Title	Study on Development of Organic Polymer-Bound Metal Complex Catalysts in Selective Reduction of Organic Compounds
Author(s)	水垣, 共雄
Citation	大阪大学, 1999, 博士論文
Version Type	VoR
URL	https://doi.org/10.11501/3155466
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Study on Development of Organic Polymer-Bound Metal Complex Catalysts in Selective Reduction of Organic Compounds

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Preface

This dissertation is a collection of the author's studies which have been carried out under the supervision of Professor Kiyotomi Kaneda at the Division of Chemical Engineering, Department of Chemical Science and Engineering, Graduate School of Engineering Science, Osaka University from 1994 to 1999.

The present thesis deals with the design of highly active and selective polymer-bound metal complex catalysts for the reduction of various organic compounds. Recently, the catalysis of polymer-bound metal complexes has attracted much interest because they have potential abilities as simply separable and reusable catalysts.

Development of the novel and highly active metal catalysts for selective reductions have been of a great importance in both academic and industrial fields. Stoichiometric reagents such as zinc powder and metal hydrides have been widely used for the reduction of many organic compounds, even at present. Despite numerous studies on the homogeneous reductions using metal complex catalysts, there are few reports on the success of the heterogeneous selective reductions using solid catalysts with aim at organic syntheses. Therefore, the author tried to prepare highly efficient polymer-bound metal complexes as heterogeneous catalysts for selective reductions of organic compounds on the basis of the unique characters of organic polymers. In addition to the development of the above prominent heterogeneous catalysts, the use of safe and cheap reducing agents such as water is also desirable from the standpoint of the environmental demand for chemical reactions.

The preparation of highly active heterogeneous catalysts using organic polymer support can provide effective methodologies for the design of the solid catalysts in molecular levels. The author hopes that this study on the polymer-bound metal complex catalysts plays an important role in the development of environmentally-benign catalysts for other selective transformations of organic compounds.

CONTENTS

Part 1.

General Introduction

1-1. Preliminary

The well-being of modern society is unimaginable without the myriad manufactures of industrial organic productions. It is not too much to say that our quality of life is much dependent on the chemical products. Therefore, developments of the novel and highly selective synthetic methods for organic transformations have been of great importance in both academic and industrial fields.

In 1990's, the human being has been faced with serious environmental problems. The hazardous materials have been discharged as wastes from chemical plants or incinerators. Hence, the chemical industry is being subjected to a maximum pressure to minimize or, preferably, to eliminate waste production in manufacturing. The challenge for chemists and chemical engineers is to develop processes that not only yield the desired products, but also are efficient and environmentally friendly. In these senses, the classical organic syntheses using stoichiometric reagents should be avoided in near future. The typical examples of the stoichiometric syntheses include (1) oxidations with dichromate and permanganate, (2) formation of ethylene oxide using Cl_2 and $Ca(OH)_2$ (chlorohydrin route), (3) reductions with zinc dust and metal hydrides, and (4) aromatic substitutions such as halogenations, sulfonations, nitrations, and the Friedel-Crafts acylations. Many of these industrial relics of a bygone age are ripe for substitution by catalytic alternatives.

Catalytic processes enjoy the advantages of proceeding efficiently under mild reaction conditions and of having high selectivities of the desired products over noncatalytic ways. Typical commercial chemical processes using catalysts already realized in practice are (1) synthesis of ethylene oxide from ethylene and molecular oxygen by Ag catalyst, (2) manufacture of acetic acid from methanol and carbon monoxide by Rh catalyst, known as the Monsanto process, (3) production of aldehydes from olefins and H_2/CO by Rh catalyst in the hydroformylation, and (4) formation of acetaldehyde from ethylene and oxygen by the Pd/Cu catalysts in the Wacker process. More clean and simple chemical processes could be realized in the future by a development of high performance catalysts based on the further merits of the catalytic method. These merits include high atom utilization of the organic reaction, omission of the emission of vast amounts of inorganic salts, minimization of steps for the final desired products, and tunability of both activity and selectivity.

The developments of high performance catalysts need a highly sophisticated design in a molecular level, which is an important objective in both academic and industrial areas. The author has been stimulated to study on the design of the high performance catalysts, which contributes to the developments of environmentally benign chemical processes. The author tried to prepare the highly efficient polymer-bound metal complexes as high performance catalysts on the basis of the unique characters of organic polymers.

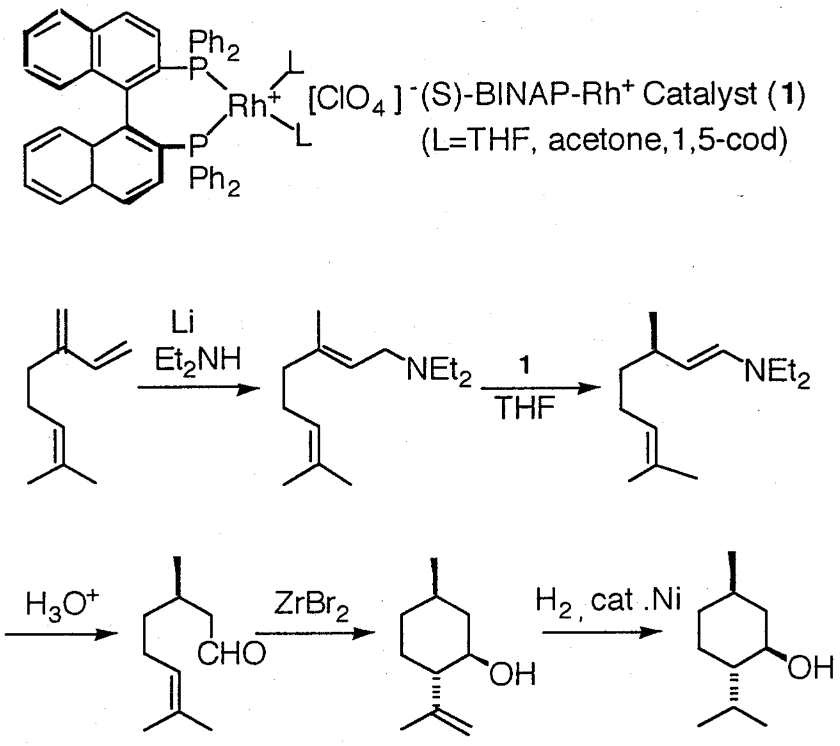
In the followings, the author reviews the developments in the design of metal complex catalysts and of heterogeneous catalysts using metal complexes through an immobilization onto organic and inorganic support materials. As a target reaction, the author mainly focused on the reduction of hydrocarbons.

1-2. Background

During the last quarter of this century, there has been great progress in the development of the transition metal complex catalysts in various organic transformations. The use of the metal complexes is considered to have some advantages over conventional heterogeneous metal catalysts as follows[1-3].

1) Homogeneity of the catalysts and substrates
2) Efficient availability of catalytically active sites
3) Reproducibility
4) Flexibility of choosing the ligands
5) High activity under the mild reaction conditions.

These advantages lead to high catalytic performances of the metal complexes in a homogeneous medium under mild reaction conditions. The most facilitating strategy to modify the catalysis of the metal complex is a permutation of the ligands in addition to the selection of the center metal. Especially, a great progress in the asymmetric synthesis of chiral compounds has been achieved by using the chiral ligands. For instance, an industrial synthesis of (-)-menthol from myrcene is accomplished by the asymmetric isomerization of geranyldiethylamine to (*S*)-citronellal - (*E*)-enamine catalyzed by a combination of cationic Rh^I complex and (*S*)-BINAP ligand. This chemical process is successfully working in Japan and the Rh catalyst can be recycled in an overall efficiency of chiral multiplication of 400000 mol product/mol Rh catalyst (**Scheme 1**). This methodology provides industrial syntheses of profens, pyrethroids, prostaglandines, and amino alcohols.



Scheme 1. Industrial Synthesis of (–)-Menthol Using (S)-BINAP-Rh^+ Catalyst.

1-2-1. Design of Multi-Phasic Catalyst Systems

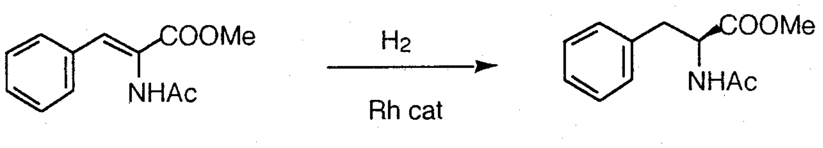
Suitable choice of the ligands makes metal complexes possible to use in multi-phasic reaction systems. In the multi-phasic catalyst system, the active catalyst species dissolve in one phase and in other phase substrates and products are miscible. Recovery procedure of the catalysts from the reaction mixture would become strikingly simple and easy. As the typical multi-phase catalysts systems, two systems of aqueous biphasic catalyst and fluorous biphasic catalyst are reviewed in the following sections.

1-2-1-1. Aqueous Biphasic Catalyst System [4-6]

By using water-soluble ligands, metal complex catalysts become water-soluble as mobile catalysts in the aqueous phase. Such a hydrophilic catalyst is insoluble in the organic phase, which could be easily separated by a simple phase separation without any chemical stress after the reaction, as illustrated in **Figure 1(a)**. Loss of the catalyst metal would be negligible because of the high polarity of the above metal catalysts and their insolubility in the organic phase.

The catalysis of aqueous homogeneous metal complexes depends on the molecular design of polar and/or water soluble ligands, *e.g.*, phosphines and amines. Typical water-soluble ligands for the homogeneous oxo Rh catalysts are shown in **Figure 2**. The solubility of metal complex catalysts in water is usually enhanced by introduction of highly polar functional groups such as -SO_3H[5], -COOH[7], -OH, -NH_2[8] and their salts into the phosphine ligands. A desired hydrophilic property of the above metal catalysts could be designed by changing the nature and number of substituents on the phosphines.

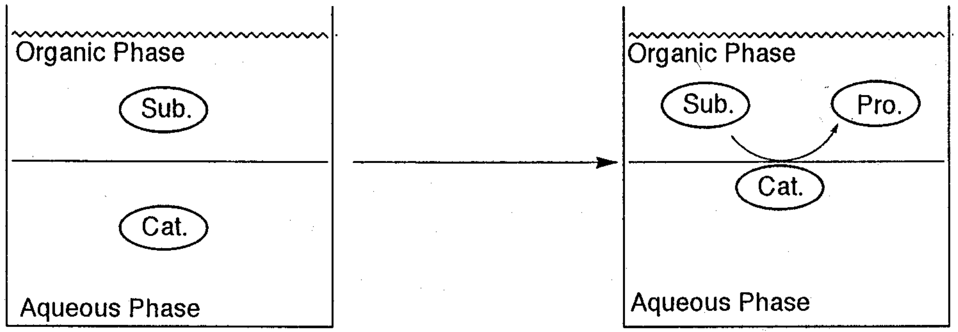
The aqueous biphasic catalyst systems have been applied for several industrial processes [8-10]. One example of valuable applications of the aqueous biphase catalyst system is an asymmetric hydrogenation of α-acetamidocinnamate using a diphosphine ligand having surface active moieties and $[RhCl(COD)]_2$ complex (**Eq. 1**) [11]. In this biphasic Rh catalyst system, the formed hydrophilic Rh complex showed higher activity than that for the corresponding one-phase system, retaining a high enantioselectivity in α-acetamido-dihydrocinnmate.



(1)

A disadvantage of the aqueous biphasic catalyst system is a limitation of the substrates used. Since the catalytic reactions take place in the aqueous phase or the boundary territory between two phases, the reaction rates in the aqueous biphasic catalyst systems strongly

(a) Aqueous Two Phase System



(b) Fluorous Biphase System

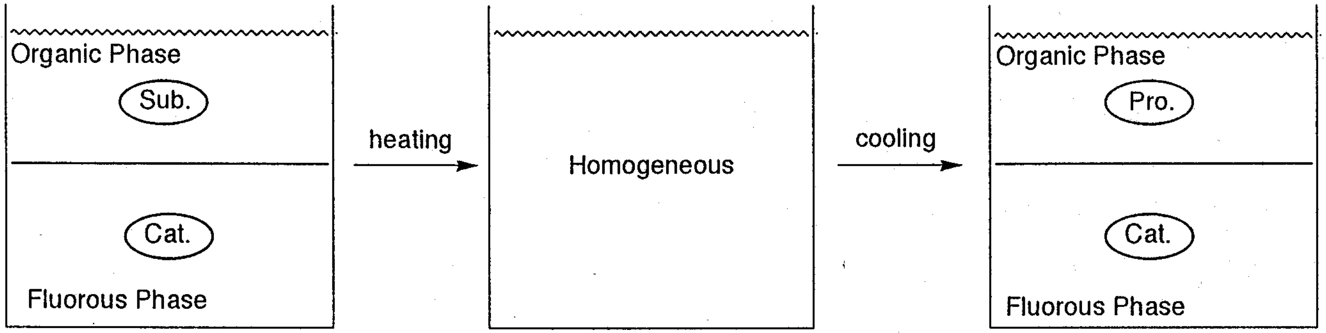
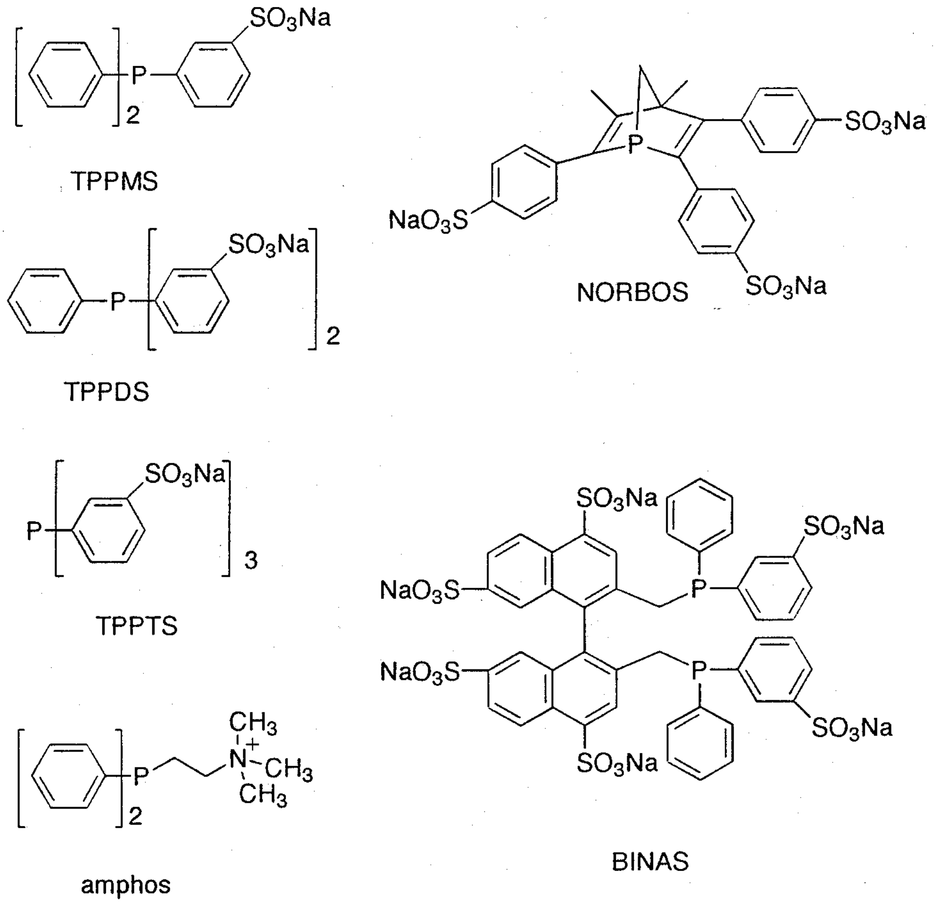


Figure 1. Schematic Models For Biphasic Catalyst Systems



TPPMS

TPPDS

TPPTS

amphos

NORBOS

BINAS

Figure 2. Typical Water-Soluble Phosphine Ligands

depend on the polarity and solubility of the substrates. In the case of the hydroformylation of 1-hexene using the water-soluble catalyst, $HRh(CO)(TPPTS)_3$ (TPPTS = triphenylphosphine *meta*-trisulfonate sodium salts), the rate determining step appears to be mass transfer of substrates to the boundary territory. The reaction rate is lower than that in the corresponding homogeneous reaction. However, in the case of propene hydroformylation, the rate in the aqueous biphasic Rh catalyst system is comparable with that in the corresponding homogeneous Rh reaction system[12].

1-2-1-2. Fluorous Biphasic Catalyst System

In spite of a great merit of the aqueous biphasic catalyst system (*vide supra*), the low solubility of many organic compounds in water limits the wide applications of aqueous metal complex catalysts. In order to overcome the above limitation, a new concept has been devised by using fluorous materials which show low solubility in the common organic solvents[13]. The term of "fluorous" is used in analogy to the term of "aqueous" in the aqueous biphasic system, because the metal catalyst exists only in the fluorous phase in place of water.

The fluorous biphasic catalyst system consists of a fluorous phase containing a catalyst and an organic phase containing substrates, as shown in **Fig. 1(b)**. The organometallic complexes can be dissolved in the fluorous phase by using the ligands with fluorocarbon moieties such as phosphines, phosphites, porphyrins, phthalocyanines, and diketonates[13]. Since the solubilities of the fluorous compounds in toluene, THF, acetone, and alcohols are low, these insoluble organic compounds can be used as solvents in the fluorous biphasic reaction system. It should be noted that a fluorous biphasic system could be homogeneous by increasing the reaction temperature, which leads to an increase of the reaction rates. The above two phases can be again separated by decreasing the temperature after the catalytic reaction, which makes the separation of the metal catalyst from the products significantly simple.

Up to the present, this convenient concept has been applied for a few catalytic reactions. One example of the fluorous biphasic catalyst system is for the hydroformylation of 1-decene using a fluoroalkylated phosphine ligand and the Rh complex. The products of C_{11} aldehydes were easily separated from the fluorous Rh catalyst phase at room temperature after the hydroformylation. It was reported that the leaching of metal complexes into the organic phase did not occur and then the catalyst could be recycled efficiently[13].

1-2-2. Design of Heterogeneous Catalysts by Immobilization of Metal Complexes

The increasing demands for environmentally benign chemical processes with high product selectivities and economically favorable reaction rates have renewed interest in the homogeneous metal catalysis. Simple and efficient separation of products from catalysts can open up the application of heterogenized homogeneous catalyst systems to the industrial processes.

In spite of the advances of the metal complex catalysts, the use of metal complexes on industrial scales has still faced on practical problems as follows. Thermal instability of the metal complex catalysts induces corrosion and plating out on the reactor wall associated with the catalyst decomposition. Difficulty of the catalyst and the ligand recovery from the reaction mixtures is also a practical problem. The latter problem of the metal separation from products is economically significant because expensive noble metal catalysts such as Rh, Pt, Pd, Ru, and Ir are desired to reuse, and also contaminants of metals and ligands must be excluded from reaction products.

In order to overcome these difficulties of the homogeneous catalyst systems, much efforts have been paid to develop heterogeneous metal catalysts by immobilization of the metal complexes on solid materials. This kind of catalysts is regarded as a new class of "hybrid catalyst"[14], which still has the advantageous characters of metal complex catalysts in homogeneous reaction systems. Furthermore, these attempts have led to the discovery of novel catalytic functions including: 1) active site isolation, 2) cooperative catalysis by several sites, 3) steric control of reaction intermediates by supports, and 4) applications for sequential reactions in the one-pot synthesis[15, 16]. Up to now, a wide variety of common organic and inorganic polymer systems have been used as solid supports for immobilized metal complex catalysts. Modification of insoluble organic and inorganic polymers with various kinds of ligand atoms is a conventional strategy for binding the metal complexes onto solid supports[17-19]. However, there are still some problems such as the metal leaching from their surface during the organic reactions and the diffusion limitation of substrates into microporous supports. In order to overcome the above problems, recent studies of the heterogenized catalysts are focused on the development of new methodology for their preparation which is based on the surface design of the supports in atomic and/or molecular levels.

In the next sections, the author reviewed the typical studies of the immobilizations of metal complexes on the organic and inorganic polymer supports which aimed at preparations of novel heterogeneous catalysts.

1-2-2-1. Organic Polymers as Catalyst Supports

Organic polymers are widely used for the supports of the polymer-bound metal complex catalysts. Such as polystyrenes, styrene-divinylbenzene copolymers, and dendrimers are considered to be catalyst supports, because they offer several advantages over the other catalyst supports as follows.

- Various kinds of functional groups can be easily introduced.
- Unlike the surface of metal oxides having acid-base characters, polymeric hydrocarbons are almost neutral which depress undesirable side reactions.
- Physical and chemical properties of organic polymers can be tune.

Accordingly, using the above unique characters of the polymers will provide to prepare the desired "tailor-made" polymer-bound metal complex catalysts [20].

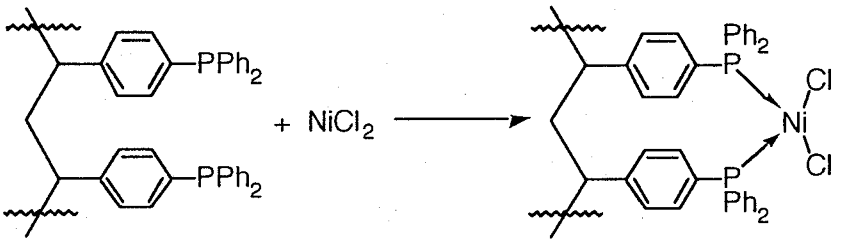
The immobilization of metal complex catalysts using the organic polymers generally involves the following steps: 1) synthesis of the unit monomers, 2) polymerization of the monomers, 3) functionalization of the obtained polymers with desired ligand groups, and 4) complexation of the functionalized polymers with metal complexes.

Polystyrenes are the most frequently adopted as organic polymers. The use of polyacrylates[21], cellulose[22], polyethylene[23], and polyoxyethylenes[24] have been also reported. As for the novel polymer materials, dendrimers will be described in Chapter 1 in

Part 3 separately.

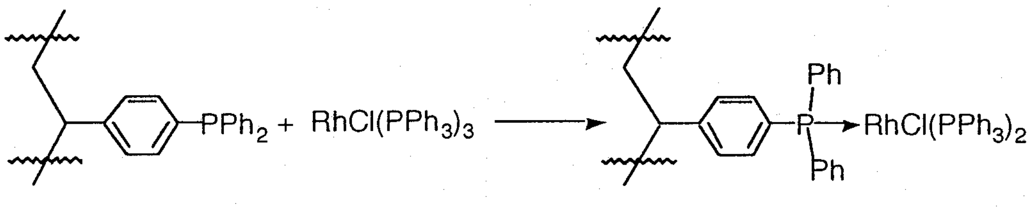
Two kinds of methods have been known as introduction of functional groups on the polymer which can chemically bind with the metal complexes. One is the copolymerization of styrene with the vinyl monomers having desired functional groups. Vinyl pyridine, diphenylallyl phosphine, and diphenylstyryl phosphine are used mainly as the above monomers. Another preparation method includes the chloromethylation step of aromatic rings on the polymer surface. Typical examples of the above functionalization of polymeric supports are summarized in **Schemes 2** and **3**.

In order to incorporate the metal complexes onto the functionalized polymers, tertiary phosphines and amines are frequently used as donor ligands. As a typical example of the direct preparation method, treatment of the functionalized polymers with a metal halide gives a polymer-bound nickel (II) complex (**Eq. 2**)[25].



(2)

The other preparation method of the polymer-bound metal complexes is the ligand displacement technique: some ligands already coordinated to a metal complex are displaced by polymer-bound ligands (**Eqs. 3 and 4**)[26, 27].



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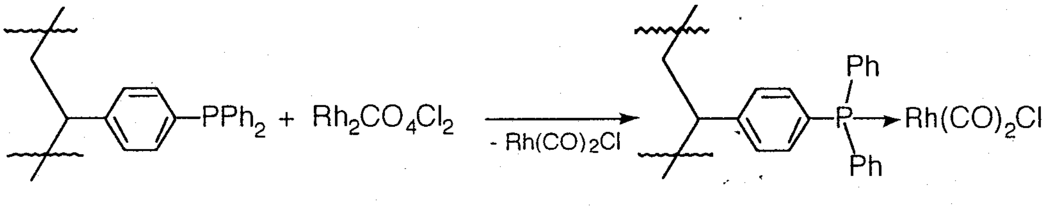

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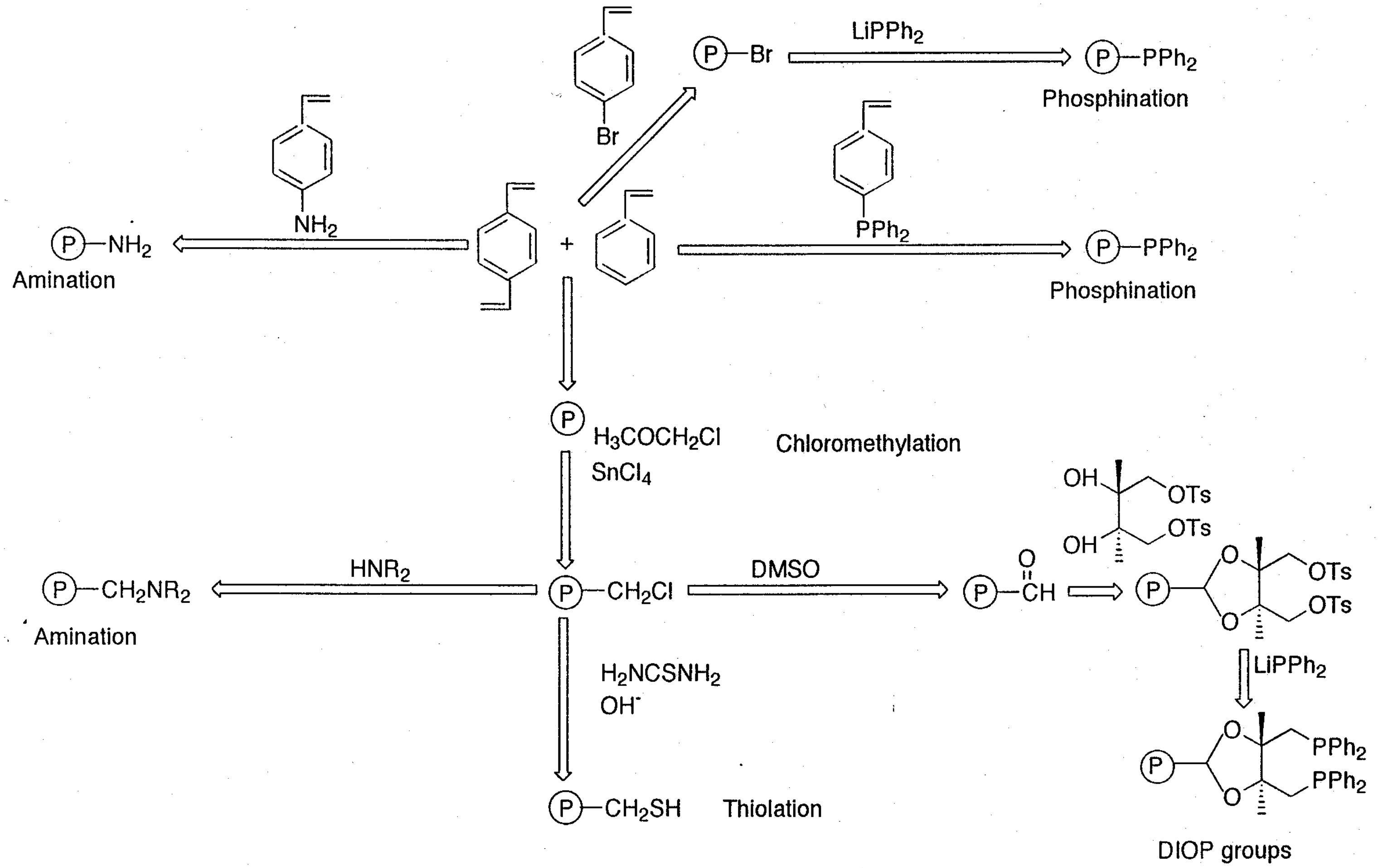
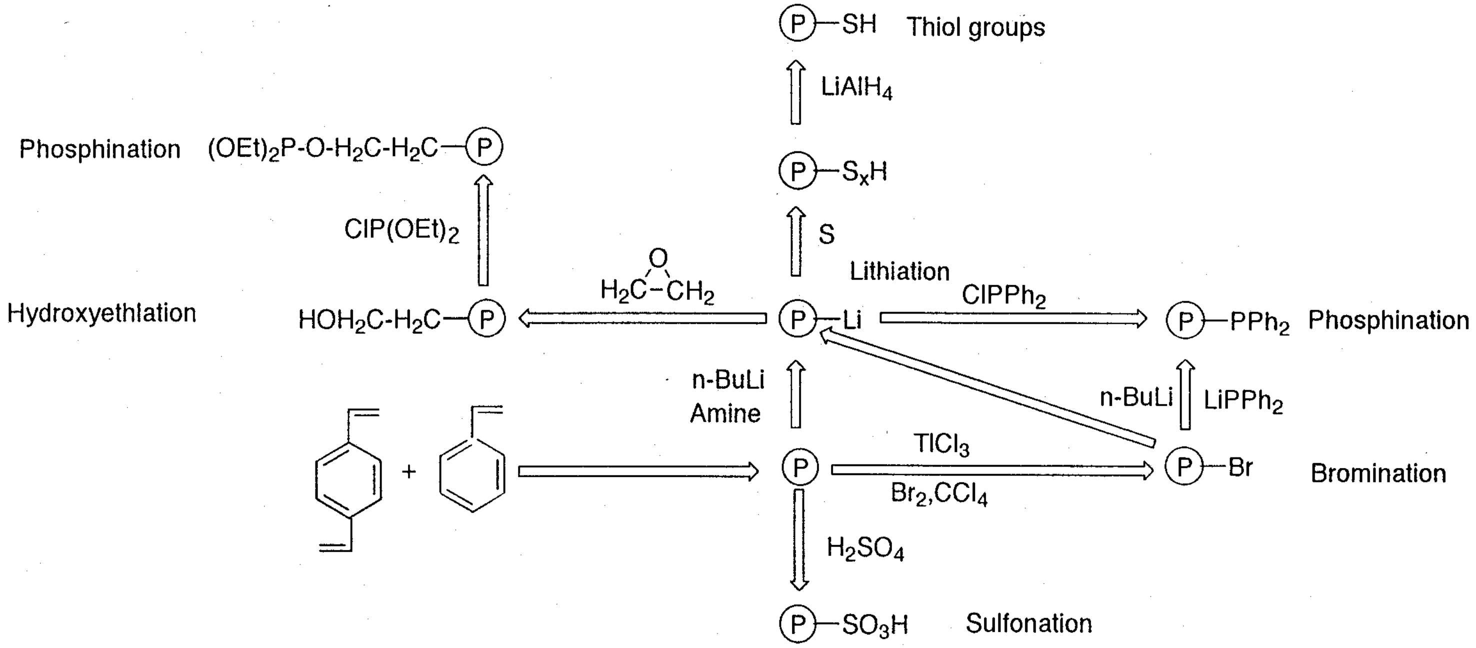
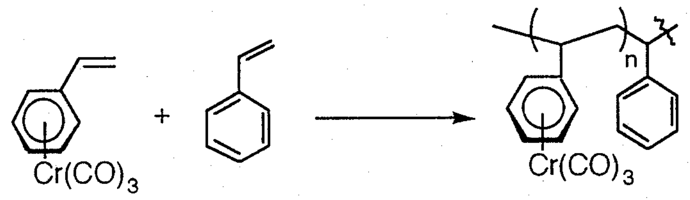


Scheme 2. Functionalization of Polymeric Supports with -Br, $-PPh_2$, $-NH_2$, - CH_2NR_2, $-CH_2SH$, and DIOP Groups.



Scheme 3. Functionalization of Polymeric Supports: Incorporation of -CH_2OH, -$CH_2CH_2P(OEt)_2$, -SH, -Br, -Li, -PPh_2, and-SO_3H Groups.

Polymerization or co-polymerization of functionalized monomeric metal complexes can also give the polymer-bound metal complexes (**Eq. 5**)[28]. An advantage of this method is that the structural homogeneity of the polymeric metal complexes can be attained. But, it is said that this methods resulted in low yields of the polymeric metal complex due to an insufficient degree of the polymerization.

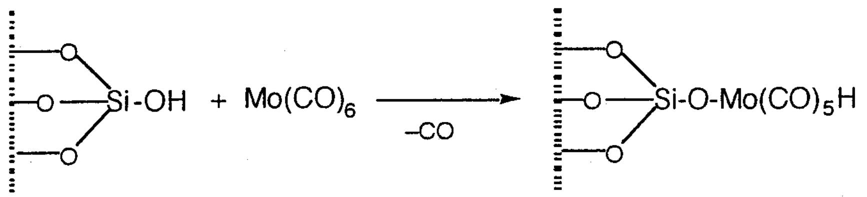


(5)

In contrast to the above neutral metal complex covalently bound to functionalized polymers, ionic metal complex species can be also formed on polymer surface through an ionic bonding onto the functionalized polymers. Examples of the ionic bonding of metal complexes to polymer supports involve supported metal clusters, *e.g.*, anionic metal carbonyl cluster complexes[29]. The fundamentals of the metal carbonyl clusters will be described in Chapter 1 in Part 2. For an example, Kaneda *et al.* have reported that the selective formation of anionic Rh carbonyl clusters from neutral clusters could be achieved using the polystyrenes functionalized with diamine groups[30].

1-2-2-2. Inorganic Polymers as Catalyst Supports

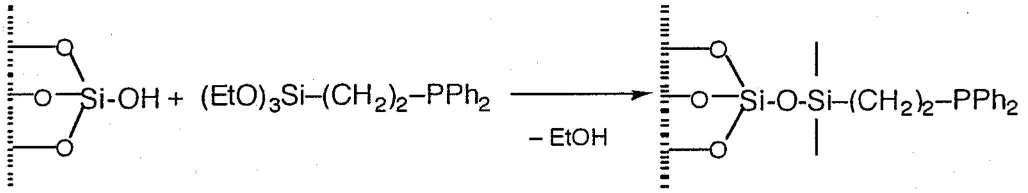
Advantages of metal oxide supports come from their rigid structure, which prevents deactivation of the active catalysts through the intermolecular interaction between them, and also the stability against higher temperatures. Silica, alumina, magnesia, glass, and clays are used as typical inorganic supports. From standpoints of availability, number and nature of surface groups, surface area, pore size, pore volume as well as form and size of the particles, silica has been a preferable inorganic support. The silica surface can be modified by the treatment of the surface silanol groups with appropriate metal complexes or with intermediate ligand groups. The direct bonding has often been used for anchoring the metal carbonyl complexes and clusters to the silica surface (**Eq. 6**)[29].



(6)

Another common technique is utilization of the spacer groups which are anchored to the support on one side and act as a ligand group on the other side. For this method, two alternative approaches have been used (routes 1 and 2). In route 1, which is demonstrated in **Eqs. 7** and **8** as a typical example[2], a ligand group is attached to the support in the first step (**Eq. 7**) and in the following step, the complexation of the phosphine-functionalized silica with a monomeric metal complex gives a supported metal complex(**Eq. 8**).

Route 1



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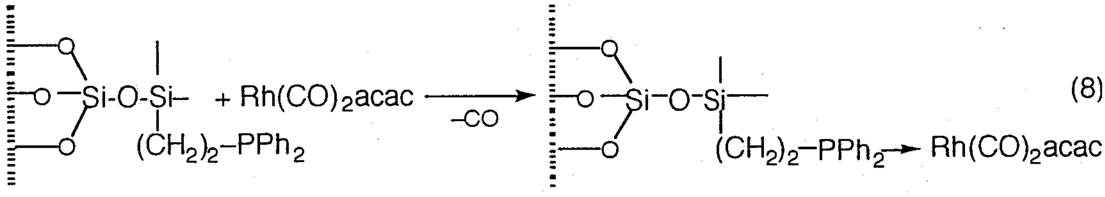
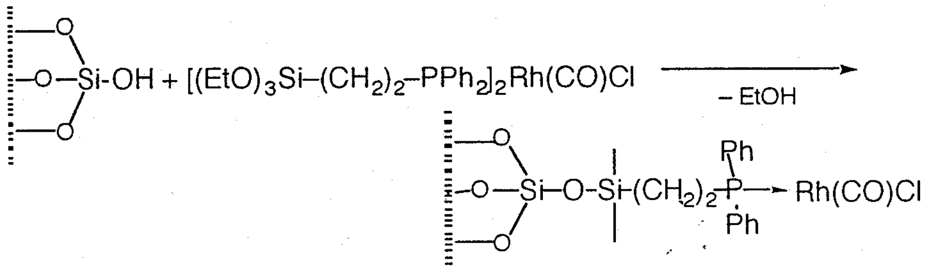


(8)

The uniformity of the catalytically active centers can be guaranteed by route 2, which involves the reaction of a metal complex bearing silicon-substituted ligands with silanol groups (**Eq. 9**)[31].

Route 2



(9)

Many immobilized metal complexes having phosphine, amine, cyano, mercapto, alkene, and cyclopentadienyl ligands have been successfully synthesized on silica surface according to the above two routes. In order to avoid undesirable side reactions on the supports after the surface modification according to routes 1 and 2, the remaining silanol groups should be treated with nonfunctionalized silylating agents. Thus, at the same time, the surface layer becomes to have more lipophilic character.

The fixation of metal complexes *via* chemi- and physisorption is usually used to control the metal particle size on the supports. The surface bonding of metal complexes *via* the impregnation technique is one of common methods particularly used for the fixation of metal carbonyl compounds[20]. The adsorbed metal carbonyl complexes may also undergo facile substitution reactions with surface groups, *e.g.*, silanol groups. Pyrolysis of the immobilized metal complexes can lead to the formation of dispersed metal particles on the supports. Entrapping of the metal complexes, so-called "ship-in-the-bottle" synthesis, could be achieved in the *in situ* preparation of cluster complexes within the pores of zeolites[32].

Other method of encapsulating the metal complexes involves polymerization and/or polycondensation reactions such as the sol-gel process[33]. The metal complexes are dissolved in the polymerizable medium and then, trapped in the polymer matrix.

A disadvantage of the use of inorganic supports is the limited number of the reactive surface groups available for further functionalization. Inorganic matrixes have an upper limit of monofunctional groups of 1-2 meq/g, although the organic matrixes have 10 meq/g of functional groups[15]. Other limitations of the immobilization using the inorganic polymers are (1) possibility of creating different sites; the metal complexes can not be fixed uniformly and (2) diffusional restrictions of substrate molecules within the pores; the immobilized metal complexes in the cavities are too large to allow the entrance of the substrates into the pores.

1-2-3. Immobilization *via* Supported Liquids

The above-described immobilization procedures generally yield the supported solid-phase catalysts. This section deals with preparation of catalysts having metal active species that are dissolved in liquid phases supported on the porous materials. The catalysis in the supported liquid phase would be similar to the corresponding homogeneous catalysis. The principal structures of both an SLPC (Supported Liquid-Phase Catalyst) and an SAPC (Supported Aqueous-Phase Catalyst) are shown in **Figure 3**. In both cases, the catalytic reaction takes place in the supported liquid (phase A) or at the interface of the supported liquid film. The reactants (phase B) in gas phase and organic phase are employed in the SLPC and the SAPC, respectively. The above supported liquids (phase A) must be insoluble in the reaction medium (phase B) to avoid the elution from the porous support.

For the SLPC system, the phase A is a solvent of low vapor pressure, *e.g.*, phthalic acid esters and ethyleneglycol. In many cases, the SLPC was used in the hydroformylation of ethylene, propene, or butene using Rh-phosphine complexes in the presence of excess PPh_3[34]. The SLPC system is not applicable with reactants or products miscible in the supported liquid phase. In contrast, the SAPC consists of a thin film of an aqueous solution of water-soluble organometallic complexes and a hydrophilic supports. For an example, controlled-porous glasses and surface modified silica with high surface areas are used for liquid reactants[35, 36]. The hydroformylation of higher olefins using Rh-TPPTS[37, 38], the Wacker oxidation[39], and asymmetric hydrogenation[40, 41] have been extensively carried out by using the above SAPC system.

Conclusively, the metal complexes can be successfully immobilized on the surfaces both of organic and inorganic supports in several manners. Throughout the many works on the immobilization of metal complexes, immobilized metallocene catalysts has been found to be promising and really satisfying catalysts in the polymerization reactions[42]. Continuous studies on the heterogenization of metal complexes willl provide us novel preparation methods of prominent catalysts for useful many organic reactions.

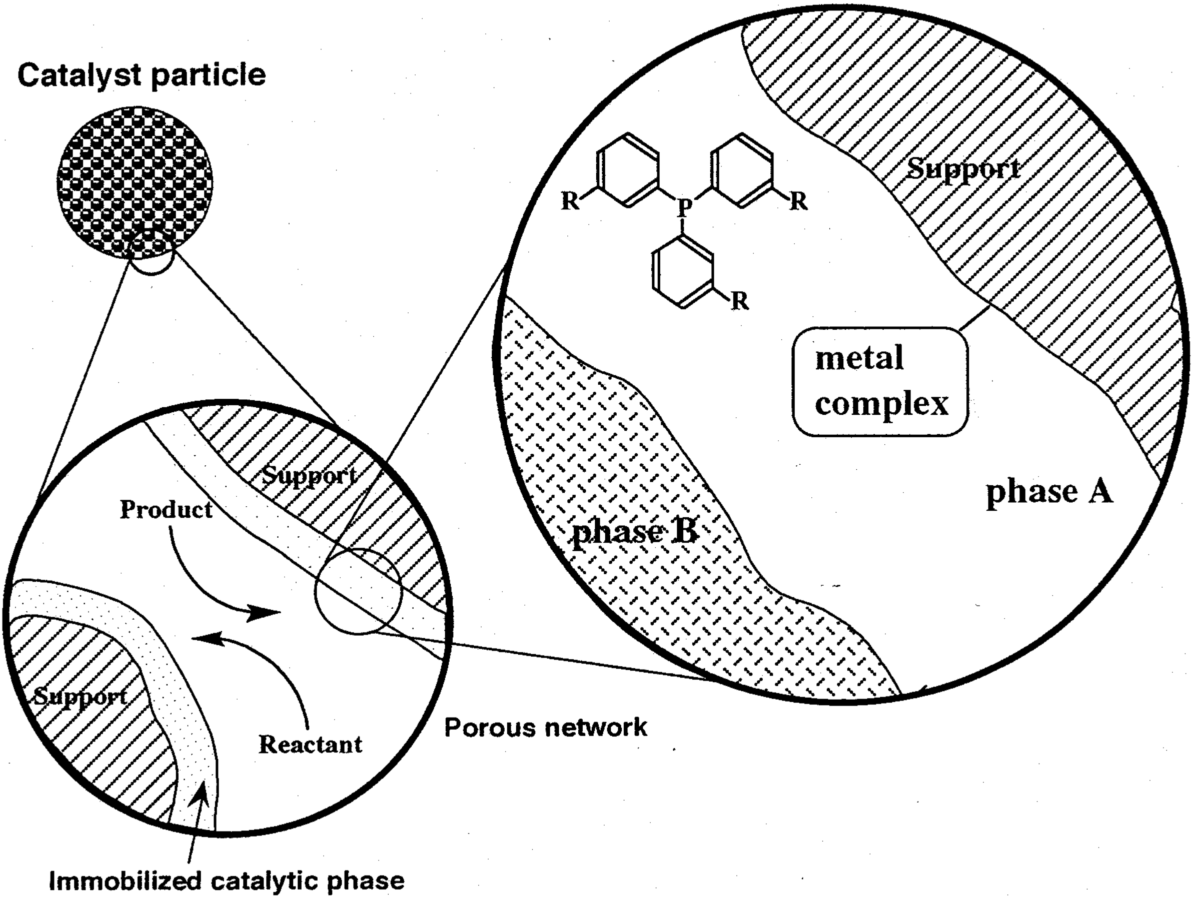


Fig. 3. Schematic of a supported liquid-phase catalyst. The liquid or water adsorbed on the porous support forms a film on the inner surface of the support.

SLPC: phase A is a nonvolatile organic solvent, *e. g.*, R = H for typical purpose; phase B in a gas phase.
SAPC: phase A is water, *e. g.*, R = SO_3Na; phase B is an organic liquid.

1-3. Purpose of This Thesis

Currently, much attention has been paid to the environmental problems. The chemical processes that not only yield the desired products, but also are efficient and environmentally friendly must be urgently developed.

Homogeneous metal complex catalysts are known to show high activity and selectivity for many organic reactions under the mild conditions. However, their instability to heat and moisture as well as high cost of noble metals and ligands prevents the use of the homogeneous catalysts in industrial processes. Therefore, the author has been stimulated to study the design of highly active polymer-bound metal complex catalysts using functionalized organic supports, which contributes to the developments of environmentally benign chemical processes with the high atom economy. In the course of this study, the author chose organic polymers of polystyrenes and dendrimers as catalyst supports because of their advantages as already described in 1-2-2-1. A new methodology for the immobilization of metal complexes using the organic polymers has been also investigated.

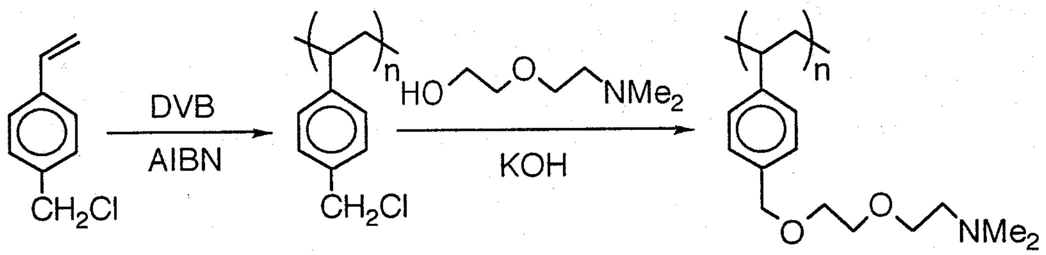
The main purpose of this thesis is to design the highly active and selective polymer-bound metal complex catalysts for the selective reduction of organic compounds. The use of the polymer-bound metal complexes for the above catalytic reactions brings the simple work-up procedures; the metal catalyst can be easily separated from the reaction mixtures and reused without any loss of the catalytic activity. In addition to the development of the prominent catalyst, safe and cheap reducing agents such as water and formic acid were used in the reductions, which contributes to one solution of the environmental problems.

1-4. Outline of This Study

The present thesis deals with the studies on the catalyst design of the polymer-bound metal complex catalysts for the efficient and selective reduction of organic compounds.

In the next section, the author prepares highly functionalized polystyrenes and then, employs them as supports for Rh carbonyl clusters to give polymer-bound Rh cluster complex catalysts. The author describes in Chapter 2 the design of multi-functionalized polystyrene

(**Eq. 10**) for the immobilization of Rh carbonyl clusters, and their catalysis in the selective reduction of carbonyl groups using water as a hydrogen source (**Eq. 11**). The polymer-bound Rh carbonyl cluster complexes with strong basicity and hydrophilicity show higher catalytic activities for the selective reduction than those of the corresponding homogeneous systems. The polymer-bound catalysts are easily separated from reaction mixtures and can be reused without any loss of the activity and selectivity for the reductions.



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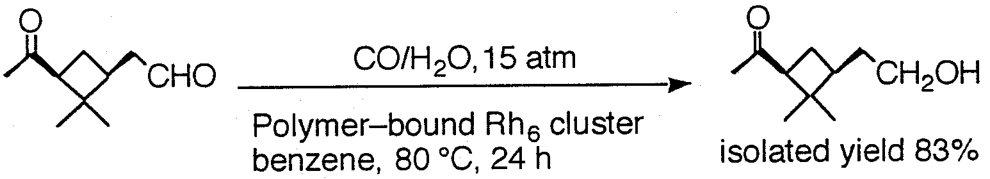
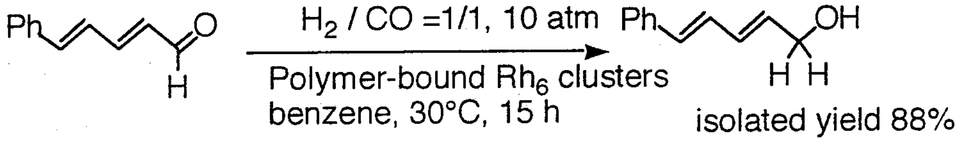


(11)

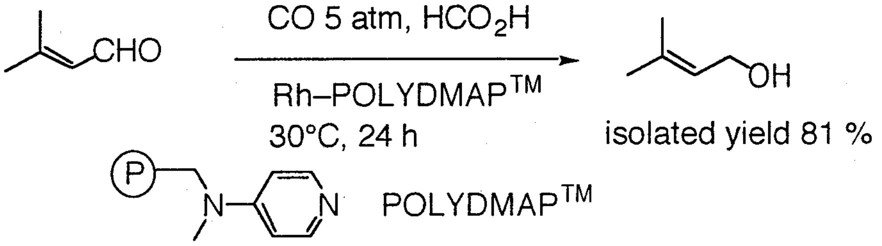
The description in Chapter 3 is the catalysis of polystyrene-bound Rh carbonyl clusters in the chemoselective reduction of α,β-unsaturated aldehydes to allylic alcohols in the presence of H_2 and CO (**Eq. 12**). The heterogeneous Rh cluster catalysts show higher activity and selectivity for the reductions than those in the corresponding homogeneous systems. The polymer-bound cluster complexes can be reused with keeping the catalytic activities in the reductions.



(12)

In Chapter 4, the author uses formic acid as a safe hydrogen source in the chemoselective reduction of α,β-unsaturated aldehydes to allylic alcohols catalyzed by polymer-bound Rh carbonyl clusters (**Eq. 13**). The homogeneous Rh cluster catalyst system using 4-

dimethylaminopyridine as an additive can be heterogenized by employing the polystyrene-bound dimethylaminopyridine (POLYDMAP). The formed POLYDMAP-bound Rh cluster catalyst can be reused without any loss of the catalytic activities.



(13)

In Part 3, the dendrimers are used as novel organic polymeric supports to develop highly active metal complex catalysts for the selective organic transformations. The author finds that the use of the surface and the interior space of dendrimers can act as catalyst binding sites. In Chapter 2, the author describes the surface functionalization of the dendrimers. The preparation of a phosphinated dendrimer-bound Pd(II) complex (**Figure 4**) and its catalysis in the selective hydrogenation of conjugated dienes to monoenes are studied (**Eq. 14**). The dendritic Pd(II) catalyst shows much higher catalytic activity in the hydrogenation than that of the corresponding low-molecular weight Pd(II) complex, and can be reused without loss of the activities.

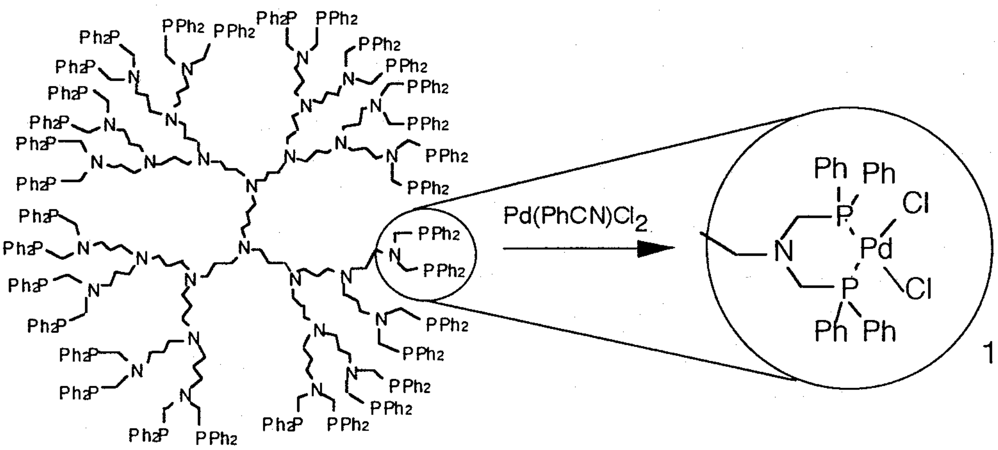


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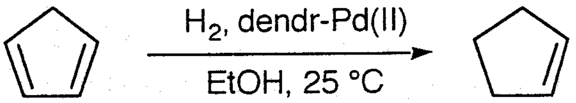
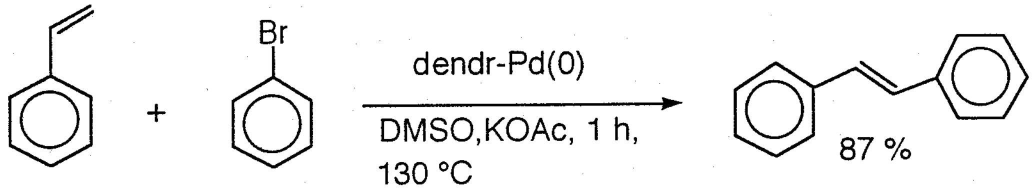
Figure 4 Schematic Illustration of Dendrimer-Bound Pd(II) Complex Catalyst



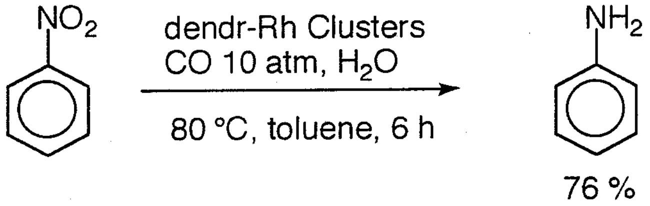
(14)

Catalysis of the dendrimer-bound Pd(0) complex in the Heck vinylic hydrogen substitution is demonstrated in Chapter 3. The dendrimer-bound Pd(0) complex prepared from the reduction of the dendritic Pd(II) complex using hydrazine gives a high stability in air and a high catalytic activity in the reaction of styrene with bromobenzene (**Eq. 15**).



(15)

In the last chapter, the utilization of interior space of the modified-dendrimers for the immobilization of Rh carbonyl clusters is described. The catalysis of the dendrimer-bound Rh clusters in the reduction of nitrobenzene using a combined reducing agent of water and CO is studied (**Eq. 16**).



(16)

Finally, the author describes overall conclusions of the present thesis. The scopes for the extensive design of the polymer-bound metal complex catalysts are stated.

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Part 2.

Catalysis of Polystyrene-Bound Rh Carbonyl Clusters

Chapter 1. Fundamentals of Metal Cluster Complexes

Recently, the study on the properties of metal clusters belongs to one of the most fascinating fields in physics and chemistry[1-3]. The metal clusters can be defined as molecules including two or more metal-metal bonds. One distinction between clusters and colloids is due to the difference in the size and colloids show a distribution of the particle sizes in solution whereas clusters keep a discrete particle size and molecular entity. There is confusion regarding the nomenclatures used to describe small metal aggregate: the terms of clusters, nano clusters, and colloids, have all been used to describe metal aggregates of quite different sizes. In order to avoid such a confusion, Schmid has proposed a definition of metal clusters and colloids: metal aggregates with the sizes smaller than 100 Å in diameter are called as metal nanoclusters and the aggregates with those bigger than 100 Å are defined as metal colloids (**Figure 1**)[2].

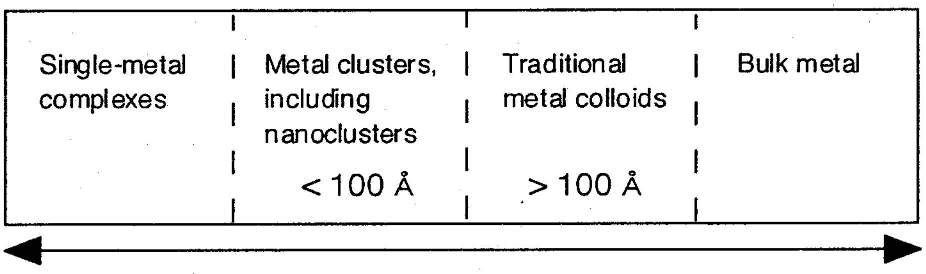


Figure 1. Schmid's Difinition of the Continuum of Metal Aggregate Sizes.

The syntheses of large metal clusters can be principally possible by following two pathways: a) the aggregation of smaller metal clusters by the thermal treatment or by controlled chemical reactions. For an example of a large transition metal clusters, $[Pt_{38}(CO)_{44}H_x]^{2-}$ was prepared by stacking smaller clusters[4]. The another pathway is b) the direct build-up from atoms in the gas phase or in solution. The latter method would produce so-called naked metal clusters. As naked clusters are chemically very reactive to aggregate spontaneously to larger units, the isolation of the clusters is not possible as they are. The preparation of the controlled metal clusters is still a challenging problem. To overcome the difficulty of preparation of such metal clusters, in the last decade, there has been an explosive growth in the number of reports on the preparation of the metal clusters and colloids by chemical reduction of simple metal salts in organic solvents[5 and 6].

The metal nanoclusters prepared from the metal atoms in the gas phase or in solutions consist of the close packed atoms. The most common structures of transition metals are the hexagonal (hcp) and the cubic close packings (ccp). Therefore, it is consequent to assume that the clusters with so-called magic numbers of atoms exist on the way from the atoms to the bulk as shown in **Table 1**. Because of their complete outer geometry, these full-shell clusters, consisting of 13 (1+12), 55 (1+12+42), 147 (1+12+42+92) (in general $10n^2+2$ atoms in the *n*th shell) atoms should be long-lived, compared with that having incomplete shells[2].

Table 1. Close-Packed *n*-Shell Clusters with Magic Numbers

n	atoms in *n* th shell	total number atoms	*n*	atoms in *n* th shell	total number atoms
1	12	13	4	162	309
2	42	55	5	252	561
3	92	147			

The synthetic methodology for metal nanoclusters has been extensively developed not only because unprecedented chemical reactions might occur on multi-metal centers as catalysts, but also because metal clusters are useful precursors of new functional materials for optical and electronic applications. The metal nanoclusters are considered to be an intermediate between mono- or di-nuclear complexes and the bulk metal, which is a surface model compounds of metal catalysts[7-13]. Many interesting reactions of small molecules with nanoclusters have been observed, which suggest that clusters have high potentiality to show unique performance in catalysis. Especially, the interaction of carbon monoxide with metal nanoclusters has been extensively studied in relation to the valuable reactions such as the Fischer-Tropsch reaction.

1-1. High Nuclearity Metal Carbonyl Cluster (HNCC) Complexes

A large number of transition metal carbonyl clusters have been synthesized and their reactivities have been studied extensively[14]. Among the metal carbonyl clusters, their flameworks consisting of more than six metal atoms are called the high nuclearity carbonyl clusters (HNCC). The first of the synthesis of the HNCC was $Rh_6(CO)_{16}$ whose structure was determined by the X ray analysis[15]. Systematic and predictable syntheses of metal cluster compounds have emerged as the results of the pioneering works by Chini[4].

There are three general methods presently available for the synthesis of HNCC: a) the oxidative coupling, b) the thermal condensation, and c) the redox-condensation of parent complexes. When suitable reagents are employed, the redox condensation allows a step by step growth of the clusters and generally gives nearly quantitative yields. On the contrary, the synthesis of HNCC by the thermal condensation is more limited and resulted low yields.

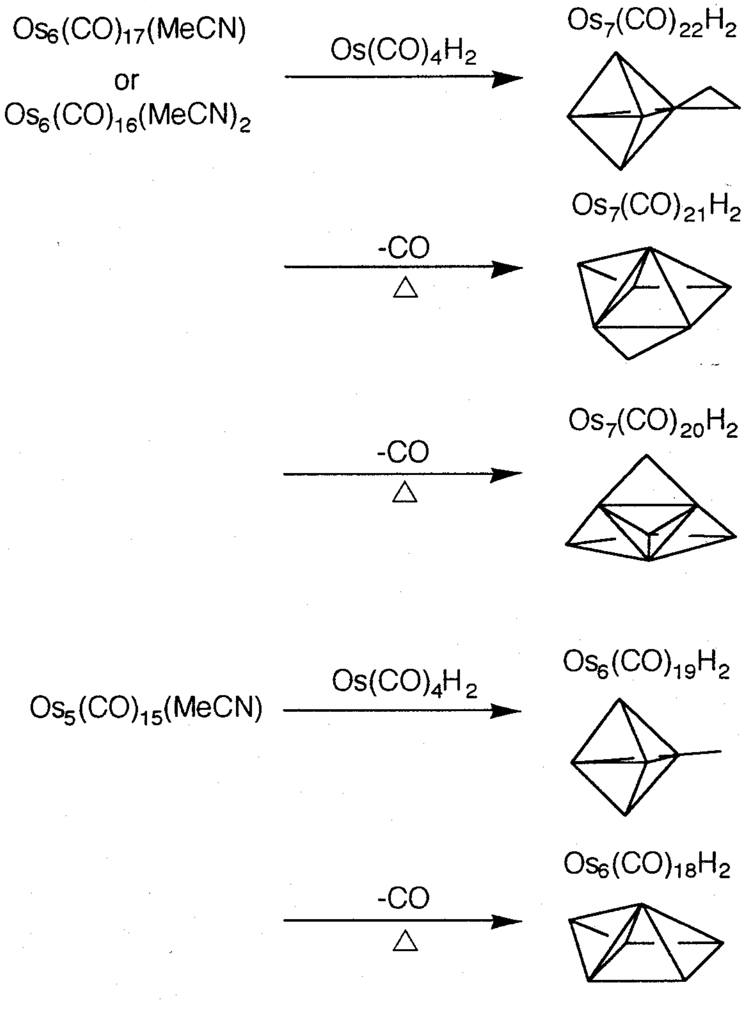
a) *Oxidative coupling of anionic clusters*

For an example, large rhodium carbide clusters could be obtained by oxidation of the $[Rh_6(CO)_{15}C]^{2-}$ dianion with Fe(III) salts (**Eq. 1**)[4]. The protonation often gives rise to unstable hydride derivatives as by-products.

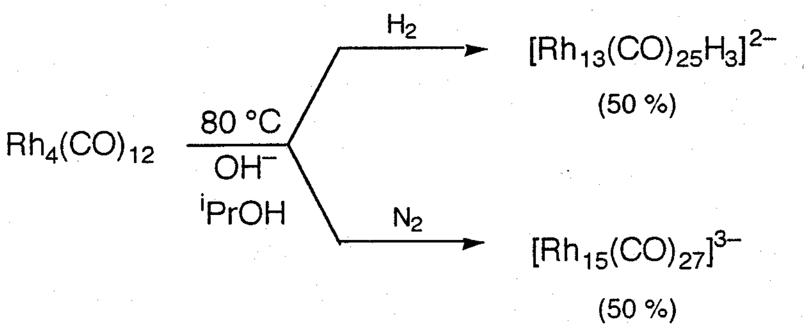
$$2[Rh_6(CO)_{15}C]^{2-} + 2H^+ \xrightarrow{Fe^{3+}} [Rh_{12}(CO)_{24}(C)_2]^{2-} + 6CO + H_2 \qquad (1)$$

b) *Thermal condensation*

The thermal condensation of preformed clusters offers high synthetic possibilities, but it requires a time-consuming and careful screening of the reaction conditions. Examples of this method are shown in **Scheme 1** for osmium [7] and **Eq. 2** for rhodium compounds[15].



Scheme 1. Thermal Condensation of Os Carbonyl Clusters.



(2)

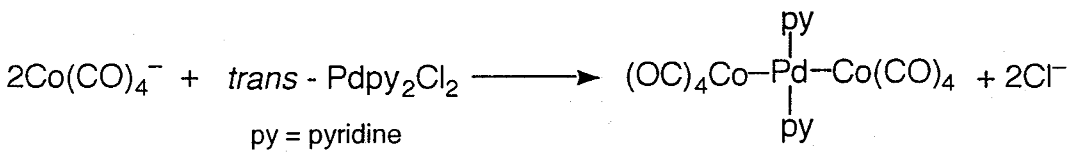
c) *Redox condensation*

The redox condensation reactions including the ligand displacement can be divided into three categories: the displacement of 1) anionic ligands, 2) CO, and 3) weakly coordinated ligands. The first example of redox condensation reaction was reported by Hieber in 1965, included in category 2 (**Eq. 3**).

$$[Fe_3(CO)_{11}]^{2-} + Fe(CO)_5 \xrightarrow[\text{THF}]{25\ ^\circ\text{C}} [Fe_4(CO)_{13}]^{2-} + 3CO \qquad (3)$$

c-1) *Displacement of anionic ligands*

Halides are the most common and easily displaced anionic ligands. When a halide ligand is displaced from a metal complex by an anionic metal complex, a metal-metal bond is usually formed. Braunstein *et al.* have prepared a variety of heteronuclear clusters containing palladium *e.g.*, reactions between metal carbonyl anions and palladium halide complexes (**Eq. 4**)[17]. This has also led to the synthesis of some unusual high nuclearity mixed metal carbonyl clusters.



$$2Co(CO)_4^- + \textit{trans}\text{-}Pdpy_2Cl_2 \longrightarrow (OC)_4Co\text{–}\underset{py}{\overset{py}{Pd}}\text{–}Co(CO)_4 + 2Cl^- \qquad (4)$$

py = pyridine

c-2) *Displacement of CO*

The displacement of CO in uncharged complex by a metal carbonyl anion is another effective method of increasing the metal nuclearity of cluster complexes in a systematic and a controllable fashion. The anion may be mononuclear (**Eq. 5**)[18] or polynuclear (**Eq. 6**) [18] and the displacement of several CO ligands and the formation of several metal-metal bonds are involved (**Eq. 7**)[19]. These are classical redox reactions.

$$\mathrm{Rh(CO)_4^-} + \mathrm{Rh_4(CO)_{12}} \longrightarrow \mathrm{[Rh_5(CO)_{15}]^-} + \mathrm{CO} \qquad (5)$$

$$\mathrm{[Ru_3(CO)_{11}]^{2-}} + \mathrm{Ru_3(CO)_{12}} \longrightarrow \mathrm{[Ru_6(CO)_{18}]^{2-}} + 5\mathrm{CO} \qquad (6)$$

$$\mathrm{[Rh_5(CO)_{15}]^-} + \mathrm{Rh(CO)_4^-} \longrightarrow \mathrm{[Rh_6(CO)_{15}]^{2-}} + 4\mathrm{CO} \qquad (7)$$

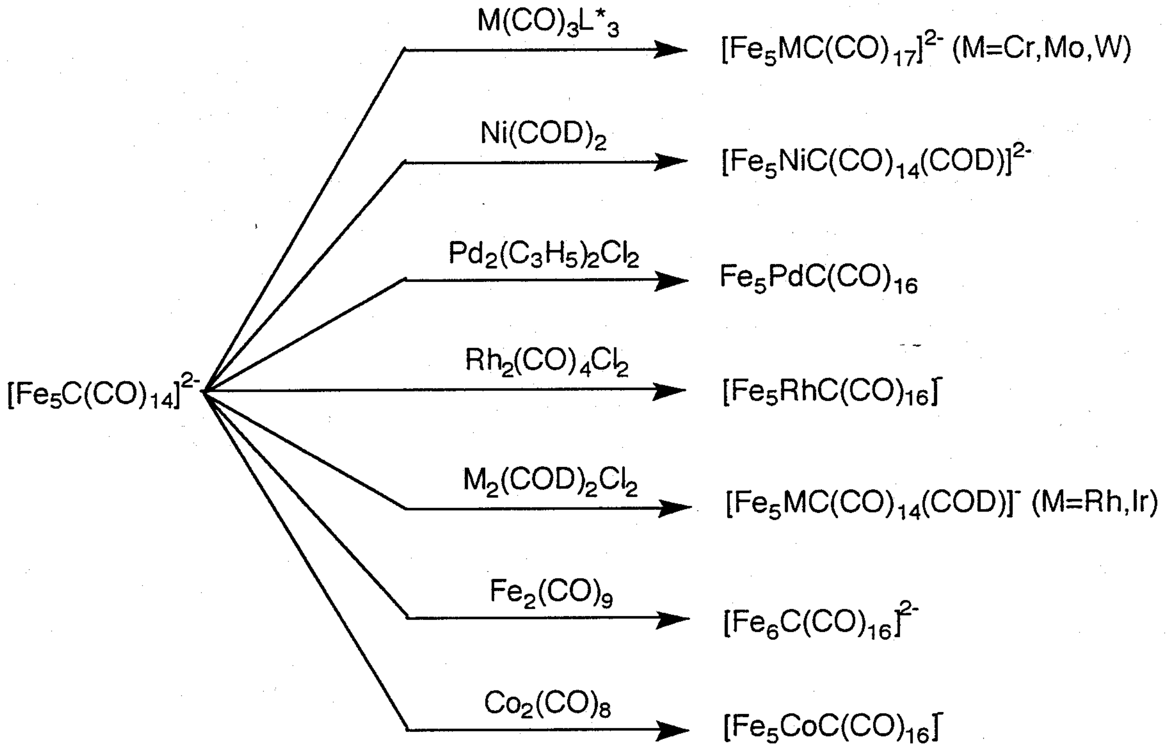
c-3) *Displacement of weakly coordinated ligands*

THF, CH_3CN, COD(cyclooctadiene), pyridine, acetone, and many alkenes are the most common examples of weakly coordinated ligands. Metal complexes containing these ligands are said to be "lightly stabilized". The lightly stabilized complexes have been used for the enlargement of high nuclearity clusters (**Eqs. 8 and 9**)[15].

$$\mathrm{[Rh_{13}(CO)_{24}]^{3-}} + \mathrm{[Rh(CO)_2(CH_3CN)_2]^+} \xrightarrow{298\ \mathrm{K}} \mathrm{[Rh_{14}(CO)_{25}H]^{3-}} + \mathrm{CO} \qquad (8)$$

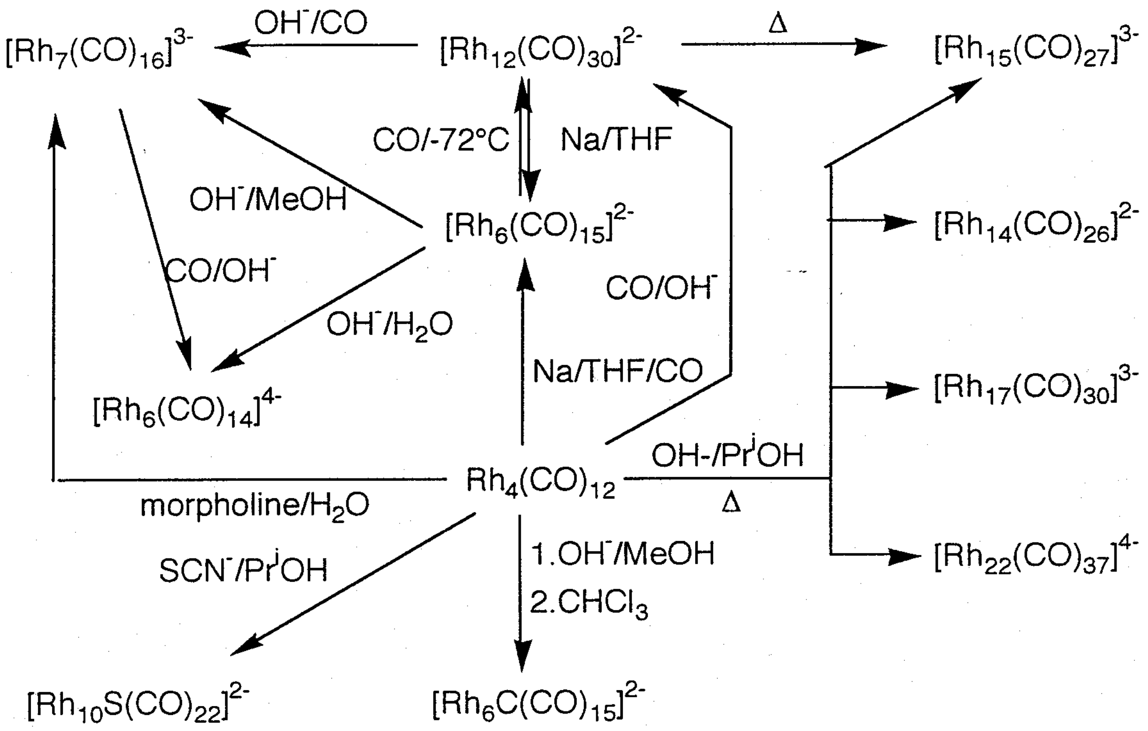
$$\mathrm{[Rh_{14}(CO)_{25}]^{4-}} + \mathrm{[Rh(CO)_2(CH_3CN)_2]^+} \xrightarrow{298\ \mathrm{K}} \mathrm{[Rh_{15}(CO)_{27}]^{3-}} \qquad (9)$$

Additional examples of redox condensations are shown in **Scheme 2**[8]. In the case of rhodium carbonyl clusters, a variety of anionic clusters have been synthesized, and the basic redox interconversions between them are outlined in **Scheme 3** [21].



*M=Cr,L=C_5H_5N ; M=Mo,L=THF ; M=W,L=MeCN

Scheme 2. Examples of Cluster Enlargements Through Redox Condensation Reactions.



Scheme 3. Redox Interconversions Between Rh Carbonyl Cluster Anions.

1-2. Catalysis of Metal Clusters

The reactivity of the metal cluster complexes might offer some opportunities to obtain high performance catalysts from the following reasons.

- Clusters could offer unique selectivity by virtue of their structures.
- Neighboring metal centers of the clusters allow multiple bonding of a single reactant molecule, providing opportunities for conversions of reactants which are impossible with mononuclear metal complexes.
- Clusters allow bonding of different reactants in neighboring positions. It should be expected that one metal atom in the bimetallic clusters specifically is chosen to bind one reactant and the other metal is chosen to bind the other.
- Effects of ligands at one metal can be transmitted to other metal center through the metal-metal bonds, which allow to design catalysts by choice of the proper ligands.

A number of reports of catalytic reactions by metal clusters include isomerizations, reductions of multiple bonds, hydroformylation, the Fischer-Tropsh synthesis, and the Water-Gas Shift Reaction, etc.[22]. In addition, there are several studies on interactions of ligands with metal clusters which are unknown for mononuclear compounds. It suggests that the unique catalysis based on clusters is the reasonable expectation[23, 24].

The metal cluster complexes are soluble in solvents and could not be easily recovered from the reaction mixtures. Furthermore, since metal-metal bonds in clusters are usually weak, the stabilization of the cluster flameworks under the reaction conditions is necessary for the cluster catalysis.

To solve these problems, the attempts to immobilize the metal clusters on the solid supports have been developed[25-28]. The immobilization of metal cluster complexes onto organic or inorganic polymers, hybrid catalysts[29], would provide a fruitful methodology for the preparation of novel heterogenized catalysts, which act as a bridge between traditional homogeneous and heterogeneous catalysts[30, 31].

Typical polymeric supports can be classified into inorganic polymers such as silica, alumina, zeolite, and clay, and organic polymers such as polystyrenes and polyamides[24].

Concerning organic polymers, cross-linked polystyrenes are widely used as supports for the metal complexes. The organic polymers have been attractive because the desired polymers could be obtained by incorporation of various functional groups on the polymers[32-35].

The purpose of this part is the development of high performance polymer-bound rhodium carbonyl cluster catalysts for the selective reduction of carbonyl groups with H_2O, H_2, and HCOOH as reducing agents in the presence of CO. Rhodium carbonyl clusters are considered to be suitable for catalysts because Rh complexes have high potential abilities as catalysts for the reductions, and the structures of Rh clusters have been well characterized crystallographically and spectroscopically. Polystyrenes seem also to be useful materials for designing polymer-bound catalysts because their physical and chemical properties could be easily controlled by incorporation of desired functional groups on their surface.

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Chapter 2. Selective Reduction of Carbonyl Compounds Catalyzed by Polymer-Bound Rh Carbonyl Clusters under the Water-Gas Shift Reaction Conditions

–Use of H_2O as a Hydrogen Source –

2-1. Introduction

The use of water as a reagent or a reaction medium in place of organic solvents is of great interests to develop environmentally friendly organic syntheses of organic compounds, because water is highly economic and non-toxic. Furthermore, the use of water would significantly decrease emission of harmful wastes[1]. Water is a unique solvent for certain stoichiometric and catalytic reactions involving organometallic compounds[2-4]. The protic and highly polar natures of water strongly influence the acid-base behavior of solutes and the formation and disruption of ion pairs. Hydrogen bonds and the extent of the hydrophobic interactions with organometallic compounds are also anticipated. The combinations of these effects sometimes lead to acceleration of reaction rates and unexpected product selectivity[2 and 3].

Applications of the aqueous media to organometallic reactions such as aqueous two phase catalysis are growing in number[2, 3, 5-8], however, there are a few example using water as a reactant in catalysis. A typical example of the known reactions where the water acts as a reagent is the "Water-Gas Shift Reaction (WGSR)". This reaction produces H_2 and CO_2 from the mixture of H_2O and CO (**Eq. 1**). H_2 required for the industrial production of ammonia is generated through this equilibrium reaction. This reaction can also be used to adjust the H_2/CO ratio in the synthesis gas, a mixture of H_2 and CO.

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (1)$$

$$(\Delta H°298 = -41 kJ/mol, \Delta G°298 = -28 kJ/mol)$$

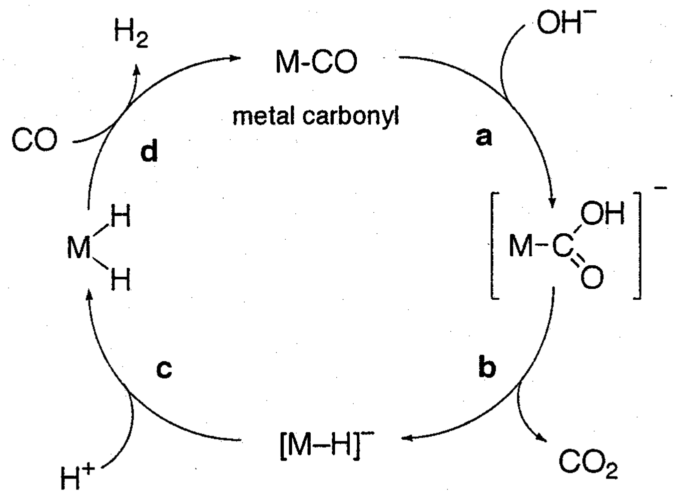
The useful rates of the reaction which could be available for the commercial plants are achieved only when catalysts and high temperatures are employed. In the typical processes, chromium(II) oxides at 350-450 °C and copper/zinc oxides at 200-300 °C are used as catalysts[9]. Since the equilibrium constant exhibits a negative temperature dependence, there is still a need to find better catalysts.

Recently, soluble metal complexes such as $Fe(CO)_5$ and their derivatives $[HFe(CO)_4]^-$, $Ru_3(CO)_{12}$, $[Rh(CO)_2I_2]^-$, and $Pt[P(^iPr)_3]_3$ have been recognized to catalyze the WGSR which provides an insight into the role of the metal in the heterogeneous catalytic reaction mechanism. In addition, the rhodium complex of $[Rh(CO)_2I_2]^-$, the key catalytic species in the Monsanto acetic acid process, is particularly efficient[10].

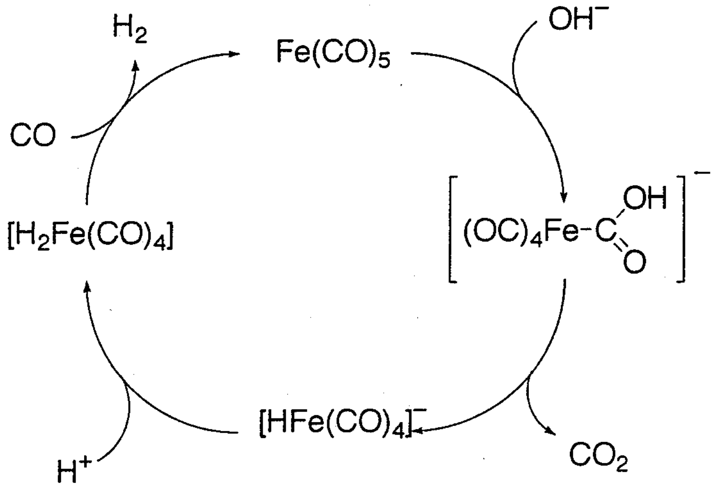
The mechanism of the WGSR catalyzed by metal carbonyl complexes has been proposed by Ford *et al.* in 1970's as shown in **Scheme 1**[11-14]. It involves a number of consecutive organometallic reactions. The first step is the nucleophilic attack at a metal-coordinated carbon monoxide by a hydroxide anion (reaction **a** in **Scheme 1**)[15]. A transition metal carboxylic acid resulting from the above step is normally unstable to decarboxylation, thus undergoing degradation to metal hydrides (reaction **b** in **Scheme 1**)[16]. The anionic hydride species takes up a proton from the aqueous medium to yield a dihydride complexes (step **c**). In the final step of **d**, the elimination of hydrogen through replacement by CO completes the catalyst cycle. A typical example of the reaction mechanism for the WGSR catalyzed by $Fe(CO)_5$ is shown in **Scheme 2**[17].

Some other metal carbonyl complexes including Rh carbonyls also show the catalytic activity in the WGSR above *ca* 50 °C[18]. The Rh carbonyl compounds are also formed *in situ* by $HRhL_3$ ($L=PEt_3$, PPr^i_3) under the WGSR conditions. Among the rhodium complexes, various Rh carbonyl clusters such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $[Rh_{12}(CO)_{30}]^{2-}$ are active catalysts; they are the most effective when ethylenediamine is added as a base under mild reaction conditions[19]. The catalyst systems have been utilized in a variety of functional group transformations under the WGSR conditions[20]. Kaneda *et al.* have explored deoxygenation of various N-O bonds[21], reduction of carbonyl groups[22], hydrohydroxymethylation of olefins[23] catalyzed by Rh carbonyl clusters under the WGSR conditions in the presence of amines (**Scheme 3**).

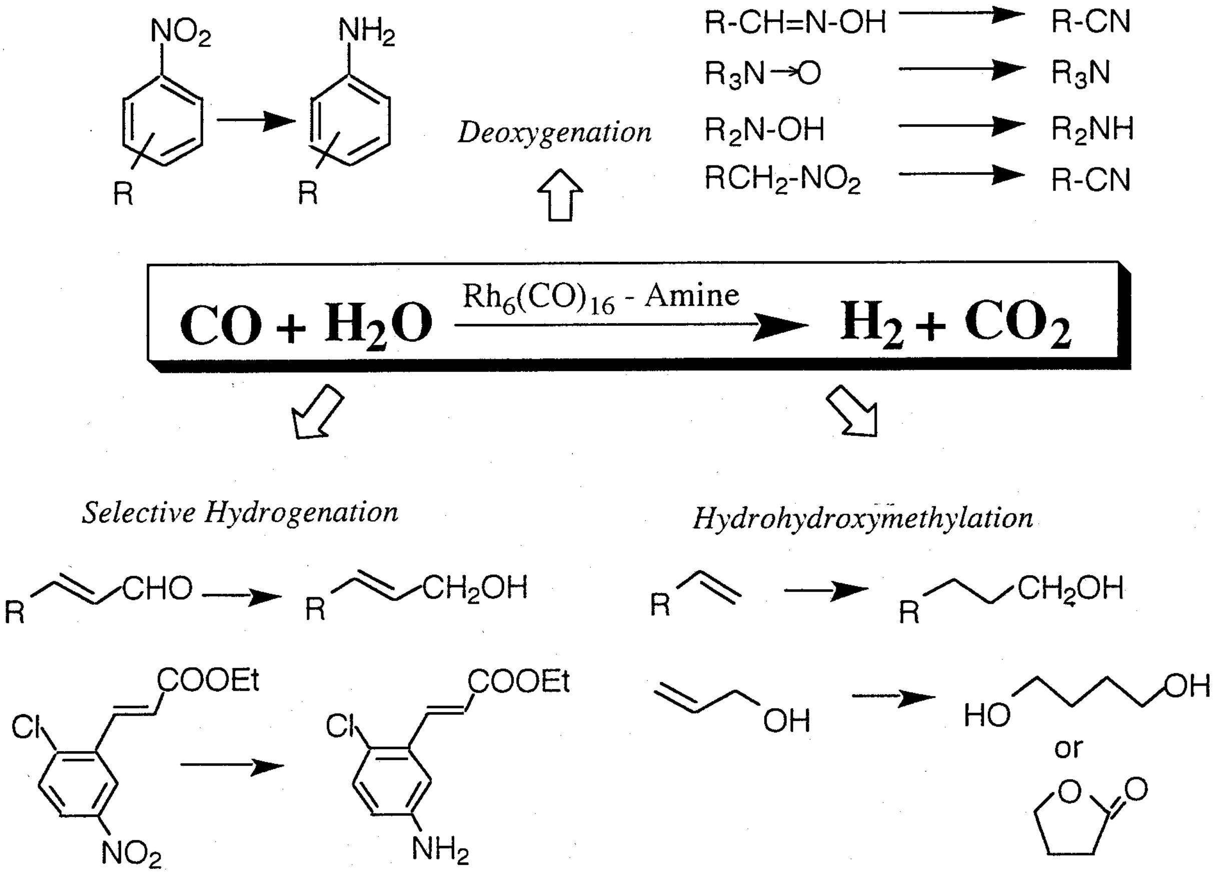
In the above homogeneous catalytic reactions, an amphiphilic solvent such as 2-ethoxyethanol was a good solvent in order to dissolve Rh clusters and water in the organic



Scheme 1. Proposed Mechanism for Metal-Catalyzed WGSR.



Scheme 2. Proposed Mechanism for the WGSR Catalyzed by $Fe(CO)_5$ Complex.



Scheme 3. Applications to Organic Syntheses of Rh Cluster Catalyst System under the WGSR Conditions.

phase. Because of the homogeneity of the reaction mixtures, it seems difficult to separate the expensive Rh cluster catalysts from the reaction mixtures in the above reactions and reuse with keeping their initial catalytic activities. The use of the solid catalysts may overcome these disadvantages of homogeneous catalytic reactions as described in Part 1. Expected advantages of using the solid supports are summarized as follows.

- Facile separation of the catalyst from the reaction mixture.
- Increase of catalyst stability through the interaction with solid surface.
- High product selectivities promoted by the interaction of active species with supports.
- Freedom of the solvent selection.

The heterogenization of the homogeneous metal complexes has been extensively attempted using inorganic solid supports such as SiO_2, MgO, and Al_2O_3, but the activities and selectivities of the immobilized metal complexes are usually insufficient, compared with the corresponding homogeneous catalyst systems[24-28]. Some problems such as the metal leaching from the surface during the organic reactions and the diffusion limitation of substrates through microporous supports also remain to be solved. On the other hands, organic polymers offer several advantages over other inorganic catalyst supports[29]:

- Various functional groups can be easily introduced.
- Unlike the surfaces of metal oxides having acid-base properties, polymeric hydrocarbons are almost neutral which suppress unfavorable side reactions.
- Physical and chemical properties of organic polymers, especially poly(styrene-divinylbenzene), can be tunable.

Based on the above superior characters, the author utilized organic polymer styrenes as solid supports for the immobilization of the Rh carbonyl clusters. The functional groups at the polymer surface can chemically bind with the metal complexes. Furthermore, it is expected that the organic polymer supports will provide biomimetic, enzyme-like high performance polymeric metal complex catalysts[30].

In this chapter, the author heterogenized the Rh carbonyl cluster complexes by designing the polystyrene surface for the selective hydrogenation of carbonyl compounds under WGSR conditions. Various amino and ether groups were introduced to the polystyrene surface, which were used as supports. It was found that the Rh cluster complexes bound to the modified polystyrene showed higher catalytic activities than the corresponding homogeneous catalyst system. The basicity and hydrophilicity of the polystyrenes were characterized in relation to the catalytic features of the immobilized Rh cluster complexes. Finally, the distinct roles of functional groups on the polymer surface in the catalysis and stability of the Rh carbonyl complexes was emphasized.

2-2. Experimental

2-2-1. General

^{1}H NMR spectra were obtained on JEOL GSX-270 or JNM-AL400 spectrometers at 270 or 400 MHz in $CDCl_3$ with TMS as an internal standard. Infrared spectra were obtained with a Shimadzu FT-IR 8200PC and JASCO FTIR-410. Analytical GLC was performed by a Shimadzu GC-8APF with flame ionization detector and GC-8AIT with thermal conductivity detector equipped with KOCL 3000T and Silicone UC W-98 columns. Elemental analysis was carried out by Perkin Elmer 2400CHN.

Aldehydes, amines, and solvents were purchased from Wako Chemicals and Tokyo Kasei, and purified according to the standard procedures and stored under a nitrogen atmosphere [31]. $RhCl_3{\bullet}3H_2O$ was obtained from N.E. Chemcat. *cis*-3-Acetyl-2,2-dimethylcyclobutane-acetaldehyde was synthesized by ozonolysis of α-pinene[32]. *p*-(Chloromethyl)styrene was purchased from SEIMI Chemical. All of the substrates and products were characterized by comparison with the literature data.

2-2-2. Preparation of Rh Carbonyl Cluster

Rhodium carbonyl clusters $Rh_6(CO)_{16}$ was prepared from $RhCl_3{\bullet}3H_2O$ according to the following procedures (**Eq. 2**).

$$RhCl_3{\cdot}3H_2O \xrightarrow[100\ ^\circ C]{CO} Rh_2(CO)_4Cl_2 \xrightarrow[KOH/MeOH]{CO} Rh_6(CO)_{16} \qquad (2)$$

2-2-2-1. Synthesis of $Rh_2(CO)_4Cl_2$

$Rh_2(CO)_4Cl_2$ was synthesized from $RhCl_3 \cdot 3H_2O$ by the reaction with CO (**Eq. 3**)[33].

$$2(RhCl_3 \cdot 3H_2O) + 6CO \xrightarrow[100\ °C]{} Rh_2(CO)_4Cl_2 + 6H_2O + 2COCl_2 \quad (3)$$

$RhCl_3 \cdot 3H_2O$ (5.7 mmol, 1.5 g) was placed on the sintered-glass filter attached to the bottom of the grass tube and heated at 100 °C in the slow up-stream of carbon monoxide. After 24 h, the red needle-like crystal was obtained (0.89 g, 80 %). IR ν_{CO} (2102 m, 2084 s, 2030 s cm^{-1}; Nujol mull, **Figure 1**).

2-2-2-2. Synthesis of Hexarhodium Carbonyl Cluster $Rh_6(CO)_{16}$

$Rh_6(CO)_{16}$ was synthesized from $Rh_2(CO)_4Cl_2$ according to the method by Chini (**Eq. 4**)[34].

$$3Rh_2(CO)_4Cl_2 + 6KOH + 7CO \longrightarrow Rh_6(CO)_{16} + 6KCl + 3CO_2 + 3H_2O \quad (4)$$

A 0.2 N KOH solution in methanol (4.0 mmol, 20 mL) was slowly added over two hours into a solution of $Rh_2(CO)_4Cl_2$ (2.0 mmol) in 35 mL of methanol under an carbon monoxide atmosphere. After stirring for 48 h, the supernatant was withdrawn and the resulted $Rh_6(CO)_{16}$ was washed with methanol for three times and vacuum dried (0.67 g, 94%). IR ν_{CO} (2080 s (br), 2069 s (sh), 2052 s (sh), 2042 m (sh), 2025 m, 2019 m (br), 1797 s (br) cm^{-1}; Nujol mull, **Figure 2**).

2-2-3. Preparation of Various Aminated Polystyrenes

Bulk polymerization of *p*-(chloromethyl)styrene and divinylbenzene (2 wt %) was carried out using α,α'-azobis-isobutyronitrile (AIBN). Various aminated polystyrenes were synthesized by the modified procedure in the literature [29]. A typical example using diethylamine as a modifier was as follows. An excess of diethylamine (30 ml) was added dropwise over 2 hours to poly(4-chloromethyl)styrene (2 g, 12.5 mmol eq. of Cl) swollen in 30 ml of 1,4-dioxane. After stirring for 48 h at room temperature, the resulted light brown polymer was filtered and washed successively with 1,4-dioxane, a 1:1 mixture of 0.1 N NaOH aq. and acetone, then aqueous acetone (50 vol. %) for several times until the filtrate

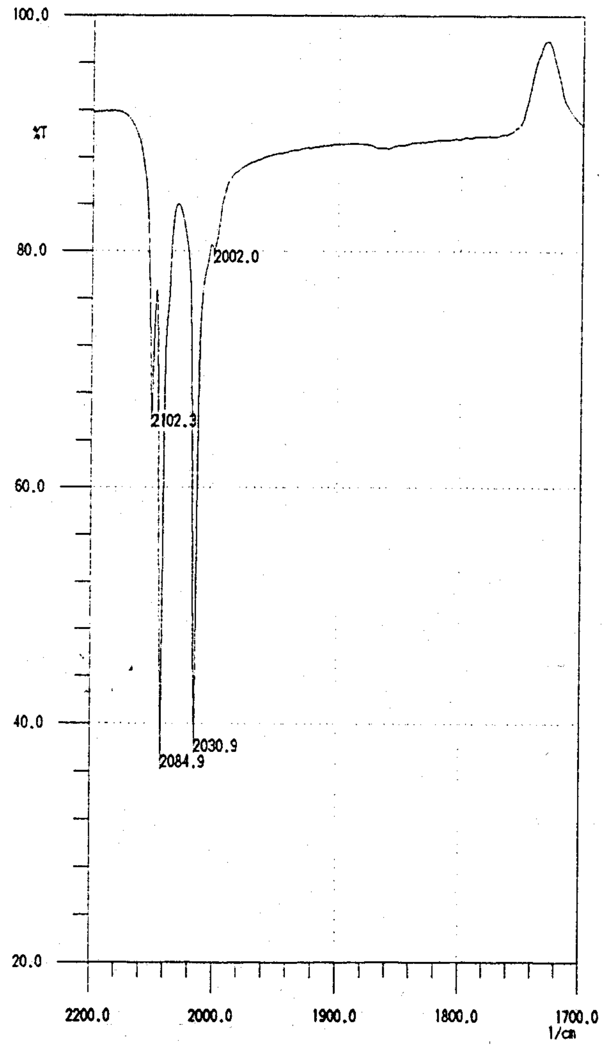


Figure 1. IR Spectrum of $Rh_2(CO)_4Cl_2$

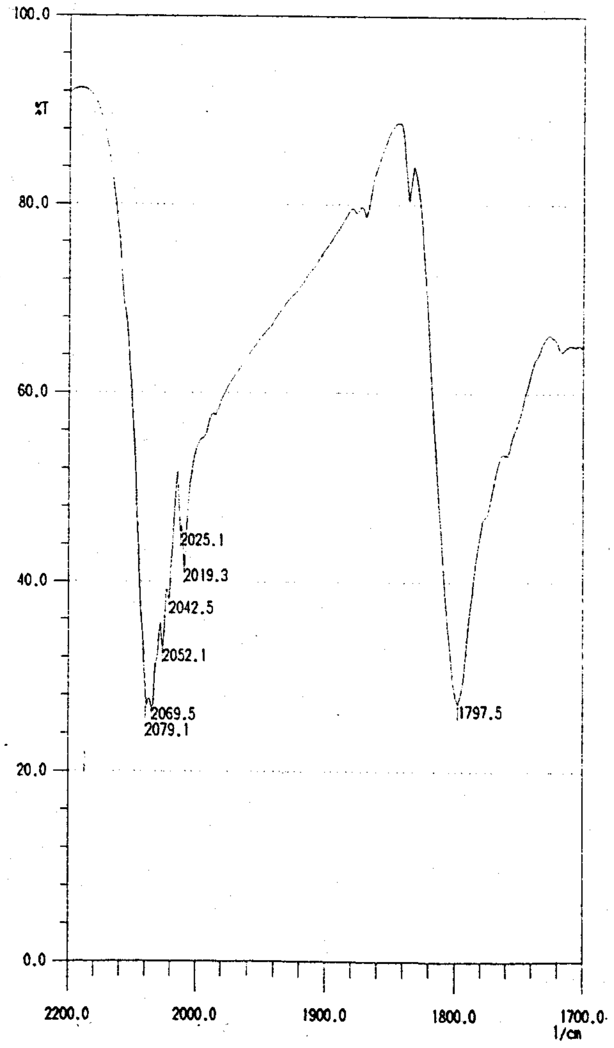


Figure 2. IR Spectrum of $Rh_6(CO)_{16}$

became neutral (usually for three times). Finally, it was washed with acetone and dried *in vacuo* at 60 °C for 24 h to give the pale yellow diethylaminated polystyrene (**1N**).

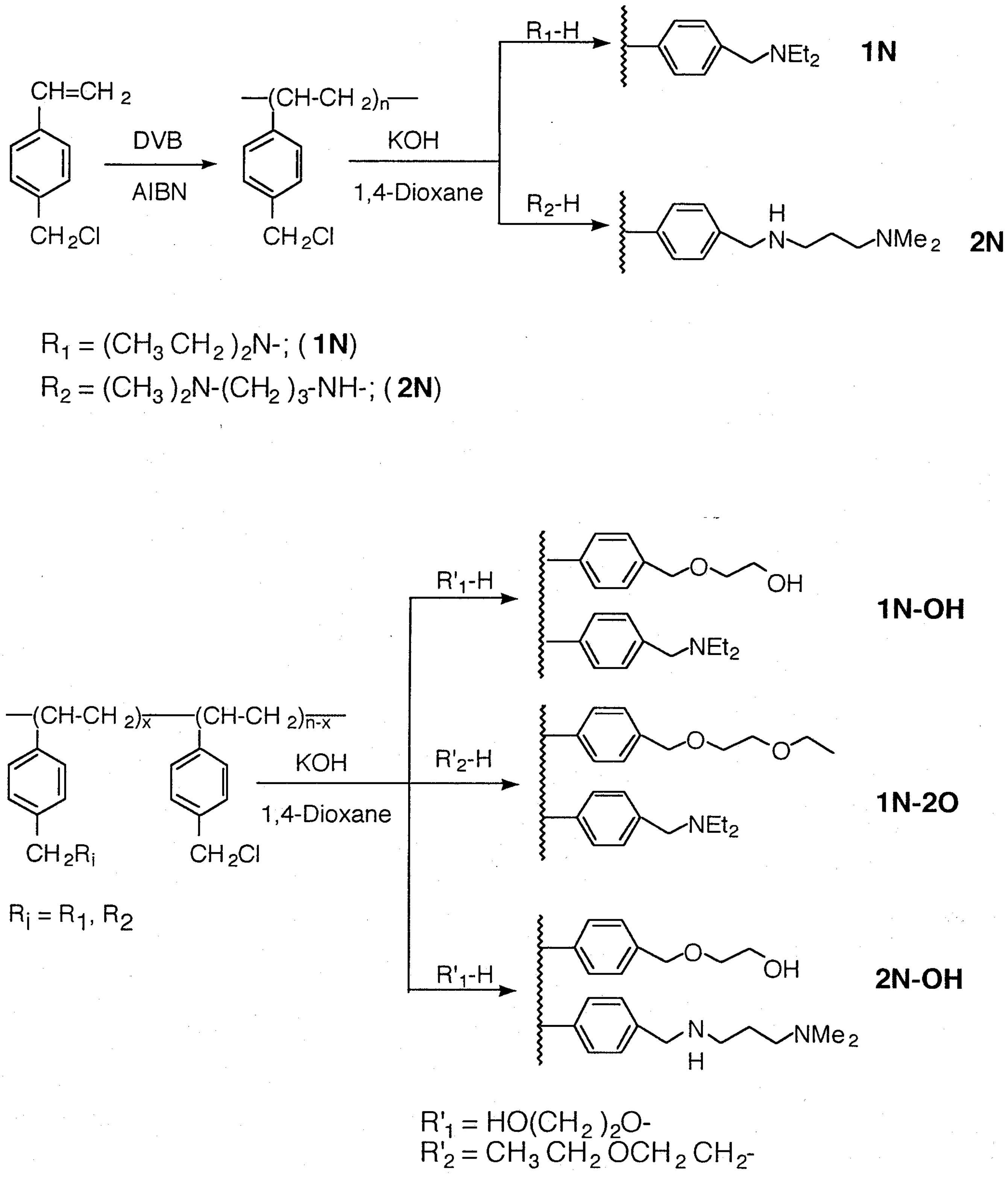
2-2-4. Preparation of Successive Multi-Functionalized Polystyrenes

The residual chloromethyl moieties in the aminated polystyrenes of **1N** and **2N** can be functionalized successively with ethylene glycol or 2-ethoxyethanol which gave multi-functionalized polystyrenes which are designated as polymer **1N-OH**, **2N-OH**, and **1N-2O**, respectively (**Scheme 4**)[35]. A typical example of the preparation of polymer **1N-OH** was as follows. Diethylaminated polymer **1N** (2 g) and solid KOH (1.1 g) was placed in a flask and allowed to swell in 30 ml of 1,4-dioxane under a nitrogen atmosphere. Then, 30 ml of ethylene glycol was added and the mixture was heated at 100 °C for 48 h with stirring. The resulting polymer was filtered and washed with 1,4-dioxane, a 1:1 mixture of 0.1 N NaOH aq. and acetone, then aqueous acetone (50 vol. %) for several times until the filtrate became neutral (usually for three times). Finally, washing with acetone and drying *in vacuo* at 60 °C for 24 h gave the brownish polymer **1N-OH**. Polymer **2N-OH** was obtained from the diaminated polystyrene **2N**. Use 2-ethoxyethanol in place of ethylene glycol gave polymer **1N-2O** from polymer **1N** having 2-(ethoxy)ethoxy moieties.

2-2-5. Preparation of Direct Multi-Functionalized Polystyrenes

Introduction of the functional groups containing amino and ether groups in one spacer was carried out by the treatment of the poly(4-chloromethyl)styrene with various aminoalcohols as shown in **Scheme 5**.

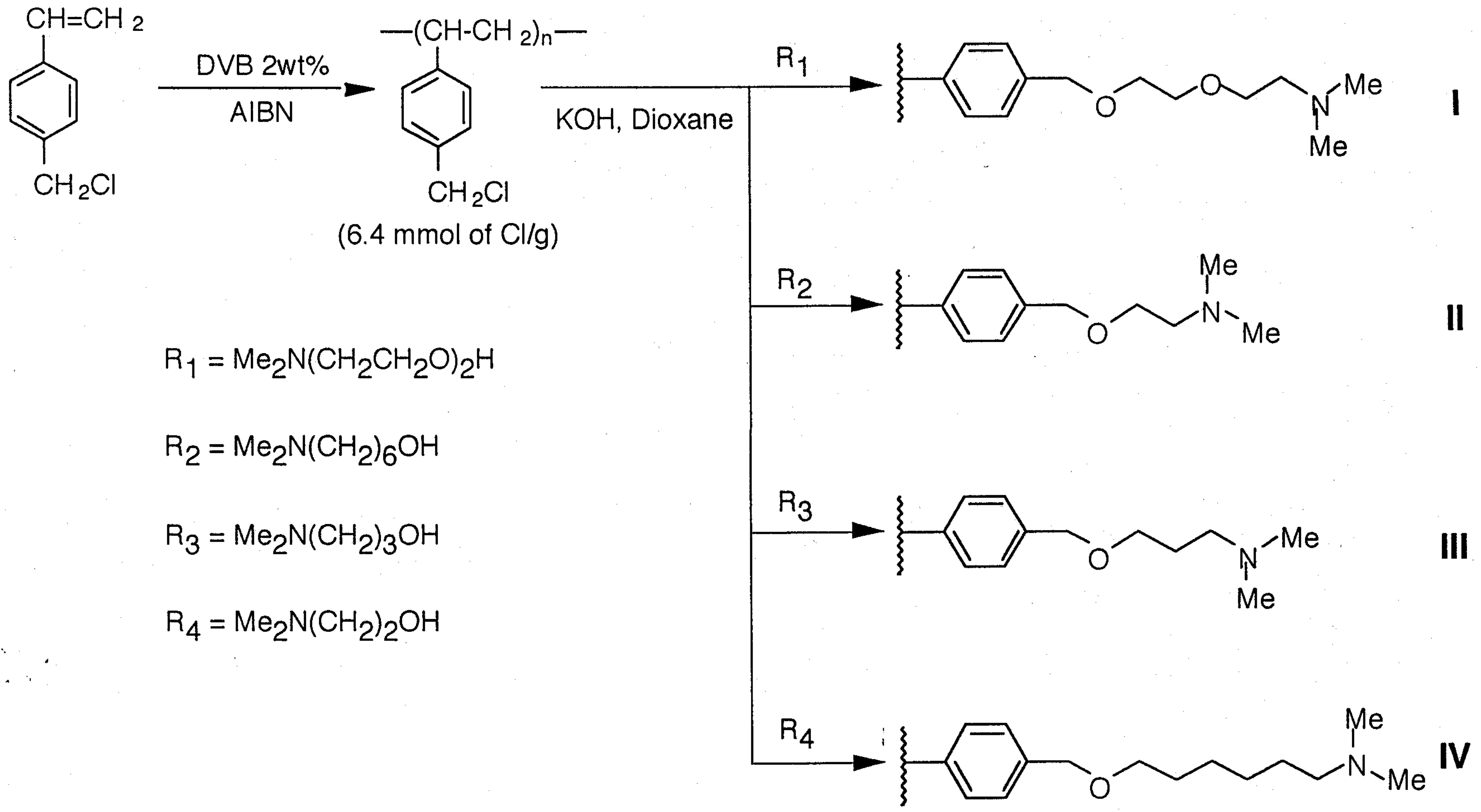
Typically, an excess of 2-(dimethylamino)ethoxyethanol (30 ml) was added dropwise over 2 hours to poly(4-chloromethyl)styrene (2 g, 12.5 mmol eq. of Cl) and solid KOH (1.1 g) swollen in 30 ml of 1,4-dioxane at 100 °C under a nitrogen atmosphere. After stirring for 48 h, the resulting light brown polymer was filtered and washed successively with 1,4-dioxane, a 1:1 mixture of 0.1 N NaOH aq. and acetone, then aqueous acetone (50 vol. %) for three times until the filtrate became neutral. Finally, washing with acetone and drying *in vacuo* at 60 °C for 24 h(**I**). *N*,*N*-Dimethylethanolamine, 3-dimethylaminopropanol, and 6-dimethylaminohexanol were also used to give polymers **II**, **III**, and **IV**, respectively.



$R_1 = (CH_3CH_2)_2N-$; (**1N**)
$R_2 = (CH_3)_2N-(CH_2)_3-NH-$; (**2N**)

$R'_1 = HO(CH_2)_2O-$
$R'_2 = CH_3CH_2OCH_2CH_2-$

Scheme 4. Successive Multi-Functionalization of Polystyrenes



$R_1 = Me_2N(CH_2CH_2O)_2H$

$R_2 = Me_2N(CH_2)_6OH$

$R_3 = Me_2N(CH_2)_3OH$

$R_4 = Me_2N(CH_2)_2OH$

Scheme 5. Direct Multi-Functionalization of Polystyrenes

2-2-6. Estimation of Amination Degrees of the Functionalized Polystyrenes

The amination degrees of the functionalized polystyrenes were estimated by N contents calculated from the elemental analysis and the titration of amino groups using method by Pillai[36]. The titration of amino groups was performed by the following procedures. Dried aminated polystyrene (100 mg) was equilibrated with 0.2 N HCl (10 ml) for 24 h at room temperature. The polymer was filtered, washed with ca 20 ml of distilled water to remove unreacted HCl. The filtrate was titrated with 0.2 N NaOH to a phenolphthalein end point.

2-2-7. Evaluation of Hydrophilicity of Polymers

Hydrophilicity of the functionalized polymers was evaluated by measuring the hygroscopic degree of the polymers. Each polymer sample of **I~IV** (200 mg) was dried at 50 °C for 24 h *in vacuo*, followed by exposing to moisture in the sealed vessel for 72 h. After the treatment, the wet samples were weighed and calculated the hygroscopic degree (H) according to the following equation [24].

$$H = (X_w - X_d) / X_d$$

X_w: weight of wet polymer . X_d: weight of dried polymer.

2-2-8. Estimation of Basicity of the Aminated Polystyrenes

The basicity of the polymer was estimated by π electron charge density of the nitrogen atom, which was calculated by the simple Hückel method as a function of number (n) of methylenes in $Ph-CH_2-O-(CH_2)_n-N(CH_3)_2$ molecules. Simple Hückel calculation was performed by the program HMO 2.2 from freeware program.

2-2-9. General Procedures for the Homogeneous Hydrogenation of Aldehydes Under Water- Gas Shift Reaction Condition

Homogeneous hydrogenation of benzaldehyde was a typical example as follows. A stainless autoclave containing $Rh_6(CO)_{16}$ (0.010 mmol) and *N,N,N',N'*-tetramethyl-1,3-propanediamine (TMPDA, 0.18 mmol) was evacuated and flushed three times with CO. A 1,4-dioxane (3.0 ml) solution of benzaldehyde (1.5 mmol) and H_2O (80 mmol) were added successively. The reaction mixture was stirred at 80 °C under 10 atm of CO for 24 h. The products were analyzed by GC.

2-2-10. General Procedures for the Heterogeneous Hydrogenation of Aldehydes Under Water-Gas Shift Reaction Conditions

Heterogeneous hydrogenation of benzaldehyde was carried out using polymer **I** and $Rh_6(CO)_{16}$ as a typical example in the following procedures. A stainless autoclave containing $Rh_6(CO)_{16}$ (0.010 mmol) and polymer **I** (40 mg, 0.18 mmol of N) was evacuated and flushed three times with CO. A benzene (3.0 ml) solution of benzaldehyde (1.5 mmol) and H_2O (80 mmol) were added successively. The reaction mixture was stirred at 80 °C under 10 atm of CO for 24 h, the reactor was cooled and the pressure was carefully released. After the resulting solid polymer was removed by filtration, the filtrate was extracted with diethylether and the organic layer was analyzed by GC. IR spectra of the polymeric catalysts after the filtration showed the formation of $[Rh_{12}(CO)_{30}]^{2-}$ as a main species. IR (2075 w (sh), 2066 w, 2035 s, 1992 s (br), 1970 s (br), 1803 w (sh), 1769 s (br) cm^{-1}; Nujol mull, **Figure 3**).

2-2-11. Recycling of the Polymer-Bound Rh Cluster Catalyst

The polymer-bound Rh cluster catalyst was subjected to reuse in the hydrogenation of benzaldehyde in the presence of H_2O and CO. The first run was carried out as the same procedures as described in the above heterogeneous hydrogenation. After the reaction mixture was stirred at 80 °C under 10 atm of CO for 24 h, the reactor was cooled and the pressure was slowly released. The solid was separated from the reaction mixture by filtration, and washed with benzene for three times in the air. The obtained polymer catalyst was placed in the autoclave, and a benzene (3.0 ml) solution of benzaldehyde (1.5 mmol) and H_2O (80 mmol) were charged successively, followed by stirring at 80 °C under 10 atm of CO for 24 h.

2-3. Results and Discussion

2-3-1. Hydrogenation of Benzaldehyde Using Various Aminated Polystyrenes

In the homogeneous hydrogenation of aldehydes using $Rh_6(CO)_{16}$ and amines under the Water-Gas Shift Reaction conditions, various kinds of solvents were scrutinized to find that 2-ethoxyethanol was an effective solvent[22]. It was proposed that the ether group in this solvent might favorably interact with Rh cluster anions, like solvation, to stabilize Rh

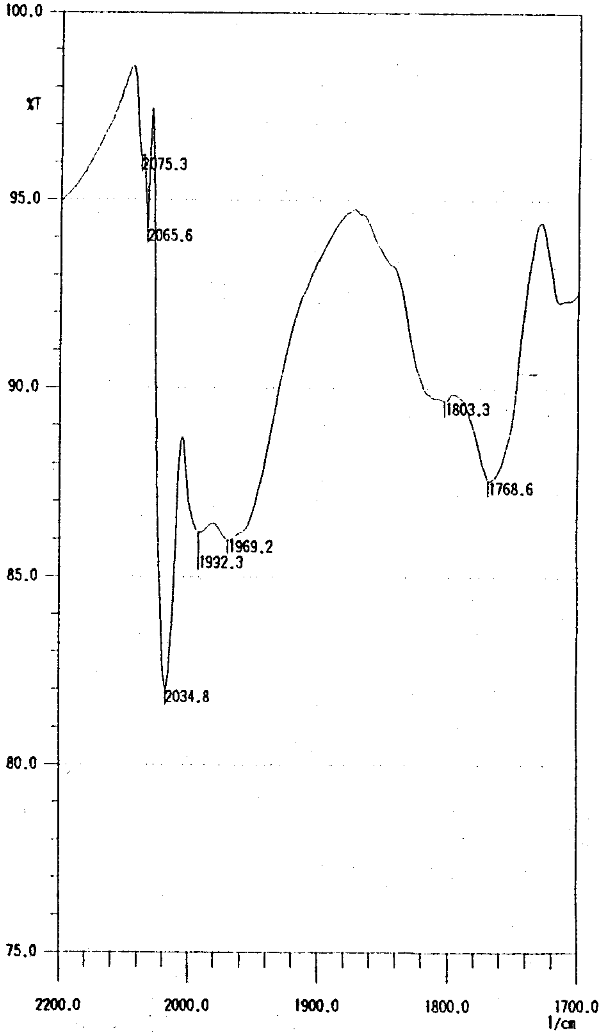


Figure 3. IR Spectrum of Polymer-Bound $[Rh_{12}(CO)_{30}]^{2-}$

cluster complexes. Similar results were observed in the other catalytic reactions with $Rh_6(CO)_{16}$ and amines, such as deoxygenation of nitro compounds[37-39], hydrohydroxymethylation of olefins[23]. The interactions of the Rh carbonyl cluster with ether and amino groups are essential for the homogeneous reaction systems. Therefore, it is reasonable to use the polymers modified with ether and amino groups as a support of the Rh carbonyl clusters.

Table 1 shows the results of the hydrogenation of benzaldehyde using CO and H_2O in the presence of $Rh_6(CO)_{16}$ and various functionalized polymers. The use of polymers of **1N** and **2N** resulted in low yields of benzyl alcohol. Further, the use of two-step functionalized polymers having ether and/or hydroxyl groups (**1N-OH**, **1N-2O**, and **2N-OH**) increased the catalytic activities. With direct multi-functionalized polymers having amino and ether groups (**I**~**IV**), hydrogenations of benzaldehyde to benzyl alcohol also occurred in high yields; especially, use of the polymer **I** showed the highest activities for the hydrogenation. In the cases with polymers **I**~**IV** having different length of the spacer, the catalytic activities decreased in the order of **I** > **IV** > **II** > **III**. These facts suggest that the catalytic activity of the hydrogenation is dependent on the length of the spacers at the polymer surface.

In addition to the length of the spacers, the author expected that hydrophilicity of the polymers might be also one of the important factors in the hydrogenation reaction catalyzed by $Rh_6(CO)_{16}$. High hydrophilicity of the polymers may increase a concentration of H_2O around the Rh cluster, which is essential for the formation of an active metal species (*vide infra*). In order to estimate the hydrophilicity of the polymers **I**~**IV**, the hygroscopic degrees of the polymers were measured by the method described in experimental section. As shown in **Table 2**, the hygroscopic degrees decreased in the order of **I** > **IV** > **III** > **II**, which indicates that the polymer **I** has the highest hydrophilicity among polymers **I**~**IV**. The result supports that the hydrophilicity of the polymer increase the catalytic activity of the hydrogenation catalyzed by Rh clusters under the WGSR conditions.

Further, hydrogenations of benzaldehyde using polymers **I**~**IV** were performed as a function of amounts of H_2O, as summarized in **Figure 4**. High yields of benzyl alcohol were obtained in the case of polymer **I** during amount of H_2O from 40 mmol to 200 mmol.

Table 1. Hydrogenation of Benzaldehyde Using Various Functionalized Polymer-Bound Rh Clusters [a]

polymer support	yield of benzyl alcohol (%)
I	95
II	85
III	57
IV	93
1N	52
1N-OH	76
1N-2O	75
2N	10
2N-OH	85

[a] Reaction conditions: benzaldehyde 1.5 mmol, $Rh_6(CO)_{16}$ 0.010 mmol, polymer 0.18 mmol of N, benzene 3.0 ml, 80 °C, H_2O 80 mmol, 24 h.

Table 2. Hygroscopic Degree of the Aminated Polymers (**I**~**IV**)

polymer	hygroscopic degree (H)		
	run 1	run 2	average
I	8.5	8.0	8.3
II	3.8	3.6	3.7
III	2.9	2.7	2.8
IV	3.7	3.4	3.6

The yields of benzyl alcohol tend to increase with increasing the amount of H_2O from 10 mmol to 80 mmol. During the amount of H_2O from 80 mmol to 160 mmol, yields of benzyl alcohol are almost constant, and decrease with large quantity of H_2O. Notably, the polymer **I** showed the highest yield at 40 mmol of H_2O. These phenomena suggest that the high hydrophilicity of the polymer **I** causes high yield of benzyl alcohol even with a small amount of H_2O.

In the homogeneous Rh catalyst systems for the reduction, the catalytic activity strongly depended on basicity of the amine additives[22]. Among the diamine series of $Me_2N(CH_2)_nNMe_2$, increasing the number (n) of methylenes facilitated the catalytic activity of the hydrogenation of aldehyde; at n=3, *N, N, N', N'*-tetramethyl-1,3-propanediamine was the most effective. Basicity of amines would correlate to the stability of the corresponding protonated amines: higher charge density at nitrogen atoms of the amines will increase stability of the protonated ammonium cations[40]. Therefore, π Electron charge density of the nitrogen atoms in the spacer moieties was estimated by the simple Hückel Calculation as a function of number (n) of methylenes in $Ph\text{-}CH_2\text{-}O\text{-}(CH_2)_n\text{-}N(CH_3)_2$. As shown in **Figure 5**, the charge densities periodically varies with respect to n of methylenes in the spacers. When the n increases, the values of the charge density converge to 1.7. The charge density of an amine with n=4 shows a low value, but displacing one carbon atom of methylenes to oxygen, like in the surface of the polymer **I**, drastically increases the π charge density to the highest value. Therefore, it is reasonable to conclude that the polymer **I** shows the highest basicity.

In the case of direct multi-functionalized polymers of **I~IV**, the ether and amino groups are homogeneously introduced into these polymer surfaces, while the both two functions are randomly incorporated to the polymers in the successive functionalized polymers of **1N-OH**, **1N-2O**, and **2N-OH**. The obtained high activities for the hydrogenation with the polymer **I~IV** can be attributed to the definite situation of two functional groups around the active Rh species. In retrospect, the polymer **I** was the best support for the polymer-bound Rh_6 cluster in the hydrogenation, which could be explained by a strong basicity and high

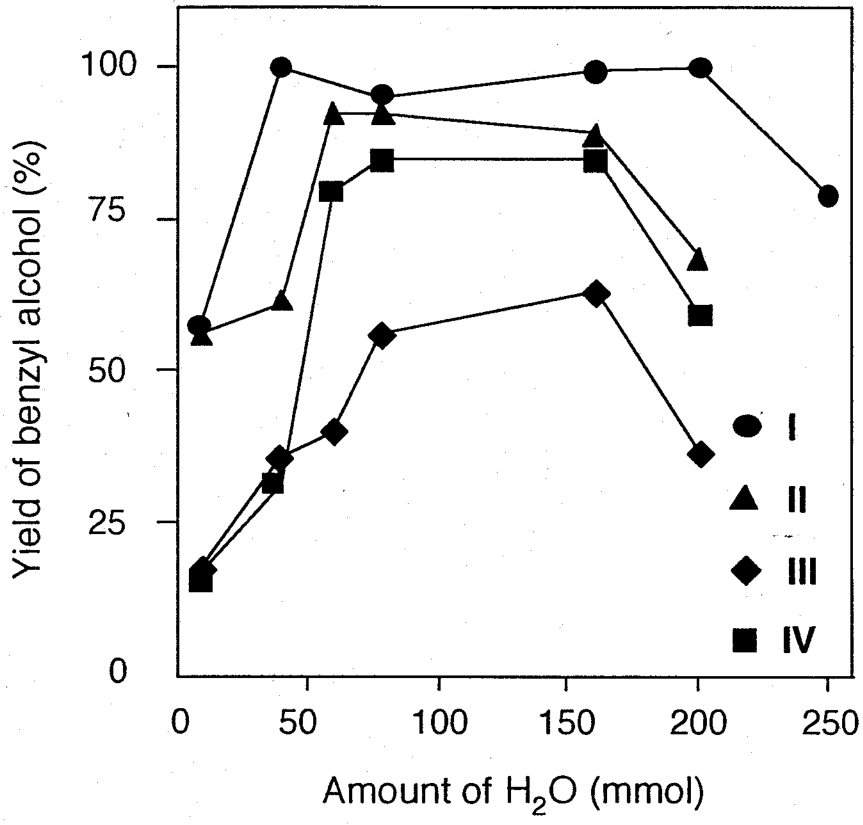


Figure 4. Influence of H_2O amounts on the hydrogenation of benzaldehyde [a]

[a] Reaction conditions: $Rh_6(CO)_{16}$ (0.010 mmol), aminated polymer (0.18 mmol of N), benzene (3.0 ml), benzaldehyde (1.5 mmol), 80°C, CO 10 atm, 24 h

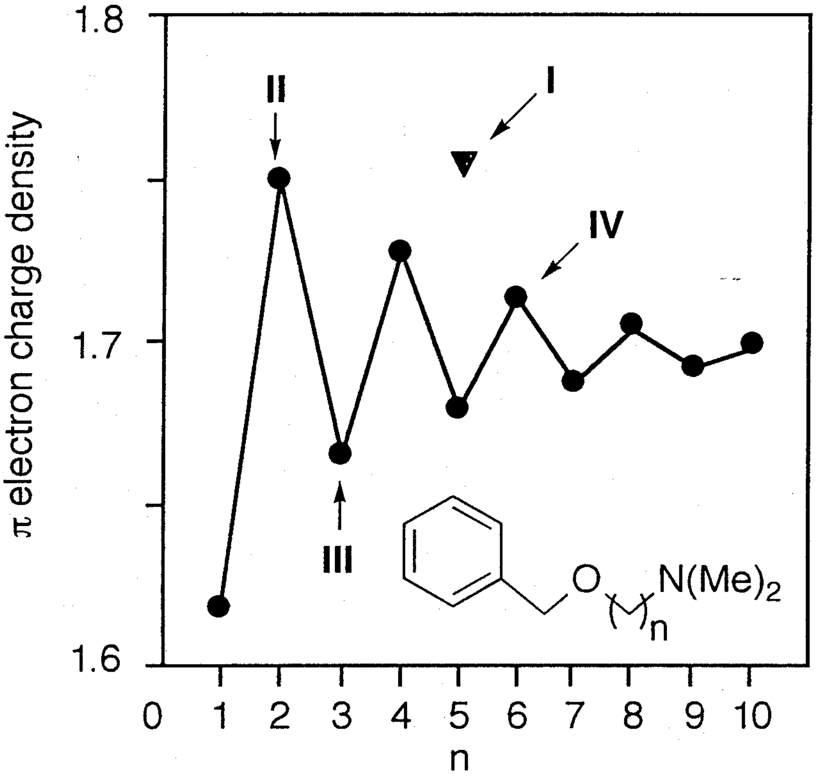


Figure 5. Simple Hückel Caluculation of π Electron Charge Density on Nitrogen Atom in Spacer Moieties.

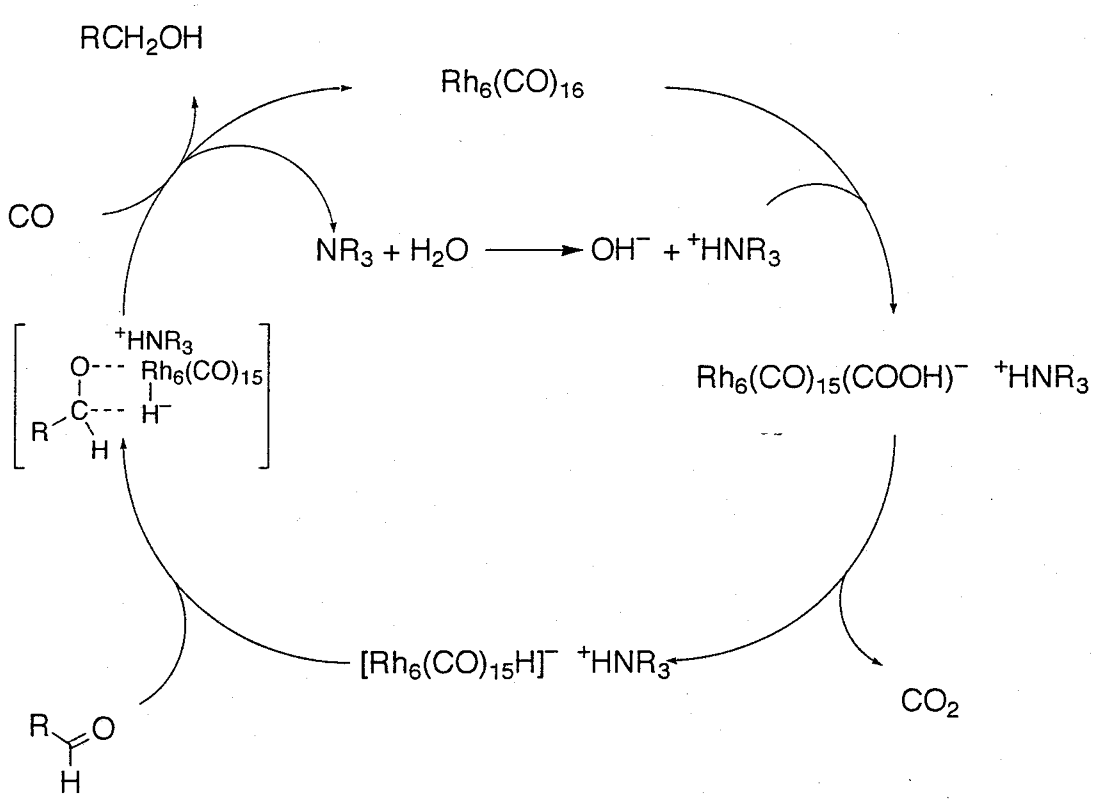
hydrophilicity of this polymer due to the introduction of the ether group in the spacers of the surface.

2-3-2. Active Species for Hydrogenation of Benzaldehyde

After the hydrogenation, the color of the polymer **I**-bound Rh cluster complexes was brownish violet, which was rapidly changed to violet in air for a few minutes. The IR spectra of this violet powder suggested formations of $[Rh_{12}(CO)_{30}]^{2-}$ as a main species and $[Rh_{14}(CO)_{25}]^{4-}$ generated from dimerization of Rh_7 species. It is known that the $[Rh_{12}(CO)_{30}]^{2-}$ anion is generated from dimerization of the unstable $[Rh_6(CO)_{15}H]^-$ species[41]. The same hydride species could be also obtained from the treatment of $Rh_6(CO)_{16}$ with the polymer **I** in the presence of H_2 and CO *via* the heterolytic splitting of molecular hydrogen[42-44].

The author think that the $[Rh_6(CO)_{15}H]^-$ anion is an active species in the present hydrogenation using CO and H_2O. This hydride Rh cluster anion of $[Rh_6(CO)_{15}H]^-$ would be formed according to **Scheme 6**; an attack of hydroxyl ion at the carbonyl moiety on $Rh_6(CO)_{16}$, followed by decarboxylation produce the hydride cluster anion[45]. The hydrogenation of benzaldehyde will occur by the nucleophilic attack of the hydride cluster anion on the carbonyl group at the aldehyde. The Rh hydride cluster anion could be stabilized in the aminated polymer through an ionic bonding with ammonium cation of the polymer as suggested in **Figure 6**. The proper length of the spacer may provide the preferable mobility of the Rh clusters in the polymer matrix.

High hydrophilicity of the polymers, which is enhanced by ether groups in the spacers, may increase concentration of H_2O in the vicinity of amino groups in the polymer. Naturally, the high basicity of polymers causes effective generation of OH^- from H_2O and in the case of polymer **I**, the formation of the active species may be facilitated by its high basicity and hydrophilicity. The definite situation of ether and amino groups in the spacer of polymer **I** could lead to favorably interact with the active hydride cluster anions, *e.g.* like solvation (**Figure 6**).



Scheme 6. Proposed Mechanism for the Hydrogenation of Aldehydes Catalyzed by Rh Carbonyl Cluster Complex.

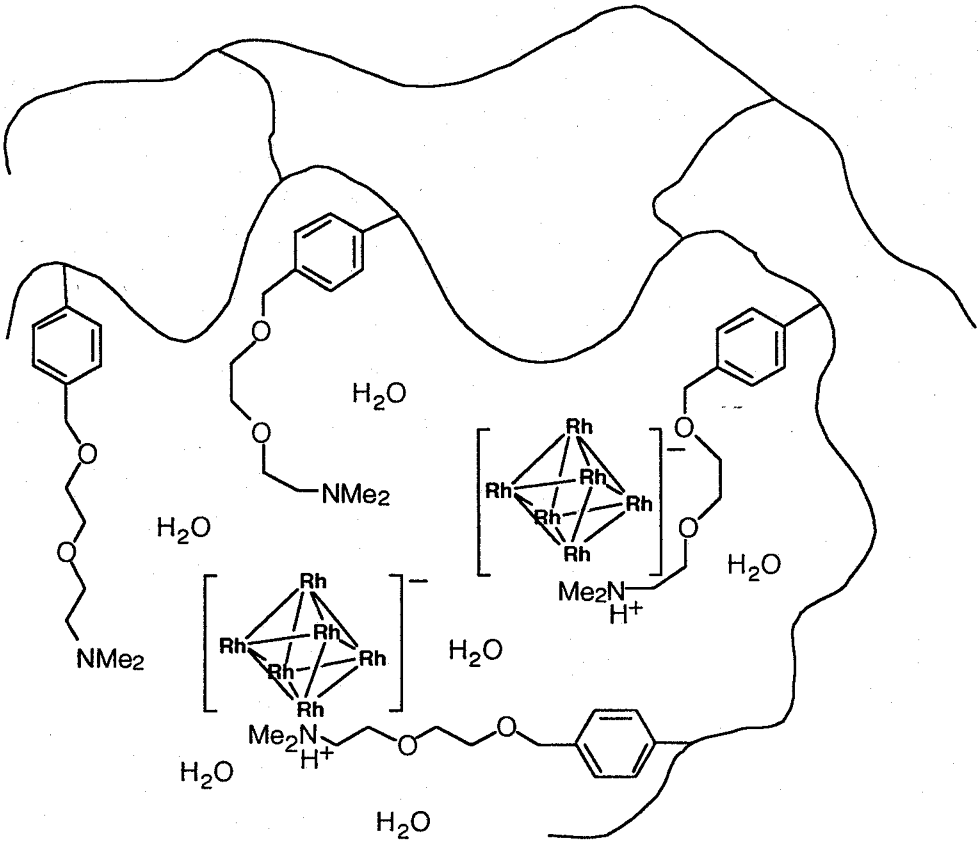
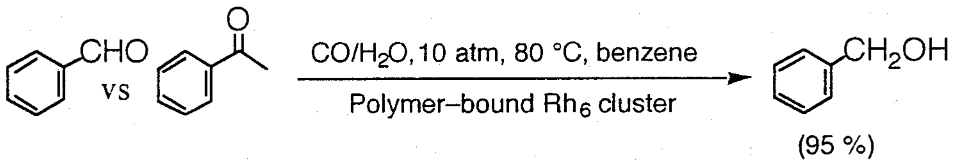


Figure 6. Schematic Image of Polymer I-Bound Rh Carbonyl Cluster Complex.
(Terminal and bridge CO are omitted for clarity.)

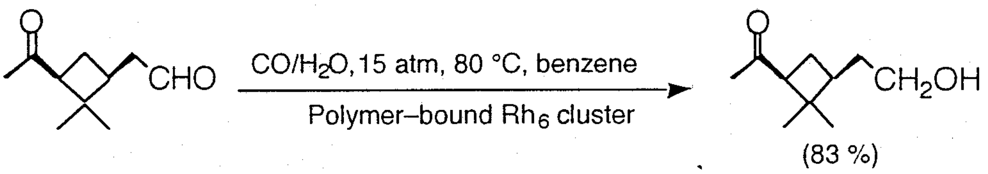
2-3-3. Hydrogenation of Various Carbonyl Compounds

The most active polymer-bound Rh carbonyl cluster complex was further applied to the hydrogenation of various carbonyl compounds in the presence of H_2O and CO. Results of the hydrogenation of various aldehydes using the polymer **I**-bound Rh catalyst were shown in **Table 3**. Many aromatic aldehydes were reduced to corresponding alcohols in high yields without hydrogenation of aromatic ring under 10~15 atm of CO in benzene solvent at 80 °C. Hydrogenolysis of substituents (entries 2, 3, and 8), reduction of nitrile (entry 7), and decarbonylation did not occur. Generally, introduction of substituents into the *para* position of benzaldehyde retarded the reduction rate. In the case of aliphatic aldehydes, corresponding alcohols were also obtained, but 1-octanal and 2-ethylbutanal showed relatively low reactivities. Hydrogenation of ketones hardly occurred under the present reaction conditions. In an intermolecular competitive hydrogenation between benzaldehyde and acetophenone using the polymer-bound Rh cluster complex, only benzyl alcohol was detected without formation of 1-phenylethanol from acetophenone (**Eq. 5**).



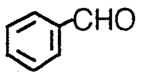
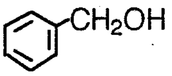
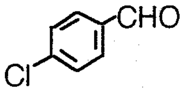
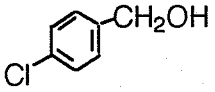
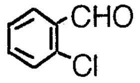
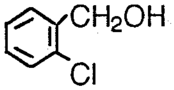
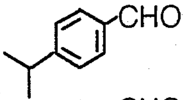
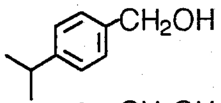
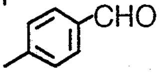
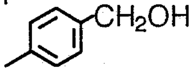
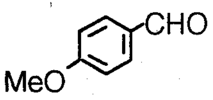
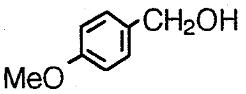
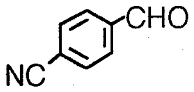
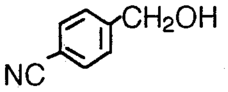
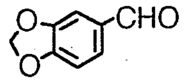
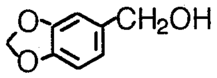
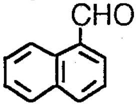
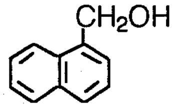
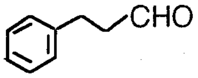
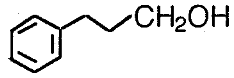
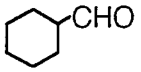
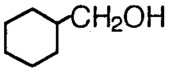
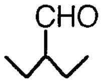
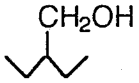
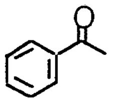
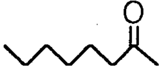
(5)

Furthermore, high chemoselectivity of the polymer-bound Rh_6 cluster catalyst could be also confirmed by the following intramolecular competitive reduction; *cis* -3-acetyl-2,2-dimethylcyclobutaneacetaldehyde gave exclusively *cis*-3-acetyl-2,2-dimethylcyclobutane-ethanol in 90 % yield (83 % isolated) without products from reduction of the ketone group (**Eq. 6**).



(6)

Table 3. Reduction of Various Aldehydes and Ketones in the Presence of CO and H_2O[a]

run	substrate	product	Pco (atm)	yields (%)[b]	
				hetero.[c]	homo.[d]
1			10	96 (82)	22
2			15	93 (86)	12
3			10	97 (87)	22
4			15	98 (87)	4
5			15	93 (87)	9
6			15	91 (83)	14
7			15	93 (89)	19
8			15	98 (83)	16
9			15	95 (85)	20
10			10	89 (82)	26
11			15	99 (91)	30
12			10	27	22
13			10	43	9
14		no reaction	10	0	0
15			10	trace	0

[a] Reaction conditions: substrate 1.5 mmol, $Rh_6(CO)_{16}$ 0.01 mmol, benzene 3.0 ml, H_2O 80 mmol, the aminated polymer 40 mg (0.18 mmol of N), 80 °C, 24 h. [b] Yields were determined by GC using internal standard technique. [c] Values in parentheses are isolated yields. In isolation of products, use of column chromatography on silica gel (Wako Gel C-200) with a 10:1 mixture of n-hexane and ethyl acetate gave pure reduction products. [d] Values are for the corresponding homogeneous system: NEt_3 0.18 mmol, H_2O 40 mmol, 1,4-dioxane 3.0 ml, 80 °C, 24 h.

It should be noted that the polymer **I**-bound Rh carbonyl cluster complex showed high activity and chemoselectivity for the hydrogenation of aldehydes, while in such chemoselective reductions, the stoichiometric reagents of metal hydrides such as $NaBH_4$, $LiAlH_4$, and metal alcoxide derivatives were widely used[46] and the examples of catalytic reductions were less reported[47-50]. Notably, a corresponding homogeneous Rh system using triethylamine in place of the functionalized polystyrene **I** showed lower activity for these reductions than the heterogeneous polymeric system using the same concentration of amine moieties, which might be due to effect of ligand concentration in polymer matrix. It should be noted that the activities of the polymer-bound catalysts are higher than those obtained in the corresponding homogeneous systems.

2-3-4. Recycling of the Polymer-Bound Rh Cluster Catalyst

The catalyst system of the polymer-bound Rh cluster complexes forms *triphase system* consisting of water, organic phase, and polymeric catalyst (**Fig.** 7)[51], which facilitates the recovery of the catalyst and the isolation of the products from the reaction mixtures. In addition of the possibility of the catalyst recovery, recyclability of the polymer **I**-bound Rh cluster catalyst was examined in the hydrogenation of benzaldehyde under the same reaction conditions as those of the fresh one. After the first run, the polymeric catalyst was easily recovered from the reaction mixtures by simple filtration. During the separation process, the color of the solid catalyst changed from brownish violet to violet which indicate the formation of $[Rh_{12}(CO)_{30}]^{2-}$. The reused catalyst after the hydrogenation was again brownish violet. The used catalyst gave 93 % yield of benzyl alcohol without appreciable loss of the activity as in the case of the fresh catalyst (96 %). Considering the result of the recycle experiment, reversible transformation of the catalytically active Rh hydride species and the stable Rh_{12} species in the polymer matrix might be occur.

It is noted that the polymer-bound Rh cluster catalysts can be easily separated from reaction mixtures by simple filtration in the air and they are reusable catalysts for the hydrogenation reactions (**Scheme** 7).

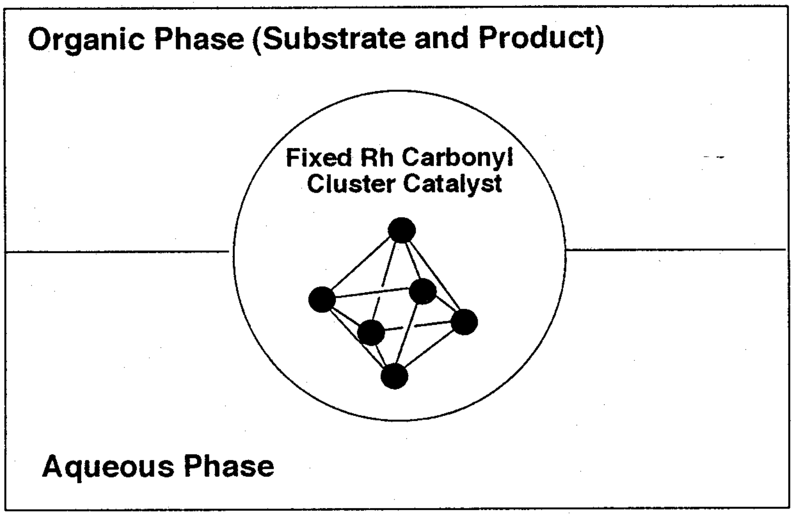
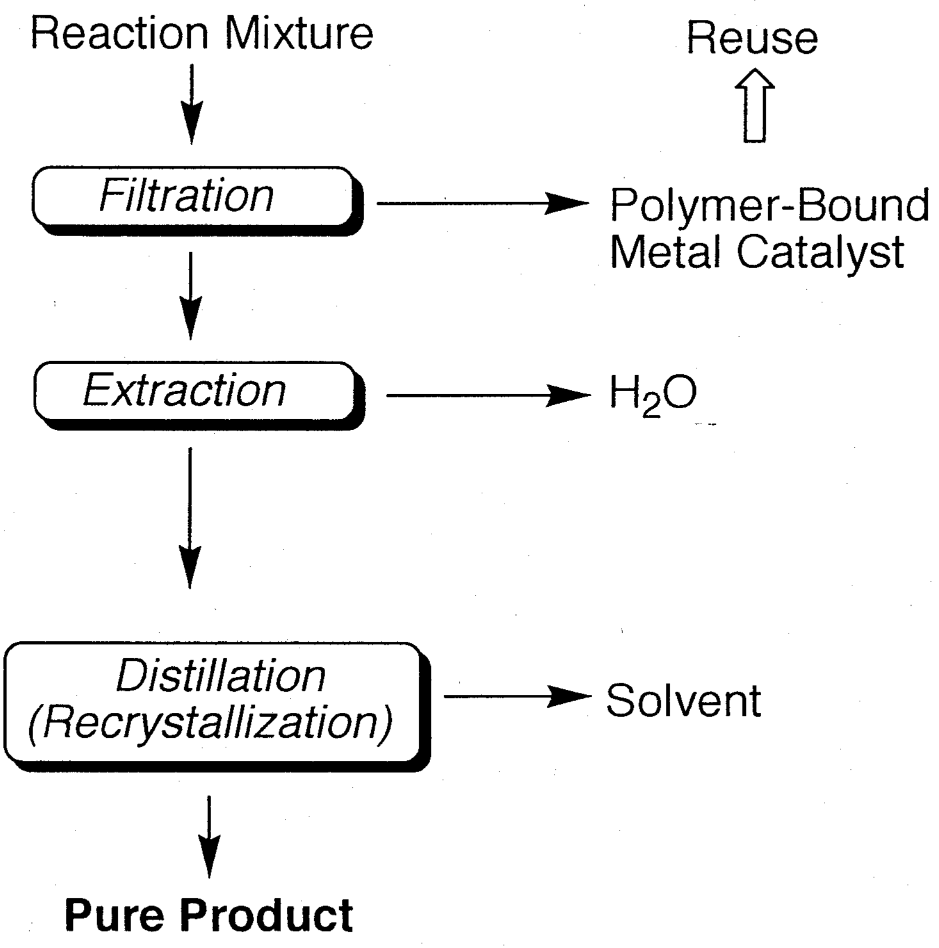


Figure 7. Triphase Catalyst System Consisted of Organic, Aqueous and Polymeric Catalyst Phases.



Scheme 7. Separation Procedures of the Triphase Catalyst System.

2-4. Conclusions

Treatment of $Rh_6(CO)_{16}$ with functionalized polymers having ether and amino groups gave the polymer-bound Rh_6 cluster complexes, which showed high catalytic activity for the hydrogenation of various aldehydes under the WGSR conditions. The catalytic activity of the polymer-bound Rh complexes is higher than that in homogeneous system without addition of amines, which might be due to effect of ligand concentration in polymer matrix. The catalytic activity for the hydrogenation was dependent on the length of spacers, and on basicity and hydrophilicity of the functionalized polymers. Especially, use of polystyrene with 2-(dimethylaminoethoxy)ethoxy moieties (polymer **I**) brought excellent catalytic activities for the hydrogenation of various aldehydes, which is due to high basicity and hydrophilicity of the surface.

The active species for the hydrogenation is proposed to be $[Rh_6(CO)_{15}H]^-$, which binds to ammonium cation of polymer through an ionic bonding. The Rh hydride cluster anion dimerizes with the elimination of hydrogen in exposure to air. The catalyst systems of the polymer-bound Rh cluster complexes forms *triphase system* consisting of water, organic phase, and polymer, which makes the work-up procedures simple; the polymeric Rh catalysts is easily separated from the organic products and water. The reversible transformation between unstable Rh hydride cluster and stable Rh_{12} cluster can be achieved by using the functionalized polystyrenes, which enable the polymeric Rh cluster to be reusable without appreciable loss of the activity and selectivity for the selective hydrogenation of aldehydes.

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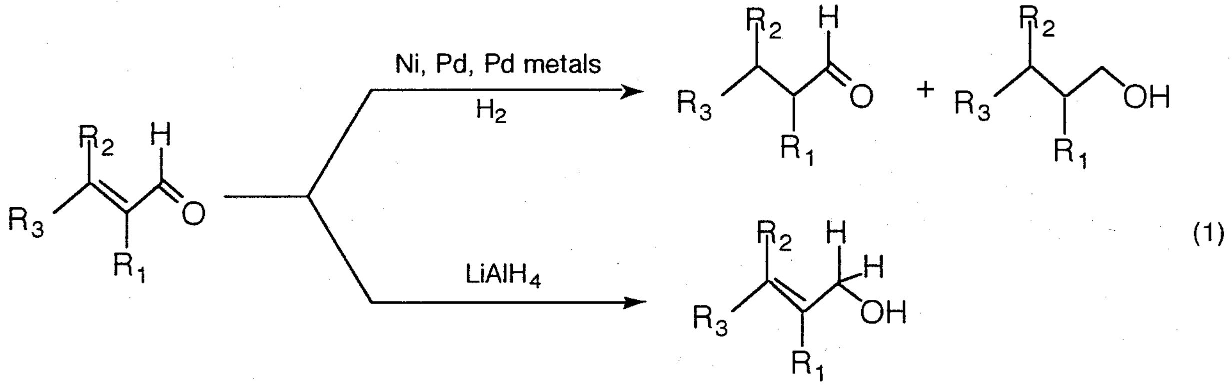
Chapter 3. Selective Hydrogenation of α, β-Unsaturated Aldehydes to Allylic Alcohols Catalyzed by Polymer-Bound Rh Carbonyl Clusters in the Presence of H_2 and CO

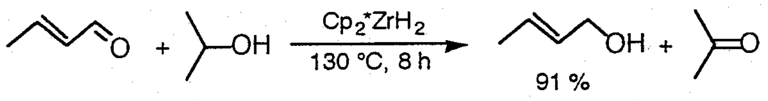
3-1. Introduction

Chemoselective reductions of α,β–unsaturated carbonyl compounds to allylic alcohols have been extensively studied because of the industrial importance of allylic alcohols in the syntheses of fine chemicals such as perfumes, flavorings, and pharmaceuticals. Hydrogenation of the carbon-carbon double bonds conjugated with carbonyl groups is readily achieved under mild conditions with a high selectivity using group VIII metal hydrogenation catalysts such as Ni, Pt, and Pd, yielding saturated aldehydes and saturated alcohols (**Eq. 1**)[1-3]. On the other hands, the catalytic reduction of the aldehyde group still remains a challenging field. So far, the stoichiometric reduction with metal hydrides such as $NaBH_4$ and $LiAlH_4$ have been generally used for the chemoselective reduction of carbonyl groups (**Eq. 1**)[4 and 5].

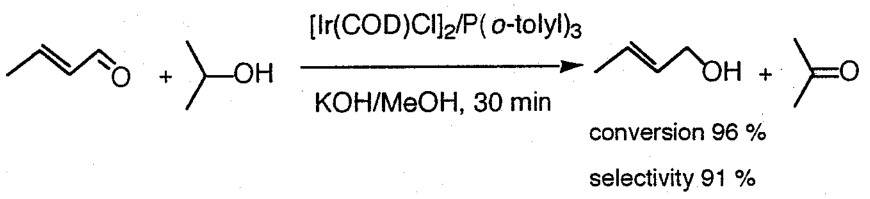


(1)

As the catalytic chemoselective reduction of α,β–unsaturated aldehydes, transfer hydrogenation using alcohols as hydrogen donors are developed[6-9]. This type of reduction has been known as the Meerwein-Pondorf-Varley reduction. Group IV A metals[10] or transition metals[11 and 12] were generally used as catalysts and both *primary* and *secondary* alcohols can be employed as hydrogen donors (**Eqs. 2, 3**).



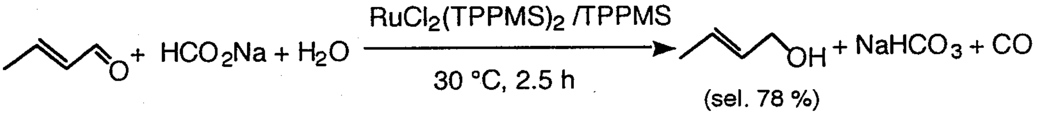
(2)



(3)

Formic acid and its salts are also used as a hydrogen source in the transfer hydrogenation. Joó *et al.* reported the selective reduction of unsaturated aldehydes to allylic alcohols in aqueous phase with water soluble Ru catalyst using sodium formate as a hydrogen donor [13 and 14]. The disadvantage of this catalytic reaction holds to the formation of sodium carbonate during the reaction leading to a basic medium, which causes degradation of ligands and thus a serious deactivation of Ru catalyst.

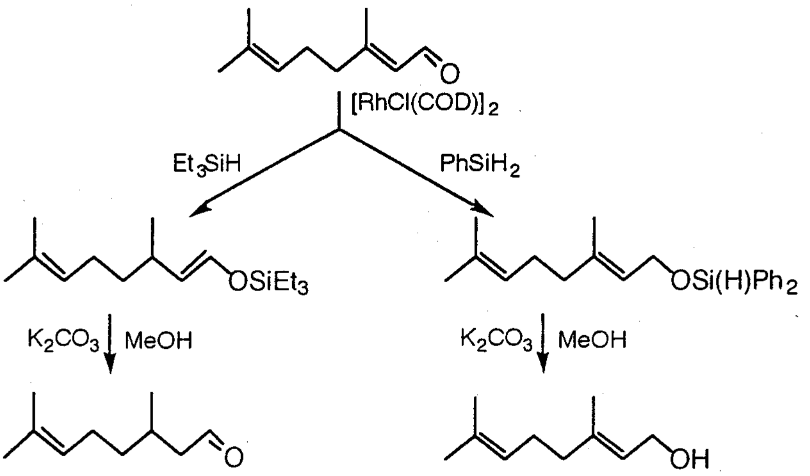
Details of these transfer hydrogenations will be described in Chapter 4.



(4)

TPPMS = (sulfophenyl)diphenylphosphine sodium salt

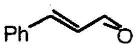
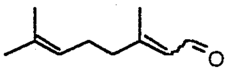
Also, transition metal catalyzed hydrosilylation has been reported as a method of chemoselective reduction of carbonyl groups (**Eq.** 5)[15]. It has been found that monohydrosilanes lead to 1,4-addition in contrast to dihydrosilanes (1,2-addition), which lead to saturated aldehydes and unsaturated alcohols, respectively. However, this method requires two step procedures to obtain the desired products.



(5)

Taking into consideration of the industrial impact, catalytic hydrogenation of α,β–unsaturated aldehydes to allylic alcohols using molecular hydrogen is the most attractive way. **Table 1** shows a few examples for the formation of allylic alcohols from α,β–unsaturated aldehydes by using transition metal complexes of Ru, Os, Ir in the presence of hydrogen molecule[16-20]. High chemoselectivity was obtained with 3-phenyl-2-propenal (cinnamaldehyde) and 3,7-dimethyl-2,6-octadienal (citral), however, high pressures of hydrogen are usually needed for the reduction catalyzed by the transition metal complexes.

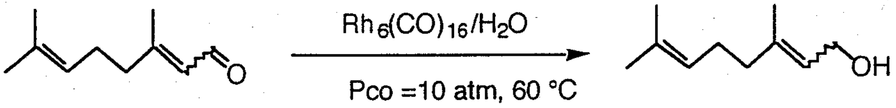
Table 1. Catalytic Hydrogenation of Various α,β–unsaturated Aldehydes

substrate	catalyst	P_{H2}, bar	T, °C	time, h	yield, %	selectivity[a], %	ref
	$Ru(CF_3CO_2)(CO)(PPh_3)_2$	15	160	6	85	60	16
	$RuCl_2(PhP(CH_2CH_2PPh_2)_2$	34	100	1,6	54	38	17
	$Os(H)(Br)(CO)(PPh_3)_3$	1	100	1	100	50	18
 Ph	$[IrCl(COD)]_2$+ PPh_2Cy	30	100	2	98	96	19
	$HRuCl(PPh_3)_3$	50	30	20	99	95	20

[a] Selectivity of corresponding allylic alcohol.

Further, water can be used as a hydrogen source. Kaneda *et al.* have already reported that a catalyst system consisting of $Rh_6(CO)_{16}$ and *N,N,N',N'*-tetramethyl-1,3-propanediamine could reduce chemoselectively carbonyl functions in α,β-unsaturated aldehydes using H_2O

and CO as shown in the following scheme[21]. It was contrast with the report that the rhodium catalysts sometimes lead to decarbonylation of aldehydes in the presence of hydrogen [22].



The author already found that the $Rh_6(CO)_{16}$ cluster immobilized on the modified polymer surface efficiently catalyzed chemoselective reduction of aldehydes in the presence of H_2O and CO, as described in Chapter 2.

In this chapter, the author applied the heterogenized Rh cluster catalyst on the modified polystyrene surface for the chemoselective reduction of α,β-unsaturated aldehydes in the presence of molecular hydrogen and CO. It was found that the polymer-bound Rh carbonyl clusters showed the higher catalytic performances in the selective hydrogenation of various α,β-unsaturated aldehydes to allylic alcohols than the corresponding homogeneous catalyst system. Furthermore, the polymer-bound Rh cluster catalyst can be reused without appreciable loss of activity and chemoselectivity for the above hydrogenations. Finally, the reaction mechanism of the reduction of aldehydes catalyzed by the immobilized $Rh_6(CO)_{16}$ cluster using H_2 and CO is proposed.

3-2. Experimental

3-2-1. General

^{1}H NMR spectra were obtained on JEOL GSX-270 or JNM-AL400 spectrometers at 270 or 400 MHz in $CDCl_3$ with TMS as an internal standard. Infrared spectra were obtained with a Shimadzu FT-IR 8200PC and JASCO FTIR-410. Analytical GLC was performed by a Shimadzu GC-8APF with flame ionization detector and GC-8AIT with thermal conductivity detector equipped with KOCL 3000T and Silicone UC W-98 columns. Elemental analysis was carried out by Perkin Elmer 2400CHN.

Aldehydes, amines, and solvents were purchased from Wako Chemicals and Tokyo Kasei, and purified according to the standard procedures and stored under a nitrogen atmosphere

[23]. $RhCl_3 \cdot 3H_2O$ was obtained from N.E. Chemcat. $Rh_6(CO)_{16}$ was prepared according to the methods by Chini as described in Chapter 2[24]. 3-Phenyl-2-butenal, *trans*–3-(4-chlorophenyl)-2-propenal, *trans*–3-(4-methoxy-phenyl)-2-propenal, (*E*, *E*)-5-phenyl-2,4-pentadienal, 3,3-diphenyl-2-propenal, and (*Z*)-2,3-diphenyl-2-propenal were synthesized according to the literature[25]. *p*-(Chloromethyl)styrene was purchased from SEIMI Chemical. All of the substrates and products were characterized by comparison with the literature data.

3-2-2. Preparation of Aminated Polystyrene

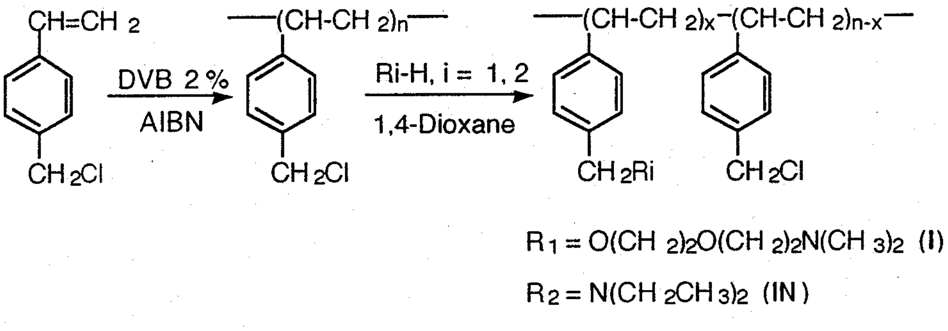
The experimental procedure for the preparation of aminated polystyrenes was described in Chapter 2 in detail.

Bulk polymerization of 4-(chloromethyl)styrene and divinylbenzene (2 wt %) was carried out using AIBN. Various aminated polystyrenes were synthesized by the modified procedure in the literature[26]. A typical example using diethylamine was as follows (**Scheme 1**). An excess of diethylamine was added dropwise to poly(4-chloromethyl)styrene swollen in 1,4-dioxane. After stirring for 48 h at room temperature, the resulting light brown polymer was filtered and washed with 1,4-dioxane, a 1:1 mixture of 0.1 N NaOH aq. and acetone, successively, then aqueous acetone (50 vol. %) for three times until the filtrate became neutral. Finally, washing with acetone and drying *in vacuo* gave the pale yellow diethylaminated polystyrene **1N**.

3-2-3. Direct Multi-Functionalization of Poly(4-chloromethyl)styrene

The experimental procedure for the preparation of aminated polystyrenes was described in Chapter 2 in detail. Introduction of the functional groups containing simultaneously amino and ether groups in the spacer was carried out by treatment of the poly(4-chloromethyl)styrene with 2-(dimethylamino)ethoxyethanol (**Scheme 1**).

An excess of 2-(2-dimethylamino)ethoxyethanol was added dropwise to poly(4-chloromethyl)styrene and solid KOH swollen in 1,4-dioxane at 100 °C under nitrogen atmosphere. After stirring for 48 h, the resulted light brown polymer was filtered and washed successively with 1,4-dioxane, a 1:1 mixture of 0.1 N NaOH aq. and acetone, then aqueous acetone (50 vol. %) for three times until the filtrate became neutral. Finally, washing with acetone and drying *in vacuo* at 60 °C for 24 h gave the pale yellow polymer **I**.



Scheme 1. Synthetic Procedures of Functionalyzed Polymers (I) and (I N)

3-2-4. Estimation of Amination Degrees of the Functionalized Polystyrenes

The experimental procedure for the preparation of aminated polystyrenes was described in Chapter 2 in detail.

The amination degrees of the functionalized polystyrenes were estimated by N contents calculated by elemental analysis and the titration method[27]. The titration of amino groups was carried out by the following procedures. Dried aminated polystyrene (100 mg) was equilibrated with 0.2 N HCl (10 ml) for 24 h at room temperature. The polymer was filtered, washed with ca 20 ml of distilled water to remove unreacted HCl. The filtrate was titrated with 0.2N NaOH to a phenolphthalein end point. The N contents were almost agree with the results obtained from the elemental analysis.

3-2-5. Homogeneous Hydrogenation of Aldehydes in the Presence of H_2 and CO

A typical example of homogeneous hydrogenation of cinnamaldehyde by $Rh_6(CO)_{16}$ in the presence of amine was as follows. To a glass liner containing $Rh_6(CO)_{16}$ (0.010 mmol) and triethylamine (0.40 mmol), a THF (3.0 ml) solution of cinnamaldehyde (1.5 mmol) was added successively under a nitrogen atmosphere. The glass liner was set in a stainless steel autoclave and then flushed three times with CO. The reaction mixture was stirred at 30 °C under 10 atm of CO and H_2 (1:1) for 15 h. The reactor was cooled and the pressure was carefully released. The GC analysis showed 84 % of cinnamyl alcohol.

3-2-6. General Procedures for the Heterogeneous Hydrogenation of Aldehydes in the Presence of H_2 and CO

Heterogeneous hydrogenation of (*E,E*)-5-phenyl-2,4-pentadienal with $Rh_6(CO)_{16}$ and polymer **I** was a typical example as follows. To a glass liner containing $Rh_6(CO)_{16}$ (0.010 mmol) and aminated polymer **I** (40 mg, 0.18 mmol of N), a benzene (3.0 ml) solution of (*E,E*)-5-phenyl-2,4-pentadienal (1.5 mmol) was added successively under a nitrogen atmosphere. The glass liner was set in a stainless steel autoclave and then flushed three times with CO. The reaction mixture was stirred at 30 °C under 10 atm of CO and H_2 (1:1) for 15 h. The reactor was cooled and the pressure was carefully released. After a solid polymer was removed by filtration, the filtrate was subjected to column chromatography to give 0.227 g of (*E,E*)-5-phenyl-2,4-pentadien-1-ol (88 %; mp 74-75 °C): ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.18 (d, $J = 4.95$ Hz, 2H), 5.90 (tt, $J = 15.34$ Hz, 1H), 6.49 (d, $J = 15.83$ Hz, 2H), 6.72 (dd, $J = 10.14$ and 15.7 Hz, 1H), 7.12-7.35 (m, 5H); IR 3350, 3000, 1445, 1380, and 995 cm^{-1}.

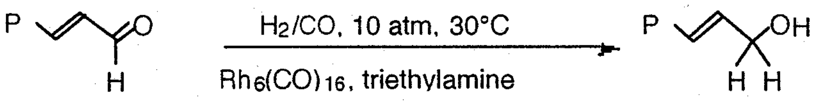
3-2-7. Recycling of the Polymer-Bound Rh Cluster Catalyst

The polymeric Rh cluster catalyst was subjected to reuse in the hydrogenation of cinnamaldehyde. The first run was carried out as the same procedures as described in the above heterogeneous hydrogenation. After the reaction mixture was stirred at 30 °C under 10 atm of H_2 and CO for 15 h, the reactor was cooled and the pressure was slowly released. The solid polymer was separated from reaction mixtures by centrifugation, and washed with benzene for three times. The washed polymeric catalyst was placed in the autoclave, and a benzene (3.0 ml) solution of cinnamaldehyde (1.5 mmol) was added successively, followed by stirring at 30 °C under 10 atm of H_2 and CO (1:1) for 15 h. The reactor was cooled and the pressure was slowly released. In the second and third experiments, the GC yields of cinnamyl alcohol were 94 and 82 %, respectively.

3-3. Results and Discussion

3-3-1. Homogeneous Hydrogenation of Cinnamaldehyde Catalyzed by Rh Carbonyl Cluster

In the homogeneous hydrogenation of cinnamaldehydes using $Rh_6(CO)_{16}$ and amines, various kinds of solvents were scrutinized to find that THF and 2-ethoxyethanol gave high yields of allylic alcohols, while methanol, benzene, toluene, and cyclohexane were poor solvents. This result is shown in **Table 2**.



(6)

In scrutiny of additives, triethylamine was an excellent for this selective hydrogenation. It seems that the ether group in the solvent might favorably interact with Rh cluster anions, like solvation, to stabilize Rh cluster complexes. Similar results were observed in the other catalytic reactions with $Rh_6(CO)_{16}$ and amines under the Water-Gas Shift Reaction conditions [28]. The interactions of the Rh cluster with ether and amino groups would be essential also for the heterogeneous reaction systems.

3-3-2. Heterogeneous Hydrogenation of Cinnamaldehyde Using the Aminated Polystyrenes

Taking the above results into a consideration, a functionalized polystyrene having both amino and ether functions **I** was prepared by a reaction of chloromethylpolystyrene with *N,N*-dimethylaminoethoxyethanol according to the **Scheme 1**.

In **Table 2**, the effect of the functional groups introduced to the polystyrene in various solvents are also shown. Use of the polymer **I** led to high yields of cinnamyl alcohol even in hydrocarbon solvents, *e.g.* use of cyclohexane gave 83 % yield of cinnamyl alcohol, while hydrogenation with the polymer **IN** without ether groups in the polymer surface resulted in 40 % yield of cinnamyl alcohol. It is notable that THF is not an excellent solvent in this heterogeneous catalyst system. After the hydrogenation of cinnamaldehyde in a THF solvent, the color of the filtrate of the reaction mixture was reddish brown, which shows elution of the Rh complexes from the aminated polymer.

Table 2. Homogeneous and Heterogeneous Hydrogenations of Cinnamaldehyde Using $Rh_6(CO)_{16}$ under H_2/CO Conditions[a]

Run	Additive	Solvent	Time (h)	Conv. (%)	Selectivity[b] (%)		
					1	**2**	**3**
1	NEt_3 (0.40 mmol)	THF	20	97	84	2	13
2	NEt_3 (0.40 mmol)	1,4-Dioxane	20	22	72	20	8
3	NEt_3 (0.40 mmol)	Methanol	20	6	61	39	0
4	NEt_3 (0.40 mmol)	Benzene	20	19	77	16	7
5	NEt_3 (0.40 mmol)	Toluene	20	26	79	15	6
6	NEt_3 (0.40 mmol)	Cyclohexane	20	10	63	25	12
7	Polymer (I)	Benzene	15	100	96	0	4
8	Polymer (I)	Toluene	15	99	85	2	13
9	Polymer (I)	Cyclohexane	15	100	83	0	17
10	Polymer (II)	Cyclohexane	15	67	60	20	20

[a] Cinnamaldehyde 1.5 mmol; $Rh_6(CO)_{16}$ 0.010 mmol; solvent 3.0 mL; $P_{H2/CO} = 4$ (1:3) atm; 30 °C.

[b] Selectivity $= i / \sum i$ (i = Yields of **1**, **2**, and **3**) . Quantitative analyses of reaction products were performed by GC. For heterogeneous system (Runs 7 - 10); polymer 40mg (0.18 mg atm of N); $P_{H2/CO} = 10$ (1:1) atm; 30 °C. **1**; Cinnamyl alcohol, **2**; 3-Phenylpropanal, **3**; 3-Phenylpropanol.

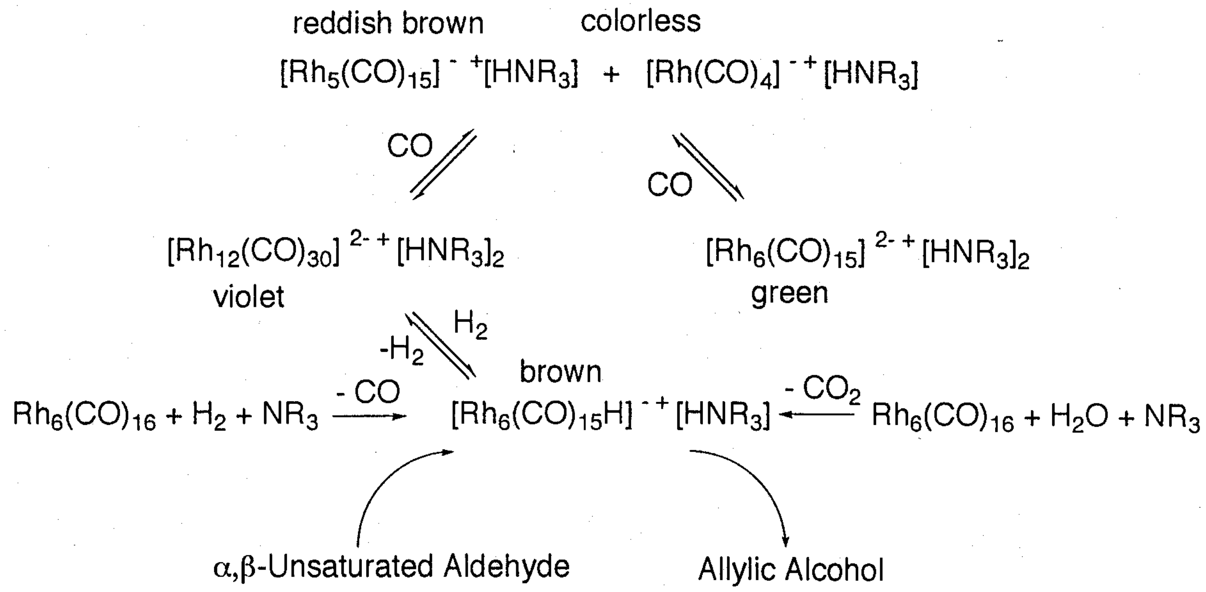
3-3-3. Active Species for Chemoselective Hydrogenation

The IR spectrum of the polymeric catalysts after the hydrogenation showed the formation of $[Rh_{12}(CO)_{30}]^{2-}$, $[Rh_6(CO)_{15}]^{2-}$, as main species and together with a small amount of $[Rh_6(CO)_{15}H]^-$. IR (2075 w (sh), 2066 m, 2035 s, 2000 m (sh), 1992 s (br), 1967 s (br), 1817 w (sh), 1803 w (sh), 1769 s (br), 1763 s (sh), 1717 w (br) cm^{-1}; Nujol mull).

In this hydrogenation, the active Rh hydride species can be generated from the heterolytic splitting reaction of molecular hydrogen with $Rh_6(CO)_{16}$ in the presence of the amines[29-31]. In the case of a reducing agent consisting of CO and H_2O, a similar hydride-metal species would be formed by an attack of hydroxyl anion to carbonyl moiety on the Rh clusters, followed by decarboxylation[32 and 33]. In a separated experiment, the reaction of the polymer **I** with $Rh_6(CO)_{16}$ under atmospheric H_2 and CO was carried out at 30 °C for 15 h. The IR spectrum of the isolated polymer-bound metal complex showed formation of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_{12}(CO)_{30}]^{2-}$ as major species with a small amount of $[Rh_6(CO)_{15}H]^-$ species (**Scheme 2**). On an exposure to air, the $[Rh_6(CO)_{15}H]^-$ and $[Rh_6(CO)_{15}]^{2-}$ species were gradually converted into $[Rh_{12}(CO)_{30}]^{2-}$ species with color changes from greenish brown to violet through reddish brown. The color change of polymer-bound Rh complexes and their IR spectra suggest the formation of $[Rh_5(CO)_{15}]^-$anion whose color is reddish brown. Therefore the author proposed the active species as $[Rh_6(CO)_{15}H]^-$. A reverse process from the Rh_{12} to the Rh_6-H species might be achieved on the polymer surface during the above hydrogenation conditions under H_2 and CO. This proposal was convinced by the fact that a spent polymeric complex containing the $[Rh_{12}(CO)_{30}]^{2-}$ species was reusable for the hydrogenation of cinnamaldehyde without loosing its high catalytic activity and selectivity.

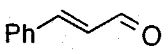
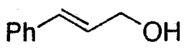
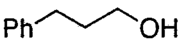
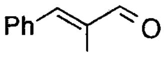
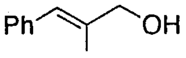
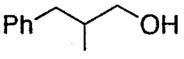
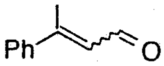
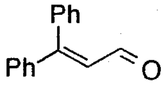
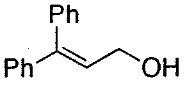
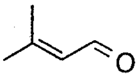
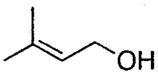
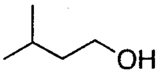
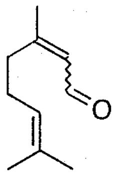
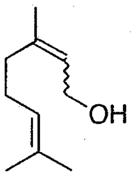
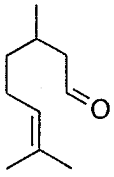
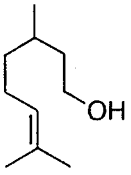
3-3-4. Chemoselective Hydrogenation of Various α,β-Unsaturated Aldehydes

Heterogeneous hydrogenations of various α,β-unsaturated aldehydes using $Rh_6(CO)_{16}$ the polymer **I** in place of amines were carried out under the conditions similar to those of the homogeneous catalyst system. The results are summarized in **Table 3** together with the corresponding homogeneous ones (Runs 4 and 10). It should be noted that the polymer-bound Rh complex has higher catalytic activity for the hydrogenation than the corresponding



Scheme 2. Interconversion of Rh Carbonyl Clusters under the Reaction Conditions

Table 3. Hydrogenation of α,β-Unsaturated Aldehydes Using Rh Carbonyl Cluster Catalysts in the Presence of H_2 and CO[a]

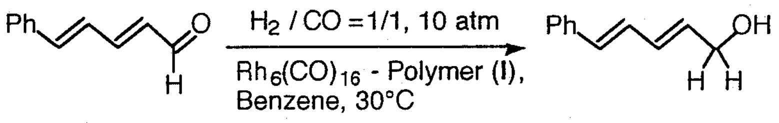
run	substrate	conv. (%)	products selectivity[b] (%)					
			1		2		3	
1		100		96 (85)[c]				4
2[d]	reuse 1	100		94				6
3[d]	reuse 2	98		82		2		16
4[e]		45		77		14		9
5		100		94 (80)[c]				6
6	 (E/Z=0.38)	100	 (E/Z=0.38)	~100				
7		99		~100 (97)[c]				
8		100		91				9
9		97		87		4		9
10[e]	(E/Z=2.01)	34	(E/Z=2.01)	84		16		0

[a] Substrate 1.5 mmol; $Rh_6(CO)_{16}$ 0.010 mmol; benzene 3.0 mL; polymer (I) 40 mg (0.18 mg atom of N); $P_{H2/CO}$ = 10 (1:1) atm; 30 °C; 15 h. 1; Unsaturated alcohol, 2; Saturated aldehyde, 3; Saturated alcohol.

[b] Selectivity = i /Σi, (i = Yields of 1, 2 and 3). Quantitative analyses of reaction products were performed by GC.

[c] Values in parentheses are isolated yields. In the isolation of products, reaction scale was three-fold under $P_{H2/CO}$ = 12 (1/1) atm and use of column chromatography on alumina with a 1:10 mixture of ethyl acetate and n-hexane gave pure reduction products. [d] A spent catalyst was recharged. [e] For homogeneous system; benzene 3.0 mL; Et_3N 0.18 mmol.

homogeneous Rh system (Runs 1 vs. 4 and 9 vs. 10)[34]. In cases of methyl substituted cinnamaldehydes, 2-methyl-3-phenyl-2-propenal gave 94 % yield of 2-methyl-3-phenyl-2-propen-1-ol, accompanied with a formation of a small amount of 2-methyl-3-phenylpropanol, and a carbonyl function was selectively reduced to afford 3-phenyl-2-buten-1-ol from 3-phenyl-2-butenal. The hydrogenation of 3,3-diphenyl-2-propenal also occurred chemoselectively to give 3,3-diphenyl-2-propen-1-ol as a sole product. Further, aliphatic α,β-unsaturated aldehydes of 3-methyl-2-butenal and citral gave rise to the corresponding allylic alcohols in high yields, respectively. Hydrogenation of citral containing two geometrical isomers (*E*/*Z*=2.01) proceeded with a high retention of C=C bond configuration (Runs 9 and 10). A similar stereospecificity could be observed in 3-phenyl-2-butenal (Run 6). This high chemoselectivity could be observed also in the hydrogenation of a diene system; (*E*,*E*)-5-phenyl-2,4-pentadienal gave (*E*,*E*)-5-phenyl-2,4-pentadien-1-ol in a high yield (Eq. 7).



(7)

In the case of α,β-unsaturated aldehydes, reduction of olefinic functions might not occur by 1, 2- addition of metal-hydride to olefinic carbons, but by the 1, 4-addition manner. Isolated olefinic function in citral was intact under the reaction conditions. 1-Octene as a common olefin was not reduced under the above conditions.

Notably, the reaction of allylic alcohols as starting materials, *e.g.* cinnamyl alcohol and geraniol resulted in a quantitative recovery of the substrates. The fact shows that both of hydrogenation and isomerization of allylic alcohols do not occur under the above reaction conditions. These results are contrast with the literature showing that an isomerization of allylic alcohols to saturated aldehydes easily occurred by metal catalysts[35].

3-3-5. Recycling of the Polymer-Bound Rh Cluster Catalyst

The polymer-bound Rh cluster catalysts are expected to be reusable catalysts in the hydrogenation of aldehydes under the H_2 and CO conditions. Recyclability of the polymer

I-bound Rh cluster catalyst was examined in the hydrogenation of cinnamaldehyde under the same reaction conditions as those of the fresh one. After the first run, the polymeric catalyst was easily recovered from the reaction mixtures by centrifugation, then charged to the second run. The used polymeric catalyst gave high yields of cinnamyl alcohol without an appreciable loss of the activity as in the case of the fresh catalyst. During the separation process, the color of the solid catalyst gradually changed from greenish brown to violet, which indicated the transformation of the active Rh hydride and $[Rh_6(CO)_{15}]^{2-}$ species to rather stable $[Rh_{12}(CO)_{30}]^{2-}$. Considering the result of the recycle experiment, a reversible transformation between the catalytically active Rh hydride species and the stable Rh_{12} species in the polymer matrix might be occur. It is noted that the polymer-bound Rh cluster catalyst can be easily separated from reaction mixtures by a simple operation in the air and they are reusable catalysts for the hydrogenation reactions.

3-4. Conclusions

The polymer-bound Rh cluster complexes obtained from the treatment of the functional polystyrene **I** having *N,N*-dimethylaminoethoxy moieties with $Rh_6(CO)_{16}$ could catalyze the chemoselective hydrogenations of α,β-unsaturated aldehydes to the corresponding allylic alcohols in high yields in the presence of H_2 and CO. The polymeric catalyst showed higher activity in the hydrogenation than the corresponding homogeneous catalyst system. The active species in the above reactions is proposed to be a $[Rh_6(CO)_{15}H]^-$ anion, which forms ion pairs with ammonium cation at the polymer surface. The reversible transformation between the unstable Rh hydride cluster and the stable Rh_{12} clusters can be achieved by using the functionalized polystyrene, which enable the polymeric Rh cluster to reuse without an appreciable loss of the activity for the selective hydrogenation of carbonyl groups of aldehydes.

3-5. References

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Chapter 4. Chemoselective Transfer Hydrogenation of α,β-Unsaturated Aldehydes to Allylic Alcohols Using Formic Acid Catalyzed by Polymer-Bound Rh Carbonyl Clusters in the Presence of CO

4-1. Introduction

The reduction of with the aid of a hydrogen donor in the presence of a catalyst is known as transfer hydrogenation[1-4]. This reaction can be generalized as shown in **Eq. 1**.

$$DH_2 + A \xrightleftharpoons{\text{cat.}} D + AH_2 \qquad (1)$$

DH_2 = hydrogen donor; A = hydrogen accepter

Various kinds of substrates have been successfully reduced by the transfer hydrogenation in the presence of catalysts [1-4]. In the hydrogen transfer reactions, most of the hydrogen donors employed are organic compounds: unsaturated hydrocarbons such as cyclohexene or cyclohexadiene, *primary* or *secondary* alcohols like methanol or 2-propanol, and formic acid and its salts have been extensively used. Among the alkylammonium formates, especially triethylamine formate have been proven to be a useful source of hydrogen due to their solubility in many organic solvents. Since dehydrogenation of formic acid derivatives is an irreversible and exothermic process, this usually overwhelms the energetic requirements of the reduction process.

In comparison with catalytic reduction using molecular hydrogen, transfer reduction using hydrogen donors has real and potential advantages[5]. Molecular hydrogen, a gas of low molecular weight and therefore high diffusibility, is easily ignited and presence considerable hazards, particularly on the large scale; the use of hydrogen donor of obviates these difficulties in that no gas containment is necessary. No pressure vessels are needed, and simple stirring of solutions is usually all that is required. Potentially, transfer methods could afford enhanced selectivity in reduction. With a catalyst and molecular hydrogen, changes of catalyst, solvent, and temperature are possible variations in reaction conditions but, with hydrogen donors, a new dimension is opened up because the choice of hydrogen donor can affect the reaction through its competitive adsorption onto the catalyst surface. Thus, rate and specificity of reduction are amenable to control through choice of hydrogen donor.

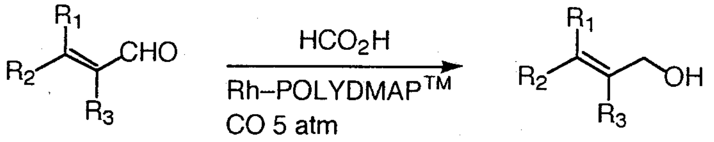
In spite of these valuable features, hydrogen transfer reduction with homogeneous catalysts has attracted much less attention than heterogeneous transfer hydrogenation using palladium metal. This can be in part a consequence of the low catalytic activity displayed by the first generation catalysts, *e.g.*, [$RuCl_2(PPh_3)_3$], which required high reaction temperatures [6], whereas the homogeneous hydrogenation catalysts like [$RuCl(PPh_3)_3$] were active in the presence of hydrogen under much milder conditions[7].

In recent years, major advantages have been achieved in the field of transfer hydrogenation. The discovery of more active catalysts and more efficient hydrogen donors has given the possibility to obtain high reaction rates under mild reaction conditions[2]. More recent developments of the homogeneous transfer hydrogenation is the asymmetric transfer hydrogenation of ketones using triethylamineformate (5:2 formic acid - triethylamine azeotropic mixture)[8].

It is well recognized that the reduction of C=C double bonds by alcohols and formic acid is thermodynamically favored and proceeds to completion under a great variety of conditions. In contrast, the reduction of carbonyl groups by alcohols suffers from unfavorable thermodynamics and it can be anticipated that the equilibrium of H transfer reduction of ketones by means of alcohols lies to the left side, particularly when *primary* alcohols are employed.

Chemoselective hydrogenation of α,β-unsaturated carbonyl compounds to the corresponding allylic alcohols has been continuously studied due to the high potential utilities of allylic alcohols[9]. The author already described in Chapter 3 that the catalyst system consisting of $Rh_6(CO)_{16}$ and amines had high activities for the chemoselective hydrogenation of α,β-unsaturated aldehydes to allylic alcohols in the presence of hydrogen and carbon monoxide[10]. Using the functionalized polystyrenes, the above catalyst system could be heterogenized to form polymer-bound Rh cluster complexes that showed high catalytic performances and highly operatable catalysts[11].

In this chapter, the author applied the Rh cluster–amine catalyst system to the transfer hydrogenation of α,β-unsaturated aldehydes to allylic alcohols using formic acid as a hydrogen donor in the presence of CO. The advantages of use of formic acid are (1) easy handling, and (2) low price, compared with other reductants such as hydrogen gas. The homogeneous catalyst system could be heterogenized by using POLYDMAP™ as an aminated polystyrene support to form a polymer-bound Rh cluster catalyst that could be recycled without a loss of high activities and selectivities for the following chemoselective hydrogenations (**Eq 2**).



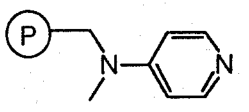
(2)

4-2. Experimental

4-2-1. General

^{1}H spectra were obtained on JEOL GSX-270 or JNM-AL400 spectrometers at 270 or 400 MHz in $CDCl_3$ with TMS as an internal standard. Infrared spectra were obtained with a JASCO FTIR-410. Analytical GLC was performed by a Shimadzu GC-8APF with flame ionization detector and GC-8AIT with thermal conductivity detector equipped with KOCL 3000T and Silicone UC W-98 columns.

Aldehydes, amines, and solvents were purchased from Wako Chemicals and Tokyo Kasei, and purified according to the standard procedures and stored under a nitrogen atmosphere [12]. 4-Dimethylaminopyridine (4-DMAP) was obtained from Koei Chemical and recrystallized from toluene prior to use. $RhCl_3 \cdot 3H_2O$ was supplied from N.E. Chemcat. $Rh_6(CO)_{16}$ was prepared by the literature procedures reported by Chini [13]. 3-Phenyl-2-butenal, *trans*–3-(4-chlorophenyl)-2-propenal, *trans*–3-(4-methoxyphenyl)-2-propenal, 3,3-diphenyl-2-propenal, and (*Z*)-2,3-diphenyl-2-propenal were synthesized according to the literature method[14]. *cis*-3-Acetyl-2,2-dimethylcyclobutaneacetaldehyde was synthesized by ozonolysis of α-pinene [15]. POLYDMAP™ was obtained from Reilly Industries and dried in vacuo prior to use. The surface structure of POLYDMAP™ is shown in **Figure 1**. This polymer has a 4-(dimethylamino)pyridino moiety on the *para* position of styrene unit in the cross-linked polystyrene support. Formic acid (99 %) was purchased from Wako Pure Chemicals and used as received. All of the substrates and products were characterized by comparison with the literature data.



Ⓟ Crosslinked polystyrene

Figure 1. Structure of the POLYDMAP^{TM}.

4-2-2. Measurement of the Degree of Swelling of the POLYDMAP.

The degree of swelling of the POLYDMAP was measured as following procedures. The dry resin beads POLYDMAP (0.2 ml) were filled in a graduated cylinder, to which was added 1 ml of THF. The polymer was treated with an ultrasonication for 1 min to remove air and was then placed for 2 h. The degree of swelling of the POLYDMAP (DS) was calculated as the swollen resin volume over the dry one (0.2 ml). The measurement of DS were performed using all solvents used in **Table 1.**

4-2-3. General Procedures for the Homogeneous Transfer Hydrogenation of Aldehydes Under Formic acid and CO

Homogeneous hydrogenation of cinnamaldehyde was carried out using 4-dimethylaminopyridine(4-DMAP) and $Rh_6(CO)_{16}$ as a typical example. To a glass liner containing 2 mmols of formic acid and 4-DMAP was added $Rh_6(CO)_{16}$ (0.005 mmol), followed by a THF (3.0 ml) solution of cinnamaldehyde (1.0 mmol) under a nitrogen atmosphere. The glass liner was set in a stainless steel autoclave and then flushed three times and pressurized to 5 atm with CO. After the reaction mixture was stirred at 30 °C for 8 h, the reactor was cooled and the pressure was slowly released. The GC analysis showed 91 % yield of cinnamyl alcohol.

Table 1. Effect of Solvents on the Homogeneous and Heterogeneous Hydrogenations of Cinnamaldehyde (**1**) Using $Rh_6(CO)_{16}$[a,b]

solvent	DS [c]	convn of **1**[d] (%)	selectivity[d] (%)		
			2	**3**	**4**
THF	2.7	91 (86)	91 (89)	1 (1)	8 (10)
1,4-Dioxane	1.8	99 (89)	82 (85)	1 (2)	17 (13)
THP	1.5	95 (88)	82 (87)	2 (1)	16 (12)
Toluene	2.1	99 (0)	66 (–)	2 (–)	32 (–)
MeOH	1.2	10 (0)	72 (–)	24 (–)	4 (–)

[a] Reaction conditions: **1** (1.0 mmol), $Rh_6(CO)_{16}$ (0.005 mmol), formic acid (2.0 mmol), 4-DMAP (2.0 mmol), solvent (3.0 mL), *Pco* = 5 atm, 30 °C, 5 h. [b] Values in parentheses are for the heterogeneous system; the POLYDMAP (100 mg, 0.14 mmol equiv of DMAP) was used. [c] Degree of swelling of the POLYDMAP^{TM}. DS: degree of swelling, Swollen resin volume/dry resin volume. [d] Determined by GC using internal standard technique. **2**, Unsaturated alcohol; **3**, saturated aldehyde; **4**, saturated alcohol.

4-2-4. General Procedure for the Heterogeneous Transfer Hydrogenation with POLYDMAP.

A typical example of the heterogeneous transfer hydrogenation of cinnamaldehyde using POLYDMAP and $Rh_6(CO)_{16}$ was as follows. POLYDMAP (100 mg, 0.14 mmol equiv of 4-DMAP) was used in place of 4-DMAP. To a glass liner containing formic acid (2 mmol) and the POLYDMAP (100 mg) was added $Rh_6(CO)_{16}$ (0.005 mmol), followed by a THF (3.0 ml) solution of cinnamaldehyde (1.0 mmol) under a nitrogen atmosphere. The glass liner was set in a stainless steel autoclave and then flushed three times and pressurized to 5 atm with CO. After the reaction mixture was stirred at 30 °C for 12 h, the reactor was cooled and the pressure was slowly released. After the separation of the solid polymer by a filtration, the GC analysis of filtrate showed 89 % of cinnamyl alcohol.

In the heterogeneous transfer hydrogenations, the product was isolated by the following procedures. After the hydrogenation procedures, the solid polymer was removed by filtration and washed three times with THF. The combined filtrate was concentrated by an evaporation and subjected to column chromatography on silica gel (Wako gel C-200) with a mixture of hexane and ethyl acetate (10:1), which afforded pure allylic alcohol. The polymer was initially golden amber, which became reddish brown after the filtration. The IR spectra of the reddish brown polymer-bound Rh complexes showed the absorption peaks at 2078, 2037, 2000, and 1819 cm^{-1}, which are attributed to the stretching of the carbonyl groups.

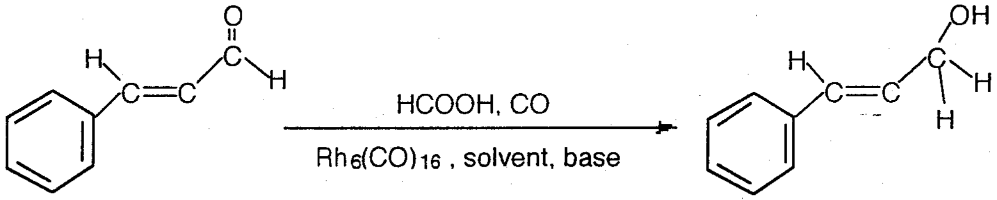
4-2-5. Recycling of the Polymer-Bound Rh Catalyst in the Transfer Hydrogenation of 3-Methyl-2-butenal.

The polymeric Rh cluster catalyst was reused in the hydrogenation of 3-Methyl-2-butenal. The first run using 3-methyl-2-butenal (1.0 mmol) was carried out in using the same procedure as described in the above heterogeneous hydrogenation. After the reaction mixture was stirred at 30 °C for 24 h, the reactor was cooled and the pressure was slowly released. The supernatant in the glass liner was withdrawn using a syringe under a nitrogen atmosphere. The residual polymeric catalyst was washed with three 5 ml aliquots of THF, followed by addition of formic acid and THF solution of the substrate, flushed three times and pressurized to 5 atm with CO, and stirred at 30 °C for 24 h. The recycling experiment was repeated four times in the same manner as in the first recycle.

4-3. Results and Discussion

4-3-1. Homogeneous Transfer Hydrogenations of Unsaturated Aldehydes

In order to attain highly chemoselective reductions of carbonyl group of the aldehyde in the presence of formic acid as a hydrogen donor, various reaction conditions (*e.g.*, CO pressures, additives, reaction temperatures, and solvents) were scrutinized in the homogeneous reaction of cinnamaldehyde as a model substrate (**Eq. 3**).



(3)

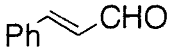
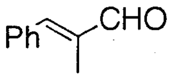
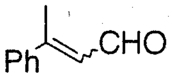
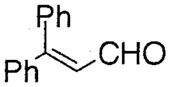
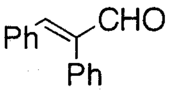
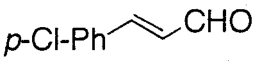
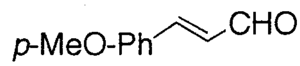
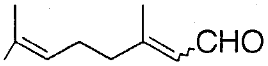
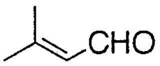
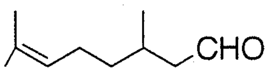
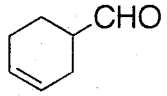
This selective hydrogenation needed base additives as was also observed in the previous hydrogenations using H_2O or H_2 as a hydrogen source. In this transfer hydrogenation, 4-(dimethylamino)pyridine (4-DMAP) was found to be the best additive, while additions of diamines as bases were ineffective in this case. This result differ from the hydrogenations by using of H_2O or H_2 that the addition of diamines are highly effective as described in the previous chapters.

Further, CO was essential for this transfer hydrogenation; at least 5 atm of CO was necessary for the efficient formation of cinnamyl alcohol. Hardly any hydrogenation occurred under a nitrogen atmosphere without any CO. The highest selectivity for the unsaturated alcohol was attained at 30 °C, and hydrogenations at higher temperatures than 30 °C resulted in poor selectivities to allylic alcohols. **Table 1** shows the effect of solvents on the catalytic activity of the homogeneous hydrogenation using formic acid together with that of the corresponding heterogeneous Rh system. Cyclic ether solvents, *e.g.*, THF, 1,4-dioxane, and tetrahydropyran were effective, while methanol and toluene were poor solvents, respectively. Among the cyclic ether solvents, the highest selectivity for cinnamyl alcohol (91%) was obtained with THF.

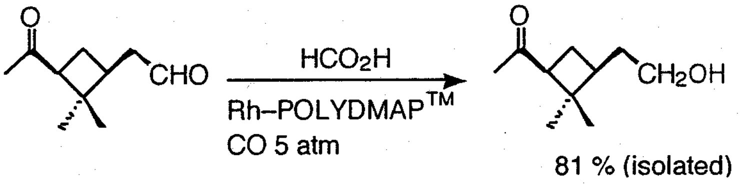
Results of the homogeneous transfer hydrogenation of various α,β-unsaturated aldehydes using 4-DMAP and THF as a solvent are shown in **Table 2** together with those obtained in the heterogeneous catalyst system (*vide infra*). Methyl-substituted cinnamaldehydes of 2-methyl-3-phenylpropenal and 3-phenyl-2-butenal showed high selectivities for the corresponding unsaturated alcohols, respectively (Table 2, entries 2 and 3). In the case of phenyl-substituted cinnamaldehydes, the chemoselective hydrogenation of 3,3-diphenyl-2-propenal occurred to give 3,3-diphenyl-2-propen-1-ol as the sole product (Table 2, entry 4), while *trans*-2,3-diphenyl-2-propenal showed a poor selectivity for the corresponding unsaturated alcohol (Table 2, entry 5). Notably, either an electron-donating or -withdrawing substituent in the para position of cinnamaldehydes did not significantly influence the chemoselectivity (Table 2, entries 6 and 7). Under these reaction conditions, dechlorination of 3-(4-chlorophenyl)-2-propenal did not occur (Table 2, entry 6). Further, citral and 3-methyl-2-butenal, typical aliphatic α,β-unsaturated aldehydes, gave the corresponding allylic alcohols in high yields, respectively (Table 2, entries 8 and 9). The isolated olefinic bond in citral remained intact under the above reaction conditions. This high chemoselectivity for the aldehyde functions in the presence of nonconjugated olefinic bonds could be observed also in citronellal and cyclohexene-4-carboxaldehyde (Table 2, entries 10 and 11). Furthermore, the transfer hydrogenations of 3-phenyl-2-butenal and citral used as mixtures of geometrical isomers (*E*/*Z* = 2.6 and 2.0) proceeded with high retention of the olefinic configuration, respectively.

In an intermolecular competitive reaction between benzaldehyde and acetophenone, benzyl alcohol was only hydrogenated product without formation of 1-phenylethanol from acetophenone. High chemoselectivity to aldehyde against ketone function was also confirmed in the intramolecular competitive hydrogenation of *cis*-3-acetyl-2,2-dimethylcyclobutaneacetaldehyde (**Eq. 4**). Only the formyl function could be reduced to afford *cis*-3-acetyl-2,2-dimethylcyclobutaneethanol in 92% yield (81% isolated). No products were obtained from reduction of the ketone group.

Table 2. Chemoselective Hydrogenation of α,β–Unsaturated Aldehydes to Unsaturated Alcohols Using Formic Acid [a,b]

entry	substrate	time (h)	convn[c] (%)	selectivity[c] (%)			Yield of **2**[d]
				2	**3**	**4**	(%)
1		8 (12)	97 (97)	91 (90)	0 (0)	9 (10)	87
2		10 (24)[e]	98 (89)	94 (94)	0 (1)	6 (5)	78
3[f]		10[e] (24)[e]	92 (86)	100 (100)	0 (0)	0 (0)	80
4		10 (24)	83 (76)	100 (100)	0 (0)	0 (0)	70
5		5 (20)	92 (72)	52 (57)	0 (8)	48 (35)	
6		5 (20)	89 (90)	88 (97)	9 (1)	3 (2)	79
7		5 (20)	92 (78)	89 (91)	4 (1)	7 (8)	67
8[g]		20 (20)	92 (68)	95 (90)	0 (5)	5[h] (5)[h]	
9		20 (24)	92 (90)	96 (99)	0 (0)	4 (1)	81
10		5 (24)	99 (92)	100[h] (100)[h]	–	0 (0)	87
11		5 (14)	96 (98)	100[i] (100)[i]	0 (0)	0 (0)	93

[a] Reaction conditions: substrate (1.0 mmol), $Rh_6(CO)_{16}$ (0.005 mmol), 4-DMAP (2.0 mmol), formic acid (2.0 mmol), THF (3.0 mL), P_{CO} = 5 atm, 30 °C. [b] Values in parentheses are for the heterogeneous system, where the POLYDMAP (100 mg, 0.14 mmol equiv of 4-DMAP) was used in place of 4-DMAP. [c] Determined by GC using internal standard technique. **2**, Unsaturated alcohol; **3**, saturated aldehyde; **4**, saturated alcohol.
[d] Isolated yields. See in experimental section about the isolation procedures. [e] Formic acid (3.0 mmol) was used. [f] Mixture of regio isomers. *E/Z* = 2.6. [g] Mixture of regio isomers. *E/Z* = 2.0. [h] Citronellol. The isolated olefinic bond is intact. [i] 3-Cyclohexene-1-methanol.



(4)

4-3-2. Heterogeneous Transfer Hydrogenations.

It is well demonstrated in the previous chapters that the use of polymer-bound metal complex catalysts can simplify the process of the isolation of products. In order to heterogenize the above homogeneous Rh–amine system by using polymer supports, POLYDMAP was used in place of 4-DMAP as a base additive since POLYDMAP has a 4-(dimethylamino)pyridino moiety on the para position of styrene unit in the cross-linked polystyrene support (**Figure 1**).

It was found that cinnamaldehyde smoothly hydrogenated to cinnamyl alcohol using POLYDMAP without an addition of 4-DMAP. As shown in **Table 1**, THF was also an effective solvent in the heterogeneous system, but the effects of solvent (except for cyclic ethers) were much different from those in homogeneous systems. For instance, the heterogeneous catalyst system did not show the activity in toluene solvent in spite of the quantitative conversion of cinnamaldehyde catalyzed by the homogeneous system in toluene. The degree of swelling of POLYDMAP (DS) in every solvent used in Table 1 was obtained by measurement of both dry and swollen polymer volumes in each solvent. Use of THF or toluene showed a high DS value, but the transfer hydrogenation did not occur with toluene. In the heterogeneous catalytic systems, it seemed that the DS in the cyclic ether solvents did not strongly affect the hydrogenation rate and product selectivity.

In the above homogeneous transfer hydrogenation, a large amount of 4-DMAP was necessary to obtain unsaturated alcohols in good yields. Typically, 2 equivalent was required. On the other hand, the heterogeneous transfer hydrogenations smoothly proceeded with POLYDMAP having a much lower amino content, even 7 % of that in the homogeneous catalyst system. This phenomenon might be due to the concentration effect of amino moieties within the polymer beads. The concentration of DMAP within the swollen volume of the beads in THF was 0.70 mmol/ml, which was similar to the value in the homogeneous reaction (0.67 mmol/ml). A very low conversion of cinnamaldehyde was obtained in the homogeneous hydrogenation with 0.14 mmol of 4-DMAP, the same amount as in the heterogeneous system. Influence of the polymer particle size was also examined. POLYDMAP beads were ground at liquid nitrogen temperature, and the resulting powder was used in a hydrogenation of cinnamaldehyde. No influence on the hydrogenation rate of cinnamaldehyde was observed when the ground POLYDMAP was used, which suggests that the active species exist on the surface of the polymer beads. Diffusion of the substrate or product through the polymer would not be a significant factor in this transfer hydrogenation using POLYDMAP.

Results of the heterogeneous hydrogenation of various α,β-unsaturated aldehydes using POLYDMAP are also shown in **Table 2**. Generally, high chemoselectivity for the hydrogenation of various aldehydes could be obtained in spite of lower hydrogenation rates than those in the homogeneous system. As expected, use of POLYDMAP could make the workup procedures very simple. The polymer-bound Rh catalysts were easily separated from the reaction mixture by filtration. Pure allylic alcohols can be easily isolated using the column chromatography.

Furthermore, the polymer-bound Rh catalyst could be reused in the hydrogenation of 3-methyl-2-butenal as shown in **Table 3**. The high catalytic activity of the polymeric complexes and high chemoselectivity for 3-methyl-2-buten-1-ol were maintained even after the fourth recycle experiments.

It should be noted that this Rh–amine catalyst system with formic acid as a hydrogen source shows higher activity than those under the same reaction conditions with H_2O or H_2. As the reason for the faster reaction rates with formic acid, the author think that the Rh hydride species could be readily generated from the Rh complex and formic acid under the reaction conditions. Since the basicity of 4-DMAP is stronger than that of TMPDA, the formation of salts with formic acid would be highly efficient and such bases could also act as strong counter cations of the hydride Rh carbonyl cluster anions. An alternative explanation

Table 3. Recycling the Polymer-Bound Rh Catalyst in the Hydrogenation of 3-Methyl-2-butenal (**1**)[a]

recycle no.	convn of **1**[b] (%)	selectivity[b] (%) **2**	**3**	**4**
fresh	90	99	0	1
1	93	99	0	1
2	90	99	0	1
3	88	99	0	1
4	88	99	0	1

[a] Reaction conditions: **1** (1.0 mmol), $Rh_6(CO)_{16}$ (0.005 mmol), the POLYDMAP (100 mg), THF (3.0 mL), formic acid (3.0 mmol), P_{CO} = 5 atm, 30 °C, 24 h. [b] Determined by GC using internal standard technique. **2**, Unsaturated alcohol; **3**, saturated aldehyde; **4**, saturated alcohol.

is formations of different Rh hydride cluster species with high activities from that observed under the conditions with H_2O or H_2. The formation of new Rh_{13} or Rh_{14} hydride clusters in the presence of HCOOH and CO has been proposed by the IR measurements.

4-4. Conclusion

In conclusion, the $Rh_6(CO)_{16}$/4-DMAP/CO system efficiently catalyzed the chemoselective transfer hydrogenation of various α,β-unsaturated aldehydes to the corresponding allylic alcohols with formic acid as a hydrogen source. The rate of the transfer hydrogenation with formic acid was higher than those with H_2O or H_2. This phenomenon can be explained in terms of the strong basicity of DMAP. By employing POLYDMAP, the above Rh cluster catalyst could be heterogenized to form a recoverable and reusable polymer-bound Rh complex without addition of DMAP .

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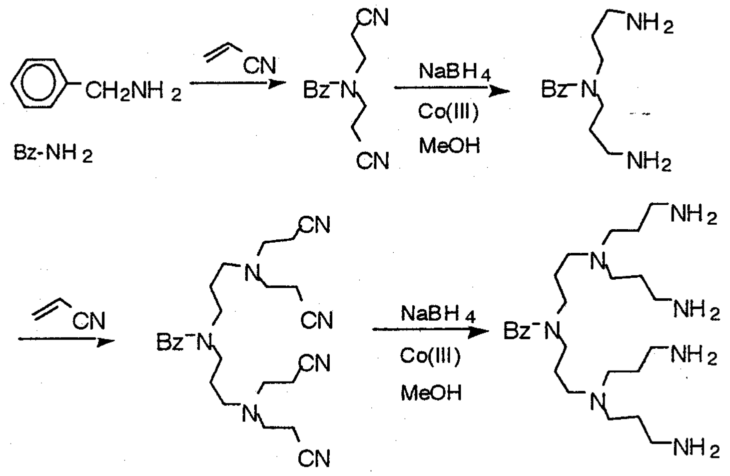
Part 3.

Catalysis of Dendrimer-Bound Metal Complex Catalysts

Chapter 1. Fundamentals of Dendrimer

Since the end of the 1970's, much attention has been paid to the new scientific areas of host-guest[1] and supramolecular chemistries[2]. In order to develop large and substrate-selective ligands, 'tentacle' [3] and 'octopus' [4 and 5] molecules were synthesized. They have long branches which radiate from central hub or macrocycles. The success of the above early researches led to the attempt of a 'cascade' synthesis by Vögtle[6], wherein an exhaustive Michael addition of acrylonitrile to an amine, followed by the reduction of the nitrile groups to *primary* amines, could theoretically be repeated to produce highly branched ligands (**Scheme 1**).



Scheme 1. Cascade Synthesis of Hyperbranched Ligand

The field of highly branched macromolecules has been also interested from the viewpoint of polymer chemistry. Tomaila *et al.* have developed the stepwise growth polymerization giving highly branched polymers with extremely low polydispersity. The polyamidoamine (PAMAM) series thus synthesized were called 'starburst dendrimers[7 and 8]. The term of dendrimer is from the Greek word *dendra* for a tree. The term 'dendrimer' is now used universally to describe highly branched, and monodispersed compounds.

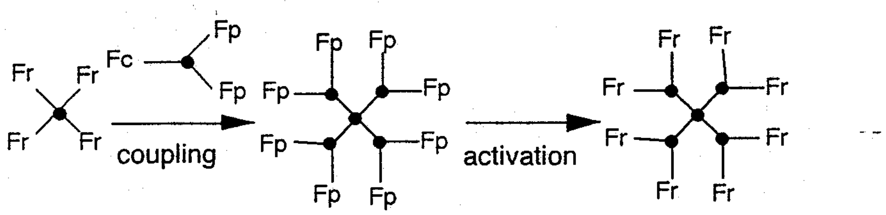
In contrast to linear polymers, dendrimers are highly branched fractal-like macromolecules with defined three-dimensional size, shape, and topology, which can be prepared with very narrow molecular weight distribution. They have a large number of untangled chain-ends and surface functional groups. Dendritic molecules can be designed as tailor-made materials to contain discrete functional domains having unique physical and chemical properties, which include controllable nanoscale dimensions, predetermined shape, precise mass, and tunable interior and surface features. Recently, a variety of dendritic molecules having organic, inorganic, and organometallic functionalities has been developed. Then, the efforts have been devoted to identifying their practical applications. It should be emphasized that dendrimers without functional moieties can still exhibit interesting chemical or physical properties. Experimental[9] and computer simulation[10] studies reveal that the interior of dendrimers consisting of solvent-filled voids can be used as hosts for encapsulation of small molecules. The entrapment of guest molecules is one of the unique properties of dendritic macromolecules.

1-1. Synthesis of Dendrimers

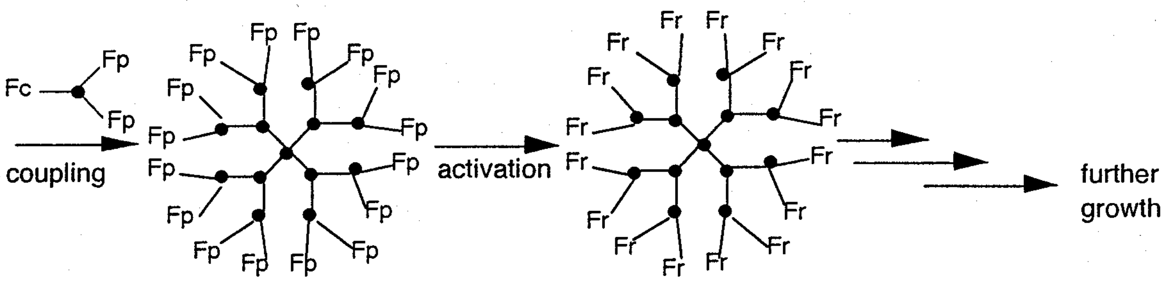
A number of sophisticated synthetic routes are available for exerting complete control of the size and shape of dendrimers. As well as the surface properties by proper selection of the peripheral functionalities, their molecular cavities can be varied by the nature of the dendritic branch and the branching junctions.

1-1-1. Divergent Methods

The divergent synthetic methods have been developed with the key contributions from Vögtle[6], Tomalia[7], and Newkome[11]. A schematic representation of divergent growth is shown in **Scheme 2**. Starting from a reactive core, a generation is grown through the coupling (Fr + Fc) to give the first generation (G1) dendrimer and then the new periphery moieties (Fp) are activated for a successive reaction with additional monomers to give the second generation dendrimer (G2). The above two steps can be repeated. The divergent approach is suitable for the production of large quantities of dendrimers, since in each adding step of the generation, the numbers of the terminal functional groups of the dendrimers are doubled. However, incomplete growth steps and side reactions often lead to the formation of



G1 (1st generation)



G2 (2nd generation)

Scheme 2. Divergent Synthetic Strategy of Dendrimers

Fr : reactive group , Fp : protected group , Fc : coupling group slightly imperfect structures of desired dendrimers. Divergently synthesized dendrimers are virtually difficult to isolate pure form from the by-products.

1-1-2. Convergent Methods

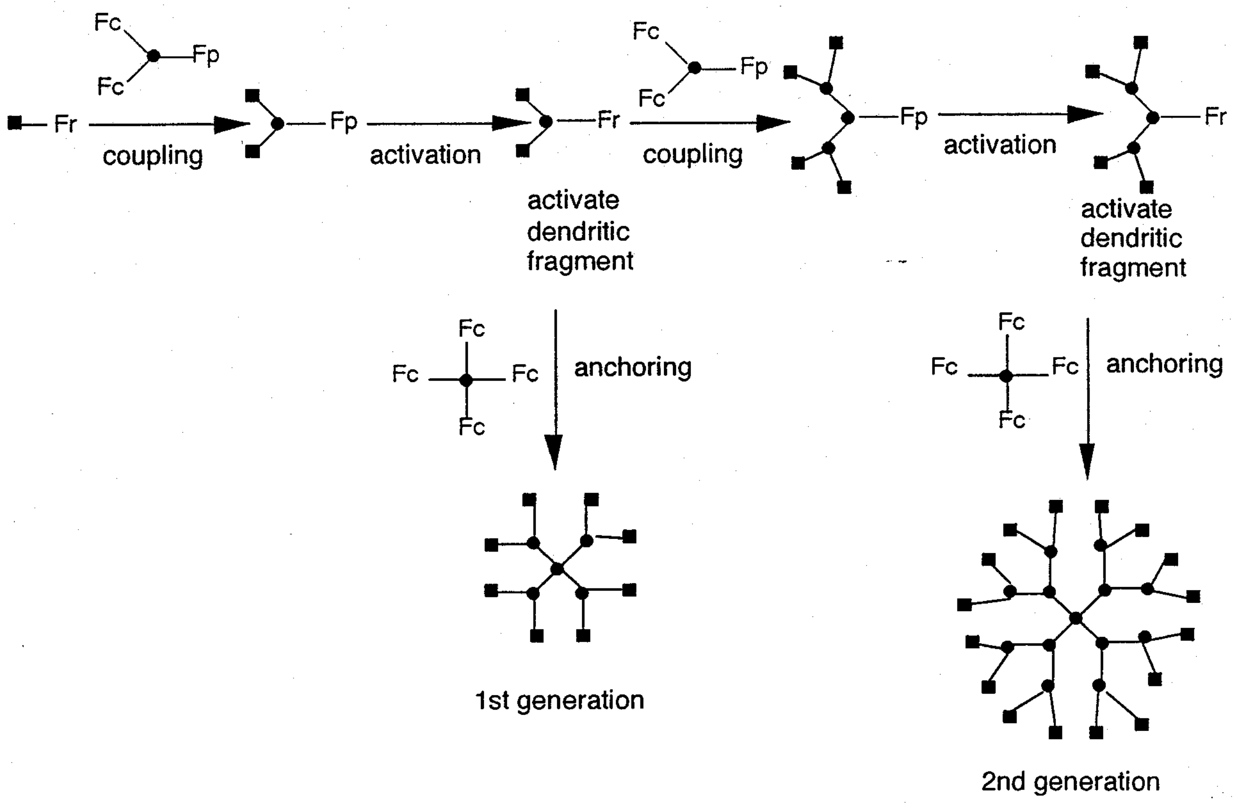
The convergent approach has been developed independently by Frechét[12] and Miller[13]. The synthesis begins at the peripheral sectors of the dendrimers and propagates toward the central core(**Scheme 3**). Advantages of the convergent growth over divergent growth stem from the fact that only two successive reactions are required for any generation-adding steps. More importantly, this protocol makes the isolation of pure dendrimers simple.

1-1-3. Hypercore Convergent Growth

This approach is initially coined by Frechét *et al.* as the double-stage convergent growth, which allowed the rapid preparation of higher generation dendrimers with monodispersity[14]. The key feature of this process involves the anchoring of small dendritic wedges onto a hyperbranched dendritic core (hypercore) which carries a large number of reactive surface groups (**Scheme 4**). The hypercore can be prepared by a convergent growth. The surface functional groups of the hypercore are less sterically hindered than those of simple non-dendritic core molecules used in the conventional convergent method.

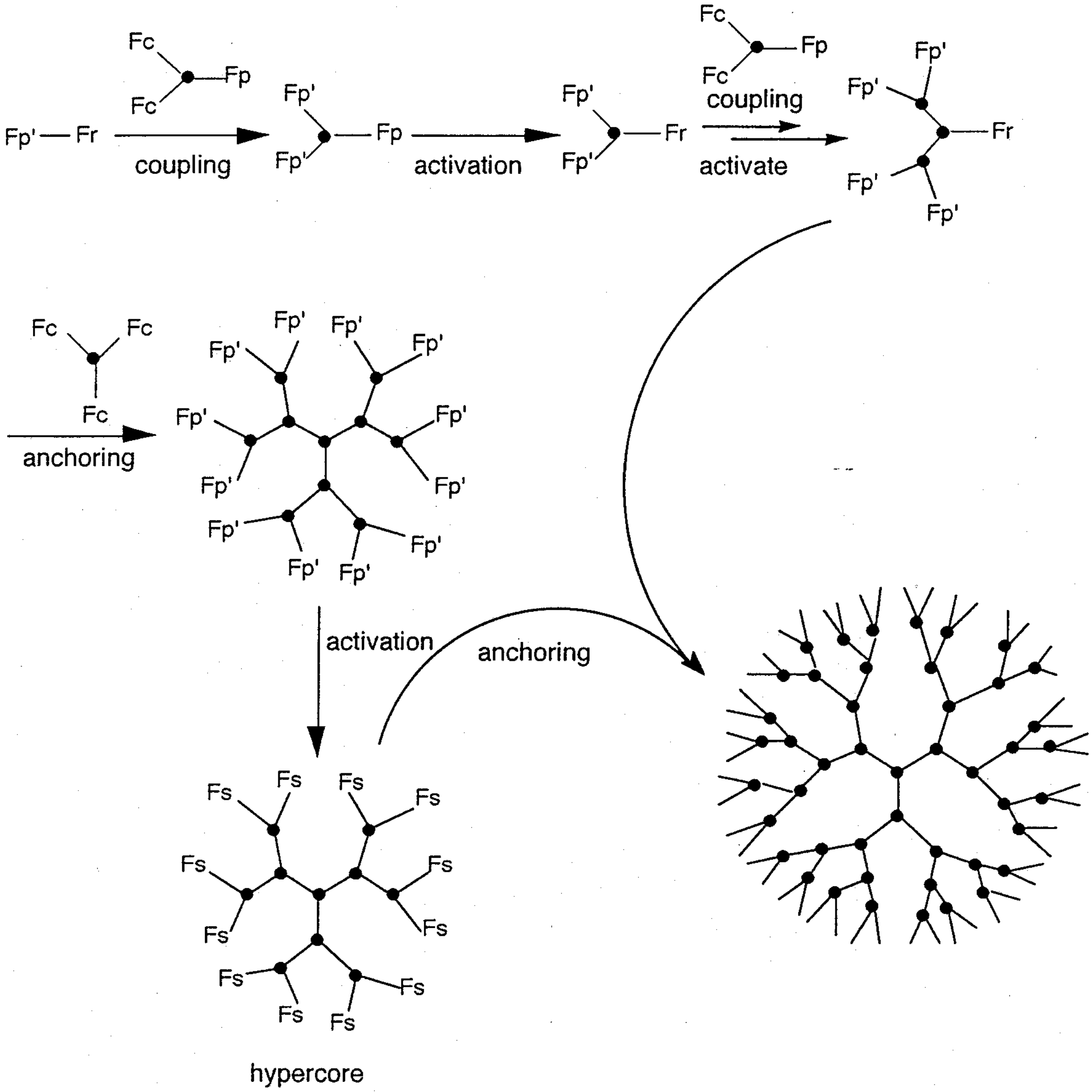
1-2. Characterizations of Dendritic Molecules

Dendrimers are usually characterized by standard polymer characterization techniques such as size exclusion chromatography (SEC), viscosity and light scattering measurements. Due to the structural regularity of dendritic molecules, NMR is often a better method in providing structural informations for dendrimers. With the advent of modern techniques in mass spectroscopy, it has become possible to ionize dendritic molecules and to determine their molecular mass with high precision. Fast atom bombardment (FAB), electrospray (ES), and matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) are especially useful for structural characterization of high molecular weight dendrimers[15].



Scheme 3. Convergent Synthetic Strategy of Dendrimer

Fr : reactive group , Fp : protected group , Fc : coupling group



Scheme 4. Hypercore Convergent Synthetic Strategy of Dendrimer

Fr : reactive group , Fp : protected group , Fc : coupling group , Fs : surface functional group

1-3. Application of Dendrimers

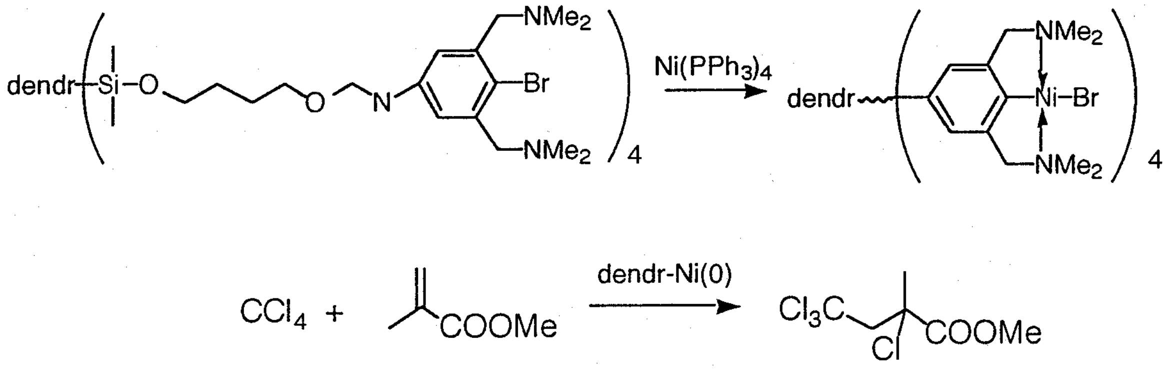
A large number of applications of dendrimers such as calibrators, catalysts, drug delivery vehicles, micelles, liquid crystals, and adhesives have been proposed[8 and 16-19]. In this section, the author reviewed to focus on their application as catalysts.

1-3-1. Catalytically Active Dendrimers

One of the important developments in dendrimer is the preparation of active dendritic catalyst systems. Two broad categories have evolved in the catalytic systems. The first strategy involves the surface incorporation of catalytic sites and the second one is the encapsulation of catalytic sites within a dendritic matrix. The former strategy allows to examine a cooperative effect on the catalytic active centers, while the latter offers opportunities to modulate catalytic activity and selectivity in organic reactions by the encapsulation.

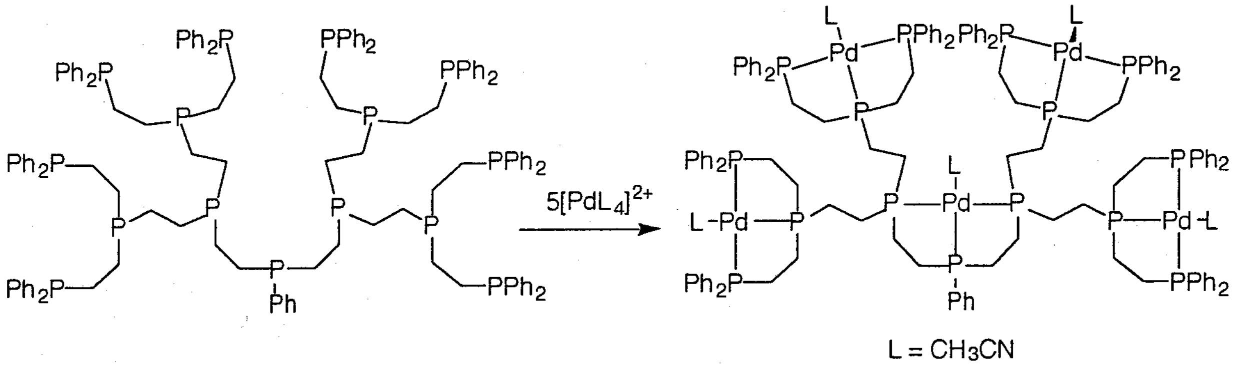
Multiple Catalytic Sites

The first example of metal dendrimer catalysts has been reported by van Koten *et al.*[20]. Aryl nickel(II) complexes located at the periphery of the silane dendrimer provide the multiple center catalysts. The diamino aryl moieties were attached to a polysilane core, followed by an oxidative addition of $Ni(PPh_3)_4$ into the diamino aryl units to give the active Ni catalyst as an orange solid. This homogeneous Ni catalyst was found to be an effective for the Kharash addition of polyhaloalkanes to olefins (**Scheme 5**). However, the catalytic activity was lower than the corresponding monomeric Ni complex and its recycle was not mentioned.



Scheme 5. Kharash Reaction of Polyhaloalkanes to Olefins

DuBois *et al.* have reported the divergent synthesis of dendritic organophosphine ligands and the electrochemical reduction of CO_2 to CO catalyzed by the Pd complexes of the phosphine dendrimers (**Scheme 6**)[21]. The dendritic catalysts had almost the same catalytic activity and selectivity as the analogous mono-palladium catalysts.



Scheme 6. Preparation of Cationic Pd Dendrimer

In order to develop the useful chiral dendritic catalysts in asymmetric syntheses, optically active amino alcohol-terminated dendrimers were synthesized and used as ligands for asymmetric addition of diethylzinc to benzaldehyde[22]. The enantioselectivity diminished with increasing the catalyst generation (Gi, i=1, 2....., n), starting from 10 % e.e. with G0 and reaching 0 % with the G5 catalyst (**Figure 1**). The conformational rigidity and surface crowding arround the metal active centers are the possible reasons for the drop in the asymmetric induction.

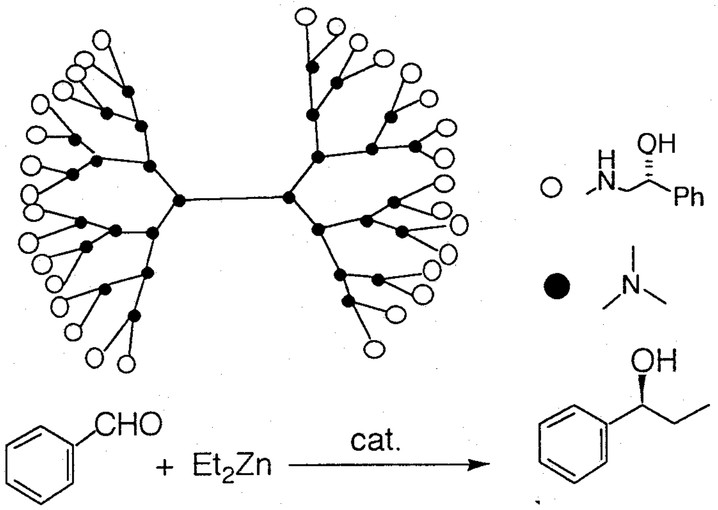


Figure 1. Asymmetric Dendritic Ligand

The first successful result of catalytically active dendrimers has been reported by Reetz *et al*[23]. The poly(propyleneimine) dendrimer with 16 chelate phosphine groups was synthesized and its palladium, rhodium, and iridium complexes were prepared (**Figure 2**). The phosphinated dendrimer-bound dimethyl palladium complex catalyzed the Heck reaction of styrene with bromobenzene. The catalytic activity was higher than the corresponding monomeric palladium complexes. Furthermore, the dendritic Pd catalyst could be recycled with a slightly lower activity than that of a fresh one. Hydroformylation of 1-octene was also carried out with the dendritic cationic rhodium complexes, whose catalytic activity was similar to those of the monomeric Rh complexes.

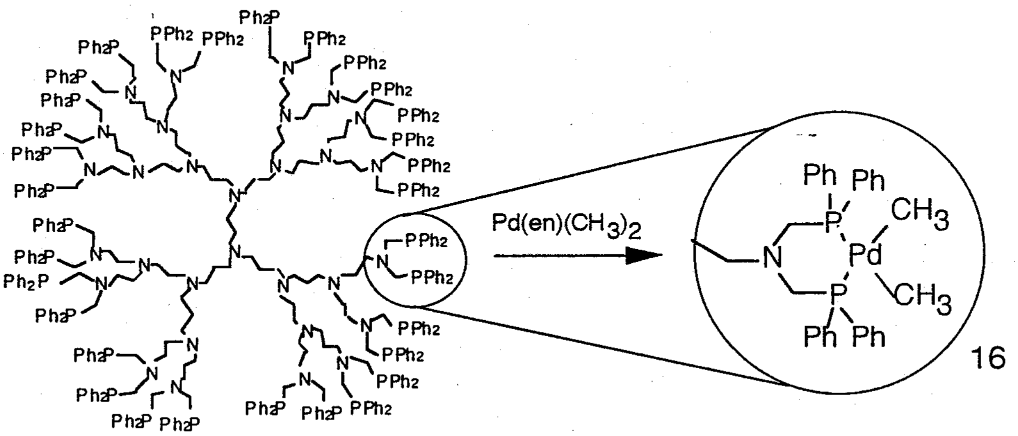
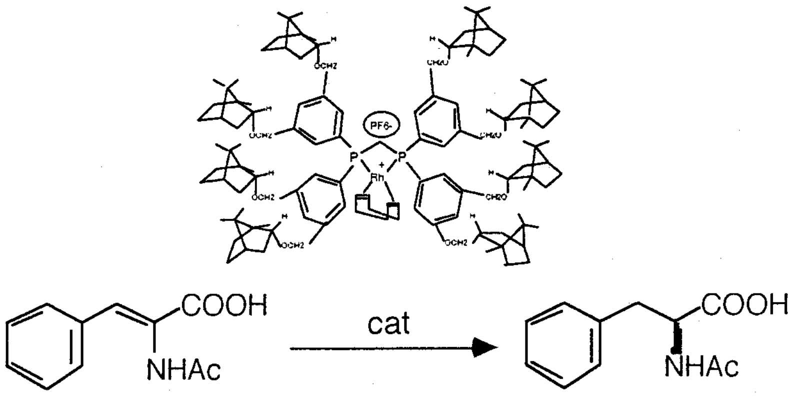


Figure 2. Dendritic $Pd(CH_3)_2$ Complex

Single Catalytic Unit Systems

An incorporation of a catalytic metal center in the interior of a dendrimer with the aim of modulating the catalytic activity is the second approach toward a catalyst design of the dendrimers. A common protocol is to attach one or several dendritic units to a catalytic center.

Brunner and Fürst have provided the first example of synthesis of a series of chiral ligands to the asymmetric catalysis (**Scheme 7**)[24]. Several dendritic ligands were prepared by attaching optically active (-)-borneol moieties with bis-(phosphino)alkanes. The rhodium complex of the dendritic ligand was used for the hydrogenation of *N*-actamidocinnamic acid, however, the product *e.e.* were extremely low (2-5 %). Subsequent works with rhodium-catalyzed hydrogenation, palladium-catalyzed allylation, or copper-catalyzed cyclopropanation resulted in also poor results[25 and 26].



Scheme 7. Asymmetric Hydrogenation of Acetamidocinnnamic Acid

The rate enhancement of the hydrogenation of a acetamidocinnamic acid was observed using a dendritic rhodium catalyst (**Figure 3**)[27]. This rate acceleration was shown to be dependent on the stereospatial arrangement of the dendritic branches on the bis(phosphine) core. Hydrogenation using 2,5-substituted ligands exhibited a 300 fold rate retardation.

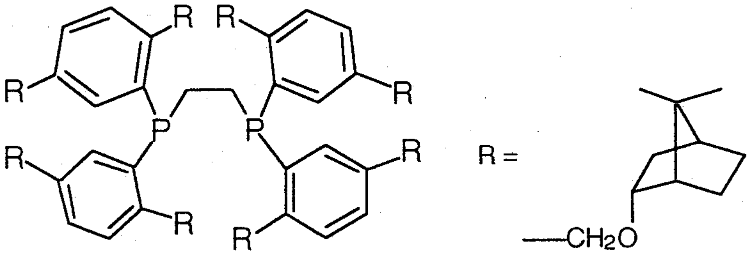


Figure 3. 2,5-Substituted Dendritic Bisphosphine Ligand

Usually, higher generation chiral dendritic catalysts tend to give products with low *e.e.*, however, the chiral pyridinyl alcohols synthesized by Bolm *et al.* have proved to be a useful for the asymmetric alkylation of benzaldehyde with diethylzinc[28]. No significant changes in the enantioselectivity were found using ligands of different generations.

The preparation of chiral polyether dendritic ligands having TADDOL moieties on the dendrimer surface has been reported by Seebach *et al*[29]. The titanium complexes of the dendrimers were capable of promoting the nucleophilic addition of diethylzinc to benzaldehyde and the [3+2] cycloaddition between 3-crotonyl-1,3-oxazolidino-2-one and (*Z*) *N*-benzylidenephenylamine *N*-oxide. However, no significant improvement of diastereo-, and enantioselectivity was observed, compared with non-dendritic titanium TADDOL complexes (**Figure 4**).

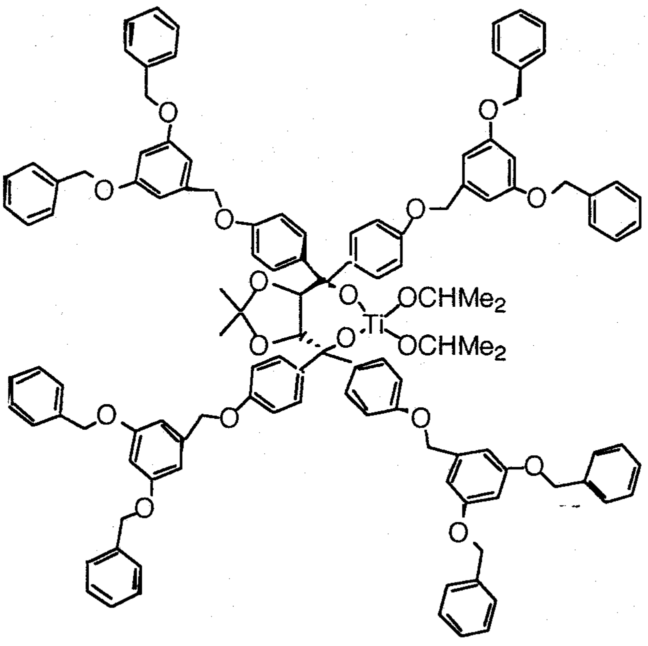


Figure 4. Schematic Presentation of Dendritic Ti-TADDOL (TADDOL = $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanol)

Moore *et al.* have reported the use of manganese containing dendritic porphyrins in the substrate-selective epoxidations (**Figure 5**)[30]. Such dendritic catalysts are analogues to enzyme molecules, which is expected to provide an enhanced substrate selectivity. In the competitive epoxidation betwen 1-alkene and cyclooctene, the G2 catalysts showed higher selectivity by the factor of 2-3 towards 1-alkenes.

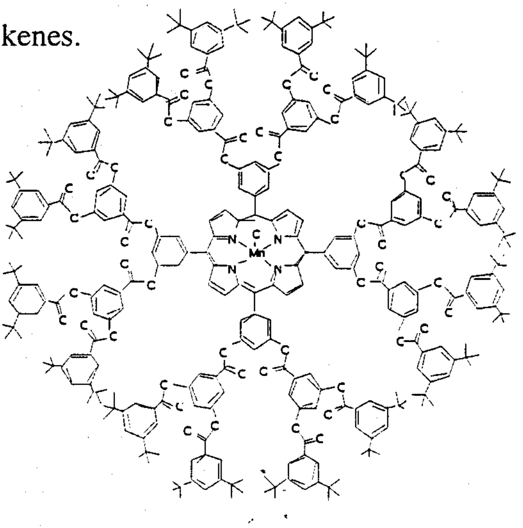


Figure 5. Dendritic Manganase Porphyrin Complex

Kinetic and mechanistic studies of the Diels-Alder reaction catalyzed by a series of dendritic bis(oxazoline) ligands were performed in the presence of copper triflate[31]. Two important mechanistic steps were revealed in this reaction. First step is a reversible binding between the copper center and the dienophile. Secondly, a bimolecular reaction between the copper-dienophile complex and the diene occurs. According to the kinetic studies, the destabilization effect on the binding strength between copper and dienophile became stronger as the increase of size of the dendritic sector. In the higher genaration of dendritic catalysts, the dendritic ligand folded the metal center to give low reaction rates.

In the course of the present studies on the catalyst design of highly functionalized polymeric metal complexes, the author chose dendrimers as catalyst supports in place of polystyrenes used in the Part 2. Based on the specific and unique characters of dendrimers reviwed above, the dendrimers are interesting materials for the catalyst supports, which have the potential possibility of designing both interior and surface functionalities.

In this part, the author primarily used the peripheral functionality of the dendrimer to bind the catalytically active sites, *i. e.*, Pd(II) and Pd(0), in selective hydrogenation of dienes and the Heck coupling reaction, respectively. Also, the interior of the dendrimers could be employed to immobilize the rhodium carbonyl clusters *via* the encapsulation, which catalyzed the reduction of nitrobenzene under the WGSR conditions.

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Chapter 2. Catalysis of Dendrimer-Bound Pd(II) Complex

- Selective Hydrogenation of Conjugated Dienes to Monoenes -

2-1. Introduction

Among many transition metals, palladium compounds are particularly useful and versatile for organic transformation such as C-C bond formation reactions, *e.g.*, C-C coupling and carbonylation[1]. Further advantages of using Pd complexes in organic syntheses are due to its inexpensiveness than Rh, Pt, and Os and its low toxicity. Hence, a number of industrial processes based on the Pd-catalyzed reactions have been developed and are now operated.

Two kinds of Pd compounds, namely Pd(II) salts and Pd(0) complexes, are frequently used. Pd(II) compounds such as $PdCl_2$, $Pd(OAc)_2$, and $Pd(acac)_2$ are commercially available and mainly employed both as unique stoichiometric oxidizing agents and precursors of Pd(0) complexes. It is well known that Pd(II) compounds coordinate to alkenes to form π-complexes[1 and 2]. A decrease in the electron density of alkenes caused by the coordination to electrophilic Pd(II) center permits the attack by various nucleophiles on the coordinated alkenes. In contrast, the electrophilic attack is commonly observed with uncoordinated alkenes. The attack of nucleophiles with formation of a carbon-palladium σ-bond is called the palladation of alkenes which leads to nucleophilic substitution or nucleophilic addition of alkenes. Typical nucleophiles known to react with coordinated alkenes are water, alcohols, carboxylic acid, amines, and active methylene compounds. In the above chemical processes, the Pd(II) species is irreversibly reduced to Pd(0) species, which results in a stoichiometric reaction.

The first example of the catalytic reactions in chemical industry with the Pd(II) species is the Wacker process, in which acetaldehyde is produced from ethylene and molecular oxygen[1]. The essence of the great success of the Wacker process is the invention of an ingenious catalytic cycle, where the reduced Pd(0) is reoxidized *in situ* to Pd(II) with $CuCl_2$, and in turn CuCl is easily reoxidized to $CuCl_2$ with oxygen. Consequently, ethylene is oxidized indirectly with oxygen without consuming $PdCl_2$ and $CuCl_2$ by the combination of these redox reactions. In addition to $CuCl_2$, some other compounds such as $Cu(OAc)_2$, $Cu(NO_3)_2$, $FeCl_3$, HNO_3, and MnO_2 are used as oxidants of the Pd(0) species. Also, organic oxidants such as benzoquinone, organic peroxides, and hydrogen peroxide are employed.

In spite of the success of the Wacker oxidation reaction using Pd(II) complexes, a number of applications of the Pd(II) in the catalytic reaction are limited, compared with those using Pd(0) complexes. Therefore, the author challenged to develop organic reactions catalyzed by Pd(II) complexes. Target reaction is a selective hydrogenation of conjugated dienes to the corresponding monoenes with hydrogen molecule under mild reaction conditions. It has been reported that the hydrogenation of dienes by conventional Pd(II) compounds such as $PdCl_2(PPh_3)_2$ is non-selective and needs high reaction temperatures, hydrogen pressures, and also toxic additives such as $SnCl_2$ to attain high selectivity to monoenes[2]. In addition, rapid and irreversible formation of Pd(0) have been often observed in homogeneous Pd systems under hydrogenation conditions, which leads to the deactivation of the Pd compounds.

In the course of the author's studies on the catalyst design of highly functionalized polymeric metal complexes [3-6], the author chose the modified dendrimers as well-defined polymeric ligands for the Pd(II) species. 115 The dendrimers are novel macromolecules with the monodispersed molecular weights, precisely determined cascade structures, and specific number of the end groups, as described in the general introduction of this part [7-11]. Surface functional groups on the dendrimers can be easily modified with various ligand atoms capable of binding metal complexes to give a number of metal-containing dendrimers[12-14]. Hence, much attention has been paid to the dendritic metal complexes as catalysts because they have structurally well-defined and specific number of active sites as well as possibilities of recovery and reuse of the catalyst [15-18].

In this chapter, it was found that the dendrimer-bound Pd(II) complex showed high catalytic activity for the selective hydrogenation of various conjugated dienes to monoenes. Further, the characteristic features of the dendrimer-bound Pd(II) complex catalysts were revealed by comparison with those of the corresponding monomeric Pd(II) complex and a typical polymeric catalyst of the polystyrene-bound Pd(II) complex[19].

2-2. Experimental

2-2-1. General

^1H, ^{13}C NMR spectra were obtained on JEOL GSX-270 or JNM-AL400 spectrometers with TMS as an internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL GSX-270 and chemical shifts are reported in ppm relative to 85 % H_3PO_4. Infrared spectra were obtained with JASCO FT/IR-410 and FT/IR-610. Analytical GLC was performed by a Shimadzu GC-8APF with flame ionization detector and GC-8AIT with thermal conductivity detector equipped with a capillary column (SPB-1, 60 m) and KOCL 3000T columns. Elemental analysis was carried out by Perkin Elmer 2400CHN. XPS were recorded on Shimadzu ESCA-KM using MgK_α radiation.

The poly(amino)dendrimer, DAB-dendr-$(NH_2)_{16}$ (Astramol™) was purchased from DSM Fine Chemicals and vacuum dried prior to use. Olefins and solvents were purchased from Wako Chemicals and Tokyo Kasei, and purified according to the standard procedures and stored under a nitrogen atmosphere[20]. Paraformaldehyde (95 %) was obtained from Nacalai Tesque and used without further purifications. Cyclopentadiene was prepared by pyrolysis of dicyclopentadiene and stored under an argon in the refrigerator[21]. Diphenylphosphine was synthesized according to the literature procedures[22]. $PdCl_2$ was obtained from Wako Pure Chemicals and used as received. $PdCl_2(PhCN)_2$ [23] and $PdCl_2(PPh_3)_2$ [24] were prepared by reported procedures. $[PhN(CH_2PPh_2)_2PdCl_2]$ was obtained by the literature methods[25 and 26]. All of the substrates and products were characterized by comparison with the literature data.

2-2-2. Preparation of Diphenylphosphinomethyl Dendrimer

The diphenylphosphinomethylated dendrimer DAB-dendr-$[N(CH_2PPh_2)_2]_{16}$ (**1**) was synthesized from DAB-dendr-$(NH_2)_{16}$ according to the method reported by Reetz *et al.*[13]. All manipulation was carried out under an N_2 atmosphere. The mixture of paraformaldehyde (7.0 mmol) and diphenylphosphine (7.7 mmol) in methanol (5 ml) was heated at 65 °C for 10 min. After cooling the mixture to room temperature, a solution of DAB-dendr-$(NH_2)_{16}$ (0.20 mmol, 3.20 mmol eq of the terminal amino groups) in methanol (3 ml) was added to the solution. The mixture was stirred for 30 min at room temperature, then toluene (15 ml) was added. The resulting mixuture became cloudy during the stirring at 65 °C, which was then allowed to further stirr for 12 h at room temperature to complete the reaction. The reaction mixture was concentrated to about 3 ml, and methanol (10 ml) was added. The product precipitated was dried *in vacuo* at 65 °C for 24 h to yield phosphinated dendrimer **1**.

2-2-3. Preparation of Dendrimer-Bound Pd(II) Complexes

Complexation of **1** with $PdCl_2(PhCN)_2$ afforded the dendrimer-bound $PdCl_2$ complex (**2**). The toluene (30 ml) solution of the phosphinated dendrimer **1** (0.172 mmol, 2.75 mmol with respect to the chelete phosphine groups) and $PdCl_2(PhCN)_2$ (2.75 mmol) was stirred at room temperature for 24 h. The light brown precipitate was obtained and the supernatant became almost colorless. The precipitate was washed with toluene (20 ml) for three times, then ether (20 ml). The pale yellow to light brown precipitate was dried under a high vacuum.

2-2-4. General Procedures for the Hydrogenation of Conjugated Dienes

Hydrogenation of cyclopentadiene was carried out using dendritic Pd catalyst **2** under an atmospheric pressure of hydrogen as a typical example in the following procedures. Dendritic catalyst **2** (0.01 mmol eq of Pd) was placed in a side armed flask attached to a gas buret and a manometer. The system was evacuated and filled with H_2, followed by addition of 5ml of EtOH and stirred for half an hour at 25 °C in order to saturate the hydrogen in the solvent and reactor. The stirring was done so rapidly that a reaction rates did not depend on the stirring speed. The volume of hydrogen uptake was continuously measured as the reaction time just after the addition of cyclopentadiene (1.3 mmol). Samples were withdrawn from the reaction mixture at regular intervals and were analyzed by gas chromatography.

2-2-5. Recycling of the Dendrimer-Bound Pd(II) Catalyst

The dendrimer-bound catalyst **2** was subjected to reuse in the hydrogenation of 1,3-COD in EtOH. After the hydrogenation, the dendritic catalyst was separated from the reaction mixture by centrifugation and washed with EtOH in the air, then dried *in vacuo* . The spent Pd catalyst and 1,3-COD and EtOH were recharged to the reactor and subjected to the second run.

2-3. Results and Discussion

2-3-1. Characterization of Dendrimer-Bound Pd(II) Complexes

Complexation of phosphinated dendrimer **1** with $PdCl_2(PhCN)_2$ afforded the dendrimer-bound $PdCl_2$ complex (**2**). $[PhN(CH_2PPh_2)_2PdCl_2]$ (**3**) was also prepared as a low-molecular weight analogue of **2**. The structures of the dendritic compounds **1** and **2** were characterized by ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR techniques. In the ^{31}P NMR spectrum of **2**, a sharp signal at $\delta = -28.0$ due to the metal-free dendrimer **1** completely disappeared and only a new signal was observed at $\delta = +7.93$ corresponding to the phosphines bound to the Pd complex. IR spectrum of **2** had broad bands at 294 cm^{-1} assigned as terminal, *cis* Pd-Cl stretching bands, which were similar to those observed in **3** [27]. XPS spectrum of **2** showed two bands at 343.4 and 338.3 eV due to Pd $3d_{3/2}$ and $3d_{5/2}$, respectively and the binding energy of Cl 2p was 197.9 eV. The above values of binding energies are comparable with those of **3** and a typical Pd(II) complex of $PdCl_2(PPh_3)_2$. The binding energies of Pd $3d_{3/2}$, $3d_{5/2}$ and Cl 2p of the complexes **3** and $PdCl_2(PPh_3)_2$ are as follows; 343.6, 338.5, and 198.0 eV for **3** and 343.6, 338.3, and 198.5 eV for $PdCl_2(PPh_3)_2$ (**Table 1**). From these results, the structure of the dendritic Pd complex **2** can be considered as a divalent DAB-dendr-$[N(CH_2PPh_2)_2Pd(II)Cl_2]_{16}$ as proposed in **Scheme 1**.

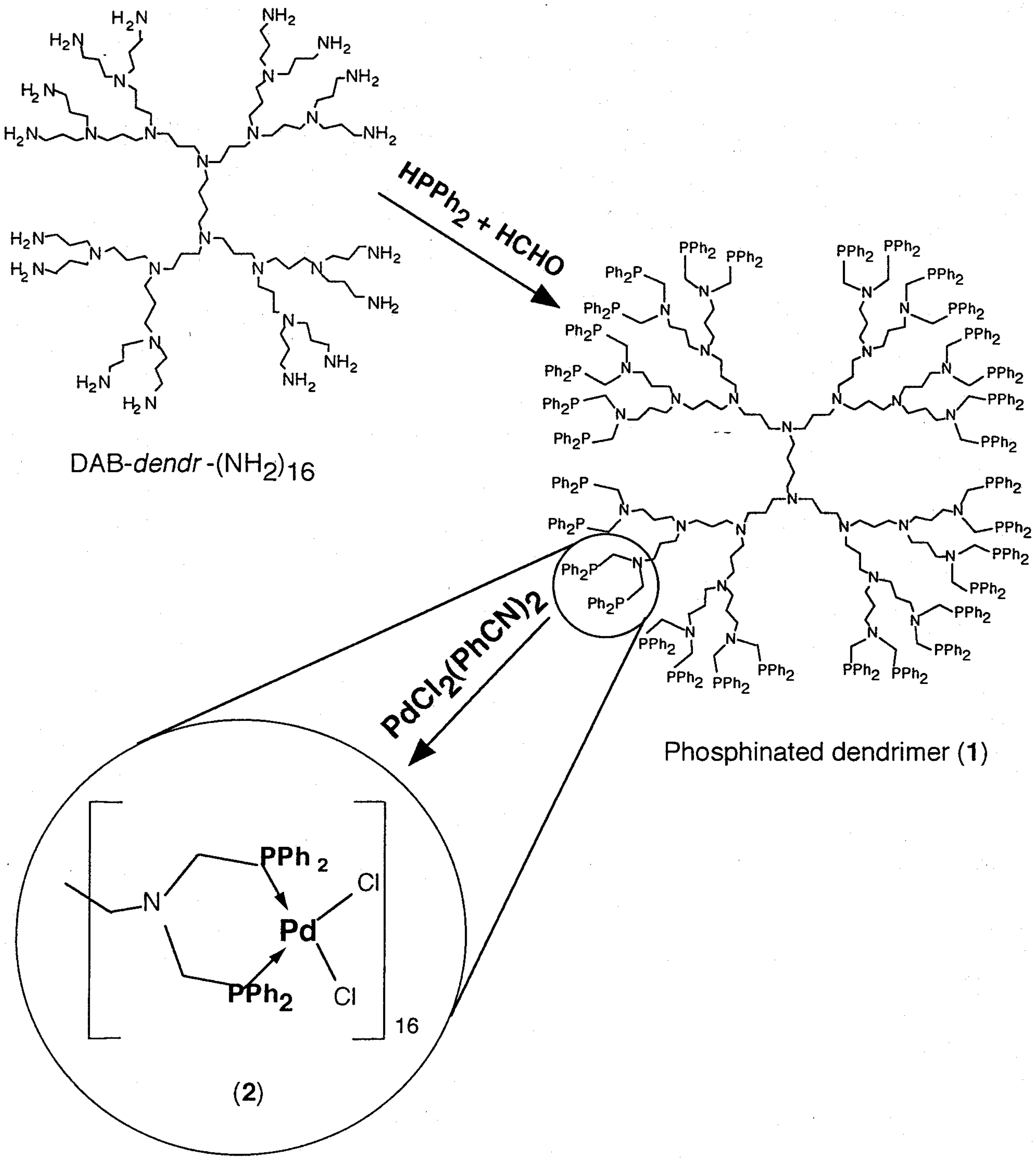
2-3-2. Hydrogenation of Dendrimer-Bound Pd(II) Catalyst

The catalytic activity of the dendritic Pd(II) **2** was examined in the hydrogenation of cyclopentadiene under an atmospheric pressure of H_2 in EtOH solvent, compared with those of the low-molecular analogue Pd(II) **3**, Pd/C, and Pd/Al_2O_3. The timecourses of hydrogen uptakes are shown in **Figure 1**. In the case of **2**, the rate of the hydrogen uptake drastically dropped after cyclopentadiene was completely consumed. At this stage, a high selectivity for the formation of cyclopentene was observed; cyclopentene was an only product without cyclopentane. Further, the successive reduction of cyclopentene occurred at an extremely slow rate when the reaction was prolonged. It has been reported that such a selective

Table 1. Pd 3d, Cl 2p, P 2p, and N1s Binding Energies(eV) of the Pd Complexes [a]

Pd complex	Pd		Cl	P	N
	3d3/2	3d5/2	2p	2p	1s
2	343.4	338.3	197.9	131.6	399.8
2 (used)	343.5	338.2	198.0	131.8	399.7
3	343.6	338.5	198.0	131.9	400.1
$PdCl_2(PPh_3)_2$	343.6	338.3	198.5	132.5	
$PdCl_2$(dppp) [b]	344.3	339.0	198.6	132.5	
$PdCl_2$	343.3	338.0	199.1		
PS-Pd(II) [c]	344.0	338.6	199.1		

[a] The binding energy values are referenced to carbon 1s (285.0 eV).
[b] dppp = 1,3-bis(diphenylphosphino)propane.
[c] Polystyrene-bound $PdCl_2$ complex. Reference 19.



Scheme 1. Synthesis of Peripheral Functionalized Dendrimer (**1**) and the Proposed Structure of Dendrimer-Bound Pd(II) Complex (**2**)

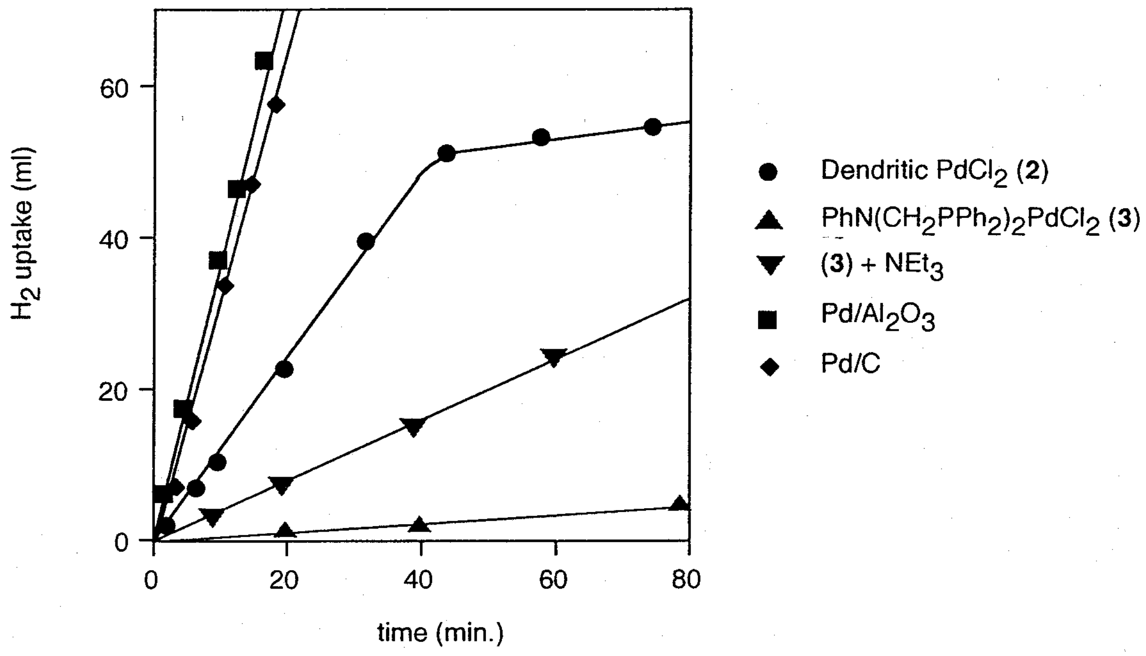


Figure 1. Timecources of H_2 Uptakes Using Various Pd Catalysts in the Hydrogenation of Cyclopentadiene

Reaction conditions: substrate 1.3 mmol, catalyst 0.01 mmol of Pd, . EtOH 5.0 mmol, H_2 1atm, 25±1 °C hydrogenation of dienes to monoenes using homogeneous Pd catalysts required high pressures of H_2 and $SnCl_2$ as an activating agent[28 and 29].

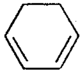
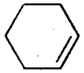
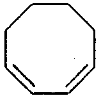
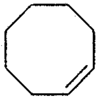
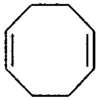
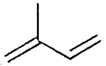
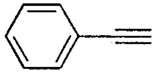
Using Pd/C and Pd/Al_2O_3 catalysts, rates of the hydrogenation was high and remained constant after the perfect consumption of the diene without a turning point of the hydrogen uptake; a competitive reduction of cyclopentadiene and cyclopentene occurred. Thus, the selectivities for the cyclopentene on these supported-Pd catalysts were significantly low. A rate of the hydrogenation with **3** was extremely low among the above Pd catalysts.

The initial rates of H_2 uptakes in the hydrogenation of various olefins are summarized in **Table 2,** together with those using the polystyrene-bound Pd catalyst [19]. The dendritic Pd(II) catalyst **2** has high activity for the hydrogenation of several cyclic conjugated dienes to monoenes. *Notably, the rates increase in the order of* $C_5 < C_6 \sim C_8$, *while the size of substrates much influences the hydrogenation rates in the case of the polystyrene-bound Pd catalyst* [19]. Reductions of non-conjugated diene and common monoolefins such as 1,5-cyclooctadiene (1,5-COD) and cyclooctene occurred slowly. An acetylenic compound of phenylacetylene was also hydrogenated to give styrene in 90 % selectivity. Nitro, carbonyl, and nitrile compounds, *e.g.*, nitrobenzene, benzaldehyde, acetophenone, and propionitrile remained intact under the above reaction conditions.

Table 3 shows the hydrogenation of 1,3-cyclooctadiene by **2** and **3** in the various solvents. Notably, in this hydrogenation, the catalytic activity of the dendritic Pd complex **2** was higher than that of the low-molecular weight Pd analogue **3** in various solvents. Generally heterogenization of metal complexes using organic polymers has disadvantages such as lowered reactivity induced by diffusion limitation of substrates, catalyst leaching, steric hindrance, and inability to totally mimic reactivity and selectivity attainable with the corresponding homogeneous ones[18]. It has been also reported that dendritic metal complex catalysts had lower activities than analogous monomeric complexes in many organic reactions [30-32]. These are not in this case using the dendritic Pd catalyst **2**.

Presumably, an active species for this selective hydrogenation is a Pd(II) hydride species derived from the following scheme on the basis of hydrogenation using the polystyrene-

Table 2. Hydrogenationof Olefins Catalyzed by Dendrimer-Bound Pd(II) Complex (**2**) and Polystyrene-bound Pd(II) Complex (PS-$PdCl_2$)[a]

substrate	initial rate (x 10^{-1} ml/min.)		substrate	initial rate (x 10^{-1} ml/min.)	
	2	PS-$PdCl_2$ [b]		**2**	PS-$PdCl_2$ [b]
	13.9	19.3		1.0 [c]	4.9
	21.7	17.1		3.3 [c]	3.3
	18.0	11.3		0.6 [c]	0.5
reuse	17.6			1.1	3.8
	18.2			4.9	13.9

[a] Reaction conditions: substrate 1.3 mmol, EtOH 5.0 mL, catalyst 0.01 mmol of Pd, 25±1 °C, H_2 1atm.
[b] Reference 19. Reaction conditions: substrate 4.3 mmol, benzene-EtOH(1:1) [13-(volume of substrate)] mL, catalyst 0.04 mmol of Pd, 25±1 °C, H_2 1atm.
[c] Reaction temperature 40±1 °C.

Table3. Hydrogenation of 1,3-Cyclooctadiene in Various Solvents Catalyzed by Dendrimer-Bound Pd (II) Complex (**2**) and $[PhN(CH_2PPh_2)_2PdCl_2]$ (**3**) [a]

solvent	initial rate (x 10^{-1} ml/min.)	
	2	**3**
EtOH	18.0 (Hetero)	0.3 (Hetero)
MeOH	13.8 (Hetero)	0.6 (Hetero)
n-BuOH	12.9 (Hetero)	1.2 (Hetero)
^{i}PrOH	9.1 (Hetero)	1.3 (Hetero)
THF	9.7 (Hetero)	1.5 (Hetero)
DMF	8.7 (*Homo*)	1.1 (*Homo*)
acetone	7.0 (Hetero)	0 (Hetero)
toluene	5.1 (Hetero)	0.2 (Hetero)
n-hexane	1.2 (Hetero)	0 (Hetero)
chloroform	0.5 (Hetero)	0 (Hetero)

[a] Reaction conditions: substrate 1.3 mmol, catalyst 0.01 mmol of Pd, solvent 5 mL, H_2 = 1atm, 25±1°C.

Hetero: heterogeneous reaction. Homo: homogeneous reaction.

bound Pd(II) catalyst [19].

$$PdCl_2(L) \xrightleftharpoons{H_2} PdHCl(L) + HCl$$

L = bisphosphine ligand.

According to the above equilibrium reaction, a generation of the Pd-H can be accelerated by the presence of bases to remove HCl. In a separated experiment, an addition of triethylamine to the corresponding low-molecular weight Pd(II) catalyst **3** increased the hydrogenation rate, as demonstrated in **Figure 1**. It is suggested that the high catalytic performance of the dendritic Pd catalyst **2** is originated from the unique structure of dendrimer that it contains many amino moieties.

Interestingly, the solubility of 2 in various solvents did not strongly influence the catalytic activities. Among the solvents used in **Table 3**, EtOH was the most effective solvent whereas the compound **2** was insoluble in EtOH. On the other hands, the hydrogenation by **2** proceeded homogeneously in DMF, but the rate of hydrogenation was not so high. Since all active sites of **2** are located on the dendrimer surface, the substrates can easily access to the active Pd sites on the surface without a steric hindrance and a diffusion limitation, which might lead to the efficient hydrogenation even in the heterogeneous system using EtOH solvent. *Vide supra*, the fact that molecular size of dienes did not affect the hydrogenation rate could be explained by the above unique situation of the functionalized dendrimer-bound Pd(II) catalyst. These phenomena are a sharp contrast to results of our previous hydrogenation using the polystyrene-bound Pd complex[19]; in order to swell the polystyrene support, a mixed solvent of benzene and ethanol must be used because the most Pd active sites exist within the polystyrene matrix.

Recycling of **2** was carried out in the heterogeneous hydrogenation of 1,3-COD in EtOH. After the hydrogenation, the dendritic Pd catalyst was separated from the reaction mixture by centrifugation and washed with EtOH in air, then dried *in vacuo* . In the case of homogeneous hydrogenations in DMF solvent, the compound **2** could be also recovered as precipitates by adding an excess of ether to the reaction mixtures. The spent Pd catalyst was used in the hydrogenation for the 2nd run. The activity and selectivity of the dendritic Pd catalyst **2** were kept in the 2nd run. The dendritic Pd catalyst maintained pale yellow color throughout the above reuse experiment. The XPS spectra of the spent catalyst showed the binding energies of Pd $3d_{3/2}$, $3d_{5/2}$ and Cl 2p were almost the same as those of the fresh ones. The IR spectrum of the spent catalyst indicated the retention of *cis* configuration of the Pd complex as was shown in fresh one.

2-4. Conclusions

In conclusions, the dendrimer-bound $PdCl_2$ complex **2** was prepared by the reaction of phosphinated dendrimer and with $PdCl_2(PhCN)_2$. The dendritic Pd(II) complex efficiently catalyzed the selective hydrogenation of conjugated dienes to monoenes under an atmospheric pressure of H_2. For the dendritic Pd catalyst, the catalytic activities was higher than that of the corresponding low-molecular weight complex and the selectivity for the monoenes was higher than those of the conventional supported Pd catalysts. The rate of the hydrogeneation on the Pd compound **2** was not severely sensitive on the size of dienes and on the solvent. Furthermore, the dendritic Pd catalyst can be easily recovered and reused without any loss of the catalytic activity and selectivity for the selective hydrogenation of dienes.

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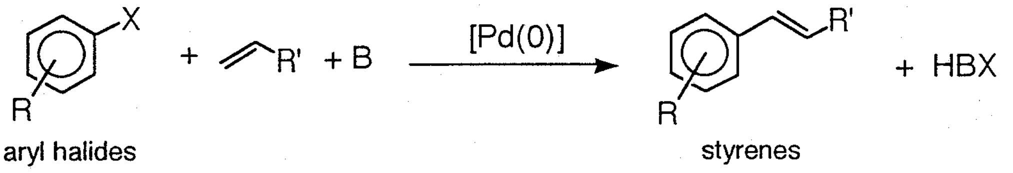
Chapter 3. Catalysis of Dendrimer-Bound Pd(0) Complex

– Heck Vinylic Hydrogen Substitution with Aryl Halides –

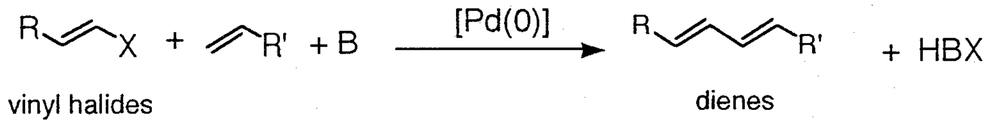
3-1. Introduction

The carbon-carbon bond formation plays an important role in organic syntheses. The most characteristic feature of Pd catalyzed organic reactions is a C-C bond formation[1 and 2]; no other transition metals than Pd can offer such versatile catalysts for the C-C bond formations.

It has been known from the pioneer works of Heck and Tsuji that some organopalladium(II) species generated *in situ* from the treatment of common Pd(II) salts with organomercury compounds convert olefins into vinylic C–C coupling products[1 and 2]. The Pd-mediated C–C coupling has been much evolved from the discovery of the direct oxidative addition of organic halides RX to Pd(0) to yield R-Pd[$(PPh_3)_2$]-X. The key step of "going catalytic" was set by Mizoroki and Heck, who independently discovered that vinylations according to **Eqs. 1** and **2** - now called "Heck olefination" or simply "Heck reaction"- can proceed with catalytic amount of Pd(0) complexes[3 and 4].



(1)

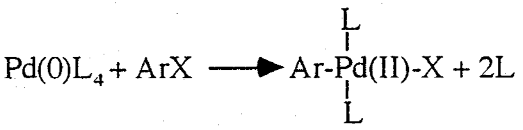


(2)

X = I, Br, N_2BF_4, COCl, CF_3SO_3 B = base: NR_3, K_2CO_3, NaOAc
[Pd(0)] = Pd(0)-phosphine complexes

In this coupling, a vinylic hydrogen can be replaced by a vinyl, aryl, or benzyl group. Therefore, the final step to product formation is the elimination of a hydrogen halide, and the presence of the bases are thus required to remove the acid their salts. Amines as well as K_2CO_3, $NaHCO_3$, and NaOAc are the common bases.

Typical catalysts for the Heck reaction are Pd(0)–phosphine complexes, *e.g.*, $Pd(PPh_3)_4$, or *in situ* generated Pd(0) species, $Pd(0)(R_3P)_n$, easily obtained by the *in situ* reduction of Pd(II) salts, generally $Pd(OAc)_2$, in the presence of phosphine ligands with several reducing agents, such as hydrazine, metal hydrides, alkenes, CO, and alcohols. Phosphines are necessary to stabilize the Pd(0) species, but the use of an excess of phosphines suppress the reaction rates. The Pd(0) species has d^{10} configuration which allows the oxidative addition of reactants, *i. e.*, aryl halide ArX (**Eq. 3**).



$$Pd(0)L_4 + ArX \longrightarrow Ar\text{-}\underset{L}{\overset{L}{Pd}}(II)\text{-}X + 2L \qquad (3)$$

L = phosphine ligand, ArX = aryl halide.

A consequent insertion of olefins undergoes regioselectively in the *syn* stereochemistry, followed by C-C coupling and the *syn* elimination of final olefinic C-C coupling products, normally exhibit the *trans* geometry.

The reactivity of aryl and vinyl halides increases in the order I > Br >> Cl, as rationally explained by the dissociation energy (D) of C-X bond: D values (kcal/mol at 298 K) of Ph-X, X= F, Cl, Br, and I are 126, 96, 81, and 65, respectively[5]. Hence, iodo derivatives are much more reactive, so that additional phosphines are not necessary. It is known that fluorides are completely unreactive with any known catalysts.

In spite of the extensive versatility of the Heck reaction, no commercial application has been seen yet. Following problems prevent the practical use of the Heck reaction.

(a) Catalyst deactivation stems from the fact that decomposition of the Pd(0) catalysts occurs usually above *ca.* 140 °C. The Pd(0) catalysts are also air sensitive.

(b) Relatively large amounts of catalysts are necessary because of the low turnover numbers.

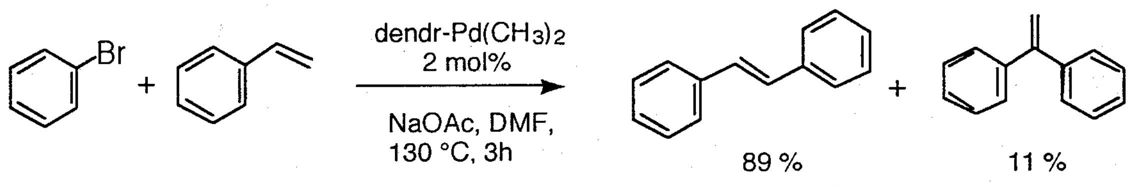
(c) Reactive substrates such as iodides and bromides are expensive. Inexpensive chlorides are not efficiently converted by the common Pd-phosphine catalyst systems.

(d) No efficient method of the catalyst recycling is at hand.

(e) The salt waste is inherent in this reaction sequence.

Therefore, even at present, the improvement of the Heck reaction are continuously studied. The stabilization of Pd(0) species seems to be an important to design the active catalysts[6 and 7].

The coordinatively unsaturated monomeric Pd(0) species could be stabilized in polystyrene matrixes[8 and 9]. Kaneda *et al.* and Pittmann *et al.* have independently reported the polystyrene-bound Pd(0) complex catalysts for the vinylic hydrogen substitution of styrene with iodobenzene. Recently, Reetz *et al.* have reported the Heck reaction of bromobenzene and styrene catalyzed by the phosphinated-dendrimer bound Pd(0) complex, generated *in situ* from the immobilized Pd(II) species (**Eq. 4**)[10]. It seems that the Pd(0) species could be stabilized by the phosphine ligands at the surface of the dendrimer.



(4)

In this chapter, the author investigated the catalysis of the peripherally functionalized dendrimer-bound Pd(0) complex in the Heck reaction. The dendrimer-bound Pd(0) complex was prepared by the *ex situ* reduction of the phosphinated dendrimer-bound Pd(II) complex with hydrazine in the presence of triphenylphosphine, and was applied for the vinyl hydrogen substitution of styrene with bromobenzene. It was found that the dendrimer-bound Pd(0) complex was stable even in air and showed high catalytic activity for the C-C coupling reaction KOAc as a base in DMSO solvent. Furthermore, the dendrimer-bound Pd catalyst was easily recovered as the precipitates from the reaction mixtures by filtration.

3-2. Experimental

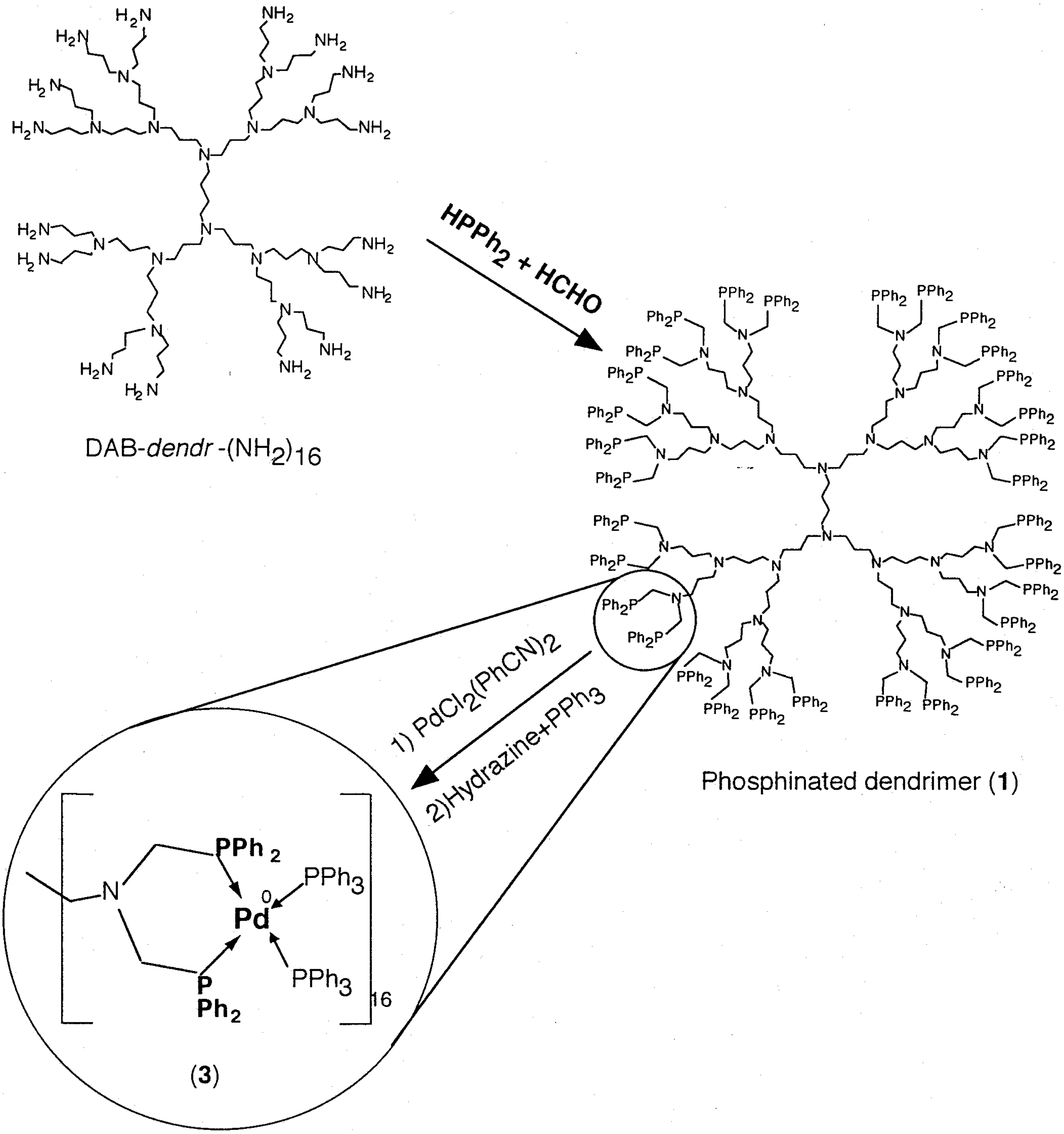
3-2-1. General

^1H, ^{13}C NMR spectra were obtained on JEOL GSX-270 or JNM-AL400 spectrometers with TMS as an internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL GSX-270 and chemical shifts are reported in ppm relative to 85% H_3PO_4. Analytical GLC was performed by a Shimadzu GC-8APF with flame ionization detector equipped with Polyester FF and OV-17 columns. XPS were recorded on Shimadzu ESCA-KM using MgK_α radiation.

The poly(amino)dendrimer, DAB-dendr-$(NH_2)_{16}$ (Astramol™) was purchased from DSM Fine Chemicals and dried in a vacuum before use. Styrene and all solvents purchased from Wako Chemicals and Tokyo Kasei were purified according to the standard procedures and stored under a nitrogen atmosphere[11]. Hydrazine hydrate (99 %) was obtained from Nacalai tesque and used without purification. All inorganic bases such as Na_2CO_3, K_2CO_3, NaOAc, KOAc were commercially available as special grade and used without purification. Triphenylphosphine was recrystallized from n-hexane under a nitrogen atmosphere prior to use. Diphenylphosphine was synthesized according to the literature procedures[12]. $PdCl_2$ was obtained from Wako Pure Chemicals and used as received. $PdCl_2(PhCN)_2$ was prepared by reported procedures[13]. All of the substrates and products were characterized by comparison with the literature data.

3-2-2. Preparation of Diphenylphosphinomethyl Dendrimer (1)

The detailed preparation method of the diphenylphosphinomethylated dendrimer DAB-dendr-$[N(CH_2PPh_2)_2]_{16}$ (**1**) was described in Chapter 4. It was synthesized by the reaction of DAB-dendr-$(NH_2)_{16}$ with paraformaldehyde and diphenylphosphine (**Scheme 1**)[10].



Scheme 1. Synthesis of Peripheral Functionalized Dendrimer (**1**) and the Proposed Structure of Dendrimer-Bound Pd(0) Complex (**3**)

3-2-3. Preparation of Dendrimer-Bound Pd(II) Complexes (2)

The phosphinated dendrimer-bound Pd(II) complex (**2**) was prepared by the reaction of **1** with $PdCl_2(PhCN)_2$ (**Scheme 1**). The detailed method was described in Chapter 4.

3-2-4. Preparation of Dendrimer-Bound Pd(0) Complexes (3)

The dendrimer-bound Pd(0) complex (**3**) was prepared by the reduction of the dendritic Pd(II) complex (**2**) with hydrazine and PPh_3 as shown in **Scheme 1** in a similar way reported by Kaneda *et al*[8]. The dendrimer-bound $PdCl_2$ complex (**2**) (0.74 mmol eq of Pd) and PPh_3 (1.6 mmol) was stirred in EtOH (3 ml) at room temperature for 4 h. Hydrazine monohydrate (6 mmol) was added dropwise to the mixtures, which allowed to stir for 2 h. The solid product was filtered and washed with EtOH (5 ml) for three times, then ether (5 ml). The reddish brown precipitate was dried under a high vacuum.

3-2-5. General Procedures for the Vinylic Hydrogen Substitution Reactions

The reaction of styrene with bromobenzene using the dendritic Pd(0) catalyst **3** was a typical example in the following procedures. The dendritic Pd catalyst **3** (0.02 mmol eq of Pd) and KOAc (2.0 mmol) were placed in a schlenk flask attached to a reflux condenser. The flask was evacuated and filled with Ar, followed by addition of styrene (1.5 mmol), bromobenzene (1.0 mmol) and 2 ml of DMSO, and stirred at 130 °C for 1 h. Samples were withdrawn from the reaction mixture at regular intervals and were analyzed by gas chromatography.

3-3. Results and Discussion

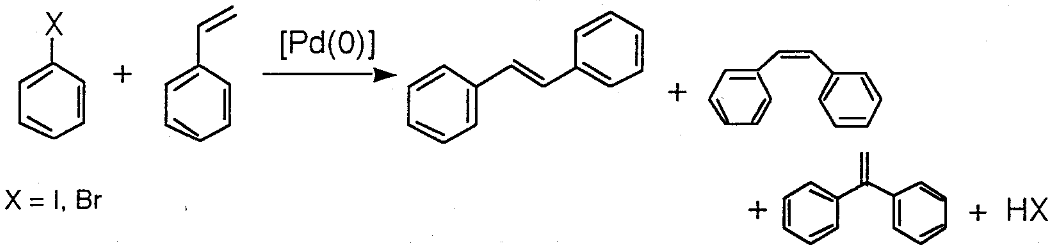
3-3-1. Characterization of Dendrimer-Bound Pd Catalyst

New dendritic Pd compound **3** was obtained from the treatment of Pd(II) dendrimer with excess hydrazine and two moles equivalent of triphenylphosphine in EtOH. The XPS spectrum of **3** showed two bands at 341.3 and 336.0 eV due to Pd $3d_{3/2}$ and $3d_{5/2}$, respectively and the binding energy of P 2p was 131.0 eV. The above values of binding energies are comparable with those of a typical Pd(0) complex of $Pd(PPh_3)_4$. The binding energies of Pd $3d_{3/2}$, $3d_{5/2}$ and P 2p of $Pd(PPh_3)_4$ are 341.4, 336.2, and 131.2 eV, respectively (**Table 1**).

From these results, the structure of the dendritic Pd complex **3** can be considered as a zerovalent DAB-dendr-$[N(CH_2PPh_2)_2Pd(0)(PPh_3)_x]_{16}$ (**Scheme 1**).

3-3-2. Vinylic Hydrogen Substitution with Aryl Halides by Dendrimer-Bound Pd(0) Catalyst (3)

In order to test the catalytic activity of the dendrimer-bound Pd(0) complex **3**, the vinylic hydrogen substitution with aryl halide was examined (**Eq. 5**)[4].



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The results of the C-C coupling of styrene with bromobenzene catalyzed by the dendrimer-bound Pd(0) complex **3** in various solvents are shown in **Table 2.**. In all the solvents employed, the products were a *E*- and *Z*- mixture of stilbenes, and the formation of 1,1-diphenylethylene was negligible. Notably, the reaction proceeded smoothly in polar aprotic solvents such as dimethylsulfoxide (DMSO) and DMF, while dimethylacetamide (DMA) and *N*-methyl-2-pyrrolidone (NMP) gave moderate yields. MeOH proved to be a poor solvent for the C-C coupling reaction. No reaction occurred in the presence triethylamine as a solvent and a base. When many solvents except for MeOH and triethylamine were used, the reaction mixtures were first orange or light brown solution which turned to red immediately at 130 °C, then to pale yellow within 10 minutes. During the reactions in DMSO and MeOH, the dendritic catalyst **3** underwent partial decomposition with formation of black palladium precipitates, while no Pd precipitates could be observed in DMF, DMAc, and NMP. Any change of **3** could not be observed in triethylamine.

Table 3 shows the effect of various bases on the catalytic activity of the dendrimer-bound Pd(0) complex **3** for the C-C coupling reaction in the DMSO solvent. Among common bases of pottasium and sodium salts, potassium acetate was found to be the most effective base, while use of K_2CO_3 or Na_2CO_3 induced rapid formation of Pd metal precipitates which resulted from a detachment of the Pd species from the dendrimer. *Vide supra*, triethylamine

Table 1. Pd 3d, Cl 2p, and P 2p Binding Energies(eV) of Various Pd Complexes [a]

Pd complex	Pd		P	Cl
	3d3/2	3d5/2	2p	2p
dendr-Pd(0) (**3**)	341.3	336.0	131.0	
$Pd(PPh_3)_4$ [b]	341.4	336.2	131.2	
PS-Pd-PPh_3 [b]	342.6	337.6	132.3	
dendr-$PdCl_2$ (**2**)	343.4	338.3	131.6	197.9
$PdCl_2((PhPCH_2)_2NPh)$	343.6	338.5	131.9	198.0
$PdCl_2(PPh_3)_2$	343.6	338.3	132.5	198.5
$PdCl_2$	343.3	338.0		199.1

[a] The binding energy values are referenced to carbon 1s (285.0 eV).
[b] Reference 8.

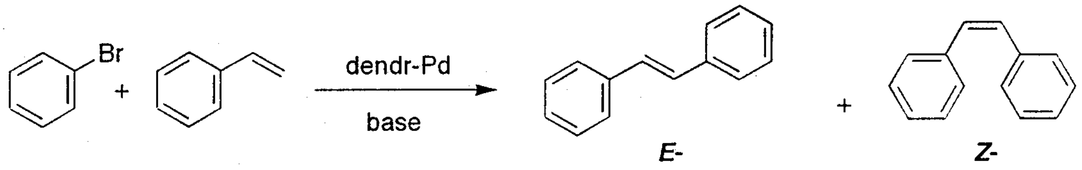

Table 2. Vinylic Hydrogen Substitution of Styrene with Bromobenzene Catalyzed by Dendrimer-Bound Pd(0) in Various Solvents [a]

solvent	conv. (%)[b]	yield (%)[b]	selectivity (%) [c] *E*- : *Z*-
DMSO	99	97	88 : 12
DMF	80	77	83 : 17
DMA	53	52	88 : 12
NMP	49	42	83 : 17
MeOH	10	10	72 : 28
NEt_3 [d]	0	0	–

[a] Reaction conditions: bromobenzene 1.0 mmol, styrene 1.5 mmol, catalyst 0.02 mol eq of Pd, solvent 2.0 mL, NaOAc 2.0 mmol, 4h, 130 °C, Ar atmosphere. [b] Coneversions and yields were based on starting bromobenzene. [c] Selectivities were determined by GC. [d] Without NaOAc.

Table 3. Vinylic Hydrogen Substitution of Styrene with Bromobenzene Using Various Bases [a]

base	conv. (%) [b]	yield (%)[b]	selectivity (%)[c] *E*- : *Z*-
KOAc	98	97	90 : 10
NaOAc	80	75	90 : 10
K_2CO_3	59	51	89 : 11
Na_2CO_3	44	40	89 : 11

[a] Reaction conditions: bromobenzene 1.0 mmol, styrene 1.5 mmol, catalyst 0.02 mol eq of Pd, solvent 2.0 mL, base 2.0 mmol, 1h, 130 °C, Ar atmosphere. [b] Coneversions and yields were based on starting bromobenzene. [c] Selectivities were determined by GC.

as an organic base was not suitable.

Notably, the turnover frequency of this catalysts system was 50 h^{-1}, which is extremely higher than that of the palladacycle catalyst recently presented as a highly active catalyst for the Heck reaction[7]. *Also, the dendritic Pd catalyst can be easily separated from the reaction mixture as a yellow precipitate by addition of excess ether after the filtration of NaOAc and its salt.*

In contrast with the results of the hydrogenations catalyzed by the dendrimer-bound Pd(II) **2** described in Chapter 2, it seems that the solubility of the dendrimer-bound catalyst **3** in the reaction media plays an important role in keeping high catalytic activity in the Heck reaction of bromobenzene with styrene. Among the solvents used in **Table 1**, the solubility of **3** in MeOH and triethylamine was extremely low, whereas **3** dissolved completely in DMSO, DMF, DMAc, and NMP solvents to form clear orange to light brown solution. These solvent effects are similar to those of typical Pd(0)-phosphine complexes, *e.g.*, $Pd(PPh_3)_4$ or an *in situ* catalyst such as $Pd(OAc)_2$-PPh_3 where the Heck reactions are efficiently conducted in polar aprotic solvents such as acetonitrile, DMSO, or DMAc[14]. The above phenomena in solutions could be also observed in the conventional Pd(0) catalysts. Usually, common Pd(0) catalysts are air sensitive, and it should be handled in an inert atmosphere. Notably, **3** was quite stable in air with maintaining the high catalytic activity. The stability of **3** might be due to the site isolation among Pd(0) on the dendrimer, which prevents aggregation of the Pd species. Stabilization of the Pd(0) species using phosphinated polystyrene supports have been also achieved by Kaneda *et al.*[8]. The coordinatively unsaturated Pd(0) species in the polystyrene matrix had a high activity in the vinylic hydrogen substitution of styrene with iodobenzene. Using a dendrimer support, Reetz *et al.* has reported that the dendrimer-bound Pd(0) complex prepared *in situ* from the phosphinated dendrimer-bound $Pd(II)(CH_3)_2$, showed a moderate catalytic activity for the Heck reaction of bromobenzene with styrene, which afforded 89 % of *trans*-stilbene and 11 % of 1,1-diphenylethylene at a conversion of 85-90 % (**Eq. 4**)[10]. *Notably, this catalyst system consisting of 3 and KOAc in DMSO solvent showed much higher activity for the reaction of bromobenzene with styrene than that of the* *dendrimer-bound Pd(0) complex*, which is prepared from the phosphinated dendrimer-bound Pd(II)$(CH_3)_2$.

3-4. Conclusions

In conclusions of this chapter, the phosphinated dendrimer-bound Pd(0) complex could be prepared *ex situ* from the reduction of the dendrimer-bound $PdCl_2$ with hydrazine in the presence of tiphenylphosphine. The dendritic Pd(0) complex is stable in air and effectively catalyze for the Heck C-C coupling reaction of styrene with less reactive bromobenzene. The catalytic activity of the dendritic Pd(0) complex is higher than those of the previously reported catalyst systems of the palladacycles and the dendrimer-bound $Pd(CH_3)_2$ complex. The phosphinated dendrimer-bound Pd(0) catalyst can be easily separated from the reaction mixture as precipitates by adding ether, which would provide a good alternative to the conventional Pd(0) complexes such as $Pd(PPh_3)_4$.

3-5. References

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Chapter 4. Catalysis of Dendrimer-Bound Rh Carbonyl Cluster Complexes

– Reduction of Nitrobenzene under WGSR Conditions –

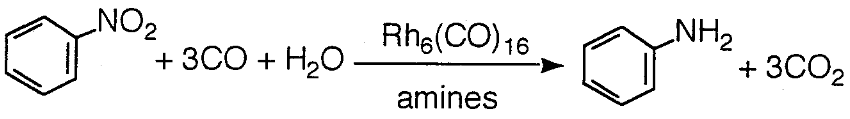
4-1. Introduction

Dendrimers are well defined, highly branched and novel macromolecules that have roughly spherical and globular shape in solution[1-5]. Their cores are relatively loosely packed and can trap guest molecules[6-8] and the dendrimers can act as unimolecular micelle-like entities by appropriate functionalization of the surface end groups. Despite the intensive researches on modification of dendrimers, guest molecules in the interior of dendrimers are limited to organic compounds. Fréchet *et al.* have reported that pyrene could be solubilized in water by employing a water-soluble dendrimer[2]. This example is based on a dynamic process; the guests can easily diffuse in or out of the dendrimer host, depending on the equilibrium conditions. Meijer *et al.* have demonstrated that it was possible to physically lock organic guest molecules in a monomolecular dendritic box[9].

The dendrimers can be considered as nanoreactors, and the ligand sites at the surface of the dendrimers can be used for the binding sites of the active components. Furthermore, the ordered domains at the atomic and/or molecular level within the interior of dendrimers may act as separators, and also be expected to control the cluster size of metals. Recently, Tomalia *et al.* have reported the synthesis of dendrimer-templated nanocomposites using inorganic compounds[10]. They used polyamidoamine dendrimers as templates and copper ions as a precursor of the cluster. A complexation of copper ions with amino groups in the dendrimer molecules, followed by the reduction gave zerovalent copper nanoclusters with the sizes over 2-4 nm.

So far, the application of dendrimers to the encapsulation of inorganic guests molecules are rare and their applications to catalyst for organic reactions have not been reported yet. It is expected that the use of the interior as metal binding sites might provide stabilization of unstable active metal species and the shape selectivities of substrates derived from the unique dendritic structures.

In this chapter, the author intended to use the interior space of dendrimers as metal binding sites, and then, synthesized alkylated dendrimers for an encapsulation of rhodium carbonyl clusters. The reduction of nitrobenzene was carried out by the dendrimer-bound Rh clusters under the Water Gas Shift Reaction (WGSR) conditions (**Eq. 1**).



(1)

It was found that the Rh carbonyl clusters bound to the alkylated dendrimers showed high catalytic activity for the above reduction, while no reaction occurred with non-dendritic low molecular weight amines such as TMPDA. The Rh cluster species could be encapsulated and stabilized in the dendrimers, which was recovered as a stable $[Rh_{12}(CO)_{30}]^{2-}$ cluster anion bound to the aminated dendrimer.

4-2. Experimental

4-2-1. General

^{1}H, ^{13}C NMR spectra were obtained on JEOL GSX-270 or JNM-AL400 spectrometers at 270 or 400 MHz in $CDCl_3$ with TMS as an internal standard. Infrared spectra were obtained with a JASCO FTIR-410. Analytical GLC was performed by a Shimadzu GC-8APF with flame ionization detector and GC-8AIT with thermal conductivity detector equipped with KOCL 3000T and Silicone UC W-98 columns.

Nitrobenzene and solvents were purchased from Wako Pure Chemicals and Tokyo Kasei, and purified according to the standard procedures and stored under a nitrogen atmosphere[11]. Formaldehyde (37 %) was used as purchased. Acid chlorides were obtained from Wako Pure Chemicals and used as received. The poly(amino)dendrimer, DAB-dendr-$(NH_2)_{16}$ (Astramol™) was purchased from DSM Fine Chemicals and dried in vacuo before use. $RhCl_3 \bullet 3H_2O$ was obtained from N.E. Chemcat. All of the substrates and products were characterized by comparison with the literature data.

4-2-2. Preparation of Rh Carbonyl Cluster

Rhodium carbonyl clusters $Rh_6(CO)_{16}$ was prepared from $RhCl_3 \cdot 3H_2O$ according to **Eq. 2** [12 and 13]. The details of the procedures have already described in Chapter 2 in Part 2.

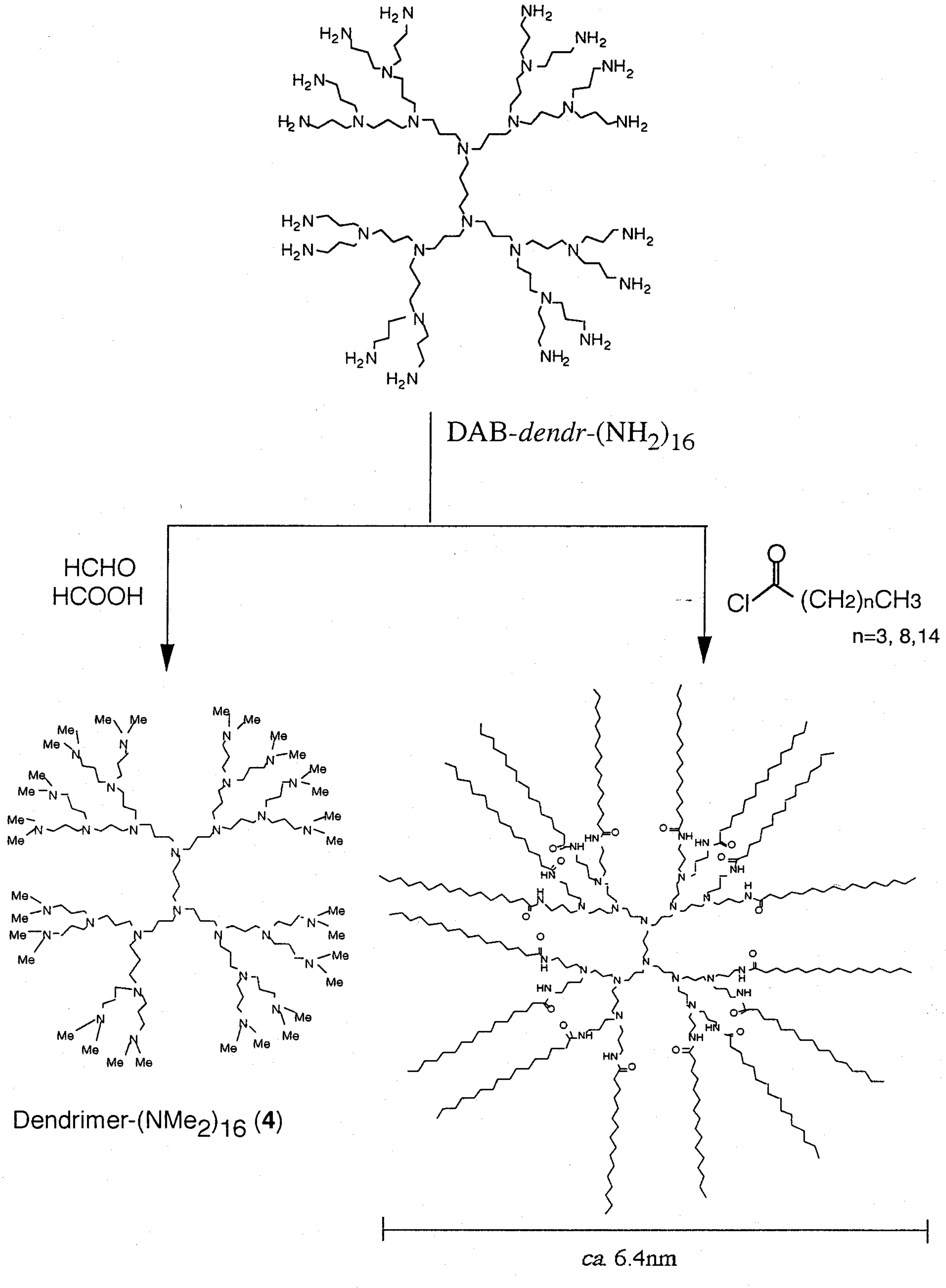
$$RhCl_3 \cdot 3H_2O \xrightarrow[100\ °C]{CO} Rh_2(CO)_4Cl_2 \xrightarrow[KOH/MeOH]{CO} Rh_6(CO)_{16} \qquad (2)$$

4-2-3. Preparation of *N,N*-Dimethylaminodendrimer, dendrimer-$(NMe_2)_{16}$ (4)

The *N,N*-dimethylation of terminal amino groups of dendrimer-$(NH_2)_{16}$ was carried out using the modified procedure of Eschweiler-Clarke Reaction as follows (**Scheme 1**). Dendrimer-$(NH_2)_{16}$ (9 g, 5.3 mmol) was placed in a 500 ml round bottom flask, and dissolved in a mixture of 70 ml of formaldehyde (37 %) and 100 ml of formic acid (99 %). The mixture was stirred at 100 °C for 3 days, then concentrated under a reduced pressure at 65 °C. Fresh formaldehyde (37 %, 70 ml) and formic acid (99 %, 100 ml) were added to the residue and further refluxed for 24 h. The sequence was repeated twice. After refluxing, 100 ml of hydrogen chloride (37 %) was added to the reaction mixtures and concentrated. Then, 300 ml of aqueous sodium hydroxide (10 %) was added to the residue, followed by addition of 10 g of solid NaOH. This alkaline mixture was extracted with ether (4 x 50 ml), and the organic layer was dried over $MgSO_4$. Evaporation of the ether solution gave the desired product of dimethylaminated dendrimer **4** as highly viscous oil (8.8 g, 76 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38 (br, 4H, $NCH_2C\mathit{H}_2C\mathit{H}_2CH_2N$), 1.55-1.62 (m, 56H, $NCH_2C\mathit{H}_2CH_2N$), 2.19-2.27 (m, 128H, $NCH_2CH_2C\mathit{H}_2N(C\mathit{H}_3)_2$), 2.36-2.46 (m, 84H, $NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N$+$NC\mathit{H}_2CH_2C\mathit{H}_2N$+$NC\mathit{H}_2CH_2CH_2N(CH_3)_2$). ^{13}C NMR (105 MHz, $CDCl_3$): δ = 24.9 ($NCH_2\mathit{C}H_2CH_2N$+$NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N$), 25.59 ($NCH_2\mathit{C}H_2CH_2N(CH_3)_2$), 45.5 ($CH_2N(\mathit{C}H_3)_2$), 52,2-52.7 ($N\mathit{C}H_2CH_2CH_2N(CH_3)_2$+$N\mathit{C}H_2CH_2\mathit{C}H_2N$), 54.5 ($N\mathit{C}H_2CH_2CH_2\mathit{C}H_2N$), 58.0 ($NCH_2CH_2\mathit{C}H_2N(CH_3)_2$).

4-2-4. Preparation of Terminal Alkylated Dendrimers, dendrimer-$(NHCOC_n)_{16}$, n = 5 (Compound 5), 10 (Compound 6), and 16 (Compound 7)

The primary amino end groups of dendrimer-$(NH_2)_{16}$ were modifies with hydrophobic alkyl chains by the procedures reported by Meijer[14-16]. Treatment of the dendrimer-$(NH_2)_{16}$



Scheme 1. Surface Modification of Dendrimer-$(NH_2)_{16}$

with various alkyl acid chlorides gave the terminal alkylated dendrimers, dendrimer-$\mathrm{(NHCOC_n)_{16}}$ ($\mathrm{C_n = (CH_2)_{n-1}CH_3}$, n = 4, 9, 15).

4-2-4-1. Preparation of Pentanoyl-Functionalized Dendrimer, dendrimer-$\mathrm{(NHCOC_4)_{16}}$(5)

To a solution of dendrimer-$\mathrm{(NH_2)_{16}}$ (1.69 g, 1.0 mmol) in THF (80 ml) added triethylamine (11.3 g, 111 mmol). Pentanoyl chloride (2.7 g, 22.5 mmol) was slowly added over a period of 10 min. After stirring for 48 h at room temperature, the white turbid solution was evaporated in vacuo. The residue was refluxed with a aqueous NaOH (1 N, 100 ml) for 2.5 h, and then the precipitate was washed with a distilled water, yielding the crude product. The product was refluxed in 50 ml of ether for an hour and decanted to remove salts. The residue was washed with ether and was dried in vacuo, yielding yellow highly viscous oil (**5**). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ =0.89 (t, 48H, $\mathrm{C\mathit{H}_3}$),1.27-1.65 (m,124H, $\mathrm{CH_3(C\mathit{H}_2)_2}$+ $\mathrm{NCH_2C\mathit{H}_2C\mathit{H}_2CH_2N}$+$\mathrm{NCH_2C\mathit{H}_2CH_2N}$+$\mathrm{NCH_2C\mathit{H}_2CH_2NHCO}$), 2.19 (t,32H, $\mathrm{C\mathit{H}_2CONH}$), 2.39-2.42 (m, 84H, $\mathrm{NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N}$+$\mathrm{NC\mathit{H}_2CH_2C\mathit{H}_2N}$+$\mathrm{C\mathit{H}_2CH_2CH_2NHCO}$), 3.26 (q, 32H, $\mathrm{C\mathit{H}_2NHCO}$), 7.10 (t, 16H, $\mathrm{N\mathit{H}CO}$). ^{13}C NMR(100MHz, $\mathrm{CDCl_3}$): δ =13.7($\mathrm{\mathit{C}H_3}$), 22.2 ($\mathrm{CH_3\mathit{C}H_2}$), 25.0 ($\mathrm{NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N}$+$\mathrm{NCH_2\mathit{C}H_2CH_2N}$), 27.2 ($\mathrm{\mathit{C}H_2CH_2NHCO}$), 27.9 ($\mathrm{\mathit{C}H_2CH_2CONH}$), 36.3 ($\mathrm{\mathit{C}H_2CONH}$), 37.9 ($\mathrm{\mathit{C}H_2NHCO}$), 51.8 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCO}$), 52.3 ($\mathrm{NCH_2CH_2\mathit{C}H_2N}$), 54.5 ($\mathrm{N\mathit{C}H_2CH_2CH_2CH_2N}$), 173.3 ($\mathrm{NH\mathit{C}O}$). IR (KBr): ν($\mathrm{cm^{-1}}$) = 3288.6 (N-H stretch), 2954.9 (C-H sat.), 1644.0 (C=O), 1552.9 (N-H bend).

4-2-4-2. Preparation of Decanoyl-Functionalized Dendrimer, dendrimer-$\mathrm{(NHCOC_9)_{16}}$ (6)

To a solution of dendrimer-$\mathrm{(NH_2)_{16}}$ (1.69 g, 1.0 mmol) in THF (80 ml) added triethylamine (11.3 g, 111 mmol). Decanoyl chloride (4.3 g, 22.5 mmol) was slowly added over a period of 10 min. After stirring for 48 h at room temperature, the white turbid solution was evaporated in vacuo. The residue was refluxed with a aqueous NaOH (1 N, 100 ml) for 2.5 h, and then the precipitate was washed with a distilled water, yielding the crude product. The product was refluxed in 50 ml of ether for an hour and centrifuged to remove salts. The residue was washed with ether and was dried in vacuo, yielding pale yellow solid of **6**. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ =0.88 (t, 48H, $\mathrm{C\mathit{H}_3}$), 1.26-1.70 (m,284H, $\mathrm{CH_3(C\mathit{H}_2)_7}$+$\mathrm{NCH_2C\mathit{H}_2C\mathit{H}_2CH_2N}$+$\mathrm{NCH_2C\mathit{H}_2CH_2N}$+$\mathrm{NCH_2C\mathit{H}_2CH_2NHCO}$), 2.18(t, 32H,

$\mathrm{C\mathit{H}_2CONH}$), 2.35-2.41 (m, 84H, $\mathrm{NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N{+}NC\mathit{H}_2CH_2C\mathit{H}_2N{+}C\mathit{H}_2CH_2CH_2NHCO}$), 3.26(q, 32H, $\mathrm{C\mathit{H}_2NHCO}$), 6.95 (t, 16H, $\mathrm{N\mathit{H}CO}$). ^{13}C NMR (105MHz, $\mathrm{CDCl_3}$): $\delta = 14.1$ ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{CH_3\mathit{C}H_2}$), 24.9 ($\mathrm{NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N{+}NCH_2\mathit{C}H_2CH_2N}$), 26.0 ($\mathrm{\mathit{C}H_2CH_2CONH}$), 27.4 ($\mathrm{\mathit{C}H_2CH_2NHCO}$), 29.4-29.6 ($\mathrm{CH_3CH_2CH_2(\mathit{C}H_2)_4}$), 36.8 ($\mathrm{CH_3CH_2\mathit{C}H_2}$), 36.7 ($\mathrm{\mathit{C}H_2CONH}$), 38.0 ($\mathrm{\mathit{C}H_2NHCO}$), 51.8 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCO}$), 52.4 ($\mathrm{NCH_2CH_2\mathit{C}H_2N}$), 56.0 ($\mathrm{N\mathit{C}H_2CH_2CH_2\mathit{C}H_2N}$), 173.5($\mathrm{NH\mathit{C}O}$). IR (KBr): $\nu(\mathrm{cm^{-1}}) = 3289.0$ (N-H stretch), 2954.4 (C-H sat.), 1644.0 (C=O), 1546.3 (N-H bend).

4-2-4-3. Preparation of Palmitoyl-Functionalized Dendrimer, dendrimer-$(\mathrm{NHCOC_{15}})_{16}$(7)

To a solution of dendrimer-$(\mathrm{NH_2})_{16}$ (1.69 g, 1.0 mmol) in THF (80 ml) added triethylamine (11.3 g, 111 mmol). Palmitoyl chloride (6.2 g, 22.5 mmol) was slowly added over a period of 10 min. After stirring for 48 h at room temperature, the white turbid solution was evaporated in vacuo. The residue was refluxed with a aqueous NaOH (1 N, 100 ml) for 2.5 h, and then the precipitate was washed with a distilled water, yielding the crude product. The product was refluxed in 50 ml of ether for an hour and centrifuged to remove salts. The residue was washed with ether and was dried in vacuo, yielding off-white solid (**7**). M.p. 77 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 0.88$ (t, 48H, $\mathrm{C\mathit{H}_3}$), 1.18-1.75 (m, 476H, $\mathrm{CH_3(C\mathit{H}_2)_{13}{+}NCH_2C\mathit{H}_2C\mathit{H}_2CH_2N{+}NCH_2C\mathit{H}_2CH_2N{+}\ NCH_2C\mathit{H}_2CH_2NHCO}$), 2.16 (t, 32H, $\mathrm{C\mathit{H}_2CONH}$), 2.31-2.45 (m, 84H, $\mathrm{NC\mathit{H}_2CH_2CH_2C\mathit{H}_2N{+}NC\mathit{H}_2CH_2C\mathit{H}_2N + C\mathit{H}_2CH_2CH_2NHCO}$), 3.25 (q, 32H, $\mathrm{C\mathit{H}_2NHCO}$), 7.26 (t, 16H, $\mathrm{N\mathit{H}CO}$). ^{13}C NMR (400MHz, $\mathrm{CDCl_3}$): $\delta = 14.1$ ($\mathrm{\mathit{C}H_3}$), 22.7 ($\mathrm{CH_3\mathit{C}H_2}$), 24.9 ($\mathrm{NCH_2\mathit{C}H_2\mathit{C}H_2CH_2N{+}NCH_2\mathit{C}H_2CH_2N}$), 26.0 ($\mathrm{\mathit{C}H_2CH_2CONH}$), 27.1 ($\mathrm{\mathit{C}H_2CH_2NHCO}$), 29.3-29.7 ($\mathrm{CH_3CH_2CH_2(\mathit{C}H_2)_{10}}$), 31.9 ($\mathrm{CH_3CH_2\mathit{C}H_2}$), 36.7 ($\mathrm{\mathit{C}H_2CONH}$), 37.8 ($\mathrm{\mathit{C}H_2NHCO}$), 51.4 ($\mathrm{\mathit{C}H_2CH_2CH_2NHCO}$), 52.2 ($\mathrm{N\mathit{C}H_2CH_2\mathit{C}H_2N}$), 54.5 ($\mathrm{N\mathit{C}H_2CH_2CH_2\mathit{C}H_2N}$), 173.8 ($\mathrm{NH\mathit{C}O}$). IR (KBr): $\nu(\mathrm{cm^{-1}}) = 3299.0$ (N-H stretch), 2918.1 (C-H sat.), 1639.9 (C=O), 1560.0 (N-H bend).

4-2-5. General Procedure of the Reduction of Nitrobenzene under WGSR Conditions.

Reduction of nitrobenzene using dendrimer **7** and $\mathrm{Rh_6(CO)_{16}}$ was a typical example as follows. A stainless autoclave containing $\mathrm{Rh_6(CO)_{16}}$ (0.010 mmol) and dendrimer **7** (0.75 mmol) was evacuated and flushed three times with CO. A toluene (2.0 ml) solution of nitrobenzene (1.0 mmol) and H_2O (40 mmol) were added successively. The reaction mixture was stirred at 80 °C under 10 atm of CO for 6 h. After the reaction, the reactor was cooled and the pressure was slowly released. The color of toluene solution was initially reddish brown which gradually changed to purple. The products were analyzed by GC.

4-3. Results and Discussion

4-3-1. Reduction of Nitrobenzene Using Various Surface Modified Dendrimers

Reductions of nitrobenzene using $Rh_6(CO)_{16}$ were carried out in the presence of various alkylated dendrimers **4-7** and *N,N,N',N'*-tetramethyl-1,3-propanediamine (TMPDA) under the WGSR conditions as shown in **Table 1**. The dendrimer **7** was the most effective among the above amines in the reduction, and yields of aniline decreased in the order of the length of the attached alkyl chains **4-7**. *It should be noted that the reduction did not occur using non-dendritic TMPDA under the reaction conditions.*

Figure 1 shows the effect of the amount of various alkylated dendrimers on yields of aniline. Among the dendrimers used here, the highest catalytic activity could be obtained with the dendrimer **7**, where a mole ratio of dendrimer to $Rh_6(CO)_{16}$ was 0.75. Also, in the cases of **5** and **6**, maximum yields of aniline were obtained at the ratio of 0.75, respectively. Uses of **6** and **7** decreased yields of aniline where mole ratios to the Rh catalyst were over 0.75. On the other hands in **4**, the aniline yield increased with increasing the amount of the dendrimer. This behavior is similar to that using a nondendritic amine TMPDA, where a large amount of TMPDA showed the high catalytic activity. A different result was obtained for the dendrimer **5**; the yield of aniline increased with increasing the ratio up to 1.0, then converged on the constant value over 1.0.

As shown in **Figure 2**, reductions of nitrobenzene using **7** in 1,2-dimethoxyethane and toluene solvents were carriied out. The reaction mixture was homogeneous in a 1,2-dimethoxyethane solvent, while the phase separation was observed in toluene. *Notably, in toluene, the yield of aniline was higher than that in 1,2-dimethoxyethane during all mole ratios of the dendrimer to the Rh carbonyl cluster.*

Table 1. Reduction of Nitrobenzene to Aniline in the Presence of H_2O and CO [a]

additives	yield (%)
dendrimer-$(NHCOC_{15})_{16}$ (**7**)	76
dendrimer-$(NHCOC_9)_{16}$ (**6**)	70
dendrimer-$(NHCOC_4)_{16}$ (**5**)	63
dendrimer-$(NMe_2)_{16}$ (**4**)	31
TMPDA	0

[a] Reaction conditions: nitrobenzene 1.0 mmol, $Rh_6(CO)_{16}$ 0.01 mmol, toluene 2.0 ml, H_2O 40 mmol, additives 0.105 mmol eq. of amino groups, 6 h, 80 °C, Pco 10 atm.
TMPDA: *N,N,N',N'*-tetramethyl-1,3-propandiamine.

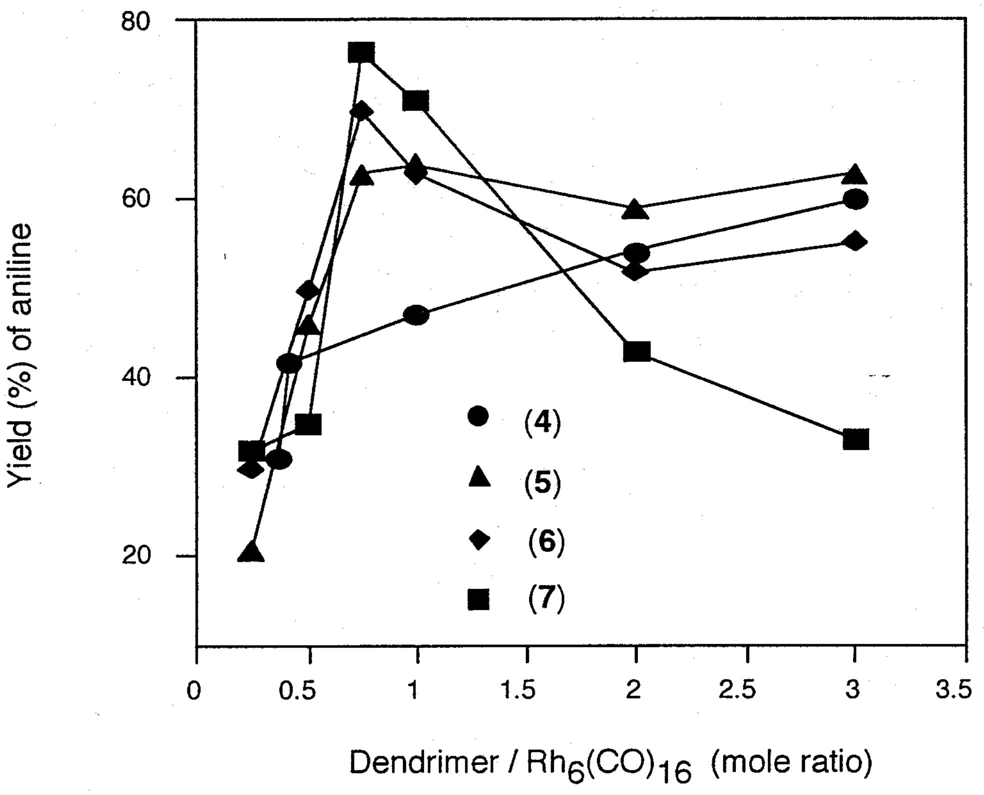


Figure 1. Reduction of Nitrobenzene in the Presence of H_2O and CO Catalyzed by Dendrimer-Bound Rh Cluster Complexes.

Reaction conditions: nitrobenzene 1.0 mmol, $Rh_6(CO)_{16}$ 0.01 mmol, toluene 2.0 ml, H_2O 40 mmol, 6 h, 80 °C, Pco 10 atm.

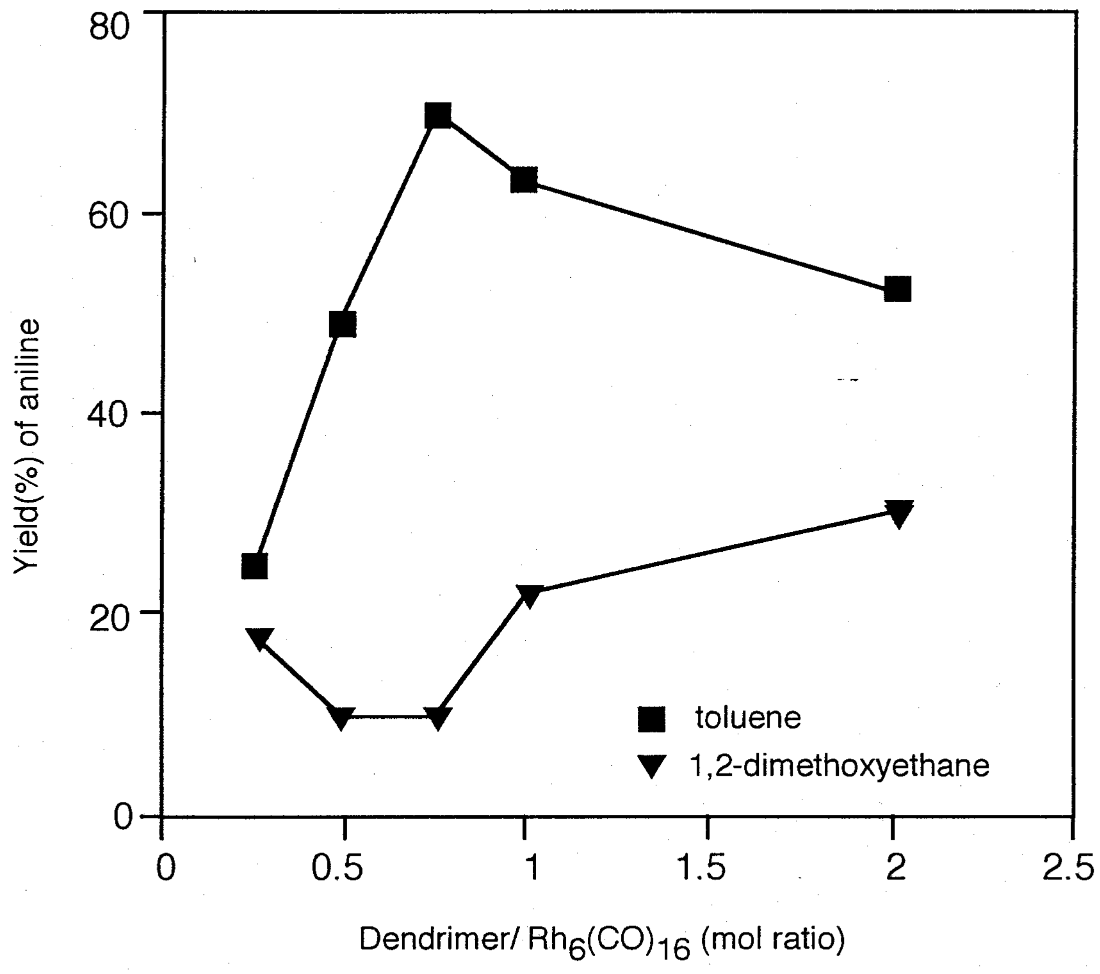


Figure 2. Effect of Solvents on Reduction of Nitrobenzene Catalyzed by dendrimer-$(NHCOC_{15})_{16}$ (**7**) -Bound Rh Cluster Complexes.

Reaction conditions: nitrobenzene 1.0 mmol, $Rh_6(CO)_{16}$ 0.01 mmol,solvent 2.0 ml, H_2O 40 mmol, 6 h, 80 °C, Pco 10 atm.

Kaneda *et al.* have already reported that the reduction of nitrobenzene was catalyzed by Rh carbonyl clusters under the WGSR conditions in the presence of amines such as TMPDA and aminated polystyrenes[17-19]. $Rh_6(CO)_{16}$ is transformed to Rh cluster anions under the above WGSR conditions, where the amines act as counter cations for the Rh cluster anions. In this case, the dendrimers might also behave as counter cations for the Rh cluster anions. Using TMPDA, a large amount of the amine was necessary to attain the high catalytic activity. Furthermore, in the heterogeneous system using aminated polystyrenes, the reaction rates were lower than that of the corresponding homogeneous catalyst system[17]. It should be noted that the combination of the dendrimer **7** and the Rh carbonyl cluster showed the high catalytic activity even in low amine contents as shown in **Table1**. This might be due to the concentration effect of the amino moieties by using dendrimers as soluble supports.

Vide supra, among the surface modified dendrimers **4** - **7**, the length of the alkyl chains influenced the yield of aniline. After the reduction with **4**, the reddish brown solution changed to purple and then dark brown together with a formation of black precipitates of Rh metal. The change of the color suggests the transformation of unstable Rh cluster anions to the stable $[Rh_{12}(CO)_{30}]^{2-}$ species. However, with dendrimer **7**, the $[Rh_{12}(CO)_{30}]^{2-}$ was kept in the dendrimer for longer time than in the case of **4**. These results are similar to that in polystyrene-bound Rh clusters as described in Chapter 2 of Part 2.

The longer alkyl chain would stabilize the Rh cluster anions by encapsulating the clusters within the dendrimer. From the results of **Figure 1**, the highest yields of aniline at a mole ratio of 0.75 in **6** and **7** suggest that the one or two Rh_6 clusters are encapsulated in one dendrimer (**Figure 3**). In the cases of dendrimers **6** and **7**, the dendrimer-bound Rh clusters could be recovered from the reaction mixture by the precipitation with adding an excess of ether. The IR spectrum of the recovered purple solid indicated the formation of the $[Rh_{12}(CO)_{30}]^{2-}$ species (**Figure 4**). However, after the reactions with the **4**, dark brown precipitates was formed in the reddish purple solution. The IR spectrum of the brownish precipitate was found to be a mixture of Rh_{13} and Rh_{12} carbonyl cluster anions (**Figure 5**).

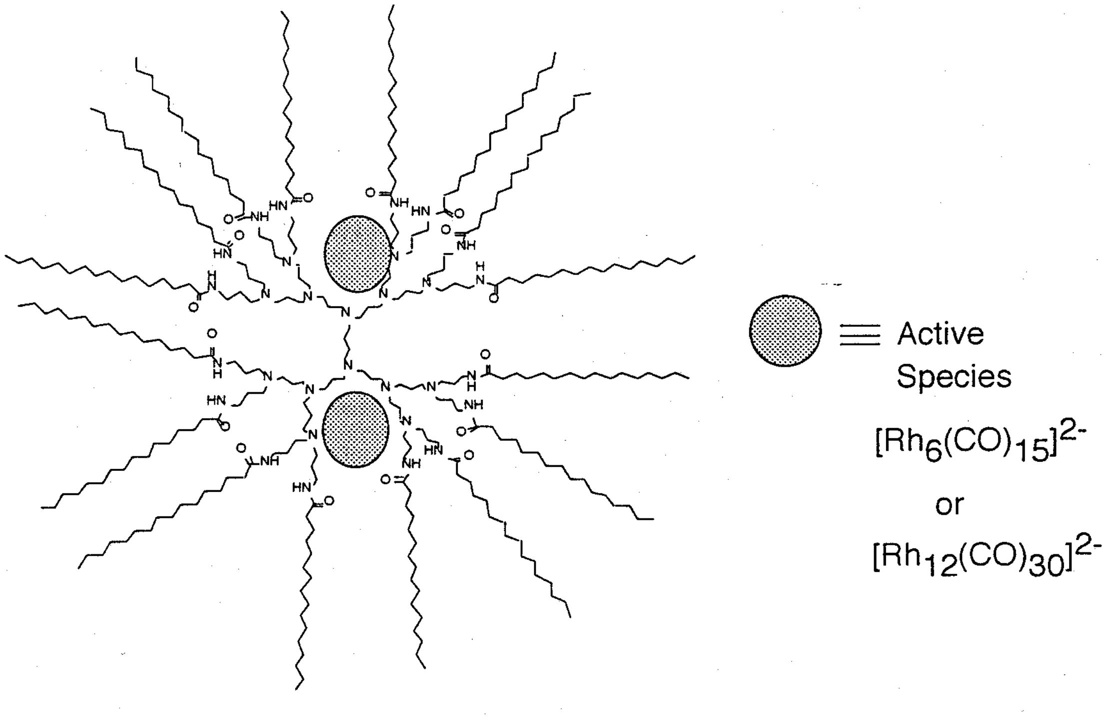


Figure 3. Schematic Illustration of Dendrimer-(**7**)-Bound Rh Cluster Complexes.

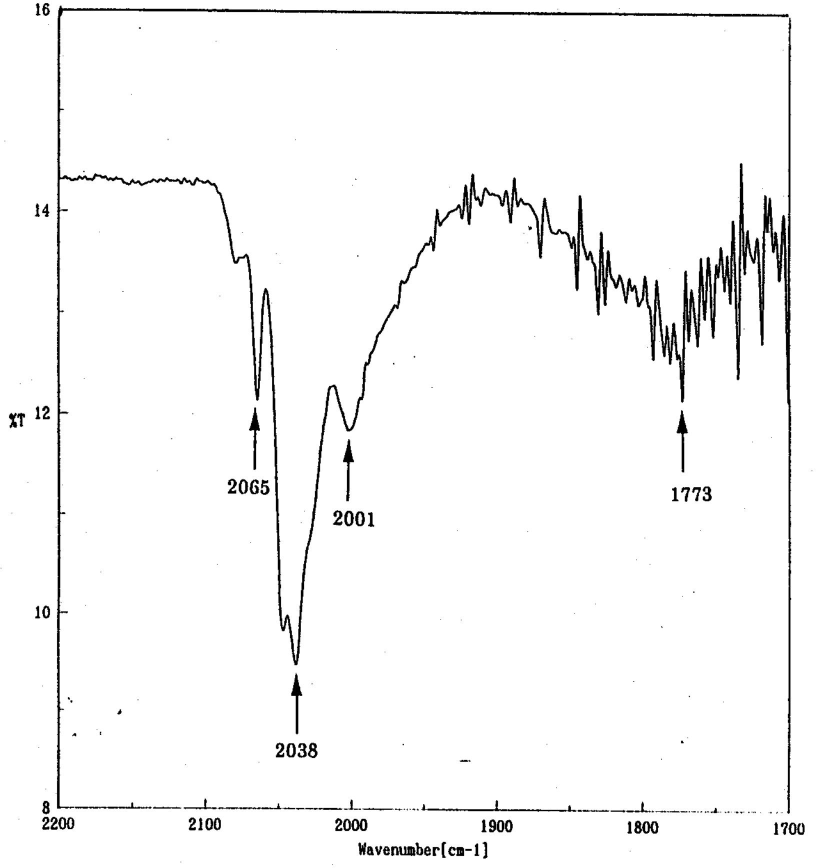


Figure 4. IR Spectrum of Dendrimer-$(NHCOC_{15})_{16}$-Bound $[Rh_{12}(CO)_{30}]^{2-}$

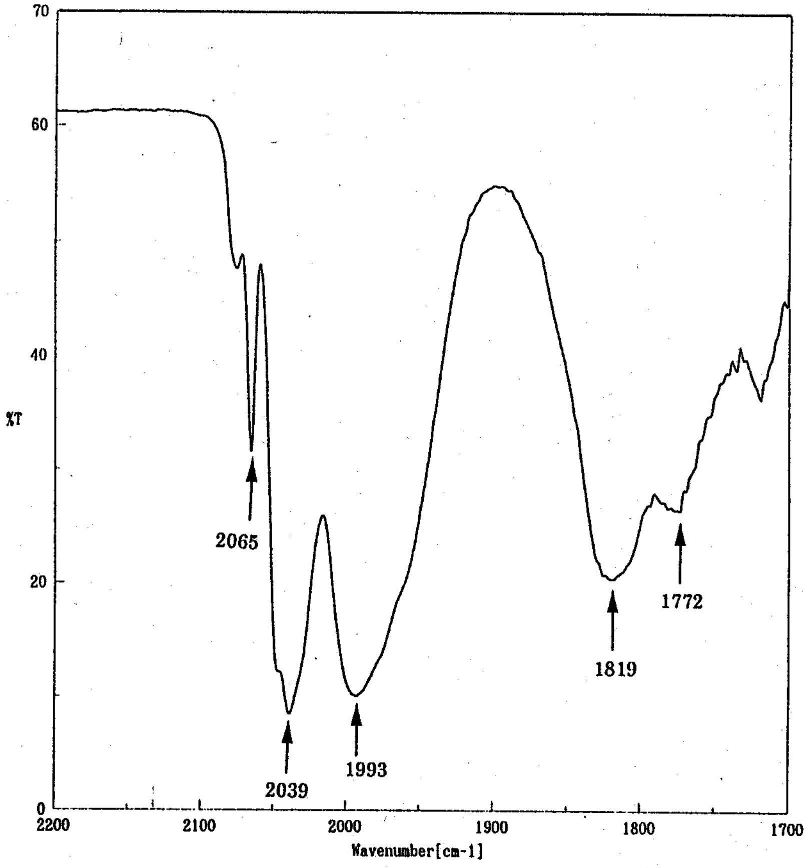


Figure 5. IR Spectrum of Dendrimer-$(NHCOC_4)_{16}$-Bound $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_{13}(CO)_{24}H_2]^{3-}$

Therefore, the author think that the **4** acts like TMPDA and the Rh cluster anions are bound to the surface amines of the dendrimer not to stabilize the active Rh species. It is said that the Rh_{12} cluster is formed through a dimerization of Rh_6 clusters or from a condensation of Rh_5 clusters. The high activity of the dendritic Rh cluster catalyst with **7** might be due to the stabilization of active Rh_6 species by the encapsulation within the dendrimers, which could prevent the formation of unfavorable Rh_{12} and Rh_{13} species.

4-4. Conclusions

The polyamine dendrimer-$(NH_2)_{16}$ could be modified with various length of alkyl chains. By treatment of the alkylated dendrimers **4-7** with $Rh_6(CO)_{16}$ under the WGSR conditions, Rh cluster anions were formed in the dendrimers. Nitrobenzene was smoothly reduced to aniline in the presence of the above dendrimer-bound Rh clusters under the WGSR conditions, while the reduction did not occur using a non-dendritic amine such as TMPDA. The concentration effect of amino moieties was observed with the dendrimers having long alkyl chain such as **6** and **7**. In this reduction, the active species are proposed to be Rh_6 cluster anions. The alkylated dendrimers **4-7** act as counter cations for the Rh cluster anions. The location of the Rh cluster anions in the dendrimers is dependent on the length of the alkyl chains introduced to the dendrimers; in the case of long alkyl chain **7**, the Rh cluster anions exist inner space of the dendrimers, while the Rh cluster anions favor peripheral amino groups of the dendrimers in the short alkyl chain **4**. The cluster framework is stabilized by encapsulation of the clusters within the internal domain.

4-5. References

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Conclusions of This Thesis

This thesis deals with the studies on the preparation and catalysis of the polymer-bound rhodium and palladium complexes for selective reductions of unsaturated aldehydes to alcohols, conjugated dienes to monoenes, and for the Heck C-C coupling reaction of olefins with aryl halides. The polymer-bound metal complex catalysts for the above reactions could be developed based on the advantageous characters of the organic polymers, *i.e.*, polystyrene and dendrimer.

In Part 1, the author surveyed the methodology of the preparation of the polymer-bound metal complexes and their catalyses in many organic reactions. The author emphasized the necessities of the highly sophisticated catalyst design from the stand point of environmental protection, which could be achieved by the heterogenization of metal complexes using organic polymer supports .

In Part 2, the fundamentals of metal cluster complexes were reviewed and the potential abilities of the clusters as novel catalysts were mentioned. The author chose $Rh_6(CO)_{16}$ as a target complex and polystyrene as a basal polymer support to aim at the synthesis of novel polymer-bound Rh carbonyl cluster catalysts in the selective reduction of carbonyl compounds. Among the various functionalized polystyrenes prepared, the polymer having 2-(dimethylaminoethoxy)ethoxy moieties was found to be the best catalyst support for the selective reduction of carbonyl compounds using H_2O or H_2 as a hydrogen source in the presence of CO. The high catalytic activity of the polymer supports can be ascribed to the length of the spacers, the high hydrophilicity, and the basicity of the polymers. Notably, the polymer-bound Rh clusters had higher catalytic activities than those of the corresponding homogeneous Rh catalyst systems. The author proposed that the active species for the selective reduction was $[Rh_6(CO)_{15}H]^-$ and the interconversion between $[Rh_6(CO)_{15}H]^-$ and $[Rh_{12}(CO)_{30}]^{2-}$ species occurred with the aid of the functionalized polystyrenes. The polymeric Rh cluster catalysts could be reused without loss of the activity and selectivity for the above reductions. In the case of H_2O as a hydrogen source, the reduction proceeded in the triphase consisted of the polymer-bound catalyst, organic phase, and aqueous phase, where the separation of the polymeric Rh catalysts from other two phases could be performed by a simple operation. The author also found that the catalyst system of $Rh_6(CO)_{16}$ and 4-dimethylaminopyridine (4-DMAP) showed a high catalytic activity for the transfer hydrogenation of α,β-unsaturated aldehydes to allylic alcohols using formic acid as an environmentally-conscious hydrogen source. Employing the polystyrene with dimethylaminopyridine moieties in place of 4-DMAP, the above Rh cluster catalyst system could be successfully heterogenized to form recoverable and reusable Rh cluster catalysts.

In Part 3, the author used dendrimers as novel supports having unique characters of tunable interior and surface properties to give dendrimer-bound Pd and Rh complexes. Two approaches of 1) entrapping of active species on the peripheral groups and 2) encapsulation of active species into the interior space were employed. A typical example of the approach 1) is for immobilizations of Pd(II) and Pd(0) complexes. The encapsulation of the Rh carbonyl cluster is a case of the latter approach. In the first approach, the author functionalized the polyaminedendrimer with 16 chelate phosphine groups on the peripheral of the dendrimer, which was used as the polymeric supports for the palladium(II) and Pd(0) complexes. Catalysis of the dendrimer-bound Pd(II) complex was examined in the selective hydrogenation of conjugated dienes to monoenes under an atmospheric pressure of hydrogen. It should be noted that the dendritic Pd(II) catalyst had higher catalytic activity and selectivity than that of the corresponding low-molecular weight palladium analogue, and the hydrogenation rates were insensitive to the size of the diene substrates. The dendritic catalyst could be easily recovered and reused keeping the activity. The dendrimer-bound Pd(0) catalyst was subjected to the Heck C-C coupling reaction of olefins with halogenated benzenes. Notably, the dendritic Pd(0) catalyst was stable in air, and efficiently catalyzed the C-C coupling reaction. The dendrimer catalysts could be easily recovered from the reaction mixtures as precipitates after the above reaction. The second approach was achieved by the functionalization of the polyaminedendrimer surface with various lengths of alkyl chains to prepare aminated dendrimers like as reverse-micelles. It was found that the surface modified dendrimers with long alkyl chains could stabilize the Rh carbonyl clusters through the encapsulation in the dendritic interior space. The dendrimer-encapsulated Rh carbonyl clusters showed higher activity for the reduction of nitrobenzene under the WGSR conditions than the homogeneous Rh complex with a non-dendritic TMPDA additive. The dendritic Rh cluster complexes could be simply recovered from the reaction mixtures by a simple precipitation method to give an anionic Rh carbonyl cluster of $[Rh_{12}(CO)_{30}]^{2-}$.

In the present thesis, the author demonstrated the catalyst design of the polystyrene- and polyaminedendrimer-bound metal complex catalysts based on the unique characters of these organic polymers. The above polymer-bound metal complex catalysts had high catalytic activities in many reductions. The polymeric metal complexes were easily separated from the reaction mixtures and were reusable catalysts, which makes the work-up procedures strikingly simple and easy. The author hopes that this environmentally-friendly polymer-bound metal complex catalysts can be applied to various organic reactions in future.

Finally, the author points out the extended developments for the preparation of highly functionalized polymer-bound metal complex catalysts as follows.

- The polymeric catalyst systems having multidentate ligands can bind with more than two metals, which would cooperatively act in the parallel and/or sequential reactions.
- The incorporation of asymmetric ligands on the polymer surface could bring exalted optical yields of the products in the peculiar reaction field induced by electrostatic and structural natures of the organic polymer.

The use of highly functionalized polymers as a support for metal cluster complexes would provide a novel preparation method homogeneously to distribute metal particles on the surfaces, which gives a clue to a clear understanding of the catalysis of supported metal particles.

List of Publications

(1) "Catalysis by Polymer-Bound Rh Carbonyl Clusters. Selective Hydrogenation of α,β-Unsaturated Aldehydes to Allylic Alcohols in the Presence of H_2 and CO",
Kiyotomi Kaneda and Tomoo Mizugaki,
Organometallics, **1996**, *15(15)*, 3247-3249.

(2) "Catalysis by Polymer-Bound Rh_6 Carbonyl Clusters. Selective Hydrogenation of Carbonyl Compounds in the Presence of CO and H_2O",
Tomoo Mizugaki, Kohki Ebitani, and Kiyotomi Kaneda,
Applied Surface Science, **1997**, *121/122*, 360-365.

(3) "Highly Chemoselective Reduction of Aldehyde Function Catalyzed by Polymer-Bound Rh_6 Cluster Complex under Water-Gas Shift Reaction Conditions",
Tomoo Mizugaki, Kohki Ebitani, and Kiyotomi Kaneda,
Tetrahedron Letters, **1997**, *30* (17), 3005-3008.

(4) "Chemoselective Transfer Hydrogenation of α,β-Unsaturated Aldehydes to Allylic Alcohols Using Formic Acid Catalyzed by Polymer-Bound Rh Carbonyl Clusters",
Tomoo Mizugaki, Yoshinori Kanayama, Kohki Ebitani, and Kiyotomi Kaneda,
Journal of Organic Chemistry, **1998**, *63*(7), 2378-2381.

(5) "Catalysis of Dendrimer-Bound Pd(II) Complex –Selective Hydrogenation of Conjugated Dienes to Monoenes–",
Tomoo Mizugaki, Masahiko Ooe, Kohki Ebitani, and Kiyotomi Kaneda,
Journal of Molecular Catalysis A: Chemical, submitted.

(6) "Selective Reduction of Nitro Compounds Catalyzed by Dendrimer-Encapsulated Rh Carbonyl Clusters",
Tomoo Mizugaki, Kazuhiro Kosumi, Kohki Ebitani, and Kiyotomi Kaneda,
in preparation.

Acknowledgment

The author wishes to express his deepest gratitude to Professor Kiyotomi Kaneda for the instructive guidance and encouragement through the present work. Hearty thanks are made to Professor Setsuji Tone, Professor Isao Komasawa, and Professor Ryoichi Kuboi (Department of Chemical Science and Engineering, Graduate School of Engineering Science, Osaka University), who acted as examiner of the dissertation, for their helpful and useful suggestions.

The author also deeply thanks Assistant Professor Kohki Ebitani (Graduate School of Engineering Science, Osaka University) for numerous discussion and encouragement. He would like to thank Associated Professor Kazushi Mashima (Graduate School of Engineering Science, Osaka University) for the helpful comments and suggestions.

The author is grateful to Associated Professor Tsunehiro Tanaka (Department of Molecular Engineering, Kyoto University), Dr. Masaki Haruta, and Dr. Mitsutaka Okumura (Osaka National Industrial Research Institute) for the XPS measurements, Dr. Remko Vreekamp and Dr. Eric Grolman (DSM Fine Chemicals) for their helpful suggestion for the modification of the dendrimer.

Thanks must be made to Mr. Yoshinori Kanayama, Mr. Kazuhiro Kosumi, Mr. Choi Kwang-Min, and Mr. Masahiko Ooe for their collaborations and lively discussion; without their devoted supports, completion of this work would not have been possible. He is indebted to all the students studied together with him at this laboratory led by Professor Kiyotomi Kaneda.

Finally, the author sincerely thanks his parents Wataru Mizugaki and Kaneko Mizugaki, his grandmother Yumi Mizugaki, and all his relatives for their constant understanding and encouragement.

Tomoo MIZUGAKI