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New pentafluorophenyl complexes with phosphine-amide ligands

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Abstract

A series of nickel(II) and palladium(II) complexes containing one or two pentafluorophenyl ligands and the phosphino-amides *o*-$Ph_2PC_6H_4CONHR$ [R = ^{i}Pr (**a**), Ph (**b**)] displaying different coordination modes have been synthesised. The chelating ability of these ligands and the influence of both coligands and the metal centre in their potential hemilabile behaviour have been explored. The crystal structure of (**b**) has been determined and reveals N–H···O intermolecular hydrogen bonding. Bis-pentafluorophenyl derivatives [$M(C_6F_5)_2$(*o*-Ph_2**P**C_6H_4C**O**-NHR)] [M = Ni; R = ^{i}Pr (**1a**); R = Ph (**1b**); M = Pd; R = ^{i}Pr (**2a**); R = Ph (**2b**)] in which (**a**) and (**b**) act as rigid P, O-chelating ligands were readily prepared from the labile precursors *cis*-[$M(C_6F_5)_2(PhCN)_2$]. X-ray structures of (**1a**), (**1b**) and (**2a**) have been established, allowing an interesting comparative structural discussion. Dinuclear [{$Pd(C_6F_5)$(tht)(μ-Cl)}$_2$] reacted with (**a**) and (**b**) yielding the monopentafluorophenyl complexes [$Pd(C_6F_5)Cl${**P**$Ph_2(C_6H_4$–C**O**NH–R)}] (R = ^{i}Pr (**3a**), Ph (**3b**)) that showed a P, O-chelating behaviour of the ligands, confirmed by the crystal structure determination of (**3a**). New cationic palladium(II) complexes in which (**a**) and (**b**) behave as P-monodentate ligands have been synthesised by reacting them with [{$Pd(C_6F_5)$(tht)(μ-Cl)}$_2$], stoichiometric $Ag(O_3SCF_3)$ and external chelating reagents such as *cod* [$Pd(C_6F_5)$(cod){**P**$Ph_2(C_6H_4$-CONH-R)}](O_3SCF_3)(R = ^{i}Pr (**4a**), Ph (**4b**)) and *2,2′-bipy* [$Pd(C_6F_5)$(bipy){**P**$Ph_2(C_6H_4$-CONH-R)}](O_3SCF_3) (R = ^{i}Pr (**5a**), Ph (**5b**)). When chloride abstraction in [{$Pd(C_6F_5)$(tht)(μ-Cl)}$_2$] is promoted by means of a dithioanionic salt as dimethyl dithiophospate in the presence of (**a**) or (**b**), the corresponding neutral complexes [$Pd(C_6F_5)${S(S)P(OMe)$_2$}{**P**$Ph_2(C_6H_4$-CONH-R)}] (R = ^{i}Pr (**6a**), Ph (**6b**)) were obtained.

Keywords: Phosphino-amide ligands; Coordination modes; Pentafluorophenyl ligands; Nickel; Palladium

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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 the last few years as a result of their versatile coordination behaviour [6,7] and their 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 their complexes in chemical sensings [9–11] and catalytic processes. It is in this last field that phosphine-amide ligands have received growing attention: the asymmetric 1,4-addition reaction of arylboronic acids with cycloalkenones is catalysed by an amidophosphine rhodium(I) complex [12], new chiral amidophosphine ligands take part in palladium-catalysed asymmetric allylic alkylation processes [13–15], amide derived phosphines possessing various *N*,*N*-dialkyl aromatic amide scaffolds have shown to be highly effective in Suzuki cross-coupling reactions [16,17], and 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 [18].

In this sense, both ligands design and studies about the conditions in which the different bonding patterns may take

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place are of considerable importance to understand and then to make use of the properties exhibited by ligands and complexes [5]. Thus, the influence of coligands in the hemilability of a given ligand, or the variations in its coordination behaviour towards different metal centres would contribute to a deeper knowledge of the ligand itself and its usefulness. We have recently reported the coordination properties of the mixed-donor bidentate ligands **a** and **b** in their first described palladium(II) complexes [19]. Ligands were made to react to several cyclometallated precursors $[Pd(C^\wedge N)(\mu\text{-}X)]_2$ [$C^\wedge N$ = phenylazophenyl, 2-pyridininphenyl, 7,8-benzoquinolyl, and 2-(2-oxazolinyl)phenyl] whose bridging units (X = Cl, AcO or OH) exhibited different acid–base behaviour, and a marked influence of the precursor employed in the final adopted bonding pattern was observed. Thus, a hemilabile behaviour of ligand **b** was just detected against μ-AcO precursors, while amide deprotonation is only achieved when μ-OH starting materials were used. On the other hand, we have contributed to the large body of work concerning pentafluorophenyl derivatives of group 10 metals [20] with the synthesis of the precursors *cis*-$[M(C_6F_5)_2(PhCN)_2]$ M = Ni, Pd [21], that have been used in the preparation and characterisation of a wide variety of complexes possessing the C_6F_5- ligand [22,23]. In this paper, we present the preparation of new mono- and bis-pentafluorophenyl complexes with phosphine-amide ligands **a** and **b**, and our structural and solution investigations on their coordination properties.

2. Experimental

2.1. General remarks

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, ^{13}C, ^{31}P) were recorded on Bruker Avance 200, 300 and 400 spectrometers. Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operated in negative 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.

The pentafluorophenyl precursors $[\{Pd(C_6F_5)(tht)(\mu\text{-}Cl)\}_2]$ and *cis*-$[M(C_6F_5)_2(PhCN)_2]$ (M = Ni, Pd) were prepared as described in the literature [20a,21]. The diphenylphosphinobenzamides *o*-$Ph_2PC_6H_4CONHR$ (R = ^{i}Pr **a**, Ph **b**) were prepared adapting a reported procedure [13].

2.2. Preparation of complexes *[M(C₆F₅)₂(o-Ph₂PC₆H₄CO-NHR)] [M = Ni; R = ⁱPr (**1a**); R = Ph (**1b**); M = Pd; R = ⁱPr (**2a**); R = Ph (**2b**)]*

The new complexes were obtained by treating *cis*-$[M(C_6F_5)_2(PhCN)_2]$ (M = Ni, Pd) with previously prepared 2-diphenylphosphine-*N*-isopropylbenzamide (**a** compounds) or 2-diphenylphosphine-*N*-phenylbenzamide (**b** compounds) in molar ratio 1:1, using CH_2Cl_2 as solvent and according to the following general method. To a dichloromethane solution (10 mL) of the corresponding precursor $[M(C_6F_{52}(PhCN)_2]$ (60 mg) was added solid 2-diphenylphoshinebenzamide. The resulting solution was stirred for 60 min, filtered through a short Celite column and then concentrated to half the volume under reduced pressure. Addition of hexane caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from dicholoromethane–hexane.

$[Ni(C_6F_5)_2(o\text{-}Ph_2PC_6H_4CO\text{-}NH^iPr)]$ (**1a**): Yield 0.089 g (72%). *Anal.* Calc. for $C_{34}F_{10}H_{22}NOPNi$: C, 55.2; H, 3.0; N, 1.9. Found: C, 55.0; H, 3.1; N, 1.8%. FT-IR (nujol mull cm^{-1}): ν(NH) 3422(s); ν(CO) 1600(vs). ^1H NMR (200 MHz, $CDCl_3$): δ(ppm):0.87 (m, 6H, ^{i}Pr), 3.63 (m, 1H, ^{i}Pr), 6.11 (s, 1H, aromatic), 7.32–7.61 (m, 14H, aromatic +NH). ^{31}P NMR (200 MHz, $CDCl_3$): δ(ppm): 18.3 (s). ^{19}F NMR (200 MHz, $CDCl_3$): δ(ppm): −115.1 (d, $2F_o$,J_{om} = 20.0), −118.9 (m, $2F_o$, J_{om} = 20.0), −161.8 (t, $1F_p$, J_{pm} = 19.8), −162.9 (t, $1F_p$, J_{pm} = 19.8), −164.3 (m, $2F_m$), −165.1 (m, $2F_m$). FAB-MS (negative mode) *m*/*z*: 572 ($M-C_6F_5$), 405 ($M-2C_6F_5$).

$[Ni(C_6F_5))_2o\text{-}Ph_2PC_6H_4CO\text{-}NHPh)]$ (**1b**): Yield 0.095 g (74%). *Anal.* Calc. for $C_{37}F_{10}H_{20}NOPNi$: C, 57.4; H, 2.6; N, 1.8. Found: C, 57.3; H, 2.7; N, 1.8%. FT-IR (nujol mull cm^{-1}): ν(NH) 3439(s); ν(CO) 1608(vs). ^1H NMR (200 MHz, $CDCl_3$): δ(ppm): 6.97–7.89 (m, 19H, aromatic + NH). ^{31}P NMR (200 MHz, $CDCl_3$): δ(ppm):7.5 (s). ^{19}F NMR (200 MHz, $CDCl_3$): δ(ppm): −115.8 (m, $2F_o$), −118.9 (m, $2F_o$), −161.9 (t, $1F_p$, J_{pm} = 18.8), −163.2 (t, $1F_p$, J_{pm} = 18.8), −164.4 (m, $2F_m$), −165.3 (m, $2F_m$). FAB-MS (negative mode) *m*/*z*: 606 ($M-C_6F_5$), 439 ($M-2C_6F_5$).

$[Pd(C_6F_5)_2(o\text{-}Ph_2PC_6H_4CO\text{-}NH^iPr)]$ (**2a**): Yield 0.083 g (68%). *Anal.* Calc. for $C_{34}F_{10}H_{22}NOPPd$: C, 51.8; H, 2.8; N, 1.8. Found: C, 51.9; H, 3.0; N, 2.0%. FT-IR (nujol mull cm^{-1}): ν(NH) 3424(s); ν(CO) 1600(vs). ^1H NMR (400 MHz, $CDCl_3$): δ(ppm): 0.88 (d, J_{HH} = 8.8, 6H, ^{i}Pr), 3.86 (m, 1H, ^{i}Pr), 6.03 (m, 1H, aromatic), 7.37–7.52 (m, 14H, aromatic + NH). ^{31}P NMR (200 MHz, $CDCl_3$): δ(ppm): 20.0 (s). ^{19}F NMR (200 MHz, $CDCl_3$): δ(ppm): −113.6 (m, $2F_o$), −116.7 (m, $2F_o$), −160.9 (t, $1F_p$, J_{pm} = 19,8), −162.1 (t, $1F_p$, J_{pm} = 19,8), −163.3 (m, $2F_m$), −164.0 (m, $2F_m$). FAB-MS (negative mode) *m*/*z*: 620 ($M-C_6F_5$), 453 ($M-2C_6F_5$).

$[Pd(C_6F_5)_2(o\text{-}Ph_2PC_6H_4CO\text{-}NHPh)]$ (**2b**): Yield 0.073 g (58%). *Anal.* Calc. for $C_{37}F_{10}H_{20}NOPPd$: C, 54.1; H, 2.4; N, 1.7. Found: C, 54.2; H, 2.4; N, 1.8%. FT-IR (nujol mull cm^{-1}): ν(NH) 3398(s); ν(CO) 1610(vs). ^1H NMR (400 MHz, $CDCl_3$): δ(ppm): 6.98–7.90 (m, 20H, aromatic + NH). ^{31}P NMR (400 MHz, $CDCl_3$): δ(ppm): 19.1 (s). ^{19}F NMR (400 MHz, $CDCl_3$): δ(ppm): −113.8 (m, $2F_o$), −116.4 (m, $2F_o$), −160.5 (t, $1F_p$, J_{pm} = 19.8), −161.9 (t, $1F_p$, J_{pm} = 19.8), −163.1 (m, $2F_m$), −163.8 (m, $2F_m$). FAB-MS (negative mode) *m*/*z*: 654 ($M-C_6F_5$), 487 ($M-2C_6F_5$).

*2.3. Preparation of complexes [Pd(C_6F_5)(Cl)(o-Ph_2-PC_6H_4CO-NHR)] [R = ^{i}Pr (**3a**); R = Ph (**3b**)]*

To a dichloromethane (10 mL) solution of the precursor [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] (0.1 g, 0.126 mmol) was added the stoichiometric amount (1:2 molar ratio) of the corresponding 2-diphenylphoshinebenzamide. The reaction was stirred at room temperature for 2 h, filtered and then concentrated under reduced pressure. The addition of pentane caused the formation of the new complexes, which were filtered off, air dried and recrystallised from acetone–pentane.

[Pd(C_6F_5)(Cl)(*o*-$Ph_2PC_6H_4$CO-NH^{i}Pr)] (**3a**): Yield 0.142 g (86%). *Anal.* Calc. for $C_{28}ClF_5H_{22}NOPPd$: C, 51.2; H, 3.4; N, 2.1. Found: C, 51.3; H, 3.4; N, 2.1%. FT-IR (nujol mull cm^{-1}): *ν*(NH) 3338(s); *ν*(CO) 1594(vs). ^{1}H NMR (300 MHz, $CDCl_3$): *δ*(ppm): 0.99 (d, $J_{HH} = 6.6$, 6H, ^{i}Pr), 4.06 (m, 1H, ^{i}Pr), 6.98–7.97 (m, 14H, aromatic), 8.66 (m, 1H, NH). ^{31}P NMR (300 MHz, $CDCl_3$): *δ*(ppm): 29,6 (t, 1P, $J_{FP} = 11{,}8$). ^{19}F NMR (300 MHz, $CDCl_3$): *δ*(ppm): −115.5 (dd, 2F$_o$, $J_{om} = 22.6$; $J_{FP} = 11.8$), −164.0 (t, 1F$_p$, $J_{pm} = 19.7$), −165.7 (m, 2F$_m$). FAB-MS (negative mode) *m/z*: 620 (M−Cl).

[Pd(C_6F_5)(Cl)(*o*-$Ph_2PC_6H_4$CO-NHPh)] (**3b**): Yield 0.111 g (64%). *Anal.* Calc. for $C_{31}ClF_5H_{20}NOPPd$: C, 53.9; H, 2.9; N, 2.0. Found: C, 54.0, H, 3.0; N, 2.1%. FT-IR (nujol mull cm^{-1}): *ν*(NH) 3265(s); *ν*(CO) 1608(vs). ^{1}H NMR (400 MHz, $CDCl_3$): *δ*(ppm): 7.19–8.29 (m, 19H, aromatic), 10.45 (m, 1H, NH). ^{31}P NMR (400 MHz, $CDCl_3$): *δ*(ppm): 30.7 (t, 1P, $J_{FP} = 11{,}8$). ^{19}F NMR (400 MHz, $CDCl_3$): *δ*(ppm): −115.7 (dd, 2F$_o$, $J_{om} = 23.5$; $J_{FP} = 11.8$), −163.7 (t, 1F$_p$, $J_{pm} = 19.8$), −165.5 (m, 2F$_m$). FAB-MS (negative mode) *m/z*: 654 (M−Cl).

*2.4. Preparation of complexes [Pd(C_6F_5)(LL){PPh_2(C_6H_4-CONH-R)}](O_3 SCF_3) [LL = cod; R = ^{i}Pr (4a), Ph (4b); LL = bipy; R = ^{i}Pr (**5a**), Ph (**5b**)]*

To a dichloromethane (cod compounds) or acetone (bipy compounds) (10 mL) solution of the precursor [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] (0.1 g, 0.126 mmol) was added the stoichiometric amount (1:2 molar ratio) of the corresponding 2-diphenylphoshinebenzamide. The reaction was stirred at room temperature for 1 h, and then Ag(O_3SCF_3) and LL ligands (bipy in 5 mL acetonitrile) were added, allowing the reaction to stir for 30 min. The AgCl precipitate was filtered and the solution then concentrated under reduced pressure to half the volume. The addition of hexane caused the formation of the new complexes, which were filtered off, air dried and recrystallised from acetone–hexane.

[Pd(C_6F_5)(cod)(*o*-$Ph_2PC_6H_4$CO-NH^{i}Pr)](O_3SCF_3) (**4a**): Yield 0.110 g (50%). *Anal.* Calc. for $C_{37}F_8H_{34}NO_4PSPd$: C, 50.6; H, 3.9; N, 1.6. Found: C, 50.8; H, 4.0; N, 1.7%. FT-IR (nujol mull cm^{-1}): *ν*(NH) 3372(s); *ν*(CO) 1594(vs). ^{1}H NMR (300 MHz, $CDCl_3$): *δ*(ppm): 0.95 (d, $J_{HH} = 6.9$, 6H, ^{i}Pr), 2.09 (m, 8H, cod), 2.98 (s, 4H, cod), 3.78 (m, 1H, ^{i}Pr), 7.17 (m, 1H, aromatic), 7.38 (m, 9H, aromatic), 7.50 (m, 2H, aromatic), 7.78 (m, 1H, aromatic), 8.10 (m, 1H, aromatic), 9.36 (m, 1H, NH). ^{31}P NMR (300 MHz, $CDCl_3$): *δ*(ppm): 30.0 (t, 1P, $J_{FP} = 11{,}3$). ^{19}F NMR (300 MHz, $CDCl_3$): *δ*(ppm): −78.1 (CF_3SO_3), −115.5 (dd, 2F$_o$, $J_{\rm om} = 21.2$; $J_{FP} = 11.3$), −157.0 (t, 1F$_p$, $J_{\rm pm} = 19.8$), −160.3 (m, 2F$_m$). FAB-MS (negative mode) *m/z*: 728 (M−O_3SCF_3).

[Pd(C_6F_5)(cod)(*o*-$Ph_2PC_6H_4$CO-NHPh)](O_3SCF_3) (**4b**): Yield 0.124 g (54%). *Anal.* Calc. for $C_{40}F_8H_{32}NO_4PSPd$: C, 52.7; H, 3.5; N, 1.5. Found: C, 52.8; H, 3.7; N, 1.6%. FT-IR (nujol mull cm^{-1}): *ν*(NH) 3364(s); *ν*(CO) 1608(vs). ^{1}H NMR (300 MHz, $CDCl_3$): *δ*(ppm): 1.81 (m, 8H, cod), 2.79 (s, 4H, cod), 7.09 (m, 2H, aromatic), 7.26 (m, 4H, aromatic), 7.39 (m, 8H, aromatic), 7.52 (m, 2H, aromatic), 7.63 (m, 1H, aromatic), 7.87 (m, 1H, aromatic), 8.39 (m, 1H, aromatic), 11.14 (m, 1H, NH). ^{31}P NMR (300 MHz, $CDCl_3$): *δ*(ppm): 29.9 (t, 1P, $J_{FP} = 12.7$). ^{19}F NMR (200 MHz, $CDCl_3$): *δ*(ppm): −77.9 (CF_3SO_3), −115.6 (dd, 2F$_o$, $J_{om} = 21.2$; $J_{FP} = 12.7$), −156.9 (t, 1F$_p$, $J_{pm} = 19.8$), −160.3 (m, 2F$_m$). FAB-MS (negative mode) *m/z*: 763 (M−O_3SCF_3).

[Pd(C_6F_5)(bipy)(*o*-$Ph_2PC_6H_4$CO-NH^{i}Pr)](O_3SCF_3) (**5a**): Yield 0.163 g (72%). *Anal.* Calc. for $C_{37}F_8H_{28}N_3O_4PSPd$: C, 49.4; H, 3.1; N, 4.7. Found: C, 49.4; H, 3.2; N, 4.7%. FT-IR (nujol mull cm^{-1}): *ν*(NH) 3312(s); *ν*(CO) 1636(s); *ν*(bipy)1540(m). ^{1}H NMR (300 MHz, $CDCl_3$): *δ*(ppm): 0.86 (d, $J_{HH} = 6.6$, 6H, ^{i}Pr), 3.50 (m, 1H, ^{i}Pr), 7.43–8.75 (m, 22H, aromatic), 8.97 (br, 1H, NH). ^{31}P NMR (300 MHz, (($CD_3)_2CO$)): *δ*(ppm): 33.1 (br, 1P). ^{19}F NMR (300 MHz, (($CD_3)_2CO$)): *δ*(ppm): −78.6 (CF_3SO_3), −115.5 (d, 2F$_o$, $J_{om} = 22.6$), −160.6 (t, 1F$_p$, $J_{pm} = 19.8$), −163.0 (m, 2F$_m$). FAB-MS (negative mode) *m/z*: 776 (M−O_3SCF_3).

[Pd(C_6F_5)(bipy)(*o*-$Ph_2PC_6H_4$CO-NHPh)](O_3SCF_3) (**5b**): Yield 0.176 g (75%). *Anal.* Calc. for $C_{40}F_8H_{26}N_3O_4PSPd$: C, 51.4; H, 2.8; N, 4.5. Found: C, 51.5; H, 2.9; N, 4.5%. FT-IR (nujol mull cm^{-1}): *ν*(NH) 3302(s); *ν*(CO) 1660(s); *ν*(bipy)1538(m). ^{1}H NMR (300 MHz, $CDCl_3$): *δ*(ppm): 6.85–8.37 (m, 27H, aromatic), 9.27 (br, 1H, NH). ^{31}P NMR (300 MHz, (($CD_3)_2CO$)): *δ*(ppm): 32.1 (br,1P). ^{19}F NMR (300 MHz, (($CD_3)_2CO$)): *δ*(ppm): −78.6 (CF_3SO_3), −116.8 (d, 2F$_o$, $J_{om} = 28.2$), −160.3 (t, 1F$_p$, $J_{pm} = 19.8$), −162.6 (m, 2F$_m$). FAB-MS (negative mode) *m/z*: 810 (M−O_3SCF_3).

*2.5. Preparation of complexes [Pd(C_6F_5){S(S)P($OMe)_2$}(o-$Ph_2PC_6H_4$CONHR)] [R = ^{i}Pr (**6a**), Ph (**6b**)]*

To a dichloromethane (10 mL) solution of the precursor [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] (0.1 g, 0.126 mmol) was added the stoichiometric amount (1:2 molar ratio) of the corresponding 2-diphenylphoshinebenzamide and (NH_4) [S(S)-P($OMe)_2$]. The reaction was stirred at room temperature for 1/2 hour, and then filtrated to eliminate the NH_4Cl

formed. The resulting solution was then concentrated under reduced pressure to half the volume and the addition of a (1:1) mixture of Et_2O–pentane resulted in the precipitation of the new complexes, which were filtered off, washed with water and pentane,air dried and recrystallised from dichloromethane–hexane.

$[Pd(C_6F_5)\{S(S)P(OMe)_2\}(o\text{-}Ph_2PC_6H_4CONH^iPr)]$ (**6a**): Yield 0.098 g (50%). *Anal.* Calc. for $C_{30}F_5H_{28}NO_3P_2S_2Pd$: C, 46.3; H, 3.6; N, 1.8. Found: C, 46.4; H, 3.7; N, 1.8%. FT-IR (nujol mull cm^{-1}): ν(NH) 3386(s); ν(CO) 1650(s); ν(PS) 690(m). ^1H NMR (300 MHz, $((CD_{32}CO))$: δ(ppm): 0.86 (d, $J_{HH} = 6.7$, 6H, ^{i}Pr), 3.83 (d, 6H, P–OCH_3, $J_{HP} = 15.0$), 4.20 (m, 1H, ^{i}Pr), 7.48 (m, 14H, aromatic), 7.84 (m, 1H, NH). ^{31}P NMR (300 MHz, $((CD_3)_2CO)$): δ(ppm): 105.40 (d, 1P, $J_{pp} = 32.8$), 30.4 (m,1P). ^{19}F NMR (300 MHz, $((CD_3)_2CO)$): δ(ppm): −113.4 (dd, $2F_o$, $J_{om} = 24.0$; $J_{FP} = 7.1$), −163.3 (t, $1F_p$, $J_{pm} = 19.8$), −164.9 (m, $2F_m$). FAB-MS (negative mode) *m*/*z*: 610 ($M-C_6F_5$).

$[Pd(C_6F_5)\{S(S)P(OMe)_2\}(o\text{-}Ph_2PC_6H_4CONHPh)]$ (**6b**): Yield 0.125 g (61%). *Anal.* Calc. for $C_{33}F_5H_{26}NO_3P_2S_2Pd$: C, 48.8; H, 3.2; N, 1.7. Found: C, 48.8; H, 3.3; N, 1.7%. FT-IR (nujol mull cm^{-1}): ν(NH) 3302(s); ν(CO) 1660(s); ν(PS) 692(m). ^1H NMR (300 MHz, $((CD_3)_2CO)$): δ(ppm): 3.61 (d, 6H, P–OCH_3, $J_{HP} = 15.3$), 7.05 (m, 1H, aromatic), 7.36 (m, 13H, aromatic), 7.55 (m, 1H, aromatic), 7.72 (m, 1H, aromatic), 7.86 (m, 2H, aromatic), 8.13 (m, 1H, aromatic), 9.60 (m, 1H, NH). ^{31}P NMR (300 MHz, $((CD_3)_2CO)$): δ(ppm): 106.30 (d, 1P, m), 30.5 (m, 1P). ^{19}F NMR (300 MHz, $((CD_3)_2CO)$): δ(ppm): −114.1 (dd, $2F_o$, $J_{om} = 21.2$, $J_{FP} = 7.1$) −162.8 (t, $1F_p$, $J_{pm} = 19.8$), −164.7 (m, $2F_m$). FAB−MS (negative mode) *m*/*z*: ($M-C_6F_5$).

2.6. *Crystal structure determination of (**b**) (**1a**), (**1b**), (**2a**) and (**3a**)*

Crystals suitable for a diffraction study were prepared by slow diffusion of hexane into their dichloromethane solutions. Data collection was performed at −173 °C on a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 6.2 cm. Diffraction data were collected based on a ω scan run. A total of 2524 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package [24] and corrected for absorption with SADABS [25]. The structures were solved by direct (**b**, **2a** and **3a**) or heavy-atom methods [26] (**1a** and **1b**) and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms [26] (Table 1). Hydrogen atoms were introduced in calculated positions and refined during the last stages of the refinement.

Table 1
Crystal data and structure refinement for compounds **b**, **1a**, **1b**, **2a** and **3a**

	b	**1a**	**1b**	**2a**	**3a · H$_2$O**
Empirical formula	$C_{25}H_{20}NOP$	$C_{34}H_{22}F_{10}NOPNi$	$C_{37}H_{20}F_{10}NOPNi$	$C_{34}H_{22}F_{10}NOPPd$	$C_{28}H_{24}ClF_5NO_2PPd$
Formula weight	381.39	740.21	774.22	787.90	674.30
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Absorption coefficient (mm^{-1})	0.154	0.772	0.734	0.729	0.904
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	$P21/a$	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$
a (Å)	9.2011(4)	11.0425(5)	23.3095(16)	19.1346(9)	9.2344(4)
b (Å)	19.5847(8)	11.6230(5)	16.0000(11)	13.5370(6)	12.1146(6)
c (Å)	11.2092(5)	13.6005(6)	17.5878(12)	26.0564(12)	12.8823(6)
α (°)	90	81.8960(10)	90	90	87.9650(10)
β (°)	101.4790(10)	66.2280(10)	95.6550(10)	110.9410(10)	71.1000(10)
γ (°)	90	74.9000(10)	90	90	83.6000(10)
V (Å^3)	1979.50 (15)	1541.05(12)	6527.5(8)	6303.5(5)	1354.96(11)
Z	4	2	8	8	2
D_{calc} ($Mg\,m^{-3}$)	1.280	1.595	1.576	1.660	1.653
F(000)	800	748	3120	3136	676
Reflections collected	22705	18173	37395	36123	15692
Independent reflections (R_{int})	4564 (0.0608)	6949 (0.0277)	7587 (0.0257)	7335 (0.0253)	6056 (0.0156)
Parameters	253	418	460	433	360
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 F^2
R_1[a]	0.0457	0.0418	0.0391	0.0342	0.0235
wR[b]	0.1102	0.1052	0.0965	0.0825	0.0645
S[c]	0.942	0.967	0.741	1.097	0.757
Maximum, minimum $\Delta\rho$ (e Å^{-3})	0.450,−0.381	0.531, −0.345	0.341, −0.234	0.690, −0.380	0.449,−0.644

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$ for reflections with $I > 2\sigma I$.

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2})$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, were $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

[c] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$; *n* is the number of reflections and *p* the total number of parameters refined.

3. Results and discussion

In dichloromethane, the labile precursors *cis*-$[M(C_6F_5)_2(PhCN)_2]$ [M = Ni, Pd] react at room temperature with *o*-$Ph_2PC_6H_4CONHR$: [R = ^{i}Pr **a** or Ph **b**] (see Section 2 for details) yielding the yellow (**1a**, **1b**) or white (**2a**, **2b**) compounds of general formula $[M(C_6F_5)_2(o\text{-}Ph_2\mathbf{P}C_6H_4C\mathbf{O}\text{-}NHR)]$ [M = Ni; R = ^{i}Pr **1a**; R = Ph **1b**; M = Pd; R = ^{i}Pr **2a**; R = Ph **2b**] in which the diphenylphosphine-benzamidate ligands display a η^2-P,O coordination mode. The characterising spectroscopic and analytical data are in agreement with the proposed structures presented in Scheme 1.

Infrared spectroscopy provides full information of the situation. All complexes show the characteristic absorptions of the C_6F_5 group [27] at ca. 1630 m, 1500 vs, 1050 s and 950 vs cm^{-1} and two bands in the 800–780 cm^{-1} region for the so-called “X-sensitive” mode of C_6F_5, typical of the *cis*-$M(C_6F_5)_2$ fragment, obviously found in compounds containing bidentate chelate ligands. A medium *ν*(NH) vibration and a *ν*(CO) absorption, lowered in energy by approximately 30 cm^{-1} with respect to those of the free ligands (**a**: 1624 cm^{-1}. **b**: 1647 cm^{-1}), indicate that the amide ligands are O-coordinated to the respective metals. The FAB mass spectrometry displays fragments corresponding to $[M^- - C_6F_5]$ and $[M^- - 2C_6F_5]$. The $^{31}P\{^1H\}$ NMR spectra of the new complexes in $CDCl_3$ consist of singlets around 19 ppm, while their ^{19}F spectra show the expected pattern of three duplicated resonance signals, consistent with the presence of two non-equivalent C_6F_5 groups, one *trans* to O and one *trans* to P. In our previous work with **a** and **b** they coordinated to different cyclometallated fragments, and we pointed out the hemilability exhibited by ligand **b** under certain conditions [19]. Here modifications in this behaviour as a result of a different chemical environment could be expected, in which the large *trans*-influence exerted by the C_6F_5 groups may play an important role labilizing the O–M bond. Indeed, when the $^{31}P\{^1H\}$spectra of **2b** was run in CD_3CN, two resonances at ca. 28 ppm and 23 ppm were growing with time, reaching after three weeks a (3/1.5/1) ratio in relation to the diminishing singlet at 19 ppm. This observation suggests that the amidic oxygen is involved in processes of coordination/dissociation, in which both the deuterated solvent and probably its water may take part, conferring on the ligand a behaviour of hemilabile P,O chelate. Attempts to isolate the hypothetical $[Pd(C_6F_5)_2(o\text{-}Ph_2\mathbf{P}C_6H_4CO\text{-}NHPh)(CH_3CN)]$ complex were unsuccessful and the parent complex **2b** was always obtained. It is worth to mention that, in agreement with our previous results [19], a stronger chelating character is attributable to **a** in comparison with **b**, since analogous studies in CD_3CN for compound **2a** displayed after three weeks, a (1/1/7) ratio for signals at 29 ppm, 22 ppm and 20 ppm. The latter resonance (being always predominant) was attributed to the P,O chelating mode. Regarding nickel complexes **1a** and **1b**, the expected affinity between hard metal-hard donor atom may explain the absence of dynamic processes that imply O-dissociation.

X-ray diffraction analysis has confirmed the structures of **b**, **1a**, **1b** and **2a**, providing a set of structural data that enrich some aspects discussed above. The molecular structure of **b** is shown in Fig. 1, showing similar values to those reported for related compounds (searched at the Cambridge Structural Database (CSD) v. 5.26. IVONOW [28], DOVWIU [29], AJIFII [30] and CEMPOZ [31]).

The angle between planes O(1)–C(7)–C(6) and C(6)–C(1)–P(1) is 53.11(13)°. This value slightly diminishes once the ligand is complexed to Ni or Pd: 38.42(22)°, 33.29(20)°

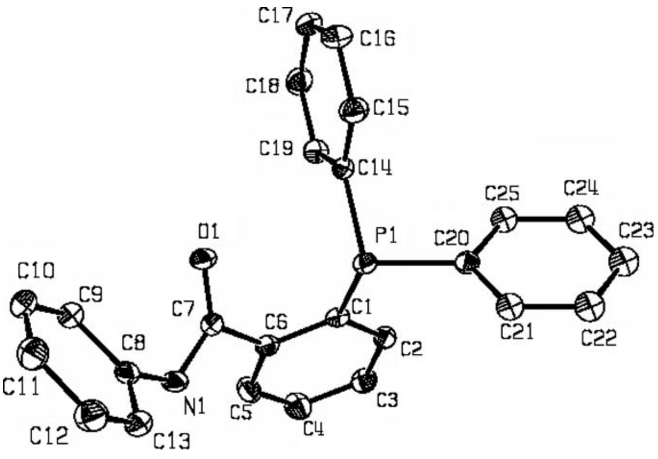
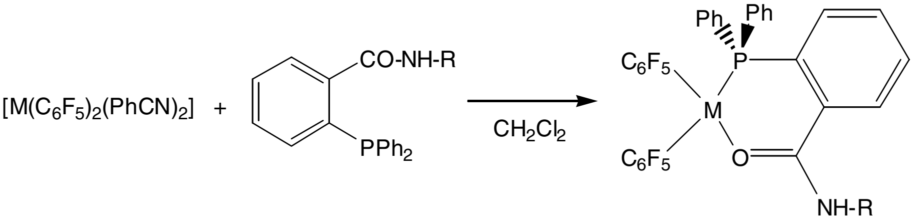


Fig. 1.



M = Ni; R = ^{i}Pr **1a**, Ph **1b**
M = Pd; R = ^{i}Pr **2a**, Ph **2b**

Scheme 1.

and 41.26(19)° for **1a**, **1b** and **2a**, respectively. The most significant difference between the solid state conformation of the free ligand **b** and the coordinated ligand in **1b** is the relative position of the phenyl rings bonded to the N–CO-moiety. In the free ligand both rings are nearly perpendicular (81.7°) while in the complex the phenyl bonded to N rotates, causing both rings to be parallel (10.2°). The crystal structure analysis reveals that **b** forms H-bonded chains (Fig. 2) due to intermolecular hydrogen bonding between NH and CO functions (distance N(1)···O(1) 2.817(2) Å and angle N(1)–H···O(1) of 152.29°. In addition Ph–N and Ph–P rings from different chains adopt a T-shaped conformation [32] with an angle of 82.7° between planes and centroid–centroid distance of 4.895 Å.

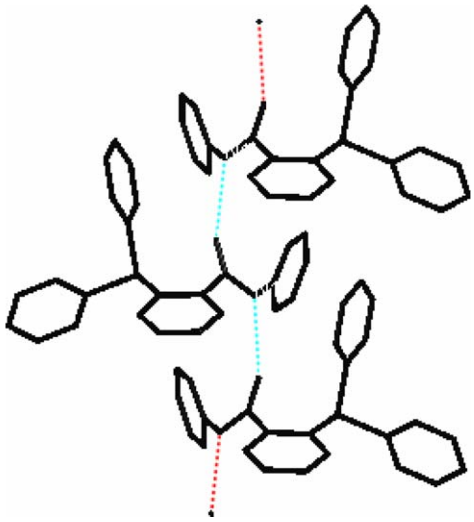


Fig. 2.

Upon coordination, no remarkable changes in bond distances are observed with respect to free **b**, except the expected elongation in the C–O distance found in the structures of the three complexes (Table 2). Neither variations in the Ni environment are detected when varying the R groups (^{i}Pr in **1a** (Fig. 3) or Ph in **1b** (Fig. 4)). Both structures have a shorter Ni(1)–C(1) compared to Ni(1)–C(7) and may be described as nearly planar, with a moderate tetrahedral distortion from the ideal square-plane [33] (Table 3). A close Ni(1)–P(1) distance has been reported in a related complex with ligand **b** and a PMe_3 group *trans*-to P instead of C_6F_5 [18].

Selected bond distances and angles for complex **2a** (Fig. 5) are given in Table 2. The Pd(1)–O(1) distance is very similar to the one we found for a cyclometallated benzoquinolyl compound, also containing the carbonyl group of **a** involved in P,O chelation to a palladium centre [19]. This fact confers a comparable *trans*-influence to C_6F_5– and a orthometallated carbon in our complexes. Ligand **a** does not behave in the same way coordinating Ni and Pd. Thus, the difference between Pd(1)–O(1) and Ni(1)–O(1) distances is higher than the difference in distances obtained by the sum of covalent radii, confirming the expected hard-hard affinity between Ni and O. Both complexes **1a** and **2a** exist as dimer in the solid state, thanks to hydrogen bonding between F(6) and N(1) atoms (distance N(1)···F(6) 2.984(2) Å and angle N(1)–H···F(6) of 150.97° and 2.983(3) Å and 151.56°, respectively).

The dinuclear complex $[\{Pd(C_6F_5)(tht)(\mu\text{-}Cl)\}_2]$ undergo ready bridge cleavage with **a** and **b** ligands affording the

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1a**, **1b**, **2a** and **3a**

	1a	**1b**	**2a**	**3a**
Ni(1)–C(1)	1.872(2)	1.880(2)		
Ni(1)–C(7)	1.931(2)	1.951(2)		
Ni(1)–P(1)	2.1799(6)	2.1848(6)		
Ni(1)–O(1)	1.9274(15)	1.9313(14)		
C(1)–Ni(1)–C(7)	89.15(9)	89.02(9)		
C(1)–Ni(1)–P(1)	93.90(7)	91.80(6)		
C(1)–Ni(1)–O(1)	176.32(8)	177.95(8)		
C(7)–Ni(1)–P(1)	174.26(7)	171.63(7)		
C(7)–Ni(1)–O(1)	91.07(8)	92.81(7)		
P(1)–Ni(1)–O(1)	86.20(5)	86.53(5)		
Pd(1)–C(1)			1.978(2)	1.9823(17)
Pd(1)–C(7)			2.079(2)	
Pd(1)–P(1)			2.2737(6)	2.2114(4)
Pd(1)–O(1)			2.1086(17)	2.0976(12)
Pd(1)–Cl(1)				2.3691(4)
C(1)–Pd(1)–C(7)			85.98(9)	
C(1)–Pd(1)–P(1)			95.26(7)	95.04(5)
C(1)–Pd(1)–O(1)			175.87(8)	178.08(6)
C(7)–Pd(1)–P(1)			178.72(6)	
C(7)–Pd(1)–O(1)			94.06(7)	
P(1)–Pd(1)–O(1)			84.73(5)	83.74(4)
C(1)–Pd(1)–Cl(1)				89.08(5)
P(1)–Pd(1)–Cl(1)				175.863(15)
O(1)–Pd(1)–Cl(1)				92.14(4)

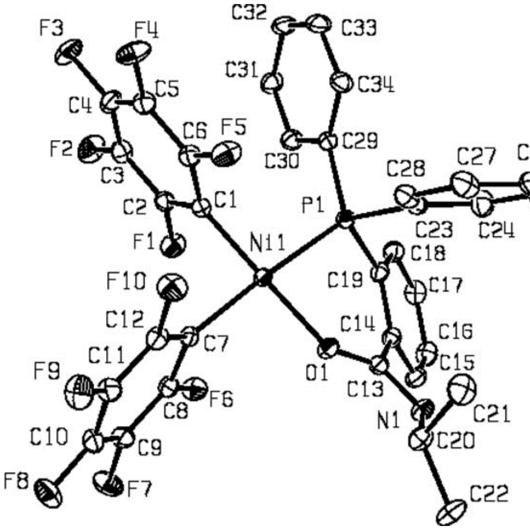


Fig. 3.

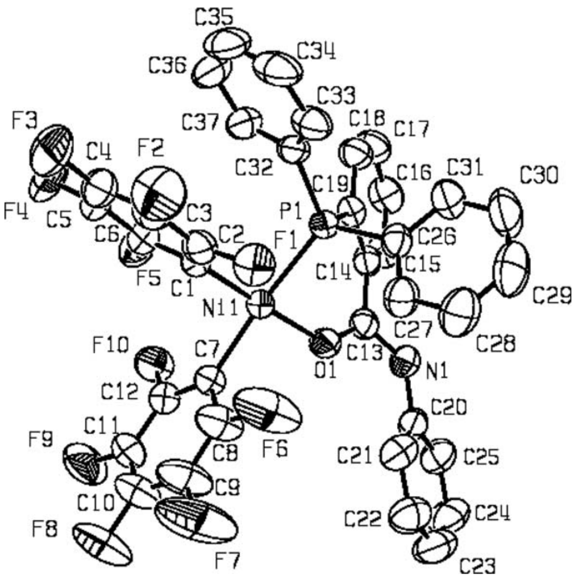


Fig. 4.

Table 3
Distortion parameters from square planar coordination

Improper torsion angles (°)	1a	1b	2a	3a
P(1)–C(1)–C(7)–Ni(1)	3.57	−6.23		
O(1)–C(7)–C(1)–Ni(1)	2.58	−0.64		
P(1)–C(1)–C(7)–Pd(1)			−0.25	
O(1)–C(7)–C(1)–Pd(1)			−2.84	
P(1)–C(1)–Cl(1)–Pd(1)				0.22
O(1)–Cl(1)–C(1)–Pd(1)				0.98

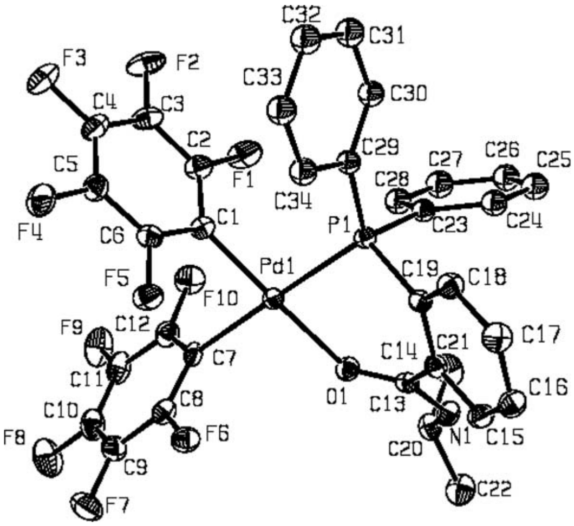
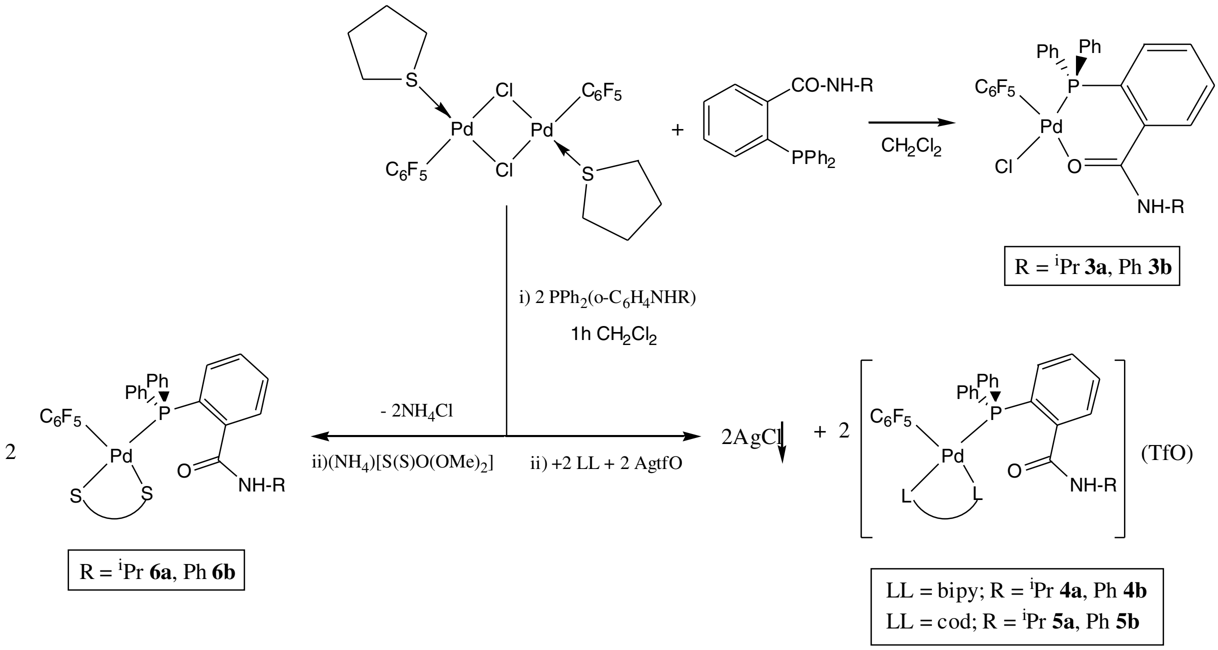


Fig. 5.

white neutral complexes [Pd(C_6F_5)Cl{**P**Ph$_2$(C_6H_4-C**O**NH-R)}] (R = ^{i}Pr **3a**, Ph **3b**) displayed in Scheme 2. Formation of a P,O chelate around the Pd centre is supported by the appearance of the ν(CO) vibration in the same range mentioned above for complexes **2a** and **2b**. A single band at ca. 800 cm^{-1} indicates the presence of just one C_6F_5 ring that, as inferred from the coupling constants obtained in their ^{31}P and ^{19}F NMR spectra, lies *trans* to the amidic oxygen. In this case, the amidic oxygen stays firmly bonded to palladium and no dynamic behaviour was detected when running the spectra in CD_3CN. Thus, the presence of a Cl$^-$ coligand is more prone to be displaced than both C_6F_5−, when comparing with **2a** and **2b**, or the chelating O- may cause the observed situation. The characterisation in solid state was completed with the FAB mass spectrometry, that showed fragments at [M$^-$−Cl], and the X-ray crystal structure determination of complex **3a**, further confirmed the proposed arrangement of ligands. An ORTEP representation of **3a** is presented in Fig. 6, and selected bond distances and angles are given in Table 2.

A very slight tetrahedral distortion of the planar palladium environment is observed in both **2a** and **3a** structures (Table 3) and a shorter Pd(1)–P(1) is found in complex **3a**, as expected from the weaker *trans*-influence of Cl− compared to C_6F_5−. A distance Pd(1)–O(1) of 2.0976(12) Å, almost identical to that in **2a** and in the previously reported [19] complex [Pd(Bzq)(*o*-Ph$_2$**P**C_6H_4C**O**-NH^{i}Pr)][PF$_6$], indicates that the group situated in *cis*-position to this bond does not hardly affect its length. Following the recent classification of Dance and Scudder [34] for PPh$_3$ based on measures of torsion angles M–P–C$_{ipso}$-C (Table 4), the conformation of Pd–PPh$_2$C$_6$H$_4$COR groups is described as *good rotor* for all the new complexes, presenting values close to those which would have the ideal rotor ($T_1 = T_2 = T_3 = 44°$). According to the classification of Allen and Taylor [35], the six membered chelated rings show a distorted *screw-boat* conformation. The torsion angles in the four new complexes do not conform to the ideal of around 10°, 8°, 14° and 7° for **1a**, **1b**, **2a** and **3a**, respectively.

New cationic complexes of general formula [Pd(C_6F_5)-(LL){**P**Ph$_2$(C_6H_4-CONH-R)}](O$_3$SCF$_3$) (LL = cod; R = ^{i}Pr **4a**, Ph **4b**; LL = bipy; R = ^{i}Pr **5a**, Ph **5b**) were obtained from the precursor [{Pd(C_6F_5)(tht)(μ-Cl)}$_2$] when it was



Scheme 2.

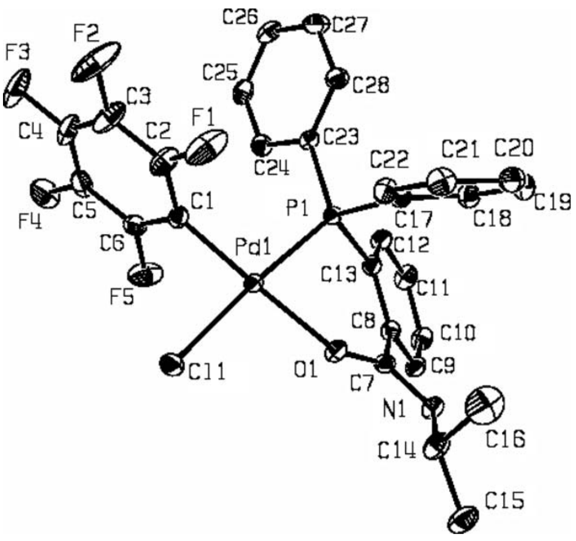


Fig. 6.

treated in successive steps with **a** or **b**, $Ag(O_3SCF_3)$ and neutral LL ligands (Scheme 2). An η^1-phosphine coordination mode for diphenylphosphine-benzamide ligands is induced under these conditions, in which, as expected, both bipy and cod show a stronger chelating ability than our ligands. The $^{31}P\{^1H\}$ NMR spectra consist of singlets at ca. 30 ppm, and the ^{19}F spectra display the three resonances of C_6F_5– and a singlet at −78 ppm corresponding to the triflate anion. Measurements of molar conductivity in acetone solutions indicate that the new complexes behave as 1:1 electrolytes [36], in accordance with the proposed formulae.

Also in order to force the η^1-phosphine coordination mode in our ligands we reacted $[\{Pd(C_6F_5)(tht)(\mu\text{-}Cl)\}_2]$ with amonic dimethyldithiophosphate, obtaining the monopentafluorophenyl complexes $[Pd(C_6F_5)\{S(S)P(OMe)_2\}\{\mathbf{P}Ph_2(C_6H_4\text{-}CONH\text{-}R)\}]$ (R = ^{i}Pr **6a**, Ph **6b**) shown in Scheme 2. In their IR spectra, the carbonyl bands appear

Table 4
Torsion angles Pd–P–C_{ipso}–C for the three phenyl rings in each of the complexes studied

	1a	1b	2a	3a
Ring 1	−47.04/133.16	−42.09/126.82	48.57/−133.35	−45.88/132.40
Ring 2	144.88/−34.04	−12.23/167.57	−149.00/27.40	140.37/−35.06
Ring 3	−66.24/102.35	109.88/−59.28	−121.88/51.14	−50.79/128.63
T (ring 1)	−47.07	−42.09	48.57	−45.88
T (ring 2)	−34.04	−12.23	27.40	−35.06
T (ring 3)	−66.24	−59.28	51.14	−50.79
T_1	34.04	12.23	27.40	35.06
T_2	47.07	42.09	48.57	45.88
T_3	66.24	59.28	51.14	50.79
T_2–T_1	13.03	29.86	21.17	10.82
T_3–T_2	19.17	17.19	2.57	4.91
Rotor type	Good rotor	Good rotor	Good rotor	Good rotor

in the range of non-coordinated oxygen, and the absorptions attributed to the coordinated dithiophosphate are observed in the 960–1050 and 630–690 regions [37]. The presence of this group is also confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, being observed a doublet resonance for the Me groups strongly coupled to P in the former, and a signal around 106 ppm that accompanies the multiplet due to **a** or **b** at 30 ppm in the latter.

4. Supplementary material

Crystallographic data (excluding structure factors) reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-278159 (**b**), CCDC-278160(**1a**), CCDC-278161 (**1b**), CCDC-278162 (**2a**) and CCDC-278163 (**3a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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