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Synthesis and characterisation of cyclometallated palladium(II) complexes with phosphine–carboxylate and phosphine–amide ligands

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The coordination properties of hybrid phosphino-amide ligands *o*-$Ph_2PC_6H_4CONHR$ [R = ^{i}Pr (**a**), Ph (**b**)] have been investigated. New cyclometallated palladium(II) complexes in which **a** and **b** act as P-monodentate ligands have been synthesised by reacting them with selected cyclometallated precursors containing bridging chloride or acetate groups. The crystal structures of the compounds [Pd(Bzq)(*o*-Ph_2**P**C_6H_4CO–N**H**^{i}Pr)(Cl)] and [Pd(Phox)(*o*-Ph_2**P**C_6H_4CO–N**H**^{i}Pr)(CH_3COO)] (Bzq = 7,8-benzoquinolyl; Phox = 2-(2-oxazolinyl)phenyl) have been determined. Hemilability of coordinated ligand **b** is detected when it appears combined with certain cyclometallated backbones. A rigid P,O-chelating behaviour of the ligands, confirmed by the crystal structure determination of [Pd(Bzq)(*o*-Ph_2**P**C_6H_4**CO**–N**H**^{i}Pr)][PF_6], is observed in complexes obtained by adding stoichiometric KPF_6 to [Pd(C^N)(μ-Cl)]$_2$ compounds. The reactions of hydroxo-bridged precursors [Pd(C^N)(μ-OH)]$_2$ with **a** and **b** afforded mononuclear derivatives in which a less common anionic P,N-binding mode is exhibited. The crystal structure of Pd(Phpy)(*o*-Ph_2**P**C_6H_4CO–**N**^{i}Pr)] (Phpy = 2-phenylpyridine) is also reported. Furthermore, related compounds with phosphino-carboxylate ligands have been prepared by direct reaction between 2-(diphenylphosphinobenzoic) acid and [Pd(C^N)(μ-CH_3COO)]$_2$ precursors, and the X-ray structures of [Pd(C^N)(*o*-Ph_2**P**C_6H_4CO**O**)] (C^N = Bzq and Phpy) have been determined.

The considerable attention received by hybrid ligands containing both a soft phosphine donor atom and a hard (*e.g.* N or O) functionality[1–4] comes from their versatile coordination behaviour[5,6] and its potential hemilability,[3,4] that make their complexes useful as the foundation for molecule-based sensors,[7–9] as well as good precursors in catalytic processes. The hard donor site dissociates readily from soft metal centres, generating a vacant site on the metal ion for substrate binding. Thus, metal complexes containing hemilabile ligands have been found to be catalytically active in a range of reactions.[4,10–16] In this sense, we have recently described the syntheses of some organometallic derivatives containing iminophosphine ligands, either with an *ortho*-metallated palladium(II) backbone[17] or pentafluorophenyl derivatives of Ni(II) and Pd(II).[18] Although phosphine–amide ligands have received comparatively less attention,[19] some anionic P,O ligands have shown recent application in the nickel-catalysed ethene oligomerization into linear α-olefins.[20–22] The asymmetric 1,4-addition reaction of arylboronic acids with cycloalkenones is catalysed by an amidophosphine rhodium(I) complex[23] and new chiral amidophosphine ligands also take part in palladium-catalysed asymmetric allylic alkylation processes.[24]

On the other hand, the di-μ-hydroxo-complexes of group 10 metals have shown to be useful precursors for the preparation of an interesting variety of compounds,[25–29] by simple acid–base reaction with protic electrophiles. We have explored[30–33] the synthesis and reactivity of a wide range of such hydroxo-bridged precursors, some of them with a cyclometallated backbone.[34] We report here our investigations on the coordination properties of the mixed-donor bidentate ligands 2-diphenylphosphine–benzoate and diphenylphosphine–benzamidate **a** and **b**, based on the use of several cyclometallated precursors [Pd(C^N)(μ-X)]$_2$ whose bridging units (X = Cl, AcO or OH) exhibit different acid–base behaviour.

Results and discussion

In dichloromethane, the chloro-bridged cyclometallated dimers [{Pd(μ-Cl)(C^N)}$_2$] [C^N = phenylazophenyl (**Azb**), 2-phenylpyridine (**Phpy**), 7,8-benzoquinolyl (**Bzq**), and 2-(2-oxazolinyl)phenyl (**Phox**)] react under the smooth conditions described in the experimental section with *o*-Ph_2-PC_6H_4CONHR: [R = ^{i}Pr (**a**) or Ph (**b**)] to afford the pale yellow products [Pd(C^N)(*o*-Ph_2**P**C_6H_4CO–NHR)(Cl)] (**1a**–**4a**, **1b**–**4b**) in which the diphenylphosphine–benzamidate ligands display an η^1-phosphine coordination mode. The characterising spectroscopic and analytical data are in agreement with the proposed structures presented in Scheme 1.

Infrared spectra of the new compounds show the characteristic absorptions of the corresponding cyclometallated ligand, a weak *ν*(NH) vibration and a *ν*(CO) absorption in the range observed for the free ligands (**a**: 1624 cm^{-1}. **b**: 1647 cm^{-1}) indicating that the amidic oxygen is not coordinated to the Pd centre. The $^{31}P\{^1H\}$-NMR spectra of the mononuclear complexes consist of singlets with chemical shifts in the usual range of a Pd(II)-bound phosphorus atom. The FAB mass spectrometry displays the expected fragments corresponding to [M$^+$–Cl], in accordance with reported data for related compounds,[35,36] and the crystal structure of [Pd(Bzq)(*o*-Ph_2**P**C_6-H_4CO–N**H**^{i}Pr)(Cl)] also confirms that the diphenylphosphine–benzamidate ligand acts in a P-monodentate form. The molecular structure of **3a** is given in Fig. 1 and selected bond lengths and angles are collected in Table 1. The Pd(1)–Cl(1) distance is similar to that found in related compounds.[37] The N(1)–Cl(1) distance (3.26 Å) and the N(1)–H ⋯ Cl(1) angle of 169° are consistent with a hydrogen-bonding type interaction. The intermolecular contact H ⋯ Cl(1) of 2.42 Å make it classifiable as "short" (≤2.52 Å).[38]

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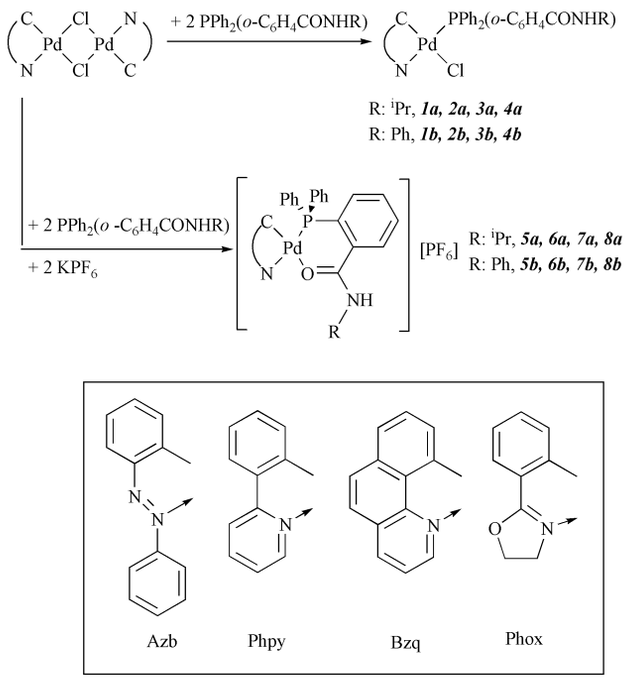
Table 1 Selected distances (Å) and angles (°) for complex **3a**

Pd(1)–C(23)	2.017(3)	Pd(1)–P(1)	2.2586(7)
Pd(1)–N(2)	2.096(2)	Pd(1)–Cl(1)	2.3905(7)
C(23)–Pd(1)–N(2)	82.05(10)	C(23)–Pd(1)–Cl(1)	170.08(8)
C(23)–Pd(1)–P(1)	94.29(8)	N(2)–Pd(1)–Cl(1)	90.29(7)
N(2)–Pd(1)–P(1)	175.53(7)	P(1)–Pd(1)–Cl(1)	93.63(2)



Scheme 1 The preparation of [Pd(C^N)(*o*-Ph$_2$**P**C$_6$H$_4$CO–NHR)(Cl)] (**1a**–**4a**, **1b**–**4b**) and [Pd(C^N)(*o*-Ph$_2$**P**C$_6$H$_4$C**O**NHR)][PF$_6$] (**5a**–**8a**, **5b**–**8b**).

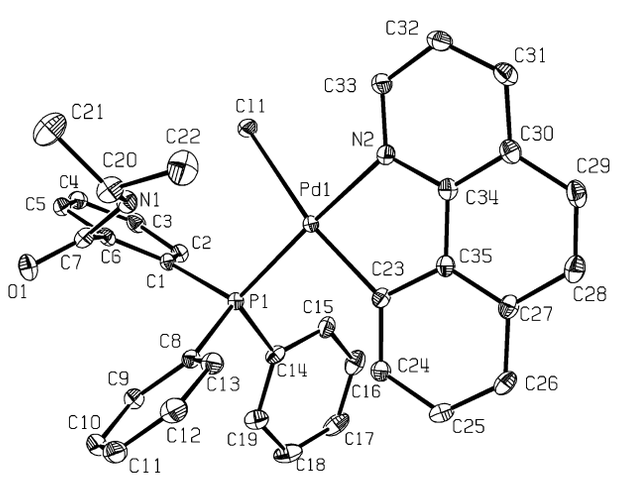


Fig. 1 The molecular structure of [Pd(Bzq)(*o*-Ph$_2$**P**C$_6$H$_4$CO–NH^{i}Pr)(Cl)], complex **3a**.

Bridge cleavage of [{Pd(μ-Cl)(C^N)}$_2$] with ligands **a** or **b** in the presence of stoichiometric KPF$_6$, afforded the white cationic complexes [Pd(C^N)(*o*-Ph$_2$**P**C$_6$H$_4$C**O**NHR)][PF$_6$] (**5a**–**8a**, **5b**–**8b**), in which a rigid P,O-chelation of the diphenylphosphine–benzamidates is induced (Scheme 1). Measurements of their molar conductivity in acetone solutions indicate that all the complexes behave as 1 : 1 electrolytes,[39] in accordance with the proposed formulae. Formation of a P,O chelate around the Pd centre is supported by the appearance of the *ν*(CO) vibration lowered in energy by approximately 30 cm^{-1} with respect to those observed in compounds **1**–**4**, and further confirmed by a crystal structure determination of **7a**. An ORTEP representation of [Pd(Bzq)(*o*-Ph$_2$**P**C$_6$H$_4$C**O**–NH^{i}Pr)][PF$_6$] is presented in Fig. 2, and selected bond distances and angles are

Table 2 Selected distances (Å) and angles (°) for complex **7a**

Pd(1)–C(23)	2.002(5)	Pd(1)–O(1)	2.110(3)
Pd(1)–N(2)	2.081 (4)	Pd(1)–P(1)	2.2384(12)
C(23)–Pd(1)–N(2)	82.03(17)	C(23)–Pd(1)–P(1)	102.05(14)
C(23)–Pd(1)–O(1)	169.59(16)	N(2)–Pd(1)–P(1)	174.06(11)
N(2)–Pd(1)–O(1)	89.85(14)	O(1)–Pd(1)–P(1)	85.58(10)

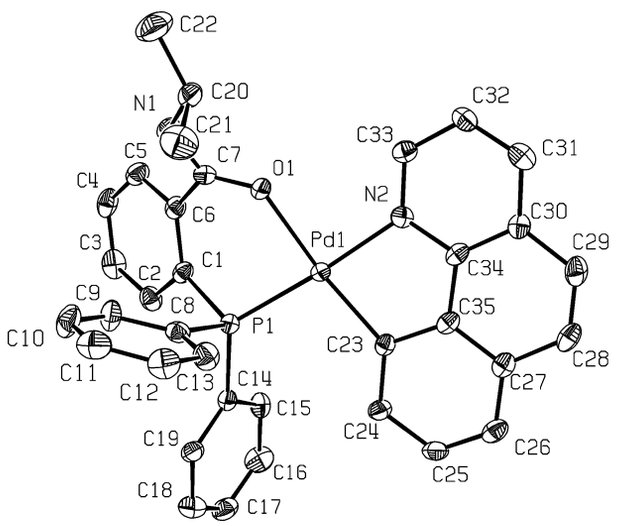
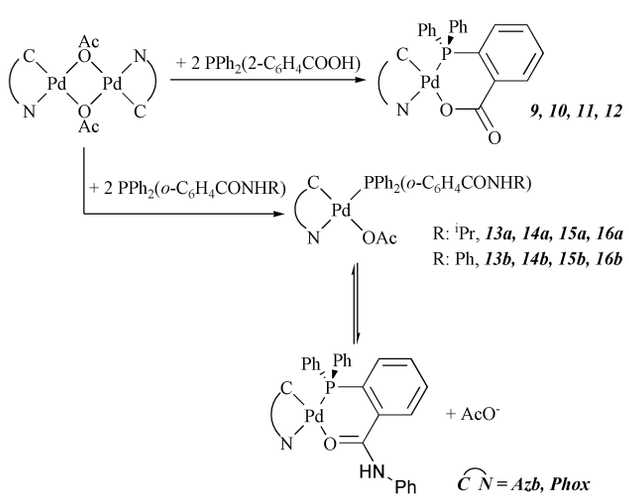


Fig. 2 An ORTEP representation of [Pd(Bzq)(*o*-Ph$_2$**P**C$_6$H$_4$C**O**–NH^{i}Pr)][PF$_6$], complex **7a**.

given in Table 2. As suggested by the IR data, the C(7)–O(1) distance of 1.261(6) Å is a bit longer in this compound with coordinated O(1) than in the other structures of this work in which ligand **a** acts as an η^1-phosphine. The Pd(1)–O(1) distance is shorter than those reported for related compounds containing a carbonyl group involved in P,O chelation to a palladium centre.[6]

The comparatively higher basicity of [{Pd(μ-AcO)(C^N)}$_2$] precursors make them useful in bridge splitting reactions with protic electrophiles,[40] and suggested a route to force a different coordination behaviour of the diphenylphosphine–benzamidate ligands. As a preliminary step in order to test this reactivity, and also to obtain the expected benzamidate hydrolysis products, we prepared the complexes [Pd(C^N)(*o*-Ph$_2$**P**C$_6$H$_4$C**OO**)] (**9**–**12**) by adding diphenylphosphinobenzoic acid to dichloromethane solutions of the corresponding [{Pd(μ-AcO)(C^N)}$_2$] starting material (Scheme 2). In the IR spectra of new complexes the carbonyl band appear at *ca*. 1700



Scheme 2 The preparation of complexes [Pd(C^N)(*o*-Ph$_2$**P**C$_6$H$_4$-C**OO**)] (**9**–**12**) and [Pd(C^N)(*o*-Ph$_2$**P**C$_6$H$_4$CO-NHR)(CH$_3$COO)] (**13a**–**16a**, **13b**–**16b**).

Table 3 Selected distances (Å) and angles (°) for complexes **10** and **11**

	10	**11**
Pd(1)–C(20)	1.996(2)	2.009(2)
Pd(1)–N(1)	2.0812(19)	2.082(4)
Pd(1)–O(1)	2.0985(15)	2.071(3)
Pd(1)–P(1)	2.2261(6)	2.2241(11)
C(20)–Pd(1)–N(1)	81.22(9)	82.08(18)
C(20)–Pd(1)–O(1)	169.62(8)	169.13(16)
N(1)–Pd(1)–O(1)	92.73(7)	87.95(7)
C(20)–Pd(1)–P(1)	100.61(7)	98.75(13)
N(1)–Pd(1)–P(1)	171.81(5)	178.93(12)
O(1)–Pd(1)–P(1)	86.57(5)	91.17(9)

cm^{-1}, and the most prominent peak observed in their FAB$^+$ spectra corresponds to M$^+$. Crystals of **10** (Fig. 3) and **11** (Fig. 4) suitable for X-ray analysis were grown by gas diffusion in chloroform–diethyl ether. In Table 3 are collected representative bond lengths and angles for both compounds. Distances in the palladium environment are very similar, as are those involving the carboxylate group. A different distortion of planar coordination is observed, being clearly tetrahedral for **10** and slightly square pyramidal for **11**.

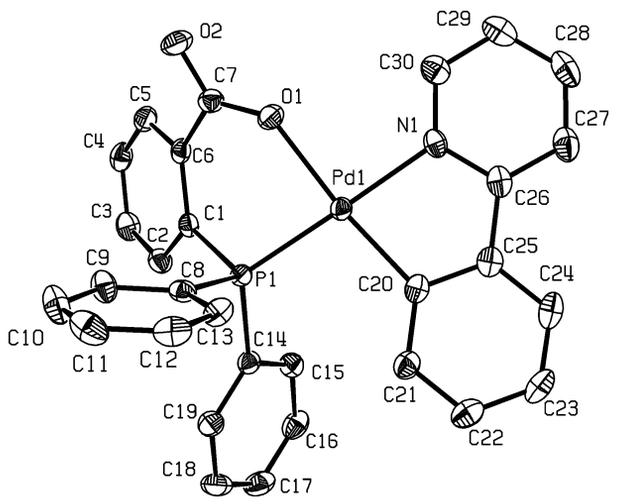


Fig. 3 An ORTEP representation of [Pd(Phpy)(*o*-$Ph_2PC_6H_4COO$)], complex **10**.

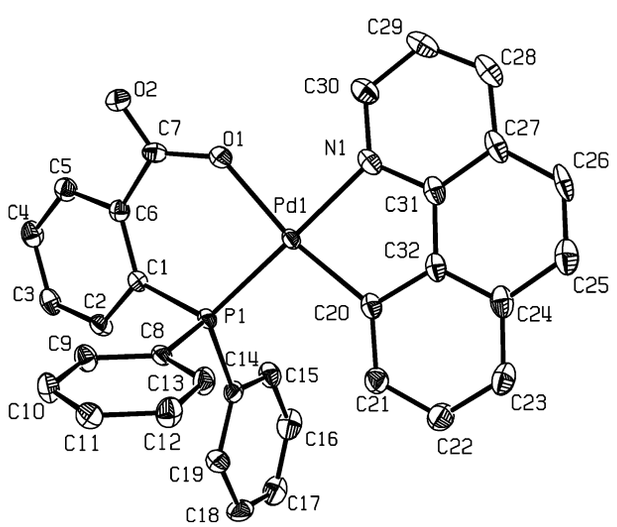


Fig. 4 An ORTEP representation of [Pd(Bzq)(*o*-$Ph_2PC_6H_4COO$)], complex **11**.

A different reaction, looking for amide deprotonation and hence a P,N-coordination mode in final compounds, was carried out between [{Pd(μ-AcO)(C^N)}$_2$] precursors and ligands **a** or **b** in a 1 : 2 molar ratio (Scheme 2). Nevertheless, [Pd(C^N)(*o*-Ph_2**P**C_6H_4CO-NHR)(CH_3COO)] compounds (**13a**–**16a**, **13b**–**16b**) containing a terminal acetate and diphenylphosphine–benzamidate ligands acting as P-monodentate were always obtained from these reactions. Thus, their IR spectra show a weak *ν*(NH) absorption and a complex carbonyl region with vibrations of both a free carbonyl fragment of the ligands and a terminal acetate coordinated to the Pd centre. The characterisation in the solid state was completed with the FAB mass spectrometry, that displays fragments at [M$^+$–CH_3COO], and the X-ray crystal structure determination of complex **16a**. The structure of [Pd(Phox)(*o*-Ph_2**P**C_6H_4CO–NH^{i}Pr)(CH_3COO)] is shown in Fig. 5 and selected bond lengths and angles are collected in Table 4. To date, just a few complexes containing *ortho*-palladated 2-(2-oxazolinyl)phenyl ligand and its derivatives have been crystallographically characterised.[42] The Pd–C and Pd–N bond lengths found for complex **16a** are longer than the values described previously. A slight square pyramidal distortion of the planar palladium environment is observed, with the Pd(1) atom displaced 0.0692(11) Å from a least-squares plane defined by the coordinated atoms. Intramolecular N(1)–H ··· O(3)$COCH_3$ hydrogen bonding is supported by the values of distance N(1) ··· O(3) (2.801 Å) and the angle N–H ··· O(3) of 172.55°. This interaction might be important to explain the equilibrium described next.[6] In solution, **13a**–**16a**, **14b** and **15b** compounds behave as expected from the solid state data: a sharp singlet around 43 ppm is observed in their $^{31}P\{^1H\}$-NMR spectra, while the ^{1}H NMR spectra show a resonance assignable to the NH proton and a broad signal corresponding to CH_3 protons in the acetate group. The presence of this group is also detected in the ^{13}C NMR spectra. However, the room temperature $^{31}P\{^1H\}$ NMR spectra of **13b** and **16b** in $CDCl_3$ consist of two singlets at *ca.* *δ* 43.5 and 35.5 (ratio: 65/35). This fact, together with an unclear duplicated aromatic region in their ^{1}H NMR spectra, suggests the presence in solution of two species in equilibrium (Scheme 2), as a result of the hemilability of ligand **b**. Thus, whereas the phosphorus atom stays firmly bonded to the metal, the amidic oxygen is involved in a process of coordination/dissociation, conferring on the ligand a behaviour of hemilabile P,O chelate.

Table 4 Selected distances (Å) and angles (°) for complex **16a**

Pd(1)–C(23)	2.025(3)	Pd(1)–O(3)	2.0897(19)
Pd(1)–N(2)	2.071 (2)	Pd(1)–P(1)	2.2521(8)
C(23)–Pd(1)–N(2)	81.21(11)	C(23)–Pd(1)–P(1)	97.25(9)
C(23)–Pd(1)–O(3)	171.26(10)	N(2)–Pd(1)–P(1)	173.71(7)
N(2)–Pd(1)–O(3)	90.09(9)	O(3)–Pd(1)–P(1)	91.31 (6)

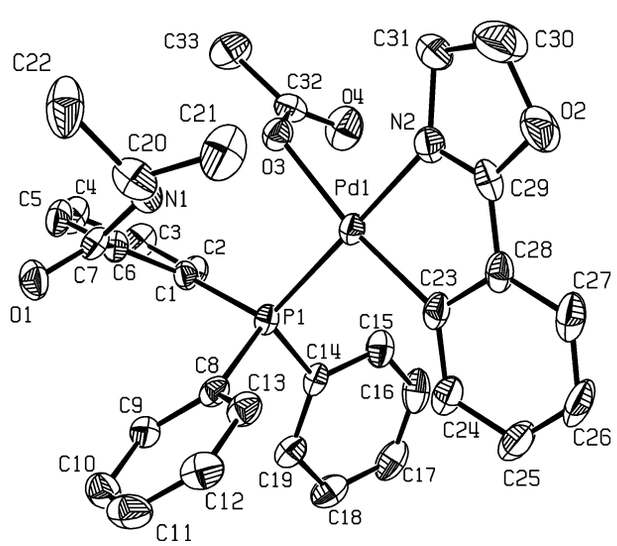
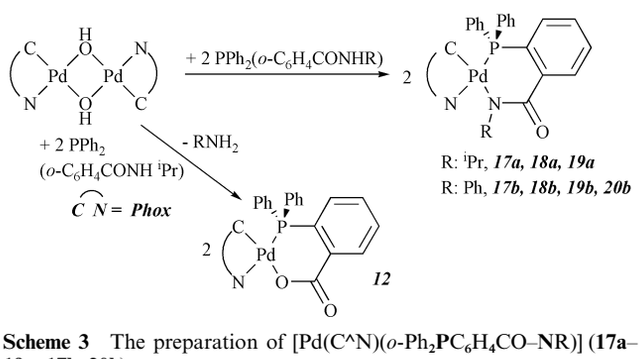


Fig. 5 The structure of [Pd(Phox)(*o*-Ph_2**P**C_6H_4CO–NH^{i}Pr)(CH_3-COO)], complex **16a**.

As CH_3COO^- displacement accompanies amide chelation, it was likely that the equilibrium was subjected to solvent dependence. Indeed, when the $^{31}P\{^1H\}$spectra were run in $(CD_3)_2CO$, a marked inversion in signal ratio is found (15/85), with predominance of the chelated ionic species. A similar result is obtained when the NMR was run in CD_3CN. Ligand hemilability is further proved when complex **13b** is treated with stoichiometric KSCN. The amide carbonyl group is then readily displaced as inferred from IR and $^{31}P\{^1H\}$-NMR data. A neat SCN absorption around 2100 cm^{-1}, and just one singlet resonance at δ 38.5 are observed, respectively. Since no analogous equilibria are detected in similar compounds with ligand **a**, a stronger chelation is attributable to it in comparison with **b**.

In order to induce amide deprotonation, the di-μ-hydroxo-complexes $[\{Pd(\mu\text{-}OH)(C\text{^}N)\}_2]$ were employed as starting materials in reactions with ligands **a** and **b**. The recognised basicity of such precursors and its usefulness in previous synthetic work prompt us to perform the reactions shown in Scheme 3 to prepare complexes [Pd(C^N)(*o*-Ph_2**P**C_6H_4CO–**N**R)] (**17a**–**19a**, **17b**–**20b**). The loss of both *ν*(NH) and *ν*(OH) bands in the IR spectra of new compounds with regards to those of the starting materials, together with the expected ^{1}H-NMR data, confirmed that the proposed reactions took place. A singlet at *ca.* 36 ppm characterises the $^{31}P\{^1H\}$-NMR spectra, and peaks assigned to M^+ are observed in FAB^+ spectrometry. Suitable crystals of complex **18a** (Fig. 6) were grown from dichloromethane–hexane confirming the proposed formulae. Selected bond lengths and angles are collected in Table 5. As far as we are aware (CSD version 5.24, updated April 2003), this is the first crystal structure in which a deprotonated phosphine–amide coordinates in a bidentate fashion to a metal centre *via* its P and N atoms.

It is noteworthy that a strong incompatibility between the 2-(2-oxazolinyl)phenyl hydroxo precursor and the diphenyl-



Scheme 3 The preparation of [Pd(C^N)(*o*-Ph_2**P**C_6H_4CO–**N**R)] (**17a**–**19a**, **17b**–**20b**).

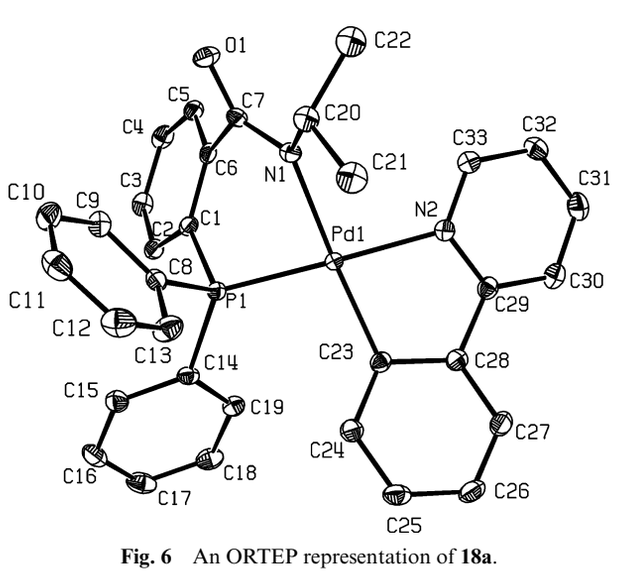


Fig. 6 An ORTEP representation of **18a**.

Table 5 Selected distances (Å) and angles (°) for complex **18a**

Pd(1)–C(23)	2.007(2)	Pd(1)–N(2)	2.1118(19)
Pd(1)–N(1)	2.1413(18)	Pd(1)–P(1)	2.2114(6)
C(23)–Pd(1)–N(2)	80.73(8)	C(23)–Pd(1)–P(1)	100.44(6)
C(23)–Pd(1)–N(1)	167.51(8)	N(2)–Pd(1)–P(1)	164.79 (5)
N(2)–Pd(1)–N(1)	98.11(7)	N(1)–Pd(1)–P(1)	83.97(5)

Table 6 Values of $|T_i|$ for each M–P-phenyl group in **3a**, **7a**, **10**, **11**, **16a** and **18a**[a]

	3a	**7a**	**10**	**11**	**16a**	**18a**
T_1	10.45	42.32	40.27	29.50	19.03	30.01
T_2	31.87	47.97	44.12	47.21	25.40	43.89
T_3	84.16	54.00	47.42	47.77	80.97	66.01

[a] The three Pd–P–C_{ipso}–C torsion angles (T_i, i = 1–3) which were in the range −90 to +90°, and they were ordered so that $T_1 < T_2 < T_3$.

phosphinobenzamide ligand **a** was found, preventing the obtention of complex **20a**. Instead of that, the product of hydrolysis **12** was isolated and characterised by several techniques as described in the experimental section. From this result, the strongest basic character of the precursors tested may be attributed to $[\{Pd(\mu\text{-}OH)(Phox)\}_2]$, being as expected the aliphatic benzamide **a** more inclined than **b** to experience hydrolysis.

The structural analyses of complexes **3a**, **7a**, **10**, **11**, **16a** and **18a** confirm the relative *cis*-position of the metallated carbon atom and the P atom of phosphino-amide ligands, with independence of its coordination mode. This is the typical arrangement of the phosphine group in cyclopalladated complexes due to the so-called *transphobia* effect.[43] The narrow NMC bite angle is also characteristic of *ortho*-metallated transition metal complexes,[44] and the values found in our crystal structures are in the expected range (see Tables 1–5). The Pd(1)–P(1) and Pd(1)–C(23) bond distances are a little longer in compounds **3a** and **16a** where ligand **a** adopts a P-monodentate coordination mode, and in the range of our previous data for related complexes.[45] The six new structures may be described as nearly planar, with rms values for the less square plane defined by the Pd and coordinated atoms in the range 0.0343–0.2261. The last value corresponds to complex **18a** that shows a moderate tetrahedral distortion from the ideal square-plane. Following the recent classification of Dance and Scudder[46] for PPh_3 based on measures of torsion angles M–P–C_{ipso}–C (Table 6), the conformation of Pd–$PPh_2C_6H_4$COR groups is described as *no rotor* for complexes **3a** and **16a**, and as *good rotor* for **7a**, **10**, **11** and **18a**. Compound **10** presents a set of T_i values very close to those which would have the ideal rotor ($T_1 = T_2 = T_3 = 44°$). The six membered chelated ring shows a distorted *screw-boat* conformation in **10** and **18a**, and a distorted *boat* conformation in **7a** and **11**, according to the classification of Allen and Taylor.[47]

Concluding remarks

The versatile coordination properties of phosphino-amide ligands *o*-$Ph_2PC_6H_4CONHR$ [R = ^{i}Pr (**a**), Ph (**b**)] have been stated by synthesising and characterising four series of cyclometallated palladium(II) complexes in which P-monodentate, P,O-bidentate or anionic P,N-bidentate coordination modes are displayed. A marked influence of the precursor employed in the final adopted pattern has been observed. Thus, a hemilabile behaviour of ligand **b** is just detected starting from μ-AcO precursors, while amide deprotonation is only achieved when μ-OH starting materials are used. It is interesting to note that stronger treatments, typically involving excess NEt_3,[48] alkoxide[35] or hydride bases,[49] are usually required to attain deprotonation in similar systems. In this sense, the hydroxo-bridged precursors reaffirm its unique characteristics. In this

study, both **a** and **b** ligands show similar properties although a more "rigid chelate" character can be conferred to **a** as no dynamic processes of its complexes have been found in solution. The crystal structure of six new complexes have been determined, confirming the proposed formulae and also providing an interesting comparative structural discussion.

Experimental

General

C, H, and N analyses were carried out with a Carlo Erba instrument. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer, using Nujol mulls between polyethylene sheets. NMR data (^{1}H, ^{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 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. Decomposition temperatures were determined on a Reichert microscope. Conductance measurements were performed with a Crison 525 conductimeter (in acetone solutions, 5×10^{-4} M). All the solvents were dried by conventional methods.

The cyclometallated precursors $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ and $[Pd(C\hat{}N)(\mu\text{-}OAc)]_2$, and $[Pd(C\hat{}N)(\mu\text{-}OH)]_2$ [C^N = phenylazophenyl (Azb), 2-phenylpyridine (Phpy), 7,8-benzoquinolyl (Bzq), and 2-(2-oxazolinyl)phenyl (Phox)] were prepared as described in the literature.[34,40,41] The diphenylphosphinobenzoic acid was purchased from Aldrich Chemical and used with further purification. The diphenylphosphinobenzamides *o*-$Ph_2PC_6H_4CONHR$ [R = ^{i}Pr (**a**), Ph (**b**)] were prepared according to reported procedures.[24]

Preparations

Complexes [Pd(C^N)(*o*-$Ph_2PC_6H_4CO$-NHR)(Cl)] [R = ^{i}Pr, C^N = phenylazophenyl (1a), 2-phenylpyridine (2a), 7,8-benzoquinolyl (3a) and 2-(2-oxazolinyl)phenyl (4a); R = Ph, C^N = phenylazophenyl (1b), 2-phenylpyridine (2b), 7,8-benzoquinolyl (3b), and 2-(2-oxazolinyl)phenyl (4b)]. The new complexes were obtained by treating $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ with previously prepared 2-diphenylphosphine-*N*-isopropylbenzamide (**a** compounds) or 2-diphenylphosphine-*N*-phenylbenzamide (**b** compounds) in molar ratio 2 : 1, using CH_2Cl_2 as solvent and according to the following general method. To a dichloromethane solution (10 mL) of the corresponding precursor $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ (60 mg) was added solid 2-diphenylphosphinebenzamide. The resulting solution was stirred for 30 min, filtered through a short Celite column and then concentrated to half volume under reduced pressure. Addition of hexane caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from dicholoromethane–hexane.

[Pd(Azb)(*o*-$Ph_2PC_6H_4CONH^iPr$)(Cl)] (**1a**) (0.085 g, 74%). Found: C, 60.9; H, 4.6; N, 6.3%. $C_{34}H_{31}ClN_3OPPd$ requires C, 60.9; H, 4.6; N, 6.3%. ν_{max}/cm^{-1}: (NH) 3388w; (CO) 1625s (Nujol). δ_H (400 MHz; $CDCl_3$): 1.07 (d, J_{HH} = 6.4 Hz, 6H, CH_3), 3.76 (m, 1H, CH), 6.40 (m, 1H), 6.73 (m, 1H), 6.90 (m, 1H), 7.18 (m, 1H), 7.34 (m, 1H), 7.40–7.70 (m, 14H), 7.87 (m, 2H), 8.04 (m, 2H), 9.61 (br, 1H, NH). δ_P ($CDCl_3$): 40.8 (s). FAB-MS (positive mode) *m*/*z*: 634 (M–Cl).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CONH^iPr$)(Cl)] (**2a**) (0.075 g, 56%). Found: C, 61.9; H, 4.8; N, 4.3%. $C_{33}H_{30}ClN_2OPPd$ requires C, 61.6; H, 4.7; N, 4.4%. ν_{max}/cm^{-1}: (NH) 3234s; (CO) 1644vs (Nujol). δ_H (400 MHz; $CDCl_3$): 1.12 (d, 6H, *J* = 6.0 Hz, CH_3), 3.51 (m, 1H, CH), 6.52 (m, 2H), 6.95 (m, 2H), 7.26–7.64 (m, 11H), 7.76–8.04 (m, 5H), 8.92 (m, 1H), 9.43 (br, 1H, NH). δ_P ($CDCl_3$): 43.1 (s). FAB-MS (positive mode) *m*/*z*: 607 (M–Cl).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONH^iPr$)(Cl)] (**3a**) (0.075 g, 60%). Found: C, 62.8; H, 4.6; N, 4.3%. $C_{35}H_{30}ClN_2OPPd$ requires C, 63.0; H, 4.5; N, 4.2%. ν_{max}/cm^{-1}: (NH) 3238s; (CO) 1649vs (Nujol). δ_H (400 MHz; $CDCl_3$): 1.10 (d, 6H, *J* = 6.6 Hz, CH_3), 3.41 (m, 1H, CH), 6.67 (m, 1H), 6.95 (m, 2H), 7.29–7.79 (m, 13H), 8.12 (m, 4H), 7.93 (br, 1H, NH), 8.35 (m, 1H), 8.79 (br, 1H, NH), 9.73 (m, 1H). δ_P ($CDCl_3$): 44.1 (s). FAB-MS (positive mode) *m*/*z*: 631 (M–Cl).

[Pd(Phox)(*o*-$Ph_2PC_6H_4CONH^iPr$)(Cl)] (**4a**) (0.083 g, 63%). Found: C, 58.4; H, 4.8; N, 4.6%. $C_{31}H_{30}ClN_2O_2PPd$ requires C, 58.6; H, 4.7; N, 4.4%. ν_{max}/cm^{-1}: (NH) 3374w; (CO) 1647vs (Nujol). δ_H (200 MHz; $CDCl_3$): 1.14 (d, J_{HH} = 6.4 Hz, 6H, CH_3), 3.29 (m, 1H, CH), 4.29 (t, 2H, J_{HH} = 9.6 Hz, NCH_2), 4.69 (t, 2H, *J* = 9.6 Hz, OCH_2), 6.31 (m, 1H), 6.54 (m, 1H), 6.87 (m, 2H), 7.12–7.46 (m, 10H), 7.85–7.99 (m, 4H), 8.59 (m, 1H). δ_P ($CDCl_3$): 43.9 (s). FAB-MS (positive mode) *m*/*z*: 600 (M–Cl).

[Pd(Azb)(*o*-$Ph_2PC_6H_4CONHPh$)(Cl)] (**1b**) (0.087 g, 67%). Found: C, 63.1; H, 4.0; N, 6.0%. $C_{37}H_{29}ClN_3OPPd$ requires C, 63.1; H, 4.1; N, 6.0%. ν_{max}/cm^{-1}: (NH) 3200w; (CO) 1675vs (Nujol). δ_H (400 MHz; $CDCl_3$): 6.32 (m, 1H), 6.59 (m, 1H), 6.97–7.54 (m, 19H), 7.86–7.99 (m, 7H), 10.40 (br, 1H, NH). δ_P ($CDCl_3$): 45.7 (s). FAB-MS (positive mode) *m*/*z*: 668 (M–Cl).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CONHPh$)(Cl)] (**2b**) (0.078 g, 55%). Found: C, 63.7; H, 4.1; N, 4.1%. $C_{36}H_{28}ClN_2OPPd$ requires C, 63.8; H, 4.2; N, 4.1%. ν_{max}/cm^{-1}: (NH) 3198w; (CO) 1690vs (Nujol). δ_H (200 MHz; $CDCl_3$): 6.40 (m, 2H), 6.87–7.08 (m, 5H), 7.27–7.58 (m, 16H), 7.74 (m, 1H), 7.94 (m, 1H), 9.69 (m, 1H), 10.57 (br, 1H, NH). δ_P ($CDCl_3$): 45.4 (s). FAB-MS (positive mode) *m*/*z*: 641 (M–Cl).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONHPh$)(Cl)] (**3b**) (0.086 g, 63%). Found: C, 65.2; H, 4.1; N, 3.8%. $C_{38}H_{28}ClN_2OPPd$ requires C, 65.1; H, 4.2; N, 4.0%. ν_{max}/cm^{-1}: (NH) 3172w; (CO) 1674vs (Nujol). δ_H (200 MHz; $CDCl_3$): 6.55 (m, 1H), 6.82 (m, 2H), 6.97 (m, 2H), 7.34–7.73 (m, 18H), 8.37 (m, 1H), 9.87 (m, 1H), 10.70 (br, 1H, NH). δ_P ($CDCl_3$): 45.7 (s). FAB-MS (positive mode) *m*/*z*: 665 (M–Cl).

[Pd(Phox)(*o*-$Ph_2PC_6H_4CONHPh$)(Cl)] (**4b**) (0.070 g, 55%). Found: C, 60.9; H, 4.2; N, 4.1%. $C_{34}H_{28}ClN_2O_2PPd$ requires C, 61.0; H, 4.2; N, 4.1%. ν_{max}/cm^{-1}: (NH) 3174w; (CO) 1667vs (Nujol). δ_H (200 MHz; $CDCl_3$): 4.29 (t, 2H, J_{HH} = 10.0 Hz, NCH_2), 4.81 (t, 2H, J_{HH} = 10.0 Hz, OCH_2), 6.28 (dd, 1H, *J* = 7.3, 4.4 Hz), 6.55 (t, 1H, *J* = 7.4 Hz), 6.84–7.04 (m, 3H), 7.15–7.57 (m, 14H), 7.99 (br, 4H), 10.58 (br, 1H, NH). δ_P ($CDCl_3$): 45.4 (s). FAB-MS (positive mode) *m*/*z*: 633 (M–Cl).

Complexes [Pd(C^N)(*o*-$Ph_2PC_6H_4CONHR$)][PF_6] [R = ^{i}Pr, C^N = phenylazophenyl (5a), 2-phenylpyridine (6a), 7,8-benzoquinolyl (7a) and 2-(2-oxazolinyl)phenyl (8a); R = Ph, C^N = phenylazophenyl (5b), 2-phenylpyridine (6b), 7,8-benzoquinolyl (7b), and 2-(2-oxazolinyl)phenyl (8b)]. The complexes were obtained by treating $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ with previously prepared 2-diphenylphosphine-*N*-isopropylbenzamide (**a** compounds) or 2-diphenylphosphine-*N*-phenylbenzamide (**b** compounds), in acetone (molar ratio 2 : 1) according to the following general method. To an acetone suspension (10 mL) of the precursor $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ (0.2 mmol) was added the stoichiometric amount of solid 2-diphenylphosphinebenzamide and KPF_6. After stirring for 30 min at room temperature, the solution was filtered through Celite 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 recrystallised from dicholoromethane–diethyl ether.

[Pd(Azb)(*o*-$Ph_2PC_6H_4CONH^iPr$)][PF_6] (**5a**) (0.137 g, 95%). Found: C, 52.5; H, 4.3; N, 5.3%. $C_{34}H_{31}F_6N_3OP_2Pd$ requires C, 52.4; H, 4.0; N, 5.4%. ν_{max}/cm^{-1}: (NH) 3377w; (CO) 1598vs, (PF_6) 849vs (Nujol). δ_H (200 MHz; $CDCl_3$): 1.20 (d, J_{HH} = 6.4 Hz, 6H, CH_3), 3.97 (m, 1H, CH), 6.18 (m, 1H), 6.64 (m, 1H), 6.77 (m, 1H), 7.10 (m, 1H), 7.29–7.57 (m, 15H), 7.94 (m, 1H), 8.07 (m, 2H), 8.26 (m, 1H), 8.97 (br, 1H, NH). δ_P ($CDCl_3$): 34.2 (s). FAB-MS (positive mode) *m*/*z*: 634 (M–PF_6).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CONH^iPr$)][PF_6] (**6a**) (0.075 g, 56%). Found: C, 52.9; H, 4.2; N, 3.9%. $C_{33}H_{30}F_6N_2OP_2Pd$ requires C, 52.6; H, 4.0; N, 3.7%. ν_{max}/cm^{-1}: (NH) 3372s; (CO) 1601vs, (PF_6) 842vs (Nujol). δ_H (200 MHz; $CDCl_3$): 1.06 (br, 6H, CH_3), 3.27 (m, 1H, CH), 6.26 (m, 1H), 6.53 (m, 1H), 6.75–7.02 (m, 3H), 7.18–7.55 (m, 14H), 7.64 (m, 1H), 7.79 (m, 1H), 8.25 (m, 1H), 8.78 (br, 1H, NH). δ_P ($CDCl_3$): 35.6 (s). FAB-MS (positive mode) *m*/*z*: 607 (M–PF_6).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONH^iPr$)][PF_6] (**7a**) (0.112 g, 77%). Found: C, 54.0; H, 4.1; N, 3.6%. $C_{35}H_{30}F_6N_2OP_2Pd$ requires C, 54.1; H, 3.9; N, 3.6%. ν_{max}/cm^{-1}: (NH) 3357s; (CO) 1593vs, (PF_6) 843vs (Nujol). δ_H (200 MHz; $CDCl_3$): 1.39 (br, 6H, CH_3), 3.34 (m, 1H, CH), 6.37 (m, 1H), 6.91 (m, 3H), 7.32–7.70 (m, 16H), 8.28 (m, 2H), 9.00 (br, 1H, NH). δ_P ($CDCl_3$): 35.7 (s). FAB-MS (positive mode) *m*/*z*: 631 (M–PF_6).

[Pd(Phox)(*o*-$Ph_2PC_6H_4CONH^iPr$)][PF_6] (**8a**) (0.141 g, 91%). Found: C, 50.0; H, 4.1; N, 3.6%. $C_{31}H_{30}F_6N_2O_2P_2Pd$ requires C, 50.0; H, 4.0; N, 3.7%. ν_{max}/cm^{-1}: (NH) 3371s; (CO) 1597vs, (PF_6) 813vs (Nujol). δ_H (200 MHz; $CDCl_3$): 1.00 (d, J_{HH} = 6.4 Hz, 6H, CH_3), 3.39 (m, 1H, CH), 4.04 (t, 2H, J_{HH} = 9.2 Hz, NCH_2), 4.74 (t, 2H, *J* = 9.2 Hz, OCH_2), 6.12 (dd, 1H, *J* = 7.5, 4.3 Hz), 6.61 (m, 1H), 6.75–6.93 (m, 2H), 7.27–7.52 (m, 13H), 8.20 (m, 1H). δ_P ($CDCl_3$): 33.5 (s). FAB-MS (positive mode) *m*/*z*: 599 (M–PF_6).

[Pd(Azb)(*o*-$Ph_2PC_6H_4CONHPh$)][PF_6] (**5b**) (0.142 g, 94%). Found: C, 54.5; H, 3.6; N, 5.3%. $C_{37}H_{29}F_6N_3OP_2Pd$ requires C, 54.6; H, 3.6; N, 5.1%. ν_{max}/cm^{-1}: (NH) 3370w; (CO) 1638s, (PF_6) 843vs (Nujol). δ_H (400 MHz; $CDCl_3$): 6.11 (m, 1H), 6.49 (m, 1H), 6.77 (m, 1H), 6.85–6.99 (m, 10H), 7.18 (m, 1H), 7.21–7.47 (m, 12H), 7.72 (m, 2H), 7.81 (m, 1H), 9.69 (br, 1H, NH). δ_P ($CDCl_3$): 39.9 (s). FAB-MS (positive mode) *m*/*z*: 665 (M–PF_6).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CONHPr$)][PF_6] (**6b**) (0.122 g, 76%). Found: C, 55.0; H, 3.7; N, 3.9%. $C_{36}H_{28}F_6N_2OP_2Pd$ requires C, 55.0; H, 3.6; N, 3.6%. ν_{max}/cm^{-1}: (NH) 3370s; (CO) 1671vs, (PF_6) 844vs (Nujol). δ_H (300 MHz; $CDCl_3$): 6.29 (m, 1H), 6.46 (m, 1H), 6.89–7.00 (m, 3H), 7.07 (m, 2H), 7.24 (m, 1H), 7.31–7.57 (m, 13H), 7.54–7.88 (m, 6H), 10.10 (br, 1H, NH). δ_P ($CDCl_3$): 41.7 (s). FAB-MS (positive mode) *m*/*z*: 641 (M–PF_6).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONHPh$)][PF_6] (**7b**) (0.141 g, 93%). Found: C, 56.1; H, 3.3; N, 3.3%. $C_{38}H_{28}F_6N_2OP_2Pd$ requires C, 56.3; H, 3.5; N, 3.4%. ν_{max}/cm^{-1}: (NH) 3360s; (CO) 1673vs, (PF_6) 841vs (Nujol). δ_H (400 MHz; $CDCl_3$): 6.55 (m, 1H), 6.8–6.99 (m, 5H), 7.30–7.99 (m, 19H), 8.40 (m, 1H), 9.83 (m, 1H). 10.66 (br, 1H, NH). δ_P ($CDCl_3$): 46.2 (s). FAB-MS (positive mode) *m*/*z*: 665 (M–PF_6).

[Pd(Phox)(*o*-$Ph_2PC_6H_4CONHPh$)][PF_6] (**8b**) (0.149 g, 92%). Found: C, 52.5; H, 3.6; N, 3.6%. $C_{34}H_{28}F_6N_2O_2P_2Pd$ requires C, 52.4; H, 3.6; N, 3.6%. ν_{max}/cm^{-1}: (NH) 3376s; (CO) 1598vs, (PF_6) 813vs (Nujol). δ_H (200 MHz; $CDCl_3$): 4.09 (m, 2H, NCH_2), 4.83 (t, 2H, J_{HH} = 9.3 Hz, OCH_2), 6.29 (dd, 1H, *J* = 7.5, 4.4 Hz), 6.75 (m, 1H), 6.92–7.34 (m, 4H), 7.49–7.81 (m, 16H), 8.21 (br, 1H), 9.51 (br, 1H, NH). δ_P ($CDCl_3$): 36.8 (s). FAB-MS (positive mode) *m*/*z*: 633 (M–PF_6).

Complexes [Pd(C^N)(*o*-$Ph_2PC_6H_4COO$)] [C^N = phenylazophenyl (9), 2-phenylpyridine (10), 7,8-benzoquinolyl (11) and 2-(2-oxazolinyl)phenyl (12)]

The complexes were obtained by treating [Pd(C^N)(μ-OAc)]$_2$ with 2-diphenylphosphinebenzoic acid (molar ratio 2 : 1) in dichloromethane according to the following general method. To a CH_2Cl_2 solution (10 mL) of the precursor [Pd(C^N)(μ-OAc)]$_2$ (0.2 mmol) was added solid 2-diphenylphosphinebenzoic acid (0.123 g, 0.4 mmol). The solution was then stirred for 30 min, and after that concentrated under reduced pressure to half volume. Addition of hexane caused precipitation of the new complexes, which were filtered off, air dried and recrystallized from dicholoromethane–diethyl ether.

[Pd(Azb)(*o*-$Ph_2PC_6H_4COO$)] (**9**) (0.032 g, 64%). Found: C, 62.5; H, 4.0; N, 4.5%. $C_{31}H_{23}N_2O_2PPd$ requires C, 62.8; H, 3.9; N, 4.7%. ν_{max}/cm^{-1}: (CO) 1720vs (Nujol). δ_H (200 MHz; $CDCl_3$): 6.24 (m, 1H), 6.68 (m, 1H), 6.81 (m, 1H), 7.13 (m, 1H), 7.31–7.58 (m, 15H), 7.98 (m, 1H), 8.18–8.23 (m, 2H), 8.36 (m, 1H). δ_P ($CDCl_3$): 34.7 (s). FAB-MS (positive mode) *m*/*z*: 593 (M^+).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4COO$)] (**10**) (0.045 g, 82%). Found: C, 63.9; H, 4.1; N, 2.3%. $C_{30}H_{22}NO_2PPd$ requires C, 63.7; H, 3.9; N, 2.5%. ν_{max}/cm^{-1}: (CO) 1642vs (Nujol). δ_H (200 MHz; $CDCl_3$): 6.35 (m, 1H), 6.56 (m, 1H), 6.92–7.00 (m, 2H), 7.41–7.70 (m, 14H), 8.04–8.10 (m, 2H), 8.33 (m, 1H), 8.98 (m, 1H). δ_P ($CDCl_3$): 35.0 (s). FAB-MS (positive mode) *m*/*z*: 566 (M^+).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4COO$)] (**11**) (0.044 g, 86%). Found: C, 65.3; H, 3.6; N, 2.5%. $C_{32}H_{22}NO_2PPd$: C, 65.1; H, 3.8; N, 2.4%. ν_{max}/cm^{-1}: (CO) 1714vs (Nujol). δ_H (200 MHz; $CDCl_3$): 6.40 (m, 1H), 6.90–7.00 (m, 2H), 7.33–7.69 (m, 16H), 8.31 (m, 1H), 8.49 (m, 1H), 9.28 (m, 1H). δ_P ($CDCl_3$): 35.8 (s). FAB-MS (positive mode) *m*/*z*: 590 (M^+).

[Pd(Phox)(*o*-$Ph_2PC_6H_4COO$)] (**12**) (0.045 g, 79%). Found: C, 60.1; H, 4.2; N, 2.7. $C_{28}H_{22}NO_3PPd$: C, 60.3; H, 4.0; N, 2.5%. ν_{max}/cm^{-1}: (CO) 1712vs (Nujol). δ_H (200 MHz; $CDCl_3$): 4.14 (t, 2H, J_{HH} = 9.4 Hz, NCH_2), 4.72 (t, 2H, *J* = 9.4 Hz, OCH_2), 6.19 (dd, 1H, *J* = 7.6, 4.4 Hz), 6.65 (m, 1H), 6.77–6.95 (m, 2H), 7.23–7.55 (m, 13H), 8.36 (m, 1H). δ_P ($CDCl_3$): 33.5 (s). FAB-MS (positive mode) *m*/*z*: 558 (M^+).

Complexes [Pd(C^N)(*o*-$Ph_2PC_6H_4CO$-NHR)(CH_3COO)] [R = ^{i}Pr, C^N = phenylazophenyl (13a), 2-phenylpyridine (14a),7,8-benzoquinolyl (15a), and 2-(2-oxazolinyl)phenyl (16a); R = Ph, C^N = phenylazophenyl (13b), 2-phenylpyridine (14b), 7,8-benzoquinolyl (15b), and 2-(2-oxazolinyl)phenyl (16b)].

The new complexes were obtained by treating [Pd(C^N)(μ-OAc)]$_2$ with previously prepared 2-diphenylphosphine-*N*-isopropylbenzamide (**a** compounds) or 2-diphenylphosphine-*N*-phenylbenzamide (**b** compounds) in molar ratio 2 : 1, using dichloromethane as solvent and according to the following general method. To a dichloromethane solution (10 mL) of the corresponding precursor [Pd(C^N)(μ-OAc)]$_2$ (60 mg) was added solid 2-diphenylphosphinebenzamide. The resulting solution was stirred for 30 min, and then concentrated to half volume under reduced pressure. Addition of hexane caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from dicholoromethane–hexane.

[Pd(Azb)(*o*-$Ph_2PC_6H_4CONH^iPr$)(CH_3COO)] (**13a**) (0.077 g, 64%). Found: C, 62.2; H, 4.9; N, 6.3%; $C_{36}H_{34}N_3O_3PPd$ requires C, 62.3; H, 4.9; N, 6.1%. ν_{max}/cm^{-1}: (NH) 3223w; (CO) 1680s, (CH_3COO) 1600s (Nujol). δ_H (200 MHz; $CDCl_3$): 1.06 (br, 6H, CH_3), 2.15 (br, 3H, CH_3COO) 3.36 (m, 1H, CH), 6.34 (m, 1H), 6.63 (m, 1H), 7.02–7.14 (m, 2H), 7.26 (m, 1H), 7.43–7.52 (m, 14H), 7.81–7.84 (m, 2H), 7.98 (dd, 2H, *J* = 7.6, 1.4 Hz), 8.92 (br, 1H, NH). δ_C ($CDCl_3$): 176.5 (s, COO), 41.8 (s, CH), 23.0 (s, CH_3COO), 22.3 (s, CH_3). δ_P ($CDCl_3$): 43.3 (s). FAB-MS (positive mode) *m*/*z*: 634 (M–CH_3COO).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CONH^iPr$)(CH_3COO)] (**14a**) (0.087 g, 69%). Found: C, 62.9; H, 4.8; N, 4.2%. $C_{35}H_{33}N_2O_3PPd$ requires C, 63.0; H, 5.0; N, 4.2%. ν_{max}/cm^{-1}: (NH) 3408w; (CO) 1594s, (CH_3COO) 1578s (Nujol). δ_H (200 MHz; $CDCl_3$): 1.02 (d, 6H, J_{HH} = 5.0 Hz, CH_3), 1.87 (br, 3H, CH_3COO), 3.42 (m, 1H, CH), 6.39 (m, 2H), 6.88 (m, 2H), 7.20 (m, 1H), 7.32–7.45 (m, 14H), 7.72–8.04 (m, 2H), 8.48 (m, 1H), 9.10 (br, 1H, NH). δ_C ($CDCl_3$): 176.9 (s, COO), 42.0 (s, CH), 23.3 (s, CH_3COO), 22.4 (s, CH_3). δ_P ($CDCl_3$): 42.9 (s). FAB-MS (positive mode) *m*/*z*: 607 (M–CH_3COO).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONH^iPr$)(CH_3COO)] (**15a**) (0.079 g, 65%). Found: C, 64.3; H, 4.9; N, 4.3%. $C_{37}H_{33}N_2O_3PPd$ requires C, 64.3; H, 4.8; N, 4.1%. ν_{max}/cm^{-1}: (NH) 3400w; (CO) 1612s, (CH_3COO) 1556s (Nujol). δ_H (200 MHz; $CDCl_3$): 1.05 (d, 6H, J_{HH} = 7.0 Hz, CH_3), 1.82 (br, 3H, CH_3COO) 3.40 (m, 1H, CH), 6.54 (m, 1H), 6.83 (m, 1H), 7.09–7.26 (m, 2H), 7.31–7.69 (m,

15H), 7.93 (br, 1H), 8.28 (m, 1H), 8.72 (m, 1H), 9.19 (br, 1H, NH). δ_C ($CDCl_3$): 176.9 (s, COO), 42.0 (s, CH), 23.2 (s, CH_3COO), 22.5 (s, CH_3). δ_P ($CDCl_3$): 43.2 (s). FAB-MS (positive mode) *m*/*z*: 631 (M–CH_3COO).

[Pd(Phox)(*o*-$Ph_2PC_6H_4CONH^iPr$)(CH_3COO)] (**16a**) (0.098 g, 77%). Found: C, 60.3; H, 4.9; N, 4.2%. $C_{33}H_{33}N_2O_4PPd$ requires C, 60.1; H, 5.0; N, 4.2%. ν_{max}/cm^{-1}: (NH) 3142w; (CO) 1675s, (CH_3COO) 1614s (Nujol). δ_H (200 MHz; $CDCl_3$): 1.16 (m, 6H, CH_3), 1.66 (br, 3H, CH_3COO) 3.42 (m, 1H, CH), 3.96 (t, 2H, J_{HH} = 9.2 Hz, NCH_2), 4.69 (t, 2H, J_{HH} = 9.4 Hz, OCH_2), 6.28 (dd, 1H, *J* = 7.5, 4.4 Hz), 6.55 (t, 1H, *J* = 7.5 Hz), 6.80–6.94 (m, 2H), 7.19 (m, 1H), 7.31–7.47 (m, 11H), 7.97 (br, 2H), 9.05 (br, 1H, NH). δ_C ($CDCl_3$): 178.4 (s, COO), 42.5 (s, CH), 21.5 (s, CH_3COO), 21.0 (s, CH_3). δ_P ($CDCl_3$): 43.4 (s). FAB-MS (positive mode) *m*/*z*: 599 (M–CH_3COO).

[Pd(Azb)(*o*-$Ph_2PC_6H_4CONHPh$)(CH_3COO)] (**13b**) (0.081 g, 64%). Found: C, 64.4; H, 4.5; N, 5.6%. $C_{39}H_{32}N_3O_3PPd$ requires C, 64.3; H, 4.4; N, 5.8%. ν_{max}/cm^{-1}: (NH) 3146w; (CO) 1677vs, (CH_3COO) 1605s (Nujol). FAB-MS (positive mode) *m*/*z*: 669 (M–CH_3COO).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CONHPh$)(CH_3COO)] (**14b**) (0.091 g, 69%). Found: C, 64.9; H, 4.2; N, 4.2%. $C_{38}H_{31}N_2O_3PPd$ requires C, 65.1; H, 4.4; N, 4.0%. ν_{max}/cm^{-1}: (NH) 3325w; (CO) 1597s, (CH_3COO) 1574s (Nujol). δ_H (200 MHz; $CDCl_3$): 1.31 (br, 3H, CH_3COO), 6.29 (m, 2H), 6.78–6.99 (m, 4H), 7.11–7.83 (m, 19H), 8.38 (m, 1H), 8.59 (m, 1H), 11.06 (br, 1H, NH). δ_C ($CDCl_3$): 177.0 (s, COO), 23.0 (s, CH_3COO). δ_P ($CDCl_3$): 44.1 (s). FAB-MS (positive mode) *m*/*z*: 642 (M–CH_3COO).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONHPh$)(CH_3COO)] (**15b**) (0.095 g, 75%). Found: C, 66.0; H, 4.5; N, 4.0%. $C_{38}H_{31}N_2O_3PPd$ requires C, 66.2; H, 4.3; N, 3.8%. ν_{max}/cm^{-1}: (NH) 3300w; (CO) 1672s, (CH_3COO) 1598s (Nujol). δ_H (200 MHz; $CDCl_3$): 1.27 (s, 3H, CH_3COO), 6.51 (m, 2H), 6.99 (m, 4H), 7.26–7.77 (m, 17H), 8.37 (m, 3H), 8.92 (m, 1H). 11.2 (br, 1H, NH). δ_C ($CDCl_3$): 176.9 (s, COO), 23.2 (s, CH_3COO). δ_P ($CDCl_3$) 43.6 (s). FAB-MS (positive mode) *m*/*z*: 666 (M–CH_3COO).

[Pd(Phox)(*o*-$Ph_2PC_6H_4CONH^iPr$)(CH_3COO)] (**16b**) (0.095 g, 71%). Found: C, 62.3; H, 4.3; N, 4.2%. $C_{33}H_{33}N_2O_4PPd$ requires C, 62.4; H, 4.5; N, 4.0%. ν_{max}/cm^{-1}: (NH) 3175w; (CO) 1675, (CH_3COO) 1621vs (Nujol). FAB-MS (positive mode) *m*/*z*: 634 (M–CH_3COO).

Complexes [Pd(C^N)(*o*-$Ph_2PC_6H_4CO$-NR)] [R = ^{i}Pr, C^N = phenylazophenyl (17a), 2-phenylpyridine (18a) and 7,8-benzoquinolyl (19a); R = Ph, C^N = phenylazophenyl (17b), 2-phenylpyridine (18b), 7,8-benzoquinolyl (19b), and 2-(2-oxazolinyl)phenyl (20b)]. The new complexes were obtained by treating [Pd(C^N)(μ-OH)]$_2$ with previously prepared 2-diphenylphosphine-*N*-isopropylbenzamide (**a** compounds) or 2-diphenylphosphine-*N*-phenylbenzamide (**b** compounds) in molar ratio 1 : 2, using dichloromethane as solvent and according to the following general method. To a dichloromethane solution (10 mL) of the corresponding precursor [Pd(C^N)(μ-OH)]$_2$ (60 mg) was added solid 2-diphenylphosphinebenzamide. The resulting solution was stirred for 30 min, filtered through a short Celite column and then concentrated to half volume under reduced pressure. Addition of hexane caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from dicholoromethane–hexane.

[Pd(Azb)(*o*-$Ph_2PC_6H_4CON^iPr$)] (**17a**) (0.115 g, 92%). Found: C, 64.4; H, 4.9; N, 6.6%. $C_{34}H_{30}N_3OPPd$ requires C, 64.4; H, 4.8; N, 6.6%. ν_{max}/cm^{-1}: (CO) 1545s (Nujol). δ_H (200 MHz; $CDCl_3$): 0.56 (d, 3H, *J* = 4.0 Hz, CH_3), 0.79 (d, 3H, *J* = 4.0 Hz, CH_3), 3.79 (m, 1H, CH), 6.58 (m, 2H), 6.85 (m, 1H), 7.16–7.26 (m, 3H), 7.36 (m, 3H), 7.36–7.59 (m, 10H), 7.90–7.93 (m, 2H), 7.98 (m, 1H). δ_P ($CDCl_3$): 35.7 (s). FAB-MS (positive mode) *m*/*z*: 634 (M^+).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CON^iPr$)] (**18a**) (0.120 g, 90%). Found: C, 65.4; H, 4.9; N, 4.8%. $C_{33}H_{29}N_2OPPd$ requires C, 65.3; H, 4.8; N, 4.6%. ν_{max}/cm^{-1}: (CO) 1537vs (Nujol). δ_H (200

Table 7 Crystal data and structure refinement for compounds **3a**, **7a**, **10**, **11**, **16a** and **18a**

	3a·MeOH	**7a**·1/2CH_2Cl_2	**10**·H_2O	**11**·2$CHCl_3$	**16a**·1/2CH_2Cl_2	**18a**
Formula	$C_{36}H_{34}ClN_2O_2PPd$	$C_{35.50}H_{31}ClF_6N_2OP_2Pd$	$C_{30}H_{24}NO_3PPd$	$C_{34}H_{24}Cl_6NO_2PPd$	$C_{33.50}H_{34}ClN_2O_4PPd$	$C_{33}H_{29}N_2OPPd$
Formula weight	699.47	819.41	583.87	828.61	701.45	606.95
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*21/*n*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*C*2/*c*	*P*21/*n*
a/Å	14.2424(7)	9.1497(6)	9.3790(5)	8.7881(7)	42.380(2)	10.7355(13)
b/Å	10.5660(5)	13.4993(8)	11.1515(7)	10.5776(8)	9.5746(7)	18.102(2)
c/Å	21.5403(10)	13.9376(8)	13.0729(6)	17.9300(14)	16.9787(11)	13.7074(17)
α/°	90	89.880 (4)	86.117(4)	95.713(1)	90	90
β/°	93.8840(10)	82.800(6)	73.468(4)	99.574(1)	109.315(4)	96.693(2)
γ/°	90	77.079 (5)	74.776(4)	95.302(1)	90	90
V/Å^3	3234.1(3)	1664.08(18)	1264.74(12)	1625.2(2)	6501.7(7)	2645.6(6)
Z	4	2	2	2	8	4
T/K	100(2)	173(2)	173(2)	100(2)	173(2)	100(2)
Reflections collected	19748	6148	4788	18989	8124	30299
μ/mm^{-1}	0.741	0.801	0.830	1.148	0.741	0.792
Independent reflections [*R*(int)]	7253 [0.0176]	5820 [0.0203]	4428 [0.0197]	7258 [0.0196]	5715 [0.0186]	6121 [0.0200]
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0389, 0.1094	0.0431, 0.1164	0.0228, 0.0577	0.0613, 0.1551	0.0306, 0.0731	0.0327, 0.0715
R_1, wR_2 (all data)	0.0412, 0.1113	0.0538, 0.1424	0.0268, 0.0589	0.0631, 0.1567	0.0444, 0.0767	0.0335, 0.0720

MHz; $CDCl_3$): 0.57 (d, 3H, J = 4.0 Hz, CH_3), 1.29 (d, 3H, J = 4.0 Hz, CH_3), 4.27 (m, 1H, CH), 6.58 (m, 2H), 6.71 (m, 1H), 7.02 (m, 1H), 7.12–7.22 (m, 3H), 7.33 (m, 3H), 7.48–7.57 (m, 7H), 7.73–7.85 (m, 3H), 8.39 (m, 1H), 8.52 (m, 1H). δ_P ($CDCl_3$): 36.7 (s). FAB-MS (positive mode) m/z: 607 (M^+).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONH^iPr$)(CH_3COO)] (**19a**) (0.09 g, 79%). Found: C, 66.8; H, 4.8; N, 4.3%. $C_{35}H_{29}N_2OPPd$ requires C, 66.6; H, 4.6; N, 4.4%. ν_{max}/cm^{-1}: (CO) 1539vs (Nujol). δ_H (200 MHz; $CDCl_3$): 1.14 (d, 6H, J_{HH} = 6.0 Hz, CH_3), 3.69 (m, 1H, CH), 6.62 (m, 2H), 6.95 (m, 3H), 7.33–7.79 (m, 9H), 7.92 (m, 6H), 8.37 (m, 2H). δ_P ($CDCl_3$): 37.1 (s). FAB-MS (positive mode) m/z: 631 (M^+).

[Pd(Azb)(*o*-$Ph_2PC_6H_4CONPh$)] (**17b**) (0.120 g, 95%). Found: C, 66.4; H, 4.0; N, 6.2%. $C_{37}H_{28}N_3OPPd$ requires C, 66.5; H, 4.2; N, 6.3%. ν_{max}/cm^{-1}: (CO) 1548s (Nujol). δ_H (300 MHz; $CDCl_3$): 6.53 (m,1H), 6.65–6.86 (m, 6H), 7.15 (m, 1H), 7.29–7.67 (m, 13H), 7.93 (m, 1H), 8.47 (m, 1H). δ_P ($CDCl_3$): 35.6 (s). FAB-MS (positive mode) m/z: 668 (M^+).

[Pd(Phpy)(*o*-$Ph_2PC_6H_4CONPh$)] (**18b**) (0.090 g, 60%). Found: C, 67.4; H, 4.3; N, 4.5%. $C_{36}H_{27}N_2OPPd$ requires C, 67.5; H, 4.2; N, 4.4%. ν_{max}/cm^{-1}: (CO) 1547vs (Nujol). δ_H (200 MHz; $CDCl_3$): 6.66 (m, 3H), 7.04 (m, 4H), 7.23 (m, 2H), 7.38–7.73 (m, 16H), 8.29 (m, 1H), 8.42 (m, 1H). δ_P ($CDCl_3$): 36.7 (s). FAB-MS (positive mode) m/z: 641 (M^+).

[Pd(Bzq)(*o*-$Ph_2PC_6H_4CONHPh$)] (**19b**) (0.05 g, 42%). Found: C, 68.8; H, 4.0; N, 4.3%. $C_{38}H_{27}N_2OPPd$ requires C, 68.6; H, 4.1; N, 4.2%. ν_{max}/cm^{-1}: (CO) 1546vs (Nujol). δ_H (200 MHz; $CDCl_3$): 6.73 (m, 3H), 7.01 (m, 1H), 7.26 (m, 2H), 7.40–7.80 (m, 16H), 8.11 (m, 1H), 8.48 (m, 2H). δ_P ($CDCl_3$): 36.8 (s). FAB-MS (positive mode) m/z: 665 (M^+).

[Pd(Phox)(*o*-$Ph_2PC_6H_4CONHPh$)] (**20b**) (0.104 g, 74%). Found: C, 64.3; H, 4.3; N, 4.2%. $C_{34}H_{27}N_2O_2PPd$ requires C, 64.5; H, 4.3; N, 4.4%. ν_{max}/cm^{-1}: (CO) 1596vs (Nujol). δ_H (300 MHz; $CDCl_3$): 2.94 (m, 2H, NCH_2), 4.38 (t, 2H, J_{HH} = 9.3 Hz, OCH_2), 6.43 (m, 1H), 6.66 (m, 2H), 6.91 (m, 2H), 7.19 (m, 3H), 7.41–7.56 (m, 14H), 8.44 (m, 1H). δ_P ($CDCl_3$): 35.8 (s). FAB-MS (positive mode) m/z: 633 (M^+).

Crystallography

Crystals suitable for a diffraction study were grown from dicholoromethane–hexane (complexes **3a**, **7a**, **10**, **16a** and **18a**) or chloroform–diethyl ether (complex **11**). Data collection for **3a**, **11** and **18a** 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 1371 (**3a**) and 2524 (**11** and **18a**) frames were collected at 0.3° intervals and 10 s $frame^{-1}$. The diffraction frames were integrated using the SAINT package[50] and corrected for absorption with SADABS.[51] Data collection for **7a**, **10** and **16a** was performed at −100 °C on a Siemens P4 diffractometer.

The structures were solved by direct (all the cases except **7a**) or heavy-atom methods[52] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms[52] (Table 7), for **3a** the solvent molecule was refined isotropically. Hydrogen atoms were introduced in calculated positions and refined during the last stages of the refinement. The highest residual peak (4.78 e $Å^{-3}$) in **11** is located at 1.343 Å from the carbon atom of a chloroform molecule. It was not possible to refine a different position for that molecule.

CCDC reference numbers 219141–219146.

See http://www.rsc.org/suppdata/dt/b3/b310843k/ for crystallographic data in CIF or other electronic format.

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References

1 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
2 G. R. Newkome, *Chem. Rev.*, 1993, **93**, 2067.
3 C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233.
4 P. Braustein and F. Naud, *Angew. Chem. Int. Ed.*, 2001, **40**, 680 and references therein.
5 G. M. Kapteijn, M. P. R. Spee, D. M. Grove, H. Kooijman, A. L. Spek and G. van Koten, *Organometallics*, 1996, **15**, 1405.
6 P. Braunstein, C. Frison, X. Morise and R. A. Adams, *J. Chem. Soc., Dalton Trans.*, 2000, 2205.
7 C. W. Rogers and M. O. Wolf, *Chem. Commun.*, 1999, 2297.
8 O. Clot, M. O. Wolf, G. P. A. Yap and B. O. Patrick, *J. Chem. Soc., Dalton Trans.*, 2000, 2729.
9 C. W. Rogers, Y. Zhang, B. O. Patrick, W. E. Jones Jr. and M. O. Wolf, *Inorg. Chem.*, 2002, **41**, 1162.
10 G. M. DiRenzo, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 6225.
11 E. K. van den Beuken, W. J. J. Smeets, A. L. Spek and B. L. Feringa, *Chem. Commun.*, 1998, 223.
12 A. Bacchi, M. Carcelli, M. Costa, A. Leporati, E. Leporati, P. Pelagatti, C. Pelizzi and G. Pelizzi, *J. Organomet. Chem.*, 1997, **535**, 107.
13 L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267.
14 B. Milani, L. Vicentini, A. Sommazzi, F. Garbassi, E. Chiarparin, E. Zangrando and G. Mestroni, *J. Chem. Soc., Dalton Trans.*, 1996, 3139.
15 A. Aeby and G. Consiglio, *J. Chem. Soc., Dalton Trans.*, 1999, 655.
16 J-X. Gao, T. Ikariya and R. Noyoro, *Organometallics*, 1996, **15**, 1087.
17 G. Sánchez, J. L. Serrano, M. A. Moral, J. Pérez, E. Molins and G. López, *Polyhedron*, 1999, **18**, 3057.
18 (*a*) G. Sánchez, J. L. Serrano, F. Ruiz and G. López, *J. Fluorine Chem.*, 1998, **91**, 165; (*b*) G. Sánchez, J. L. Serrano, F. Momblona, F. Ruiz, J. García, J. Pérez, G. López, P. A. Chaloner and P. Hitchcock, *Polyhedron*, 2001, **20**, 571.
19 (*a*) T. Satyanarayana and K. V. Reddy, *Transition Met. Chem.*, 1994, **19**, 283; (*b*) J. D. G. Correia, A. Domingos, A. Paulo and I. Santos, *J. Chem. Soc., Dalton Trans.*, 2000, 2477.
20 J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.*, 1998, **22**, 467.
21 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
22 W. Keim, *Angew. Chem., Int. Ed.*, 1990, **29**, 235.
23 M. Kuriyama, K. Nagai, K. Yamada, Y. Miwa, T. Taga and K. Tomioka, *J. Am. Chem. Soc.*, 2002, **124**, 8932.
24 T. Mino, K. Kashihara and M. Yamashita, *Tetrahedron: Asymmetry*, 2001, **12**, 287.
25 G. Sánchez, J. L. Serrano, J. García, G. López, J. Pérez and E. Molins, *Inorg. Chim. Acta*, 1999, **287**, 37.
26 G. Sánchez, F. Ruiz, M. D. Santana, G. García, G. López, J. A. Hermoso and M. Martínez-Ripoll, *J. Chem. Soc., Dalton Trans.*, 1994, 19.
27 J. Ruiz, V. Rodríguez, G. López, P. A. Chalonner and P. B. Hitchcock, *Organometallics*, 1996, **15**, 1662.
28 S. Kannan, A. J. James and P. R. Sharp, *Inorg. Chim. Acta*, 2003, **345**, 8.
29 L. Díez, P. Espinet and J. A. Miguel, *J. Chem. Soc., Dalton Trans.*, 2001, 1189.
30 G. Sánchez, J. A. Muñoz, M. J. Vidal, G. García and G. López, *J. Organomet. Chem.*, 1993, **463**, 239.
31 J. Ruiz, V. Rodríguez, G. López, P. A. Chalonner and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 1997, 4271.
32 G. Sánchez, J. L. Serrano, J. Pérez, M. C. Ramírez de Arellano, G. López and E. Molins, *Inorg. Chim. Acta*, 1999, **295**, 13.
33 G. Sánchez, J. L. Serrano, J. Pérez, M. C. Ramírez de Arellano and G. López, *Polyhedron*, 2000, **19**, 1395.
34 J. Ruiz, N. Cutillas, V. Rodríguez, J. Sampedro, G. López, P. A. Chalonner and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 1999, 2939.
35 M. B. Smith and A. M. Z. Slawin, *Inorg. Chim. Acta*, 2000, **299**, 172.
36 P. Bhattacharyya, T. Q. Ly, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 2001, **20**, 1803.
37 J. Vicente, A. Arcas, D. Bautista and M. C. Ramírez Arelllano, *J. Organomet. Chem.*, 2002, **603**, 164.
38 G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton and A. G. Orpen, *Chem. Commun.*, 1998, 653.
39 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
40 I. Aiello, A. Crispini, M. Ghedini, M. La Deda and F. Barigelletti, *Inorg. Chim. Acta*, 2000, **308**, 121.

41 I. P. Smoliakova, K. J. Keuseman, D. C. Haagenson, D. M. Wellmann, P. B. Colligan, N. A. Kataeva, A. V. Churakov, L. G. Kuz'mina and V. V. Dunina, *J. Organomet. Chem.*, 2000, **603**, 86.
42 D. L. Peterson, K. J. Keuseman, N. A. Kataeva, L. G. Kuz'mina, J. A. K. Howard, D. C. Haagenson, V. V. Dunina and I. P. Smoliakova, *J. Organomet. Chem.*, 2002, **654**, 66.
43 J. Vicente, J. A. Arcas, A. D. Farkland and M. C. Ramírez de Arellano, *Chem. Eur. J.*, 1999, **5**, 3066.
44 M. C. Etter and A. R. Siedle, *J. Am. Chem. Soc.*, 1983, **105**, 643.
45 J. L. Serrano, L. García, J. Pérez, E. Pérez, J. Vives, G. Sánchez, G. López, E. Molins and A. G. Orpen, *Polyhedron*, 2002, **21**, 1589.
46 I. Dance and M. Scudder, *J. Chem. Soc., Dalton Trans.*, 2000, 1579.
47 F. H. Allen and R. Taylor, *Acta Crystallogr.*, 1991, **B47**, 404.
48 N. G. Jones, M. L. H. Green, I. C. Vei, L. H. Rees, S. I. Pascu, D. Watkin, A. Cowley, X. Morise and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, 2002, 2491.
49 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian and J. Fisher, *J. Chem. Soc., Dalton Trans.*, 1995, 863.
50 SAINT, Bruker AXS Inc, Madison, WI, version 6.22.
51 G. M. Sheldrick, SADABS, Program for area detector adsorption correction, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
52 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997; G. M. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis, University of Göttingen, Germany, 1998, release 97-2.