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Reactivity of cyclometallated semicarbazone complexes of Pd(II): crystal and molecular structures of [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}(PPh$_3$)][ClO$_4$] and [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P*,*P*,*P*}][Cl]

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Abstract

Treatment of the cyclometallated complexes [Pd{4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)NH$_2$}(Cl)] (**a**), [Pd{C$_6$H$_4$C(Et)=NN(H)-C(=O)NH$_2$}(Cl)] (**b**) and [Pd{3,4-Me$_2$C$_6$H$_2$C(Me)=NN(H)C(=O)NH$_2$}(Cl)] (**c**) with tertiary monophosphine ligands in a complex–phosphine 1:1 molar ratio yielded [C, N] bonded cyclometallated complexes [Pd{4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)NH$_2$}-(Cl)(L)] (**1a**–**4a**), [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}(Cl)(L)] (**1b**–**4b**) and [Pd{3,4-Me$_2$C$_6$H$_2$C(Me)=NN(H)C(=O)NH$_2$}(Cl)(L)] (**1c**–**4c**), [L = PPh$_3$, PMePh$_2$, PEtPh$_2$ and PEt$_2$Ph]. Reaction of **a**, **b** and **c** with silver perchlorate, prior to the treatment with the monophosphine gave the [C, N, O] bonded cyclometallated complexes [Pd{4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)NH$_2$}-(L)][ClO$_4$] (**5a**–**8a**), [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}(L)][ClO$_4$] (**5b**–**8b**) and [Pd{3,4-Me$_2$C$_6$H$_2$C(Me)=NN(H)C(=O)NH$_2$}(L)]-[ClO$_4$] (**5c**–**8c**). Reaction of **a**, **b** and **c** with tertiary monophosphines in a complex–phosphine 1:2 ratio gave the C only bonded non-cyclometallated complexes [Pd{4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)NH$_2$}(PEt$_2$Ph)$_2$(Cl)] (**9a**), [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}-(PPh$_3$)$_2$(Cl)] (**9b**) and [Pd{3,4-Me$_2$C$_6$H$_2$C(Me)=NN(H)C(=O)NH$_2$}(PEt$_2$Ph)$_2$(Cl)] (**9c**). Treatment of **a**, **b** and **c** with the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine (trifos) yielded the non-cyclometallated complexes [Pd{4-[MeC$_6$H$_3$C-(Me)=NN(H)C(=O)NH$_2$}{L-*P*,*P*,*P*}][Cl] (**10a**), [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}{L-*P*,*P*,*P*}][Cl] (**10b**) and [Pd{3,4-Me$_2$C$_6$H$_2$C-(Me)=NN(H)C(=O)NH$_2$}{L-*P*,*P*,*P*}][Cl] (**10c**) (L = (Ph$_2$PCH$_2$CH$_2$)$_2$PPh). The complexes were characterised by their elemental analysis (C, H, N) and by IR and ^{31}P-{^{1}H} and ^{1}H-NMR spectroscopy. [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}(PPh$_3$)][ClO$_4$] (**5b**) and [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P*,*P*,*P*}][Cl] (**10b**) were characterised crystallographically. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclometallated; Semicarbazone; Palladium

1. Introduction

Since the first cyclometallated complex was synthesised, cyclometallation has become an important part of organometallic chemistry and several reviews covering the subject have appeared [1–5]. Cyclometallated compounds show important applications, such as their use in regiospecific organic and organometallic reactions [6], in insertion reactions [7] and in the synthesis of new metal mesogenic compounds [8] and catalytic materials [9]. Nitrogen donor ligands are known to undergo facile cyclometallation. In previous work, we have shown that potentially terdentate lignads such as Schiff bases [10,11], semicarbazones [12] and thiosemicarbazones

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[13] undergo facile metallation with palladium(II), palladium(0) and platinum(II) to give compounds with two five-membered fused rings at the metal centre (Fig. 1).

When [C, N, O] and [C, N, N] derivatives are treated with neutral ligands, such as tertiary phosphines cleavage of the oxygen–metal or of the nitrogen–metal bonds occurs prior to the ring-opening of the five-membered metallacycle upon continued reaction with the corresponding phosphine. If the cyclometallated compound is treated first with a silver(I) salt, the chloride ligand is removed from as silver chloride and the vacant co-ordination site is occupied by the phosphine. Reactivity of the [C, N, S] derivatives is clearly different to that shown by [C, N, O] and [C, N, N] derivatives. This stems from the distinct nature of the compounds. On the one hand, the semicarbazone compounds are usually mononuclear species **II** and the thiosemicarbazone ones are tetramers **III**, and on the other, the $Pd–S_{chelating}$ bond is sufficiently strong to hinder cleavage by nucleophiles; this always gives compounds with two fused five-membered rings at the metal. Herein, we report the reactivity of semicarbazone cyclometallated compounds which can be directed to cleavage of: (a) only the Pd–O bond; (b) the Pd–Cl bond with substitution of the chloride ligand; (c) the Pd–O and Pd–N bonds; and (d) the Pd–O, Pd–N and Pd–Cl bonds, simultaneously. The first three cases (a, b) and (c), may be modelled by reaction with tertiary monophosphines, and the last one (d), proceeds via reaction with triphosphines such as bis(2-diphenylphosphinoethyl)phenylphosphine (triphos). The crystal structures of two compounds pertaining to cases (b) and (d) are described; an interesting feature of the latter is the close contact, in the solid state, between the palladium atom and the imino nitrogen atom.

2. Results and discussion

2.1. Reactivity of the cyclometallated complexes

The compounds described in this paper were characterised by elemental analysis and by IR spectroscopy (data in Section 3) and by ^{1}H- and ^{31}P-$\{^{1}$H$\}$-NMR spectroscopy (Table 1).

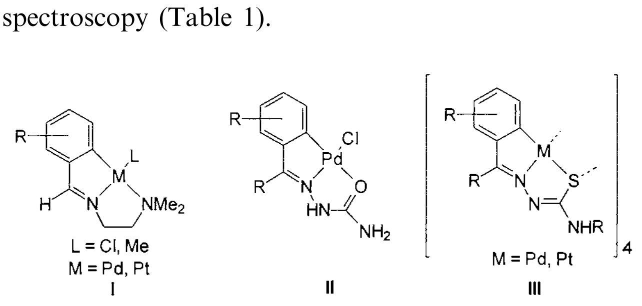


Fig. 1.

2.1.1. Pd–O bond cleavage

Treatment of the cyclometallated compounds **a**, **b** and **c** with tertiary monophosphines (see Scheme 1) in 1:1 molar ratio gave the complexes $[Pd\{4\text{-}MeC_6H_3C(Me)=NN(H)C(=O)NH_2\}(Cl)(L)]$ (**1a**–**4a**), $[Pd\{C_6H_4C(Et)=NN(H)C(=O)NH_2\}(Cl)(L)]$ (**1b**–**4b**) and $[Pd\{3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2\}(Cl)(L)]$ (**1c**–**4c**) [L = PPh_3, $PMePh_2$, $PEtPh_2$ and PEt_2Ph]. The compounds were pure air-stable solids which were fully characterised (see Section 3 and Table 1). The $\nu(C{=}O)$ stretching frequency was shifted from its position in the IR spectra of the starting material, **a**–**c**, to higher frequency, i.e. a value similar to the one in the free ligand. Also, the NH resonance in the ^{1}H-NMR spectra was shifted to lower frequency and its value was close to that in the spectra of the ligands. These findings are in accordance with the presence of an unco-ordinated C=O group formed upon Pd–O bond cleavage and opening of the PdNNCO ring [12,14].

The H5 proton resonance was shifted to a lower frequency and also showed coupling to the ^{31}P nucleus with ^{4}J(PH5) values in the range 5.2–6.4 Hz. The C(4)–Me signal in the ^{1}H-NMR spectra of compounds **1a**–**4a** and **1c**–**4c** showed a strong upfield shift, ca. 0.6 ppm, due to shielding by a phenyl ring from the phosphine [15]. This implies that the phosphine ligand is in a *cis* position to the metallated ring, thus placing the chloride ligand *trans* to the metallated carbon atom. Therefore, the incoming phosphine imposes a rearrangement of the co-ordinated atoms on the palladium metal. Further proof was given by the phosphorus resonance in the ^{31}P-$\{^{1}$H$\}$-NMR spectra, which was in accordance with a phosphorus-to-nitrogen *trans* geometry [16]; and also, by the ν(Pd–Cl) stretching mode, typical of a chloride ligand *trans* to a ligand of high *trans* influence such as the phenyl carbon atom.

2.1.2. Pd–Cl bond cleavage through chlorine abstraction

Treatment of compounds **a**, **b** and **c** with silver perchlorate followed by the appropriate tertiary monophosphine in 1:1 molar ratio gave the mononuclear compounds $[Pd\{4\text{-}MeC_6H_3C(Me)=NN(H)C(=O)NH_2\}(L)][ClO_4]$ (**5a**–**8a**), $[Pd\{C_6H_4C(Et)=NN(H)C(=O)NH_2\}(L)][ClO_4]$ (**5b**–**8b**) and $[Pd\{3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2\}(L)][ClO_4]$ (**5c**–**8c**) [L = PPh_3, $PMePh_2$, $PEtPh_2$ and PEt_2Ph] as air-stable solids which were fully characterised (see Section 3 and Table 1). They were 1:1 electrolytes as was shown by molar conductivity measurements in dry acetonitrile. Both the $\nu(C{=}O)$ stretching frequency in the IR spectra and the resonance assigned to the NH proton in the ^{1}H-NMR spectra were in agreement with Pd–O and Pd–N co-ordination [12,14] (see Section 3 and Table 1). Thus, the palladium atom is co-ordinated to the imine nitrogen atom and to the oxygen atom of the semicarbazone

Table 1
^{31}P- [a] and ^{1}H-NMR [b] data [c,d]

Compound	^{31}P	Aromatic	Others
Ligand [e]		7.60[d, 2H, H^2, H^6, 8.2 [f]]	8.80[br, 1H, NH]
		7.21[d, 2H, H^3, H^5, 8.2 [f]]	6.4[br, 2H, NH_2]
			2.38[s, 3H, Me]
			2.28[s, 3H, Me]
a [e]		6.83–7.15[m, 3H, H^2, H^3, H^5]	10.2[br, 1H, NH]
			2.21[s, 3H, Me]
			2.18[s, 3H, Me]
1a [e]	37.0 s	7.01[d, 1H, H^2, 7.7 [f]]	9.3[br, 1H, NH]
		6.74[d, 1H, H^3, 7.7 [f]]	6.7[br, 2H, NH_2]
		5.97[d, 1H, H^5, 5.4 [g]]	2.45[s, 3H, Me]
			1.70[s, 3H, Me [h]]
2a [e,k]	21.5 s	7.22[d, 1H, H^2, 7.5 [f]]	9.0[br, 1H, NH]
			6.9[br, 2H, NH_2]
		5.95[d, 1H, H^5, 6.2 [g]]	2.21[s, 3H, Me]
			1.66[s, 3H, Me [h]]
3a [e]	33.8 s	7.21[d, 1H, H^2, 7.7 [f]]	9.0[br, 1H, NH]
			6.7[br, 2H, NH_2]
		6.05[d, 1H, H^5, 5.8 [g]]	2.21[s, 3H, Me]
			1.64[s, 3H, Me [h]]
4a	33.0 s	7.17[d, 1H, H^2, 7.7 [f]]	9.8[br, 1H, NH]
		6.79[d, 1H, H^3, 7.7 [f]]	5.0[br, 2H, NH_2]
		6.18[d, 1H, H^5, 6.0 [g]]	2.42[s, 3H, Me]
			1.90[s, 3H, Me [h]]
5a	35.5 s	6.94[d, 1H, H^2, 7.7 [f]]	10.61[s, 1H, NH]
		6.76[d, 1H, H^3, 7.7 [f]]	5.1[br, 2H, NH_2]
		5.88[d, 1H, H^5, 5.0 [g]]	2.35[s, 3H, Me]
			1.74[s, 3H, Me [h]]
6a [k]	18.4 s	6.93[d, 1H, H^2, 7.7 [f]]	10.62[d, 1H, NH, 4.6 [m]]
		6.78[d, 1H, H^3, 7.7 [f]]	5.2[br, 2H, NH_2]
		6.00[d, 1H, H^5, 5.3 [g]]	2.32[s, 3H, Me]
			1.87[s, 3H, Me [h]]
7a	32.1 s	6.93[d, 1H, H^2, 7.7 [f]]	10.63[d, 1H, NH, 4.5 [m]]
		6.77[d, 1H, H^3, 7.7 [f]]	2.38[s, 3H, Me]
		5.99[d, 1H, H^5, 4.3 [g]]	1.78[s, 3H, Me [h]]
8a	32.2 s	6.90[d, 1H, H^2, 7.7 [f]]	10.62[d, 1H, NH, 4.4 [m]]
		6.76[d, 1H, H^3, 7.7 [f]]	5.8[br, 2H, NH_2]
		5.99[d, 1H, H^5, 5.0 [g]]	2.31[s, 3H, Me]
			1.83[s, 3H, Me [h]]
9a	8.1 s	6.88[d, 1H, H^2, 7.7 [f]]	8.9 [n][br, 1H, NH]
		6.63[d, 1H, H^3, 7.7 [f]]	4.8[br, 2H, NH_2]
		6.76[s, 1H, H^5]	2.08[s, 3H, Me]
			1.65[s, 3H, Me [h]]
10a	85.8 t		11.5[br, 1H, NH]
	41.3 d	6.59[d, 1H, H^3, 7.7 [f]]	5.5[br, 2H, NH_2]
		5.67[d, 1H, H^5, 6.9 [g]]	2.36[s, 3H, Me]
			1.57[s, 3H, Me [h]]
Ligand [e]		7.82[dd, 1H, H^2, 7.8 [f], 1.4 [i]]	9.64[br, 1H, NH]
		7.36[m, H^3, H^4, H^5, H^6,]	6.57[s, 2H, NH_2]
			2.72[q, 2H, Et, 7.5 [f]]
			1.19[t, 3H, Et, 7.5 [f]]
b [e]		7.3–6.9[m, 4H]	10.6 [br, 1H, NH]
			2.63[q, 2H, Et, 7.5 [f]]
			1.11[t, 3H, Et, 7.5 [f]]
1b	35.7 s	7.09[d, 1H, H^2, 7.4 [f]]	9.5 [n][br, 1H, NH]
		6.96[t, 1H, H^3, 7.4[f]]	6.82[n][s, 2H, NH_2]
		6.55[dt, 1H, H^4, 7.4 [f], 1.3 [i]]	2.91[q, 2H, Et, 7.6 [f]]
		6.20[dd, 1H, H^5, 7.4 [f], 6.2 [g]]	1.38[t, 3H, Et, 7.6 [f]]
2b [k]	20.3 s	7.21[d, 1H, H^2, 7.4 [f]]	9.0 [n][br, 1H, NH]
		6.96[t, 1H, H^3, 7.4 [f]]	6.7 [n][br, 2H, NH_2]
		6.63[t, 1H, H^4, 7.4 [f]]	2.87[q, 2H, Et, 7.5 [f]]
		6.38[dd, 1H, H^5, 7.4 [f], 5.8 [g]]	1.33[t, 3H, Et, 7.5 [f]]

Table 1 (Continued)

Compound	^{31}P	Aromatic	Others
3b	32.9 s	7.57[d, 1H, H^2, 7.5 [f]]	9.2 [n][br, 1H, NH]
		6.95[t, 1H, H^3, 7.5 [f]]	6.7 [n][br, 2H, NH_2]
		6.59[t, 1H, H^4, 7.5 [f]]	2.71[q, 2H, Et, 7.6 [f]]
		6.37[dd, 1H, H^5, 7.5 [f], 5.2 [g]]	1.16[t, 3H, Et, 7.6 [f]]
4b	32.3 s	7.13[dd, 1H, H^2, 7.4 [f], 1.3 [i]]	9.2 [n][br, 1H, NH]
		6.96[dt, 1H, H^3, 7.4 [f], 0.6 [i]]	6.7 [n][br, 2H, NH_2]
		6.63[dt, 1H, H^4, 7.4 [f], 1.3 [i]]	2.82[q, 2H, Et, 7.8 [f]]
		6.38[m, 1H, H^5, 7.4 [f], 0.6 [i], 5.2 [g]]	1.27[t, 3H, Et, 7.8 [f]]
5b	35.4 s	7.08[dd, 1H, H^2, 7.6 [f], 1.5 [i]]	10.72[d, 1H, NH, 4.7 [m]]
		6.98[dt, 1H, H^3, 7.6 [f], 0.7 [i]]	4.9[br, 2H, NH_2]
		6.58[dt, 1H, H^4, 7.6 [f], 1.5 [i]]	2.77[q, 2H, Et, 7.6 [f]]
		6.19[m, 1H, H^5, 7.6 [f], 0.7 [i], 5.3 [g]]	1.35[t, 3H, Et, 7.6 [f]]
6b [k]	18.7 s	7.08[d, 1H, H^2, 7.5 [f]]	10.7[br, 1H, NH]
		6.99[t, 1H, H^3, 7.5 [f]]	6.0[br, 2H, NH_2]
		6.70[t, 1H, H^4, 7.5 [f]]	2.75[q, 2H, Et, 7.6 [f]]
		6.32[dd, 1H, H^5, 7.5 [f], 6.4 [g]]	1.32[t, 3H, Et, 7.6 [f]]
7b	32.2 s	7.06[dd, 1H, H^2, 7.6 [f], 1.6 [i]]	10.9[br, 1H, NH]
		6.97[dt, 1H, H^3, 7.6 [f], 0.7 [i]]	6.0[br, 2H, NH_2]
		6.66[dt, 1H, H^4, 7.6 [f], 1.6 [i]]	2.78[q, 2H, Et, 7.7 [f]]
		6.30[m, 1H, H^5, 7.6 [f], 0.7 [i], 5.3 [g]]	1.34[t, 3H, Et, 7.7 [f]]
8b	32.6 s	7.06[dd, 1H, H^2, 7.6 [f], 1.8 [i]]	10.74[d, 1H, NH, 4.5 [m]]
		6.99[t, 1H, H^3, 7.6 [f]]	5.2[br, 2H, NH_2]
		6.73[dt, 1H, H^4, 7.6 [f], 1.8 [i]]	2.74[q, 2H, Et, 7.6 [f]]
		6.28[dd, 1H, H^5, 7.6 [f], 5.0 [g]]	1.33[t, 3H, Et, 7.6 [f]]
9b	9.0 s		9.5 [n][d, 1H, NH]
		6.92[t, 1H, H^3, 7.6 [f]]	6.81 [n][s, 2H, NH_2]
		6.52[dt, 1H, H^4, 7.6 [f], 1.1 [i]]	2.72[q, 2H, Et, 7.5 [f]]
		6.42[d, 1H, H^5, 7.6 [f]]	1.27[t, 3H, Et, 7.5 [f]]
10b	86.4 t		10.8[br, 1H, NH]
	41.4 d	6.82[t, 1H, H^3, 7.5 [f]]	5.3[br, 2H, NH_2]
		6.39[t, 1H, H^4, 7.5 [f]]	
		5.98[t, 1H, H^5, 7.5 [f], 7.5 [g]]	1.09[t, 3H, Et, 7.6 [f]]
Ligand [e]		7.45[s, 1H, H^2]	9.2[br, 1H, NH]
		7.40[d, 1H, H^6, 7.7 [f]]	6.4[br, 2H, NH_2]
		7.14[d, 1H, H^5, 7.7 [f]]	2.30[s, 3H, Me]
			2.29[s, 3H, Me]
			2.19[s, 3H, Me [h]]
c [e]		7.1–6.8 m	10.1[br, 1H, NH]
			2.17[s, 3H]
			2.13[br, 6H]
1c	36.0 s	6.87[s, 1H, H^2]	9.2 [n][br, 1H, NH]
		5.89[d, 1H, H^5, 5.4 [g]]	6.7 [n][br, 2H, NH_2]
			2.18[s, 3H, Me]
			2.08[s, 3H, Me]
			1.61[s, 3H, Me [h]]
2c [e,k]	21.0 s	7.11[s, 1H, H^2]	8.95[s, 1H, NH]
		5.90[d, 1H, H^5, 6.4 [g]]	6.7[br, 2H, NH_2]
			2.20[s, 3H, Me]
			2.02[s, 3H, Me]
			1.56[s, 3H, Me [h]]
3c [e]	33.7 s	7.11[s, 1H, H^2]	9.0[br, 1H, NH]
		5.99[d, 1H, H^5, 6.0 [g]]	6.7[br, 2H, NH_2]
			2.22[s, 3H, Me]
			2.02[s, 3H, Me]
			1.56[s, 3H, Me [h]]
4c [e]	32.1 s	7.08[s, 1H, H^2]	9.0[br, 1H, NH]
		6.06[d, 1H, H^5, 6.0 [g]]	6.7[br, 2H, NH_2]
			2.18[s, 3H, Me]
			2.03[s, 3H, Me]
			1.72[s, 3H, Me [h]]
5c	35.2 s	6.80[s, 1H, H^2]	10.58[d, 1H, NH, 4.3 [m]]
		5.81[d, 1H, H^5, 5.2 [g]]	4.3[br, 2H, NH_2]

Table 1 (Continued)

Compound	^{31}P	Aromatic	Others
			2.35[s, 3H, Me]
			2.10[s, 3H, Me]
			1.64[s, 3H, Me [h]]
6c [k]	18.8 s	6.80[s, 1H, H^2]	10.64[d, 1H, NH, 4.5 [m]]
		5.92[d, 1H, H^5, 5.3 [h]]	5.0[br, 2H, NH$_2$]
			2.33[s, 3H, Me]
			2.10[s, 3H, Me]
			1.67[s, 3H, Me [h]]
7c	33.3 s	6.79[s, 1H, H^2]	10.65[d, 1H, NH, 4.5 [m]]
		5.92[d, 1H, H^5, 5.1 [g]]	5.1[br, 2H, NH$_2$]
			2.34[s, 3H, Me]
			2.09[s, 3H, Me]
			1.79[s, 3H, Me [h]]
8c	32.3 s	6.79[s, 1H, H^2]	10.62[d, 1H, NH, 4.5 [m]]
		5.94[d, 1H, H^5, 5.0 [g]]	5.0[br, 2H, NH$_2$]
			2.32[s, 3H, Me]
			2.10[s, 3H, Me]
			1.83[s, 3H, Me [h]]
9c	8.36 s	6.65[s, 1H, H^2]	8.8 [n][br, 1H, NH]
		6.77[s, 1H, H^5]	4.5[br, 2H, NH$_2$]
			2.28[s, 3H, Me]
			2.19[s, 3H, Me]
			1.99[s, 3H, Me [h]]
10c	87.7 t		10.6[br, 1H, NH]
	43.0 d	5.56[d, 1H, H^5, 8.9 [g]]	5.1[br, 2H, NH$_2$]
			2.29[s, 3H, Me]
			2.03[s, 3H, Me]
			1.75[s, 3H, Me [h]]

[a] In $CDCl_3$ unless otherwise stated. Measured at 100.6 MHz (ca. ± 20°C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4.

[b] In $CDCl_3$ unless otherwise stated. Measured at 250 or 300 MHz; chemical shifts (δ) in ppm (± 0.01) to high frequency of $SiMe_4$.

[c] Coupling constants in Hz.

[d] s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt doublet of triplets; q, quadruplet; m, multiplet; br, broad. The metallated phenyl ring carbon atoms are numbered from 1 (semicarbazone functionality) to 6 (metallated carbon).

[e] In DMSO-d^6.

[f] $^3J(HH)$.

[g] $^4J(PH)$.

[h] C(4)–Me.

[i] $^4J(HH)$.

[k] $\delta(CH_3PPh_2) = 2.19$ d (**2a**), 2.11 d (**6a**), 2.14 d (**2b**), 2.10 d (**6b**), 2.18 d (**2c**), 2.10 d (**6c**); $^2J(CH_3P) = 10.5$ (**2a**), 9.4 (**6a**), 10.0 (**2b**), 9.7 (**6b**), 10.6 (**2c**), 10.4 (**6c**).

[m] $^4J(PNH)$.

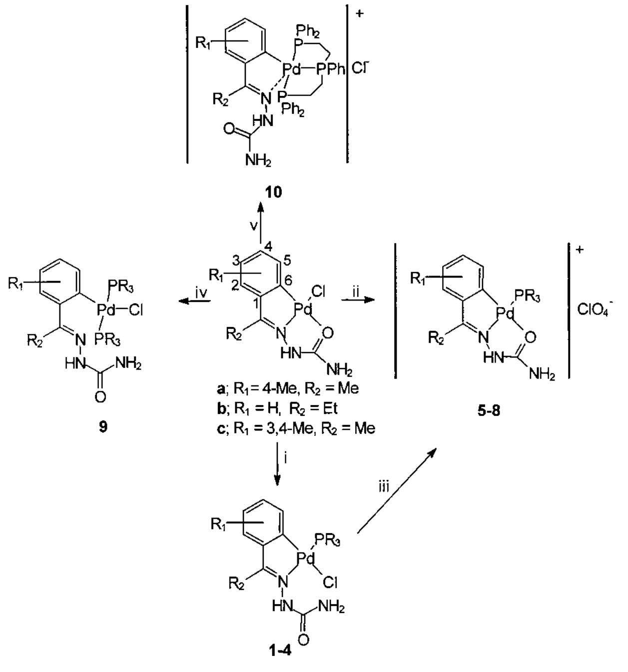
[n] Signal taken from a spectrum in DMSO-d^6.

ligand, giving compounds with two fused five-membered rings at the metal. The phosphine ligand occupies the fourth co-ordination site which was left vacant after the removal of the chloride ligand. The absence of the ν(Pd–Cl) stretching mode in the IR spectra of the complexes ascertains that chloride was removed quantitatively. The H5 proton resonance shows coupling to the ^{31}P nucleus, ca. 6.4–4.3 Hz, and was shifted to a lower frequency, in accordance with the above results.

An alternative route to the synthesis of these complexes was the treatment of compounds **1a**–**4a**, **1b**–**4b** or **1c**–**4c**, as appropriate, with silver perchlorate; upon removal of the chloride ligand, the oxygen atom occupies the vacant co-ordination site *trans* to carbon. The X-ray structure of complex **5a** was solved confirming the spectroscopic data.

2.1.3. Pd–O and Pd–N bond cleavage

Reaction of complexes **a**, **b** and **c** with tertiary monophosphines in a 1:2 ratio gave the non-cyclometallated complexes [Pd{4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)NH$_2$}(PEt$_2$Ph)$_2$(Cl)] (**9a**), [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}(PPh$_3$)$_2$(Cl)] (**9b**) and [Pd{3,4-Me$_2$C$_6$H$_2$C(Me)=NN(H)C(=O)NH$_2$}(PEt$_2$Ph)$_2$(Cl)] (**9c**). The ν(C=O) stretching frequency ca. 1690 cm^{-1} and the NH resonance of ca. 9.0 ppm seem to indicate that the Pd–O bond is absent in the complexes. Furthermore, no coupling of the H5 proton resonance to the ^{31}P nucleus was observed. This is attributable to cleavage of the Pd–N bond and consequent opening of the five-membered ring, so that, the metallated phenyl ring may rotate freely about the Pd–C bond bringing its plane at 90° to the palladium co-ordination plane [16]. A singlet resonance was observed in the $^{31}P-\{^1H\}$-NMR spectra of the complexes indicating a P–Pd–P *trans* geometry. Its value was strongly shifted to a lower frequency as compared to the compounds with the phosphine *trans* to the nitrogen, which reflects the stronger *trans* influence of phosphorus as opposed to nitrogen. These data point to complexes, where the Pd–O and Pd–N bonds have been cleaved, so that the organic ligand is bonded to the metal atom solely by the σPd–C bond. The Pd–Cl bond remains, but the chloride ligand has changed its co-ordination position from *cis* to carbon to *trans* to carbon, a geometry imposed by the incoming phosphine ligands.



Scheme 1. (i) PR_3 (acetone, 1:1 ratio); (ii) $AgClO_4$, PR_3 (acetone); (iii) $AgClO_4$; (iv) PR_3 (acetone, 1:2 ratio); (v) triphos (acetone).

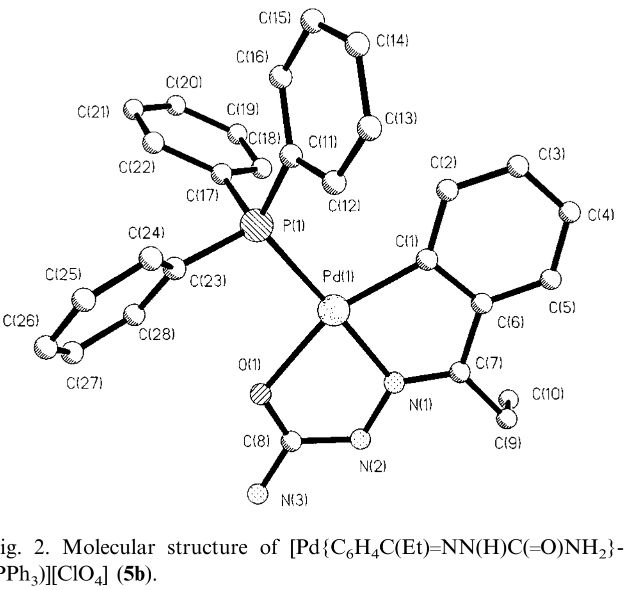


Fig. 2. Molecular structure of $[Pd\{C_6H_4C(Et)=NN(H)C(=O)NH_2\}(PPh_3)][ClO_4]$ (**5b**).

2.1.4. Pd–O, Pd–N and Pd–Cl bond cleavage

Treatment of **a**, **b** and **c** with the phosphine bis(2-diphenylphosphinoethyl)phenylphosphine in 1:1 molar ratio yielded the complexes $[Pd\{4\text{-}MeC_6H_3C(Me)=NN(H)C(=O)NH_2\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][Cl]$ (**10a**), $[Pd\{C_6H_4C(Et)=NN(H)C(=O)NH_2\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][Cl]$ (**10b**) and $[Pd\{3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2\}\{(Ph_2PCH_2\text{-}CH_2)_2PPh\text{-}P,P,P\}][Cl]$ (**10c**). The compounds were 1:1 electrolytes as shown by the conductivity measurements in dry acetonitrile. The phosphorus resonances in the $^{31}P-\{^1H\}$-NMR spectra were downfield shifted from their values in the free phosphine suggesting co-ordination of the phosphorus atoms to the metal centre. A triplet signal was assigned to the central ^{31}P nucleus, which was *trans* to the phenyl carbon atom, and a doublet was assigned to the two equivalent mutually *trans* phosphorus nuclei, which appeared at a lower frequency in accordance with the high *trans* influence of the phosphine ligand [17]. The H5 proton resonance was coupled to the central phosphorus nucleus only with ^4J(PH5) in the range 8.9–6.9 Hz; no coupling was observed between H5 and the two terminal phosphorus nuclei in accordance with the ca. 90° angle between the metallated phenyl ring and the palladium co-ordination plane. These observations agree with co-ordination of the palladium atom to the carbon atom and to three phosphorus atoms with subsequent Pd–O, Pd–N and Pd–Cl bond cleavage as shown by the value of the ν(C=O) stretching frequency and the absence of ν(Pd–Cl). Surprisingly, the NH resonance in the ^1H-NMR spectra showed a downfield shift from its value in the spectra of the free ligands. These findings were confirmed by the X-ray crystal structure resolution of one of the compounds, **10b**.

2.1.5. Crystal structure of $[Pd\{C_6H_4C(Et)=NN(H)C(=O)NH_2\}(PPh_3)][ClO_4]$ (5b)

Suitable crystals of the title compound were grown by slowly evaporating a chloroform solution. The molecular structure is illustrated in Fig. 2. Crystal data are given in the Table 2 and selected bond distances and angles with estimated standard deviations are shown in Table 3.

The crystal structure comprises the cation **5b**, a perchlorate ion and a chloroform molecule. The palla-

Table 2
Crystal data and structure refinement

	5b	**10b**
Formula	$C_{29}H_{28}N_3O_5PCl_4Pd$	$C_{46.63}H_{47.63}N_3OP_3Cl_{8.88}Pd$
M_r	777.71	1179.93
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
Cell dimensions		
a (Å)	11.2771(2)	38.364(8)
b (Å)	13.2373(1)	11.292(6)
c (Å)	22.2874(3)	25.122(5)
β (°)	96.6457(9)	90
V (Å^3)	3304.67(8)	10883(7)
Z	4	8
μ (mm^{-1})	0.975	0.902
Crystal size (mm)	0.60 × 0.50 × 0.40	0.64 × 0.40 × 0.30
$2\theta_{max}$ (°)	56	45
Reflections:		
collected	22784	7804
unique	7942 ($R_{int} = 0.13$)	6639 ($R_{int} = 0.04$)
Transmissions	1.00, 0.72	No absorption correction
No. of parameters	388	674
S	1.009	1.012
R [F, $I > 2\sigma(I)$]	0.0607	0.0721
wR [F^2, all data]	0.1605	0.1724
Max. Δ/σ	0.001	0.001
Max. ρ (e Å^{-3})	1.102	0.660

dium(II) atom is bonded to the aryl carbon C(1), the imine nitrogen N(1) and the oxygen O(1) of the semicarbazone ligand and to a phosphorus atom of the triphenylphosphine ligand P(1).

The Pd–N(1) bond distance of 2.017(4) Å is within the expected value based on the sum of the covalent radii [18] of palladium (1.31 Å) and nitrogen (sp^2) (0.7 Å) and similar to other distances reported [12,19]. The Pd–C(1), 2.002(5) and Pd(1)–P(1), 2.275(1) Å, bond distances are somewhat shorter than the values predicted from their covalent radii [18], but similar to values found earlier [12,19]. The Pd–O(1) bond distance (2.168(4) Å) is longer than the expected value of 1.97 Å, and shows the *trans* influence of the aryl carbon atom and similar to others reported [12]. The C(8)–O(1), 1.257(6) Å and N(1)–N(2), 1.374(6) Å bond distances are similar to the values found in non-co-ordinated semicarbazone ligands [20]. The sum of angles about the palladium atom is 359.99° with the only noteworthy deviation being the somewhat reduced [N(1)–Pd(1)–C(1)] bond angle consequent upon chelation.

The geometry around the palladium atom is planar (r.m.s. = 0.0118 Å; plane 1). The metallated ring [Pd, C(1), C(6), C(7), N(1)] and the co-ordination ring [Pd, N(1), N(2), C(8), O(1)] are also planar (r.m.s. = 0.0181 Å; plane 2) and (r.m.s. = 0.0145 Å; plane 3), respectively. Angles between planes are as follows: plane 1/plane 2 = 0.8°; plane 1/plane 3 = 2.3°; plane 2/plane 3 = 2.1°.

In the solid state the molecules of **5b** are bridged by the perchlorate counterion which forms hydrogen bonds with the thiosemicarbazone N(2) and N(3) hydrogen atoms (see Fig. 3) (N(2)–H(2A)···O(4), 2.827(9) Å, H(2A)···O(4), 1.97 Å, 158.5°; N(3)–H(3A)···O(3), 3.100(9) Å, H(3A)···O(3), 2.22 Å, 168.8°; N(3)–H(3B)···O(5), 3.177(12) Å, H(3B)···O(5), 2.31 Å, 161.0°; N(3)–H(3B)···O(2), 3.367(14), H(3B)···O(2), 2.57 Å, 148.5°). The H-bonded molecules are stacked in pseudo-parallel polymeric planes.

*2.1.6. Crystal structure of [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}{$(Ph_2PCH_2CH_2)_2PPh$-P,P,P}][Cl] (**10b**)*

Suitable crystals of the title compound were grown by slowly evaporating a chloroform solution. The molecular structure is illustrated in Fig. 4. Crystal data are given in the Table 2 and selected bond distances and angles with estimated standard deviations are shown in Table 3.

The structure of **10b** comprises two, almost identical, discrete [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}{$(Ph_2PCH_2CH_2)_2PPh$-*P*,*P*,*P*}]$^+$ cations, two chloride anions and five full-occupancy and one 25% occupancy chloroform solvent molecules. The palladium(II) is bonded to four atoms: three phosphorus from the terdentate bis(2-diphenylphosphinoethyl)phenylphosphine and to the *ortho* carbon atom of the semicarbazone. A short contact between the N(1) imino carbon atom and the palladium atom is observed (Pd(1)–N(1) and Pd(2)–N(1a) distances of 2.61(1) and 2.59(1)°, respectively) far from the Pd–N bond length of 2.23(2) Å in an authentic five-co-ordinate Pd(II) complex [21]. Such weak interactions in the range 2.576(4)–2.805(5) Å have been described before [22]. As a consequence of this interaction, the square planar geometry around the palladium atom is severely distorted.

The palladium atom is 0.486 Å out of the plane through P(1), P(2), P(3), C(5) (plane 1, r.m.s. = 0.0086 Å). C(5)–Pd(1)–P(2) and P(3)–Pd(1)–P(1) bond angles of 171.2(6) and 154.9(2)° show the mentioned distortion. The metallated phenyl ring is planar (C(5), C(6), C(7), C(8), C(9), C(10); plane 2, r.m.s. = 0.0080 Å) and forms an angle with plane 1 of 105.0°. The Pd(1)–C(5) bond length, 2.093(18) Å is longer than the Pd(1)–C(1), 2.002(5) bond distance as a consequence of the *trans* influence of the phosphorus atom. The Pd–P bond lengths (Pd(1)–P(1), 2.323(6) Å; Pd(1)–P(2), 2.283(6) Å; Pd(1)–P(3), 2.289(6) Å) are similar to those found in related Pd(II) complexes [23] and suggest that slightly partial double bond between the palladium an phosphorus atoms may exist [24].

The molecular units are stacked in dimers held together by intermolecular hydrogen bonding (see Fig. 5) between one amido hydrogen and the oxygen

Table 3
Selected bond distances (Å) and angles (°) for complexes **5b** and **10b**

	5b		**10b**		
Bond distances					
Pd(1)–C(1)	2.002(5)	Pd(1)–C(5)	2.09(1)	Pd(2)–C(5A)	2.07(2)
Pd(1)–N(1)	2.017(4)	Pd(1)–P(2)	2.283(6)	Pd(2)–P(2A)	2.298(7)
Pd(1)–O(1)	2.168(4)	Pd(1)–P(3)	2.289(6)	Pd(2)–P(1A)	2.311(6)
Pd(1)–P(1)	2.275(1)	Pd(1)–P(1)	2.323(6)	Pd(2)–P(3A)	2.332(6)
O(1)–C(8)	1.257(6)	Pd(1)–N(1)	2.61(1)	Pd(2)–N(1A)	2.59(1)
N(1)–C(7)	1.284(6)	N(1)–C(11)	1.24(2)	N(1A)–C(11A)	1.26(2)
N(1)–N(2)	1.374(6)	N(1)–N(2)	1.38(2)	N(1A)–N(2A)	1.39(2)
N(2)–C(8)	1.366(7)	N(2)–C(12)	1.39(3)	N(2A)–C(12A)	1.40(2)
N(3)–C(8)	1.321(7)	N(3)–C(12)	1.35(3)	N(3A)–C(12A)	1.35(3)
		O(1)–C(12)	1.20(3)	O(1A)–C(12A)	1.21(2)
Bond angles					
C(1)–Pd(1)–N(1)	81.0(2)	C(5)–Pd(1)–P(2)	171.2(6)	C(5A)–Pd(2)–P(2A)	170.4(6)
C(1)–Pd(1)–O(1)	157.6(2)	C(5)–Pd(1)–P(3)	96.0(5)	C(5A)–Pd(2)–P(3A)	93.4(6)
N(1)–Pd(1)–O(1)	76.6(2)	C(5)–Pd(1)–P(1)	91.4(6)	C(5A)–Pd(2)–P(1A)	94.8(6)
C(1)–Pd(1)–P(1)	101.0(2)	P(2)–Pd(1)–P(3)	84.3(2)	P(2A)–Pd(2)–P(1A)	84.2(2)
N(1)–Pd(1)–P(1)	177.1(1)	P(2)–Pd(1)–P(1)	84.9(2)	P(2A)–Pd(2)–P(1A)	84.2(2)
O(1)–Pd(1)–P(1)	101.3(1)	P(3)–Pd(1)–P(1)	154.9(2)	P(1A)–Pd(2)–P(3A)	154.3(2)
C(8)–O(1)–Pd(1)	111.6(4)	C(5)–Pd(1)–N(1)	70.7(6)	C(5A)–Pd(2)–N(1A)	72.8(6)
C(7)–N(1)–N(2)	124.2(4)	P(2)–Pd(1)–N(1)	117.1(4)	P(2A)–Pd(2)–N(1A)	116.1(4)
C(7)–N(1)–Pd(1)	120.1(3)	P(3)–Pd(1)–N(1)	117.0(4)	P(3A)–Pd(2)–N(1A)	87.3(4)
N(2)–N(1)–Pd(1)	115.7(3)	P(1)–Pd(1)–N(1)	88.0(4)	P(1A)–Pd(2)–N(1A)	118.4(4)
C(8)–N(2)–N(1)	114.7(4)	C(11)–N(1)–N(2)	119(2)	C(11A)–N(1A)–N(2A)	119(2)
C(2)–C(1)–C(6)	116.7(5)	N(2)–N(1)–Pd(1)	130(1)	N(2A)–N(1A)–Pd(2)	132(1)
		C(12)–N(2)–N(1)	121(2)	C(12A)–N(2A)–N(1A)	118(2)
		O(1)–C(12)–N(3)	125(2)	O(1A)–C(12A)–N(3A)	123(2)
		O(1)–C(12)–N(2)	122(2)	O(1A)–C(12A)–N(2A)	123(2)
		N(3)–C(12)–N(2)	112(2)	N(3A)–C(12A)–N(2A)	114(2)

(N(3)–H(3c)···O(1a), 2.98(2) Å, 179.4°; N(3A)–H(3a)···O(1), 2.93(2) Å, 178.5°).

3. Experimental

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

3.1. Materials and instrumentation

Solvents were purified by standard methods [25]. Chemicals were reagent grade. The phosphines PPh_3, $PMePh_2$, $PEtPh_2$, PEt_2PPh and $(Ph_2PCH_2CH_2)_2PPh$ (triphos) were purchased from Aldrich–Chemie. Compounds **a**, **b** and **c** were prepared according to procedures described elsewhere [12]. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo Erba Elemental Analyser, Model 1108. NMR spectra were obtained as $CDCl_3$ or DMSO-d^6 solutions and referenced to $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P-{^1H}) and were recorded on Bruker WM250, and AMX-300 spectrometers. All chemical shifts were reported downfield from standards.

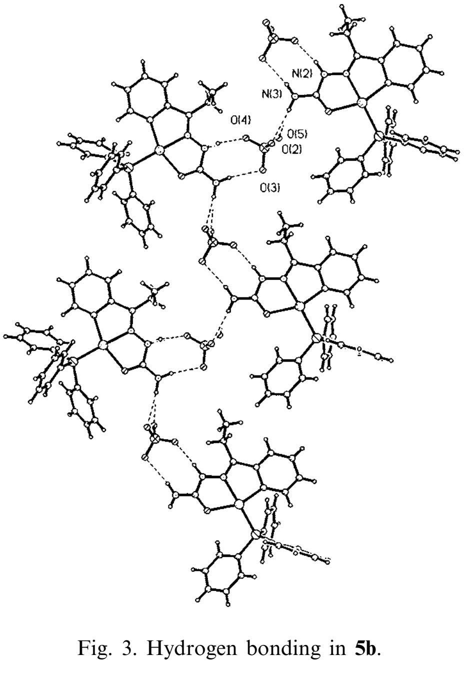


Fig. 3. Hydrogen bonding in **5b**.

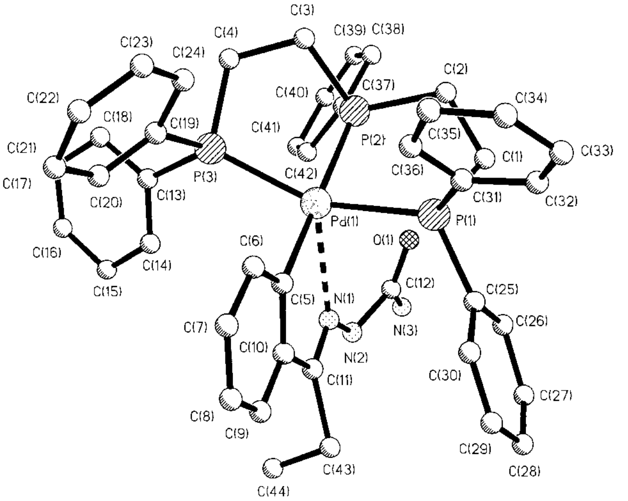


Fig. 4. Molecular structure of [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}-{(Ph_2P–$CH_2CH_2)_2PPh$-*P*,*P*,*P*}][Cl] (**10b**).

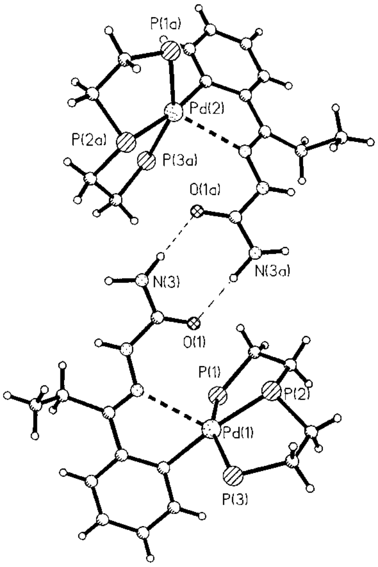


Fig. 5. Hydrogen bonding in **10b** (phenyl ring atoms have been omitted for clarity).

3.2. Preparations

3.2.1. Preparation of [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}(Cl)(PPh_3)] (*1a*)

PPh_3 (39 mg, 0.15 mmol) was added to a suspension of a (50 mg, 0.15 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h, the resulting white solid filtered off and dried in air. Yield 60% (Found: C, 56.3; H, 4.6; N, 7.3. $C_{28}H_{27}N_3OClPdP$ requires C, 56.6; H, 4.6; N, 7.1%); IR (ν_{max}/cm^{-1}) 1710 s (C=O), 1620 m (C=N), 290 w (Pd–Cl).

Compounds **2a**–**4a**, **1b**–**4b** and **1c**–**4c** were obtained following a similar procedure as white or pale yellow solids (**1a**, **1c** and **3c**).

3.2.2. [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}-(Cl)($PMePh_2$)] (*2a*)

Yield 62% (Found: C, 51.6; H, 4.5; N, 7.9. $C_{23}H_{25}N_3OClPdP$ requires C, 51.9; H, 4.7; N, 7.9%); IR (ν_{max}/cm^{-1}) 1709 s (C=O), 1604 m (C=N), 290 w (Pd–Cl).

3.2.3. [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}-(Cl)($PEtPh_2$)] (*3a*)

Yield 82% (Found: C, 53.1; H, 4.7; N, 7.9. $C_{24}H_{27}N_3OClPdP$ requires C, 53.8; H, 5.0; N, 7.7%); IR (ν_{max}/cm^{-1}) 1716 s (C=O), 1616 m (C=N), 290 w (Pd–Cl).

3.2.4. [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}-(Cl)(PEt_2Ph)] (*4a*)

Yield 79% (Found: C, 48.0; H, 5.5; N, 8.4. $C_{20}H_{27}N_3OClPdP$ requires C, 48.2; H, 5.4; N, 8.4%); IR (ν_{max}/cm^{-1}) 1713 s (C=O), 1608 m (C=N), 295 w (Pd–Cl).

3.2.5. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}-(Cl)(PPh_3)] (*1b*)

Yield 75% (Found: C, 56.6; H, 4.7; N, 7.0. $C_{28}H_{27}N_3OClPdP$ requires C, 56.6; H, 4.6; N, 7.1%); IR (ν_{max}/cm^{-1}) 1691 s (C=O), 1626 m (sh) (C=N), 285 w (Pd–Cl).

3.2.6. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}-(Cl)($PMePh_2$)] (*2b*)

Yield 67% (Found: C, 52.0; H, 4.6; N, 7.6. $C_{23}H_{25}N_3OClPdP$ requires C, 51.9; H, 4.7; N, 7.9%); IR (ν_{max}/cm^{-1}) 1690 s (C=O), 1629 m (C=N), 305 w (Pd–Cl).

3.2.7. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}-(Cl)($PEtPh_2$)] (*3b*)

Yield 81% (Found: C, 53.6; H, 4.8; N, 7.5. $C_{24}H_{27}N_3OClPdP$ requires C, 53.8; H, 5.0; N, 7.7%); IR (ν_{max}/cm^{-1}) 1713 s (C=O), 1627 m (C=N), 297w (Pd–Cl).

3.2.8. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}-(Cl)(PEt_2Ph)] (*4b*)

Yield 79% (Found: C, 47.9; H, 5.1; N, 8.4. $C_{20}H_{27}N_3OClPdP$ requires C, 48.2; H, 5.4; N, 8.4%); IR (ν_{max}/cm^{-1}) 1712 s(C=O), 1629 m (C=N), 280 w (Pd–Cl).

3.2.9. [Pd{3,4-$Me_2C_6H_2C(Me)$=NN(H)C(=O)NH_2}-(Cl)(PPh_3)] (*1c*)

Yield 69% (Found: C, 57.5; H, 4.5; N, 6.6. $C_{29}H_{29}N_3OClPdP$ requires C, 57.2; H, 4.8; N, 6.9%); IR (ν_{max}/cm^{-1}) 1710 s (C=O), 1614 m (sh) (C=N), 285 w (Pd–Cl).

3.2.10. [Pd{3,4-$Me_2C_6H_2C(Me)$=NN(H)C(=O)NH_2}(Cl)($PMePh_2$)] (**2c**)

Yield 91% (Found: C, 52.4; H, 5.2; N, 7.6. $C_{24}H_{27}N_3OClPdP$ requires C, 52.8; H, 5.0; N, 7.7%); IR (ν_{max}/cm^{-1}) 1722 s (C=O), 1610 w (C=N), 292 w (Pd–Cl).

3.2.11. [Pd{3,4-$Me_2C_6H_2C(Me)$=NN(H)C(=O)NH_2}(Cl)($PEtPh_2$)] (**3c**)

Yield 79% (Found: C, 53.8; H, 4.9; N, 7.3. $C_{25}H_{29}N_3OClPdP$ requires C, 53.6; H, 5.2; N, 7.5%); IR (ν_{max}/cm^{-1}) 1713 s (C=O), 1612 m (sh) (C=N), 280 w (Pd–Cl).

3.2.12. [Pd{3,4-$Me_2C_6H_2C(Me)$=NN(H)C(=O)NH_2}(Cl)(PEt_2Ph)] (**4c**)

Yield 80% (Found: C, 49.0; H, 5.4; N, 8.0. $C_{21}H_{29}N_3OClPdP$ requires C, 49.2; H, 5.7; N, 8.2%); IR (ν_{max}/cm^{-1}) 1720 s (C=O), 1618 m (C=N), 286 w (Pd–Cl).

3.2.13. Preparation of [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}(PPh_3)][ClO_4] (**5a**)

A suspension of **a** (50 mg, 0.15 mmol) in acetone (15 cm^3) was treated with silver perchlorate (32 mg) and stirred for 2 h. The solution was filtered through Celite to eliminate the AgCl precipitate. PPh_3 (39 mg, 0.15 mmol) was added to the filtrate and the solution stirred for 4 h, the solvent removed and the product recrystallised from dichloromethane–hexane to give the desired complex as a white solid. Yield 81% (Found: C, 50.5; H, 4.2; N, 6.4. $C_{28}H_{27}N_3O_5ClPdP$ requires C, 51.1; H, 4.1; N, 6.4%); IR (ν_{max}/cm^{-1}) 1655 s (C=O), 1640 s (sh) (C=N); specific molar conductivity, $\Lambda_m = 193\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

Compounds **6a**–**8a**, **5b**–**8b** and **5c**–**8c** were synthesised following a similar procedure as white or yellow (**7b**, **5c** and **6c**) solids.

3.2.14. [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}($PMePh_2$)][ClO_4] (**6a**)

Yield 92% (Found: C, 46.3; H, 4.2; N, 6.8. $C_{23}H_{25}N_3O_5ClPdP$ requires C, 46.3; H, 4.2; N, 7.0%); IR (ν_{max}/cm^{-1}) 1656 m (C=O), 1634 s (sh) (C=N); specific molar conductivity, $\Lambda_m = 213\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.15. [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}($PEtPh_2$)][ClO_4] (**7a**)

Yield 72% (Found: C, 47.4; H, 4.2; N, 6.6. $C_{24}H_{27}N_3O_5ClPdP$ requires C, 47.2; H, 4.5; N, 6.9%); IR (ν_{max}/cm^{-1}) 1655 s (C=O), 1634 s (sh) (C=N); specific molar conductivity, $\Lambda_m = 166\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.16. [Pd{4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2}(PEt_2Ph)][ClO_4] (**8a**)

Yield 65% (Found: C, 42.1; H, 4.9; N, 7.4. $C_{20}H_{27}N_3O_5ClPdP$ requires C, 42.7; H, 4.8; N, 7.5%); IR (ν_{max}/cm^{-1}) 1655 s (C=O), 1637 s (C=N); specific molar conductivity, $\Lambda_m = 193\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.17. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}(PPh_3)][ClO_4] (**5b**)

Yield 81% (Found: C, 51.5; H, 4.1; N, 6.4. $C_{28}H_{27}N_3O_5ClPdP$ requires C, 51.1; H, 4.1; N, 6.4%); IR (ν_{max}/cm^{-1}) 1649 m (C=O), 1626 m (sh) (C=N); specific molar conductivity, $\Lambda_m = 169\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.18. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}($PMePh_2$)][ClO_4] (**6b**)

Yield 92% (Found: C, 46.4; H, 4.1; N, 6.8. $C_{23}H_{25}N_3O_5ClPdP$ requires C, 46.3; H, 4.2; N, 7.0%); IR (ν_{max}/cm^{-1}) 1655 m (C=O), 1626 m (sh) (C=N); specific molar conductivity, $\Lambda_m = 183\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.19. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}($PEtPh_2$)][ClO_4] (**7b**)

Yield 72% (Found: C, 47.3; H, 4.5; N, 6.7. $C_{24}H_{27}N_3O_5ClPdP$ requires C, 47.2; H, 4.5; N, 6.9%); IR (ν_{max}/cm^{-1}) 1655 s (C=O), 1626 m (sh) (C=N); specific molar conductivity, $\Lambda_m = 170\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.20. [Pd{$C_6H_4C(Et)$=NN(H)C(=O)NH_2}(PEt_2Ph)][ClO_4] (**8b**)

Yield 65% (Found: C, 42.7; H, 4.7; N, 7.4. $C_{20}H_{27}N_3O_5ClPdP$ requires C, 42.7; H, 4.8; N, 7.5%); IR (ν_{max}/cm^{-1}) 1651 s (C=O), 1637 s (C=N); specific molar conductivity, Λ_m=175 $\Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.21. [Pd{3,4-$Me_2C_6H_2C(Me)$=NN(H)C(=O)NH_2}(PPh_3)][ClO_4] (**5c**)

Yield 83% (Found: C, 51.6; H, 4.3; N, 6.1. $C_{29}H_{29}N_3O_5ClPdP$ requires C, 51.8; H, 4.3; N, 6.2%); IR (ν_{max}/cm^{-1}) 1649 m (C=O), 1631 m (sh) (C=N); specific molar conductivity, $\Lambda_m = 200\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.22. [Pd{3,4-$Me_2C_6H_2C(Me)$=NN(H)C(=O)NH_2}($PMePh_2$)][ClO_4] (**6c**)

Yield 91% (Found: C, 46.9; H, 4.6; N, 6.7. $C_{24}H_{27}N_3O_5ClPdP$ requires C, 47.2; H, 4.5; N, 6.9%); IR (ν_{max}/cm^{-1}) 1655 s (C=O), 1635 m (sh) (C=N); specific molar conductivity, $\Lambda_m = 175\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.23. [Pd{3,4-$Me_2C_6H_2C(Me)$=NN(H)C(=O)NH_2}($PEtPh_2$)][ClO_4] (**7c**)

Yield 68% (Found: C, 48.1; H, 4.7; N, 6.7. $C_{25}H_{29}N_3O_5ClPdP$ requires C, 47.2; H, 4.5; N, 6.9%); IR (ν_{max}/cm^{-1}) 1651 s (C=O), 1632 m ν(C=N); specific molar conductivity, $\Lambda_m = 180\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.24. [Pd{3,4-$Me_2C_6H_2$C(Me)=NN(H)C(=O)NH_2}(PEt_2Ph)][ClO_4] (**8c**)

Yield 72% (Found: C, 44.0; H, 5.2; N, 7.1. $C_{21}H_{29}N_3O_5ClPdP$ requires C, 43.8; H, 5.1; N, 7.3%); IR (ν_{max}/cm^{-1}) 1655 s (C=O), 1633 s (C=N); specific molar conductivity, $\Lambda_m = 193\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.25. Preparation of [Pd{4-MeC_6H_3C(Me)=NN(H)-C(=O)NH_2}(PEt_2Ph)$_2$(Cl)] (**9a**)

PEt_2Ph (50 mg, 0.30 mmol) was added to a suspension of **a** (50 mg, 0.15 mmol) in dichloromethane (15 cm^3). The solution was stirred for 4 h. The solvent was removed and the product recrystallised from dichloromethane–hexane to give the desired complex as a pale yellow solid. Yield 87% (Found: C, 54.6; H, 6.2; N, 6.3. $C_{30}H_{42}N_3OClPdP_2$ requires C, 54.3; H, 6.4; N, 6.3%); IR (ν_{max}/cm^{-1}) 1680 s (C=O), 1581 m (sh) (C=N), 300 w ν(Pd–Cl).

Compounds **9b** and **9c** were synthesised following a similar procedure as white solids.

3.2.26. [Pd{C_6H_4C(Et)=NN(H)C(=O)NH_2}(PPh_3)$_2$(Cl)] (**9b**)

Yield 91% (Found: C, 64.5; H, 4.6; N, 4.8. $C_{46}H_{42}N_3OClPdP_2$ requires C, 64.5; H, 4.9; N, 4.9%); IR (ν_{max}/cm^{-1}) 1691 s (C=O), 1628 m (sh) (C=N), 295 w ν(Pd–Cl).

3.2.27. [Pd{3,4-$Me_2C_6H_2$C(Me)=NN(H)C(=O)NH_2}-(PEt_2Ph)$_2$(Cl)] (**9c**)

Yield 86% (Found: C, 54.8; H, 6.6; N, 6.6. $C_{31}H_{44}N_3OClPdP_2$ requires C, 54.9; H, 6.5; N, 6.2%); IR (ν_{max}/cm^{-1}) 1691 s (C=O), 1583 m (C=N), 273 w (Pd–Cl).

3.2.28. Preparation of [Pd{4-MeC_6H_3C(Me)=NN(H)C(=O)NH_2}{($Ph_2PCH_2CH_2$)$_2$PPh-P,P,P}][Cl] (**10a**)

To a suspension of **1a** (40 mg, 0.12 mmol) in dichloromethane (25 cm^3) ($Ph_2PCH_2CH_2$)$_2$PPh (64 mg, 0.12 mmol) was added and the mixture stirred at room temperature for 4 h. The solvent was removed and the product recrystallised from dichloromethane–hexane to give the desired complex as a white solid. Yield 88% (Found: C, 60.8; H, 5.1; N, 4.8. $C_{44}H_{45}N_3OClPdP_3$ requires C, 61.0; H, 5.2; N 4.8%); IR (ν_{max}/cm^{-1}) 1692 s (C=O), 1587 m (C=N); specific molar conductivity, $\Lambda_m = 104\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

Compounds **10b** and **10c** were obtained following a similar procedure as white solids.

3.2.29. [Pd{C_6H_4C(Et)=NN(H)C(=O)NH_2}-{($Ph_2PCH_2CH_2$)$_2$PPh-P,P,P}][Cl] (**10b**)

Yield 77% (Found: C, 61.2; H, 5.1; N, 4.8. $C_{44}H_{45}N_3OClPdP_3$ requires C, 61.0; H, 5.2; N 4.8%); IR (ν_{max}/cm^{-1}) 1691 s (C=O), 1585 m ν(C=N); specific molar conductivity, $\Lambda_m = 115\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.30. [Pd{3,4-$Me_2C_6H_2$C(Me)=NN(H)C(=O)NH_2}-{($Ph_2PCH_2CH_2$)$_2$PPh-P,P,P}][Cl] (**10c**)

Yield 77% (Found: C, 61.0; H, 5.5; N, 4.6. $C_{45}H_{47}N_3OClPdP_3$ requires C, 61.4; H, 5.5; N 4.8%); IR (ν_{max}/cm^{-1}) 1685 s (C=O), 1587 m (C=N); specific molar conductivity, $\Lambda_m = 112\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.3. Single-crystal X-ray diffraction analysis

3.3.1. Crystal structure determination of complex **5a**

Three-dimensional, room temperature X-ray data were collected in the θ range 2.88–28.00° on a Siemens Smart CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of data collected from frames each covering 0.3° in omega. Of the 22784 reflections measured, all of which were corrected from Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.7240 and 1.0000), 4256 independent reflections exceeded the significance level $|F|/\sigma|F| > 4.0$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in the calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0607$ ($wR_2 =$ 0.1605, for all 7942 data, 338 parameters, mean and maximum $\delta/\sigma = 0.000$, 0.001) with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -1.255 and 1.102 e Å^{-3}. The structure solution and refinement were carried out using the program package SHELX-97 [26].

3.3.2. Crystal structure determination of complex **10b**

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Nicolet R3 diffractometer by the omega scan method. Of the 7804 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 4694 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by blocked cascade least-squares methods on F^2. Hydrogen atoms were included in the calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0721$ ($wR_2 =$ 0.1724, for all 6639 unique data; 686 parameters, mean and maximum $\delta/\sigma = 0.000$, 0.002), with allowance for the thermal anisotropy of all palladium, phosphorus, nitrogen and whole occupancy chlorine atoms only. Geometric constrains were used in all chloroform solvent molecules. Minimum and maximum final electron density -0.456 and 0.660 e Å^{-3}. Complex scattering factors were taken from the program package SHELX-97 [26].

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre CCDC no. 132746 and 132747 for compounds **5b** and **10b**, respectively.

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