Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 4809–4815
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Preparation and properties of palladium(II) complexes of 3-oxo-1-(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphapropenes

Katsunori Nishide, Hongze Liang, Shigekazu Ito *, Masaaki Yoshifuji *

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

Received 21 April 2005; received in revised form 21 July 2005; accepted 22 July 2005
Available online 31 August 2005

Abstract

Kinetically stabilized 3-oxo-1,3-diphosphapropenes were prepared by oxidation of 1,3-diphosphapropenes with *m*-CPBA or from reaction of the corresponding phosphaethenyllithium with phosphinic chloride. The 3-oxo-1,3-diphosphapropenes were used as *P*,*O*-unsymmetrical bidentate ligands and the catalytic activity of the palladium(II) complexes in some cross-coupling reactions was investigated.

Keywords: Phosphorus ligand; Phosphaalkene; Palladium complex; X-ray crystallography; Cross-coupling reaction

1. Introduction

Chemistry of low-coordinated phosphorus compounds has greatly developed in recent years and we have reported a number of kinetically stabilized phosphaethenes with a bulky Mes* (2,4,6-tri-*t*-butylphenyl) group [1,2]. Phosphaethenes with the P=C bond, which exhibits unique properties such as π-electron accepting effect, are novel and attractive ligands for synthetic catalysts [3]. Indeed, DPCB (=3,4-diphosphinidenecyclobutene) has afforded several unique catalysts for organic reactions [3]. We recently reported preparation and coordination chemistry of kinetically stabilized 2-methyl-3,3-diphenyl-1,3-diphosphapropene **1a** [4,5] which was used as ligands for transition-metal complexes. Compound **1a** contains both a low-coordinated sp^2 phosphorus and a normal sp^3 phosphino phosphorus in the molecular system. Basically, **1a** predominantly forms an *E*-configuration to avoid steric congestion between the Mes* group and the PPh_2 moiety, which enables the 1,3-diphosphapropene to act as a chelating ligand in the complex formation. Indeed, **1a** afforded chelate transition-metal complexes of tungsten(0), palladium(II) and platinum(II) [4]. On the other hand, 2-chloro-3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphapropene [Mes*P=C(Cl)–PPh_2: **1a-Cl**] afforded neither palladium nor platinum complex, though it afforded mono-coordinated and chelate tungsten complexes [5], suggesting that the substituent on the sp^2 carbon in 1,3-diphosphapropenes is important for complexation [6].

The 1,3-diphosphapropene systems can be transformed chemically into other molecular structures. We recently reported sulfurization of **1a** to the corresponding 3-thioxo-1,3-diphosphapropene **2a** and utilization of **2a** as a ligand for transition-metal complexes [7]. 3-Thioxo-1,3-diphosphapropene consists of the P=C–P=S skeleton and behaves as a *P*,*S*-chelating ligand to afford the corresponding five-membered transition-metal complexes. The palladium(II) complexes containing the ligated 3-thioxo-1,3-diphosphapropene are stable in air and moisture, and can be used for catalytic reactions such as the Sonogashira and the Suzuki cross-coupling reactions [7] (see Chart 1).

* Corresponding authors. Tel.: +81 22 795 6560.
E-mail addresses: ito@synchem.chem.tohoku.ac.jp (S. Ito), yoshifj@mail.tains.tohoku.ac.jp (M. Yoshifuji).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.07.075

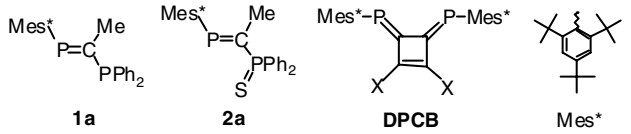
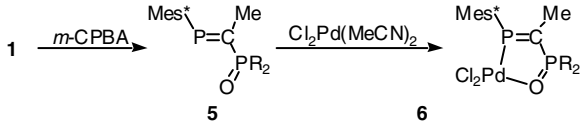


Chart 1.



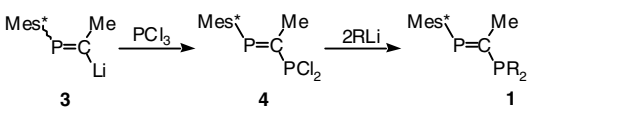
Scheme 2.

The oxygen atom in phosphine oxides coordinates on metals. Moreover, a number of biphosphine monoxides have been developed and utilized as catalysts for organic reactions [8]. Therefore, combination of phosphaethene and phosphine oxide is expected to provide novel ligands that are useful for exploring new catalysts. In this paper, we report preparation of novel 1,3-diphosphapropene and 3-oxo-1,3-diphosphapropene derivatives. Coordination chemistry of P═C–P═O ligands as well as catalytic activities has also been investigated.

2. Results and discussion

Compound **1a** was prepared according to our previous report [4]. Compound **3**, prepared from (*Z*)-2-bromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene and butyllithium [9], was allowed to react with phosphorus trichloride to give 2-methyl-3,3-dichloro-1,3-diphosphapropene **4** [$\delta_P = 316$, 168 ($^2J_{PP} = 596$ Hz)] almost quantitatively. Air- and moisture-sensitive **4** was characterized only by ^{31}P NMR spectroscopy and *E*-configuration was identified from a large $^2J_{PP}$ value. Steric congestion between the Mes* group and the PCl_2 moiety is responsible for the formation of **4** of *E*-form. Compound **4** was allowed to react with two equivalents of organolithium reagent to give the corresponding 1,3-diphophapropene derivatives (**1b**–**d**) (Scheme 1). Indeed, **4** is a promising reagent to prepare various 1,3-diphosphapropenes. Molecular structure of **1c** was successfully analyzed by X-ray crystallography (30% of molecules in the crystal were 3-oxo-1,3-diphosphapropene **5c**) [10]. The structure of **1c** is similar to that of **1a-Cl** [6].

The 1,3-diphosphapropenes **1a**–**d** were allowed to react with an equimolar amount of *m*-chloroperbenzoic acid (*m*-CPBA) to give the corresponding 3-oxo-1,3-diphosphapropenes **5a**–**d** in 70–75% yields (Scheme 2). No oxidation on the sp^2 phosphorus in **1** was observed under the employed conditions. Alternatively, 2-chloro-3-oxo-1,3-diphosphapropene **5a-Cl** was prepared from



Scheme 1.

the reaction of (*Z*)-1-chloro-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium and $Ph_2P(O)Cl$ in 34% yield, whereas attempts to obtain **5a-Cl** from **1a-Cl** by using *m*-CPBA resulted in decomposition of the substrate. A single crystal of **5c** was employed for X-ray crystallography and Fig. 1 shows an ORTEP drawing of the molecular structure. Selected metric parameters are displayed in Table 1. The P1–C1–P2–O1 skeleton takes an *s*-cis form with the torsion angles of $\Theta = 12.3(2)°$, which is similar to a 3-thioxo-1,3-diphosphapropene [7]. The P1–C1 distance indicates a P═C double bond [1], and the P2–O distance is close to the corresponding data of triphenylphosphine oxide (1.46 Å) [11].

3-Oxo-1,3-diphosphapropenes **5a**–**d** afforded the corresponding dichloropalladium(II) complexes **6a**–**d** in 75–85% yields [7]. Similarly, **5a-Cl** was allowed to react with $PdCl_2(CH_3CN)_2$ to generate the corresponding dichloropalladium(II) complex, but it gradually decomposed affording unidentified products [12]. The palladium(II) complex **6a** was recrystallized from a mixture of CH_2Cl_2 and toluene to afford single crystals, one of which was employed for X-ray crystallography. The molecular structure of **6a** and selected metric parameters are displayed in Fig. 2 and Table 1, respectively. The structure around the palladium atom in **6a** revealed a square-planar structure. The Pd–P1–C1–P2–O five-membered chelate ring is almost planar [Θ(Pd–P1–C1–P2) = 0.6(3)°, Θ(P1–C1–P2–O) = −13.0(4)°] , which is similar to the structure of **7a** [7b]. The Pd–Cl1 bond of 2.326(1) Å is longer than that of Pd–Cl2 [2.257(2) Å] indicating the greater *trans* influence of the P═C moiety

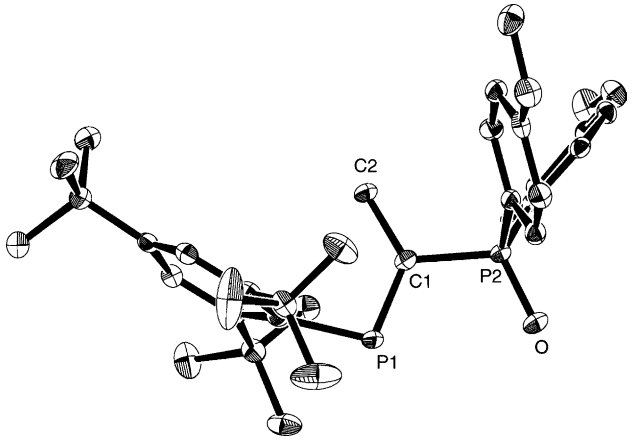


Fig. 1. Molecular structure of **5c** (40% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) of **5c** and **6a**

	Complex **5c**	Complex **6a**
P1–C1	1.673(3)	1.671(6)
P1–C_{Mes^*}	1.858(3)	1.812(5)
P2–O1	1.486(2)	1.513(4)
P2–C1	1.814(3)	1.794(5)
P2–C_{arom}	1.814(3)	1.783(6)
P2–C_{arom}	1.798(3)	1.784(6)
C1–C2	1.507(4)	1.501(8)
Pd–Cl1		2.326(1)
Pd–Cl2		2.257(2)
Pd–P1		2.208(1)
Pd–O		2.075(4)
C1–P1–C_{Mes^*}	99.8(1)	113.0(3)
P1–C1–P2	115.2(2)	109.4(3)
P1–C1–C2	127.5(2)	128.6(4)
P2–C1–C2	116.9(2)	122.0(4)
O–P2–C1	112.4(1)	109.7(2)
O–P2–C_{arom}	112.5(1)	110.4(3)
O–P2–C_{arom}	113.6(1)	110.5(2)
C_{arom}–P2–C_{arom}	107.2(1)	112.9(3)
Cl1–Pd–Cl2		93.90(6)
Cl1–Pd–P1		174.98(8)
Cl1–Pd–O		91.0(1)
Cl2–Pd–P1		90.62(5)
Cl2–Pd–O		174.6(1)
P1–Pd–O		84.6(1)
Pd–P1–C1		112.3(2)
Pd–P1–C_{Mes^*}		134.7(2)
Pd–O–P2		120.3(2)

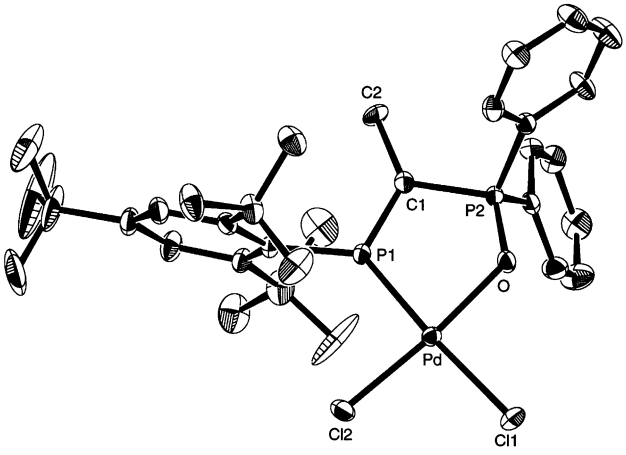


Fig. 2. Molecular structure of **6a** with 30% probability ellipsoids. Hydrogen atoms and the solvent molecules (dichloromethane) are omitted for clarity.

than that of the P═O moiety. The P1–C1 distance of **6a** is longer than that in **7a** [1.644(9) Å] [7b]. The P2–O distance of **6a** is comparable to that for **8** [1.509(11) Å] [13a] or for $[Ph_2PCH_2P(=O)Ph_2][Pd(Me)Cl]$ [1.508(4) Å] [13b]. The P1–Pd and Pd–O distances of **6a** are comparable to the corresponding distances of **7a** [2.186(3) Å] and **8** [2.088(12) Å] [13a], respectively (see Chart 2).

To estimate the catalytic activity of **6**, we employed the Sonogashira coupling reaction [14]. Iodobenzene

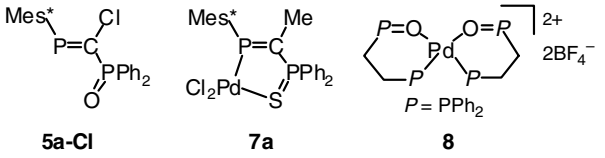
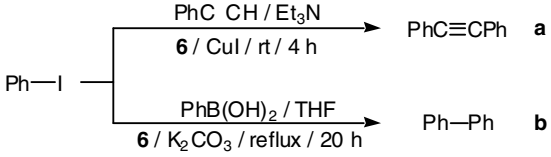


Chart 2.

(2.0 mmol) in triethylamine (8 mL) reacted with phenylacetylene (2.0 mmol) at room temperature in the presence of **6** (0.050 mmol) and copper(I) iodide (0.050 mmol) for 4 h at room temperature to afford the corresponding diphenylacetylene. Table 2 summarizes the results of the Sonogashira reactions (Scheme 3(a)). The catalytic activity of **6** is inferior to that of **7a** [7b], suggesting a considerable π-accepting effect of P═C moiety as well as a smaller electron-donating effect of the P═O moiety. In Table 2, **6c** gave the best result, indicating that the *p*-anisyl groups might facilitate the oxidative addition relatively with other complexes. On the other hand, the catalytic activity of **6** in the Suzuki reaction [15] in Scheme 3(b) [conditions: iodobenzene (2.0 mmol), phenylboric acid (2.0 mmol), **6** (0.080 mmol), potassium carbonate (4.0 mmol), THF (15 mL), reflux 20 h] is moderate (Table 3) and similar to the catalytic activity of **9** [16]. We are studying to establish other catalytic reaction systems which are suitable to 3-oxo-1,3-diphosphapropenes (see Chart 3).



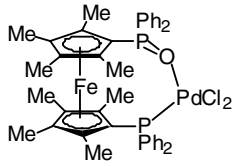
Scheme 3.

Table 2
Sonogashira reaction (Scheme 3(a))

Catalyst	Yield (%)
6a	35
6b	60
6c	68
6d	39

Table 3
Suzuki reaction (Scheme 3(b))

Catalyst	Yield (%)
6a	71
6b	60
6c	57
6d	64



9

Chart 3.

3. Conclusion

We have demonstrated the preparation of 3-oxo-1,3-diphosphapropenes **5a**–**d** which have been used as the P=C–P=O chelate ligands of palladium(II) complexes **6a**–**d**. The molecular structure of **6a** was confirmed by the X-ray crystallography. The catalytic activities of **6** in some cross-coupling reactions were investigated as a property of 3-oxo-1,3-diphosphapropene ligands. Although **6** did not show efficient catalytic activity in the Sonogashira or Suzuki coupling reactions, the preliminary results prompt us to survey unique activity of the P=C–P=O ligands.

4. Experimental

4.1. Preparation of *4*

To a solution of (*Z*)-2-bromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene (0.50 g, 1.30 mmol) in THF (20 mL) was added butyllithium (1.30 mmol) at −78 °C. To the reaction mixture containing **3** was added phosphorus trichloride (ca. 2.5 mmol) in Et_2O (10 mL) at −78 °C. After being warmed to room temperature, the volatile materials were removed in vacuo and the residue was extracted with hexane. Removal of the solvent afforded **4**: 0.52 g (1.30 mmol, >99% yield).

4.2. Preparation of *1b*

To a THF solution of *p*-bromotoluene (2.60 mmol) was added *t*-butyllithium at −78 °C, and stirred for 0.5 h. The reaction mixture was added to a solution of **4** (ca. 1.30 mmol) in THF at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed in vacuo and the residual materials were purified by silica-gel column chromatography (hexane/AcOEt = 19:1) to afford **1b**: 294 mg (0.57 mmol) (44% yield). Colorless amorphous solid; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 289.0 (d, $^2J_{PP}$ = 243 Hz), 8.5 (d, $^2J_{PP}$ = 243 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.53–7.49 (m, 6H, arom), 7.27–7.25 (m, 4H, arom), 2.45 (s, 6H, *p*-CH_3), 1.59 (s, 18H, *o*-*t*Bu), 1.37 (s, 9H, *p*-*t*Bu), 1.48–1.43 (m, 3H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 181.3 (dd, $^1J_{PC}$ = 59 Hz, $^1J_{PC}$ = 30 Hz, P=*C*), 153.6 (s, *o*-C of Mes*), 150.1 (s, *p*-C of Mes*), 139.4 (dd, $^1J_{PC}$ = 68 Hz, $^3J_{PC}$ = 24 Hz, *ipso*-C of Mes*), 138.9 (s, *p*-Tol), 134.2 (d, $^2J_{PC}$ = 19 Hz, *o*-Tol), 133.7 (dd, $^1J_{PC}$ = 16 Hz, $^3J_{PC}$ = 4 Hz, *ipso*-Tol), 129.5 (d, $^3J_{PC}$ = 7 Hz, *m*-Tol), 122.0 (s, *m*-C of Mes*), 38.3 (s, *o*-*C*Me_3), 35.3 (s, *p*-*C*Me_3), 33.2 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 31.8 (s, *p*-C*Me*$_3$), 22.5 (dd, $^2J_{PC}$ = 15 Hz, $^2J_{PC}$ = 11 Hz, P=C*Me*), 21.8 (s, *p*-$C_6H_4CH_3$).

4.3. Preparation of *1c*

To a THF solution of *p*-bromoanisole (2.60 mmol) was added *t*-butyllithium at −78 °C, and stirred for 0.5 h. The reaction mixture was added to a solution of **4** (ca. 1.30 mmol) in THF at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed in vacuo and the residual materials were purified by silica-gel column chromatography (hexane/AcOEt = 19:1) to afford **1c**: 356 mg (0.65 mmol) (50% yield). Colorless amorphous solid; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 284.8 (d, $^2J_{PP}$ = 214 Hz), 7.8 (d, $^2J_{PP}$ = 214 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.51–7.47 (m, 4H, arom), 7.43 (s, 2H, arom), 6.96–6.94 (m, 4H, arom), 3.85 (s, 6H, OCH_3), 1.51 (s, 18H, *o*-*t*Bu), 1.42 (dd, $^3J_{PH}$ = 14 Hz, $^3J_{PH}$ = 10 Hz, 3H, CH_3), 1.37 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 182.3 (dd, $^1J_{PC}$ = 61 Hz, $^1J_{PC}$ = 29 Hz, P=*C*), 162.6 (d, $^4J_{PC}$ = 2 Hz, *p*-Anis), 153.6 (s, *o*-C of Mes*), 150.1 (s, *p*-C of Mes*), 139.6 (dd, $^1J_{PC}$ = 68 Hz, $^3J_{PC}$ = 20 Hz, *ipso*-C of Mes*), 135.8 (d, $^2J_{PC}$ = 20 Hz, *o*-Anis), 128.1 (dd, $^1J_{PC}$ = 16 Hz, $^3J_{PC}$ = 10 Hz, *ipso*-Anis), 122.0 (s, *m*-C of Mes*), 114.4 (d, $^3J_{PC}$ = 8 Hz, *o*-Anis), 55.6 (s, *p*-$C_6H_4OCH_3$), 38.4 (s, *o*-*C*Me_3), 35.3 (s, *p*-*C*Me_3), 33.1 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 32.0 (s, *p*-C*Me*$_3$), 22.8 (dd, $^2J_{PC}$ = 32 Hz, $^2J_{PC}$ = 17 Hz, P=C*Me*).

4.4. Preparation of *1d*

To an Et_2O solution of butyllithium (2.60 mmol) was added a solution of **4** (ca. 1.30 mmol) in THF at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed in vacuo and the residue was purified by silica-gel column chromatography (hexane/AcOEt = 19:1) to afford **1d**: 264 mg (0.59 mmol) (45% yield). Pale yellow oil; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 277.0 (d, $^2J_{PP}$ = 214 Hz), −5.4 (d, $^2J_{PP}$ = 214 Hz); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.47 (s, 2H, arom), 7.43 (s, 2H, arom), 1.55 (s, 18H, *o*-*t*Bu), 1.35 (s, 9H, *p*-*t*Bu), 1.75–1.30 (m, 21H, *n*Bu, Me); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ = 183.4 (dd, $^1J_{PC}$ = 60 Hz, $^1J_{PC}$ = 32 Hz, P=*C*), 153.7 (s, *o*-C of Mes*), 150.0 (s, *p*-C of Mes*), 139.1 (dd, $^1J_{PC}$ = 68 Hz, $^3J_{PC}$ = 20 Hz, *ipso*-C of Mes*), 122.2 (s, *m*-C of Mes*), 38.3 (s, *o*-*C*Me_3), 35.3

(s, *p*-*C*Me$_3$), 33.0 (d, $^4J_{PC} = 7$ Hz, *o*-C*Me*$_3$), 31.8 (s, *p*-C*Me*$_3$), 28.9 (d, $^2J_{PC} = 14$ Hz, *C*H$_2$), 26.4 (dd, $^1J_{PC} = 18$ Hz, $^3J_{PC} = 14$ Hz, *C*H$_2$), 24.8 (d, $^3J_{PC} = 12$ Hz, *C*H$_2$), 21.5 (dd, $^2J_{PC} = 15$ Hz, $^2J_{PC} = 10$ Hz, P=C*Me*), 14.1 (s, *C*H$_3$).

4.5. Oxidation of *1* with m-CPBA

A solution of **1a** (0.550 g, 1.13 mmol) and *m*-CPBA (1.13 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residual solid was purified by silica-gel column chromatography (hexane/AcOEt = 1:1) to afford **5a**; 0.43 g (0.85 mmol) (75% yield). Compound **5a**: Colorless crystals, mp 168–169 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 320.9$ (d, $^2J_{PP} = 115$ Hz), 33.0 (d, $^2J_{PP} = 115$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.86$–7.81 (m, 4H, arom), 7.48–7.43 (m, 6H, arom), 7.40 (s, 2H, Mes*), 1.50–1.47 (m, 3H, CH$_3$), 1.47 (s, 18H, *o*-*t*Bu), 1.29 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 172.1$ (dd, $^1J_{PC} = 76$ Hz, $^1J_{PC} = 64$ Hz, P=*C*), 153.8 (s, *o*-C of Mes*), 151.0 (s, *p*-C of Mes*), 136.3 (dd, $^1J_{PC} = 66$ Hz, $^3J_{PC} = 18$ Hz, *ipso*-C of Mes*), 132.5 (dd, $^1J_{PC} = 102$ Hz, $^3J_{PC} = 4$ Hz, *ipso*-Ph), 132.5 (d, $^3J_{PC} = 9$ Hz, *m*-Ph), 132.2 (d, $^4J_{PC} = 2$ Hz, *p*-Ph), 128.7 (d, $^2J_{PC} = 12$ Hz, *o*-Ph), 122.5 (s, *m*-C of Mes*), 38.2 (s, *o*-*C*Me$_3$), 35.3 (s, *p*-*C*Me$_3$), 33.2 (d, $^4J_{PC} = 7$ Hz *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 22.9 (dd, $^2J_{PC} = 14$ Hz, $^2J_{PC} = 6$ Hz, P=C*Me*); IR (KBr) $\nu = 1178$ (P=O) cm^{-1}; HR-ESI-MS found: *m*/*z* 527.2603; calcd for $C_{32}H_{42}OP_2 \cdot Na$ ($M^+ + Na$): 527.2603. Compounds **5b-d** were prepared in a similar manner. Compound **5b** (70% yield): Colorless solid, mp 164–165 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 318.2$ (d, $^2J_{PP} = 116$ Hz), 33.2 (d, $^2J_{PP} = 116$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.74$–7.69 (m, 4H, arom), 7.40 (s, 2H, arom), 7.25–7.23 (m, 4H, arom), 2.34 (s, 6H, *p*-CH$_3$), 1.49–1.43 (m, 3H, CH$_3$), 1.43 (s, 18H, *o*-*t*Bu), 1.29 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 172.9$ (dd, $^1J_{PC} = 76$ Hz, $^1J_{PC} = 64$ Hz, P=*C*), 153.8 (s, *o*-C of Mes*), 150.9 (s, *p*-C of Mes*), 142.3 (d, $^4J_{PC} = 3$ Hz, *p*-Tol), 136.6 (dd, $^1J_{PC} = 67$ Hz, $^3J_{PC} = 18$ Hz, *ipso*-C of Mes*), 132.6 (d, $^3J_{PC} = 10$ Hz, *m*-Tol), 129.4 (dd, $^1J_{PC} = 105$ Hz, $^3J_{PC} = 3$ Hz, *ipso*-Tol), 129.4 (d, $^2J_{PC} = 12$ Hz, *o*-Tol), 122.4 (s, *m*-C of Mes*), 38.2 (s, *o*-*C*Me$_3$), 35.3 (s, *p*-*C*Me$_3$), 33.1 (d, $^4J_{PC} = 7$ Hz *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 22.0 (s, *p*-C$_6$H$_4$*C*H$_3$), 20.9 (dd, $^2J_{PC} = 14$ Hz, $^2J_{PC} = 5$ Hz, P=C*Me*); IR (KBr) $\nu = 1184$ (P=O) cm^{-1}. Compound **5c** (75% yield): Colorless solid, mp 140–142 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 316.8$ (d, $^2J_{PP} = 116$ Hz), 32.6 (d, $^2J_{PP} = 116$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.70$–7.66 (m, 4H, arom), 7.33 (s, 2H, arom), 6.90–6.88 (m, 4H, arom), 3.70 (s, 6H, *p*-OCH$_3$), 1.42–1.31 (m, 3H, CH$_3$), 1.37 (s, 18H, *o*-*t*Bu), 1.23 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 173.6$ (dd, $^1J_{PC} = 77$ Hz, $^1J_{PC} = 63$ Hz, P=*C*), 162.6 (d, $^4J_{PC} = 2$ Hz, *p*-Anis), 153.6 (s, *o*-C of Mes*), 150.7 (s, *p*-C of Mes*), 136.6 (dd, $^1J_{PC} = 67$ Hz, $^3J_{PC} = 18$ Hz, *ipso*-C of Mes*), 134.2 (d, $^3J_{PC} = 11$ Hz, *m*-Anis), 123.9 (d, $^1J_{PC} = 110$ Hz, *ipso*-Anis), 122.3 (s, *m*-C of Mes*), 114.1 (d, $^2J_{PC} = 13$ Hz, *o*-Anis), 55.6 (s, *p*-C$_6$H$_4$O*C*H$_3$), 38.2 (s, *o*-*C*Me$_3$), 35.3 (s, *p*-*C*Me$_3$), 33.1 (d, $^4J_{PC} = 5$ Hz, *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 20.8 (dd, $^2J_{PC} = 14$ Hz, $^2J_{PC} = 5$ Hz, P=C*Me*); IR (KBr) $\nu = 1176$ (P=O) cm^{-1}. Compound **5d** (70% yield): Colorless crystals, mp 120–121 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 309.8$ (d, $^2J_{PP} = 92$ Hz), 47.0 (d, $^2J_{PP} = 92$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.33$ (s, 2H, arom), 1.37 (s, 18H, *o*-*t*Bu), 1.83–1.30 (m, 21H, *n*Bu, Me), 1.23 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 172.1$ (pt, $(^1J_{PC} + {}^1J_{PC})/2 = 64$ Hz, P=*C*), 153.7 (s, *o*-C of Mes*), 150.9 (s, *p*-C of Mes*), 135.8 (dd, $^1J_{PC} = 66$ Hz, $^3J_{PC} = 15$ Hz, *ipso*-C of Mes*), 122.3 (s, *m*-C of Mes*), 38.2 (s, *o*-*C*Me$_3$), 35.3 (s, *p*-*C*Me$_3$), 33.0 (d, $^4J_{PC} = 11$ Hz, *o*-C*Me*$_3$), 31.6 (s, *p*-C*Me*$_3$), 29.3 (dd, $^1J_{PC} = 67$ Hz, $^3J_{PC} = 7$ Hz, *C*H$_2$), 24.6 (d, $^2J_{PC} = 15$ Hz, *C*H$_2$), 24.2 (d, $^3J_{PC} = 3$ Hz, *C*H$_2$), 20.6 (dd, $^2J_{PC} = 15$ Hz, $^2J_{PC} = 5$ Hz, P=C*Me*), 14.0 (s, *C*H$_3$); IR (KBr) $\nu = 1170$ (P=O) cm^{-1}.

4.6. Preparation of *5a-Cl*

To a solution of 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (0.500 g, 1.43 mmol) in THF (20 mL) was added butyllithium (1.58 mmol) at −100 °C. After being stirred for 10 min, diphenylphosphinic chloride (1.60 mmol) was added to the reaction mixture. The reaction mixture was stirred for 1 h at −100 °C and was allowed to warm to room temperature. The solvent was removed in vacuo and silica-gel column chromatography (hexane/AcOEt 2:1) gave **5a-Cl** (0.257 g, 34% yield). Colorless crystals, mp 163–164 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 319.7$ (d, $^2J_{PP} = 80$ Hz), 30.0 (d, $^2J_{PP} = 80$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.87$–7.84 (m, 4H, arom), 7.55–7.53 (m, 2H, arom), 7.48–7.46 (m, 4H, arom), 7.42 (s, 2H, arom), 1.43 (s, 18H, *o*-*t*Bu), 1.32 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 158.7$ (pt, $(^1J_{PC} + {}^1J_{PC})/2 = 83$ Hz, P=*C*), 153.9 (s, *o*-C of Mes*), 151.7 (s, *p*-C of Mes*), 133.5 (dd, $^1J_{PC} = 61$ Hz, $^3J_{PC} = 11$ Hz, *ipso*-C of Mes*), 132.7 (s, *o*-Ph), 132.64 (s, *p*-Ph), 132.61 (s, *m*-Ph), 131.1 (dd, $^1J_{PC} = 107$ Hz, $^3J_{PC} = 2$ Hz, *ipso*-Ph), 122.8 (s, *m*-C of Mes*), 38.2 (s, *o*-*C*Me$_3$), 35.4 (s, *p*-*C*Me$_3$), 33.3 (d, $^4J_{PC} = 7$ Hz *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$); IR (KBr) $\nu = 1190$ cm^{-1} (P=O).

4.7. Preparation of *6*

A solution of **5a** (200 mg, 0.397 mmol) and $PdCl_2(CH_3CN)_2$ (0.397 mmol) in dichloromethane (30 mL) was stirred at room temperature for 0.5 h. Hexane

(10 mL) was added to the reaction mixture and the precipitates were collected by filtration. Purification by silica-gel column chromatography (hexane/AcOEt = 1:2) afforded **6a**: 230 mg (0.337 mmol) (85%). Yellowish-brown solid (CH_2Cl_2/toluene), mp 144–145 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 255.1$ (d, $^2J_{PP} = 62$ Hz), 65.0 (d, $^2J_{PP} = 62$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.79$–7.75 (m, 6H, arom), 7.62–7.60 (m, 4H, arom), 7.55–7.54 (m, 2H, arom), 1.70 (s, 18H, *o*-*t*Bu), 1.32 (s, 9H, *p*-*t*Bu), 1.37–1.30 (m, 3H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 156.6$ (d, $^2J_{PC} = 3$ Hz, *o*-C of Mes*), 156.1 (s, *p*-C of Mes*), 153.7 (dd, $^1J_{PC} = 78$ Hz, $^1J_{PC} = 28$ Hz, P=*C*), 134.8 (d, $^3J_{PC} = 2$ Hz, *m*-C of Mes*), 132.4 (d, $^3J_{PC} = 11$ Hz, *m*-Ph), 130.0 (d, $^2J_{PC} = 13$ Hz, *o*-Ph), 125.9 (d, $^1J_{PC} = 8$ Hz, *ipso*-Ph), 124.9 (d, $^4J_{PC} = 9$ Hz, *p*-Ph), 116.7 (d, $^1J_{PC} = 10$ Hz, *ipso*-C of Mes*), 39.6 (s, *o*-*C*Me$_3$), 35.8 (s, *p*-*C*Me$_3$), 34.7 (s, *o*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$), 19.7 (dd, $^2J_{PC} = 15$ Hz, $^2J_{PC} = 6$ Hz, P=C*Me*). IR (KBr) $\nu = 1120$ (P=O) cm^{-1}; HR-ESI-MS found: *m*/*z* 645.1431; calcd for $C_{32}H_{42}ClOP_2Pd$ (M^+–Cl): 645.1429. Complexes **6b-d** were prepared in a similar manner. Complex **6b** (84% yield): Yellowish-brown solid, mp 163–164 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 250.7$ (d, $^2J_{PP} = 62$ Hz), 65.4 (d, $^2J_{PP} = 62$ Hz);^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.55$–7.50 (m, 4H, arom), 7.42 (s, 2H, Mes*), 7.29 (brs, 4H, arom), 2.31 (s, 6H, *p*-CH_3), 1.52 (s, 18H, *o*-*t*Bu), 1.31 (dd, $^3J_{PH} = 29$ Hz, $^3J_{PH} = 15$ Hz, 3H, CH_3), 1.19 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 156.5$ (s, *o*-C of Mes*), 155.9 (s, *p*-C of Mes*), 155.4 (dd, $^1J_{PC} = 77$ Hz, $^1J_{PC} = 29$ Hz, P=*C*), 145.7 (s, *m*-C of Mes*), 132.3 (d, $^3J_{PC} = 11$ Hz, *m*-Tol), 130.3 (d, $^2J_{PC} = 13$ Hz, *o*-Tol), 124.8 (d, $^4J_{PC} = 9$ Hz, *p*-Tol), 122.0 (dd, $^1J_{PC} = 110$ Hz, $^3J_{PC} = 7$ Hz, *ipso*-Tol), 116.7 (d, $^1J_{PC} = 8$ Hz, *ipso*-C of Mes*), 39.5 (s, *o*-*C*Me$_3$), 35.7 (s, *p*-*C*Me$_3$), 34.6 (s, *o*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$), 22.3 (s, *p*-$C_6H_4CH_3$), 19.9 (dd, $^2J_{PC} = 15$ Hz, $^2J_{PC} = 6$ Hz, P=C*Me*); IR (KBr) $\nu = 1119$ (P=O) cm^{-1}. Complex **6c** (82% yield): Yellowish-brown solid, mp 175–177 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 249.0$ (d, $^2J_{PP} = 64$ Hz), 64.8 (d, $^2J_{PP} = 64$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.64$–7.59 (m, 4H, arom), 7.47 (d, $^3J_{PH} = 4$ Hz, 2H, Mes*), 7.04–7.01 (m, 4H, arom), 3.83 (s, 6H, *p*-OCH_3), 1.59 (s, 18H, *o*-*t*Bu), 1.38 (dd, $^3J_{PH} = 30$ Hz, $^3J_{PH} = 14$ Hz, 3H, CH_3), 1.25 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 164.6$ (d, $^4J_{PC} = 3$ Hz, *p*-Anis), 156.6 (d, $^3J_{PC} = 3$ Hz, *m*-C of Mes*), 155.9 (s, *p*-C of Mes*), 155.5 (dd, $^1J_{PC} = 76$ Hz, $^1J_{PC} = 3$ Hz, P=*C*), 134.5 (d, $^3J_{PC} = 12$ Hz, *m*-Anis), 124.8 (d, $^2J_{PC} = 9$ Hz, *o*-C of Mes*), 116.8 (d, $^1J_{PC} = 3$ Hz, *ipso*-C of Mes*), 116.7 (d, $^1J_{PC} = 8$ Hz, *ipso*-Anis), 115.6 (d, $^2J_{PC} = 14$ Hz, *o*-Anis), 55.2 (s, *p*-$C_6H_4OCH_3$), 39.5 (s, *o*-*C*Me$_3$), 35.7 (s, *p*-*C*Me$_3$), 34.6 (s, *o*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$), 19.9 (dd, $^2J_{PC} = 15$ Hz, $^2J_{PC} = 6$ Hz, P=C*Me*); IR (KBr) $\nu = 1119$ (P=O) cm^{-1}. Complex **6d** (75% yield): Yellowish-brown amorphous solid; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) $\delta = 249.0$ (d, $^2J_{PP} = 50$ Hz), 90.0 (d, $^2J_{PP} = 50$ Hz); ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.49$ (d, 2H, $^3J_{PH} = 3$ Hz, arom), 1.63 (s, 18H, *o*-*t*Bu), 1.45 (dd, $^3J_{PH} = 30$ Hz, $^3J_{PH} = 15$ Hz, 3H, CH_3), 2.05–1.40 (m, 18H, *n*Bu), 1.20 (s, 9H, *p*-*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) $\delta = 157.1$ (dd, $^1J_{PC} = 64$ Hz, $^1J_{PC} = 29$ Hz, P=*C*), 156.5 (d, $^3J_{PC} = 3$ Hz, *o*-C of Mes*), 155.9 (s, *p*-C of Mes*), 124.8 (d, $^2J_{PC} = 9$ Hz, *m*-C of Mes*), 116.9 (brd, $^1J_{PC} = 7$ Hz, *ipso*-C of Mes*), 39.5 (s, *o*-*C*Me$_3$), 35.7 (s, *p*-*C*Me$_3$), 34.8 (s, *o*-C*Me*$_3$), 31.3 (s, *p*-C*Me*$_3$), 27.9 (dd, $^1J_{PC} = 65$ Hz, $^3J_{PC} = 6$ Hz, *C*H$_2$), 24.2 (d, $^2J_{PC} = 15$ Hz, *C*H$_2$), 23.6 (d, $^3J_{PC} = 5$ Hz, *C*H$_2$), 19.6 (dd, $^2J_{PC} = 16$ Hz, $^2J_{PC} = 7$ Hz, P=C*Me*), 14.1 (s, *C*H$_3$); IR (KBr) $\nu = 1122$ (P=O) cm^{-1}.

4.8. X-ray crystallography for **5c**

$C_{34}H_{46}O_3P_2$, $M = 564.68$, crystal dimensions: $0.20 \times 0.20 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 16.3881(6)$ Å, $b = 10.2144(3)$ Å, $c = 19.9335(6)$ Å, $\beta = 108.0622(7)°$, $V = 3172.3(2)$ $Å^3$, $Z = 4$, $T = 133$ K, $2\theta_{max} = 55.0°$, $\rho = 1.182$ g cm^{-1}, μ(Mo Kα) = 0.168 mm^{-1}, $F_{000} = 1216$, 25165 measured reflections, 7108 unique reflections ($R_{int} = 0.044$), $R_1 = 0.057$ ($I > 2.0\sigma(I)$), $R_w = 0.132$ (all data) (CCDC-269267).

4.9. X-ray crystallography for **6a**

$C_{32}H_{42}Cl_2OP_2Pd \cdot CH_2Cl_2$, $M = 766.87$, crystal dimensions: $0.25 \times 0.20 \times 0.20$ mm^3, monoclinic, space group $P2_1$ (No. 4), $a = 8.8009(3)$ Å, $b = 16.1300(6)$ Å, $c = 13.2923(5)$ Å, $\beta = 103.307(2)°$, $V = 1936.3(3)$ $Å^3$, $Z = 2$, $T = 223$ K, $2\theta_{max} = 55.0°$, $\rho = 1.387$ g cm^{-1}, μ(Mo Kα) = 0.907 mm^{-1}, $F_{000} = 788$, 14672 measured reflections, 4303 unique reflections ($R_{int} = 0.040$), $R_1 = 0.042$ ($I > 2.0\sigma(I)$), $R_w = 0.052$ (all data) (CCDC-249371).

4.10. Sonogashira coupling reaction

A solution of iodobenzene (2.0 mmol), phenylacetylene (2.0 mmol), catalyst (**6**, 0.050 mmol), and copper(I) iodide (0.050 mmol) in triethylamine (8 mL) was stirred for 4 h at room temperature. The volatile materials were removed in vacuo and the residue was extracted with hexane. Silica-gel column chromatography (hexane) of the hexane extracts afforded diphenylacetylene.

4.11. Suzuki coupling reaction

A solution of iodobenzene (2.0 mmol), phenylboric acid (2.0 mmol), catalyst (**6**, 0.080 mmol), and potassium carbonate (4.0 mmol) in THF (15 mL) was refluxed for 20 h. After being cooled to room temperature, the reaction mixture was concentrated in vacuo. The residue

was extracted with hexane and purified by silica-gel column chromatography (hexane) to afford biphenyl.

Acknowledgments

This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 13303039 and 14044012) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. H. Liang is grateful to the Japan Society for the Promotion of Science for the Postdoctoral Fellowships for Foreign Researchers.

References

[1] (a) M. Regitz, O.J. Scherer, Multiple Bonds and Low Coordination in Phosphorus Chemistry, Georg Thieme Verlag, Stuttgart, 1990;
(b) K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998.

[2] (a) M. Yoshifuji, J. Chem. Soc., Dalton Trans. (1999) 3343;
(b) M. Yoshifuji, J. Organomet. Chem. 611 (2000) 210.

[3] (a) F. Mathey, Angew. Chem. Int. Ed. 42 (2003) 1578;
(b) L. Weber, Angew. Chem. Int. Ed. 41 (2002) 563;
(c) M. Yoshifuji, J. Synth. Org. Chem. Jpn. (Yuki Gosei Kagaku Kyokai-Shi) 61 (2003) 1116;
(d) F. Ozawa, M. Yoshifuji, C. R. Chimie 7 (2004) 747.

[4] H. Liang, K. Nishide, S. Ito, M. Yoshifuji, Tetrahedron Lett. 44 (2003) 8297.

[5] S. Ito, M. Yoshifuji, Chem. Commun. (2001) 1208.

[6] We recently reported an activation of the C–Cl bond in **1a-Cl** in the presence of a palladium reagent: H. Liang, S. Ito, M. Yoshifuji, Z. Anorg. Allg. Chem. 630 (2004) 1177.

[7] (a) S. Ito, H. Liang, M. Yoshifuji, Chem. Commun. (2003) 398;
(b) H. Liang, S. Ito, M. Yoshifuji, Org. Lett. 6 (2004) 425;
(c) H. Liang, S. Ito, M. Yoshifuji, Org. Biomol. Chem. 1 (2003) 3054;
(d) S. Ito, H. Liang, M. Yoshifuji, J. Organomet. Chem. 690 (2005) 2531.

[8] V.V. Grushin, Chem. Rev. 104 (2004) 1629.

[9] (a) S. Ito, S. Kimura, M. Yoshifuji, Chem. Lett. (2002) 708;
(b) S. Ito, S. Kimura, M. Yoshifuji, Bull. Chem. Soc. Jpn. 76 (2003) 405.

[10] The oxidized product **5c** seemed to have been formed during the recrystallization. Crystal data: $C_{34}H_{46}O_{2.3}P_2$, $M = 553.48$, crystal dimensions: $0.20 \times 0.20 \times 0.15$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 16.4465(6)$ Å, $b = 10.1438(3)$ Å, $c = 19.8486(6)$ Å, $\beta = 107.7497(8)°$, $V = 3153.7(2)$ Å^3, $Z = 4$, $T = 153$ K, $2\theta_{max} = 55.0°$, $\rho = 1.166$ g cm^{-1}, μ(Mo Kα) $= 0.167$ mm^{-1}, $F_{000} = 1193$, 23096 measured reflections, 6975 unique reflections ($R_{int} = 0.061$), $R_1 = 0.061$ ($I > 2.0\sigma(I)$), $R_w = 0.148$ (all data) (CCDC-268951). Both compounds **1c** and **5c** were observed in ca. 2:1 ratio in ^{31}P NMR spectrum after attempted recrystallization of **1c**.

[11] J.A. Thomas, T.A. Hamor, Acta Crystallogr., Sect. C 49 (1993) 355.

[12] The observed complex [$\delta_P = 257.7$, 57.8 ($^2J_{PP} = 71$ Hz)] gradually decomposed affording an unidentified complex [$\delta_P = 47.3$, 29.6 ($^2J_{PP} = 5$ Hz)].

[13] (a) R.J. Coyle, Y.L. Slovokhotov, M.Y. Antipin, V.V. Grushin, Polyhedron 17 (1998) 3059;
(b) I. Brassat, U. Englert, W. Keim, D.P. Keitel, S. Killat, G.-P. Suranna, R. Wang, Inorg. Chim. Acta 280 (1998) 150.

[14] (a) K. Sonogashira, in: F. Diederich, P.J. Stang (Eds.), Metal-catalyzed Cross-coupling Reactions, Wiley–VCH, Weinheim, 1998;
(b) K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. (1975) 4467.

[15] (a) A. Suzuki, H.C. Brown, Suzuki Coupling, Organic Syntheses via Boranes, vol. 3, Aldrich, Milwaukee, 2003;
(b) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.

[16] O.V. Gusev, T.A. Peganova, A.M. Kalsin, N.V. Vologdin, P.V. Petrovskii, K.A. Lyssenko, A.V. Tsvetkov, I.P. Beletskaya, J. Organomet. Chem. 690 (2005) 1710.