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Homoleptic palladium complexes with phosphine-amide or iminophosphine ligands

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ABSTRACT

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Dedicated to Prof. Jonathan R. Dilworth

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1. Introduction

Hybrid ligands that contain distinct chemical functions [1–5], such as soft phosphine and hard (e.g. N or O) donor atoms, have attracted continuous interest during last years as a result of their versatile coordination behaviour [6,7] and its potential hemilability [3–5]. These properties have been exploited in several ways, as the "weak-link approach" for the synthesis of supramolecular structures [8] or the use of some ligands and its complexes in chemical sensing [9-11] and catalytic processes. It is in this last field that phosphine-amide ligands have received growing attention. For example, the asymmetric 1,4-addition reaction of arylboronic acids with cycloalkenones is catalysed by an amidophosphine rhodium(I) complex [12], and also amide derived phosphines (Aphos) possessing various N,N-dialkyl aromatic amide scaffolds have shown to be highly effective in Suzuki cross-coupling reactions [13,14]. The last generation of such Aphos ligands has been able to promote room-temperature coupling of unactivated and sterically hindered aryl chlorides [15] and a recent review explored the use of catalysts containing hemilabile ligands in the Suzuki reaction [16]. Also 2-diphenylphosphinobenzamido nickel complexes have found application in ethylene polymerization, showing that slight variations in the ligand frame produce drastic changes

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The reaction between Pd(dba)₂ and phosphino-amide ligands yielded the unexpected Pd(II) homoleptic complexes [Pd(*o*-Ph₂PC₆H₄CO-NR)₂] [R = ⁱPr (1), Ph (2), 4-MeC₆H₄ (3), 4-FC₆H₄ (4)], in which an κ^2 -P,N coordination mode for diphenylphosphine-benzamidate ligands is observed. In order to induce amide protonation in the ligands and subsequent κ^2 -P,O coordination, compounds (1-4) were treated with HClO₄(aq) to give cationic complexes [Pd(*o*-Ph₂PC₆H₄CO-NHR)₂][ClO₄]₂ (5-8). These complexes and the analogous with iminophosphine ligands [Pd(*o*-Ph₂PC₆H₄CH=N-R)₂] [ClO₄]₂ [R = ⁱPr (9), Ph (10)] can be alternatively obtained when [PdCl₂(PhCN)₂] is treated with AgClO₄ in the presence of the corresponding ligand. The reaction of Pd(dba)₂ with iminophosphines has also been explored, yielding in this case the Pd(0) derivatives [Pd(*o*-Ph₂PC₆H₄CH=N-R)₂] [R = ⁱPr (1), Ph (12)]. X-ray structures of (3), (4), (5), (8) and (9) have been established, allowing an interesting comparative structural discussion.

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in the catalytic behaviour [17]. In this sense, we have recently studied the coordination properties of these mixed-donor bidentate ligands in their first described ruthenium(II) [18] and palladium(II) complexes containing cyclometallated [19] or pentafluorophenyl co-ligands [20].

On the other hand, metal complexes containing iminophosphine ligands prepared by condensation of 2-(diphenylphosphino)benzaldehyde with primary amines $(o-Ph_2PC_6H_4CH=N-R)$ were first reported in the early nineties by Dilworth an other authors [21-23]. Since then palladium iminophosphine complexes have also been known to act as versatile catalysts for many different reactions, such as the copolymerization of carbon monoxide and ethylene [24], the hydrosilylation of ketones [25] and Heck [26,27], Suzuki [25,28-30] and Stille couplings [31-34]. In this last reaction in situ mixtures of Pd(dba)₂ with the above mentioned iminophosphines (o-Ph₂PC₆H₄CH=N-R) have shown outstanding efficiency [34]. We present in this paper as an extension of previous work the synthesis and characterization of homoleptic-iminophosphine Pd(0) complexes that, as mentioned above, have not been isolated before although its catalytic activity have been demonstrated when used in situ. The new analogous cationic compounds of Pd(II) prepared as perchlorate salts are reported too. The study of the coordination behaviour of diphenylphosphine-benzamide ligands o-Ph₂PC₆H₄CO-NHR, containing steric and electronically differentiated substituents, in its reactions against Pd(dba)₂ and [PdCl₂(PhCN)₂] is also described.





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2. Experimental

2.1. Methods and materials

C, H and N analyses were carried out with a Carlo Erba instrument. IR spectra were recorded on a Perkin–Elmer spectrophotometer 16F PC FT–IR, using Nujol mulls between polyethylene sheets. NMR data (¹H, ³¹P) were recorded on Bruker Avance 200 and 300 spectrometers. Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operated in positive mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25 KeV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000. All the solvents were dried by conventional methods.

Pd(dba)₂ [35], the diphenylphosphinobenzamide *o*-Ph₂P-C₆H₄-CO-NH-R (R = ⁱPr, Ph, 4-MeC₆H₄ or 4-FC₆H₄ and iminophosphine ligands *o*-Ph₂PC₆H₄CH=N-R (R = ⁱPr or Ph) were prepared by reported procedures [20,21].

2.2. Synthesis

2.2.1. Preparation of complexes $[Pd(o-Ph_2PC_6H_4CO-NR)_2] [R = {}^{i}Pr (1), Ph (2), 4-MeC_6H_4 (3), 4-FC_6H_4 (4)]$

To a red solution of $[Pd(dba)_2]$ (200 mg, 0,35 mmol) in 20 mL of dicholoromethane was added the stoichiometric amount of the corresponding 2-diphenylphosphinebenzamide (0.70 mmol, molar ratio 1:2). The reaction was stirred at room temperature for 24 h and then it was evaporated to half volume under reduced pressure. Addition of diethyl ether caused precipitation of the new yellow complexes, which were filtered off, air dried and recrystallised from CH₂Cl₂/ether. The same results were obtained when the reactions were performed under air or N₂ atmosphere.

[Pd(o-Ph₂PC₆H₄CO-N-ⁱPr)₂] (1): (72% yield). Mp = 155 °C. *Anal.* Calc. for C₄₄H₄₂N₂O₂P₂Pd: C, 66.1; H, 5.3; N, 3.5. Found: C, 65.8; H, 5.7; N, 3.6.%. FT-IR (nujol, cm⁻¹): ν (CO) 1623 (s), 1574 (vs). ¹H NMR (200 MHz, CDCl₃): δ (ppm): 8.26 (m, 2H, P-C₆H₄-CO-), 7.88-7.24 (m, 24H, 20H PPh₂ + 4H P-C₆H₄-CO-), 6.43 (m, 2H, P-C₆H₄-CO-), 3.70 (m, 2H, CH-ⁱPr), 1.05 (d, J_{HH} = 6.0 Hz, 6H, CH₃-ⁱPr), 0.65 (d, J_{HH} = 6.0 Hz, 6H, CH₃-ⁱPr). ³¹P NMR (300 MHz, CDCl₃): δ (ppm): 32.5 (s). FAB-MS (positive mode) *m/z*: 799 (M⁺+1).

[Pd(o-Ph₂PC₆H₄CO-N-Ph)₂] (**2**) (80% yield). Mp = 177 °C. *Anal.* Calc. for C₅₀H₃₈N₂O₂P₂Pd: C, 69.3; H, 4.4; N, 3.2. Found: C, 69.4; H, 4.7; N, 3.3.%. FT-IR (nujol, cm⁻¹): ν (CO) 1655 (s), 1580 (vs). ¹H NMR (200 MHz, CDCl₃): δ (ppm): 8.11 (m, 2H, P-C₆H₄-CO-), 7.92-7.31 (m, 32H, 20H PPh₂ + 10H N-Ph + 2H P-C₆H₄-CO-), 6.58 (m, 2H, P-C₆H₄-CO-). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 33.3 (s). FAB-MS (positive mode) *m/z*: 867 (M⁺ + 1).

[Pd(o-Ph₂PC₆H₄CO-N-C₆H₄-4Me)₂] (**3**) (74% yield). Mp = 196 °C. *Anal.* Calc. for C₅₂H₄₂N₂O₂P₂Pd: C, 69.8; H, 4.7; N, 3.1 Found: C, 69.5; H, 5.1; N, 3.3%. FT-IR (nujol, cm⁻¹): ν (CO) 1612 (s), 1593 (vs). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.97 (m, 2H, P-C₆H₄-CO-), 7.52-7.35 (m, 12H, 8H PPh₂ + 4H N-C₆H₄-CH₃), 7.22 (m, 2H, P-C₆H₄-CO-), 7.09 (m, 2H, P-C₆H₄-CO-), 6.86 (m, 12H, PPh₂), 6.68 (m, 4H, N-C₆H₄-CH₃), 6.57 (m, 2H, P-C₆H₄-CO-), 2.16 (s, 6H, CH₃). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 33.2 (s). FAB-MS (positive mode) *m/z*: 894 (M⁺).

[Pd(o-Ph₂PC₆H₄CO-N-C₆H₄-4F)₂] (**4**) (68% yield). Mp = 206 °C. Anal. Calc. for C₅₀H₃₆F₂N₂O₂P₂Pd: C, 66.5; H, 4.0; N, 3.1. Found: C, 66.4; H, 4.4; N, 3.4.%. FT-IR (nujol, cm⁻¹): v(CO) 1604(s), 1576 (vs). ¹H NMR (200 MHz, CDCl₃): δ (ppm) 8.02 (m, 2H, P-C₆H₄-CO-), 7.52-7.35 (m, 12H, 8H PPh₂ + 4H N-C₆H₄-F), 7.22 (m, 2H, P-C₆H₄-CO-), 7.19 (m, 2H, P-C₆H₄-CO-), 6.90 (m, 12H, PPh₂), 6.58 (m, 6H, 4H N-C₆H₄-F + 2H P-C₆H₄-CO-). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 33.5 (s). ¹⁹F NMR (200 MHz, CDCl₃): δ (ppm): -120.3 (s). FAB-MS (positive mode) *m/z*: 902 (M⁺). 2.2.2. Preparation of complexes $[Pd(o-Ph_2PC_6H_4CO-NHR)_2][ClO_4]_2$ $[R = {}^{i}Pr(5), Ph(6), 4-MeC_6H_4(7), 4-FC_6H_4(8)]$

2.2.2.1. Method A. The new complexes were obtained by treating a dichloromethane solution of the corresponding complexes (1-4) (100 mg, 20 mL) with stoichiometric amount of 1.16 M HClO₄ aqueous solution (molar ratio: 1:2). After 1 h stirring at room temperature, the mixture was concentrated to half volume under reduced pressure. Addition of diethyl ether caused precipitation of the new yellow complexes (**5–8**), which were filtered off, washed with ether, air dried and recrystallized from CH₂Cl₂/ether.

2.2.2.2. Method B. To a solution of $[PdCl_2(PhCN)_2]$ (100 mg, 0,26 mmol) in 10 mL of dichloromethane, the stoichiometric amount of the corresponding 2-diphenylphosphinebenzamide (0.52 mmol, molar ratio 1:2) and AgClO₄ (108 mg, 0.52 mmol) were added. The precipitation of AgCl started immediately. After 30 min of stirring at room temperature the precipitate was removed, and the resulting clear solution was evaporated to half volume. A yellow precipitate formed after addition of diethyl ether and then it was filtered off and washed with ether. The complexes (**5–8**) were recrystallised from CH₂Cl₂/ether.

[Pd(o-Ph₂PC₆H₄CO-NH⁻ⁱPr)₂][ClO₄]₂ (**5**): (73% yield).. Mp = 235 °C. *Anal.* Calc. for C₄₄H₄₄Cl₂N₂O₁₀P₂Pd: C, 52.8; H, 4.4; N, 2.8. Found: C, 53.1; H, 4.6; N, 2.7.%. FT–IR (nujol, cm⁻¹): *v*(NH) 3287, *v*(CO) 1584 (vs), *v*(ClO₄) 1093 (vs). ¹H NMR (300 MHz, CDCl₃): *δ* (ppm): 8.89 (m, 2H, NH), 8.30 (m, 2H, P–C₆H₄–C), 7.92 (m. 2H, P–C₆H₄–C), 7.65–7.51 (m, 10H, 2H P–C₆H₄–C + 8H PPh₂), 7.40–7.28 (m, 12H, PPh₂), 6.90 (m, 2H, P–C₆H₄–C), 3.95 (m, 2H, CH⁻ⁱPr), 0.94 (d, *J*_{HH} = 6.0 Hz, 12H, CH₃-ⁱPr). ³¹P NMR (300 MHz, CDCl₃): *δ* (ppm) 44.5(s). FAB-MS (positive mode) *m*/*z*: 898 (M⁺-ClO₄), 797 (M⁺-2ClO₄).

[Pd(o-Ph₂PC₆H₄CO-NH-Ph)₂][ClO₄]₂ (**6**): (68% yield). Mp = 194 °C. *Anal.* Calc. for C₅₀H₄₀Cl₂N₂O₁₀P₂Pd: C, 56.2; H, 3.8; N, 2.6. Found: C, 56.1; H, 4.0; N, 2.8.%. FT-IR (nujol, cm⁻¹): ν (CO) 1578 (vs), ν (ClO₄) 1097 (vs). ¹H NMR (200 MHz, CDCl₃): δ (ppm): 10.49 (br, 2H, NH), 8.41 (m, 2H, P-C₆H₄-C), 7.83 (m, 2H, P-C₆H₄-C), 7.69-7.16 (m, 32H, 20H PPh₂ + 10H N-Ph + 2H P-C₆H₄-CO-), 6.95 (m, 2H, P-C₆H₄-C). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 43.2 (s). FAB-MS (positive mode) *m/z*: 867 (M⁺-2ClO₄ + 1).

[Pd(o-Ph₂PC₆H₄CO-NH-C₆H₄-4Me)₂][ClO₄]₂ (**7**) (69% yield). Mp = 231 °C. *Anal.* Calc. for C₅₂H₄₄Cl₂N₂O₁₀P₂Pd: C, 57.0; H, 4.1; N, 2.6. Found: C, 57.2; H, 4.3; N, 2.9.%. FT-IR (nujol, cm⁻¹): ν (NH) 3371 (s), ν (CO) 1577 (vs), ν (ClO₄) 1103 (vs). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 10.51 (s, 2H, NH), 8.46 (m, 2H, P-C₆H₄-C), 7.88 (m, 2H, P-C₆H₄-C), 7.55-7.48 (m, 6H, 2H P-C₆H₄-C+4H N-C₆H₄-CH₃), 7.36-7.28 (m, 20 H PPh₂) 7.05 (m, 4H, N-C₆H₄-Me), 6.94 (m, 2H, P-C₆H₄-C), 2.27 (s, 6H, CH₃). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 43.3 (s). FAB-MS (positive mode) *m/z*: 995 (M⁺-ClO₄), 894 (M⁺-2ClO₄).

[Pd(o-Ph₂PC₆H₄CO-NH-C₆H₄-4F)₂][ClO₄]₂ (**8**) (75% yield). Mp = 191 °C. *Anal.* Calc. for C₅₀H₃₈Cl₂F₂N₂O₁₀P₂Pd: C, 54.4; H, 3.5; N, 2.5. Found: C, 54.7; H, 3.9; N, 2.8.%. FT-IR (nujol, cm⁻¹): ν (NH) 3336 (s), ν (CO) 1580 (vs), ν (ClO₄) 1100 (vs). ¹H NMR (200 MHz, CDCl₃): δ (ppm): 11.05 (br, 2H, NH), 8.46 (m, 2H, P-C₆H₄-C), 7.85 (m, 2H, P-C₆H₄-C), 7.75 (m, 2H, P-C₆H₄-C), 7.69-7.62 (m, 16H, 12H PPh₂ + 4H N-C₆H₄-F), 7.40-7.30 (m, 10H, 8H aromatics +2H P-C₆H₄-C), 6.99 (m, 4H N-C₆H₄-F). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 41.4 (s). ¹⁹F NMR (200 MHz, CDCl₃): δ (ppm): -120.3(s). FAB-MS (positive mode) *m/z*: 903 (M⁺-2ClO₄).

2.2.3. Preparation of complexes $[Pd(o-Ph_2PC_6H_4CH=N-R)_2] [ClO_4]_2$ $[R = {}^{i}Pr (\mathbf{9}), Ph (\mathbf{10})]$

To a solution of [PdCl₂(PhCN)₂] (100 mg, 0,26 mmol) in 10 mL of dichloromethane, the stoichiometric amount of the corresponding iminophosphine (0.52 mmol, CH₂Cl₂ solution) and AgClO₄ (108 mg, 0.52 mmol) were added. The precipitation of AgCl started immedi-

ately. After 30 min of stirring at room temperature the precipitate was removed, and the resulting clear solution was evaporated to half volume. An orange precipitate formed after addition of diethyl ether and then it was filtered off and washed with ether. The complexes (9 and 10) were recrystallised from CH₂Cl₂/ether.

 $[Pd(o-Ph_2PC_6H_4CH=N^{-i}Pr)_2][ClO_4]_2$ (9): (64% yield). Mp = 190 °C. Anal. Calc. for C₄₄H₄₄Cl₂N₂O₈P₂Pd: C, 54.6; H, 4.5; N, 2.9. Found: C, 54.8; H, 4.7; N, 3.0.%. FT-IR (nujol, cm⁻¹): v(C=N) 1646 (s), $v(CIO_4)$ 1090 (vs). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.00 (s, 2H, HC=N), 7.91 (m, 2H, P-C₆H₄-C), 7.80-6.23 (m. 24H, 4 P-C₆H₄-C + 20H PPh₂), 6.86 (m, 2H, P-C₆H₄-C), 3.55 (m, 2H, CH-ⁱPr), 0.94 (d, $J_{\rm HH}$ = 6.6 Hz, 12H, CH₃-ⁱPr). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 32.5(s). FAB-MS (positive mode) *m/z*: 869 (M⁺-ClO₄).

 $[Pd(o-Ph_2PC_6H_4CH=N-Ph)_2][ClO_4]_2$ (10): (61% vield). Mp = 193 °C. Anal. Calc. for $C_{50}H_{40}Cl_2N_2O_8P_2Pd$: C, 58.0; H, 3.9; N, 2.7. Found: C, 58.2; H, 4.1; N, 3.0.%. FT-IR (nujol, cm⁻¹): v(C=N) 1622 (s), $v(ClO_4)$ 1097 (vs), ¹H NMR (200 MHz, CDCl₃); δ (ppm); 8.20 (s, 2H, HC=N), 7.65 (m, 2H, P-C₆H₄-C), 7.41 (m, 2H, P-C₆H₄-C), 7.21-6.95 (m. 32H, 2H P-C₆H₄-C + 20H PPh₂ + 10H N-Ph), 6.81 (m, 2H, P-C₆H₄-C), ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 35.2 (s). FAB-MS (positive mode) *m/z*: 937 (M⁺-ClO₄).

2.2.4. Preparation of complexes $[Pd(o-Ph_2PC_6H_4CH=N-R)_2] [R = {}^{i}Pr$ (11). Ph (12)]

To a red solution of [Pd(dba)₂] (200 mg, 0,35 mmol) in 20 mL of dichloromethane was added the stoichiometric amount of the corresponding iminophosphine previously prepared (0.70 mmol, CH₂Cl₂ solution). The reaction was stirred at room temperature for 1 h and then it was evaporated to half volume under reduced pressure. Addition of diethyl ether caused precipitation of the new yellow/orange complexes, which were filtered off, air dried and recrystallised from CH₂Cl₂/ether. The same results were obtained when the reactions were performed under air or N₂ atmosphere.

 $[Pd(o-Ph_2PC_6H_4CH=N^{-i}Pr)_2]$ (11): (62% yield). Mp = 95 °C. Anal. Calc. for C₄₄H₄₄N₂P₂Pd: C, 68.7; H, 5.7; N, 3.6. Found: C, 69.0; H, 5.9; N, 3.8.%. FT-IR (nujol, cm⁻¹): v(C=N) 1650(s), 1591(s). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8,63 (br, 2H, CH=N), 8.12-6.12(m, 28H, arom.) 3.28 (m, 2H, CH⁻ⁱPr) 1,19 (d, J_{HH} = 6.9 Hz, 12H, CH₃-ⁱPr). ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 29.1(s). FAB-MS (positive mode) m/z: 683 (M⁺-2ⁱPr).

 $[Pd(o-Ph_2PC_6H_4CH=N-Ph)_2]$ (12): (85% yield). Mp = 117 °C. Anal. Calc. for C₅₀H₄₀N₂P₂Pd: C, 71.8; H, 4.8; N, 3.3. Found: C, 72.0; H, 5.0; N, 3.3.%. FT-IR (nujol, cm⁻¹): v(C=N) 1650(s), 1590(s). ¹H NMR (200 MHz, CDCl₃): δ (ppm): 8.53 (s, 2H, HC=N), 7.90-6.95 (m. 36H, 6H P-C₆H₄-C + 20H PPh₂ + 10H N-Ph), 6.90 (m, 2H, P- C_6H_4 -C), ³¹P NMR (300 MHz, CDCl₃): δ (ppm) 31.2 (s). FAB-MS (positive mode) *m/z*: 836 (M⁺).

2.3. Crystal structure determination of (3), (4), (5), (8) and (9)

Crystals of (**3**) $(0.14 \times 0.06 \times 0.06 \text{ mm}^3)$, (**4**) $(0.09 \times 0.06 \times 10^3)$ 0.04 mm³), (5) $(0.11 \times 0.10 \times 0.08 \text{ mm}^3)$, (8) $(0.15 \times 0.08 \times 10^{-3})$ 0.06 mm³) and (9) $(0.25 \times 0.11 \times 0.10 \text{ mm}^3)$ suitable for a diffraction study were prepared by slow diffusion of hexane into their dichloromethane solutions, mounted on glass fibre and transferred to a Bruker Smart CCD diffractometer at -173 °C. The crystallographic data are summarised in Table 1. Mo K α radiation was used $(\lambda = 0.71073 \text{ Å})$. The structures were solved by direct methods (excepting (8) that was done by Patterson methods) and refined anisotropically on F^2 [36].

The ranges of *hkl* were $-13 \le h \le 13$, $-15 \le k \le 15$, $-25 \le l \le 25$ for (**3**), $-22 \le h \le 23$, $-15 \le k \le 15$, $-24 \le l \le 24$ for (4), $-13 \le h \le 13$, $-23 \le k \le 22$, $-32 \le l \le 32$ for (5), $-15 \leq h \leq 16$, $-26 \leq k \leq 25$, $-24 \leq l \leq 25$ for (**8**) and $22 \leq h \leq 23$, $-22 \le k \le 21$, $-25 \le l \le 24$ for (**9**), respectively. Hydrogen atoms were introduced in calculated positions, except in complexes (3) and (8) where hydrogen atoms positions belonging to water mole-

Table	1
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	3	4	5	8	9
Empirical formula	C ₅₂ H ₄₂ N ₂ O ₂ P ₂ Pd.2H ₂ O	$C_{50}H_{36}F_2N_2O_2P_2Pd$	C44H44Cl2N2O10P2Pd	C ₅₀ H ₃₈ Cl ₂ F ₂ N ₂ O ₁₀ P ₂ Pd.H ₂ O	C44H44Cl2N2O8P2Pd.CH2Cl2
Formula weight	931.25	903.15	1000.05	1122.08	1052.98
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Absorption coefficient (mm ⁻¹)	0.546	0.607	0.667	0.647	0.770
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	ΡĪ	C2/c	Pbnn	P21/n	P21/n
a (Å)	10.7736(5)	17.8316(16)	10.2127(4)	12.4876(5)	13.8266(11)
b (Å)	11.4828(5)	12.3863(11)	17.8225(8)	19.6641(7)	16.8343(14)
c (Å)	19.3207(9)	18.4784(6)	24.5073(11)	19.2333(7)	19.4930(16)
α (°)	77.7550(10)	90	90	90	90
β (°)	75.2820(10)	104.784(2)	90	91.152(1)	90.286(1)
γ (°)	73.3040(10)	90	90	90	90
$V(Å^3)$	2189.20 (17)	3946.2(6)	4460.7(3)	4717.1(3)	4537.2(6)
Ζ	2	4	4	4	4
D_{calc} (Mg m ⁻³)	1.413	1.520	1.489	1.580	1.542
F(000)	960	1840	2048	2280	2152
Reflections collected	25543	22567	48947	54276	51122
Independent reflections (<i>R</i> _{int})	9487 (0.0433)	4593 (0.0599)	5328 (0.0591)	11001 (0.0588)	10479 (0.0518)
Parameters	566	267	270	639	569
Refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on <i>F</i> ²
R_1^a	0.0469	0.0453	0.0746	0.0620	0.1080
wR ₂ ^b	0.0960	0.1065	0. 1923	0.1313	0.2513
Sc	1.057	1.079	0.905	1.099	1.068
Maximum, minimum $\Delta \rho$	0.618, -0.708	0.664, -0.6415	2.536, -2.514	1.762, -1.386	2.529, -1.966

^a $R_1 = \sum ||F_0| - |F_C|| / \sum |F_0|$ for reflections with $I > 2\sigma I$.

^b $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, were $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program. ^c $S = \{\Sigma[w(F_0^2 - F_c^2)^2]/(n-p)\}^{1/2}$; n is the number of reflections and p the total number of parameters refined.

cules were refined. Data are of poor quality, assessed by a mean value of I/sig(I) always lower than 10. For this reason in complex (**8**) a ClO_4^- anion show high thermal parameters. Because U_{ij} values on neighbouring atoms tend to be similar DELU, SIMU and ISOR restraints [36] were applied. In complex (**9**) ISOR was applied to a dichloromethane molecule. Data were corrected for absoption with SADABS [37].

Complex (5) exhibits crystallographic C_2 symmetry. In one perchlorate the chlorine atom lies on a C_2 axis, so only two positions were refined for oxygen atoms. In the second perchlorate chlorine and one oxygen atom lie on a C_2 axis (special positions). The remaining oxygen atoms were found in general positions with a 50% occupation factor.

3. Results and discussion

3.1. Oxidative addition reactions of diphenylphosphine-benzamides to Pd(0)

In dichloromethane, the precursor $Pd(dba)_2$ reacts at room temperature with o-Ph₂P-C₆H₄-CO-NH-R yielding the yellow compounds of general formula [Pd(o-Ph₂PC₆H₄CO-NR)₂] [R = ⁱPr (1),

Ph (**2**), 4-MeC₆H₄ (**3**), 4-FC₆H₄ (**4**)] in which an κ^2 -P,N coordination mode for diphenylphosphine-benzamidate ligands is observed. The spectroscopic and analytical data are in agreement with the proposed structures presented in Scheme 1. Thus, the loss of v(NH)bands in their IR spectra and the presence of v(CO) absorptions in the range observed for the free ligands (1604–1655 cm⁻¹) gives a first support for the formation of a P–N chelate around the Pd centre [19,20], confirmed by the FAB mass spectrometry that displays fragments corresponding to M⁺ or M⁺ + 1. The presence of diphenylphosphine-benzamidate ligands is also observed by ³¹P{1H} NMR spectroscopy, the spectra consisting of singlets around 33 ppm. This data is in agreement with those obtained in the characterization of cyclopalladated compounds with anionic diphenilphosphine-benzamidate ligands [19].

Thus, under our conditions the expected complexes of Pd(0) and diphenylphosphinobenzamides are not stable and instead Pd(II) complexes were obtained. The formation of related Pd(II) complexes was mentioned by Trost et al. [38,39] in the reaction of Pd₂(dba)₃ whit the chiral bidentate ligand (15,25)-(-)-1,2-diamino-cyclohexane-*N*,*N'*-bi(2-diphenylphosphino-1-benzoyl) and recently the mechanism of formation of such Pd(II) complexes with a very similar Trost type ligands has been explored by Amatore



Scheme 1. Preparation of homoleptic derivatives (1–4) with κ^2 -P,N coordination mode.



Scheme 2. Proposed routes for the formation of complexes (1-4).

Table 2	
Selected bond lengths (Å) and angles	(°).

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Bond length (Å)/ angle(°)	(3)	(4)	(5)	(8)	(9)
$\begin{array}{cccccccc} Pd(1)-P(1) & 2.2594(8) & 2.2454(7) & 2.2268(11) & 2.2292(10) & 2.2572(19) \\ Pd(1)-P(2) & 2.2584(8) & & 2.2145(10) & 2.255(2) \\ Pd(1)-O(1) & & & 2.051(3) & 2.066(3) \\ Pd(1)-O(2) & & & & & & & & & \\ N(1)-Pd(1)-R(1) & 89.33(9) & & & & & & & & & & \\ N(2) & & & & & & & & & & & & \\ N(1)-Pd(1)-P(1) & 81.19(7) & 83.86(7) & & & & & & & & & & & \\ N(1)-Pd(1)-P(2) & 167.17(7) & & & & & & & & & & & & & & \\ N(2)-Pd(1)-P(1) & 165.91(6) & & & & & & & & & & & & & & \\ N(2)-Pd(1)-P(2) & 82.71(7) & & & & & & & & & & & & & & & & & & \\ N(2)-Pd(1)-P(2) & 108.35(3) & & & & & & & & & & & & & & & & & & &$	Pd(1)–N(1) Pd(1)–N(2)	2.091(2) 2.092(2)	2.094(2)			2.116(6) 2.104(7)
$\begin{array}{cccccccc} Pd(1)-P(2) & 2.2584(8) & 2.2145(10) & 2.255(2) \\ Pd(1)-O(1) & 2.051(3) & 2.066(3) \\ Pd(1)-O(2) & 2.039(3) & \\ N(1)-Pd(1)-R(1) & 89.33(9) & 89.7(2) \\ N(2) & & & & \\ N(1)-Pd(1)-P(1) & 81.19(7) & 83.86(7) & 87.14(17) \\ N(1)-Pd(1)-P(2) & 167.17(7) & 165.23(18) \\ N(2)-Pd(1)-P(1) & 165.91(6) & 165.04(19) \\ N(2)-Pd(1)-P(2) & 82.71(7) & 87.28(19) \\ P(1)-Pd(1)-P(2) & 108.35(3) & 103.88(4) & 99.29(7) \\ \end{array}$	Pd(1) - P(1)	2.2594(8)	2.2454(7)	2.2268(11)	2.2292(10)	2.2572(19
$\begin{array}{ccccccc} Pd(1)-O(1) & 2.051(3) & 2.066(3) \\ Pd(1)-O(2) & 2.039(3) \\ N(1)-Pd(1)- & 89.33(9) & 89.7(2) \\ N(2) & & & & & & & \\ N(1)-Pd(1)-P(1) & 81.19(7) & 83.86(7) & 87.14(17) \\ N(1)-Pd(1)-P(2) & 167.17(7) & 165.23(18) \\ N(2)-Pd(1)-P(1) & 165.91(6) & 165.04(19) \\ N(2)-Pd(1)-P(2) & 82.71(7) & 87.28(19) \\ P(1)-Pd(1)-P(2) & 108.35(3) & 103.88(4) & 99.29(7) \\ \end{array}$	Pd(1) - P(2)	2.2584(8)			2.2145(10)	2.255(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Pd(1) - O(1)			2.051(3)	2.066(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Pd(1) - O(2)	80.22(0)			2.039(3)	80 7(2)
N(1)-Pd(1)-P(1) 81.19(7) 83.86(7) 87.14(17) N(1)-Pd(1)-P(2) 167.17(7) 165.23(18) N(2)-Pd(1)-P(1) 165.91(6) 165.04(19) N(2)-Pd(1)-P(2) 82.71(7) 87.28(19) P(1)-Pd(1)-P(2) 108.35(3) 103.88(4) 99.29(7)	N(1) - Pu(1) - N(2)	89.55(9)				89.7(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(1) - Pd(1) - P(1)	81.19(7)	83.86(7)			87.14(17)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(1)-Pd(1)-P(2)	167.17(7)				165.23(18
N(2)-Pd(1)-P(2) 82.71(7) 87.28(19) P(1)-Pd(1)-P(2) 108.35(3) 103.88(4) 99.29(7)	N(2)-Pd(1)-P(1)	165.91(6)				165.04(19
P(1)-Pd(1)-P(2) 108.35(3) 103.88(4) 99.29(7)	N(2)-Pd(1)-P(2)	82.71(7)				87.28(19)
	P(1)-Pd(1)-P(2)	108.35(3)			103.88(4)	99.29(7)
N(1)-Pd(1)- 90.38(13)	N(1) - Pd(1) -		90.38(13)			
N(1)#1	N(1)#1					
N(1)#1-Pd(1)- 164.99(6) P(1)	N(1)#1-Pd(1)- P(1)		164.99(6)			
P(1)-Pd(1)- P(1)#1 104.91(4) 101.90(6)	P(1)-Pd(1)- P(1)#1		104.91(4)	101.90(6)		
P(1)-Pd(1)-O(1) 87.25(9) 84.93(8)	P(1) - Pd(1) - O(1)			87.25(9)	84.93(8)	
P(1)-Pd(1)- 167.65(9) 168.72(8)	P(1)-Pd(1)-			167.65(9)	168.72(8)	
O(1)#1 ^a	O(1)#1 ^a					
O(1)-Pd(1)- 85.00(18) 85.42(11)	O(1)-Pd(1)-			85.00(18)	85.42(11)	
O(1)#1 ^a	O(1)#1 ^a					
P(2)-Pd(1)-O(1) 167.72(8)	P(2) - Pd(1) - O(1)				167.72(8)	
P(2)-Pd(1)-O(2) 86.59(8)	P(2)-Pd(1)-O(2)				86.59(8)	

^a O(2) in (**8**).

and Jutand [40]. According to their proposal, Pd(II) complexes would be generated by either oxidation of $Pd^{0}(\text{fosfine-amide})_{2}$ by air or an alternative reaction involving intramolecular activation of one N–H bond by the Pd(0) centre leading to a Pd(II) hydride. In this case subsequent intramolecular deprotonation would give the complexes **1–4** (Scheme 2). X-ray diffraction analysis has confirmed the structures of (**3**) and (**4**), providing a set of structural data that enrich some aspects discussed above. Selected bond distances and angles are presented in Table 2 and their molecular structures are shown in Figs. 1 and 2, respectively. The bond



Fig. 1. ORTEP diagram of complex (3) with the atom numbering scheme; displacement ellipsoids are drawn at the 50% propability level.

lengths and angles around Pd are similar in both complexes and also in the range of those found in the few related complexes described previously [19,40]. Complex (**3**) is involved in four hydrogen bondings with two H₂O molecules forming infinite chains as shown in Fig. 3 (distance $O(2) \cdots O(3)$ 2.782(3) Å and angle O(3)– H(54) $\cdots O(2)$ 170(4)°; distance $O(2) \cdots O(3)$ 2.856(4) Å and angle O(3)–H(53) $\cdots O(2)$ 173(4)°; distance $O(1) \cdots O(4)$ 2.840(3) Å and angle O(4)–H(55) $\cdots O(1)$ 166(4)°; distance $O(1) \cdots O(4)$ 2.797(4) Å and angle O(4)-H(56) $\cdots O(1)$ 168.(5)°).

3.2. Synthesis and characterization of P,O-diphenylphosphinebenzamide complexes of palladium(II)

In order to induce amide protonation in the ligands, and a likely κ^2 -P.O coordination mode according to our previous studies with nickel and palladium organometallic complexes, compounds (1-**4**) were treated with $HClO_4(aq)$ in dichloromethane as described in the experimental section, to yield yellow cationic complexes $[Pd(o-Ph_2PC_6H_4CO-NHR)_2][ClO_4]_2$ [R = i-Pr (5), Ph (6), 4-MeC₆H₄ (7), 4-FC₆H₄ (8)]. The presence of both v(NH) and $v(ClO_4)$ bands in their IR spectra accompanied by a noticeable change in the carbonyl region, in comparison with the corresponding precursors, confirmed that the proposed reactions took place. Alternatively, the complexes were prepared by reaction of the labile complex [PdCl₂(PhCN)₂] with the 2-diphenylphosphine-benzamide (molar ratio 1:2) ligands and AgClO₄ in CH₂Cl₂. After elimination of the precipitated AgCl, complexes (5-8) were isolated as perchlorate salts. The positive FAB mass spectra of the complexes shows signals at m/z due to the $[Pd(o-Ph_2PC_6H_4CO-NHR)_2]^+$ and $[Pd(o-Ph_2PC_6H_4CO-NHR)_2]^+$ $Ph_2PC_6H_4CO-NHR)_2(ClO_4)$ ⁺ fragments. A singlet shifted towards low field compared to P,N-chelated neutral compounds characterizes the ³¹P{1H} NMR spectra, and the expected pattern is observed in the ¹H NMR with significant presence of amidic proton resonance at low field. Measurements of their molar conductivity in acetone solutions indicate that all the complexes behave as 1:1 electrolytes [41], in accordance with the proposed formulae.

It was possible to grow X-ray quality crystals that after diffraction study have confirmed the structures of, (**5**) and (**8**). Each of them consisted of a cationic complex $[Pd(o-Ph_2PC_6H_4CO-$



Fig. 2. ORTEP diagram of complex (4) with the atom numbering scheme; displacement ellipsoids are drawn at the 50% propability level.



Fig. 3. Molecules of (3) joining into infinite chains with O1 and O2 bridged by two H₂O molecules.



Fig. 4. ORTEP diagram of complex (5); displacement ellipsoids are drawn at the 50% probability level.



Fig. 5. X-ray crystal structure of (8). Displacement ellipsoids are drawn at 50% probability.

 $NHR)_2]^{2+}$ (Figs. 4 and 5, respectively) and two ClO_4^- anions, with just one of them involved in hydrogen bonding with the amidic nitrogens. Thus a ClO_4^- anion in complex (**5**) links by hydrogen bond two units of complex in a C_2 symmetry (distance $N(1) \cdots O(2) 2.898(5)$ Å and angle $N(1)-H(1) \cdots O(2) 164.0^\circ$) generating a linear chain (Fig. 6). In complex (**8**) there are also hydrogen bonding characterized by the distance $N(2) \cdots O(3)$ of 3.019(4) Å and the angle $N(2)-H(2) \cdots O(3)$ of 157.8° , and distance $O(11) \cdots O(10)$ of 2.812(14) Å and the angle $O(11)-H(11B) \cdots O(10)$ of $164.(11)^\circ$, respectively.

Selected bond lengths and angles listed in Table 2 are very similar in both complexes.

The Pd(1)–O(1) distances are shorter than those reported for related compounds containing a carbonyl group involved in P,O chelation to a palladium centre [7,19].

3.3. Synthesis and characterization of homoleptic Pd(II) and Pd(0) iminophosphine complexes

Following an analogous route as the one described above, $[PdCl_2(PhCN)_2]$ reacts in dichloromethane with iminophosphines (molar ratio 1:2) and the stoichiometric amount of AgClO₄ to yield the homoleptic cationic complexes $[Pd(o-Ph_2PC_6H_4CH=N-R)_2][ClO_4]_2$ [R = ⁱPr (**9**), Ph (**10**)] (Scheme 3).

The cationic palladium complexes are air-stable yellow solids and their infrared spectra show a single strong band in the double bond region attributed to the C=N stretching vibrations, shifted to lower frequencies than in free ligands. The complexes also exhibit the characteristic absorptions of the CIO_4^- anion at ca. 1100 and 600 cm⁻¹ and measurements of their molar conductivity in acetone solutions indicate that they behave as 2:1 electrolytes [41], in accordance with the proposed formulae. The ³¹P NMR spectra of the compounds consist of singlets with chemical shifts in the usual range of Pd(II) iminophosphine complexes [42–45]. The positive FAB-MS spectra of the complexes show the peaks for the M⁺-



Fig. 6. View of the ClO_4^- – H-bonded chains in complex (8).



Scheme 3. Preparation of homoleptic Pd(II) iminophosphine complexes.



Fig. 7. ORTEP diagram of complex (**9**) with the atom numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

ClO₄ ion and additional peaks for M^+ -2ClO₄, [Pd(o-Ph₂PC₆H₄CH=N-R)][ClO₄] and [Pd(o-Ph₂PC₆H₄CH=N-R)][ClO₄].

We reported in 2001 [43] the preparation of (**9**) by a similar route using $KClO_4$ instead of the silver salt. The characterization data obtained then are in agreement with the ones presented here, that are completed with the determination of the molecular structure by a single-crystal diffraction study. Selected bond distances and angles are presented in Table 2 and Fig. 7 displays an ORTEP drawing of the complex cation.

The five new structures may be described as planar and their deviation from the planar coordination has been quantified by

Table 4 Pd-P-C_{ipso}-C torsion angles (°) for three phenyl ring in complexes (3), (4), (5), (8) and (9).

Table 3					
Conformation a	and deformation () of six-membered	rings for	complexes (3)	, (4), (5)
(8) and (9).					

	(3)		(4)	(5)	(8)		(9)	
Pd N C C C	1.00	1.00	0.99 SB	1.00			0.94	0.97
Р	SB	SB		SB			SB	SB
	11 °	9 °	0.01 TB	14 °			0.06	0.03
							HC	HC
			13 °				6 °	5 °
Pd P C C C					0.91	0.65 E		
0					SB			
					0.09	0.26		
					В	HC		
					15°	0.09		
						SB		
						12 °		

measures of improper torsion angles: $w_1 = 7.19$ and $w_2 = 5.30^\circ$ for (**3**), $w_1 = -9.77$ and $w_2 = -7.58^\circ$ for (**4**), $w_1 = 5.26$ and $w_2 = 7.06^\circ$ for (**5**), $w_1 = 2.62$ and $w_2 = 7.16^\circ$ for (**8**) and $w_1 = -10.24$ and $w_2 = -8.78^\circ$ for (**9**) [46]. These values correspond to a moderate tetrahedral distortion from the ideal square-plane. The six membered chelate rings involving the Pd atom show a distorted *screw-boat* conformation except for the Pd1–N1–C19–C18–C13 ring of (**8**) when they are evaluated by the classification method for $\sigma = 10$ [47]. The mean deviation from the torsion angles between the closest ideal conformation and found in our complexes ranges 5–15° (Table 3).

Following the classification of Dance and Scudder [48] for PPh₃ based on measures of torsion angles M–P–C_{ipso}–C (Table 4), the conformation of Pd–PPh₂C₆H₄COR groups is described as *no rotor* for complexes (**5**) and the group Pd1–P2–C–C of (**8**) and as *good ro-tor* for the rest. Compounds (**3**) and (**4**) present a set of T_i values very close to those which would have the ideal rotor $(T_1 = T_2 = T_3 = 44^\circ)$ (Fig. 8).

	(3)		(4)	(5)	(8)		(9)	
Ring 1	128.53	-49.41	47.34	-42.77	-54.11	-24.48	44.75	44.18
	-48.85	129.42	-139.20	144.32	131.76	157.17	-142.86	-142.27
Ring 2	144.40	131.39	-139.72	-59.61	145.72	5.74	16.85	-163.01
-	-38.13	-54.43	43.54	120.42	-30.53	-177.46	-163.89	19.01
Ring 3	112.07	-38.07	-122.80	-5.95	123.57	115.45	-122.43	56.44
	-65.70	144.22	54.26	165.34	-56.90	-61.23	59.21	-125.19
T (ring 1)	-48.85	-49.41	47.34	-42.77	-54.11	-24.48	44.75	44.18
T (ring 2)	-38.13	-54.43	43.54	-59.61	-30.53	5.74	16.85	19.01
T (ring 3)	-65.70	-38.07	54.26	-5.95	-56.90	-61.23	59.21	56.44
T_1	-65.70	-54.43	43.54	-59.61	-56.90	-61.23	16.85	19.01
T ₂	-48.85	-49.41	47.34	-42.77	-54.11	-24.48	44.75	44.18
T ₃	-38.13	-38.07	54.26	-5.95	-30.53	5.74	59.21	56.44
$T_2 - T_1$	16.85	4.52	3.80	16.84	2.79	36.75	27.90	25.17
$T_{3} - T_{2}$	10.72	11.9	6.92	36.82	23.58	30.22	14.46	12.26
Kind of rotor	good rotor	good rotor	good rotor	no rotor	good rotor	no rotor	good rotor	good rotor



Fig. 8. A drawing of the ideal rotor.

complexes Homoleptic-iminophosphine Pd(0)[Pd(o- $Ph_2PC_6H_4CH=N-R_2$ [R = ⁱPr (11), Ph (12)] were obtained by reaction of a fresh dichloromethane solution of these ligands with Pd(dba)₂ at room temperature. It is worth it to point out the low decomposition temperatures of the new complexes, which are stable on air for weeks. In contrast with analogous Pd(II) complexes, their IR spectra display several overlapped absorptions in the carbonyl region. The ³¹P NMR spectra of the new iminophosphine complexes consist of singlets slightly shifted to high field if compared with related organometallic Pd(II) compounds [42-45] and the analogous cationic complexes described above.

The proposed formulae of the new complexes are also confirmed by FAB mass spectrometry, which displays a different fragmentation pattern compared to that of (9) and (10).

4. Conclusion

New homoleptic palladium(II) complexes with diphenylphosphine-benzamide ligands exhibiting different coordination modes have been prepared by different synthetic routes and characterized by spectroscopic techniques and single crystal X-ray diffraction analysis. Reaction of o-Ph₂PC₆H₄CO-NR with Pd(dba)₂ did not yield the expected Pd⁰ complexes, unstable under our conditions, and instead this reaction produced complexes in which a κ^2 -P,N coordination mode to Pd(II) is observed. Homoleptic iminophosphine derivatives of both Pd(0) and Pd(II) were readily prepared by direct reaction of the N^P ligands with whether Pd(dba)₂ or labile [PdCl₂(PhCN)₂] in presence of AgClO₄.

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Appendix A. Supplementary data

CCDC 721716, 721717, 721718, 721719 and 721720 contains the supplementary crystallographic data (3), (4), (5), (8) and (9). 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.ica.2009.07.003.

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