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Synthesis and structure of orthopalladated complexes derived from prochiral iminophosphoranes and phosphorus ylides

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Abstract

The iminophosphorane $Ph_2MeP{=}NPh$ (**1**) reacts with $Pd(OAc)_2$ to give the orthopalladated $[Pd(\mu\text{-}Cl)\{C_6H_4(PPh(Me){=}NPh\text{-}\kappa\text{-}C,N)\text{-}2\}]_2$ (**2**) as the racemic mixture, which reacts with Tl(acac) to give $[Pd(acac)\{C_6H_4(PPh(Me){=}NPh\text{-}\kappa\text{-}C,N)\text{-}2\}]$ (**3**). The X-ray structure of (**3**) has been determined by diffraction methods. The phosphorus ylide $Ph_2MeP{=}CHC(O)Ph$ (**5**) reacts with $Pd(OAc)_2$ to give the dinuclear $[Pd(\mu\text{-}Cl)\{C_6H_4(PPh(Me)CHC(O)Ph\text{-}\kappa\text{-}C,C)\text{-}2\}]_2$ (**6**) as a mixture of isomers. Complex (**6**) reacts with Tl(acac), PPh_3 or $AgClO_4$/dppe giving the mononuclear derivatives $[Pd(acac)\{C_6H_4(PPh(Me)CHC(O)Ph\text{-}\kappa\text{-}C,C)\text{-}2\}]$ (**7**), $[PdCl\{C_6H_4(PPh(Me)CHC(O)Ph\text{-}\kappa\text{-}C,C)\text{-}2\}PPh_3]$ (**8**) and $[Pd\{C_6H_4(PPh(Me)CHC(O)Ph\text{-}\kappa\text{-}C,C)\text{-}2\}(dppe\text{–}P,P')][ClO_4)$ (**9**), as mixtures of stereoisomers with high diastereomeric excess.

Keywords: Cyclometallated; CH-bond activation; Iminophosphoranes; Phosphorus ylides; Palladium

1. Introduction

The activation of C–H bonds induced by transition metals is, at present, one of the most active fields of research in organometallic chemistry due to its implications, among others, in fundamental steps in catalytic cycles, in the functionalization of simple substrates through orthometallation, and in other relevant chemical processes [1–29]. While this type of reaction has been extensively studied with a large variety of substrates, metallations developed with iminophosphoranes are still scarcely represented [30–45]. The iminophosphoranes are compounds of general structure $R_3P{=}NR'$ (R = alkyl, aryl; R′ = alkyl, aryl, acyl, ...) that have numerous applications in organic chemistry (e.g., aza-Wittig reaction), either as neutral or as anionic reagents, and behave as good ligands [46–48]. In addition, they show notable analogies with the phosphorus ylides $R_3P{=}CR'(R'')$ [46].

The orthometallation of these two species, iminophosphoranes $R_3P{=}NR'$ [30–45] and phosphorus ylides $R_3P{=}C(R')(R'')$ [49–57], is produced, in the vast majority of cases, regioselectively at the Ph rings of the phosphine unit. Some recent contributions have shown, however, that it is possible to obtain orthopalladated complexes derived from CH activation at Ph rings belonging to the R′ or R″ substituents of the ylidic carbon and, more precisely, belonging to benzamide moieties [45].

Aiming to expand the scope of this type of orthometallated derivatives we have studied the C–H bond activation process, induced by Pd(II) salts, in the iminophosphorane ligand $Ph_2MeP{=}NPh$ (**1**) and in the ylide ligand $Ph_2MeP{=}CHC(O)Ph$ (**5**), both containing a pro-chiral phosphorus center. The results obtained show that the palladation is produced at one phenyl ring of the PPh_2Me

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group, giving complexes with a stereogenic P center and, in the case of the ylides, with an additional chiral carbon center. In the latter, the final arrangement occurs with high diastereoselective induction.

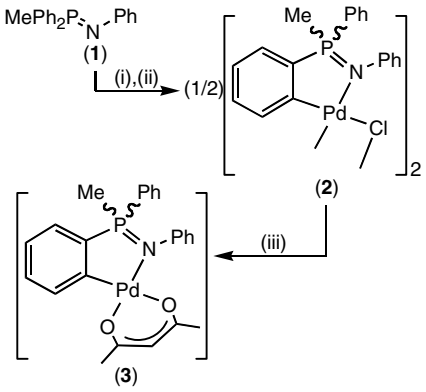
2. Results and discussion

The iminophosphorane $Ph_2MeP{=}NPh$ (**1**) was prepared following Staudinger method [58], by reaction of N_3Ph with PPh_2Me in dry CH_2Cl_2. Phenylazide was prepared following also reported methods [59], by reaction of aniline with $NaNO_2$ and NaN_3 in H_2O at 0 °C for 5 h. The IR spectrum of **1** shows a strong absorption at 1314 cm^{-1}, due to the P=N stretch [60–62], and the $^{31}P\{^1H\}$ NMR spectrum shows a single peak at 5.89 ppm. These results are similar to those observed in related species such as $Ph_3P{=}NPh$ [32].

The reactivity of **1** with $Pd(OAc)_2$ (OAc = acetate) has been investigated. The treatment of $Pd(OAc)_2$ with **1** (1:1 molar ratio) in refluxing toluene, and further reaction of the acetate intermediate with excess LiCl in methanol gives a very insoluble solid, whose stoichiometry corresponds to the orthometallated complex $[Pd(\mu\text{-}Cl)\{C_6H_4(PPh(Me){=}NPh\text{-}\kappa\text{-}C,N)\text{-}2\}]_2$ (**2**) (Scheme 1). The N-bonding of the iminophosphorane can be inferred from the IR spectrum, since a decrease on the P=N stretch is observed. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows the presence of three signals, one of them containing two overlapped peaks, in the range around 45–50 ppm. The range of chemical shifts denotes the presence of the metallacycle $[Pd(C_6H_4PR_2{=}NR')]$ [32], and means that a palladation has occurred at the phenyl ring of the phosphonium unit. The proposed structure is represented in Scheme 1, and shows that the P atom has been transformed into an stereogenic center. Taking into account these facts, the presence of four peaks in the $^{31}P\{^1H\}$ NMR spectrum of **2** can be easily explained. Complex **2** is dinuclear and it is obtained as a mixture of geometric isomers (*cis* and *trans*), with two stereogenic P centers each. A signal is observed for each one of the four diastereoisomers: *cis* (RR/SS), *cis* (RS/SR), *trans* (RR/SS) and *trans* (RS/SR). The high insolubility of **2** in the usual organic solvents prevented a more detailed spectroscopic characterization of **2**.

For this reason, complex **2** was reacted with Tl(acac) (molar ratio 1:2) in CH_2Cl_2 to obtain the mononuclear acetylacetonate derivate $[Pd(acac\text{-}O,O')\{C_6H_4(PPh(Me){=}NPh\text{-}\kappa\text{-}C,N)\text{-}2\}]$ (**3**) (Scheme 1), which is adequately soluble in organic solvents. Its $^{31}P\{^1H\}$ NMR spectrum shows a single peak at 48.6 ppm, in the same region than those observed for **2**. The ^1H NMR spectrum of **3** shows the high-field signals assigned to the acac ligand and to the methyl group of the phosphine ligand. Full assignment of the aromatic signals due to the $Pd(C_6H_4)$ fragment was performed with the help of a ^1H–^1H COSY experiment, and were found at 7.20–7.27 (2H), 7.45–7.49 (1H) and 7.94 (1H) ppm, while the protons assigned to the $P\text{-}C_6H_5$ ring appear at 7.68 (H_m), 7.75 (H_p) and 8.08 (H_o) ppm.

The molecular structure of **3** was determined through X-ray diffraction methods. A molecular drawing of complex **3** is shown in Fig. 1, crystallographic data and parameters concerning data collection and structure solution and refinement are summarized in Table 1 and selected bond distances and angles are presented in Table 2. Complex **3** crystallizes on the orthorhombic system, on the centrosymmetric space group Pbca. Although **3** is quiral, the crystal as a whole is racemic. The absolute configuration of the phosphorus atom depicted in the structure shown in Fig. 1 is *S*. The Pd atom is located on a square-planar environment, surrounded by the iminic nitrogen N(1), the metallated carbon C(7), and the two oxygen atoms O(1) and O(2) of the chelating acac ligand. The sum of the bond angles around the palladium is almost 360.0°. Although the orthometallated ligand is remarkably warped, the environment around the Pd is planar. The Ph ring and the Me group at the palladacycle occupy the axial and equatorial positions, respectively. The axial location of the bulkiest group probably responds to a minimization of intramolecular interactions. The Pd(1)–N(1) [2.046(5) Å] and the Pd(1)–C(7) [1.973(6) Å] bond distances are statistically identical than those found in related complexes like



Scheme 1. (i) $Pd(OAc)_2$/toluene/Δ; (ii) LiCl/MeOH; (iii) Tl(acac).

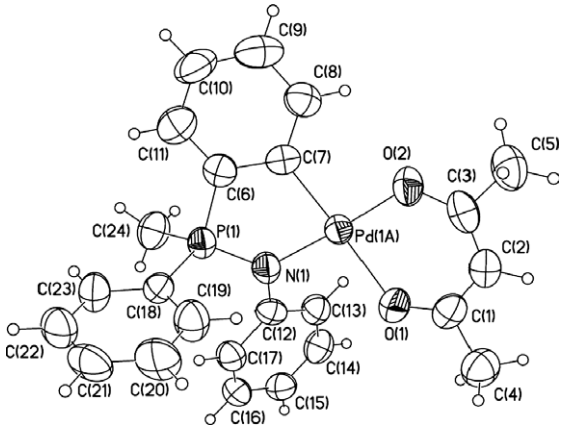


Fig. 1. Molecular structure of complex **3**. Ellipsoids are drawn at 50% probability level.

Table 1
Crystal data and structure refinement for compound **3**

Empirical formula	$C_{24}H_{24}NO_2PPd$
Formula weight	495.81
Temperature (K)	100(1)
Radiation (l, Å)	Mo Kα (0.71073)
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	16.0446(14)
b (Å)	14.8842(11)
c (Å)	17.8088(13)
V (Å^3)	4252.9(6)
Z	8
D_{calc} (Mg/m^3)	1.549
μ (mm^{-1})	0.968
Crystal size (mm^3)	0.14 × 0.12 × 0.04
Reflections collected	14188
Independent reflections	3742 ($R_{int} = 0.0750$)
Data/restraints/parameters	3742/0/275
Goodness-of-fit on F^2	1.035
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0548$; $wR_2 = 0.0949$
R indices (all data)	$R_1 = 0.1039$; $wR_2 = 0.1100$
Largest difference in peak, hole (e Å^{-3})	0.433 and −0.377

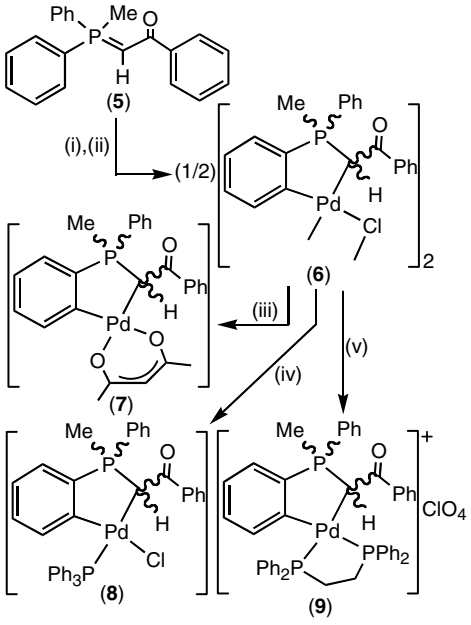
Table 2
Selected bond distances (Å) and angles (°) for compound **3**

Pd1–C7	1.973(6)	Pd1–N1	2.046(5)
Pd1–O1	2.106(5)	Pd1–O2	1.987(4)
P1–N1	1.600(5)	P1–C6	1.787(6)
P1–C18	1.802(6)	N1–C12	1.400(7)
C7–Pd1–N1	85.2(2)	C7–Pd1–O2	90.4(2)
N1–Pd1–O1	93.2(2)	O1–Pd1–O2	91.14(18)
Pd1–C7–C6	118.2(5)	C7–C6–P1	114.0(5)
C6–P1–N1	102.6(3)	P1–N1–Pd1	113.8(3)

[Pd(κ^2-C,N–C_6H_4(PPh_2=NC_6H_4Me-4′)-2)(μ-OAc)]$_2$ [2.050(2)Å] [42] and [Pd(κ^2-C,N–$C_6H_4PPh_2$=NPh)(μ-Cl)]$_2$ [2.047(2) Å] [63]. The acac group behaves as an *O*,*O*′-chelate ligand and is bonded to the Pd atom giving a six membered ring. The distances Pd(1)–O(2) [1.987(4) Å] and Pd(1)–O(1) [2.106 Å] are quite different, reflecting the different *trans* effect of the nitrogen atom and the arylic carbon. However, the two distances are in good agreement with other structures where the acetilacetonate also behaves as a chelate ligand coordinated to a Pd centre [64]. Other internal parameters of the metallated iminophosphorane ligand do not deviate from published values [65].

The α-ketostabilized ylide [Ph_2MeP=CHC(O)Ph] (**5**) was synthesized following reported procedures, with minor changes (see Section 4) [66,67]. Phenacyl bromide reacts with PPh_2Me to give the corresponding phosphonium salt, [Ph_2MePCH_2C(O)Ph]Br (**4**), which in turn reacts with Na_2CO_3 in MeOH/H_2O at 25 °C giving **5** as an air-stable white solid [66,67]. The IR spectrum of **5** shows a strong absorption at 1504 cm^{-1} due to the carbonyl stretch. This band clearly appears at lower energies compared to that found in the salt **4** (1661 cm^{-1}) due to the charge delocalization present in this kind of compounds. The $^{31}P\{^1H\}$ NMR spectrum shows a signal at 10.82 ppm, shielded with respect to that found in **4** (23.13 ppm), as is typical for carbonyl-stabilized ylides [49].

Treatment of **5** with $Pd(OAc)_2$ (1:1 molar ratio) in refluxing CH_2Cl_2, and further reaction of the acetate intermediate with excess LiCl in methanol gives a yellow solid, whose stoichiometry corresponds to the palladated complex [Pd(μ-Cl){C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}]$_2$ (**6**) (Scheme 2). Ylide **5** can undergo a C–H activation process at two different positions, almost equivalents, namely the phenyl ring of the benzoyl fragment and the phenyl ring of the phosphine group (Fig. 2). We have recently reported that the preferred position for palladation on the related ylides Ph_3P=CHC(O)Ph [45] is the phenyl ring bonded to the P atom, being the activation of the benzoyl ring only possible in these species in the absence of Ph rings at the P atom. In addition, we have also reported that the palladation of the benzoyl ring is possible when iminophosphoranes Ph_3P=NC(O)Ph are considered [45]. Therefore, although both activations could in principle occur, it seems that, for ylides, palladation at the PPh_3 group is the expected process. The IR spectrum of **6** shows a sharp absorption, due to the ν_{CO} stretch, shifted to higher frequency with respect to the corresponding absorption in



Scheme 2. (i) $Pd(OAc)_2/CH_2Cl_2/\Delta$; (ii) LiCl/MeOH; (iii) Tl(acac); (iv) PPh_3; (v) $AgClO_4$/THF/dppe.

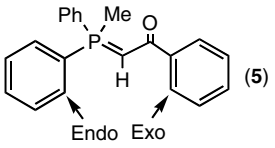


Fig. 2. Possible orthometallation sites of the prochiral phosphorus ylide (**5**).

the free ligand **5**, this fact indicating that the ylide is C-bonded to the Pd center. The $^{31}P\{^{1}H\}$ NMR spectrum of **6** shows eight different signals in the range 15.5–20 ppm. The presence of such high number of signals can be easily explained taking into account: (i) that the palladation has been produced at one of the Ph rings of the phosphine moiety; (ii) the C-bonding of the ylide, and (iii) that **6** is dinuclear in nature. Thus, the generated Pd{C_6H_4-(PPh(Me)CHC(O)Ph-κ-C,C)-2} ligand contains two stereogenic centers, the P atom and the C atom, and two diastereoisomers could be expected for each palladated unit. Moreover, this palladated unit can be arranged, in a dinuclear complex, in *cis* and *trans* orientations, this giving a total of eight *cis* diastereosiomers and additional eight *trans* diastereoisomers. Although the total number of ^{31}P NMR peaks arising from these considerations exceeds the number of signals observed in the spectrum, we must take into account the possible overlap of peaks and that not all isomers would be obtained with the same molar ratio.

In order to simplify the characterization of the palladated ligand, a decrease in the number of diastereoisomers is desirable, and further reactivity of **6** has been performed. Reactions of cleavage of the chloride bridges and substitutions of the halide by other neutral or anionic ligands, which should give mononuclear derivatives, have been attempted. The reaction of **6** with Tl(acac) (1:2 molar ratio), PPh_3 (1:2 molar ratio) or $AgClO_4$/dppe (1:2:2 molar ratio) gives the mononuclear derivatives [Pd(acac){C_6H_4(PPh(Me)CHC(O)-Ph-κ-C,C)-2}] (**7**), [PdCl{C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}PPh_3] (**8**) and [Pd{C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}-(dppe–P,P′)](ClO_4) (**9**) (see Scheme 2).

Complexes **7**–**9** show correct elemental analyses and mass spectra. The IR spectra of **7**–**9** show the presence of absorptions assigned to the different functional groups: two strong absorptions due to the υ_{CO} stretch of the acac ligand (1564, 1514 cm^{-1}) in **7** and one intense band in the range 1615–1625 cm^{-1} due to the υ_{CO} stretch of the ylidic carbonyl, amongst them. The ^{1}H NMR spectra show in all cases two sets of signals, corresponding to the presence of two diastereoisomers (R_PR_C/S_PS_C) and (R_PS_C/S_PR_C). The relative abundance varies from one to another, but all syntheses occur with notable diastereomeric excess, probably related with the fact that the two stereogenic centers are very near. Observed molar ratios are 5/1 (d.e. = 67%, complex **7**), 7/1 (d.e. = 75%, complex **8**) and 6.7/1 (d.e. = 74%, complex **9**). Similar d.e. have been reported for Pd(II) complexes with (sulfinylmethyl)phosphonium ylide ligands, which also contain two adjacent stereogenic centers (the Cα atom and the sulfur atom) [68]. The ^{1}H NMR spectrum of **7** shows expected signals due to the methyl and CH protons of the acac ligand (around 2 and 5 ppm, respectively), while the ylidic protons appear around 4.50 ppm as doublets with a small coupling constant $^{2}J_{PH}$, typical for C–bonding of the ylides. For complex **8**, the ylidic protons appear as doublets of doublets, meaning that each proton is coupled with two different P nuclei (PPh_3 and PPh_2Me). The coupling constants found ($^{2}J_{PH}$ = 8.8 Hz and $^{3}J_{PH}$ = 6.8 Hz) suggest that the PPh_3 is located *trans* to the ylidic carbon[49], in good agreement with the *transphobia* between the PPh_3 and the arylic carbon [69–71]. Similar conclusions can be derived from the analysis of the ^{1}H NMR spectrum of **9**, although in this case the extensive overlap of peaks avoids a careful inspection.

In order to determine the absolute configurations of the stereogenic centers on the most abundant diastereomer in **7**–**9**, NOE experiments were carried out in **8**, as a representative example. Irradiation of the ylidic proton results in clear NOEs in signals due to the ortho protons of the benzoyl ring, ortho protons of the P–phenyl ring and in P–Me protons. On the other hand, saturation at the ortho protons of the benzoyl group induces clear NOEs in signals assigned to the neighbor meta protons and in the ylidic proton, while saturation at the ortho protons of the PPh group produces strong NOEs at the meta protons of the same ring, at the ylidic protons and at the methyl group. With this sequence of NOE effects, the most plausible steric arrangement at the ylidic P and C atoms is that containing one Ph ring of the P atom and the bulkiest C(O)Ph group of the Cα atom in axial positions but in different sides of the molecular plane, while the methyl group of the P atom and the ylidic proton Cα–H are located in equatorial positions. In good agreement with the structures depicted in Scheme 2, the $^{31}P\{^{1}H\}$ NMR spectra of **7**–**9** also show two sets of signals, due to the two possible diastereoisomers. That of **7** shows two singlets around 20 ppm, these signals appearing in the same range that those observed in **6**, and suggesting that the palladacycle has not been altered. The $^{31}P\{^{1}H\}$ NMR spectrum of **8** shows the expected pairs of doublets, and in that of **9** the P,P'-bonding mode of the dppe is evident, since it shows three low-field signals [72], one due to the ylide and the other two to the dppe ligand (range 43–54 ppm).

3. Conclusion

New cyclopalladated complexes have been obtained through CH bond activation processes on the iminophosphorane $Ph_2MeP{=}NPh$ (**1**) and on the ylide ligand $Ph_2MeP{=}CHC(O)Ph$ (**5**). Although there are two competing cyclometallation positions, the palladation is produced selectively at the phenyl rings of the PPh_2Me unit, giving [Pd(μ-Cl){C_6H_4(PPh(Me)=NPh-κ-C,N)-2}]$_2$ (**2**) and [Pd(μ-Cl){C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}]$_2$ (**6**), which are obtained as mixtures of isomers. The corresponding acac derivatives allow a complete characterization of the cyclometallated ligands, including X-ray determination. The reactivity of (**6**) with anionic chelating (**7**), neutral monodentate (**8**), or neutral chelating (**9**) ligands promotes the cleavage and/or substitution of the chloride bridging system and the synthesis of new mononuclear species, in which the five-membered metallacycle remains stable.

4. Experimental

4.1. General methods

Solvents were dried and distilled under argon using standard procedures. Elemental analyses were performed on a Perkin–Elmer 2400-B microanalyser. Infrared spectra (4000–400 cm^{-1}) were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer from nujol mulls between polyethylene sheets. ESI/APCI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Helium served as a cooling gas for the ion trap and collision gas for MS_n experiments. Other mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (δ, ppm; J, Hz) were recorded on $CDCl_3$ or CD_2Cl_2 solutions at room temperature (other temperatures are specified) on Bruker ARX-300 or Avance-400 spectrometers. The ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual solvent signal while the $^{31}P\{^1H\}$ NMR spectra was referenced to external H_3PO_4 (85%).

4.2. Synthesis

4.2.1. Synthesis of $Ph_2MeP{=}NPh$ (1)

The iminophosphorane (**1**) has been obtained using the Staudinger method [58]. To a solution of N_3Ph [59] (1.36 g, 11.9 mmol) in dry CH_2Cl_2 (20 ml) under Ar atmosphere, a solution of PPh_2Me (2.21 g, 11.9 mmol) in dry CH_2Cl_2 (20 ml) was added dropwise during 20 min. The evolution of N_2 is evident even from the first steps of the addition. The mixture was stirred at 25 °C until N_2 evolution ceased (≈4 h), and then it was evaporated to dryness. **1** was obtained as a yellow solid. Yield: 3.43 g (100%). Anal. Calc. for $C_{19}H_{18}NP$ (291.3): C, 78.33; H, 6.23; N, 4.81. Found: C, 78.15; H, 6.76; N, 4.35%. MS (MALDI+): m/z (%) = 292 (100) $[M+H]^+$. IR (ν, cm^{-1}): 1314 (ν_{PN}). ^1H NMR ($CDCl_3$): $\delta = 2.15$ (d, 3H, $^2J_{PH} = 9.6$, PMe), 6.68 (t, 1H, $^3J_{HH} = 6.0$, H_p, Ph), 6.78 (d, 2H, $^3J_{HH} = 5.7$, H_o, Ph), 7.04 (t, 2H, $^3J_{HH} = 5.7$, H_m, Ph), 7.46–7.57 (m, 6H, $H_m + H_p$, PPh_2), 7.76 (m, 4H, H_o, PPh_2). $^{31}P\{^1H\}$NMR ($CDCl_3$): $\delta = 5.89$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 15.22$ (d, $^1J_{PC} = 74.9$, PMe), 117.36 (C_p, Ph), 122.92 (d, $^3J_{PC} = 18.8$, C_o, Ph), 128.79 (d, $^4J_{PC} = 2.6$, C_m, Ph), 128.87 (d, $^3J_{PC} = 11.9$, C_m, PPh_2), 131.44 (d, $^2J_{PC} = 9.4$, C_o, PPh_2), 131.54 (d, $^1J_{PC} = 94$, C_i, PPh_2), 131.79 (C_p, PPh_2), 151.23 (d, $^2J_{PC} = 1.8$, C_i, Ph).

4.2.2. Synthesis of $[Pd(\mu\text{-}Cl)\{C_6H_4(PPh(Me){=}NPh\text{-}\kappa\text{-}C,N)\text{-}2\}]_2$ (2)

To a solution of **1** (0.300 g, 1.04 mmol) in dry toluene (15 ml) under Argon atmosphere, $Pd(OAc)_2$ (0.235 g, 1.04 mmol) was added, and the resulting mixture was refluxed for 2 h. After the reaction time, some decomposition (presence of black Pd^0) is evident. The cooled suspension was filtered, the solid was dissolved in MeOH and treated with an excess of anhydrous LiCl (0.775 g, 17.8 mmol). A grey solid immediately precipitated, which was filtered, washed with MeOH (20 ml) and Et_2O (50 ml) and dried in vacuo. This grey solid was recrystallized from CH_2Cl_2 giving **2** as a yellow solid, which was characterized by NMR as a mixture of the *cis* and *trans* isomers in 1/1 molar ratio. Yield: 0.175 g (39.4%). Anal. Calc. for $C_{38}H_{34}Cl_2N_2P_2Pd_2$ (864.4): C, 52.80; H, 3.96; N, 3.24. Found: C, 52.66; H, 4.46; N, 3.60%. MS (MALDI+): m/z (%) = 864 (10) $[M]^+$. IR (ν, cm^{-1}): 1254 (ν_{PN}). ^1H NMR (dmso-d_6): $\delta = 2.30$ (d, $^2J_{PH} = 12.5$, PMe, both), 6.83–8.18 (m, 28H, PPh_2, both). $^{31}P\{^1H\}$NMR (dmso-d_6): $\delta = 46.78$, 48.49, 48.74 (2P).

4.2.3. Synthesis of $[Pd(acac\text{-}O,O')\{C_6H_4(PPh(Me){=}NPh\text{-}\kappa\text{-}C,N)\text{-}2\}]$ (3)

To a solution of **2** (0.372 g, 0.429 mmol) in CH_2Cl_2 (5 ml) Tl(acac) (0.260 g, 0.858 mmol) was added, resulting in the immediate precipitation of TlCl. This suspension was stirred for 1 h at 25 °C and then filtered over Celite. The clear yellow solution was evaporated to dryness and the residue treated with cold Et_2O (10 ml), to give **3** as a yellow solid. Yield: 0.341 g (80.33%). Complex **3** was recrystallized from $CHCl_3/OEt_2$, giving crystals of $\mathbf{3}\cdot 2CHCl_3$, which were used for analytical purposes. Anal. Calc. for $C_{24}H_{24}NO_2PPd \cdot 2CHCl_3$ (734.6): C, 42.51; H, 3.57; N, 1.90. Found: C, 42.36; H, 4.26; N, 2.49. MS (MALDI+): m/z (%): 396 (20) $[M-acac]^+$. IR (ν, cm^{-1}): 1582 (ν_{CO}), 1515 (ν_{CO}), 1261 (ν_{PN}). ^1H NMR ($CDCl_3$): $\delta = 1.87$ (s, 3H, Me, acac), 2.24 (s, 3H, Me, acac), 2.32 (d, 3H, $^2J_{PH} = 12.3$, PMe), 5.47 (s, 1H, CH, acac), 7.01–7.13 (m, 2H, H_p(NPh) + 1H (C_6H_4)), 7.20–7.27 (m, 5H, 1H (C_6H_4) + $2H_o$ + $2H_m$ (NPh)), 7.47 (m, 1H, C_6H_4), 7.68 (m, 2H, H_m, PPh), 7.75 (m, 1H, H_p, PPh), 7.94 (d, 1H, $^3J_{HH} = 7.6$, C_6H_4), 8.08 (dd, 2H, $^3J_{HH} = 8.0$, $^3J_{PH} = 11.5$, H_o, PPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 12.11 (Me, acac), 12.70 (Me, acac), 27.49 (d, $^1J_{CP} = 16.1$, PMe), 100.03 (CH, acac), 122.15 (d, $^4J_{CP} = 2.0$, C_m, NPh), 124.32 (d, $J_{CP} = 14.3$, C_6H_4), 126.54 (d, $J_{CP} =$ 22.6, C_6H_4), 127.57 (d, $^2J_{CP} = 9.5$, C_6H_4), 127.89 (C_p, NPh), 129.10 (d, $^3J_{CP} = 11.4$, C_m, PPh), 130.20 (d, $^4J_{CP} =$ 3.2, C_p, PPh), 131.08 (d, $^2J_{CP} = 9.64$, C_o, PPh), 131.67 (d, $^1J_{CP} = 82.5$, C_i, PPh), 132.34 (C_6H_4), 132.48 (d, $^3J_{CP} =$ 2.4, C_o, NPh), 140.19 (d, $^1J_{CP} = 138.5$, C_2, C_6H_4), 146.18 (d, $^2J_{CP} = 3.3$, C_i, NPh), 151.91 (d, $^2J_{CP} = 21.3$, C_1, C_6H_4), 185.28 (CO, acac), 188.04 (CO, acac). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 48.6$.

4.2.4. Synthesis of $Ph_2MeP{=}CHC(O)Ph$ (5)

The ylide $Ph_2MeP{=}CHC(O)Ph$ **5** was prepared following the general method reported by Ramírez et al. [66] in two steps. The reaction of phenacyl bromide (1.500 g, 7.54 mmol) with PPh_2Me (1.40 ml, 7.54 mmol) in THF at r.t. for 24 h gives the salt $[Ph_2MePCH_2C(O)Ph]Br$ (**4**)

(2.78 g, 92.4%) [67]. In the second step, the phosphonium **4** (1.00 g, 2.51 mmol) reacts with Na_2CO_3 (0.27 g, 2.51 mmol) in MeOH/H_2O (1/7, 80 ml), giving **5** as a white solid. Yield: 0.45 g (56.7%). Selected spectroscopic data: IR (ν, cm^{-1}): 1504 (ν_{CO}). ^1H NMR ($CDCl_3$): $\delta = 2.35$ (d, 3H, $^2J_{PH} = 14.0$, PMe), 4.14 (s, br, 1H, PCH), 7.2-7.29 (m, 3H, H_m, H_p, PhC(O)), 7.42 (m, 4H, H_m, PPh_2), 7.48 (td, 2H, H_p, PPh_2, $^3J_{HH} = 6.8$, $^4J_{HH} = 1.2$), 7.63 (dd, 4H, H_o, PPh_2, $^3J_{PH} = 12.4$, $^3J_{HH} = 6.8$), 7.87 (dd, 2H, H_o, PhC(O)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 10.82$.

4.2.5. Synthesis of [Pd(μ-Cl){C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}]$_2$ (6)

To a solution of **5** (1.000 g, 3.14 mmol) in CH_2Cl_2 (10 ml), $Pd(OAc)_2$ (0.710 g, 3.14 mmol) was added, and the resulting mixture was refluxed with vigorous stirring for 24 h. After the reaction time, the solvent was evaporated and the yellow solid residue was dissolved in 15 ml of MeOH and anhydrous LiCl (0.130 g, 3.140 mmol) was added. Immediately a yellow solid (**6**) precipitated. The stirring was maintained during 30 min at room temperature and the resulting suspension was filtered. The yellow solid was washed with MeOH (10 ml) and Et_2O (50 ml) and air dried. **6** was characterized (NMR) as a mixture of eight diastereoisomers with a molar ratio 1.00/0.59/0.67/2.23/3.47/1.34/0.98/0.43. Yield: 1.380 g (95.7%). Complex **6** was recrystallized from CH_2Cl_2/OEt_2, giving crystals of **6**·CH_2Cl_2, which were used for analytical purposes. Anal. Calc. $C_{42}H_{36}Cl_2O_2P_2Pd_2CH_2Cl_2$ (1003.3): C, 51.47; H, 3.82. Found: C, 51.52; H, 3.61. MS (MALDI+): m/z (%) = 881 (50) $[M-Cl]^+$. IR (ν, cm^{-1}): 1614 (ν_{CO}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 15.91$, 16.12, 17.23, 18.12, 18.95, 19.11, 19.69, 19.90.

4.2.6. Synthesis of [Pd(acac-O,O′){C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}] (7)

Complex **7** was prepared following an experimental method similar to that described for **3**, but using **6** as starting compound. Thus, **6** (0.150 g, 0.16 mmol) was reacted with Tl (acac) (0.100 g, 0.33 mmol), giving **7** as a yellow solid, which was characterized as a mixture of two diastereoisomers in 5/1 molar ratio (d.e. = 66.7%). Yield: 0.110 g (61.5%). Anal. Calc. for $C_{26}H_{25}O_3PPd$ (522.9): C, 59.21; H, 4.82. Found: C, 58.91; H, 4.93%. MS (MALDI+): m/z (%) = 523 (55) $[M]^+$. IR (ν, cm^{-1}): 1625 (ν_{CO}, ylide), 1564 (ν_{CO}, acac), 1514 (ν_{CO}, acac). ^1H NMR ($CDCl_3$): $\delta = 1.53$ (s, Me, acac, maj.), 1.75 (s, Me, acac, min), 1.91 (s, Me, acac, maj.), 1.94 (s, Me, acac, min), 2.45 (d, $^2J_{PH} = 12.6$, PMe, min), 2.48 (d, $^2J_{PH} = 13.2$, PMe, maj.), 4.46 (d, $^2J_{PH} = 2.4$, CHP, maj.), 4.50 (d, $^2J_{PH} = 4.8$, CHP, min), 5.11 (s, CH, acac, maj.), 5.17 (s, CH, acac, min), 6.98–7.09 (m, H_6 and H_5, C_6H_4, both), 7.17–7.21 (m, H_4, C_6H_4, both), 7.24 (m, H_m, PhC(O), min), 7.28 (t, $^3J_{HH} = 7.3$, H_m, PhC(O), maj.), 7.34 (t, $^3J_{HH} = 7.3$, H_p, PhC(O), min), 7.38 (t, $^3J_{HH} = 7.2$, H_p, PhC(O), maj.), 7.45–7.49 (m, H_m, PPh, both), 7.52–7.56 (m, H_p, PPh, both), 7.66 (dd, $^3J_{HH} = 7.8$, $^4J_{HH} = 2.6$, H_3, C_6H_4, min), 7.68 (dd,$^3J_{HH} = 7.4$, $^4J_{HH} = 2.1$, H_3, C_6H_4, maj.), 7.83 (m, H_o, PPh, maj.), 7.99 (m, H_o, PPh, min), 8.06 (d, $^3J_{HH} = 7.2$, H_o, PhC(O), min), 8.10 (d, $^3J_{HH} = 7.2$, H_o, PhC(O), maj.). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 11.94$ (d, PMe, maj., $^1J_{PC} = 52.3$), 14.00 (d, PMe, min, $^1J_{PC} = 62.2$), 27.61 (Me, acac, maj.), 27.84 (Me, acac, min), 27.97 (Me, acac, maj.), 28.02 (Me, acac, min), 30.78 (d, CHP, maj., $^1J_{PC} = 63.0$), 35.14 (d, CHP, min, $^1J_{PC} = 62.8$), 99.45 (CH, acac, maj.), 99.57 (CH, acac, min), 124.40 (d, C_5, C_6H_4, min, $^4J_{PC} = 13.5$), 124.75 (d, C_5, C_6H_4, maj., $^4J_{PC} = 13.3$), 125.31 (d, C_i, PPh, min, $^1J_{PC} = 67.9$), 128.29 (d, C_6, C_6H_4, maj., $^3J_{PC} = 16.6$), 128.64 (d, C_6, C_6H_4, min, $^4J_{PC} = 16.4$), 127.51 (C_m, PhCO, min), 127.62 (C_m, PhCO, maj.), 127.31 (d, C_i, PPh, maj., $^1J_{PC} = 77.1$), 128.63 (d, C_o, PhCO, maj., $^4J_{PC} = 1.4$), 128.84 (d, C_o, PhCO, min, $^4J_{PC} = 1.4$), 128.94 (d, C_m, PPh, min, $^3J_{PC} = 11.2$), 129.41 (d, C_m, PPh, maj., $^3J_{PC} = 11.2$), 130.23 (d, C_4, C_6H_4, min, $^3J_{PC} = 3.4$), 130.38 (d, C_4, C_6H_4, maj., $^3J_{PC} = 3.4$), 131.56 (d, C_o, PPh, maj., $^2J_{PC} = 9.3$), 131.63 (C_p, PhCO, min), 131.81 (C_p, PhCO, maj.), 132.60 (d, C_p, PPh, maj., $^4J_{PC} = 2.8$), 132.76 (d, C_p, PPh, min, $^4J_{PC} = 2.8$), 133.01 (d, C_o, PPh, min, $^2J_{PC} = 9.4$), 133.72 (d, C_3, C_6H_4, maj., $^2J_{PC} = 15.1$ Hz), 138.07 (d, C_i, PhCO, min, $^3J_{PC} = 5.2$ Hz), 138.34 (d, C_2, C_6H_4, min, $^1J_{PC} = 115.7$), 138.48 (d, C_i, PhCO, maj, $^3J_{PC} = 8.1$ Hz), 138.69 (d, C_2, C_6H_4, maj., $^1J_{PC} = 103.9$), 157.99 (d, C_1, C_6H_4, min, $^2J_{PC} = 22.1$), 158.34 (d, C_1, C_6H_4, maj., $^2J_{PC} = 20.6$), 186.04 (CO, acac, maj.), 186.51 (CO, acac, min), 186.79 (CO, acac, min), 186.89 (CO, acac, maj.), 195.00 (d, CO, ylide, min. $^2J_{PC} = 4.6$), 198.59 (d, CO, ylide, maj., $^2J_{PC} = 3.9$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.21$ (C_6H_4-2-PPhMe, min), 21.43 (C_6H_4-2-PPhMe, maj.).

4.2.7. Synthesis of [PdCl{C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}PPh_3] (8)

Solid PPh_3 (0.086 g, 0.33 mmol) was added to a suspension of **6** (0.150 g, 0.16 mmol) in 5 ml of CH_2Cl_2. The initial suspension gradually dissolved and, after 30 min stirring at r.t., a pale yellow solution was obtained. After the reaction time, any remaining insoluble material was filtered over Celite and discarded. The resulting solution was evaporated to dryness and the oily residue was treated with 20 ml of Et_2O, giving **8** as a white solid. The solid was characterized (NMR) as a mixture of diastereoisomers in 7/1 molar ratio (d.e. = 75%). Yield: 0.092 g (77%). Anal. Calc. $C_{39}H_{33}ClOP_2Pd$ (721.6): C, 64.92; H, 4.61. Found: C, 64.88; H, 4.55%. MS (MALDI+): m/z (%) = 686 (100) $[M-Cl]^+$. IR (ν, cm^{-1}): 1615 (ν_{CO}). ^1H NMR ($CDCl_3$): $\delta = 2.20$ (d, $^2J_{PH} = 12.4$, PMe, maj.), 2.54 (d, $^2J_{PH} = 12.6$, PMe, min), 5.01 (m, CHP, min), 5.20 (dd, $^2J_{PH} = 7.6$, $^3J_{PH} = 6.8$, CHP, maj.), 6.11–6.25 (m, H_6 and H_5, C_6H_4, min), 6.35 (m, H_6, C_6H_4, maj.), 6.43 (t, $^3J_{HH} = 7.6$, H_5, C_6H_4, maj.), 6.77 (m, H_4, C_6H_4, min), 6.85 (td, $^4J_{PH} = 4.8$, $^3J_{HH} = 7.0$, H_4, C_6H_4, maj.), 7.10 (td, $^3J_{HH} = {}^3J_{HH} = 7.4$, $^4J_{PH} = 1.6$, H_m, PPh_3, maj.), 7.16–7.18 (m, H_3, C_6H_4, both, H_m, PPh_3, min), 7.22 (t, H_p, PPh_3, both), 7.27–7.37 (m, H_o, PPh_3, maj., H_m,

PhC(O), maj., H_p, PhC(O), maj.), 7.41 (m, H_o, PPh_3, min), 7.46 (m, H_m, PPh, maj.), 7.56 (t, $^3J_{HH} = 6.8$, H_p, PPh, maj.), 7.69 (m, H_o, PPh, min), 7.99 (dd, $^3J_{PH} = 12.4$, $^3J_{HH} = 7.2$, H_o, PPh, maj.), 8.26 (d, $^3J_{HH} = 7.2$, H_o, PhC(O), min), 8.41 (d, $^3J_{HH} = 7.2$, H_o, PhC(O), maj.) (some signals of the minor component could not be assigned due to extensive overlapping). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 11.56$ (d, $^3J_{PP} = 20.0$, C_6H_4-2-PPhMe, min), 15.22 (d, $^3J_{PP} = 19.3$, C_6H_4-2-PPhMe, maj.), 31.43 (d, Pd–PPh_3, maj.), 32.24 (d, Pd–PPh_3, min).

4.2.8. Synthesis of [Pd{C_6H_4(PPh(Me)CHC(O)Ph-κ-C,C)-2}($Ph_2PCH_2CH_2PPh_2$)]ClO_4 (9)

To a suspension of **6** (0.150 g, 0.16 mmol) in THF (20 ml) $AgClO_4$ (0.068 g, 0.33 mmol) was added, and the resulting mixture was stirred at r.t. for 30 min with exclusion of light. The grey suspension was then filtered through a Celite pad. To the freshly prepared solution of the solvate, dppe (0.130 g, 0.33 mmol) was added. The resulting pale-yellow solution was stirred at r.t. for 4 h, then the solvent was evaporated to dryness and the residue treated with Et_2O (10 ml) to give **9** as a white solid. Yield: 0.290 g (95.0%). **9** was characterized (NMR) as a mixture of two diastereoisomers in 6.7/1 molar ratio (d.e. = 74%). Anal. Calc. for $C_{47}H_{42}ClO_5P_3Pd$ (921.6): C, 61.25; H, 4.59. Found: C, 60.98; H, 4.41%. MS (MALDI+): *m*/*z*, (%) = 822 (100) $[M-ClO_4]^+$. IR (*v*, cm^{-1}): 1617 (v_{CO}). ^1H NMR ($CDCl_3$): $\delta = 1.73$ (m, CH_2, dppe, maj.), 2.25 (d, $^2J_{PH} = 12.5$, PMe, maj.), 2.59–2.76 (m, CH_2, dppe, maj.), 4.41 (m, CHP, maj.), 6.76–7.84 (m, aromatic protons, PPh_2, C_6H_4, Ph-C(O), both.). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.95$ (dd, $^3J_{PP} = 17.7$, $^3J_{PP} = 27.8$, C_6H_4PMe, minor.), 26.93 (dd, $^3J_{PP} = 17.6$, $^3J_{PP} = 32.0$, C_6H_4PMe, maj.), 43.78 (dd, $^3J_{PP} = 28.2$, $^3J_{PP} = 22.8$, PPh_2 *trans* CH, min), 44.44 (dd, $^3J_{PP} = 32.2$, $^3J_{PP} = 22.4$, PPh_2 *trans* CH, maj.), 50.83 (dd, $^3J_{PP} = 17.7$, $^3J_{PP} = 22.3$, PPh_2 *cis* CH, maj.), 53.24 (dd, $^3J_{PP} = 17.7$, $^3J_{PP} = 22.7$, PPh_2 *cis* CH, min).

4.3. X-ray crystallography

4.3.1. Data collection

Crystals of **3** of adequate quality for X-ray measurements were grown by vapour diffusion of Et_2O into a CH_2Cl_2 solution of **3** at room temperature. A single crystal was mounted at the end of a quartz fiber in a random orientation, covered with magic oil and placed under the cold stream of nitrogen. Data collection was performed at 100 K on an Bruker Smart CCD diffractometer using graphite-monocromated Mo Kα radiation ($\lambda = 0.71073$ Å). An hemisphere of data was collected based on three ω and Φ-scans runs. The diffraction frames were integrated using the program SAINT [73] and the integrated intensities were corrected for absorption with SADABS [74].

4.3.2. Structure solution and refinement

The structure was solved and developed by Patterson and Fourier methods [75]. In the final steps of the refinement, a strong peak Q of residual electron density remained at 1.08 Å of the Pd atom, without chemical sense. This problem was not solved using three different crystals of different batches, performing the data collection at different temperatures or using other different strategies. In the Patterson map the vector Pd···Q is clear, meaning that this electron density is real and not an error of the model. We assumed the existence of two different crystallographic domains, in 93% and 7% relative abundance. This Q peak should then correspond to the Pd atom of the second minor component. The next heavy atom of the minor component should be the P atom, with assigned electron density in the difference maps of about 1 e $Å^{-3}$. This atom (and the following lighter atoms) could not be observed in the final difference maps. Attempts to refine one complete model at 93% occupancy also failed, probably due to the fact that this model includes the atoms of the 7% occupancy model. Finally, the proposed model contains two Pd atoms with 93% and 7% occupancies and full occupancy for the rest of the molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations [76].

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Appendix A. Supplementary material

CCDC 664274 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.012.

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