# Inorganic Chemistry
### Article

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

**Xavier Morise,*,[†] Pierre Braunstein,*,[†] and Richard Welter[‡]**

*Laboratoire de Chimie de Coordination and Laboratoire DECMET, UMR 7513 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France*

The new bifunctional ligands Ph$_2$PCH=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$_2${Ph$_2$PCH=C(Ph)OP(O)(OPh)$_2$}$_2$] (**2b**), [PdCl{Ph$_2$PCH=C(Ph)OP(O)(OEt)$_2$}-($\mu$-Cl)]$_2$ (**3a**), [Pd(dmba){Ph$_2$PCH=C(Ph)OP(O)(OEt)$_2$}][PF$_6$] (**8a′**), and *cis*-[Pd{Ph$_2$PCH=C(Ph)OP(O)OEt)$_2$}][BF$_4$]$_2$ (**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.[1–3] 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[1,4,5] and/or the possible occurrence of hemilabile behavior of these ligands.[1,2,6,7]

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.[8–11] 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[12] and hybrid organic–inorganic or layered metal–phosphonate materials.[12–14] Recent advances in this area include the synthesis

* To whom correspondence should be addressed. E-mail: morise@chimie.u-strasbg.fr (X.M.); braunst@chimie.u-strasbg.fr (P.B.).
† Laboratoire de Chimie de Coordination.
‡ Laboratoire DECMET.

(1) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.
(2) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680.
(3) (a) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Progr. Inorg. Chem.* **1999**, *48*, 233. (b) Lindner, E.; Pautz, S.; Haustein, M. *Coord. Chem. Rev.* **1996**, *15*, 145 and references therein.
(4) Keim, W.; Behr, A.; Kraus, G. *J. Organomet. Chem.* **1983**, *377*, 251.
(5) Hoberg, H.; Ballesteros, A.; Sigan, A.; Jegat, C.; Milchereit, A. *Synthesis* **1991**, 395.
(6) Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207.
(7) Braunstein, P.; Chauvin, Y.; Nähring, J.; DeCian, A.; Fischer, J.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1996**, *15*, 5551.
(8) DeBolster, M. W. G.; Goeneveld, W. L. In *Topics in Phosphorus Chemistry*; Griffith, E. J., Grayson, M., Eds.; Wiley: New York, 1976; Vol. 8, p 273 and references therein.
(9) Gahagan, M.; Mackie, R. K.; Cole-Hamilton, D. J.; Cupertino, D. C.; Harman, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**.
(10) Weis, K.; Rombach, M.; Vahrenkamp, H. *Inorg. Chem.* **1993**, *32*, 2470.
(11) (a) Morise, X.; Braunstein, P.; Welter, R. *C. R. Chimie* **2003**, *6*, 91. (b) Kingsley, S.; Chandrasekhar, V.; Incarvito, C. D.; Lam, M. K.; Rheingold, A. L. *Inorg. Chem.* **2001**, *40*, 5890.
(12) Deemie, R. W.; Rao, M.; Knight, D. A. *J. Organomet. Chem.* **1999**, *585*, 162.
(13) Deniaud, D.; Schöllorn, B.; Mansuy, D.; Rouxel, J.; Battioni, P.; Bujoli, B. *Chem. Mater.* **1995**, *7*, 995.
(14) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420.

of water soluble tertiary phosphines,[15−19] and rhodium complexes of phosphino−phosphonate ligands have been used in the catalytic carbonylation of methanol[20−22] or in styrene hydroformylation.[23,24] $PtCl_2$−$SnCl_2$ hydroformylation catalysts with phosphonated triarylphosphines have also been reported recently.[25]

As part of our ongoing interest in the chemistry of multifunctional phosphine ligands containing hard and soft donor functions,[26−34] we describe here the preparation of the first enolphosphato−phosphine ligands, $Ph_2PCH=CPh$-[$OP(O)(OR)_2$] [**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 $^1H$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ 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% $H_3PO_4$ in $H_2O$ with downfield chemical shifts reported as positive.

(15) Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 3500.
(16) Herring, A. M.; Steffey, B. D.; Miedaner, A.; Wander, S. A.; DuBois, D. L. *Inorg. Chem.* **1995**, *34*, 1100.
(17) Schull, T. L.; Fettinger, J. C.; Knight, D. A. *Inorg. Chem.* **1996**, *35* (5), 6717.
(18) Callahan, K. P.; DiGiacomo, P. M.; Dines, M. B. U.S. Patent 4386013, 1983.
(19) Bischoff, S.; Kant, M. *Catal. Today* **2001**, *66*, 183.
(20) Freiberg, J.; Weigt, A.; Dilcher, H. *J. Prakt. Chem.* **1993**, *335*, 337.
(21) Weigt, A.; Bishoff, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *102*, 91.
(22) Bischoff, S.; Weigt, A.; Miessner, H.; Lücke, B. *J. Mol. Catal. A: Chem.* **1996**, *107*, 339.
(23) Le Gall, I.; Soulier, E.; Salaün, J.-Y.; des Abbayes, H. *J. Organomet. Chem.* **1998**, *567*, 13.
(24) Köckritz, A.; Bischoff, S.; Kant, M.; Siefken, R. *J. Mol. Catal. A: Chem.* **2001**, *174*, 119.
(25) Ellis, D. D.; Harrison, G.; Orpen, A. G.; Phetmung, H.; Pringle, P. G.; deVries, J. G.; Oevering, H. *J. Chem. Soc., Dalton Trans.* **2000**, 671.
(26) Braunstein, P.; Gomes-Carneiro, T. M.; Matt, D.; Balegroune, F.; Grandjean, D. *J. Organomet. Chem.* **1989**, *367*, 117.
(27) Braunstein, P.; Morise, X.; Bénard, M.; Rohmer, M.-M.; Welter, R. *Chem. Commun.* **2003**, 610.
(28) Braunstein, P.; Douce, L.; Balegroune, F.; Grandjean, D.; Bayeul, D.; Dusausoy, Y.; Zanello, P. *New J. Chem.* **1992**, *16*, 925.
(29) Andrieu, J.; Braunstein, P.; Dusausoy, Y.; Ghermani, N. E. *Inorg. Chem.* **1996**, *35*, 7174.
(30) Andrieu, J.; Braunstein, P.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1996**, *35*, 5975.
(31) Braunstein, P.; Charles, C.; Tiripicchio, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1996**, 4365.
(32) Andrieu, J.; Braunstein, P.; Naud, F.; Adams, R. D. *J. Organomet. Chem.* **2000**, *601*, 43.
(33) Braunstein, P.; Chauvin, Y.; Fischer, J.; Olivier, H.; Strohmann, C.; Toronto, D. V. *New J. Chem.* **2000**, *24*, 437.
(34) Camus, J.-M.; Morales, D.; Andrieu, J.; Richard, P.; Poli, R.; Braunstein, P.; Naud, F. *J. Chem. Soc., Dalton Trans.* **2000**, 2577.

The $^1H$ NMR chemical shifts of the aromatic protons have been omitted for clarity, since they are unexceptional.

The chlorophosphates $ClP(O)(OR)_2$ (Aldrich) were degassed before use. $AgBF_4$ (Avocado) and $TlPF_6$ (Strem) were dried overnight in vacuo before use. The compounds $Ph_2PCH_2C(O)Ph$,[35a] [$PdCl_2(COD)$],[36] [$Pd(Me)Cl(COD)$],[37] [$Pd(dmba)(\mu$-$Cl)]_2$,[38] [$Pd(\eta^3$-$C_3H_5)(\mu$-$Cl)]_2$,[39] [$Pd(NCMe)_4](BF_4)_2$,[40] and $Ph_2PN(Me)PPh_2$[35b,c] were prepared according to the literature.

**Syntheses. $Ph_2PCH=C(Ph)OP(O)(OEt)_2$ (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 $Ph_2PCH_2C(O)Ph$ (3.04 g, 10.0 mmol) was then added, at room temperature. This resulted in gas ($H_2$) evolution, whereas the solution progressively turned yellow-orange. After the evolution of $H_2$ 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 $CH_2Cl_2$, and the volatiles were evaporated, affording a beige solid, which was washed with $Et_2O$ (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.

**$Ph_2PCH=C(Ph)P(O)(OPh)_2$ (1b).** This compound was obtained as a white powder, in a manner similar to **1a** from $Ph_2PCH_2C(O)$-Ph (3.04 g, 10.0 mmol) and $ClP(O)(OPh)_2$ (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.

**[$PdCl_2\{Ph_2PCH=C(Ph)OP(O)(OEt)_2\}_2$] (2a).** Solid [$PdCl_2$(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 $CH_2Cl_2$ 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 $Et_2O$ (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 $C_{48}H_{52}Cl_2O_8P_4Pd$ ($M$ = 1058.146): C, 54.49; H, 4.95. Found: C, 54.32; H, 4.82.

**[$PdCl_2\{Ph_2PCH=C(Ph)OP(O)(OPh)_2\}_2$] (2b).** This complex was obtained as a yellow-orange solid, in a manner similar to **2a** from [$PdCl_2(COD)$] (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;

(35) (a) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765. (b) Wang, F. T.; Najdzionek, J.; Leneker, K. L.; Wasserman, H.; Braitsch, D. M. *Synth. React. Inorg. Metal-Org. Chem.* **1978**, *8*, 119. (c) Sekabunga, E. J.; Smith, M. L.; Webb, T. R.; Hill, W. E. *Inorg. Chem.* **2002**, *41*, 1205.
(36) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413.
(37) Lapido, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.
(38) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
(39) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *29*, 220.
(40) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1984**, *23*, 3257.

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

| compd | | $^1H$ NMR, $\delta$ [a] | | $^{31}P\{^1H\}$ NMR, $\delta$ [a] | | IR, cm$^{-1}$ [b] |
|---|---|---|---|---|---|---|
| | | H enolate of P ligand | other | P | PO | $\nu$(P=O) |
| $Ph_2PCH\!=\!C(Ph)OP(O)(OEt)_2$ | **1a** | 6.20 (dd, $^2J$(PH) = 3.1, $^4J$(PH) = 1.4) | 1.18 (dt, 6H, $CH_2CH_3$, $^3J$(HH) = 7.0, $^4J$(PH) = 1.0); 4.08 (m, 4H, $OCH_2$) | −29.8 | −7.0 | 1277s |
| $Ph_2PCH\!=\!C(Ph)OP(O)(OPh)_2$ | **1b** | 6.33 (dd, $^2J$(PH) = 3.5, $^4J$(PH) = 1.1) | | −28.4 | −18.0 | 1313s |
| $[PdCl_2\{PPh_2CH\!=\!C(Ph)OP(O)(OEt)_2\}_2]$ | **2a** | 6.24 (dt, $^2J$(PH) = 7.3, $^4J$(PH) = 1.6) (*trans* isomer) | 0.97 (t, 12H, $CH_2CH_3$, $^3J$(HH) = 7.1); 3.69 (m, 8H, $OCH_2$) | 4.6 (*trans*) | −8.1 (*trans*) | 1269s[c] |
| | | 5.62 (dd, $^2J$(PH) = 11.0, $^4J$(PH) = 2.1) (*cis* isomer) | 1.03 (t, 12H, $CH_2CH_3$, $^3J$(HH) = 7.1); 3.69 (m, 8H, $OCH_2$) | 12.1 (*cis*) | −8.0 (*cis*) | |
| $[PdCl_2\{PPh_2CH\!=\!C(Ph)OP(O)(OPh)_2\}_2]$ | **2b** | 6.54 (dt, $^2J$(PH) = 7.6, $^4J$(PH) = 1.7) (*trans* isomer) | | 4.8 (*trans*) | −19.6 (*trans*) | 1302s |
| | | 5.87 (dd, $^2J$(PH) = 11.4, $^4J$(PH) = 1.9) (*cis* isomer) | | 12.1 (*cis*) | −19.6 (*cis*) | |
| $[PdCl\{PPh_2CH\!=\!C(Ph)OP(O)(OEt)_2\}(\mu\text{-}Cl)]_2$ | **3a** | 5.92 (d br, $^2J$(PH) = 10.2, $^4J$(PH) not resolved) | 1.11 (t, 12H, $CH_2CH_3$, $^3J$(HH) = 7.0); 3.86 (m, 8H, $OCH_2$) | 13.7 | −8.6 | 1272s |
| $[PdCl\{PPh_2CH\!=\!C(Ph)OP(O)(OPh)_2\}(\mu\text{-}Cl)]_2$ | **3b** | 6.18 (d br, $^2J$(PH) = 10.9, $^4J$(PH) not resolved) | | 13.8 | −20.1 | 1294s[d] |
| $[PdMe\{PPh_2CH\!=\!C(Ph)OP(O)(OEt)_2\}(\mu\text{-}Cl)]_2$ | **4a** | 6.33 (br, $^2J$(PH) and $^4J$(PH) not resolved) | 0.75 (d, 6H, PdMe, $^3J$(PH) = 3.0); 1.11 (t, 12H, $CH_2CH_3$, $^3J$(HH) = 7.0); 4.15 (m br, 8H, $OCH_2$) | 19.9 | −5.3 | 1276s[c] |
| $[PdMe\{PPh_2CH\!=\!C(Ph)OP(O)(OPh)_2\}(\mu\text{-}Cl)]_2$ | **4b** | 5.97 (d br, $^2J$(PH) = 8.5, $^4J$(PH) = not resolved) | 0.77 (d, 6H, PdMe, $^3J$(PH) = 2.3) | 21.1 | −19.5 | 1299s |
| $[Pd(dmba)Cl\{PPh_2CH\!=\!C(Ph)OP(O)(OEt)_2\}]$ | **5a** | 6.02 (dd, $^2J$(PH) = 6.2, $^4J$(PH) = 1.3) | 1.04 (t, 6H, $CH_2CH_3$, $^3J$(HH) = 7.1); 2.84 (d, 6H, $NMe_2$, $^4J$(PH) = 3); 3.77 (m, 4H, $OCH_2$); 4.08 (d, 2H, $NCH_2$, $^4J$(PH) = 1.4) | 20.9 | −7.5 | 1272s |
| $[Pd(dmba)Cl\{PPh_2CH\!=\!C(Ph)OP(O)(OPh)_2\}]$ | **5b** | 6.32 (dd, $^2J$(PH) = 6.4, $^4J$(PH) = 1.7) | 2.77 (d, 6H, $NMe_2$, $^4J$(PH) = 2.3); 4.08 (d, 2H, $NCH_2$, $^4J$(PH) = 1.7) | 20.8 | −19.4 | 1304s |
| $[Pd(\eta^3\text{-allyl})Cl\{PPh_2CH\!=\!C(Ph)OP(O)(OEt)_2\}]$ [e] | **6a** | 6.02 (dd, $^2J$(PH) = 5.4, $^4J$(PH) = 1.2) | 1.06 (dt, 6H, $CH_2CH_3$, $^3J$(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 $H_d$, $^3J$($PH_d$) ≈ $^3J$($H_cH_d$) ≈ 7.2); 5.66 (m, 1H, allyl $H_c$) | 4.0 | −7.7 | 1281s |
| $[Pd(\eta^3\text{-allyl})Cl\{PPh_2CH\!=\!C(Ph)OP(O)(OPh)_2\}]$ [e] | **6b** | 6.21 (dd, $^2J$(PH) = 5.8, $^4J$(PH) = 1.2) | 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 $H_d$, $^3J$($PH_d$) ≈ $^3J$($H_cH_d$) ≈ 7.0); 5.41 (m, 1H, allyl $H_c$) | 5.3 | −19.2 | 1304s |
| $[PdMe(NCMe)\{Ph_2PCH\!=\!C(Ph)OP(O)(OEt)_2\}][BF_4]$ | **7a** | 6.29 (dd, $^2J$(PH) = 6.0, $^4J$(PH) = 2.4) | 0.58 (d, 3H, PdMe, $^3J$(PH) = 2.5); 1.11 (dt, 6H, $CH_2CH_3$, $^3J$(HH) = 7.0, $^4J$(PH) = 1.3); 2.32 (s, 3H, MeCN); 4.08 (m, 4H, $OCH_2$) | 22.9 | −6.1 | 1227s |
| $[PdMe(NCMe)\{Ph_2PCH\!=\!C(Ph)OP(O)(OPh)_2\}][BF_4]$ | **7b** | 6.37 (dd, $^2J$(PH) = 5.2, $^4J$(PH) = 2.3) | 0.59 (d, 3H, PdMe, $^3J$(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, $^2J$(PH) = 4.9, $^4J$(PH) = 2.3) | 0.59 (d, 3H, PdMe, $^3J$(PH) = 2.3); 2.23 (s, 3H, MeCN) | 21.4 | −16.1 | 1241s |
| $[Pd(dmba)\{PPh_2CH\!=\!C(Ph)OP(O)(OEt)_2\}][BF_4]$ | **8a** | 6.32 (dd, $^2J$(PH) = 7.6, $^4J$(PH) = 2.7) | 1.07 (dt, 6H, $CH_2CH_3$, $^3J$(HH) = 7.1, $^4J$(PH) = 1.4); 2.82 (d, 6H, $NMe_2$, $^4J$(PH) = 2.6); 4.01 (m, 4H, $OCH_2$); 4.10 (d, 2H, $NCH_2$, $^4J$(PH) = 1.2) | 24.0 | −7.7 | 1228s |
| $[Pd(dmba)\{PPh_2CH\!=\!C(Ph)OP(O)(OEt)_2\}][PF_6]$ | **8a′** | 6.37 (dd, $^2J$(PH) = 7.5, $^4J$(PH) = 2.7) | 1.09 (dt, 6H, $CH_2CH_3$, $^3J$(HH) = 7.0, $^4J$(PH) = 1.4); 2.79 (d, 6H, $NMe_2$, $^4J$(PH) = 2.5); 3.94 (m, 4H, $OCH_2$); 4.09 (d, 2H, $NCH_2$, $^4J$(PH) = 1.2) | 24.2 | −7.5 | 1240s |
| $[Pd(dmba)\{PPh_2CH\!=\!C(Ph)OP(O)(OPh)_2\}][BF_4]$ | **8b** | 6.50 (dd, $^2J$(PH) = 6.9, $^4J$(PH) = 2.4) | 2.47 (d, 6H, $NMe_2$, $^4J$(PH) = 1.9); 4.02 (s, 2H, $NCH_2$, $^4J$(PH) not resolved) | 23.5 | −17.3 | 1240s |

**Table 1.** (Continued)

| compd | | H enolate of P ligand | other | P | PO | IR, cm$^{-1b}$ $\nu$(P=O) |
|---|---|---|---|---|---|---|
| | | | | **$^{31}$P{$^1$H} NMR, $\delta^a$** | | **IR, cm$^{-1b}$** |
| $[Pd(\eta^3\text{-allyl})\{PPh_2CH=C(Ph)OP(O)\text{-}(OEt)_2\}][BF_4]^e$ | **9a** | 6.41 (dd, $^2J$(PH) = 3.6, $^4J$(PH) = 1.8) | 1.08 (dt, 6H, CH$_2$C$H_3$, $^3J$(HH) = 7.0, $^4J$(PH) = 1.3); 3.10 (br, overlapping signals, 2H, allyl H$_b$ and H$_a$); 4.00 (m, 4H, OCH$_2$); 4.26 (br, 1H, allyl H$_d$ or H$_e$); 5.01 (br, 1H, allyl H$_d$ or H$_e$); 6.01 (apparent quint, 1H, allyl H$_c$) | 11.3 | −6.5 | 1208s$^d$ |
| $[Pd(\eta^3\text{-allyl})\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}][BF_4]^e$ | **9b** | 6.56 (br, $^2J$(PH) and $^4J$(PH) not observed) | 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$_c$) | 11.3 | −16.0 | 1226s |
| *cis*-$[Pd\{PPh_2CH=C(Ph)OP(O)\text{-}(OEt)_2\}_2][BF_4]_2$ | **10a** | 6.79 (dd, $^2J$(PH) = 10.5, $^4J$(PH) = 2.5) | 1.13 (dt, 12H, CH$_2$C$H_3$, $^3J$(HH) = 7.1, $^4J$(PH) = 1.3); 4.05 (m, 8H, OCH$_2$) | 28.4 (d, $J$(PP) = 16) | −11.0 (d) | 1221s |
| *cis*-$[Pd\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}_2][BF_4]_2$ | **10b** | 6.99 (dd, $^2J$(PH) = 10.0, $^4J$(PH) = 2.5) | | 29.4 (d, $J$(PP) = 16) | −21.0 (d) | 1244s$^c$ |
| $[PdMe\{PPh_2CH=C(Ph)OP(O)\text{-}(OEt)_2\}\{PPh_2CH=C(Ph)OP(O)\text{-}(OEt)_2\}][BF_4]$ | **11a** | 6.31 (m br) | 0.28 (m br, 3H, Pd-Me); 0.99 (m, 12H, CH$_2$C$H_3$); 3.66 (m, 4H, OCH$_2$), 4.09 (m, 4H, OCH$_2$) | 13.3 | −6.6 | 1272s, 1225s |
| $[PdMe\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}][BF_4]$ | **11b** | 6.28 (m) | 0.56 (apparent t, 3H, Pd-Me $^3J$(PH) = 6.4) | 13.9 | −18.3 | 1310s, 1243s |
| $[PdCl\{PPh_2N(Me)PPh_2\}\text{-}\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}][CF_3SO_3]$ | **12** | 6.30 (dd, $^2J$(PH) = 12.0, $^4J$(PH) = 3.0) | 2.56 (dd, $^2J$(PH) = 11.6 and 11) | 2.3 (d, $^2J$(PP) = 480, P of **1b**); 32.5 (dd, $^2J$(PP) = 480 and 46, P*N*P *trans* to **1b**); 37.6 (d, $^2J$(PP) = 46, PN*P cis* to **1b**) | −20.0 | 1271s |
| $[PdMe\{PPh_2NHC(O)Me\}\text{-}\{PPh_2CH=C(Ph)OP(O)\text{-}(OEt)_2\}][BF_4]$ | **13a** | 5.84 (dd, $^2J$(PH) = 4.0, $^4J$(PH) = 3.7) | 0.80 (dd, 3H, Pd-Me, $^3J$(PH) = 6.4 and 5.8); 0.93 (m, 6H, CH$_2$C$H_3$); 2.40 (s, 3H, C(O)CH$_3$); 3.66 (m, 4H, OCH$_2$); 9.56 (br, 1H, NH) | 8.8 (d, P of **1a**, $^2J$(PP) = 401); 70.8 (d, PNH) | −6.1 | 1271s [1608s, $\nu$(CO)] |
| $[PdMe\{PPh_2NHC(O)Me\}\text{-}\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}][BF_4]$ | **13b** | 6.08 (m) | 0.85 (m, 3H, Pd-Me); 2.14 (s, C(O)CH$_3$); 9.57 (br, 1H, NH) | 8.5 (d, P of **1b**, $^2J$(PP) = 412); 71.0 (d, PN) | −17.8 | 1301s [1608s, $\nu$(CO)] |
| $[PdMe\{PPh_2CH=C(Ph)OP(O)\text{-}(OEt)_2\}\{PPh_2CH_2C(O)Ph\}]\text{-}[BF_4]$ | **14a** | 6.43 (m) | 0.33 (dd, 3H, Pd-Me, $^3J$(PH) = 6.4 and 6.2); 0.75 (m, 6H, CH$_2$C$H_3$); 3.53 (m, 4H, OCH$_2$); 4.36 (m, 2H, PCH$_2$) | 15.0 (P of **1a**, $J$(PP) = 408);$^f$ 18.3 (PCH$_2$)$^g$ | −6.8 | 1223s [1672s, $\nu$(CO)] |
| $[PdMe\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}\{PPh_2CH_2C(O)Ph\}]\text{-}[BF_4]$ | **14b** | 6.30 (m) | 0.63 (dd, 3H, Pd-Me, $^3J$(PH) = 6.7 and 5.9); 4.31 (dd, 2H, PCH$_2$, $^2J$(PH) = 10.2, $^4J$(PH) = 1.6) | 12.5 (P of **1b**, $J$(PP) = 401);$^f$ 23.2 (PCH$_2$)$^g$ | −17.9 | 1241s [1672, $\nu$(CO)] |
| $[PdMe\{PPh_2CH=C(Ph)OP(O)\text{-}(OEt)_2\}\{PPh_2CH=C(Ph)OP(O)\text{-}(OPh)_2\}][BF_4]$ | **17** | 6.10 (m, P−C$H$=CPh of **1b**); 6.40 (m, P−C$H$=CPh of **1a**) | 0.50 (m, 3H, Pd-Me); 0.84 (m, 6H, CH$_2$C$H_3$); 3.55 (m, 4H, OCH$_2$) | 12.1 (P of **1b**, $^2J$(PP) = 404);$^f$ 16.6 (P of **1a**)$^g$ | −7.6 (**1a**) −18.1 (**1b**) | 1310s (**1b**) 1226vs (**1a**) |

$^a$ Recorded in CDCl$_3$ unless otherwise stated, coupling constants in Hz, aromatic protons are omitted for clarity since their chemical shifts are totally unexceptional. $^b$ Recorded in Nujol unless otherwise stated. $^c$ In KBr. $^d$ In CDCl$_3$. $^e$ Numbering of the allylic protons as pictured:
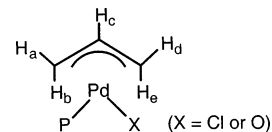


$^f$ Part A of an AB spin system. $^g$ Part B of an AB spin system.

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$_2$Cl$_2$ solution of **2b**.

**[PdCl{Ph$_2$PCH=C(Ph)OP(O)(OEt)$_2$}($\mu$-Cl)]$_2$ (3a).** This complex was obtained as an orange solid, in a manner similar to **2a** from [PdCl$_2$(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 $Et_2O$ into a $CH_2Cl_2$ solution of **2b**.

**[PdCl{Ph₂PCH=C(Ph)OP(O)(OPh)₂}(μ-Cl)]₂ (3b).** This complex was obtained as an orange solid, in a manner similar to **2a** from $[PdCl_2(COD)]$ (0.345 g, 1.2 mmol) and **1b** (0.648 g, 1.2 mmol). Yield: 0.760 g (88%). Anal. Calcd for $C_{64}H_{52}Cl_2O_8P_4Pd_2$ ($M = 1427.63$): C, 53.85; H, 3.67. Found: C, 54.17; H, 3.81.

**[PdMe{Ph₂PCH=C(Ph)OP(O)(OEt)₂}(μ-Cl)]₂ (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 $C_{50}H_{58}Cl_2O_8P_4Pd_2$ ($M = 1194.62$): C, 50.27; H, 4.89. Found: C, 50.17; H, 4.84.

**[PdMe{Ph₂PCH=C(Ph)OP(O)(OPh)₂}(μ-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 $C_{66}H_{58}Cl_2O_8P_4Pd_2$ ($M = 1386.82$): C, 57.16; H, 4.22. Found: C, 56.98; H, 4.11.

**[Pd(dmba)Cl{Ph₂PCH=C(Ph)OP(O)(OEt)₂}] (5a).** Solid [Pd-(dmba)(μ-Cl)]₂ (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, $CH_2Cl_2$ (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 $Et_2O$ (2 × 15 mL) and pentane (20 mL). Complex **5a** was obtained as a green-yellow solid (0.645 g, 89%). Anal. Calcd for $C_{33}H_{38}ClNO_4P_2Pd$ ($M = 716.48$): C, 55.32; H, 5.35; N, 1.95. Found: C, 55.60; H, 5.22; N, 1.97.

**[Pd(dmba)Cl{Ph₂PCH=C(Ph)OP(O)(OPh)₂}] (5b).** This complex was obtained as a pale green-yellow solid, in a manner similar to **5a** from [Pd(dmba)(μ-Cl)]₂ (0.331 g, 0.6 mmol) and **1b** (0.643 g, 1.2 mmol). Yield: 0.853 g (87%). Anal. Calcd for $C_{41}H_{38}ClNO_4P_2Pd$ ($M = 812.56$): C, 60.61; H, 4.71; N, 1.72. Found: C, 60.81; H, 4.86; N, 1.71.

**[Pd(η³-C₃H₅)Cl{Ph₂PCH=C(Ph)OP(O)(OEt)₂}] (6a).** This complex was obtained as a yellow solid, in a manner similar to **5a** from [Pd(η³-C₃H₅)(μ-Cl)]₂ (0.205 g, 0.56 mmol) and **1a** (0.493 g, 1.12 mmol). Yield: 0.635 g (91%). Anal. Calcd for $C_{27}H_{31}ClO_4P_2Pd$ ($M = 623.34$): C, 52.03; H, 5.01. Found: C, 51.72; H, 4.94.

**[Pd(η³-C₃H₅)Cl{Ph₂PCH=C(Ph)OP(O)(OPh)₂}] (6b).** This complex was obtained as a yellow solid, in a manner similar to **5a** from [Pd(η³-C₃H₅)(μ-Cl)]₂ (0.165 g, 0.43 mmol) and **1b** (0.461 g, 0.86 mmol). Yield: 0.590 g (94%). Anal. Calcd for $C_{35}H_{31}ClO_4P_2Pd$ ($M = 719.44$): C, 58.43; H, 4.34. Found: C, 58.04; H, 4.30.

**[PdMe(NCMe){Ph₂PCH=C(Ph)OP(O)(OEt)₂}](BF₄) (7a).** To a MeCN (20 mL) solution of **4a** (0.109 g, 0.18 mmol) was added in one portion solid $AgBF_4$ (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 $Et_2O$ (2 × 15 mL). Compound **7a** was obtained as a pale brown powder (0.132 g, 84% yield). Anal. Calcd for $C_{27}H_{32}BF_4NO_4P_2Pd$ ($M = 689.71$): C, 47.02; H, 4.68; N, 2.03. Found: C, 46.68; H, 4.33; N, 1.66.

**[PdMe(NCMe){Ph₂PCH=C(Ph)OP(O)(OPh)₂}](BF₄) (7b).** This complex was obtained as a beige powder, in a manner similar to **7a** from **4b** (0.094 g, 0.067 mmol) and $AgBF_4$ (0.026 g, 0.136 mmol). A 1/1 mixture of MeCN and $CH_2Cl_2$ was used, owing to the poor solubility of **4b** in pure MeCN. Yield: 0.084 g (79%). Anal. Calcd for $C_{35}H_{32}BF_4NO_4P_2Pd$ ($M = 785.80$): C, 53.50; H, 4.10; N, 1.78. Found: C, 53.56; H, 4.18; N, 1.80.

**[PdMe(NCMe){Ph₂PCH=C(Ph)OP(O)(OPh)₂}](PF₆) (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 $TlPF_6$ (0.123 g, 0.354 mmol). Yield: 0.256 g (86%). Anal. Calcd for $C_{35}H_{32}F_6NO_4P_3Pd$ ($M = 843.96$): C, 49.81; H, 3.82; N, 1.66. Found: C, 49.72; H, 3.66; N, 1.80.

**[Pd(dmba){Ph₂PCH=C(Ph)OP(O)(OEt)₂}](BF₄) (8a).** This complex was obtained as a yellow powder, in a manner similar to **7b**, using $CH_2Cl_2$ as solvent, from **5a** (0.094 g, 0.13 mmol) and $AgBF_4$ (0.025 g, 0.13 mmol). Yield: 0.072 g (72%). Anal. Calcd for $C_{33}H_{38}BF_4NO_4P_2Pd$ ($M = 767.83$): C, 51.62; H, 4.99; N, 1.82. Found: C, 51.76; H, 4.94; N, 1.90.

**[Pd(dmba){Ph₂PCH=C(Ph)OP(O)(OEt)₂}](PF₆) (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 $TlPF_6$ (0.070 g, 0.2 mmol). Yield: 0.135 g (82%). Anal. Calcd for $C_{33}H_{38}F_6NO_4P_3Pd$ ($M = 825.99$): 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 $Et_2O$ into a $CH_2Cl_2$ solution of **8a′**.

**[Pd(dmba){Ph₂PCH=C(Ph)OP(O)(OPh)₂}](BF₄) (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 $AgBF_4$ (0.098 g, 0.5 mmol). Yield: 0.376 g (87%). Anal. Calcd for $C_{41}H_{38}BF_4NO_4P_2Pd$ ($M = 863.92$): C, 57.00; H, 4.43; N, 1.62. Found: C, 57.17; H, 4.48; N, 1.71.

**[Pd(η³-C₃H₅){Ph₂PCH=C(Ph)OP(O)(OEt)₂}](BF₄) (9a).** To a $CH_2Cl_2$ (20 mL) solution of **6a** (0.150 g, 0.24 mmol) was added in one portion solid $AgBF_4$ 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 $Et_2O$ (2 × 15 mL). Compound **9a** was obtained as a pale green-brown powder (0.120 g, 75% yield). Anal. Calcd for $C_{27}H_{31}BF_4O_4P_2Pd$ ($M = 674.70$): C, 48.07; H, 4.63. Found: C, 47.85; H, 4.77.

**[Pd(η³-C₃H₅){Ph₂PCH=C(Ph)OP(O)(OPh)₂}](BF₄) (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 $AgBF_4$ (0.050 g, 0.25 mmol, excess). Yield: 0.118 g (81%). Anal. Calcd for $C_{35}H_{31}BF_4O_4P_2Pd$ ($M = 770.79$): C, 54.54; H, 4.05. Found: C, 54.17; H, 3.69.

**cis-[Pd{Ph₂PCH=C(Ph)OP(O)(OEt)₂}₂](BF₄)₂ (10a).** Solid [Pd(NCMe)₄](BF₄)₂ (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 $CH_2Cl_2$ (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 $Et_2O$ (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 $C_{48}H_{52}B_2F_8O_8P_4Pd$ ($M = 1160.85$): 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 $Et_2O$ into a $CH_2Cl_2$ solution of **10a**.

**cis-[Pd{Ph₂PCH=C(Ph)OP(O)(OPh)₂}₂](BF₄)₂ (10b).** This complex was obtained as a yellow solid, in a manner similar to **10a** from [Pd(NCMe)₄](BF₄)₂ (0.098 g, 0.22 mmol) and **1b** (0.236 g, 0.44 mmol). Yield: 0.262 g (88%). Anal. Calcd for $C_{64}H_{52}B_2F_8O_8P_4Pd$ ($M = 1353.03$): C, 56.81; H, 3.87. Found: C, 57.12; H, 3.67.

**[PdMe{Ph₂PCH=C(Ph)OP(O)(OEt)₂}{Ph₂PCH=C(Ph)OP-(O)(OEt)₂}][BF₄] (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 CH₂Cl₂ (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 Et₂O (10 mL) and pentane (10 mL). Complex **11a** was obtained as a pale brown solid (0.075 g, 95% yield). Anal. Calcd for C₄₉H₅₅-BF₄O₈P₄Pd ($M$ = 1089.08): C, 54.04; H, 5.09. Found: C, 54.44; H, 5.38.

**[PdMe{Ph₂PCH=C(Ph)OP(O)(OPh)₂}{Ph₂PCH=C(Ph)OP-(O)(OPh)₂}][BF₄] (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 C₆₅H₅₅BF₄O₈P₄Pd·0.5 CH₂Cl₂ ($M$ = 11281.26 + 42.47): C, 59.43; H, 4.26. Found: C, 59.55; H, 4.36.

**[PdCl{Ph₂PN(Me)PPh₂}{Ph₂PCH=C(Ph)OP(O)(OPh)₂}][CF₃-SO₃] (12).** [PdCl₂(COD)] (0.365 g, 1.278 mmol) and Ph₂PN(Me)-PPh₂ (0.510 g, 1.278 mmol) were placed in a Schlenk flask and degassed in vacuo, before CH₂Cl₂ (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 Et₂O (2 × 10 mL) and hexane (15 mL), which afforded [PdCl₂{Ph₂PN(Me)PPh₂}] as a pale yellow solid (0.665 g, 90% yield,³¹P{¹H} NMR: δ 31 ppm). The latter was suspended in a CH₂Cl₂/acetonitrile mixture (ratio: 1/1, 25 mL), before AgSO₃-CF₃ (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 Et₂O (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 C₅₈H₄₉ClF₃NO₇P₄PdS ($M$ = 1226.84): C, 56.78; H, 4.03; N, 1.14. Found: C, 56.39; H, 4.08; N, 1.21.

**[PdMe{Ph₂PNHC(O)Me}{Ph₂PCH=C(Ph)OP(O)(OEt)₂}]-[BF₄] (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 Ph₂-PNHC(O)Me (0.018 g, 0.077 mmol). Yield: 0.063 g (92%). Anal. Calcd for C₃₉H₄₃BF₄NO₅P₃Pd ($M$ = 891.91): C, 52.52; H, 4.86; N, 1.57. Found: C, 52.28; H, 4.91; N, 1.69.

**[PdMe{Ph₂PNHC(O)Me}{Ph₂PCH=C(Ph)OP(O)(OPh)₂}]-[BF₄] (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 Ph₂-PNHC(O)Me (0.013 g, 0.056 mmol). Yield: 0.048 g (88%). Anal. Calcd for C₄₇H₄₃BF₄NO₅P₃Pd ($M$ = 988.00): C, 57.14; H, 4.39; N, 1.42. Found: C, 57.38; H, 4.51; N, 1.31.

**[PdMe{Ph₂PCH=C(Ph)OP(O)(OEt)₂}{Ph₂PCH₂C(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 Ph₂-PCH₂C(O)Ph (0.020 g, 0.067 mmol) in 90% yield (0.058 g), or from [PdMe{Ph₂PCH₂C(O)Ph}(NCMe)][BF₄] (**16**) (0.055 g, 0.099 mmol) and **1a** (0.043 g, 0.099 mmol) in 92% yield (0.087 g). It could not be separated from **11a** and [PdMe{Ph₂PCH₂C(O)Ph}{Ph₂-PCH₂C(O)Ph}][BF₄] (**15**). The relative ratio **14a/11a/15**, determined by ³¹P{¹H} NMR spectroscopy, is 9:1:1. Anal. Calcd for C₄₅H₄₆-BF₄O₅P₃Pd·0.5CH₂Cl₂ ($M$ = 952.99 + 42.47): C, 54.90; H, 4.76. Found: C, 55.29; H, 4.63.

**[PdMe{Ph₂PCH=C(Ph)OP(O)(OPh)₂}{Ph₂PCH₂C(O)Ph}]-[BF₄] (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 Ph₂PCH₂C(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 ³¹P{¹H} NMR spectroscopy, is 4:1:1. Yield: 0.050 g (97%). Anal. Calcd for C₅₃H₄₆BF₄O₅P₃Pd·0.5CH₂Cl₂ ($M$ = 1049.08 − 42.47): C, 58.87; H, 4.34. Found: C, 58.62; H, 4.26.

**[PdMe{Ph₂PCH=C(Ph)OP(O)(OEt)₂}{Ph₂PCH=C(Ph)OP-(O)(OPh)₂}][BF₄] (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 ³¹P{¹H} NMR spectroscopy, is 4:1:1. Anal. Calcd for C₅₇H₅₅-BF₄O₈P₄Pd ($M$ = 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 Kα radiation λ = 0.71073 Å) (*trans*-**2b**, **3a**, and **18**), an Enraf-Nonius CAD4 diffractometer (graphite monochromated Mo Kα radiation λ = 0.71073 Å) (**8a′**), and a Philips PW1100 diffractometer (graphite monochromated Cu Kα radiation λ = 1.54184 Å) (**10a**). The structures were solved using the direct-methods program SIR,⁴¹ except for **18**, for which the SHELXS-97 was used.⁴² Subsequent full-matrix least-squares refinements were carried out using the SHELXL-97 program.⁴² 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 Ph₂-PCH=C(Ph)OP(O)(OR)₂ (1).** Deprotonation of Ph₂PCH₂C-(O)Ph³⁵ᵃ with KH, in THF at room temperature, yielded the corresponding enolate K[Ph₂PCH⋯C(⋯O)Ph] **A**,⁴³ which was reacted in situ with ClP(O)(OR)₂ to afford the new phosphine−phosphates Ph₂PCH=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)NPh₂] were reacted with Ph₂PCl, to give the keto-phosphine Ph₂PCH₂C(O)Ph³⁵ᵃ and the bisphosphine (Ph₂P)₂-CHC(O)NPh₂,³⁰ respectively. The ³¹P{¹H} NMR spectra of **1a,b** consisted in a single phosphine resonance at ca. δ −29, accompanied by a signal at lower field, δ −7.0 (**1a**) or −18.0 (**1b**), which was ascribed to the phosphate moiety (Table 1). In addition, both ¹H NMR spectra showed only one enolate resonance (Table 1). The absence of any $J$(PP)

(41) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. SIR Program. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(42) Sheldrick, G. M. *SHELXL97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(43) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C.; Dedieu, A.; Ingold, F.; Braunstein, P. *Organometallics* **1993**, *12*, 4359.

**Scheme 1**



**Scheme 2**
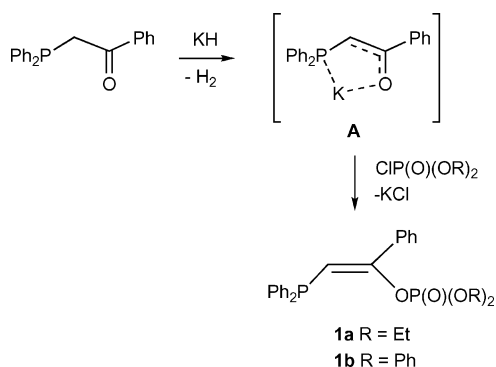


coupling in the $^{31}$P{$^1$H} NMR spectra and the magnitude of the $^2J$(PH) for the enolate protons (3.1 and 3.5 Hz for **1a** and **1b**, respectively) suggested that only the *Z*-isomers were obtained in this reaction. This was confirmed by the X-ray structures of some of the Pd complexes obtained 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).[43] Then, subsequent reactions with chlorophosphates would lead to the *Z*-isomers of **1**. Similar intermediates have been reported for the deprotonated form of methylenediphosphonates, β-ketophosphonates, or phosphine oxides.[44−46]

**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 ν(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 (Δδ = +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$_2$PCH=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.[47] 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 $^{31}$P resonances of the phosphine moieties of the *trans* isomers occurred at higher field than those of the *cis* isomer (δ ca. 4.7 vs 12.1),[48−50] whereas in the $^1$H NMR spectra, the opposite trend was observed for
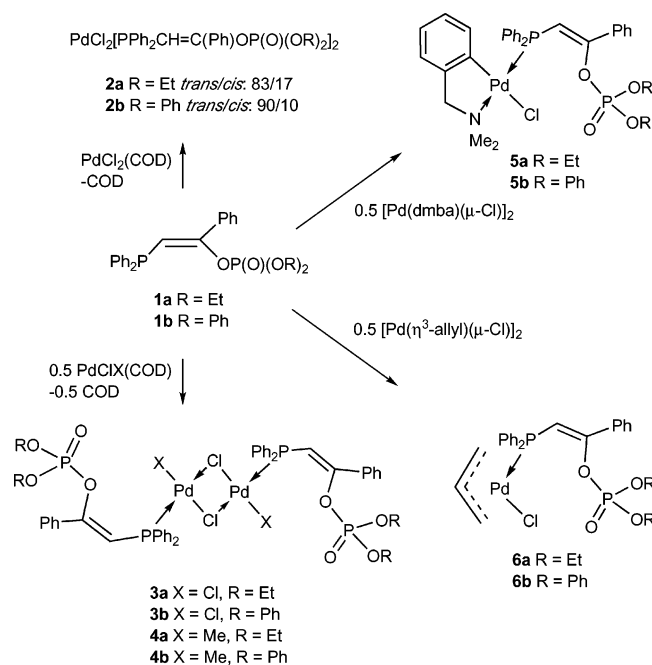
the enolate proton resonances (Table 1). Interestingly, in the latter case, the signals for the *cis* and *trans* isomers showed not only different intensities, but also different patterns. Indeed, in contrast to the doublet of doublets observed for the *cis* isomer, the enolate protons of the *trans* 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.[51,52]

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$_2$PCH=C(Ph)OP-(O)(OEt)$_2$}(μ-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 $^1$H NMR spectra of **5a,b**, the $^4J$(PH) couplings observed for the NMe$_2$ and CH$_2$ 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).[53,54] The $^{31}$P resonances of the η$^3$-allyl complexes **6a,b** were observed at higher field (δ ca. 5) than those of **5a,b** (δ ca. 20.8). Both the chemical shifts and the patterns of the $^1$H allylic resonances of **6a,b** resemble those reported for other [(η$^3$-allyl)PdCl(PR$_3$)] complexes (Table 1).[55,56]

(44) Iorga, B.; Savignac, P. *J. Organomet. Chem.* **2001**, *624*, 203 and references therein.

(45) Evreinov, V. I.; Antoshin, A. E.; Safronova, Z. V.; Kharitonov, A. V.; Tsvetkov, E. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 873.

(46) Truter, M. R.; Lestas, C. N. *J. Chem. Soc. A* **1971**, 738.

(47) *trans* and *cis* isomers refer to the arrangement of the P atoms around the Pd center.

(48) Verstuyft, A. W.; Lewis, W. C.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 1495.

(49) Nelson, J. H.; Rahn, J. A.; Bearden, W. H. *Inorg. Chem.* **1987**, *26*, 2193.

(50) Burrows, A. D.; Mahon, M. F.; Palmer, M. T. *J. Chem. Soc., Dalton Trans.* **2000**, 1669.

(51) Verstuyft, A. W.; Nelson, J. H.; Redfield, D. A.; Cary, L. W. *Inorg. Chem.* **1976**, *15*, 1128.

(52) Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1977**, *16*, 2776.

(53) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

(54) Braunstein, P.; Frison, C.; Morise, X.; Adams, R. D. *J. Chem. Soc., Dalton Trans.* **2000**, 2205.

(55) Faller, J. W.; Blankenship, C.; Whitmore, B.; Sena, S. *Inorg. Chem.* **1985**, *24*, 4483.

(56) Braunstein, P.; Naud, F.; Dedieu, A.; Rohmer, M.-M.; DeCian, A.; Rettig, S. J. *Organometallics* **2001**, *20*, 2966.

**Table 2.** Selected Crystallographic Data for Complexes *trans*-**2b**, **3a**·2Et₂O, **8a**′, **10a**·CH₂Cl₂, and **18**
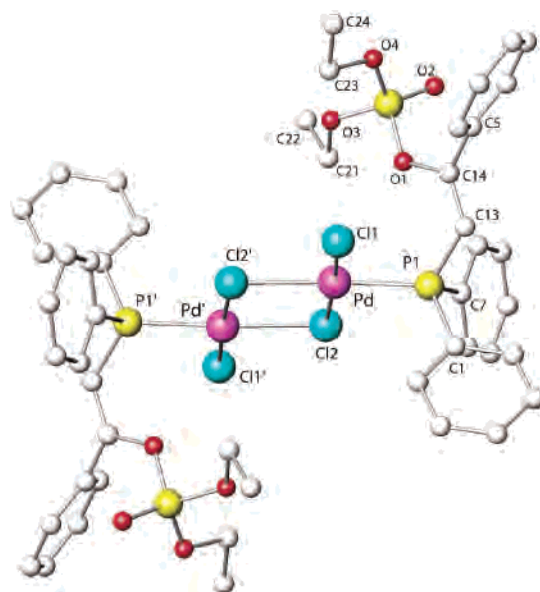
| | *trans*-**2b** | **3a**·2Et₂O | **8a**′ | **10a**·CH₂Cl₂ | **18** |
|---|---|---|---|---|---|
| formula | $C_{64}H_{52}Cl_2O_8P_4Pd$ | $C_{48}H_{52}Cl_4O_8P_4Pd_2 \cdot C_4H_{10}O$ | $C_{33}H_{38}F_6NO_4P_3Pd$ | $C_{48}H_{32}B_2F_8O_8P_4Pd \cdot CH_2Cl_2{}^a$ | $C_{23}H_{26}BF_4N_2OPPd$ |
| fw | 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 | $P\bar{1}$ | $C2/c$ | $P2_1/c$ | $Pnna$ | $P\bar{1}$ |
| $T$/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) |
| $\alpha$/deg | 71.93(5) | 90 | 90 | 90 | 99.023(5) |
| $\beta$/deg | 86.04(5) | 96.923(3) | 100.346(5) | 90 | 104.466(5) |
| $\gamma$/deg | 77.52(5) | 90 | 90 | 90 | 95.540(5) |
| $V$/Å³ | 2865.7(9) | 5775.0(2) | 3675.1(2) | 5546.5(8) | 1199.2(10) |
| $Z$ | 2 | 4 | 4 | 4 | 2 |
| $F(000)$ | 1280 | 2664 | 1680 | 2464 | 576 |
| $\mu$/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 |
| $R_w$ | 0.1054 | 0.1599 | 0.1233 | 0.1615 | 0.1171 |

*a* The 20 OEt protons have not been included owing to the significant disorder oberved for these groups.
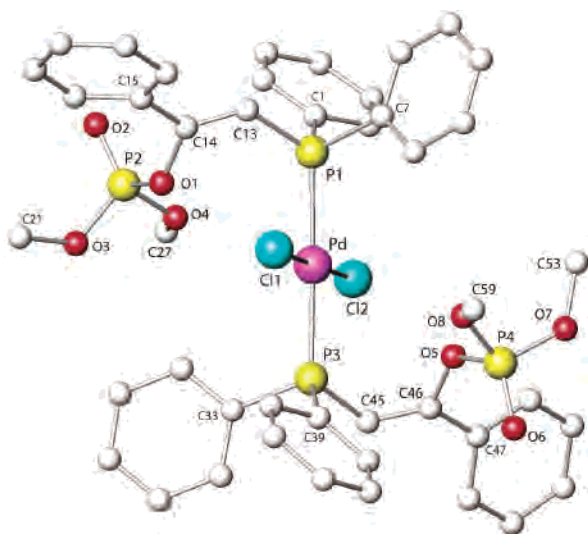


**Figure 1.** ATOMS view of the molecular structure of *trans*-**2b**; for better clarity, only the *ipso* carbon atoms of the phenyl groups of the phosphate moieties have been represented.



**Figure 2.** ATOMS view of the molecular structure of **3a**·2Et₂O.

**Crystal Structures of *trans*-2b and 3a.** Views of the crystal structures of *trans*-[PdCl₂{Ph₂PCH=C(Ph)OP(O)-(OPh)₂}₂] (**2b**) and [PdCl{Ph₂PCH=C(Ph)OP(O)(OEt)₂}(μ-Cl)]₂ (**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*-[PdCl₂(L)₂][50,57,58] and [PdCl(L)(μ-Cl)]₂ complexes (L = phosphine).[59,60] Bond

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 Ph₂P 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 penta-coordinated 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 negligible, 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

(57) Leznoff, D. B.; Rancurel, C.; Sutter, J. P.; Rettig, S. J.; Pink, M.; Kahn, O. *Organometallics* **1999**, *18*, 5097.

(58) Pitter, S.; Dinjus, E.; Jung, B.; Gorls, H. *Z. Naturforsch., B* **1996**, *51*, 934.
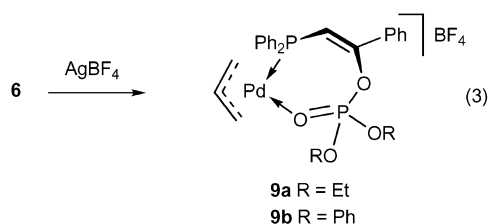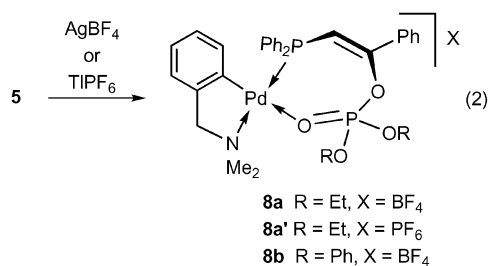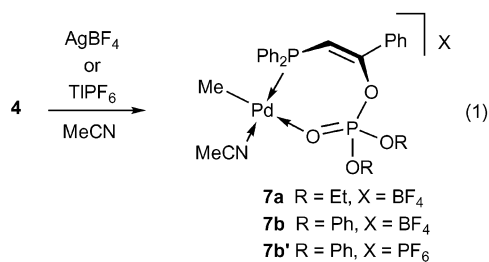
(59) Coles, S. J.; Faulds, P.; Hurthouse, M. B.; Kelly, D. G.; Ranger, G. C.; Toner, A. J.; Walker, N. M. *J. Organomet. Chem.* **1999**, *586*, 234.

(60) 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 chloro-derivatives **4**−**6** with AgBF$_4$ (or TlPF$_6$ 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$^{-1}$) than those of **4**−**6**. A slight low field shift of the $^1$H and $^{31}$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** | | **3a** | |
|---|---|---|---|
| Pd−Cl1 | 2.2924(6) | Pd−Cl1 | 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′** and **10a·**CH$_2$Cl$_2$

| **8a′** | | **10a·**CH$_2$Cl$_2$ | |
|---|---|---|---|
| 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$_2$PCH=C(Ph)OP-(O)(OEt)$_2$}][PF$_6$] (**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.[61−66] 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
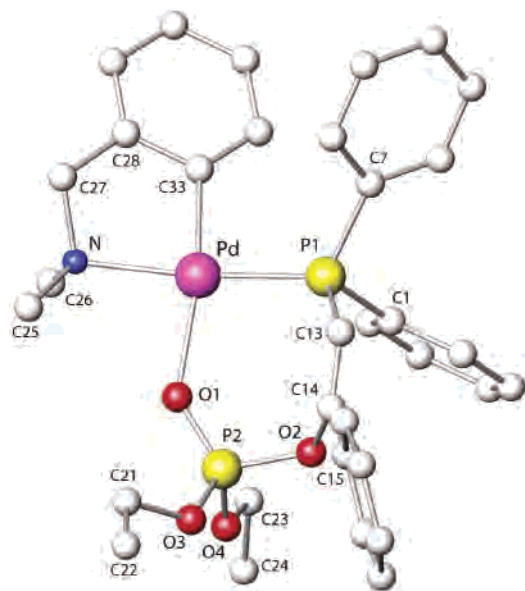
**Figure 3.** ATOMS view of the molecular structure of the cation in **8a′**.

related systems.[61,62,66,67] 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 seven-membered 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 six-membered P,O-metallocycles, which range from 80° to 85°[61–63,65,68–71] and 88° to 93.5°,[64,72–77] respectively. In the case of a Pd atom chelated with a BINAPO ligand (BINAPO = 2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthalene), the P,O-bite angle of the resulting eight-membered ring [90.9(1)°][78] is also more acute than in **8a′**. As a probable

(61) Braunstein, P.; Matt, D.; Nobel, D.; Bouaoud, S.-E.; Grandjean, D. *J. Organomet. Chem.* **1986**, *301*, 401.
(62) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.
(63) Andrieu, J.; Braunstein, P.; Dusausoy, Y.; Ghermani, N. E. *Inorg. Chem.* **1996**, *35*, 7174.
(64) Coyle, R. J.; Slovokhotov, Y. L.; Antipin, M. Y.; Grushin, V. V. *Polyhedron* **1998**, *17*, 3059.
(65) Ma, J.-F.; Kojima, Y.; Yamamoto, Y. *J. Organomet. Chem.* **2000**, *616*, 149.
(66) Mattheis, C.; Braunstein, P. *J. Organomet. Chem.* **2001**, *621*, 218.
(67) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *J. Chem. Soc., Chem. Commun.* **1987**, 489.
(68) Lindner, E.; Schmid, M.; Wegner, P.; Nachtigal, C.; Steimann, M.; Fawzi, R. *Inorg. Chim. Acta* **1999**, *296*, 103.
(69) Slawin, A. M. Z.; Smith, M. B.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 1283.
(70) Matt, D.; Sutter-Beydoun, N.; Brunette, J. P.; Balegroune, F.; Grandjean, D. *Inorg. Chem.* **1993**, *32*, 3488.
(71) Braunstein, P.; Douce, L.; Fischer, J.; Craig, N. C.; Goetz-Grandmont, G.; Matt, D. *Inorg. Chim. Acta* **1992**, *194*, 151.
(72) Leung, P.-H.; He, G.; Lang, H.; Liu, A.; Loh, S.-K.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, *56*, 7.
(73) Gül, N.; Nelson, J. H. *Tetrahedron* **2000**, *56*, 71.
(74) Butts, C. P.; Crosby, J.; Lloyd-Jones, G. C.; Stephen, S. C. *J. Chem. Soc., Chem. Commun.* **1999**, 1707.
(75) Bei, X.; Uno, T.; Norris, J.; Turner, H. W.; Weinberg, W. H.; Guram, A. S.; Petersen, J. L. *Organometallics* **1999**, *18*, 1840.
(76) Leung, P.-H.; Lang, H.; White, A. J. P.; Williams, D. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2961.
(77) Leung, P.-H.; Loh, S.-K.; Vittal, J. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1997**.

**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)°] is more acute (by 2–5°) than those found in other complexes containing both dmba and P,O-chelates.[61–63,65,66,69] 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*-[PdCl₂{Ph₂PCH=C(Ph)OPPh₂}], in which the Pd, P, C, C, O, and P atoms are almost coplanar.[53] Thus, increasing the ring size by one unit leads to a remarkable change of the conformation of the metallocycle.
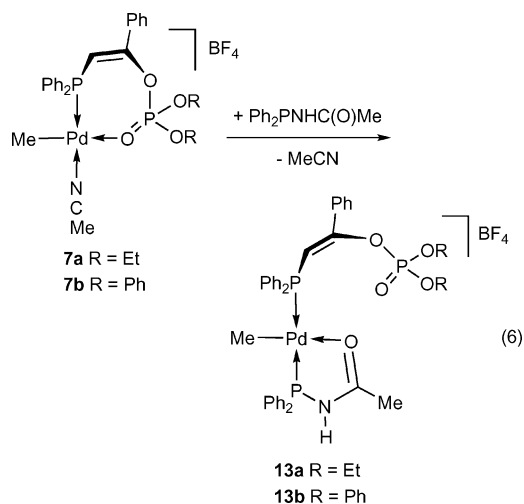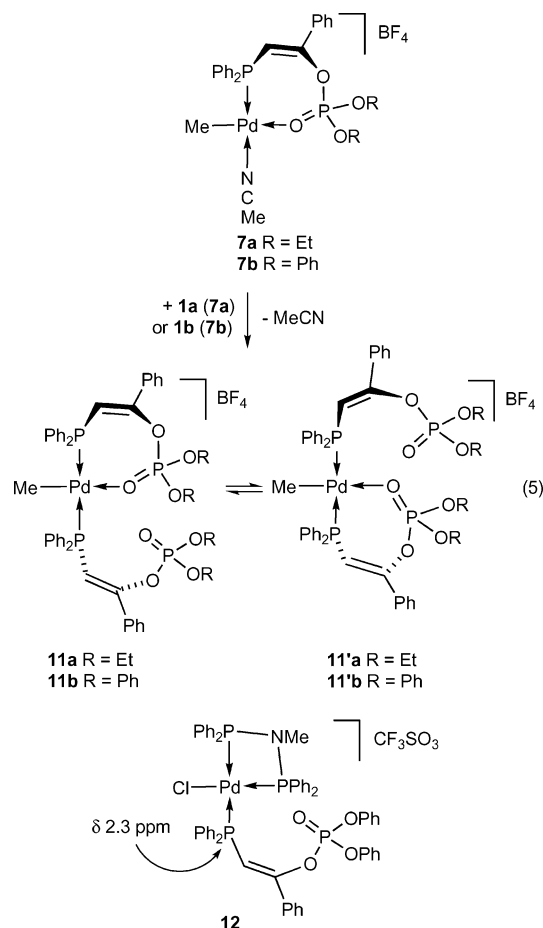
Treatment of the chloro-bridged dimers **4a,b** with AgBF₄ or TlPF₆ afforded the mononuclear derivatives **7**, for which stabilization is achieved by coordination of a solvent molecule (acetonitrile). Interestingly, this reaction was regioselective, with formation, as sole product, of the isomer in 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.[54] Reaction of [Pd(NCMe)₄][BF₄]₂ with 2 mol equiv of **1** led to the formation of complexes **10a,b** (eq 4). In the IR spectrum, the *ν*(P=O) vibrations are observed at 1221 and 1244 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 ³¹P resonances of **7**–**9**, those of the Ph₂P 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 ³¹P{¹H} 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.[64,71,72,79] When [Pd(NCMe)₄][BF₄]₂ was reacted with only 1 mol equiv of

(78) Gladiali, S.; Pulacchini, S.; Fabbri, D.; Manassero, M.; Sansoni, M. *Tetrahedron: Asymmetry* **1998**, *9*, 391.
(79) Redwine, K. D.; Wilson, W. L.; Moses, D. G.; Catalano, V. J.; Nelson, J. H. *Inorg. Chem.* **2000**, *39*, 3392.

**Figure 5.** ATOMS view of the molecular structure of the cation in **10a·CH₂Cl₂**.

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.



**10a** R = Et
**10b** R = Ph

The proposed structure was confirmed by an X-ray determination of *cis*-[Pd{Ph₂PCH=C(Ph)OP(O)(OEt)₂}₂]- [BF₄]₂ (**10a·CH₂Cl₂**). 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·CH₂Cl₂** 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 $C_2$ 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.[64,71,72,79] 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){Ph₂PCH=C(Ph)OP(O)- (OEt)₂}][PF₆] (**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·CH₂Cl₂**, 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 ³¹P{¹H} NMR spectrum showed only two singlets at δ 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** (δ 21.5), where this ligand behaves as a P,O-chelate, and in **12** (δ 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** ⇌ **11b′**, resulting from the P,O-ligand acting alternatively as a chelating or monodentate ligand (eq 5). The ¹H NMR data are consistent with the proposed structure. Thus, the resonance for the methyl protons is a triplet [³*J*(PH) ≈ ³*J*(P′H) ≈ 6.4 Hz], the two PPh₂ 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 ν(P=O) vibrations at 1310 and 1243 cm⁻¹ were observed for the free and coordinated P=O function, respectively. A similar hemilabile behavior has been observed for the P,O-ligands Ph₂PNRC(O)Me (R = H, Me) and Ph₂- PCH₂C(O)Ph in complexes analogous to **11b**, i.e., [PdMe- (P,O)₂][PF₆].[54] 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 ³¹P NMR spectrum, which consisted of two singlets at δ 13.3 ppm (PPh₂) 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 [ν(P=O): 1225 cm⁻¹] while the other one is only P-coordinated [ν(P=O): 1272 cm⁻¹].

**7a** R = Et
**7b** R = Ph

**11a** R = Et
**11b** R = Ph

**11'a** R = Et
**11'b** R = Ph

(5)

δ 2.3 ppm

**12**

**7a** R = Et
**7b** R = Ph

+ Ph₂PNHC(O)Me
− MeCN

(6)

**13a** R = Et
**13b** R = Ph

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 Ph₂PNHC-(O)Me[54] 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 δ 70.8 and 8.8 ppm, which were ascribed to the Ph₂P moieties of the acetamidophosphine and **1a**, respectively. The $^2J$(PP) value of 401 Hz indicates a *trans* arrangement of these two nuclei around the Pd center. The range of $^{31}$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$^{-1}$, ascribed to coordinated C=O of Ph₂PNHC(O)-Me (free ligand: 1715 cm$^{-1}$)[54] and free P=O of **1a**, respectively. In the $^1$H NMR spectrum, the enolate resonance occurred at δ 5.84 ppm, whereas the NH proton was observed at δ 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 $^1$H resonance of the enolate proton, which resonated in **13b** at lower field than in **13a** (δ 6.08 ppm).

If the acetamido phosphine Ph₂PNHC(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 β-ketophosphine Ph₂PCH₂C(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**[54] (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 δ 15.0 and 18.3 ppm, ascribed to the Ph₂P 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.[54] The magnitude of the $^2J$(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 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 $^{31}$P{$^1$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 Ph₂PCH₂C(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.
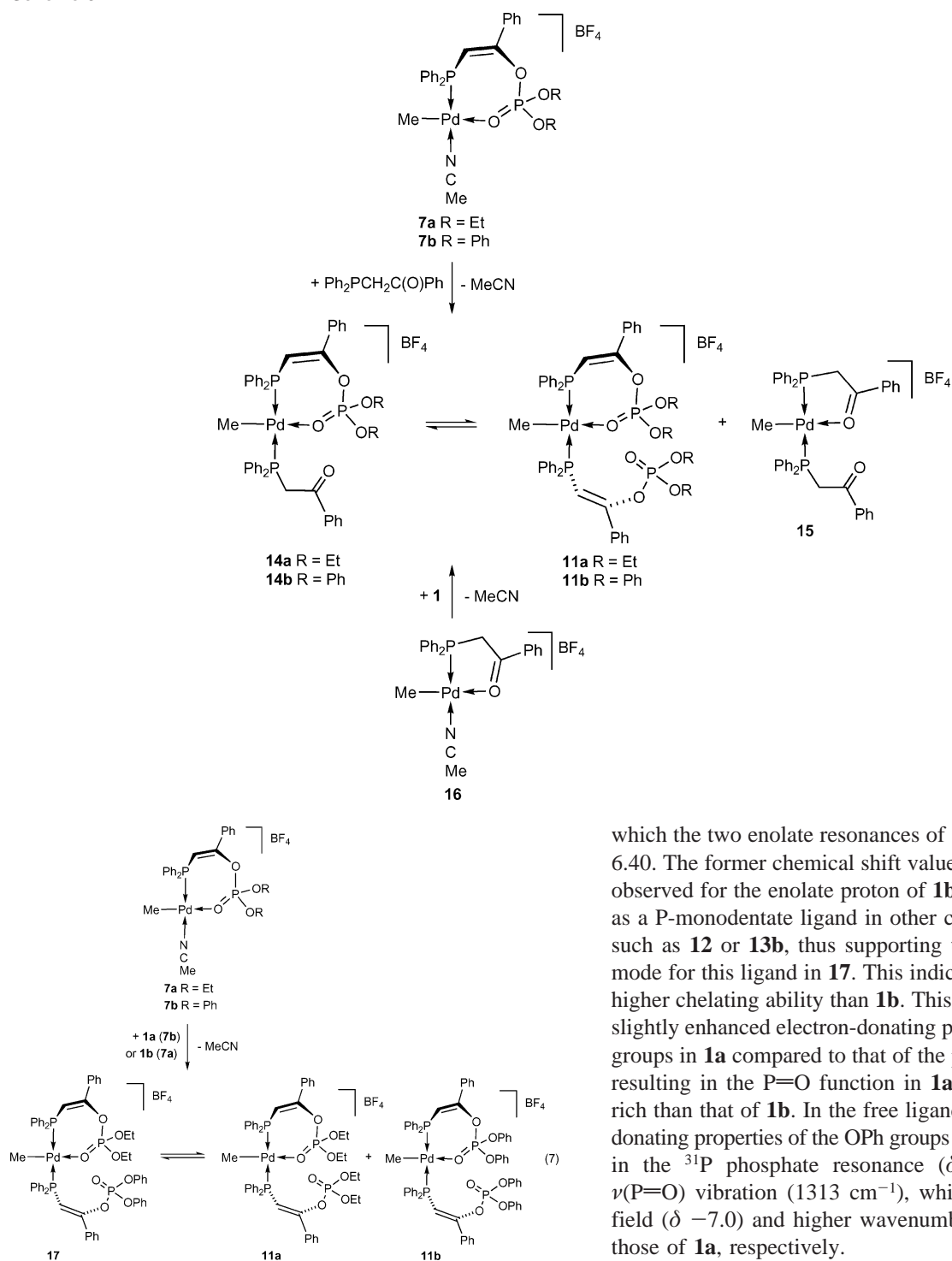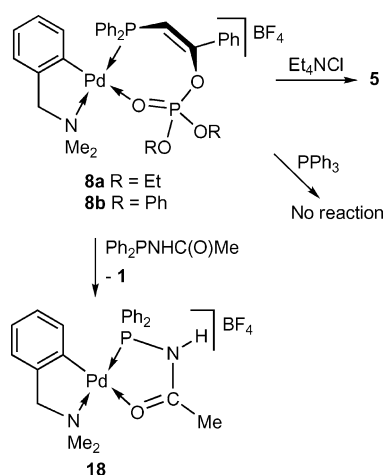
Although ligand redistribution is observed, these experiments indicate a higher chelating ability of **1a** and **1b** than Ph₂PCH₂C(O)Ph. Not only was chelation of the latter not observed in the presence of coordinated **1a** or **1b** (see **14a** and **14b**), but the enolphosphatophosphine **1a** 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 Ph₂PCH₂C(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).

**Scheme 3**

which the two enolate resonances of **17** occur at $\delta$ 6.10 and 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 electron-rich than that of **1b**. In the free ligands, the lower electron-donating properties of the OPh groups in **1b** are also reflected in the $^{31}$P phosphate resonance ($\delta$ −18.0) and in the $\nu$(P=O) vibration (1313 cm$^{-1}$), which occurred at higher field ($\delta$ −7.0) and higher wavenumbers (1277 cm$^{-1}$) than those of **1a**, respectively.

When complexes **8** were reacted with 1 mol equiv of Et$_4$NCl, the coordinated phosphates were substituted by Cl$^-$ and the neutral chloro-complexes **5** obtained (Scheme 4). Interestingly, in the presence of PPh$_3$ no reaction was observed, the P,O-chelates in **8** being not displaced. However, treatment of these complexes with the functional phosphine Ph$_2$PNHC(O)Me[54] 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$_2$PNHC(O)Me}][BF$_4$] (**18**),[54] in which the incoming

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 $^2J$(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,O-chelate while the other one is P-monocoordinated. The $^{31}$P chemical shifts for both the phosphine and phosphate moieties in **17** suggested the chelating ligand to be **1a**. Additional evidence came from the $^1$H NMR spectrum in

**Scheme 4**



**8a** R = Et
**8b** R = Ph

**18**

**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 five-membered metallocycle in **18**, due to the known chelating ability of Ph₂PNHC(O)Me.[54] It also reflects the importance of keeping a relatively hard donor atom (oxygen) *trans* to the σ-bonded carbon donor (antisymbiotic effect). This would clearly not have been possible with PPh₃ as a donor. Note that treatment of **8** with the β-ketophosphine Ph₂PCH₂C-(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){Ph₂PNHC(O)Me}][BF₄] (**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 NMe₂ 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 Ph₂PNHC(O)Me. A slightly longer Pd−O bond length was found in [PdMe{Ph₂PNHC(O)Me}{Ph₂PNHC(O)Me}][O₃-
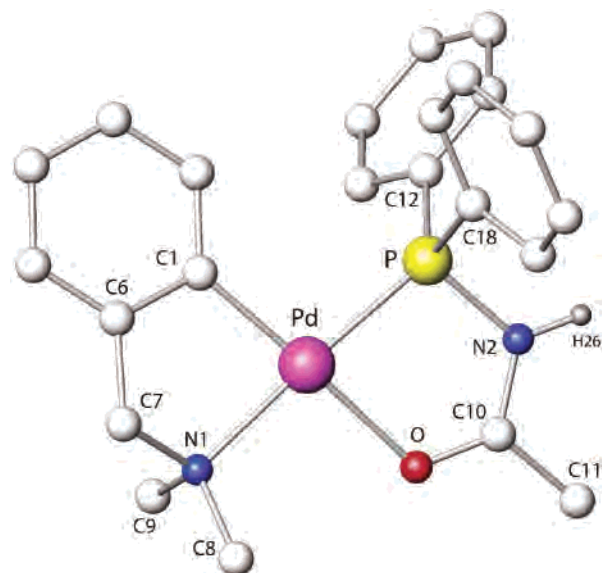


**Figure 7.** ATOMS view of the molecular structure of the cation in **18**.

SCF₃] [2.181(4) Å].[54] In the latter, the Pd−P bond lengths of 2.307(2) and 2.265(2) Å, for the monodentate and chelate ligands, respectively,[54] 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.

**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