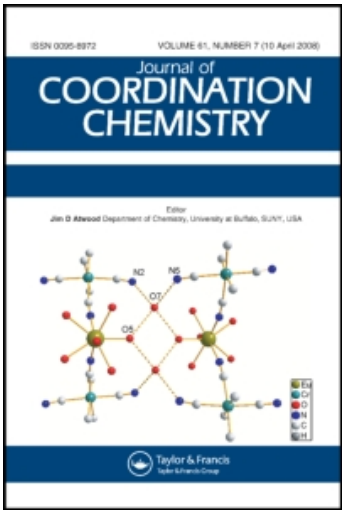

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New Palladium(II) Complexes with a Tridentate PNO Ligand

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NEW PALLADIUM(II) COMPLEXES WITH A TRIDENTATE PNO LIGAND

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The synthesis of neutral and cationic palladium complexes containing the tridentate monoanionic ligand [2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O]$^-$ is described. Deprotonation of the Schiff base formed by condensation of 2-(diphenylphosphino)benzaldehyde with 2-aminophenol in the presence of the appropriate palladium precursor ([Pd(AcO)$_2$] or [$PdCl_2(PhCN)_2$]) form the corresponding neutral complexes [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(AcO)] (**1**) or [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(Cl)] (**2**) in good yield. The first reacts smoothly with thiols and activated phenols to give complexes of general formula [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(X)] (X = OC_6F_5 (**3**), SEt (**4**), S^{t}Bu (**5**), SC_6H_5 (**6**), SC_6H_4-4Me (**7**), SC_6H_4-4NO_2 (**8**)). When the chloro complex is treated with silver perchlorate and tertiary phosphines (L) the cationic derivatives [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(L)][ClO_4] (L = PPh_3 (**9**), $PMePh_2$ (**10**), PMe_2Ph (**11**), PEt_3 (**12**)) were obtained. The new complexes were characterized by partial elemental analyses and spectroscopic methods (IR, ^{1}H, ^{19}F and ^{31}P NMR).

Keywords: Tridentate ligand; Iminophosphine; Palladium complexes

INTRODUCTION

Bidentate phosphine-based ligands containing both hard and soft donor atoms have been a subject of considerable interest in many areas of coordination chemistry [1,2] and homogeneous catalysis [3], since they combine strong coordination via phosphorus with a hemilabile donor for transient stabilization of intermediates during reaction sequences.

Among the most widely studied ligands with these characteristics are the pyridylphosphines and the iminophosphines, from which palladium complexes have been recently reported [4–9]. However, only a small number of heterotridentate phosphines exist which have both oxygen and nitrogen properly placed for metal coordination, taking the forms PNO, PON or OPN depending upon the relative position of the donors [10]. Several PNO ligands, typically built from a diphenylphosphine unit, and its respective complexes have been described [11–18], and interesting catalytic properties

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have been pointed out in some cases [19,20]. The Schiff base synthesized by condensation of 2-(diphenylphosphino)benzaldehyde with 2-aminophenol, together with some iron, cobalt and rhenium complexes was first described by Dilworth and coworkers [11]. Since then just a few complexes with Group 10 metals [17] and ruthenium [21] have been described.

Here we report the synthesis and characterization of the new neutral palladium complex containing this PNO ligand [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(AcO)] (**1**) and its reactivity involving replacement of the AcO^- group. We also include our synthesis of [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(Cl)] (**2**), recently described [17], and further investigation of its chemistry as a precursor of new cationic complexes.

EXPERIMENTAL

C, H, N and S analyses were carried out with a Perkin-Elmer 240C microanalyzer. IR spectra were recorded on a Perkin-Elmer spectrophotometer 16F PC FT-IR, using nujol mulls between polyethylene sheets. NMR data were recorded on a Bruker AC 200E (^1H) or a Varian Unity 300 (^1H, ^{31}P, ^{19}F) spectrometer. Conductance measurements were performed with a Crison 525 conductimeter (in acetone, 5×10^{-4} M). All the solvents were dried by standard methods before use. The precursor [$PdCl_2(PhCN)_2$] [22] and the PNO ligand [11] were prepared according to reported procedures. [$Pd(AcO)_2$] was obtained commercially and used as received.

Preparation of Complexes [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(AcO)] (1) and [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(Cl)] (2)

Complex (**2**) was prepared by adding a stochiometric amount of NEt_3 and [$PdCl_2(PhCN)_2$] (0.1 mmol) to a dichloromethane solution (15 mL) of the PNO ligand (0.1 mmol). The mixture was stirred at room temperature for 3 h and then concentrated under reduced pressure to half volume. Addition of diethyl ether caused precipitation of the new red complex, which was filtered off, air dried and recrystallized from dichloromethane–ether. Complex (**1**) was obtained following the same procedure, using [$Pd(AcO)_2$] as starting material instead of [$PdCl_2(PhCN)_2$], and without addition of NEt_3 to the reaction mixture.

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(AcO)] (**1**) was obtained in 72% yield. Anal. Calcd. for $C_{27}H_{22}NO_3PPd$(%): C, 59.4; H, 4.0; N, 2.6. Found: C, 59.6; H, 3.9; N, 2.7. IR (cm^{-1}): 1580 (C=N str). ^1H NMR ($CDCl_3$, 20°C) δ 1.5 (s, 3H, CH_3), 6.3–7.8 (m, 18H, C_6H_4; Ph), 8.2 (d, 1H, CH=N, $J_{HP} = 2.3$). ^{31}P-{^1H}NMR ($CDCl_3$, 20°C) δ 28.7 (s).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(Cl)] (**2**) was obtained in 80% yield. Anal. Calcd. for $C_{25}ClH_{19}NOPPd$(%): C, 57.5; H, 3.6; N, 2.7. Found: C, 57.6; H, 3.6; N, 2.7. IR (cm^{-1}): 1580 (C=N str). ^1H NMR ($CDCl_3$, 20°C) δ 6.3–7.8 (m, 18H, C_6H_4; Ph), 8.5 (s, 1H, CH=N). ^{31}P-{^1H}NMR ($CDCl_3$, 20°C) δ 32.0 (s).

Preparation of Complexes [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(X)] (X = OC_6F_5 (3), SEt (4), S^{t}Bu (5), SC_6H_5 (6), SC_6H_4-4Me (7), SC_6H_4-4NO_2 (8))

The complexes were obtained by treating [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(AcO)] (40 mg, 0.73 mmol) with the corresponding protic electrophile (molar ratio 1 : 1

except for complex (**3**) molar ratio 1 : 5) in dichloromethane (15 mL). The resulting solution was stirred at room temperature for 3 h and then concentrated under reduced pressure to half volume. Addition of diethyl ether caused precipitation of the new complexes, which were filtered off, air dried and recrystallized from dichloromethane–ether.

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(OC_6F_5)] (**3**) was obtained in 68% yield. Anal. Calcd. for $C_{31}F_5H_{19}NOPPd$(%): C, 57.0; H, 2.9; N, 2.1. Found: C, 56.8; H, 2.9; N, 2.2. IR (cm^{-1}): 1584 (C=N str). ^{1}H NMR ($CDCl_3$, 20°C) δ 6.3–7.8 (m, 18H, C_6H_4; Ph), 8.4 (s, 1H, CH=N). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 32.0 (s). ^{19}F-{^{1}H}NMR ($CDCl_3$, 20°C) δ −163.2 (dd, $2F_o$, $J_{om} = 20.3$), −170.0 (t, $2F_m$, $J_{mp} = 21.2$), −180.0 (m, $1F_p$).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(SEt)] (**4**) was obtained in 70% yield. Anal. Calcd. for $C_{27}H_{24}NOPSPd$(%): C, 59.2; H, 4.4; N, 2.5; S, 5.8. Found: C, 59.4; H, 4.5; N, 2.7; S, 5.8. IR (cm^{-1}): 1582 (C=N str). ^{1}H NMR ($CDCl_3$, 20°C) δ 1.3 (m, 3H, CH_2CH_3), 2.7 (m, 2H, CH_2CH_3), 6.2–7.6 (m, 18H, C_6H_4; Ph), 8.5 (s, 1H, CH=N). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 36.5 (s).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(S^tBu)] (**5**) was obtained in 80% yield. Anal. Calcd. for $C_{29}H_{28}NOPSPd$(%): C, 60.5; H, 4.8; N, 2.4; S, 5.5. Found: C, 60.4; H, 4.9; N, 2.4; S, 5.6. IR (cm^{-1}): 1580 (C=N str). ^{1}H NMR ($CDCl_3$, 20°C) δ 1.4 (s, 9H, CH_3), 6.2–7.8 (m, 18H, C_6H_4; Ph), 8.6 (s, 1H, CH=N). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 34.2 (s).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(SC_6H_5)] (**6**) was obtained in 72% yield. Anal. Calcd. for $C_{31}H_{24}NOPSPd$(%): C, 62.5; H, 4.0; N, 2.3; S, 5.4. Found: C, 62.6; H, 4.1; N, 2.4; S, 5.5. IR (cm^{-1}): 1580 (C=N str). ^{1}H NMR ($CDCl_3$, 20°C) δ 6.2–7.8 (m, 23H, C_6H_4; Ph), 8.6 (s, 1H, CH=N). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 34.2 (s).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(SC_6H_4-4Me)] (**7**) was obtained in 65% yield. Anal. Calcd. for $C_{32}H_{26}NOPSPd$(%): C, 63.0; H, 4.3; N, 2.3; S, 5.2. Found: C, 62.9; H, 4.1; N, 2.3; S, 5.3. IR (cm^{-1}): 1580 (C=N str). ^{1}H NMR ($CDCl_3$, 20°C) δ 2.1 (s, 3H, Me), 6.2–7.6 (m, 22H, C_6H_4; Ph), 8.5 (s, 1H, CH=N). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 34.2 (s).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(SC_6H_4-4NO_2)] (**8**) was obtained in 75% yield. Anal. Calcd. for $C_{31}H_{26}N_2O_3PSPd$(%): C, 57.8; H, 4.0; N, 4.3; S, 5.0. Found: C, 57.9; H, 4.0; N, 4.3; S, 5.2. IR (cm^{-1}): 1580 (C=N str). ^{1}H NMR ($CDCl_3$, 20°C) δ 6.2–7.6 (m, 22H, C_6H_4; Ph), 8.5 (s, 1H, CH=N). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 33.7 (s).

Preparation of Complexes [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(L)][ClO_4] (L = PPh_3 (9), $PMePh_2$ (10), PMe_2Ph (11), PEt_3 (12))

The cationic derivatives were obtained by treating complex (**2**) with the corresponding phosphine (molar ratio 1 : 1) in acetone according to the following general method. A stochiometric amount of $AgClO_4$ was added to an acetone (15 mL) solution of the precursor [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(Cl)] (53.6 mg, 0.1 mmol). The reaction was kept stirring at room temperature for 30 min and then the AgCl precipitate was removed by filtration. A solution of the corresponding phosphine (0.1 mmol) in acetone (5 mL) was added to the resulting filtrate and the mixture was stirred for 30 min at room temperature. The solvent was then removed under reduced pressure and addition of

diethyl ether caused precipitation of the new complexes, which were filtered off, air dried and recrystallized from dichloromethane–ether.

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(PPh_3)][ClO_4] (**9**) was obtained in 82% yield. Anal. Calcd. for $C_{43}ClH_{34}NO_5P_2Pd$(%): C, 60.9; H, 4.0; N, 1.6. Found: C, 60.9; H, 4.0; N, 1.5. IR (cm^{-1}): 1582 (C=N str), 625, 544, 520 (PPh_3). Λ_M ($\Omega^{-1}\,mol^{-1}\,cm^2$): 127. ^{1}H NMR ($CDCl_3$, 20°C) δ 6.2–8.3 (m, 33H, C_6H_4; Ph), 9.2 (d, 1H, CH=N, $J_{HP} = 14.6$). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 31.4 (d, PPh_3), 34.3 (d, PNO, $J_{PP} = 23.3$).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}($PMePh_2$)][ClO_4] (**10**) was obtained in 75% yield. Anal. Calcd. for $C_{43}ClH_{34}NO_5P_2Pd$(%): C, 58.0; H, 4.1; N, 1.8. Found: C, 57.9; H, 4.2; N, 1.7. IR (cm^{-1}): 1582 (C=N str), 890, 624 ($PMePh_2$). Λ_M ($\Omega^{-1}\,mol^{-1}\,cm^2$): 133. ^{1}H NMR ($CDCl_3$, 20°C) δ 2.0 (s, 3H, Me), 6.5–8.3 (m, 28H, C_6H_4; Ph), 9.1 (d, 1H, CH=N, $J_{HP} = 14.4$). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 7.8 (d, $PMePh_2$), 33.6 (d, PNO, $J_{PP} = 26.9$).

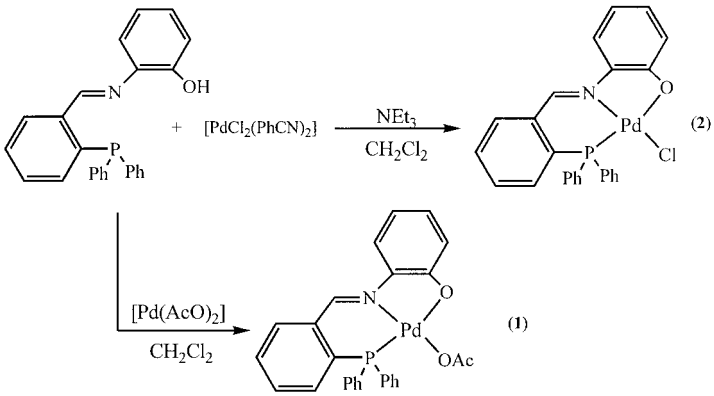
[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(PMe_2Ph)][ClO_4] (**11**) was obtained in 80% yield. Anal. Calcd. for $C_{33}ClH_{30}NO_5P_2Pd$(%): C, 54.7; H, 4.1; N, 1.9. Found: C, 55.0; H, 4.0; N, 1.7. IR (cm^{-1}): 1582 (C=N str), 960, 916, 428 (PMe_2Ph). Λ_M ($\Omega^{-1}\,mol^{-1}\,cm^2$): 135. ^{1}H NMR ($CDCl_3$, 20°C) δ 1.7 (s, 6H, Me), 6.5–8.3 (m, 23H, C_6H_4; Ph), 8.7 (d, 1H, CH=N, $J_{HP} = 14.3$). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 7.8 (d, PMe_2Ph), 33.6 (d, PNO, $J_{PP} = 26.8$).

[Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(PEt_3)][ClO_4] (**12**) was obtained in 75% yield. Anal. Calcd. for $C_{31}ClH_{34}NO_5P_2Pd$(%): C, 52.8; H, 4.8; N, 2.0. Found: C, 52.7; H, 4.9; N, 1.9. IR (cm^{-1}): 1582 (C=N str), 758 (PEt_3) Λ_M ($\Omega^{-1}\,mol^{-1}\,cm^2$): 120. ^{1}H NMR ($CDCl_3$, 20°C) δ 1.1 (m, 9H, CH_2CH_3), 1.6 (m, 6H, CH_2CH_3), 6.5–8.2 (m, 18H, C_6H_4; Ph), 8.7 (d, 1H, CH=N, $J_{HP} = 13.2$). ^{31}P-{^{1}H}NMR ($CDCl_3$, 20°C) δ 31.7 (d, PEt_3), 32.6 (d, PNO, $J_{PP} = 24.8$).

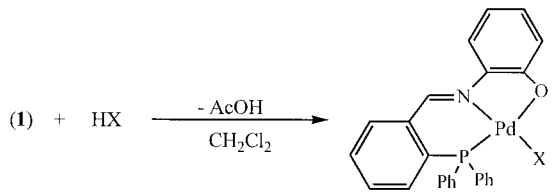
RESULTS AND DISCUSSION

In dichloromethane, the palladium precursors $[Pd(AcO)_2]$ or $[PdCl_2(PhCN)_2]$ react under mild conditions with the tridentate monoanionic ligand [2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4OH] previously prepared [11], to give the expected compounds [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(AcO)] (**1**) or [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(Cl)] (**2**) in good yield (Scheme 1). A stoichiometric amount of NEt_3 was needed to achieve ligand deprotonation when $[PdCl_2(PhCN)_2]$ was used as starting material, whereas the inherent basicity of $[Pd(AcO)_2]$ was enough for this aim, and no extra-base was added. The new complexes are air stable red solids that show negligible molar conductance and have been characterized by elemental analysis, ^{1}H and ^{31}P-{^{1}H} NMR and infrared spectroscopy (see Experimental Section).

Complex (**1**) may be a suitable precursor of new neutral complexes by reacting with ligands which could protonate the acetate anion (Scheme 2). Thus, aliphatic and aromatic thiols easily react with [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(AcO)] to give the corresponding thiolate complexes [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(X)]. Attempts to obtain the equivalent alkoxo-complexes under the same conditions or with an excess of reactant under extended reflux were unsatisfactory, yielding the starting material. This is probably due to the inherent instability of Pd-alkoxo bonds together

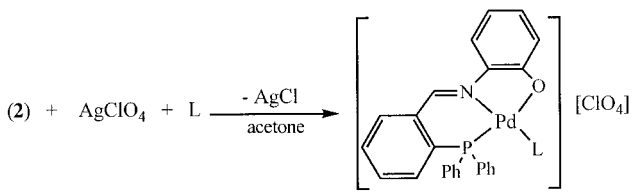


SCHEME 1 Synthesis of the new precursors (**1**) and (**2**).



X = OC_6F_5 (**3**), SEt (**4**), S^{t}Bu (**5**), SC_6H_5 (**6**), SC_6H_4-4Me (**7**), SC_6H_4-4NO_2 (**8**).

SCHEME 2 Reactivity of complex (**1**) against protic ligands.



L = PPh_3 (**9**), $PMePh_2$ (**10**), PMe_2Ph (**11**), PEt_3 (**12**).

SCHEME 3 Synthesis of new cationic complexes.

with insufficient acidity of these ligands, and the reaction was just achieved when an excess of a strongly activated alcohol (C_6F_5OH) was added.

New cationic derivatives of general formula [Pd{2-(2-$Ph_2PC_6H_4$–CH=N)C_6H_4O}(L)][ClO_4] were prepared by treating complex (**2**) with 1 equiv. of $AgClO_4$ in acetone. After elimination of the precipitated AgCl, a solution of the corresponding phosphine was added, and the new complexes were isolated as their perchlorate salts (Scheme 3).

Both neutral and cationic complexes are air-stable red solids and have been characterized by elemental analysis, ^{1}H, ^{19}F and ^{31}P-{^{1}H} NMR and infrared spectroscopy (see Experimental Section). The infrared spectra of all compounds show a single medium band around 1580 cm^{-1}, attributed to the C=N stretching vibration of the

iminophosphine ligand coordinated to Pd and shifted to lower frequencies than in the free ligand [11,21,23], together with the respective absorptions of the incoming ligands. Typical absorptions corresponding to the perchlorate anion [24] at 1085 cm^{-1} (ν_3 ClO_4) and 620 cm^{-1} (ν_4 ClO_4) also appear in the IR spectra of cationic complexes (**9**–**12**), whose acetone solutions exhibit conductances in the range 120–135 $\Omega^{-1}\,cm^2\,mol^{-1}$ as expected for 1 : 1 electrolytes [25].

The ^1H and ^{31}P-{^1H} NMR data of the new complexes are collected in the Experimental Section. ^1H spectra of neutral derivatives display the expected resonances for the iminophosphine ligand, which are little perturbed on complexation [11], and the signals attributed to the corresponding monodentate anionic ligand. The ^{31}P NMR spectra of the new neutral compounds consist of singlets with chemical shifts in the range observed for Pd(II) complexes. This shift is clearly influenced by the anionic ligand placed *cis*- to the phosphorus atom and falls in the range 37 and 44 ppm for O- and S-donors, respectively, in agreement with previously reported data for related compounds [18,22].

The presence of the PNO ligand is also confirmed in cationic compounds by ^1H NMR spectroscopy, and the appreciable coupling to the phosphorus atom exhibited by the imine proton is the only remarkable feature. ^{31}P NMR spectra of compounds (**9**–**12**) show two doublet signals in the expected range, due to the PNO and the neutral ligand respectively and with a typical value of $J_{P\text{-}P}$ for *cis*- arrangement in complexes of square-planar geometry.

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