modeling the behavior of an enzyme system quite closely.

An example of a potentially useful complex which tends to polymerize in solution is titanocene, $TiCp_2$ (Cp = cyclopentadienide anion). This is formed when the corresponding dichloride is treated with a reducing agent, such as sodium naphthalide, a Grignard reagent, or an organolithium reagent. C. Gibbons has successfully coordinated an analog of $TiCp_2Cl_2$ to the styrene-divinylbenzene copolymer beads using a benzyl linkage to give 1 on the polymer.[15] He found that treatment of the polymer-supported catalyst with butyllithium in hexane produces an active hydrogenation catalyst for olefins. In the analagous homogeneous system, Brintzinger has determined that most of the titanocene is present as an insoluble polymeric hydride.[16,17] If the monomeric hydride complex is more active as a hydrogenation catalyst than the polymer hydride, then the supported titanocene may be much more active, provided that the support matrix keeps the active metal centers



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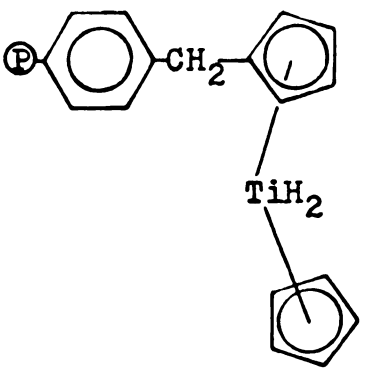

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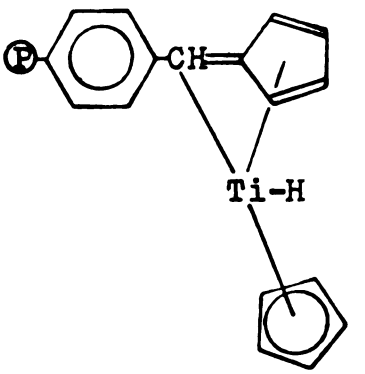
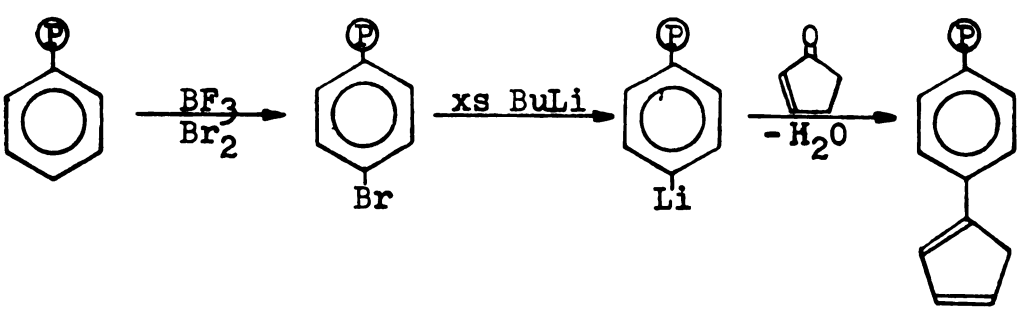


3

apart. The active species on the polymer may be either 2 or 3, both of which are known for the decamethyl analog of titanocene,[17b] a complex in which dimerization is impossible for steric reasons. The formation of 3 should be reversible, leading to 2 in the presence of hydrogen, if the decamethyl analog is a reasonable model compound. It is possible that the formation of 3 might be less reversible than the carbon-hydrogen insertion reaction in the decamethyl complex, so that removal of the benzylic methylene group from a position adjacent to the cyclopentadienyl ring might activate the supported complex more.

One goal of the research reported here was the development of the synthetic route in Scheme 3, as a means of testing the proposal that removal of the benzylic methylene group might activate the supported titanocene more.



Scheme 3

Two other goals related to the use of supported titanocene as a hydrogenation catalyst were the verification of the presence of most of the titanocene within the interior of the polymer and the further investigation of substrates which might be hydrogenated using this

catalyst. To achieve the first goal, samples of whole and ground beads were used as hydrogenation catalysts. If the majority of the catalytic sites lay within the interior of the polymer, the grinding of the beads would be expected to increase the rate of hydrogenation, because the substrates would no longer have to diffuse through the pore structure of the polymer beads to reach the catalyst. Comparison with homogeneous catalyst samples should also determine if there is an activation of the catalyst by supporting it on a rigid polymer matrix. The second goal, further evaluation of the substrates activated for hydrogenation by the supported catalyst, can be easily met by testing the desired substrates. Substrates of interest include dienes, alkynes, unsaturated ketones, and aromatic systems.

Titanocene has also been used as a nitrogen fixation vehicle by several researchers. Dimeric titanocene seems to be required for these fixations,[17b,18,19] so it would seem that if the supported titanocene system prevents dimer formation then no nitrogen should be fixed by the supported system. This may be tested by using the conventional procedures for nitrogen fixation and testing for the formation of ammonia. While both the van Tamelin[18] and Vol'pin-Shur nitrogen fixation systems require dimeric titanocene for ammonia formation, Vol'pin and Shur[19] have reported that aniline is formed in their nitrogen fixation method from a monomeric titanocene species when

phenyllithium is used to reduce titanocene dichloride to titanocene. If a nitrogen fixation is attempted using supported catalyst with some homogeneous titanocene present, then the amount of aniline formed should increase relative to the amount of ammonia formed.

The question of whether or not the polymer matrix is rigid enough to prevent nearby ligands from chelating supported complexes arose during our work. Several researchers have worked on this problem with varied results. Some have found that chelation or other interactions of polymer-supported species occurs only when a high degree of substitution, over 1 mmol per g of beads, or when the substrates used are able to bond to sites over 10 Å apart are present.[20,21,22] Others favor chelation as a major factor even at 1 mmol per g of beads levels of substitution.[23]

A study of supported titanocene's nitrogen fixation behavior, as mentioned above, would give some valuable information on this subject. However, other experiments more specifically designed to answer the question of whether or not chelation is a major factor could be run also. The treatment of phosphinated copolymer beads with solutions of $[RhCl(COE)_2]_2$ (COE = cyclooctene) or $RhCl(CO)(P\phi_3)_2$ followed by analysis of the solutions for free COE or $P\phi_3$ should give a fairly accurate measure of the amount of chelation on the polymer, provided that the stoichiometry of the ligand displacement is known.

The primary areas of investigation covered by this work, then, were (1) whether polymer support of homogeneous catalysts was feasible, (2) whether such supported catalysts displayed altered selectivity compared to their homogeneous analogs, (3) whether new, more active catalysts could be synthesized using this approach, and (4) whether chelation by polymer-supported ligands would be a problem.

RESULTS AND DISCUSSION

Supported Wilkinson's Catalyst

The first research goal was the successful support of a known homogeneous catalyst, Wilkinson's Catalyst, on a styrene-divinylbenzene copolymer matrix. The attachment of a diphenylphosphine moiety to this was carried out using the method outlined in Scheme 2 (page 5). Phosphination of the copolymer such that the product had 0.5 to 1.0 mmol of phosphine per g of beads was sought.

In the first actual phosphinated beads preparation, 200-400 mesh 2% divinylbenzene-styrene copolymer beads were used. These were chloromethylated with $SnCl_4$ and $ClCH_2OCH_2CH_3$[9] and were found to have 0.9 meq of chloride per g of beads by analysis. The analytical technique used was to reflux the polymer in pyridine and then determine the chloride content of the pyridine using standard Volhard analysis.[24] Lithiodiphenylphosphide prepared by the method of Tamborski, et al., was then used to phosphinate the copolymer. Repetition of the chloride analysis procedure after phosphination resulted in only 0.05 meq of chloride per g of beads remaining on the beads, and an elemental analysis indicated the presence of 0.62 mmol of phosphine per g of beads.

A sample of the phosphinated beads was equilibrated with an excess of Wilkinson's Catalyst in acetonitrile for eight days. After removal of the solvent and repeated rinses with fresh acetonitrile, the beads were vacuum dried and tested for their activity as hydrogenation catalysts. These 'Batch A' catalyst beads catalyzed the hydrogenation of cyclohexene at a rate of 0.046 ml of hydrogen per minute.

In an attempt to create catalyst beads of a higher level of activity, another method of preparation was tried. More of the phosphinated copolymer beads were used, but this time they were treated with $[RhCl(C_3H_6)_2]_2$ in a solvent of THF-ethanol.[25] After three days of stirring at ambient temperatures, the golden-yellow beads were analyzed and were found to have 0.127 mmol of rhodium per g of beads. Hydrogenation tests were performed using 1-hexene, cyclohexene, and Δ^2-cholestene as substrates. The steroid was used to determine if most of the catalytic sites were within the interior of the beads, since it was expected that its large size would restrict its ability to diffuse through the pore structure of the beads to the catalytic sites. The observed rates, which were 1.12, 0.173, and 0.003 ml of hydrogen per minute for 1-hexene, cyclohexene, and Δ^2-cholestene respectively, seem to verify the idea that most of the catalyst is within the interior of the beads. In order to investigate the nature of the substrate size selectivity with the supported catalytic system, a

larger batch of beads was prepared for use instead of these 'Batch B' beads.

Some 200-400 mesh 2% divinylbenzene-styrene beads, chloromethylated by T. K. Brunck, were phosphinated with lithiodiphenylphosphide. The beads had 1.0 meq of chloride per g of beads before phosphination and 0.3 meq of chloride per g after phosphination, so their estimated phosphine content was 0.7 mmol per g of beads. Catalyst 'Batch C' and 'Batch D' were prepared by the equilibration of portions of these phosphinated beads with Wilkinson's Catalyst in benzene. Batch C, which weighed about 2 g, was used for only two cyclohexene reductions before it stopped functioning. The reduction rates of those two reductions were 0.575 and 0.025 ml of hydrogen per minute.

Batch D, which weighed about 3 g, was used for a number of reductions, with a variety of substrates, as listed in Table 1. In these reductions, cyclohexene was used as a reference substrate; it was reduced before and after every other substrate to provide a reference rate for the determination of the relative reduction rate of each olefin. For Δ^2-cholestene, cyclohexene was injected into the system after one day of steroid reduction measurements. It was expected that the rates would parallel the size of each substrate, if most of the catalyst was supported within the interior of the polymer beads. The expectations seem to have been well fulfilled, for the reduction rates do in fact closely parallel the size of the substrates. The

TABLE 1

BATCH D SUPPORTED WILKINSON'S CATALYST [a]
COMPARATIVE REDUCTION RATES *vs.*
WILKINSON'S CATALYST

Substrate tested	Relative rates		Mean absolute rates [b]	
	Beads	$RhCl(P\phi_3)_3$	Beads	$RhCl(P\phi_3)_3$
Cyclohexene	1.00	1.00 (1.00)[c]	0.87	0.21 (1.30)[c]
1-Hexene	2.31	1.12	1.86	0.24
1-Octadecene	0.67	0.85	0.52	0.18
Cyclododecene	0.19	0.90	0.19	0.19
Cyclooctene	0.40	0.85	0.38	0.18
Δ^2-Cholestene	0.03	0.67 (0.42)[c]	0.01	0.14 (0.55)[c]

[a] 3 g sample of beads; $RhCl(P\phi_3)_3$ at 2.4 mM

[b] in ml of hydrogen per minute; ± 0.05 ml of hydrogen per minute

[c] run with 10 % palladium on charcoal as the catalyst

same reductions were run using homogeneous Wilkinson's Catalyst to reduce the substrates to determine which rate differences were primarily due to the catalyst itself and not the diffusion restrictions of the polymer. These are also listed in Table 1. Table 1 includes both the relative rates, using cyclohexene as the reference compound, and the actual measured rates of reduction. The rate of cyclohexene reduction given is the mean of six measurements, but when the relative reduction rate of each substrate on the beads was calculated, the cyclohexene rate used for comparison was the mean of the reductions run immediately before and after the other substrate. For the steroid, the relative rate was determined by injecting cyclohexene into the system while the steroid was being reduced and measuring the new reduction rate. The reduction rate before injection of cyclohexene was then subtracted, to give a cyclohexene reduction rate of 0.309 ml of hydrogen per minute.

The data of Table 1 clearly indicate that size selectivity is a major factor in the supported system under investigation, with larger substrates increasingly less reactive due to their inability to diffuse into the polymer to the catalytic sites. This behavior is substantially different from ordinary heterogeneous catalysts, as may be seen when the relative rates of reduction of cyclohexene and Δ^2-cholestene with the heterogeneous catalyst 10% Palladium on Charcoal are compared. These relative rates are also listed in Table 1.

The fairly low reduction rates of the Batch D beads prompted the preparation of a larger batch of new catalyst beads using supported Wilkinson's Catalyst, known as 'Batch E'. These were prepared as the beads of Batches C and D had been, but were of a 30-80 mesh size, so that filtration operations with these beads were simpler. The improved handling characteristics of these beads may have contributed to their greater rhodium content, which was determined to be 0.33 meq of rhodium per g of beads.

A ten gram sample of the Batch E beads was used in an extensive series of reductions with over 75 reductions catalyzed without a major loss in activity. After an initial activity drop from 3.7 ml of hydrogen per minute to 2.2 ml of hydrogen per minute for 1-hexene, the beads lost only 10% of their activity over the next 30 reductions. For these reductions, which are listed in Table 2, the standard substrate used was 1-hexene. This was reduced before and after each other substrate and the relative rates listed are based on comparisons with these rates. Homogeneous Wilkinson's Catalyst was again used for comparison reduction rates. The reduction pattern of the substrates used in this study duplicated that of the substrates in the study using the Batch D beads; substrates of larger bulk were reduced more slowly than smaller substrates.

Among the alkenes listed in Table 2 are two with hydroxy groups in their structures, allyl alcohol and 4-pentene-1-ol. These were chosen to further investigate

TABLE 2

BATCH E SUPPORTED WILKINSON'S CATALYST [a]
COMPARATIVE REDUCTION RATES *vs.*
WILKINSON'S CATALYST

Substrate	Relative rates		Mean absolute rates [b]	
	Beads	$RhCl(P\phi_3)_3$	Beads	$RhCl(P\phi_3)_3$
1-Hexene	1.00	1.00	2.15	4.69
Cyclohexene	1.18	0.77	2.16	3.59
3,5,5-Trimethyl-1-hexene	0.52	0.57	1.00	2.68
Norbornene	1.27	0.40	1.87	1.89
1-Dodecene	0.70	0.87	0.87	4.06
Allyl alcohol	0.64	0.92	2.98	4.33
4-Pentene-1-ol	1.00	0.50	1.46	2.34
1-Hexene [c]	1.00	1.81	1.88	8.51
4-Pentene-1-ol [c]	0.56	----	1.05	----

[a] 10 g sample of beads; $RhCl(P\phi_3)_3$ at 1.0 mM

[b] in ml of hydrogen per minute, $\pm$ 0.10 ml of hydrogen per minute

[c] solvent = 1:1 benzene-ethanol; all other reductions done in pure benzene.

the selectivity effects of the polymer support on the catalyst. If the nonpolar matrix exhibits substantial interaction with the substrates, reduction rates of the polar alcohols should be considerably slower than when they are reduced by homogeneous Wilkinson's Catalyst. Such an effect is observed for allyl alcohol, which is reduced 25 to 50% slower than 1-hexene using the supported catalyst but at the same rate as 1-hexene using homogeneous Wilkinson's Catalyst. For 4-pentene-1-ol, very little relative rate change is noted.

The effect of increasing the polarity of the solvent mixture was investigated using 1:1 benzene-ethanol as the solvent for bead reductions. Under these conditions, 4-pentene-1-ol showed a substantial rate difference from that of 1-hexene. The 1-hexene rate seemed to increase by 10% while the 4-pentene-1-ol rate decreased by 50%, most probably due to a greater preference of the alcohol for the more polar solvent mixture. The 1-hexene would tend to migrate more into the polymer because of its nonpolar nature, resulting in an increase in reduction rate. The effects of polarity on substrate selectivity seem to be less dramatic than those of size, but nevertheless a clear effect is present.

One problem encountered in the use of the Batch E beads was caused by their activity. It was found that for some of the more reactive substrates, such as 1-hexene, the reduction rate observed was not limited by the rate

of diffusion of the substrate into the beads alone, but also by the ability of hydrogen to diffuse into the solvent. This was detected when it was observed that the rate of hydrogen uptake was dependent on the rate of stirring. When the amount of beads used was reduced to 2 g, no changes in rates were observed when the stirring speed was varied over its entire range, even with 1-hexene as the substrate.

A new set of reductions, using just 1-hexene, cyclohexene, and cyclooctene, was run using the 2 g sample of Batch E beads. These three alkenes were used because it was felt that their sizes varied enough to indicate trends in size selectivity. Solvents of pure benzene and 1:1 benzene-ethanol were used for all three alkenes. The results are listed in Table 3. All substrates undergo at least a 100% increase in reduction rate on going to the more polar solvent mixture, indicating that the preference of the nonpolar substrates for the nonpolar polymer matrix is a larger factor than the size restrictions of the polymer's pores. A drop in the relative rate of the two cyclic alkenes compared to 1-hexene does seem to have occured, probably due to the pore shrinkage which occurs in the more polar solvent.

Figure 1 is a plot of the relative reduction rates observed for 1-hexene, cyclohexene, and cyclooctene in the data of Tables 1,2, and 3. As can be seen in Figure 1, the general trend among the supported catalyst systems is toward

TABLE 3

BATCH E SUPPORTED WILKINSON'S CATALYST [a]
SOLVENT AND SIZE EFFECTS

Substrate used	Solvent used	Hydrogenation rate [b]	Relative rate
1-Hexene	ØH	0.67	1.00
Cyclohexene	ØH	0.53	0.79
Cyclooctene	ØH	0.12	0.18
1-Hexene	ØH-EtOH	2.97	4.43
Cyclohexene	ØH-EtOH	2.19	3.27
Cyclooctene	ØH-EtOH	0.36	0.54

[a] 2 g sample of beads

[b] in ml of hydrogen per minute ± 0.05 ml of hydrogen per min.

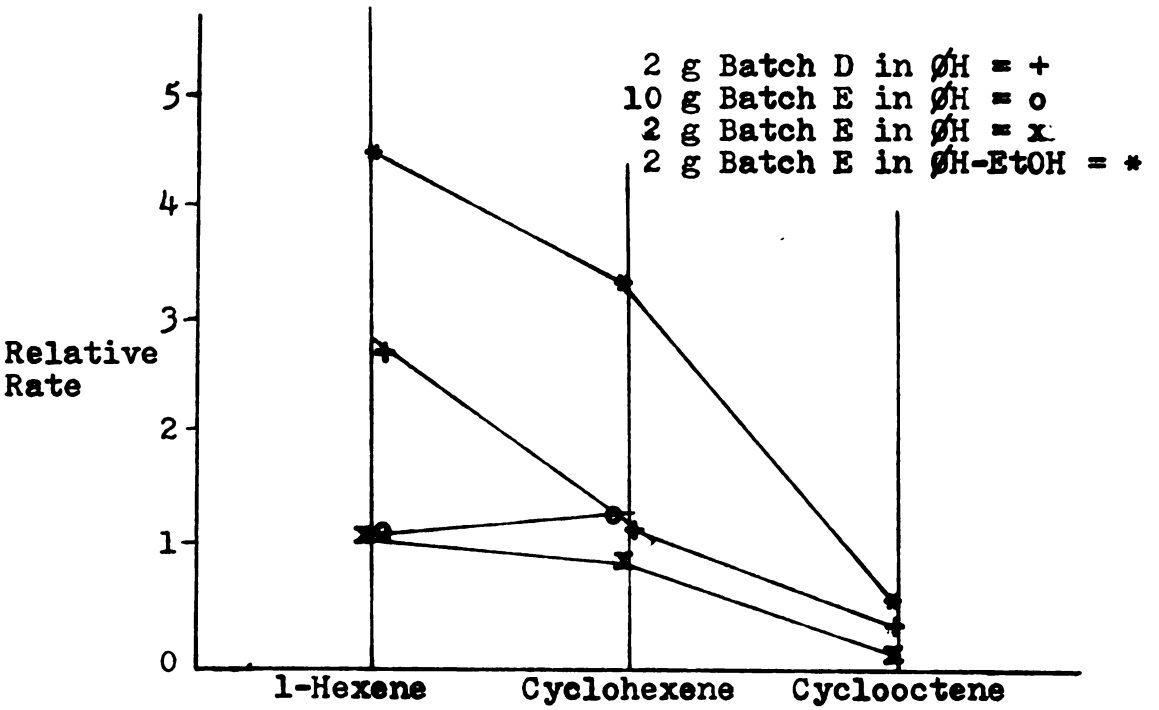


FIGURE 1

RELATIVE REDUCTION RATES, BATCHES D AND E

slower rates for larger substrates. Although the 10 g sample of Batch E seemed to reduce cyclohexene a bit faster than 1-hexene, in general the reduction rates of different substrates follow the expected pattern.

The greater selectivity of the beads, when the solvent is more polar and the pores are therefore smaller, can be seen in the increase in the slope of the curve in going from the 2 g Batch E beads in benzene (x) to 1:1 benzene-ethanol (*).

Summary of studies on supported Wilkinson's Catalyst. The above research indicated that:

1. Support of a functioning homogeneous catalyst on a styrene-divinylbenzene copolymer matrix is possible.

2. Such a system has most of the supported catalyst within the interior of the matrix used.

3. The supported catalyst displays size and polar selectivity toward substrates which is not observed with the homogeneous catalyst.

4. The supported catalyst may be reused many times without regeneration, in contrast to the homogeneous equivalent.

Supported Titanocene

Hydrogenation studies. The attachment of dicyclopentadienyldichlorotitanium (IV) , also known as titanocene dichloride, to a styrene-divinylbenzene copolymer via a benzylic linkage has been accomplished by C. Gibbons.[15] He found that the supported complex could be reduced with alkyllithium reagents and used as a hydrogenation catalyst. A similar reaction had already been observed for the homogeneous system.[16] Two further experiments were done with these beads relating to their use in hydrogenations.

In the first study, the ability of the supported titanocene to catalyze the hydrogenation of a variety of substrates was tested. These are listed in Table 4. For each of the reductions recorded, 0.015 ± 0.001 mmol of supported titanocene was used to reduce 0.5 ml of substrate.

TABLE 4

BENZYL-SUPPORTED TITANOCENE HYDROGENATIONS

Substrate	Hydrogenation rate[a] (ml of H_2/ minute)
1,5-Cyclooctadiene	1.54
1,3-Cyclooctadiene	1.81
Styrene	2.05
1-Hexyne	Polymer
3-Hexyne	1.26
Benzyl acetate	No Rxn. (?)
Vinyl acetate	No Rxn. (?)
3-cholestene-4-one	No Rxn. (?)

[a] ± 0.10 ml of H_2/minute

Both octadienes were readily reduced to their completely saturated counterparts, as was 3-Hexyne. These three reductions were monitored by gas chromatography to detect any isomerization or partially reduced intermediates present during the course of the reduction. No isomerization or partially reduced products was detected. The formation of a cloudy solution of polymer when 1-Hexyne reduction was attempted is understandable, since the homogeneous system is known to polymerize terminal alkynes.[27] Styrene forms ethylbenzene quantitatively. The three other substrates tested all contain oxygen and thus could quite possibly deactivate the titanocene, since the reaction of oxygen-containing functional groups with low-valent titanium is known.[28] Titanocene might also be acting as a nucleophile in these systems, leading to unreactive products with the substrates.[29] The former reaction is more common for titanium. The homogeneous titanocene system has been used to catalyze alkene, diene, and alkyne hydrogenation as well, but it has been reported to polymerize styrene in an excess of hydrogen.[16,27]

One property of the homogeneous titanocene system is its ability to reform $TiCp_2Cl_2$ upon treatment with HCl.[17b] If such a reaction could be carried out with the supported titanocene system, it could be reused. To test the possibility of this approach to making the supported titanocene "recyclable", a sample of the pale grey active polymer was exposed to air, at which exposure it immediately became tan,

the color of deactivated supported catalyst. This was then treated with dry HCl gas while suspended in absolute ethanol. The beads became pink (the color of the beads before activation) within five minutes. After hexane rinsing and drying under vacuum, the beads were activated with butyllithium and used for the reduction of a sample of 1-hexene. The reduction rate observed on the first use of the beads was 1.75 ml of hydrogen per minute; the beads after recycling produced a rate of 1.82 ml of hydrogen per minute. Regeneration of the catalyst appears to be possible.

One other experiment done with the benzyl-supported titanocene system used sodium naphthalide to activate the beads. This was to verify the usefulness of the same reducing agents used for the activation of the homogeneous titanocene system. A reduction using 1-hexene gave a rate of 0.45 ml of hydrogen per minute. Although less active than the butyllithium-activated beads, these beads were still quite good as a catalyst.

Confirmation of the presence of most of the titanocene within the interior of the beads, as was done for the Wilkinson's catalyst beads, was desired. A different method was used for the titanocene beads, however. If most of the catalyst is within the interior of the beads, then substrates will have to pass through the pores of the beads before being reduced. As was observed for the Wilkinson's Catalyst beads, such a passage limits the rate of reduction because the diffusion into the beads requires time. If the

bead structure is destroyed, however, a great rate increase should be observed, because diffusion through the pores to get to the catalytic sites will not be necessary. Identical quantities of cyclohexene were reduced using samples of the same amount of beads with and without grinding the beads in a mortar and pestle before activation. The whole beads had a reduction rate of 88.7 ml of hydrogen per minute per meq of titanium; the rate for the ground beads was 714 ml of hydrogen per minute per meq of titanium. The belief that most of the supported titanocene was within the beads seemed to be clearly supported by this result.

The question of whether or not titanocene was activated by supporting it on the polymer matrix was considered and an answer sought by comparing the reduction rate on non-supported and supported titanocene. Two reductions were run using homogeneous titanocene with the same procedure and quantities as had been used in the whole bead-ground bead rate comparisons. The reduction rate observed was 28 ml of hydrogen per minute per meq of titanium. This was clearly much slower than the supported titanocene reductions. A one to two hour induction period was also observed when the homogeneous system was used. During this, the reduction rate was only 20% of the maximum value. The supported system had the same reduction rate from the beginning of catalyzed reductions until less than 5% of the substrate was left, at which time the rate began to drop off.

Since the possible presence of 3 (page 7) was felt to be a way in which the benzyl-supported titanocene might be deactivated, the synthetic process of Scheme 3 (page 8) was applied to some 20% divinylbenzene-styrene copolymer beads. The synthetic conditions were first developed using non-polymeric systems because analysis of the products is simpler when they are not on the polymer support.[30] The synthetic procedure worked for the non-polymeric attempts, and was then applied to the polymer. Bromination of the first batch of beads run was done using the method of Olah,[31] with $FeCl_3$ and bromine in nitromethane. This yielded a highly brominated polymer with over 3 meq of bromide per g of beads. The polymer contained some residual iron salts, however, which proved difficult to remove. After lithiation and treatment with cyclopentenone, only 0.058 meq of titanium per g of beads were successfully attached to the polymer. When used as a catalyst, however, the beads proved to be more active than the benzylic-supported titanocene beads, with a reduction rate of 106 ml of hydrogen per meq of titanium for cyclohexene reduction. This is a 13% increase relative to the reduction rate found with the whole beads having benzylic-supported titanocene. This preparation also has the advantage of not requiring the use of chloromethylethyl ether to functionalize the basic polymer. This ether has been found to be a potent carcinogen.

Another preparation of "phenyl-supported" titanocene used the same lithiation and cyclopenteneone reaction

sequence as the preceding batch, but the bromination was done using BF_3 as the catalyst. A lower degree of bromination was obtained, but the final product had a much higher percentage of titanium substitution, 0.546 meq of titanium per g of beads.

Nitrogen fixation studies. Homogeneous titanocene has been used for nitrogen fixations by several different workers. The method of van Tamelin uses sodium naphthalide in THF with $TiCp_2Cl_2$ to give ammonia which may be trapped out of a nitrogen stream passed through the reaction solution.[18] In the method of Vol'pin and Shur, $TiCp_2Cl_2$ in diethyl ether is treated with an organolithium or Grignard reagent under 100-200 atmospheres of nitrogen.[19] Hydrolysis is necessary to form ammonia in the Vol'pin-Shur system, and the formation of arylamines is observed when aryllithium reagents are used to reduce titanocene dichloride. Both nitrogen fixation procedures were run using the supported titanocene as the source of titanocene. Homogeneous titanocene reactions were also performed to determine the correct conditions for nitrogen fixation and to verify the validity of the analytical methods used.

Researchers in titanocene nitrogen fixation are all agreed that dimeric titanocene is involved in the formation of reduced nitrogen.[17-19] It would seem that if the supporting matrix in the polymer-supported titanocene system is rigid enough to prevent association of the supported titanocene, then no ammonia formation should be observed in

fixation attempts using the beads. This was found to be the case. Although homogeneous titanocene produced ammonia in both the van Tamelin and Vol'pin-Shur systems when attempted fixations were run, no significant amounts of ammonia were ever produced by the supported titanacene beads.

Analytical methods differed for the two systems. For the van Tamelin method, the nitrogen stream was passed through a gas washing tower containing aqueous H_2SO_4. This was then boiled down and either simply tested for ammonia content with Nessler's Reagent[32] after being made basic or else titrated with a standard NaOH solution if the H_2SO_4 solution was of a known concentration. For the Vol'pin-Shur fixations, Nessler's Reagent or Kjeldahl analysis was used. For the latter, the acidic hydrolysis mixture was made basic, steam distilled into boric acid solution, and titrated with standardized HCl solution to quantitatively determine the amount of ammonia formed.[33] Since phenyllithium was used as the reductant in the Vol'pin-Shur fixations, aniline yields were determined by benzene extraction of the steam distillate and gas chromatographic determination of the aniline using a durene standard.

No ammonia was ever detected using van Tamelin's method with polymer-supported catalyst only. When the homogeneous system was used, ammonia was clearly detected, but when a combination of supported catalyst and homogeneous catalyst were used, no ammonia could be detected, even though both quantitative and qualitative methods of

analysis were used. Many problems were encountered with the nitrogen flow system and evaporation of the solvent despite the inclusion of a THF bubbler before the reaction flask, so the Vol'pin-Shur method was used for most of the bead nitrogen fixation experiments.

Table 5 summarizes a series of nitrogen fixations run using the Vol'pin-Shur method of nitrogen fixation. Systems using homogeneous titanocene were run three times and were found to give ammonia on all three runs according to Nessler's Reagent. Four runs were then done with quantitative analysis of the products, giving the first four items in Table 5. The first two used identical quantities of reagents; the third used twice as much reducing agent, and the fourth was a blank run under argon. Two bead nitrogen fixations follow. These were analyzed quantita-

TABLE 5

VOL'PIN-SHUR NITROGEN FIXATIONS

Titanocene form	Reactants used		Products found[a]	
	mmol Ti	mmol ØLi	mmol NH_3	mmol $ØNH_2$
Homogeneous	2.41	17.0	0.41	0.02
Homogeneous	2.40	17.0	0.32	0.02
Homogeneous	2.40	34.0	0.66	0.03
Homogeneous	2.40	17.0	0.01	0.00
Supported	2.16	17.0	0.02	0.00
Supp. + Homog.	4.40	34.0	0.80	0.09

[a] $\pm$ 0.01 mmol

tively also. The first used the same quantities of reagents as the first two homogeneous reactions, while the second used equal amounts of homogeneous and supported titanium with as much reducing agent as the third homogeneous reaction.

The failure to detect any significant amounts of ammonia in trials using only supported catalyst was expected, as mentioned earlier, because dimeric titanocene is necessary and dimerization of the supported titanocene is probably difficult. The results tend to confirm further the idea that this polymer support can keep the active metal centers apart. Another attempted nitrogen fixation using the supported system was done with Nessler's Reagent used to test for ammonia. The results were also negative.

If dimeric titanocene is indeed necessary for the fixation of nitrogen, attempted fixation using homogeneous titanocene plus supported titanocene might lead to the formation of some dimer pairs by supported and homogeneous titanocene molecules, increasing the yield of ammonia. This is observed, as seen in the last item of Table 5. Another interesting and significant fact can be seen in this last item of Table 5. The ratio of ammonia to aniline in the homogeneous systems is ca. 20; in the mixed homogeneous-supported titanocene system it is 9. If, as Vol'pin and Shur propose, their system forms aniline by a monomeric titanocene reaction (with some form of fixed nitrogen possibly

from a former dimer) then in the mixed system, there is a much greater chance that monomeric formation of aniline will occur, because only half of the supported titanocene is dimerized with homogeneous titanocene at best. The 50% increase in the amount of aniline formed is then quite reasonable. This result adds further credence to the indications of reduced aggregate formation found in the hydrogenation experiments with supported titanocene.

Summary of studies on supported titanocene. The titanocene studies in hydrogenation and nitrogen fixation have established the following:

1. Supported titanocene reduces dienes and inner alkynes to alkanes without isomerization or detectable formation of intermediate monalkenes.

2. Terminal alkynes and oxygen-containing substrates are not reduced, though some reaction may occur.

3. Organolithium reagents or sodium naphthalide both activate supported $TiCp_2Cl_2$ for hydrogenation catalysis.

4. Supported titanocene may be reconverted to its dichloride by treatment with HCl gas.

5. Removal of the benzylic methylene group from a position adjacent to the supported cyclopentadienide results in increased activity.

6. Supported titanocene is mostly within the interior of the beads in this system.

7. Aggregation of titanocene supported on the copolymer is difficult or impossible.

8. Supported titanocene is active in nitrogen fixation only when homogeneous titanocene is present in solution as well.

Chelation Studies

Although some of the above results would seem to indicate that the supported catalysts are held far enough apart so that metal-metal interactions are difficult if not impossible, the question of whether or not polymer-attached ligands are mobile enough to chelate with supported complexes and thereby deactivate them is a recurring one[20-23]. It was decided that the equilibration of a labile complex with the phosphinated copolymer, followed by the measurement of the amount of freed ligand, would give some information relating to this question. Two different complexes were chosen for these studies, the rhodium complex of cyclooctene (COE), a very labile dimeric complex, and rhodium Vaska complex, a less labile monomeric complex. The use of Wilkinson's Catalyst itself proved impractical because at the concentrations necessary for accurate free triphenylphosphine determination dimerization occurred with the release of triphenylphosphine (Reaction 1).

Reaction 1 $$2\ RhCl(P\phi_3)_3 \rightleftharpoons [RhCl(P\phi_3)_2]_2 + 2\ P\phi_3$$

The extent of ligand displacement in both systems used was measured by gas chromatography. This proved

fairly simple for the COE dimer reactions but difficult for the Vaska complex reactions, which had to be run near the lower limits of detection for triphenylphosphine. Thus the results in the Vaska system are less reliable.

$[RhCl(COE)_2]_2$ studies. The COE dimer complex was used in reactions with 2% and 20% divinylbenzene-styrene copolymer beads. The 2% beads used had 0.8 mmol of phosphine per g of beads, while the 20% beads used had either 0.9 or 0.4 mmol of phosphine per g of beads. In all the cases tested, supported phosphine was present in at least a four-fold excess relative to the complex.

Twenty percent divinylbenzene beads with 0.9 mmol of phosphine per g of beads were equilibrated with the COE complex (phosphine:complex = 6.8 mmol:1.41 mmol) in benzene and sampled at two hours, one day, and nineteen days after solvent addition. Free COE levels detected were 2.45, 2.90, and 2.10 $\pm$ 0.30 mmol at the respective times. The solution was removed and treated with excess triphenylphosphine to free any COE in solution as the rhodium complex.[34] The analysis which followed indicated 2.25 mmol of COE were present, so virtually no rhodium COE complex was present was present in the solution; it had coordinated to the polymer. The overall results indicated that half the complexed COE had been freed, presumably displaced by phosphine ligands. The degree of bidentate chelation indicated was about 70%.

Samples of the above beads were treated with triphenylphosphine to prove that 3 mmol of COE were still on them.

One sample tested was treated with triphenylphosphine under nitrogen; a second sample was treated with triphenylphosphine under hydrogen. The former was analyzed for free COE after three hours; the latter was analyzed for cyclooctane after one and five hours. Both samples were expected to contain 0.08 mmol of COE. The first produced 0.07 mmol of COE and the second produced 0.08 mmol of cyclooctane (both ± 0.01 mmol of hydrocarbon).

A further test was run using the same batch of phosphinated copolymer beads that was used in the above equilibration as well as some of the 2% beads containing 0.8 mmol of phosphine per g of beads. A blank containing $[RhCl(COE)_2]_2$ and two standards containing the complex and triphenylphosphine were also run. After injection of benzene, the bead-containing reactions were analyzed one day later, while the others were analyzed after seven hours. The amounts of reagents used and the results are listed in Table 6. Note that two other standards using the rhodium complex and triphenylphosphine were run and are also included in Table 6.

As may be seen from Table 6, free COE was present only when a phosphine of some form was present. All of the complex still in solution in these tests was removed before analysis by passing the solution sample through a short column of alumina, which held the highly polar complex but allowed COE to pass freely. The amount of COE that was freed, however, was 25 to 50% more than would be

TABLE 6

PHOSPHINE BEADS CHELATION STUDIES
$[RhCl(COE)_2]_2$ EQUILIBRATION

Sample	mmol COE present	mmol phosphine present	Form of phosphine present	mmol free COE [a] detected
1	0.484	0.65	2% DVB Beads [b]	0.31
2	0.532	0.85	2% DVB Beads [b]	0.34
3	0.444	0.64	20% DVB Beads [c]	0.23
4	0.196	----	none	less than 0.02
5	0.216	0.27	$P\phi_3$	0.20
6	0.248	0.49	$P\phi_3$	0.27
1'	0.568	0.218	$P\phi_3$	0.32
2'	0.488	0.261	$P\phi_3$	0.32

[a] $\pm$ 0.03 mmol

[b] 0.8 mmol of phosphine per g of beads

[c] 0.9 mmol of phosphine per g of beads

expected from a 1:1 stoichiometric displacement of COE by the phosphine component in the homogeneous standard systems. Thus an accurate determination of the degree of chelation would seem to be difficult to obtain, though the chelation indicated should be the upper limit of that actually occuring. From the results in Table 6, the degree of chelation indicated in samples 1, 2, and 3 respectively was 156, 154, and 107% bidentate chelation. Chelations of over 100% indicate tridentate chelation. Although samples 1 and 3 used virtually the same amount of supported phosphine and the same amount of complex, the latter had considerably less chelation indicated. This is reasonable, since the 20% divinylbenzene beads used in sample 3 should have a less mobile matrix than the 2% divinylbenzene beads used in samples 1 and 2.

A third chelation study was made using 20% divinylbenzene beads with only 0.4 mmol of phosphine per g of beads. Patchornik found that self-condensations of enolizable esters on polymer supports were very low when substitution was kept low,[20] so it was hoped that a lower degree of phosphination would decrease the amount of chelation occuring. Samples of these beads were equilibrated with the COE complex while two more standards using the complex plus triphenylphosphine were also run. Both were sampled at 3 and 50 hours; Table 7 lists the results.

Note that a very high degree of chelation, beyond expectations for this system, was indicated. At the end of

TABLE 7

PHOSPHINE BEADS CHELATION STUDIES
$[RhCl(COE)_2]_2$ EQUILIBRATION

Sample	mmol COE present	mmol phosphine present	Form of phosphine present	mmol free COE[a] detected	
				3 hr	50 hr
1	0.981	0.220	$P\phi_3$	0.232	0.252
2	0.794	0.560	$P\phi_3$	0.558	0.589
3	0.945	2.7	20% DVB Beads[b]	0.575	0.624
4	0.795	2.1	20% DVB Beads[b]	0.511	0.614

[a] ± 0.03 mmol

[b] 0.4 mmol of phosphine per g of beads

fifty hours, the beads in sample 3 analyzed as having 164% bidentate chelation and those in sample 4 as having 210% bidentate chelation. No larger excess of supported phosphine was present in this experiment than in the previous ones. The only difference was the method used to prepare the phosphinated polymer itself. Whereas the previous experiments used phosphinated copolymer prepared via the chloromethylated copolymer, this batch used polymeric phosphine prepared from directly brominated beads which were treated with butyllithium followed by chlorodiphenylphosphine. It may be that this method produces a polymer having "bunched" phosphines on the polymer which are able to chelate more than the phosphine ligands on the other polymers.

$RhCl(CO)(P\phi_3)_2$ studies. Two samples of phosphinated 20% divinylbenzene-styrene copolymer beads containing 1.25 mmol of phosphine per g of beads were equilibrated with the rhodium Vaska complex. A standard reference sample containing triphenylphosphine and the complex was also run, but the formation of solid material made its results difficult to use. The solutions were analyzed after passage through an alumina column to remove any complex still in solution. The Vaska complex was found to release all its triphenylphosphine when injected into the gas chromatograph, so all but the last analyses used no alumina columns. The results of the analyses are recorded in Table 8. After the experiment was completed, the beads used in sample 3 were washed, dried, and submitted for microanalysis. This indicated the presence of 0.043 mmol of rhodium per g of beads.

Based on the Vaska complex not present in solution, 0.025 mmol of rhodium per g of beads had been expected, with an upper limit of 0.034 mmol of rhodium per g of beads if all the complex present had been coordinated to the polymer. Clearly the microanalytical results are unreliable.

While the results obtained in this experiment had an estimated error of 15-20% (because the work was at the lower limits of detection of triphenylphosphine) they also seemed to verify the presence of bidentate chelation. Indeed, because virtually all of the triphenylphosphine present was detected either as free phosphine or dissolved complex, bidentate chelation of the supported complex seems to be 100%. In both samples 2 and 3 a very large molar excess of phosphine was present, and that may have contributed to the amount of chelation observed, since if even 5 or 10% of the copolymer phosphine ligands were near enough to chelate a metal, then with time an equilibrium state favoring the chelated metal would be approached. It should be considered also that the degree of chelation calculated for the COE system assumes no breakage of the chloride bridges in the dimer, although this is quite possible. If chloride bridge breakage were a common occurance, then the tridentate chelation occuring could be less than that determined by assuming that the bridging remains intact. This can be understood when it is recognized that two separate rhodium atoms coordinated completely to polymeric phosphine ligands would give a chelation percentage of 300% by the method which assumes chloride bridging is intact, while the actual

TABLE 8

PHOSPHINE BEADS CHELATION STUDIES
$RhCl(CO)(P\phi_3)_2$ EQUILIBRATION

Sample	Total mmol $P\phi_3$ present	mmol free $P\phi_3$ detected[a]							
		1 hr	15 hr	40 hr	65 hr	90 hr	140 hr	165 hr	final
1[b]	1:129	---	0.18[f]	---	---	---	---	---	---
2[c]	0.514	0.28	0.48	0.47	0.44	0.52	0.48	0.54	0.50[e] 0.46[f]
3[d]	0.566	0.34	0.55	0.50	0.49	0.57	0.56	0.56	0.59[e] 0.42[f]

[a] ± 0.08 mmol

[b] 0.441 mmol $RhCl(CO)(P\phi_3)_2$ + 0.247 mmol $P\phi_3$; formed solid precipitate

[c] 0.257 mmol $RhCl(CO)(P\phi_3)_2$ + 6.0 mmol polymer-supported phosphine

[d] 0.283 mmol $RhCl(CO)(P\phi_3)_2$ + 10.0 mmol polymer-supported phosphine

[e] before passage through alumina to remove dissolved $RhCl(CO)(P\phi_3)_2$

[f] after passage through alumina to remove dissolved $RhCl(CO)(P\phi_3)_2$

percentage would be 200%, since every rhodium atom would have a tridentate chelation form (100% would represent complete bidentate chelation). This computational problem only arises beyond the bidentate chelation level, however, so that if one major species is present in the systems using COE complex treatment, the predominance of bidentate chelation is confirmed.

Summary of chelation studies. The overall pattern of the chelation studies tends to confirm the presence of bidentate chelation in systems which have more mobile polymer matrices (i.e., 2% divinylbenzene copolymer systems) while indicating that in less mobile polymer matrix systems (i.e., 20% divinylbenzene copolymer systems) which have the ligand well distributed throughout the polymer, chelation may be effectively kept at a low level. This would correlate well with the results of experiments with the supported titanocene system which seem to favor a low level of interaction between adjacent metal centers on the 20% divinylbenzene matrix used.

GENERAL SUMMARY AND SUGGESTED FURTHER RESEARCH

This research was directed toward answering four major questions, as outlined in the introduction. The answers obtained are:

1. Polymer support of a homogeneous catalyst is feasible.[36]

2. Altered selectivity is displayed by these supported catalysts, based on the size and the polarity of the substrates used.[36,37]

3. New catalysts of greater activity than their homogeneous analogs can be synthesized by this method of polymer support.[38]

4. Chelation may be a problem in polymeric systems which have flexible (low cross-linked) matrices and/or high degrees of ligand substitution.[38]

As with any research, many new ideas have been promoted by this work, and problems which still need much effort to solve them have been encountered. This researcher suggests that more work might be profitably directed toward the following problems:

1. Analysis of the supported systems. This has been the greatest problem in this work, because the polymer matrix often blocks or overpowers analyses of the supported metals. One recent reviewer has pinpointed this as

the biggest problem in studies of supported systems.[30] Application of more sensitive methods such as Fourier transform far infrared spectroscopy and electron microprobe studies have been undertaken by some of my coworkers and seem to be yielding useful information. The use of color changes and microanalyses has reached its limits in most of our work.

2. More complete determination of the factors involved in chelation and ways to control them would seem to be a possible means of producing more active catalysts, and is again dependent upon the improvement of analytical methods.

3. The nature of the supported titanocene system would seem to be a fruitful area of investigation. This system is extremely active in hydrogenation reactions, and it might be possible to use it in the production of aryl amines if a small amount of homogeneous titanocene could be used to provide a catalytic nitrogen fixing system.

4. Now that a method of putting cyclopentadienide ligands onto the polymer without chloromethylation is available, the investigation of other "sandwich" complexes supported on the polymer might be undertaken. Although in this researcher's opinion more reactive metal complexes than titanocene (which is very reactive) might attack the support, it is possible that many new or improved catalytic processes could be carried out on the supported system. It is certainly true that greater effective catalyst concentrations are attainable using this approach.

5. The development of a "flow-through" system for catalytic reactions is a long-term pipe dream for this method of catalysis. With methods such as the use of cyclic ethers as a hydrogen source for alkene reductions with Wilkinson's Catalyst currently being reported in the literature,[35] the possibility of such flow systems becomes more likely and should be investigated.

6. Further investigation of the selectivity of the supported systems as well as kinetic studies of the bead reaction are obvious research efforts one could suggest. Both of these areas are already under investigation.

EXPERIMENTAL

Introduction

All NMR spectra were run on a Varian T-60 spectrometer using intermal TMS in a solvent of deuteriochloroform. Spectra are given in δ units as parts per million downfield from tetramethylsilane. Mass spectra were run on a Hitachi Perkin-Elmer RMU-6 by L. Guile. All gas chromatographs were taken on a Varian Aerograph Model 90-P using ¼" columns. Microanalyses were done by Spang Microanalytical Laboratory or Galbraith Laboratories (Rh analyses) except for titanium analyses, which were done by E.S. Chandreasekaren.[39]

Lithium reagents were purchased from Alfa Inorganics. Phosphines were supplied by Pressure Chemical Co. All polymer beads used in the reactions were gifts of The Dow Chemical Company. All solvents used were reagent grade, purchased from either J.T. Baker or Mallinckrodt.

Bead Syntheses

Supported Wilkinson's Catalyst Batches A and B. A 15 g sample of 2% DVB (Divinylbenzene)-styrene copolymer beads was treated with 5 g of $SnCl_4$ and 125 ml of $ClCH_2OCH_2CH_3$ according tho the method of Pepper, Paisley, and Young.[9] The stirred reaction was halted after five hours by the addition of 200 ml of 1:3 dioxane-H_2O. After stirring overnight, the liquid was drained off and four 1:1 dioxane-H_2O rinses (100 ml each) were carried out. The following sequence of solvent washes was then performed:

1. 3:2 dioxane-H_2O
2. 3:1 dioxane-10%HCl
3. 9:1 dioxane-10%HCl
4. 9:1 dioxane-H_2O
5. Pure dioxane
6. 1:1 dioxane-benzene
7. Benzene
8. Benzene

The damp, pale pink beads were vacuum dried. When dry, they were white. Volhard analysis[24] indicated a chloride substitution of 0.9 meq of chloride per g of beads.

A 12 g sample of the chloromethylated beads (10.8 meq of chloride) was refluxed with a solution of lithiodiphenylphosphide prepared the previous day from 8.02 g of chlorodiphenylphosphine (40 mmol) and 1.4 g of lithium metal clippings (200 mmol) in 100 ml of THF.[10] After 36 hours, the reaction was terminated by the addition of 100 ml of aqueous saturated NH_4Cl solution. After stirring for 1.5 hours, the solution was drained off and the beads were rinsed with 50 ml aliquots of the following solvents:

1. 1:1 dioxane-10%HCl
2. 1:1 dioxane-10%HCl
3. 1:1 dioxane-H_2O
4. 3:1 dioxane-H_2O
5. Dioxane
6. 3:1 dioxane-benzene
7. 1:1 dioxane-benzene
8. 1:3 dioxane-benzene
9. Benzene
10. Benzene

After vacuum drying, Volhard analysis[24] indicated the presence of 0.05 meq of chloride per g of beads. An elemental analysis was also performed.

Analysis: 89.35 % C 7.74 % H 1.96 % P

This is 0.62 mmol of phosphine per g of beads.

Batch A of the supported Wilkinson's Catalyst beads was prepared by refluxing 1.37 g of the phosphine beads (0.85 mmol of phosphine) with 1.07 g of Wilkinson's Catalyst (1.16 mmol) in 100 ml of acetonitrile for eight days. Some crystals of the dimer of Wilkinson's Catalyst, $[RhCl(P\phi_3)_2]_2$, were observed. The solvent was removed and the beads were rinsed with acetonitrile and vacuum dried.

Batch B of the supported Wilkinson's Catalyst beads was prepared by a different route. Propene was bubbled through 2.6 g of $RhCl_3 \cdot 3H_2O$ (10 mmol) in 100 ml of 1:1 THF-ethanol for three days to form $[RhCl(C_3H_6)_2]_2$.[25] A 2.06 g sample of phosphine beads (1.27 mmol of phosphine) was then added to the solution a week later. The supported phosphine ligands displaced some of the propene ligands, producing Wilkinson's Catalyst on the beads. After three days, the liquid was removed and the golden-yellow beads were rinsed with three 10 ml THF rinses and three 10 ml benzene rinses.

After vacuum drying, a sample of the beads was taken for elemental analysis.

Analysis: 86.38 % C 7.54 % H 1.46 % P 1.31 % Rh

This is 0.47 mmol of phosphine and 0.127 meq of rhodium per g of beads.

Supported Wilkinson's Catalyst Batches C and D. Lithiodiphenylphosphide prepared from 11 g of chlorodiphenylphosphine (50 mmol) and 1.8 g of lithium metal clippings (257 mmol) in 50 ml of THF[10] was used to phosphinate 7 g of 2% DVB-styrene copolymer beads which had been chloromethylated by T. K. Brunck (7 meq of chloride; these beads had 1.0 meq of chloride per g by Volhard analysis[24]).

Syringe techniques were used to work with these beads, because their 200-400 mesh size had been found to clog frit pores with Batches A and B. The supernatant solution was removed with a syringe after stirring for one day at ambient temperatures. Five THF rinses (50 ml each) were performed, accompanied by ten minutes of stirring between each solvent addition and removal. Saturated aqueous NH_4Cl solution was injected into the bead flask to destroy any residual phospho-lithium reagent. The following 50 ml rinses were then carried out:

1. 1:1 dioxane-H_2O
2. 1:1 dioxane-10% HCl
3. 5:1 dioxane-10% HCl
4. 10:1 dioxane-10% HCl
5. Dioxane
6. 3:1 dioxane-benzene
7. 1:1 dioxane-benzene
8. Benzene

The beads were vacuum dried and analyzed for chloride content using the Volhard method.[24] A chloride content of 0.3 meq per g beads was found, indicating a maximum phosphine content of ca. 0.7 mmol of phosphine per g of beads.

Batch C of the supported Wilkinson's Catalyst beads was prepared by equilibrating 2.25 g of the phosphinated beads (1.6 mmol of phosphine) with 1.78 g of Wilkinson's Catalyst in 30 ml of benzene. These were stirred for one week, then drained and repeatedly rinsed with benzene. Two days of rinsing were necessary before the rinse solutions had no more coloration. The beads were then vacuum dried.

Batch D of the supported Wilkinson's Catalyst beads was prepared by 3.2 g of phosphinated beads (2.2 mmol of phosphine) with 3,22 g of Wilkinson's Catalyst (3.5 mmol) in 40 ml of benzene under argon for one month. Rinsing with benzene was carried out for four days. The beads were then vacuum dried.

Supported Wilkinson's Catalyst Batch E. Treatment of 20 g of 30-80 mesh, 2% DVB-styrene copolymer beads with 160 ml of $ClCH_2OCH_2CH_3$ and 4 g of $SnCl_4$ was carried out at room temperature, for a total of five hours. The liquid was drained off through a fritted filter, and 150 ml rinses of aqueous dioxane, aqueous dioxane plus 5% HCl, and dioxane (twice) were performed. Vacuum drying followed.

The entire batch of beads was treated with lithiodiphenylphosphide made from 2.8 g of lithium metal (400 mmol) and 17.6 g of chlorodiphenylphosphine (80 mmol) in 300 ml of

THF. This was stirred at reflux for one day, then cooled and hydrolyzed with 100 ml of saturated aqueous NH_4Cl after 100 ml of the reaction solution had been removed. After three hours, the aqueous solution was removed, and the following 150 ml rinses were performed:

1. 1:1 THF-H_2O
2. 1:1 THF-5% HCl
3. 1:1 THF-H_2O
4. 7:3 THF-H_2O
5. THF
6. 1:1 THF-benzene
7. Benzene
8. Benzene

The beads were then vacuum dried.

All of the phosphinated beads were then equilibrated with 13.2 g of Wilkinson's Catalyst in 350 ml of benzene for twelve days. They were then rinsed repeatedly with benzene over a two week period (at least two rinses each day). The deep-red beads were vacuum dried, and a sample was taken for elemental analysis.

Analysis: 82.90% C 6.71% H 3.30% P 1.39% Cl 3.43% Rh

This is 0.33 meq of rhodium per g of beads.

Benzyl-supported titanocene dichloride. Following the procedure developed by C. Gibbons,[15] a sample of beads with the benzyl-supported form of titanocene dichloride was prepared. A 12 g sample of 30-80 mesh 2% divinylbenzene-styrene copolymer beads was treated with 100 ml of $ClCH_2OCH_2CH_3$ and 3.5 g of $SnCl_4$ for five hours at ambient temperatures. The beads were then washed with aqueous dioxane containing ca. 5% HCl three times, aqueous dioxane

four times, and dry dioxane five times. Vacuum drying followed.

Sodium dispersion (1.1g, 48 meq) was allowed to react with 4 ml of freshly-distilled cyclopentadiene (50 mmol) in 150 ml of THF under argon. The chloromethylated beads were added and the solution was stirred for three days. To terminate the reaction, 20 ml of THF containing 2 ml of 10% HCl was injected with stirring. The solution was drained off and several more rinses were carried out, using a total of 400 ml of THF containing 10 ml of 10% HCl. Three more rinses with 100 ml aliquots of dry THFwere followed with vacuum drying.

The golden-yellow beads were suspended in 50 ml of THF and 25 ml of 2.4 M methyllithium in diethyl ether was added. The reaction was cooled in a dry ice-acetone bath for five hours and then the solvent was removed, followed by four 40 ml THF rinses. The beads were vacuum dried. $TiCpCl_3$ [40] (13.5 g, 60 mmol) was then added to the dry beads. Benzene (150 ml) was then added and the solution was stirred. The beads, which should have had ca. 10 meq of active sites, began to turn dark pink within ten minutes. The solution was drained after eighteen hours and six dioxane rinses were performed, followed by vacuum drying.

1-Phenyl-cyclopentene. This was synthesized in a model of the proposed reaction of Scheme 3 (page 8) before attempting the reaction on the polymer support.

To 5 ml of Eastman grade cyclopentanone dried over 4A molecular sieves in 10 ml of diethyl ether (4.75 g, 57 mmol) 40 ml of 1.6 M phenyllithium in diethyl ether (64 mmol) was added slowly over an hour, with stirring and cooling in an ice bath to maintain a solution temperature below 10°C. After fifteen minutes of further stirring, 20 ml of H_2O was added. The organic layer was separated, washed with saturated sodium chloride and aqueous NH_4Cl, and dried over anhydrous $MgSO_4$. The yellow solution was reduced to a volume of 5 ml on a rotary evaporator. Distillation gave a fraction collected at 230-240°C which weighed 0.5 g. Its NMR spectrum matched that reported for the title compound by Ketley and McClanahan:[41] 7.2-7.6 (m), 6.18(t), 2.3-2.8 (m), and 1.8-2.2 (m), area ratio = 5:1:4:2.

1-Phenyl-1,3-cyclopentadiene. A method similar to that reported by Riemschneider, et al., was used.[42] The title compound was synthesized as the second model for Scheme 3 (page 8) before applying the Scheme to the polymer support.

2-Cyclopentene-1-one was made via its ethylene glycol ketal according to the method of DePuy, et al.[43] The ketal was converted to the ketone by treatment with one equivalent of 0.02% aqueous oxalic acid, and was distilled just before use (b.p. = 150-155°C). The ketone's NMR spectrum consisted of multiplets at 7.85, 6.20, 2.70, and 2.35 with respective relative areas of 1:1:2:2.

Dropwise addition of 9 ml of 2-cyclopentene-1-one

(9 g, 0.11 mol) to 100 ml of 2 M phenyllithium in benzene (0.20 mol) was done over a fifteen minute period while the reaction was kept at less than 10°C in an ice bath. The solution was stirred for thirty minutes and then 50 ml of H_2O was slowly added to it. The benzene layer was separated and dried over molecular sieves overnight at 0°C.

Removal of the benzene on a rotary evaporator left a yellow viscous liquid which was distilled at aspirator vacuum. The fraction collected a 160°C (ca.1 g) closely matched the NMR spectrum expected for the dimer of 1-phenyl-1,3-cyclopentadiene, based on comparison to the spectrum of the dimer of cyclopentadiene itself. The spectrum consisted of multiplets at 7.5, 6.3, and 1-4 (areas 10:2:8). The mass spectrum had a very strong parent peak at m/e = 142 (calculated for 1-phenyl-1,3-cyclopentadiene is 142.08). Major peaks also occured at m/e = 141,115,40,44,41,39,57 and 69 (decreasing magnitude).

Riemschneider reported that 2-phenyl-1,3-cyclopentadiene formed when 2-hydroxy-2-phenyl-1,3-cyclopentadiene was distilled and rapidly rearranged to 1-phenyl-1,3-cyclopentadiene and dimerized.[42] The tendency of the product to yellow and harden in air which was reported was also observed.

Phenyl-supported titanocene dichloride. The first synthesis of the title system began with the bromination of 22 g of 20% DVB-styrene copolymer beads using 110 g $FeCl_3$ and 32 g of bromine (0.20 mol) in 200 ml of nitromethane. The reaction

was stirred in the dark and monitored by measuring its oxidizing ability. Periodically, 1.00 ±0.01 ml aliquots of the solution were removed and added to 1.7 g of KI in 25 ml of H_2O; the free I_2 formed was then titrated with standard $Na_2S_2O_3$ using a starch indicator.[33b] The reaction had ended after two days. The beads were then rinsed with 150 ml portions of:

1. 5% HCl
2. H_2O (twice)
3. 1:1 5% HCl-THF
4. 1:5 5% HCl-THF
5. THF (three times)

The polymer was then washed with THF in a soxhlet extractor overnight and vacuum dried. An elemental analysis was done.

Analysis: 67.92 % C 6.58 % H 25.34 % Br

This is 3.2 meq of bromide per g of beads.

A 26.3 g sample of the beads (84 meq bromide) in 25 ml of benzene was treated with 100 ml of 2.4 M butyllithium in hexane for four days. The beads were then washed with three 50 ml THF rinses and suspended in 40 ml of THF. As the suspension was stirred, 8.2 g of 2-cyclopentene-1-one (0.10 mol) was added. Stirring was continued for one day. The beads were then washed with 75 ml rinses of 1:1 benzene-ethanol, 1:1 benzene-1% ethanolic HCl, H_2O, and absolute ethanol (three times). The beads were then vacuum dried, followed by overnight extraction with dioxane in a soxhlet extractor. They were analyzed.

Analysis: 84.10 % C 7.82 % H 4.68 % Br

Thus, 0.6 meq of bromide per g of beads is still present.

The cyclopentadiene-containing polymer (10 g) was treated with 50 ml of 2.4 M methyllithium in diethyl ether with an additional 50 ml of diethyl ether added. The evolution of methane gas was monitored with a gas buret until it stopped, at which time ca. 700 ml of gas had been evolved (30 mmol). Three THF rinses were carried out, and the beads were then stirred with 11 g of $TiCpCl_3$ (50 mmol) in 125 ml of THF for twenty days. The beads were treated with THF in a soxhlet extractor for two days, vacuum dried, and analyzed for titanium content.[39]

Analysis: 0.058 meq of titanium per g of beads

These beads were used for all the phenyl-supported titanocene reactions reported in this thesis.

The second synthesis of the title system followed the same general pattern as the first synthesis, but with a new bromination procedure. 118 g of 20% DVB-styrene beads was brominated using 7 g BF_3 and 16 g bromine (0.10 mol of both) in 500 ml of nitromethane. The reaction was carried out for one day in the dark. At the end of the reaction period, ca. 5% of the beads floated at the top of the solution, while the remainder settled to the bottom. It was concluded that the less dense beads were unbrominated (and therefore less dense) so they were siphoned off and discarded. The remaining beads were rinsed with nitromethane, methanol, methylene chloride, and then vacuum dried.

Analysis: 85.54% C 7.62% H 6.78% Br

This is 0.8 meq of bromide per g of beads.

Treatment of 20.18 g of the brominated beads (17 meq of bromide) with 50 ml of 1.9 M butyllithium in hexane (95 mmol) and 100 ml of hexane was done for 36 hours. The resulting light tan beads were rinsed five times with THF and then 75 ml of THF was added to suspend the beads. Slow addition of 2.0 g of 2-cyclopentene-1-one (24 mmol) to the cooled solution produced an immediate change in the color of the beads to white, but they gradually yellowed during the three days of stirring which followed. Two wet THF rinses and seven dry THF rinses preceded vacuum drying of the beads with gentle heating (50°C). An analysis was run.

Analysis: 89.04 % C 7.90 % H less than 0.1 % Br

The entire 20 g batch of cyclopenteneone-treated beads was suspended in 100 ml of diethyl ether in a dry ice bath and treated with 50 ml of 0.8 M methyllithium in ether for three days. They were rinsed three times with diethyl ether and then vacuum dried. $TiCpCl_3$ (5.6 g, 0.025 mol) was added to the beads with 200 ml of benzene. This was stirred for three days, washed with three benzene rinses, and extracted with THF overnight in a soxhlet extractor. The vacuum dried beads were non-uniform dark red-pink in color. A titanium analysis was run on these beads also.[39]

Analysis: 0.546 meq of titanium per g of beads

The bromination using BF_3 seems to produce much more supported titanocene in the product, possibly because no residual iron salts are left on the polymer.

Hydrogenations

All solvents used were reagent grade, further purified and deoxygenated by refluxing and distillation under nitrogen with sodium (or potassium)-benzophenone in the distillation flask. Ethanol was dried, deoxygenated, and purified by distillation from sodium ethoxide and diethyl phthalate under nitrogen. Solvents were kept dry and oxygen-free by storage under nitrogen and transferal with syringes.

Wilkinson's Catalyst[11] was prepared from freshly recrystallized triphenylphosphine (Pressure Chemical Company) and $RhCl_3 \cdot 3H_2O$ (Engelhard Industries). Titanocene dichloride was used as purchased from Alfa Inorganics. Naphthalene was used as purchased from Eastman Kodak.

All of the liquid substrates were distilled from sodium under nitrogen, except for allyl alcohol, which was distilled from diallyl phthalate and sodium alloxide under nitrogen, and 1-hexyne, which was distilled from molecular sieves under nitrogen. Δ^2-cholestene was prepared from cholesterol by the method of Douglas, et al.,[44] while benzyl acetate was prepared from sodium acetate and benzyl chloride in dimethylformamide, a very simple and straightforward reaction. The 4-cholestene-3-one used was made by K. Patel.

The apparatus used, refered to below as "the hydrogenator", consisted of a normal atmospheric pressure hydrogenation apparatus, with gas burets of 250 or 50 ml used for volume measurements. The leveling bulb was placed so that at

any time except when volume readings were actually being made the system was operating at a slight negative pressure, thereby preventing leaks from giving false hydrogen uptake data. The process refered to as "hydrogen flushing" consisted of a minimum of three vacuum cycles of better than 5 torr vacuum with alternate hydrogen addition to remove virtually all oxygen from the system before solvent addition.

Two additions were made to the hydrogenator during the course of the research project: a temperature bath for the reaction flask, kept at 25 $\pm$0.5°C, and SAM. SAM was an automated hydrogen addition system, which replaced the buret-leveling bulb system of uptake measurement. SAM automatically allowed a fixed amount of gas to enter the system whenever a chosen partial vacuum was reached, giving an electric pulse with each aliquot. The pulse was fed to a strip-chart recorder, and thus gave a measure of the time at which each aliquot was introduced. Whenever SAM and/or the bath have been used, the specific expermental description mentions it.

Alkenes were purchased from Aldrich Chemical Co. and from Chemical Samples Co.; alkynes were purchased form Farchan Research Laboratories.

All reductions were stirred using magnetic stirrers with stir bars of the appropriate size in the reaction vessels.

The benzyl-supported titanocene catalyst beads used for hydrogenations were prepared by C. Gibbons[15] and W. Bonds and had 0.37 meq titanium per g of beads.[39]

Batch A supported Wilkinson's Catalyst hydrogenations. These were run in a Schlenk tube, using 3 ml of benzene which was injected after hydrogen flushing of the system. After thirty minutes of equilibration, 5 ml of cyclohoxene was injected and the hydrogen volume was measured over a four day period. The reduction rate was 0.046 ml of hydrogen per minute. The beads were then rinsed and dried under vacuum.

Batch B supported Wilkinson's Catalyst hydrogenations. These beads were also tested in a Schlenk tube. For the first trial, a solvent mixture of 30 ml of THF and 5 ml of benzene was injected into the Schlenk tube after hydrogen flushing. After thirty minutes, 0.5 ml of 1-hexene was injected and the hydrogen uptake was measured for twenty-seven hours. A reduction rate of 1.12 ml of hydrogen per minute was observed. The beads were then rinsed with THF and benzene and vacuum dried.

Reductions of 1.0±0.1 M initial concentrations of alkenes in benzene were carried out for cyclohexene, Δ^2-cholestene, and mixtures of the two olefins using 10 ml total solution volumes. Cyclohexene was observed to be reduced at 0.173 ml of hydrogen per minute, while 0.003 ml of hydrogen per minute was the steroid's rate. The beads were rinsed with benzene and vacuum dried between each use.

Batch C supported Wilkinson's Catalyst hydrogenations. All of the batch C beads were placed in a 100 ml Schlenk tube and connected to the hydrogenator. After hydrogen flushing,

benzene (10.5 ml) was injected into the tube via a septum in the sidearm. After ca. one hour of stirring under hydrogen, 1.2 ml of cyclohexene was injected (initial olefin concentration = 1.0 M). The hydrogen volume was monitored for several hours. The solvent was removed by syringe and the beads were vacuum dried. This reaction was repeated. The first reduction had a rate of 0.575 ml of hydrogen per minute; the second was 0.025 ml of hydrogen per minute.

Batch D supported Wilkinson's Catalyst hydrogenations. The entire batch was placed in a Schlenk tube and flushed with hydrogen after attachment to the hydrogenator and 9.5 ml of benzene was injected; after stirring for one hour, 1.0 ml of cyclohexene was injected and the hydrogen volume was measured with time until the reduction was complete. The beads were rinsed with benzene three times and vacuum dried.

After returning the Schlenk tube to the hydrogenator and hydrogen flushing, 5 ml of benzene was injected; 1.61 g of Δ^2-cholestene in 2 ml of benzene was injected after one hour (initial olefin concentration 0.7 M) and hydrogen volume vs. time readings were taken for two days. Cyclohexene (1.0 ml) was then injected, and the uptake rate was monitored for six more hours. The beads were rinsed with benzene and vacuum dried.

The entire batch was then transfered to a specially-designed 300 ml round-bottomed flask equipped with two sidearms. Both sidearms had stopcocks, with one having a fritted filter

where it met the flask wall. Thus all solution additions and removals were done without having to remove the flask from the hydrogenator.

The beads were used for the reduction of several alkenes, to determine the relative rates of reduction of each. All alkenes were at 1.0 ±0.1 M initial concentrations in benzene. Each alkene was injected into the beads already equilibrated under hydrogen for one hour, and hydrogen uptake was measured for at least two hours (results in Table 1, page 15). Cyclohexene was used as a reference, run before and after the reduction of every other alkene. Cyclohexene, 1-hexene, cyclododecene,[26] 1-octadecene, and cis-cyclooctene were reduced.

Batch E supported Wilkinson's Catalyst hydrogenations.

A 10 g sample of the beads was used in the same specially-designed flask which had been used for the Batch D beads, immersed in the 25°C bath. Reductions of 1-hexene, allyl alcohol, 4-pentene-1-ol, 3,5,5-trimethyl-1-hexene, cyclohexene, norbornene, and 1-dodecene were done. 1-hexene was used as the reference compound, reduced before and after each other alkene. The substrates were all reduced in benzene, using a total solution solution volume of 20 ml and initial olefin concentrations of 1.0 ±0.1 M. 1-hexene and 4-pentene-1-ol were also reduced in 1:1 benzene-ethanol, using the same volumes and substrate concentrations as used for plain benzene. The hydrogen uptake was measured every fifteen minutes for

the first 1.5-2.0 hours of the reduction. The results are in Table 2 (page 18).

Another series of reductions was done using the same reaction flask with only 2 g of beads and 10 ml total solution volumes. All of these measurements were done with the stirring bar's speed varied frequently during the course of the reduction and volume readings made every five minutes, to confirm that the rate of hydrogen diffusion into the solution was not a limiting factor in the relative rates measured. 1-hexene, cyclooctene, and cyclohexene were used in plain benzene and 1:1 benzene-ethanol for this reaction series, all at 1.0 $\pm$0.1 M initial concentrations, with the reduction flask in the 25°C water bath. The results of these reductions are in Table 3 (page 21).

Benzyl-supported titanocene hydrogenations. Following the general method of C. Gibbons,[15] a sample of benzyl-supported titanocene dichloride beads weighing 0.040 $\pm$0.003 g was weighed into a 100 ml sidearm round-bottomed flask. After attachment to the hydrogenator and hydrogen flushing, the beads were treated with 0.18 ml of 2 M butyllithium in hexane and 5 ml of hexane. After stirring for three hours, 0.5 ml of substrate was injected and hydrogen volume readings were taken every five to ten minutes for two to four hours. The substrates tested were 1,5-cyclooctadiene, 1,3-cyclooctadiene, 1-hexyne, 3-hexyne, benzyl acetate, vinyl acetate, styrene, and 4-cholestene-3-one. For the latter four, two 5 ml hexane

rinses were carried out before the substrate was tested in another 5 ml of hexane. The two cyclooctadiene and the 3-hexyne reductions were periodically monitored via gas chromatography (5', 20% NaCl on Silica Gel at 240°C) to see if intermediate monoolefins were present. The results are listed in Table 4 (p23).

One sample of the benzyl-supported titanocene dichloride beads was tested using sodium naphthalide as the reducing agent. For this test, the same procedure as followed above was used, except that 1 ml of 0.23 M sodium naphthalide in THF was added to the beads in 5ml of THF. After stirring for two hours, three 6 ml hexane rinses were carried out and 5 ml of hexane was added. After another hour, 0.5ml of 1-hexene was injected and the hydrogen volume was read for 3 hours. The rate observed was 0.45 ml of hydrogen per minute.

Another set of reductions was done with these beads, using SAM to monitor the reduction. 0.036 g of beads were treated with 1 ml of 2 M butyllithium in hexane and 5ml of hexane, and were then used to reduce 0.5 ml of cyclohexene after an hour. The reduction was monitored to completion. The same reduction procedure was repeated using 0.040 g of the beads which had been thoroughly ground in a mortar and pestle before use. The whole beads produced a rate of 88.7 ml of hydrogen per minute per meq of titanium; the ground beads produced one of 714 ml of hydrogen per minute per meq of titanium.

Bead regeneration. A 0.043 g sample of the benzyl-supported titanocene dichloride beads used above was weighed into a 100 ml sidearm round-bottomed flask, attached to the hydrogenator, and flushed with hydrogen; 5 ml of hexane and 0.13 ml of 2.2 M butyllithium in hexane was injected, stirred for 1.5 hours, and then 0.5 ml of 1-hexene was injected. The hydrogen volume was measured every five minutes for one hour after injection. The rate observed was 1.75 ml of hydrogen per minute.

The flask was removed from the hydrogenator, the solvent was removed, and 5 ml of absolute ethanol was added. The beads went from pale grey (active catalyst) to pale brown (inactivated catalyst) immediately. Dry HCl was then bubbled through the solution. The beads became pink in less than two minutes, the color they are before activation with a reducing agent. Four hexane rinses and vacuum drying were performed.

The HCl treated beads were now run through exactly the same cycle of hydrogenation which they had been run through on their initial use, with the same amounts of reagents and the time intervals as used earlier. The reduction was monitored for seventy minutes, at which time the reduction was complete. The rate observed was 1.82 ml of hydrogen per minute.

Phenyl-supported titanocene hydrogenations. A 0.036 g sample of the beads was placed in a 50 ml sidearm round-bottomed flask and attached to the hydrogenator. After hydrogen

flushing, 0.25 ml of 2.4 M butyllithium in hexane and 20 ml of hexane were injected. An hour later, two 10 ml hexane rinses were carried out. The beads were then stirred in 10 ml of hexane for 15 minutes, followed by the injection of 0.25 ml of cyclohexene. The hydrogen volume was measured every five minutes for an hour and then at two and 2.5 hours after injection. The beads were somewhat ground up during the course of the reduction. A rate of 106 ml of hydrogen per minute per meq of Ti was observed.

Wilkinson's Catalyst hydrogenations. A series of reductions were run using $RhCl(P\phi_3)_3$[11] at 2.4 ±0.1 mM concentration in benzene with alkene concentrations of 0.70 ±0.02 M initially. In each reduction, the dry catalyst was weighed into a 25 ml sidearm pear-shaped flask, attached to the hydrogenator, flushed with hydrogen, equilibrated with hydrogen in benzene for an hour, and then the substrate was injected. Hydrogen volume was monitored for at least four hours. The substrates used were Δ^2-cholestene, cyclohexene, cyclododecene,[26] 1-hexene, cyclooctene, and 1-octadecene. All except the steroid were reduced at least twice. The results are recorded in Table 1 (page 15).

Another series of reductions was performed, using 1.00 ±0.05 mM Wilkinson's Catalyst concentrations and 1.00 ±0.05 M initial olefin concentrations. Benzene was used as the solvent for reductions of 1-hexene, cyclohexene, cyclooctene, 1-dodecene, 3,5,5-trimethyl-1-hexene, allyl alcohol, norborene, and 4-pentene-1-ol; a mixture of equal volumes of

benzene and ethanol was used as a solvent for reductions of 1-hexeneand 4-pentene-1-ol as well. The results of all these reductions are recorded in Table 2 (page 18).

10% Palladium on Charcoal hydrogenations. A 0.187 g sample of 10% Palladium on Charcoal was weighed into a Schlenk tube, and 1.61 g of 80% Δ^2-cholestene (20% cholestane) was added. Benzene (5 ml) was added and the system was attached to the hydrogenator and flushed with hydrogen. The rate of hydrogen consumption was monitored until the reduction was complete. A reduction rate of 0.55 ml of hydrogen per minute had been observed; 0.7 ml of cyclohexene was now injected and its rate of hydrogenation was also measured. A rate of 1.30 ml of hydrogen per minute was observed for cyclohexene.

Homogeneous titanocene hydrogenations. A 0.0125 g sample of $TiCp_2Cl_2$ (50 mmol) was weighed out into a 100 ml sidearm round-bottomed flask, attached to the hydrogenator, and flushed with hydrogen; 1 ml of 2.0 M butyllithium was then injected, followed by 5 ml of hexane. This was stirred for thirty minutes, and then 0.5 ml of cyclohexene was added. The reduction was monitored using SAM, with the reaction vessel immersed in the 25°C bath. A rate of reduction of 28 ml of hydrogen per minute per meq of titanium was observed after an initial induction period of an hour which had a rate of 5.6 ml of hydrogen per minute per meq of titanium.

The reaction was rerun using 0.0145 g of $TiCp_2Cl_2$ (58 mmol); all other quantities and procedures were the same. A reduction rate of 28 ml of hydrogen per minute per meq titanium was again observed, as was an induction period of an hour.

Nitrogen Fixations

All solvents were dried and degassed by distillation from sodium (or potassium) and benzophenone under nitrogen.

Naphthalene was used as purchased from Eastman Kodak. $TiCp_2Cl_2$ was used as purchased from Alfa Inorganics. The nitrogen gas used was high purity dry nitrogen used as sold by Airco. All supported titanocene used was prepared by C. Gibbons and W. Bonds, with 0.86 meq of titanium per g of beads.

van Tamelin fixation using benzyl-supported titanocene. A 0.81 g sample of naphthalene (6.3 mmol) was reacted with 0.155 g of sodium metal (6.7 mmol) in 25 ml of THF in a Schlenk tube with a magnetic stir bar under argon for twelve hours; 1.305 g of beads (1.12 mmol of titanocene dichloride) was then added with an additional 10 ml THF. Nitrogen saturated with THF was then bubbled through the system into a gas washing tower filled with 100 ml of 20% H_2SO_4 for one day. The washing tower solution was then boiled down to 50 ml and a 10 ml sample of it was made basic with NaOH solution. This was tested with Nessler's Reagent[32] for the presence of ammonia. Wet litmus and odor tests were also done. No ammonia was detected.

The reaction was repeated, using 1.81 g of naphthalene (14 mmol), 0.65 g of sodium (28 mmol), 75 ml of THF, 0.252 g of $TiCp_2Cl_2$ (1 mmol) and 1.34 g of beads (1.15 mmol of titanium) with the same gas passage system. The 0.0838 N H_2SO_4 solution used in the washing tower was boiled down to 50 ml after passing nitrogen through the system for eight hours. After the addition of sufficient distilled water to bring the acid solution back to its original volume, it was titrated with 0.101 N NaOH using bromcresol green as the indicator; 41 ml of base was required, indicating no ammonia formation.

Vol'pin-Shur fixation using benzyl-supported titanocene. All fixations were done using 1000-1500 psi nitrogen in an autoclave previously flushed with nitrogen, at ambient temperatures with continual stirring during the pressurized period of the reaction. To 2.6 g of beads (2.2 mmol titanocene dichloride) put into the autoclave's glass insert before the autoclave was sealed 10 ml of 1.7 M phenyllithium in 7:3 benzene-diethyl ether (17 mmol) and 100 ml of diethyl ether were added. The system was pressurized and stirred for two days, then depressurized and acidified with 20 ml of absolute methanol and 20 ml of 20% H_2SO_4. After stirring the resulting solution for two hours in the autoclave, the solution was removed and boiled down to 25 ml. It was made basic with aqueous NaOH and tested for ammonia using Nessler's Reagent[32] and odor tests. The solution was also extracted with 2 ml of benzene and subjected to gas chromatography to detect any

aniline present (5' Carbowax at 150°C). No ammonia or aniline was detected.

The above reaction sequence was repeated using 2.7 g of beads (2.2 mmol) with 10 ml of 1.7 M phenyllithium (17 mmol) and 100 ml of diethyl ether. Analysis for ammonia and aniline consisted of steam distillation of the basified methanol-and-acid-treated reaction mixture into 4% boric acid.[33a] The boric acid solution was extracted with 2 ml of benzene and this extract was dried over NaOH and gas chromatographed using a durene standard to determine the amount of aniline formed. The boric acid solution was then titrated with 0.0482 M HCl using bromcresol green as the indicator to determine the amount of ammonia formed. A total of 0.40 ml of standard HCl was needed, indicating the formation of 0.02 mmol of NH_3; no aniline was detected.

The reaction was repeated a third time, using 0.60 g of $TiCp_2Cl_2$ (2.4 mmol), 2.47 g of beads (2.1 meq of titanium), 80 ml of diethyl ether, and 20 ml of 1.7 M phenyllithium (34 mmol). The same steam distillation, boric acid collection and HCl titration,[33a] and gas chromatography analysis procedures were used as in the previous reaction. The formation of 0.80 mmol of ammonia and 0.09 mmol of aniline were indicated by the analyses run.

van Tamelin fixation using homogeneous titanocene. A 0.54 g sample of $TiCp_2Cl_2$ (2.1 mmol) was placed in a Schlenk tube, capped with a septum, and flushed with argon. Addition of

120 ml of 0.1 M sodium naphthalide in THF obtained from W. Bonds was then performed and the reaction was stirred rapidly for ten minutes. A syringe needle was then inserted through the septum so that it entered the solution. Nitrogen passed through the needle could escape the Schlenk tube via the tube's sidearm, pass through a tube and into a gas washing tower filled with 120 ml of 20% H_2SO_4. After one day of nitrogen passage, the tower's contents were boiled down to 50 ml, cooled, and then a 5 ml sample was made basic with aqueous NaOH and tested for ammonia with Nessler's Reagent,[32] wet litmus, and by odor testing. Ammonia was detected.

Vol'pin-Shur fixation using homogeneous titanocene. The following procedure was used for repeated trials: while the assembled autoclave was flushed with nitrogen, 0.60±0.02g of $TiCp_2Cl_2$ (2.4 mmol) was weighed into a Schlenk tube and treated with 8 ml of 1.7 M phenyllithium (13.6 mmol) and 100 ml of diethyl ether under argon; this was stirred for one hour and then transfered to the autoclave using a syringe. The autoclave was pressurized to 1200-1500 psi nitrogen for two to three days. After release of the pressure, the system was worked up with 20 ml of absolute methanol and 20 ml of 20% H_2SO_4, which was stirred for thirty minutes after addition. The solution was then removed and boiled down to 20 ml. It was then made basic and analyzed for ammonia. Three runs were analyzed using Nessler's Reagent.[32] Ammonia was present

in all three runs. Two more runs were done, using the Kjeldahl method of quantitative ammonia analysis.[33a] A last run was made using 20 ml of phenyllithium solution. The results are recorded in Table 5 (page 30).

A blank was run to test the Kjeldahl method's steam distillation-boric acid collection system for background base levels. The usual reaction sequence and quantities of reagents were used, but the system was never exposed to nitrogen. The analysis indicated the presence of 0.01 mmol of ammonia (0.20 ml of 0.0482 M HCl were required for titration of the boric acid solution). No aniline was indicated by gas chromatographic testing.

Chelation Studies

$[RhCl(COE)_2]_2$ studies. All analyses were done using either a 5', 5 % SE-30 on Chromosorb W gas chromatography column at 125°C or a 5', 3 % SE-30 on Varaport-30 column at 120°C. The latter was slightly better. For each analysis, 0.5 ml of the solution was withdrawn from the reaction flask and passed through a one inch column of alumina in a disposable pipet tube to remove the complex from solution, leaving only free COE. All solvents were dry and oxygen-free, and all reactions were carried out under nitrogen or argon.

Some phosphinated 20 % DVB beads were prepared for equilibration studies by reacting them with lithiodiphenylphosphide made from 7.5 ml of chlorodiphenylphosphine (40 mmol) and 1.5 g of lithium metal (210 mmol) in 250 ml of THF. The

beads used (20.0 g) had already been chloromethylated by C. Gibbons, who determined that they contained 1.03 meq of chloride per g of beads.[24] After phosphination, less than 5 % of the original chloride was still present, meaning a maximum phosphine content of ca. 0.9 mmol per g of beads.

To 7.64 g of the above phosphinated beads (6.8 mmol of phosphine) in a Schlenk tube, 1.01 g of $[RhCl(COE)_2]_2$ (1.41 mmol, 5.64 mmol of COE) and 0.298 g of durene were added. The solution was stirred and sampled at two hours, one day, and nineteen days after the addition of solvent. The free COE detected was 2.45, 2.90, and 2.10 mmol at the respective sampling times. The solution was removed from the beads after the last sample and three 5 ml benzene washes were performed. The rinses were added to the solution removed earlier and the entire benzene solution was treated with 0.925 g of triphenylphosphine (3.5 mmol) to release COE from any of the complex which might still be in solution. The triphenylphosphine-treated liquid was then analyzed for free COE; 2.25 mmol was detected. The beads were further rinsed and then vacuum dried. A 0.2159 g sample of the dried reddish beads was treated with 0.0434 g of triphenylphosphine (0.166 mmol) and 0.0200 g of durene under nitrogen in 3 ml of benzene for three hours, then sampled for free COE content. Gas chromatographic analysis indicated 0.07 mmol of free COE was present. Another sample weighing 0.2073 g was treated with 0.0392 g of triphenylphosphine (0.150 mmol) and 0.0129 g of durene in 5 ml of benzene under hydrogen and analyzed for

cyclooctane after one and five hours. After one hour, 0.06 mmol of cyclooctane was detected; at five hours, 0.08 mmol was present.

A sample of 2% Divinylbenzene-styrene copolymer beads phosphinated by E. Sweet having at least 0.8 mmol of phosphine per g of beads were also tested for chelation, with another sample of the 20% cross-linked beads used above. A blank sample and two samples using triphenylphosphine were also used, as follows:

Sample	g Durene	$[RhCl(COE)_2]_2$ g	$[RhCl(COE)_2]_2$ mmol	Phosphine Component form	Phosphine Component g
1	0.0161	0.0870	0.121	2% beads	0.8292
2	0.0199	0.0954	0.133	2% beads	1.0697
3	0.0208	0.0795	0.111	20% beads	0.7129
4	0.0064	0.0350	0.049	-- none --	
5	0.0101	0.0390	0.054	$P\emptyset_3$	0.0708
6	0.0144	0.0447	0.062	$P\emptyset_3$	0.1294

Each sample was treated with benzene after flushing with argon; 3 ml was used for samples 1-3 and 1 ml for samples 4-6. The samples were stored under argon, periodically shaken, and analyzed after 7 hours for samples 4-6 and after one day for samples 1-3. The results are listed in Table 6 (page 36).

Two more reference reactions were run, using triphenylphosphine and $[RhCl(COE)_2]_2$ in 1.5 ml of benzene under argon. Sample 1' used 0.0152 g durene, 0.1020 g $[RhCl(COE)_2]_2$ (0.142 mmol), and 0.0571 g $P\emptyset_3$. Sample 2' used 0.0148 g durene, 0.0875 g $[RhCl(COE)_2]_2$ (0.122 mmol), and 0.0685 g $P\emptyset_3$. These were stirred for twelve hours under argon and then sampled

for COE. See Table 6 (page 36) for the results.

Another sample of phosphinated beads was prepared by treatment of 20 g of brominated 20% Divinylbenzene-styrene copolymer beads (16 mmol of bromide) with 40 ml of 2.2 M butyllithium in hexane under nitrogen for one day, followed by four 50 ml THF rinses and treatment with 1.7 g of chlorodiphenylphosphine (7.7 mmol) in 75 ml of THF for twelve hours. These beads were then rinsed with 50 ml aliquots of: 1) Saturated aqueous NH_4Cl (twice) 2) Water (twice) 3) 1:1 THF-water 4) 2:1 THF-water 5) THF (four times) followed by vacuum drying. They were then used in the following experiment:

Sample	g Durene	$[RhCl(COE)_2]_2$ g	mmol	Phosphine Component form	g
1	0.0202	0.1759	0.245	$P\emptyset_3$	0.0577
2	0.0301	0.1423	0.198	$P\emptyset_3$	0.1466
3	0.0345	0.1540	0.236	beads	5.0
4	0.0220	0.1425	0.198	beads	3.8

10 ml toluene was added to each flask after nitrogen flushing and analyses were carried out after three and fifty hours. The results are listed in Table 7 (page 38).

$RhCl(CO)(P\emptyset_3)_2$ studies. A 15 g sample of 20% Divinylbenzene-styrene copolymer beads was treated with 100 ml chloromethyl-ethyl ether and 4 g of stannic chloride for five hours, then washed with dioxane-5% HCl three times, aqueous dioxane twice, and soxhlet extracted overnight with dry dioxane. These were then treated with lithiodiphenylphosphide[10] made from 1.40 g of lithium metal clippings (0.20 mol) and 8.0 ml of chlorodiphenylphosphine (0.04 mol) in 100 ml of THF under nitrogen

for two days and then worked up with deoxygenated solutions (100 ml each) of: 1) Saturated aqueous NH_4Cl, 2) Water (twice), 3) 1:1 Water-THF, 4) 1:2 Water-THF, 5) THF (four times). They were vacuum dried for two days and analyzed.

Analysis: 87.82 % C 7.36 % H 3.82 % P 1.04 % Cl

This is 1.25 mmol of phosphine per g of beads. This batch of beads was used for the following chelation study:

Sample	g Tetracosane	Phosphine g	Phosphine form	$RhCl(CO)(P\phi_3)_2$ g	$RhCl(CO)(P\phi_3)_2$ mmol[45]
1	0.0482	0.0648	$P\phi_3$	0.3046	0.441
2	0.0487	4.8	beads	0.1777	0.257
3	0.0929	8.2	beads	0.1954	0.283

Each sample was placed in a vial which was sealed and flushed with nitrogen; 20 ml of benzene was added to samples 1 and 2 and 25 ml of benzene was added to sample 3. The vials were then sampled (0.5 ml each time) for gas chromatography on a 9" 6% SE-30 on Chromosorb W column at 190°C. Analyses were performed at 1, 15, 40, 65, 90, 140, and 165 hours after solvent addition. A sample of the solution in vial 2 was taken at 175 hours and analyzed before and after passage through a one inch alumina column to remove any $RhCl(CO)(P\phi_3)_2$ in solution. The same test was done with the sample 3 solution after 216 hours of elapsed time. The results of all the analyses of this system are given in Table 8 (page 41).

The beads of sample 3 were washed with benzene, vacuum dried, and submitted for elemental analysis.

Analysis: 87.33 %C 7.33 %H 3.81 %P 0.70 %Cl 0.44 %Rh

The analysis indicates the presence of 1.23 mmol of phosphine and 0.043 meq of rhodium per g of beads.

A test of the amount of triphenylphosphine freed by the Vaska complex on injection into the gas chromatograph was performed. A solution of 0.0174 g of Vaska complex, $RhCl(CO)(P\phi_3)_2$ (0.0252 mmol, 0.0504 mmol of triphenylphosphine) and 0.0122 g of triphenylphosphine (0.0466 mmol) was prepared. Toluene (20 ml) and a standard (tetracosane, 0.0118 g) were added and the closed system was stirred under nitrogen. Gas chromatographic analysis was carried out on the solution after one and three days (9" SE-30 column at 190°C). For both analyses, the solution was analyzed with and without passage through a one inch column of alumina in a disposable pipet tube. The alumina removed all of the Vaska complex from solution, but allowed free passage of triphenylphosphine in solution. The one day sample analysis indicated the presence of 0.097 mmol of triphenylphosphine before alumina treatment and 0.044 mmol of triphenylphosphine after alumina; the three day sample analysis indicated the presence of 0.094 mmol of triphenylphosphine before alumina treatment and 0.047 mmol of triphenylphosphine after alumina. All of the above are $\pm$ 0.005 mmol of triphenylphosphine. The results seem to clearly indicate that all of the triphenylphosphine on the rhodium Vaska complex is lost on injection into the gas chromatograph, and is detected and measured accurately.

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