

# Enhanced Catalysis Based on the Surface Environment of the Silica-supported Metal Complex

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## **Abstract**

Silica-supported metal complex catalysts have been developed and used for organic transformations. The surface environment around the supported metal complex enhances the catalysis based on a unique surface effect. The design of the linker ligand structure induces the formation of a highly reactive, coordinatively unsaturated metal complex on the silica surface due to the isolated environment. In contrast to the site-isolation effect, accumulated metal complexes and co-catalysts on the same surface facilitate the acceleration of the catalytic reaction by concerted catalysis. The immobilization of multi-active sites also promotes the tandem catalysis and development of complex products from simple molecules through successive reactions. Surface silanol species originating from the silica support also participate in the catalysis. The control of the immobilization density/location of metal complex/co-immobilized functionality/surface silanol is a key factor for the achievement of site-isolation/concerted catalysis. The direct interaction between the metal complex and co-immobilized functionality facilitates the formation of unique reactive species. The confinement effect of the pore structure of the support enhances the accumulation of active species in mesopores, which boosts the reaction rate, and slightly changes the ligand conformation, which increases the enantioselectivity. The direct support electronic effect is also one of the key factors affecting the surface organometallic chemistry (SOMC) and photooxidation of linker metal complexes. These acceleration effects were detected in both supported homogeneous catalysis and SOMC. Not only the local structure of the metal complex and its ligand, but also the surface environment play the most important roles in enhancing the catalysis. In this review, representative examples of silica-supported metal complexes whose catalysis is significantly enhanced by their surface long-range environment are summarized. The

contributions of recent developments of spectroscopic techniques, including DNP-enhanced solid-state NMR and XAFS, which support the evaluation of such long-range interactions, are also discussed. The surface design of the silica-supported metal complex facilitates highly active, selective, and durable catalysis.

**Keywords:** supported catalyst, metal complex, silica, concerted effect, confinement effect

## 1. Introduction

Homogeneous metal complexes play pivotal roles in the generation of catalytically active species for the production of important chemical intermediates and pharmaceuticals. Controlling the ligand structure is one of the most important factors affecting their catalytic performances including the activity, selectivity, and durability. With respect to heterogeneous catalysts, numerous studies have been carried out in the field of supported metal complex catalysts.[1-5] The catalytic performance of supported metal complexes also depends on the ligand structure. However, there are many other factors affecting the catalysis of supported metal complexes because of the complex nature of the surface environment. In other words, the potential to increase the metal complex catalysis on a support by controlling its surface environment is unlimited. This approach differs from the enhancement of the catalysis in homogeneous cases, which is mainly based on the tuning of the ligand structure.

Figure 1 summarizes the interactions of a supported metal complex catalyst, which potentially enhance its catalytic performance. As defined by Copéret et al., supported metal complex catalysts can be divided into supported homogeneous catalysts (SHC),

which are based on the grafting of ligands on the support surface with a methylene linker sharing covalent bonds with the support surface, and surface organometallic chemistry (SOMC), which refers to the direct attachment of metal sites onto the solid surface with ancillary ligands. [6-8] Another method for ligand immobilization is noncovalent bonding such as hydrogen bonding with surface hydroxyl groups and cation–anion interactions. The concept of ligand immobilization is similar to that of SHC. In all cases, the support surface affects the catalysis of the immobilized metal complex. In SHC, it is often considered that immobilization leads to a low performance due to steric hindrance and the heterogeneous nature of the surface. On the other hand, this unique support effect can be used to increase the catalytic performance including the reaction rate, regio- and stereoselectivity, and durability, which is the main target of this review. The surface effects can be summarized as follows.

(i) Site isolation: As shown in Figure 1, the site-isolation effect of a metal complex is one of the most widely known phenomena that increases the stability of coordinatively unsaturated metal sites. Due to immobilization, metal complexes cannot connect with each other, preventing the dimerization of metal species and coordination of additional ligands. The formation of a unique metal complex is also possible because of the isolated environment.

(ii) Concerted catalysis: Another positive surface effect is the direct/indirect interaction with co-immobilized functionalities. Several active species can accumulate on the catalyst surface. These active species participate in the catalytic reaction, which is accelerated by the immobilized metal complex through cooperative catalysis: substrate molecules are concertedly activated by two or more active species. An application of concerted catalysis is the attachment of oligomers. Attached active species have specific

interactions with each active site in an oligomer (intramolecular) or with another oligomer (intermolecular). In addition to immobilized active sites, surface functional groups, such as Si-OH of the SiO<sub>2</sub> support, may activate polar substrates by hydrogen bonding and/or electron withdrawal.

(iii) Direct interaction: The covalently bonded functionality can directly activate an immobilized metal complex. The functionality acts as a simple additional ligand and enhances the catalysis, or the surface reaction of the functionality with the metal complex induces the generation of different active complex structures, resulting in a high catalytic activity and selectivity.

(iv) Confinement effect: Metal complexes immobilized in micro/mesopores often have different reactivities. The product selectivity, activity, and stereoselectivity frequently change due to the confined space. The appropriate size of the metal complex, including its ligand and/or co-catalyst, significantly enhances the reaction rate and product selectivity.

(v) Direct electronic effect: Directly immobilized metal complex was often affected by the surface electronic effect. In the case of SOMC, this effect is strong. The appropriate selection of metal-oxide supports is mandatory for SOMC. Another direct effect is the photoinduced surface plasmon of metal nanoparticles.

(vi) Tandem catalysis: The immobilization of more than two metal complexes on the support surface enables a tandem reaction. Successive reactions occur on each metal complex site, leading to the final product in a single reactor. Site isolation of the two metal complexes enables the coexistence of reactive and unstable metal complexes in the same reaction media.

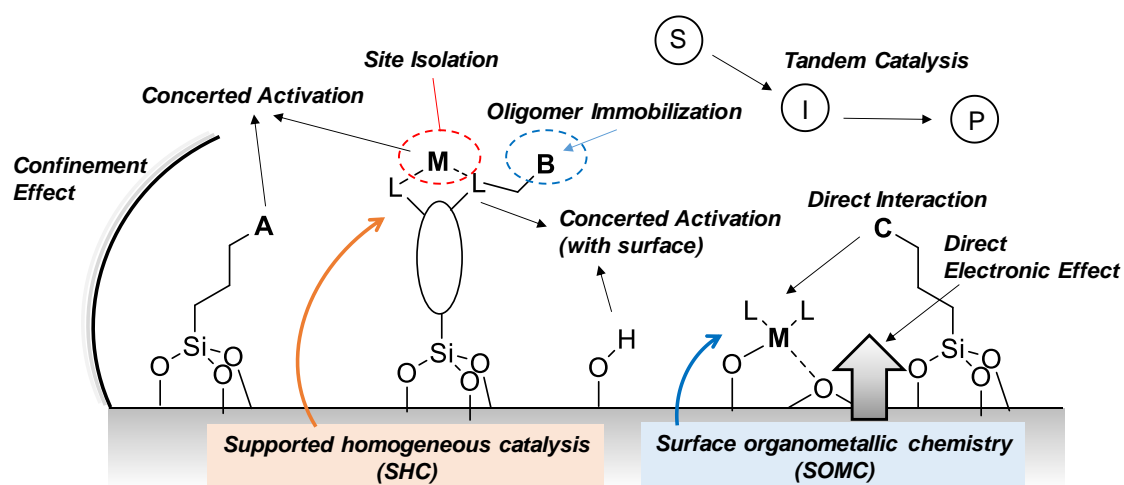
These “positive” surface effects strongly enhance the productivities of both SHC and

SOMC. They can be observed in various types of support materials such as polymers, MOFs, and metal oxides. However, we restrict our discussion to silica-based support materials. Silica is one of the most well-known supports for catalytically active metal complexes. Silica has density-tunable surface hydroxyl groups (Si-OH).[1,8] The reaction between the surface Si-OH and trialkoxysilyl group of the metal ligand (silane-coupling reaction) is one of the most famous ways of the covalent attachment of a metal complex (SHC). Surface silanol groups can also be used for the direct attachment of metal complexes via cation exchange and/or coordination of surface oxygen atoms (SOMC). Possible types of attachment of the metal complex onto the silica surface are summarized in Figure 2. Covalent grafting of a ligand is possible through post-immobilization using the silane-coupling reaction (Figure 2a) and incorporation during the sol-gel preparation of the silica matrix itself (Figure 2b). Ionic interactions, including hydrogen bonding between carboxylic acid groups or fluorine atoms and surface silanol, are also possible. SHC preparation procedures (Figures 2c and d). In SOMC, the surface density of silanol strongly affects the structure of the metal complex: the pretreatment of support SiO<sub>2</sub> at high temperature leads to a low density of Si-OH, resulting in a metal complex with isolated silanol (Figure 2e). On the other hand, a slightly higher density of Si-OH leads to the formation of di- or tridentate Si-O-M complexes, as shown in Figure 2f.

The variety of possible silica morphologies, including mesoporous, microporous (zeolites), layered, and nonporous structures, is another advantage for catalytic support materials.[9,10] The surface properties of silica are basically inert during catalysis. However, the surface Si-OH group has a specific reactivity, such as hydrogen bonding and electron withdrawal, which benefits the catalytic reaction. The incorporation of additional atoms into the siloxane network (most famously Al) can dramatically change

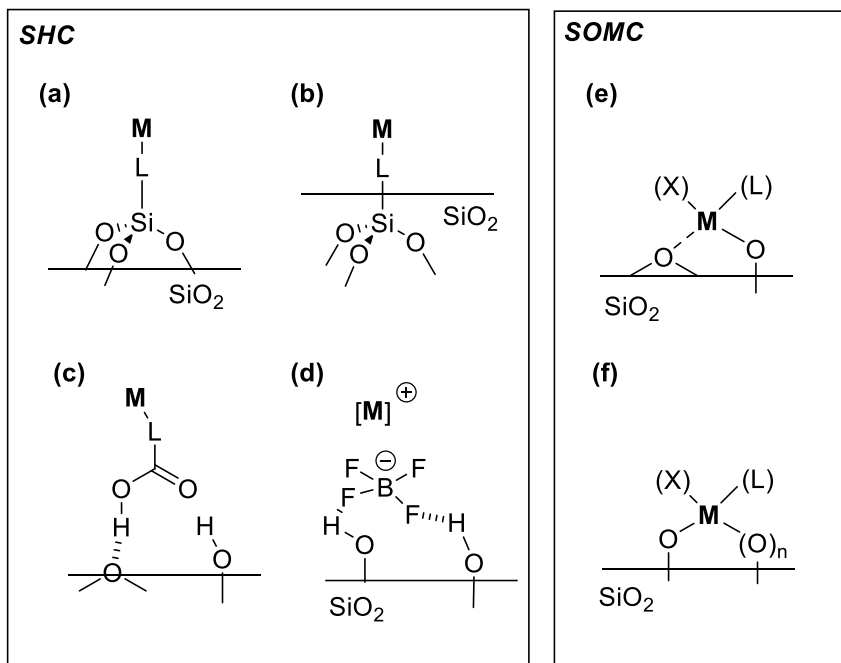
the surface acidity.

Many review papers have been published in the field of silica-supported metal complex catalysis, which focus on the immobilization strategy,[12-14] use of special support structures,[15-18] hybrid materials including organocatalysis [19-22] and metal nanoparticles,[23] photo-induced promotion effects,[24-25] and catalyst recycling.[26] In contrast, this review deals with a variety of silica-supported metal complex catalysts that are enhanced by one or more of the above-mentioned unique surface effects. The supported catalyst structure, design strategy, and representative superior catalytic performance are discussed in comparison with those of homogeneous counterparts and/or simply immobilized catalysts. Several examples have already been summarized in short reviews with similar concepts in the 2000s.[27,28] Many recent examples are included in this review because of the high research activity with respect to supported metal complex catalysis. This review is divided into four sections based on the types of enhanced catalysis: Isolated Metal Complex for Enhanced Catalysis (Section 2); Concerted Effect on Surface for Enhanced Catalysis (Section 3), Confinement Effect/Molecular Imprinting for Enhanced Catalysis (Section 4), and Supported Metal Complexes Designed through SOMC (Section 5).



**Figure 1.** Interactions of a supported metal complex catalyst for the enhancement of the catalysis





**Figure 2.** Possible ways of attachment of a metal complex on the silica surface. (a) Attachment via silane-coupling reaction with surface Si-OH; (b) co-condensation of a functional group with silica matrix; (c) interaction between an acidic functionality, such as carboxylic group, with surface Si-O-Si/Si-OH; (d) hydrogen bonding between counter anion ( $\text{BF}_4^-$ ) and surface Si-OH; direct attachment of metal complex onto silica surface with (e) relatively low and (f) high Si-OH density.

## 2. Isolated Metal Complex for Enhanced Catalysis

The supported monomeric Pd complex frequently changes its structure to metallic particles during the catalytic reaction, especially hydrogenation and cross-coupling reactions.[29,30] Therefore, an appropriate ligand structure, attachment technique, and reaction conditions must be selected. In addition, the supported catalyst must be characterized during and after catalysis. One of the most famous reactions involving Pd catalysts is hydrogenation. Both Pd complexes and Pd nanoparticles show a high performance with respect to the hydrogenation of organic compounds using molecular H<sub>2</sub>. The Pd complex and an appropriate ligand, a molecular palladium catalyst, can be used for selective hydrogenation. Recently, the hydrodeoxygenation of aromatic alcohols has received much attention due to the utilization of lignin, a plant biomass containing an oxygenated polyaromatic structure, as a source of aromatic compounds. DeLucia et al. reported a silica-supported terpyridine-Pd complex for the hydrodeoxygenation of model biomass compounds.[31] The terpyridine-Pd complex with a carboxylic group is attached to the silica surface. The supported Pd complex exhibits a high activity and selectivity with respect to the hydrodeoxygenation of benzyl alcohol to toluene (**Scheme 1**). The toluene selectivity significantly decreases when a precursor complex and silica-supported premade Pd nanoparticles are used. In such cases, the major products are methyl cyclohexane and its derivatives due to the promotion of benzene ring hydrogenation by Pd(0) nanoparticles. In other words, the supported terpyridine-Pd complex was stable and prevents aggregation. The mercury test also indicates the maintenance of the Pd complex structure during the reaction. The catalytic activity of the supported Pd catalyst was measured for at least ten cycles. The presence of the Pd complex and absence of Pd

nanoparticles in the recovered catalyst were determined by solid-state nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) measurement, respectively. The energy calculation of the model surface structure reveals a strong interaction between the -OH of the carboxylic acid group and the surface oxygen of the Si-O-H(or Si) group.

It has been reported that metal complexes with *N*-heterocyclic carbene (NHC) ligands are useful ligands for catalysis tuning, and a variety of immobilization approaches have been studied.[32] Conley et al. reported a silica-supported NHC-Pd complex and its catalysis for the semihydrogenation of alkynes.[33] Molecular level characterization was also performed using DNP-enhanced solid-state NMR. The structure and catalytic results of the immobilized NHC-Pd complexes are shown in **Scheme 2**. Catalyst structures including NHC, aromatics, and  $\pi$ -allyl groups were fully characterized by DNP-enhanced 1D  $^{13}\text{C}$  CPMAS NMR and 2D  $^1\text{H}$ - $^{13}\text{C}$  HETCOR NMR analysis. The immobilized NHC-Pd has a high catalytic activity and selectivity, with 89% *Z*-alkene selectivity at 99% conversion. The homogeneous counterpart has a slightly lower selectivity for the *Z*-product. The selectivity is significantly low for Pd nanoparticles, indicating the catalysis of the NHC-Pd complex on the  $\text{SiO}_2$  surface. The catalyst can be used for the *Z*-selective semihydrogenation of other internal and terminal alkynes. There have been many reports on supported Pd complex catalysts for hydrogenation reactions for which immobilized ligands with high coordination abilities, such as NHC,[34] triaza donor,[35] and Schiff base,[36] are used.

Corma et al. reported an Au(I)-heterocyclic carbene (NHC) complex as a hydrogenation and cross-coupling reaction catalyst.[37] The Au(I)-NHC complex can be easily immobilized on the silica surface by a simple silane coupling reaction. In the case of the hydrogenation of diethyl citraconate, the supported catalyst has a higher reaction

rate (TOF) than the homogeneous analogue (**Scheme 3**). There are several reasons for the higher performance of the supported catalysts. The site-isolation effect of the supported catalyst prevents the Au–NHC complex from decomposing during the reaction. The supported catalyst has a good recyclability with respect to the hydrogenation reaction; similar reaction rates and product yields were observed after 4th reuse experiment.

Other supported metal complexes with a NHC ligand are summarized in **Scheme 4**. Romanenko and co-workers reported NHC-Ir complex on silica surface for hydrogenation of *trans*-stilbene. The maximum TON of 8000 was significantly higher than the corresponding homogeneous catalyst (<1000).[38] A supported Ru-pincer catalyst containing a NHC group was also reported for hydrogenation of CO<sub>2</sub> to formate with superior performances than a homogeneous Ru analogue.[39] Other silica-supported Ru-NHCs applied for alkene metathesis reaction: Samantary and co-workers investigated the effect of rigidity of the linker structure on the metathesis catalysis as well as interaction between Ru center and silica surface.[40] Other recently reported immobilized Ir-pincer complex[41] and Ru-thiolate[42] catalysts were used for CO<sub>2</sub> hydrogenation and alkene methathesis, respectively.

For supported Pt complex catalysts, Prignano and Trogler reported silica-supported bis(trialkylphosphine)platinum oxalate in 1987.[43] The alkylphosphine ligand was immobilized onto a silica surface with a Pt(C<sub>2</sub>O<sub>4</sub>)(SMe<sub>2</sub>)<sub>2</sub> precursor. The immobilized Pt catalyst is active with respect to the hydrosilylation of alkenes under UV irradiation (**Scheme 5**). Recently, Huo et al. reported a Pt(II) complex with bulky Schiff base ligands.[44] This catalyst system is also applicable to the hydrosilylation reaction: a maximum TON of 3623 was obtained from the reaction of 1-octene and trimethoxyhydrosilane.

Mori et al. reported a [Pt(tpy)Cl]Cl (tpy: terpyridine) catalyst for the photooxidation of alkenes.[45] The Pt complex, [Pt(tpy)Cl]Cl, can be easily attached to the mesoporous silica surface with an immobilized aminopropyl group. The photooxidation catalytic activity (total TON) strongly depends on the loading amount of Pt on the mesoporous silica support (**Scheme 6**). This dependency is in agreement with the intensity of the luminescence emission of the <sup>3</sup>MLCT of the supported Pt complex under degassing conditions: the luminescence intensity first increases from 0.2 wt.% to 0.4 wt.% and then decreases with increasing load ( $\geq 0.8$  wt.%) with increasing <sup>3</sup>MMLCT band due to the aggregation of the supported Pt complex. In the presence of O<sub>2</sub>, the catalyst with a load of 0.4 wt.% may effectively produce active oxygen species by energy- and/or electron-transfer reactions from the excited state of the Pt complex. The homogeneous Pt complex has a much lower catalytic activity due to aggregation. The same authors also reported the hydrogen evolution reaction from an acetate buffer solution and EDTA using a supported Pt complex catalyst.

Sawamura et al. reported silica-supported cage-type phosphine ligands for a variety of highly efficient organic transformations catalyzed by transition metals including palladium.[45-48] A compact phosphine ligand, silicon-constrained monodentate alkylphosphine (SMAP), was immobilized on the silica surface using its isolated form, suggesting the formation of a highly reactive 1:1 metal/P complex on the surface. The compact shape of the ligand also enables the reaction of sterically hindered substrates. The silica-SMAP/Pd system is applicable to the Suzuki–Miyaura cross-coupling reaction of chloroarenes with bulky groups such as 2,6-dimethylchlorobenzene and 2,6-diphenylchlorobenzene.[46] Note that the activity of silica-SMAP/Pd is higher than that of homogeneous systems using XPhos and SPhos in the case of bulky substrates. Silica-

supported 9-phospha-10-silatriptycenes (silica-TRIP) was also developed as a solid ligand of Pd for Suzuki–Miyaura coupling.[47] **Scheme 7** presents the results of the Suzuki–Miyaura coupling of chlorotoluene and phenylboronic acid. Silica-TRIP and silica-SMAP catalysts exhibit a much better performance than their homogeneous analogues.[47] This reaction rarely occurs with simple  $\text{PPh}_3$ . The same group also investigated silica-supported tripod and monopod triarylphosphines (silica-3p-TPP and silica-1p-TPP).[48] The structure and cross-coupling results are shown in **Scheme 7**. Silica-3p-TPP is a good ligand compared with silica-1-TPP. The results of the solid-state NMR analysis reveal the formation of an undesired 1/2 Pd/P complex in Silica-1p-TPP/Pd. On the other hand, Silica-3p-TPP and the direct attachment of cage-type phosphine ligands, SMAP and TRIP, on the silica surface selectively yielded isolated 1/1 P/Pd complexes. Various other silica-supported Pd complexes have been used for cross-coupling reactions. Please see references [49-62] regarding recent examples of Heck, Suzuki–Miyaura, Negishi, and Sonogashira reactions.

Sawamura et al. reported the hydrosilylation of bulky ketones using a Rh complex attached to a silica-supported compact phosphane ligand (SMAP: silicon-constrained alkylphosphane).[63,64] The supported catalyst was characterized with high-resolution solid-state NMR. The catalyst showed an excellent catalytic performance with respect to the hydrosilylation of sterically hindered ketones with hydrosilanes containing bulky groups such as isopropyl and tertiary butyl substituents (**Scheme 8**). On the other hand, homogeneous Rh catalysts with either SMAP structures or other general phosphine ligands hardly showed a catalytic performance under the same reaction conditions. The exceptionally spare environment of the supported Rh complex due to both the site-isolation effect and compact SMAP ligand facilitates the excellent performance with

respect to the hydrosilylation reaction of tough substrates. Sawamura et al. also reported C(sp<sup>3</sup>)-H borylation using a supported triarylphosphine reagent (TRIP).[65,66] As shown in **Scheme 9**, the combination of a [Rh(OMe)(cod)]<sub>2</sub> precursor and silica-TRIP promotes the C-H borylation of *N,N*-dimethylacetamide yielding mono- and di-borylated products, whereas other heterogeneous and homogeneous reaction systems using various ligands, including Rh-TRIP, did not show a considerable catalytic activity. The methyl group and internal methylenes, such as *N*-pivaloylpyrrolidine, can be reacted using the silica-TRIP-Rh catalyst systems. In addition, the same research group expanded the silica-supported compact phosphine ligand strategy to various Rh-catalyzed reactions such as the hydrogenation of hindered ketones [67] and aromatic C-H borylation.[68]

Sawamura et al. reported the conjugate reduction of  $\alpha,\beta$ -unsaturated carbonyl and carboxyl compounds as an example of a supported Cu catalyst for reduction reactions.[69] Polymethylhydrosiloxane was used as the reducing agent. The silica-SMAP acted as a heterogeneous ligand of the Cu acetate precursor, resulting in a high yield of the corresponding saturated carbonyl compounds. Other phosphine ligands, including homogeneous Ph-SMAP, were not effective. Regarding supported Cu complex catalysis, bond-forming reactions, such as aldehyde-alkyne-amine (A<sup>3</sup>) coupling,[70] the addition of alkynes to imines,[71] and click chemistry [72,73] have been reported.

The Ir complex has been mainly highlighted as a highly active homogeneous catalyst for the C-H activation reaction. Smith et al. initially reported Ir-catalyzed C-H borylation using a homogeneous Ir complex.[74,75] Hartwig–Miyaura C-H borylation is a widely known C-H activation procedure [76-80] and the combination of the bipyridine ligand and Ir-hydroxo or –methoxide cyclooctadiene complex yields an efficient catalyst for the C-H borylation reaction.[78] Recently, the heterogenization of the Ir complex has

been applied to various solid media such as metal-organic-frameworks (MOFs)[81-84] and covalent organic frameworks (COFs) [85]. A minireview of heterogeneous Ir catalysts has also been published [86]. Silica is also an effective solid support for Ir complexes. Sawamura et al. reported silica-supported SMAP as a heterogeneous ligand of the Ir-catalyzed aromatic C-H borylation.[87-89] As shown in **Scheme 10**, silica-SMAP-Ir has a high catalytic activity with respect to the C-H borylation of methyl benzoate with  $\text{pin}_2\text{B}_2$ , yielding 89% *ortho*-borylated product with a high regioselectivity. The amount of Ir catalyst can be decreased to 0.005 mol% while maintaining the high product yield, realizing an excellent TON of 20000 for 3 h. Interestingly, the C-H borylation suddenly stopped when the SMAP ligand was used as a homogeneous Ir catalyst. Various homogeneous ligands and several Ir/ligand ratios were examined, however, a catalytic reaction rarely occurred. This comparison indicates that a unique structure forms on the silica surface with a SMAP ligand: site-isolation phenomena on a solid surface may play pivotal roles in the construction of highly active and coordinately unsaturated Ir sites. Sawamura et al. expanded the compact phosphine ligand to Ir-catalyzed reactions. Silica-supported TRIP is also an efficient heterogeneous ligand for Ir-catalyzed  $\text{C}(\text{sp}^3)\text{-H}$  borylation [90] and C-H borylation of quinolones at the C8 position.[91]

Another efficient way to heterogenize the Ir complex is to immobilize the Ir-bipyridine complex by a silane coupling reaction. Jones et al. reported a mesoporous silica-supported Ir-bipyridine complex with a methylene linker.[92] The reported catalyst has a good stability. The initial reaction rate gradually decreased; however, a 94% yield was achieved at 3rd reuse experiment after a prolonged reaction time. Inagaki et al. demonstrated periodic mesoporous organosilica (PMO) as a support for the Ir complex.[93-95] The



PMO containing a bipyridine ligand (Bpy-PMO) acted as an excellent support for the Ir-cyclooctadiene species. With respect to the borylation reaction of benzene, a high TON of 728 was achieved with the Bpy-PMO-Ir catalyst. A comparison of the catalytic activity with other homogeneous and heterogeneous Ir catalysts is shown in **Scheme 11**. The Bpy-PMO was determined to be the best support for the borylation of benzene compared with the silica-supported Ir-bipyridine complex with a methylene linker. Surprisingly, the performance of Bpy-PMO-Ir was superior to that of its homogenous analogue. The Bpy-PMO-Ir catalyst showed a good durability and recyclability and the catalyst maintained a high catalytic activity at least three times. On the other hand, the homogeneous analogue was completely deactivated after the first run. The isolated Ir sites on the well-defined Bpy-PMO wall prevented an undesired deactivation and increased its durability. The wide applicability of the Bpy-PMO-Ir catalyst enhances the borylation of various substituted benzenes as well as heteroaromatics.[94] Regarding the POM ligand for site-isolation, Wang and co-workers reported Bpy-PMO-Mn catalyst for efficient CO<sub>2</sub> photoreduction.[96]

Supported Ir-bipyridine catalysis is strongly affected by the support environment. Based on these previous studies of supported Ir catalysis, our group investigated the effects of the linker length as well as co-immobilized molecules on the C-H borylation reaction catalyzed by silica-supported Ir-bipyridine.[97] Interestingly, the methylene linker length strongly affects the catalytic performance: the reaction rate of the C1 linker (SiO<sub>2</sub>/bpy(C1)/Ir) is more than five times higher than that of the C4 linker. The catalytic activity of SiO<sub>2</sub>/bpy(C1)/Ir with respect to the reaction of benzene is comparable to that of its homogeneous analogue, that is, 4,4'-dimethyl-2,2'-bipyridyl. In addition, the co-immobilization of tertiary amine onto SiO<sub>2</sub>/bpy(C1)/Ir significantly increases the

catalytic performance of aromatic substrates with specific substitution groups such as benzonitrile (**Scheme 12**). The results of *in situ* FTIR analysis of the supported tertiary amine indicate interactions among benzonitrile–silanol–amine, which may enhance the adsorption of aromatic substrates and affect the C-H activation catalysis.

Yang and Rioux reported a silica-supported Rh complex for C-S bond formation.[98,99] The supported Rh complex with a simple diamine linker facilitates the *Z*-selective hydrothiolation of terminal alkynes.[99] The supported Rh complex showed 99% selectivity toward the *Z* product with a good catalytic activity (**Scheme 13**). The reaction also proceeded with a homogeneous Rh complex. However, the *E*-selectivity was 94% without the diamine ligand. With diamine, the *Z*-selectivity increased in the case of the homogeneous catalyst. However, both the activity and *Z*-selectivity of the heterogeneous catalyst were higher.

An enhanced enantioselectivity was observed in a periodic mesoporous organosilica (PMO)-supported Rh catalyst used for enantioselective hydrogenation combined with horse liver alcohol dehydrogenase (HLADH).[100] As shown in **Scheme 14**, the catalytic cycle of the enantioselective hydrogenation by HLADH is assisted by the NADH-NAD<sup>+</sup> cycle catalyzed by a Rh catalyst with formate as a hydrogen donor. Both the substrate conversion and enantioselectivity of the product (*S*)-4-phenyl-2-butanol with a PMO-supported Rh complex (91%, >98% ee) were higher than those of the homogeneous Rh-bipyridine catalyst (80%, 87% ee). Mesoporous silica (FSM-16) represents a good support for the enantioselectivity, whereas the use of amorphous silica did not improve the performance. In the case of a homogeneous catalyst, the Rh catalyst was adsorbed onto HLADH, resulting in the deactivation of HLADH. In the case of PMO-supported Rh, the direct interaction between the Rh site and HLADH is prevented, which

induces the maintenance of the catalytic activity and selectivity. The interaction was also prevented in the case of FSM-16. However, the catalytic activity decreased because of the different immobilization methods: the direct immobilization of Rh onto the PMO surface results in a higher catalytic performance.

Fukaya et al. reported a stable tripodal linker unit for the immobilization of a chiral ligand during asymmetric hydrogenation (**Scheme 15**).<sup>[101]</sup> The hydrogenation of (*Z*)- $\alpha$ -(acetamido)cinnamic acid occurred in the presence of a Rh precursor and immobilized chiral ligand and 98% of the corresponding product was yielded, with an ee of 95%. The low leaching levels of P and Rh atoms induced an excellent recyclability of the catalyst. Regarding robust and chiral catalysis, Saito and Kobayashi reported a supported chiral Rh complex via acid-base and electrostatic interactions using silica-supported primary amine and heteropoly acid.<sup>[102]</sup>

Various ruthenium complex catalysts have been reported for oxidation, reduction, hydrogen transfer, and metathesis reactions. Recently, the selective decomposition of formic acid to CO<sub>2</sub> and H<sub>2</sub> has received much attention due to the use of formic acid as a hydrogen carrier. Gan et al. reported a silica-supported Ru-phosphine catalyst for the selective decomposition of formic acid to CO<sub>2</sub> and H<sub>2</sub>.<sup>[103]</sup> The supported catalyst was prepared by the silane coupling reaction of a phosphine ligand with a methylene linker, followed by complexation with [RuCl<sub>2</sub>(mTPPTS)<sub>2</sub>]<sub>2</sub> (mTPPTS=*meta*-trifluoromethylated triphenylphosphine). The catalytic activity of the supported catalyst strongly depended on the linker length. The highest TOF of 660 h<sup>-1</sup> was obtained with the C2 linker (**Scheme 16**). This value is higher than that of the homogeneous Ru complex analogue (480 h<sup>-1</sup>). After the optimization of the reaction conditions, the TOF value increased to 2780 h<sup>-1</sup>. Interestingly, no Ru leaching was observed. The catalyst showed a good durability and

the TON increased up to 71000 after 18 recycles.

The formation of unsaturated metal complexes can be achieved due to the site-isolation effect on the silica surface. Tada et al. reported silica-supported unsaturated Ru complex catalysts for oxidation reactions.[104,105] A well-known monomeric Ru complex was prepared from *N*-arylsulfonyl-1,2-ethylenediamine and  $[\text{Ru}_2(p\text{-cymene})_2\text{Cl}_4]$ . Subsequently, the Ru complex was attached to the silica surface. The supported Ru complex exhibited a high catalytic activity with respect to the epoxidation of stilbene using  $\text{O}_2$  and isobutylaldehyde (**Scheme 17A**),[104] whereas the precursor monomeric Ru complex was much less active under similar reaction conditions (10% conversion, 71% select). The results of spectroscopic analyses, including UV/Vis, NMR, FTIR, and XAFS, and DFT calculations imply the formation of three-coordinate Ru species during the reaction.[105] The same supported Ru catalyst was further activated by photoirradiation under an  $\text{O}_2$  atmosphere.[106] The activated singlet-state Ru complex showed a good performance with respect to the photooxidation of cyclohexane under  $\text{O}_2$  with a total TOF of  $6.3 \text{ h}^{-1}$  (**Scheme 17B**). Site isolation on the silica surface resulted in the formation of coordinatively unsaturated Ru complexes with a high reactivity.

Many other supported Ru complexes have been reported as efficient heterogeneous catalysts for hydrogenation,[107] hydrogen transfer reactions,[108] alkene and alkane oxidation,[109] and metathesis reactions[110,111].

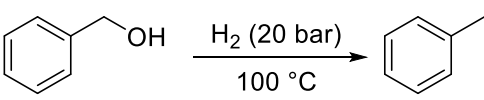
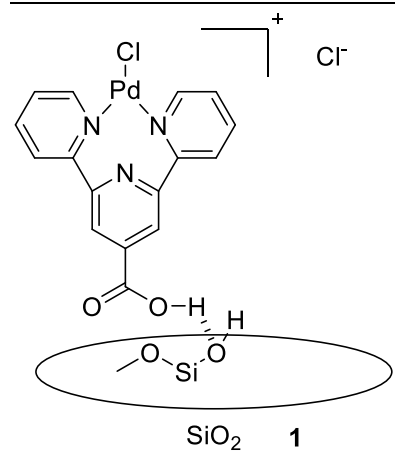
Che et al. reported a silica-supported Fe complex for oxidative carbon–carbon bond-forming reactions.[112] The substituted terpyridine ligand was immobilized on the SBA-15 surface, followed by complexation using the  $\text{Fe}(\text{ClO}_4)_2$  precursor forming the supported Fe terpyridine complex. The oxidative coupling between indole and tetrahydroisoquinoline was investigated using TBHP as an oxidant. The reaction with the

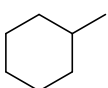
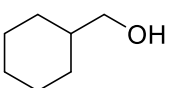
supported Fe complex yielded 80% of the corresponding coupling product, whereas the selectivity decreased based on the use of a homogeneous Fe-terpyridine complex analogue (**Scheme 18**). The catalyst can be widely applied as a substrate for the coupling of indoles, pyrroles, and alkynes with various amines. The supported terpyridine ligand can be reused; however,  $\text{Fe}(\text{ClO}_4)_2$  is required for the recycling experiment.

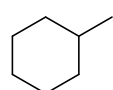
Hikichi et al. reported an SBA-15-supported Fe complex catalyst for the oxidation of alkenes.[113] An Fe complex with a  $\beta$ -ketiminate ligand is attached to the silica surface by a silane coupling reaction and the addition of  $\text{FeCl}_3$  leads to the formation of the surface Fe complex (**Scheme 19**). The prepared catalyst has a good catalytic performance with respect to the oxidation of cyclohexene using  $\text{H}_2\text{O}_2$  as an oxidant. The total TON of the SBA-15-supported catalyst was 8.3 and 57.1 at room temperature and 80 °C, respectively. When amorphous silica was used as a support at room temperature, the TON decreased to 5.2. The uniform surface of SBA-15 enables the efficient formation of a coordinatively unsaturated Fe complex. A homogeneous catalyst with two ketamine ligands has a lower catalytic activity at room temperature, indicating the site-isolation effect of the supported catalyst. Supported Fe catalysts with organoborate ligands have also been used for the oxidation of cycloalkenes by the same research group.[114,115] Nakazawa et al. reported supported Co complexes used for alkane oxidation reactions.[116] A triazolyl-group-containing tetradentate ligand was prepared on a silica surface and the ligand was treated with a methanol solution of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  to obtain the supported Co complex (**Scheme 20**). The prepared catalyst was used for the oxidation of cyclohexane using mCPMA as an oxidant. The catalytic performance of the supported catalyst was similar to that of the homogeneous Co complex with similar ligands. Other supported Co, Ni, and Fe complexes have been reported as catalysts for alkane oxidation

reactions.[117-119]

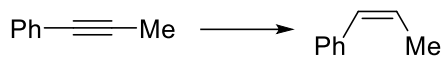
**Scheme 1.** Hydrodeoxygenation of benzyl alcohol using Pd catalysts [31]

		
Catalyst	Conv.	Select.
 SiO <sub>2</sub> <b>1</b>	> 99%	> 99%
Pd complex	> 99%	< 5% <sup>[a]</sup>
Pd nanoparticles	> 99%	24% <sup>[b]</sup>
Pd nanoparticles + Hg	0%	0%
Supported Pd Complex <b>1</b> + Hg	95%	> 99%

<sup>[a]</sup> major product  and 

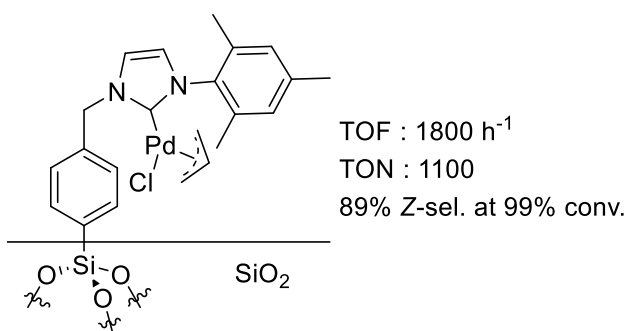
<sup>[b]</sup> other major product 

**Scheme 2.** Semihydrogenation of alkynes using Pd catalysts [33]




---

**Heterogeneous**

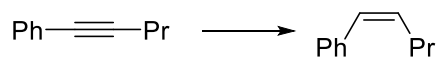


**Homoegenous**

[BnMesNHC]Pd(C<sub>3</sub>H<sub>5</sub>)Cl 84% Z-sel. at 95% conv.

**Nanoparticle**  
(20 nm)

74% Z-sel. at >90%conv




---

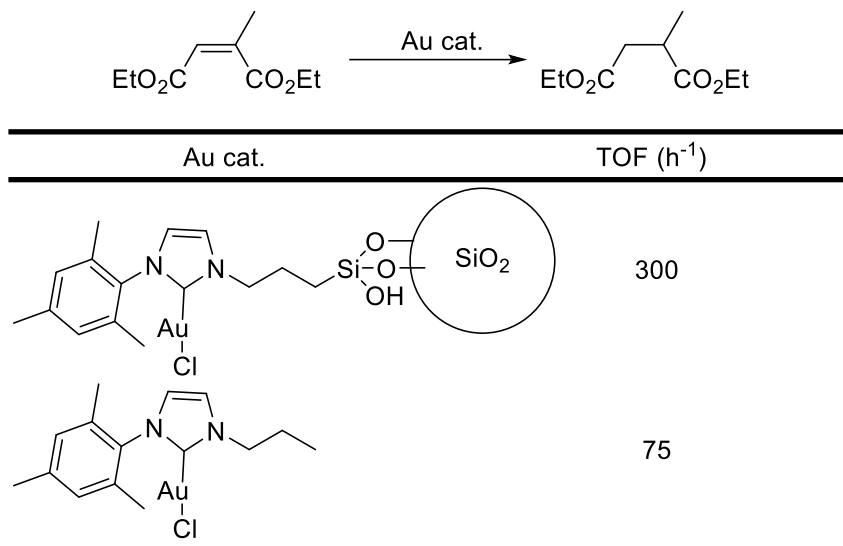
**Heterogeneous**

TOF : 13200 h<sup>-1</sup>  
TON : 3300  
92% Z-sel. at 99% conv.

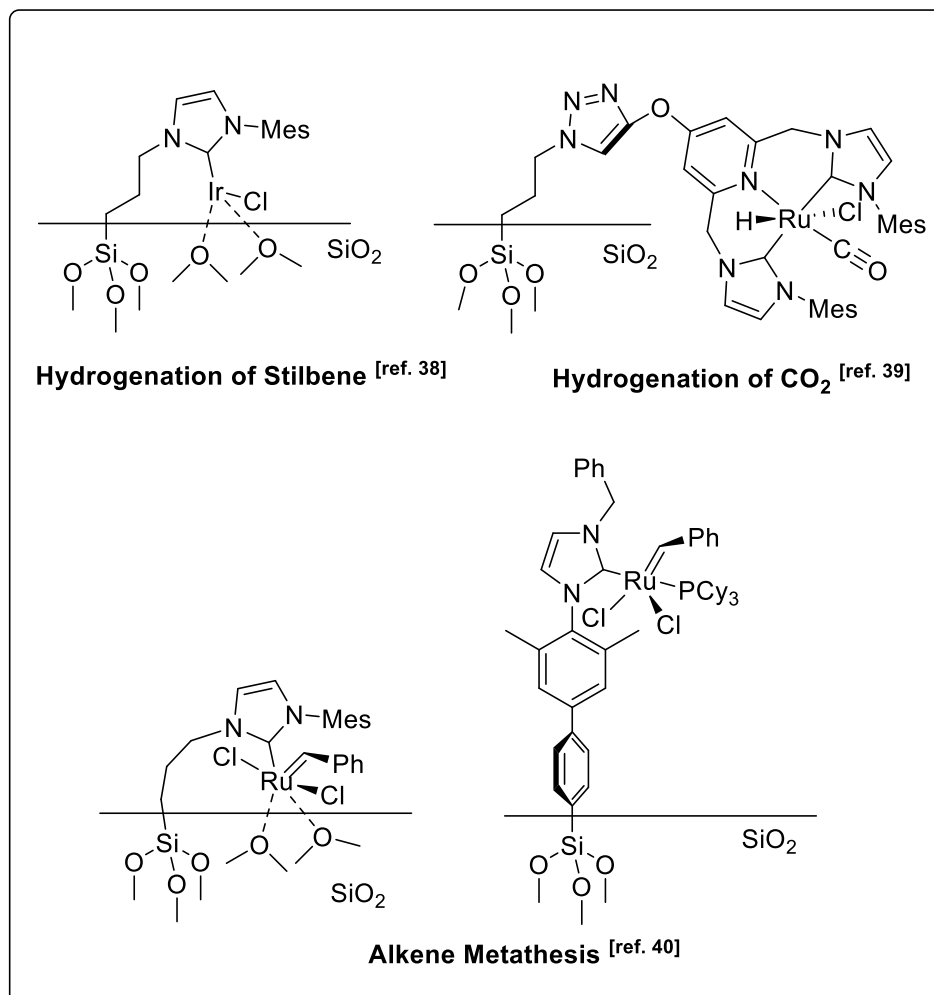
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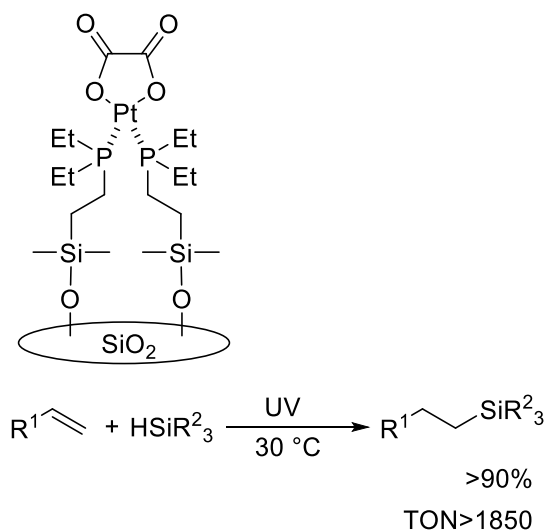
**Scheme 3.** Silica-supported Au–NHC complex for hydrogenation [37]



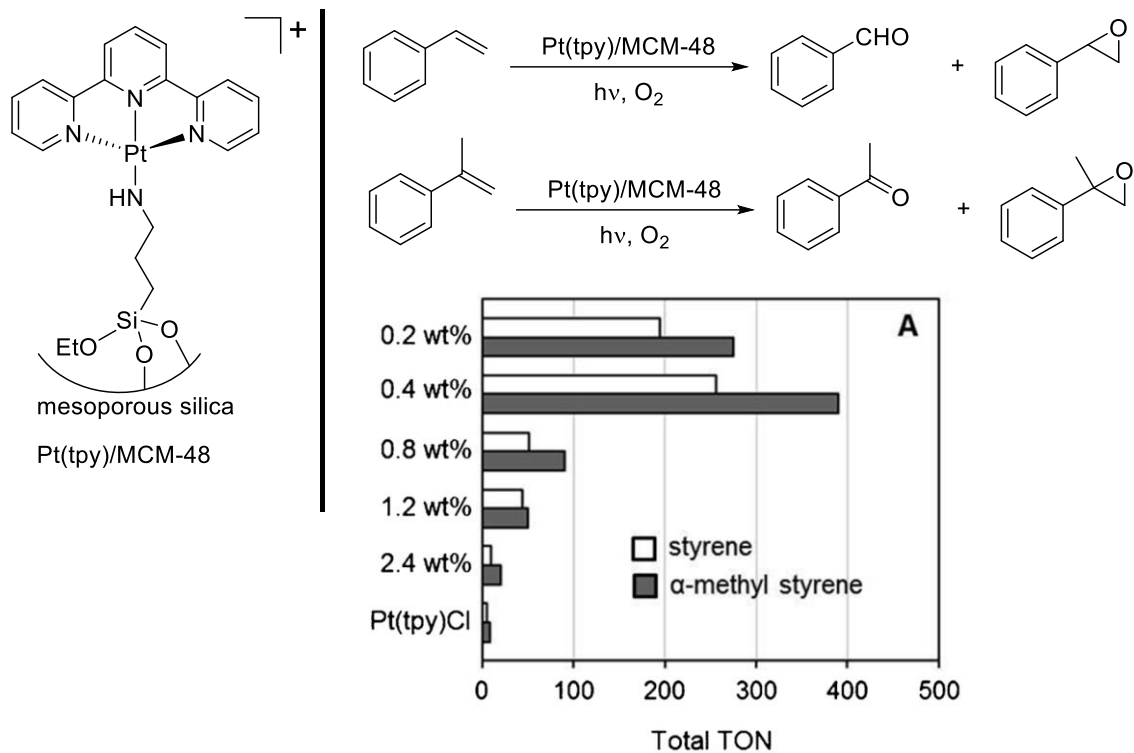
**Scheme 4.** Examples of silica-supported metal complex catalysts with a NHC ligand [38-40]



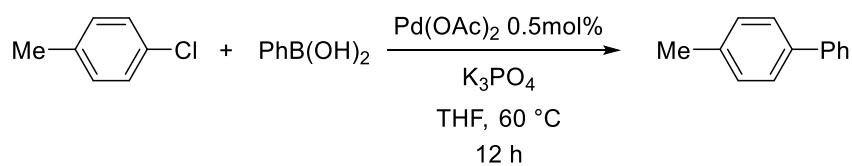
**Scheme 5.** Hydrosilylation of olefins catalyzed by a supported Pt complex [43]



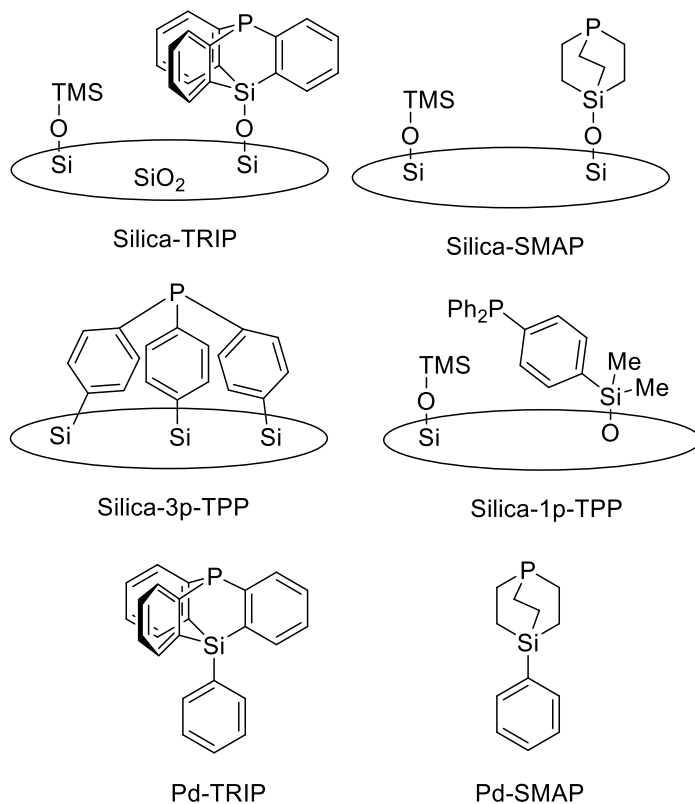
**Scheme 6.** Supported Pt complex catalyst for the photooxidation of styrenes (Adapted from ref. [45] Copyright Wiley-VCH GmbH. Reproduced with permission.)



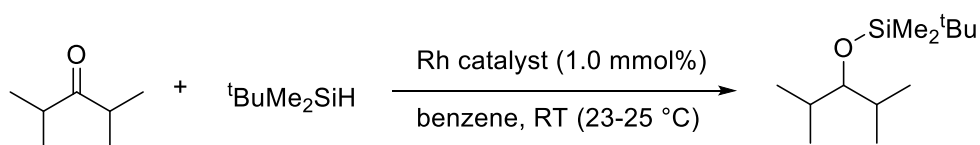
**Scheme 7.** Suzuki–Miyaura cross-coupling of chlorotoluene catalyzed by a Pd complex [47b]



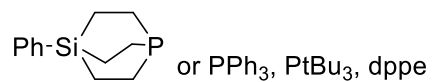
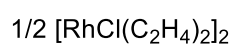
Ligand	Yield
Silica-TRIP	93%
Silica-SMAP (10 h)	82%
Silica-3p-TPP	83%
Silica-1p-TPP	9%
Ph-TRIP	0%
Ph-SMAP	0%
PPh <sub>3</sub>	< 1%



**Scheme 8.** Hydrosilylation of diisopropyl ketone using a silica-SMAP-Rh catalyst [63]

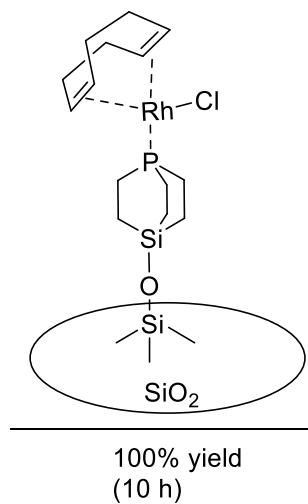


**Homogeneous**



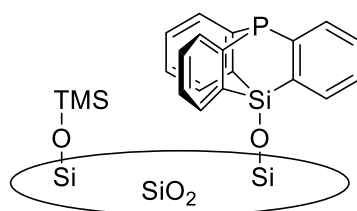
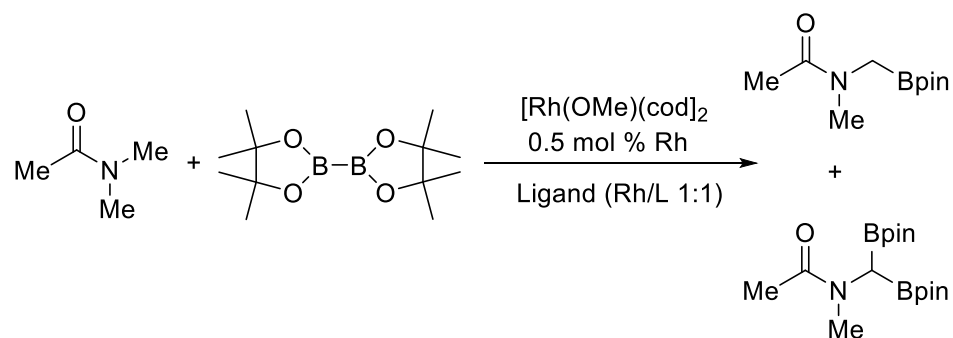
< 2 % Conv.  
(10 h)

**Heterogeneous**

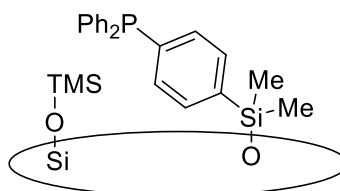


100% yield  
(10 h)

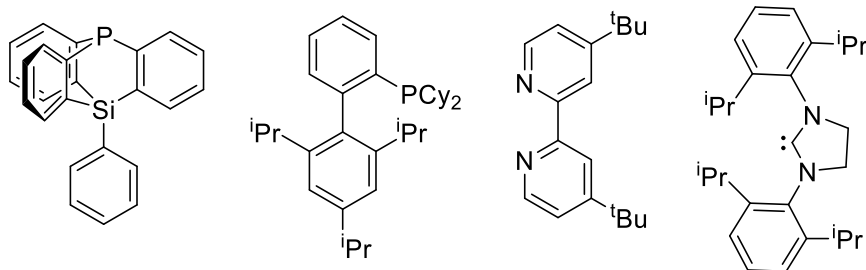
**Scheme 9.** Borylation of C(sp<sup>3</sup>)-H using a Rh complex catalyst [65,66]



**Silica-TRIP**  
**126% Yield**

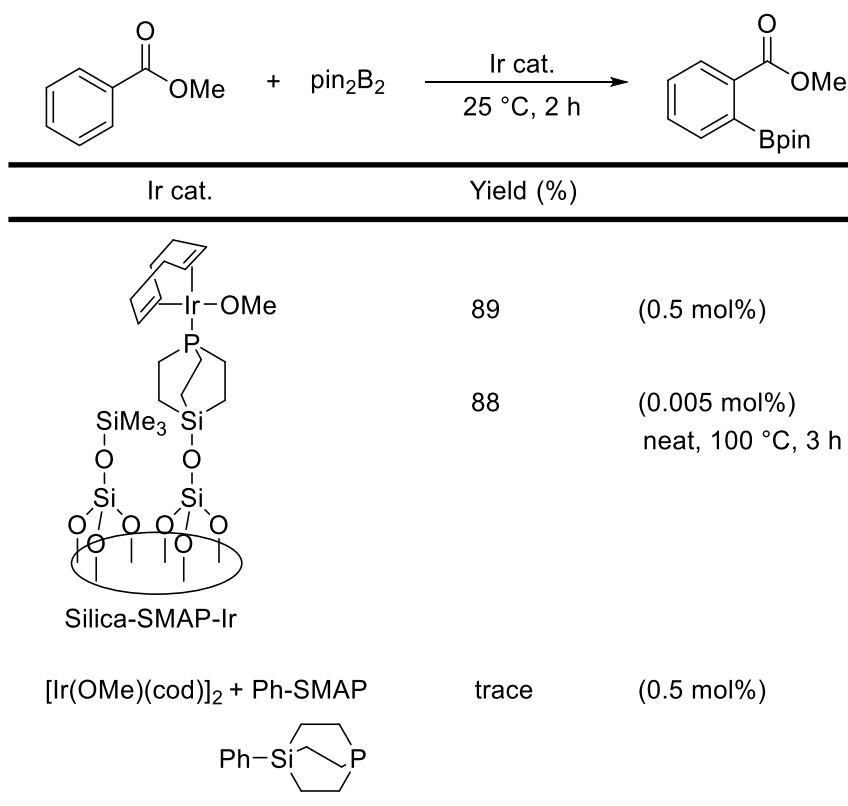


**Silica-TPP**  
**5% Yield**



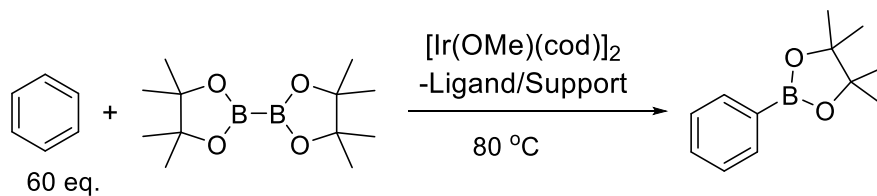
**Homogeneous TPPIR, Other phosphines, dtphy, STPr: 0 % Yield**

**Scheme 10.** C-H borylation of methyl benzoate using a silica-SMAP-Ir catalyst [87]

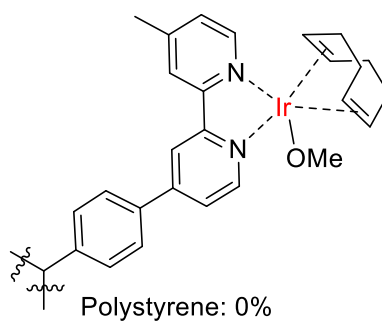
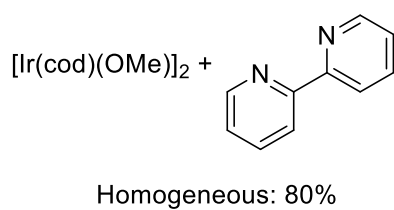
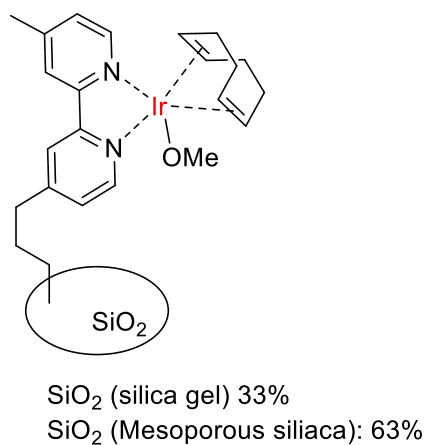
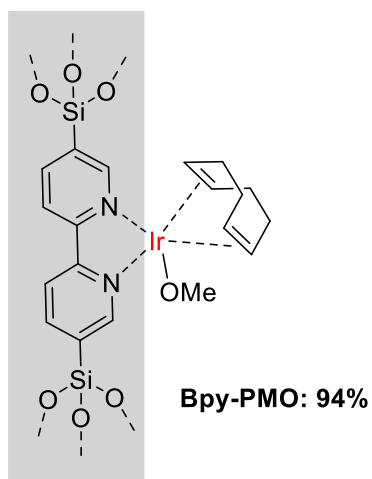




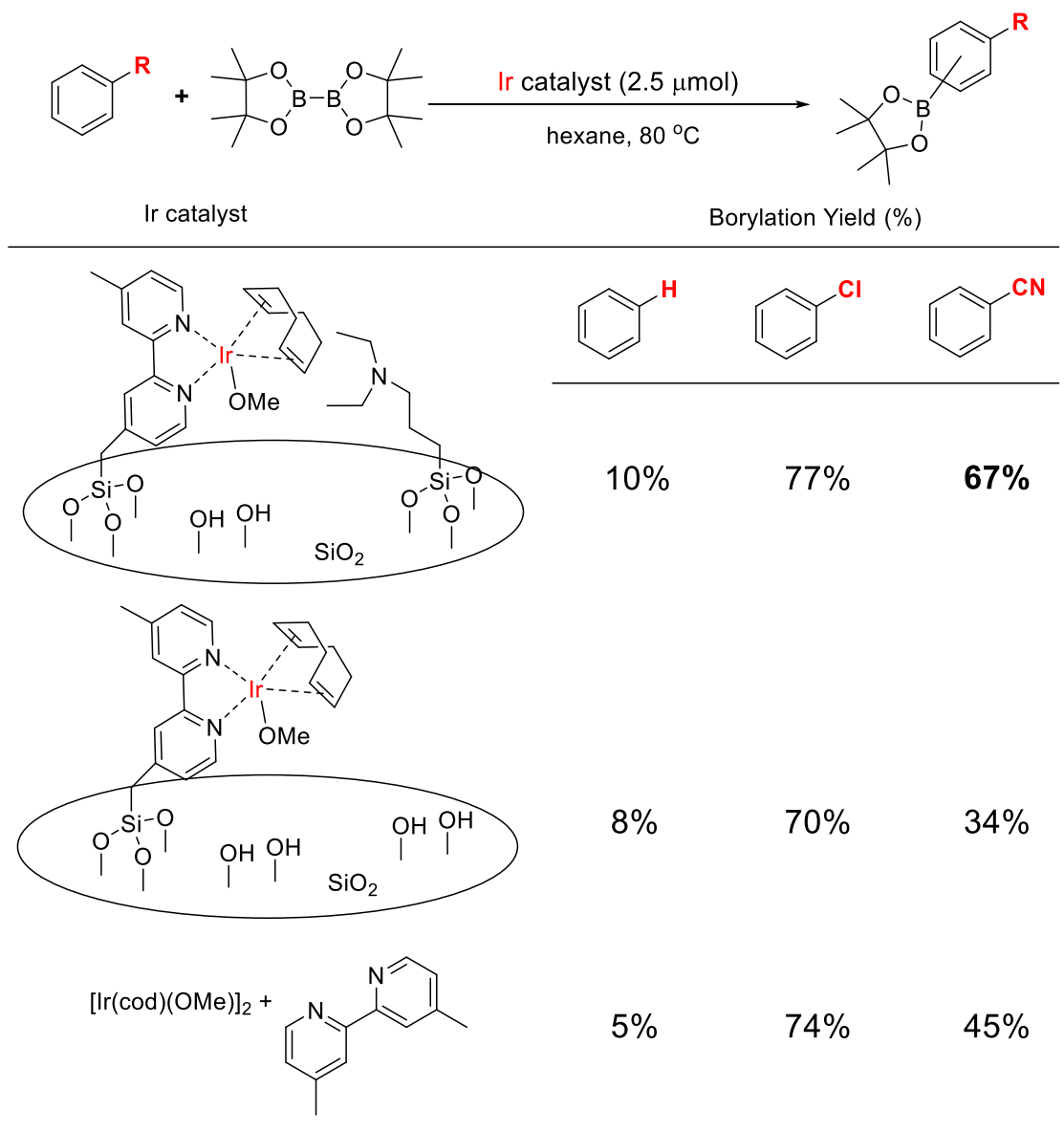
**Scheme 11.** C-H borylation of benzene using Bpy-POM-Ir and a heterogeneous/homogeneous Ir-bipyridine catalyst [93]



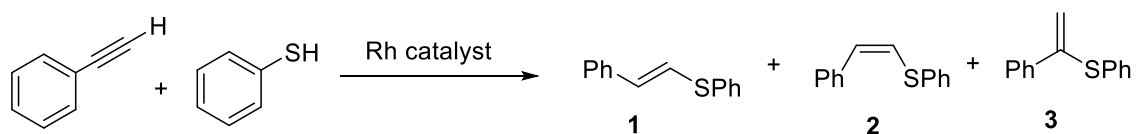
Ir catalyst: Borylation yield



**Scheme 12.** Silica-supported Ir-bipyridine for the C-H borylation of benzene and substituted benzene [97]

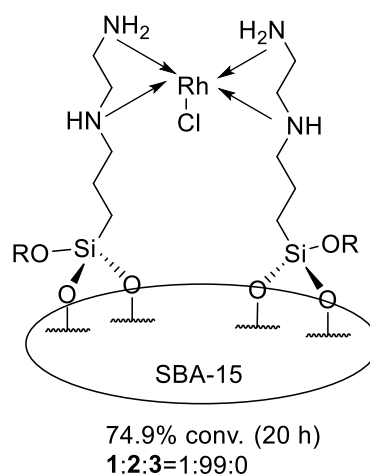


**Scheme 13.** Hydrothiolation of phenylacetylene using Rh complex catalysts [99]

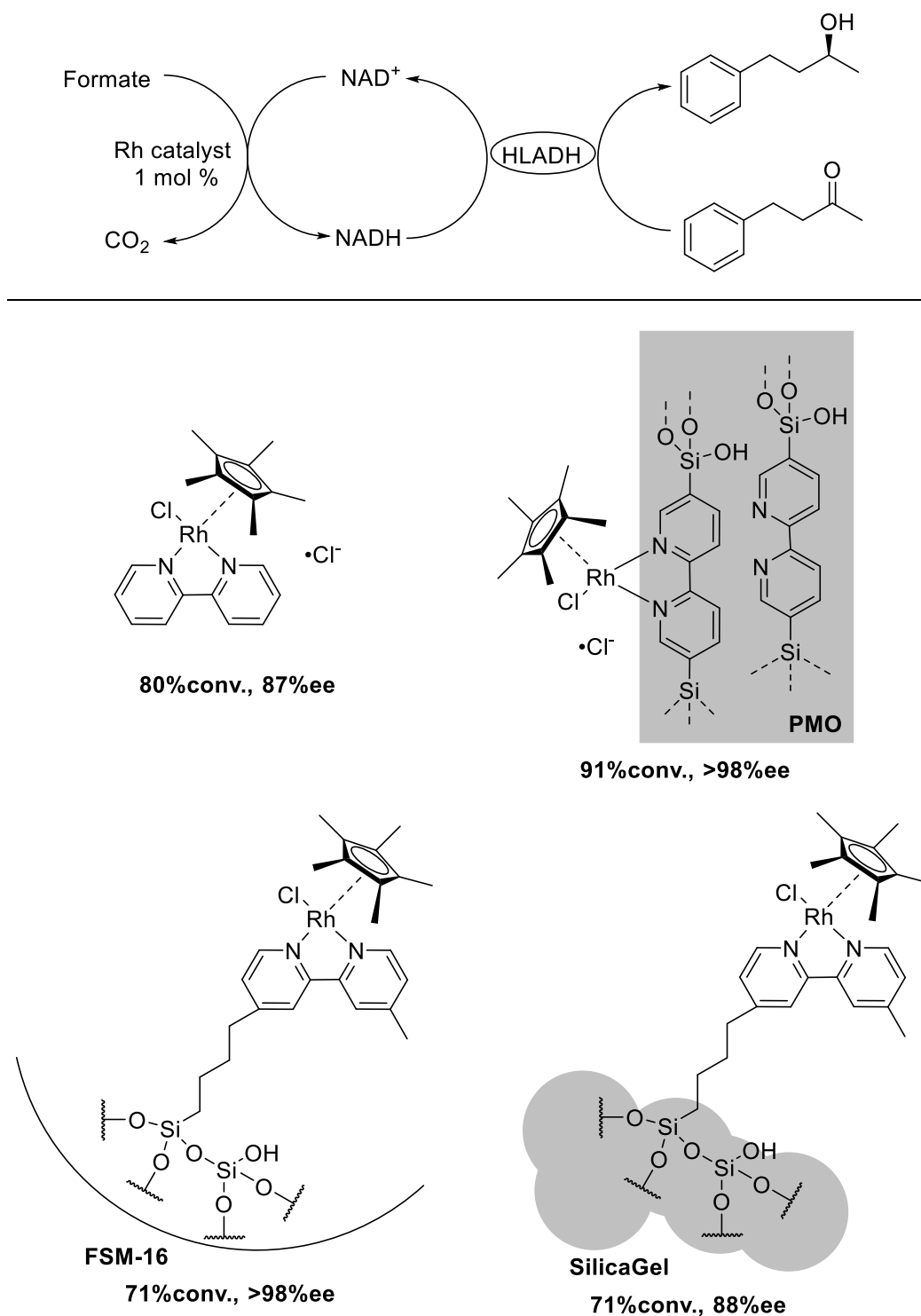


$\text{RhCl}(\text{PPh}_3)_3$   
98% conv. (45 min)  
1:2:3=94:0:6

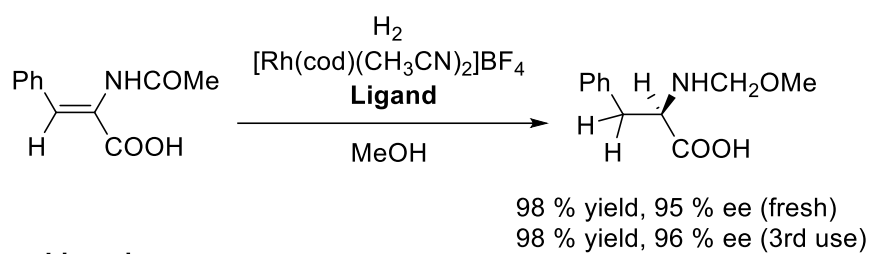
$\text{RhCl}(\text{PPh}_3)_3$   
+  
 $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$   
61.2% conv. (20 h)  
1:2:3=4:96:0



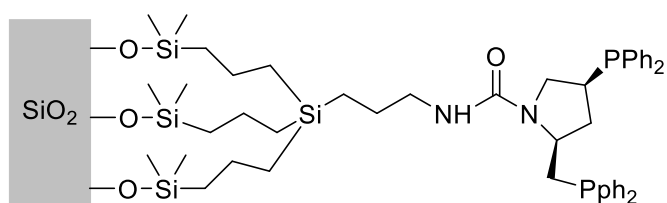
**Scheme 14.** Asymmetric hydrogenation with the Rh catalyst-HLDAH combined system  
[100]



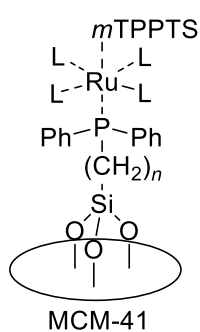
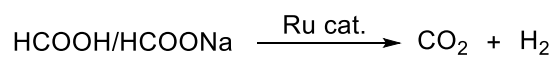
**Scheme 15.** Asymmetric hydrogenation catalyzed with the Rh complex with a phosphine ligand immobilized by a tripodal linker unit [101]



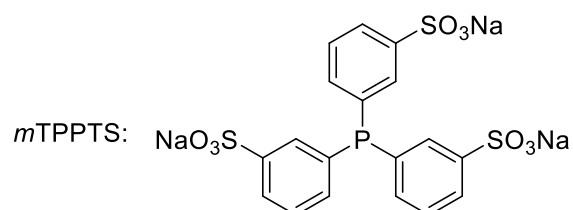
**Ligand**



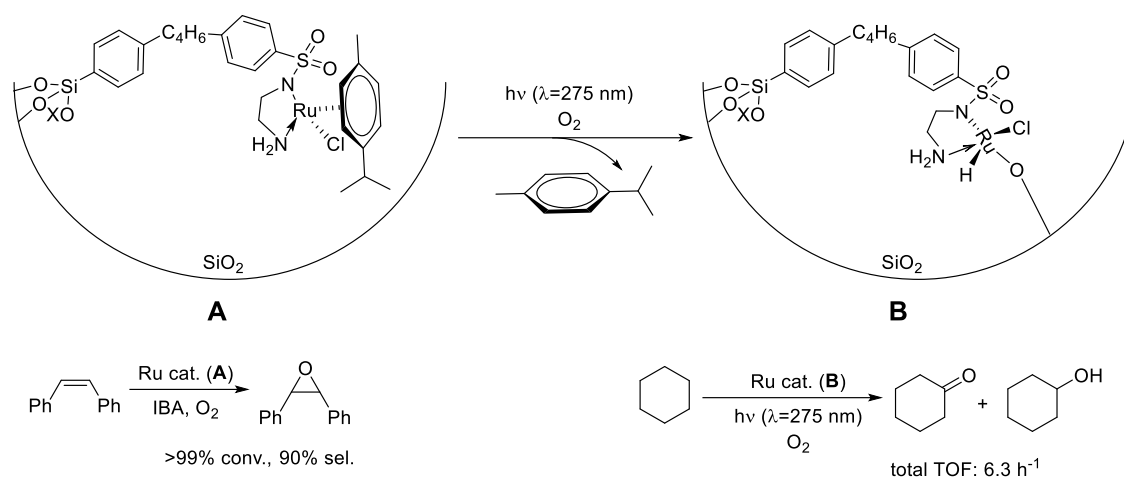
**Scheme 16.** Selective decomposition of formate to CO<sub>2</sub> and H<sub>2</sub> using a supported Ru complex [103]



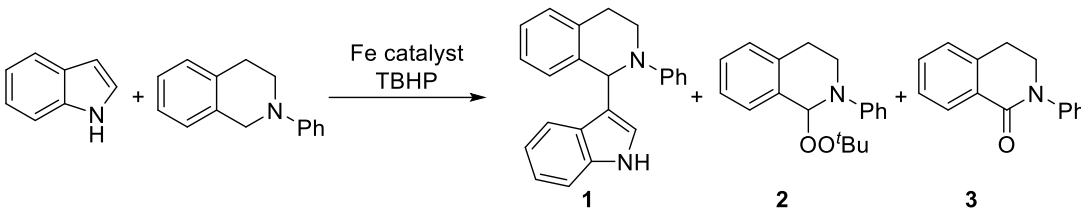
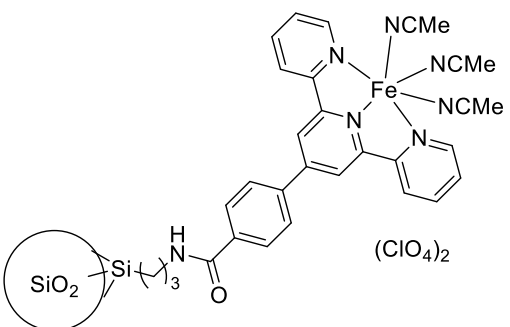
(CH <sub>2</sub> ) <sub>n</sub>	TOF (h <sup>-1</sup> )
C1	640
C2	660
C3	150
C4	200
Ru(II)/ <i>m</i> TPPTS	480



**Scheme 17.** Silica-supported Ru complex for (A) alkene epoxidation and (B) alkane photooxidation [104,106]



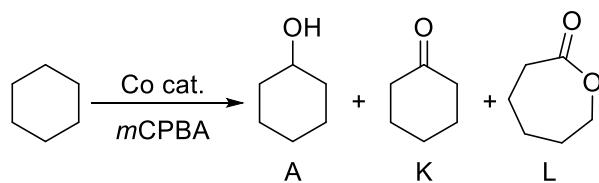
**Scheme 18.** Oxidative coupling of indole and a tetrahydroisoquinoline using Fe complex catalysts [112]

				
Fe catalyst	Conv. (%)	1 (%)	2 (%)	3 (%)
$[\text{Fe}(\text{Cl}_3\text{terpy})_2](\text{ClO}_4)_2$ 4,4',4''-trichloro-2,2':6',2''-tripyridine	>99	63	0	21
 $(\text{ClO}_4)_2$	>99	80	8	6

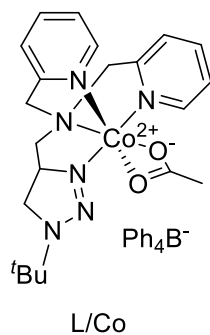
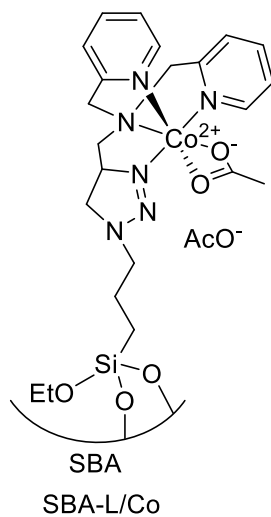




**Scheme 20.** Oxidation of cyclohexane using supported Co complex catalysts [116]



Co cat.	TON		
	A	K	L
SBA-L/Co (3 h)	745	80	25
L/Co (2 h)	604	98	14



### 3. Concerted Effect on Surface for Enhanced Catalysis

Surface-induced chiral synthesis was reported by Córdova et al. [120] Both chiral pyrrolidine derivatives and diamonopalladium complexes were immobilized on the same silica surface. Click chemistry was used for amine immobilization to provide the supported organocatalyst. The prepared catalyst was used for the asymmetric cascade transformation of unsaturated aldehydes and nucleophilic alkynes (**Scheme 21**). As shown in Scheme, the nucleophilic addition to the aldehyde (Michael reaction) occurs via the iminium activation mechanism, followed by a cyclization reaction promoted by a Pd site affording carbocycle products. The use of a supported bifunctional catalyst yielded 73% of the corresponding product, with a diastereomer ratio (*dr*) of 87:13 and enantiomer ratio (*er*) of 95:5. The reaction was also applied to the synthesis of spirocyclic oxindoles. After the optimization of the reaction conditions, the *er* increased to 97.5:2.5. Without Pd, cyclization products were not obtained. The cyclization product was also obtained by using a homogeneous asymmetric organocatalyst precursor and PdCl<sub>2</sub>. However, the *er* slightly decreased (94.5:5.5), indicating the synergistic effect of the bifunctional surface.

The palladium-catalyzed allylation of nucleophiles (Tsuji–Troost reaction) is one of the most powerful procedures for introducing reactive allyl groups to nucleophilic compounds. After the initial discovery of the reactivity of  $\pi$ -allylpalladium by Tsuji[121] and Trost[122], numerous studies have been carried out using homogeneous and heterogeneous palladium catalysts.[123-126] The Pd-catalyzed Tsuji–Troost reaction is promoted by base additives, which increase the nucleophilicity of the donor substrates such as active methylene compounds. This reaction mechanism encouraged us to design a bifunctional catalyst with both a Pd complex and organic base, such as a tertiary amine, on the same SiO<sub>2</sub> surface.[127,128] As shown in **Scheme 22**, the Tsuji–Troost reaction of

ethyl acetoacetate and allyl methyl carbonate was examined using supported diaminopalladium catalysts. The silica-supported diaminopalladium–tertiary amine catalyst ( $\text{SiO}_2/\text{diamine}/\text{Pd}/\text{NEt}_2$ ) has the highest catalytic activity, leading to a quantitative yield of the product. The product yield decreases to 26% based on the use of the supported catalyst containing only the Pd complex ( $\text{SiO}_2/\text{diamine}/\text{Pd}$ ) and the yield does not improve by the addition of silica-supported tertiary amine ( $\text{SiO}_2/\text{NEt}_2$ ). These results indicate that both the Pd complex and tertiary amine must be located on the same silica surface to increase the allylation catalysis. Under the same conditions, the homogeneous diaminopalladium analogue is almost inactive. The proposed reaction mechanism includes the cooperative activation of an allylating agent and a nucleophile by the Pd complex and tertiary amine, respectively.

Studer et al. reported a silica-supported Pd complex–amine system that was prepared via click chemistry.[129] An azide group was immobilized on the silica surface via a silane coupling reaction, followed by azide–alkyne coupling using 2-ethynylpyridine providing a triazole-pyridyl ligand on the silica surface. Various amines were functionalized on the same silica surface and the complexation of  $\text{PdCl}_2$  with the ligand led to the formation of bifunctional catalysts (**Scheme 23**). Immobilization of tertiary amines, especially the aminoamide group, performs much better, yielding 96% of the corresponding double allylation product compared with the catalyst only containing the Pd complex (77% yield of the mono-allylated product). Other functionalities, such as tertiary and primary amines, also accelerate the allylation reaction, selectively providing mono-allylated products.

The Pd complex–tertiary amine catalyst was improved by our group by using a bisphosphine–Pd complex and DABCO as Pd and amine sites ( $\text{SiO}_2/\text{PP-Pd}/\text{DABCO}$ ),

respectively.[130,131] The catalyst structure and performance are summarized in **Scheme 24**. Co-immobilization of DABCO enhances the catalytic performance of the Pd complex. After the optimization of the reaction conditions, various nucleophiles, such as dicarbonyls and phenols, were applied to generate the corresponding mono- and diallylated products with high turnover numbers (TONs). The prepared SiO<sub>2</sub>/PP-Pd catalysts were characterized using several spectroscopic techniques including solid-state NMR and Pd K-edge X-ray absorption fine structure (XAFS). The extended X-ray absorption fine structure (EXAFS) curve-fitting analysis indicates that the Debye–Waller factor (DW) is strongly affected by the co-immobilized functionality. After the immobilization of large molecules, such as DABCO and *n*-hexyl groups, the DW values increased.[131,132] This result suggests that the Pd complex conformation is affected by the co-immobilized functionality, whereas the basic coordination structures are the same. In other words, the surface functionalities are located in close proximity and can interact with substrates together and activate them cooperatively. Similar DW value changing was also observed due to different morphologies of the silica support.[133]

Cooperation between the immobilized Pd complex and support silica surface is another interesting effect that increases the Pd catalysis. In the field of supported organocatalysis, it is well known that surface silanol groups can assist in catalytic reactions.[134-138] González-Arellano et al. reported that the olefin hydrogenation rate of a supported Pd–Ni complex was enhanced by surface acidity.[139] The hydrogenation intermediate was stabilized by surface acidity. In the case of allylation, allylic alcohol has received much attention as an allylating agent due to the formation of water as the sole byproduct.[140,141] It is well known that hydrogen bonding between allylic alcohol and protonic additives enhances the allylation using allylic alcohols.[142-146] Therefore, the

use of a silica-supported Pd complex with surface Si-OH should be effective for the allylation of nucleophiles using allylic alcohols.[147,148] The reaction results are summarized in **Scheme 25**. The use of a mesoporous silica-supported PP-Pd complex (MS/PP-Pd) enhances the reaction of ethyl acetoacetate with allylic alcohol. After the removal of the surface Si-OH, the catalytic activity decreases. Under these reaction conditions, the homogeneous Pd counterpart exhibits a very low activity. The interaction between allylic alcohol and surface Si-OH was detected by *in situ* FT-IR and solid-state NMR. The polar environment of the silica surface with silanol enhances the C-O bond cleavage of the allylic alcohols.

The use of cationic metal complexes with BF<sub>4</sub> anions is an interesting approach with respect to the immobilization of metal complexes on silica surfaces. Shu et al. demonstrated the use of a silica-supported cationic Au complex for region- and enantioselective intramolecular lactonization.[149] The hydrogen bonding of the F atom and surface Si-OH enables the stable immobilization of Ph<sub>3</sub>PAuBF<sub>4</sub> onto the silica SBA-15 surface. The supported catalyst accelerates the intramolecular lactonization of an allenic acid due to the enhancement of protodeauration by Si-OH. The reaction was completed within 2 min with the supported catalyst, whereas it lasted for 120 min with homogeneous Ph<sub>3</sub>PAuBF<sub>4</sub> (**Scheme 26A**). The supported catalyst showed a high regioselectivity with respect to the cyclization reaction of alkynic acid and a very high regioselectivity of the 5-membered cyclic product compared with the homogeneous catalyst (**Scheme 26B**). The supported cationic Au catalyst system can be applied to the enantioselective cyclization of allenic acid. As shown in **Scheme 26C**, the supported catalyst with chiral ligand L\* yields a lactonization product with a high enantiomer excess (95% ee). In the case of the homogeneous counterpart with the same ligand, an

enantioselectivity was not observed. In the control experiment, the authors examined the reaction using other supports such as MCM-41 and nonmesoporous silica. An enantioselectivity was still observed with other silica materials, suggesting the participation of the surface Si-OH group in the catalytic cycle rather than the confinement effect. The supported Au catalyst could be reused at least 11 times without any enantioselectivity loss, whereas the Au amount gradually decreased. Other silica-supported Au(I) complex catalysts have also been applied using directly attached phosphine ligands with methylene linkers [150-152].

An interesting example of the cooperative catalysis of a supported Rh complex was observed during the hydrogenation of aromatic rings. Angelici et al. initially reported a silica-supported Rh complex-metallic Pd particle bifunctional catalyst system for the hydrogenation of arenes.[153-159] Representative results are summarized in **Table 1**. [154] The hydrogenation of the benzene ring of methyl benzoate and phenol rarely occurred using SiO<sub>2</sub>-supported Pd particle under 4 atm of H<sub>2</sub>. The SiO<sub>2</sub>-supported Rh complex yielded a small amount of the hydrogenation product from methyl benzoate, whereas it was almost inactive with respect to phenol hydrogenation. Surprisingly, the silica-supported both Rh complex and metallic Pd provided an excellent yield of both hydrogenation products in a shorter reaction time than the Rh complex alone. The TON value of the Rh site was 2900 for the reaction of phenol. In a similar reaction system, a detailed hydrogenation mechanism was demonstrated by Barbaro et al.[160-162] The EXAFS and FTIR analyses and control experiments revealed that the Rh complex and Pd nanoparticles are located in close proximity and directly interact with the activated arene under hydrogenation conditions.[161] This catalyst system, monomeric Rh complex, and metallic Pd particles, might be applicable to hydroformylation.[163] The incorporation of

the two functionalities into one silica sol-gel matrix is also suitable for arene hydrogenation.[164] As shown in **Table 2**, the SiO<sub>2</sub>-supported Rh dimer catalyst with metallic Pd particles has the highest reaction rate with respect to the hydroformylation of 1-octene.[163] Regarding hydroformylation of alkenes, many supported Rh complexes with phosphine ligands, such as xantphos, have been used.[165-180]

Vizza et al. reported a supported triphosphine sulfos ( $-\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$ ) Pd complex on SiO<sub>2</sub> obtained via hydrogen bonding between the silica surface and SO<sub>3</sub><sup>-</sup> group.[181] As mentioned above, this supported Rh complex was used in a bifunctional system with metallic Pd.[160,161] The catalyst, SiO<sub>2</sub>-sulphos-Rh, shows a good performance with respect to the hydrogenation of enones, nitriles, and heteroarenes.[182,183] The enantioselective hydrogenation of alkenes has also been applied.[184]

The Rh-catalyzed 1,4-addition reaction of phenylboronic acid is one of the most powerful tools for the construction of β-arylcarbonyl compounds.[185-192] It was also reported that a silica-supported diamine ligand is effective for heterogeneous Rh complex catalysts with respect to 1,4-addition reactions with the support of co-immobilized tertiary amines.[193] The bifunctional catalyst, that is, the SiO<sub>2</sub>-supported diamonorrhodium complex with tertiary amine (SiO<sub>2</sub>/diamine/Rh/NEt<sub>2</sub>), can accelerate the catalysis by electron donation from the tertiary amine to the boron atom of the phenylboronic acid, which weakens the Ph-B bond and thus enhances the transformation step. The interaction between the amine and boron was revealed by solid-state <sup>11</sup>B MAS NMR.[193] As shown in **Scheme 27**, the TOF of the Rh site strongly depends on the total surface density of the Rh complex and tertiary amine, indicating that the distance between the Rh complex and tertiary amine is a critical factor affecting the acceleration. A method using a probe



molecule that can interact with both the diamine ligand and tertiary amine revealed that the appropriate surface distance between the Rh complex and tertiary amine should be shorter than 8 Å.[194] The 1,4-addition reaction rate significantly depends on the support morphology. When mesoporous silica was used as a support for both the Rh complex and tertiary amine, a maximum TON of 8500 was obtained, with a yield of 82%.[195]

Fernandes et al. demonstrated the control of silica-supported Cu catalysis by surface molecular engineering using additional functionalities such as *N*-methylimidazole ligand (NMI) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).[196,197] In the aerobic oxidation of benzyl alcohol, NMI and TEMPO act as additional ligands for the Cu-pyridyltriazol complex and co-catalyst for the hydride elimination from the Cu-alkoxide intermediate, respectively. As shown in **Scheme 28**, the trifunctional catalyst, that is, silica-supported Cu complex/NMI/TEMPO, has the highest reaction rate (TOF) with respect to the aerobic oxidation of benzyl alcohol ( $55.1 \times 10^{-2} \text{ min}^{-1}$ ).[196] A moderate reaction rate was observed in the case of a supported bifunctional catalyst with an additional homogeneous component such as silica-supported Cu complex/TEMPO with homogeneous NMI ( $25.4 \times 10^{-2} \text{ min}^{-1}$ ). The TOF of the bifunctional catalyst without additional NMI was only  $1.3 \times 10^{-2} \text{ min}^{-1}$ . This result strongly implies the significant acceleration by the immobilized NMI. A simple homogenous mixture of three components yielded a much lower efficiency ( $11.9 \times 10^{-2} \text{ min}^{-1}$ ). This is an interesting and unique effect of the multifunctionalized catalytic surface. To investigate the detailed positioning of these three components, that is, Cu, NMI, and TEMPO, oligomers were immobilized onto silica surfaces with a controlled order by the same group.[198,199] As shown in **Scheme 29**, the order of the components strongly affects the catalytic activity: the position of NMI must be close to that of the Cu complex in the case of the supported

catalyst. On the other hand, the homogeneous oligomer catalyst exhibits different phenomena. In addition, the co-immobilization of triethylene glycol methyl ether on the silica surface with the Cu/NMI/TEMPO oligomer decreases the reaction rate ( $8.1 \times 10^{-2} \text{ min}^{-1}$ ). These results indicate that intermolecular interactions between neighboring Cu/NMI/TEMPO oligomer pairs are necessary to increase the reaction rate, suggesting the presence of intermolecular Cu complex–NMI interactions. The appropriate orientation of supported TEMPO/NMI/Cu enhances the catalytic activity, whereas the homogeneous nature induces insignificant differences in the catalytic activity, even under a different order of functionalities.

The Cu-bis(oxazoline) complex (Cu-BOX) catalyzes the asymmetric reactions of Lewis acids. Iwasawa et al. reported silica-supported Cu-BOX catalysts for asymmetric Diels–Alder reactions.[200,201] The homogeneous Cu-BOX-OTf catalyst promoted the reaction between cyclopentadiene and 2-acryloyl-2-oxazolidinone, yielding 98% conversion and an endo product with an ee of 27%. This ee value is higher than that of Cu-BOX-ClO<sub>4</sub> (5% ee). After immobilization of the Cu-BOX catalyst onto the silica surface, the enantioselectivity decreased to 14% ee. However, the ee value increased to 63% after the co-immobilization of the methacryloxypropyl group on the same silica surface (**Scheme 30**). Other functional groups, such as octyl and diamino groups, did not increase the enantioselectivity. The results of Cu K-edge XAFS, X-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR) analyses did not indicate a significant change in the local coordination structure of the Cu complex after the co-immobilization of organic groups. Strong interactions between the Cu-BOX and methacryloxypropyl group were not observed. However, the FTIR analysis indicated that the methacryloxypropyl group might interact with polar functionalities, such as NH, in

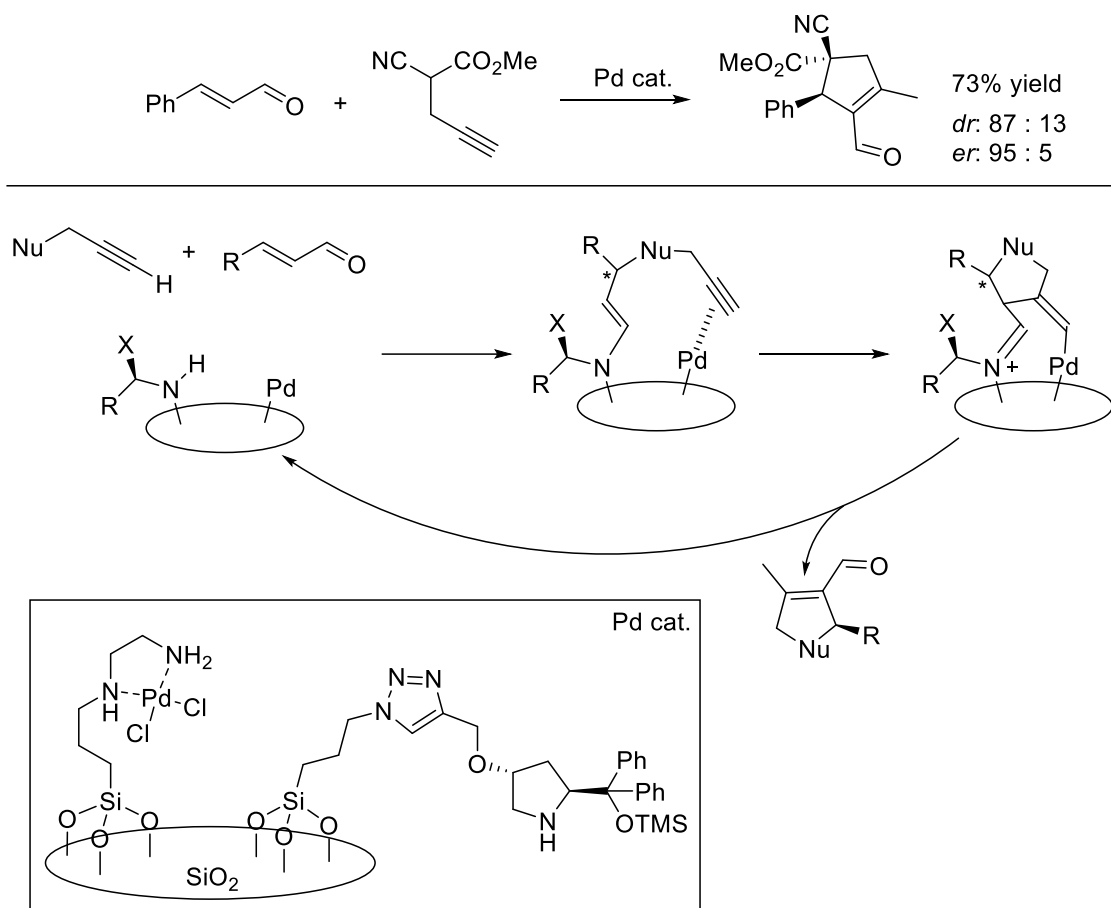
the BOX ligand. The immobilized organic group occupies the space around the Cu-BOX and weak interactions may enhance the chirality. Similar examples of surface-enhanced enantioselectivity by surrounding environment have been reported for other metal complexes. Details are shown in next Section.

A  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex immobilized on  $\text{SiO}_2@\text{Ag}$  has been reported by Mori et al. as a supported metal complex catalyst based on which localized surface plasmon resonance can be controlled.[202] Plasmonic Ag nanoparticles coated with  $\text{SiO}_2$  enhanced the excitation rate and quantum efficiency of the attached Ru-bipyridine complex under photoirradiation conditions. The  $\text{SiO}_2$  layer was functionalized by a carboxylic acid group through a silane coupling reaction and  $[\text{Ru}(\text{bpy})_3]^{2+}$  was then attached via electrostatic interactions. The electron transfer from the Ru complex to the molecular oxygen activated the oxidation reaction of alkenes under visible-light irradiation at room temperature. For example, the TON of  $\alpha$ -methylstyrene oxidation using the  $\text{SiO}_2@\text{Ag}$ -supported Ru complex was two times higher than that of a simple  $\text{SiO}_2$  support (**Scheme 31**). On the other hand, the direct attachment of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex to the Ag nanoparticle decreased the catalytic activity due to the quenching of the excited  $[\text{Ru}(\text{bpy})_3]^{2+}$ . These results are in good agreement with the PL emission intensity of the Ru complex. The plasmon resonance frequency at 400 nm due to Ag nanoparticle is close to the excitation frequency of  $[\text{Ru}(\text{bpy})_3]^{2+}$ .

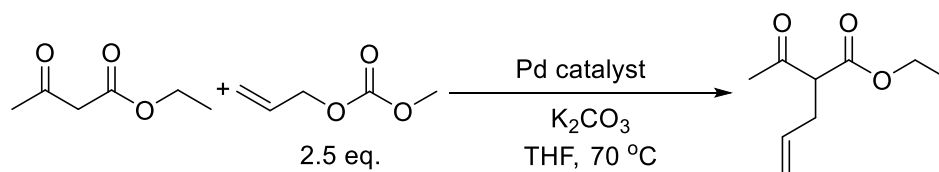
A tandem reaction using one silica catalyst with more than two incorporated metal complexes is an effective approach to prepare multi-functionalized organic molecules. Several review papers have been published including tandem reaction approaches using multifunctionalized heterogeneous catalysts.[203] Liu et al. reported a shell-type silica nanosphere, which can be used to immobilize both Pd complexes and chiral Ru

catalysts.[204] Based on the ship-in-bottle synthesis of the IPr–Pd complex inside the silica shell followed by the complexation of the Ru precursor onto the pre-immobilized chiral ligand, a silica nanosphere containing both an IPr–Pd complex and chiral Ru complex was obtained (**Scheme 32**). The catalyst is utilized for the tandem Suzuki–Miyaura coupling–asymmetric hydrogen transfer reaction of chloroacetophenones. The bifunctional catalyst system led to a high yield of corresponding alcohols with high enantioselectivities. The reaction also occurred using a homogeneous counterpart. However, the heterogeneous catalyst has a higher activity and selectivity in several substrates (**Scheme 32**). The preparation of the silica support with a three-dimensional (3D) printing approach was also reported for the tandem reaction using two types of metal complexes.[205] The Pd and Cu complexes were separately attached to different 3D-printed silica supports. The two catalyst sets were used for the tandem click reaction–Sonogashira/Stille/Suzuki–Miyaura coupling. For example, the three substrates, that is, 2-iodobenzylbromide, NaN<sub>3</sub>, and alkynes, were effectively converted to the corresponding substituted 1,2,3-triazoles (**Scheme 33**).

**Scheme 21.** Silica-supported organocatalyst and Pd complex for enantioselective cyclization [120]



**Scheme 22.** Tsuji–Trost reaction catalyzed by a silica-supported Pd complex–tertiary amine [127]



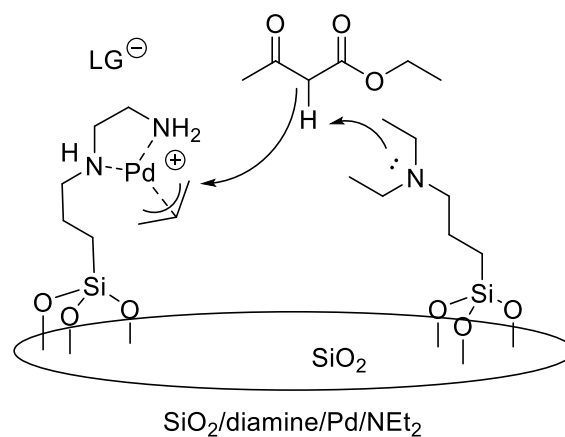
Pd catalyst: Yield

$SiO_2$ /diamine/Pd/ $NEt_3$ : >99%

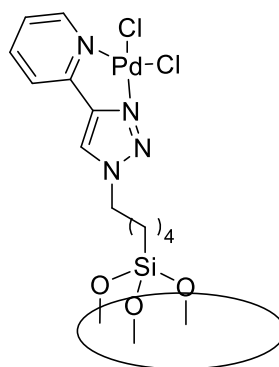
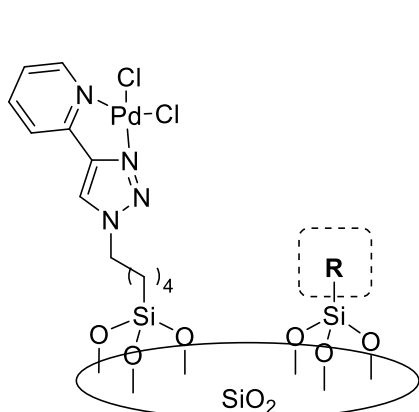
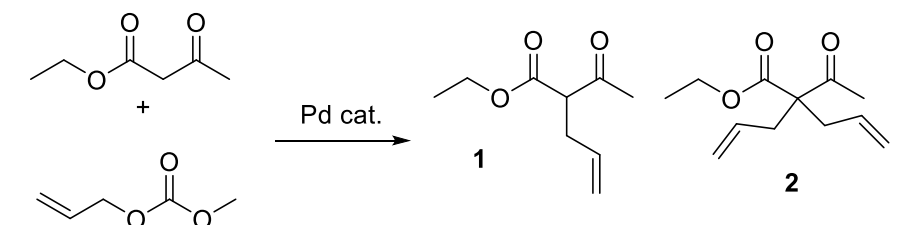
$SiO_2$ /diamine/Pd: 26%

$SiO_2$ /diamine/Pd  
+  $SiO_2/NEt_3$ : 28%

Dichloro(ethylenediamine)-  
palladium(II): 0%



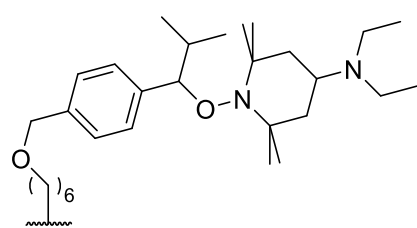
**Scheme 23.** Tsuji–Trost reaction catalyzed by a silica-supported Pd complex [129]



**1:** 77%

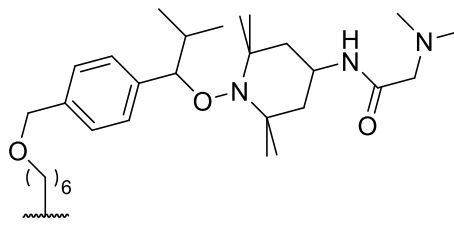
**2:** 0% (24 h)

**R =**



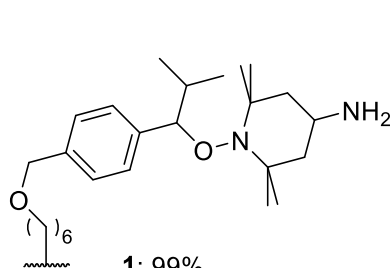
**1:** 99%

**2:** 0% (12 h)



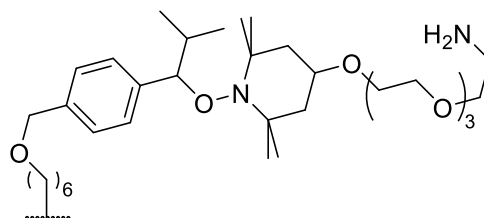
**1:** 0%

**2:** 96% (18 h)



**1:** 99%

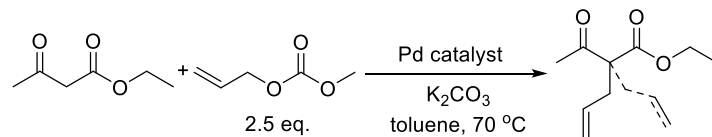
**2:** 0% (18 h)



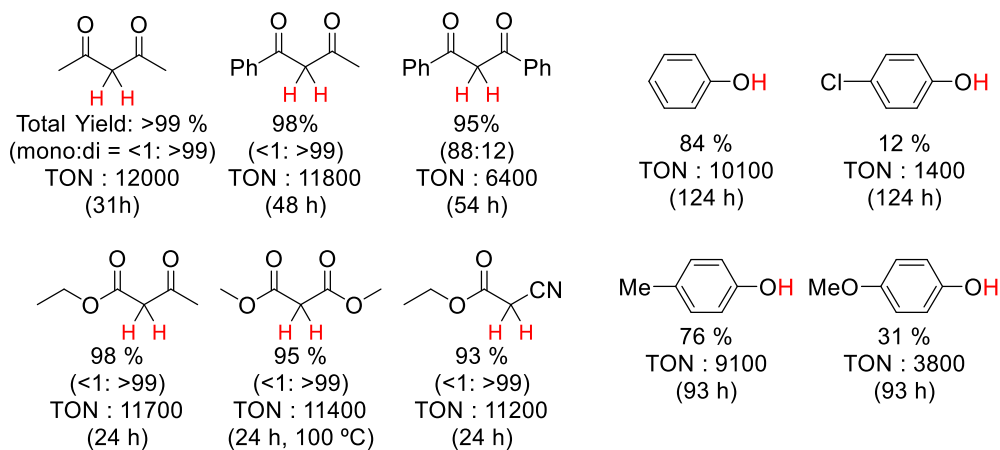
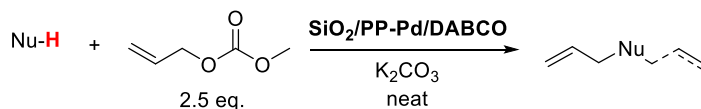
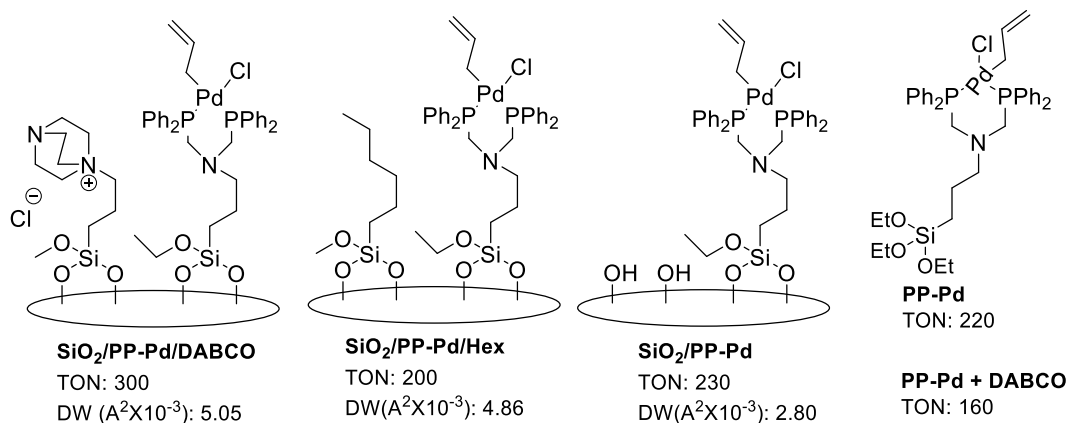
**1:** 93%

**2:** 0% (18 h)

**Scheme 24.** Silica-supported Pd-bisphosphine complex for the Tsuji–Trost reaction [131]

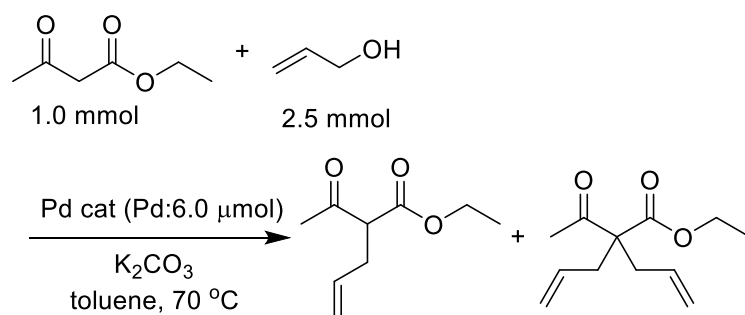


Catalyst/ TON/ DW factor by CF of Pd K-edge EXAFS

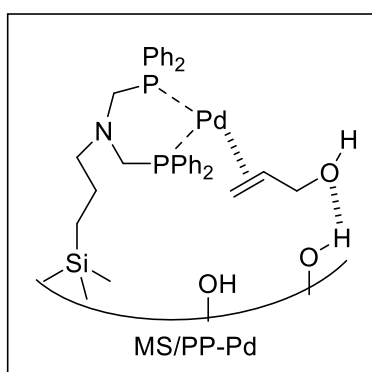




**Scheme 25.** Allylation of ethyl acetoacetate using allylic alcohol [147]

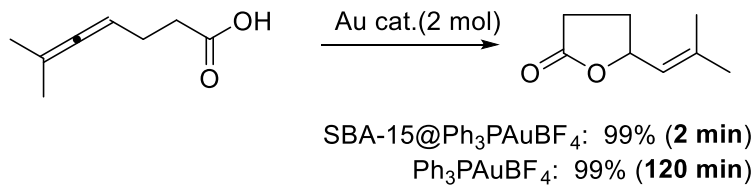


Pd cat	yield (mono/di) [%]	TON
MS/PP-Pd	47/3	87
MS/PP-Pd (calcination)	38/1	68
MS/PP-Pd/Me (trated with MeSi(OMe) <sub>3</sub> )	19/0	31
PP-Pd	6/0	10

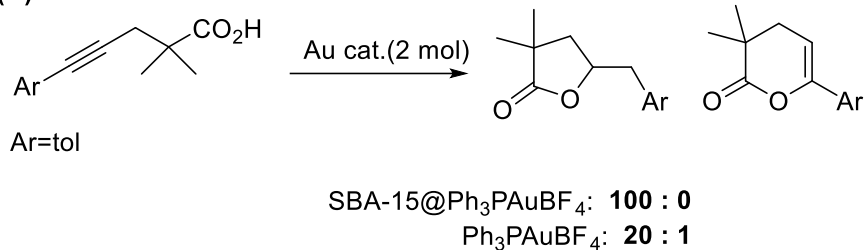


**Scheme 26.** SBA-15-suported  $\text{Ph}_3\text{PAuBF}_3$  for lactonization reactions [149]

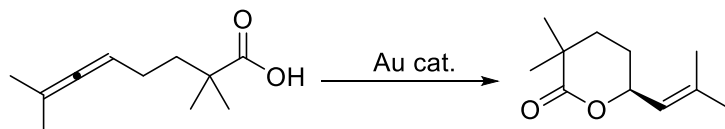
(A)



(B)

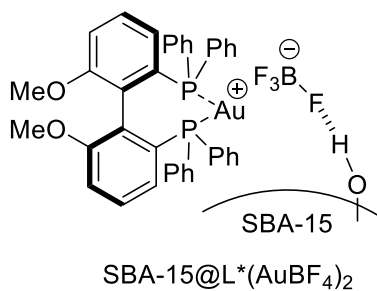


(C)

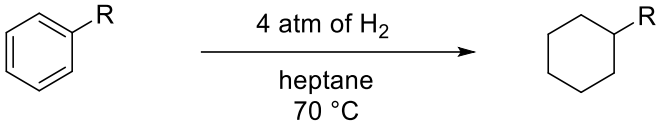
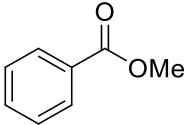
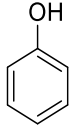
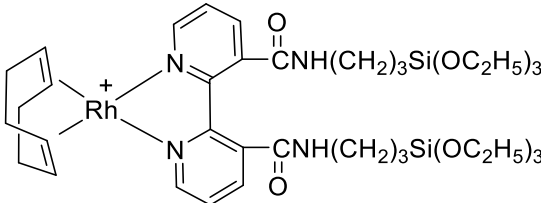
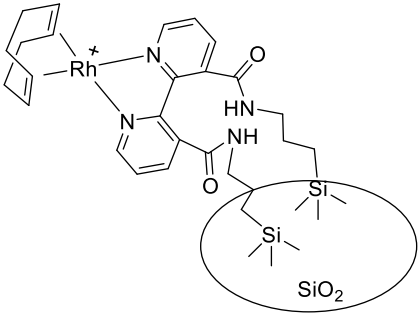
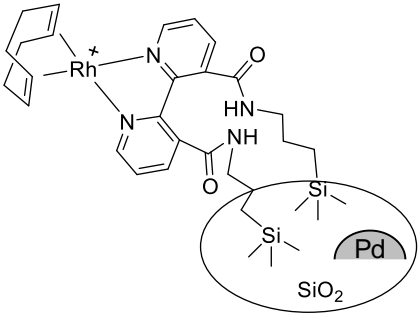


hetero.: SBA-15@ $\text{L}^*(\text{AuBF}_4)_2$  84% yeid, 95%ee

homo.:  $\text{L}^*(\text{AuBF}_4)_2$  90% yeid, 0%ee

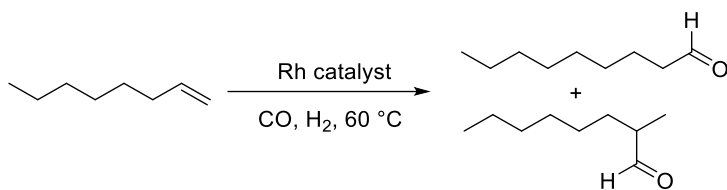
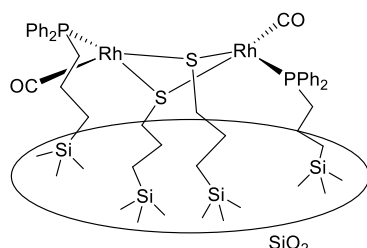
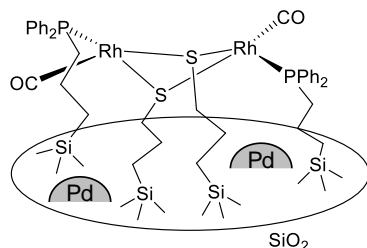


**Table 1.** Silica-supported Rh complex–metallic Pd catalyst for the hydrogenation of arenes [154]

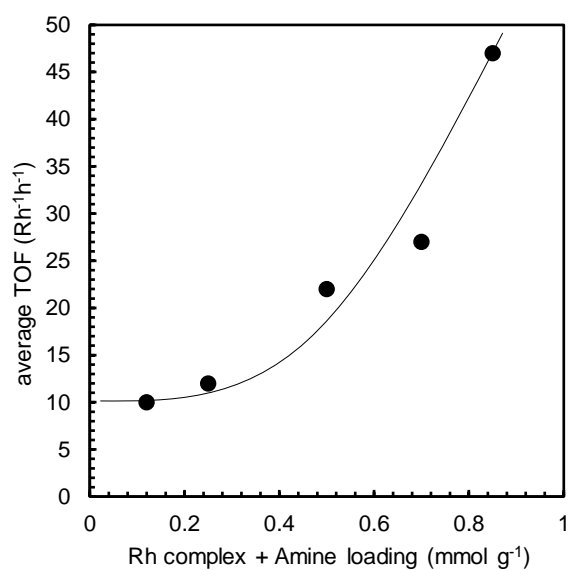
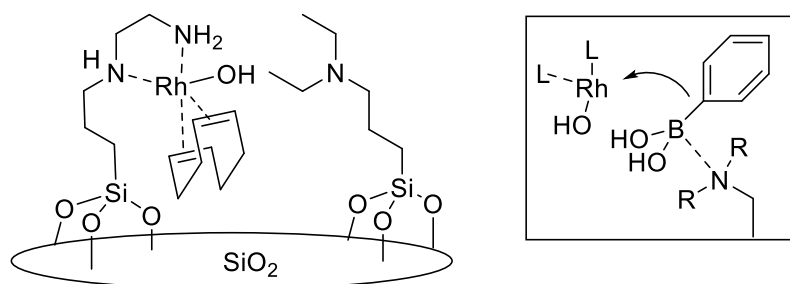
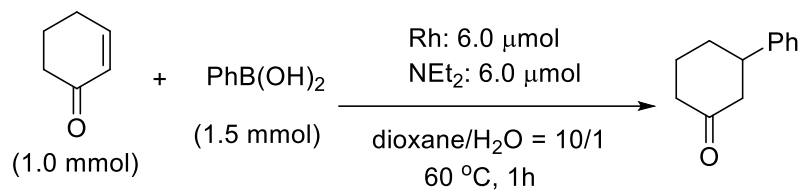
		
Catalyst	Conversion/TON of Rh	
		
SiO <sub>2</sub> /Pd	18%/- (3 h)	0%/0 (18 h)
	0%/0 (2 h)	0%/0 (10 h)
	23%/120 (4 h)	0%/0 (18 h)
	100%/720 (0.5 h)	100%/2900 <sup>[a]</sup> (7 h)

[a] cyclohexanone 58.8%, cyclohexanol 41.2%.

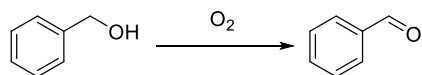
**Table 2.** Silica-supported Rh complex-metallic Pd catalyst for the hydrogenation of arenes [163]

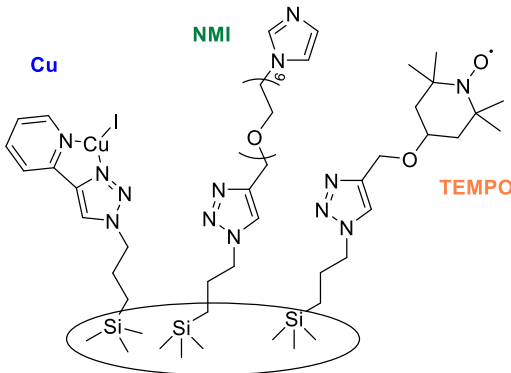
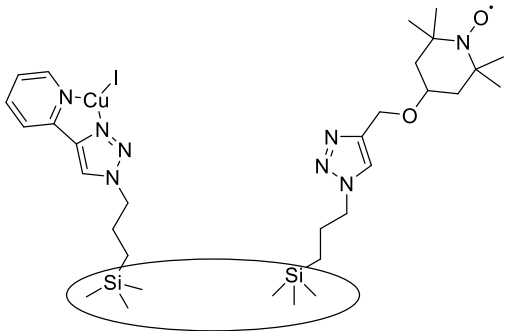
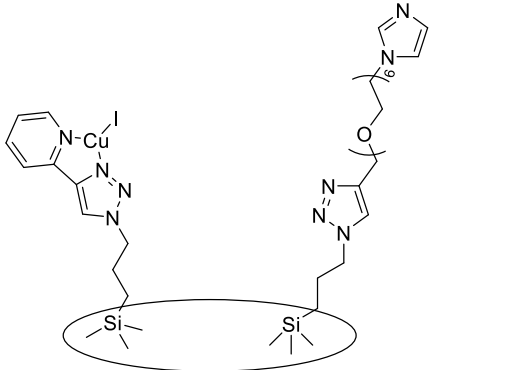
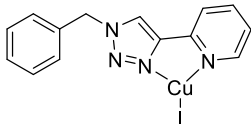
	
Catalyst	Conversion (time)/TOF
$\text{cis-Rh}_2[\mu\text{-S}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2\text{-}[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2(\text{CO})_2$ (Homogeneous complex)	Conversion: 44.1% (28 h) TOF: $0.11 \text{ min}^{-1}$
	Conversion: 98.2% (21 h) TOF: $0.49 \text{ min}^{-1}$
	Conversion: 98.6% (23.5 h) TOF: $0.88 \text{ min}^{-1}$

**Scheme 27.** 1,4-addition of phenylboronic acid using a SiO<sub>2</sub>-supported diaminorhodium-tertiary amine catalyst [193]

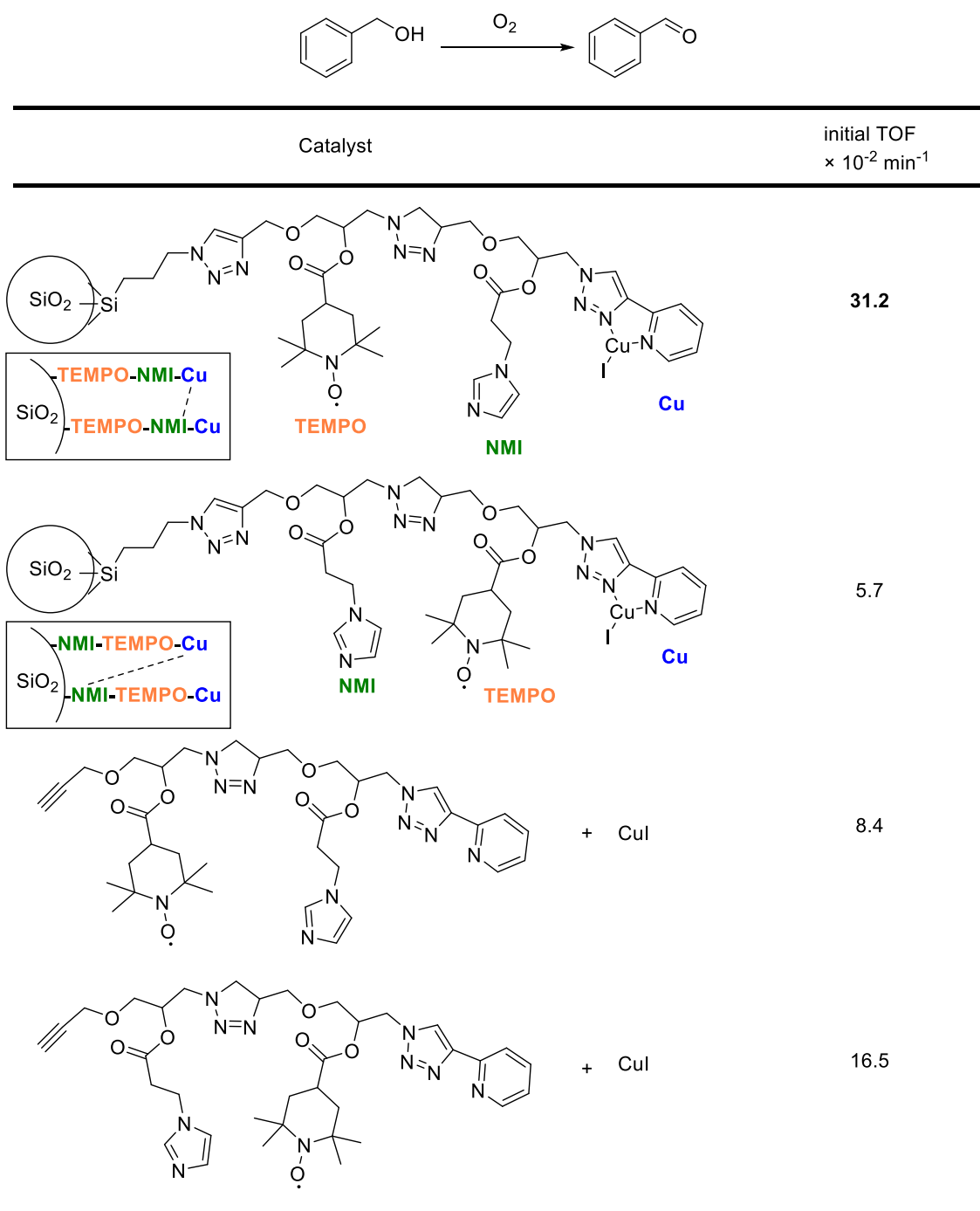


**Scheme 28.** Supported Cu-complex with NMI and TEMPO group for the aerobic oxidation of benzyl alcohol [196]

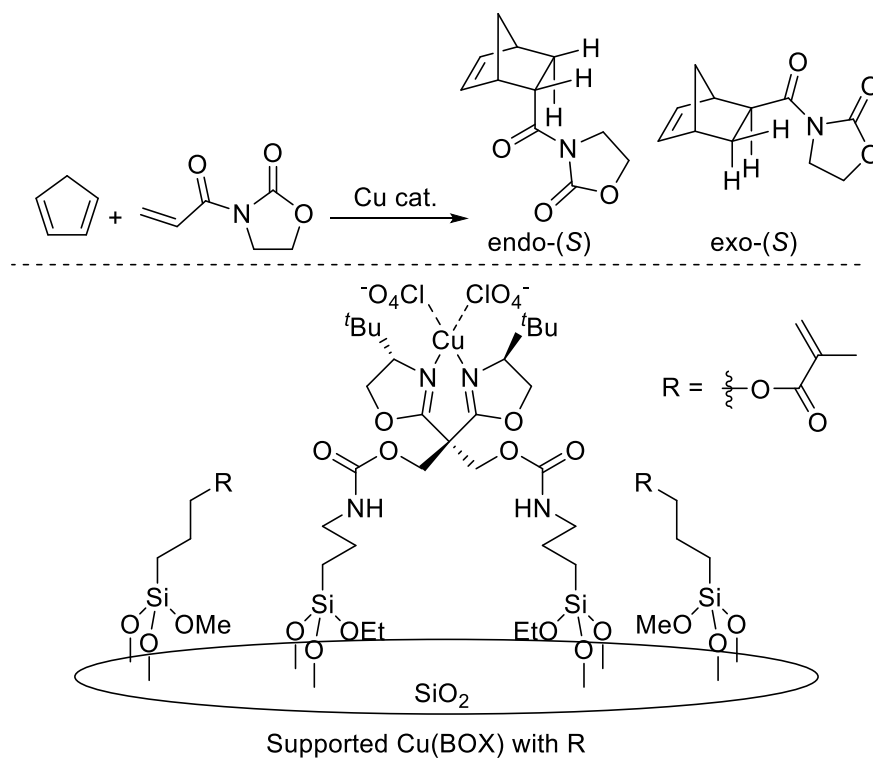


Catalyst	initial TOF × 10 <sup>-2</sup> min <sup>-1</sup>	
	55.1	
	+ NMI	25.4
	+ TEMPO	22.7
NMI + 	+ TEMPO (2:1:1)	11.9

**Scheme 29.** Supported Cu-NMI-TEMPO oligomer and comparison of their reaction rate with homogeneous oligomers [198]



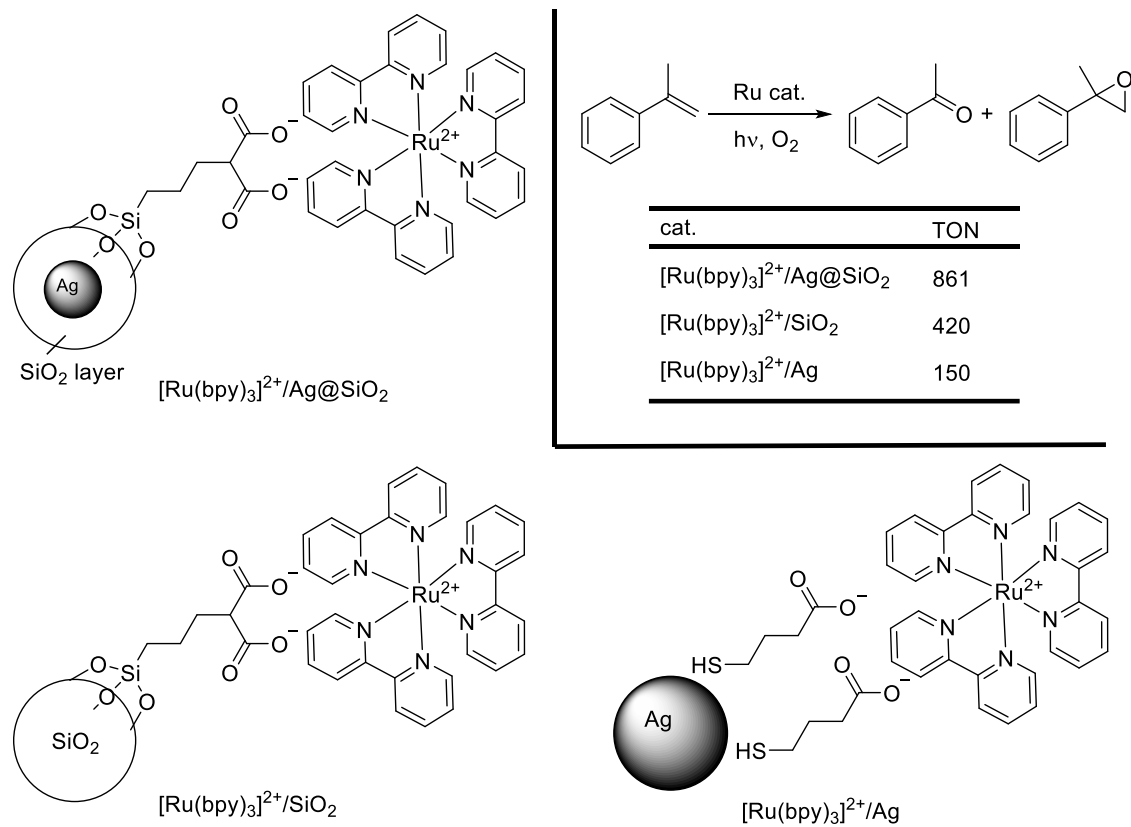
**Scheme 30.** Enantioselective Diels–Alder reaction promoted by a supported Cu complex with co-immobilized functionalities [201]



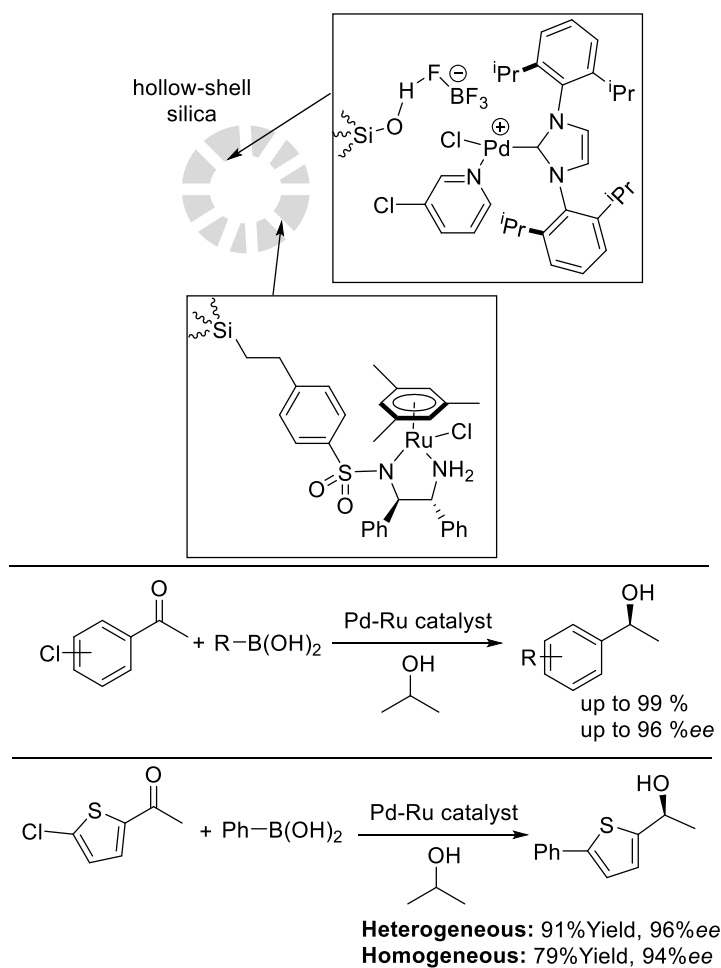
Cu cat.	conv. (%)	ee(S) of endo (%)
Cu(BOX)(OTf) <sub>2</sub> homogeneous	98 (4 h)	27
Supported Cu(BOX)	>99 (24 h)	14
Supported Cu(BOX) with R	>99 (24 h)	63



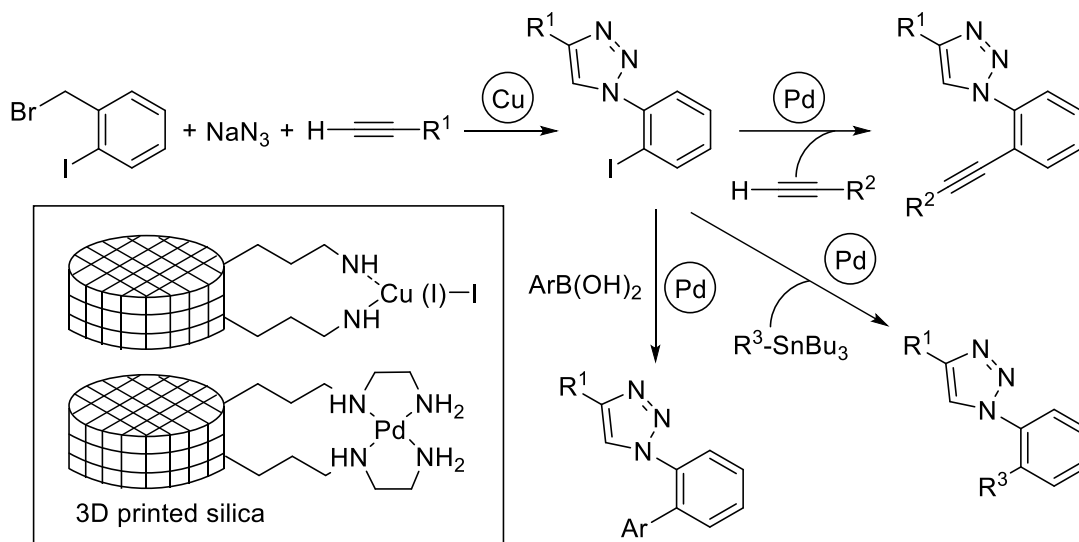
**Scheme 31.** Ag@SiO<sub>2</sub>-supported [Ru(bpy)<sub>3</sub>]<sup>2+</sup> for photooxidation of  $\alpha$ -methylstyrene [202]



**Scheme 32.** Hollow-shell silica-supported IPr-Pd complex and chiral Ru catalyst for the tandem Suzuki–Miyaura coupling–asymmetric hydrogen transfer reaction [204]



**Scheme 33.** 3D-printed silica-supported Pd and Cu complex for the tandem click reaction–Sonogashira/Stille/Suzuki–Miyaura coupling [205]



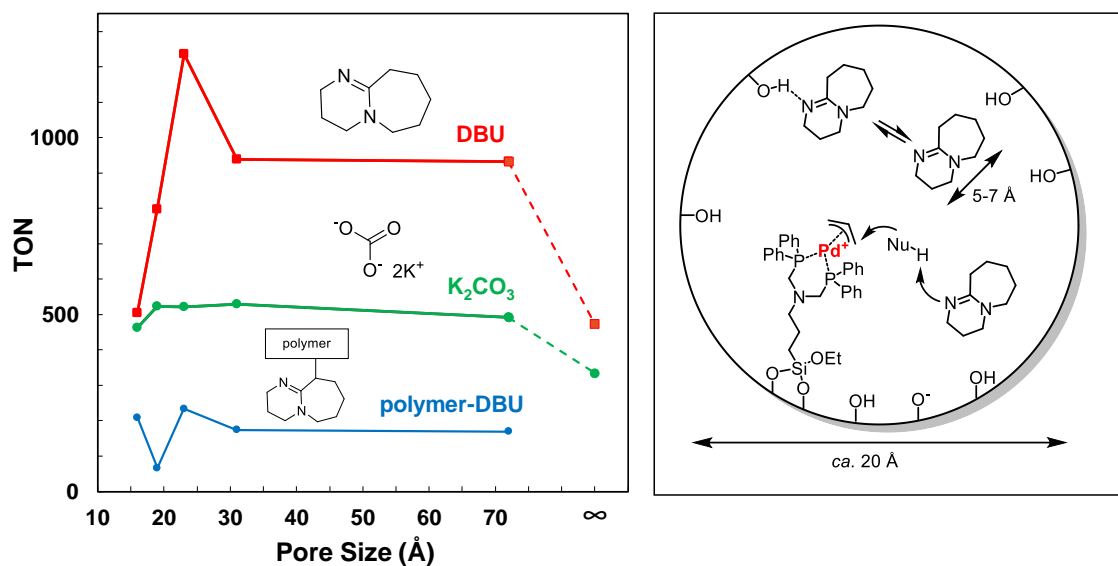
### 3. Confinement Effect/Molecular Imprinting for Enhanced Catalysis

The advantage of mesoporous supports is the active site accumulation effect. Li et al. reported the accumulation of a Co(salen) complex in an SBA-16 cavity.[206] The Co complex has a much higher activity with respect to the kinetic resolution of epoxide compared with homogeneous catalysis because of the cooperation of the two Co complexes in the cavity. The amine–silanol cooperative catalysis in the mesopores is also enhanced. Jones et al. reported the effect of the pore size on the aldol-type condensation reaction.[207] Our group also investigated the effect of the pore size on Pd-catalyzed allylation reactions.[208] **Figure 3** indicates that the effect of the pore size depends on the base additive. Based on the use of  $K_2CO_3$ , a frequently used inorganic base, the catalytic performance could be maintained at pore sizes ranging from 16 to 31 Å, whereas the maximum catalytic performance was observed for DBU at 23 Å. In the case of polymer-supported DBU as an additive, the catalytic activity is much lower for all catalysts because of the large size of the base compared with the pore size. Kinetic studies of the allylation using the MS/PP-Pd-DBU system imply that the maximum pre-exponential factor ( $A$ ) is reached at a size of 23 Å, whereas the activation energy insignificantly changes ( $E_a = 66.1\text{--}73.3 \text{ kJ mol}^{-1}$ ). These results indicate that the confinement of an appropriate pore enhances the accumulation of active species, DBU, and the Pd complex, resulting in a high catalytic performance.

An enhanced enantioselectivity by confinement effect has been reported in Rh complex-catalyzed reactions. **Table 3** shows the enantioselective hydrogenation of a diketone to the corresponding hydroxylketone catalyzed by the Rh complex located in the silica mesopores.[209] Both the reaction rate and enantioselectivity of the corresponding alcohol increased with the decrease in the size of mesopores. In addition, the structure of

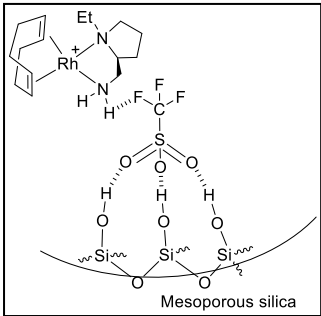
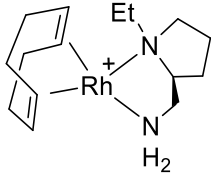
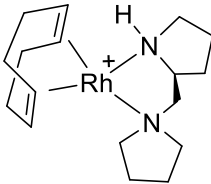
the asymmetric ligand of the Rh complex strongly depends on the catalysis. Note that the use of homogeneous Rh complexes with the same ligand does not yield a good performance in terms of both the catalytic activity (turnover frequency: TOF) and enantioselectivity. In addition to the above-mentioned example, there are many recent reports [210-222] and reviews [223-231] on approaches for asymmetric catalytic reactions using mesoporous supports or other heterogeneous media in both metal complex catalysis and organocatalysis.

A molecularly imprinted approach was tested for the chemoselective Pd-catalyzed Suzuki–Miyaura cross-coupling reaction. Muratsugu et al. reported a selective coupling reaction using a silica-supported Pd complex imprinted by SiO<sub>2</sub>-matrix overlayers.[232] The prepared imprinted catalyst was characterized by several spectroscopic techniques, indicating the presence of a Pd complex in the SiO<sub>2</sub>-matrix overlayer. As shown in **Scheme 34**, the template molecule (gray) structure is similar to the cross-coupling product with the *meta*-substituted group. The Suzuki–Miyaura coupling results are summarized in **Scheme 34**. The performance of the simple supported Pd complex is similar to that of *ortho*, *meta*, and *para*-propenyl iodobenzene with phenylboronic acid, whereas the reactivity of *ortho*-substituted iodobenzene is significantly lower in the case of the imprinted catalyst. Both *meta*- and *para*-substituted iodobenzenes might not be strongly affected by the cavity structure. The steric hindrance of the template cavity leads to a unique reactivity, which depends on the similarity of the substrate structure and cavity. There are various shape-selective approaches for silica-supported metal complex catalysis using the molecular imprinting technique.[233-244]

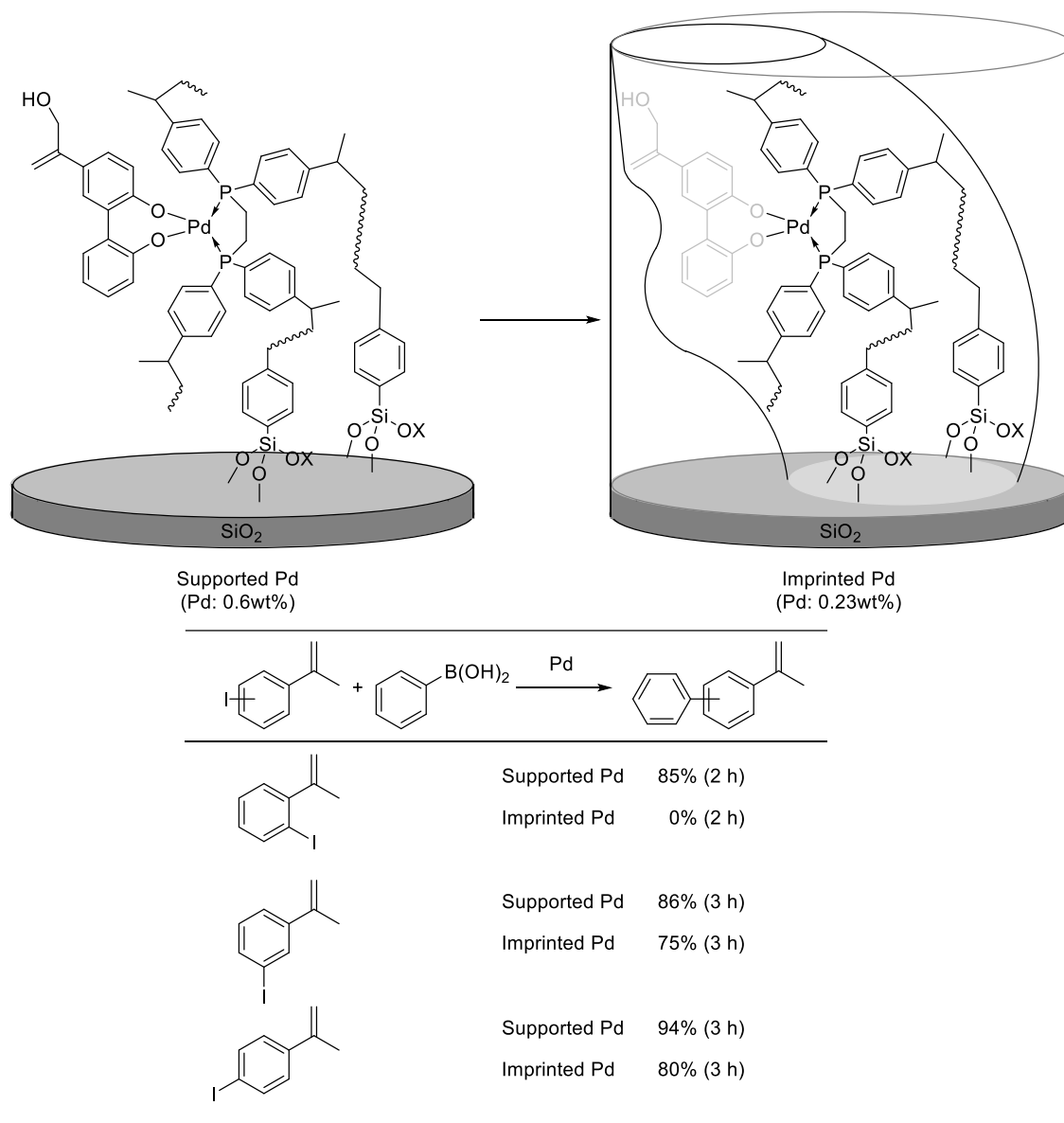


**Figure 3.** (left) Dependency of the TON of allylation on the pore size of the mesoporous silica support and (right) image of accumulation of DBU into a mesopore with appropriate pore size [208]

**Table 3.** Effect of the support pore size on the Rh complex-catalyzed enantioselective hydrogenation [209]

<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> <chem>COC(=O)C(=O)c1ccccc1</chem>  <math>\xrightarrow[40\text{ }^{\circ}\text{C, 30 min, MeOH 30 mL}]{\text{H}_2\text{ 20 bar, Rh / MS cat. 50 mg}}</math> <chem>COC(=O)[C@H](O)c1ccccc1</chem> </div> <div style="margin-left: 20px;">  </div> </div>				
Rh/MS Cat.	Pore size Å	Conversion (%)	TOF (h <sup>-1</sup> )	ee (%)
	38	82.6	542	82
	60	67.1	440	65
	250	44.6	292	0
	Homogeneous (2 h)	62	46	0
	38	92.8	643	85
	60	63.0	436	72
	250	60.7	420	65
	Homogeneous	46.2	145	53

**Scheme 34.** Pd complex catalyst imprinted on SiO<sub>2</sub> for the selective cross-coupling reaction [232]





#### 4. Supported metal complexes designed through SOMC

The SOMC concept has been applied to a variety of metal complexes, including Pd, Ni, Rh, and Ru, for organic transformation.[6] The use of both appropriate precursor metal complexes and pretreated silica supports enables the formation of active species on surfaces. Apler et al. carried out pioneering work on Pd complexes, which were directly immobilized onto silica surfaces for hydroamination.[245] As shown in **Scheme 35**, the reaction between the surface Si-OH and *trans*-[PdMe(NO<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>] leads to a silica-supported Pd complex and CH<sub>4</sub> formation. The supported catalyst has a good performance with respect to the intramolecular hydroamination of aminoalkynes (**Scheme 35**). The reaction of 5-phenyl-4-pentyn-1-amine leads to a quantitative yield of the corresponding cyclic imine. The reaction rate of the supported Pd catalyst is higher than that of the precursor metal complex.

Ishitani et al. reported asymmetric 1,4-addition using a silica-supported Ni catalyst.[246] Nickel-diamine complexes are known to be good enantioselective homogeneous catalysts for conjugate addition. The Ni-diamine complex can be easily attached to the silica MCM-41 surface via a simple wetness impregnation method. The reaction between dimethyl malonate and nitroalkene with 1 mol% of the supported Ni-diamine complex led to a quantitative yield of the corresponding product, with 90% ee (**Scheme 36**). The homogeneous catalyst NiI<sub>2</sub> with the same chiral ligand led to an ee of 90%, whereas the yield decreased to 46%. Supported Ni-diamine can be used on various substrates. The active site structure was clarified by Ni K-edge XAFS analysis (**Scheme 36**). This catalyst system is also applicable to the flow reactor: sequential 1,4-addition and reductive cyclization of dimethyl malonate and a nitroalkene yielded 89% of the corresponding  $\gamma$ -lactam, with 87% ee, suggesting that the catalyst system is truly

heterogeneous. Regarding another grafted Ni catalysis on a silica surface, a supported dinuclear Ni species for hydrogenation was also reported.[247]

A Rh-grafted on a silica surface with additional ligands was reported by Marciniak et al. as a heterogeneous hydrosilylation catalyst.[248-250] A Rh dimer with a cyclooctadiene (cod) ligand can be easily grafted on the silica surface in monomeric Rh form with the remaining cod ligand. The catalyst has a high activity and recyclability with respect to the hydrosilylation of terminal olefins (**Scheme 37**). The reaction mechanism was carefully analyzed by solid-state NMR spectroscopy of the reaction intermediates such as the Si-Rh-H species that formed after oxidative addition. Our research group also reported a silica-supported Rh complex with a co-immobilized tertiary amine for hydrosilylation.[251,252] As shown in **Scheme 38**, the catalytic activity was significantly improved by the co-immobilization of tertiary amines. After optimizing the reaction conditions, a TON value of up to 1900000 was achieved. The Rh K-edge XAFS, DNP-enhanced  $^{15}\text{N}$  CP/MAS NMR, and *in situ* FTIR analyses revealed that the tertiary amine weakly interacts with the cod ligand on the Rh site and the ligand exchange process is accelerated.[253] The Rh-grafted silica catalyst for the hydrosilylation of olefins has also been summarized in several reviews.[254,255] A Ru-grafted silica catalyst was also reported by Marciniak and co-workers for alkene metathesis reactions.[256]

The SOMC approach has also been applied to the synthesis of silica-supported metal complexes such as Mo, W, Ta, Zr, Ti, Cr, Nb, group 3 metals, and lanthanides. Recently, several comprehensive reviews have been published by Copéret et al. [257-259]. Therefore, brief introductions and very recent examples are summarized here.

**Scheme 39** summarizes important examples of silica-supported metal complex catalysts that are based on the SOMC concept. Grafted Mo and W alkylidene complexes

show excellent performance in alkene metathesis reactions.[260-262] Alkynes and alkane metathesis reactions have also been reported for other silica-supported Mo, W, Ta, and Re catalysts.[263-267] The supported Ta imido complex is active with respect to the heterometathesis reaction.[268] The heterogeneous Ta catalyst promotes the reaction between *N*-sulfinylamines and ketones, yielding the corresponding imines. Silica-supported Ta catalysts have a higher activity than their homogenous counterparts. The supported Ta catalysts were also active in the hydroamination [269,270] and H-D exchange reaction.[271] Recently, other titanium imido complexes active in the heterometathesis reaction have been reported (**Scheme 40**).[272] The silica-supported Ti imido complex with the 2,5-dimethylpyrrol ligand has an excellent reaction rate with respect to the oxo/imido heterometathesis of benzophenone and *N*-sulfinyl-*p*-toluidine. The reaction rate is superior to that reported for highly active Ta, Mo, and V catalysts. A supported cyclopentadienyl Zr alkyl complex has also been reported as an ethylene polymerization catalyst (**Scheme 39**).[273] The complex structure, its cation form, is strongly affected by the support: the catalytic activity for ethylene polymerization increases in the order of SiO<sub>2</sub> < silica-alumina (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) < Al<sub>2</sub>O<sub>3</sub>.

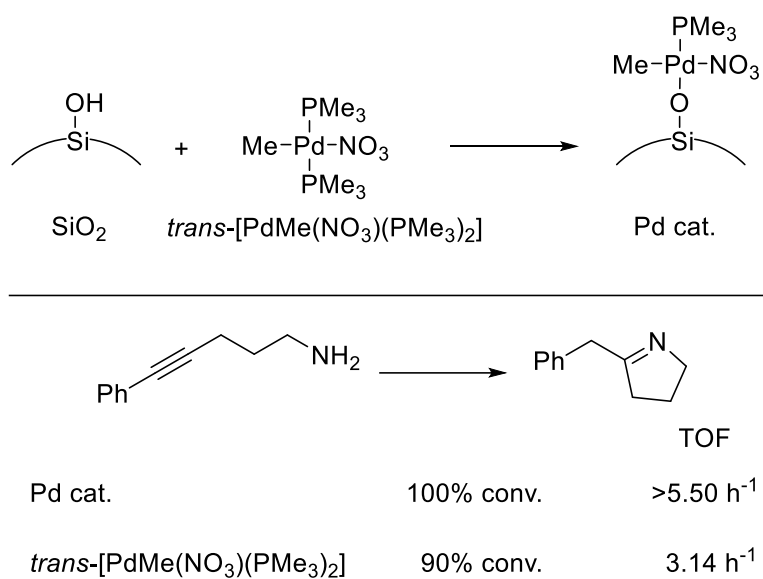
Wang et al. reported a silica-supported organolanthanum catalyst for the borylation of epoxides.[274] A La precursor complex, La{C(SiHMe<sub>2</sub>)<sub>3</sub>}, was directly attached to mesoporous silica nanospheres (MSN; **Scheme 41**). The silica support was treated at 550 and 700 °C under vacuum, denoted as MSN<sub>500</sub> and MSN<sub>700</sub>, respectively. The La precursor reacts with the surface Si-OH and a part of the La complex reacts with two Si-OH groups due to the higher Si-OH density of MSN<sub>500</sub>, resulting in the formation of both bipodal and monopodal La complexes on the SiO<sub>2</sub> surface. On the other hand, the catalyst prepared from MSN<sub>700</sub> yields a single La species in the monopodal form. The two

prepared catalysts were fully characterized by solid-state  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^1\text{H}$ - $^{29}\text{Si}$  HETCOR NMR analyses. The catalyst was employed for the reaction between the epoxide and HBpin. As shown in **Scheme 41**, the catalytic activity of the  $\text{La@MSN}_{700}$  catalyst is higher than that of its La precursor complex or similar. The  $\text{La@MSN}_{500}$  also has a comparable or slightly lower performance than  $\text{La@MSN}_{700}$ , which depends on the substrate molecules. The reaction intermediates, surface La-boran complexes and organoborans that reacted on the silica surface, were investigated using various solid-state  $^{11}\text{B}$  MAS NMR techniques.

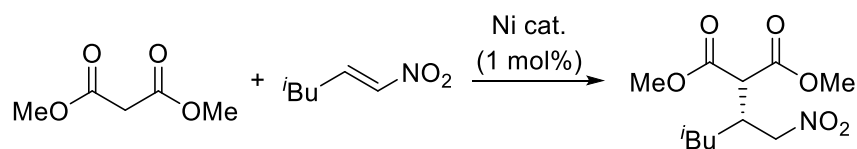
It has been reported that silica-supported Mn catalysts prepared from Mn complexes are hydrosilylation, hydroborylation, and transesterification catalysts.[275] As shown in **Scheme 42**, the surface Mn sites were prepared from a  $\text{Mn}(\text{N}(\text{TMS})_2)_2(\text{THF})$  complex and  $\text{SiO}_2$  treated at  $700\text{ }^\circ\text{C}$  under vacuum ( $\text{SiO}_{2-700}$ ). The isolated Si-OH induced the formation of a monomeric Mn complex on the silica surface. The surface complex was then treated at  $400\text{ }^\circ\text{C}$  under vacuum, leading to the formation of  $\text{Mn/SiO}_{2-400}$  as an isolated Mn site on the silica surface without ligands. The formation of Lewis acidic  $\text{Mn}^{\text{II}}$  sites was confirmed by FTIR, EPR, and XANES analyses. The prepared  $\text{Mn/SiO}_{2-400}$  has a high catalytic performance with respect to the hydroborylation and hydrosilylation of aldehydes and ketones. Conventional MnO did not show any catalytic activity for this reaction. The isolated Mn site on  $\text{SiO}_2$  can be used for the hydroborylation of secondary alcohols with bulky substitution groups such as tertiary butyl groups. A different Mn precursor of  $\text{Mn}_2[\text{OSi}(\text{OtBu})_3]_4$  was used to prepare the silica-supported catalyst. The catalyst was slightly less active for transesterification than  $\text{Mn/SiO}_{2-400}$  because of the hydrophobicity attributed to the remaining TMS group of  $\text{Mn/SiO}_{2-400}$ . Similar concept was applied to preparation of a site-isolated Co catalyst for C-H activation.[276]

A surface organohafunium complex was developed for ethylene homo- and 1-octene copolymerization.[277] The complex structure is illustrated in **Scheme 43**. Sulfonated aluminum and sulfonated zirconium were selected as support materials. Sulfonated aluminum showed better performance with respect to both homo- and copolymerization. The supported Hf complex with two methyl groups showed a higher activity for polymerization, whereas a superior 1-octene incorporation ratio was observed for the complex with the naphthyl group. The surface electronic effect induces different immobilization structures, supporting the group 4 metal complex via SOMC. In the case of electron-deficient supports, such as sulfonate aluminum,  $\text{Hf}^{\text{+}}\text{-support}^{-}$  interactions were generated, resulting in a high polymerization reaction performance. The appropriate selection of support is mandatory for active and selective metal complex-catalyzed reactions.[278]

**Scheme 35.** Intermolecular hydroamination of alkyne using a Pd complex [245]



**Scheme 36.** Asymmetric 1,4-addition using a supported Ni-diamine catalyst and its local structure [246]

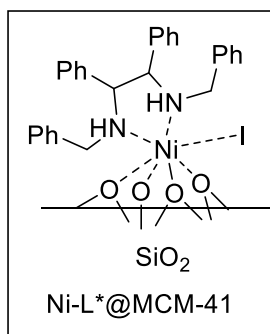
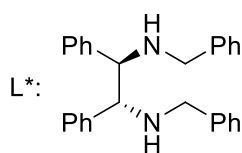


Ni-L\*@MCM-41

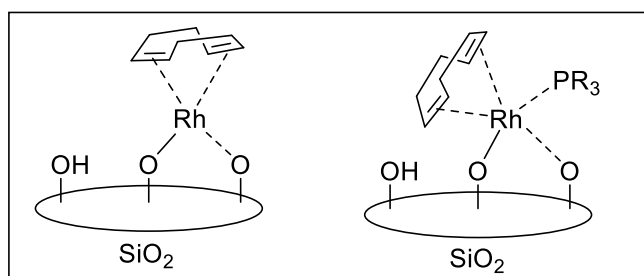
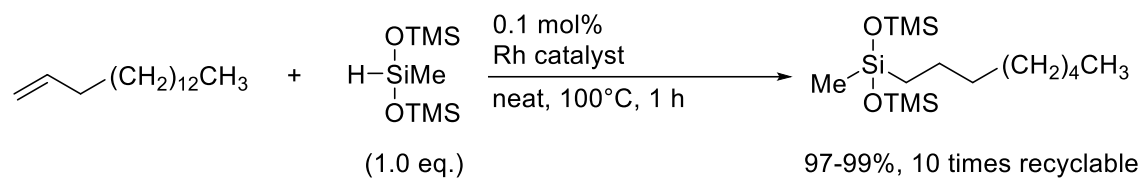
>99% yield, 90%ee

NiI<sub>2</sub> + L\*

46% yield, 90%ee

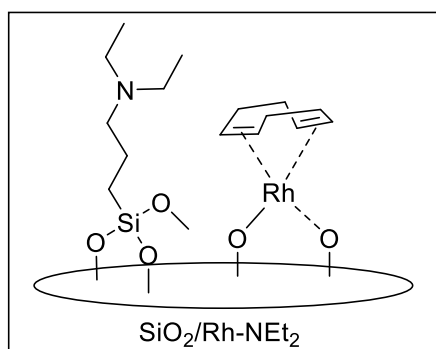
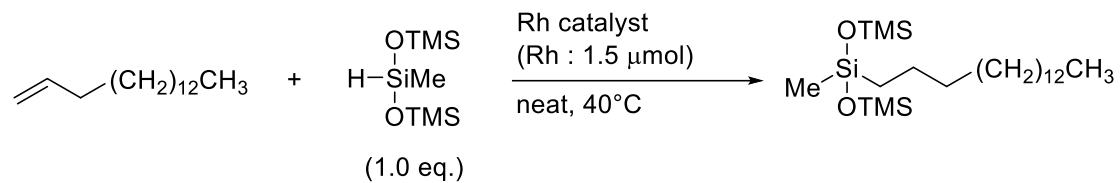


**Scheme 37.** Hydrosilylation of terminal olefin catalyzed with a silica-grafted Rh-cod complex [248-250]



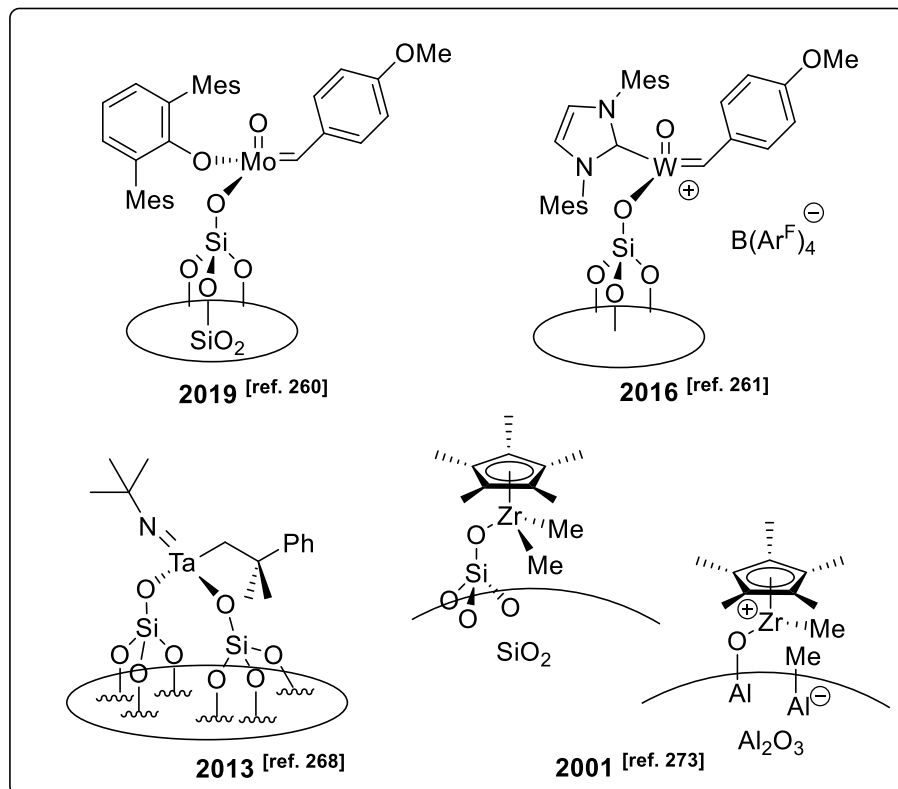


**Scheme 38.** Enhanced hydrosilylation catalysis by the co-immobilization of tertiary amine with a grafted Rh complex [251]

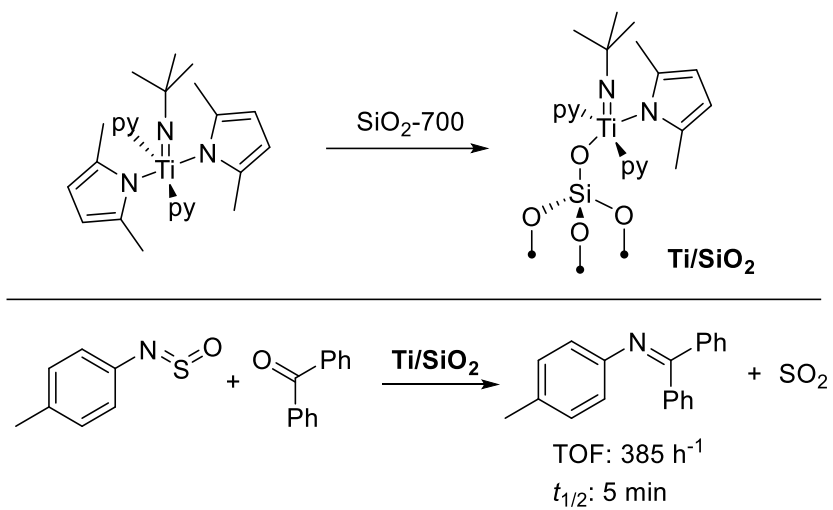


catalyst	yield (time)
SiO <sub>2</sub> /Rh-NEt <sub>2</sub>	96% (15 min)
SiO <sub>2</sub> /Rh	9% (30 min)
SiO <sub>2</sub> /NEt <sub>2</sub>	<1% (120 min)

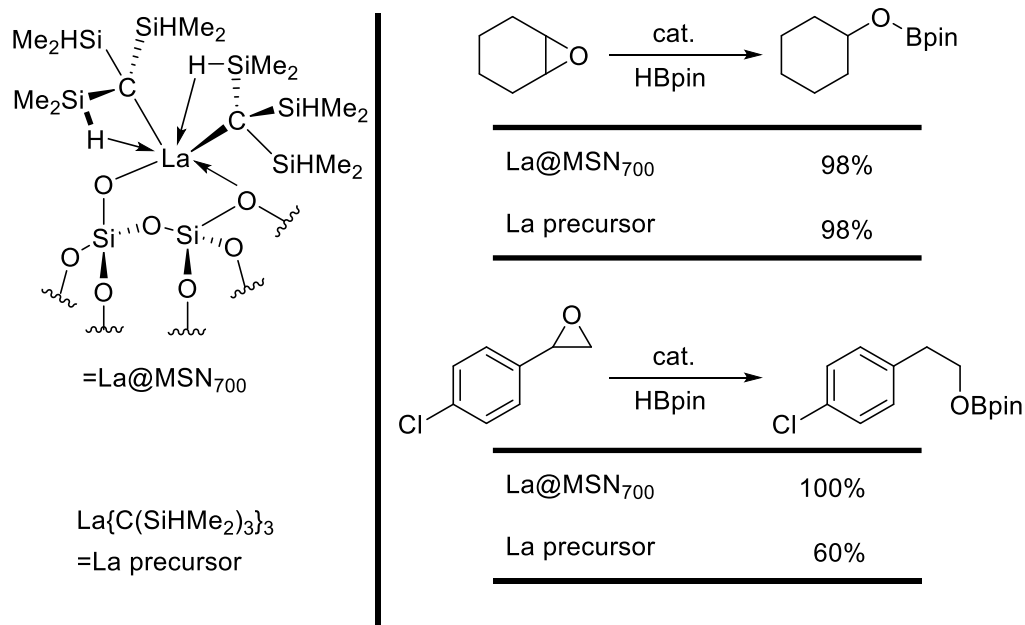
**Scheme 39.** Examples of silica-supported metal complex catalysts synthesized via SOMC [260,261,268,273]



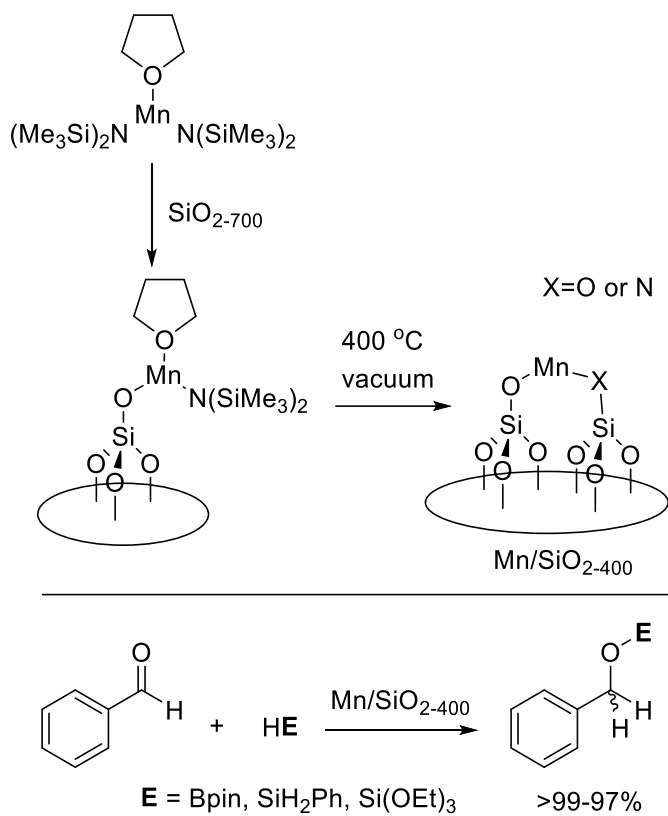
**Scheme 40.** Silica-supported Ti imido complex for oxo/imido heterometathesis [272]



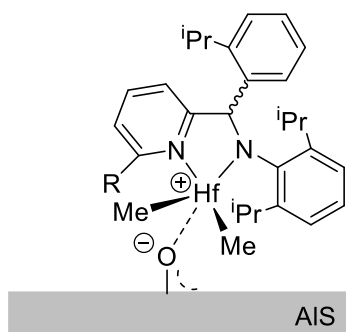
**Scheme 41.** Structure of the surface Lanthanum complex on MSN and its catalysis for the borylation of epoxide [274]



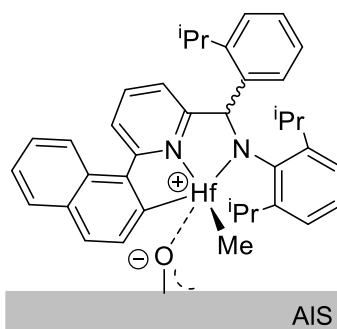
**Scheme 42.** Preparation of a surface Mn site on SiO<sub>2</sub> and its catalysis for hydroborylation and hydrosilylation [275]



**Scheme 43.** Metal sulfonate-supported organohafnium catalyst for homo- and copolymerization [277]



*Active for ethylene homo- and 1-octene copolymerization*



*High 1-octene incorporation ratio*

## 5. Summary and Outlook

Silica-supported metal complex hybrid catalysts with precisely controlled active site environments effectively enhance the catalytic performance including the activity, selectivity, and durability. In this review, we provided representative examples of silica-supported metal complexes with enhanced catalysis. Among the acceleration effects, “the site isolation” of active metal complexes on heterogeneous surfaces enables the creation of a novel metal complex structure on the silica surface. For example, silica-supported cage-type phosphane ligands act as efficient supports for isolated Pd, Rh, and Ir metal complexes [47,63,65,87]. The supported Fe complex structure is affected by the support morphology: the use of amorphous silica induces the coordination of two attached ligands around one Fe center, whereas an active 1/1 = Fe/ligand complex formed on the SBA-15 support surface.[113] Due to the site-isolation effect, coordinatively unsaturated surface metal complexes have a much higher performance than their homogeneous counterparts.

Cooperative catalysis between two different functionalities is one of the most powerful tools to enhance the catalytic performance. The Tsuji–Trost reaction is accelerated by bifunctional surfaces with both Pd complexes and tertiary amines. In such cases, the substrate molecules are activated synergistically.[127] The immobilization of oligomers is an effective procedure for enhancing the cooperativity of metal complexes and functionalities. The supported Cu complex-TEMPO-NMI oligomer system induces a high catalytic activity for the aerobic oxidation of alcohols.[198] Weak interactions of surface species also affect the catalytic activity: hydrosilylation catalyzed by the grafted Rh complex is accelerated by co-immobilized amine; the maximum TON is 1900000.[251] In addition to the organic functionality, surface silanol/metal nanoparticles also act as co-catalysts in the supported metal complex reaction.[148,153]

The confinement effect is an advantage of supported catalysis. A chiral Rh complex attached to the inside of mesoporous silica induces an increase in both the reaction rate and enantioselectivity.[209] In the case of the Pd complex-based additive system, the results of kinetic analysis reveal that the accumulation of active species in pores with an appropriate size enhances the contact frequency of the active species and substrate, leading to a high reaction rate.[208] Another important function of mesopores is the prevention of active sites from undesired interactions. The one-pot asymmetric reaction system using a PMO-supported Rh complex and enzyme leads to high product yield and enantioselectivity due to the prevention of the interaction with each other.[100] Related to the confinement effect, the molecular imprinting approach has further advantages because an on-demand void space can be designed to enhance the catalysis. A molecular imprinting approach using a silica matrix was developed for metal complex catalysis.[232]

Novel immobilization techniques have also been developed and utilized for supported metal complex catalysts. Regarding covalent bonding on a silica surface, tripodal immobilization of the silane-coupling reagent leads to lower levels of both metal and phosphine ligand leaching.[101] Ligands with carboxylic acid/sulfonic acid groups could flexibly and strongly interact with the silica surface, especially with the surface silanol group.[31,161] Such a catalyst system exhibits a good stability and durability. Ionic interactions between Si-OH and  $\text{BF}_4^-$  anions associated with cationic metal complexes are also frequently utilized.[149] The direct attachment of metal sites onto silica surfaces has also received much attention in SOMC. In the case of SOMC, the ligand attached to the metal site as well as the surface properties, such as electron-deficient phenomena, affect the catalytic activity.



Surface density of both active species and silanol group is essential to create the surface enhanced catalysis. Mori and co-workers reported an appropriate loading of a Pt complex for phoooxidation reaction.[45] The photoluminescence analysis of MLCT and MMLCT transitions could be used as an indicator of the surface dispersion of catalytically active species itself. Increasing the surface density facilitates specific interactions between the metal complex and co-immobilized organic functionality. For example, the surface density of the immobilized Rh complex and tertiary amine affects the catalytic activity (TOF) of Rh with respect to the 1,4-addition reaction of phenylboronic acid.[193] Careful selection of preheating conditions of a silica support is one of the critical factors to determine the active site structure, especially in the case of SOMC. For example, the structure and catalytic activity of surface La sites could be controlled by the density of silanol, resulting a uniform active species.[274] Regarding a novel grafting technique, Choi and co-workers recently reported the use of bidentate disilicate framework for the selective production of a specific surface Pt complex.[279] The catalytic performance often significantly increased by the site-isolation/cooperative catalysis design, however, unfortunately, especially in the case of bifunctional catalytic surface, it is not easy to control the distance between two different functionalities precisely. The use of a weak interaction in the precursor solution including both of active species is one of the potential solutions to control their cooperativity.[251]

To understand the enhancement of catalysis by the surface environment, precise spectroscopic analyses of the local structure around active metal centers and long-range interactions between a metal complex and surface/other functionality are mandatory. The DNP-enhanced solid-state NMR spectroscopy [280-282] was conducted for the immobilized NHC-Pd complex.[33] The  $^1\text{H}$ - $^{13}\text{C}$  HETCOR NMR with long contact times

facilitates the detection of long-range correlation between allyl/mesityl carbon and surface TMS sites, indicating the close location of the Pd metal center and silica surface. The X-ray reflectivity measurements of a supported Rh complex on a model SiO<sub>2</sub> crystal surface also indicated a similar lying structure of the complex with the methylene linker.[194] The XAFS analysis also provided information on the interaction between the metal complex and co-immobilized molecules. The Pd K-edge EXAFS analysis of the silica-supported Pd complex indicated that the DW factor increases with increasing bulkiness of the co-immobilized molecules, suggesting the close proximity of the co-immobilized functionality.[131] However, quantitative parameters with respect to long-range information about the activity/selectivity enhancing the interactions among the metal complex, silica surface, pore size, and co-immobilized molecules remain unexplored. Spectroscopic techniques for long-range analysis must be further developed.

Reaction sequences on multi-active sites, including metal complexes, are also advantageous for tandem catalysis. Several reaction systems exhibit a better performance than a homogeneous mixture of the two counterparts.[204] In addition to tandem reactions, two or more active species should cooperate in a single reaction in such cases. The mixing of two catalytically active sites and the precise control of these positions should facilitate consecutive synergistic catalysis. Based on the above-mentioned approaches to enhance the catalysis, novel design concepts for supported catalysts, such as the use of two types of metal complexes for synergistic activation, will be established along with molecular-level characterization, resulting in highly efficient and challenging molecular transformations.

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