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New mono- and bis(pentafluorophenyl)palladium(II) complexes with iminophosphine ligands. Crystal structure of $[Pd(C_6F_5)(SC_6H_5)(o\text{-}Ph_2PC_6H_4{-}CH{=}N^iPr)]$

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Abstract

The synthesis of new mono- and bis(pentafluorophenyl) derivatives of palladium(II) with the mixed-donor bidentate ligands *o*-$Ph_2PC_6H_4{-}CH{=}NR$ (RN–P) has been achieved. The new complexes of general formula $[Pd(C_6F_5)_2(RN{-}P)]$ [R = Me (**1**), Et (**2**), ^{n}Pr (**3**) ^{i}Pr (**4**), ^{t}Bu (**5**), Ph (**6**), NH–Me (**7**)] and $[Pd(C_6F_5)Cl(RN{-}P)]$ [R = Me (**8**), ^{i}Pr (**9**), NH–Me (**10**)] have been, respectively, prepared by reaction between the labile precursors *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ or $[\{Pd(C_6F_5)(tht)(\mu\text{-}Cl)\}_2]$ (tht = tetrahydrothiophene) and the corresponding iminophosphines. Complex (**9**) undergoes metathetical exchange of chloride with anionic monodentate ligands when reacting with alkaline salts, giving the complexes of formula $[Pd(C_6F_5)X(^iPrN{-}P)]$ [X = Br (**11**), I (**12**), CN (**13**), SCN (**14**), SC_6H_5 (**15**), *p*-SC_6H_4Me (**16**), *p*-$SC_6H_4NO_2$ (**17**), OMe (**18**)]. Furthermore, when the chloropentafluorophenyl complex (**9**) was treated with silver trifluoromethanesulfonate in the presence of tertiary phosphines, the cationic derivatives $[Pd(C_6F_5)(L)(^iPrN{-}P)](CF_3SO_3)$ [L = PEt_3 (**19**), PMe_2Ph (**20**), $PMePh_2$ (**21**)] were obtained in good yield. The new complexes were characterized by partial elemental analyses and spectroscopic methods (IR, ^{1}H, ^{19}F and ^{31}P NMR). The molecular structure of complex (**15**) has been determined by a single-crystal diffraction study, showing that the iminophosphine act as chelating ligand with coordination around the palladium atom slight distorted from the square-planar geometry. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chelate complexes; Pentafluorophenyl palladium derivatives; Iminophosphines; Crystal structures

1. Introduction

During the last few years there has been a growing interest in the chemistry of polydentate ligands with both hard and soft donor atoms [1–7]. The metal complexes with N and P donor atoms display a variety of coordination modes well beyond those of P–P or N–N ligands [8]. Furthermore, these ligands show particular behaviour binding soft metal centres such as Pd(II) and Pt(II) that make their complexes good precursors in catalytic processes [9–16]. Thus, it has been found that some complexes with N–P ligands are suitable for palladium-catalyzed allylic alkylation [17], oligomerization of olefins [18,19], homogeneous hydrogenation of double and triple C–C bonds [20] and copolymerization of CO/olefins [21–23]. Among the most widely studied ligands with these characteristics are the pyridylphosphines and the iminophosphines that we present in this work, from which palladium complexes have been profusely reported since 1992 [13–17,24–29]. In this sense, we have described in recent work the syntheses of some organometallic derivatives containing iminophosphine ligands, either with an *ortho*-metalated palladium (II) backbone [30]

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or accompanying a bis(pentafluorophenyl)nickel (II) fragment [31] as a result of directly reacting the precursor *cis*-[Ni(C_6F_5)$_2$(PhCN)$_2$] with the corresponding ligands.

Here we report the preparation of new mono- and bis(pentafluorophenyl) derivatives of palladium(II) with iminophosphine ligands by means of the ligand-exchange reaction between the labile complexes [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] [30] and *cis*-[Pd(C_6F_5)$_2$-(PhCN)$_2$] [33], well known as convenient precursors for the synthesis of pentafluorophenyl compounds [34,35], and iminophosphines. Further reactivity of the complex [Pd (C_6F_5)Cl(^{i}PrN–P)] towards interchange of chloride to give neutral and cationic derivatives has also been investigated.

2. Experimental

2.1. Materials and physical measurements

C, H, N and S analyses were carried out with a Perkin–Elmer 240C microanalyser. 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 (^{1}H) or a Varian Unity 300 (^{1}H, ^{19}F, ^{31}P{^{1}H}) spectrometer using as standards $SiMe_4$, $CFCl_3$ and H_3PO_4, respectively. Conductance measurements were performed with a Crison 525 conductimeter (in acetone, 5×10^{-4} M).

The pentafluorophenyl precursors [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] and *cis*-[Pd(C_6F_5)$_2$(PhCN)$_2$] were prepared by the published methods [32,33]. The iminophosphine ligands were prepared according to reported procedures [11] and all the solvents were dried by standard methods before use.

2.2. Preparation of the complexes [Pd(C_6F_5)$_2$(RNP)] [R = Me (1), Et (2), ^{n}Pr (3) ^{i}Pr (4), ^{t}Bu (5), Ph (6), NH–Me (7)]

The complexes were obtained by treating [Pd(C_6F_5)$_2$(PhCN)$_2$] with the corresponding iminophosphine (molar ratio 1:1) in acetone according to the following general method. To an acetone (5 ml) solution of the precursor [Pd(C_6F_5)$_2$(PhCN)$_2$] (0.07 g, 0.129 mmol) was added the calculated amount of iminophosphine in acetone solution previously prepared. The reaction was stirred at room temperature for 30 min. Upon complete solvent evaporation, the crude product was precipitated with hexane/^{i}PrOH and then filtered off, washed with hexane and air dried. Yellow crystals of the compounds **1**–**7** were obtained in high yield by recrystallization from dichloromethane–hexane.

[Pd(C_6F_5)$_2$(*o*-$Ph_2PC_6H_4$–CH=NMe)] (**1**) was obtained in 80% yield (80 mg). *Anal.* Calc. for $C_{32}F_{10}H_{18}NPPd$: C, 51.7; H, 2.4; N, 1.9. Found: C, 51.9; H, 2.4; N, 1.9%. IR (Nujol, cm^{-1}): 1644 (C = N str). ^{1}H NMR ($CDCl_3$) δ: 3.4 (s, 3H, Me); 7.5 (m, 11H); 7.7 (m, 3H); 8.5 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: −114.2 (d, 2F$_o$, J_{om} = 27.7); −115.3 (m, 2F$_o$); −162.5 (t, 1F$_p$, J_{pm} = 19.8); −164.4 (m, 1F$_p$ + 2F$_m$); −165.6 (m, 2F$_m$). ^{31}P NMR ($CDCl_3$) δ: 26.0 (s).

[Pd(C_6F_5)$_2$(*o*-$Ph_2PC_6H_4$–CH=NEt)] (**2**) was obtained in 80% yield (78 mg). *Anal.* Calc. for $C_{33}F_{10}H_{20}NPPd$: C, 52.3; H, 2.7; N, 1.9. Found: C, 52.0; H, 2.5; N, 1.8%. IR (Nujol, cm^{-1}): 1634 (C=N str). ^{1}H NMR ($CDCl_3$) δ: 1.2 (t, 3H, CH_3); 3.5 (q, 2H, CH_2, J_{HH} = 7.1); 7.4 (m, 11H); 7.8 (m, 3H); 8.5 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: −114.2 (d, 2F$_o$, J_{om} = 27.4); −115.0 (m, 2F$_o$); −162.5 (t, 1F$_p$, J_{om} = 19.8); −164.4 (m, 1F$_p$ + 2F$_m$); −165.5 (m, 2F$_m$). ^{31}P NMR ($CDCl_3$) δ: 25.6 (s).

[Pd(C_6F_5)$_2$(*o*-$Ph_2PC_6H_4$–CH=N^{n}Pr)] (**3**) was obtained in 84% yield (83 mg). *Anal.* Calc. for $C_{34}F_{10}H_{22}NPPd$: C, 52.9; H, 2.9; N, 1.8. Found: C, 52.8; H, 2.8; N, 2.0%. IR (Nujol, cm^{-1}): 1632 (C=N str). ^{1}H NMR ($CDCl_3$) δ: 0.5 (t, 3H, CH_3, J_{HH} = 7.3); 1.8 (m, 2H, CH_2); 2.8 (m, 2H, CH_2N); 7.5 (m, 11H); 7.8 (m, 3H); 8.5 (s, 1H, CH = N). ^{19}F NMR ($CDCl_3$) δ: −114.1 (d, 2F$_o$, J_{om} = 28.2); −115.2 (m, 2F$_o$); −162.4 (t, 1F$_p$, J_{pm} = 19.8); −164.3 (m, 1F$_p$ + 2F$_m$); −165.5 (m, 2F$_m$). ^{31}P NMR ($CDCl_3$) δ: 25.2 (s).

[Pd(C_6F_5)$_2$(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**4**) was obtained in 90% yield (89 mg). *Anal.* Calc. for $C_{34}F_{10}H_{22}NPPd$: C, 52.9; H, 2.9; N, 1.8. Found: C, 52.9; H, 2.9; N, 1.9%. IR (Nujol, cm^{-1}): 1632 (C = N str). ^{1}H NMR ($CDCl_3$) δ: 1.1 (d, 6H, CH_3, J_{HH} = 6.5); 3.8 (sep, 1H, CH); 7.4 (m, 11H); 7.6 (m, 1H); 7.8 (m, 1H); 8.0 (m, 1H); 8.5 (s, 1H, CH = N). ^{19}F NMR ($CDCl_3$) δ: −114.2 (m, 2F$_o$); −115.0 (m, 2F$_o$); −162.6 (t, 1F$_p$, J_{pm} = 20.0); −164.4 (m, 1F$_p$ + 2F$_m$); −165.6 (m, 2F$_m$). ^{31}P NMR ($CDCl_3$) δ: 26.5 (s).

[Pd(C_6F_5)$_2$(*o*-$Ph_2PC_6H_4$–CH=N^{t}Bu)] (**5**) was obtained in 86% yield (87 mg). *Anal.* Calc. for $C_{35}F_{10}H_{24}NPPd$: C, 53.5; H, 3.1; N, 1.8. Found: C, 53.7; H, 3.0; N, 1.8%. IR (Nujol, cm^{-1}): 1632 (C=N str). ^{1}H NMR ($CDCl_3$) δ: 1.0 (s, 9H, CH_3); 7.2 (m, 2H); 7.5 (m, 10H); 7.9 (m, 1H); 8.0 (m, 1H); 8.5 (d, 1H, CH=N, J_{HP} = 3.1). ^{19}F NMR ($CDCl_3$) δ: −113.5 (br, 2F$_o$); −116.1 (br, 2F$_o$); −162.8 (t, 1F$_p$, J_{pm} = 19.8); −164.2 (t, 1F$_p$, J_{pm} = 19.8); −165.6 (m, 4F$_m$). ^{31}P NMR ($CDCl_3$) δ: 28.0 (s).

[Pd(C_6F_5)$_2$(*o*-$Ph_2PC_6H_4$–CH=NPh)] (**6**) was obtained in 90% yield (93 mg). *Anal.* Calc. for $C_{37}F_{10}H_{20}NPPd$: C, 55.1; H, 2.5; N, 1.7. Found: C, 54.9; H, 2.4; N, 1.9%. IR (Nujol, cm^{-1}): 1602 (C=N str). ^{1}H NMR ($CDCl_3$) δ: 7.4 (m, 19H); 8.6 (d, 1H, CH=N, J_{HP} = 3.2). ^{19}F NMR ($CDCl_3$) δ: −114.2 (d, 2F$_o$, J_{om} = 30.0); −115.0 (m, 2F$_o$); −162.7 (t, 1F$_p$, J_{pm} = 19.8); −164.4 (m, 1F$_p$ + 2F$_m$); −165.6 (m, 2F$_m$). ^{31}P NMR ($CDCl_3$) δ: 23.6 (s).

[Pd(C_6F_5)$_2$(*o*-$Ph_2PC_6H_4$–CH=NNHMe)] (**7**) was obtained in 89% yield (87 mg). *Anal.* Calc. for $C_{32}F_{10}H_{19}N_2PPd$: C, 50.6; H, 2.5; N, 3.7. Found: C, 50.8; H, 2.4; N, 1.9%. IR (Nujol, cm^{-1}): 3420 (N–H), 1632 (C=N str). ^1H NMR ($CDCl_3$) δ: 3.0 (d, 3H, Me, $J_{HH} = 3.9$); 7.5 (m, 10H); 7.7 (m, 4H); 8.2 (d, 1H, CH=N, $J_{HP} = 5.0$). ^{19}F NMR ($CDCl_3$) δ: –114.2 (d, $2F_o$, $J_{om} = 30.5$); –114.5 (m, $2F_o$); –162.4 (t, $1F_p$, $J_{pm} = 19.8$); –164.4 (t, $1F_p$, $J_{pm} = 19.8$); –164.5 (m, $2F_m$); –165.6 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 30.4 (s).

*2.3. Preparation of the complexes [Pd(C_6F_5)Cl(RN–P)] [R = Me (**8**), ^{i}Pr (**9**), NH–Me (**10**)]*

The complexes were obtained by treating [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] with the corresponding iminophosphine (molar ratio 1:2) in dichloromethane according to the following general method. To a dichloromethane (5 ml) solution of the precursor [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] (0.068 g, 0.086 mmol) was added the calculated amount of iminophosphine in dichloromethane solution previously prepared. The reaction was stirred at room temperature for 2 h. The white solution was concentrated under reduced pressure to half volume and the addition of hexane caused precipitation of the new complexes, which were filtered off and air-dried. White crystals of the compounds were obtained in high yield by recrystallization from dichloromethane–hexane.

[Pd(C_6F_5)Cl(*o*-$Ph_2PC_6H_4$–CH=NMe)] (**8**) was obtained in 90% yield (94 mg). *Anal.* Calc. for $C_{26}ClF_5H_{18}NPPd$: C, 60.0; H, 2.9; N, 2.3. Found: C, 59.9; H, 2.9; N, 2.3%. IR (Nujol, cm^{-1}): 1634 (C=N str). ^1H NMR ($CDCl_3$) δ: 3.9 (s, 3H, Me); 7.4 (m, 14H, aromatic); 8.0 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: –116.6 (dd, $2F_o$, $J_{om} = 21.4$); –161.8 (t, $1F_{pm}$, $J = 19.2$); –163.8 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 31.3 (t, $J_{PF} = 11.9$).

[Pd(C_6F_5)Cl(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**9**) was obtained in 85% yield (93 mg). *Anal.* Calc. for $C_{28}ClF_5H_{22}NPPd$: C, 52.5; H, 3.4; N, 2.2. Found: C, 52.7; H, 3.5; N, 2.2%. IR (Nujol, cm^{-1}): 1632 (C=N str). ^1H NMR ($CDCl_3$) δ: 1.2 (d, 6H, CH_3, $J_{HH} = 6.5$); 5.3 (sep, 1H, CH); 7.4 (m, 14H, aromatic); 8.0 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: –116.4 (d, $2F_o$, $J_{om} = 24.5$); –162.0 (t, $1F_p$, $J_{pm} = 19.2$); –163.8 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 30.6 (t, $J_{PF} = 11.0$).

[Pd(C_6F_5)Cl(*o*-$Ph_2PC_6H_4$–CH=NNHMe)] (**10**) was obtained in 85% yield (91 mg). *Anal.* Calc. for $C_{26}ClF_5H_{19}N_2PPd$: C, 49.8; H, 3.0; N, 4.5. Found: C, 49.6; H, 3.1; N, 4.4%. IR (Nujol, cm^{-1}):1634 (C=N str). ^1H NMR ($CDCl_3$) δ: 2.9 (s, 3H, Me); 7.3 (m, 14H, aromatic); 8.5 (d, 1H, CH=N, $J_{PH} = 4.0$). ^{19}F NMR ($CDCl_3$) δ: –116.8 (d, $2F_o$, $J_{om} = 21.4$); –161.6 (t, $1F_p$, $J_{pm} = 20.0$); –163.6 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 30.8 (t, $J_{PF} = 11.4$).

*2.4. Preparation of the complexes [Pd(C_6F_5)X(^{i}PrN–P)] [X = Br (**11**), I (**12**), CN (**13**), SCN (**14**), SC_6H_5 (**15**), p-SC_6H_4Me (**16**), p-$SC_6H_4NO_2$ (**17**), OMe (**18**)]*

Compounds **11**–**14** were obtained by reacting stoichiometric amounts (1:1) of complex **9** and the corresponding potassium salt KX in 10 ml of acetone. After 2 h stirring at boiling temperature the KCl formed was removed by filtration and the resulting solution concentrated under reduced pressure to half volume. The addition of hexane caused precipitation of the new complexes, which were filtered off and air-dried.

[Pd(C_6F_5)Br(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**11**) was obtained in 70% yield. *Anal.* Calc. for $C_{28}BrF_5H_{22}NPPd$: C, 49.1; H, 3.2; N, 2.0. Found: C, 49.2; H, 3.1; N, 2.2%. IR (cm^{-1}): 1632 (C=N str). ^1H NMR ($CDCl_3$): 1.2 (d, 6H, CH_3, $J_{HH} = 6.5$); 5.4 (sep, 1H, CH); 7.4 (m, 14H, aromatic); 8.0 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$): –115.7 (d, $2F_o$, $J_{om} = 24.5$); –162.1 (t, $1F_p$, $J_{pm} = 19.2$); –163.9 (m, $2F_m$). ^{31}P NMR ($CDCl_3$): 29.6 (br).

[Pd(C_6F_5)I(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**12**) was obtained in 68% yield. *Anal.* Calc. for $C_{28}IF_5H_{22}NPPd$: C, 45.9; H, 3.0; N, 1.9. Found: C, 45.7; H, 3.1; N, 1.7%. IR (cm^{-1}): 1628 (C=N str). ^1H NMR ($CDCl_3$): 1.2 (d, 6H, CH_3, $J_{HH} = 6.5$); 5.4 (sep, 1H, CH); 7.4 (m, 14H, aromatic); 8.0 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$): –113.8 (d, $2F_o$, $J_{om} = 23.1$); –162.3 (t, $1F_p$, $J_{pm} = 20.3$); –164.0 (m, $2F_m$). ^{31}P NMR ($CDCl_3$): 25.8 (br).

[Pd(C_6F_5)(CN)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**13**) was obtained in 75% yield. *Anal.* Calc. for $C_{29}F_5H_{22}N_2PPd$: C, 55.2; H, 3.5; N, 4.4. Found: C, 55.0; H, 3.2; N, 4.3%. IR (cm^{-1}): 2350 (CN str), 1634 (C=N str). ^1H NMR ($CDCl_3$): 1.3 (d, 6H, CH_3, $J_{HH} = 6.5$); 5.8 (sep, 1H, CH); 7.4 (m, 14H, aromatic); 8.0 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$): –115.4 (d, $2F_o$, $J_{om} = 22.0$); –161.8 (t, $1F_p$, $J_{pm} = 20.3$); –163.8 (m, $2F_m$). ^{31}P NMR ($CDCl_3$): 25.8 (br).

[Pd(C_6F_5)(SCN)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**14**) was obtained in 90% yield. *Anal.* Calc. for $C_{29}F_5H_{22}N_2PSPd$: C, 52.5; H, 3.3; N, 4.2; S, 4.8. Found: C, 52.3; H, 3.2; N, 4.36; S, 4.8%. IR (cm^{-1}): 2078 (CN str), 1640 (C=N str). ^1H NMR ($CDCl_3$): 1.3 (d, 6H, CH_3, $J_{HH} = 6.5$); 4.7 (sep, 1H, CH); 7.4 (m, 14H, aromatic); 8.1 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$): –117.4 (d, $2F_o$, $J_{om} = 24.0$); –160.7 (t, $1F_p$, $J_{pm} = 19.5$); –163.2 (m, $2F_m$). ^{31}P NMR ($CDCl_3$): 31.8 (br).

To obtain complexes **15**–**17** the corresponding thiol (0.062 mmol) was first reacted with a 10 ml solution of MeONa/MeOH for 15 min. Complex **9** (0.062 mmol) was then added and the mixture was stirred at room temperature for 1 h. Concentration of the resulting solution under reduced pressure to half volume precipitated the yellow solids that were filtered off, washed with diethyl ether and air-dried.

[Pd(C_6F_5)(SC_6H_5)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**15**) was obtained in 70% yield (31 mg). *Anal.* Calc. for $C_{34}F_5H_{27}NPSPd$: C, 57.2; H, 3.8; N, 1.9; S, 4.5. Found: C, 57.4; H, 3.6; N, 1.9; 4.7%. IR (Nujol, cm^{-1}): 1632 (C=N str). ^1H NMR ($CDCl_3$) δ: 1.1 (d, 6H, CH_3, $J_{HH} = 6.5$); 5.1 (m, 1H, CH); 7.1 (m, 19H, aromatic); 8.0 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: −115.3 (d, $2F_o$, $J_{om} = 30.7$); −163.6 (t, $1F_p$, $J_{pm} = 20.3$); −164.4 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 24.3 (s).

[Pd(C_6F_5)(SC_6H_4Me)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**16**) was obtained in 75% yield (34 mg). *Anal.* Calc. for $C_{35}F_5H_{29}NPSPd$: C, 57.8; H, 4.0; N, 1.9; S, 4.4. Found: C, 58.0; H, 3.7; N, 1.7; 4.2%. IR (Nujol, cm^{-1}): 1628 (C=N str). ^1H NMR ($CDCl_3$) δ: 1.2 (d, 6H, CH_3, $J_{HH} = 6.5$); 2.1 (s, 3H, Me); 5.1 (sep, 1H, CH); 7.1 (m, 18H, aromatic); 8.0 (s, 1H, CH = N). ^{19}F NMR ($CDCl_3$) δ: −115.5 (d, $2F_o$, $J_{om} = 25.0$); −164.2 (t, $1F_p$, $J_{pm} = 20.3$); −164.7 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 24.1 (s).

[Pd(C_6F_5)($SC_6H_4NO_2$)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**17**) was obtained in 70% yield (33 mg). *Anal.* Calc. for $C_{34}F_5H_{26}N_2O_2PSPd$: C, 53.8; H, 3.4; N, 3.7; S, 4.2. Found: C, 54.2; H, 3.2; N, 3.9; 4.2%. IR (Nujol, cm^{-1}): 1634 (C=N str), 1568 (NO). ^1H NMR ($CDCl_3$) δ: 1.0 (d, 6H, CH_3, $J_{HH} = 6.5$); 5.0 (sep, 1H, CH); 7.5 (m, 18H, aromatic); 8.1 (d, 1H, CH=N, $J_{PH} = 8.6$). ^{19}F NMR ($CDCl_3$) δ: −115.2 (d, $2F_o$, $J_{om} = 28.8$); −161.4 (t, $1F_p$, $J_{pm} = 22.3$); −163.7 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 25.8 (s).

[Pd(C_6F_5)(OCH_3)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**18**) was obtained in 80% yield (31 mg) by treating a 5 ml solution of complex **9** (0.062 mmol) in methanol with a KOH/MeOH solution (10 ml). The mixture was then stirred at room temperature for 1 h. Addition of hexane caused the precipitation of a white solid that was filtered off, washed with diethyl ether and air-dried. *Anal.* Calc. for $C_{29}F_5H_{25}NOPPd$: C, 54.8; H, 3.9; N, 2.2. Found: C, 54.5; H, 3.8; N, 2.4%. IR (Nujol, cm^{-1}): 1632 (C=N str). ^1H NMR ($CDCl_3$) δ: 1.2 (d, 6H, CH_3, $J_{HH} = 6.5$); 3.4 (s, 3H, OMe); 5.4 (sep, 1H, CH); 7.4 (m, 14H, aromatic); 8.0 (s, 1H, CH = N). ^{19}F NMR ($CDCl_3$) δ: −115.2 (d, $2F_o$, $J_{om} = 21.5$); −161.4 (t, $1F_p$, $J_{pm} = 19.2$); −163.7 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 30.3 (s).

2.5. Preparation of the complexes [Pd(C_6F_5)(L)(^{i}PrN–P)](CF_3SO_3) [L = PEt_3 (**19**), PMe_2Ph (**20**), $PMePh_2$ (**21**)]

The complexes were obtained according to the following general method. To a dichloromethane (5 ml) solution of complex **9** (0.065 mmol) was added the stoichiometric amount (1:1) of silver triflate and the corresponding phosphine. The reaction was stirred at room temperature for 1 h and then filtered to remove the AgCl formed. The resulting solution was concentrated under reduced pressure to half volume and the addition of hexane caused precipitation of the new complexes, which were filtered off and air-dried. White crystals of the compounds were obtained by recrystallization from dichloromethane–hexane.

[Pd(C_6F_5)(PEt_3)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)][TfO] (**19**) was obtained in 75% yield (47 mg). *Anal.* Calc. for $C_{35}F_8H_{37}NO_3P_2SPd$: C, 48.2; H, 4.2; N, 1.6; S, 3.7. Found: C, 48.0; H, 4.5; N, 1.7; 4.0%. IR (Nujol, cm^{-1}): 1634 (C=N str), 760 (PEt_3). $\Lambda_M = 123\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR ($CDCl_3$) δ: 1.0 (m, 6H, PCH_2); 1.2 (d, 6H, ^{i}Pr, $J_{HH} = 6.4$); 1.6 (m, 9H, CH_3); 4.0 (m, 1H, ^{i}Pr); 7.8 (m, 14H, aromatic); 8.6 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: −114.7 (m, $2F_o$); −158.5 (t, $1F_p$, $J_{pm} = 19.2$); −160.9 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 16.4 (d, P_A, PEt_3); 24.3 (d, P_B, $J_{AB} = 405.2$).

[Pd(C_6F_5)($PMePh_2$)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)][TfO] (**20**) was obtained in 78% yield (48 mg). *Anal.* Calc. for $C_{42}F_8H_{35}NO_3P_2SPd$: C, 52.9; H, 3.7; N, 1.5; S, 3.4. Found: C, 52.8; H, 3.7; N, 1.3; 3.4%. IR (Nujol, cm^{-1}): 1634 (C=N str), 892 ($PMePh_2$). $\Lambda_M = 135\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR ($CDCl_3$) δ: 0.9 (d, 6H, ^{i}Pr, $J_{HH} = 6.4$); 1.7 (d, 6H, PMe_2, $J_{PH} = 9.9$); 3.8 (sep, 1H, ^{i}Pr); 7.6 (m, 19H, aromatic); 8.5 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: −114.6 (d, $2F_o$, $J_{om} = 21.4$); −159.8 (t, $1F_p$, $J_{pm} = 19.2$); −161.3 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 7.3 (d, P_A, PMe_2Ph); 25.6 (d, P_B, $J_{AB} = 419.4$).

[Pd(C_6F_5)(PMe_2Ph)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)][TfO] (**21**) was obtained in 82% yield (47 mg). *Anal.* Calc. for $C_{37}F_8H_{33}NO_3P_2SPd$: C, 49.8; H, 3.7; N, 1.6; S, 3.6. Found: C, 49.9; H, 3.9; N, 1.6; 3.7%. IR (Nujol, cm^{-1}): 1632 (C=N str), 914 (PMe_2Ph). $\Lambda_M = 115\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR ($CDCl_3$) δ: 0.9 (d, 6H, ^{i}Pr, $J_{HH} = 6.5$); 2.2 (d, 3H, PMe, $J_{PH} = 9.0$); 3.8 (sep, 1H, ^{i}Pr); 7.4 (m, 24H, aromatic); 8.6 (s, 1H, CH=N). ^{19}F NMR ($CDCl_3$) δ: −115.2 (m, $2F_o$); −158.8 (t, $1F_p$, $J_{pm} = 23.0$); −160.8 (m, $2F_m$). ^{31}P NMR ($CDCl_3$) δ: 5.8 (d, P_A, $PMePh_2$); 25.0 (d, P_B, $J_{AB} = 421.4$).

2.6. Crystal structure determination of [Pd(C_6F_5)(SC_6H_5)(*o*-$Ph_2PC_6H_4$–CH=N^{i}Pr)] (**15**)

X-ray experiment was carried out on an Enraf Nonius CAD4 diffractometer using a graphite monochromated Mo Kα radiation. The crystallographic data are shown in Table 1. An empirical ψ-scan mode absorption correction was made.

Data for **15** were collected using a single crystal of approximate dimensions $0.4 \times 0.4 \times 0.2$ mm^3. The range of *hkl* was $0 \le h \le 16$, $0 \le k \le 13$, $-17 \le l \le 16$ corresponding to $2\Theta_{max} = 44°$. The structure was solved by direct methods SHELXS-97 [36] and refined on F^2 by full-matrix least-squares techniques [36] on F^2 using anisotropic thermal parameters for non-H atoms.

3. Results and discussion

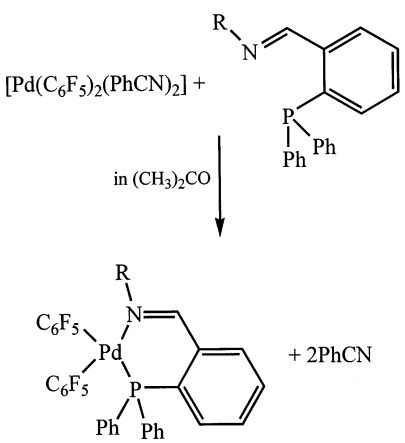
3.1. bis(Pentafluorophenyl) complexes

In acetone, *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ reacts with iminophosphines (molar ratio 1:1) under mild conditions to give the corresponding neutral square-planar complexes $[Pd(C_6F_5)_2(RN–P)]$ shown in Scheme 1.

Table 1
Crystal data and structure refinement for $[Pd(C_6F_5)(S\ C_6H_5)(^iPrNP)]$

Empirical formula	$C_{34}H_{27}F_5NPPdS$
Formula weight	714.00
Temperature (K)	293(2) K
Wavelength (Å)	0.7107 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	15.961(3)
b (Å)	12.594(3)
c (Å)	16.171(4)
α (°)	90
β (°)	103.45(2)
γ (°)	90
V (Å^3)	3161.4(12)
Z	4
D_{calc} (Mg m^{-3})	1.500
Absorption coefficient (mm^{-1})	0.757
Crystal size (mm)	$0.40 \times 0.40 \times 0.20$
θ Range for data collection (°)	2.07 to 21.97
Reflections collected	4026
Independent reflections	3866 [$R_{int} = 0.0348$]
Number of reflections with $I > 2s(I)$	2761
Max/min transmission	1.00, 0.89
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3866/0/388
Goodness-of-fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	R_1 [a] = 0.0432, wR_2 [b] = 0.0824
R indices (all data)	$R_1 = 0.0752$, $wR_2 = 0.0942$

[a] $R_1 = ||F_o| - |F_c||/|F_o|$.
[b] $wR_2 = [[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]]^{0.5}$.



R = Me (**1**), Et (**2**), n-Pr (**3**), i-Pr (**4**), t-Bu (**5**), Ph (**6**), MeNH (**7**)

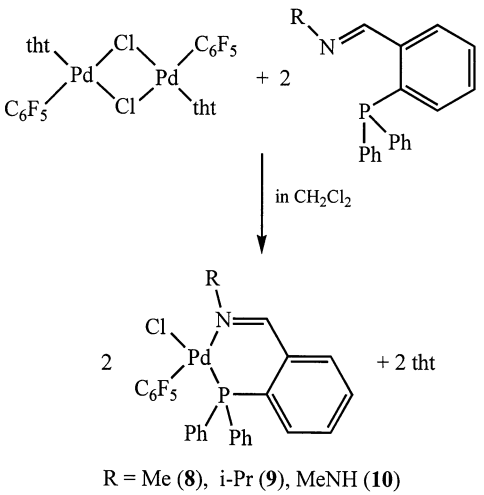
Scheme 1.

The new bis(pentafluorophenyl)-palladium derivatives **1**–**7** with iminophosphines are air-stable, white solids. The IR spectra of these compounds show the characteristic absorptions of the C_6F_5 group [37] at ca. 1630 m, 1490 vs, 1050 s and 950 vs cm^{-1}. The presence of two bands in the 800–780 cm^{-1} region for the so called 'X-sensitive' mode of the C_6F_5 ligand is characteristic of the *cis*-$M(C_6F_5)_2$ fragment [38], which obviously appears in compounds containing bidentate chelate ligands. The most relevant IR bands attributed to the ligands in all the iminophosphine complexes appear in the 1650–1600 cm^{-1} region. Thus, the IR spectra of the complexes show a single strong band in this region assigned to the C=N stretching vibration, shifted to lower frequencies than in the free ligands.

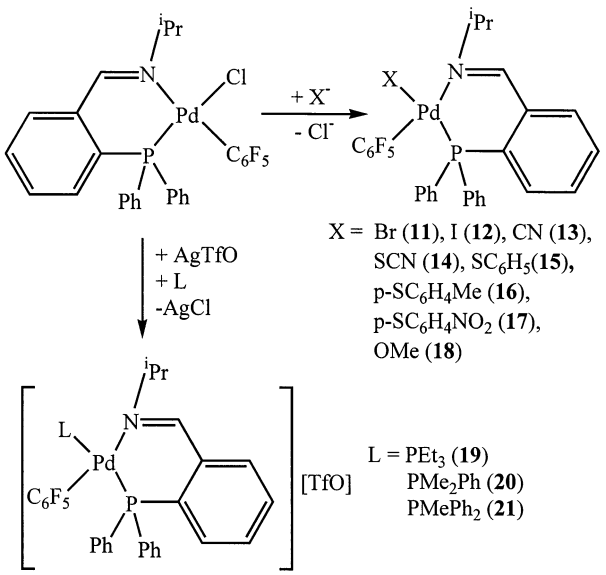
The ^{1}H NMR spectra show the corresponding aliphatic and aromatic signals, with a typical iminic singlet or doublet resonance in the 8–8.5 ppm region depending on the strength of the coupling to the phosphorus atom [11]. The ^{31}P NMR spectra of the iminophosphine compounds consist of singlets with chemical shifts in the range observed for Pd(II) complexes and the ^{19}F NMR spectra show the expected pattern of three duplicated resonance signals, consistent with the presence of two nonequivalent C_6F_5 groups, one *trans* to N and one *trans* to P. Thus, there are two different *ortho*-F resonances: a lower field doublet attributed to the C_6F_5 ring *trans* to N and a higher field multiplet caused by additional coupling with the *trans* P atom. The ^{19}F NMR spectrum of complex **5** at room temperature, as observed previously for the nickel analogues [31], shows broad resonances in the *ortho*- and *meta*-F regions, suggesting that the bulky *t*-butyl group slows down the 'free' rotation of the C_6F_5 rings. The spectrum recorded at −20°C revealed that, at this temperature, the rotation is sufficiently sluggish to make the *ortho*-F atoms distinguishable by their different chemical shifts, and three 2:1:1 doublet resonances are observed. A similar behaviour was found for the *meta*- and *para*-F resonances, resolved as four signals with relative intensities of 1:2:2:1 at −20°C.

3.2. Mono(pentafluorophenyl) complexes

The addition of the corresponding iminophosphine to a solution of the chloro-bridged precursor $[\{Pd(C_6F_5)(tht)\}_2(\mu\text{-}Cl)_2]$ (molar ratio 1:2), in dichloromethane, leads to the formation of the organometallic complexes presented in Scheme 2. The chloride derivatives **8**–**10** are white solids the IR spectra of which show the characteristic absorptions of the pentafluorophenyl group [38], together with a medium band assigned to the Pd–Cl (at 296 cm^{-1}) vibration



Scheme 2.



Scheme 3.

and a strong absorption around 1630 cm^{-1} corresponding to the iminophosphine ligands.

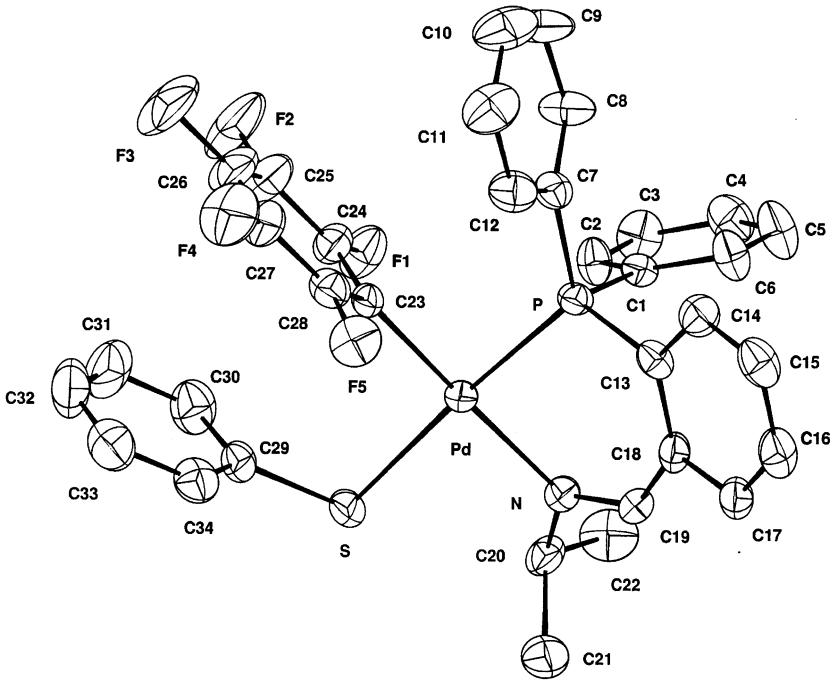
The chloro–pentafluorophenyl palladium(II) complexes have shown to be convenient precursors for the synthesis of new monopentafluorophenyl derivatives by means of chloride metathesis reactions with other monodentate anionic ligands. Thus, when $[Pd(C_6F_5)Cl(o\text{-}Ph_2PC_6H_4–CH=N^iPr)]$ (**9**) was made react with several alkaline salts in acetone, the corresponding products (**11**–**18**) of chloride metathesis were obtained (Scheme 3). The synthesis of the new cationic derivatives (**19**–**21**) is also achieved when complex **9** reacts in acetone with silver trifluoromethane sulfonate, in the presence of neutral ligands (tertiary phosphines). The precipitation of silver chloride allows the coordination of the neutral ligands and the obtention of the new mixed-ligand complexes.

The IR spectra of the neutral (**11**–**18**) and cationic (**19**–**21**) monopentafluorophenyl complexes show as most remarkable feature the expected disappearance of the Pd–Cl stretching absorption and the new bands corresponding to the incoming ligands, collected in Section 2. The presence of iminophosphine ligands in the new complexes is also confirmed by ^1H NMR spectroscopy, as the three signals in ^{19}F-spectra with relative intensity of 2:1:2 revealed the presence of a C_6F_5 ring bound to palladium. Again a hindered rotation situation is observed for complex **19**, and three broad resonances appear in the ^{19}F NMR spectrum at room temperature. The spectrum recorded at $-40°C$ shows the expected pattern of two doublet signals corresponding to two nonequivalent *ortho*-F atom, a triplet for *para*-F and two still broad resonances for *meta*-F.

A single resonance at approximately 31 ppm was observed in the $^{31}P\{^1H\}$ NMR spectra of compounds (**8**–**10**), where a weak F_o–P coupling (ca. 11 Hz) was detected. This small value suggests a *cis*-geometry of the C_6F_5 ring and the P atom around the palladium centre, as does the fact that phosphorus resonance is variably shifted in compounds (**11**–**18**) depending on the different anionic ligand placed *trans*- to the iminophosphinic–P. This extent is confirmed from the X-ray crystal structure determination of complex **15** and in accordance with previously reported data for related compounds [39]. The relative geometrical disposition of N–P ligand and C_6F_5 ring coordinating palladium is also kept in the cationic complexes (**19**–**21**), as revealed in their ^{31}P MNR data. Thus, two doublet signals characteristic of an AX system are observed, with coupling constant values up to 400 Hz indicating a *trans*-situation of P-atoms of iminophosphine and tertiary phosphine, as shown in Scheme 4.

3.3. X-ray structure of $[Pd(C_6F_5)(SC_6H_5)(o\text{-}Ph_2PC_6H_4–CH=N^iPr)]$ (15)

Selected bond distances and angles of **15** are presented in Table 2. The coordination around palladium is approximately square planar. The main distortion is the NPdP bite angle of 86.1(2)° similar to other palladium complexes with iminophosphines [30]. The Pd–S distance is similar to that found in others thiolate complexes *trans* to a phosphorus atom [40]. The palladium-bound C_6F_5 group is nearly orthogonal to the palladium square plane; the angle between the plane defined by PdPNS and the plane of the Pd-bound C_6F_5 group is 87.3(2)°. The chelate six-membered ring of the iminophosphine is not coplanar with the N–Pd–P coordination plane: the imino carbon C19 and the *ortho*



Scheme 4.

Table 2
Selected bond lenghts (Å) and bond angles (°) for complex **15**

Bond lengths			
Pd–C(23)	2.002(6)	Pd–N	2.103(5)
Pd–P	2.245(2)	Pd–S	2.357(2)
Bond angles			
C(23)–Pd–N	177.5(2)	C(23)–Pd–S	91.0(2)
N–Pd–P	86.1(2)	P–Pd–S	175.8(1)
N–Pd–S	90.8(2)	C(29)–S–Pd	110.8(2)
C(23)–Pd–P	92.2(2)		

disubstituted phenyl group of the N–P ligand lie on the same side out of the NPdP plane (with a dihedral angle of 129.6(2)° between the N–Pd–P plane and the phenyl C13–C18 mean plane).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151215. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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