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Base controlled (1,1)- and (1,2)-hydrophosphination of functionalized alkynes

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Abstract

The (1,1)- and (1,2)-addition of diphenylphosphine to 3-butyn-2-one and ethyl propiolate can be controlled chemoselectively by regulating the amount of triethylamine as the external base and in the presence of the chiral organopalladium(II) template derived from (*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine.

The synthesis of functionalized chiral phosphines is considered important since these ligands play vital roles in transition metal catalyzed reactions.[1] The addition of secondary phosphines to carbon–carbon multiple bonds is generally considered a straightforward and efficient organic synthetic process.[2] However, this approach continues to pose considerable challenges in the preparation of oxygen-sensitive and highly reactive phosphines. Transition metal complex-assisted hydrophosphination reactions have been reported.[3] In general, metal complexes offer better stabilization and selectivity in hydrophosphination reactions than other reaction promoters such as strong bases,[4] acids[5] and free radicals.[6] We have previously reported a series of chiral complex-promoted asymmetric 1,2-addition reactions with alkynes in the absence of an external base promoter.[7] Herein we present the preparation of functionalized diphosphines from substituted alkynes via a simple chiral palladium template-promoted hydrophosphination reaction. By regulating the amount of triethylamine, as a mild external base, the (1,1)- and (1,2)-addition pathways could be controlled chemoselectively. It is important to note that the functionalized 1,1-diphosphine products could not be produced by the traditional addition reaction using 1,1-bis(diphenylphosphino)-ethylene as the starting material.[8]

In the absence of triethylamine, diphenylphosphine shows no reactivity towards the functionalized alkynes **2a** and **2b** under ambient conditions, even in the presence of the standard chiral reaction promoter (*R*)-**3**.[7] In the presence of 2 mol % of triethylamine and the chiral palladium complex (*R*)-**3**, the reaction between diphenylphosphine and 3-butyn-2-one **2a** proceeded smoothly at −78 °C generating a 1:2 mixture of the stereoisomeric 1,1-addition products **4a** and **5a** regiospecifically (Scheme 1). The keto groups in these two isomeric product complexes are located on the opposite side of the square-plane. Prior to purification, the ^{31}P NMR spectrum of the crude reaction product in $CDCl_3$ exhibited two pairs of doublets at δ −18.8, 9.6 ($J_{PP} = 52$ Hz, minor product) and −18.5, 8.2 ($J_{PP} = 54$ Hz, major product), respectively. The 202 MHz ^{31}P NMR spectrum did not detect the presence of any sterically favourable (1,2)-addition products in the crude mixture. The isomeric mixture was then treated with concentrated hydrochloric acid to remove the chiral naphthylamine ligand to afford a single dichloro complex **6a** in 85% yield. The ^{31}P NMR spectrum of **6a** in CD_2Cl_2 exhibited a sharp singlet at δ −37.5. The X-ray structure of **6a** is shown in Figure 1. Interestingly, both the P(1)–C(13)–P(2) [92.8(1)°] and the P(1)–Pd(1)–P(2) [74.5(1)°] angles within the 4-membered ring are both rather small (see Tables 1 and 2).

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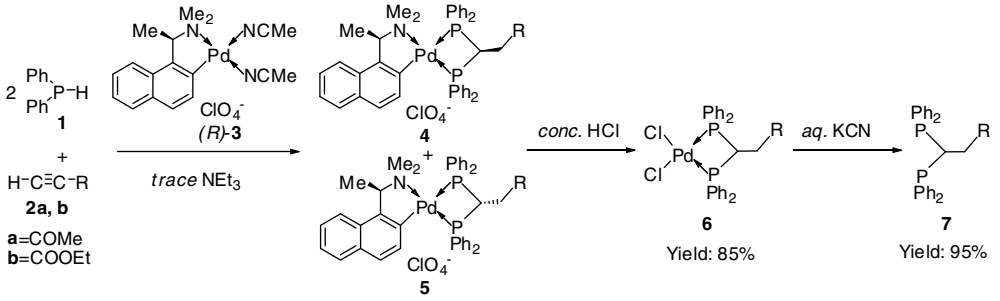


Scheme 1.

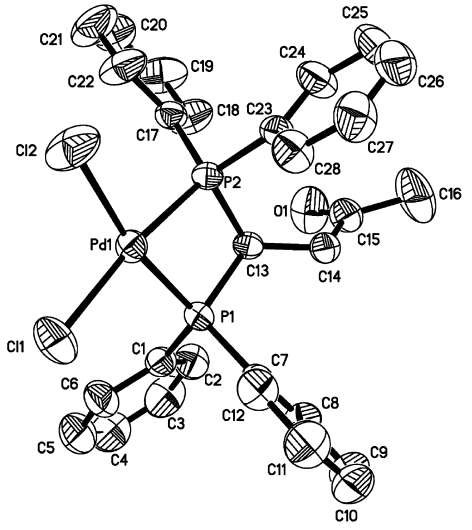


Fig. 1. Molecular structure of dichloro complex **6a**.

Table 1
Selected bond lengths (Å) and bond angles (°) of **6a**

Pd(1)–P(2)	2.2289(5)
Pd(1)–P(1)	2.2322(6)
Pd(1)–Cl(1)	2.3494(7)
Pd(1)–Cl(2)	2.3544(8)
P(1)–C(13)	1.8654(19)
P(2)–C(13)	1.8639(19)
C(13)–C(14)	1.528(3)
C(14)–C(15)	1.520(3)
P(2)–Pd(1)–P(1)	74.534(19)
P(2)–C(13)–P(1)	92.83(9)
P(2)–Pd(1)–Cl(1)	171.79(3)
P(1)–Pd(1)–Cl(1)	97.28(3)
P(2)–Pd(1)–Cl(2)	94.31(3)
P(1)–Pd(1)–Cl(2)	168.52(3)
Cl(1)–Pd(1)–Cl(2)	93.84(3)

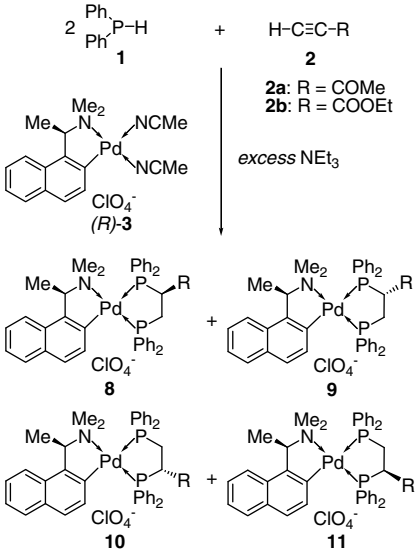
Treatment of a CH_2Cl_2 solution of **6a** with aqueous potassium cyanide liberated the keto-substituted diphosphine **7a** as a white solid in 95% yield. The ^{31}P NMR spectrum of the liberated ligand in $CDCl_3$ exhibited a sharp singlet at δ −5.3.

Interestingly, when the above hydrophosphination of 3-butyn-2-one **2a** was performed under similar reaction conditions but in the presence of excess triethylamine (20 equiv), the reaction proceeded exclusively via the (1,2)-addition pathway (Scheme 2). In $CDCl_3$, the 202 MHz ^{31}P NMR spectrum of the crude mixture indicated the four diastereomeric (1,2)-addition products only: four pairs of doublets were recorded with the intensity ratio of ca. 7:1:1:1 at δ

Table 2
Crystallographic data for complexes **6a**, **6b**, **8a** and **8b**

Formula	**6a** $C_{28}H_{26}Cl_2OP_2Pd$	**6b** $C_{29}H_{28}Cl_2O_2P_2Pd$	**8a** $C_{44}H_{47}ClNO_{5.50}P_2Pd$	**8b** $C_{43}H_{44}ClNO_6P_2Pd{\cdot}0.5CH_2Cl_2$
M	617.73	647.75	881.62	917.05
Space group	Cc	$P2(1)/c$	$P2(1)2(1)2$	$P2(1)$
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
a (Å)	17.3953(7)	20.6239(7)	29.8157(17)	19.6133(8)
b (Å)	8.7688(3)	16.0221(5)	10.9192(6)	9.4188(3)
c (Å)	18.2530(6)	18.0126(5)	13.2866(7)	23.1706(9)
V (Å^3)	2699.2(2)	5586.9(3)	4325.6(4)	4078.0(3)
Z	4	8	4	4
T (K)	298(2)	173(2)	298(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	1.024	0.995	0.610	0.714
R_1 (obs. data)[a]	0.0244	0.0408	0.0661	0.0540
wR_2 (obs. data)[b]	0.0575	0.0944	0.1167	0.1564
Flack parameter			−0.02(6)	0.01(3)

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.
[b] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_0)^2 + (aP)^2 + bP$.



Scheme 2.

45.1, 48.9 ($J_{PP} = 32$ Hz, major signals); 45.4, 48.3 ($J_{PP} = 32$ Hz); 29.2, 64.2 ($J_{PP} = 32$ Hz) and 41.0, 70.5 ($J_{PP} = 22$ Hz), respectively. Thus the spectroscopic study revealed that all the four possible diastereomeric 1,2-addition products **8a**–**11a** were generated in the hydrophosphination reaction. The major isomer **8a** was subsequently crystallized from acetone–diethyl ether as pale yellow prisms in 40% yield. The molecular structures and the absolute stereochemistry of **8a** were determined by X-ray crystallography (Fig. 2). The absolute chirality at C(16) is *S*. The P(2)–Pd(1)–P(1) bond angle [84.8(1)°] in **8a** is significantly larger than its counterpart in complex **6a** (Table 3). Unfortunately, the treatment of **8a** with concentrated hydrochloric acid generated the *racemic* dichloro complex **12a** in 90% yield (Scheme 3). The 202 MHz ^{31}P NMR spectrum of **12a** in $CDCl_3$ exhibited a pair of doublets at δ 47.4, 70.6 ($J_{PP} = 9$ Hz).

The racemization of the chiral keto-substituted diphosphine ligand is attributed to the classic keto–enol tautomerism of the carbonyl functionality during the acid treatment. This stereo-dynamic process readily disturbed the chirality of the stereogenic carbon centre in the chiral diphosphine ligand. To avoid this intrinsic problem, the keto group in the original alkyne was replaced by its ester analogue. Thus, in the presence of excess triethylamine (2 equiv), the hydrophosphination of ethyl propiolate **2b**

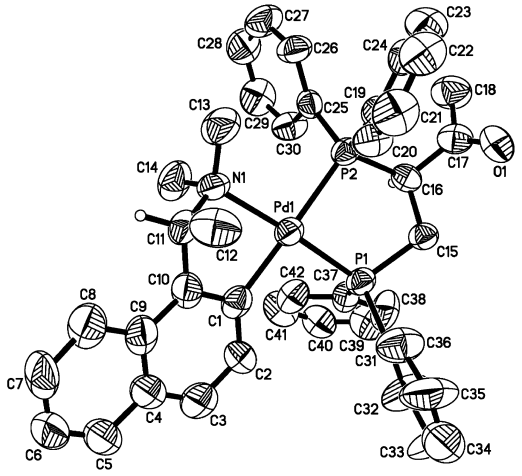
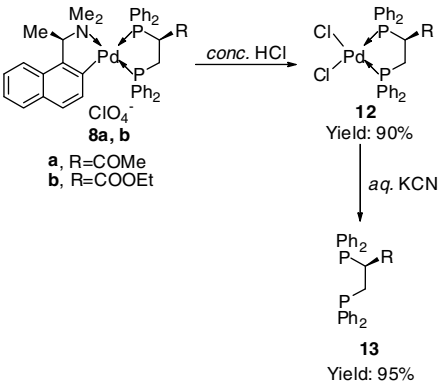


Fig. 2. Molecular structure of the cationic complex **8a**.



Scheme 3.

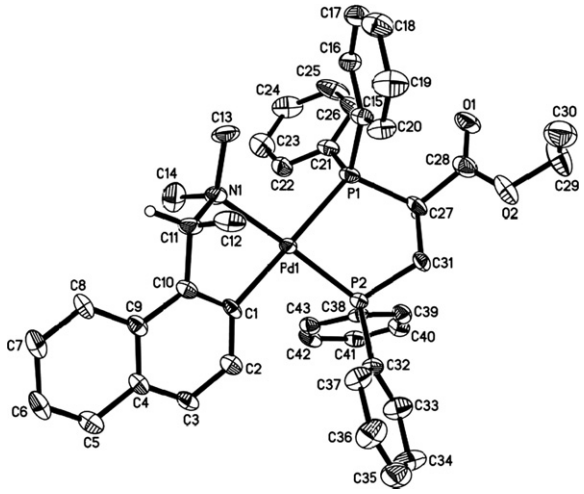


Fig. 3. Molecular structure of the cationic complex **8b**.

Table 3
Selected bond lengths (Å) and bond angles (°) of **8a**

Pd(1)–C(1)	2.042(11)
Pd(1)–N(1)	2.141(6)
Pd(1)–P(1)	2.246(2)
Pd(1)–P(2)	2.345(3)
C(16)–P(2)	1.860(9)
C(15)–C(16)	1.534(13)
C(15)–P(1)	1.822(10)
C(16)–C(17)	1.496(15)
C(1)–Pd(1)–N(1)	80.8(4)
C(1)–Pd(1)–P(1)	96.0(3)
N(1)–Pd(1)–P(1)	176.0(3)
C(1)–Pd(1)–P(2)	177.8(3)
N(1)–Pd(1)–P(2)	98.3(2)
P(1)–Pd(1)–P(2)	84.82(9)

Table 4
Selected bond lengths (Å) and bond angles (°) of **8b**

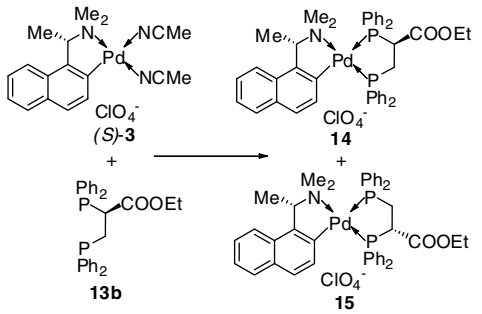
Pd(1)–C(1)	2.063(5)
Pd(1)–N(1)	2.162(5)
Pd(1)–P(2)	2.2440(14)
Pd(1)–P(1)	2.3814(13)
P(1)–C(27)	1.871(6)
P(2)–C(31)	1.833(5)
C(27)–C(28)	1.528(8)
C(27)–C(31)	1.532(8)
C(1)–Pd(1)–N(1)	79.4(2)
C(1)–Pd(1)–P(2)	97.44(16)
N(1)–Pd(1)–P(2)	176.62(13)
C(1)–Pd(1)–P(1)	179.16(16)
N(1)–Pd(1)–P(1)	99.80(13)
P(2)–Pd(1)–P(1)	83.33(5)

at −78 °C gave only three of the four possible (1,2)-addition diastereomeric products (Scheme 2).

In $CDCl_3$, the 202 MHz ^{31}P NMR spectrum of the crude product showed three pairs of doublets with the intensity ratio of ca. 18:3:1 at δ 47.6, 48.9 ($J_{PP} = 32$ Hz); 28.5, 66.4 ($J_{PP} = 33$ Hz) and 35.4, 69.9 ($J_{PP} = 26$ Hz), respectively. The major product **8b** was isolated from dichloromethane–diethyl ether as pale yellow prisms in 55% yield. The molecular structures and the absolute stereochemistry of **8b** were determined by X-ray crystallography (Fig. 3 and Table 4). The treatment of complex **8b** with concentrated hydrochloric acid gave the enantiomerically pure dichloro complex **12b** in 90% yield, with $[\alpha]_{436}$ −78 (*c* 0.5, CH_2Cl_2, 24 °C). In contrast to its keto-analogue, the absolute stereochemistry of the chiral diphosphine ligand in **12b** remained unchanged during the acidic treatment, as the ester group was not involved in a similar tautomerism process. As shown in Scheme 3, the treatment of a CH_2Cl_2 solution of **12b** with aqueous potassium cyanide liberated the optically pure diphosphine **13b** as a white solid in 95% yield, with $[\alpha]_{436}$ −33 (*c* 1.0, CH_3Cl, 24 °C). The ^{31}P NMR spectrum of the free diphosphine in $CDCl_3$ exhibited a pair of doublets at δ −16.6, 2.4 ($J_{PP} = 24$ Hz).

The optical purity of the liberated chiral diphosphine was confirmed by the quantitative recoordination of **13b** to (*R*)-**3**: the 202 MHz ^{31}P NMR spectrum of the crude product showed only two pairs of doublets with similar intensity at δ 47.6, 48.9 ($J_{PP} = 32$ Hz) and 28.5, 66.4 ($J_{PP} = 33$ Hz). The spectroscopic signals confirmed the formation of **8b** and its regio-isomer **10b**. In a further test of optical purity, the diastereomers **14** and **15** were prepared from **8b** and the equally accessible (*S*)-**3** (Scheme 4). The ^{31}P NMR spectrum of the crude product showed two clearly different pairs of doublets with similar intensity at δ 35.4, 69.9 ($J_{PP} = 26$ Hz) and 47.5, 47.9 ($J_{PP} = 31$ Hz).

Interestingly, the reaction rate and the (1,1)- and (1,2)-chemoselectivity of the hydrophosphination reaction are sensitive to the functionality present on the reacting alkyne. The ester-substituted alkyne **2b** appeared to favour the (1,2)-addition pathway. Thus when the amount of triethylamine was reduced to 2 mol %, the hydrophosphination reaction between diphenylphosphine and **2b** at −78 °C continued to give mostly the (1,2)-addition products. In contrast to the similar reaction involving keto-alkyne **2a**, only a small quantity of (1,1)-addition ester products, together with some as yet unidentified materials were generated under these conditions. The optimum condition for the synthesis of the (1,1)-addition products required the presence of 20 mol % of triethylamine and the reaction was conducted at room temperature. Under these conditions, a 2:3 mixture of the two stereoisomeric (1,1)-addition products **4b** and **5b** could be obtained in 50% isolated yield (Scheme 1). Treatment of the mixture with concentrated hydrochloric acid generated a single dichloro complex **6b**, quantitatively. As shown in Figure 4, the X-ray structural analysis of **6b** revealed that it has a similar molecular orientation to its keto counterpart **6a** (Table 5). There are no major steric repulsions around the ester functional group in **6b**. Thus, apart from the quantity of the external base used, the electronic properties of the functional group in the substituted-alkynes also play a major role in reaction mechanism of the current hydrophosphination reaction for the chemoselective formation of the (1,1)- and (1,2)-addition products. We are currently investigating the mod-



Scheme 4.

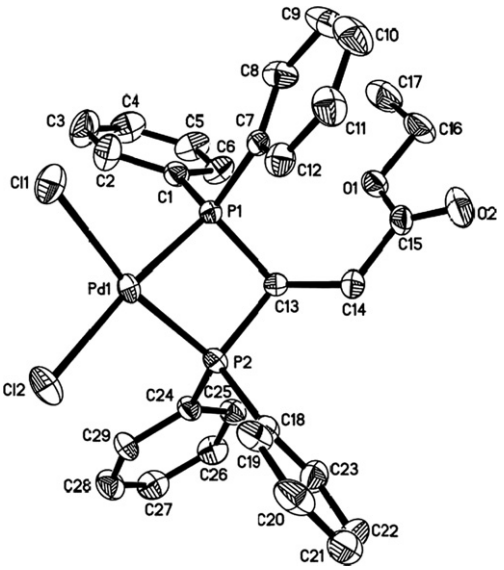


Fig. 4. Molecular structure of dichloro complex **6b**.

Table 5
Selected bond lengths (Å) and bond angles (°) of **6b**

Pd(1)–P(1)	2.2207(8)
Pd(1)–P(2)	2.2382(9)
Pd(1)–Cl(1)	2.3607(10)
Pd(1)–Cl(2)	2.3622(9)
P(1)–C(13)	1.866(3)
P(2)–C(13)	1.871(3)
C(13)–C(14)	1.536(5)
C(14)–C(15)	1.528(5)
P(1)–Pd(1)–P(2)	74.23(3)
P(1)–C(13)–P(2)	92.10(15)
P(1)–Pd(1)–Cl(1)	93.58(4)
P(2)–Pd(1)–Cl(1)	167.73(4)
P(1)–Pd(1)–Cl(2)	172.76(4)
P(2)–Pd(1)–Cl(2)	98.54(4)
Cl(1)–Pd(1)–Cl(2)	93.65(4)

ifications of the (1,1)-hydrophosphination reaction to generate a family of asymmetric 4-membered metal chelates .

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Proton NMR spectra were recorded at 300 MHz on a Bruker ACF300 NMR spectrometer. All the ^{31}P NMR spectra were recorded at 202 MHz on a Bruker ACF500 NMR spectrometer.

CCDC-667577 [for complex **6a**], -667578 [for complex **8a**], -667579 [for complex **8b**] and -667580 [for complex **6b**] contain the supplementary crystallographic data for this letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cdcc.cam.ac.uk/data_request/cif.

Selected physical and spectroscopic data for **6a**: Mp 212–214 °C. Anal. Calcd for $C_{28}H_{26}Cl_2OP_2Pd$: C, 54.4; H, 4.2. Found: C, 54.1; H, 4.0. ^{31}P NMR (CD_2Cl_2): δ −37.5; ^{1}H NMR (CD_2Cl_2): δ 1.42 (s, 3H, CO*Me*), 2.23 (dt, 2H, $^3J_{HH} = 7.6$ Hz, $J_{PH} = 15.1$ Hz, PCCH_2), 5.23 (tt, 1H, $^3J_{HH} = 7.6$ Hz, $J_{PH} = 10.6$ Hz, PC*H*), 7.44–8.17 (m, 20H, aromatics).

Selected physical and spectroscopic data for **6b**: Mp 197–199 °C. Anal. Calcd for $C_{29}H_{28}Cl_2O_2P_2Pd$: C, 53.8; H, 4.4. Found: C, 53.5; H, 4.6. ^{31}P NMR (CDCl3): δ −37.3; ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 3H, $^3J_{HH} = 7.1$ Hz, COOCH$_2$CH_3), 2.20 (dt, 2H, $^3J_{HH} = 8.0$ Hz, $J_{PH} =$ 15.1 Hz, PCCH_2), 3.81 (q, 2H, $^3J_{HH} = 7.1$ Hz, COOCH_2 CH$_3$), 5.19 (tt, 1H, $^3J_{HH} = 8.0$ Hz, $J_{PH} = 10.6$ Hz, PC*H*), 7.48–8.24 (m, 20H, aromatics).

Selected physical and spectroscopic data for **7a**: ^{31}P NMR ($CDCl_3$): δ −5.3; ^{1}H NMR (CD_2Cl_2): δ 1.36 (s, 3H, CO*Me*), 2.53 (dt, 2H, $^3J_{HH} = 5.4$ Hz, $J_{PH} = 9.1$ Hz, PCCH_2), 4.19 (tt, 1H, $^3J_{HH} = J_{PH} = 5.4$ Hz, PC*H*), 7.25–7.56 (m, 20H, aromatics).

Selected physical and spectroscopic data for **7b**: ^{31}P NMR ($CDCl_3$): δ −5.9; ^{1}H NMR ($CDCl_3$): δ 0.96 (t, 3H, $^3J_{HH} = 7.2$ Hz, COOCH$_2$CH_3), 2.41 (dt, 2H, $^3J_{HH} =$ 5.9 Hz, $J_{PH} = 9.2$ Hz, PCCH_2), 3.56 (q, 2H, $^3J_{HH} = 7.2$ Hz, COOCH_2CH$_3$), 3.91 (tt, 1H, $^3J_{HH} = J_{PH} = 5.9$ Hz, PC*H*), 7.28–7.60 (m, 20H, aromatics).

Selected physical and spectroscopic data for **8a**: Mp 203–204 °C; $[\alpha]_D$ −58 (*c* 0.5, CH_2Cl_2, 24 °C). Anal. Calcd for $C_{42}H_{42}ClNO_5P_2Pd$: C, 59.7; H, 5.0; N, 1.7. Found: C, 59.2; H, 5.4; N, 1.6. ^{31}P NMR ($CDCl_3$): δ 45.1, 48.9 ($J_{PP} = 33$ Hz); ^{1}H NMR ($CDCl_3$): δ 1.88 (s, 3H, CO*Me*), 1.95 (d, 3H, $^3J_{HH} = 6.1$ Hz, CH*Me*), 2.43 (d, 3H, $J_{PH} =$ 1.2 Hz, N*Meeq*), 2.51 (dd, 3H, $J_{PH} = J_{P'H} = 3.7$ Hz, N*Meax*), 2.76–2.88 (m, 1H, P^{2}C*H*H′), 2.95–3.06 (m, 1H, P^{2}CH*H*′), 3.77–3.88 (m, 1H, P^{1}C*H*COMe), 4.48 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.1$ Hz, C*H*Me), 6.87–8.19 (m, 26H, aromatics).

Selected physical and spectroscopic data for **8b**: Mp 182–184 °C; $[\alpha]_D$ −110 (*c* 0.5, CH_2Cl_2, 24 °C). Anal. Calcd for $C_{43}H_{44}ClNO_6P_2Pd$: C, 59.0; H, 5.1; N, 1.6. Found: C, 58.6; H, 5.2; N, 1.6. ^{31}P NMR ($CDCl_3$): δ 47.6, 48.9 ($J_{PP} = 32$ Hz); ^{1}H NMR ($CDCl_3$): δ 0.87 (t, 3H, $^3J_{HH} =$ 7.1 Hz, COOCH$_2$CH_3), 1.96 (d, 3H, $^3J_{HH} = 6.2$ Hz, CH*Me*), 2.48 (d, 3H, $J_{PH} = 1.2$ Hz, N*Meeq*), 2.61 (dd, 3H, $J_{PH} = J_{P'H} = 3.7$ Hz, N*Meax*), 2.89–3.00 (m, 1H, P^{2}C*H*H′), 3.06–3.16 (m, 1H, P^{2}CH*H*′), 3.17–3.29 (m, 1H, P^{1}C*H*COOEt), 3.78–3.94 (m, 2H, COOCH_2CH$_3$), 4.55 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.2$ Hz, C*H*Me), 6.87–8.26 (m, 26H, aromatics).

Selected physical and spectroscopic data for **12a**: Mp 188–189 °C. Anal. Calcd for $C_{28}H_{26}Cl_2OP_2Pd$: C, 54.4; H, 4.2. Found: C, 54.1; H, 4.0. ^{31}P NMR ($CDCl_3$): δ 47.4, 70.6 ($J_{PP} = 9$ Hz); ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 3H, CO*Me*), 2.57–2.68 (m, 1H, P^{2}C*H*H′), 2.75–2.87 (m, 1H, P^{2}CH*H*′), 3.66–3.78 (m, 1H, P^{1}C*H*COMe), 7.46–8.15 (m, 20H, aromatics).

Selected physical and spectroscopic data for **12b**: Mp 257–258 °C; $[\alpha]_{436}$ −78 (*c* 0.5, CH_2Cl_2, 24 °C). Anal. Calcd for $C_{29}H_{28}Cl_2O_2P_2Pd$: C, 53.8; H, 4.4. Found: C, 53.4; H, 4.4. ^{31}P NMR ($CDCl_3$): δ 49.0, 73.6 ($J_{PP} = 9$ Hz); ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, $^3J_{HH} = 7.1$ Hz, COOCH$_2$CH_3), 2.72–3.01 (m, 2H, PCH_2CHCOOEt), 3.47–3.61 (m, 1H, PC*H*COOEt), 3.82–3.85 (m, 2H, COOCH_2CH$_3$), 7.43–8.13 (m, 20H, aromatics).

Selected physical and spectroscopic data for **13b**: $[\alpha]_{436}$ −33 (*c* 1.0, CH_3Cl, 24 °C). ^{31}P NMR ($CDCl_3$): δ −16.6, 2.4 ($J_{PP} = 24$ Hz); ^{1}H NMR($CDCl_3$): δ 0.93 (t, 3H, $^3J_{HH} = 7.1$ Hz, COOCH$_2$CH_3), 2.16–2.26 (m, 1H, PCH′*H*CHCOOEt), 2.60–2.73 (m, 1H, PC*H*′HCHCOOEt), 3.19–3.28 (m, 1H, PC*H*COOEt), 3.68–3.89 (m, 2H, COOCH_2CH$_3$), 7.26–7.38 (m, 20H, aromatics).

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References and notes

1. (a) *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, England, 1990; (b) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857–871; (c) Pietrusiewicz, K. M.;

Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375–1411; (d) Quin, L. D. *A Guide to Organophosphorus Chemistry*; John Wiley and Sons, 2000.
2. (a) Wicht, D. K.; Glueck, D. S. In *Catalytic Hetero-functionalization*; Togni, A., Grutzmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Chapter 5; (b) Engel, R.; Cohen, J. L. I. *Synthesis of Carbon–Phosphorus Bonds*, 2nd ed.; CRC Press: Boca Raton, FL, 2003.
3. (a) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079–3159; (b) Sadow, A. D.; Togni, A. *J. Am. Chem. Soc.* **2005**, *127*, 17012–17024; (c) Treichel, P. M.; Wong, W. K. *J. Organomet. Chem.* **1978**, *157*, C5–C9; (d) Malish, W.; Rehmann, F. J.; Jehle, H.; Reising, J. *J. Organomet. Chem.* **1998**, *570*, 107–112.
4. Bunlaksananusorn, T.; Knochel, P. *Tetrahedron Lett.* **2002**, *43*, 5817–5819 and references cited therein.
5. Song, Y.; Mok, K. F.; Leung, P. H. *Inorg. Chem.* **1998**, *37*, 6399–6401.
6. (a) Rauhut, M. M.; Currier, H. A.; Semsel, A. M.; Wystrach, V. P. *J. Org. Chem.* **1996**, *26*, 5138–5145; (b) Deprele, S.; Montchamp, J. L. *J. Org. Chem.* **2001**, *66*, 6745–6755.
7. (a) Tang, L.; Zhang, Y.; Luo, D.; Li, Y.; Mok, K. F.; Yeo, W. C.; Leung, P. H. *Tetrahedron Lett.* **2007**, *48*, 33–35; (b) Pullarkat, S. A.; Ding, Y.; Li, Y.; Tan, G. K.; Leung, P. H. *Inorg. Chem.* **2006**, *45*, 7455–7463; (c) Yeo, W. C.; Tee, S. T.; Tan, G. K.; Koh, L. L.; Leung, P. H. *Inorg. Chem.* **2004**, *43*, 8102–8109.
8. (a) Hassan, F. S. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 3011–3016; (b) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1527–1530; (c) King, G.; Higgins, S. J.; Hopton, A. *J. Chem. Soc., Dalton Trans.* **1992**, 3403–3409.