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Isomeric Preference in Complexes of Palladium(II) with Chelating P,N-Donor Ligands

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Square-planar complexes [PdCl{κ^2-(RN = $CHC_6H_4PPh_2$)R′}] (R′ = Cl; R = 4-$CH_3C_6H_4$, **1a**; R = 2-$CH_3OC_6H_4$, **1b**; R = 2-HOC_6H_4, **1c**; R′ = CH_3; R = 4-$CH_3C_6H_4$, **2a**; R = 2-$CH_3OC_6H_4$, **2b**; R = 2-HOC_6H_4, **2c**) have been prepared and characterized. In complexes **2a–c** only formation of one isomer was observed. The Pd–methyl bond arranges in a *cis* position to the phosphane fragment of the P,N chelating ligand. Reaction of complexes **2a–c** in acetonitrile with $AgBF_4$ led to removal of the chlorido ligand and coordination of acetonitrile for **2a**. However, for **2b** and **2c** coordination of the oxygen was observed and the chelating P,N ligands became tricoordinate. DFT calculations developed on models of the complexes displayed that the isomer with the methyl ligand coordinated in the *cis* position to the phosphane ligand were harder (or had a bigger HOMO/LUMO gap)

Introduction

In recent years, phosphorus and nitrogen donor ligands have been among the most attractive and useful ligands used in catalysis because of the presence of both soft and hard donor atoms, which allows for interesting complexation properties.[1,2] Complexes with these kinds of ligands have found application as catalysts in a wide range of reactions.[2–8]

The properties of a number of P,P- and P,N-donor ligands in a variety of chemical environments have been recently studied, building a map of bidentate ligand space that has potential applications in predictions about novel or untested ligands.[9] The coordination of P,N-donor chelating ligands to synthesize four-coordinate complexes can give rise to different isomers when the ancillary ligands are different. This isomeric possibility can be important in catalytic processes, as the activity of each isomer could not be the same. Schubert et al. have reported the C–Cl/Si–H exchange catalyzed by [PtClMe(P,N)] complexes.[10] Despite the fact that it is possible to propose two isomers, they have found that only the isomer with the chlorido ligand coordinated *cis* to the phosphane fragment is the active catalytic species.

In this context, the Maximum Hardness Principle (MHP)[11,12] and antisymbiosis[13–15] can be very useful tools in order to understand what the most stable isomer is. In this work we report the syntheses and characterization of complexes of palladium(II) with P,N-donor ligands. In some cases these complexes can give rise to *cis*,*trans* isomers, but we have found the formation of only one of them. DFT calculations are used to rationalize this preferential formation (or others) on the basis of the MHP and are in good agreement with the antisymbiosis rule.

Results and Discussion

Syntheses of the Complexes

The P,N-donor ligands were prepared by simple condensation of the aldehyde 2-diphenylphosphanylbenzaldehyde with a slight excess of 4-toluidine (**a**), 2-anisidine (**b**), or 2-aminophenol (**c**) in methanol solution in a similar way to those previously reported.[16–19] Reactions of equimolar amounts of ligands (**a–c**) with [$PdCl_2$(COD)] or [PdCl(COD)Me] [COD = 1,5-cyclooctadiene] in THF solution afforded the complexes [$PdCl_2$(P,N)] (**1a–c**) or [PdClMe(P,N)] (**2a–c**), respectively, in high yields (Scheme 1).

A downfield shift of the phosphane signals (approximately 30 ppm for dichlorido complexes and 38 ppm for chloridomethyl complexes) in ^{31}P NMR with respect to the free ligand reflects the coordination of the phosphane to the palladium metal. For complexes **2a–c** it is possible to propose the formation of two isomers depending on the orientation of the methyl and chlorido ligands with respect to

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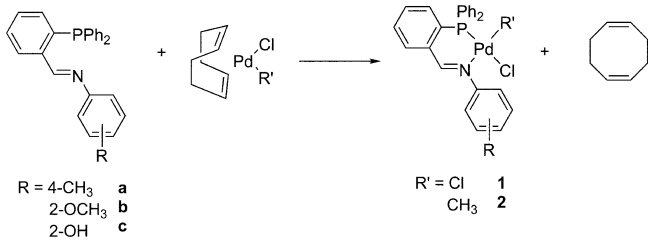
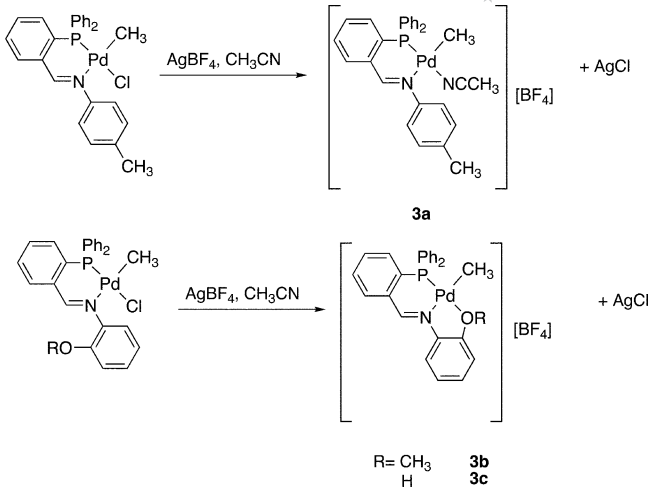


Scheme 1. Syntheses of complexes **1** and **2**.

the phosphane-imine ligand. Nevertheless, the presence of only one signal in the ^{31}P NMR spectra is indicative of the formation of only one isomer. The ^{1}H NMR spectrum shows that the methyl group coordinated *cis* to the phosphorus atom appears as a doublet with a coupling constant $J_{P\text{-}H} \approx 3.4$ Hz for complexes **2a** and **2b**, and 2.7 Hz for complex **2c**. These small values for the coupling constants are indicative of the formation of the isomer in which the phosphane fragment and the methyl group are orientated in the *cis* position. The observed values for complexes **2a** and **2b** are in good agreement with the value reported for a *cis* arrangement of the methyl group and phosphane in complexes of palladium; however, the observed value for complex **2c** is smaller, but not that far off the values of the related compounds. NOESY experiments showed the presence of NOE between the methyl group and the aromatic protons of the phenyl groups bonded to the phosphorus atom. These experiments confirm the configuration in which the methyl group is bonded in a *cis* position to the phosphorus atom (and *trans* to the nitrogen atom) of the chelating ligand. This result is in good agreement with previous published results of similar complexes.[16,20,21]

The reaction of complexes **2a**–**c** with $AgBF_4$ in acetonitrile yielded the removal of the chlorido ligand but the result depends on the coordinating nature of the ligands. For complex **2a** the reaction afforded the substitution of the chlorido ligand by an acetonitrile ligand keeping the position of the methyl group with respect to the chelating ligand (i.e. the coordinated methyl group remains in a *cis* position to the phosphorus atom). For complexes **2b** and **2c** the same reaction afforded the removal of the chlorido ligand without the incorporation of acetonitrile as a ligand. Instead of this, we observed the coordination of the oxygen atom of the methoxy (**b**) or hydroxy (**c**) groups, which became terdentate ligands with two chelating rings, as depicted in Scheme 2. The terdentate behavior of the ligand precludes the formation of different isomers and the only possibility for the methyl group is to remain bonded to the palladium in a *cis* position to the phosphorus atom.

The elimination of the halogen to produce cationic complexes moves the signal of the coordinated phosphane to lower fields, from 38, 37, or 39 ppm (for **2a**, **2b**, or **2c**, respectively) to 40, 44, or 42 ppm (for **3a**, **3b**, or **3c**, respectively). The chemical shift of the methyl group bonded to the palladium atom moves to higher fields and this change is stronger from complex **2a** to **3a** (from 0.7 ppm to 0.46 ppm) than in the other complexes.



Scheme 2. Syntheses of compounds **3**.

Structural Characterization of Complex 2b

The slow evaporation of the solvent of a solution of complex **2b** in $CDCl_3$ afforded single crystals suitable for X-ray diffraction studies. The molecular structure of complex **2b** is shown in Figure 1, and selected bond lengths, bond angles, and torsion angles are given in Table 1.

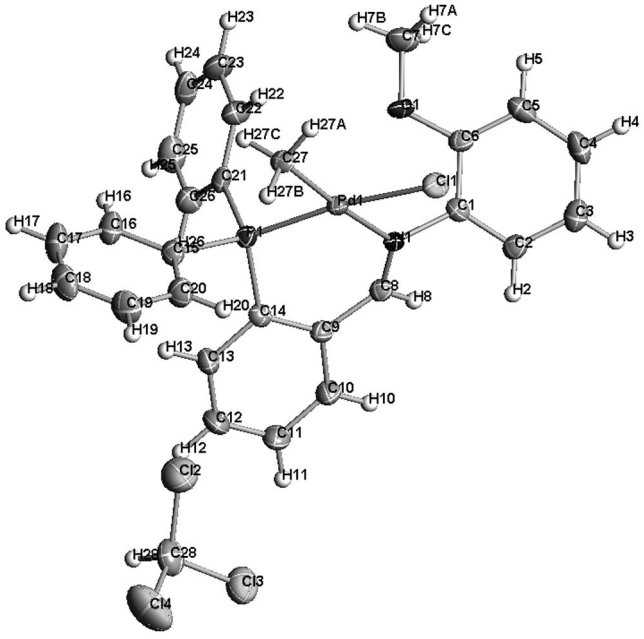


Figure 1. Structure of complex **2b**. A chloroform molecule of crystallization is represented. Selected bond lengths and angles are summarized in Table 1.

The chelating ligand binds to the metal through a phosphorus donor P(1) and secondary imine donor N(1). The P(1)–Pd(1)–N(1) bond angle is 89.09(8)°. The coordination around the palladium atom is slightly distorted from planarity with a torsional angle N(1)–P(1)–C(27)–Cl(1) of 10.41°. The six-membered chelating ring is folded and the torsional angle C(14)–P(1)–Pd(1)–N(1) is 38.7°. This non-

Table 1. Selected bond lengths [Å] and angles [°] for compound **2b**.

Pd(1)–C(27)	2.054(3)	Pd(1)–N(1)	2.159(3)
Pd(1)–P(1)	2.1861(10)	Pd(1)–Cl(1)	2.3843(10)
C(8)–C(9)	1.463(5)	C(8)–H(8)	0.9500
P(1)–C(14)	1.818(4)	C(9)–C(14)	1.411(5)
N(1)–C(8)	1.270(4)		
C(27)–Pd(1)–N(1)	173.91(12)	C(27)–Pd(1)–P(1)	90.49(11)
N(1)–Pd(1)–P(1)	89.09(8)	C(27)–Pd(1)–Cl(1)	89.31(11)
N(1)–Pd(1)–Cl(1)	91.94(8)	P(1)–Pd(1)–Cl(1)	172.00(3)
C(8)–N(1)–Pd(1)	128.7(2)	N(1)–C(8)–C(9)	127.3(3)
C(14)–C(9)–C(8)	126.0(3)	C(9)–C(14)–P(1)	122.0(3)
C(27)–Pd(1)–P(1)–C(14)	–147.37(16)	N(1)–Pd(1)–P(1)–C(14)	38.70(14)
Cl(1)–Pd(1)–P(1)–C(14)	–58.8(3)	C(27)–Pd(1)–N(1)–C(8)	–117.8(11)
P(1)–Pd(1)–N(1)–C(8)	–31.7(3)	Cl(1)–Pd(1)–N(1)–C(8)	140.4(3)
Pd(1)–N(1)–C(8)–C(9)	4.5(5)	N(1)–C(8)–C(9)–C(14)	18.5(6)
Pd(1)–P(1)–C(14)–C(9)	–34.6(3)		

planarity of the six-membered chelating ring gives rise to twist-boat (δ/λ)[22] chirality in the molecule.[23–30] Taking into account this source of chirality, it is possible to propose two enantiomers for these complexes. Figure 2 displays fragments of the nonplanar chelating rings. Both enantiomers crystallize together in the unit cell as required by the space group $P2_1/c$ (see Figure 2).

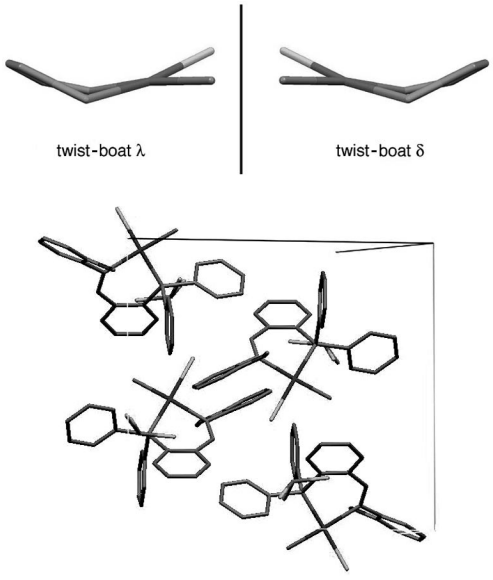


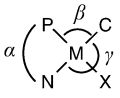
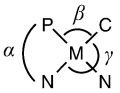
Figure 2. Fragments of the nonplanar chelating rings and packing in the unit cell (hydrogen atoms and solvent molecules omitted for clarity).

Structural Preference

For complexes **2a**–**c** and for the cationic complex of compound **3a** it is possible to propose two different isomers considering the relative position around the metallic center. Nevertheless, the spectroscopic characterization in solution of all complexes along with the solid state characterization for complex **2b** indicates that only one isomer was formed and in all cases this isomer is the one which locates the methyl group bonded to the palladium atom in a *cis* position to the phosphorus atom of the chelating ligand.

A search in the Cambridge Structural Database (CSD,[31,32] version 5.29, November 2007) for structures of palladium and platinum with a similar coordination environment of a phosphorus atom, a nitrogen atom, a carbon atom, and a halogen restricted to an angle P–Pd–N close to 90° (see Table 2) displayed 71 hits with 83 structures of complexes of palladium or platinum with this coordination environment and in all of them the carbon atom coordinated to the palladium locates in the *cis* position to the phosphorus atom as we have found in our complexes. A similar search replacing a halogen atom for a nitrogen atom, trying to find similar situations to the complex **3a**, displayed 120 hits with 153 structures. In 149 of the 153 structures the disposition of the atoms was exactly the same as we found in **3a**, and the four structures that do not match ours have additional chelating rings that impose an alternative conformation. In three cases a pincer N~C~N chelating ligand imposes the coordination of the phosphorus atom in a *trans* position to the carbon atom.[33] In the fourth outlying case it is a P~N~C chelating ligand that imposes a *trans* coordination of the phosphorus and carbon atoms.[34]

Table 2. CSD results for searches of analogous compounds to **2** and **3a**.

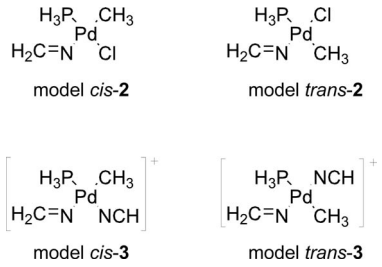
Entry to CSD		Results	
	75° < α < 105°	83/83 β ≈ 90°	83/83 γ ≈ 180°
	75° < α < 105°	149/153 β ≈ 90°	149/153 γ ≈ 180°
		4/153 β ≈ 180°	4/153 γ ≈ 90°

This observed structural preference can be interpreted on the basis of the Maximum Hardness Principle, which states that "molecules arrange themselves to be as hard as possible."[12] Taking into account Koopmans's theorem, the chemical hardness (η) is related to the HOMO/LUMO gap as half the energy gap between the two orbitals.[11,12]

$$\eta = (E_{LUMO} - E_{HOMO})/2$$

In order to confirm the relationship between the observed structural preference and the chemical hardness, theoretical calculations have been developed on simplified models of our complexes. The models were constructed considering both possibilities of relative orientation of the ligands around the metallic center, i.e. the methyl group bonded to the palladium atom can be orientated *cis* or *trans* to the phosphorus atom of the chelating ligand as can be seen in Scheme 3.

In the models for the neutral complexes (*cis*-2 and *trans*-2) we found that the HOMO/LUMO gap for the model *cis*-2 is 4.66 eV and for *trans*-2 the value is 4.11 eV. The bigger



Scheme 3. Simplified models for theoretical calculations of complexes **2** and cations of compounds **3**.

gap (with a difference of 0.55 eV or 12.6 kcal/mol) in *cis*-2 means that *cis*-2 corresponds to a harder complex and a more stable configuration for the complexes, according to the MHP.

Checking the electronic structure of these models, we can see that in both cases the LUMO has a similar structure which can be described mainly as a π^* (p_z–p_z) orbital centered in the double bond C–N. This antibonding orbital displays a weak π^* interaction with the metal which involves a d orbital of the palladium atom. For the model *cis*-2, this orbital corresponds to a π^* interaction between the d_{xz} orbital of the palladium atom and the p_z atomic orbital of the chlorido ligand. For the model *trans*-2 we found that the HOMO is a molecular orbital with an in plane π^* character built, mainly, by a combination of the atomic orbitals d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ of the palladium atom and the p_y atomic orbital of the chlorido ligand. For the same model, analyzing HOMO-1 (which is very close in energy to HOMO) we find now a π^* interaction between the d_{xz} orbital of the palladium atom and the p_z orbital of the chlorido ligand for the model *trans*-2 (analogous to the HOMO of the model *cis*-2). In the case of the model *cis*-2 HOMO-1 corresponds to a molecular orbital of π^* analogous to HOMO of the model *trans*-2. Analyzing the shape of the molecular orbitals for these two models we can state that HOMO and HOMO-1 have exchanged their order in energies and for model *trans*-2 these two levels are very similar in energy. The phosphorus atomic orbitals have a very small participation in the frontier orbitals.

A similar calculation carried out for models of cationic complexes (model *cis*-3 and model *trans*-3) showed that the HOMO/LUMO gap for *cis*-3 is 5.41 eV and for *trans*-3 the value is 5.05 eV. As in the neutral complexes, the model *cis*-3 corresponds to the more stable configuration, as found in our complex and in the structural database (the difference between the gaps is 0.36 eV or 8.40 kcal/mol).

For both cationic models (model *cis*-3 and model *trans*-3), HOMO has mainly a d_{z^2} character along with a small participation of orbital p_y of the methyl carbon. The interaction between both atomic orbitals is σ*, and the participation of the atomic orbital p_y is bigger in model *trans*-3 than in model *cis*-3. This means that the antibonding interaction is stronger and the energy of the HOMO is higher in model *trans*-3 than in model *cis*-3. For *cis*-3 LUMO is mainly composed of an antibonding interaction between the $d_{x^2-y^2}$ atomic orbital of the palladium atom and the p_y atomic orbital of the carbon. The analogous molecular orbital in model *trans*-3 is LUMO+1, and in this model LUMO is composed mainly of a π^* interaction of the C–N bond in the imine ligand. In model *cis*-3 LUMO+1 is composed mainly of a π^* interaction of the C–N bond in the imine ligand, very similar to LUMO in model *trans*-3. In brief, we observe the order inversion of LUMO and LUMO+1 in models *cis*-3 and *trans*-3 (Figure 3).

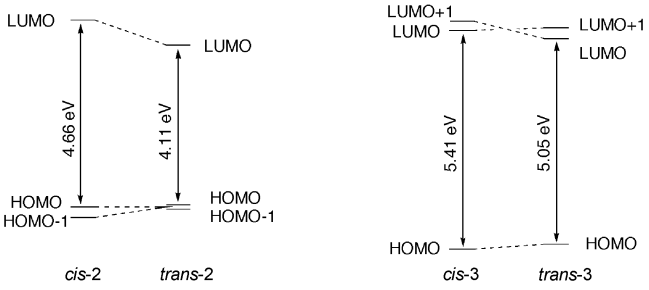


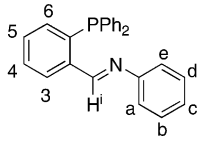
Figure 3. Relative energies of frontier orbitals in models **2** (left) and **3** (right).

Conclusions

The square-planar complexes of palladium(II) with P,N-donor ligands can generate different isomers when the ancillary ligands are different. When these two ligands are chlorido and methyl, the methyl group locates in a *cis* position to the phosphane fragment of the chelating ligand. This is the only isomer detected in solution. The solid-state characterization for one of these complexes (**2b**) is in complete agreement with the facts observed in solution. The extraction of the chlorido ligand maintains the methyl group coordinated in a *cis* position to the phosphorus atom. This isomeric preference can be understood on the basis of the Maximum Hardness Principle. DFT calculations developed for models of the complexes displayed that the isomer with the methyl ligand coordinated in a *cis* position to the phosphane ligand was harder (or had a bigger HOMO/LUMO gap). These calculations confirm the predictions of the antisymbiosis rule.

Experimental Section

General Methods: Elemental analyses (C,H,N) were performed with a LECO CHNS-932 apparatus. ^{1}H NMR spectra were obtained with a Varian Unity Inova 400-MHz spectrometer with $SiMe_4$ as internal standard at 25 °C. Ligands **b**[17,19] and **c**[17,19] were synthesized as reported in the literature. [$PdCl_2$(1,5-COD)][36] and [PdMeCl(1,5-COD)][37] were synthesized as reported. Numbering used for the ligands:



Syntheses

[$C_{26}H_{22}NP$] (a): To a solution of 2-diphenylphosphanylbenzaldehyde (1082.5 mg, 3.70 mmol) in anhydrous methanol (40 mL) under N_2 was added *p*-toluidine (907 mg, 8.46 mmol) and the reaction mixture was stirred at room temperature overnight. After that time the mixture was kept at –18 °C for two hours to induce crystallization. The product was obtained as a yellow solid collected by filtering through a fritted filter and washed with cold methanol. Yield: 1053.9 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 2.32 (s, 3 H, -CH_3), 6.85 (d, $J_{H,H}$ = 8.40 Hz, 2 H, H^o), 6.92 (m, 1 H, H^4), 7.09 (d, $J_{H,H}$ = 8.1 Hz, 2 H, H^m), 7.32 (m, 11 H, -Ph_2 + H^5), 7.44 (m, 1 H, H^3), 8.20 (m, 1 H, H^6), 9.08 (d, $J_{H,P}$ = 5.2 Hz, 1 H, H^i) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$, 20 °C.): δ = 21.23, 76.94, 77.26, 77.57, 109.99, 115.47, 121.14, 128.16, 128.20, 128.85, 128.92, 128.99, 129.15, 129.18, 129.34, 129.83, 129.97, 130.96, 130.97, 133.72, 134.18, 134.21, 134.38, 134.42, 136.03, 136.59, 138.55, 138.74, 139.44, 139.61, 149.29, 158.16, 158.37 ppm. ^{31}P NMR (161.92 MHz, $CDCl_3$, 20 °C): δ = –12.28 ppm. $C_{26}H_{22}N$ (379.43): calcd. C 82.3, H 5.84, N 3.69; found C 81.99, H 5.55, N 3.88.

[Pd($C_{26}H_{22}NP$)Cl_2] (1a): Complex [$PdCl_2$(1,5-COD)] (104.0 mg, 3.64 mmol) was dissolved in dichloromethane (15 mL). To this solution ligand **a** (140.4 mg, 3.70 mmol) was added. The mixture was stirred at room temperature for 2 h. The solution was concentrated in vacuo and the product was precipitated with diethyl ether. A yellow solid was filtered off, washed with diethyl ether, and then dried under vacuum. Yield: 205.6 mg (86%). ^{1}H NMR (300 MHz, [D_6]DMSO, 20 °C): δ = 2.30 (s, 3 H, -CH_3), 7.03 (m, 1 H, H^6), 7.16 (d, $J_{H,H}$ = 8.7 Hz, 2 H, H^{b,d}), 7.35 (d, $J_{H,H}$ = 8.3 Hz, 2 H, H^{a,e}), 7.58 (m, 10 H, -Ph_2), 7.80 (t, $J_{H,H}$ = 7.5 Hz, 1 H, H^5), 7.95 (t, $J_{H,H}$ = 7.4 Hz, 1 H, H^4), 8.17 (m, 1 H, H^3), 8.64 (s, 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, [D_6]DMSO, 20 °C): δ = 30.31 ppm. $C_{26}H_{22}Cl_2NPPd$ (556.76): calcd. C 56.09, H 3.98, N 2.52; found C 55.97, H 3.89, N 2.71.

[Pd($C_{26}H_{22}NOP$)Cl_2] (1b): The same procedure was followed as for **1a**. The compounds used were: complex [$PdCl_2$(1,5-COD)] (109.2 mg, 3.82 mmol) and ligand **b** (154.2 mg, 3.90 mmol). A yellow solid was collected as product. Yield: 206.9 mg (94%). ^{1}H NMR (400 MHz, [D_6]DMSO, 20 °C): δ = 3.79 (s, 3 H, -OCH_3), 7.00 (t, $J_{H,H}$ = 7.45 Hz, 1 H, H^b), 7.09 (m, 1 H, H^d), 7.14 (m, 1 H, H^6), 7.27 (m, 1 H, H^a), 7.33 (m, 1 H, H^c), 7.65 (m, 10 H, -Ph_2), 7.86 (m, 1 H, H^5), 7.99 (m, 1 H, H^4), 8.20 (m, 1 H, H^3), 8.72 (s, 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, [D_6]DMSO, 20 °C): δ = 30.67 ppm. $C_{26}H_{22}Cl_2NOPPd$ (572.76): calcd. C 54.25, H 3.87, N 2.45; found C 54.35, H 3.81, N 2.38.

[Pd($C_{25}H_{20}NOP$)Cl_2] (1c): The same procedure was followed as for **1a**. The compounds used were: complex [$PdCl_2$(1,5-COD)] (106.0 mg, 3.71 mmol) and ligand **c** (145.2 mg, 3.81 mmol). A yellow solid was collected as product. Yield: 199.2 mg (96%). ^{1}H NMR (400 MHz, [D_6]DMSO, 20 °C): δ = 6.71 (m, 1 H, H^b), 6.85 (m, 1 H, H^d), 7.10 (m, 1 H, H^c), 7.21 (t, $J_{H,H}$ = 8.95 Hz, 1 H, H^5), 7.35 (d, $J_{H,H}$ = 7.9 Hz, 1 H, H^a), 7.60 (m, 10 H, -Ph_2), 7.80 (t, $J_{H,H}$ = 7.6 Hz, 1 H, H^6), 7.94 (t, $J_{H,H}$ = 7.7 Hz, 1 H, H^4), 8.21 (m, 1 H, H^3), 8.80 (s, 1 H, H^i), 9.22 (br., OH) ppm. ^{31}P NMR (161.92 MHz, [D_6]DMSO, 20 °C): δ = 30.90 ppm. $C_{25}H_{20}Cl_2NOPPd$ (558.73): calcd. C 53.74, H 3.61, N 2.51; found C 53.53, H 3.52, N 2.66.

[Pd($C_{26}H_{22}NP$)ClMe] (2a): Complex [PdCl(1,5-COD)Me] (105.5 mg, 3.98 mmol) was dissolved in dichloromethane (15 mL). To this solution ligand **a** (154.6 mg, 4.05 mmol) was added. The mixture was stirred at room temperature for 5 d. No solid was seen during this time. The solution was concentrated in vacuo and the product was precipitated with hexane. A yellow solid was filtered off, washed with hexane, and then dried under vacuum. Yield: 190.6 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.70 (d, $J_{H,P}$ = 3.3 Hz, 3 H, Pd-CH_3), 2.33 (s, 3 H, -CH_3), 7.14 (m, 5 H, H^6 + H$^{a–e}$ + H$^{b–d}$), 7.49 (m, 11 H, -Ph_2 + H^5), 7.62 (m, 2 H, H^3 + H^4), 8.19 (d, $J_{H,P}$ = 2 Hz, 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, $CDCl_3$, 20 °C): δ = 38.41 ppm. $C_{27}H_{25}ClNPPd$ (536.34): calcd. C 60.46, H 4.7, N 2.61; found C 59.99, H 4.50, N 2.84.

[Pd($C_{26}H_{22}NOP$)ClMe] (2b): The same procedure was followed as for **2a**. The compounds used were: complex [PdCl(1,5-COD)Me] (101.9 mg, 3.84 mmol) and ligand **b** (153.0 mg, 3.87 mmol). A yellow solid was collected as product. Yield: 212.3 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.63 (d, $J_{H,P}$ = 3.4 Hz, 3 H, Pd-CH_3), 3.79 (s, 3 H, -OCH_3), 6.93 (m, 1 H, H^5), 6.97 (m, 1 H, H^d), 7.05 (dd, $J_{H,H}$ = 1.85, 7.6 Hz, 1 H, H^a), 7.15 (t, $J_{H,H}$ = 8.5 Hz, 1 H, H^6), 7.20 (td, $J_{H,H}$ = 1.9, 7.9 Hz, 1 H, H^c), 7.49 (m, 12 H, -Ph_2 + H^4 + H^b), 7.62 (m, 1 H, H^3), 8.24 (s, 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, $CDCl_3$, 20 °C): δ = 37.42 ppm. $C_{27}H_{25}ClNOPPd$ (552.34): calcd. C 58.71, H 4.56, N 2.54; found C 58.34, H 4.48, N 2.52.

[Pd($C_{26}H_{23}NOP$)ClMe] (2c): The same procedure was followed as for **2a**. The compounds used were: complex [PdCl(1,5-COD)Me] (130.1 mg, 4.90 mmol) and ligand **c** (187.7 mg, 4.92 mmol). A yellow solid was collected as product. Yield: 223.3 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.71 (d, $J_{H,P}$ = 2.7 Hz, 3 H, Pd-CH_3), 6.79 (br., -OH), 7.14 (m, 2 H, H^d + H^6), 7.19 (m, 1 H, H^b), 7.46 (m, 10 H, -Ph_2), 7.54 (m, 3 H, H^4 + H^5 + H^c), 7.65 (m, 2 H, H^3 + H^a), 8.31 (br., 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, $CDCl_3$, 20 °C): δ = 39.38 ppm. $C_{26}H_{23}ClNOPPd$ (538.31): calcd. C 58.01, H 4.31, N 2.60; found C 57.84, H 4.50, N 2.59.

[Pd(MeCN)($C_{26}H_{26}N_2P$)Me]BF_4 (3a): Complex **2a** (44.6 mg, 0.083 mmol) was dissolved in dichloromethane (30 mL). To this solution MeCN (2 mL) and $AgBF_4$ (19.8 mg, 0.102 mmol) were added. The mixture was stirred for 2 h at room temperature. The white precipitate of AgCl was removed by filtering through celite. The solution was concentrated under vacuum and the product was precipitated by the addition of hexane. A pale yellow solid was collected as product. Yield: 40.5 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.46 (d, $J_{H,P}$ = 1.8 Hz, 3 H, Pd-CH_3), 1.93 (s, 3 H, NCMe overlapped with a small amount of free acetonitrile), 2.36 (s, 3 H, -CH_3), 7.15 (m, 3 H, H^6 + H^{a+e}), 7.25 (m, 2 H, H^{b+d}), 7.42 (m, 4 H, Ph_2), 7.52 (m, 4 H, -Ph_2), 7.58 (m, 3 H, -Ph_2 + H^5), 7.77 (t, $J_{H,H}$ = 7.6 Hz, 1 H, H^4), 7.90 (m, 1 H, H^3), 8.37 (s, 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, $CDCl_3$, 20 °C): δ = 40.13 ppm. $C_{29}H_{28}BF_4N_2PPd$ (628.74): calcd. C 55.40, H 4.49, N 4.46; found C 55.02, H 4.65, N 3.98.

[Pd($C_{26}H_{22}NOP$)Me]BF_4·0.25CH_3CN (3b): The same procedure was followed as for **3a**. The compounds used were: complex **2b** (67.4 mg, 0.125 mmol), $AgBF_4$ (27.5 mg, 0.141 mmol), and MeCN (2 mL). A yellow solid was collected as product. Yield: 30.8 mg (44%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.56 (s, 3 H, Pd-CH_3), 4.22 (s, 3 H, -OCH_3), 7.26 (m, 3 H, H^6 + H^b + H^d), 7.38 (m, 1 H, H^c), 7.44 (m, 8 H, -Ph_2), 7.58 (m, 3 H, -Ph_2 + H^5), 7.83 (m, 1 H, H^4), 7.91 (d, $J_{H,H}$ = 8.8 Hz, 1 H, H^a), 8.35 (m, 1 H, H^3), 9.20 (s, 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, $CDCl_3$, 20 °C): δ = 44.12 ppm. $C_{27}H_{25}BF_4NOPPd$·0.25CH_3CN (613.96): calcd. C 53.80, H 4.23, N 2.85; found C 53.95, H 4.28, N 2.78.

[Pd($C_{25}H_{20}NOP$)Me]BF_4·0.25CH_3CN (3c): The same procedure was followed as for **3a**. The compounds used were: complex **2c** (51.9 mg, 0.096 mmol), $AgBF_4$ (20.2 mg, 0.104 mmol), and MeCN (2 mL). A yellow solid was collected as product. Yield: 35.6 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.61 (s, 3 H, Pd-CH_3), 6.74 (br., 1 H, -OH), 7.15 (m, 2 H, -Ph_2+H^d), 7.42 (m, 5 H,

-Ph_2 + H^b + H^6), 7.50 (m, 8 H, -Ph_2 + H^5 + H^c), 7.58 (d, $J_{H,H}$ = 8.2 Hz, 1 H, H^a), 7.70 (t, $J_{H,H}$ = 7.7 Hz, 1 H, H^4), 7.87 (m, 1 H, H^3), 8.31 (br., 1 H, H^i) ppm. ^{31}P NMR (161.92 MHz, $CDCl_3$, 20 °C): δ = 42.45 ppm. $C_{26}H_{23}BF_4NOPPd\cdot0.25CH_3CN$ (599.93): calcd. C 52.96, H 3.93, N 2.38; found C 52.17, H 4.19, N 2.00.

X-ray Crystallography: Crystallographic data for compound **2b** were collected with a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[38] Intensities were integrated[39] from several series of exposures, each exposure covering 0.3° in ω, and the total dataset being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[40] The structure was solved by direct methods and refined by least-squares on weighted F^2 values for all reflections (see Table 3).[41] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 3. Complex neutral-atom scattering factors were used.[42] CCDC-702771 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structure refinement for **2b**.

Empirical formula	$C_{28}H_{26}Cl_4NOPPd$
Formula weight	671.67
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
a	11.436(3) Å
b	14.400(3) Å
c	17.133(4) Å
α	90°
β	90.810(4)°
γ	90°
Volume	2821.2(11) Å^3
Z	4
Density (calculated)	1.581 Mg/m^3
Absorption coefficient	1.116 mm^{-1}
F(000)	1352
Crystal size[35]	0.30 × 0.10 × 0.10
θ range for data collection	1.78–25.00°
Index ranges	$-13 \le h \le 13$, $-17 \le k \le 17$, $-20 \le l \le 20$
Reflections collected	26641
Independent reflections	4947 [R_{int} = 0.0499]
Completeness to θ = 25.00°	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.894 and 0.840
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	4947/0/327
Goodness-of-fit on F^2	S = 1.149
R indices [for 4268 reflections with $I > 2\sigma(I)$]	R_1 = 0.0318, wR_2 = 0.0807
R indices (for all 4947 data)	R_1 = 0.0405, wR_2 = 0.1008
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$ a = 0.0497, b = 1.0878
Largest diff. peak and hole	0.510 and –0.467 e Å^{-3}

Computational Study: DFT calculations were performed with the hybrid method known as B3LYP, in which the Becke three-parameter exchange functional[43] and the Lee–Yang–Parr correlation functional were used,[44] implemented in the Gaussian 03 (Revision B.04) program suite.[35] Pd and P atoms were described using an effective core potential (LANL2DZ) for the inner electrons[45,46] adding a f-polarization shell for Pd (ζ_f = 1.472)[47] and a d-polarization for P (ζ_d = 0.387).[48] The basis set for C, N, Cl, and H elements was split-valence and included polarization functions in all atoms [abbreviated as 6-31G(d,p)].[49]

Supporting Information (see footnote on the first page of this article): Tables of optimized structures for models **2** and **3**.

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