

Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with Water Yielding (*E*)-1-Alkenylphosphine Oxides

Azusa Kondoh, Hideki Yorimitsu,* and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510

Received November 19, 2007; E-mail: yori@orgrxn.mbox.media.kyoto-u.ac.jp

Treatment of 1-alkynylphosphines with a rhodium catalyst in 1,4-dioxane/H_2O at reflux provides (*E*)-1-alkenylphosphine oxides in good yields with perfect stereoselectivity. The reaction proceeds as follows. Oxidative addition of 1-alkynylphosphine to rhodium followed by hydrolysis yields the corresponding terminal alkyne and diphenylphosphine oxide. Rhodium-catalyzed hydrophosphinylation of the terminal alkyne then proceeds to afford (*E*)-1-alkenylphosphine oxide.

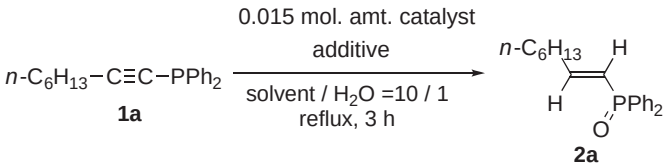
We have been interested in the use of 1-alkynylphosphines as precursors of new phosphines.[1] Here, we report a new transformation of 1-alkynylphosphines. 1-Alkynylphosphines react with water in the presence of a rhodium catalyst to provide the corresponding (*E*)-1-alkenylphosphine oxides[2] with perfect stereoselectivity. This is an interesting formal hydration reaction of 1-alkynylphosphines from mechanistic and synthetic points of view.

Results and Discussion

Treatment of 1-octynyldiphenylphosphine (**1a**) under [RhCl(cod)]$_2$ catalysis in 1,4-dioxane/H_2O (10/1) at reflux provided (*E*)-1-octenyldiphenylphosphine oxide (**2a**) in 84% NMR yield and 73% isolated yield (Table 1, Entry 1). Other rhodium complexes such as [Rh(OH)(cod)]$_2$ also showed catalytic activity (Entry 2). Addition of PPh_3 (2 mol. amt. to Rh) as a ligand had no effect on the reaction (Entry 3). In contrast, when BINAP (1 mol. amt. to Rh) or $P(OEt)_3$ (2 mol. amt. to Rh) was used instead of PPh_3, the reaction was completely inhibited (Entries 4 and 5). Rh(acac)$_3$ and an iridium catalyst, [IrCl(cod)]$_2$, were inactive (Entries 6 and 7).

1,4-Dioxane/H_2O was the choice of solvent. Although the

Table 1. Optimization of Reaction Conditions

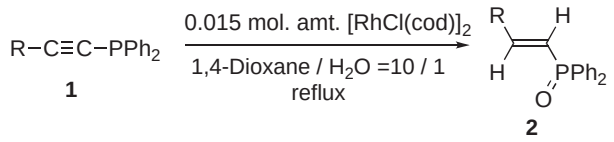


Entry	Catalyst	Additive	Solvent[f)]	Yield[a)]/%
1	[RhCl(cod)]$_2$	None	1,4-Dioxane	84 (73)
2	[Rh(OH)(cod)]$_2$	None	1,4-Dioxane	75
3	[RhCl(cod)]$_2$	PPh_3[b)]	1,4-Dioxane	85
4	[RhCl(cod)]$_2$	BINAP[c)]	1,4-Dioxane	0
5	[RhCl(cod)]$_2$	$P(OEt)_3$[b)]	1,4-Dioxane	0
6	Rh(acac)$_3$	None	1,4-Dioxane	0
7	[IrCl(cod)]$_2$	None	1,4-Dioxane	0
8	[RhCl(cod)]$_2$	None	Toluene[g)]	0–84
9	[RhCl(cod)]$_2$	None	THF	0
10	[RhCl(cod)]$_2$	None	CH_3CN	0
11	[RhCl(cod)]$_2$	None	$ClCH_2CH_2Cl$[g)]	0
12[d)]	[RhCl(cod)]$_2$	None	1,4-Dioxane	0
13[e)]	[RhCl(cod)]$_2$	None	1,4-Dioxane	0–84

a) Based on ^{31}P NMR with a sufficient first decay period. Isolated yields are in parentheses. b) 2 mol. amt. to Rh. c) 1 mol. amt. to Rh. d) The reaction was performed without H_2O. e) The reaction was performed with H_2O (3 mol. amt. to **1a**). f) The reaction is homogeneous unless otherwise noted. g) The reaction proceeded in a two-phase medium.

Published on the web April 10, 2008; doi:10.1246/bcsj.81.502

Table 2. Synthesis of (*E*)-1-Alkenylphosphine Oxide[a)]



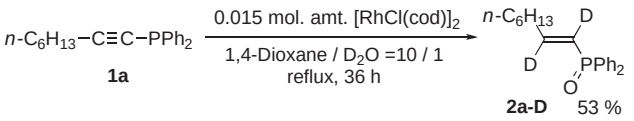
R	Yield[b)]/%	Time/h
Ph (**1b**)	72	6
i-Pr (**1c**)	69	8
t-Bu (**1d**)	0	8
o-$MeOC_6H_4$ (**1e**)	72	21
p-$MeOC_6H_4$ (**1f**)	75	7
p-AcC_6H_4 (**1g**)	62	5
2-Pyridyl (**1h**)	0	12
PhCH(OH) (**1i**)	0	12

a) Reaction conditions: **1** (0.50 mmol), $[RhCl(cod)]_2$ (0.0075 mmol), 1,4-dioxane (3 mL), H_2O (0.30 mL). b) Isolated yields.

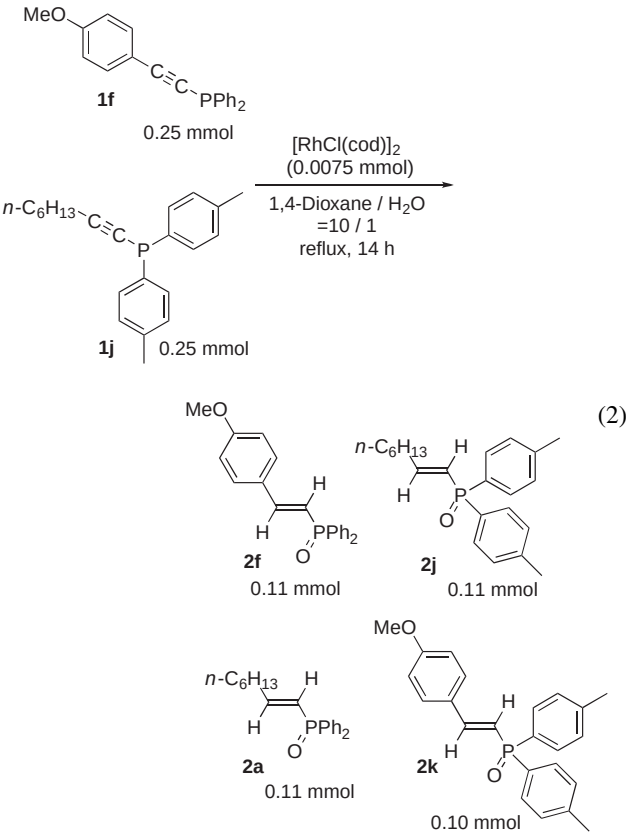
reaction proceeded in a toluene/H_2O mixed solvent, the reaction suffered from poor reproducibility (Entry 8). When toluene was used, the reaction proceeded in a two-phase medium. The erratic amount of water in the nonpolar organic phase would be responsible for the poor reproducibility. When THF or acetonitrile was used instead of 1,4-dioxane, the reaction did not proceed, albeit the reaction is homogeneous (Entries 9 and 10). The reaction in a 1,2-dichloroethane/H_2O biphasic medium failed, probably because of the highly hydrophobic nature of 1,2-dichloroethane (Entry 11). The use of 1,4-dioxane without H_2O resulted in complete recovery of **1a** (Entry 12). When the amount of H_2O was reduced to three molar amounts to the alkynylphosphine, poor reproducibility was observed (Entry 13). The amount of water in the organic phase is the key for reproducibility.

The scope of 1-alkynylphosphines was investigated (Table 2). Although a bulky *t*-butyl group of **1d** completely suppressed the reaction,[3] phenyl- and isopropyl-substituted alkynylphosphines **1b** and **1c** underwent the reaction. The reactions of methoxyphenyl-substituted **1e** and **1f** and *p*-acetylphenyl-substituted **1g** proceeded smoothly. However, neither pyridine-containing **1h**, hydroxy group-containing **1i**, nor 1-octynyldicyclohexylphosphine reacted.

To reveal the mechanism of this reaction, we carried out the following two experiments. First, D_2O was used instead of H_2O. As a result, a product deuterated at the two alkenyl positions was obtained as the sole product (eq 1). From a mechanistic point of view, it is worth noting that the reaction in 1,4-dioxane/D_2O was slow (vide infra). Next, a mixture of **1f** and **1j** was exposed to the reaction conditions. In this case, four 1-alkenylphosphine oxides were obtained in almost equal amounts (eq 2). This result suggests that cleavage of the C_{sp}–P bonds of 1-alkynylphosphines would occur.

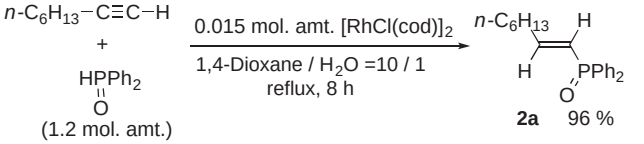


(1)

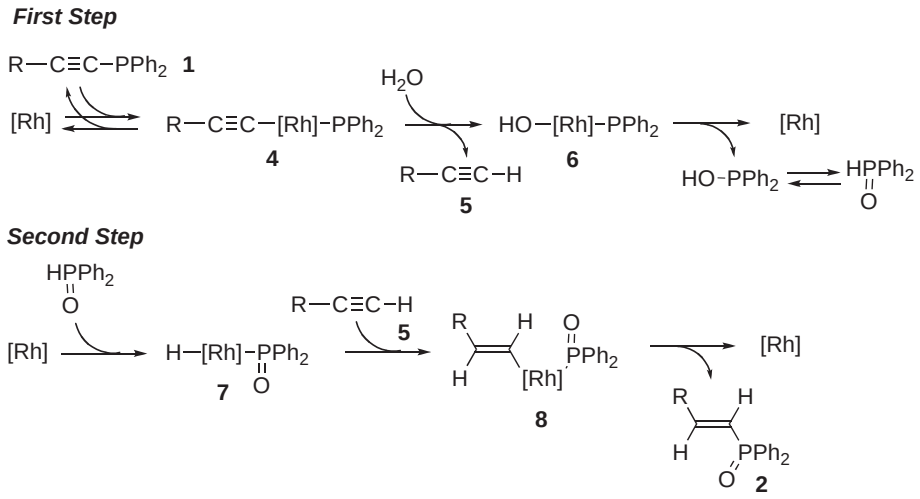


(2)

Based on these results, we assume that the reaction mechanism is as follows (Scheme 1). This reaction seems to consist of two steps. In the first step, C–P bond cleavage proceeds. Oxidative addition of 1-alkynylphosphine to a Rh^I complex occurs to yield **4**. The oxidative addition would be reversible because no reaction took place in the absence of water (vide supra). Protonation with H_2O followed by reductive elimination provides 1-alkyne **5** and diphenylphosphine oxide. In the second step, rhodium-catalyzed hydrophosphinylation of 1-alkyne with diphenylphosphine oxide proceeds to yield 1-alkenylphosphine oxide. Oxidative addition of diphenylphosphine oxide occurs to afford **7**. Hydrorhodation of alkyne **5** followed by reductive elimination provides the product **2**. Such a rhodium-catalyzed hydrophosphinylation reaction has been reported.[4] Actually, treatment of 1-octyne with diphenylphosphine oxide under the reaction conditions provided (*E*)-1-octenyldiphenylphosphine oxide in high yield (eq 3). This result supports the proposed mechanism. During the reaction, accumulation of neither diphenylphosphine oxide, 1-alkyne, nor rhodium hydride **7** was observed. Therefore, oxidative addition of diphenylphosphine oxide to a Rh^I complex is not rate-determining. The protonolysis of **4** would be the rate-determining step, since the use of D_2O retarded the reaction (eq 1).



(3)



Scheme 1. Plausible reaction mechanism.

Conclusion

We have found a reaction for the synthesis of (*E*)-1-alkenylphosphine oxides from 1-alkynylphosphines. The reaction is an interesting formal hydration reaction that involves carbon–phosphorus bond cleavage with a rhodium complex. Transition metal-mediated carbon–phosphorus bond cleavage has been an attractive topic in organometallic chemistry.[5,6] The present reaction gives new information on the reactivity of 1-alkynylphosphine under rhodium catalysis.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ or C_6D_6 with tetramethylsilane as an internal standard. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in $CDCl_3$ or C_6D_6 with 85% H_3PO_4 solution as an external standard. NMR yields were determined by fine ^{31}P NMR spectra with $(MeO)_3P{=}O$ as an internal standard. The first delay of ^{31}P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F_{254}. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. 1-Alkynylphosphines were prepared according to the literature.[1a]

Typical Procedure for Rhodium-Catalyzed Reaction to Yield (*E*)-1-Alkenylphosphine Oxides. Synthesis of **2a** is representative. $[RhCl(cod)]_2$ (3.7 mg, 0.0075 mmol) was placed in a 20-mL reaction flask under argon. 1,4-Dioxane (3.0 mL), H_2O (0.30 mL), and 1-octynyldiphenylphosphine (**1a**, 0.15 g, 0.50 mmol) were sequentially added. The resulting solution was stirred for 4 h at reflux. After the mixture was cooled to room temperature, water (10 mL) was added, and the product was extracted with dichloromethane (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded **2a** (0.11 g, 0.37 mmol, 73%) as a white solid.

Characterization Data. Phosphines **1a**,[7] **1b**,[7] **1c**,[1a] **1d**,[8] **1e**,[1c] **1f**,[9] **1g**,[1a] **1h**,[10] and **1i**,[1a] and phosphine oxides **2a**,[11] **2b**,[11] **2c**,[12] and **2f**[13] showed the same spectroscopic data as those described in the literature.

Bis(4-methylphenyl)-1-octynylphosphine (1j): IR (neat) 3015, 2928, 2853, 2178, 1905, 1598, 1496, 1456, 1395, 1184, 1094, 1019, 803, 624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.0 Hz, 3H), 1.27–1.37 (m, 4H), 1.46 (dd, J = 7.5, 7.5 Hz, 2H), 1.61 (dd, J = 7.5, 7.5 Hz, 2H), 2.33 (s, 6H), 2.43 (dt, J = 1.5, 7.5 Hz, 2H), 7.13–7.17 (m, 4H), 7.47–7.53 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.30, 20.64, 21.53, 22.81, 28.53, 28.55, 31.29, 76.23 (d, J = 1.6 Hz), 109.94 (d, J = 3.9 Hz), 129.24 (d, J = 7.6 Hz), 132.36 (d, J = 21.0 Hz), 133.84 (d, J = 4.9 Hz), 138.68; ^{31}P NMR ($CDCl_3$) δ −36.38. Found: C, 82.18; H, 8.62%. Calcd for $C_{22}H_{27}P$: C, 81.95; H, 8.44%.

(*E*)-1-Diphenylphosphinyl-2-(2-methoxyphenyl)ethene (2e): IR (nujol) 2923, 2853, 1598, 1484, 1461, 1247, 1181, 1004, 821, 744, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H), 6.90 (d, J = 8.5 Hz, 1H), 6.94 (dd, J = 18.0, 24.0 Hz, 1H), 6.95 (dd, J = 8.5, 8.5 Hz, 1H), 7.33 (dd, J = 8.5, 8.5 Hz, 1H), 7.44–7.55 (m, 7H), 7.73–7.83 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 55.41, 111.16, 119.69 (d, J = 104.1 Hz), 120.57, 124.12 (d, J = 17.1 Hz), 128.49 (d, J = 11.9 Hz), 128.76 (d, J = 1.0 Hz), 131.20, 131.43 (d, J = 10.0 Hz), 131.65 (d, J = 2.4 Hz), 133.35 (d, J = 104.5 Hz), 143.00 (d, J = 4.9 Hz), 158.08; ^{31}P NMR ($CDCl_3$) δ 23.09. Found: C, 75.11; H, 5.62%. Calcd for $C_{21}H_{19}O_2P$: C, 75.44; H, 5.73%. Mp: 150.5–152.0 °C.

4-[(*E*)-2-(Diphenylphosphinyl)ethenyl]acetophenone (2g): IR (nujol) 2924, 2853, 1678, 1603, 1438, 1359, 1270, 1182, 1107, 1000, 806, 746, 728, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.59 (s, 3H), 6.97 (dd, J = 17.5, 22.0 Hz, 1H), 7.44–7.57 (m, 7H), 7.60 (d, J = 8.0 Hz, 2H), 7.70–7.79 (m, 4H), 7.95 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.63, 122.45 (d, J = 101.8 Hz), 127.83, 128.66 (d, J = 11.9 Hz), 128.79, 131.29 (d, J = 10.0 Hz), 132.01 (d, J = 2.5 Hz), 132.47 (d, J = 105.9 Hz), 137.80, 139.24 (d, J = 17.6 Hz), 145.93 (d, J = 3.4 Hz), 197.26; ^{31}P NMR ($CDCl_3$) δ 22.00. Found: C, 76.23; H, 5.54%. Calcd for $C_{22}H_{19}O_2P$: C, 76.29; H, 5.53%. Mp: 176.0–177.5 °C.

(*E*)-1-Bis(4-methylphenyl)phosphinyl-1-octene (2j): IR (neat) 2927, 2856, 1629, 1603, 1453, 1400, 1182, 1118, 1101, 807,

656 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, $J = 7.0$ Hz, 3H), 1.21–1.34 (m, 6H), 1.45 (tt, $J = 7.0$, 7.5 Hz, 2H), 2.26 (dt, $J = 6.5$, 7.5 Hz, 2H), 2.36 (s, 6H), 6.17 (dd, $J = 17.0$, 24.0 Hz, 1H), 6.66 (ddt, $J = 17.0$, 19.5, 6.5 Hz, 1H), 7.21–7.26 (m, 4H), 7.51–7.59 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.95, 21.48 (d, $J = 1.0$ Hz), 22.46, 27.80 (d, $J = 1.0$ Hz), 28.73, 31.47, 34.40 (d, $J = 16.8$ Hz), 122.00 (d, $J = 102.6$ Hz), 129.11 (d, $J = 12.5$ Hz), 130.05 (d, $J = 106.4$ Hz), 131.24 (d, $J = 10.5$ Hz), 141.92 (d, $J = 2.9$ Hz), 152.24 (d, $J = 1.4$ Hz); ^{31}P NMR ($CDCl_3$) δ 22.02. HRMS (EI^+) (m/z) Observed: 340.1954 ($\Delta = -0.7$ ppm). Calcd for $C_{22}H_{29}OP$ [M^+]: 340.1956.

(*E*)-1,2-Dideuterio-1-diphenylphosphinyl-1-octene (2a-D): IR (nujol) 2923, 2854, 1593, 1546, 1438, 1180, 1120, 722, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, $J = 7.0$ Hz, 3H), 1.20–1.36 (m, 6H), 1.46 (tt, $J = 7.5$, 7.5 Hz, 2H), 2.27 (dt, $J = 2.0$, 7.5 Hz, 2H), 7.40–7.53 (m, 6H), 7.64–7.71 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.48, 27.76, 28.74, 31.48, 34.27 (d, $J = 16.3$ Hz), 121.09 (dt, $J = 101.3$, 24.8 Hz), 128.42 (d, $J = 12.0$ Hz), 131.23 (d, $J = 10.0$ Hz), 131.58 (d, $J = 2.9$ Hz), 133.22 (d, $J = 104.5$ Hz), 152.46 (t, $J = 23.4$ Hz); ^{31}P NMR ($CDCl_3$) δ 21.78. ^2H NMR ($CDCl_3$) δ 6.20, 6.73. HRMS (EI^+) (m/z) Observed: 314.1767 ($\Delta = -0.4$ ppm). Calcd for $C_{20}H_{23}D_2OP$ [M^+]: 314.1769. Mp: 58.0–60.0 °C.

(*E*)-2-Bis(4-methylphenyl)phosphinyl-1-(4-methoxyphenyl)-ethene (2k): IR (nujol) 2924, 2855, 1602, 1511, 1464, 1438, 1378, 1307, 1257, 1176, 1100, 1020, 1002, 823, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.39 (s, 6H), 2.82 (s, 3H), 6.64 (dd, $J =$ 17.5, 22.0 Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 7.23–7.31 (m, 4H), 7.39 (dd, $J = 17.5$, 19.5 Hz, 1H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.59–7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.53 (d, $J = 1.0$ Hz), 55.31, 114.13, 116.78 (d, $J = 105.9$ Hz), 128.06 (d, $J = 18.1$ Hz), 129.21 (d, $J = 12.4$ Hz), 129.14, 130.10 (d, $J = 107.4$ Hz), 131.36 (d, $J = 10.5$ Hz), 142.06 (d, $J = 2.4$ Hz), 146.51 (d, $J = 3.8$ Hz), 161.01; ^{31}P NMR ($CDCl_3$) δ 23.19. HRMS (EI^+) (m/z) Observed: 362.1433 ($\Delta = -0.8$ ppm). Calcd for $C_{23}H_{23}O_2P$ [M^+]: 362.1436. Mp: 148.0–149.5 °C.

This work was supported by Grants-in-Aid for Scientific Research and COE Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. A.K. acknowledges JSPS for financial support.

References

1 a) A. Kondoh, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2007**, *129*, 4099. b) A. Kondoh, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, *9*, 1383. c) S. Kanemura, A. Kondoh, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, *9*, 2031. d) A. Kondoh, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2007**, *129*, 6996.

2 1-Alkenylphosphine oxides are useful in organic chemistry: M. Niu, H. Fu, Y. Jiang, Y. Zhao, *Chem. Commun.* **2007**, 272, and references cited therein.

3 The *t*-butyl group would retard the oxidative addition (Scheme 1). Treatment of *t*-butylacetylene with diphenylphosphine oxide under conditions similar to those in eq 3 led to smooth hydrophosphinylation.

4 L.-B. Han, C.-Q. Zhao, M. Tanaka, *J. Org. Chem.* **2001**, *66*, 5929.

5 a) P. E. Garrou, *Chem. Rev.* **1985**, *85*, 171. b) J. V. Ortiz, Z. Havlas, R. Hoffmann, *Helv. Chim. Acta* **1984**, *67*, 1. c) S. A. Macgregor, *Chem. Soc. Rev.* **2007**, *36*, 67. d) A. W. Parkins, *Coord. Chem. Rev.* **2006**, *250*, 449.

6 a) A. Inoue, H. Shinokubo, K. Oshima, *J. Am. Chem. Soc.* **2003**, *125*, 1484. b) L. K. Hwang, Y. Na, J. Lee, Y. Do, S. Chang, *Angew. Chem., Int. Ed.* **2005**, *44*, 6166. c) M. Sakamoto, I. Shimizu, A. Yamamoto, *Chem. Lett.* **1995**, 1101. d) B. E. Segelstein, T. W. Butler, B. L. Chenard, *J. Org. Chem.* **1995**, *60*, 12. e) D. K. Morita, J. K. Stille, J. R. Norton, *J. Am. Chem. Soc.* **1995**, *117*, 8576. f) F. E. Goodson, T. I. Wallow, B. M. Novak, *J. Am. Chem. Soc.* **1997**, *119*, 12441. g) H. Nakazawa, Y. Matsuoka, Y. Nakagawa, K. Miyoshi, *Organometallics* **1992**, *11*, 1385.

7 P. Bharathi, M. Periasamy, *Organometallics* **2000**, *19*, 5511.

8 F.-E. Hong, Y.-C. Lai, Y.-J. Ho, Y.-C. Chang, *J. Organomet. Chem.* **2003**, *688*, 161.

9 M. Bernechea, N. Lugan, B. Gil, E. Lalinde, G. Lavigne, *Organometallics* **2006**, *25*, 684.

10 V. V. Afanasiev, I. P. Beletskaya, M. A. Kazankova, I. V. Efimova, M. U. Antipin, *Synthesis* **2003**, 2835.

11 L.-B. Han, N. Choi, M. Tanaka, *Organometallics* **1996**, *15*, 3259.

12 P. Mauleón, A. A. Núñez, I. Alonso, J. C. Carretero, *Chem. Eur. J.* **2003**, *9*, 1511.

13 N. Vinokurov, A. Michrowska, A. Szmigielska, Z. Drzazga, G. Wójciuk, O. M. Demchuk, K. Grela, K. M. Pietrusiewicz, H. Butenschön, *Adv. Synth. Catal.* **2006**, *348*, 931.