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Title: **Reactivity of Metal Ions Bound to Water-Soluble Polymers**

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Reactivity of Metal Ions Bound to Water-Soluble Polymers

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Abstract

The intent of this work is to determine the effectiveness of catalysts covalently bound to polymers and to understand the consequences of supporting the catalysts on catalyst efficiency and selectivity. Rhodium phosphine complexes with functional groups for coupling to polymers were prepared. These catalyst precursors were characterized using standard techniques including IR, NMR, and elemental analysis. Studies on the modified catalysts showed that they were still active hydrogenation catalysts. However, tethering of the catalysts to polyamines gave systems with low hydrogenation activity. Analogous biphasic systems were also explored. Phosphine ligands with a surfactant-like structure have been synthesized and used to prepare catalytically active complexes of palladium. The palladium complexes were utilized in Heck-type coupling reactions (e.g. coupling of iodobenzene and ethyl acrylate to produce ethyl cinnamate) under vigorously stirred biphasic reaction conditions, and were found to offer superior performance over a standard water-soluble palladium catalyst under analogous conditions.

Background and Research Objectives

Catalysis plays an ever more important role in U.S. industry as pressure to produce cleaner and cheaper materials grows. Heterogeneous catalysts currently dominate the field of large-scale industrial chemical synthesis. In contrast, commercial applications of homogeneous catalysts are rare. While homogenous systems typically operate at relatively mild temperatures and exhibit activities and selectivities unknown for their heterogeneous counterparts, it has long been recognized that many homogeneous reactions are not commercially viable because of problems associated with the separation, recovery and re-use of the highly expensive catalysts. In addition, reactions with homogeneous catalysts are generally carried out in organic solvents, which present problems of flammability, toxicity and significant cost. Two primary problems must be addressed before homogeneous catalysis gains widespread acceptance within the chemical industry. The catalyst must be able to be quickly separated from the product at the end of the reaction and subsequently reused, and organic solvents must be replaced with more environmentally benign solvent systems such as water. The goal of our research has been to

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chemical industry. The catalyst must be able to be quickly separated from the product at the end of the reaction and subsequently reused, and organic solvents must be replaced with more environmentally benign solvent systems such as water. The goal of our research has been to develop novel catalytic systems to overcome *both* of these problems by incorporating the catalysts into water-soluble or miscible supports to enable the ready separation of the catalysts from the reaction products and replacement of traditional organic solvents.

The concept of tethering catalysts to overcome both catalyst loss and separations problems has been evaluated. Generally, these efforts have focused upon the immobilization of organometallic species responsible for catalysis on solid supports. There have been many reports of "heterogenization" of homogeneous catalysts by coupling them to silica, alumina and polystyrene.[1] While these systems do deter catalyst loss and improve product separation (recovery), they are less desirable from a chemical standpoint. The act of supporting these catalysts on a heterogeneous substrate often has a deleterious effect upon their performance: tethering of the catalyst on a rigid support limits reactions rates, and renders the catalyst less efficient. As a result, the performance of such heterogeneous catalysts only approximates those of their homogeneous counterparts.

Proposed concepts for the replacement of organic solvents have focused primarily upon the use of water-soluble catalysts, most commonly those bearing sulfonated triarylphosphine ligands, and this field has attracted considerable interest in recent years. Water-soluble catalysts are often used to carry out reactions in aqueous solution on water-soluble substrates such as carboxylic acids and alcohols. This procedure avoids the use of organic solvents, but does suffer from several drawbacks: (i) catalyst recycle is hampered by the fact that catalyst, substrate and product(s) are all water-soluble; (ii) the number of water-soluble organic substrates is limited. Current industrial applications of water-soluble catalysts are limited to substrates that have significant water solubility. Thus Rhône-Poulenc currently operates a water-soluble catalyst-based process for the hydroformylation of propene to butanal on a 330,000 tons/yr. scale. The process cannot be extended to longer chain olefins due to their negligible solubility in water, and consequential mass-transport limitations on reaction rates as the substrates have to cross a phase boundary.[2] Clearly systems that maintain catalyst separability, but allow for high miscibility with organic reactants, would be a significant breakthrough for homogeneous catalysis.

The objective of this research was to demonstrate techniques for covalently coupling well-defined molecular catalysts to water-soluble polymers and to evaluate the resulting systems for catalytic activity in aqueous and biphasic systems. In addition, we sought to examine the potential for these systems to form active metal binding pockets similar to those seen in enzymatic systems. The practical goal is to provide economically feasible and "environmentally

green" catalysts in which the selectivity and activity can be controlled through modification of the polymeric support. The scientific goal is to understand the reactivity of the metal center in these macromolecular systems and to understand and control the effect that the polymeric matrix has on the active site. In this sense, the approach is analogous to bioinorganic chemistry which seeks to understand the intrinsic reactivity of metals within biological systems and define the role the protein matrix has in altering and controlling that chemistry. A key feature of this approach is that the molecular chemistry of the active catalyst is well defined so the effect of tethering to a macromolecule and subsequent modifications to the polymer can be readily evaluated.

This approach has several additional advantages. First, the polymeric support will impart aqueous solubility to catalysts generally attainable only in organic systems, thus expanding the range of catalysts that can be used in aqueous or biphasic systems and eliminating the need for hazardous solvents. In addition, the macromolecular nature of the polymers will mitigate loss of precious metal catalysts *while retaining the advantages of homogeneous systems*. This will greatly reduce the economic constraints on catalyst composition and allow for the substitution of more active and efficient species based on rhodium, iridium and ruthenium for those utilizing the base metals such as nickel and cobalt. Of particular importance to the success of this approach is that the selectivity of these systems can be controlled by altering the physical properties of the polymer. The hydrophobicity and thus the solubility of reactants in these systems can be varied through polymer modification. As part of this facet of the work, we examined the reactivity of supported catalysts in biphasic solvent systems.

In liquid-liquid biphasic systems the catalytic complex remains in one phase while the products remain separated in a second, immiscible phase. Our concept is to employ novel micelle-forming catalysts which, because of their hydrophilic segments, can partition into and be "supported" by the aqueous phase of a biphasic water/organic system. The catalytically active, metal-containing portions of the catalyst structure will be oriented directly into the bulk organic (reactant) phase. The goals of this aspect of our research were twofold: To prepare effective active catalysts which will adopt micelle structures that are, in effect, "supported" in the aqueous phase; and to replace organic solvents with a biphasic system containing the organic reactants and an aqueous phase which contains the catalyst.

Importance to LANL's Science and Technology Base and National R&D Needs

We believe that this work demonstrates that the field of aqueous catalysis can be extended to include macromolecular materials with superior catalytic and physical properties. This will have tremendous implications in industrial processes, open a new avenue to "environmentally green" production and encourage collaboration with industrial partners. The research program will also elucidate the chemistry of transformations occurring within macromolecular

environments. Through systematically modifying the polymeric framework around the catalytic site, effects of hydrophobicity, dielectric strength and hydrogen bonding on the catalytic reactivity can be studied without modifying the actual catalytic unit.

Scientific Approach and Accomplishments

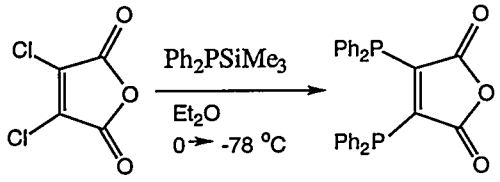
I. Water-Soluble Polymers as Carriers for Homogeneous Catalysts

Well-defined molecular catalysts have been covalently linked to soluble polymers and their physical and catalytic activity in aqueous, organic and biphasic systems evaluated. To demonstrate the reactivity of soluble supported metal centers, we devised methods to prepare phosphine-functionalized polymers for incorporation of catalytically active metals into our soluble polymer systems. This work focused on well defined and active catalysts in aqueous systems: rhodium phosphine hydrogenation catalysts.[3] These catalysts are generally prepared by the addition of a diphosphine ligand to a dimeric rhodium diene species to form the four coordinate catalytic species, **I**. A large number of diphosphine ligands have been used with

$$[Rh(diene)Cl]_2 + 2\ \text{diphosphine} \longrightarrow 2\ \underset{\mathbf{I}}{[Rh(diene)(diphosphine)]^+}\ Cl^-$$

surprisingly little effect on the efficacy of the hydrogenation reaction. In the course of this research project, four chelating phosphine systems were prepared which would allow for direct coupling of the diphosphines to polymeric systems. Prior to incorporation into the soluble support, the rhodium complex of each phosphine was prepared and the catalytic activity fully characterized. It is important to have this data as a base for which to evaluate the success of catalysts that are incorporated into the selected polymers. In addition, data such as this is invaluable in understanding the chemical and reactivity changes that could occur when any catalyst is coupled to a soluble support.

Synthesis of diphosphine ligands. The water-soluble polymers chosen as supports for soluble catalysts are polyamines. The three selected for study were linear polyvinyl amine, the spherical dendrimer Starburst PAMAM generation 4, and a polymer with irregular structure, polyethylenimine. Figure 1 shows the chemical structure of these polymer systems. All have active primary amines to which the catalyst species can be attached via strong amide linkages. The first system explored was 2,3-(diphenyl phosphino)maleic anhydride (PMA). This ligand effectively binds metals without destroying the anhydride moiety.[5] Subsequent reaction of the ligand with monomeric or polymeric amines gives an amide linkage. The result is a series of complexes, which serve as models for catalysts bound to polymeric supports. **Scheme 1** shows the formation of the new



rhodium diphosphine hydrogenation catalyst and the subsequent reaction of this ligand with both molecular and polyamines. During the course of this work a complex with an additional coordinated triphenylphosphine (PPh_3) was also prepared. This 5-coordinate Rh species was of interest for catalytic studies as well. The proposed mechanism for olefin hydrogenation requires that both olefin and hydrogen are bound to the catalytic metal center. The presence of an additional PPh_3 ligand should inhibit this reaction and give lower conversion rates of olefin. Addition of nucleophiles, ethanol and ethylenediamine proceeded cleanly to ring-opened products analogous to those which would be formed when the catalysts were reacted with polymeric species. Catalytic studies of all these species were done to establish conditions for attaching the rhodium complexes to the polymers and to determine the intrinsic reactivity of the metal center so that comparisons to the polymeric systems can be made.

Two other chelating phosphines were prepared as part of this study. They were also designed for facile coupling to polymeric systems. Figure 2 shows the structures of the diphosphines, PPR (2-hydroxy-1,3-bisdiphenyl-phosphinopropane) and PEA (N,N, bis-(diphenylphosphine-ethylacetamide). Complexes of these ligands with the starting rhodium catalyst were prepared analogously to the Rh-(PMA) complex as shown in Figure 3 with the PPR ligand. All complexes were fully characterized by using standard inorganic techniques (NMR, IR, and Elemental Analysis) prior to initiating baseline catalytic studies.

A third method for incorporating phosphines into polymeric supports was also examined. This route relied on modification of the polymer backbone and attachment of the phosphine directly to the linker. One example of this approach is a two-step process that uses (dimethylamino)-diphenylphosphine [$N(CH_3)_2PPh_2$] as a phosphorus source. This procedure was modeled after a literature preparation and involves addition of an alcohol functionality to several polyamines, **P**. Several other routes to phosphine incorporation into soluble polymers were also demonstrated. Unfortunately, while phosphine ligands were incorporated into polymers using this type of method, reaction of the polymeric species with rhodium catalyst precursors gave unresolvable mixtures of catalysts by phosphorus NMR. Given the heterogeneous nature of the product, no catalytic studies with this material were initiated.

$$\mathbf{P}\text{-}CH_2CH_2NH_2 + BrCH_2CH_2OH \longrightarrow \mathbf{P}\text{-}CH_2CH_2NH\text{-}CH_2CH_2OH + HBr$$

$$\mathbf{P}\text{-}CH_2CH_2NH\text{-}CH_2CH_2OH + N(CH_3)_2PPh_2 \longrightarrow \mathbf{P}\text{-}CH_2CH_2NH\text{-}CH_2CH_2O\text{-}PPh_2 + HN(CH_3)_{2(g)}$$

To prepare polymer tethered catalysts, Rh(NBD)(PMA) was reacted with PAMAM generation 4.0 dendrimer. ^{31}P NMR confirmed that the catalyst was bound to the support.

Catalytic Studies. Hydrogenation reactions using each of the untethered catalysts were done at room temperature under an atmosphere of hydrogen using a 500:1 substrate (1-octene) to catalyst ratio with acetone as the solvent. Reaction products and product distributions were followed by Gas Chromatography (GC) or GC-Mass Spectroscopy. Table 1 shows the first order reaction rates for both the hydrogenation and isomerization reactions for the unsupported complexes. For comparison, we also measured rates for $Rh(NBD)(PPh_3)_2$ that is one of the most stable and active homogeneous rhodium hydrogenation catalysts reported in the literature.[3] The electronic and steric structure of catalysts can be quite important in catalytic hydrogenation. Comparison to the simple triphenylphosphine complex allows us to directly evaluate if our phosphine ligands modified for coupling to polymers negatively impacted catalytic hydrogenation. As seen in Table 1, there was some variation in both hydrogenation and isomerization rates for the new catalysts. Notable is the Rh(NBD)(PPR) complex which has

Table 1. Hydrogenation and isomerization rates for rhodium catalysts as ClO_4^- salts.

Catalyst	**$k_1(s^{-1})$ Hydrogenation**	**$k_2(s^{-1})$ Isomerization**
$Rh(NBD)(PPh_3)_2$	16.0	90.2
Rh(NBD)(PMA)	2.0	2.5
$Rh(NBD)(PMA)(PPh_3)$	0.5	0.9
Rh(NBD)(PMAET)	2.4	6.9
Rh(NBD)(PPR)	17.2	13.4
Rh(NBD)(PEA)	1.3	1.7

hydrogenation rates that are slightly higher than those observed for the $Rh(NBD)(PPh_3)_2$, and with much higher selectivity against the undesired isomerization products. It is interesting to note that both catalysts with the PMA ligand (ring intact or ring opened) were less effective hydrogenation catalysts. Clearly, electronic factors are strongly effecting catalyst reactivity. Another interesting feature of our systems was the generally lower substrate isomerization rate. For the baseline catalyst, isomerization occurred at a much higher rate (5 times faster) than did

hydrogenation. For our catalysts, the isomerization and hydrogenation rates were quite similar. One possible explanation of this result is that the modified phosphine ligands have larger steric requirements around the Rh center, making rearrangement of the olefin less favored.

As anticipated, the 5-coordinate rhodium PMA catalyst with the additional triphenyl phosphine, Rh(NBD)(PMA)(PPh_3), was much less reactive than all other catalysts evaluated. In order to understand this rate change, the NMR spectra of the catalyst with H_2 was obtained. The ^1H and ^{31}P spectra indicate a structure where the chelating phosphine is trans to or opposite of the coordinated hydride. Normally, the position trans to the hydride would be labile, allowing substrate access to the coordination sphere. The presence of the additional phosphine in the rhodium coordination sphere does not allow this, hence the observed reduced reaction rates for this species.

Hydrogenation studies were also undertaken for tethered catalyst systems. Unfortunately, attempts to perform hydrogenations under the conditions used for the untethered systems were of limited success. It was concluded that the catalytically active metal, Rh, was no longer bound to the phosphine ligands. It is possible that the multiple amine sites on the polymer assist in the release of Rh from the active site. Continuing studies in this area should focus on polymers that do not have competing binding sites for Rh. During the course of this work, Andersson and Malmstrom reported the formation and catalytic properties of Rh complexes bound to water-soluble polymers.[4] This system, while fully characterized, was also not suitable for catalytic studies. Given this, efforts were focused on the development of biphasic catalysts.

II. Biphasic Catalysis

The ability of the catalyst to adopt a micellar structure serves a number of purposes. While the micelle itself is held together by both hydrophilic and hydrophobic forces, the catalyst segment at the end of the alkyl chain is still free to take up a configuration that is most favorable to the reaction. Thus, when compared to a solid-supported catalyst, micellar catalysts exhibit the characteristic features of homogeneous catalysts, high reactivity, selectivity and reproducibility under mild conditions. An additional benefit of this type of catalyst results from the volume of information available concerning the physical and chemical properties of surfactants and micelles, which makes it relatively straightforward to tailor the properties of the ligand to those desired for a particular application. Despite this, very little work has been carried out using surfactant-like ligands in biphasic catalysis systems.[6] Some reported catalyst systems have a structure that renders them surfactant-like, but they are still found to be rather easily extracted into the organic phase and then behave like a standard organic-soluble catalyst system.

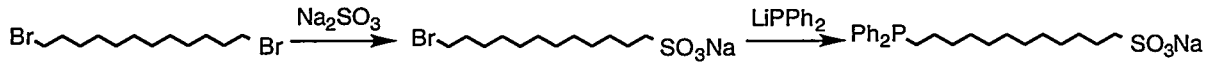
Consider the preparation of a hydrogenation catalyst coordinated by surfactant-like phosphine ligands, which may be represented schematically as shown in Figure 4. When such a

catalyst is placed into a stirred, biphasic reaction system where water and an organic compound serve as solvents (in which $Volume_{org.\ phase} > Volume_{aq.\ phase}$), it would be expected to promote the formation of reversed micelles, *i.e.* very finely dispersed aqueous droplets in a bulk organic phase. The ionic head-group of the surfactant ligand would be expected to be oriented into the aqueous phase. The hydrophobic (catalytically active) tail of the molecule will be oriented directly into the bulk organic (reactant) phase and will thus come into intimate contact with the reactants without the need for any crossing of phase boundaries.

Although we have shown idealized spherical micelle structures in the figures, geometric packing requirements of the irregularly shaped surfactant-like ligands may lead to ellipsoidal, disk-shaped and rod-like structures, which are the more commonly encountered micelle shapes. At the conclusion of the reaction, stirring is stopped and the emulsion breaks into two phases. The catalyst-containing aqueous phase may be decanted and re-used, while the organic phase will contain only product(s) with no organic solvents to be removed. Thus we will have addressed two of the most fundamental problems that have prevented homogeneous catalysis from gaining wide acceptance and usage within the chemical industry.

Typically, micelle formation in aqueous solution is promoted by molecules that contain a long-chain (>10 carbon atom) hydrophobic alkyl group, and a hydrophilic, ionic head-group (such as tetraalkyl ammonium or sulfonate) at one end. Micelle formation may also be promoted by neutral molecules that possess a long-chain alkyl group in combination with a hydrophilic segment such as a hydroxyl-terminated polyethylene glycol.

We have investigated synthetic methods for the preparation of surface-active phosphine ligands and performed some preliminary experiments in this area. Treatment of 1,12-dibromododecane with sodium sulfite in water/ethanol leads to the formation of the mono-sulfonate species, which may be treated with an equivalent of lithium diphenylphosphide to produce the surface-active phosphine as shown below. This ligand may be complexed with palladium *via* reaction with $PdCl_2(PhCN)_2$ in THF solvent.



The resulting complex was found to be water soluble and to carry out biphasic catalysis much more efficiently than analogous water-soluble palladium catalysts bearing TPPTS ($P(C_6H_4\text{-}m\text{-}SO_3Na)_3$) ligands. Thus in a trial reaction, the surfactant-like palladium catalyst $PdCl_2[Ph_2P(CH_2)_{12}SO_3Na]_2$ was added to a vigorously stirred biphasic mixture containing water, iodobenzene, ethyl acrylate and triethylamine (substrate:catalyst ratio = 125:1). After 3 hours at 80 °C, ^1H NMR analysis of the product layer (which may be obtained simply by

decanting it away from the aqueous phase) showed conversion to trans-ethyl cinnamate in a yield of 32% (Figure 5). An identical reaction was then performed using a standard water-soluble catalyst $PdCl_2[P(C_6H_4\text{-m-}SO_3Na)_3]_3$. In this case the yield of trans-ethyl cinnamate was 2%, owing to the fact that either catalyst or reactants have to cross a phase boundary in order to undergo reaction. Although the reaction takes place under conditions of vigorous stirring the reaction mixture phases separate cleanly after stirring is halted.

Similar palladium-catalyzed coupling reactions were also performed using different substrates. In the case of phenylacetylene and iodobenzene, the coupling product diphenylacetylene was obtained in 75% yield after 4 hours of stirring at ambient temperature (Figure 6). The catalyst:substrate ratio was 1:170, and once again the product was separated from the aqueous phase by simple decantation.

The catalyst also performed well in the coupling of aryl halides with olefins. Thus using a catalyst:substrate ratio of 1:140, styrene was coupled with iodobenzene to form a 4:1 mixture of *trans*-stilbene and diphenylethylene in 72 % overall yield after 90 h at 80 °C (Figure 7). Coupling of iodobenzene with the activated olefin 3,4-dihydropyran also occurred over a period of 90 h at 80° C in 33% yield (Figure 8).

This initial investigation into biphasic catalysis has demonstrated the efficacy of this technique for homogeneous catalysis. Future work in this area will include the design and synthesis of a range of surfactant-like phosphine ligands bearing both ionic and non-ionic hydrophilic groups, and the formation of rhodium- and palladium-based catalyst systems incorporating these ligands.

III. Binding Pockets for Anions: Mimics for Enzyme Binding Sites

A new area of interest in the area of homogeneous catalysis and metal ion reactivity is synthetic analogs for enzyme active sites. The final aspect of this study on reactivity of metal ions bound to soluble polymers incorporated this concept by trying to understand if systems based on water-soluble polymers could be organized to form pockets for binding specific substrates. We chose to investigate the binding of metal oxyanions to modified star-burst dendrimers because this requires organization to maximize electrostatic and hydrogen bonds rather than formation of coordinate covalent bonds. These studies have been summarized for publication, so the treatment of the work within this report will be brief.

A series of modified dendrimers with hydrogen bonding groups were synthesized. These molecules, along with the parent PAMAM 4.0 compound, bind arsenate, chromate, and phosphate even in the presence of competing anions such as chloride. Selectivity is achieved through bringing together moieties with a combination of electrostatic and hydrogen bonding capabilities. These interactions are analogous to the binding types that allow high specificity in

anion binding in enzyme systems.[7] In order to maintain structural control to enhance selectivity, more rigid polymeric dendrimers were selected for initial examination. Starburst PAMAM dendrimer generation 4.0, which is based on a *N*-(ethylamino)-propionamide repeating unit ($CH_2CH_2CONHCH_2HC_2NH_2$), was chosen as our base molecule for several reasons. The net positive charge of the dendrimer backbone provides an electrostatic attraction for anion binding. The 64 primary amine sites on the generation 4.0 dendrimer are easily modified, and the dendrimer is large enough (14K MW) to be retained by an ultrafiltration membrane. As shown in Figure 9, the dendrimer was modified with different ligands to provide three types of hydrogen bonding interactions with anions. In PAMAM-OH, 18% of these amines were modified with bromoethanol to give a mixture of amine and hydroxy sites. PAMAM-PZ was formed by DCC catalyzed condensation with 2-carboxy-pyrazine; 5% modification of the primary amine sites was achieved.

The maximum anion capacity of the three dendrimers was measured in the presence of an excess of anion. Despite the lack of covalent attachment of the anion to the dendrimer, these capacities are of similar magnitude to those of cations such as lead or cadmium, with up to 0.28 mg of anion bound per mg of dendrimer (Table 2). The dendrimers retain their high capacity at higher ionic strength; if a mixture of oxyanions is present, total ion capacity for PAMAM 4.0 and PAMAM-OH remains almost unchanged. The capacity of PAMAM-PZ actually increases, which suggests that unfavorable *intramolecular* interactions were disrupted at higher ionic strength, allowing the oxyanions access to binding sites on the dendrimer.

The selectivity for oxyanion binding versus chloride was also investigated (Figure 10). Phosphate binding in the presence of 0.03 M NaCl was relatively unaffected in the case of PAMAM 4.0 and only slightly decreased with PAMAM-OH. As in the mixed anion experiments above, the capacity of PAMAM-PZ dramatically increased, again suggesting that this dendrimer has strong intramolecular interactions. The combination of hydrogen bonding and electrostatic interactions are designed to give a specific site for an oxyanion. Such pockets are formed by selective anion-binding proteins and have been observed with in crystal structures of anions bound inside of aza-crown ether molecules.[8] Selective binding sites are

Table 2. Molar capacity of modified dendrimer complexes for oxyanions.

Polymer	CrO_4^{2-}	AsO_4^{3-}	PO_4^{3-}
PAMAM 4.0	1.99	1.74	1.62
PAMAM-OH	2.39	1.28	2.07
PAMAM-PZ	1.17	1.08	0.40

also proposed to exist in dendrizymes (dendrimer complexes for catalysis that mimic enzymes).[9] The ability to bind the oxyanions even in the presence of excess halide suggests that the dendrimers may form such pockets in solution.

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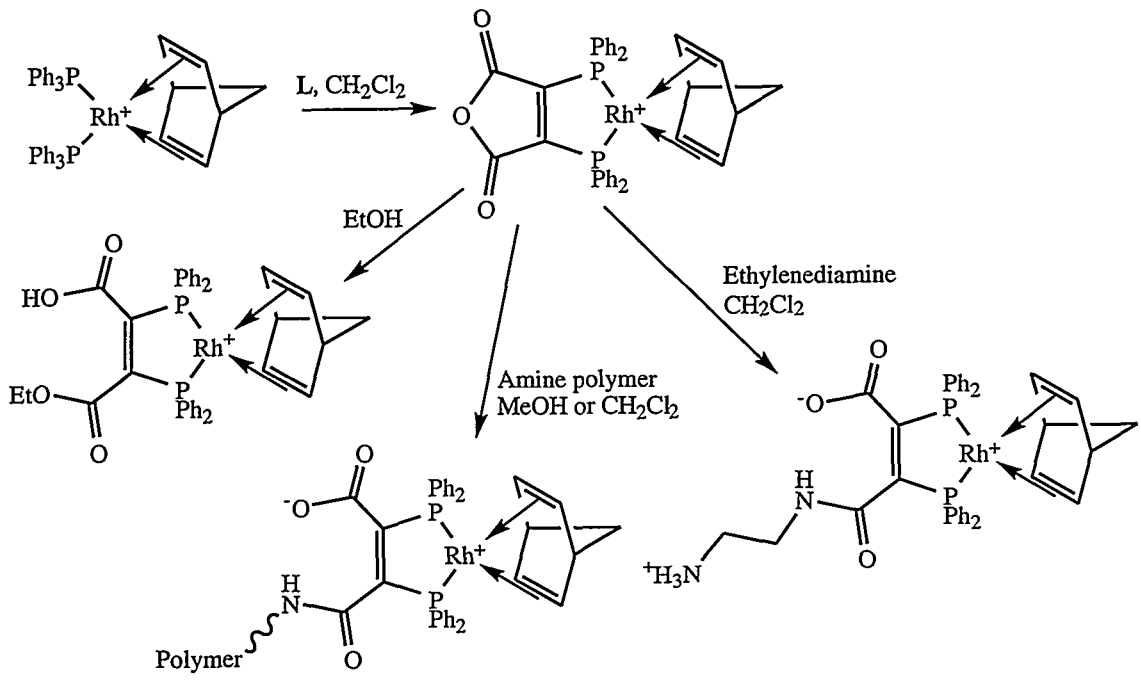
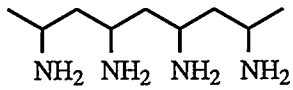
Schemes

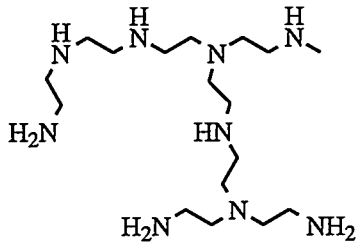


Scheme 1. Formation of the Rh-PMA catalyst and subsequent coupling reactions with alcohols, amines and polymers.

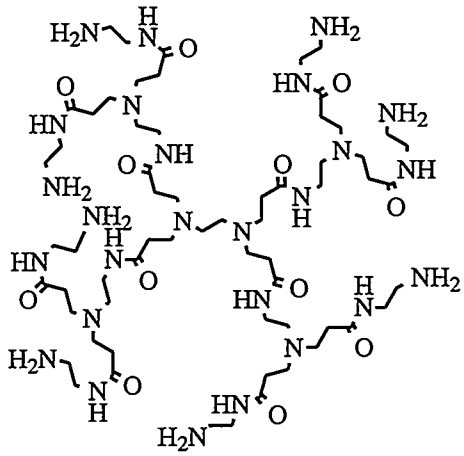
Figures follow:



Polyvinylamine

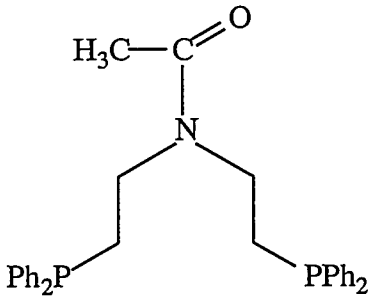


Polyethylenimine

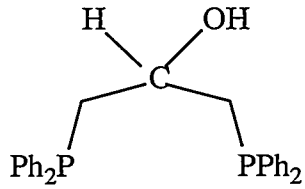


Starburst PAMAM denrimer generation 2

Figure 1. Polymers used in this study as soluble supports for homogeneous rhodium hydrogenation catalysts.



N,N-bis(diphenylphosphino-ethyl)acetamide
(PEA)



2-hydroxy-(1,3-bis(diphenyl-phosphino))propane
(PPR)

Figure 2. Structures of the diphosphines, PPR (2-hydroxy-1,3-bisdiphenyl-phosphinopropane) and PEA (N,N, bis-(diphenylphosphine-ethylacetamide).

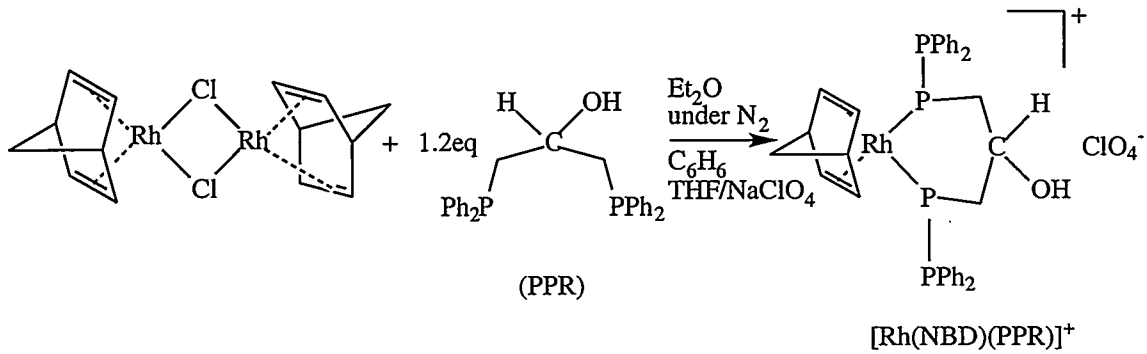


Figure 3. Synthesis of the Rhodium PPR catalysts from the rhodium dimer $[RhCl(NBD)]_2$. NBD is Norbornadiene.

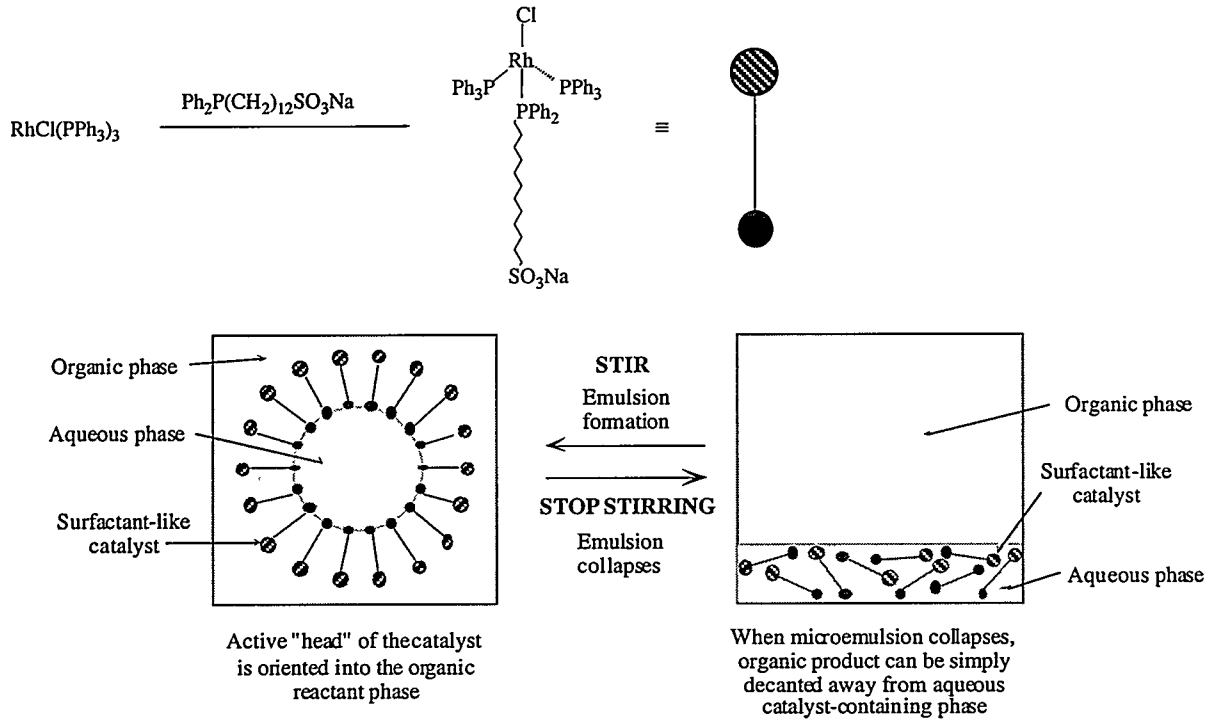
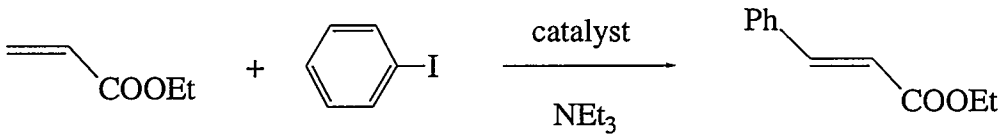


Figure 4. Schematic representation of micellar catalysts and their use in biphasic systems.

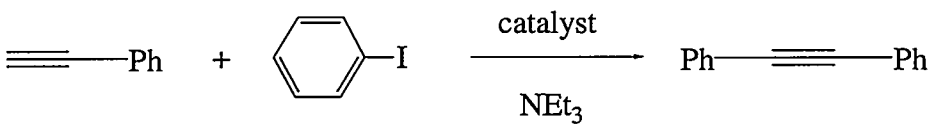


Conditions: Substrate:Catalyst ratio = 125:1

H_2O/organic biphasic system, 80 °C, 3 h

Catalyst	Yield
$PdCl_2[Ph_2P(CH_2)_{12}SO_3Na]_2$	32%
$PdCl_2[P(C_6H_4\text{-}m\text{-}SO_3Na)_3]_2$	2%

Figure 5. Comparison of a micellar catalyst, $PdCl_2[Ph_2P(CH_2)_{12}SO_3Na]_2$ with a standard water soluble catalyst, $PdCl_2[P(C_6H_4\text{-m-}SO_3Na)_3]_3$ in the coupling of iodobenzene and ethyl acrylate (substrate:catalyst ratio = 125:1) to give trans-ethyl cinnamate.

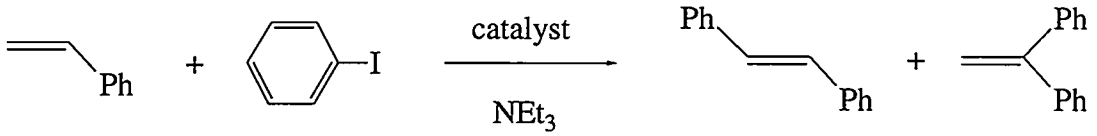


Conditions: Substrate:Catalyst ratio = 170:1

H_2O/organic biphasic system, 20 °C, 4 h

Catalyst	Yield
$PdCl_2[Ph_2P(CH_2)_{12}SO_3Na]_2$	75%

Figure 6. Coupling of phenylacetylene and iodobenzene to give diphenylacetylene using a Pd micellar catalyst. The catalyst:substrate ratio was 1:170.



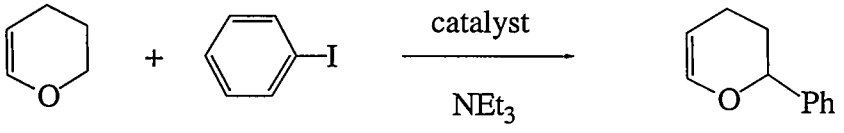
Conditions: Substrate:Catalyst ratio = 140:1

H_2O/organic biphasic system, 80 °C, 90 h

Catalyst	Yield
$PdCl_2[Ph_2P(CH_2)_{12}SO_3Na]_2$	72%

trans-stilbene:diphenylethylene ratio ca. 4:1

Figure 7. Coupling of aryl halides with olefins. Using a catalyst:substrate ratio of 1:140, styrene was coupled with iodobenzene to form a 4:1 mixture of *trans*-stilbene and diphenylethylene in 72 % overall yield.



Conditions: Substrate:Catalyst ratio = 194:1

H_2O/organic biphasic system, 80 °C, 90 h

Catalyst	Yield
$PdCl_2[Ph_2P(CH_2)_{12}SO_3Na]_2$	33%

Figure 8. Coupling reaction of iodobenzene with the activated olefin 3,4-dihydropyran at 80° C.

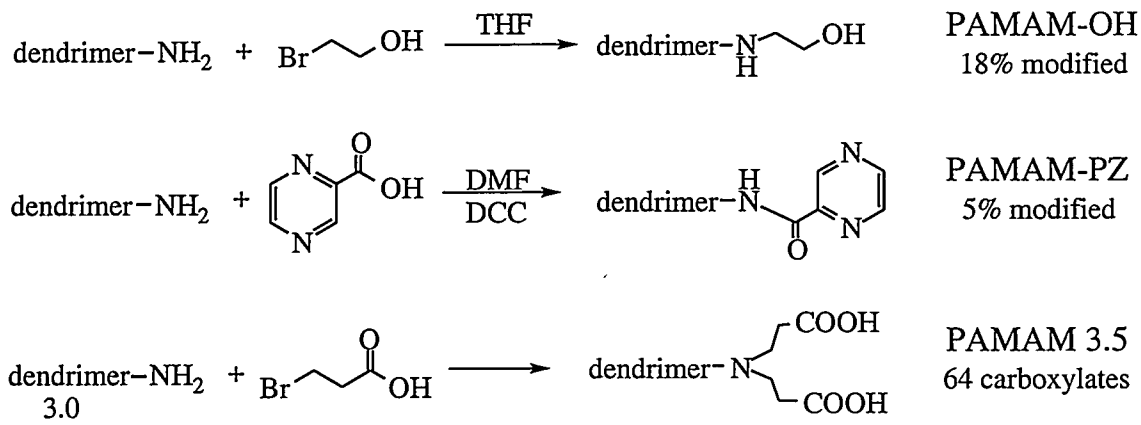


Figure 9. Synthesis of the three modified dendrimers used for anion binding experiments.

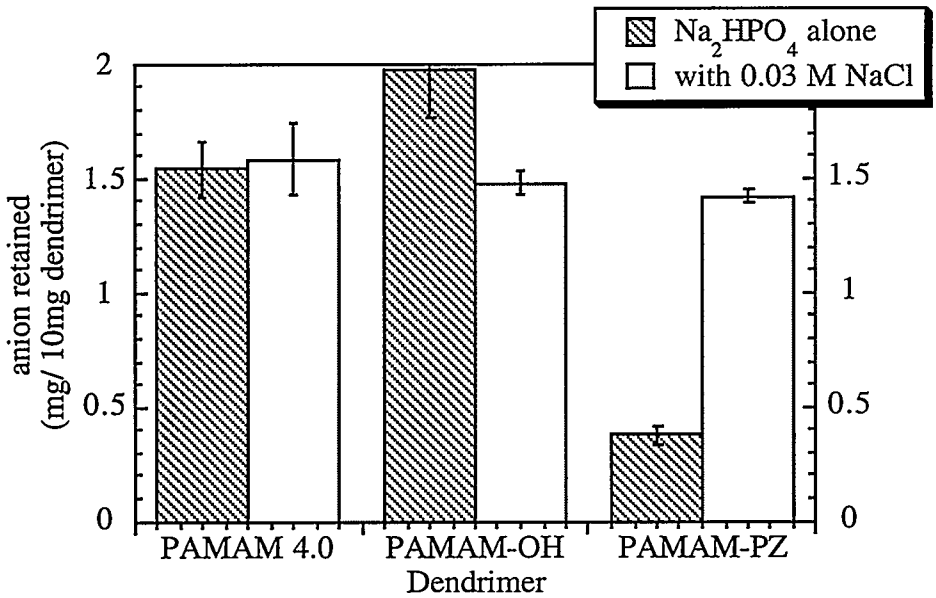


Figure 10. Phosphate capacity from 0.015 M Na_2HPO_4 alone, or in the presence of 0.03 M NaCl. The chloride does not compete significantly for binding sites on the dendrimers (4.0 and -OH), but binding of phosphate dramatically increases on the pyrazine derivative.