

# Phosphines Having a 2,3,4,5-Tetraphenylphenyl Moiety: Effective Ligands in Palladium-Catalyzed Transformations of Aryl Chlorides

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Three new triarylphosphines were prepared that have a 2,3,4,5-tetraphenylphenyl (TPPh) moiety on one of the phenyl rings (at the *ortho*, *meta*, or *para* position) of triphenylphosphine. Among them, the *ortho* derivative is particularly effective to utilize unactivated aryl chlorides in three different palladium-catalyzed reactions, i.e., Suzuki–Miyaura coupling, Mizoroki–Heck reaction, and silylation with  $\text{Me}_3\text{SiSiMe}_3$ . On the other hand, the corresponding *meta* and *para* derivatives are not effective as ligands at all in these catalytic reactions. X-ray crystal structures of Pd(0) complexes having the effective phosphines (*ortho* derivatives) as ligands show that  $\eta^2$ -coordination on the TPPh moiety is general and operative to realize a highly active catalyst system.

## Introduction

Dendrimers consisting of a 2,3,4,5-tetraphenylphenyl (TPPh) moiety are receiving considerable attention as polyphenylene nanomaterials due to their eminent optical and electrical properties.<sup>1</sup> We have recently found that the new pyridine ligand (**1**) having a TPPh moiety at the 3-position is an excellent ligand in a palladium-catalyzed air oxidation of alcohols to suppress Pd black formation and maintain catalytic activity for a long time.<sup>2</sup> We also reported that the new chiral diamine ligand (**2**) having a TPPh moiety realizes high selectivity in kinetic resolution of axially chiral 2,2'-dihydroxy-1,1'-biaryls by palladium-catalyzed alcoholysis.<sup>3</sup> The rigid and spatially spread TPPh moiety on the pyridine (**1**) and the diamine (**2**) ligands has a pronounced effect on these catalytic reactions.

Phosphines are also very important ligands in homogeneous transition metal catalysis.<sup>4</sup> In the present study, we prepared new triarylphosphines bearing TPPh on one of the phenyl rings of triphenylphosphine (*ortho*: **3**, *meta*: **4**, *para*: **5**). Among them, **3** is a particularly efficient ligand to utilize unactivated aryl chlorides<sup>5</sup> in three different palladium-catalyzed reactions, i.e., Suzuki–Miyaura coupling,<sup>6</sup> Mizoroki–Heck reaction,<sup>7</sup> and silylation with  $\text{Me}_3\text{SiSiMe}_3$ .<sup>8</sup>

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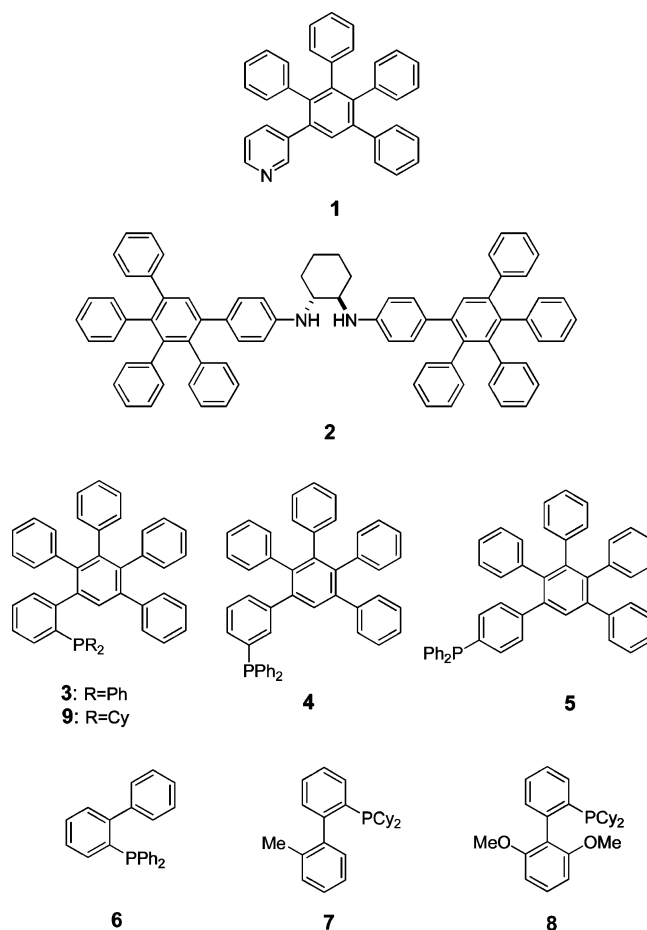
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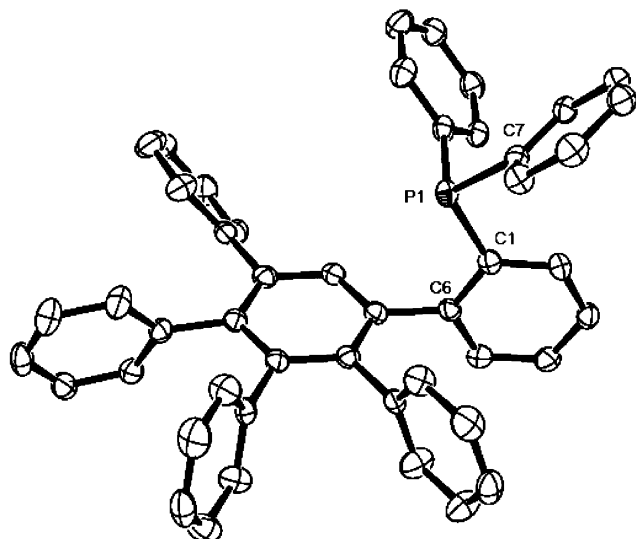
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## Results and Discussion

Novel phosphines (**3**, **4**, and **5**) were synthesized straightforwardly by lithiation of the corresponding bromides followed

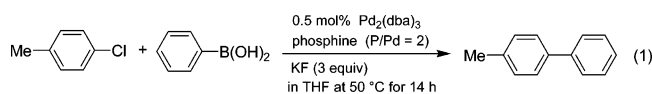
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**Figure 1.** ORTEP drawing of **3** with thermal ellipsoids at the 50% probability level.

by treatment with  $\text{Ph}_2\text{PCl}$ . The molecular structure of **3** determined by crystallographic analysis is shown in Figure 1.<sup>9</sup> The structure shows that the TPPh moiety spatially spreads out and the lone pair of the phosphorus atom points to the TPPh unit due to steric repulsion between the TPPh and the phenyl rings on the phosphorus.

The triarylphosphines **3**, **4**, and **5** were employed as a ligand in Suzuki–Miyaura coupling of an unactivated aryl chloride, 4-chlorotoluene, with phenylboronic acid in the presence of  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (dba = dibenzylideneacetone, 1,5-diphenyl-1,4-pentadien-3-one) and KF in THF at 50 °C (eq 1). In the reaction, **3** as the ligand smoothly afforded 4-methylbiphenyl in 92% yield. In contrast, the use of the corresponding *meta* (**4**) and *para* (**5**) derivatives gave no coupling adduct and the starting materials remained unchanged. Without a phosphine ligand or with a phosphine such as diphenyl(2-phenylphenyl)phosphine (**6**),<sup>10</sup>  $\text{PPh}_3$ , tri(*o*-tolyl)phosphine, tris(2,4,6-trimethylphenyl)phosphine, tri(4-methoxyphenyl)phosphine, 1,2-bis-(diphenylphosphino)ethane (DPPE), and ( $\pm$ )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), almost no conversions of 4-chlorotoluene were observed in eq 1. Thus, **3** is a very unique phosphine to activate and utilize unactivated aryl chlorides<sup>5</sup> in the coupling reaction.



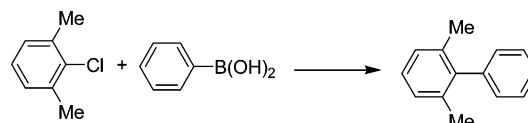
Very basic and bulky phosphines such as  $\text{P}(t\text{-Bu})_3$ ,<sup>11</sup>  $\text{PCy}_3$  (Cy = cyclohexyl),<sup>11</sup> **7**,<sup>12</sup> and **8**<sup>13</sup> have been reported as efficient ligands in Suzuki–Miyaura coupling of unactivated aryl chlorides. However, the basicity of **3** is not very high and is

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(9) Crystal data of **3**:  $\text{C}_{48}\text{H}_{35}\text{P}$ , triclinic, space group  $P\bar{1}$  (#2), colorless,  $a = 12.414(3)$  Å,  $b = 12.782(3)$  Å,  $c = 23.901(5)$  Å,  $\alpha = 76.984(6)^\circ$ ,  $\beta = 71.554(6)^\circ$ ,  $\gamma = 86.812(6)^\circ$ ,  $V = 3504.6(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = -160$  °C,  $d_{\text{calcd}} = 1.218$  g cm<sup>-3</sup>,  $\mu(\text{Mo}, K\alpha) = 1.12$  cm<sup>-1</sup>, observed reflections 30 955 ( $I > 3\sigma(I)$ ),  $R_1 = 0.0625$ ,  $wR_2 = 0.165$ , GOF = 1.540.

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**Table 1.** Suzuki–Miyaura Coupling of 2-Chloro-1,3-dimethylbenzene with Phenylboronic Acid with Various Phosphines<sup>a</sup>



entry	phosphine	conditions <sup>a</sup>	yield (%) <sup>b</sup>
1	<b>3</b>	A	92 (84)
2	$\text{P}(t\text{-Bu})_3$	A	12
3	$\text{PCy}_3$	A	24
4	<b>7</b>	A	3
5	<b>8</b>	A	2
6	<b>9</b>	A	51
7	<b>3</b>	B	82
8	$\text{P}(t\text{-Bu})_3$	B	6
9	$\text{PCy}_3$	B	0
10	<b>7</b>	B	2
11 <sup>c</sup>	<b>7</b>	B	61
12	<b>8</b>	B	0
13	<b>9</b>	B	32
14	<b>3</b>	C	1
15	$\text{P}(t\text{-Bu})_3$	C	10
16	$\text{PCy}_3$	C	6
17	<b>7</b>	C	10
18	<b>8</b>	C	>99
19	<b>9</b>	C	50
20 <sup>d</sup>	<b>9</b>	C	>99

<sup>a</sup> Conditions A: aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol),  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (0.005 mmol), phosphine (0.012 mmol), KF (3 mmol), in THF (1 mL) at 50 °C for 14 h. Conditions B: aryl chloride (0.5 mmol), phenylboronic acid (0.75 mmol),  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (0.005 mmol), phosphine (0.02 mmol),  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  (1.5 mmol), in toluene (1.7 mL) at 50 °C for 14 h. Conditions C: aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol),  $\text{Pd}(\text{OAc})_2$  (0.005 mmol), phosphine (0.005 mmol),  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  (3 mmol), in THF (1 mL) at room temperature for 14 h. <sup>b</sup> Determined by GC. Isolated yield in parentheses. <sup>c</sup> At 110 °C. <sup>d</sup> For 32 h.

comparable to that of triaryl phosphines.<sup>14,15</sup> Therefore, the efficacy of **3** as the ligand was compared with these representative phosphines of high basicity using 2-chloro-1,3-dimethylbenzene as a hindered substrate. It is well-known that the Suzuki–Miyaura coupling reaction is considerably affected by the nature of the catalyst precursor, the added base, and solvent.<sup>6,11–13</sup> Therefore, the efficacy of the phosphine ligands was examined under three different reaction conditions (Table 1): conditions A ( $\text{Pd}_2(\text{dba})_3$ –KF in THF at 50 °C),<sup>11a</sup> conditions B ( $\text{Pd}_2(\text{dba})_3$ – $\text{K}_3\text{PO}_4$  in toluene at 50 °C),<sup>12,13b</sup> and conditions C ( $\text{Pd}(\text{OAc})_2$ – $\text{K}_3\text{PO}_4$  in THF at room temperature).<sup>13a</sup> Under conditions A, **3** afforded the product in 92% yield (entry 1), although the basic phosphine ligands such as  $\text{P}(t\text{-Bu})_3$ ,  $\text{PCy}_3$ ,

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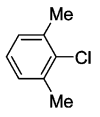
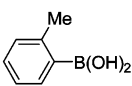
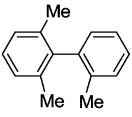
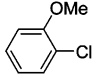
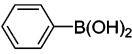
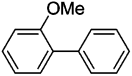
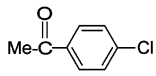
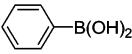
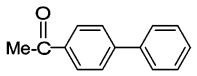

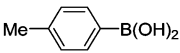
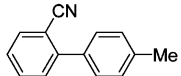
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(14) (a) Basicity of phosphines is evaluated by theoretical calculation (B3LYP/6-31G(d,p) level) of the molecular electrostatic potential minimum ( $V_{\text{min}}$ ) according to the method of Koga et al.<sup>14b</sup>  $V_{\text{min}}$  values (in kcal/mol) for the representative phosphines are as follows: **3**: –34.0, **4**: –35.3, **5**: –35.6, **6**: –34.8,  $\text{PPh}_3$ : –34.8,  $\text{P}(t\text{-Bu})_3$ : –45.2,  $\text{PCy}_3$ : –43.9, **7**: –47.4, **8**: –47.3, **9**: –44.9. More negative  $V_{\text{min}}$  values indicate more basic phosphines. (b) Suresh, C. H.; Koga, N. *Inorg. Chem.* **2002**, *41*, 1573–1578.

(15) (a) So far several phosphines<sup>13a,15b,c</sup> having comparable basicity to triaryl phosphines were found to be effective in Suzuki–Miyaura coupling of unactivated aryl chlorides. (b) Liu, S.; Choi, M. J.; Fu, G. C. *Chem. Commun.* **2001**, 2408–2409. (c) Yin, J.; Rainka, M. P.; Zhang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162–1163.

**Table 2. Suzuki–Miyaura Coupling of Various Aryl Chlorides with Arylboronic Acids<sup>a</sup>**

Entry	Aryl chloride	Boronic acid	mmol of cat Temp, Time	Product	Yield <sup>b</sup> (%)
1			2.5 × 10 <sup>-3</sup> mmol 65 °C, 8 h		93
2			2.5 × 10 <sup>-3</sup> mmol 50 °C, 8 h		97
3 <sup>c</sup>			3.5 × 10 <sup>-4</sup> mmol 50 °C, 16 h		91
4			5 × 10 <sup>-3</sup> mmol rt, 24 h		91

<sup>a</sup> Conditions: aryl chloride (1.0 mmol), arylboronic acid (1.5 mmol), KF (3 mmol), cat. Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (3.5 × 10<sup>-4</sup> to 5 × 10<sup>-3</sup> mmol), **3** (8.4 × 10<sup>-4</sup> to 1.2 × 10<sup>-2</sup> mol; P/Pd = 1.2), in THF (1 mL). <sup>b</sup> Isolated yields. <sup>c</sup> 4-Chloroacetophenone (1.4 mmol).

**7**, and **8** afforded the product in only low yields (2–24%, entries 2–5). Similar results were obtained under conditions B: **3** provided the product in 82% yield (entry 7), while the yields were low (0–6%) with the representative basic phosphine ligands (entries 8–10 and 12). With **7** as the ligand, the yield was 2% at 50 °C (entry 10), and the product was obtained in 61% yield when the reaction temperature was raised to 110 °C (entry 11). In contrast, under conditions C, **3** (the product in 1% yield, entry 14) as well as P(*t*-Bu)<sub>3</sub>, PCy<sub>3</sub>, and **7** (the product in 6–10% yields, entries 15–17) were not effective ligands at all, but **8** afforded the product almost quantitatively (entry 18). Even **3** is a very poor ligand under conditions C. Tuning the basicity of the phosphine might affect the efficiency. So, the corresponding dicyclohexyl derivative (**9**) was prepared and was used as the ligand in the catalytic reaction. As expected, **9** is much more basic than **3** ( $V_{\text{min}}^{14} = -44.9$  kcal/mol for **9**,  $-34.0$  kcal/mol for **3**). X-ray crystal structure analysis indicates that **9** has a very similar structure in which the lone pair on the phosphorus atom points to the TPPh moiety (see Figure S1 in the Supporting Information). Under conditions A, **9** (the product in 51% yield, entry 6) was not as effective as **3** (entry 1). Under conditions B, **9** (the product in 32% yield, entry 13) was not a better ligand than **3** either (entry 7). However under conditions C, **9** turned out to be a superior ligand to **3**, affording the product in 50% yield in 14 h (entry 19) and >99% yield in 32 h (entry 20). Thus, the phosphines **3** and **9**, having a TPPh moiety, are quite effective and unique ligands in the Suzuki–Miyaura coupling of unactivated aryl chlorides.

Several aryl chlorides and arylboronic acids were cross-coupled efficiently with **3** as the ligand (Table 2). The reaction between 2-chloro-1,3-dimethylbenzene and 2-methylphenylboronic acid successfully proceeded to afford 2,2',6,6'-trimethylbiphenyl in 93% yield (entry 1). 2-Chloroanisole provided the desired biphenyl in 97% yield (entry 2). Activated aryl chlorides with electron-withdrawing substituents gave the products in high yields with a low catalyst loading (0.05 mol %) (entry 3) or at room temperature (entry 4).

To further examine the efficacy of the phosphine ligands, **3** and **9**, having a TPPh moiety, two more palladium-catalyzed reactions, the Mizoroki–Heck reaction<sup>7</sup> and the silylation

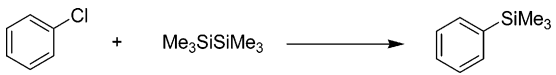
**Table 3. Mizoroki–Heck Reaction of Chlorobenzene with Methyl Acrylate with Various Phosphines<sup>a</sup>**

entry	phosphine	yield (%) <sup>b</sup>
1	<b>3</b>	>99 (98)
2	<b>4</b>	0
3	<b>5</b>	0
4	<b>6</b>	2
5	PPh <sub>3</sub>	1
6	P( <i>t</i> -Bu) <sub>3</sub>	63
7	PCy <sub>3</sub>	0
8	<b>7</b>	13
9	<b>8</b>	10
10	<b>9</b>	24

<sup>a</sup> Conditions: chlorobenzene (1 mmol), methyl acrylate (2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.015 mmol), phosphine (0.06 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.1 mmol) in 1,4-dioxane (1 mL), under reflux for 22 h. <sup>b</sup> Determined by GC. Isolated yield in parentheses.

reaction with Me<sub>3</sub>SiSiMe<sub>3</sub>,<sup>8</sup> were carried out. In the Mizoroki–Heck reaction of chlorobenzene with methyl acrylate (Table 3), the *ortho* derivative (**3**) was highly effective as the ligand to afford the desired product in >99% yield (entry 1), while the *meta* (**4**) and the *para* (**5**) derivatives did not afford the product at all and chlorobenzene remained unchanged (entries 2 and 3). With other triarylphosphines such as **6** and PPh<sub>3</sub>, conversions of chlorobenzene were very low (entries 4 and 5). As for the basic phosphines, P(*t*-Bu)<sub>3</sub> as the ligand showed substantial catalytic activity (the product in 63% yield, entry 6), as reported by Fu et al.<sup>16</sup> However, PCy<sub>3</sub>, **7**, and **8** gave the product in only 0%, 13%, and 10% yields, respectively (entries 7–9). The dicyclohexylphosphine **9** was not as effective as **3** and provided the product in 24% yield (entry 10).

In the silylation of chlorobenzene with Me<sub>3</sub>SiSiMe<sub>3</sub> (Table 4), the *ortho* derivative (**3**) afforded the silylated product in 77% yield (entry 1), while again *meta* (**4**) and *para* (**5**) derivatives were almost ineffective as the ligand (entries 2 and 3). With

**Table 4.** Palladium-Catalyzed Silylation of Chlorobenzene with Hexamethyldisilane with Various Phosphines<sup>a</sup>


entry	phosphine	yield (%) <sup>b</sup>
1	<b>3</b>	77
2	<b>4</b>	2
3	<b>5</b>	0
4	<b>6</b>	1
5	PPh <sub>3</sub>	1
6	P( <i>t</i> -Bu) <sub>3</sub>	62
7	PCy <sub>3</sub>	12
8	<b>7</b>	55
9	<b>8</b>	24
10	<b>9</b>	94

<sup>a</sup> Conditions: chlorobenzene (0.5 mmol), hexamethyldisilane (2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.0075 mmol), phosphine (0.03 mmol; P/Pd = 2), LiF (0.55 mmol), at 110 °C for 48 h. <sup>b</sup> Determined by GC.

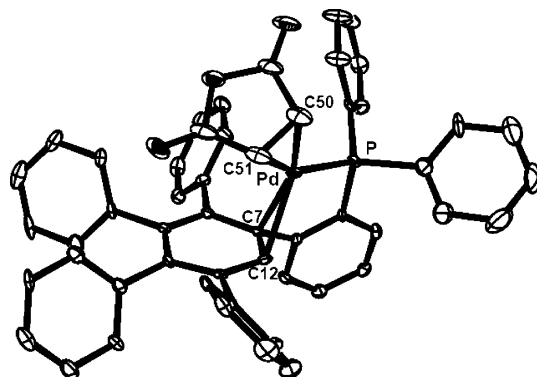
triarylphosphines such as **6** and PPh<sub>3</sub>, conversions of chlorobenzene were very low (entries 4 and 5). Basic phosphines such as P(*t*-Bu)<sub>3</sub> and **7** could be used in the reaction to afford the product in 62% (entry 6) and 55% (entry 8) yields, respectively. However, PCy<sub>3</sub> and **8** were not effective as the ligand, providing the product only in 12% (entry 7) and 24% (entry 9) yields, respectively. Noteworthy is that in the silylation reaction **9** was a more effective ligand than **3** to afford the product in 94% yield (entry 10).

In these palladium-catalyzed reactions using unactivated aryl chlorides as substrates (Tables 1–4), the phosphine ligands **3** and **9**, having a TPPh moiety at the *ortho* position, realize high catalytic activity. To elucidate why **3** is a very efficient ligand in these catalytic reactions, stoichiometric reactions of **3** with Pd(dba)<sub>2</sub><sup>17</sup> were carried out at 50 °C in THF-*d*<sub>8</sub> for 1 h at the three P/Pd ratios of 1, 2, and 3. The reactions were monitored by <sup>31</sup>P NMR. At P/Pd = 1, the <sup>31</sup>P resonance of free (uncoordinated) **3** at –12.7 ppm almost disappeared in 1 h and a new complex (**10**) appeared at 18.2 ppm. With P/Pd = 2 and 3, the complex **10** remained intact, and with an increase in the P/Pd ratio the peak intensity of the free **3** at –12.7 ppm increased. These results may suggest that complex **10** would be a *mono*(phosphine)palladium species with a composition such as Pd(**3**)(dba). However, all trials to isolate complex **10** were unsuccessful, because the complex was rather unstable and decomposed during the isolation procedures.

After several trials, we successfully stabilized the complex by substituting the dba ligand with maleic anhydride. First, the reaction of **3** with Pd(dba)<sub>2</sub> at 50 °C in THF-*d*<sub>8</sub> for 1 h was carried out at P/Pd = 1, which afforded complex **10** (<sup>31</sup>P resonance at 18.1 ppm) in 88% NMR yield. Then, to that reaction mixture at room temperature was added 1.2 equiv of maleic anhydride. The reaction was very clean. In 17 h, complex **10** disappeared and a new complex, **11**, having a <sup>31</sup>P resonance at 24.7 ppm, was given in 98% NMR yield. By concentrating the solution and adding pentane to it, single crystals of complex **11** suitable for X-ray crystal analysis were successfully obtained.

The molecular structure of **11** is shown in Figure 2.<sup>18</sup> Selected distances and angles are listed in Table 5. Complex **11** bears only the phosphine **3** and maleic anhydride as the ligands. The most characteristic feature of **11** is the intramolecular  $\eta^2$ -coordination

(17) In the catalytic reactions (Tables 1–4), Pd(dba)<sub>2</sub> as a catalyst precursor showed the same catalytic activity as Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>. Therefore, in the stoichiometric reaction, Pd(dba)<sub>2</sub> was employed in place of Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> since Pd(dba)<sub>2</sub> provided cleaner reactions.

**Figure 2.** ORTEP drawing of **11** with thermal ellipsoids at the 50% probability level.

dination of one of the phenyl rings of the TPPh moiety, as clearly shown by the short Pd–C7 and Pd–C12 distances of 2.376(3) and 2.361(3) Å, respectively. The phenyl ring containing C(7) and C(12) considerably deformed from planarity: the mean deviations from the plane of the corresponding phenyl rings are 0.0384 Å for **11** (Figure 2) and 0.0049 Å for **3** (Figure 1). The  $\eta^2$ -coordination stabilizes the *mono*(phosphine) species by adding two more electrons to the Pd(0) center. With the dicyclohexylphosphine **9**, similar clean reaction with Pd(dba)<sub>2</sub> (P/Pd = 1) afforded the Pd(**9**)(dba) complex, **12** (<sup>31</sup>P resonance at 30.3 ppm), in 99% NMR yield. The reaction of **12** with maleic anhydride similarly provided the Pd(**9**)(maleic anhydride) complex, **13** (<sup>31</sup>P resonance at 38.0 ppm), in 99% NMR yield. The X-ray crystal structure of **13** is very similar to that of **11**, with the same intramolecular  $\eta^2$ -coordination (see Figure S2 in the Supporting Information).

Very recently, Buchwald et al. reported less common  $\eta^1$ -coordination<sup>13</sup> with a Pd(0) complex having **8** as a ligand. The X-ray crystal structures of **11** and **13** (Figures 2 and S2) indicate that the more common  $\eta^2$ -coordination<sup>15c</sup> is a very characteristic feature of the ligands **3** and **9**, having a TPPh moiety. The  $\eta^2$ -coordination is only possible with the *ortho* derivatives **3** and **9**. With the *meta* (**4**) and the *para* (**5**) derivatives, such  $\eta^2$ -coordination and the resulting high catalytic activity cannot be expected. In the catalytic reactions, the intramolecular  $\eta^2$ -coordination stabilizes the *mono*-phosphine species, but the  $\eta^2$ -ligand would be labile and dissociate to generate highly unsaturated Pd(0) species having **3** or **9**, which must be the responsible species for the high catalytic activities in the three different palladium-catalyzed reactions of unactivated aryl chlorides (Tables 1–4). These observations clearly indicate that the  $\eta^n$ -coordination ( $n = 2$  or  $1$ ) facilitated by properly designed ligand such as **3**, **9**, and **8** is very general and operative to realize highly active catalyst systems.

## Experimental Section

**Preparation of 3.** To a dry and degassed solution of 2'-bromo-2,3,4,5-tetraphenylbiphenyl<sup>19</sup> (1.08 g, 2 mmol) in THF (24 mL) at –78 °C was added *n*-butyllithium (2.2 mmol, 1.59 M in hexane) dropwise over 2 min, and the resulting yellow suspension was stirred vigorously at –50 °C for 2.5 h. To the suspension at –78 °C was added chlorodiphenylphosphine (485 mg, 2.2 mmol)

(18) Crystal data of **11**·(C<sub>4</sub>H<sub>8</sub>O): C<sub>56</sub>H<sub>45</sub>O<sub>4</sub>PPd, triclinic, space group P1̄ (#2), pale yellow,  $a = 9.977(9)$  Å,  $b = 12.097(8)$  Å,  $c = 18.97(2)$  Å,  $\alpha = 85.60(6)^\circ$ ,  $\beta = 83.22(7)^\circ$ ,  $\gamma = 76.05(3)^\circ$ ,  $V = 2203.3(36)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = -160$  °C,  $d_{\text{calcd}} = 1.386$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 5.06$  cm<sup>-1</sup>, observed reflections 8318 ( $I > 3\sigma(I)$ ),  $R_1 = 0.0520$ ,  $wR_2 = 0.1540$ , GOF = 1.027.

(19) For a preparation method of this new compound, see the Supporting Information.

**Table 5. Selected Bond Lengths and Angles of 11**

length (Å)		angle (deg)	
Pd–P1	2.312(1)	P–Pd–C7	82.65(9)
Pd–C7	2.376(3)	P–Pd–C12	102.89(9)
Pd–C12	2.361(3)	P–Pd–C50	115.4(1)
Pd–C50	2.104(4)	P–Pd–C51	153.9(1)
Pd–C51	2.135(4)	P–Pd–C7	82.65(9)

dropwise over 3 min. The reaction mixture was allowed to warm to room temperature in 2 h with stirring. The solvent and all the volatiles were thoroughly removed under vacuum. To the residue were added chloroform (100 mL) and water (40 mL), and the whole solution was shaken vigorously in a separatory funnel. The separated organic layer was washed with water (40 mL), then brine (40 mL), and dried over  $\text{Na}_2\text{SO}_4$ . The solution was filtered and concentrated in vacuo to afford a crude product as viscous materials. The crude product was dissolved in chloroform (6 mL) and precipitated by pouring the solution into methanol (55 mL). A white powder was collected and dried in vacuo. Recrystallization from degassed propionitrile (10 mL) under an argon atmosphere afforded pure product as colorless crystals in 45% yield (579 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.34–7.23 (m, 9H), 7.20–6.81 (m, 24H), 6.66–6.64 (m, 2H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.6 (d,  $J_{\text{CP}} = 32$  Hz), 141.6, 141.3, 140.4, 140.11, 140.08, 140.0 (d,  $J_{\text{CP}} = 6.3$  Hz), 139.4, 139.23, 139.21, 138.5 (d,  $J_{\text{CP}} = 14$  Hz), 137.2 (d,  $J_{\text{CP}} = 13$  Hz), 136.4 (d,  $J_{\text{CP}} = 12$  Hz), 134.3 (d,  $J_{\text{CP}} = 21$  Hz), 133.6 (d,  $J_{\text{CP}} = 1.7$  Hz), 133.0 (d,  $J_{\text{CP}} = 18$  Hz), 132.3 (d,  $J_{\text{CP}} = 3.0$  Hz), 131.7, 131.5, 131.4, 130.9 (d,  $J_{\text{CP}} = 5.6$  Hz), 129.8, 128.5, 128.4 (d,  $J_{\text{CP}} = 7.4$  Hz), 128.2 (d,  $J_{\text{CP}} = 5.6$  Hz), 127.9, 127.8, 127.2, 127.0, 126.9, 126.8, 126.6, 126.4, 125.58, 125.54, 125.48, 125.2.  $^{31}\text{P}$  NMR (240 MHz,  $\text{CDCl}_3$ ):  $\delta$  –12.4. FD-MS  $m/z$ : 642 (100%,  $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{48}\text{H}_{35}\text{P}$ : C, 89.69; H, 5.49. Found: C, 89.40; H, 5.49.

**Procedure for Suzuki–Miyaura Coupling (Table 1, entry 1).** KF (174 mg, 3 mmol) was dried in vacuo in a 20 mL Schlenk flask with heating (heat gun) for 1 min. Then, phenylboronic acid (183 mg, 1.5 mmol),  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$  (5.2 mg, 0.005 mmol), and the phosphine **3** (7.7 mg, 0.012 mmol) were added to the flask, and the whole system was evacuated and backfilled with argon three times. Under an argon atmosphere, 2-chloro-1,3-dimethylbenzene (1 M in THF, 1 mL) was added, and the resulting suspension was stirred at room temperature for 10 min. The reaction was carried out at 50 °C for 14 h. After the reaction, the reaction mixture was diluted with ethyl acetate (15 mL) and filtered. GC analysis with an internal standard, tridecane (39 mg, 0.21 mmol), showed that 2,6-dimethylbiphenyl<sup>12</sup> was obtained in 92% yield. The product

was isolated in 84% yield by column chromatography (silica gel with hexane as an eluent).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45–7.41 (m, 2H), 7.36–7.32 (m, 1H), 7.19–7.11 (m, 5H), 2.04 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.3, 141.6, 136.5, 129.5, 128.9, 127.8, 127.5, 127.1, 21.3. MS (EI)  $m/z$ : 182 ( $\text{M}^+$ ), 167.

**Procedure for the Mizoroki–Heck Reaction.**  $\text{Cs}_2\text{CO}_3$  (385 mg, 1.1 mmol) was dried in vacuo in a 20 mL Schlenk flask with heating (heat gun) for 1 min. Then, the flask was charged with  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$  (16 mg, 0.015 mmol) and the phosphine **3** (39 mg, 0.06 mmol), and the whole system was evacuated and backfilled with argon three times. Under an argon atmosphere, chlorobenzene (1 M in 1,4-dioxane, 1 mL) and methyl acrylate (172 mg, 2 mmol) were added. The resulting suspension was stirred at room temperature for 10 min. The reaction was carried out under reflux (oil bath at 110 °C) for 22 h. After the reaction, the reaction mixture was diluted with diethyl ether (15 mL) and filtered. GC analysis with tridecane (37 mg, 0.20 mmol) as an internal standard showed that methyl *trans*-cinnamate was obtained in >99% yield. The product was isolated in 98% yield (159 mg) by column chromatography (silica gel with EtOAc/hexane = 2/98 as an eluent), and its  $^1\text{H}$  NMR, GC, and TLC were identical to an authentic sample from Wako Pure Chemical.

**Procedure for Silylation of Chlorobenzene with Hexamethyldisilane.** LiF (14 mg, 0.55 mmol) was dried in vacuo in a 20 mL Schlenk flask with heating (heat gun) for 1 min. Then, the flask was charged with  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$  (7.8 mg, 0.0075 mmol) and the phosphine **3** (19 mg, 0.03 mmol), and the whole system was evacuated and backfilled with argon three times. Under an argon atmosphere, hexamethyldisilane (293 mg, 2 mmol) and chlorobenzene (56 mg, 0.5 mmol) were added, and the resulting suspension was stirred at room temperature for 10 min. The reaction was carried out at 110 °C for 48 h. After the reaction, the reaction mixture was diluted with ether (15 mL) and filtered. GC analysis with tridecane (18 mg, 0.10 mmol) as an internal standard showed that phenyltrimethylsilane was obtained in 77% yield. The product was isolated by distillation in 33% yield as a colorless oil, and its  $^{13}\text{C}$  NMR and GC were identical to an authentic material from Aldrich.

**Supporting Information Available:** Experimental details, characterization of new compounds, and X-ray crystal structures of **9** and **13**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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