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Forum

Homogeneous Nanosize Palladium Catalysts

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Expanding the catalytic environment to a nanosize must be one of the most promising ways to improve the performance of homogeneous catalysts. In this Forum Article, recent developments in homogeneous nanosize palladium catalysts are reviewed. It contains solubilized palladium nanoparticles, metalated dendrimers, and complexes with well-defined nanosized ligands. These systems realize efficient catalyst recycling, unique selectivity, suppression of metal aggregation, and remarkable enhancement of the catalytic activity.

Introduction

Many heterogeneous catalysts are nanosized, and some of them have fabricated nanostructures.[1] However, these catalysts are usually “prepared” rather than “synthesized” using highly empirical methods. On the other hand, homogeneous transition-metal catalysts are usually discrete molecules and can be synthesized by ligand design in a defined and rational way. In many cases, molecular modeling by theoretical calculation is also very useful for the design. A homogeneous Pd-catalyzed reaction is one of the most versatile methods for synthesizing useful and necessary molecules. However, in homogeneous catalysis, there is a persistent problem that metal aggregation and precipitation cause catalyst decomposition and a considerable loss of catalytic activity. So far, to improve the catalyst performance, modification of the catalysts is usually carried out within close proximity of a metal center (within a few angstroms). In fact, this conventional method is very effective in developing efficient catalysts. However, recently the catalytic environment can be expanded to a nanosize, and this unique environment will add new properties to homogeneous catalysis. Here recent progress in homogeneous nanosize Pd catalysts is surveyed.

Soluble Pd Nanoparticle

Nanoparticles are used as catalysts for a variety of organic and inorganic reactions.[2] Nearly monodisperse Pd nanoparticles were prepared within the interiors of hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers (G*n*-OH, where G*n* represents the *n*th generation; Figure 1). These materials are soluble in water and stable, either dry or solvated, for at least several months.[3] These dendrimer-encapsulated catalysts are active in the hydrogenation of allyl alcohols. Noteworthy is the fact that the dendrimer moieties can act as a mesh nanofilter: higher-generation dendrimer catalysts (G8 > G6 > G4) or larger allylic alcohols (substrates in Table 1) resulting in lower turnover frequencies (Table 1).[4] These size selectivities were not possible with conventional catalyst systems. Not only hydrophilic dendrimers but also hydrophobic perfluorinated polyether-derivatized poly(propylene imine) (PPI) dendrimers containing Pd^0 nanoparticles were prepared.[5] They could be dried to a residue and fully redissolved again in a variety of perfluorinated solvents without detectable agglomeration or precipitation. They were good catalysts in the Mizoroki–Heck reaction[6] of aryl halides with *n*-butyl acrylate using a fluorocarbon/hydrocarbon solvent system, which is useful for catalyst recovery: the product was dissolved in the hydrocarbon, and the fluoro phase retained the catalyst. Pd^0

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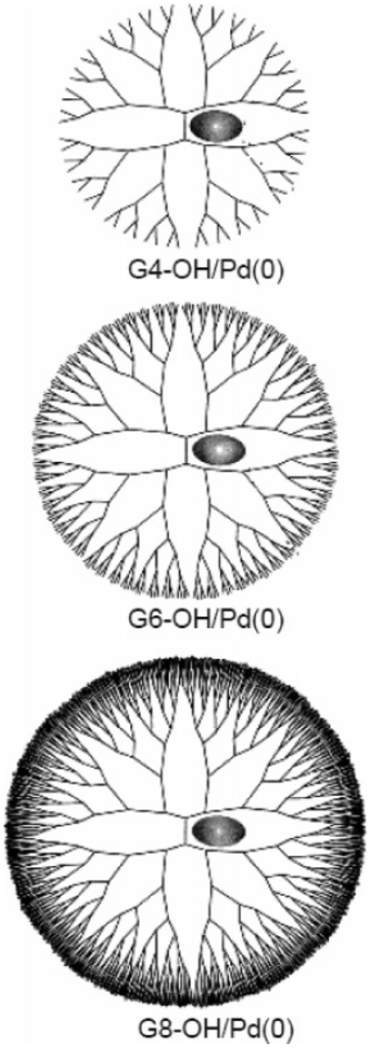


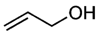
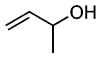
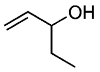
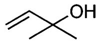
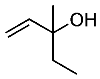
Figure 1. Pd^0 nanoparticles within the interiors of PAMAM dendrimers (G*n*-OH).

nanoparticles within the PPI dendrimers bearing triethoxybenzamide groups were unique catalysts for substrate-specific hydrogenation of polar olefins.[7] Fréchet-type dendrimers with a peripheral disulfide[8] or a phosphine[9] moiety successfully afforded Pd nanoparticles, which are active catalysts in Suzuki−Miyaura coupling. These dendrimer catalysts were soluble in common organic solvents such as toluene, tetrahydrofuran (THF), and dichloromethane but insoluble in methanol. Thus, the soluble catalytic environment around Pd nanoparticles provides unique selectivity and catalytic activity.

Peripheral Multiple-Pd Catalyst Systems

Nanosize Pd complexes bearing multiple-Pd centers on the periphery were synthesized and used as catalysts. Although their nanosize catalytic environments could not influence the catalytic activity and selectivity very efficiently, the nanosize structures often favored catalyst recycling and separation.

Table 1. Hydrogenation Using a G*n*-OH/Pd^0 Catalyst[a]

	TOF / mol H_2 (mol Pd)$^{-1}$ h^{-1}		
Substrates	G4-OH/Pd(0)	G6-OH/Pd(0)	G8-OH/Pd(0)
	480	450	120
	450	380	93
	260	280	68
	150	75	62
	100	40	50

[a] The reactions were carried out at 25 ± 2 °C with 2×10^{-4} M Pd^0 composite catatysts in a $MeOH/H_2O$ (4:1, v/v) mixture. The turnover frequency (TOF) was calculated on the basis of H_2 uptake.

Reetz et al. reported the first example of PPI dendrimers peripherally modified with Pd−phosphine complexes[10] and utilized them as catalysts in Mizoroki−Heck and hydroformylation reactions. Metalated pincer complexes have been successfully applied as homogeneous catalysts.[11] For example, nanosize multimetallic NCN-pincer Pd^{II} complexes (**1**−**4**) were prepared (Figure 2).[12a] They are active catalysts in the double Michael reaction between methyl vinyl ketone and ethyl α-cyanoacetate.[12b] The catalytic activities per the Pd^{II} center of multi-NCN−Pd^{II} catalysts (**1**−**3**) are similar, indicating that all of the Pd^{II} centers in **1**−**3** act as independent catalytic sites. Interestingly, the dodecakis-NCN−Pd^{II} catalyst (**4**) showed an almost threefold increase in the catalytic activity per Pd^{II} center. A molecular modeling study shows that on average the metal sites of **4** are in closer proximity to each other, suggesting cooperative effects between the Pd^{II} centers during catalysis. These nanosize catalysts (**1**−**4**) could be recycled by means of nanofiltration,[13] and retentions greater than 99.9% were found using commercially available nanofiltration membranes.[14] A polymer-enlarged catalyst formed from $(1\text{-}Ad)_2P$-substituted poly(methylstyrene) and a Pd source such as $PdCl_2(PhCN)_2$ was active[15] in Suzuki−Miyaura,[16] Sonogashira,[17] and Mizoroki−

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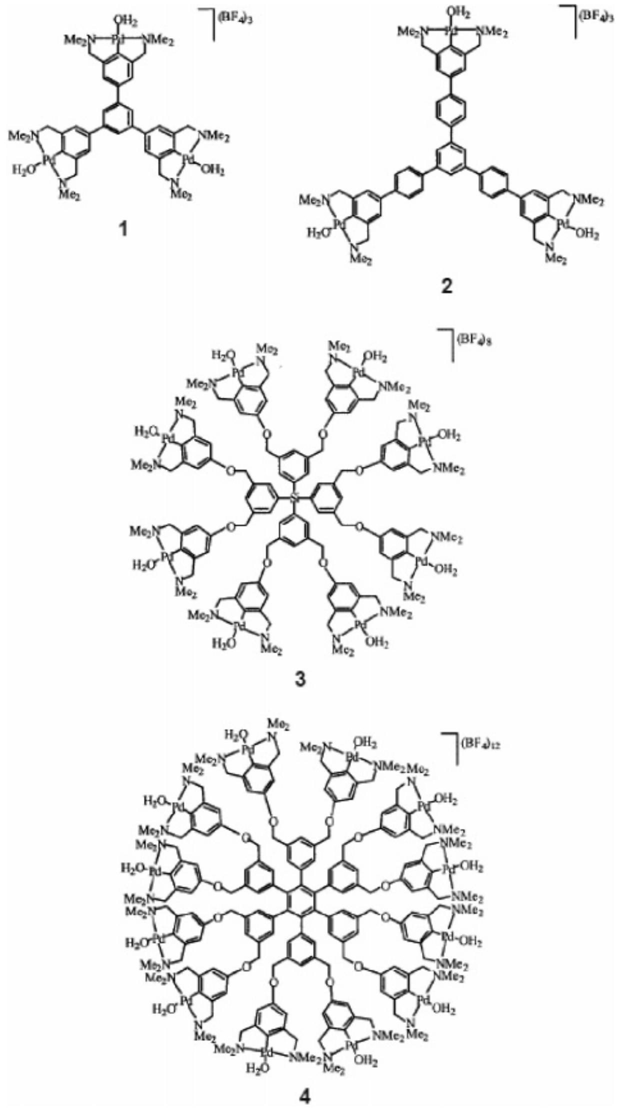

Figure 2. Nanosize multimetallic NCN-pincer Pd^{II} complexes.

Heck[6] reactions of aryl bromides and chlorides. These catalysts also could be recycled in nanofiltration separation systems, in which the linear 5000 Da polymer backbone was sufficiently large to be retained virtually quantitatively by a nanofiltration membrane.

Double phosphinomethylation of primary amino groups on the first, third, fourth, and fifth generations of PPI dendrimers were carried out, giving 4, 16, 32, and 64 chelate phosphines on the periphery (**5a**−**d** in Figure 3), respectively. Treatment of the dendrimers with $PdCl_2(PhCN)_2$ followed by reduction with hydrazine monohydrate in the presence of PPh_3 led to the formation of dendritic Pd^0 complexes (**6a**−**d**). The nanosize Pd complexes **6** catalyzed the amination of *cis*-3-acetoxy-5-carbomethoxycyclohex-1-ene with morpholine (Figure 4).[18] Notably, the stereoselectivity for the

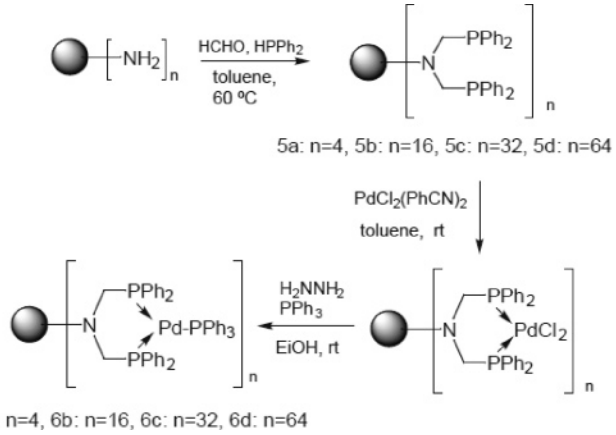

Figure 3. Preparation of dendritic Pd^0 complexes (**6**).

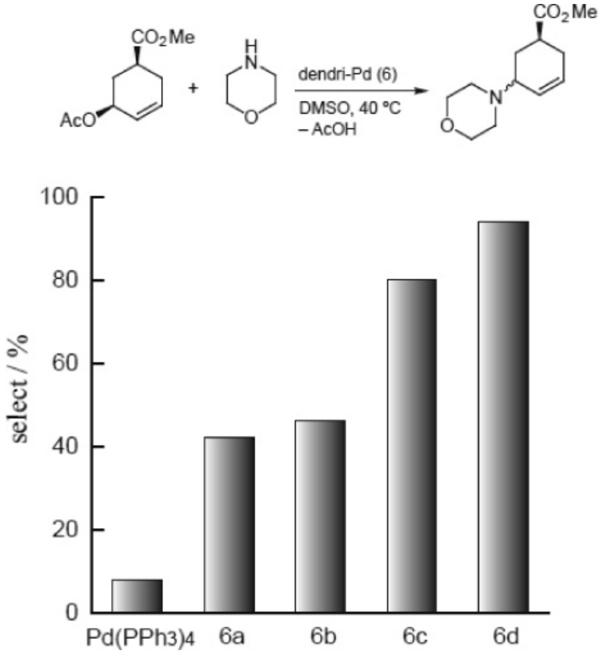

Figure 4. Generation dependence on the selectivity. Selectivity (%) = [(cis − trans)/(cis + trans)] × 100: 8% with $Pd(PPh_3)_4$, 42% with **6a**, 46% with **6b**, 80% with **6c**, and 94% with **6d**.

cis product increased with an increase in the size (generation) of the catalysts. Nucleophilic attack to a surface (π-allyl)-palladium intermediate from the Pd side would be strongly shielded. Further, encapsulating Pd−phosphine complexes within PPI dendrimers showed the positive dendrimer effect[19,20] in which the rate of the Mizoroki−Heck reaction increased with an increase in the size of the dendrimers.

Isolated and well-characterized dendrimer Pd complexes **7-G1** (the first generation with six terminal Pd units) and **7-G3** (the third generation with 24 terminal Pd units) were prepared (Figure 5).[21] Complex **8-G3** was prepared in situ by mixing a dendrimer of the third generation with $Pd(OAc)_2$ (P/Pd = 4/1). These complexes were active as catalysts in the Stille coupling reaction[22] of iodobenzene with tributylvi-

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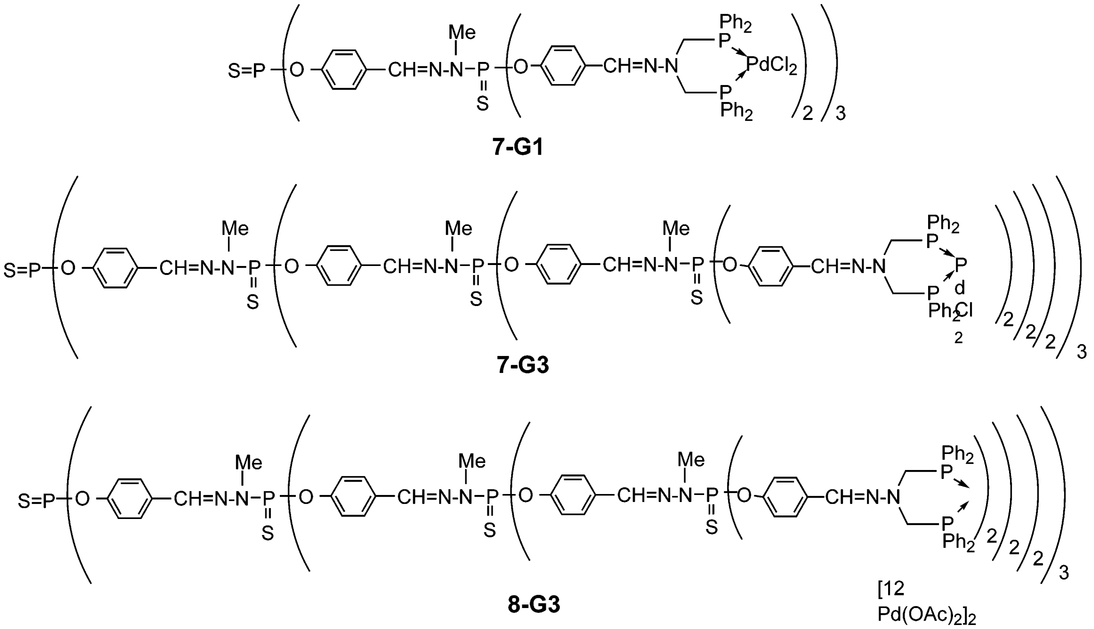
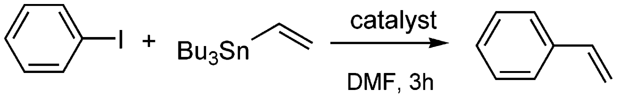


Figure 5. Pd complexes with P-containing dendrimers.

Table 2. Stille Coupling Using **7** or **8** as a Catalyst[a]



entry	catalyst	mol % Pd	T/°C	conv/%
1	**7-G1**	1	90	100
2	**7-G3**	1	90	100
3	**7-G3** (cycle 1)	5	50	100
4	**7-G3** (cycle 2)	5	50	95
5	**7-G3** (cycle 1)	2	50	100
6	**7-G3** (cycle 2)	2	50	92
7	**8-G3**	1	80	100
8	**8-G3** (cycle 1)	5	50	100
9	**8-G3** (cycle 2)	5	50	100
10	**8-G3** (cycle 3)	5	50	100
11	$P(2\text{-furyl})_3/Pd(OAc)_2$	5	50	100

[a] Iodobenzene (5.34 mmol), tributylvinyltin (5.34 mmol), in *N*,*N*-dimethylformamide (20 mL).

nyltin (Table 2). They showed reactivity comparable to that of $P(2\text{-furyl})_3/Pd(OAc)_2$,[23] which is well-known as one of the most active catalysts for the Stille coupling reaction (entry 11). These nanosize Pd complexes **7-G3** and **8-G3** were easily recovered (precipitated) by adding ether into a reaction mixture. Recycled complexes showed good catalytic activity in the reaction (entries 3−6 and 8−10).

Single-Pd Catalyst System

With a multimetal system described above, each center has different catalytic environments. Thus, catalytic activity and selectivity were often difficult to regulate. In contrast, a single metal center in a well-designed nanosize catalytic environment may utilize the unique property and realize unusual catalytic activity or selectivity. The second-generation dendrimer−phosphine complex with Pt^0 at the core was synthesized (Figure 6A).[24] Molecular modeling of the complex by B3LYP/LANL2DZ-PM3/MOZYME[25] visualized a nanosized flattened globular structure with a diameter of 4.4 nm. Interestingly, as the optimization proceeded, several cavities appeared around the Pt center (Figure 6B), which might be utilized as a guest room in catalytic reactions.

A Pd catalyst shows good catalytic activity in an aerobic oxidation of alcohols.[26,27] However, in a reaction, the Pd black formed very easily. [26a,d,e,27] We reported a new catalyst system that suppresses the Pd black formation even under air and with a high (>1000) S/C (substrate/catalyst) ratio.[28] Dendrimers having a 2,3,4,5-tetraphenylphenyl (TPPh) moiety were synthesized by Müllen et al. and utilized as polyphenylene nanomaterials.[29] We are interested in their spatially spread and rigid structure and synthesized novel pyridine ligands (**9** and **10** in Figure 7) bearing a TPPh or its higher dendritic[30] moiety. These new pyridine ligands, as well as pyridine (Py), 3-phenylpyridine (3-PhPy), 3,5-

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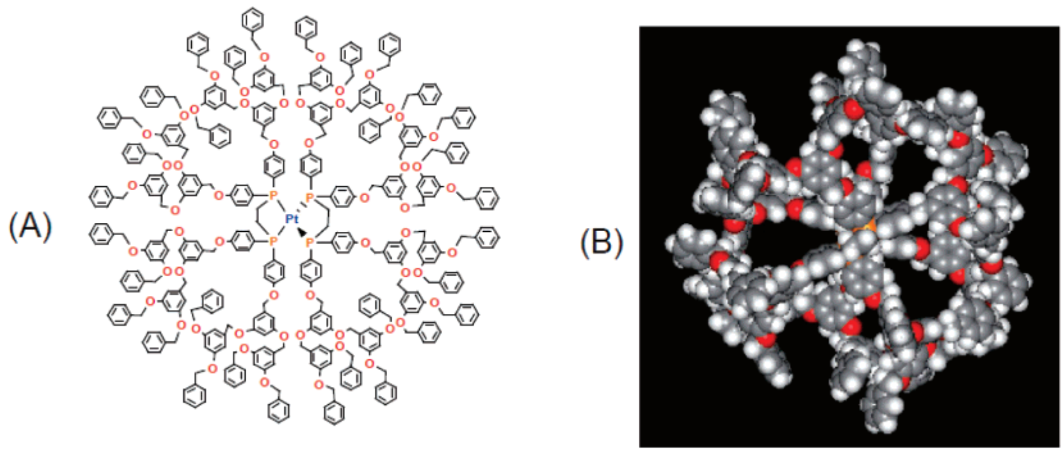
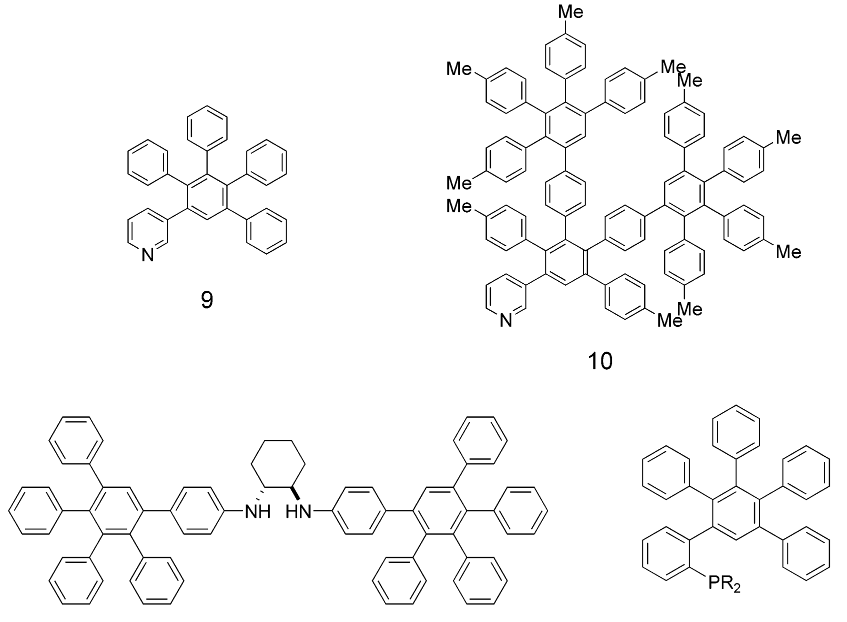


Figure 6. Second-generation dendrimer−phosphine complex with Pt^0 at the core.



9

10

11

12: R=Ph, 13: R=Cy

Figure 7. Ligands bearing TPPh moieties.

diphenylpyridine (3,5-Ph_2Py), and 2,2′-bipyridine, readily reacted with $Pd(OAc)_2$ in toluene and afforded the $Pd(OAc)_2$(ligand)$_2$ complexes almost quantitatively. These complexes were used as catalysts for the air oxidation of alcohols (Table 3).[28] X-ray structures of Pd $(OAc)_2(Py)_2$[31] and $Pd(OAc)_2$(**9**)$_2$[28] are shown in parts A and B, respectively, of Figure 8. Because good single crystals suitable for X-ray analysis were not obtained, a structure of $Pd(OAc)_2$(**10**)$_2$ was optimized by ONIOM[32] (B3LYP/LANL2DZ-UFF) calculation and is shown in Figure 8C. It is evident that TPPh and its higher dendritic moieties at the 3 position of the Py ring of **9** and **10** spatially spread out and cover the wide area over the long range from the Pd center. The longest distances between the edges of the complexes are 2.9 nm for $Pd(OAc)_2$(**9**)$_2$ (Figure 8B) and 4.7 nm for $Pd(OAc)_2$(**10**)$_2$ (Figure 8C). $Pd(OAc)_2(Py)_2$ catalyzed the oxidation of 1-phenylethanol to afford acetophenone in 23% yield at 80 °C with 0.1 mol % catalyst (entry 2 in Table 3). However, at this moment, all of the Pd catalyst decomposed completely into Pd black, and the oxidation stopped. The palladium acetate complexes having 3-PhPy or 3,5-Ph_2Py also resulted in complete Pd black formation to afford the product in low yields (entries 3 and 4). In contrast, $Pd(OAc)_2$(**9**)$_2$ afforded acetophenone in 87% yield without Pd black formation (entry 5). The higher dendritic analogue $Pd(OAc)_2$(**10**)$_2$ was a more efficient catalyst, realizing the highest TON = 1480 with S/C = 2000 (entry 7). With other alcohols, the ligands **9** and **10** also suppress Pd black formation, while the Py ligand resulted in complete Pd black formation (entries 8−20).

Concerning catalytically inactive species like Pd black in homogeneous catalysis, there have been very few spectroscopic studies, even though they are indispensable to explore highly active catalysts. Recently, we utilized matrix-assisted laser desorption ionization time-of-flight (MALDI TOF) mass to examine oligomer formation of $Pd(OAc)_2(L)_2$ (L =

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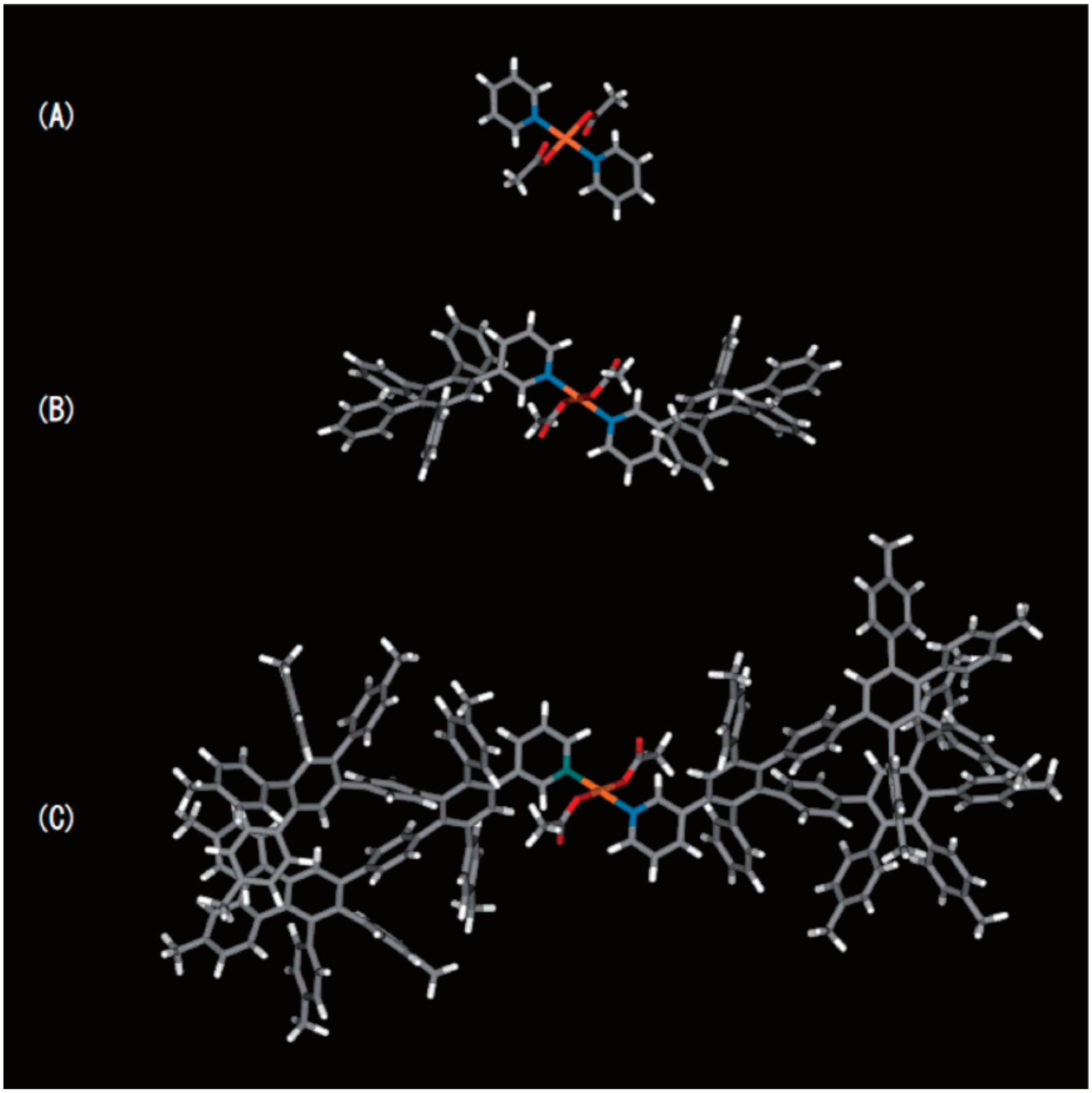

Figure 8. X-ray structures of (A) $Pd(OAc)_2(Py)_2$ and (B) $Pd(OAc)_2(\mathbf{9})_2$ and the ONIOM (B3LYP/LANL2DZ-UFF)-optimized structure of (C) $Pd(OAc)_2(\mathbf{10})_2$.

Py, 3-PhPy, 3,5-Ph_2Py, and **9**) as an early stage of Pd black formation (catalyst deactivation).[33] MALDI TOF mass successfully detected Pd oligomers and showed that the degree of the Pd oligomerization was influenced by the Py ligands considerably and this ligand effect was very similar to the one observed for Pd black formation in the air oxidation of alcohols.[28]

The diamine ligand (**11**) bearing a TPPh moiety is very effective in a Pd-catalyzed kinetic resolution of axially chiral 2,2′-dihydroxy-1,1′-biaryls by alcoholysis of vinyl ethers.[34] The reaction proceeded with high selectivity for various kinds of biaryls. This process is applicable to not only binaphthols but also biphenols, which have been considered to be difficult for the enantioselective synthesis by known catalytic methods.

Phosphines are also very important ligands in homogeneous transition-metal catalysis. Recently, we found that the phosphines (**12** and **13** in Figure 7)[35] that have a TPPh moiety at the ortho position are effective ligands to utilize aryl chlorides in three different Pd-catalyzed reactions such as Suzuki−Miyaura coupling (Table 4), the Mizoroki−Heck reaction, and silylation with $Me_3SiSiMe_3$. In contrast, the corresponding meta and para derivatives did not afford the products at all. X-ray crystal structures of the Pd^0 complexes having **12** (Figure 9) or **13** as a ligand show that η^2 coordination on the TPPh moiety occurs, and this interaction will be operative to realize highly active catalyst systems. Such η^2 coordination is not possible with the meta and para derivatives.

As a new class of phosphines, the first bowl-shaped phosphine (BSP), tris(2,2″,6,6″-tetramethyl-*m*-terphenyl-5′-yl)phosphine (**14**; R = Me, R′ = H, in Figure 10), was synthesized.[36] The diameter (*l* in Figure 10) of **14** is 1.95 nm, and the BSP (**14**) is a very bulky phosphine. However, the nature of the bulkiness is quite different between the BSP

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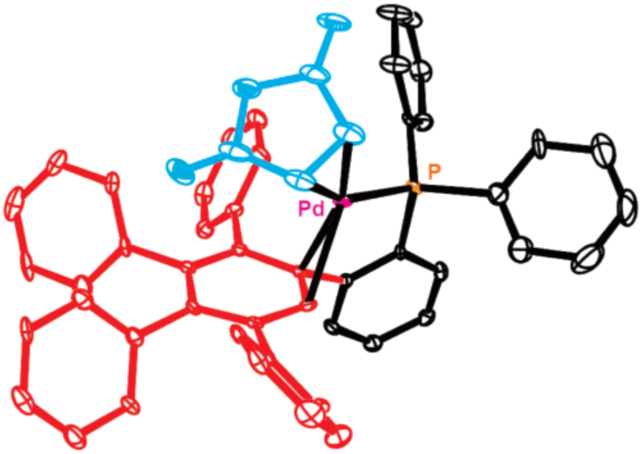


Figure 9. ORTEP drawing of [palladium(**12**)(maleic anhydride)] with thermal ellipsoids at 50% probability levels.

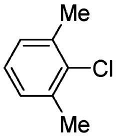
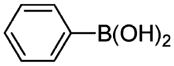
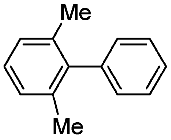
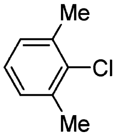
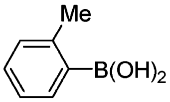
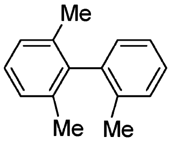
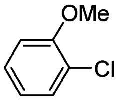
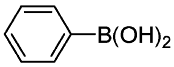
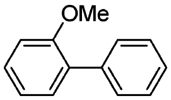
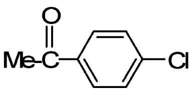
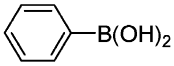
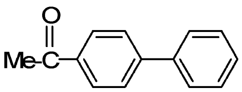
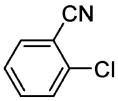
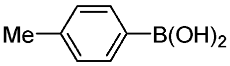
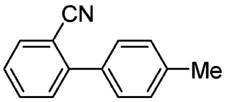
Table 3. Effect of Py Ligands on Pd-Catalyzed Air Oxidation of Alcohols[a]

entry	alcohol	ligand[b]	time/h	yield/%[c]	Pd black formation[d]
1	1-phenylethanol	none	24	trace	+
2		Py	24	23	+
3		3-PhPy	6	34	+
4		3,5-Ph_2Py	6	32	+
5		**9**	72	87	−
6		**10**	72	>99 (95)	−
7[e]		**10**	96	74	−
8	2-octanol	Py	2	21	+
9		**9**	96	69	−
10		**10**	96	79(75)	−
11	benzyl alcohol	Py	2	23	+
12		**9**	48	74	−
13		**10**	48	78	−
14	2-heptanol	Py	8	27	+
15		**9**	72	52	−
16		**10**	72	72	+
17	3,3-dimethyl-2-butanol	Py	4	32	−
18		**9**	96	89	−
19	2-hexanol	Py	2	24	+
20		**9**	96	72	−

[a] S/C = 1000. [b] The ligand of the $Pd(OAc)_2(ligand)_2$. [c] Determined by gas chromatography. Isolated yields are in parentheses. [d] +: complete Pd black formation. −: no Pd black formation. [e] S/C = 2000.

and conventional bulky phosphines such as $P(t\text{-}Bu)_3$. The bulkiness of the BSP occurs on the periphery of the phosphine (at the rim of the bowl) with substantial empty space around the P atom. In contrast, $P(t\text{-}Bu)_3$ has severe steric congestion within close proximity of the P atom. Various BSP ligands were prepared and used in the Rh-catalyzed hydrosilylation of ketones and ketimines.[37] In the catalytic reaction, BSP ligands markedly accelerated the reaction as compared with conventional phosphine ligands such as PPh_3 and $P(t\text{-}Bu)_3$. Although neither basicity nor the

Table 4. Suzuki−Miyaura Coupling of Aryl Chlorides with **12** as a Ligand[a]

Entry	Aryl chloride	Boronic acid	mmol of cat Temp, Time	Product	Yield[b] (%)
1			5×10^{-3} mmol 50 °C, 14 h		84
2			2.5×10^{-3} mmol 65 °C, 8 h		93
3			2.5×10^{-3} mmol 50 °C, 8 h		97
4[c]			3.5×10^{-4} mmol 50 °C, 16 h		91
5			5×10^{-3} mmol rt, 24 h		91

[a] Conditions: aryl chloride (1.0 mmol), arylboronic acid (1.5 mmol), KF (3 mmol), catalyst $Pd_2(dba)_3\cdot CHCl_3$ (3.5×10^{-4}−5×10^{-3} mmol), **12** (8.4×10^{-4}−1.2×10^{-2} mol; P/Pd = 1.2), in THF (1 mL). [b] Isolated yields. [c] 4-Chloroacetophenone (1.4 mmol).

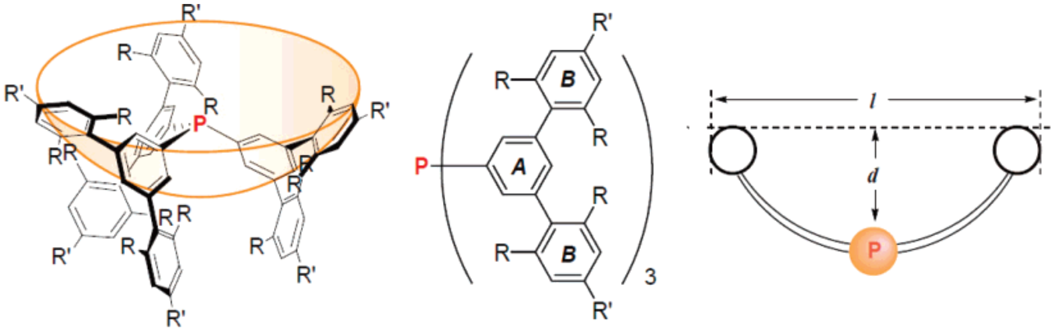


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Figure 10. Bowl-shaped phosphine.

cone angle of the phosphines showed evident correlations with the efficacy of the ligands, the depth (*d* in Figure 10) of the bowls affect the reaction and deeper bowls provide more active catalysts. Furthermore, BSPs were found to be a highly effective ligands in Pd-catalyzed Suzuki−Miyaura coupling of unactivated aryl chlorides,[38] in which deeper bowl ligands afforded more active catalysts. In both of the catalytic reactions, coordination of the BSP is successfully regulated to provide *mono*(phosphine) species and these highly unsaturated species would be responsible for the highly active catalytic reactions.

In conclusion, homogeneous nanosize Pd catalysts are very promising to realize new reactivity, selectivity, and efficient catalyst recycling. Excellent design and well-defined structures should be crucial for successful results.

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