Palladium Alkyl Complexes Containing β-Phosphonato−Phosphine P,O Ligands and Their Reactivity toward CO-Ethylene or -Acrylate Insertion

Adel Hamada and Pierre Braunstein*

Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France

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Neutral and cationic square-planar Pd(II) complexes containing the β-phosphonato-phosphine ligand *rac*-$Ph_2PCH(Ph)P(O)(OEt)_2$ (**1**) or the new α-silyl-phosphonato-phosphine ligand $Ph_2PCH(SiMe_3)$-$P(O)(OMe)_2$ (**4**) have been prepared. Reaction of **4** with $[Pd(\mu\text{-}Cl)(dmba)]_2$ (dmba = *o*-$C_6H_4CH_2NMe_2$) afforded an equilibrium mixture of $[Pd(dmba)\{Ph_2PCH(SiMe_3)P(O)(OMe)_2\}]Cl$ (**5**) and $[PdCl(dmba)\{Ph_2PCH(SiMe_3)P(O)(OMe)_2\}]$ (**5′**), which illustrates the hemilabile behavior of the ligand in this system. From the stepwise insertion reaction of CO and ethylene into the Pd−C bond of $[PdCl(Me)\{Ph_2PCH(Ph)P(O)(OEt)_2\}]$ (**2a**), the metallacyclic complex $[Pd\{CH_2CH_2C(O)Me\{Ph_2PCH(Ph)P(O)$-$(OEt)_2\}][BF_4]$ (**10**) was obtained which features the first acetyl−ethylene coupling product containing a phosphine−phosphonate ligand. Chloride abstraction from **2a** led to the cationic complex $[PdMe(NCMe)\{Ph_2PCH(Ph)P(O)(OEt)_2\}][BF_4]$ (**8**), which reacted sequentially with CO and methyl acrylate to afford $[Pd\{CH[C(O)OMe][CH_2C(O)Me]\}\{Ph_2PCH(Ph)P(O)(OEt)_2\}][BF_4]$ (**11**). The reaction between **8** and the P,O-ligand $Ph_2PNHC(O)Me$ resulted in an equilibrated ligand exchange where the heteroleptic system is preferred over the mixture of the two homoleptic complexes. The complexes **2a** and **10**·1/2$CHCl_3$ have been characterized by X-ray diffraction and represent rare examples of crystal structures showing a (diethyl)methylphosphonate ligand coordinated to a metal center.

Introduction

Heterodifunctional P,O ligands combine a soft phosphorus donor moiety with a harder oxygen functionality and are receiving much attention not only as potentially hemilabile ligands but also because of the interesting and often unique properties and reactivity of their transition metal complexes.[1−6] Among the large number of known metal complexes with P,O ligands, those which associate a phosphine and a phosphonate, phosphinate, or phosphate function are relatively scarce and have mainly been described with one or more phosphonate groups -$P(O)(OR)_2$ (R = alkyl, aryl) as the oxygen donor function.[7−10] The transformation of phosphonic esters into the corresponding acids -$P(O)(OH)_2$ or salts -$P(O)(OM)_2$ (M = Na, Li...) allows the formation of hydrosoluble compounds.[11] It is also interesting to note that condensation processes involving phosphonate functions have been applied to the preparation of catalysts[11b,d] or to the immobilization of metal complexes.[11b,d,12−17]

We have recently described Pd(II) complexes in which a heterofunctional enolphosphato−phosphine $Ph_2PCH{=}CPh$-$[OP(O)(OR)_2]$[7] or the β-phosphonatophosphine $Ph_2PCH(Ph)$-$P(O)(OEt)_2$ (**1**) behaved as a rigid and/or hemilabile P,O chelate.[9]

The chelating ability of **1** was compared to that of other potential P,O chelates, and on the basis of competition experiments, **1** was found to be a stronger chelate than the related

* To whom correspondence should be addressed. Fax: (+33) (0)3 90 24 13 22. E-mail: braunstein@chimie.u-strasbg.fr.

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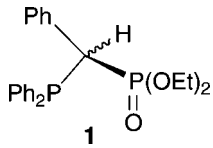

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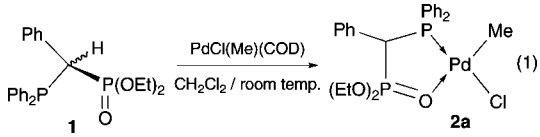
keto- or amido-phosphine P,O-ligands $Ph_2PCH_2C(O)Ph$[18] and $Ph_2PCH_2C(O)NPh_2$,[19] respectively. We describe here organometallic Pd(II) methyl complexes with the P,O chelate **1** and, as a continuation of previous work in this area,[20−23] the formation of metallacyclic complexes resulting from the initial CO-ethene or CO-methyl acrylate insertions into their Pd−Me bond.

Results and Discussion

The Pd(II) complex [PdCl(Me){$Ph_2PCH(Ph)P(O)(OEt)_2$}] (**2a**) was obtained in 93% yield by the reaction of the β-phosphonatophosphine **1** with [PdCl(Me)(COD)] (COD = 1,5-cyclooctadiene, C_8H_{12}) (eq 1). Its IR ν(PO) absorption band at 1186 cm^{-1} and its ^{31}P NMR spectrum (AB spin system, $^{2+3}J(P,P) = 45$ Hz) are consistent with the structure drawn.



The structure of **2a** in the solid state was established by X-ray diffraction. An ORTEP view of one molecule of **2a** is presented in Figure 1, and selected bond distances and angles are given in Table 1. The P═O oxygen and the phosphine donor atoms chelate the metal center and, as expected for a Pd(II) complex with d^8 electronic configuration, the overall coordination geometry around the metal is square-planar. The trans relationship between the soft phosphine and Cl ligands and the harder oxygen and methyl groups, respectively, is consistent with previous findings with the Pt analog of **2a**[24] and in related systems.[22,25−27] The phenyl group attached to the carbon atom α to the phosphorus atoms is almost orthogonal to the metal coordination plane.

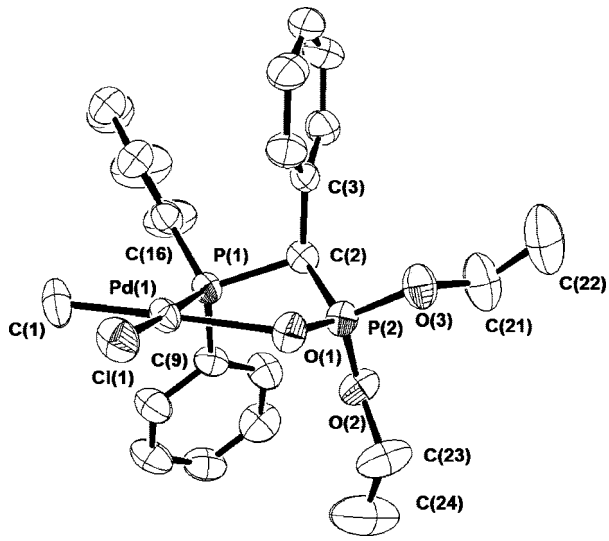
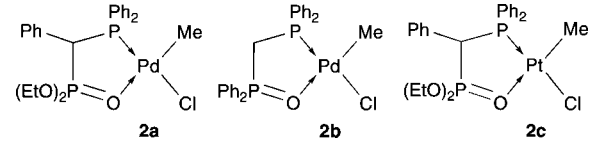


Figure 1. ORTEP view of one molecule of [PdCl(Me){$Ph_2PCH(Ph)P(O)(OEt)_2$}] (**2a**). Thermal ellipsoids enclose 50% of the electron density (H atoms are not shown).

It is interesting to note that with the related diphosphine-phosphonate ligands $(Ph_2P)_2CHP(O)(OR)_2$ (R = Me, Ph), spontaneous deprotonation of the PCHP moiety was observed with Pd(II) precursor complexes containing a basic enough ligand, such as a methyl or a cyclometalated dmba chelate (dmbaH = $C_6H_5CH_2NMe_2$).[28] Here, in contrast, the Pd-bound methyl ligand does not promote the deprotonation of ligand **1**.

Complex **2a** is related to the P,O diphosphine monooxide Pd(II) complex [PdMeCl{$Ph_2PCH_2P(O)Ph_2$}] (**2b**)[29] and to the Pt(II) complex with ligand **1**, [PtMeCl{$Ph_2PCH(Ph)P(O)(OEt)_2$}] (**2c**).[24] The geometry around the metal centers is square planar and a comparison between the structural parameters of **2a**, **2b** and **2c** is provided in Table 1.



The Pd−P distance of 2.219(1) Å in **2a** is in agreement with literature data for related P,O systems such as the diphosphine monoxide complex **2b**[29] and is shorter than Pd−P bonds for dppm complexes in general,[30] whereas the Pd−O distance of 2.265(2) Å is significantly longer. This is consistent with the trans influence of the methyl group, which forms a strong bond to palladium as indicated by the Pd−C(1) bond length of 2.029(3) Å. This value is at the lower limit for Pd−C(sp^3) bonds and is much shorter than the sum of the covalent radii of Pd(II) and C(sp^3) (2.07 Å). The Pd−Cl distance of 2.362(1) Å falls in the expected range for a *trans* Cl−Pd−P arrangement.[18,29,30] Although no classical intermolecular hydrogen bonding was detected in complex **2a**, non-conventional C(23)−H(23)···Cl(1) hydrogen bonds are present (Figure 2) that involve a Cl ligand and a C-*H* atom of a POC$H_2$$CH_3$ methylene group. Furthermore, intermolecular interactions exist between Cl(1) and the PC(2)H(2)P hydrogen and the phenyl C(4)−H(4) hydrogen atoms.

The dimethyl(diphenylphosphino)(trimethylsilyl)methylphosphonate ligand **4** (eq 2), which is related to **1**, was synthesized from the silylphosphonate **3** (prepared by Savignac's procedure using methyl(dimethyl)phosphonate, see Experimental Section),[31] by deprotonation with LDA or *n*-BuLi and treatment of the resulting anion with PPh_2Cl. Its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ consisted of two doublets at δ −16.8 and 33.0 ($^2J(P,P) = 19$ Hz) for the phosphine and the phosphonate functions, respectively. These values are similar to those found for its

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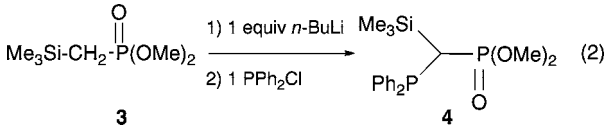
Table 1. Comparison of Selected Structural Data between Complexes 2a, 2b, and 2c

	2a	2b		2c
Pd−C(1)	2.029(3)	2.024(6)	Pt−C(1)	2.0316(4)
Pd−Cl	2.362(1)	2.378(2	Pt−Cl	2.389(2)
Pd−P(1)	2.219(1)	2.204(2)	Pt−P(1)	2.145(2)
Pd−O(1)	2.265(2)	2.2761(4)	Pt−O(1)	2.231(5)
C(1)−Pd−O(1)	178.3(1)	174.8(2)	C(1)−Pt−O(1)	176.40(1)
Cl−Pd−P(1)	176.4(2)	171.69(6)	−	−
C(1)−Pd−Cl	89.8(2)	90.6(2)	C(1)−Pt-Cl	88.92(6)
P(1)−Pd−O(1)	87.77(6)	89.2(1)	P(1)−Pt−O(1)	89.8(1)

diethyl analog.[32] In the ^{1}H NMR spectrum of **4** ($CDCl_3$), the $SiMe_3$ protons give rise to a signal at 0.05 ppm, the PCHP proton to a doublet of doublets centered at 2.45 ppm (^2J(PO,H) = 22.2 Hz, ^2J(P,H) = 1.2 Hz), whereas the magnetically inequivalent MeO groups resonate as two doublets at 3.32 and 3.47 ppm (^3J(PO,H) = 11.1 Hz). In the IR spectrum (KBr), the ν(P═O) vibration was found at 1248 s cm^{-1}.



(2)

For comparison, **4** was reacted with $[Pd(\mu\text{-Cl})(dmba)]_2$ (dmba = o-$C_6H_4CH_2NMe_2$) in a 2:1 ratio, which afforded a yellow solid. The presence of two species was confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. At room temperature, the ^{31}P{^{1}H} NMR spectrum ($CDCl_3$) consisted of two pairs of doublets at δ 34.2 (^{2+3}J(P,P) = 34 Hz) and 29.5 (^{2+3}J(P,P) = 34 Hz) and at δ 28.2 (^2J(P,P) = 7 Hz), and 26.3 (^2J(P,P) = 7 Hz) which are suggested to correspond to the P═O and P resonances of [Pd(dmba){$Ph_2PCH(SiMe_3)P(O)(OMe)_2$}]Cl (**5**) and [PdCl(dmba){$Ph_2PCH(SiMe_3)P(O)(OMe)_2$}] (**5′**), respectively (for the ^{31}P{^{1}H} NMR spectrum, see Figure S-1, Supporting Information). The smaller value of the J(PP) coupling constant in the monodentate vs the chelate form of the ligand is consistent with previous observations.[9] The hemilability of coordinated **4** (Scheme 1) would result in solution in a slow equilibrium on the NMR time scale between **5** and **5′**.[33]

Addition of $AgBF_4$ to the **5/5′** mixture in a NMR tube led to anion exchange and induced the quantitative formation of the cationic complex [Pd(dmba){$Ph_2PCH(SiMe_3)P(O)(OMe)_2$}]-[$BF_4$] (**6**) (see Experimental Section and Figure S-2, Supporting Information).

1. CO/Olefin Insertion into a Pd−Me Bond. The palladium catalyzed alternating insertion of carbon monoxide and olefins leads to the formation of polyketones, and theoretical and experimental studies have established the kinetic and thermodynamic factors that control the chain growth by alternating CO and olefin migratory insertion into the metal−alkyl or metal−acyl bond, respectively.[5,34−51] Palladium complexes containing P,P chelating ligands are effective in CO/ethylene[42,45−47,52−55] and CO/propylene[35,56] copolymerization, whereas aromatic olefins, such as styrene and its derivatives, are efficiently copolymerized when N,N ligands chelate the palladium center.[57−61] The interest for unsymmetrical bidentate ligands, particularly of the P,N-[2,4,62] and P,O types,[6,20,22,25,63,64] is motivated by the simultaneous presence of donor groups with different stereoelectronic properties and trans-effect/influence and by their potential hemilabile behavior in metal complexes.[33]

In 2002, Drent et al. reported the use of alkoxyarylphosphine ligands bearing sulfonic acid groups that, when combined *in situ* with palladium acetate or [Pd_2(dba)$_3$], were able to promote the formation of nonalternating polyketones from carbon monoxide and ethylene.[65,66] Furthermore, the copolymerization of ethylene and methyl acrylate afforded copolymers with the

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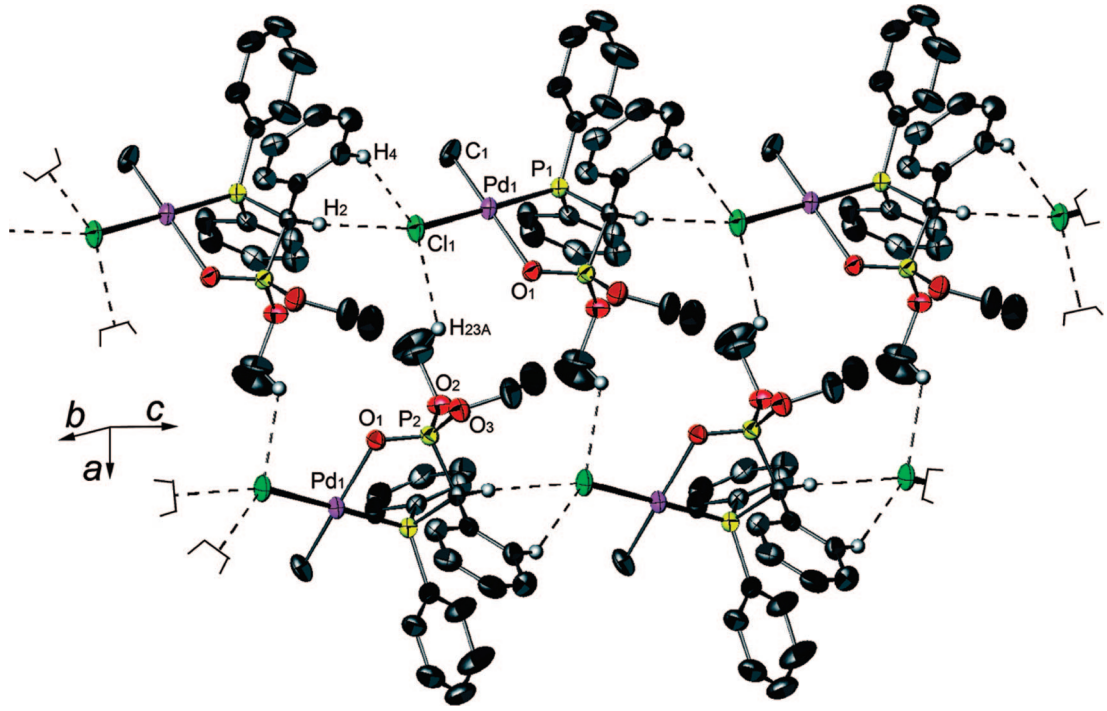
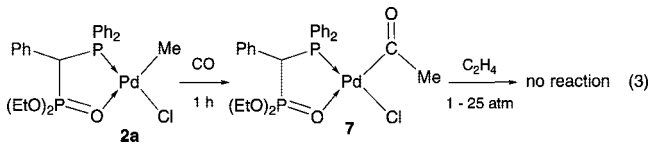


Figure 2. View of the intermolecular interactions in the solid-state structure of **2a**. The square-brackets indicate the directions of the polymeric network. Symmetry operations: (i) $x, y, -1+z$; (ii) $0.5-x, y, -0.5+z$.

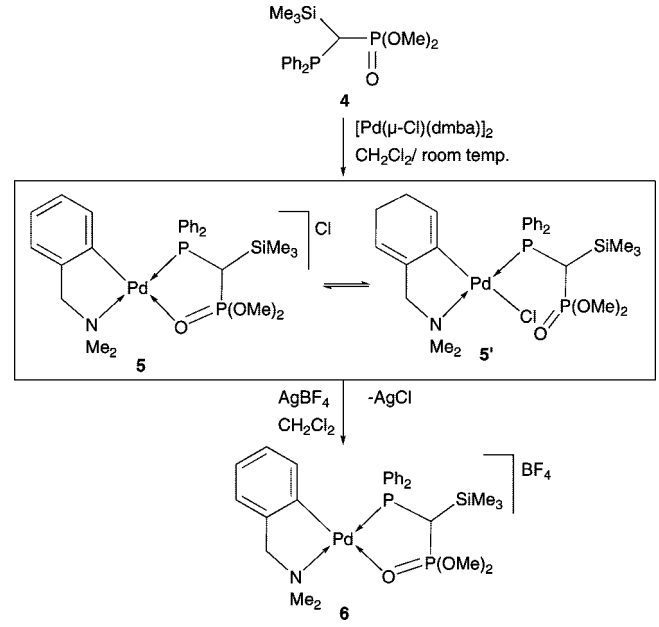
acrylate units statistically placed in the polyethylene chain. This was the first example of transition metal catalysis providing a low temperature/low pressure route to such copolymers.

1.1. CO Insertion into the Pd−Me Bond of a Neutral Pd(II) Complex. Insertion of CO into the Pd−Me bond of complex **2a** in CH_2Cl_2 under mild conditions resulted in the formation of the acetyl complex **7** (eq 3), which is characterized by a ν(CO) absorption at 1711 cm^{-1} in the IR spectrum and by $^{31}P\{^1H\}$ NMR resonances at δ 23.6 (d, $^{2+3}J(P,P) = 44$ Hz, PPh_2) and 34.1 (d, $^{2+3}J(P,P) = 44$ Hz, PO). This indicates that the acyl ligand resides in *cis* position relative to the phosphine donor, like the methyl ligand in **2a**. Complex **7** did not insert ethylene under usual conditions (see eq 3).



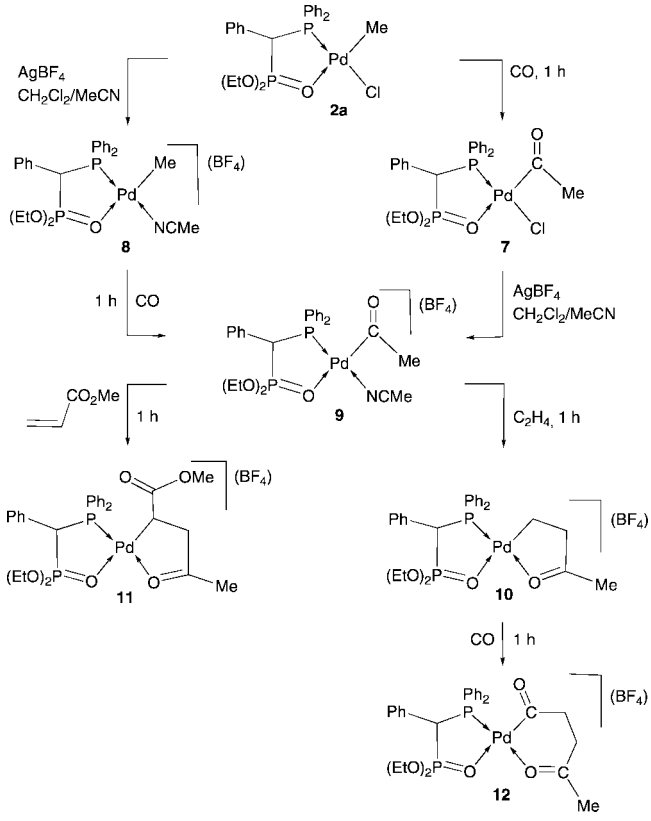
1.2. Stepwise Ethene/methylacrylate/CO Insertion into the Pd−Me Bond of Cationic Pd(II) Complexes Containing a P,O Chelate. We have previously structurally characterized Pd(II) complexes resulting from CO/ethene insertion and containing a P,O or a P,N ligand.[20−22,25] and considering the interest in the copolymerization of olefins with polar monomers, we have also structurally characterized Pd(II) complexes resulting from insertion of methyl acrylate into a Pd(II)−acetyl bond.[22,23] Expecting for a cationic complex a higher reactivity than that of the corresponding neutral complex, we have prepared [PdMe(NCMe){$Ph_2PCH(Ph)P(O)(OEt)_2$}][BF_4] (**8**) by reaction of **2a** with one molar equiv of $AgBF_4$ in a 50/50 mixture of acetonitrile and dichloromethane (Scheme 2). At room temperature, its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed two doublets at δ 37.4 (P, $^{2+3}J(P,P) = 40$ Hz) and 38.8 (PO, $^{2+3}J(P,P) = 40$ Hz).

Scheme 1



The acetyl complex **9** was prepared either from **7** by chloride abstraction in the presence of MeCN or by carbonylation reaction of **8** (Scheme 2). It is characterized by a ν(CO) vibration at 1716 cm^{-1} in the IR spectrum and two doublets in the $^{31}P\{^1H\}$ NMR spectrum at δ 26.5 (PPh_2, $^{2+3}J(P,P) = 40$ Hz) and 35.6 (PO, $^{2+3}J(P,P) = 40$ Hz). Only one isomer of the acetyl complex was observed, in which the C(O)Me group is cis to the P donor atom, as indicated by the typical shift of the ^{31}P resonance of the phosphine donor when going from **8** to **9** ($\Delta\delta = -11$ ppm). The stability of complex **9** in the solid state or in solution contrasts with observations made with other cationic acetyl−palladium complexes which rapidly decomposed.[38,67]

Scheme 2. All Reactions Were Performed at Room Temperature



Insertion of ethylene into the Pd−acyl bond of **9** occurred at ambient temperature and pressure and afforded complex **10**. The reaction was completed after ca. 1 h. Coordination of the ketonic oxygen to palladium (ν(CO) = 1637 cm^{-1}) leads to a stabilizing chelation that disfavors β-hydrogen elimination. Complex **10** is stable at room temperature for several minutes in solution and for months in the solid state, in contrast to other chelated complexes with a P,P or a P,O chelate.[68,69] The ^{1}H NMR spectrum of **10** shows for the CH_2 protons of the inserted ethylene second order multiplets (for the Pd-CH_2 and CH_2C═O protons), consistent with the presence of a stereogenic center in the molecule (see Experimental Section). This complex features the first acetyl−ethylene coupling product containing a phosphine−phosphonate ligand.

The structure of **10** in **10** · 1/2$CHCl_3$ was determined by X-ray diffraction (Figure 3). The Pd(II) center is chelated by P,O and C,O ligands, with a cis arrangement of the two oxygen atoms that forms a O(1)−Pd−O(4) angle of 93.0(2)°.

The phenyl group at C(2) assumes a different orientation in **2a** and **10** (see Figure 4). In complex **2a**, it occupies an axial site with respect to the chelate mean plane whereas in **10**, it is in an equatorial position. The angle between the C(2)−C_{ipso} bond and the P1−C(2)−P2 plane is 127.70(1)° and 135.69(1)° in **2a** and **10**, respectively. The Pd−C(24) distance of 2.008(7) Å compares well with that in related molecules.[20−22]

After the insertion of ethylene into the palladium−acetyl bond of the cationic complex **9**, we examined the insertion of methyl

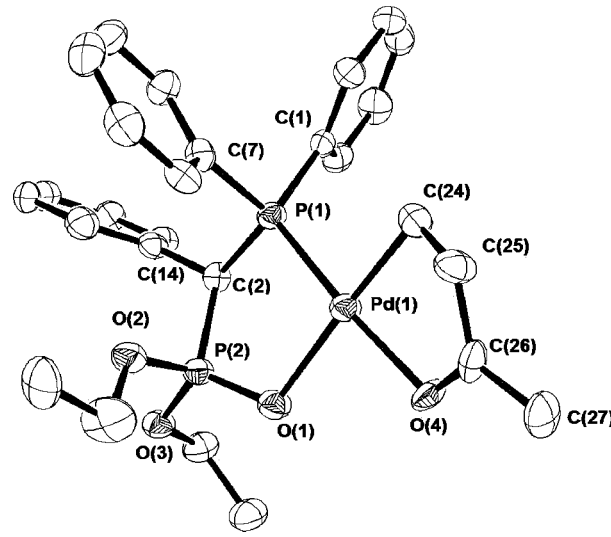


Figure 3. View of the molecular structure of the cation in complex **10** · 1/2$CHCl_3$ (H atoms are not shown). Selected bond lengths [Å] and angles [deg]: Pd−P(1) 2.208(2), Pd−O(1) 2.201(5), Pd−C(24) 2.008(7), Pd−(O4) 2.132(4), C(24)−(25) 1.54(1), C(25)−C(26) 1.49(1), C(26)−O(4) 1.247(8), C(26)−C(27) 1.49(1), P(1)−C(2) 1.858(6), P(2)−C(2) 1.812(7); P(1)−Pd−O(4) 175.4(2), P(1)−Pd−O(1) 91.4(2), P(1)−C(2)−P(2) 106.0(3), C(24)−Pd−O(4) 82.9(2), O(1)−Pd−O(4) 93.0(2).

acrylate, a reaction of high current interest (Scheme 2).[20,21,66,70] This reaction is more demanding than that of ethylene, but it was found to be much faster than recently observed for related Pd(II) complexes with P,O ligands.[20] It occurred within 1 h at ambient temperature and pressure and led to the formation of complex **11**. Owing to the presence of two stereogenic centers in this 2,1-insertion product, it was obtained as a 65/35 mixture of diastereoisomers, as indicated by ^{31}P{^{1}H} NMR (two AB spin systems) and ^{1}H NMR spectroscopy (see Experimental Section).

A solution of the P,O chelate complex **10** in CH_2Cl_2 was purged with CO to form the α-keto chelate complex **12** (Scheme 1). Although the desired complex could not be isolated pure, the IR spectrum showed two ν(C═O) vibrations at 1659 and 1708 cm^{-1} assigned to the coordinated ketonic and acyl CO, respectively.

2. Competing Chelation Experiments. To evaluate the chelating ability of ligand **1** in the presence of another P,O donor

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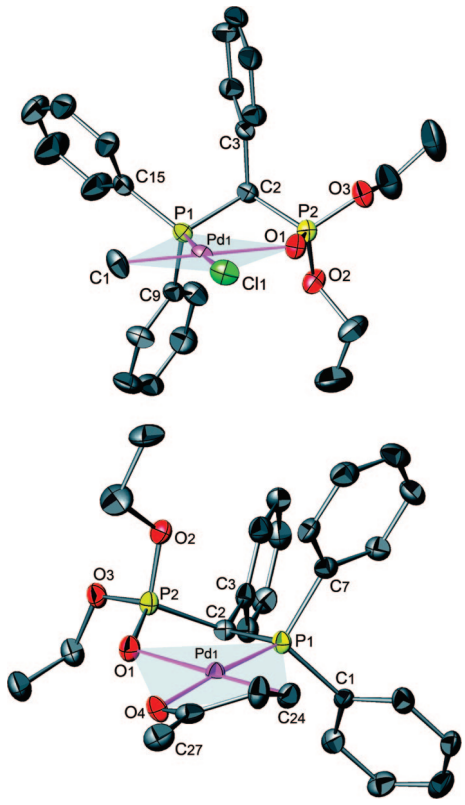

Figure 4. Views of the comparative orientations of the C(2)-bound phenyl group in the PC(Ph)P moiety in complexes **2a** (top) and **10** (bottom).

ligand, we first reacted a molar equiv of **1** with complex **8** and obtained complex **13**. A dynamic, temperature-dependent intramolecular dynamic equilibrium **13**⇌**13′** takes place (Scheme 3), as indicated by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S-3, Supporting Information), where the two phosphonato P═O groups alternatively bind to the Pd center. This mutual exchange of the two P═O functions is facilitated by the proximity of the uncoordinated oxygen atoms and results in hemilabile bahavior.[33] Because of the presence of two stereogenic centers in the molecule, a mixture of diastereoisomers was obtained, in an approximate 1:1 ratio, that we did not attempt to separate. For each diastereoisomer, the phosphines give rises to a triplet in the dynamic regime owing to coupling with two P═O functions. At lower temperature, the P═O resonance remains broad owing to the presence of diastereoisomers with very similar chemical shifts.

We then reacted the acetamidophosphine ligand $Ph_2PNHC(O)Me$ with **8** in a 1:1 ratio (Scheme 3). This afforded complex **14**, which contains both ligands but with **1** being chelated to the metal. From this heteroleptic complex, a ligand exchange reaction affords a mixture of the homoleptic complexes **13** and **15**, with **14** being the major species present at equilibrium (Scheme 3). This indicates that the heteroleptic system is preferred over the mixture of the two homoleptic ones. Complex **15** has been reported previously, and it was found that its monodentate and chelating ligands are in dynamic exchange, resulting in a broad ^{31}P NMR resonance at δ 60.2 ppm.[19]

In conclusion, we have prepared new square-planar Pd(II) complexes containing the β-phosphonato-phosphine ligand *rac*-$Ph_2PCH(Ph)P(O)(OEt)_2$ (**1**) or the new α-silyl-phosphonato−phosphine ligand $Ph_2PCH(SiMe_3)P(O)(OEt)_2$ (**4**) and examples of hemilabile behavior were described in the former case. The first acetyl−ethylene coupling product containing a phosphine-phosphonate ligand, $[Pd\{CH_2CH_2C(O)Me\{Ph_2PCH(Ph)P(O)\}(OEt)_2\}][BF_4]$(**10**), was obtained from the stepwise insertion reaction of CO and ethylene into the Pd−C bond of $[PdCl(Me)\{Ph_2PCH(Ph)P(O)(OEt)_2\}]$ (**2a**). The cationic complex $[PdMe(NCMe)\{Ph_2PCH(Ph)P(O)(OEt)_2\}][BF_4]$ (**8**) reacted sequentially with CO and methyl acrylate to afford $[Pd\{CH[C(O)OMe][CH_2C(O)Me]\}\{Ph_2PCH(Ph)P(O)(OEt)_2\}][BF_4]$ (**11**). However, further insertion reaction of ethylene into the newly formed Pd−C bond was not observed under our experimental conditions.

Experimental Section

General Considerations. All the reactions and manipulations were carried out under an inert atmosphere of purified nitrogen using standard Schlenk tube techniques. Solvents were purified over appropriate drying agents and freshly distilled under nitrogen before use. 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 analysis were performed by the "Service de microanalyses" (Université de Strasbourg, France). Infrared spectra were recorded in the 4000−400 cm^{-1} range in the solid state (KBr) on a Bruker IF66FT or Perkin-Elmer 1600 Series FTIR or, pure, on a Thermo Nicolet 6700 instrument, equipped with a SMART Orbit Diamond ATR accessory. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13, 121.49, and 75.5 MHz, respectively.

Synthesis. The compounds *rac*-$Ph_2PCH(Ph)P(O)(OEt)_2$,[9] $Ph_2PNHC(O)Me$,[19] and $[PdCl(Me)(COD)]$[71] (COD = 1,5-cyclooctadienne, C_8H_{12}) and $[Pd(\mu\text{-}Cl)(dmba)]_2$[72] were prepared according to literature procedures.

$[PdCl(Me)\{Ph_2PCH(Ph)P(O)(OEt)_2\}]$ (2a). In a 100 mL Schlenk tube containing [PdCl(Me)(COD)] (1.30 g, 4.92 mmol) in CH_2Cl_2 (25 mL) was added $Ph_2PCH(Ph)P(O)(OEt)_2$ (**1**) (2.03 g, 4.92 mmol). The solution was stirred for 20 min at room temperature and the solvent was removed under reduced pressure. The beige residue was washed with diethyl ether (2 × 20 mL) and pentane (2 × 20 mL) and dried in vacuum overnight to afford a beige powder. Yield 1.93 g (93%). Anal. Found: C, 50.83; H, 5.17%. Calcd for $C_{24}H_{29}ClO_3P_2Pd$: C, 50.63; H, 5.13%. X-ray quality crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. ^1H NMR ($CDCl_3$): δ 0.91 (t, 3H, $^3J(P,H)$ = 1.6 Hz, $PdCH_3$), 1.05 (m, 6H, CH_3CH_2O), 3.91 (dd, 1H, $^2J(P,H)$ = 1.94 Hz, $^2J(PO,H)$ = 7.14 Hz, PCHPh), 4.05 (m, 4H, CH_3CH_2O), 7.08−7.86 (m, 15H, aromatics); $^{31}P\{^1H\}$ NMR ($CDCl_3$): AB spin system δ_A 35.6 (d, $^{2+3}J(P,P)$ = 45 Hz, PPh_2), δ_B 36.0 (d, $^{2+3}J(P,P)$ = 45 Hz, PO). IR (KBr): $\nu(P=O)$ 1186 s cm^{-1}.

$(MeO)_2P(O)CH_2SiMe_3$ (3). In a 250 mL Schlenk tube containing a solution of *n*-BuLi in hexane (20.13 mL, 32.23 mmol, 1.6 M Aldrich) cooled at −20 °C, was added a solution of diisopropylamine (3.500 g, 32.23 mmol) in THF (30 mL). After the reaction mixture was stirred for 10 min, a solution of $MeP(O)(OMe)_2$ (2.000 g, 16.11 mmol) in THF (30 mL) was added, and the mixture was further stirred for 10 min during which the temperature was kept below −65 °C. It was then cooled again to −78 °C, and a solution of MeSiCl (1.750 g, 1.98 mL, 16.11 mmol) in THF (20 mL) was added dropwise. The temperature was then allowed to warm to 0 °C while stirring was maintained. The reaction mixture was quenched at −20 °C by addition of a degassed 5N HCl solution

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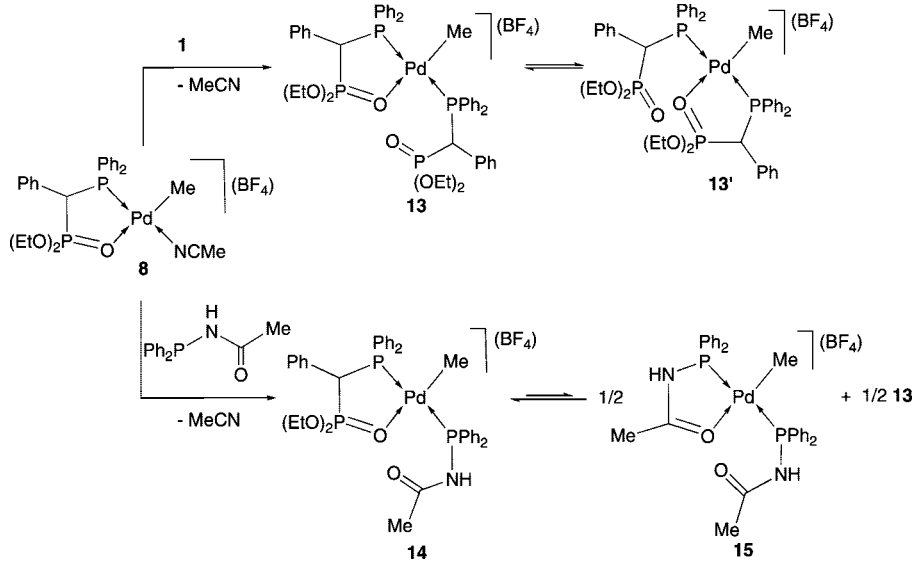
Scheme 3. All Reactions Were Performed at Room Temperature in CH_2Cl_2



until pH 4 was reached. The organic layer was then collected and the aqueous phase was extracted with diethyl ether (2 × 20 mL). The combined organic phases were then dried over degassed $MgSO_4$, the solvent was evaporated under reduced pressure, affording a liquid compound (yield 2.470 g, 78%). ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 9H, $SiCH_3$), 0.94 (2H, d, ^2J(PO,H) = 22.0 Hz, P(O)CH_2Si), 3.53 (6H, d, ^3J(PO,H) = 11.1 Hz, OCH_3); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.8 (s, PO); IR (THF): ν(P═O) 1250 s cm^{-1}.

$Ph_2PCH(SiMe_3)P(O)(OMe)_2$ (4). In a 250 mL Schlenk tube cooled to −78 °C was placed a solution of *n*-BuLi in hexane (3.18 mL, 5.09 mmol, 1.6 M Aldrich) to which was added a solution of $Me_3SiCH_2P(O)(OMe)_2$ (**3**) (1.000 g, 5.09 mmol) in THF (20 mL). The mixture was stirred for 10 min. during which the temperature was kept below −78 °C, and a solution of Ph_2PCl (1.120 g, 0.91 mL, 5.09 mmol) in THF (10 mL) was added. After it was stirred for 15 min, the mixture was brought back to room temperature over 10 min, the solvents were eliminated under reduced pressure, and the solid was washed with hexane (2 × 10 mL). The compound was extracted with diethyl ether (2 × 20 mL). After filtration and removal of the volatiles under vacuum, ligand **4** was obtained as a yellow solid (0.968 g, 50%). ^{1}H NMR ($CDCl_3$): δ 0.05 (s, 9H, $SiMe_3$), 2.45 (dd, 1H, ^2J(PO,H) = 22.2 Hz, ^2J(P,H) = 1.2 Hz, PCHP), 3.32 (d, 3H, ^3J(PO,H) = 11.1 Hz, $POCH_3$), 3.47 (d, 3H, ^3J(PO,H) = 11.1 Hz, $POCH_3$), 7.20−7.80 ppm (10H, m, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.8 (d, ^2J(P,P) = 19 Hz, PPh_2), 33.0 (d, ^2J(P,P) = 19 Hz, PO); IR (KBr): ν(P═O) 1248 cm^{-1}.

[PdCl(dmba){$Ph_2PCH(SiMe_3)P(O)(OMe)_2$}] (5′). Solid [Pd($\mu$-Cl)(dmba)]$_2$ (0.619 g, 1.12 mmol) and **4** (0.853 g, 2.24 mmol) were placed in a Schlenk flask and CH_2Cl_2 (20 mL) was added at ambient temperature. The yellow solution was stirred for 2 h and the volatiles were removed under reduced pressure. The residue was washed with Et_2O (2 × 10 mL) and pentane (2 × 20 mL), which afforded a yellow solid (0.761 g, 40%). Anal. Found: C, 43.49; H, 5.01; N 1.84%. Calcd for $C_{27}H_{38}ClNO_3P_2PdSi \cdot 1.5CH_2Cl_2$: C, 42.85; H, 5.27; N 1.78%. ^{1}H NMR ($CDCl_3$): δ 0.16 (s, 9H, $SiMe_3$), 2.80 (d, 6H, ^4J(P,H) = 2.7 Hz, NMe_2), 2.84 (d, 6H, ^4J(P,H) = 2.5 Hz, NMe_2), 3.50 (dd, 2H, ^2J(H,H) = 7.9 Hz, NCH_2), 3.74 (d, 6H, ^3J(PO,H) = 11.3 Hz, OCH_3), 3.89 (dd, 1H, ^2J(P,H) = 4.2 Hz, ^2J(PO,H) = 21.3 Hz, PCHP), 6.63−7.96 (14H, m, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 26.3 (d, ^2J(P,P) = 7.0 Hz), 28.2 (d, ^2J(P,P) = 7.0 Hz). IR (pure): ν(P═O) 1261 m cm^{-1}.

[Pd(dmba){$Ph_2PCH(SiMe_3)P(O)(OMe)_2$}][$BF_4$] (6). Solid **5** (0.200 g, 0.30 mmol) and $AgBF_4$ (0.060 g, 0.30 mmol) were mixed in a Schlenk flask and CH_2Cl_2 (15 mL) was added at ambient temperature. The yellow mixture was stirred for 1 h, and after filtration, the volatiles were removed under reduced pressure. The residue was washed with diethyl ether (2 × 10 mL) and pentane (2 × 10 mL), which afforded a yellow solid (0.160 g, 78%). Anal. Found: C, 44.86; H, 5.38; N, 1.98. Calcd for $C_{27}H_{38}BF_4NO_3P_2PdSi \cdot 1/3CH_2Cl_2$: C, 44.60; H, 5.29; N, 1.90. ^{1}H NMR ($CDCl_3$): δ 0.68 (s, 9H, $SiMe_3$), 1.16 (s, 3H, NMe), 1.18 (s, 3H, NMe), AB spin system: 2.87 (^2J(H,H) = 5.0 Hz, Me_2NCHH), 2.90 ^2J(H,H) = 5.0 Hz, Me_2NCHH), 3.32 (dd, 1H, ^2J(PO,H) = 16.9 Hz, ^2J(P,H) = 12 Hz, PCHP), 3.72 (d, 3H, ^3J(P,H) = 1.7 Hz, POMe), 3.75 (d, 3H, ^3J(P,H) = 1.7 Hz, POMe), 6.33−7.96 (14H, m, aromatics); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.1 (d, ^{2+3}J(P,P) = 29 Hz, PPh_2), 44.9 (d, ^{2+3}J(P,P) = 29 Hz, PO); IR (KBr): ν(P═O) 1178 cm^{-1}.

[PdCl{C(O)Me}{$Ph_2PCH(Ph)P(O)(OEt)_2$}] (7). A CH_2Cl_2 solution of **2** was placed under a CO atmosphere and stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the powder was washed with diethyl ether (2 × 20 mL) and pentane (2 × 20 mL). It was then dried in vacuum overnight to afford a pale green powder. Anal. Found: C, 50.23; H, 4.96%. Calcd for $C_{25}H_{29}ClO_4P_2Pd$: C, 50.27; H, 4.89%. ^{1}H NMR ($CDCl_3$): δ 1.05 (m, 6H, CH_3CH_2O), 2.20 (d, ^4J(P,H) = 1.0 Hz, 3H, CH_3CO), 4.05 (m, 4H, CH_3CH_2O), 4.22 (dd, 1H, ^2J(P,H) = 22.2, 12.7 Hz, PCHPh), 7.13−7.80 (m, 15H, Ph); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.6 (d, ^{2+3}J(P,P) = 44 Hz, PPh_2), 34.1 (d, ^{2+3}J(P,P) = 44 Hz, PO). IR (KBr): ν(CO) 1711 s cm^{-1}.

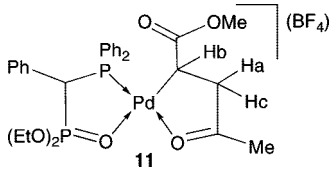
[PdMe{NCMe}{$Ph_2PCH(Ph)P(O)(OEt)_2$}][BF_4] (8). Complex **2** (1.52 g, 2.67 mmol) was dissolved in a 1:1 CH_2Cl_2/MeCN mixture (20 mL) and $AgBF_4$ (0.52 g, 2.67 mmol) was added at room temperature. The reaction mixture was stirred for 2 h. After filtration and removal of the volatiles under vacuum, the residue was washed with diethyl ether (2 × 20 mL) and pentane (2 × 20 mL) and dried in vacuum overnight to afford a pale brown powder. Anal. Found: C, 47.26; H, 4.88; N, 1.88%. Calcd for $C_{26}H_{32}BF_4NO_3P_2Pd$: C, 47.19; H, 4.87; N, 2.12%. ^{1}H NMR ($CDCl_3$): δ 0.81 (d, ^2J(P,H) = 1.5 Hz, 3H, $PdCH_3$), 1.04 (t, 3H, ^3J(H,H) = 7 Hz, CH_3CH_2O), 1.09 (t, 3H, ^3J(H,H) = 7.0 Hz, CH_3CH_2O), 2.40 (s, 3H, $NCCH_3$), 4.06 (m, 4H, CH_3CH_2O), 4.65 (dd, ^{1}H,^2J(P,H) = 20.8, 14.1 Hz), 7.15−7.94 (m, 15H, Ph).^{31}P{^{1}H} NMR ($CDCl_3$): δ 37.4 (d, ^{2+3}J(P,P) = 40 Hz, PPh_2), 38.8 (d, ^{2+3}J(P,P) = 40 Hz, PO).

[Pd{C(O)Me}$(NCMe)_2$}{$Ph_2PCH(Ph)P(O)(OEt)_2$}][BF_4] (9). The reaction of **7** (0.135 g, 0.22 mmol) with $AgBF_4$ (0.044 g, 0.22 mmol) afforded the new acetyl complex as a beige powder (0.12 g, 80%). Anal. Found: C, 44.97; H, 4.52%. Calcd. for $C_{27}H_{32}BF_4NO_4P_2Pd \cdot 0.5\ CH_2Cl_2$: C, 45.11; H, 4.54. NMR ^{1}H ($CDCl_3$): δ 1.14 (t, 3H, ^3J(H,H) = 7 Hz, CH_3CH_2O), 1.16 (t, 3H,

^3J(H,H) = 7 Hz, CH_3CH$_2$O), 2.04 (d, 3H, ^4J(P,H) = 1.1 Hz, C(O)CH$_3$), 2.24 (s, 3H, NCCH$_3$), 4.06 and 4.21 (m, 4H, CH$_3$CH_2O), 4.8 (dd, 1H, ^2J(P,H) = 33, 27 Hz, PCHPh), 7.03−7.80 (m, 15H, Ph); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 26.5 (d, ^{2+3}J(P,P) = 40 Hz, PPh$_2$), 35.6 (d, ^{2+3}J(P,P) = 40 Hz, PO). IR (KBr): ν(CO) 1716 s cm^{-1}.

[Pd{CH$_2$CH$_2$C(O)Me}{Ph$_2$PCH(Ph)P(O)(OEt)$_2$}][BF$_4$] (10). Complex **10** was prepared by stirring a solution of complex **9** (0.15 g, 0.21 mmol) in CH$_2$Cl$_2$ (30 mL) under 1 atm of ethylene. A pale-green solid was obtained after washing with pentane and diethyl ether (2 × 20 mL), which was dried under vacuum (0.12 g, 88%). Crystals suitable for X-ray diffraction were obtained by recrystallization from CHCl$_3$/pentane. Anal. found: C, 46.15; H, 5.05%. Calcd for C$_{27}$H$_{33}$BF$_4$O$_4$P$_2$Pd·0.5 CH$_2$Cl$_2$: C, 45.93; H, 4.77. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.12 (t, 6H, ^3J(H,H) = 6.9 Hz, CH_3CH$_2$O), 1.72−1.75 (m, 1H, PdCHHCH$_2$), 1.93−1.97 (m, 1H, PdCHHCH$_2$), 3.06 and 3.16 (ABM$_2$ spin system (A = B = M = H), 2H, ^2J(H,H) = 12 Hz, ^3J(H,H) = 3 Hz, PdCH$_2$CH_2), 4.07−4.20 (m, 4H, CH$_3$CH_2O), 4.71 (dd, 1H, ^2J(PO,H) = 21.9 Hz, ^2J(P,H) = 14.4 Hz, PCHP), 7.15−7.92 (m, 15H, aromatics); ^{31}P{^{1}H} NMR (CDCl$_3$): AB spin system δ 37.2 (d, ^{2+3}J(P,P) = 38 Hz, Ph$_2$P) and 38.4 (d, ^{2+3}J(P,P) = 38 Hz, PO); IR(KBr): ν(CO) 1637, ν(PO) 1175 cm^{-1}.

[Pd{CH[C(O)OMe][CH$_2$C(O)Me]}{Ph$_2$PCH(Ph)P(O)(OEt)$_2$}][BF$_4$] (11). Methyl acrylate (15.6 mmol) was added to a solution of **9** (0.12 g, 0.17 mmol) in CH$_2$Cl$_2$ (40 mL). The solution was stirred for 1 h at room temperature. After filtration and removal of the volatiles under vacuum, the pale gray residue was washed with diethyl ether (2 × 15 mL) and pentane (2 × 20 mL) and dried in vacuum to afford complex **11** (0.10 g, 79%). Anal. Found: C, 45.37; H, 5.08%. Calcd for C$_{29}$H$_{35}$BF$_4$O$_6$P$_2$Pd·0.5CH$_2$Cl$_2$: C, 45.68; H, 4.67. ^{31}P{^{1}H} NMR (CDCl$_3$): (diastereoisomeric ratio 1/2: 65/35), major diastereoisomer: δ 36.1 and 38.6 (AB spin system, ^2J(P,P) = 38 Hz); minor diastereoisomer: δ 34.9 and 37.7 (AB spin system, ^2J(P,P) = 39 Hz). The labeling of the protons is shown below:



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^{1}H NMR (300 MHz, CDCl$_3$): δ 1.08−1.19 (m, 2 × 6H, OCH$_2$CH_3), 2.51 (s, 3H, CH$_3$CO, major diastereoisomer), 2.62 (s, 3H, CH$_3$CO, minor diastereoisomer), 2.99 (s, 3H, CH$_3$COO), minor diastereoisomer), 3.15 (s, 3H, CH$_3$COO, major diastereoisomer), 3.27 (dd, ^3J(Ha,Hb) = 6.5 Hz, ^2J(Hb,Hc) = 18.8 Hz, major diastereoisomer), 3.62 (dd, ^3J(Ha,Hb) = 5.3 Hz, ^2J(Hb,Hc) = 18.3 Hz, minor diastereoisomer). ^{1}H NMR (500 MHz, CDCl$_3$): 2.25 (apparence of dt, ^3J(Ha,Hb) = 1.1 Hz, ^2J(Ha,Hc) = 6.2 Hz, ^3J(Hb,P) = 2.6 Hz, Ha major diastereoisomer), 2.51 (s, 3H, CH$_3$CO, major diastereoisomer), 2.62 (s, 3H, CH$_3$CO, minor diastereoisomer), 2.74 (dd, ^3J(Ha,Hb) = 1.6 Hz, ^2J(Ha,Hc) = 6.0 Hz, ^4J(Ha,P) = 2.4 Hz, Ha, minor diastereoisomer), 3.27 (dd, ^3J(Ha,Hb) = 6.5 Hz, ^2J(Hb,Hc) = 18.8 Hz, major diastereoisomer, Hc), 3.62 (dd, ^3J(Ha,Hb) = 5.3 Hz, ^2J(Hb,Hc) = 18.3 Hz, minor diastereoisomer, Hc), 2.99 (s, 3H, CH$_3$COO), minor diastereoisomer), 3.15 (s, 3H, CH$_3$COO, major diastereoisomer), 3.99−4.13 (m, 4H, OCH_2CH$_3$, major diastereoisomer), 6.93−7.96 (br, 40, aromatics); IR(KBr): ν(PO) 1167 cm^{-1}, ν(COcoord.) 1632 cm^{-1}, ν(COuncoord.) 1710 cm^{-1}.

Table 2. Crystal Data and Details of the Structure Determination for 2a and 10·1/2CHCl$_3$

	2a	(**10**·1/2CHCl$_3$)
Chemical formula	C$_{24}$H$_{29}$ClO$_3$P$_2$Pd	2(C$_{27}$H$_{33}$O$_4$P$_2$Pd)·2 (BF$_4$)·CHCl$_3$
M_r	569.26	1472.74
Cell setting, space group	Orthorhombic, *Aba*2	Monoclinic, *Pc*
Temp. (K)	173(2)	173(2)
a (Å)	32.473(5)	9.6834(2)
b, (Å)	17.736(3)	16.8383(4)
c (Å)	8.873(2)	19.4651(5)
β (deg)	90	99.3120(10)
V (Å^3)	5110.3(16)	3132.00(13)
Z	8	2
D_{calc} (Mg m^{-3})	1.480	1.562
radiation	Mo Kα	Mo Kα
F(000)	2320	1492
μ (mm^{-1})	0.98	0.88
Crystal size (mm)	0.10 × 0.10 × 0.10	0.35 × 0.25 × 0.10
R_{int}	0.038	0.052
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.080, 1.02	0.049, 0.128, 1.00
ρ_{max}, ρ_{min} (e Å^{-3})	30.0, 2.4	1.03, −1.09
n° of reflexions ($I > 2\sigma(I)$)	5525	8323
n° of parameters	280	733

[Pd{C(O)CH$_2$CH$_2$C(O)Me}{Ph$_2$PCH(Ph)P(O)(OEt)$_2$}][BF$_4$] (12). A solution of **10**(0.090 g, 0.129 mmol) in CH$_2$Cl$_2$ (30 mL) was purged with CO. The product was not isolated pure. IR (KBr): ν(COuncoord.) 1708, ν(COcoord.) 1659, ν(P═O) 1178 cm^{-1}.

[PdMe{Ph$_2$PCH(Ph)P(O)(OEt)$_2$}{Ph$_2$PCH(Ph)P(O)(OEt)$_2$}][BF$_4$] (13). To a Schlenk tube containing **8** (0.300 g, 0.45 mmol) dissolved in CH$_2$Cl$_2$ (25 mL) was added **1**. The solution was stirred for 90 min at room temperature, and the solvent was removed under vacuum. The residue was washed with diethyl ether (2 × 20 mL) and pentane (2 × 20 mL) and dried in vacuum overnight to afford a gray solid (0.400, 50%) as a mixture as diasteroisomers (*ca*. 1:1). (Anal. Found: C, 53.83; H, 5.20. Calcd for C$_{47}$H$_{55}$O$_6$P$_4$PdBF$_4$: C, 54.65; H, 5.37%). ^{1}H NMR (CDCl$_3$): δ 0.31 (t, 3H, ^3J(P,H) = 6.0 Hz, PdCH$_3$, diastereoisomer 1), 0.37 (dd, 3H, ^3J(P,H) = 5.7 and 6.1 Hz, PdCH$_3$, diastereoisomer 2), 1.01−1.10 (m, 2 × 12H, OCH$_2$CH_3, diastereoisomers 1 + 2), 3.78−3.98 (m, 8H, OCH_2CH$_3$, diastereoisomer 1), 4.01−4.16 (m, 8H, OCH_2CH$_3$, diastereoisomer 2), 4.80 (t, 2H, ^2J(P,H) = 10.4 Hz) and 4.88 (d, 2H, ^2J(P,H) = 9.0 Hz) (we cannot state for which PCHP proton or diastereoisomer), 7.14−7.83 (m, 30H, diastereoisomers 1 + 2); ^{31}P{^{1}H} NMR complicated pattern, owing to the presence of diastereoisomers, which includes, at low temperature (240 K): δ 28.9 (t, J(P,P) = 23 Hz, PPh$_2$, diastereoisomer 2), 29.9 (t, J(P,P) = 21 Hz, PPh$_2$, diastereoisomer 1), and a broad multiplet centered at δ 32.3 for PO. IR(KBr): ν(PO) 1248 and 1163 cm^{-1}.

[PdMe{Ph$_2$PCH(Ph)P(O)(OEt)$_2$}{Ph$_2$PNHC(O)Me}][BF$_4$] (14). The ligand Ph$_2$PNHC(O)Me (0.037 g, 0.15 mmol) was added to a solution of **8** (0.10 g, 0.151 mmol) dissolved in CH$_2$Cl$_2$ (25 mL), the solution was stirred for 2 h at room temperature, and the solvent was removed under vacuum. The beige residue was washed with diethyl ether (2 × 20 mL) and pentane (2 × 20 mL) and dried under vacuum overnight to afford a beige solid (0.07 g, 61%). Anal. Found: C, 53.22; H, 4.93; N, 1.49. Calcd for C$_{38}$H$_{43}$BF$_4$O$_4$NP$_3$Pd: C, 52.83; H, 5.02; N, 1.62. ^{1}H NMR (CDCl$_3$): δ 0.41 (br t, 3H, ^3J(H,H) ∼ 3 Hz, PdCH$_3$), 0.96 (t, 3H, ^3J(H,H) = 7.0 Hz, OCH$_2$CH_3), 1.06 (t, 3H, ^3J(H,H) = 6.9 Hz, OCH$_2$CH_3), 2.42 (s, 3H, NCOCH$_3$), 3.67−3.99 (m, 4H, OCH_2CH$_3$), 4.85 (d of virtual triplets, 1H, ^2J(H,H) = 24 Hz, ^{2+4}J(H,H) = 12 Hz, PCHP), 7.14−8.28 (m, 25H), 9.25 (br, 1H, NH); ^{31}P{^{1}H} NMR: δ 28.9 (br

d, ^2J(P,P) = 404 Hz, CP), 26.3 (br, PO), 67.8 (d, ^2J(P,P) = 404 Hz, PN). IR(KBr): ν(COuncoord.) 1702s, ν(COcoord.) 1606s, ν(POuncoord.) 1240s, ν(POcoord.) 1162s cm^{-1}.

Crystal Structure Determinations. Crystals of **2a** and **10** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution of the complex at 5 °C. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (Table 2). Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software[73,74] and the refinement was by full-matrix least-squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors (d_{C-H} = 0.95 Å, U_{11} = 0.04). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Center as Supplementary publication no CCDC 706582 and 70658. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: $^{31}P\{^1H\}$ NMR spectrum of the equilibrium mixture **5**/**5′** (Figure S-1), $^{31}P\{^1H\}$ NMR resonances of **6** (Figure S-2), and $^{31}P\{^1H\}$ NMR spectrum of complex **13** at different temperatures (Figure S-3). Crystallographic details for all structures in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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