Accounts

New Design in Homogeneous Palladium Catalysis: Study of Transformation of Group 14 Element Compounds and Development of Nanosize Palladium Catalysts[†]

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This account reports an overview of our findings in homogeneous Pd-catalyzed reactions. Herein we describe the new design in reactions of Group 14 element compounds and in homogeneous nanosize Pd catalysts. In the early stages of our study, we developed Pd-catalyzed transformations of allylic esters with disilanes, silylcyanides and acylsilanes to the corresponding silylation, cyanation and acylation products, respectively. We also developed a Pd-catalyzed three component coupling reaction of Group 14 element compounds involving 1,3-diene and acid chlorides to form β,γ-unsaturated ketone as a single product. Recently, we focus our attention on modifying the catalytic environment by nanosize Pd in order to improve the performance of Pd catalysts. These nanosystems realize efficient catalytic environment with remarkable enhancement in catalytic activity and unprecedented selectivity.

Key Words : Palladium, Homogeneous catalysis, Group 14 element compounds, Nanosize

Introduction

Pd-catalyzed reactions have been developed as one of the most versatile methods for the synthesis of various useful organic molecules.[1] A wide range of Pd catalysts have been employed in many carbon-carbon bond formation reactions such as Suzuki-Miyaura,[2] Mizoroki-Heck,[3] Stille[4] and Sonogashira[5] coupling reactions. Oxidation of organic molecules including Wacker reaction,[6] oxidative coupling[7] and aerobic oxidation of alcohol[8] are also important reactions.

A serious problem in Pd catalysis is decomposition of the homogeneous catalysts into inactive bulk metal, *i.e.*, palladium black. To improve performance of Pd catalysts, modification of catalysts is necessary and this is usually carried out within a close proximity of a metal center (within a few angstroms). This conventional method is effective to develop active catalysts in various reactions. However, recently the catalytic environment is expanded to a nanosize, and this unique environment has the potential to add new properties to homogeneous catalysis.[9]

In this account, we overview our findings in homogeneous Pd-catalyzed reactions, in which organosilanes and/or -stannanes are converted very efficiently to afford a variety of products.[10] We also describe homogeneous nanosize Pd catalysts.[9] Well-defined nanosize ligands realize efficient and unique catalyst system.

Development of Pd-Catalyzed Reactions of Group 14 Element Compounds

Reactions of Allylic Esters with Disilanes. Pd(0)-catalyzed nucleophilic substitution of allylic esters *via* η^3-allylpalladium intermediate is one of the most important homogeneous catalysis reactions.[1] We have developed Pd-catalyzed silylation,[11] cyanation[12,13] and acylation[14] reactions.
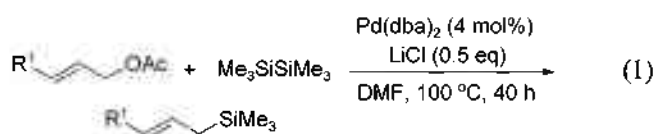
Silylation of allylic esters must be a promising synthetic method of allylic silanes, which have a large number of applications in organic synthesis.[15] Allylic acetates are smoothly silylated using organodisilane in the presence of the Pd(dba)$_2$-LiCl catalyst system at 100 °C (eq. 1).[11] Aliphatic and alicyclic acetates are readily silylated with Me$_3$SiSiMe$_3$ without β-hydride elimination. Addition of
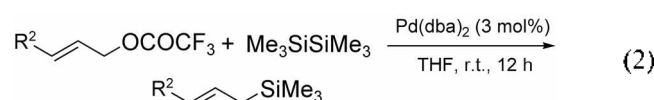
Yasushi Tsuji received his Ph D. in 1981 from Kyoto University under supervision of Prof. Y. Takegami. Subsequently, he became an Assistant Professor at Kyoto University. From 1986-1987, he conducted postdoctoral research with Prof. Tobin J. Marks at Northwestern University, USA. In 1989, he was appointed to Associate Professor at Gifu University. In 1998, he was Associate Professor at Institute for Molecular Science, then promoted to Professor at Hokkaido University in the same year. In 2006, he moved back to Kyoto University. He was

honored with the Chemical Society of Japan Award for Creative Work in 2002. His current research interest is development of homogeneous molecular catalysts with unique function.
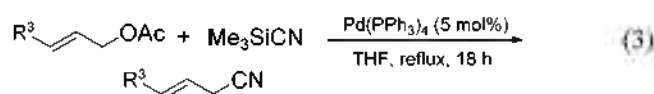Tetsuaki Fujihara received his Ph D. in 2001 from Hokkaido University under supervision of Prof. Y. Sasaki and Prof. T. Imamura. Subsequently, he conducted postdoctoral research with Prof. K. Tanaka at Institute for Molecular Science. In 2004, he moved to Hokkaido University as a postdoctoral fellow in Prof. Y. Tsuji's group. He was appointed an Assistant Professor at Kyoto University in 2006. His research interest is focused on the development of molecular catalysts bearing dendritic frameworks.

$$R^1 \diagdown\diagup OAc + Me_3SiSiMe_3 \xrightarrow[\text{DMF, 100 °C, 40 h}]{\substack{\text{Pd(dba)}_2 \text{ (4 mol\%)} \\ \text{LiCl (0.5 eq)}}} \qquad (1)$$

$$R^1 \diagdown\diagup SiMe_3$$

lithium chloride is indispensable; no products are obtained without the salt. Remarkable improvement of the silylation is realized by employing allylic trifluoroacetates in place of acetates as the substrate. The silylation proceeds even at room temperature and the added LiCl is not necessary in the catalytic system (eq. 2).
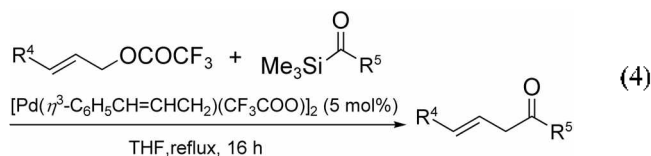
$$R^2 \diagdown\diagup OCOCF_3 + Me_3SiSiMe_3 \xrightarrow[\text{THF, r.t., 12 h}]{\text{Pd(dba)}_2 \text{ (3 mol\%)}} \qquad (2)$$

$$R^2 \diagdown\diagup SiMe_3$$

Reactions of Allylic Esters with Silylcyanides. We found the first example of cyanation of allylic esters catalyzed by a Pd complexes.[12] The reaction of allylic acetates with Me₃SiCN in the presence of Pd(PPh₃)₄ affords allylic cyanides regio- and stereoselectively (eq. 3). The choice of catalyst precursor is very important. Pd(PPh₃)₄ and Pd(CO)-(PPh₃)₃ show high catalytic activity. However, other representative precursors such as Pd(dba)₂, Pd(OAc)₂ and

$$R^3 \diagdown\diagup OAc + Me_3SiCN \xrightarrow[\text{THF, reflux, 18 h}]{\text{Pd(PPh}_3)_4 \text{ (5 mol\%)}} \qquad (3)$$

$$R^3 \diagdown\diagup CN$$

PdCl₂(PPh₃)₂ are not effective. Propargylic carbonates are also cyanated with Me₃SiCN in the presence of Pd(PPh₃)₄ as a catalyst.[13]

Reactions of Allylic Esters with Acylsilanes. When the reaction of 3-phenylpropionyltrimethylsilane with cinnamyl
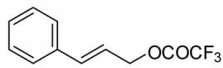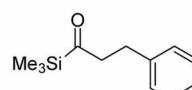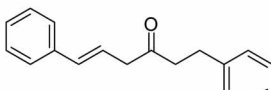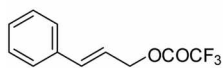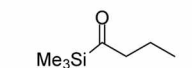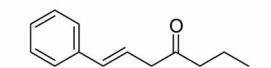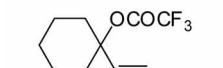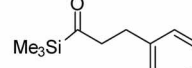
trifluoroacetate was carried out in the presence of catalytic amount of [Pd(η^3-C₆H₅CH=CHCH₂)(CF₃COO)]₂ in THF, the acylation product was obtained in 78% yield (eq. 4 and Table 1).[14] The product is only β,γ-unsaturated ketone, and no α,β-unsaturated isomers are detected. The acylation reaction of cinnamyl trifluoroacetate with various acylsilanes gives the corresponding (E)-β,γ-unsaturated ketones

$$R^4 \diagdown\diagup OCOCF_3 + Me_3Si\overset{O}{\underset{}{\diagdown}}R^5$$

$$\xrightarrow[\text{THF, reflux, 16 h}]{[\text{Pd}(\eta^3\text{-C}_6\text{H}_5\text{CH=CHCH}_2)(\text{CF}_3\text{COO})]_2 \text{ (5 mol\%)}} R^4 \diagdown\diagup\overset{O}{\underset{}{\diagdown}}R^5 \qquad (4)$$

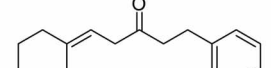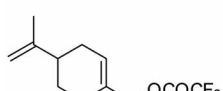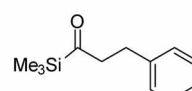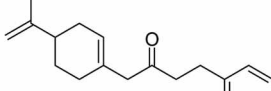regio- and stereoselectively (Table 1). Noteworthy is that leaving group of the allylic ester affects the reaction considerably. The trifluoroacetates give the highest yields. The corresponding cinnamyl pentafluoropropionate and dichlorofluoroacetate afforded the products in 67% and 54%, respectively. The cinnamyl carbonate only provided the product in 7% yield. Furthermore, the corresponding trichloroacetate and acetate did not give any acylation product at all. DFT calculation using a model compound suggests that the lowering LUMO level of η^3-allylpalladium species containing CF₃COO moiety would be indispensable.

A possible catalytic cycle of these series of reactions is shown in Scheme 1. The catalytic cycle will be initiated by the oxidative addition of allylic ester to Pd(0) species to give an η^3-allylpalladium complex (step a). Subsequently, the complex reacts with the corresponding organosilanes to afford the corresponding intermediate (step b). Finally, reductive elimination can provide the desired product and regenerates the active catalyst species (step c). In the reactions of allylic esters, the silyl moiety effectively traps

Table 1. Pd-catalyzed acylation of allylic trifluoroacetates[a]

$$R^4 \diagdown\diagup OCOCF_3 + Me_3Si\overset{O}{\underset{}{\diagdown}}R^5 \longrightarrow R^4 \diagdown\diagup\overset{O}{\underset{}{\diagdown}}R^5$$

Allyl trifluoroacetate	Acylsilane	Product	Yield (%)[b]
			60(78)
			55(65)
			46
			36(49)

[a]Allylic trifluoroacetate (1.0 mmol), acylsilane (0.5 mmol), [Pd(η^3-C₆H₅CH=CHCH₂)(CF₃COO)]₂ (0.025 mmol), THF, reflux, 16 h. [b]Isolated yields. Numbers in parentheses show GC yield.
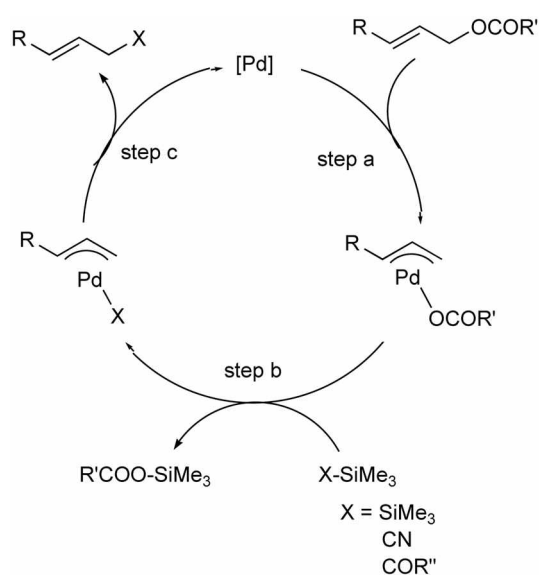
Scheme 1

the oxygen-containing leaving groups by forming the Si-O bond. Strong oxophilicity of the silicon atom may be an important driving force for these successful reactions.

The Pd-catalyzed acylation can be carried out with acylstannanes.[16] The reaction serves as a complementary method to the acylation with the acylsilanes. In particular, the acylation is profitable in the acylation of unsubstituted allyl trifluoroacetate and benzoylation of allylic trifluoroacetates.

1,4-Carbosilylation of 1,3-Dienes. Silicon-carbon bonds are prepared by a wide range of methods such as hydrosilylation.[15] Among them, addition of C-Si bond to unsaturated substrates, carbosilylation,[17] might be far more beneficial. We have developed a Pd-catalyzed three component coupling reaction of organodisilanes, 1,3-dienes and acid chlorides to afford allylic silanes as the product.[18]

An acid chloride reacts with a hexamethyldisilane and a 1,3-butadiene in the presence of a catalytic amount of Pd(dba)₂ to afford the coupling product in high yield (eq. 5 and Table 2). The carbon and the silyl substituents are introduced regio- and steroselectively at the 1- and 4-positions of the butadiene providing only (*E*) isomer as listed in Table 2. Effects of reaction conditions and catalyst precursors were examined. As a solvent, toluene gives the best results; THF and DMF lower the yields considerably. As a catalyst precursor, Pd(dba)₂, which is a naked Pd(0) complex without donating ligands, is most effective. Pd(PPh₃)₄ and PdCl₂(PPh₃)₂ are not active as the catalyst. In the reaction, the decarbonylation from the acid chlorides

(5)
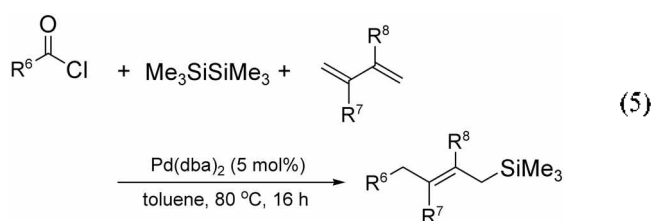
**Table 2.** 1,4-Carbosilylation of 1,3-diene using acid chlorides and Me₃SiSiMe₃[a]

Acid chloride	1,3-Diene	Product	Yield (%)[b]
			86
			90
			77
			94[c]
			78[c]
			72[c]
			82[d]
			47[e]

[a]Acid chloride (0.5 mmol), Me₃SiSiMe₃ (0.5 mmol), 1,3-diene (1.5 mmol), Pd(dba)₂ (0.025 mmol; 5 mol%), toluene, 80 °C, 4 h. [b]Isolated yields. [c](*E*)-Isomer. [d](*E*)/(*Z*) = 75/25. [e](*E*)/(*Z*) = 65/35.

takes place completely. Highly unsaturated nature of the Pd catalyst-center might facilitate such a fast and complete decarbonylation. When the reaction is carried out under carbon monoxide atmosphere, consumption of an acid chloride is low and the desired coupling product is not obtained.

A possible catalytic cycle for the reaction *via* the decarbonylation is shown in Scheme 2. Oxidative addition of the acid chloride to the Pd(0) species initiates the catalytic cycle and affords acyl palladium species. After the decarbonylation, the 1,3-diene inserts into the resulting Pd-C bond providing the allylchloropalladium intermediate. Transmetallation of the disilane with the intermediate may provide allylsilyl species with a concomitant formation of the silyl chloride. Finally, reductive elimination affords the allylic silane as the product and regenerates the Pd(0) active catalyst.

We also developed metal-catalyzed addition of organosilylstannanes (Si-Sn) to 1,3-dienes[19] or alkenes.[20] Organo-
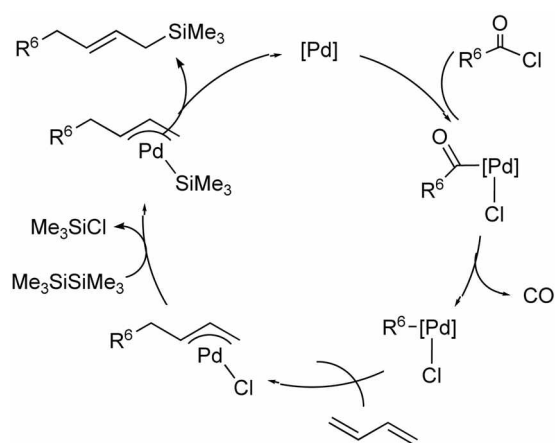
Scheme 2

distannanes (Sn-Sn)[21,22] and -disilanes (Si-Si)[22,23] also add to 1,3-dienes efficiently. Pd and Pt complexes containing *cis*-bis(stannyl)bis(phosphine)[24,25] and *cis*-bis(silyl)bis(phosphine)[25] moieties show unique fluxional behavior called twist-rotation.

Development of Well-Defined Nanosize Ligands

Bowl-Shaped Phosphine Ligands. Phosphines are one of the most important types of ligands in a homogeneous transition-metal catalyzed reaction. Thus, various phosphine compounds have been designed to bring about high catalytic activity and selectivity.[26] As a new class of phosphines, a bowl-shaped phosphine (BSP), tris(2,2",6,6"-tetramethyl-*m*-terphenyl-5'-yl)phosphine (**1b**: R^9 = Me, R^{10} = H in Scheme 3), was reported.[27] The bulkiness of BSP occurs on the periphery of the phosphine (at the rim of the bowl) with substantial empty space around the phosphorus atom as shown in Figure 1. On the contrary, P(*t*-Bu)₃ has severe steric congestion within close proximity of the phosphorus atom. Thus, the nature of bulkiness is quite different between BSP and P(*t*-Bu)₃. Our interest was focused on the application of BSP in catalysis.[28,29]

We found that BSP ligands were highly effective in Pd-catalyzed Suzuki-Miyaura coupling[2] of unactivated aryl chlorides,[29] which are more difficult to be used as the substrates.[30] The reaction was carried out using 4-chloro-toluene as the substrate in the presence of Pd₂(dba)₃ and ligand in THF at 50 °C (Table 3). Although the BSP ligand **1a** having a *m*-terphenyl group without any substituent affords the product only in 1% (entry 1), the BSP ligands **1b**, **1c** and **1d** bearing methyl substituents at the 2,2",6,6" positions of the *m*-terphenyl group afford the product in 50%, 74%, and 86% yields, respectively (entries 2-4). Interestingly, a BSP ligand **1e** bearing the higher dendritic moiety as the ligand provids the product in 89% yield (entry 5). In contrast, representative triarylphosphines such as PPh₃, P(*o*-Tol)₃, and P(Mes)₃ give almost no coupling adduct (entries 6-8). P(*t*-Bu)₃ and PCy₃ are not so effective as shown in entries 9 and 10.

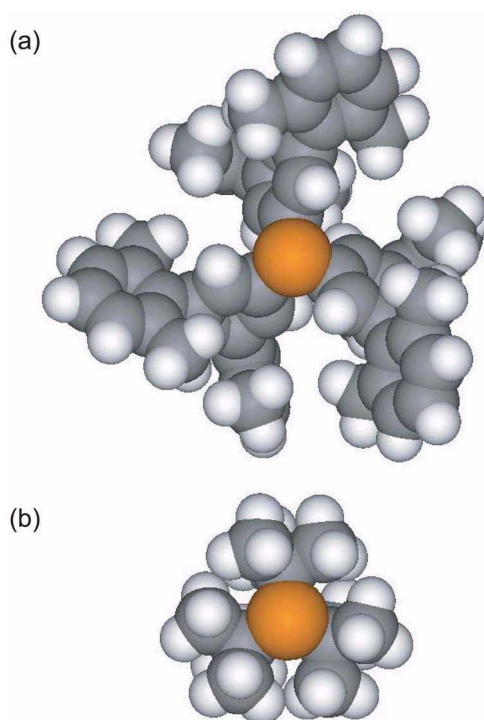To elucidate the different effectiveness of BSP in the

Figure 1. Optimized structures of (a) BSP (**1b**) and (b) P(*t*-Bu)₃ by HF/6-31G(d)-CONFLEX/MM3.

coupling reaction (entries 1-5 in Table 3), two critical parameters, basicity and cone angle, of the phosphines were examined. So far, these two electronic and steric parameters successfully rationalize influence of phosphine ligands in many transition-metal catalyzed reactions. The basicity of phosphines is evaluated by two methods: theoretical calculation (HF/6-31G(d)) of the molecular electrostatic potential (V_{min}[31]: more negative values indicate more basic

Table 3. Effect of triarylphosphine ligands on the Suzuki-Miyaura coupling of 4-chlorotoluene with phenylboronic acid[a]
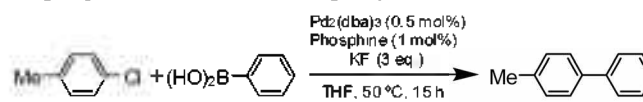
Entry	Ligand	Basicity		Cone angle (deg)[b]	Yield (%)[d]
		V_{min}[b]	$^1J_{P-Se}$		
1	**1a**	−41.6	766	193	1
2	**1b**	−41.0	770	205	50
3	**1c**	−42.8	741	210	74
4	**1d**	−42.5	743	221	86
5	**1e**	−39.8	770	268	89
6	PPh₃	−42.2	735	168	0
7	P(*o*-tol)₃	−44.4	732	218	1
8	P(Mes)₃	−44.6	−[c]	243	0
9	P(*t*-Bu)₃	−54.4	686	181	0
10	PCy₃	−54.4	674	188	13

[a]Reaction conditions: 4-chlorotoluene (1.0 mmol), phenylboronic acid (1.5 mmol), KF (3.0 mmol), THF (1 mL), Pd₂(dba)₃·CHCl₃ (0.005 mmol), ligand (0.010 mmol; P/Pd = 1), 50 °C, 15 h. [b]HF/6-31G(d). [c]Corresponding phosphine selenide is not available. [d]GC yield.

phosphines) and $^1J_{P-Se}$ coupling constants[32] of the corresponding phosphine selenides Se=PR$_3$ (smaller values correspond to higher basicity). In addition, the cone angles of the phosphines were measured according to Tolman's definition[33] using structures optimized by the HF/6-31G(d)-CONFLEX/MM3 calculations. These electronic and steric parameters are listed in Table 3. The effective (**1a-1e**) and the ineffective (**1a**) BSP have essentially similar basicity comparable to those of triarylphosphines such as PPh$_3$. Furthermore, a particular range of the cone angles for the effective ligands cannot be determined. Thus, neither the basicity nor the cone angle shows evident correlations with the efficacy of the phosphines.

In order to understand this phenomenon, we turned our attention to the shape of BSP. The depths (*d*) and the diameters (*l*) of BSP (**1a-1e**) measured on the optimized (HF/6-31G(d)-CONFLEX/MM3) structures are shown in Scheme 3. It is noteworthy that the deeper bowls (**1b-1e**) are apparently effective, but the shallower bowl (**1a**) is not. This observation is very much comparable to the case of the rhodium-catalyzed hydrosilylation of ketones with BSP.[28]

Ligands with Tetraphenylphenyl Moiety. Dendritic frameworks have received considerable attention to develop new materials including catalysts.[34] Among them, a 2,3,4,5-tetraphenylphenyl (TPPh) and its higher dendritic moieties developed by Müllen and co-workers have been utilized as building blocks for polyphenylene nanomaterials.[35] We are interested in their spatially spread and rigid structure of the
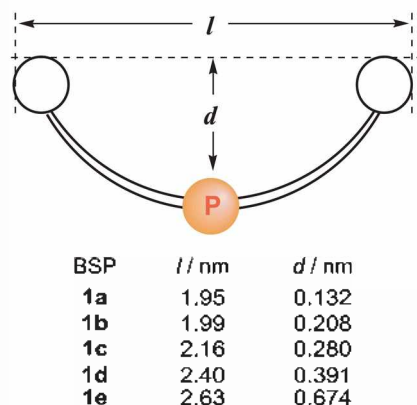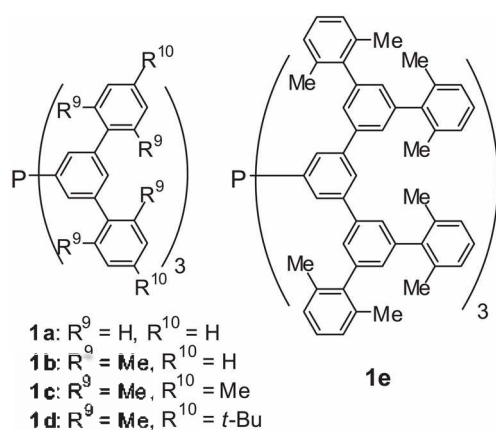
TPPh moiety.[36-38]

A series of triarylphosphines bearing a TPPh moiety on one of the phenyl rings of triphenylphosphine (*ortho-*: **2a**, *meta-*: **2b**, *para-*: **2c**) were synthesized (Scheme 4).[36] The X-ray crystal structure of the Pd(0) complex having **2a** as a ligand shows the η-coordination geometry on the TPPh moiety (Figure 2). Actually, the phosphine **2a** was employed as a ligand in Suzuki-Miyaura coupling[2] of 4-chlorotoluene with phenylboronic acid in the presence of Pd$_2$(dba)$_3$ in THF at 50 °C (S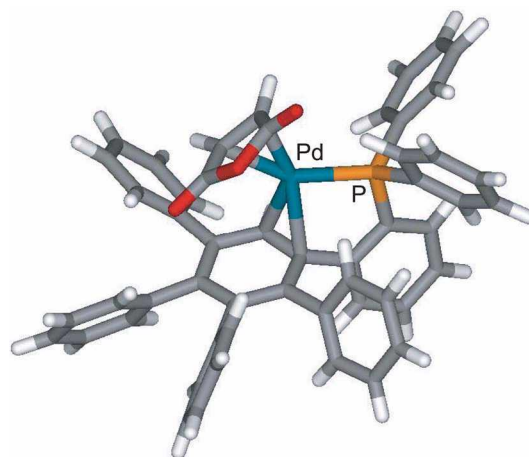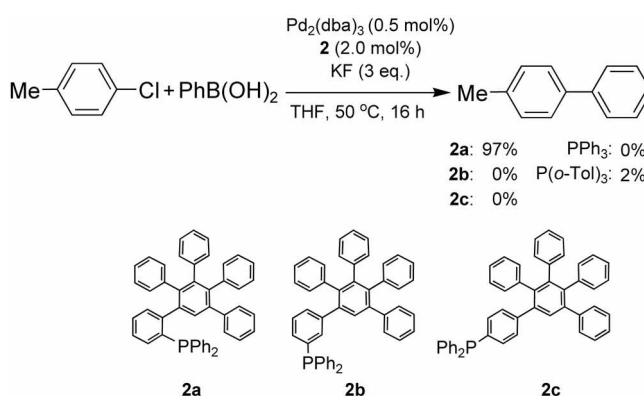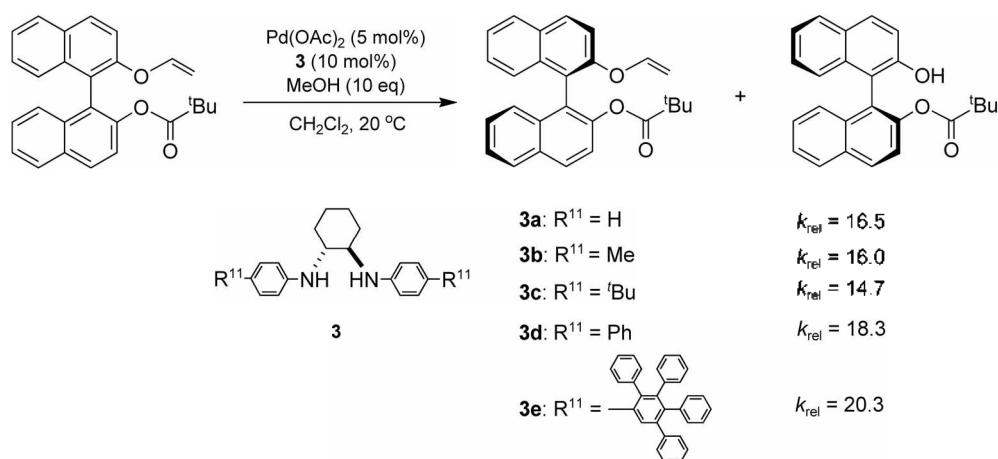cheme 4). In the reaction, **2a** as the ligand smoothly affords 4-methylbiphenyl in 97% yield. In contrast, the use of the corresponding *meta-* (**2b**) and *para-* (**2c**) derivatives gives no coupling adducts and the starting materials remain unchanged. With a conventional phosphines such as PPh$_3$ and P(*o*-Tol)$_3$, almost no conversion of 4-chlorotoluene is observed. Thus, the phosphine **2a** is a very unique phosphine to activate and utilize unactivated aryl chlorides[30] in the coupling reaction.

The diamine ligand bearing TPPh moieties (**3e**) was found to be very effective in a Pd-catalyzed kinetic resolution of axially chiral 2,2'-dihydroxy-1,1'-biaryls by alcoholysis of vinyl ethers (Scheme 5).[37] The kinetic resolution of racemic substrates was performed in the presence of Pd(OAc)$_2$, chiral secondary diamine and methanol. A diamine ligand **3a** derived from (*R,R*)-1,2-cyclohexanediamine shows higher selectivity than those of typical chiral ligands such as

1a: R^9 = H, R^{10} = H
1b: R^9 = Me, R^{10} = H
1c: R^9 = Me, R^{10} = Me
1d: R^9 = Me, R^{10} = *t*-Bu

1e

BSP	*l* / nm	*d* / nm
1a	1.95	0.132
1b	1.99	0.208
1c	2.16	0.280
1d	2.40	0.391
1e	2.63	0.674

Scheme 3

Figure 2. Crystal Structure of Pd (**2a**)(maleic anhydrate).

Me—⟨⟩—Cl + PhB(OH)$_2$
Pd$_2$(dba)$_3$ (0.5 mol%)
2 (2.0 mol%)
KF (3 eq.)
THF, 50 °C, 16 h
→ Me—⟨⟩—⟨⟩

2a: 97%   PPh$_3$: 0%
2b: 0%   P(*o*-Tol)$_3$: 2%
2c: 0%

2a   **2b**   **2c**

Scheme 4

3a: R^{11} = H k_{rel} = 16.5

3b: R^{11} = Me k_{rel} = 16.0

3c: R^{11} = ^{t}Bu k_{rel} = 14.7

3d: R^{11} = Ph k_{rel} = 18.3

3e: R^{11} = k_{rel} = 20.3
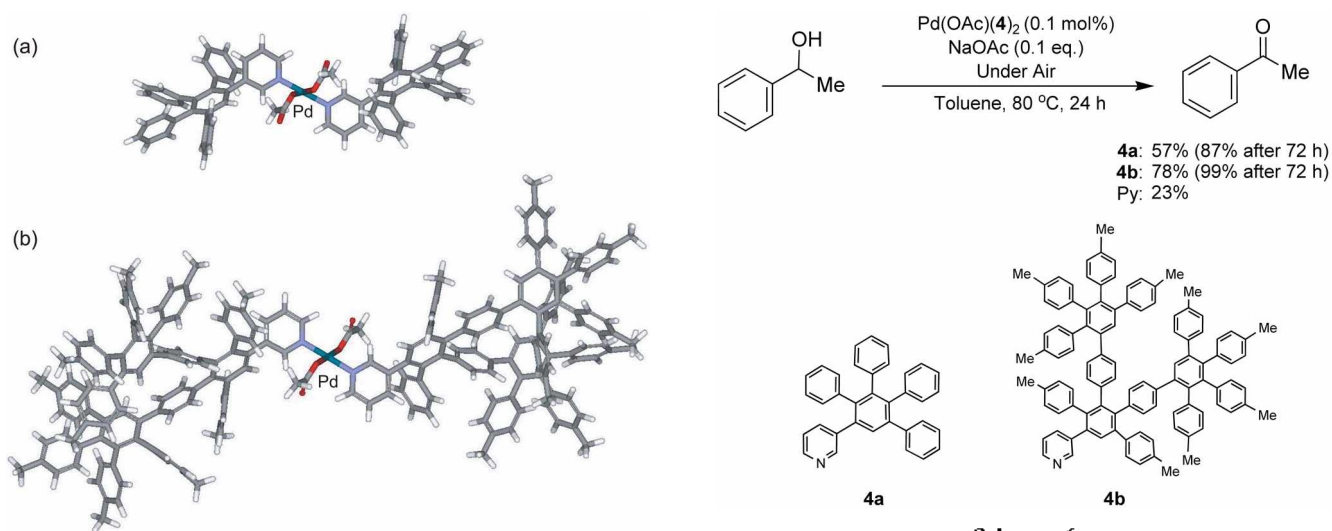
Scheme 5

Figure 3. Crystal Structure of (a) Pd(OAc)$_2$(4a)$_2$ and an optimized (ONIOM method:B3LYP/LANL2DZ-UFF) structure of (b) Pd(OAc)$_2$(4b)$_2$.

Scheme 6

BINAP (k_{rel} = 1.3) and (−)-sparteine (k_{rel} = 1.4). The ligand **3d** having phenyl groups gives slightly higher selectivity. Interestingly, the ligand **3e** bearing the TPPh moiety affords the best result with regard to selectivity and reactivity. When 2-methoxyethanol is used as an alcohol, the k_{rel} is improved to 41.2 for **3e** as the ligand. This is applicable not only to binaphthols but also to biphenols, which have been considered to be difficult for the enantioselective synthesis by known catalytic methods.

A series of novel pyridine ligands bearing a TPPh and its higher dendritic frameworks (**4a** and **4b**) were synthesized (Scheme 6).[38] The reaction of **4a** with Pd(OAc)$_2$ affords Pd(OAc)$_2$(**4a**) quantitatively. X-ray structure of Pd(OAc)$_2$ (**4a**)$_2$ and an optimized structure of Pd(OAc)$_2$(**4b**)$_2$ by ONIOM[39] (B3LYP/LANL2DZ-UFF) calculation are shown in Figure 3. It is evident that the TPPh and its higher dendritic moieties at the 3-position of the pyridine ring of **4a** and **4b** spatially spread out and cover a wide area in a long-range from the Pd center. The longest distances between the

edges of the complexes are 2.9 nm for Pd(OAc)$_2$(**4a**)$_2$ and 4.7 nm for Pd(OAc)$_2$(**4b**)$_2$. However, steric congestion around the Pd center is essentially the same as that of corresponding pyridine complex Pd(OAc)(Py)$_2$,[40] implying that the large substituent at the 3-position would not obstruct the metal center.

To evaluate the efficacy of **4a** as a ligand, the Pd-catalyzed oxidation of alcohols[8] was examined. Pd(OAc)$_2$(**4a**)$_2$ catalyzes the oxidation of 1-phenylethanol to afford acetophenone in 87% yield at 80 °C with 0.1 mol% catalyst (Scheme 6). After 72 h, no Pd black forms in the catalytic system. The higher dendritic analogue Pd(OAc)$_2$(**4b**)$_2$ provides the product in 99% yield. Although Pd(OAc)$_2$(Py)$_2$ catalyzes the oxidation in 23% yield, the Pd catalyst completely decomposes into Pd black and the reaction stops at this moment. Thus, the spatially spread frameworks suppresses the Pd black formation and maintains the catalytic activity for a long time. Degree of the Pd oligomerization was investigated by use of MALDI TOF mass spectroscopy.[41] Oligomerization of Pd(OAc)$_2$(L)$_2$ (L = Py, 3-PhPy, 3,5-Ph$_2$Py, and **4a**) is influenced by the pyridine ligands considerably.

With regard to the development of nanosize ligands, we have synthesized rhodium(I) complexes with *N*-heterocyclic carbene ligands bearing both rigid[42] and flexible[43] dendritic frameworks, and phosphine ligands bearing calix[4]arene[44] and calix[6]arene[45] functionalities. Application of these ligands in the Pd-catalyzed reactions is under investigation.

Conclusion

This account describes the new design in Pd-catalyzed reactions of Group 14 element compounds and also the homogeneous nanosize Pd catalysts. Pd-catalyzed new transformations of allylic esters and three component coupling reactions employing organosilanes and -stannanes were carried out. Strong oxophilicity of the silicon atom may be an important driving force for these successful reactions. Recent development of homogeneous nanosize Pd catalysts strongly suggests that excellent design and well-defined structures of ligands should be intrinsic for successful results.

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