Inorg. Chem. 2003, 42, 7752-7765



# Enolphosphato–Phosphines: A New Class of P,O Ligands

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Received January 27, 2003

The new bifunctional ligands  $Ph_2PCH=CPh[OP(O)(OR)_2]$  (1) (1a, R = Et; 1b, R = Ph) represent the first examples of P,O derivatives resulting from the association of a phosphine moiety and an enolphosphate group. The *Z* stereochemistry about the double bond provides a favorable situation for these ligands to act as P,O-chelates. Neutral and cationic Pd(II) complexes have been synthesized and characterized, in which 1a or 1b acts either as a P-monodentate ligand or a P,O-chelate, via coordination of the oxygen atom of the P=O group. In the latter case, it has been observed that phosphines 1a and 1b can display a hemilabile behavior, owing to successive dissociation and recoordination of the O atom. Competition experiments revealed that phosphine 1a presents a higher chelating ability than 1b, a feature ascribed to the more electrodonating properties of the ethoxy groups in 1a compared to the phenoxy groups in 1b. P,O-Chelation affords seven-membered metallocycles, which is unusual for P,O-chelates. Complexes *trans*-[PdCl<sub>2</sub>{Ph\_2PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}] (2b), [PdCl{Ph\_2PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}-

 $(\mu$ -Cl)]<sub>2</sub> (3a), [Pd(dmba){Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}][PF<sub>6</sub>] (8a'), and *cis*-[Pd{Ph<sub>2</sub>PCH=C(Ph)OP(O)OEt)<sub>2</sub>}][BF<sub>4</sub>]<sub>2</sub> (10a) have been structurally characterized. Interestingly, the seven-membered rings in 8a' and 10a adopt a sofa conformation with the double bond lying almost perpendicular to the plane containing the Pd, the two P, and the two O atoms.

## Introduction

Recent review articles have illustrated the considerable current interest in organometallic complexes containing functional phosphine ligands, in particular for catalytic processes.<sup>1–3</sup> Numerous P,O-ligands in which a phosphine moiety is associated with carboxylate, ketone, alcohol, ether, ester, sulfoxide, or phosphine oxide functions have been prepared. Many of their metal complexes display catalytic properties often related to the electronic properties of the P,O-chelating ligand<sup>1,4,5</sup> and/or the possible occurrence of hemilabile behavior of these ligands.<sup>1,2,6,7</sup>

Surprisingly, phosphine ligands containing a phosphoryl function, i.e., phosphonate, phosphinate or phosphate, have received relatively little attention, although it is established that the P=O group can coordinate to a metal center via the oxygen atom.<sup>8-11</sup> Thus, such ligands may be considered as potential P,O-chelates or assembling ligands in the formation of bi- or polynuclear species. They could also represent valuable precursors to supported catalysts<sup>12</sup> and hybrid organic—inorganic or layered metal—phosphonate materials.<sup>12–14</sup> Recent advances in this area include the synthesis

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10.1021/ic030032y CCC: \$25.00 © 2003 American Chemical Society Published on Web 10/25/2003

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of water soluble tertiary phosphines,<sup>15–19</sup> and rhodium complexes of phosphino–phosphonate ligands have been used in the catalytic carbonylation of methanol<sup>20–22</sup> or in styrene hydroformylation.<sup>23,24</sup> PtCl<sub>2</sub>–SnCl<sub>2</sub> hydroformylation catalysts with phosphonated triarylphosphines have also been reported recently.<sup>25</sup>

As part of our ongoing interest in the chemistry of multifunctional phosphine ligands containing hard and soft donor functions,<sup>26–34</sup> we describe here the preparation of the first enolphosphato–phosphine ligands, Ph<sub>2</sub>PCH=CPh-[OP(O)(OR)<sub>2</sub>] [**1a** (R = Et)] and [**1b** (R= Ph)], and their palladium complexes.

#### **Experimental Section**

**General.** All the reactions and manipulations were carried out under an inert atmosphere of purified nitrogen using standard Schlenk tube techniques. Solvents were dried and distilled under nitrogen before use: hexane, pentane, and toluene over sodium, tetrahydrofuran and diethyl ether over sodium—benzophenone, and dichloromethane over calcium hydride. Nitrogen (Air liquide, R-grade) was passed through BASF R3-11 catalyst and molecular sieves columns to remove residual oxygen and water. Elemental C, H, and N analyses were performed by the Service de Microanalyses (Université Louis Pasteur, Strasbourg). Infrared spectra were recorded on an IFS 66 Bruker FT-IR spectrometer. The <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 300.1, 121.5, and 75.5 MHz, respectively, on a Bruker AC300 instrument. Phosphorus chemical shifts were externally referenced to 85% H<sub>3</sub>-PO<sub>4</sub> in H<sub>2</sub>O with downfield chemical shifts reported as positive.

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The <sup>1</sup>H NMR chemical shifts of the aromatic protons have been omitted for clarity, since they are unexceptional.

The chlorophosphates ClP(O)(OR)<sub>2</sub> (Aldrich) were degassed before use. AgBF<sub>4</sub> (Avocado) and TlPF<sub>6</sub> (Strem) were dried overnight in vacuo before use. The compounds Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph,<sup>35a</sup> [PdCl<sub>2</sub>(COD)],<sup>36</sup> [Pd(Me)Cl(COD)],<sup>37</sup> [Pd(dmba)( $\mu$ -Cl)]<sub>2</sub>,<sup>38</sup> [Pd( $\eta$ <sup>3-</sup>C<sub>3</sub>H<sub>5</sub>)( $\mu$ -Cl)]<sub>2</sub>,<sup>39</sup> [Pd(NCMe)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>40</sup> and Ph<sub>2</sub>PN(Me)PPh<sub>2</sub><sup>35b,c</sup> were prepared according to the literature.

Syntheses. Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub> (1a). A THF suspension (30 mL) of KH (0.600 g, 15.0 mmol) was prepared in a Schlenk flask connected to a bubbler. Solid Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph (3.04 g, 10.0 mmol) was then added, at room temperature. This resulted in gas (H<sub>2</sub>) evolution, whereas the solution progressively turned yelloworange. After the evolution of H<sub>2</sub> had ceased (ca. 10 min), the reaction mixture was stirred for 20 min. Meanwhile, dry and degassed ClP(O)(OEt)2 (1.725 g, 1.44 mL, 10.0 mmol) was placed in a Schlenk flask, equipped with a filter frit containing a 1 cm pad of dry Celite, and was cooled to -60 °C. The filtered THF solution was then added, and after 2 min, the cold bath was removed and the reaction mixture stirred for 2 h, during which its color progressively turned beige. The solvent was then removed in vacuo. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the volatiles were evaporated, affording a beige solid, which was washed with Et2O (20 mL) and pentane (20 mL) and dried in vacuo. The phosphine 1a was obtained as a beige (slightly sticky) powder (3.700 g, 84% yield). In order to obtain analytically pure material, 1a (ca. 0.200 g) was dissolved in 3 mL and precipitated upon addition of pentane (15 mL). The beige precipitate was filtered and dried overnight in vacuo. Anal. Calcd for  $C_{24}H_{26}O_4P_2$  (M = 440.420): C, 65.45; H, 5.95. Found: C, 65.58; H, 5.82.

**Ph<sub>2</sub>PCH=C(Ph)P(O)(OPh)<sub>2</sub> (1b).** This compound was obtained as a white powder, in a manner similar to **1a** from Ph<sub>2</sub>PCH<sub>2</sub>C(O)-Ph (3.04 g, 10.0 mmol) and ClP(O)(OPh)<sub>2</sub> (2.07 mL, 10.0 mmol). Yield: 4.400 g (82%). The same procedure as that described for **1a** was applied to obtain analytically pure **1b**. Anal. Calcd for  $C_{32}H_{26}O_4P_2$  (M = 536.509): C, 71.64; H, 4.88. Found: C, 71.82; H, 4.96.

**[PdCl<sub>2</sub>{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}]** (2a). Solid [PdCl<sub>2</sub>-(COD)] (0.285 g, 1.0 mmol) and **1a** (0.880 g, 2.0 mmol) were placed in a Schlenk flask and degassed in vacuo for 5 min. Then, 20 mL of freshly distilled CH<sub>2</sub>Cl<sub>2</sub> was added, and the mixture was stirred for 15 min at room temperature, after which the volatiles were removed in vacuo. The yellow residue was washed with Et<sub>2</sub>O (2 × 15 mL) and pentane (2 × 15 mL) and dried under reduced pressure. Complex **2a** was obtained as a yellow powder (0.855 g, 81% yield). Both *cis* and *trans* isomers were formed (see text, Table 1). Anal. Calcd for C<sub>48</sub>H<sub>52</sub>Cl<sub>2</sub>O<sub>8</sub>P<sub>4</sub>Pd (M = 1058.146): C, 54.49; H, 4.95. Found: C, 54.32; H, 4.82.

[PdCl<sub>2</sub>{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}<sub>2</sub>] (2b). This complex was obtained as a yellow-orange solid, in a manner similar to 2a from [PdCl<sub>2</sub>(COD)] (0.055 g, 0.19 mmol) and 1b (0.203 g, 0.38 mmol). Yield: 0.205 g (86%). Both *cis* and *trans* isomers were formed. Anal. Calcd for  $C_{64}H_{52}Cl_2O_8P_4Pd$  (M = 1250.32): C, 61.48;

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## Table 1. Selected IR and $^{1}H$ and $^{31}P\{^{1}H\}$ NMR Data of $1{-}18$

|  |            | $^{1}\mathrm{H}$ NMR, $\delta$ $^{a}$   |  | $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR, $\delta^{a}$ |                      | IR,                |
|--|------------|---|--|---|----------------------|--------------------|
| compd  |            | H enolate of P ligand   | other  | Р   | РО                   | v(P=O)             |
| Ph <sub>2</sub> PCH=C(Ph)OP(O)(OEt) <sub>2</sub>   | 1a         | 6.20 (dd, ${}^{2}J(PH) = 3.1$ ,<br>${}^{4}J(PH) = 1.4$ )  | 1.18 (dt, 6H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J$ (HH) = 7.0,<br>${}^{4}J$ (PH) = 1.0); 4.08 (m, 4H, OCH <sub>2</sub> )  | -29.8   | -7.0                 | 1277s              |
| Ph <sub>2</sub> PCH=C(Ph)OP(O)(OPh) <sub>2</sub>   | 1b         | 6.33 (dd, ${}^{2}J(PH) = 3.5$ ,<br>${}^{4}J(PH) = 1.1$ )  | - ( ) ( ) 2)   | -28.4   | -18.0                | 1313s              |
| [PdCl <sub>2</sub> {PPh <sub>2</sub> CH=C(Ph)OP(O)-<br>(OEt) <sub>2</sub> } <sub>2</sub> ] | 2a         | 6.24 (dt, ${}^{2}J(PH) = 7.3$ ,<br>${}^{4}J(PH) = 1.6$ )<br>( <i>trans</i> isomer)                        | 0.97 (t, 12H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J$ (HH) = 7.1);<br>3.69 (m, 8H, OCH <sub>2</sub> )  | 4.6 ( <i>trans</i> )                                  | -8.1 (trans)         | 1269s <sup>c</sup> |
|  |            | $5.62 \text{ (dd, } {}^{2}J(\text{PH}) =$<br>11.0, ${}^{4}J(\text{PH}) = 2.1)$<br>( <i>cis</i> isomer)    | 1.03 (t, 12H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J$ (HH) = 7.1);<br>3.69 (m, 8H, OCH <sub>2</sub> )  | 12.1 ( <i>cis</i> )                                   | -8.0 ( <i>cis</i> )  |                    |
| [PdCl <sub>2</sub> {PPh <sub>2</sub> CH=C(Ph)OP(O)-<br>(OPh) <sub>2</sub> } <sub>2</sub> ] | 2b         | $6.54 	ext{ (dt, }^{2}J(PH) = 7.6,$<br>${}^{4}J(PH) = 1.7) 	ext{ (trans isomer)}$                         |  | 4.8 (trans)   | -19.6 (trans)        | 1302s              |
|  |            | 5.87 (dd, <sup>2</sup> <i>J</i> (PH) =<br>11.4, <sup>4</sup> <i>J</i> (PH) = 1.9)<br>( <i>cis</i> isomer) |  | 12.1 (cis)  | -19.6 ( <i>cis</i> ) |                    |
| $[PdCl{PPh_2CH=C(Ph)OP(O)-(OEt)_2}(\mu-Cl)]_2$   | <b>3</b> a | 5.92 (d br, ${}^{2}J(PH) =$<br>10.2, ${}^{4}J(PH)$<br>not resolved)                                       | 1.11 (t, 12H, $CH_2CH_3$ , ${}^3J(HH) = 7.0$ );<br>3.86 (m, 8H, $OCH_2$ )  | 13.7  | -8.6                 | 1272s              |
| $[PdCl{PPh_2CH=C(Ph)OP(O)-(OPh)_2}(\mu-Cl)]_2$   | 3b         | $6.18 (d br, {}^{2}J(PH) =$<br>10.9, {}^{4}J(PH)<br>not resolved)   |  | 13.8  | -20.1                | 1294s <sup>d</sup> |
| $[PdMe{PPh_2CH=C(Ph)OP(O)-(OEt)_2}(\mu-Cl)]_2$   | 4a         | 6.33 (br, ${}^{2}J(PH)$<br>and ${}^{4}J(PH)$<br>not resolved)   | 0.75 (d, 6H, PdMe, ${}^{3}J(PH) = 3.0$ ); 1.11<br>(t, 12H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J(HH) = 7.0$ );<br>4.15 (m br, 8H, OCH <sub>2</sub> )  | 19.9  | -5.3                 | 1276s <sup>c</sup> |
| [PdMe{PPh <sub>2</sub> CH=C(Ph)OP(O)-<br>(OPh) <sub>2</sub> }( <i>µ</i> -Cl)] <sub>2</sub> | 4b         | 5.97 (d br, ${}^{2}J(PH) =$<br>8.5, ${}^{4}J(PH) =$<br>not resolved)                                      | 0.77 (d, 6H, PdMe, ${}^{3}J(PH) = 2.3$ )   | 21.1  | -19.5                | 1299s              |
| $[Pd(dmba)Cl{PPh_2CH=C(Ph)-OP(O)(OEt)_2}]$   | 5a         | 6.02 (dd, ${}^{2}J(PH) = 6.2$ ,<br>${}^{4}J(PH) = 1.3$ )  | 1.04 (t, 6H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J$ (HH) = 7.1);<br>2.84 (d, 6H, NMe <sub>2</sub> , ${}^{4}J$ (PH) = 3); 3.77 (m, 4H, OCH <sub>2</sub> ); 4.08 (d, 2H, NCH <sub>2</sub> , ${}^{4}J$ (PH) = 1.4)   | 20.9  | -7.5                 | 1272s              |
| $[Pd(dmba)Cl{PPh_2CH=C(Ph)-OP(O)(OPh)_2}]$   | 5b         | $6.32 (dd, {}^{2}J(PH) = 6.4, {}^{4}J(PH) = 1.7)$   | 2.77 (d, 6H, NMe <sub>2</sub> , ${}^{4}J(PH) = 2.3$ ); 4.08<br>(d, 2H, NCH <sub>2</sub> , ${}^{4}J(PH) = 1.7$ )  | 20.8  | -19.4                | 1304s              |
| $[Pd(\eta^3-allyl)Cl{PPh_2CH=C(Ph)-OP(O)(OEt)_2}]^e$                                       | 6a         | 6.02 (dd, ${}^{2}J(PH) = 5.4$ ,<br>${}^{4}J(PH) = 1.2$ )  | $ \begin{array}{l} 1.06 \; (dt,  6H,  CH_2 CH_3,  {}^3J(HH) = 7.0, \\ {}^4J(PH) = 0.8); \; 3.11 \; (d, \; 1H, \; allyl \; H_b, \\ {}^3J(H_bH_c) = 11.0); \; 3.43-3.86 \\ (overlapping signals, \; 6H, \; OCH_2 \; and \\ allyl \; H_a \; and \; H_e); \; 4.72 \; (apparent \; t, \; 1H, \\ allyl \; H_d, \; {}^3J(PH_d) \approx {}^3J(H_cH_d) \approx 7.2); \\ 5.66 \; (m, \; 1H, \; allyl \; H_c) \end{array} $ | 4.0   | -7.7                 | 1281s              |
| $[Pd(\eta^3-allyl)Cl{PPh_2CH=C(Ph)-OP(O)(OPh)_2}]^e$                                       | 6b         | 6.21 (dd, ${}^{2}J(PH) = 5.8$ ,<br>${}^{4}J(PH) = 1.2$ )  | $ \begin{array}{l} 2.99 \; (d,\; 1H,\; allyl\; H_b,\; {}^3J(H_bH_c) = 12.0); \\ 3.58 \; (d,\; 1H,\; allyl\; H_a,\; {}^3J(H_aH_c) = 5.8); \\ 3.60 \; (dd,\; 1H,\; allyl\; H_e,\; {}^3J(PH_e) = 13.7, \\ {}^3J(H_cH_e) = 10.4); \; 4.62 \; (apparent\; t,\; 1H, \\ allyl\; H_d,\; {}^3J(PH_d) \approx {}^3J(H_cH_d) \approx 7.0); \\ 5.41 \; (m,\; 1H,\; allyl\; H_c) \end{array} $                                | 5.3   | -19.2                | 1304s              |
| $[PdMe(NCMe){Ph_2PCH=C(Ph)OP(O)-(OEt)_2}][BF_4]$   | 7a         | $6.29 (dd, {}^{2}J(PH) = 6.0, {}^{4}J(PH) = 2.4)$   | 0.58 (d, 3H, PdMe, ${}^{3}J(PH) = 2.5$ ); 1.11<br>(dt, 6H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J(HH) = 7.0$ ,<br>${}^{4}J(PH) = 1.3$ ); 2.32 (s, 3H, MeCN);<br>4.08 (m, 4H, OCH <sub>2</sub> )  | 22.9  | -6.1                 | 1227s              |
| [PdMe(NCMe){Ph <sub>2</sub> PCH=C(Ph)OP(O)-<br>(OPh) <sub>2</sub> }][BF <sub>4</sub> ]     | 7b         | 6.37 (dd, ${}^{2}J(PH) = 5.2$ ,<br>${}^{4}J(PH) = 2.3$ )  | 0.59 (d, 3H, PdMe, ${}^{3}J(PH) = 2.4$ ); 2.24 (s, 3H, MeCN)   | 21.5  | -16.1                | 1240s              |
| $[PdMe(NCMe){Ph_2PCH=C(Ph)OP(O)-(OPh)_2}][PF_6]$   | 7b′        | 6.37 (dd, ${}^{2}J(PH) = 4.9$ ,<br>${}^{4}J(PH) = 2.3$ )  | 0.59 (d, 3H, PdMe, <sup>3</sup> <i>J</i> (PH) = 2.3); 2.23<br>(s, 3H, MeCN)  | 21.4  | -16.1                | 1241s              |
| [Pd(dmba){PPh <sub>2</sub> CH=C(Ph)OP(O)-<br>(OEt) <sub>2</sub> }][BF <sub>4</sub> ]       | 8a         | 6.32 (dd, ${}^{2}J(PH) = 7.6$ ,<br>${}^{4}J(PH) = 2.7$ )  | 1.07 (dt, 6H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J$ (HH) = 7.1,<br>${}^{4}J$ (PH) = 1.4); 2.82 (d, 6H, NMe <sub>2</sub> ,<br>${}^{4}J$ (PH) = 2.6); 4.01 (m, 4H, OCH <sub>2</sub> );<br>4.10 (d, 2H, NCH <sub>2</sub> , ${}^{4}J$ (PH) = 1.2)  | 24.0  | -7.7                 | 1228s              |
| [Pd(dmba){PPh <sub>2</sub> CH=C(Ph)OP(O)-<br>(OEt) <sub>2</sub> }][PF <sub>6</sub> ]       | 8a′        | 6.37 (dd, ${}^{2}J(PH) = 7.5$ ,<br>${}^{4}J(PH) = 2.7$ )  | 1.09 (dt, 6H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J$ (HH) = 7.0,<br>${}^{4}J$ (PH) = 1.4); 2.79 (d, 6H, NMe <sub>2</sub> ,<br>${}^{4}J$ (PH) = 2.5); 3.94 (m, 4H, OCH <sub>2</sub> );<br>4.09 (d, 2H, NCH <sub>2</sub> , ${}^{4}J$ (PH) = 1.2)  | 24.2  | -7.5                 | 1240s              |
| $[Pd(dmba){PPh_2CH=C(Ph)OP(O)-(OPh)_2}][BF_4]$   | 8b         | 6.50 (dd, ${}^{2}J(PH) = 6.9$ ,<br>${}^{4}J(PH) = 2.4$ )  | 2.47 (d, 6H, NMe <sub>2</sub> , <sup>4</sup> <i>J</i> (PH) = 1.9); 4.02<br>(s, 2H, NCH <sub>2</sub> , <sup>4</sup> <i>J</i> (PH) not resolved)   | 23.5  | -17.3                | 1240s              |

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### New Class of P,O Ligands

#### Table 1. (Continued)

|   |     | $^{1}$ H NMR, $\delta$ $^{a}$  |   | $^{31}P{^{1}H}$ NMR, $\delta^{a}$   |   | IR, $-1b$                                   |
|---|-----|--|---|---|---|---|
| compd   |     | H enolate of P ligand  | other   | Р   | РО  | $\nu$ (P=O)                                 |
| $[Pd(\eta^3-allyl){PPh_2CH=C(Ph)OP(O)-(OEt)_2}][BF_4]^e$  | 9a  | $6.41 \text{ (dd, } {}^{2}J(\text{PH}) = 3.6,$<br>${}^{4}J(\text{PH}) = 1.8)$              | 1.08 (dt, 6H, CH <sub>2</sub> CH <sub>3</sub> , <sup>3</sup> J(HH) =<br>7.0, <sup>4</sup> J(PH) = 1.3); 3.10 (br,<br>overlapping signals, 2H, allyl<br>H <sub>b</sub> and H <sub>a</sub> ); 4.00 (m, 4H,<br>OCH <sub>2</sub> ); 4.26 (br, 1H, allyl H <sub>d</sub><br>or H <sub>e</sub> ); 5.01 (br, 1H, allyl H <sub>d</sub><br>or H <sub>e</sub> ); 6.01 (apparent quint,<br>1H, allyl H <sub>c</sub> ) | 11.3  | -6.5                                      | 1208s <sup>d</sup>                          |
| $[Pd(\eta^3-allyl){PPh_2CH=C(Ph)OP(O)-(OPh)_2}][BF_4]^e$  | 9b  | 6.56 (br, <sup>2</sup> <i>J</i> (PH)<br>and <sup>4</sup> <i>J</i> (PH)<br>not observed)    | $\begin{array}{l} 2.87 \ (br,  1H,  allyl  H_a  or  H_b);  3.29 \\ (br,  1H,  allyl  H_a  or  H_b);  3.75 \\ (m,  1H,  allyl  H_d  or  H_e);  4.59 \\ (br,  1H,  allyl  H_d  or  H_e);  5.75 \\ (m,  1H,  allyl  H_c) \end{array}$  | 11.3  | -16.0                                     | 1226s                                       |
| <i>cis</i> -[Pd{PPh <sub>2</sub> CH=C(Ph)OP(O)-<br>(OEt) <sub>2</sub> } <sub>2</sub> ][BF <sub>4</sub> ] <sub>2</sub> | 10a | $6.79 (dd, {}^{2}J(PH) = 10.5, {}^{4}J(PH) = 2.5)$   | 1.13 (dt, 12H, CH <sub>2</sub> CH <sub>3</sub> , ${}^{3}J$ (HH) =<br>7.1, ${}^{4}J$ (PH) = 1.3); 4.05<br>(m, 8H, OCH <sub>2</sub> )   | 28.4 (d, $J(PP) = 16$ )   | -11.0 (d)                                 | 1221s                                       |
| $cis$ -[Pd{PPh <sub>2</sub> CH=C(Ph)OP(O)-<br>(OPh) <sub>2</sub> }2][BF <sub>4</sub> ] <sub>2</sub>                   | 10b | $6.99 \text{ (dd, } {}^{2}J(\text{PH}) = 10.0,  {}^{4}J(\text{PH}) = 2.5)$                 |   | 29.4 (d,<br>J(PP) = 16)   | -21.0 (d)                                 | 1244s <sup>c</sup>                          |
| $\begin{tabular}{lllllllllllllllllllllllllllllllllll$   | 11a | 6.31 (m br)  | 0.28 (m br, 3H, Pd-Me); 0.99<br>(m, 12H, CH <sub>2</sub> CH <sub>3</sub> ); 3.66<br>(m, 4H, OCH <sub>2</sub> ), 4.09<br>(m, 4H, OCH <sub>2</sub> )  | 13.3  | -6.6                                      | 1272s, 1225s                                |
| $[PdMe{PPh_2CH=C(Ph)OP(O)-(OPh)_2}{PPh_2CH=C(Ph)OP(O)-(OPh)_2}][BF_4]$  | 11b | 6.28 (m)   | 0.56 (apparent t, 3H, Pd-Me ${}^{3}J(PH) = 6.4$ )   | 13.9  | -18.3                                     | 1310s, 1243s                                |
| $[PdCl{PPh_2N(Me)PPh_2}- {PPh_2CH=C(Ph)OP(O)- (OPh)_2}][CF_3SO_3]$  | 12  | $6.30 (dd, {}^{2}J(PH) = 12.0, {}^{4}J(PH) = 3.0)$   | 2.56 (dd, ${}^{2}J(PH) = 11.6$ and 11)  | 2.3 (d, <sup>2</sup> <i>J</i> (PP) =<br>480, P of <b>1b</b> );<br>32.5 (dd, <sup>2</sup> <i>J</i> (PP) =<br>480 and 46,<br><i>PNP trans</i> to <b>1b</b> );<br>37.6 (d, <sup>2</sup> <i>J</i> (PP) =<br>46, <i>PNP cis</i> to <b>1b</b> ) | -20.0                                     | 1271s                                       |
| $[PdMe{PPh_2NHC(O)Me}-{PPh_2CH=C(Ph)OP(O)-(OEt)_2}][BF_4]$  | 13a | 5.84 (dd, ${}^{2}J(PH) = 4.0$ ,<br>${}^{4}J(PH) = 3.7$ )                                   | 0.80 (dd, 3H, Pd-Me, ${}^{3}J(PH) =$<br>6.4 and 5.8); 0.93 (m, 6H,<br>CH <sub>2</sub> CH <sub>3</sub> ); 2.40 (s, 3H,<br>C(O)CH <sub>3</sub> ); 3.66 (m, 4H,<br>OCH <sub>2</sub> ); 9.56 (br, 1H, NH)   | 8.8 (d, P of <b>1a</b> ,<br>${}^{2}J(PP) = 401$ );<br>70.8 (d, PNH)   | -6.1                                      | 1271s<br>[1608s,<br>ν(CO)]                  |
| $[PdMe{PPh_2NHC(O)Me}-{PPh_2CH=C(Ph)OP(O)-(OPh)_2}][BF_4]$  | 13b | 6.08 (m)   | 0.85 (m, 3H, Pd-Me); 2.14<br>(s, C(O)CH <sub>3</sub> ); 9.57<br>(br, 1H, NH)  | 8.5 (d, P of <b>1b</b> ,<br>${}^{2}J(PP) = 412$ );<br>71.0 (d, PN)  | -17.8                                     | 1301s<br>[1608s,<br>ν(CO)]                  |
| $[PdMe{PPh_2CH=C(Ph)OP(O)-(OEt)_2}{PPh_2CH_2C(O)Ph}]-[BF_4]$  | 14a | 6.43 (m)   | 0.33 (dd, 3H, Pd-Me, ${}^{3}J(PH) =$<br>6.4 and 6.2); 0.75 (m, 6H,<br>CH <sub>2</sub> CH <sub>3</sub> ); 3.53 (m, 4H,<br>OCH <sub>2</sub> ); 4.36 (m, 2H, PCH <sub>2</sub> )  | 15.0 (P of <b>1a</b> ,<br>$J(PP) = 408);^{f}$<br>18.3 (PCH <sub>2</sub> ) <sup>g</sup>  | -6.8                                      | 1223s<br>[1672s,<br>v(CO)]                  |
| $[PdMe{PPh_2CH=C(Ph)OP(O)-(OPh)_2}{PPh_2CH_2C(O)Ph}]-[BF_4]$  | 14b | 6.30 (m)   | 0.63 (dd, 3H, Pd-Me, ${}^{3}J(PH) =$<br>6.7 and 5.9); 4.31 (dd, 2H,<br>PCH <sub>2</sub> , ${}^{2}J(PH) =$ 10.2,<br>${}^{4}J(PH) =$ 1.6)   | 12.5 (P of <b>1b</b> ,<br>J(PP) = 401); <sup>f</sup><br>23.2 (PCH <sub>2</sub> ) <sup>g</sup>   | -17.9                                     | 1241s<br>[1672,<br>v(CO)]                   |
| $[PdMe{PPh_2CH=C(Ph)OP(O)-(OEt)_2}{PPh_2CH=C(Ph)OP(O)-(OPh)_2}[BF_4]$   | 17  | 6.10 (m, P–C <i>H</i> =CPh<br>of <b>1b</b> ); 6.40 (m,<br>P–C <i>H</i> =CPh of <b>1a</b> ) | 0.50 (m, 3H, Pd-Me); 0.84<br>(m, 6H, CH <sub>2</sub> CH <sub>3</sub> ); 3.55<br>(m, 4H, OCH <sub>2</sub> )  | 12.1 (P of <b>1b</b> ,<br>${}^{2}J(PP) = 404);^{f}$<br>16.6 (P of <b>1a</b> ) <sup>g</sup>  | -7.6 ( <b>1a</b> )<br>-18.1 ( <b>1b</b> ) | 1310s ( <b>1b</b> )<br>1226vs ( <b>1a</b> ) |

<sup>*a*</sup> Recorded in CDCl<sub>3</sub> unless otherwise stated, coupling constants in Hz, aromatic protons are omitted for clarity since their chemical shifts are totally unexceptional. <sup>*b*</sup> Recorded in Nujol unless otherwise stated. <sup>*c*</sup> In KBr. <sup>*d*</sup> In CDCl<sub>3</sub>. <sup>*e*</sup> Numbering of the allylic protons as pictured:



<sup>f</sup> Part A of an AB spin system. <sup>g</sup> Part B of an AB spin system.

H, 4.19. Found: C, 61.34; H, 4.26. Yellow crystals, suitable for X-ray analysis, were obtained by slow diffusion of hexane into a  $CH_2Cl_2$  solution of **2b**.

[PdCl{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}( $\mu$ -Cl)]<sub>2</sub> (3a). This complex was obtained as an orange solid, in a manner similar to 2a from [PdCl<sub>2</sub>(COD)] (0.285 g, 1.0 mmol) and 1a (0.440 g, 1.0

mmol). Yield: 0.585 g (91%). Anal. Calcd for  $C_{48}H_{52}Cl_4O_8P_4Pd_2$  (M = 1235.45): C, 46.67; H, 4.24. Found: C, 46.66; H, 4.31. Orange crystals, suitable for X-ray analysis, were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of **2b**.

[PdCl{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}( $\mu$ -Cl)]<sub>2</sub> (3b). This complex was obtained as an orange solid, in a manner similar to **2a** from [PdCl<sub>2</sub>(COD)] (0.345 g, 1.2 mmol) and **1b** (0.648 g, 1.2 mmol). Yield: 0.760 g (88%). Anal. Calcd for C<sub>64</sub>H<sub>52</sub>Cl<sub>2</sub>O<sub>8</sub>P<sub>4</sub>Pd<sub>2</sub> (M = 1427.63): C, 53.85; H, 3.67. Found: C, 54.17; H, 3.81.

[PdMe{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}( $\mu$ -Cl)]<sub>2</sub> (4a). This complex was obtained as a beige solid, in a manner similar to 2a from [Pd(Me)Cl(COD)] (0.265 g, 1.0 mmol) and 1a (0.440 g, 1.0 mmol). Yield: 0.512 g (86%). Anal. Calcd for C<sub>50</sub>H<sub>58</sub>Cl<sub>2</sub>O<sub>8</sub>P<sub>4</sub>Pd<sub>2</sub> (M = 1194.62): C, 50.27; H, 4.89. Found: C, 50.17; H, 4.84.

 $[PdMe{Ph_2PCH=C(Ph)OP(O)(OPh)_2}(\mu-Cl)]_2$  (4b). This complex was obtained as a beige solid, in a manner similar to **2a** from [Pd(Me)Cl(COD)] (0.211 g, 0.8 mmol) and **1b** (0.429 g, 0.8 mmol). Yield: 0.493 g (89%). Anal. Calcd for C<sub>66</sub>H<sub>58</sub>Cl<sub>2</sub>O<sub>8</sub>P<sub>4</sub>Pd<sub>2</sub> (M = 1386.82): C, 57.16; H, 4.22. Found: C, 56.98; H, 4.11.

[Pd(dmba)Cl{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}] (5a). Solid [Pd-(dmba)( $\mu$ -Cl)]<sub>2</sub> (0.276 g, 0.5 mmol) and 1a (0.440 g, 1.0 mmol) were placed in a Schlenk flask and degassed in vacuo for 5 min. Then, CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added, and the reaction mixture was stirred for 0.5 h at room temperature. The volatiles were removed under vacuum, and the residue was washed with Et<sub>2</sub>O (2 × 15 mL) and pentane (20 mL). Complex **5a** was obtained as a greenyellow solid (0.645 g, 89%). Anal. Calcd for C<sub>33</sub>H<sub>38</sub>ClNO<sub>4</sub>P<sub>2</sub>Pd (M = 716.48): C, 55.32; H, 5.35; N, 1.95. Found: C, 55.60; H, 5.22; N, 1.97.

[Pd(dmba)Cl{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}] (5b). This complex was obtained as a pale green-yellow solid, in a manner similar to **5a** from [Pd(dmba)( $\mu$ -Cl)]<sub>2</sub> (0.331 g, 0.6 mmol) and **1b** (0.643 g, 1.2 mmol). Yield: 0.853 g (87%). Anal. Calcd for C<sub>41</sub>H<sub>38</sub>-ClNO<sub>4</sub>P<sub>2</sub>Pd (M = 812.56): C, 60.61; H, 4.71; N, 1.72. Found: C, 60.81; H, 4.86; N, 1.71.

 $[Pd(\eta^3-C_3H_5)Cl\{Ph_2PCH=C(Ph)OP(O)(OEt)_2\}]$  (6a). This complex was obtained as a yellow solid, in a manner similar to **5a** from  $[Pd(\eta^3-C_3H_5)(\mu-Cl)]_2$  (0.205 g, 0.56 mmol) and **1a** (0.493 g, 1.12 mmol). Yield: 0.635 g (91%). Anal. Calcd for  $C_{27}H_{31}ClO_4P_2$ -Pd (M = 623.34): C, 52.03; H, 5.01. Found: C, 51.72; H, 4.94.

 $[Pd(\eta^3-C_3H_5)Cl\{Ph_2PCH=C(Ph)OP(O)(OPh)_2\}]$  (6b). This complex was obtained as a yellow solid, in a manner similar to **5a** from  $[Pd(\eta^3-C_3H_5)(\mu-Cl)]_2$  (0.165 g, 0.43 mmol) and **1b** (0.461 g, 0.86 mmol). Yield: 0.590 g (94%). Anal. Calcd for  $C_{35}H_{31}ClO_4P_2$ -Pd (M = 719.44): C, 58.43; H, 4.34. Found: C, 58.04; H, 4.30.

[PdMe(NCMe){Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}](BF<sub>4</sub>) (7a). To a MeCN (20 mL) solution of 4a (0.109 g, 0.18 mmol) was added in one portion solid AgBF<sub>4</sub> (0.036 g, 0.09 mmol). The reaction mixture was stirred for 2 h, during which it became almost colorless and a pale gray precipitate was formed. After filtration over a Celite pad and evaporation of the volatiles under reduced pressure, the residue was washed with Et<sub>2</sub>O (2 × 15 mL). Compound 7a was obtained as a pale brown powder (0.132 g, 84% yield). Anal. Calcd for C<sub>27</sub>H<sub>32</sub>BF<sub>4</sub>NO<sub>4</sub>P<sub>2</sub>Pd (M = 689.71): C, 47.02; H, 4.68; N, 2.03. Found: C, 46.68; H, 4.33; N, 1.66.

[PdMe(NCMe){Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}](BF<sub>4</sub>) (7b). This complex was obtained as a beige powder, in a manner similar to **7a** from **4b** (0.094 g, 0.067 mmol) and AgBF<sub>4</sub> (0.026 g, 0.136 mmol). A 1/1 mixture of MeCN and CH<sub>2</sub>Cl<sub>2</sub> was used, owing to the poor solubility of **4b** in pure MeCN. Yield: 0.084 g (79%). Anal. Calcd for  $C_{35}H_{32}BF_{4}NO_{4}P_{2}Pd$  (M = 785.80): C, 53.50; H, 4.10; N, 1.78. Found: C, 53.56; H, 4.18; N, 1.80.

[PdMe(NCMe){Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}](PF<sub>6</sub>) (7b'). This complex was obtained as a pale yellow powder, in a manner similar to **7b** from **4b** (0.245 g, 0.177 mmol) and TlPF<sub>6</sub> (0.123 g, 0.354 mmol). Yield: 0.256 g (86%). Anal. Calcd for  $C_{35}H_{32}F_6$ -NO<sub>4</sub>P<sub>3</sub>Pd (M = 843.96): C, 49.81; H, 3.82; N, 1.66. Found: C, 49.72; H, 3.66; N, 1.80.

 $[Pd(dmba){Ph_2PCH=C(Ph)OP(O)(OEt)_2}](BF_4)$  (8a). This complex was obtained as a yellow powder, in a manner similar to **7b**, using CH<sub>2</sub>Cl<sub>2</sub> as solvent, from **5a** (0.094 g, 0.13 mmol) and AgBF<sub>4</sub> (0.025 g, 0.13 mmol). Yield: 0.072 g (72%). Anal. Calcd for C<sub>33</sub>H<sub>38</sub>BF<sub>4</sub>NO<sub>4</sub>P<sub>2</sub>Pd (*M* = 767.83): C, 51.62; H, 4.99; N, 1.82. Found: C, 51.76; H, 4.94; N, 1.90.

[Pd(dmba){Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}](PF<sub>6</sub>) (8a'). This complex was obtained as a yellow-orange powder, in a manner similar to 8a from 5a (0.143 g, 0.199 mmol) and TlPF<sub>6</sub> (0.070 g, 0.2 mmol). Yield: 0.135 g (82%). Anal. Calcd for  $C_{33}H_{38}F_6NO_4P_3$ -Pd (M = 825.99): C, 47.99; H, 4.64; N, 1.70. Found: C, 47.64; H, 4.48; N, 1.56. Orange crystals, suitable for X-ray analysis, were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of 8a'.

 $[Pd(dmba){Ph_2PCH=C(Ph)OP(O)(OPh)_2}](BF_4)$  (8b). This complex was obtained as a pale-orange powder, in a manner similar to 8a from 5b (0.406 g, 0.499 mmol) and AgBF<sub>4</sub> (0.098 g, 0.5 mmol). Yield: 0.376 g (87%). Anal. Calcd for C<sub>41</sub>H<sub>38</sub>BF<sub>4</sub>NO<sub>4</sub>P<sub>2</sub>-Pd (M = 863.92): C, 57.00; H, 4.43; N, 1.62. Found: C, 57.17; H, 4.48; N, 1.71.

 $[Pd(\eta^3-C_3H_5){Ph_2PCH=C(Ph)OP(O)(OEt)_2}](BF_4)$  (9a). To a CH<sub>2</sub>Cl<sub>2</sub> (20 mL) solution of **6a** (0.150 g, 0.24 mmol) was added in one portion solid AgBF<sub>4</sub> in excess (0.070 g, 0.35 mmol). The reaction mixture was stirred overnight. After filtration over a Celite pad and evaporation of the volatiles under reduced pressure, the residue was washed with Et<sub>2</sub>O (2 × 15 mL). Compound **9a** was obtained as a pale green-brown powder (0.120 g, 75% yield). Anal. Calcd for C<sub>27</sub>H<sub>31</sub>BF<sub>4</sub>O<sub>4</sub>P<sub>2</sub>Pd (M = 674.70): C, 48.07; H, 4.63. Found: C, 47.85; H, 4.77.

 $[Pd(\eta^3-C_3H_5){Ph_2PCH=C(Ph)OP(O)(OPh)_2}](BF_4)$  (9b). This complex was obtained as a yellow-brown solid, in a manner similar to **9a** from **6b** (0.138 g, 0.19 mmol) and AgBF<sub>4</sub> (0.050 g, 0.25 mmol, excess). Yield: 0.118 g (81%). Anal. Calcd for C<sub>35</sub>H<sub>31</sub>-BF<sub>4</sub>O<sub>4</sub>P<sub>2</sub>Pd (M = 770.79): C, 54.54; H, 4.05. Found: C, 54.17; H, 3.69.

*cis*-[Pd{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (10a). Solid [Pd(NCMe)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (0.071 g, 0.16 mmol) and 1a (0.141 g, 0.32 mmol) were placed in a Schlenk flask and degassed in vacuo, before CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added at room temperature. The reaction mixture turned pale yellow and was stirred for 1 h. The volatiles were removed under reduced pressure, and the residue was washed with Et<sub>2</sub>O (2 × 10 mL) and pentane (2 × 10 mL). Complex 10a was obtained as a yellow-orange powder (0.154 g, 83% yield). Anal. Calcd for C<sub>48</sub>H<sub>52</sub>B<sub>2</sub>F<sub>8</sub>O<sub>8</sub>P<sub>4</sub>Pd (M = 1160.85): C, 49.66; H, 4.52. Found: C, 49.74; H, 4.30. Orange crystals, suitable for X-ray analysis, were obtained by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of 10a.

*cis*-[Pd{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (10b). This complex was obtained as a yellow solid, in a manner similar to 10a from [Pd(NCMe)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (0.098 g, 0.22 mmol) and 1b (0.236 g, 0.44 mmol). Yield: 0.262 g (88%). Anal. Calcd for C<sub>64</sub>H<sub>52</sub>B<sub>2</sub>F<sub>8</sub>-O<sub>8</sub>P<sub>4</sub>Pd (M = 1353.03): C, 56.81; H, 3.87. Found: C, 57.12; H, 3.67.

[PdMe{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}{Ph<sub>2</sub>PCH=C(Ph)OP-(O)(OEt)<sub>2</sub>}][BF<sub>4</sub>] (11a). Solid 7a (0.050 g, 0.072 mmol) and 1a (0.032 g, 0.072 mmol) were placed in a Schlenk flask and degassed in vacuo, before CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added at room temperature. The reaction mixture was stirred for 15 min, and the volatiles were removed under reduced pressure. The residue was washed with Et<sub>2</sub>O (10 mL) and pentane (10 mL). Complex 11a was obtained as a pale brown solid (0.075 g, 95% yield). Anal. Calcd for C<sub>49</sub>H<sub>55</sub>-BF<sub>4</sub>O<sub>8</sub>P<sub>4</sub>Pd (M = 1089.08): C, 54.04; H, 5.09. Found: C, 54.44; H, 5.38.

 $[PdMe{Ph_2PCH=C(Ph)OP(O)(OPh)_2}{Ph_2PCH=C(Ph)OP-(O)(OPh)_2}][BF_4] (11b).$  This complex was obtained as a yellow solid, in a manner similar to 11a, from 7b (0.108 g, 0.137 mmol) and 1b (0.074 g, 0.137 mmol). Yield: 0.165 g (94%). Anal. Calcd for C<sub>65</sub>H<sub>55</sub>BF<sub>4</sub>O<sub>8</sub>P<sub>4</sub>Pd·0.5 CH<sub>2</sub>Cl<sub>2</sub> (M = 11281.26 + 42.47): C, 59.43; H, 4.26. Found: C, 59.55; H, 4.36.

 $[PdCl{Ph_2PN(Me)PPh_2}{Ph_2PCH=C(Ph)OP(O)(OPh)_2}][CF_3-$ SO3] (12). [PdCl2(COD)] (0.365 g, 1.278 mmol) and Ph2PN(Me)-PPh<sub>2</sub> (0.510 g, 1.278 mmol) were placed in a Schlenk flask and degassed in vacuo, before CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added at room temperature. The reaction mixture was stirred for 30 min, and the volatiles were removed under reduced pressure. The residue was washed with Et<sub>2</sub>O (2  $\times$  10 mL) and hexane (15 mL), which afforded [PdCl<sub>2</sub>{Ph<sub>2</sub>PN(Me)PPh<sub>2</sub>}] as a pale yellow solid (0.665 g, 90% yield, <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  31 ppm). The latter was suspended in a CH<sub>2</sub>Cl<sub>2</sub>/acetonitrile mixture (ratio: 1/1, 25 mL), before AgSO<sub>3</sub>-CF<sub>3</sub> (0.296 g, 1.152 mmol) was added. The reaction mixture was stirred for 3 h at room temperature, filtered over a pad of dried Celite, and 1b (0.617 g, 1.150 mmol) was added. After stirring for 30 min, the volatiles were removed under reduced pressure. The residue was washed with Et<sub>2</sub>O (15 mL) and pentane (15 mL), which afforded 12 as a red-orange solid. Yield: 1.326 g (94% based on **1b**, 84% overall). Anal. Calcd for  $C_{58}H_{49}ClF_3NO_7P_4PdS$  (M =

[PdMe{Ph<sub>2</sub>PNHC(O)Me}{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}]-[BF<sub>4</sub>] (13a). This complex was obtained as a pale brown solid, in a manner similar to 11a, from 7a (0.053 g, 0.077 mmol) and Ph<sub>2</sub>-PNHC(O)Me (0.018 g, 0.077 mmol). Yield: 0.063 g (92%). Anal. Calcd for C<sub>39</sub>H<sub>43</sub>BF<sub>4</sub>NO<sub>5</sub>P<sub>3</sub>Pd (M = 891.91): C, 52.52; H, 4.86; N, 1.57. Found: C, 52.28; H, 4.91; N, 1.69.

1226.84): C, 56.78; H, 4.03; N, 1.14. Found: C, 56.39; H, 4.08;

N, 1.21.

[PdMe{Ph<sub>2</sub>PNHC(O)Me}{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}] [BF<sub>4</sub>] (13b). This complex was obtained as an off-white solid, in a manner similar to 11a, from 7b (0.044 g, 0.056 mmol) and Ph<sub>2</sub>-PNHC(O)Me (0.013 g, 0.056 mmol). Yield: 0.048 g (88%). Anal. Calcd for C<sub>47</sub>H<sub>43</sub>BF<sub>4</sub>NO<sub>5</sub>P<sub>3</sub>Pd (M = 988.00): C, 57.14; H, 4.39; N, 1.42. Found: C, 57.38; H, 4.51; N, 1.31.

 $[PdMe{Ph_2PCH=C(Ph)OP(O)(OEt)_2}{Ph_2PCH_2C(O)Ph}]-$ [BF4] (14a). This complex was obtained as a pale brown solid, in a manner similar to 11a, from 7a (0.046 g, 0.067 mmol) and Ph\_2-PCH\_2C(O)Ph (0.020 g, 0.067 mmol) in 90% yield (0.058 g), or

from  $[PdMe{Ph_2PCH_2C(O)Ph}(NCMe)][BF_4]$  (16) (0.055 g, 0.099 mmol) and 1a (0.043 g, 0.099 mmol) in 92% yield (0.087 g). It

[PdMe{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OPh)<sub>2</sub>}{Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph}]-[BF<sub>4</sub>] (14b). This complex was obtained as a pale yellow-brown solid, in a manner similar to 11a, from 7b (0.039 g, 0.049 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph (0.015 g, 0.049 mmol) in 97% yield (0.050 g), or from 16 (0.055 g, 0.099 mmol) and 1b (0.053 g, 0.099 mmol) in 92% yield (0.097 g). It could not be separated from 11b and 15. The relative ratio 14b/11b/15, determined by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, is 4:1:1. Yield: 0.050 g (97%). Anal. Calcd for C<sub>53</sub>H<sub>46</sub>BF<sub>4</sub>O<sub>5</sub>P<sub>3</sub>Pd·0.5CH<sub>2</sub>Cl<sub>2</sub> (M = 1049.08 - 42.47): C, 58.87; H, 4.34. Found: C, 58.62; H, 4.26.

[PdMe{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}{Ph<sub>2</sub>PCH=C(Ph)OP-(O)(OPh)<sub>2</sub>}][BF<sub>4</sub>] (17). This complex was obtained as a yellow solid, in a manner similar to **11a**, from **7a** (0.060 g, 0.087 mmol) and **1b** (0.046 g, 0.087 mmol) in 93% yield (0.096 g), or from **7b** (0.075 g, 0.095 mmol) and **1a** in 96% yield (0.105 g). It could not be separated from **11a** and **11b**. The ratio **17/11a/11b**, determined by <sup>31</sup>P{<sup>1</sup>H</sup>} NMR spectroscopy, is 4:1:1. Anal. Calcd for C<sub>57</sub>H<sub>55</sub>-BF<sub>4</sub>O<sub>8</sub>P<sub>4</sub>Pd (M = 1185.17): C, 57.77; H, 4.68. Found: C, 58.01; H, 4.83.

**X-ray Collection and Structure Determinations.** The X-ray data were collected on an Enraf-Nonius KappaCCD diffractometer (graphite monochromated Mo K $\alpha$  radiation  $\lambda = 0.71073$  Å) (*trans*-**2b**, **3a**, and **18**), an Enraf-Nonius CAD4 diffractometer (graphite monochromated Mo K $\alpha$  radiation  $\lambda = 0.71073$  Å) (**8a**'), and a Philips PW1100 diffractometer (graphite monochromated Cu K $\alpha$  radiation  $\lambda = 1.54184$  Å) (**10a**). The structures were solved using the direct-methods program SIR,<sup>41</sup> except for **18**, for which the SHELXS-97 was used.<sup>42</sup> Subsequent full-matrix least-squares refinements were carried out using the SHELXL-97 program.<sup>42</sup> All non-hydrogen atoms were refined with anisotropic parameters. The hydrogen atoms were included in their calculated positions and refined with a riding model.

## **Results and Discussion**

Synthesis of the Phosphine-Phosphate Ligands Ph<sub>2</sub>- $PCH=C(Ph)OP(O)(OR)_2$  (1). Deprotonation of  $Ph_2PCH_2C$ -(O)Ph<sup>35a</sup> with KH, in THF at room temperature, yielded the corresponding enolate K[Ph<sub>2</sub>PCH--C(--O)Ph] A,<sup>43</sup> which was reacted in situ with ClP(O)(OR)<sub>2</sub> to afford the new phosphine-phosphates  $Ph_2PCH=C(Ph)OP(O)(OR)_2$  (1a) (R = Et) and (1b) (R = Ph) in high yields (>80%) (Scheme 1). Although this selective P-O bond formation was anticipated, owing to the known oxophilicity of phosphorus, it contrasts with the selective P-C coupling observed when the lithium salts Li[CH2 --- C(--- O)Ph] or Li[Ph2PCH--- $C(--O)NPh_2$  were reacted with  $Ph_2PCl$ , to give the ketophosphine Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph<sup>35a</sup> and the bisphosphine (Ph<sub>2</sub>P)<sub>2</sub>-CHC(O)NPh<sub>2</sub>,<sup>30</sup> respectively. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **1a,b** consisted in a single phosphine resonance at ca.  $\delta$  -29, accompanied by a signal at lower field,  $\delta$  -7.0 (1a) or -18.0 (1b), which was ascribed to the phosphate moiety (Table 1). In addition, both <sup>1</sup>H NMR spectra showed only one enolate resonance (Table 1). The absence of any J(PP)

could not be separated from **11a** and [PdMe{Ph<sub>2</sub>PCH<sub>2</sub>C( $\dot{O}$ )Ph}{Ph<sub>2</sub>-PCH<sub>2</sub>C(O)Ph}][BF<sub>4</sub>] (**15**). The relative ratio **14a**/**11a**/**15**, determined by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, is 9:1:1. Anal. Calcd for C<sub>45</sub>H<sub>46</sub>-BF<sub>4</sub>O<sub>5</sub>P<sub>3</sub>Pd•0.5CH<sub>2</sub>Cl<sub>2</sub> (M = 952.99 + 42.47): C, 54.90; H, 4.76. Found: C, 55.29; H, 4.63.

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Scheme 1



coupling in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra and the magnitude of the <sup>2</sup>*J*(PH) for the enolate protons (3.1 and 3.5 Hz for **1a** and **1b**, respectively) suggested that only the *Z*-isomers were obtained in this reaction. This was confirmed by the X-ray structures of some of the Pd complexes obtained with **1** (vide infra) since no isomerization about the C=C double bond is anticipated upon metal coordination. We propose that the stereoselectivity of the reaction results from the formation of the five-membered intermediate **A** (Scheme 1).<sup>43</sup> Then, subsequent reactions with chlorophosphates would lead to the *Z*-isomers of **1**. Similar intermediates have been reported for the deprotonated form of methylenediphosphonates,  $\beta$ -ketophosphonates, or phosphine oxides.<sup>44-46</sup>

Neutral Complexes. Reactions of 1a,b with neutral Pd-(II) precursors led to the formation of complexes 2-6a,b, as a result of either substitution of a cyclooctadiene (COD) ligand (2-4a,b) or cleavage of chloro-bridged dimers (5,6a,b) (Scheme 2). Their spectroscopic data clearly indicate that the enolphosphato-phosphines (1) behave as monodentate-P ligands (Table 1). Thus, the  $\nu$ (P=O) vibrations of 2-6a,b occurred in the same region as those of the free ligands 1. In the  ${}^{31}P{}^{1}H$  NMR spectra, P-coordination was reflected in the low field shift ( $\Delta \delta = +34$  to 51 ppm) observed for the phosphine resonances by comparison with those of 1, whereas the phosphate signals remain unaffected (Table 1). Complexes  $[PdCl_2{Ph_2PCH=C(Ph)OP(O)(OR)_2}_2]$ (2) (a, R = Et; b, R = Ph) were obtained as mixtures of *trans/cis* isomers, with a predominance of the *trans* isomer.<sup>47</sup> Yet, this was more pronounced in 2b, for which the structure of the *trans* isomer was confirmed by X-ray diffraction, with a trans/cis ratio of 90/10, as compared to the 83/17 ratio found for **2a**. Note that the <sup>31</sup>P resonances of the phosphine moieties of the trans isomers occurred at higher field than those of the *cis* isomer ( $\delta$  ca. 4.7 vs 12.1),<sup>48-50</sup> whereas in the <sup>1</sup>H NMR spectra, the opposite trend was observed for

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the enolate proton resonances (Table 1). Interestingly, in the latter case, the signals for the *cis* and *trans* isomers showed not only different intensities, but also different patterns. Indeed, in contrast to the doublet of doublets observed for the *cis* isomer, the enolate protons of the *trans* isomer gave a doublet of virtual triplets, as a result of the existence of a strong *trans-J*(PP') coupling between the P atoms of the two phosphines moieties.<sup>51,52</sup>

The reaction of [Pd(X)Cl(COD)] (X = Cl, Me) with 1 mol equiv of 1 led, exclusively, to the chloride-bridged dimers **3a,b** and **4a,b**, respectively. Mononuclear species, in which 1 would act as a P,O-chelate, have not been detected. The X-ray structure of  $[PdCl{Ph_2PCH=C(Ph)OP-(O)(OEt)_2}(\mu-Cl)]_2$  (**3a**) has been determined (vide infra).

The dmba (*N*,*N*-dimethylbenzylamine) complexes **5**–**6** presented spectroscopic characteristics similar to those of **2**–**4**. In the <sup>1</sup>H NMR spectra of **5a**,**b**, the <sup>4</sup>*J*(PH) couplings observed for the NMe<sub>2</sub> and CH<sub>2</sub> protons of the dmba ligand, which range from 1.4 to 3 Hz, are in accordance with a *trans* arrangement of P and N atoms around the Pd center (Table 1, Scheme 2).<sup>53,54</sup> The <sup>31</sup>P resonances of the  $\eta^3$ -allyl complexes **6a**,**b** were observed at higher field ( $\delta$  ca. 5) than those of **5a**,**b** ( $\delta$  ca. 20.8). Both the chemical shifts and the patterns of the <sup>1</sup>H allylic resonances of **6a**,**b** resemble those reported for other [( $\eta^3$ -allyl)PdCl(PR<sub>3</sub>)] complexes (Table 1).<sup>55,56</sup>

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Table 2. Selected Crystallographic Data for Complexes trans-2b, 3a·2Et<sub>2</sub>O, 8a', 10a·CH<sub>2</sub>Cl<sub>2</sub>, and 18

|                            | trans-2b        | $3a \cdot 2Et_2O$                             | 8a'             | $10a \cdot CH_2Cl_2$                         | 18              |
|----------------------------|-----------------|---|-----------------|--|-----------------|
| formula                    | C64H52Cl2O8P4Pd | $C_{48}H_{52}Cl_4O_8P_4Pd_2 \cdot C_4H_{10}O$ | C33H38F6NO4P3Pd | $C_{48}H_{32}B_2F_8O_8P_4Pd\cdot CH_2Cl_2^a$ | C23H26BF4N2OPPd |
| fw                         | 1250.32         | 1309.58                                       | 825.99          | 1225.62                                      | 570.64          |
| color                      | yellow          | orange  | orange          | orange                                       | yellow          |
| cryst syst                 | triclinic       | monoclinic                                    | monoclinic      | orthorhombic                                 | triclinic       |
| space group                | $P\overline{1}$ | C2/c  | $P2_{1}/c$      | Pnna   | $P\overline{1}$ |
| T/K                        | 293             | 173   | 293             | 173  | 173             |
| a/Å                        | 12.402(2)       | 24.9753(4)                                    | 10.3847(5)      | 17.133(3)                                    | 10.172(5)       |
| b/Å                        | 13.622(2)       | 9.8367(3)                                     | 21.2069(5)      | 22.051(5)                                    | 11.129(5)       |
| c/Å                        | 18.275(4)       | 23.6794(4)                                    | 16.9638(5)      | 14.681(3)                                    | 11.190(5)       |
| α/deg                      | 71.93(5)        | 90  | 90              | 90   | 99.023(5)       |
| $\beta/\text{deg}$         | 86.04(5)        | 96.923(3)                                     | 100.346(5)      | 90   | 104.466(5)      |
| γ/deg                      | 77.52(5)        | 90  | 90              | 90   | 95.540(5)       |
| V/Å <sup>3</sup>           | 2865.7(9)       | 5775.0(2)                                     | 3675.1(2)       | 5546.5(8)                                    | 1199.2(10)      |
| Ζ                          | 2               | 4   | 4               | 4  | 2               |
| F(000)                     | 1280            | 2664  | 1680            | 2464   | 576             |
| $\mu/\text{mm}^{-1}$       | 0.585           | 0.970   | 0.702           | 5.346  | 0.890           |
| data measured              | 10981           | 6593  | 7444            | 3368   | 14964           |
| data with $I > 2\sigma(I)$ | 8675            | 5492  | 5361            | 2610   | 13091           |
| R                          | 0.0385          | 0.0501  | 0.0497          | 0.0582                                       | 0.0436          |
| $R_{ m w}$                 | 0.1054          | 0.1599  | 0.1233          | 0.1615                                       | 0.1171          |

<sup>a</sup> The 20 OEt protons have not been included owing to the significant disorder oberved for these groups.



**Figure 1.** ATOMS view of the molecular structure of *trans-2b*; for better clarity, only the *ipso* carbon atoms of the phenyl groups of the phosphate moieties have been represented.

**Crystal Structures of** *trans*-2b and 3a. Views of the crystal structures of *trans*-[PdCl<sub>2</sub>{Ph<sub>2</sub>PCH=C(Ph)OP(O)-(OPh)<sub>2</sub>}<sub>2</sub>] (2b) and [PdCl{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}( $\mu$ -Cl)]<sub>2</sub> (3a) are shown in Figures 1 and 2, respectively, with crystallographic data in Table 2 and selected bond lengths and angles in Table 3. There is an effective center of symmetry in complex 2b, at the Pd center, which is not crystallographically imposed. In both complexes, the Pd center adopts a square planar geometry. Bond lengths and angles involving the Pd, P, and Cl atoms are within the same range as those reported for other *trans*-[PdCl<sub>2</sub>(L)<sub>2</sub>]<sup>50,57,58</sup> and [PdCl(L)( $\mu$ -Cl)]<sub>2</sub> complexes (L = phosphine).<sup>59,60</sup> Bond



Figure 2. ATOMS view of the molecular structure of 3a·2Et<sub>2</sub>O.

distances and angles within the phosphate moieties are nonexceptional. The C(13)-C(14) (2b and 3a) and C(45)-C(46) (2b) bond distances, which range from 1.323(3) to 1.330(6) Å (Table 3), are in agreement with the presence of a double bond between these atoms. The cis arrangement of the Ph<sub>2</sub>P and phosphate groups about these double bonds confirms the formation of 1 as the Z-isomer. In both complexes, the phosphate groups bend toward the Pd center, thus leading the enolate O atoms of the phosphate moieties to occupy almost an apical position above (or below) the metal. However, it seems reasonable to assume that this results from the favorable cis geometry of ligand 1, rather than from an inclination toward the formation of pentacoordinated species. Indeed, the O(1)-Pd and O(5)-Pd distances in **2b** (3.549 and 3.460 Å, respectively) and the O(1)-Pd distance in **3a** (3.272 Å) only suggest weak, if not negligeable, O···Pd interactions. Another feature of note is the fact that, in **3a**, the C(1)-C(6), P(1), Pd, and Cl(2') atoms

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<sup>(60)</sup> Newkome, G. M.; Evans, D. W.; Fronczek, F. R. Inorg. Chem. 1987, 26, 3500.

are within the same plane, which is almost perpendicular to that containing the Pd, Cl, and P atoms.

Cationic Complexes. The cationic complexes 7-9a,b have been prepared by reaction of the corresponding chloroderivatives 4-6 with AgBF<sub>4</sub> (or TlPF<sub>6</sub> in the case of **7b**' and 8a') (eqs 1-3). Halide abstraction occurs under mild conditions, and 7-9 have been isolated in high yields after purification (see Experimental Section). These new complexes are stabilized by coordination of the phosphate function of 1 via the oxygen atom of the P=O groups, which leads to the formation of seven-membered ring metallocycles. The latter represent, to the best of our knowledge (SciFinder search), the first examples of metallocycles of this size involving a P,O-chelate. Selected spectroscopic data of 7-9 are given in Table 1. As a result of the O-coordination, the  $\nu$ (P=O) vibrations of 7–9 occurred at shorter wavenumbers (ca. 60 cm<sup>-1</sup>) than those of **4–6**. A slight low field shift of the <sup>1</sup>H and <sup>31</sup>P resonances of the P,O-ligands was observed, by comparison with those of the corresponding neutral complexes 4-6 (Table 1). Note that there is no observable  $^{3+4}J(PP)$  coupling.



 Table 3.
 Selected Bond Lengths (Å) and Angles (deg) for trans-2b and 3a

| trans-2b    | •         | <u> </u>    |           |  |
|-------------|-----------|-------------|-----------|--|
| Pd-C11      | 2 2924(6) | Pd-C11      | 2 288(2)  |  |
| Pd-Cl2      | 2.2926(6) | Pd-Cl2      | 2.334(2)  |  |
| Pd-P1       | 2.3432(6) | Pd-Cl2'     | 2.438(2)  |  |
| Pd-P3       | 2.3570(6) | Pd-P1       | 2.244(2)  |  |
| P1-C13      | 1.811(2)  | P1-C13      | 1.805(4)  |  |
| C13-C14     | 1.323(3)  | C13-C14     | 1.330(6)  |  |
| C14-O1      | 1.408(3)  | C14-O1      | 1.395(5)  |  |
| O1-P2       | 1.578(2)  | O1-P2       | 1.603(3)  |  |
| O2-P2       | 1.443(2)  | O2-P2       | 1.462(4)  |  |
| O3-P2       | 1.576(2)  | O3-P2       | 1.557(4)  |  |
| O4-P2       | 1.570(2)  | O4-P2       | 1.554(3)  |  |
| P3-C45      | 1.801(2)  |             |           |  |
| C45-C46     | 1.323(3)  |             |           |  |
| C46-O5      | 1.403(3)  |             |           |  |
| O5-P4       | 1.586(2)  |             |           |  |
| O6-P4       | 1.449(2)  |             |           |  |
| O7-P4       | 1.563(2)  |             |           |  |
| O8-P4       | 1.567(2)  |             |           |  |
| Cl1-Pd-Cl2  | 178.94(3) | Cl1-Pd-Cl2  | 176.71(5) |  |
| Cl1-Pd-P1   | 87.48(2)  | Cl1-Pd-Cl2' | 92.19(4)  |  |
| Cl1-Pd-P3   | 91.94(2)  | Cl1-Pd-P1   | 88.39(4)  |  |
| Cl2-Pd-P3   | 91.95(2)  | Cl2-Pd-Cl2' | 84.76(4)  |  |
| Cl2-Pd-P3   | 88.65(2)  | Cl2-Pd-P1   | 94.60(4)  |  |
| P1-Pd-P3    | 178.72(2) | Cl2'-Pd-P1  | 177.31(4) |  |
| P1-C13-C14  | 129.8(2)  | P1-C13-C14  | 124.9(3)  |  |
| C13-C14-C15 | 125.2(2)  | C13-C14-C15 | 124.1(4)  |  |
| C13-C14-O1  | 119.7(2)  | C13-C14-O1  | 116.4(4)  |  |
| C14-O1-P2   | 126.6(2)  | C14-O1-P2   | 128.0(3)  |  |
| P3-C45-C46  | 124.2(2)  |             |           |  |
| C45-C46-C47 | 127.0(2)  |             |           |  |
| C45-C46-O5  | 117.4(2)  |             |           |  |
| C46-O5-P4   | 125.4(2)  |             |           |  |

Table 4. Selected Bond Lengths (Å) and Angles (deg) for  $8a^\prime$  and  $10a{\cdot} CH_2Cl_2$ 

| 8a'        |          | $10a \cdot CH_2Cl_2$ |          |  |
|------------|----------|----------------------|----------|--|
| Pd-P1      | 2.249(2) | Pd-P1                | 2.225(2) |  |
| Pd-O1      | 2.178(4) | Pd-O4                | 2.108(6) |  |
| Pd-N       | 2.127(4) | P1-C13               | 1.792(6) |  |
| Pd-C33     | 1.983(5) | C13-C14              | 1.321(8) |  |
| P1-C13     | 1.803(5) | C14-O1               | 1.417(7) |  |
| C13-C14    | 1.321(7) | O1-P2                | 1.558(5) |  |
| O1-P2      | 1.478(4) | P2-O2                | 1.526(5) |  |
| P2-O2      | 1.583(4) | P2-O3                | 1.557(7) |  |
| P2-O3      | 1.540(4) | P2-O4                | 1.448(7) |  |
| P2-O4      | 1.543(4) |                      |          |  |
| O2-C14     | 1.411(6) |                      |          |  |
| N-C25      | 1.492(8) |                      |          |  |
| N-C26      | 1.474(8) |                      |          |  |
| N-C27      | 1.487(7) |                      |          |  |
| P1-Pd-O1   | 95.3(2)  | P1-Pd-P1'            | 99.6(2)  |  |
| P1-Pd-N    | 170.7(2) | P1-Pd-O4             | 90.6(2)  |  |
| P1-Pd-C33  | 95.1(2)  | P1-Pd-O4'            | 165.0(2) |  |
| O1-Pd-N    | 88.6(2)  | O4-Pd-O4'            | 81.9(4)  |  |
| O1-Pd-C33  | 167.7(2) | Pd-P1-C13            | 103.2(2) |  |
| N-Pd-C33   | 82.1(2)  | P1-C13-C14           | 128.6(4) |  |
| P1-C13-C14 | 126.4(4) | C13-C14-O1           | 119.4(6) |  |
| O1-P2-O2   | 112.6(2) | O1-P2-O4             | 112.5(3) |  |
| C13-C14-O2 | 118.4(4) |                      |          |  |

The crystal structure of  $[Pd(dmba){Ph_2PCH=C(Ph)OP-}]$ (O)(OEt)<sub>2</sub>][PF<sub>6</sub>] (**8a**') has been determined. Crystallographic

(O)(OEt)<sub>2</sub>}][PF<sub>6</sub>] (8a') has been determined. Crystallographic data and selected bond lengths and angles are given in Tables 2 and 4, respectively. A view of the molecular structure of the cation in 8a' is shown in Figure 3. The coordination around the Pd center is best described as distorted square planar, with O(1)-Pd-C(33) and P(1)-Pd-N angles of

167.7(2)° and 170.7(2)°, respectively. Chelation of the Pd center by the dmba ligand is reflected in the Pd–N and Pd–C(33) distances of 2.127(4) and 1.983(5) Å, respectively, and in the N–Pd–C(33) angle of 82.1(2)°. These values are similar to those reported for other complexes containing this ligand.<sup>61–66</sup> Coordination of the P(1) atom [Pd–P(1) = 2.249(2) Å] occurs in *cis* position to the aryl group of the dmba ligand (antisymbiotic effect), as already observed in



Figure 3. ATOMS view of the molecular structure of the cation in 8a'.

related systems.<sup>61,62,66,67</sup> The Pd–O(1) distance of 2.178(4) Å clearly indicates the presence of a dative bond between these two atoms, thus confirming the chelation of the Pd by the enolphosphato–phosphine ligand, **1a**. To the best of our knowledge, there is no other structurally characterized sevenmembered mononuclear metallocycle involving a P,O-chelate (CSD search). The P,O-bite angle [P(1)–Pd–O(1) = 95.1-(1)°] is more obtuse than those reported for five- and sixmembered P,O-metallocycles, which range from 80° to  $85^{\circ 61-63,65,68-71}$  and  $88^{\circ}$  to  $93.5^{\circ}$ ,<sup>64,72–77</sup> respectively. In the case of a Pd atom chelated with a BINAPO ligand (BINAPO = 2-diphenylphosphino-2'-diphenylphosphinyl-1,1'-binaph-thalene), the P,O-bite angle of the resulting eight-membered ring [90.9(1)°]<sup>78</sup> is also more acute than in **8a**'. As a probable

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Figure 4. CrystalMaker view of the ligand environment at the Pd center in the cation of 8a', showing the puckering of the seven-membered ring.

consequence of the obtuse P(1)-Pd-O(1) angle, the P(1)-Pd-C(33) angle  $[95.1(2)^{\circ}]$  is more acute (by 2–5°) than those found in other complexes containing both dmba and P,O-chelates.<sup>61–63,65,66,69</sup> The most striking feature is the distortion observed in the seven-membered chelate resulting in a puckered sofa conformation (Figure 4). Thus, whereas the Pd, P(1), O(2), P(2), and O(1) atoms are almost coplanar within 0.106(5) Å, C(13) and C(14) deviate from the plane by 1.245(5) and 1.166(5) Å, respectively. A dihedral angle of 120.2(5)° is observed between the best plane passing through Pd, P(1), O(2), P(2), and O(1) and that containing C(13), C(14), and C(15) (the *ipso* carbon atom of the phenyl ring attached to the double bond). This contrasts with the situation observed for the six-membered ring complex *cis*-

[PdCl<sub>2</sub>{Ph<sub>2</sub>PCH=C(Ph)OPPh<sub>2</sub>}], in which the Pd, P, C, C, O, and P atoms are almost coplanar.<sup>53</sup> Thus, increasing the ring size by one unit leads to a remarkable change of the conformation of the metallocycle.

Treatment of the chloro-bridged dimers 4a,b with AgBF<sub>4</sub> or TIPF<sub>6</sub> afforded the mononuclear derivatives 7, for which stabilization is achieved by coordination of a solvent molecule (acetonitrile). Interestingly, this reaction was regioselective, with formation, as sole product, of the isomer in which the Me group is in a *cis* position to the P atom  $[{}^{3}J(PH) = ca. 2.5 Hz]$  (eq 1). Although this arrangement is consistent with the antisymbiotic effect, it contrasts with that encountered in related complexes, of the type [PdMe-(NCMe)(P,O)], for which mixtures of *cis* and *trans* isomers were obtained.<sup>54</sup> Reaction of [Pd(NCMe)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> with 2 mol equiv of 1 led to the formation of complexes 10a,b (eq 4). In the IR spectrum, the  $\nu$ (P=O) vibrations are observed at 1221 and 1244  $\text{cm}^{-1}$  for **10a** and **10b**, respectively (Table 1), which unambiguously establishes coordination of the P=O groups to the Pd centers. By comparison with the <sup>31</sup>P resonances of 7-9, those of the Ph<sub>2</sub>P groups in 10 underwent a low field shift of ca. 7 ppm, whereas those of the phosphate functionalities were shifted toward higher field by ca. 5 ppm. Both <sup>31</sup>P{<sup>1</sup>H} NMR spectra consisted of only two signals, indicating that only one geometric isomer was formed. The magnitude of the J(PP) value (16 Hz) and other spectroscopic data suggested the formation of the cis isomer.<sup>64,71,72,79</sup> When [Pd(NCMe)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> was reacted with only 1 mol equiv of

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Figure 5. ATOMS view of the molecular structure of the cation in  $10a \cdot CH_2CI_2$ .

1, complexes 10 were also formed and unreacted Pd starting material was recovered. No other products were detected, showing that the formation of the bis-P,O-chelates 10 is thermodynamically favored.



The proposed structure was confirmed by an X-ray determination of *cis*-[Pd{Ph<sub>2</sub>PCH=C(Ph)OP(O)(OEt)<sub>2</sub>}<sub>2</sub>]-[BF<sub>4</sub>]<sub>2</sub> (**10a**·CH<sub>2</sub>Cl<sub>2</sub>). Crystallographic data and selected bond lengths and angles are given in Tables 2 and 4, respectively. A view of the molecular structure of the cation in **10a**·CH<sub>2</sub>Cl<sub>2</sub> is shown in Figure 5, confirming that the Pd center is chelated by two enolphosphato-phosphine ligands **1a**. The phosphine moieties occupy mutually *cis* positions [P(1)-Pd-P(1') = 99.6(2)°], and a *C*<sub>2</sub> axis passes through the Pd center. The Pd-P(1) [2.225(2) Å] and Pd-O(4) [2.108(6) Å] bond distances are within the expected range for bis-P,O-chelated palladium complexes.<sup>64,71,72,79</sup> The coordination environment of the palladium atom is best described as distorted square planar, with a P(1)-Pd-O(4') angle of 165.0(2)°. Interatomic bond lengths and angles within the P,O-ligand are in the

expected range. As in  $[Pd(dmba){Ph_2PCH=C(Ph)OP(O)-(OEt)_2}][PF_6]$  (8a'), the seven-membered ring adopts a sofa conformation, with C(13) and C(14) deviating from the mean plane passing through the Pd-P(1)-O(1)-P(2) and O(4)



**Figure 6.** CrystalMaker view of the ligand environment at the Pd center in the cation of **10a**·CH<sub>2</sub>Cl<sub>2</sub>, showing the puckering of the seven-membered rings.

atoms by 1.232(7) and 1.283(7) Å, respectively. A partial view of the puckering of the chelate rings is depicted in Figure 6. The dihedral angle between the latter plane and that containing the C(13), C(14), and C(15) atoms is more acute than in **8a'** [111.9(7)° vs 120.2(5)°].

Reaction of 7b with 1 mol equiv of 1b afforded the new complex 11b (eq 5). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed only two singlets at  $\delta$  13.9 and -18.3 ppm, which were ascribed to the phosphine and phosphate moieties, respectively (Table 1). The former value is intermediate between the chemical shifts observed for **1b** in **7b** ( $\delta$  21.5), where this ligand behaves as a P,O-chelate, and in 12 ( $\delta$  2.3), in which it is P-monocoordinated in trans position to another phosphine moiety. This suggests the occurrence in solution of a fast equilibrium on the NMR time scale  $11b \Rightarrow 11b'$ , resulting from the P,O-ligand acting alternatively as a chelating or monodentate ligand (eq 5). The <sup>1</sup>H NMR data are consistent with the proposed structure. Thus, the resonance for the methyl protons is a triplet  $[{}^{3}J(PH) \approx {}^{3}J(P'H)$  $\approx$  6.4 Hz], the two PPh<sub>2</sub> groups appearing equivalent as a result of the equilibrium already mentioned (Table 1). The different coordination modes adopted by the two ligands 1b in 11b were evidenced in the solid state IR spectrum (KBr pellet). Two  $\nu$ (P=O) vibrations at 1310 and 1243 cm<sup>-1</sup> were observed for the free and coordinated P=O function, respectively. A similar hemilabile behavior has been observed for the P,O-ligands  $Ph_2PNRC(O)Me$  (R = H, Me) and  $Ph_2$ -PCH<sub>2</sub>C(O)Ph in complexes analogous to 11b, i.e., [PdMe- $(P,O)_2$  [PF<sub>6</sub>].<sup>54</sup> Complex **11a**, prepared from **7a** and **1a**, showed in solution the same dynamic behavior as that observed for 11b (eq 5). In particular, this was reflected in the <sup>31</sup>P NMR spectrum, which consisted of two singlets at  $\delta$ 13.3 ppm (PPh<sub>2</sub>) and -6.6 ppm (phosphate) (Table 1). As for **11b**, the solid state IR spectrum revealed a static situation with one ligand **1a** acting as a P,O-chelate [ $\nu$ (P=O): 1225 cm<sup>-1</sup>] while the other one is only P-coordinated [ $\nu$ (P=O):  $1272 \text{ cm}^{-1}$ ].



The chelating ability of 1a and 1b was further compared to that of other P,O-ligands. Reaction of complexes 7a and 7b with 1 mol equiv of the acetamidophosphine Ph<sub>2</sub>PNHC-(O)Me<sup>54</sup> led to the formation of a single product, **13a** and 13b, respectively (eq 6). The  ${}^{31}P{}^{1}H{}$  NMR spectrum of 13a showed two doublets at  $\delta$  70.8 and 8.8 ppm, which were ascribed to the Ph<sub>2</sub>P moieties of the acetamidophosphine and 1a, respectively. The  ${}^{2}J(PP)$  value of 401 Hz indicates a *trans* arrangement of these two nuclei around the Pd center. The range of <sup>31</sup>P chemical shifts indicates that the pre-existing P.O-chelate in 7a has been displaced by the incoming acetamidophosphine ligand.54 This was confirmed by the IR spectrum which showed two strong vibrations at 1608 and 1271 cm<sup>-1</sup>, ascribed to coordinated C=O of Ph<sub>2</sub>PNHC(O)-Me (free ligand: 1715 cm<sup>-1</sup>)<sup>54</sup> and free P=O of 1a, respectively. In the <sup>1</sup>H NMR spectrum, the enolate resonance occurred at  $\delta$  5.84 ppm, whereas the NH proton was observed at  $\delta$  9.56 ppm. The spectroscopic data of **13b** are similar to those of 13a and are consistent with the proposed structure. The only noticeable difference concerns the <sup>1</sup>H resonance of the enolate proton, which resonated in 13b at lower field than in 13a ( $\delta$  6.08 ppm).

If the acetamido phosphine Ph<sub>2</sub>PNHC(O)Me clearly presents a higher chelating ability than **1a** and **1b**, a different situation was observed when the complexes **7a** and **7b** were reacted with the  $\beta$ -ketophosphine Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph. In both cases, a mixture of products was obtained. The reaction with **7a** led to the formation of the new complex **14a** (main



product) and of **11a** and **15<sup>54</sup>** (Scheme 3). This was clearly evidenced in the  ${}^{31}P{}^{1}H$  NMR spectrum, which showed the signals of an AB spin system for 14a at  $\delta$  15.0 and 18.3 ppm, ascribed to the Ph<sub>2</sub>P moieties of **1a** and the ketophosphine, respectively. In the latter case, the chemical shift is characteristic for this ligand being P-monocoordinated to a cationic Pd center.<sup>54</sup> The magnitude of the  ${}^{2}J(PP)$  value (408 Hz) is indicative of a mutual trans arrangement of these nuclei. The proposed structure of 14a is consistent with the presence in the IR spectrum (KBr) of two strong vibrations at 1672 and 1223  $\text{cm}^{-1}$ , corresponding to the free C=O and coordinated P=O functions, respectively. Interestingly, when complex  $16^{54}$  was treated with 1 mol equiv of 1a, the same reaction mixture was obtained (Scheme 3). This suggests the existence of a thermodynamic equilibrium between 14a and 11a and 15 (Scheme 3), and in situ <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy gave a relative ratio of 9:1:1, respectively.

Similarly, a mixture of products consisting of 14b, 11b, and 15 was obtained from 7b and Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph, or from 16 and 1b. The spectroscopic data are consistent with the proposed structure for 14b (Table 1). However, the three products are present in different proportions to the previous mixture. Indeed, the ratio 14b and 11b and 15 was 4:1:1, respectively.

Although ligand redistribution is observed, these experiments indicate a higher chelating ability of 1a and 1b than Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph. Not only was chelation of the latter not observed in the presence of coordinated 1a or 1b (see 14a and 14b), but the enolphosphatophosphine 1a or 1b displaces the pre-existing P,O-chelate in 16. It is interesting that chelation of 1a and 1b in 7a and 7b, respectively, gives rise to more stable complexes than that of Ph<sub>2</sub>PCH<sub>2</sub>C(O)Ph in 16. Furthermore, the observed product ratios, with a stronger predominance of 14a than 14b, suggest different chelating abilities for the two enolphosphato-ligands 1a and 1b. Thus, we set out to prepare a complex containing both ligands, which could compete for chelation around the metal center. Complexes 7a and 7b were treated with 1 mol equiv of 1b and 1a, respectively. Both reactions led to the formation of 17, as the main product, accompanied with that of 11a and **11b**, with similar relative ratios of 4:1:1, respectively (eq 7).

Me

17



The spectroscopic data are consistent with the proposed structure of 17 (Table 1). In the  ${}^{31}P{}^{1}H$  NMR spectrum, the two phosphine moieties give rise to an AB system at  $\delta$ 16.6 and 12.1 ppm, with a  ${}^{2}J(PP)$  value of 404 Hz. This indicates a static situation in 17, with the two phosphine groups being trans to each other, and evidences the fact that one of the enolphosphatophosphine ligands acts as a P,Ochelate while the other one is P-monocoordinated. The <sup>31</sup>P chemical shifts for both the phosphine and phosphate moieties in 17 suggested the chelating ligand to be 1a. Additional evidence came from the <sup>1</sup>H NMR spectrum in 6.40. The former chemical shift value is very similar to that observed for the enolate proton of 1b when this ligand acts as a P-monodentate ligand in other cationic Pd complexes, such as 12 or 13b, thus supporting the same coordination mode for this ligand in 17. This indicates that 1a presents a higher chelating ability than 1b. This is probably due to the slightly enhanced electron-donating properties of the ethoxy groups in 1a compared to that of the phenoxy groups in 1b, resulting in the P=O function in 1a being more electronrich than that of 1b. In the free ligands, the lower electrondonating properties of the OPh groups in 1b are also reflected in the <sup>31</sup>P phosphate resonance ( $\delta$  -18.0) and in the  $\nu$ (P=O) vibration (1313 cm<sup>-1</sup>), which occurred at higher field ( $\delta$  -7.0) and higher wavenumbers (1277 cm<sup>-1</sup>) than those of 1a, respectively.

BF₄

When complexes 8 were reacted with 1 mol equiv of Et<sub>4</sub>NCl, the coordinated phosphates were substituted by Cl<sup>-</sup> and the neutral chloro-complexes 5 obtained (Scheme 4). Interestingly, in the presence of PPh<sub>3</sub> no reaction was observed, the P,O-chelates in 8 being not displaced. However, treatment of these complexes with the functional phosphine Ph<sub>2</sub>PNHC(O)Me<sup>54</sup> resulted not only in the opening of the P,O-chelate, as observed in 13a,b, but in the complete displacement of 1. Thus, the known complex [Pd(dmba)- $\{Ph_2PNHC(O)Me\}\}$ [BF<sub>4</sub>] (18),<sup>54</sup> in which the incoming Scheme 4



Table 5. Selected Bond Lengths (Å) and Angles (deg) for 18

| C1-Pd    | 1.988(2)  | C10-C11  | 1.500(3) |
|----------|-----------|----------|----------|
| C6-C7    | 1.502(3)  | N1-Pd    | 2.123(2) |
| C7-N1    | 1.491(2)  | N2-P     | 1.722(2) |
| C10-O    | 1.246(2)  | Pd-O     | 2.140(2) |
| C10-N2   | 1.352(2)  | Pd-P     | 2.217(2) |
|          |           |          |          |
| C1-Pd-O  | 175.90(6) | C7-N1-Pd | 106.6(1) |
| N1-Pd-P  | 175.63(4) | C10-O-Pd | 117.0(2) |
| N1-Pd-O  | 95.16(6)  | N2-P-Pd  | 99.36(6) |
| C1-Pd-N1 | 83.10(7)  | O-C10-N2 | 121.6(2) |
| C1-Pd-P  | 99.24(6)  | C10-N2-P | 119.3(2) |
| O-Pd-P   | 82.75(5)  |          |          |

acetamidophosphine acts as P,O-chelate, was obtained in almost quantitative yields (Scheme 4). This most likely results from the formation of the entropically favored fivemembered metallocycle in **18**, due to the known chelating ability of Ph<sub>2</sub>PNHC(O)Me.<sup>54</sup> It also reflects the importance of keeping a relatively hard donor atom (oxygen) *trans* to the  $\sigma$ -bonded carbon donor (antisymbiotic effect). This would clearly not have been possible with PPh<sub>3</sub> as a donor. Note that treatment of **8** with the  $\beta$ -ketophosphine Ph<sub>2</sub>PCH<sub>2</sub>C-(O)Ph led to untractable mixtures of products, which mainly resulted from complex ligand redistribution reactions.

Crystal Structure of 18. During the course of this study,

X-ray quality crystals of  $[Pd(dmba){Ph_2PNHC(O)Me}][BF_4]$ (18) have been obtained. Crystallographic data and selected bond lengths and angles are given in Tables 2 and 5, respectively. A view of the molecular structure of the cation in 18 is shown in Figure 7. The geometry around the Pd center is square planar, with C(1)-Pd-O and P-Pd-N(1) angle values of 175.90(6)° and 175.63(4)°, respectively. The Pd is chelated by the dmba moiety, and as expected, coordination of the P atom occurs in *trans* position to the N atom of the NMe<sub>2</sub> group, as observed in 8a' (vide supra). The Pd-O distance of 2.140(2) Å is indicative of an effective bond between these two atoms and of the P,O -chelation of Ph<sub>2</sub>PNHC(O)Me. A slightly longer Pd-O bond length was found in [PdMe{Ph<sub>2</sub>PNHC(O)Me}{[Ph<sub>2</sub>PNHC(O)Me}][O<sub>3</sub>-

Figure 7. ATOMS view of the molecular structure of the cation in 18.

 $SCF_3$ ] [2.181(4) Å].<sup>54</sup> In the latter, the Pd–P bond lengths of 2.307(2) and 2.265(2) Å, for the monodentate and chelate ligands, respectively,<sup>54</sup> are also longer than that found in **18** [2.217(2) Å]. The other bond distances and angles involving the dmba and P,O-ligands are within the expected range.

## Conclusion

We have prepared the first P,O-ligands combining a phosphine moiety and an enolphosphate function. In their palladium complexes, they can either monocoordinate the metal center via their P atom or act as P,O-chelates, in which case they may display a hemilabile behavior. The sofa conformation observed for the seven-membered metallocycles, obtained by P,O-chelation of these ligands, results in an interesting face discrimation in square planar complexes. This may be of future interest for regio/stereoselective chemical transformations. The fact that the ethoxy ligand **1a** appears to be a better chelate than its phenoxy analogue **1b** suggests that fine-tuning of the electron-donating properties of this class of ligands, and hence the reactivity of their metal complexes, could be achieved by changing the nature of the substitutents of the phosphate functionality.

Acknowledgment. We are grateful to Dr. A. DeCian and Mrs. N. Gruber for assistance with the crystal structure determinations. This work was supported by the Centre National de la Recherche Scientifique and the Ministère Délégué à la Recherche et aux Nouvelles Technologies.

**Supporting Information Available:** Crystallographic data in CIF format and ORTEP plots. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic material can also be obtained from the CCDC, the deposition numbers being CCDC 215457–215461.

IC030032Y

Inorganic Chemistry, Vol. 42, No. 24, 2003 7765