

## Highlight Review

# Recent Development of Homogeneous Transition Metal Catalysts with Nanosize Ligands

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### Abstract

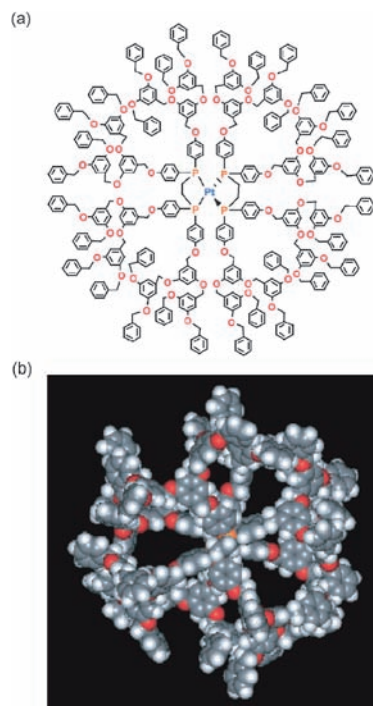
Expanding catalytic environment to a nanosize is one of the most promising ways to improve performance of homogeneous catalysts. In this highlight review, recent development in homogeneous transition metal catalysts with well-defined nanosize ligands is overviewed. These systems realize efficient catalysts with remarkable enhancement of catalytic activity, suppression of metal aggregation, and unprecedented selectivity.

### Introduction

Homogeneous transition metal catalysts are usually discrete molecules and can be synthesized with ligand designed in a defined and rational way. To improve performance of homogeneous catalysts, modification of catalysts is very important and this is usually carried out within a close proximity of a metal center (within a few angstroms). This is effective way to develop efficient catalysts for various reactions such as C–C bond-forming reactions,<sup>1</sup> asymmetric reactions,<sup>2</sup> and metathesis.<sup>3</sup> Inspired by their findings, we set out to expand catalytic environment to nanosize by modification of ligands.<sup>4</sup> Here recent progress in homogeneous transition metal catalysts with nanosize ligands is overviewed. To expand a molecular size, dendritic frameworks including flexible or rigid moieties, sterically congested *m*-terphenyl and its higher dendritic frameworks, and a calix[6]-arene functionality were introduced onto phosphine, pyridine, and *N*-heterocyclic carbene ligands.

### Ligands with Flexible Dendritic Frameworks

Development of organometallic dendrimers is imperative, since the dendritic moieties will bring about unique catalytic environment to realize novel catalytic performance.<sup>5</sup> We have been interested in Fréchet-type<sup>6</sup> flexible dendrimers constructed by benzyl ether groups. A series of phosphine compounds with the flexible dendritic frameworks were developed<sup>7</sup> since phosphines<sup>8</sup> are very important ligands in homogeneous transition metal catalysis. The second-generation dendrimer–phosphine complex with a Pt<sup>0</sup> at the core **1** was synthesized and characterized (Figure 1a). Molecular modeling of the complex by B3LYP/LANL2DZ-PM3/MOZYME visualized a flattered globular structure with a diameter of 4.4 nm. Interestingly, as the optimization proceeded, several cavities appeared around the Pt center (Figure 1b), which might be utilized as a guest

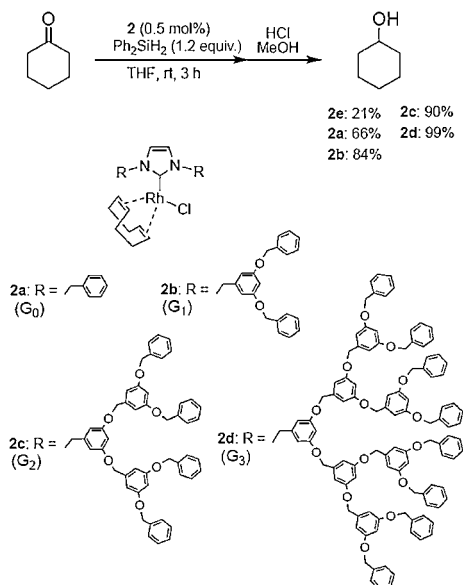


**Figure 1.** A Pt<sup>0</sup> complex bearing dendritic phosphine ligands **1**. (a) Molecular structure. (b) Space-filling model of the complex calculated by B3LYP/LANL2DZ-PM3/MOZYME.

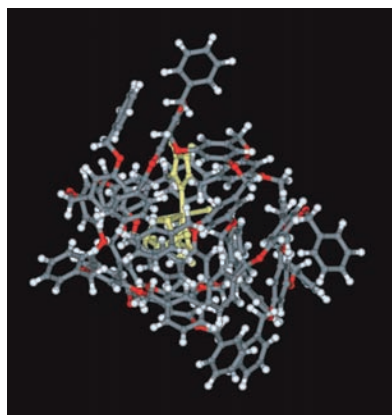
space in catalytic reactions.

A series of Rh<sup>I</sup> complexes with *N*-heterocyclic carbene (NHC)<sup>9</sup> ligands bearing flexible dendritic frameworks, G<sub>0</sub> **2a**, G<sub>1</sub> **2b**, G<sub>2</sub> **2c**, and G<sub>3</sub> **2d** were synthesized and the catalytic performance was examined (Scheme 1).<sup>10</sup> In the hydrosilylation<sup>11</sup> of cyclohexanone, RhCl(COD)[Me<sub>2</sub>(C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>)] (**2e**) only showed low catalytic activities: a yield of cyclohexanol after 3 h was 21%. The catalytic activity was enhanced by introducing G<sub>0</sub>–G<sub>3</sub> substituents onto the NHC ligand: the product was obtained in 66%, 84%, 90%, and 99% yields with **2a**, **2b**, **2c**, and **2d** as the catalyst, respectively. Noteworthy is that the yields gradually increased with increasing the dendrimer generation: a positive dendritic effect was evident. Aromatic rings of G<sub>0</sub>–G<sub>3</sub> might interact with the rhodium metal and cause the evident positive dendrimer effect, as suggested by an optimized structure of **2d** calculated by ONIOM<sup>12</sup> (B3LYP/LANL2DZ:UFF) method (Figure 2).

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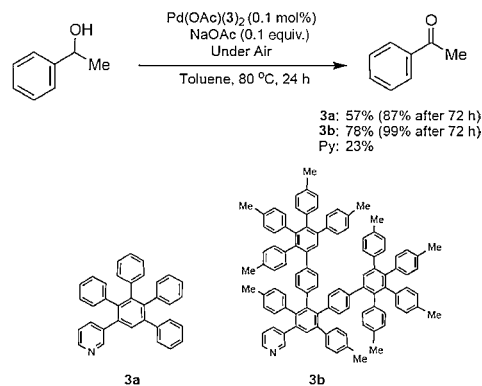
Scheme 1.

Figure 2. An optimized structure of **2d** by ONIOM calculation.

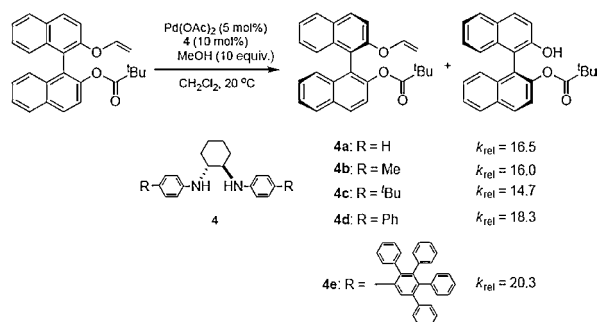
### ◆ Ligands with Rigid Dendritic Frameworks

Dendritic frameworks having a 2,3,4,5-tetraphenylphenyl (TPPh) moiety developed by Müllen and co-workers have been utilized as building blocks for polyphenylene nanomaterials.<sup>13</sup> We are interested in their spatially spread and rigid structures.

A series of pyridine ligands including **3a** and **3b**, which bear a TPPh and its higher dendritic frameworks were synthesized (Scheme 2).<sup>14</sup> Although Pd catalyst shows a good catalytic activity in an aerobic oxidation of alcohols,<sup>15</sup> Pd black forms very easily in a reaction. Pd(OAc)<sub>2</sub>(Py)<sub>2</sub> catalyzed the oxidation of 1-phenylethanol to afford acetophenone in 23% yield at 80 °C with 0.1 mol % catalyst under air (Scheme 2). However, at this moment, all the Pd catalysts decomposed completely into Pd black and the oxidation stopped. In contrast, Pd(OAc)<sub>2</sub>(**3a**)<sub>2</sub> afforded acetophenone in 87% yield after 72 h without the Pd black formation. The higher dendritic analogue Pd(OAc)<sub>2</sub>(**3b**)<sub>2</sub> provided the product in 99% yield. Interestingly, Pd(OAc)<sub>2</sub>(**3b**)<sub>2</sub> was more efficient catalyst, realizing the highest TON = 1480 with S/C = 2000.<sup>14</sup> MALDI-TOF mass was used to examine



Scheme 2.

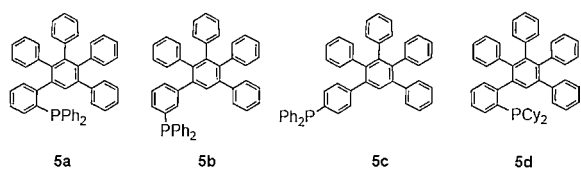


Scheme 3.

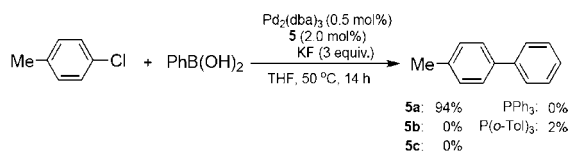
oligomer formation of Pd(OAc)<sub>2</sub>(L)<sub>2</sub> (L = Py, 3-PhPy, 3,5-Ph<sub>2</sub>Py, and **3a**) as an early stage of the Pd black formation (catalyst deactivation).<sup>16</sup> As a result, degree of the Pd oligomerization is influenced by the pyridine ligands considerably, and this ligand effect was similar to one observed for Pd black formation in the catalysis.

The diamine ligand **4e** bearing TPPh moieties was found to be very effective in a palladium-catalyzed kinetic resolution of axially chiral 2,2'-dihydroxy-1,1'-biaryls by alcoholysis of vinyl ethers (Scheme 3).<sup>17</sup> The kinetic resolution of racemic substrates was performed in the presence of Pd(OAc)<sub>2</sub>, chiral secondary diamine and methanol. A diamine ligand **4a** derived from (*R,R*)-1,2-cyclohexanediamine showed higher selectivity ( $k_{rel} = 16.5$ ) than that of typical chiral ligand such as BINAP ( $k_{rel} = 1.3$ ). The ligand **4d** bearing phenyl groups gave slightly higher selectivity ( $k_{rel} = 18.3$ ). Interestingly, the ligand **4e** bearing TPPh moieties afforded the best result with regard to selectivity and reactivity ( $k_{rel} = 20.3$ ). When 2-methoxyethanol was used as an alcohol, the  $k_{rel}$  value was improved to 41.2 for **4e** as the ligand. These are applicable not only to binaphthols but also to biphenols, which have been considered to be difficult for the enantioselective synthesis by known catalytic methods.

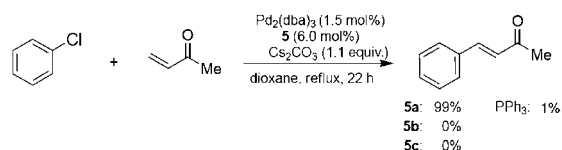
Recently, we have synthesized phosphines bearing a TPPh moiety on one of the phenyl rings of triphenylphosphine (*ortho*:- **5a**, *meta*:- **5b**, *para*:- **5c**) as shown in Scheme 4.<sup>18</sup> The structure of **5a** was determined by X-ray crystallographic analysis (Figure 3a). Interestingly, the structure shows that the TPPh moiety spatially spreads out and the lone pair of the phosphorus atom points above the TPPh unit. The phosphines **5a**, **5b**, and **5c** were employed as a ligand in Suzuki–Miyaura coupling<sup>19</sup> of 4-chlorotoluene with phenylboronic acid in the presence of



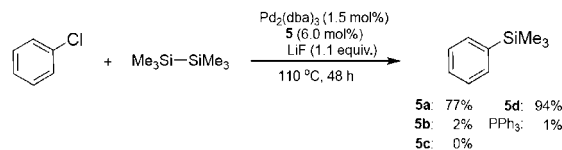
## Suzuki-Miyaura Coupling



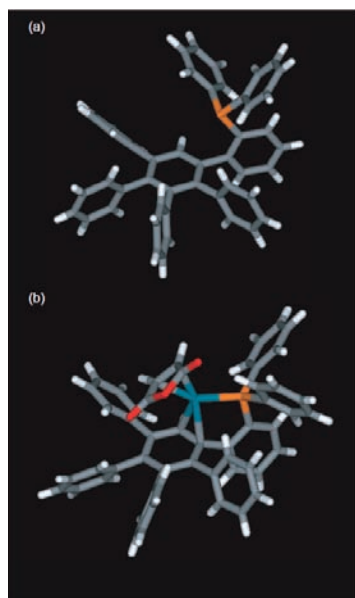
## Mizoroki-Heck Reaction



## Silylation with Disilane

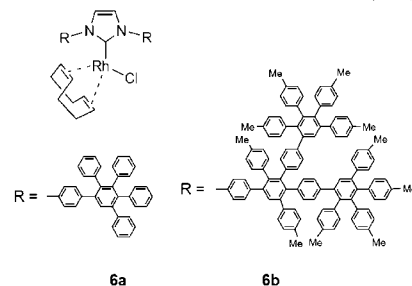
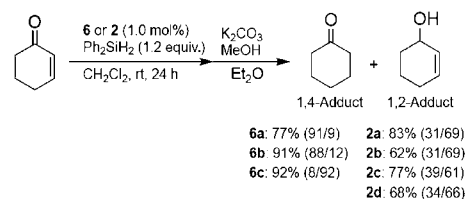


Scheme 5.

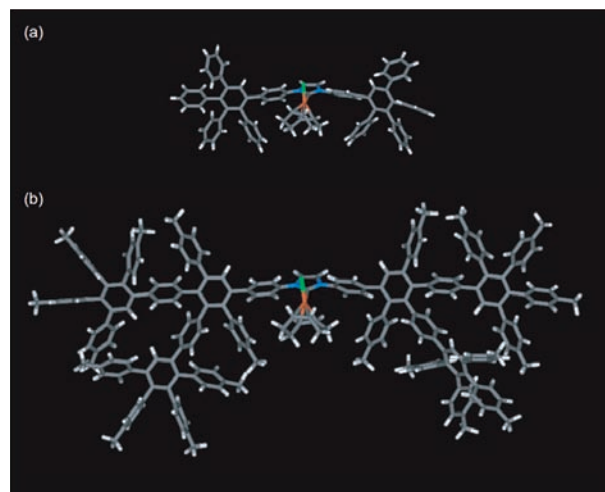


**Figure 3.** Crystal structures of (a) **5a** and (b)  $\text{Pd}(\mathbf{5a})$  (mareic unhydrate).

$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  and KF in THF at 50 °C (Scheme 5). In the reaction, **5a** as the ligand smoothly afforded 4-methylbiphenyl in 97% yield. In contrast, the use of the corresponding meta- (**5b**) and para- (**5c**) derivatives gave no coupling adduct and the starting materials remained unchanged. With conventional phosphines such as  $\text{PPh}_3$  and  $\text{P}(o\text{-Tol})_3$ , almost no conversion of 4-chlorotoluene was observed. Furthermore, the ligand **5a** was also



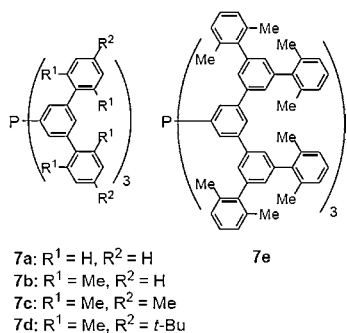
Scheme 6.



**Figure 4.** Molecular structures of **6**. (a) Crystal structure of **6a** and (b) the optimized structure of **6b** obtained by ONIOM calculation.

effective in Mizoroki–Heck reaction.<sup>20</sup> In the case of silylation of chlorobenzene with  $\text{Me}_3\text{SiSiMe}_3$ , the cyclohexyl derivative **5d** was found to be more effective (Scheme 5).<sup>18</sup> Thus, the phosphines **5a** and **5d** were very unique phosphines to activate and utilize unactivated aryl chlorides<sup>21</sup> in the coupling reaction. The X-ray crystal structure of a  $\text{Pd}^0$  complex having **5a** as the ligand showed that the TPPh moiety has  $\eta^2$ -coordination on the  $\text{Pd}^0$ , which might be general and operative to realize highly active catalysts (Figure 3b).

We designed and synthesized  $\text{Rh}^{\text{I}}$  complexes with NHC ligands bearing the TPPh and its higher dendritic moieties, **6a** and **6b** (Scheme 6).<sup>22</sup> The molecular structure of **6a** was successfully determined by X-ray crystal structural analysis (Figure 4a). An optimized structure of **6b** (Figure 4b) were obtained by ONIOM<sup>12</sup> calculation (B3LYP/LANL2DZ:UFF). As a result, **6b** was a bigger nanosize complex with the longest distance between the edges of the two dendritic frameworks being 4.9 nm. To elucidate efficacy of the complexes in catalysis, the hydrosilylation of 2-cyclohexen-1-one with  $\text{Ph}_2\text{SiH}_2$  was carried out in the presence of a catalytic amount (1 mol %) of **6** in  $\text{CH}_2\text{Cl}_2$  at



Scheme 7.

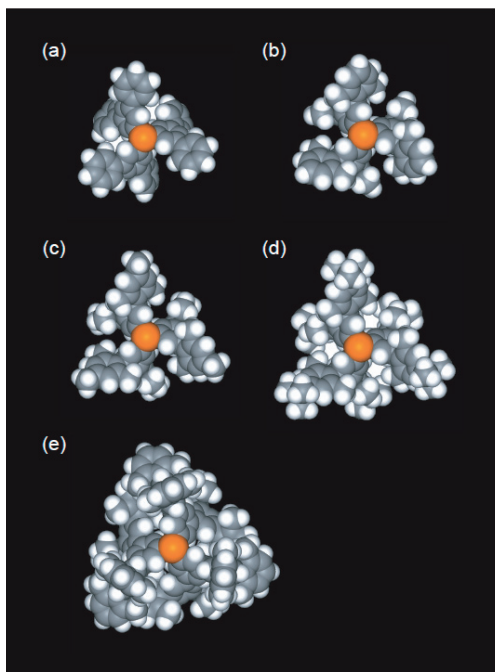
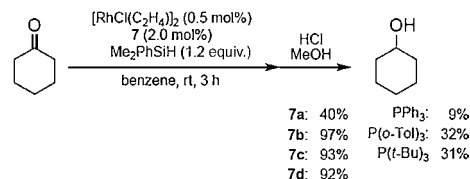


Figure 5. Optimized structures of BSP; (a) **7a**, (b) **7b**, (c) **7c**, (d) **7d**, and (e) **7e**.

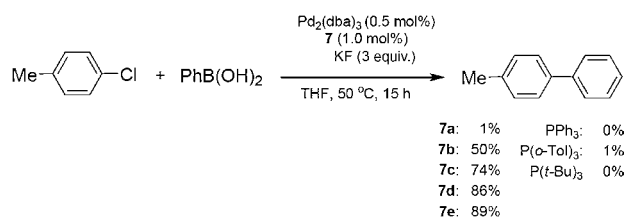
room temperature. **6a** as a catalyst afforded the 1,4-adduct (cyclohexanone) in 91% selectivity with a smaller amount of the 1,2-adduct (2-cyclohexen-1-ol) in 77% total yield after the desilylation (Scheme 6). The complex **6b** also provided the 1,4-adduct in 88% selectivity. Noteworthy is that these 1,4-selectivities obtained with Ph<sub>2</sub>SiH<sub>2</sub> were totally opposite to one obtained with RhCl(COD)[(Mes)<sub>2</sub>(C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>)] (**6c**) as a catalyst, in which the 1,2-adduct was afforded exclusively. On the other hand, the complex with flexible dendritic frameworks **2a–2d** as the catalyst afforded the 1,2-adduct mainly with similar selectivities (61%–69%). The rigid and spatially spread structures of **6a** and **6b** might be crucial to cause the 1,4-regioselectivity.

### ◆ Bowl-shaped Phosphine Ligands

As a new class of phosphines, the first bowl-shaped phosphine (BSP), tris(2,2',6,6'-tetramethyl-*m*-terphenyl-5'-yl)phosphine (**7b**: R<sup>1</sup> = Me, R<sup>2</sup> = H in Scheme 7), was reported by Goto, Kawashima, et al.<sup>23</sup> The nature of bulkiness is quite different between BSP and a conventional bulky phosphine such as



Scheme 8.



Scheme 9.

P(*t*-Bu)<sub>3</sub>. 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 5. In contrast, P(*t*-Bu)<sub>3</sub> has severe steric congestion within close proximity of the phosphorus atom. Our interest was focused on the application of BSP in catalysis.<sup>24,25</sup>

BSP was employed as the ligand in hydrosilylation of cyclohexanone in the presence of [RhCl(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (P/Rh = 2) and Me<sub>2</sub>PhSiH as a silylation agent. After 3 h, BSP **7b**, **7c**, and **7d** bearing methyl substituents at the 2,2',6,6'' positions of the *m*-terphenyl group afforded the product in 97%, 93%, and 92% yields, respectively (Scheme 8).<sup>24</sup> A BSP **7a** having a *m*-terphenyl group without any substituents and conventional phosphine ligands such as PPh<sub>3</sub> and P(*o*-Tol)<sub>3</sub> gave the product in 40%, 9%, and 32% yields, respectively. The BSP ligands **7b–7d** markedly accelerated the reaction using ketones and ketimines as substrates.<sup>24</sup>

Recently, a series of BSP ligands were found to be highly effective in palladium-catalyzed Suzuki–Miyaura coupling of unactivated aryl chlorides.<sup>25</sup> The BSP effectively worked as a ligand in the coupling of 4-chlorotoluene with phenylboronic acid in the presence of Pd<sub>2</sub>(dba)<sub>3</sub> with KF as a base in THF at 50 °C (Scheme 9). Although the BSP ligand **7a** gave 4-methylbiphenyl only in 1%, the BSP ligands **7b**, **7c**, and **7d** afforded the product in 50%, 74%, and 86% yields, respectively. Interestingly, **7e**<sup>26</sup> bearing the higher dendritic frameworks provided the product in 89% yield. In contrast, representative phosphines such as PPh<sub>3</sub>, P(*o*-Tol)<sub>3</sub>, and P(*t*-Bu)<sub>3</sub> gave almost no coupling adduct under such mild condition. To understand the efficacy of BSP in the catalysis, we turned our attention to a shape of BSP. The depths (*d*) and the diameters (*l*) of BSP (**7a–7e**) were measured on the optimized structures obtained by the HF/6-31G(d)-CONFLEX/MM3 calculations and listed in Figure 6. A depth of the bowl (*d*), not the diameter (*l*), is a critical parameter to determine effectiveness of the BSP ligands. In these reactions, coordination of BSP is successfully regulated and the resulting mono(phosphine) species would be responsible for the high catalytic activities.

### ◆ Calix[6]arene Phosphine Ligands

Calix[6]arene is a cyclic hexamer consisting six phenol units

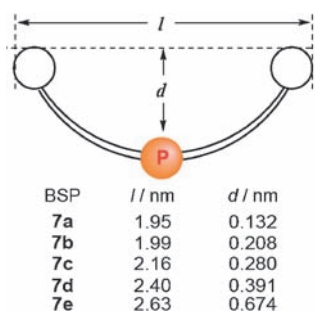
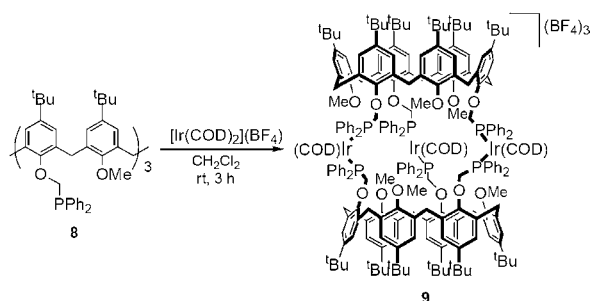


Figure 6. Depths and diameters of BSPs.



Scheme 10.

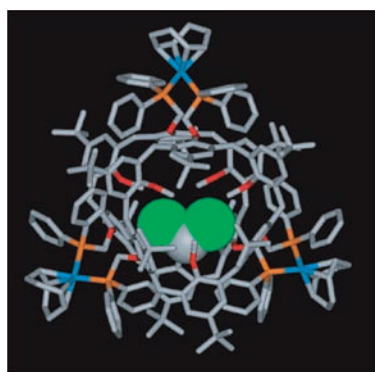
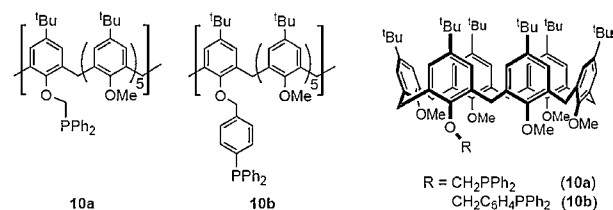


Figure 7. Crystal structure of **9**.

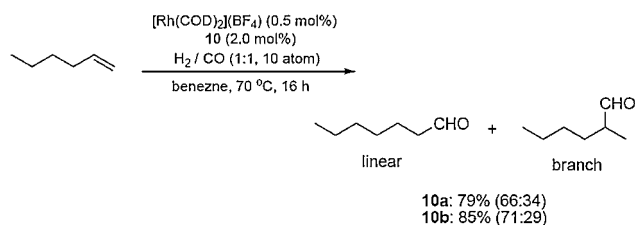
connected by methylene bridges in ortho position.<sup>27</sup> The molecules can be functionalized to provide a range of interesting molecular architectures. Among them, the combination between calixarenes and phosphine functionalities, namely phosphinocalixarenes<sup>28–30</sup> have received considerable attention since phosphine ligands generally play an important role in transition-metal-catalyzed reactions.

We synthesized a 1,3,5-triphosphinocalix[6]arene (**8**) which functioned as a tripodal phosphine ligand (Scheme 10). <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and 2D ROESY NMR spectra showed that **8** had a cone conformation in which all phenyl ring orient syn to each other. The reaction of **8** with [Ir(COD)<sub>2</sub>](BF<sub>4</sub>) in CH<sub>2</sub>Cl<sub>2</sub> afforded a novel capsule-shaped Ir<sup>I</sup> complex **9** (Scheme 10).<sup>28</sup> The X-ray crystal structure of **9** showed that one CH<sub>2</sub>Cl<sub>2</sub> molecule was encapsulated in cavity (Figure 7). Detailed analysis based on <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy as well as theoretical calculations indicated that the complex **9** encapsulated solvent molecules size-selectively.

We recently reported that synthesis and characterization of



Scheme 11.



Scheme 12.

phosphinocalix[6]arenes having mono-*O*-diphenylphosphino-methyl- and mono-*O*-(4-diphenylphosphinophenyl)methyl functionalities **10a** and **10b** as the first example of monodentate phosphane ligands bearing the calix[6]arene moiety (Scheme 11).<sup>29</sup> Although NMR study suggested **10a** and **10b** had cone conformation in solution as displayed in Scheme 11, the X-ray structural analysis clarified **10a** adapted 1,2,3-alternate conformation in which three pairs of diametrically opposite phenyl rings oriented anti to each other. The DFT calculation showed that the cone conformation was slightly more stable than the 1,2,3-alternate conformation by 0.36 kcal/mol for **10a** and 0.96 kcal/mol for **10b**. These monophosphinocalix[6]arenes were employed in rhodium-catalyzed hydroformylation<sup>31</sup> of 1-hexene to show good catalytic activity (Scheme 12).

## ◆ Summary and Future Outlook

Recent development in homogeneous transition metal catalysts with well-defined nanosized ligands was overviewed. These systems realize efficient catalysts with remarkable enhancement of catalytic activity, suppression of metal aggregation, and unique selectivity. Excellent design and well-defined structures should be crucial for successful results.

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