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2,2′-Bis(diphenylphosphino)-1,1′-biphenyl: New Entry of Bidentate Triarylphosphine Ligand to Transition Metal Catalysts

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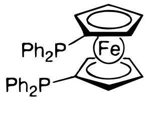
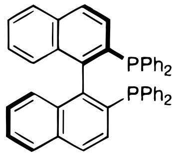
The bidentate triaryl phosphine 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (dpbp) was examined as a supporting ligand in several transition metal catalysts. The dpbp complexes showed superior catalytic activity to the corresponding complexes of other bisphosphines in Pd-catalyzed Grignard cross-coupling and Rh-catalyzed Michael addition of boronic acid. In the Pd-catalyzed Grignard cross-coupling of *sec*-BuMgCl, the Pd-dpbp catalyst showed nearly perfect secondary selectivity in the product. This selectivity is much higher than that of Pd catalysts with other standard bisphosphines and is comparable only with that of the corresponding Pd-dppf catalyst. Dpbp was also applied to Rh-catalyzed conjugate addition of boronic acids to enones, and the $\mathrm{Rh(acac)(C_2H_4)_2}$/dpbp catalyst exhibited excellent catalytic activity, which is far better than the corresponding catalyst with dppb. The structure of the dpbp complex $\mathrm{PdCl_2}$(dpbp) was studied by X-ray single-crystal structure determination, which clarified the bite angle of dpbp in the complex being 92.24°.

Introduction

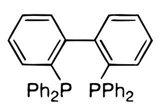
Tertiary phosphines have played very important roles as supporting ligands in transition metal chemistry. The characteristics of phosphine ligands are featured by two factors: one is electronic characteristics, and the other is steric. These characteristics are easily controlled simply by changing the substituents on the phosphorus atoms. The other important way of modifying the steric characteristics is connecting two (or more) phosphine units to make them function as bidentate (or polydentate) ligands. A variety of bidentate phosphines have been employed for coordination chemistry, organometallics, and transition metal catalysts. However, examples of "triaryl" bidentate phosphines are very rare, because of lack of suitable aromatic spacers between the two phosphorus atoms. Two triarylbisphosphines, dppf[1] and binap,[2] have been frequently employed with fair success in transition metal catalysis.[3] A representative example is application to Pd-catalyzed amination recently reported by Hartwig (with dppf)[4] and Buchwald (with binap).[5] Binap, which is a rather expensive chiral phosphine, was employed in the amination, although the reaction was *not* asymmetric. This fact prompted us to examine applications of 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (dpbp) to the palladium-catalyzed amination and other transition metal-catalyzed reactions. Surprisingly, since the first reliable report on dpbp synthesis in 1996,[6,7] no applications to transition metal catalysts have been reported except a preliminary communication on an Ir-dpbp system.[8] During our studies, we have found some examples in which dpbp complexes show superior reactivity to analogous complexes with other common bidentate phosphines. Furthermore, we have conducted X-ray crystallography of a dpbp complex, $\mathrm{PdCl_2}$(dpbp), which has clarified some aspects of dpbp, including its bite angle. Here we report our observations.



dppf



(*R*)-binap



dpbp

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(1) Dppf = 1,1′-bis(diphenylphosphino)ferrocene. Gan, K.-S.; Hor, T. S. A. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; pp 3−104.

(2) Binap = 2,2′-bis(diphenylphosphino)-2, 2′-binaphthyl. (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. (b) Miyashita, A.; Takaya, H.; Souchi, T.; Noyori, R. *Tetrahedron* **1984**, *40*, 1245.

(3) Recently, van Leeuwen et al. prepared a series of triarylbisphosphines of large bite angles and applied them to transition metal-catalyzed reactions. (a) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081. (b) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998**, 25. (c) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998**, 155. (d) Sadighi, J. P.; Harris, M. C.; Buchwald, S. L. *Tetrahedron Lett.* **1998**, *39*, 5327.

(4) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852, and references therein.

(5) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805, and references therein.

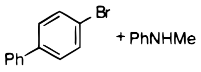
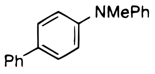
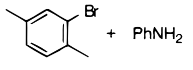
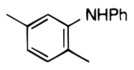
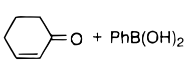
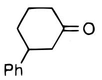
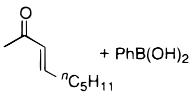
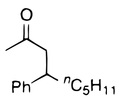
(6) (a) Desponds, O.; Schlosser, M. *J. Organomet. Chem.* **1996**, *507*, 257. (b) The first report on dpbp synthesis[6c] was found to be erroneous by Miyamoto et al. Miyamoto, T. K.; Matsuura, Y.; Okuda, K.; Ichida, H.; Sasaki, Y. *J. Organomet. Chem.* **1989**, *373*, C8. (c) Uehara, A.; Bailar, J. C., Jr. *J. Organomet. Chem.* **1982**, *239*, 1.

(7) Bennett et al. obtained a small amount of dpbp as a reductive elimination product from orthometalated complexes. See: (a) Bennett, M. A.; Bhargava, S. K.; Griffiths, K. D.; Robertson, G. B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 260. (b) Bennett, M. A.; Bhargava, S. K.; Hockless, D. C. R.; Welling, L. L.; Willis, A. C. *J. Am. Chem. Soc.* **1996**, *118*, 10469. (c) Bennett. M. A.; Contel, M.; Hockless, D. C. R.; Welling, L. L. *Chem. Commun.* **1998**, 2401.

(8) Yamagata, T.; Iseki, A.; Tani, K. *Chem. Lett.* **1997**, 1215.

10.1021/om9909587 CCC: $19.00

Table 1. Transition Metal Reactions Catalyzed by Dpbp Complexes

entry	catalyst	reagents	product	time/h	yield/%[a]
Palladium-catalyzed amination[b]					
1	$Pd_2(dba)_4$ + dpbp (5 mol % Pd)			2	97
2	$Pd_2(dba)_4$ + dpbp (5 mol % Pd)			5	>99
Palladium-catalyzed Grignard cross-coupling[c]					
3	$PdCl_2$(dpbp) (1 mol %)	PhBr + *sec*-BuMgCl	*sec*-BuPh	6	93[d, e]
4	$PdCl_2$(binap) (1 mol %)			6	95[d, f]
5	$PdCl_2$(dpbp) (1 mol %)	CH_2=CMeBr + *sec*-BuMgCl	*sec*-BuCMe=CH_2	12	84[d, g]
6	$PdCl_2$(binap) (1 mol %)			12	88[d, h]
Rhodium-catalyzed conjugate addition of boronic acid[i]					
7	Rh(acac)$(C_2H_4)_2$ + dpbp (3 mol %)			3	90
8	Rh(acac)$(C_2H_4)_2$ + dppb (3 mol %)			3	48
9	Rh(acac)$(C_2H_4)_2$ + dpbp (3 mol %)			3	94
10	Rh(acac)$(C_2H_4)_2$ + dppb (3 mol %)			3	21

[a] Isolated yield by silica gel chromatography unless otherwise noted. [b] In toluene at 100 °C with NaO^{t}Bu. [c] In Et_2O at 20 °C. [d] Determined by GC using tridecane as an internal standard. [e] 0.8% of *n*-BuPh was detected. [f] 0.4% of *n*-BuPh was detected. [g] 0.6% of *n*-BuCMe=CH_2 was detected. [h] 0.8% of *n*-BuCMe=CH_2 was detected. [i] In dioxane/H_2O (10/1) at 100 °C.

Results

Transition Metal-Catalyzed Reactions. The dpbp ligand was applied to three representative transition metal-catalyzed reactions: Pd-catalyzed amination, Pd-catalyzed Grignard cross-coupling, and Rh-catalyzed conjugate addition of boronic acid. The results are summarized in Table 1.

First, dpbp was applied to the palladium-catalyzed amination according to a procedure developed by Buchwald et al. for a Pd/binap catalyst (eq 1).[9] As expected, the Pd-dpbp catalyst showed reasonable catalytic activity for the C–N bond forming reaction (Table 1, entries 1 and 2). In the two representative examples, the catalyst generated in situ from $Pd_2(dba)_4$ and dpbp gave the amination products in very high yield in the presence of NaO^{t}Bu as base.

$$\text{Ar-Br} + \text{HNRR'} \xrightarrow[\text{Na-O}^t\text{Bu, toluene, 100 °C}]{\text{Pd}_2(\text{dba})_4/\text{dpbp}} \text{Ar-NRR'} \qquad (1)$$

Palladium-catalyzed cross-coupling reaction of Grignard reagents with aryl- or alkenyl halides is a powerful synthetic tool in modern synthetic chemistry. However, introduction of secondary alkyl groups using corresponding Grignard reagents still remains one of the most problematic reactions in this field, since it is accompanied by isomerization of the *sec*-alkyl moieties into the corresponding *n*-alkyls and/or reduction of the halides. The palladium–dppf catalyst was found to be especially effective for this problem.[10] The palladium catalyst with the dpbp ligand was examined in the cross-coupling reaction and showed nearly perfect *sec*-/*n*-selectivity like the Pd-dppf system (Table 1, entries 3 and 5).[10] The reaction of *sec*-butylmagnesium chloride with bromobenzene or 2-bromopropene was carried out in the presence of 1 mol % of $PdCl_2$(dpbp) in Et_2O (eq 2). After appropriate reaction time, *sec*-BuPh or *sec*-BuCMe=CH_2 was obtained in 93 or 84% yield with >99% selectivity. The two reactions were also run under the same conditions using an analogous Pd-binap catalyst, $PdCl_2$(binap), for comparison (Table 1, entries 4 and 6). As we expected, the Pd-binap catalyst showed reactivity and selectivity very similar to those by the Pd-dpbp catalyst. The choice of solvent is very important for the high selectivity of the reaction. In THF, the product from bromobenzene and *sec*-BuMgCl was obtained as a ca. 79/21 mixture of *sec*-/*n*-butylbenzene. The diminished *sec*-/*n*-selectivity in THF was observed for the Pd/dppf catalyst as well.

$$\text{R-Br} + sec\text{-BuMgCl} \xrightarrow[\text{Et}_2\text{O, 20 °C}]{\text{PdCl}_2(\text{dpbp})} sec\text{-BuR } (+\ n\text{-BuR}) \qquad (2)$$

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[9] Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215.

[10] Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

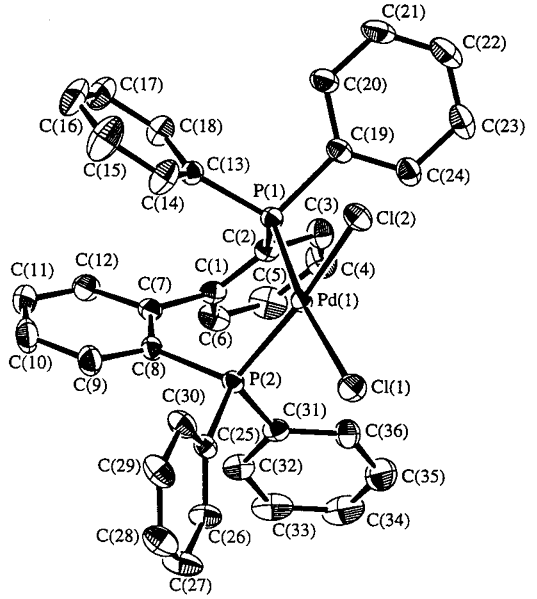
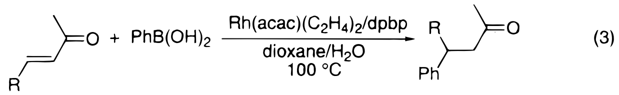


Figure 1. ORTEP drawing of $PdCl_2(dpbp)\cdot CHCl_3$ with 35% thermal ellipsoids. All hydrogen atoms and cocrystallized $CHCl_3$ are omitted for clarity.

The third reaction examined is rhodium-catalyzed conjugate addition of boronic acids to enones (eq 3; Table 1, entries 7−10). This relatively new reaction reported by Miyaura and co-workers is synthetically useful because it requires no moisture-sensitive reagents; however, reported yields of the reaction were not always satisfactory.[11] It was found that the chemical yields of the products were dramatically improved by employing a $Rh(acac)(C_2H_4)_2$/dpbp system as a catalyst instead of the originally reported $Rh(acac)(CO)_2$/dppb catalyst. Several modifications were made in the improved reaction conditions reported here, which included the rhodium precursor, the phosphine ligand, and the solvent. The reactions were also run using a corresponding $Rh(acac)(C_2H_4)_2$/dppb catalyst for comparison. It seems that application of dpbp is the most important for the enhancement of catalytic activity, since the catalyst with dppb exhibits much lower activity under the same conditions (Table 1, entries 7 vs 8 and 9 vs 10).



(3)

X-ray Crystal Structure of $PdCl_2$(dpbp). The complex $PdCl_2$(dpbp) was readily and quantitatively obtained from an equimolar mixture of $PdCl_2$(cod) and dpbp in dichloromethane. Recrystallization from $CHCl_3$/hexane gives prismatic crystals, and the structure was clarified by X-ray single-crystal structure determination (Figure 1). Selected crystallographic data are summarized in Table 2, and selected bond lengths and angles are listed in Table 3. It is revealed that the crystal contains a solvent molecule ($CHCl_3$) per formula unit (cocrystallized chloroform molecules are omitted from the ORTEP drawing for clarity), although no interaction is observed between the complex and the cocrystallized chloroform. The single crystal employed for crystallography consists of one of the enantiomers of $PdCl_2$(dpbp), which originates from atropisomerism of the coordinating dpbp. That is, $PdCl_2(dpbp)\cdot CHCl_3$ crystallizes as a racemic mixture. In accordance with this, a randomly picked single crystal of $PdCl_2(dpbp)\cdot CHCl_3$ exhibits optical rotation in chloroform ($[\alpha]^{20}_D$ ±4.3 (*c* 0.15, $CHCl_3$)). The overall molecular structure of the complex is C_2 symmetric with a small distortion. The angle P(1)−Pd(1)−P(2) is 92.24(4)°, while ∠Cl(1)−Pd(1)−Cl(2) is 88.21(5)°. The geometry around the Pd center is described as skewed square planar, which can be ascribed to the large bite angle of the dpbp ligand: the dihedral angle between the PdP_2 plane and the $PdCl_2$ plane is 14.40°. The Pd−P distances and the Pd−Cl distances are in the typical range for $PdCl_2$(P−P) complexes.[10,12]

Table 2. Crystallographic Data for $PdCl_2(dpbp)\cdot CHCl_3$

formula	$C_{37}H_{29}P_2Cl_5Pd$
fw	819.25
color, habit	yellow, prismatic
cryst size (mm)	0.16 × 0.30 × 0.36
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	10.524(4)
b (Å)	18.018(4)
c (Å)	19.060(4)
β (deg)	93.88(2)
V (Å^3)	3605(1)
Z	4
D_{calc} (g cm^{-3})	1.509
μ (cm^{-1})	10.00
F_{000}	1648.00
radiation type	Mo Kα
wavelength (Å)	0.71069
T (K)	300
$2\theta_{max}$ (deg)	55
total no. of data	8785
no. of unique data	8540
no. of obsd data	5353 ($I > 3.00\sigma(I)$)
no. of variables	494
R,[a] R_w[b]	0.040, 0.040
gof	1.87
residual ρ (e Å^{-3})	+0.73, −0.63

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $PdCl_2(dpbp)\cdot CHCl_3$

Bond Distances (Å)			
Pd(1)−Cl(1)	2.352(1)	P(1)−C(2)	1.833(5)
Pd(1)−Cl(2)	2.340(1)	P(1)−C(13)	1.804(5)
Pd(1)−P(1)	2.268(1)	P(1)−C(19)	1.821(5)
Pd(1)−P(2)	2.253(1)	P(2)−C(8)	1.832(4)
C(1)−C(7)	1.501(6)	P(2)−C(25)	1.817(5)
		P(2)−C(31)	1.804(5)

Bond Angles (deg)			
Cl(1)−Pd(1)−Cl(2)	88.21(5)	Pd(1)−P(1)−C(2)	114.4(1)
Cl(1)−Pd(1)−P(1)	169.53(5)	Pd(1)−P(1)−C(13)	107.2(2)
Cl(1)−Pd(1)−P(2)	90.52(5)	Pd(1)−P(1)−C(19)	109.4(2)
Cl(2)−Pd(1)−P(1)	90.84(5)	Pd(1)−P(2)−C(8)	115.5(2)
Cl(2)−Pd(1)−P(2)	169.69(5)	Pd(1)−P(2)−C(25)	110.5(2)
P(1)−Pd(1)−P(2)	92.24(4)	Pd(1)−P(2)−C(31)	113.7(2)

Discussion

It is interesting to compare the structures of $PdCl_2$(P−P) complexes, which are reported with a series of

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(11) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 4229.

(12) (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432. (b) Makhaev, V. D.; Dzhabieva, Z. M.; Konovalikhin, S. V.; D'yachenko, O. A.; Belov, G. P. *Russ. J. Coord. Chem.* **1996**, *22*, 563.

Table 4. Correlation of P−Pd−P and Cl−Pd−Cl Angles in $PdCl_2$(P−P) with Catalytic Activity in *sec*-BuMgCl Cross-Coupling with PhBr

			yield/%[a]	
P−P	P−Pd−P/deg	Cl−Pd−Cl/deg	*sec*-BuPh	*n*-BuPh
dppe	85.8[b]	94.2[b]	0	0
dppp	90.6[b]	90.8[b]	43	19
dppb	94.51[c]	89.78[c]	51	25
dpbp	92.24	88.21	93	1
dppf	99.07[d]	87.8[d]	95	2

[a] Results from ref 3c or 10 except data of dpbp. [b] Taken from ref 12a. [c] Taken from ref 12b. [d] Taken from ref 10.

bisphosphines such as dppe,[12a] dppp,[12a] dppb,[12b] and dppf.[10] Compared to these ligands, the bite angle of the coordinating dpbp is unremarkable: it is larger than those of dppe and dppp, while much smaller than those of dppb[13] and dppf (Table 4). On the other hand, the Cl−Pd−Cl angle in $PdCl_2$(dpbp) is characteristically small, second only to that of the dppf species (Table 4). When these d^8 four-coordinate complexes take square planar geometry, a linear correlation is expected between the P−Pd−P bite angles and the Cl−Pd−Cl angles. Indeed, this is the case with the exception of the dpbp species. The irregularity of $PdCl_2$(dpbp) is a consequence of large distortion from the planar structure.

Among the three catalytic reactions examined here, the palladium-catalyzed cross-coupling of *sec*-BuMgCl has been most extensively investigated, including effects of a variety of bidentate phosphine ligands.[3c,10] In the previous reports, reactivity and selectivity of the palladium catalysts were explained in connection with the bite angles of the phosphine ligands.[3c,10] However, the $PdCl_2$(dpbp) catalyst does not show a correlation between the bite angle and its reactivity/selectivity compared to the examples examined in the previous reports.[3c,10] The bite angle of dpbp in $PdCl_2$(dpbp) is moderate, although its selectivity is very high, which is comparable only with dppf, the bite angle of which is the largest (Table 4). The Cl−Pd−Cl angles may be more responsible for regulating the reactivity. Indeed the order of the Cl−Pd−Cl angles shows good agreement with the selectivity in the Grignard cross-coupling (Table 4).

In the catalytic cycle of the Grignard cross-coupling, the *sec*-Bu-Pd-R intermediate undergoes two different processes in the next step. One is reductive elimination to give the desired product *sec*-Bu-R; the other is isomerization to *n*-Bu-Pd-R species via successive β-hydride elimination and readdition, which will lead to the main side product *n*-Bu-R.[10] To achieve high selectivity, acceleration of the former process and/or diminution of the latter are required. The electronic nature of dpbp as triarylphosphine (weaker σ-donor) may stabilize the Pd^0 intermediate, which results in easier reductive elimination from *sec*-Bu-Pd-R prior to the isomerization. In view of this discussion, dpbp complexes are expected to be effective for many other catalytic reactions, especially those involving reductive elimination as crucial steps.

Concluding Remarks

The utility of dpbp as a supporting ligand in transition metal catalysts has been demonstrated by applying it to several catalytic reactions. Some part of the reactivity of the dpbp catalysts may be ascribed to the unique electronic characteristics of dpbp as a triarylbisphosphine, which is a rare example of this class of compounds. The phosphine is readily obtained in a bulk scale starting from inexpensive materials.[6a] The low-cost availability and the unique electronic features of dpbp will find further application of this ligand in transition metal chemistry. We propose here that it is worth trying dpbp when suitable phosphine ligands are surveyed in transition metal catalysts.

Experimental Section

General Comments. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk technique under predried nitrogen or with glovebox techniques under prepurified argon. Tetrahydrofuran, diethyl ether, dioxane, and toluene were distilled from sodium benzophenone−ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. Dpbp was prepared by either the reported method[6a] or a method employed for synthesis of 2,2′-bis[bis(3,5-dimethylphenyl)phosphino]-1,1′-biphenyl (see below).[14] $PdCl_2$(cod),[15] $Pd_2(dba)_4$,[16] and Rh(acac)$(C_2H_4)_2$[17] were synthesized as reported. All amines were purchased from Wako Pure Chemical Industries and were purified by passing through a short column of alumina. 2-Bromopropene was purchased from Aldrich Chemical Co. and used as received. All the other chemicals were purchased from either Tokyo Chemical Industry or Wako Pure Chemical Industries and used without further purification. Reaction progress was monitored by analytical TLC using 0.25 mm Merck F-254 silica gel glass plates. Visualization of the TLC plates was achieved by an UV illumination. NMR spectra were recorded on a JEOL JNM LA500 spectrometer (^1H, 500 MHz; ^{31}P, 202 MHz). ^1H NMR chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4. Optical rotations were measured on a JASCO DIP-370 polarimeter. X-ray crystallographic analyses were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα radiation. All the products from the catalytic reactions described in this paper are known compounds and characterized by comparison of their spectroscopic data with those previously reported.

2,2′-Bis(diphenylphosphinyl)-1,1′-biphenyl. To a mixture of ditriflate of 2,2′-biphenol (22.1 g, 49.1 mmol; prepared from 2,2′-biphenol and Tf_2O in CH_2Cl_2 in the presence of pyridine), diphenylphosphine oxide (29.8 g, 147 mmol), Pd(OAc)$_2$ (1.12 g, 5.0 mmol), and 1,4-bis(diphenylphosphino)butane (2.13 g, 5.0 mmol) were added dimethyl sulfoxide (220 mL) and diisopropylethylamine (38.0 g, 294 mmol). The heterogeneous mixture was stirred at 100 °C for 15 h. After cooling to room temperature, the reaction mixture was evaporated to dryness under reduced pressure. The dark brown residue was dissolved in $CHCl_3$, and the chloroform solution was washed with saturated NaCl twice, dried over $MgSO_4$,

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[13] Dppb has a tendency to behave as a bridging ligand. The Pd-dppb catalyst precursor employed for the cross-coupling was the mononuclear species;[12b] however, a possibility of isomerization into polynuclear species in solution could not be excluded. See: Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971.

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filtered, and then concentrated under reduced pressure. The residue was chromatographed on silica gel with acetone as an eluent to give the title compound as white crystals; yield 20.7 g (37.3 mmol, 76%). The material showed identical NMR spectra with those reported previously.[6a]

2,2′-Bis(diphenylphosphino)-1,1′-biphenyl. To a mixture of 2,2′-bis(diphenylphosphinyl)-1,1′-biphenyl (12.9 g, 23.3 mmol) and NEt_3 (40 mL) in xylene (300 mL) was added $HSiCl_3$ (16.0 g, 118 mmol) under nitrogen at 0 °C. The mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was quenched with a small amount of saturated $NaHCO_3$ (ca. 30 mL) and warmed to 100 °C. The resulting suspension was filtered while it was hot, and the solid was washed with hot toluene. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was recrystallized from hot toluene to give three crops of the phosphine as colorless crystals (11.3 g, 93%). The material showed identical NMR spectra with those reported previously.[6a]

Palladium-Catalyzed Amination. A mixture of aryl bromide (0.50 mmol), amine (0.60 mmol), sodium *tert*-butoxide (0.70 mmol), $Pd_2(dba)_4$ (12.5 μmol), and dpbp (38 μmol) was placed in a Schlenk flask under Ar. To this was added toluene (2 mL), and the suspension was stirred at 100 °C until the starting material had been completely consumed (checked by GC). The solution was allowed to cool to room temperature, diluted with Et_2O, and then filtered. After removing the solvent, the residue was chromatographed on silica gel. All the products were determined to be >98% pure by ^1H NMR and GC analysis.

Palladium-Catalyzed Grignard Cross-Coupling. A Schlenk flask was charged with $PdCl_2(dpbp)$ (7.0 mg, 10 μmol) under nitrogen. To this were added *sec*-butylmagnesium chloride (ca. 1.0 mol/L in Et_2O, 2 mL), bromobenzene or 2-bromopropene (1.0 mmol), and tridecane (0.20 mmol, an internal standard) successively by means of syringe at −78 °C. Then, the mixture was stirred at 20 °C until the starting material had been completely consumed (checked by GC). Samples were hydrolyzed with 10% HCl, and the ethereal layer was separated and analyzed by GC.

Rhodium-Catalyzed Conjugate Addition. A mixture of phenylboronic acid (122 mg, 1.00 mmol), $Rh(acac)(C_2H_4)_2$ (3.1 mg, 12 mmol), and dpbp (7.3 mg, 14 mmol) was placed in a Schlenk flask under nitrogen. To this were added dioxane (1 mL), water (0.1 mL), and enone (0.40 mmol) by means of syringe. The mixture was stirred for 3 h at 100 °C, then the solvents were removed under reduced pressure at room temperature. The residue was extracted with ethyl acetate three times, and the combined organic layer was washed with saturated $NaHCO_3$ twice. After removing the solvent, the residue was purified by chromatography on silica gel.

Dichloro[2,2′-bis(diphenylphosphino)-1,1′-biphenyl]-palladium. A mixture of $PdCl_2(cod)$ (286 mg, 1.00 mmol) and dpbp (533 mg, 1.02 mmol) in dichloromethane (30 mL) was stirred for 1 h at room temperature, then all the volatiles were removed under reduced pressure. The yellow residue was dissolved in a minimum amount of dichloromethane and recrystallized by slow diffusion of pentane into the concentrated dichloromethane solution at room temperature, yielding yellow prismatic crystals; yield 829 mg (80% as $PdCl_2(dpbp)\cdot 4CH_2Cl_2$). Prolonged evacuation of the crystals at 150 °C gave the solvent-free complex. An analytically pure sample, which was suitable for X-ray single-crystal structure determination, was obtained by recrystallization from chloroform/hexane as mono-$CHCl_3$ cocrystals, mp 190 °C (dec). ^1H NMR ($CDCl_3$, 26 °C): δ 6.68 (dd, J = 4.2 and 7.3 Hz, 2H), 6.89−6.95 (m, 4H), 7.12 (t, J = 7.1 Hz, 2H), 7.24−7.27 (m, 4H), 7.35−7.41 (m, 6H), 7.43−7.46 (m, 2H), 7.67 (dd, J = 7.6 and 12.2 Hz, 4H), 7.86 (dd, J = 7.2 and 10.9 Hz, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 26 °C): δ 27.1 (s). $[\alpha]^{20}_D$ 4.3 (c 0.15, $CHCl_3$; absolute value). Anal. Calcd for $C_{37}H_{29}Cl_5P_2Pd$ (as mono-$CHCl_3$ cocrystals): C, 54.25; H, 3.57. Found: C, 54.05; H, 3.38.

X-ray Structure Determination of $PdCl_2(dpbp)\cdot CHCl_3$. A crystal of suitable size was mounted on a glass fiber using an adhesive agent, and it was then transferred to a goniostat for characterization and data collection. An automated search for peaks in the range 29.07° < 2θ < 29.97° followed by analysis revealed a primitive monoclinic cell. Following intensity data collection (6° < 2θ < 55°), the additional conditions $h + 1 \neq 2n$ for $h01$ and $k \neq 2n$ for $0k0$, uniquely determined space group $P2_1/n$. Azimuthal scans of several reflection indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.71050×10^{-7}).

The structure was solved by direct methods (SIR92) and expanded using Fourier techniques. In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters, and the hydrogen atoms were varied with isotropic thermal parameters. The final difference map was reasonably clean, the largest peak being 0.73 and the deepest hole −0.63 e/Å^3.

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Supporting Information Available: Tables of crystallographic data for $PdCl_2(dpbp)\cdot CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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