## **Generation of Copper(I) Complexes with a Tethered Olefin-Phosphine Ligand from CuCl-Mediated Reaction** of Alkenylzirconocene with R<sub>2</sub>PCl

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 $\alpha$ -Substituted alkenylzirconocenes, Cp<sub>2</sub>Zr(OSiMe<sub>3</sub>){C(R)=C(R)CH<sub>2</sub>CH=CH<sub>2</sub>} (R = Pr (1a); R = Ph(1c), which were prepared in situ by the reaction of zirconacyclopentenes with (allyloxy)trimethylsilane, reacted with R'2PCl in the presence of CuCl to give the Cu(I) complexes  $[(\mu - Cl)Cu(PR'_2C(R) = C(R)CH_2CH = CH_2)]_2$  (R = Pr, R' = Ph (2a); R = Pr, R' = *i*-Pr (2b); R = Ph, R' = i Pr (2c)) with tethered olefin-phosphine ligands bidentately coordinating to copper(I) in good to high yields. The molecular structures of **2a** and **2c** were determined by single-crystal X-ray diffraction studies.

## Introduction

Phosphine compounds have been widely used as ligands in coordination chemistry and transition-metal catalysts. We have investigated the preparative methods for phosphine compounds from organozirconocene complexes.<sup>1</sup> Zirconacyclopentanes and zirconacyclopentenes reacted with Ph<sub>2</sub>PCl to form alkylphosphine and homoallylphosphine compounds, respectively.<sup>2</sup> These phosphine compounds were formed by a selective reaction of the  $Zr-C(sp^3)$  bonds. It is known that reactions of zirconacyclopentadienes, which have two  $Zr-C(sp^2)$ bonds in one molecule, with  $PhPCl_2$  afforded cyclic phosphorus compounds.<sup>3</sup> In contrast, acyclic  $\alpha$ -substituted alkenylzirconocene compounds such as 1 do not react with Ph<sub>2</sub>PCl to afford alkenylphosphines.<sup>4</sup> In this paper, we report that reactions of alkenylzirconocene 1 with R'<sub>2</sub>PCl were realized in the presence of CuCl. Unexpectedly, in this reaction the Cu(I) complex 2 with the tethered olefin-phosphine compound 3 as a bidentate ligand was obtained.

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## **Results and Discussion**

Transmetalation of  $Zr-C(sp^2)$  bonds to  $Cu-C(sp^2)$ bonds using CuCl has proven very efficient for novel organic transformation reactions.<sup>1</sup> The trisubstituted alkenylzirconocenes 1<sup>5</sup> did not react with Ph<sub>2</sub>PCl, even at high temperature. When CuCl was added, the reaction proceeded rapidly and cleanly (Scheme 1). Transmetalation of  $Zr-C(sp^2)$  bonds to  $Cu-C(sp^2)$  bonds is essential for this reaction. Very interestingly, the in situ

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**Figure 1.** ORTEP drawing of **2a**. The symmetry-equivalent atoms, which are labeled with asterisks, are generated by the symmetry operator 1 - x, -y, 2 - z.



**Figure 2.** ORTEP drawing of complex **2c**. The symmetry-equivalent atoms, which are labeled with asterisks, are generated by the symmetry operator 2 - x, -y, 2 - z.

formed tethered olefin-phosphine compounds behaved as chelating ligands and coordinated with the regenerated CuCl to afford Cu(I) complexes, providing a direct synthesis of Cu(I) complexes.<sup>6-8</sup> Copper(I) complexes **2a** (R = n-Pr, R' = Ph), **2b** (R = n-Pr, R' = i-Pr), and **2c** (R= Ph, R' = i-Pr), were formed in 83%, 72%, and 85% yields, respectively. Purification by column gave pure compounds in 43%, 50%, and 55% yields, respectively. Copper(I) complexes with olefin ligands are of great importance in biochemistry and synthetic organic chemistry.<sup>9,10</sup> The simultaneous coordination of the olefin moiety and the phosphorus atom in a tethered phosphine–olefin to a metal center is rare.<sup>6–8</sup> There is only one structurally characterized Cu(I) complex of this kind,<sup>8d</sup> to our knowledge. In the literature case, CuBr<sub>2</sub> was used as the copper source and reduced in methanol upon coordination.<sup>8d</sup>

The X-ray single-crystal structures of **2a** and **2c** are given in Figures 1 and 2, respectively, which show that these complexes are chlorine-bridged dimers with the copper atom bonded to two chloride ions, the tertiary phosphine, and the double bond of the olefin. The C–C distances of the terminal double bond in **2a** and **2c** are

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1.360(9) and 1.353(4) Å, respectively, which do not differ significantly from the corresponding data reported (1.362(6) Å in a Cu(I)–ethylene complex,<sup>8f</sup> 1.34(2) Å in a Cu(I) complex with N-olefin ligands<sup>8c</sup>) but are shorter than that in an analogous zirconocene complex (1.435(3) Å)<sup>6</sup> and longer than that in the aforementioned literature case (1.262(9) Å).<sup>8d</sup> The distances of 2.307(1) Å (Cu(1)–Cl(1)), 2.241(1) Å (Cu(1)–P(1)), 2.180(5) Å (Cu(1)–C(1)), and 2.222(6) Å (Cu(1)–C(2)) for **2a** and 2.3926(8) Å (Cu(1)–Cl(1)), 2.2486(7) Å (Cu(1)–P(1)), 2.203(3) Å (Cu(1)–C(4)), and 2.216(3) Å (Cu(1)–C(5)) for **2c** all lie within reasonable range.

As a control experiment, free tethered phosphineolefin compound **3a** ( $\mathbf{R} = n$ -Pr,  $\mathbf{R}' = Ph$ ) was prepared in an alternative way from alkenylzirconocenes **1a** (Scheme 2). Addition of 1 equiv of CuCl to a THF solution of **3a** afforded **2a** in quantitative NMR yield. Interestingly, phosphine-olefin compounds **5** and **7** 



behaved only as monodentate ligands toward CuCl, forming complexes **6** and **8** in 75% and 73% isolated yields, respectively. A plausible explanation of this result is that ligands **3** possess a favorable conformation for chelating the Cu(I) atom due to the double bond in the chain between the phosphorus and the olefin moiety.

Comparison of NMR spectral data between the free ligand **3a** and its Cu(I) complex reveals clean formation of the Cu(I) complex **2a**. The <sup>1</sup>H NMR spectrum of **2a** shows the chemical shifts of the alkenyl protons are shifted by 0.5 ppm to higher field.<sup>8c,d</sup> The <sup>13</sup>C NMR signal of the terminal alkenyl carbon appeared at 89.8 ppm (=CH<sub>2</sub>) with an upfield shift of 16 ppm compared with the free ligand **3a**.<sup>8c,d</sup> The <sup>31</sup>P NMR spectrum of **2a** showed a broad singlet at -5.1 ppm.<sup>8d</sup> The <sup>31</sup>P NMR chemical shift shows a shift of 5 ppm compared with the free ligand **3a**. These changes in chemical shifts were all consistent with those reported and indicated that phosphorus and the terminal double bond coordinate to the Cu atom simultaneously.<sup>8c,d,f</sup>

When copper-phosphine complex **2a** was treated with 2.2 equiv of sodium diethyldithiocarbamate, free phosphine **3a** was formed in 95% NMR yield and purification by short-column chlomatography afforded pure **3a** in 84% isolated yield (Scheme 3).



All reactions involving organometallic compounds were carried out under nitrogen. Tetrahydrofuran (THF) was distilled and dried with sodium benzophenone ketyl. Zirconocene dichloride was purchased from Nichia Corp. EtMgBr (0.96 M solution in THF), EtMgCl (0.97 M solution in THF), t-BuLi (1.50 M soluton in hexane), and chlorodiphenylphosphine were purchased from Kanto Chemical Co. Inc. Other phosphine compounds were purchased from Aldrich Chemical Co., Inc. Alkynes and olefins were purchased from TCI Co. Ltd. Unless otherwise noted, chemicals were used without further purification.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer.

{[(5-(*E*)-Propyl-4,7-octadien-4-yl)diphenylphosphine]- $Cu(\mu$ -Cl)<sub>2</sub> (2a). A 50 mL Schlenk tube was charged with Cp<sub>2</sub>ZrCl<sub>2</sub> (731 mg, 2.5 mmol) and THF (8 mL) under N<sub>2</sub>. To this solution was added EtMgCl (0.97 M, 5.10 mL, 5.0 mmol) at -78 °C followed by stirring for 1 h. After addition of 4-octyne (296  $\mu$ L, 2.0 mmol), the mixture was gradually warmed to 0 °C and stirred for 3 h. To the orange reaction mixture was added (allyloxy)trimethylsilane (0.69 mL, 4.0 mmol) at 0 °C, and then the mixture was warmed to 50  $^\circ C$  and stirred for 3 h. To the mixture cooled to 0 °C were added CuCl (223 mg, 2.25 mmol) and Ph<sub>2</sub>PCl (376 µL, 2.0 mmol). After it was stirred for 2 h at room temperature, the light orange reaction mixture was quenched with 3 N HCl and the pale yellow aqueous layer was extracted with ethyl acetate. The extract combined with the organic layer was washed with brine and dried over MgSO<sub>4</sub>. The title compound was obtained from column chromatography (1/3 ethyl acetate/hexane) as a white solid (387 mg, 0.43 mmol, 43% isolated yield). Mp: 150-152° dec. NMR yield: 83%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  0.46 (t, J = 7.2 Hz, 6H), 0.61-0.77 (m, 4H), 1.01 (t, J = 7.3 Hz, 6H), 1.46-1.63(m, 4H), 2.02-2.31 (m, 8H), 3.01 (d, J = 5.5 Hz, 4H), 4.40-4.58 (m, 4H), 5.02-5.22 (m, 2H), 7.17-7.62 (m, 20H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  14.09, 14.38, 21.62, 23.31, 33.78, 38.55 (d), 38.84 (d), 89.78 (d), 111.77, 125.04 (d), 128.60 (d), 129.93, 131.19 (d), 133.63 (d), 155.09 (d). <sup>31</sup>P NMR (CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>):  $\delta$ -5.07. IR (Nujol, cm<sup>-1</sup>): 1599 (m), 1558 (m), 1375 (m), 1095 (s), 898 (m), 744 (s), 698 (s). Anal. Calcd for C<sub>46</sub>H<sub>58</sub>Cl<sub>2</sub>Cu<sub>2</sub>P<sub>2</sub>: C, 63.44; H, 6.71; Cl, 8.14. Found: C, 63.52; H, 6.81; Cl, 8.02.

{[(5-(*E*)-Propyl-4,7-octadien-4-yl)diisopropylphos**phine**]**Cu**(*µ*-**Cl**)<sub>2</sub> (**2b**). The reaction was carried out in the same way as described above using <sup>i</sup>Pr<sub>2</sub>PCl (1.0 M, THF solution, 2.0 mL, 2.0 mmol) instead of Ph<sub>2</sub>PCl. The desired complex 2b was formed in 72% NMR yield. Isolation and purification by column chromatography on silica gel (1/12 ethyl acetate/hexane) afforded 2b as a colorless solid (366 mg, 0.50 mmol, 50% isolated yield). Mp: 65-67 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  0.90–1.02 (m, 12H), 1.10 (dd, J= 7.0, 15.5 Hz, 12H), 1.34 (dd, J = 6.9, 16.9 Hz, 12H), 1.48–1.52 (m, 8H), 2.11– 2.28 (m, 12H), 2.96 (d, J = 6.1 Hz, 4H), 4.28–4.38 (m, 4H), 4.90-5.02 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si): δ 13.89, 14.41, 19.45 (d), 19.88 (d), 20.86, 23.70 (d), 23.91, 33.04, 37.61 (d), 38.72 (d), 86.27, 109.45, 125.39 (d), 156.75 (d).  $^{31}\mathrm{P}$  NMR (CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>):  $\delta$  15.3. IR (Nujol, cm<sup>-1</sup>): 1593 (m), 1545 (m), 1381 (s), 1101 (s), 873 (s), 675 (m). Anal. Calcd for C<sub>34</sub>H<sub>66</sub>Cl<sub>2</sub>-Cu<sub>2</sub>P<sub>2</sub>: C, 55.57; H, 9.05; Cl, 9.65. Found: C, 55.61; H, 9.03; Cl, 9.65.

{[(1,2-Diphenyl-1,4-pentadien-1-yl)diisopropylphosphine]Cu( $\mu$ -Cl)<sub>2</sub> (2c). The reaction was carried out in the same way as described above, using diphenylacetylene (357 µL, 2.00 mmol) instead of 4-octyne. The desired complex 2c was formed in 85% NMR yield. Isolation and purification by column chromatography on silica gel (1/12 ethyl acetate/ hexane) afforded 2c as a colorless solid. Recrystallization from a THF/hexane mixuture afforded the title compound as colorless crystals (475 mg, 0.545 mmol, 55% isolated yield). Mp: 139–141°C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  1.09 (dd, J = 7.0, 15.9 Hz, 12H), 1.23 (dd, J = 6.9, 16.7 Hz, 12H), 2.02-2.21 (m, 4H), 3.45 (d, J = 6.1 Hz, 4H), 4.46–4.58 (m, 4H), 5.25–5.40 (m, 2H), 6.63-7.07 (m, 20H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si): δ 19.07 (d), 19.63 (d), 23.99 (d), 40.93 (d), 90.16 (d), 110.65, 126.45, 126.51, 127.65, 127.70, 127.73, 129.70, 131.28 (d), 139.32 (d), 144.18 (d), 158.35 (d).  ${}^{31}$ P NMR (CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>):  $\delta$  9.75. IR (Nujol, cm<sup>-1</sup>): 1599 (m), 1560 (m), 1379 (m), 1263 (m), 1024 (s), 883 (s), 802 (s), 765 (s), 700 (s). Anal. Calcd for C<sub>48</sub>H<sub>58</sub>Cl<sub>2</sub>-Cu<sub>2</sub>P<sub>2</sub> C, 63.44; H, 6.71; Cl, 8.14. Found: C, 63.38; H, 6.78; Cl, 8.21.

(5-(E)-Propyl-4,7-octadien-4-yl)diphenylphosphine (3a). To the copper-phosphine complex 2a (89.7 mg, 0.0996 mmol) were added sodium diethyldithiocarbamate trihydrate (49.7 mg, 0.221 mmol) and 5 mL of THF. The solution changed from colorless to dark yellow immediately. After the mixture was stirred for 2 h at room temperature, the solvent was removed in vacuo. The desired compound 3a was formed in 95% NMR yield. The purification through silica gel short-column chromatography (1/25 ethyl acetate/hexane) gave free phosphine 3a in 84% isolated yield (58.8 mg, 0.167 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  0.45 (t, J = 7.4 Hz, 3H), 0.62–0.73 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H), 1.47-1.61 (m, 2H), 2.05-2.16 (m, 2H), 2.17-2.27 (m, 2H), 3.39-3.46 (m, 2H), 4.96-5.10 (m, 2H), 5.72–5.86 (m, 1H), 7.18–7.52 (m, 10H).  $^{13}\mathrm{C}$  NMR (CDCl\_3, Me<sub>4</sub>Si):  $\delta$  14.17, 14.39, 21.81, 23.36, 33.77 (d), 34.71 (d), 38.36 (d), 115.54, 127.70 (d), 128.00, 130.37 (d), 133.06 (d), 136.63, 137.67 (d), 152.16 (d). <sup>31</sup>P NMR (CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>):  $\delta$  –9.95. IR (Nujol, cm<sup>-1</sup>): 1635 (m), 1597 (m), 1182 (m), 1114 (m), 1089 (m), 1068 (m), 1026 (m), 995 (m), 912 (s), 742 (s), 696 (s).

**Diphenyl(4-penten-1-yl)phosphine (5).** <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  1.46–1.62 (m, 2H), 1.98–2.23 (m, 4H), 4.89–5.06 (m, 2H), 5.68–5.82 (m, 1H), 7.20–7.68 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  25.15 (d), 27.35 (d), 35.02 (d), 115.05, 128.33 (d), 128.33, 132.61 (d), 138.00, 138.77 (d). <sup>31</sup>P NMR (CDCl<sub>3</sub>, Ph<sub>3</sub>P):  $\delta$  –16.86. IR (Nujol, cm<sup>-1</sup>): 1639 (m), 1186 (m), 1118 (m), 1097 (m), 1068 (m), 1026 (m), 999 (m), 912 (s), 738 (s), 696 (s).

[Diphenyl(4-penten-1-yl)phosphine]CuCl (6). To a suspension of CuCl (50.1 mg, 0.51 mmol) in THF (5 mL) was added diphenyl(4-penten-1-yl)phosphine (129 mg, 0.51 mmol), and then the mixture was stirred at room temperature for 6 h. After the solvent was removed in vacuo, the residue was extracted with chloroform through flash column chromatograpy on silica gel. Removal of the solvent in vacuo gave the title compound as a colorless oil (134 mg, 75% isolated yield). NMR yield: 92%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si): δ 1.62-1.83 (m, 2H), 1.97-2.29 (m, 4H), 4.74-4.92 (m, 2H), 5.46-5.63 (m, 2H), 7.16-7.38 (m, 6H), 7.60-7.79 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  24.00 (d), 26.51 (d), 34.74 (d), 111.65, 128.39 (d), 129.58, 132.87 (d), 133.34 (d), 134.23. <sup>31</sup>P NMR (CDCl<sub>3</sub>, Ph<sub>3</sub>P):  $\delta$  -11.41. IR (Nujol, cm<sup>-1</sup>): 1639 (m), 1242 (s), 1186 (w), 1101 (s), 1045 (m), 1028 (m), 999 (m), 914 (s), 740 (s), 696 (s).

(3-Propyl-(3*E*)-pentenyl)diphenylphosphine (7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  0.83–0.93 (m, 6H), 1.24–1.38 (m, 4H), 1.90–2.16 (m, 8H), 5.15 (t, *J*=7.1 Hz, 1H), 7.27–7.35 (m, 6H), 7.38–7.46 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  13.89, 14.10, 21.48, 23.12, 26.98 (d), 29.78, 31.97, 32.89 (d), 125.25, 128.34 (d), 128.34, 132.69 (d), 138.81 (d), 139.35 (d). <sup>31</sup>P NMR (CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>):  $\delta$  –15.97. IR (Nujol, cm<sup>-1</sup>): 1589 (m), 1186 (m), 1143 (m), 1099 (s), 1070 (m), 1028 (m), 999 (m), 941 (m), 893 (m), 738 (s), 694 (s). HRMS: *m*/*z* calcd for C<sub>22</sub>H<sub>29</sub>P 324.2007, found 324.2027.

 Table 1. Crystallographic Data for Complexes 2a

 and 2c

	2a	2c
formula	$C_{46}H_{58}Cl_2Cu_2P_2$	$C_{46}H_{58}Cl_2Cu_2P_2$
M <sub>r</sub>	870.91	870.91
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	14.8691(9)	19.8191(2)
<i>b</i> (Å)	10.3391(6)	8.3541(2)
<i>c</i> (Å)	15.7226(10)	14.5945(4)
$\beta$ (deg)	114.650(2)	111.162(1)
Z	2	2
V (Å <sup>3</sup> )	2196.8(2)	2253.47(9)
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	11.94	11.63
cryst size (mm <sup>3</sup> )	$0.20\times0.30\times0.40$	$0.30\times0.30\times0.50$
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.32	1.283
F(000)	912	912
no. of rflns measd	12 963	13 114
no. of unique rflns $(R_{int})$	5032 (0.026)	9970 (0.028)
no. of rflns obsd $(I > 2\sigma(I))$	3259	7014
no. of params refined	235	351
$R^a$	0.054	0.053
$R_{\rm w}{}^b$	0.069	0.068

 ${}^{a}R = \sum ||F_{0}| - |F_{c}|| / \sum |F_{0}|. \ ^{b}R_{w} = [\sum w(|F_{0}| - |F_{c}|)^{2} / \sum w|F_{0}|^{2}]^{1/2}, \ w = [\sigma_{c}^{2}(F_{0}) + (p^{2}/4)|F_{0}|^{2}]^{-1}.$ 

Table 2. Selected Bond Lengths (Å) and Angles(deg) for Complex 2a

Cu(1)-P(1)	2.241(1)	Cu(1)-C(1)	2.180(5)
Cu(1) - C(2)	2.222(6)	C(1) - C(2)	1.360(9)
Cu(1)-Cl(1)	2.307(1)	Cu(1)-Cl(1*)	2.557(1)
C(1) - Cu(1) - C(2)	36.0(2)	C(1)-C(2)-C(3)	129.1(8)
P(1)-Cu(1)-Cl(1)	117.82(4)	$P(1)-Cu(1)-Cl(1^*)$	113.56(5)
$Cl(1) - Cu(1) - Cl(1^*)$	96.83(4)	$Cu(1) - Cl(1) - Cu(1^*)$	83.17(4)
P(1)-Cu(1)-C(1)	121.2(2)	P(1)-Cu(1)-C(2)	92.4(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 2c

$\begin{array}{ccccccc} Cu(1)-P(1) & 2.2486(7) & Cu(1)-C(5) & 2.216(3) \\ Cu(1)-C(4) & 2.203(3) & C(4)-C(5) & 1.353(4) \\ Cu(1)-Cl(1) & 2.3926(8) & Cu(1)-Cl(1^*) & 2.40107(8) \\ \end{array}$		· 0/		
$\begin{array}{ccccc} Cu(1)-C(4) & 2.203(3) & C(4)-C(5) & 1.353(4) \\ Cu(1)-Cl(1) & 2.3926(8) & Cu(1)-Cl(1^*) & 2.40107(8) \\ \end{array}$	Cu(1)-P(1)	2.2486(7)	Cu(1)-C(5)	2.216(3)
$\begin{array}{ccccc} Cu(1)-Cl(1) & 2.3926(8) & Cu(1)-Cl(1^*) & 2.40107(8) \\ C(4)-Cu(1)-C(5) & 35.7(1) & C(3)-C(4)-C(5) & 126.5(4) \\ P(1)-Cu(1)-Cl(1) & 117.12(3) & P(1)-Cu(1)-Cl(1^*) & 111.18(3) \\ Cl(1)-Cu(1)-Cl(1^*) & 96.50(2) & Cu(1)-Cl(1)-Cu(1^*) & 83.50(2) \\ P(1)-Cu(1)-C(5) & 126.35(9) & P(1)-Cu(1)-C(4) & 90.74(8) \\ \end{array}$	Cu(1) - C(4)	2.203(3)	C(4)-C(5)	1.353(4)
$\begin{array}{ccccc} C(4)-Cu(1)-C(5) & 35.7(1) & C(3)-C(4)-C(5) & 126.5(4) \\ P(1)-Cu(1)-Cl(1) & 117.12(3) & P(1)-Cu(1)-Cl(1^*) & 111.18(3) \\ Cl(1)-Cu(1)-Cl(1^*) & 96.50(2) & Cu(1)-Cl(1)-Cu(1^*) & 83.50(2) \\ P(1)-Cu(1)-C(5) & 126.35(9) & P(1)-Cu(1)-C(4) & 90.74(8) \\ \end{array}$	Cu(1)-Cl(1)	2.3926(8)	$Cu(1) - Cl(1^*)$	2.40107(8)
	C(4)-Cu(1)-C(5) P(1)-Cu(1)-Cl(1) Cl(1)-Cu(1)-Cl(1) P(1)-Cu(1)-C(5)	35.7(1) 117.12(3) 96.50(2) 126.35(9)	$\begin{array}{c} C(3)-C(4)-C(5)\\ P(1)-Cu(1)-Cl(1^*)\\ Cu(1)-Cl(1)-Cu(1)\\ P(1)-Cu(1)-C(4) \end{array}$	126.5(4) 111.18(3) *) 83.50(2) 90.74(8)

{**[(3-Propyl-(3***E***)-pentenyl)]diphenylphosphine}**CuCl (8). The reaction was carried out in the same way as described in the case of **6**, using **7** instead of **5**. NMR yield: 89%. Isolated yield: 73%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  0.74 (t, J = 7.4 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H), 1.16–1.32 (m, 4H), 1.83–1.96 (m, 4H), 2.17–2.32 (m, 4H), 5.10 (t, J = 7.1 Hz, 1H), 7.18–7.32 (m, 6H), 7.59–7.73 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  13.81, 13.97, 21.35, 22.95, 26.64 (d), 29.71, 31.80, 31.85, 125.15, 128.29 (d), 129.38, 132.88 (d), 133.59 (d), 139.09 (d). <sup>31</sup>P NMR (CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>):  $\delta$  –10.92. IR (Nujol, cm<sup>-1</sup>): 1587 (m), 1377 (m), 1186 (m), 1143 (m), 1099 (s), 1070 (m), 1028 (m), 999 (m), 941 (m), 910 (m), 893 (m), 736 (s), 694 (s).

**X-ray Crystallography.** A colorless prismatic crystal of **2a** or **2c** having approximate dimensions of  $0.2 \times 0.3 \times 0.4$  mm<sup>3</sup> for **2a** and  $0.30 \times 0.30 \times 0.50$  mm<sup>3</sup> for **2c** was mounted in a glass capillary and sealed under argon. X-ray data were collected on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710$  69 Å). A total of 44 images were collected with 2 different goniometer settings. Data were processed by the PROCESS-AUTO program package. The linear absorption coefficients,  $\mu$ , for Mo K $\alpha$  radiation were 11.94 cm<sup>-1</sup> for **2a** and 11.63 cm<sup>-1</sup> for **2c**, and a numerical absorption correction using the program NUMABS<sup>11</sup>

<sup>(11)</sup> Higashi, T. Program for Absorption Correction; Rigaku Corp., Tokyo, Japan, 1999.

was applied. The structures were solved by direct methods (SIR92<sup>12</sup>) and expanded using Fourier techniques (DIRDIF94<sup>13</sup>). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **2c** were located from difference maps and refined isotropically, while those of complex **2a** were placed in calculated positions. All calculations were performed using the teXsan<sup>14</sup> crystallographic software package of Molecular Structure Corp.

Table 1 gives crystallographic data for complexes **2a** and **2c**, while Tables 2 and 3 give bond distances and angles for **2a** and **2c**, respectively.

(13) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(14) Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 & 1999. Acknowledgment. Part of this work was supported by the Ministry of Education, Science, Sport and Culture of Japan. Z.X. thanks the National Natural Science Foundation of China (Grant No. 29702001), the National Science Fund for Distinguished Young Scholars (Grant No. 29825105), and the Peking University President Fund for financial support for part of this work.

**Supporting Information Available:** Tables of crystallographic data and data collection and solution and refinement details, positional and thermal parameters, and bond distances and angles for **2a** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000592U

<sup>(12)</sup> Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.