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Homoleptic palladium complexes with phosphine-amide or iminophosphine ligands

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ABSTRACT

The reaction between $Pd(dba)_2$ and phosphino-amide ligands yielded the unexpected Pd(II) homoleptic 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**)], 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 $HClO_4$(aq) to give cationic complexes [Pd(*o*-$Ph_2PC_6H_4CO$-NHR)$_2$][ClO_4]$_2$ (**5**-**8**). These complexes and the analogous with iminophosphine ligands [Pd(*o*-$Ph_2PC_6H_4CH$=N-R)$_2$] [ClO_4]$_2$ [R = ^{i}Pr (**9**), Ph (**10**)] can be alternatively obtained when [$PdCl_2(PhCN)_2$] is treated with $AgClO_4$ 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*-$Ph_2PC_6H_4CH$=N-R)$_2$] [R = ^{i}Pr (**11**), Ph (**12**)]. X-ray structures of (**3**), (**4**), (**5**), (**8**) and (**9**) have been established, allowing an interesting comparative structural discussion.

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 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*-$Ph_2PC_6H_4CH$=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*-$Ph_2PC_6H_4CO$–NHR, containing steric and electronically differentiated substituents, in its reactions against $Pd(dba)_2$ and [$PdCl_2(PhCN)_2$] 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 (^{1}H, ^{31}P) 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*-Ph_2P–C_6H_4–CO–NH–R (R = ^{i}Pr, Ph, 4-MeC_6H_4 or 4-FC_6H_4 and iminophosphine ligands *o*-$Ph_2PC_6H_4CH$=N-R (R = ^{i}Pr 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 CH_2Cl_2/ether. The same results were obtained when the reactions were performed under air or N_2 atmosphere.

[Pd(o-$Ph_2PC_6H_4CO$–N–^{i}Pr)$_2$] (**1**): (72% yield). Mp = 155 °C. *Anal.* Calc. for $C_{44}H_{42}N_2O_2P_2Pd$: 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). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm): 8.26 (m, 2H, P-C_6H_4-CO–), 7.88–7.24 (m, 24H, 20H PPh_2 + 4H P–C_6H_4–CO–), 6.43 (m, 2H, P-C_6H_4-CO–), 3.70 (m, 2H, CH-^{i}Pr), 1.05 (d, J_{HH} = 6.0 Hz, 6H, CH_3-^{i}Pr), 0.65 (d, J_{HH} = 6.0 Hz, 6H, CH_3-^{i}Pr). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 32.5 (s). FAB-MS (positive mode) *m/z*: 799 (M^++1).

[Pd(o-$Ph_2PC_6H_4CO$–N–Ph)$_2$] (**2**) (80% yield). Mp = 177 °C. *Anal.* Calc. for $C_{50}H_{38}N_2O_2P_2Pd$: 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). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm): 8.11 (m, 2H, P–C_6H_4–CO–), 7.92–7.31 (m, 32H, 20H PPh_2 + 10H N-Ph + 2H P–C_6H_4–CO–), 6.58 (m, 2H, P–C_6H_4–CO–). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm) 33.3 (s). FAB-MS (positive mode) *m/z*: 867 (M^+ + 1).

[Pd(o-$Ph_2PC_6H_4CO$–N–C_6H_4–4Me)$_2$] (**3**) (74% yield). Mp = 196 °C. *Anal.* Calc. for $C_{52}H_{42}N_2O_2P_2Pd$: 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). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.97 (m, 2H, P–C_6H_4–CO–), 7.52–7.35 (m, 12H, 8H PPh_2 + 4H N–C_6H_4–CH_3), 7.22 (m, 2H, P–C_6H_4–CO–), 7.09 (m, 2H, P–C_6H_4–CO–), 6.86 (m, 12H, PPh_2), 6.68 (m, 4H, N–C_6H_4–CH_3), 6.57 (m, 2H, P–C_6H_4–CO–), 2.16 (s, 6H, CH_3). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm) 33.2 (s). FAB-MS (positive mode) *m/z*: 894 (M^+).

[Pd(o-$Ph_2PC_6H_4CO$–N–C_6H_4–4F)$_2$] (**4**) (68% yield). Mp = 206 °C. *Anal.* Calc. for $C_{50}H_{36}F_2N_2O_2P_2Pd$: C, 66.5; H, 4.0; N, 3.1. Found: C, 66.4; H, 4.4; N, 3.4.%. FT–IR (nujol, cm^{-1}): ν(CO) 1604(s), 1576 (vs). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.02 (m, 2H, P–C_6H_4–CO–), 7.52–7.35 (m, 12H, 8H PPh_2 + 4H N–C_6H_4–F), 7.22 (m, 2H, P–C_6H_4–CO–), 7.19 (m, 2H, P–C_6H_4–CO–), 6.90 (m, 12H, PPh_2), 6.58 (m, 6H, 4H N–C_6H_4–F + 2H P–C_6H_4–CO–). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm) 33.5 (s). ^{19}F NMR (200 MHz, $CDCl_3$): 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 $HClO_4$ 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 CH_2Cl_2/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 $AgClO_4$ (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 CH_2Cl_2/ether.

[Pd(o-$Ph_2PC_6H_4CO$–NH–^{i}Pr)$_2$][ClO_4]$_2$ (**5**): (73% yield).. Mp = 235 °C. *Anal.* Calc. for $C_{44}H_{44}Cl_2N_2O_{10}P_2Pd$: C, 52.8; H, 4.4; N, 2.8. Found: C, 53.1; H, 4.6; N, 2.7.%. FT–IR (nujol, cm^{-1}): ν(NH) 3287, ν(CO) 1584 (vs), ν(ClO_4) 1093 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.89 (m, 2H, NH), 8.30 (m, 2H, P–C_6H_4–C), 7.92 (m. 2H, P–C_6H_4–C), 7.65–7.51 (m, 10H, 2H P–C_6H_4–C + 8H PPh_2), 7.40–7.28 (m, 12H, PPh_2), 6.90 (m, 2H, P–C_6H_4–C), 3.95 (m, 2H, CH-^{i}Pr), 0.94 (d, J_{HH} = 6.0 Hz, 12H, CH_3-^{i}Pr). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm) 44.5(s). FAB-MS (positive mode) *m/z*: 898 (M^+-ClO_4), 797 (M^+-2ClO_4).

[Pd(o-$Ph_2PC_6H_4CO$–NH–Ph)$_2$][ClO_4]$_2$ (**6**): (68% yield). Mp = 194 °C. *Anal.* Calc. for $C_{50}H_{40}Cl_2N_2O_{10}P_2Pd$: 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(ClO_4) 1097 (vs). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm): 10.49 (br, 2H, NH), 8.41 (m, 2H, P–C_6H_4–C), 7.83 (m, 2H, P–C_6H_4–C), 7.69–7.16 (m, 32H, 20H PPh_2 + 10H N-Ph + 2H P–C_6H_4–CO–), 6.95 (m, 2H, P–C_6H_4–C). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm) 43.2 (s). FAB-MS (positive mode) *m/z*: 867 (M^+-2ClO_4 + 1).

[Pd(o-$Ph_2PC_6H_4CO$–NH–C_6H_4–4Me)$_2$][ClO_4]$_2$ (**7**) (69% yield). Mp = 231 °C. *Anal.* Calc. for $C_{52}H_{44}Cl_2N_2O_{10}P_2Pd$: 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(ClO_4) 1103 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.51 (s, 2H, NH), 8.46 (m, 2H, P–C_6H_4–C), 7.88 (m, 2H, P–C_6H_4–C), 7.55–7.48 (m, 6H, 2H P–C_6H_4–C + 4H N–C_6H_4–CH_3), 7.36–7.28 (m, 20 H PPh_2) 7.05 (m, 4H, N–C_6H_4–Me), 6.94 (m, 2H, P–C_6H_4–C), 2.27 (s, 6H, CH_3). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm) 43.3 (s). FAB-MS (positive mode) *m/z*: 995 (M^+-ClO_4), 894 (M^+-2ClO_4).

[Pd(o-$Ph_2PC_6H_4CO$–NH–C_6H_4–4F)$_2$][ClO_4]$_2$ (**8**) (75% yield). Mp = 191 °C. *Anal.* Calc. for $C_{50}H_{38}Cl_2F_2N_2O_{10}P_2Pd$: 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(ClO_4) 1100 (vs). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm): 11.05 (br, 2H, NH), 8.46 (m, 2H, P–C_6H_4–C), 7.85 (m, 2H, P–C_6H_4–C), 7.75 (m, 2H, P–C_6H_4–C), 7.69–7.62 (m, 16H, 12H PPh_2 + 4H N–C_6H_4–F), 7.40–7.30 (m, 10H, 8H aromatics +2H P–C_6H_4–C), 6.99 (m, 4H N–C_6H_4–F). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm) 41.4 (s). ^{19}F NMR (200 MHz, $CDCl_3$): δ (ppm): −120.3(s). FAB-MS (positive mode) *m/z*: 903 (M^+-2ClO_4).

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

To a solution of $[PdCl_2(PhCN)_2]$ (100 mg, 0,26 mmol) in 10 mL of dichloromethane, the stoichiometric amount of the corresponding iminophosphine (0.52 mmol, CH_2Cl_2 solution) and $AgClO_4$ (108 mg, 0.52 mmol) were added. The precipitation of AgCl started immedi-