

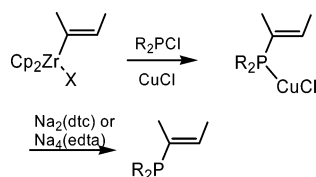
## Alkenylzirconocene-Mediated Preparation of Alkenylphosphines

Taichi Miyaji,<sup>†</sup> Zhenfeng Xi,<sup>‡</sup> Masamichi Ogasawara,<sup>†</sup> Kiyohiko Nakajima,<sup>§</sup> and Tamotsu Takahashi<sup>\*†</sup>

Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, and SORST, Japan Science and Technology Agency (JST), Kita-ku, Sapporo 001-0021, Japan, College of Chemistry, Peking University, Beijing 100871, China, and Department of Chemistry, Aichi University of Education, Igaya, Kariya, Aichi 448-8542, Japan

tamotsu@cat.hokudai.ac.jp

Received May 23, 2007



Alkenylphosphines with various substituents were prepared by the reaction of an alkenylzirconocene with a chlorophosphine. Reactions of ( $\alpha$ -unsubstituted alkenyl)zirconocenes with  $\text{Ph}_2\text{P-Cl}$  or  $\text{PhP-Cl}_2$  gave the corresponding alkenylphosphines in good yields. On the other hand, direct reactions of ( $\alpha$ -unsubstituted alkenyl)zirconocenes with  $\text{Pr}_2\text{P-Cl}$  did not proceed. Analogously, ( $\alpha$ -substituted alkenyl)zirconocenes did not react with chlorophosphines directly. However, these reactions proceeded in the presence of  $\text{CuCl}$  affording the corresponding alkenylphosphines as  $\text{CuCl}$  complexes. Treatment of the copper complexes with  $\text{Na}_2(\text{dtc})$  ( $\text{dtc} = N,N$ -diethyldithiocarbamate) or  $\text{Na}_4(\text{edta})$  liberated free alkenylphosphines from the copper centers. The overall protocol could be applicable to preparation of a variety of alkenylphosphines from alkynes via alkenylzirconocene species.

### Introduction

Tertiary phosphines are arguably one of the most important ancillary ligands in organotransition-metal chemistry.<sup>1</sup> Among such compounds, those with alkenyl moieties have attracted considerable attention because the alkenyl substituents provide potential for further functionalization of the alkenylphosphines with the aid of transition-metal catalysts/reagents.<sup>2,3</sup> Coordination chemistry of alkenylphosphines has been explored as well.<sup>4</sup> A classical method of preparing alkenylphosphine derivatives

is a coupling reaction of an alkenyl-Grignard or an alkenyl-lithium reagent with an appropriate halophosphorus compound.<sup>5</sup> Hydrophosphorylation of alkynes has been developed recently as an alternative method to prepare these compounds.<sup>6,7</sup>

We have been interested in reactions between organozirconium nucleophiles and phosphorus electrophiles.<sup>8–11</sup> In a previous paper, we reported reactions of a ( $\beta$ -allylalkenyl)-

\* To whom correspondence should be addressed.

<sup>†</sup> Hokkaido University.

<sup>‡</sup> Peking University.

<sup>§</sup> Aichi University of Education.

(1) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 4986. (b) Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741. (c) Andersen, N. G.; Keay, B. A. *Chem. Rev.* **2001**, *101*, 997.

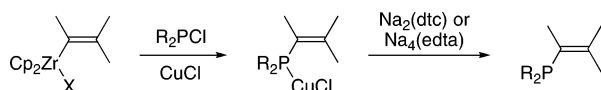
(2) (a) Leung, P.-H. *Acc. Chem. Res.* **2004**, *37*, 169. (b) Aw, B. H.; Leung, P. H. *Tetrahedron: Asymmetry* **1994**, *7*, 1167. (c) Aw, B.-H.; Hor, T. S. A.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W.; Leung, P.-H. *Inorg. Chem.* **1997**, *36*, 2138. (d) Leung, P. H.; Selvaratnam, S.; Cheng, C. R.; Mok, K. F.; Rees, N. H.; McFarlane, W. *Chem. Commun.* **1997**, 751. (e) Liu, A.; Mok, K. J.; Leung, P.-H. *Chem. Commun.* **1997**, 2397. (f) Song, Y.; Mok, K. F.; Leung, P. H.; Chan, S. H. A. *Inorg. Chem.* **1998**, *37*, 6399. (g) Qin, Y.; Selvaratnam, S.; Vittal, J. J.; Leung, S. H. *Organometallics* **2002**, *21*, 5301.

(3) (a) Timmer, M. S. M.; Ova, H.; Filippov, D. V.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron Lett.* **2000**, *41*, 8635. (b) Stoianova, D. S.; Hanson, P. R. *Org. Lett.* **2001**, *3*, 2765. (c) Chatterjee, A. K.; Choi, T.-L.; Grubbs, R. H. *Synlett* **2001**, 1034. (d) Demchuk, O. M.; Pietrusiewicz, K. M.; Michrowska, A.; Grela, K. *Org. Lett.* **2003**, *5*, 3217. (e) Bauer, E. B.; Gladysz, J. A. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 2, Chapter 2.11, p 403.

(4) (a) Fryzuk, M. P.; Gao, X.; Rettig, S. *Can. J. Chem.* **1995**, *73*, 1175. (b) Ji, H.-L.; Nelson, J. H.; De Cian, A.; Fischer, J.; Solujic, L.; Milosavljevic, E. B. *Organometallics* **1992**, *11*, 401. (c) Barthel-Rosa, L. P.; Maitra, K.; Fischer, J.; Nelson, J. H. *Organometallics* **1997**, *16*, 1714. (d) Giordano, R.; Sappa, E.; Predieri, G.; Tiripicchio, A. *J. Organomet. Chem.* **1997**, *547*, 49. (e) Malisch, W.; Rehm, F.-J.; Jehle, H.; Reising, J. *J. Organomet. Chem.* **1998**, *570*, 107. (f) Coles, S. J.; Jaulds, I.; Hursthouse, M. B.; Kelly, D. G.; Toner, A. *J. Polyhedron* **2000**, *19*, 1271. (g) Duraczynska, D.; Nelson, J. H. *Dalton Trans.* **2003**, 449.

(5) Maier, L. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 1, Chapter 1, p 32.

## SCHEME 1



zirconocene with  $R_2PCl$  in the presence of  $CuCl$ .<sup>8c</sup> In the reaction, a phosphine–olefin species generated in situ was trapped by  $Cu(I)$  as a chelating ligand. Treatment of the  $Cu$  complex with  $Na_2(dtc)$  or  $Na_4(edta)$  dissociated the coordinating phosphine–olefin ligand from the metal center, and the free ligand was isolated in a pure form.

In this report, we have examined application of the overall protocol for the synthesis of a variety of alkenylphosphines (Scheme 1). Because various alkenylzirconocene species of different substitution patterns can be easily prepared from easily available materials via (i) oxidative addition of an alkenyl halide to  $Cp_2Zr(II)$ ,<sup>12</sup> (ii) hydrozirconation of an alkyne with the Schwartz's reagent,<sup>13</sup> or (iii) zirconacyclopentene-mediated carbosilylation of an alkyne<sup>14</sup> (Scheme 2), reactions of such alkenylzirconocenes with appropriate phosphorus electrophiles should provide a general route to alkenylphosphines. During the investigation, it was found that transmetalation of the alkenyl moieties from  $Zr(IV)$  to  $Cu(I)$  was required to facilitate the

(6) (a) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571. (b) Han, L.-B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259. (c) Han, L.-B.; Hua, R.; Tanaka, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 94. (d) Zhao, C.-Q.; Han, L.-B.; Goto, M.; Tanaka, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1929. (e) Kazankova, M. A.; Efimova, I. V.; Kochetkov, A. N.; Afanas'ev, V. V.; Beletskaya, I. P.; Dixneuf, P. H. *Synlett* **2001**, 497. (f) Wicht, D. K.; Glueck, D. S. In *Catalytic Heterofunctionalization*; Togni, A., Grutzmacher, H., Eds.; Wiley-VCH: Weinheim, 2001; Chapter 5, p 143.

(7) For other methods of preparing alkenylphosphines, see: (a) Walsh, E. N.; Beck, T. M.; Woodstock, W. H. *J. Am. Chem. Soc.* **1955**, *77*, 929. (b) Maier, L.; Seyferth, D.; Stone, F. G. A.; Rochow, E. G. *J. Am. Chem. Soc.* **1957**, *79*, 5884. (c) Aguiar, A. M.; Daigle, D. *J. Am. Chem. Soc.* **1964**, *86*, 2299. (d) Clark, P. W.; Cartis, J. L. S.; Garrou, P. E.; Hartwell, G. E. *Can. J. Chem.* **1974**, *52*, 1714. (e) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748. (f) Ichikawa, J.; Yonemaru, L.; Minami, T. *Synlett* **1992**, 833. (g) Lipshutz, B. H.; Buzard, D. J.; Yun, C. S. *Tetrahedron Lett.* **1999**, *40*, 201. (h) Kazankova, M. A.; Lutsenko, S. V.; Beletskaya, I. P. *Tetrahedron Lett.* **1999**, *40*, 569. (i) Kazankova, M. A.; Chirkov, E. A.; Kochetkov, A. N.; Efimova, I. V.; Beletskaya, I. P. *Tetrahedron Lett.* **1999**, *40*, 573. (j) Gilbertson, S. R.; Ju, Z.; Starkey, G. W. *Tetrahedron Lett.* **1999**, *40*, 8509. (k) Zhong, P.; Huang, X.; Xiong, Z.-X. *Synlett* **1999**, 721.

(8) (a) Takahashi, T.; Kotori, M.; Hara, R.; Xi, Z. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591. (b) Kotori, M.; Xi, Z.; Takahashi, T. *J. Synth. Org. Chem., Jpn.* **1997**, *55*, 958. (c) Miyaji, T.; Xi, Z.; Nakajima, K.; Takahashi, T. *Organometallics* **2001**, *20*, 2859.

(9) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

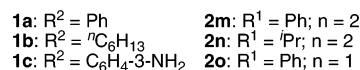
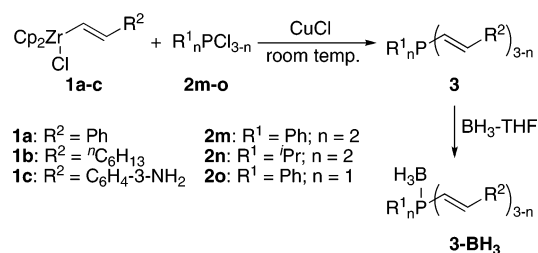
(10) Reactions of zirconacyclopentadienes with chlorodiphenylphosphine in the presence of  $CuCl$  were reported, see: (a) Doherty, S.; Knight, J. G.; Robins, E. G.; Scanlan, T. H.; Champkin, P. A.; Clegg, W. *J. Am. Chem. Soc.* **2001**, *123*, 5110. (b) Doherty, S.; Robins, E. G.; Nieuwenhuyzen, M.; Knight, J. G.; Champkin, P. A.; Clegg, W. *Organometallics* **2002**, *21*, 1383.

(11) For preparation of (*E*)-2-arylvinylphosphonate from the reaction of (*E*)-2-arylvinylzirconocene and chlorophosphonate using  $CuBr$  as a catalyst, see: Zhong, P.; Huang, X.; Xiong, Z.-X. *Synlett* **1999**, 721.

(12) Takahashi, T.; Kotori, M.; Fischer, R.; Nishihara, Y.; Nakajima, K. *J. Am. Chem. Soc.* **1995**, *117*, 11039.

(13) (a) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115. (b) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (c) Igau, A. In *Catalytic Heterofunctionalization*; Togni, A., Grutzmacher, H., Eds.; Wiley-VCH: Weinheim, 2001; Chapter 8, p 253. (d) Lipshutz, B. H.; Pfeiffer, S. S.; Noson, K.; Tomioka, T. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, 2002; Chapter 4, p. 110.

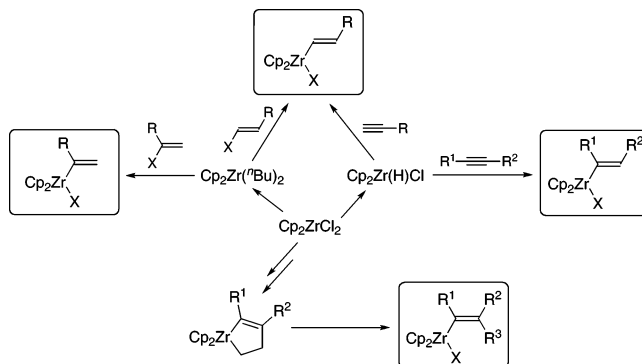
(14) (a) Takahashi, T.; Aoyagi, K.; Hara, R.; Suzuki, N. *Chem. Commun.* **1993**, 1043. (b) Takahashi, T.; Suzuki, N.; Kageyama, M.; Kondakov, D. Y.; Hara, R. *Tetrahedron Lett.* **1993**, *40*, 4811. (c) Takahashi, T.; Kondakov, D. Y.; Suzuki, N. *Tetrahedron Lett.* **1993**, *41*, 6571. (d) Takahashi, T.; Xi, C.; Ura, Y.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *112*, 3228.

TABLE 1. Preparation of ( $\alpha$ -Unsubstituted alkenyl)phosphines 3

entry	$Cp_2Zr(alkenyl)Cl$ <b>1</b>	$R^1_nPCl_{3-n}$ <b>2</b>	$CuCl$ (%)	product <b>3</b>	yield <sup>d</sup> (%)
1	<b>1a</b>	<b>2m</b>		<b>3am</b>	78 (87)
2	<b>1b</b>	<b>2m</b>		<b>3bm</b>	76 (90)
3	<b>1a</b>	<b>2n</b>		NR	
4 <sup>b</sup>	<b>1a</b>	<b>2n</b>	15	<b>3an-BH<sub>3</sub></b>	33 (37)
5 <sup>c</sup>	<b>1c</b>	<b>2n</b>	15	<b>3cn</b>	67
6	<b>1a</b>	<b>2o</b>		<b>3ao</b>	55 (98)
7 <sup>b</sup>	<b>1b</b>	<b>2o</b>		<b>3bo-BH<sub>3</sub></b>	33 (46)

<sup>a</sup> Isolated yields by silica gel chromatography. NMR yields are given in parentheses. <sup>b</sup> Reaction mixture was treated with 1.5 equiv of  $BH_3-THF$ . <sup>c</sup> Reaction mixture was treated with 2.2 equiv of  $Na_2(btc)$  (vide infra).

## SCHEME 2



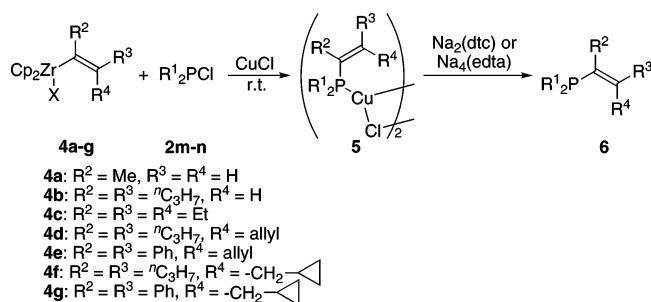
reactions of sterically encumbered substrates/reagents. We report herein details of the synthesis of alkenylphosphines via alkenylzirconocenes.

## Results and Discussion

Reactions of ( $\alpha$ -Unsubstituted alkenyl)zirconocene Species.

When an alkenylzirconium compound **1a**, which was derived from phenylacetylene by hydrozirconation, was treated with  $Ph_2PCl$  **2m** in THF at room temperature, the reaction proceeded smoothly to give diphenyl( $\beta$ -styryl)phosphine **3am** in 87% yield (Table 1, entry 1).<sup>15</sup> Analogously, (1-octenyl)diphenylphosphine **3bm** was obtained in 90% yield from **1b** and **2m** (entry 2). On the other hand, reactions of **1a** with **2n**, which was with sterically demanding isopropyl substituents, did not proceed under the identical conditions (entry 3). It was found that addition of a catalytic amount of  $CuCl$  (15%)<sup>8c,10,11</sup> realized the reaction between **1a** and **2n**. The corresponding alkenylphosphine **3an**, which was air-sensitive, was isolated as a stable  $BH_3$ -adduct after treating the crude reaction mixture with  $BH_3-THF$  (entry 4, see also entry 5).<sup>16</sup> A reaction of **1a** with 0.5 equiv of dichlorophenylphosphine **2o** under identical conditions also proceeded smoothly in the absence of  $CuCl$  and the correspond-

(15) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1988**, *53*, 4425.

TABLE 2. Preparation of ( $\alpha$ -Substituted alkenyl)phosphines 6

entry	alkenyl-Zr <b>4</b>	R <sup>1,2</sup> PCl <b>2</b>	yield of <b>5</b> <sup>a</sup> (%)	Cu scavenger	yield of <b>6</b> <sup>a</sup> (%)
1	<b>4a</b>	<b>2m</b>	63 (84), <b>5am</b>	Na <sub>2</sub> (dtc)	67 (84), <b>6am</b>
2	<b>4b</b>	<b>2m</b>	<i>b</i>	Na <sub>2</sub> (dtc)	65 (88), <b>6bm</b>
3	<b>4c</b>	<b>2m</b>	70 (80), <b>5cm</b>	Na <sub>2</sub> (dtc)	66 (94), <b>6cm</b>
4 <sup>c</sup>	<b>4c</b>	<b>2m</b>	<i>b</i>	Na <sub>2</sub> (dtc)	49 (71), <b>6cm</b>
5	<b>4c</b>	<b>2n</b>	50 (81), <b>5cn</b>	Na <sub>4</sub> (edta)	44 (–), <b>6cn</b>
6	<b>4d</b>	<b>2m</b>	<i>b</i>	Na <sub>2</sub> (dtc)	78 (90), <b>6dm</b>
7	<b>4d</b>	<b>2n</b>	50 (72), <sup>d</sup> <b>5dn</b>	Na <sub>4</sub> (edta)	52 (–), <b>6dn</b>
8 <sup>e</sup>	<b>4e</b>	<b>2n</b>	<i>b</i>	Na <sub>2</sub> (dtc)	75 (88), <b>6en</b>
9	<b>4f</b>	<b>2m</b>	56 (78), <b>5fm</b>	Na <sub>2</sub> (dtc)	73 (80), <b>6fm</b>
10	<b>4f</b>	<b>2n</b>	55 (75), <b>5fn</b>	Na <sub>2</sub> (dtc)	71 (85), <b>6fn</b>
11 <sup>e</sup>	<b>4g</b>	<b>2n</b>	64 (83), <b>5gn</b>	Na <sub>4</sub> (edta)	73 (83), <b>6gn</b>

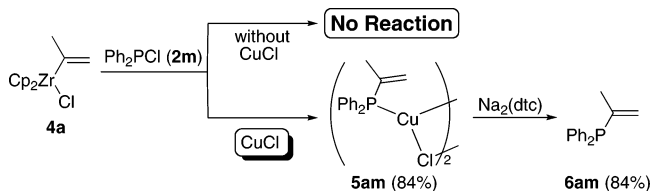
<sup>a</sup> Isolated yields by silica gel chromatography. NMR yields are given in parentheses. <sup>b</sup> The corresponding Cu complexes were not isolated. <sup>c</sup> A catalytic amount of CuCl (0.2 equiv) was used. <sup>d</sup> Taken from ref 8c. <sup>e</sup> The first step was carried out at 50 °C.

ing dialkenylphosphine **3ao** was obtained in good yield (entry 6). Note that a reaction of **1a** and **2o** in a 1:1 molar ratio also afforded **3ao** as a sole coupling product, and no monoalkenylchlorophosphine was detected. This indicates that substitution of the second P–Cl bond by the alkenylmetal reagent was faster than the first one.

**Reactions of ( $\alpha$ -Substituted alkenyl)zirconocene Species.** When alkenylzirconium species **4a**, which was generated in situ by oxidative addition of 2-chloropropene to the Negishi's reagent Cp<sub>2</sub>Zr<sup>n</sup>Bu<sub>2</sub>,<sup>12</sup> was treated with Ph<sub>2</sub>PCl **2m** in the presence of 1 equiv of CuCl, the reaction proceeded smoothly to give a dinuclear [( $\mu$ -Cl)Cu(I)]<sub>2</sub> complex **5am** in 84% yield (Table 2, entry 1). In a <sup>31</sup>P NMR spectrum of the copper complex, only one broad signal was observed at  $\delta$  0.6, which was assignable to phosphorus coordinating to the copper center. In the absence of CuCl, the desired alkenylphosphine was not formed even at elevated temperature (80 °C, bath temperature). In this reaction, transmetalation of the Zr-alkenyl moiety to a Cu(I) center was essential as reported previously.<sup>8c,10,11</sup> When Na<sub>2</sub>(dtc) was added to the reaction mixture containing the phosphine-copper complex **5am**, the color of the solution immediately changed from pale yellow to dark yellow giving free diphenyl(2-propenyl)phosphine **6am** in 84% yield (Scheme 3). The <sup>31</sup>P NMR spectrum of **6am** showed upper field shift of the signal, indicating the dissociation of the phosphine.

In the same way, ( $\alpha,\beta$ -disubstituted alkenyl)zirconocene **4b**, generated from the Schwartz's reagent Cp<sub>2</sub>Zr(H)Cl and 4-octyne, reacted with **2m** in the presence of CuCl, and after treatment with Na<sub>2</sub>(dtc) the corresponding alkenylphosphine **6bm** was obtained in 88% yield (Table 2, entry 2). This reaction also did not proceed in the absence of CuCl.

SCHEME 3

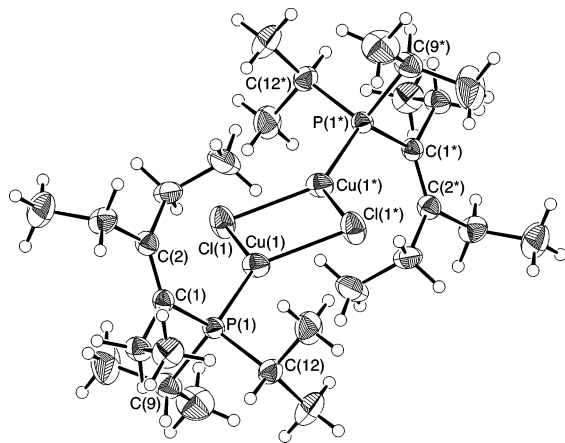


(Persubstituted alkenyl)zirconocene compounds can be easily prepared from alkynes and zirconocene dichloride (Scheme 2). We reported various carbonyl zirconation of alkynes utilizing reactions of a zirconacyclopentene with methanol,<sup>14a</sup> allyloxytrimethylsilane,<sup>14b</sup> or 4-bromo-1-butene.<sup>14c</sup> These reactions give alkenylzirconocene compounds with ethyl (**4c**), allyl (**4d-e**), or cyclopropylmethyl (**4f-g**) substituents at the  $\beta$ -position of the alkenyl moieties, respectively. The alkenylzirconocene species were generated *in situ* and reacted with chlorophosphine derivatives (**2m,n**) in the presence of CuCl affording the dinuclear [( $\mu$ -Cl)Cu]<sub>2</sub> complexes **5** coordinated by the corresponding alkenylphosphines in good yields (Table 2, entries 3, 5, 7, and 9–11). When diphenylacetylene was used for generating the (persubstituted alkenyl)zirconocenes, a higher temperature was required to accomplish the reaction (Table 2, entry 11).

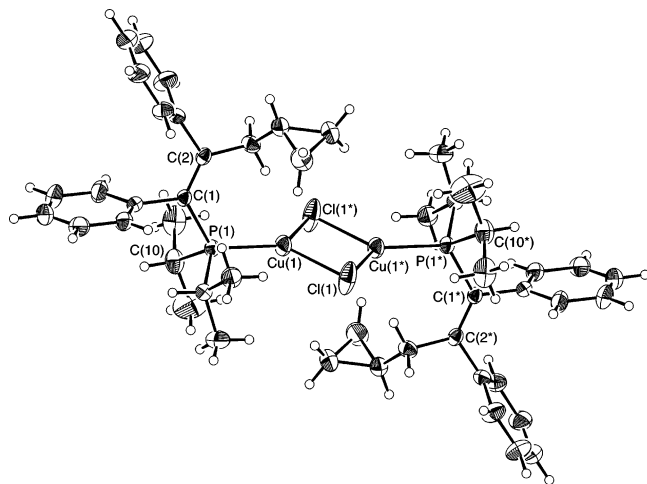
As mentioned above, treatment of the copper complexes with Na<sub>2</sub>(dtc) induced dissociation of the coordinating alkenylphosphines and the free phosphines **6** were isolated in pure form. This protocol could be extended to one-pot synthesis of free alkenylphosphines from alkynes without isolating the intermediary copper complexes (Table 2, entries 2, 4, 6, and 8). Aqueous Na<sub>4</sub>(edta) was also applicable as a Cu(I) scavenger (Table 2, entries 5, 7, and 11). For the one-pot procedure, a catalytic amount of CuCl (20 mol %) was enough to give **6cm**, albeit in the moderate yield (Table 2, entry 4).

The X-ray single-crystal structures of **5cn** and **5gn** are given in Figures 1 and 2, respectively. These results showed the

(16) (a) Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287. (b) Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998**, *178–180*, 665. (c) Carboni, B.; Monnier, L. *Tetrahedron* **1999**, *55*, 1197. (d) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.



**FIGURE 1.** ORTEP drawing of **5cn** 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Cu(1)–P(1) = 2.191(7), Cu(1)–Cl(1) = 2.3205(9), Cu(1)–Cl(1\*) = 2.3216(9), C(1)–C(2) = 1.332(4); Cl(1)–Cu(1)–P(1) = 131.93(3), Cl(1\*)–Cu(1)–P(1) = 129.75(3), Cl(1)–Cu(1)–Cl(1\*) = 98.11(3), Cu(1)–Cl(1)–Cu(1\*) = 81.89(3).



**FIGURE 2.** ORTEP drawing of **5gn** 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Cu(1)–P(1) = 2.191(1), Cu(1)–Cl(1) = 2.280(2), Cu(1)–Cl(1\*) = 2.325(2), C(1)–C(2) = 1.346(6); Cl(1)–Cu(1)–P(1) = 131.11(5), Cl(1\*)–Cu(1)–P(1) = 128.14(6), Cl(1)–Cu(1)–Cl(1\*) = 100.34(5), Cu(1)–Cl(1)–Cu(1\*) = 79.66(5).

formation of bis( $\mu$ -chloride) dimers in which the alkenylphosphines and Cu(I) were complexed with a 1:1 molar ratio.

## Conclusions

In summary, this work describes the general method for the preparation of a variety of alkenylphosphines via alkenylzirconocene compounds. When an alkenyl group had no substituent at the  $\alpha$ -position, alkenylzirconocene reacted with  $\text{Ph}_2\text{PCl}$  or  $\text{PhPCl}_2$  directly. On the other hand, a reaction of ( $\alpha$ -unsubstituted alkenyl)zirconocene with  $^i\text{Pr}_2\text{PCl}$  required addition of Cu-

(I) salt to proceed. Analogously, ( $\alpha$ -substituted alkenyl)zirconocene species reacted with chlorophosphines in the presence of CuCl, affording the corresponding alkenylphosphine as Cu(I) complexes. Free alkenylphosphines were obtained by the treatment of the alkenylphosphine–Cu(I) complexes with  $\text{Na}_2(\text{dtc})$  or  $\text{Na}_4(\text{edta})$ .

## Experimental Section

**Preparation of Alkenylphosphines by the Direct Reaction of an Alkenylzirconocene with a Chlorophosphine.** To a THF solution of  $\text{Cp}_2\text{Zr}(\text{alkenyl})\text{X}$  (1.1 equiv to  $\text{R}_2\text{PCl}$  or 2.2 equiv to  $\text{RPCl}_2$ ), which was generated in situ as reported previously,<sup>12,13</sup> was added  $\text{R}_n\text{PCl}_{3-n}$  (**2**) by means of syringe at 0 °C. After the mixture was stirred for 3 h at room temperature, the reaction mixture was treated with  $\text{BH}_3\cdot\text{THF}$  (1.2 equiv) if necessary. The product was extracted with hexane or  $\text{Et}_2\text{O}$  and then purified by column chromatography on silica gel. The yields of the alkenylphosphines **3** are described in Table 1. The characterization data of the products are listed in the Supporting Information.

**Preparation of Alkenylphosphines from an Alkenylzirconocene and a Chlorophosphine in the Presence of CuCl.** To a THF solution of  $\text{Cp}_2\text{Zr}(\text{alkenyl})\text{X}$  (1.1 equiv to  $\text{R}_2\text{PCl}$  or 2.2 equiv to  $\text{RPCl}_2$ ), which was generated in situ as reported previously,<sup>12–14</sup> was added  $\text{R}_2\text{PCl}$  (**2**) by means of syringe at 0 °C. Subsequently, an appropriate amount of CuCl (see Tables 1 and 2) was added to the mixture at this temperature. After the mixture was stirred for 3 h at room temperature, the reaction mixture was treated with  $\text{Na}_2(\text{dtc})$  (2.0 equiv) or  $\text{Na}_4(\text{edta})$  (2.0 equiv) at the same temperature. The mixture was diluted with hexane and then filtered. After removal of the volatiles, the product was purified by column chromatography on silica gel. The yields of the alkenylphosphines **3** and **6** are described in Tables 1 and 2. The compound **6dm** is known compound and was characterized by comparison of the spectral data with those reported previously.<sup>8c</sup> The characterization data of the other products are listed in the Supporting Information.

**Preparation of Dinuclear Copper/Chlorophosphine Complexes (5).** To a THF solution of  $\text{Cp}_2\text{Zr}(\text{alkenyl})\text{X}$  (**4**), which was generated in situ as reported previously,<sup>13,14</sup> were added  $\text{R}_2\text{PCl}$  (1.0 equiv) and CuCl (1.2 equiv) successively at 0 °C. After the mixture was stirred for 3 h at room temperature, the resulting black solution was quenched with 3 N HCl, extracted with ethyl acetate, washed with brine, and dried over  $\text{MgSO}_4$ . After filtration, the yellow solution was concentrated and subjected to purification through column chromatography on silica gel. The yields of the copper complexes **5** are described in Table 2. The characterization data of the complexes are listed in the Supporting Information.

**Acknowledgment.** Z.X. thanks the National Natural Science Foundation of China (29702001), the National Science Fund for Distinguished Young Scholars (29825105), and the Peking University President Fund for financial support for part of this work.

**Supporting Information Available:** Characterization data and NMR spectra for all new compounds; crystallographic data for **5cn** and **5gn** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO071089V