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Cylometallated semicarbazone complexes of palladium(II). Crystal and molecular structure of $[\{Pd[C_6H_4C(Et){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)][ClO_4]_2$

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Abstract

Treatment of the semicarbazones $4\text{-}MeC_6H_4C(Me){=}NN(H)C({=}O)NH_2$ **a**, $3,4\text{-}Me_2C_6H_3C(Me){=}NN(H)C({=}O)NH_2$ **b** and $C_6H_5C(Et){=}NN(H)C({=}O)NH_2$ **c**, gave the [C,N,O] cyclometallated compounds $[Pd\{4\text{-}MeC_6H_3C(Me){=}NN(H)C({=}O)NH_2\}(Cl)]$ **1a**, $[Pd\{3,4\text{-}Me_2C_6H_2C(Me){=}NN(H)C({=}O)NH_2\}(Cl)]$ **1b** and $[Pd\{C_6H_4C(Et){=}NN(H)C({=}O)NH_2\}(Cl)]$ **1c**, after C–H activation. Treatment of compounds **1a**, **1b**, and **1c** with silver perchlorate followed by treatment with tertiary diphosphine ligands gave the dinuclear [C,N,O] cyclometallated compounds $[\{Pd[4\text{-}MeC_6H_3C(Me){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}L)][ClO_4]_2$ **2a**–**7a**, $[\{Pd[3,4\text{-}Me_2C_6H_2C(Me){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}L)][ClO_4]_2$ **2b**–**7b**, $[\{Pd[C_6H_4C(Et){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}L)][ClO_4]_2$ **2c**–**7c**, [L = $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_2PPh_2$ (dppe), *trans*-$Ph_2PCH{=}CHPPh_2$ (*trans*-dppe), $Ph_2PC({=}CH_2)PPh_2$ (vdpp) and $Ph_2PCH_2PPh_2$ (dppm)] as 1:2 electrolytes. Reaction of **1a** and **1c** with diphosphines gave the dinuclear [C,N] cyclometallated compounds $[\{Pd[4\text{-}MeC_6H_3C(Me){=}NN(H)C({=}O)NH_2](Cl)\}_2(\mu\text{-}L)]$ **8a**, **9a**, $[\{Pd[C_6H_4C(Et){=}NN\text{–}(H)C({=}O)NH_2](Cl)\}_2(\mu\text{-}L)]$ **8c**, **9c**, [L = $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb)]. The complexes were characterised by their elemental analysis (C,H,N) and by IR and $^{31}P\{^1H\}$ and ^1H-NMR data, and $[\{Pd[C_6H_4C(Et){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)][ClO_4]_2$ **(3c)** was characterised crystallographically. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclometallated; Semicarbazone; Palladium

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1. Introduction

Since the first cyclometallated complex was described cyclometallation has become very important in organomeAtallic chemistry [1–5] and in associated areas such as in regioespecific organic and organometallic reactions [6], in insertion reactions [7], in the synthesis of new metal mesogenic compounds [8], and in catalytic materials [9]. Nitrogen-donor ligands are known to undergo facile metallation with formation of the classical five-membered metallacycle. Recently we have become interested in the synthesis and reactivity of palladium and platinum cyclometallated compounds with potentially terdentate [C,N,N] ligands and we have described some chemistry of these ligands related to their reactivity with tertiary phosphines and diphosphines [10] J.M. Vila, M. Gayoso, M.T. Pereira, M. López Torres, J.J. Fernández, A. Fernández, and J.M. Ortigueira (Unpublished results). It is our purpose to extend our research to the related terdentate [C,N,O] systems, in particular semicarbazones, which should produce cyclometallated complexes in which the ligand is bonded through carbon, nitrogen and oxygen, giving compounds with two fused rings; examples of other

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terdentate [C,N,O] systems have been reported [11–13]. In the present paper we report the synthesis and reactivity of new semicarbazone cyclometallated compounds with bonds at palladium to the aryl carbon, imine nitrogen and oxygen atoms. We considered that removal of the chlorine at palladium by treatment with silver perchlorate, should render a vacant coordination site which could be occupied by the phosphine giving compounds with the two fused rings intact, whereas treatment with the phosphine in the absence of the silver salt should give ring openning reactions, and this is what we have done. In either case novel dinuclear complexes may be obtained with the diphosphines $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2P(CH_2)_3PPh_2$ (dppp), $Ph_2P(CH_2)_2PPh_2$ (dppe), *trans*-$Ph_2PCH{=}CHPPh_2$ (*trans*-dppe), $Ph_2PC({=}CH_2)PPh_2$ (vdpp) and $Ph_2PCH_2PPh_2$ (dppm) bridging the two palladium centres. The X-ray crystal structure of one of these compounds is reported.

2. Results and discussion

2.1. Reactions of the ligands

The compounds described in this paper were characterised by elemental analysis and by IR spectroscopy (data in Section 3) and by ^1H and $^{31}P\{^1H\}$ (Table 1) and ^{13}C-NMR spectroscopy (for the free ligands and **1a**, **1b** and **1c** only; Section 3). Treatment of the semicarbazone ligands **a**, **b** or **c** with $Li_2[PdCl_4]$ in methanol gave compounds $[Pd\{4\text{-}MeC_6H_3C(Me){=}NN(H)C({=}O)NH_2\}(Cl)]$ **1a**, $[Pd\{3,4\text{-}Me_2C_6H_2C(Me){=}NN(H)C({=}O)NH_2\}(Cl)]$ **1b** and $[Pd\{C_6H_3C(Et){=}NN\text{–}(H)C({=}O)NH_2\}(Cl)]$ **1c**, respectively (Scheme 1). The metallated organic moiety is bonded to the palladium atom in each case through the aryl C6 carbon atom, the imine nitrogen atom, and the oxygen atom. The lower frequency shift of the $\nu(C{=}O)$ band is in accordance with coordination of the amide oxygen to the metal center ([14]a,b). The $\nu(PdCl)$ values confirm the *trans* geometry of the chlorine atom with respect to the imine nitrogen. The compounds were sufficiently soluble in DMSO-d_6, although some signals were broad in the ^1H-NMR spectra. Nevertheless, the NH resonance could be correctly assigned, and it is shifted to lower field in agreement with coordination of the C(=O)NH group to palladium [13]. This shift is not observed in compounds where the Pd–O bond has been cleaved (vide infra). The C=O, C=N, C1 and C6 resonances in the ^{13}C-NMR spectra are downfield shifted from those of the parent free ligands, confirming metallation and Pd–N coordination had taken place [15].

Treatment of compounds **1a**, **1b** and **1c** with silver perchlorate followed by the appropriate tertiary diphosphine in a 2:1 molar ratio gave the dinuclear compounds $[\{Pd[4\text{-}MeC_6H_3C(Me){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}L)][ClO_4]_2$ **2a–7a**, $[\{Pd[3,4\text{-}Me_2C_6H_2C\text{–}(Me){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}L)][ClO_4]_2$ **2b–7b**, $[\{Pd[C_6H_4C(Et){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}L)][ClO_4]_2$ **2c–7c**, [L = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb) $Ph_2PC((CH_2)PPh_2$ (vdpp) and *trans*-$Ph_2PCH{=}CHPPh_2$ (*trans*-dppe)], in which the diphosphine ligand bridges two metal centers which are in turn bonded to a terdentate semicarbazone [C,N,O] system. The compounds were pure air-stable solids, which were fully characterised (see Section 3 and Table 1); they are soluble in the more common organic solvents. They are 1:2 electrolytes as was shown by molar conductivity measurements in dry acetonitrile. The chlorine atom has been quantitatively removed as silver chloride, as is confirmed by the absence of the $\nu(PdCl)$ band in the IR spectra, to yield compounds with the metal center bonded to four different atoms in a square-planar environment. The H5 resonance shows a high-field shift and coupling to the ^{31}P atom (see Table 1); for compounds with dppe, dppp and dppb, this signal is a doublet or a doublet of doublets, as is the case; whereas in compounds with dppm, vdpp, and *trans*-dppe, the resonance appears as a multiplet. The $^1H\{^{31}P\}$ spectra brings the H5 resonance to a singlet in the **a** and **b** complexes, and to a doublet of doublets in the **c** complexes.

Treatment of compunds **1a**, **1b** and **1c** with the appropriate tertiary diphosphine in a 2:1 molar ratio gave the dinuclear compounds $[\{Pd[4\text{-}MeC_6H_3C(Me){=}NN(H)C({=}O)NH_2](Cl)\}_2(\mu\text{-}L)]$ **8a**, **9a**, $[\{Pd[C_6H_4C(Me){=}NN\text{–}(H)C({=}O)NH_2](Cl)\}_2(\mu\text{-}L)]$ **8c**, **9c**, [**8a**, **8c**: L = $Ph_2P(CH_2)_4PPh_2$ (dppp); **9a**: L = $Ph_2P(CH_2)_2PPh_2$ (dppe); **9c**: L = $Ph_2P(CH_2)_3PPh_2$ (dppp)], in which the diphosphine ligand bridges two metal centers which are bonded to a bidentate semicarbazone [C,N] system. The compounds were air-stable solids, which were fully characterised (see Section 3 and Table 1); compounds **8a** and **9a** were too insoluble for their NMR determination. The low values of the molar conductivity measurements in dry acetonitrile, precludes their formulation as electrolyte species. The $\nu(C{=}O)$ stretch clearly shows there is no Pd–O bond in the complexes; as proof, in **8c** and **9c** the NH resonance is not low field shifted with respect to the free ligand (vide supra). The shift of the $\nu(Pd\text{–}Cl)$ stretch towards lower wavenumbers suggests the chlorine atom is *trans* to the higher *trans* influence aryl carbon atom. Also noticable is the higher value of $^4J[PH(5)]$ in the ^1H-NMR spectra of **8c** and **9c** as compared to the analogous electrolyte compounds, **2c** and **3c**.

Reaction of compounds **8a**, **8c**, **9a**, **9c** with silver perchlorate gave removal of the chlorine ligand and rearrangement of the compounds to yield complexes **2a**, **2c**, **4a**, **3c**, respectively, with the palladium atom bonded to a terdentate [C,N,O] system.

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

Compound	31P	Aromatic	Others
a[e]		7.59[d, 2H, H^2, H^6, 8.3[f]] 7.19[d, 2H, H^3, H^5, 8.3[f]]	9.32[s, 1H, NH] 6.48[s, 2H, NH_2] 2.38[s, 3H, Me] 2.22[s, 3H, Me]
1a[e]		7.15–6.84 m	10.2[br, 1H, NH] 2.21[s, 3H, Me] 2.18[s, 3H, Me]
2a	32.1s	7.12[d,1H, H^2, 7.6[f]] 6.84[d, 1H, H^3, 7.6[f]] 6.08[d, 1H, H^5, 4.1[g]]	10.8[br, 1H, NH] 7.0[br, 2H, NH_2] 2.35[s, 3H, Me] 1.85[s, 3H, Me[h]]
3a	32.1s	7.12[d,1H, H^2, 7.8[f]] 6.82[d, 1H, H^3, 7.8[f]] 6.05[d, 1H, H^5, 5.0[g]]	10.8[br, 1H, NH] 7.0[br, 2H, NH_2] 2.36[s, 3H, Me] 1.80[s, 3H, Me[h]]
4a	32.9s	7.01[d,1H, H^2, 7.7[f]] 6.80[d, 1H, H^3, 7.7[f]] 5.57[d, 1H, H^5, 4.0[g]]	10.13[d, 1H, NH, 4.0[i]] 7.0[br, 2H, NH_2] 1.76[s, 3H, Me[h]]
5a	32.8s	7.12[d,1H, H^2, 8.0[f]] 6.85[d, 1H, H^3, 8.0[f]] 6.08[m, 1H, H^5]	10.8[br, 1H, NH] 6.9[br, 2H, NH_2] 2.38[s, 3H, Me] 1.79[s, 3H, Me[h]]
6a[k]	41.8s	7.05[d,1H, H^2, 7.6[f]] 6.81[d, 1H, H^3, 7.6[f]] 5.95[m, 1H, H^5]	10.6[br, 1H, NH] 6.8[br, 2H, NH_2] 2.34[s, 3H, Me] 1.78[s, 3H, Me[h]]
7a[l]	27.0s	6.86[d,1H, H^2, 7.7[f]] 6.52[d, 1H, H^3, 7.7[f]] 5.97[m, 1H, H^5]	10.8[br, 1H, NH] 2.37[s, 3H, Me] 1.60[s, 3H, Me[h]]
b[l]		7.45[s,1H, H^2] 7.40[d, 1H, H^6, 7.7[f]] 7.14[d, 1H, H^5, 7.7[f]]	9.25[s, 1H, NH] 6.47[s, 2H, NH_2] 2.30[s, 3H, Me] 2.29[s, 3H, Me] 2.19[s, 3H, Me]
1b[e]		7.1–6.8m	10.1[br, 1H, NH] 2.17[s, 3H, Me] 2.19[s, 3H, Me]
2b	28.5s	6.48[s,1H, H^2] 5.83[d, 1H, H^5, 5.1[f]]	10.5[br, 1H, NH] 6.8[br, 2H, NH_2] 2.35[s, 3H, Me] 2.08[s, 3H, Me] 1.77[s, 3H, Me[h]]
3b	32.2s	7.05[s,1H, H^2] 5.98[d, 1H, H^5, 5.0[f]]	10.7[br, 1H, NH] 6.4[br, 2H, NH_2] 2.37[s, 3H, Me] 1.74[s, 3H, Me[h]]
4b	32.5s	6.89[s,1H, H^2] 5.49[d, 1H, H^5, 5.3[f]]	10.14[d, 1H, NH, 4.2[i]] 6.9[br, 2H, NH_2] 1.69[s, 3H, Me[h]]
5b	36.7s	7.07[s,1H, H^2] 6.03[m, 1H, H^5]	10.8[br, 1H, NH] 6.9[br, 2H, NH_2] 2.41[s, 3H, Me] 2.12[s, 3H, Me] 1.72[s, 3H, Me[h]]
6b	42.2s	6.97[s,1H, H^2] 5.97[m, 1H, H^5]	10.5[m, 1H, NH] 6.6[br, 2H, NH_2] 2.31[s, 3H, Me] 2.13[s, 3H, Me] 1.63[s, 3H, Me[h]]
7b[l]	27.2s	6.75[s,1H, H^2] 5.87[m, 1H, H^5]	10.8[br, 1H, NH] 7.1[br, 2H, NH_2] 2.35[s, 3H, Me]

Table 1 (continued)

Compound	31P	Aromatic	Others
			1.95[s, 3H, Me]
			1.49[s, 3H, Me[h]]
c[e]		7.82[dd, 1H, H^2, 7.8[f], 1.4[m]]	9.64[s, 1H, NH]
		7.36[m, H^3, H^4, H^5, H^6]	6.57[s, 2H, NH_2]
			2.72[q, 2H, Et, 7.8[f]]
			1.19[t, 3H, Et, 7.8[f]]
1c[e]		7.3–6.9m	10.6[br, 1H, NH]
			2.63[q, 2H, Et, 7.5[f]]
			1.11[t, 3H, Et, 7.5[f]]
2c	33.1s	7.26[dd, 1H, H^2, 7.6[f], 1.3[m]]	11.1[s, 1H, NH]
		7.03[t, 2H, H^3, 7.6[f]]	7.1[s, 2H, NH_2]
		6.71[dt, 1H, H^4, 7.6[f], 1.3[m]]	2.84[q, 2H, Et, 7.6[f]]
		6.38[dd, 1H, H^5, 7.8[f], 5.2[g]]	1.25[t, 3H, Et, 7.6[f]]
3c	26.7s	7.30[dd, 1H, H^2, 7.6[f], 1.4[m]]	10.91[d, 1H, NH, 4.2[i]]
		7.05[t, 1H, H^3, 7.6[f]]	7.1[br, 2H, NH_2]
		6.73[dt, 1H, H^4, 7.6[f], 1.4[m]]	1.25[t, 3H, Et, 7.6[f]]
		6.39[dd, 1H, H^5, 7.8[f], 5.4[g]]	
4c	30.6s	7.20[dd, 1H, H^2, 7.6[f], 1.4[m]]	10.7[br, 1H, NH]
		7.02[t, 1H, H^3, 7.6[f]]	7.0[br, 2H, NH_2]
		6.62[dt, 1H, H^4, 7.6[f], 1.4[m]]	2.68[q, 2H, Et, 7.5[f]]
		6.13[dd, 1H, H^5, 7.6[f], 5.8[g]]	1.20[t, 3H, Et, 7.5[f]]
5c	31.8s	7.31[dd, 1H, H^2, 7.6[f], 1.4[m]]	10.9[br, 1H, NH]
		7.05[t, 1H, H^3, 7.6[f]]	7.0[br, 2H, NH_2]
		6.64[dt, 1H, H^4, 7.6[f], 1.4[m]]	1.20[t, 3H, Et, 7.6[f]]
		6.35[m, 1H, H^5, 7.6[f]]	
6c[j,k]	30.95s	7.0–6.9[m, 2H, H^2, H^3]	10.4[br, 1H, NH]
		6.46[dt, 1H, H^4, 7.6[f], 1.7[m]]	5.2[br, 2H, NH_2]
		5.95[m, 1H, H^5, 7.6[f]]	2.63[q, 2H, Et, 7.6[f]]
			1.22[t, 3H, Et, 7.6[f]]
7c[l]	21.1s	6.95[d, 1H, H^2, 7.6[f]]	11.0[br, 1H, NH]
		6.67[m, 2H, H^3, H^4]	2.79[q, 2H, Et, 7.6[f]]
		6.2[m, 1H, H^5]	1.25[t, 3H, Et, 7.6[f]]
8c[e]	37.2s	7.36[d, 1H, H^2, 7.3[f]]	9.2[br, 1H, NH]
		6.94[t, 1H, H^3, 7.3[f]]	6.76[br, 2H, NH_2]
		6.56[t, 1H, H^4, 7.3[f]]	2.68[q, 2H, Et, 7.5[f]]
		6.30[t, 1H, H^5, 7.3[f], 7.3[g]]	1.50[t, 3H, Et, 7.5[f]]
9c[e]	34.9s	7.35[d, 1H, H^2, 7.3[f]]	9.3[br, 1H, NH]
		6.95[t, 1H, H^3, 7.3[f]]	6.89[br, 2H, NH_2]
		6.57[t, 1H, H^4, 7.3[f]]	2.65[q, 2H, Et, 7.5[f]]
		6.27[t, 1H, H^5, 7.3[f], 7.3[g]]	1.55[t, 3H, Et, 7.5[f]]

[a] In $(CD_3)_2CO$ 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 $(CD_3)_2CO$ 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.

[e] In DMSO-d_6.

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

[g] $^4J(PH5)$.

[h] C(3)–Me.

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

[j] In $CDCl_3$.

[k] $\delta([PC({=}CH_2)P]$: (**6a**), 7.18, $N = 43$; (**6c**), 7.16, $N = 46$.

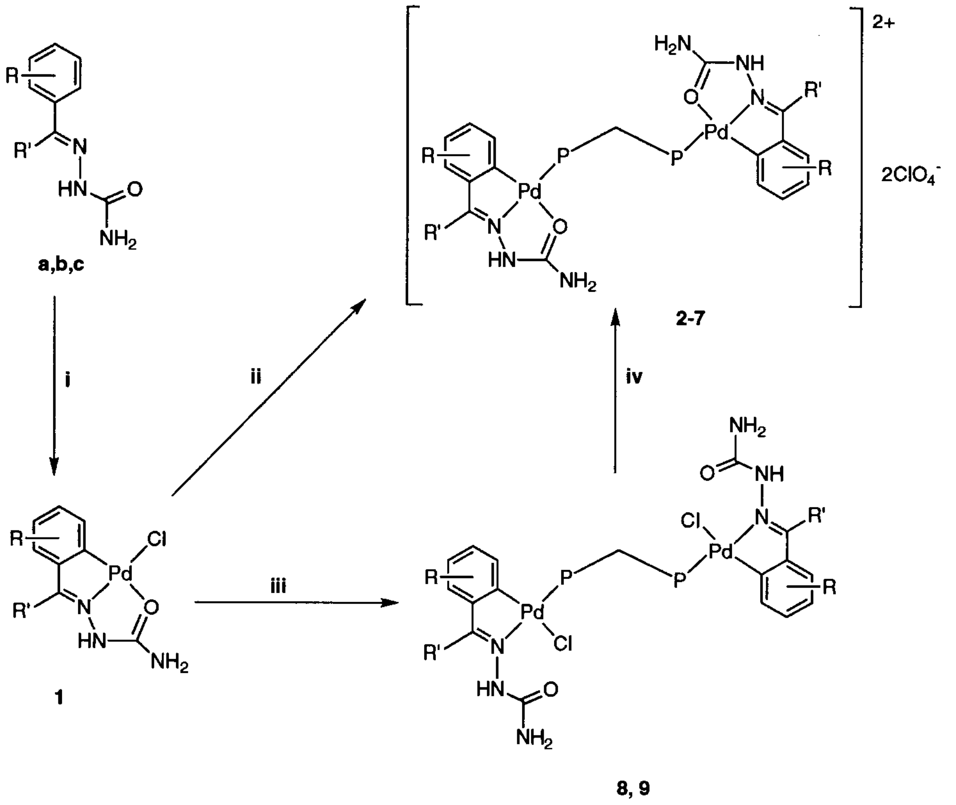
[l] $[(PCH_2P)]$: (**7a**), 4.42m; (**7b**), 4.2m; (**7c**), 4.46 m.

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

2.2. Crystal structure of $[\{Pd[C_6H_4C(Et){=}NN(H)C({=}O)NH_2]\}_2(\mu\text{-}Ph_2P{-}(CH_2)_3PPh_2)][ClO_4]_2$ **3c**

Suitable crystals of the title compound were grown from slowly evaporating a chloroform solution. The molecular structure is illustrated in Fig. 1. Crystal data are given in Table 2. Fractional coordinates and isotropic thermal parameters are listed in Table 3. Selected bond lengths and bond angles with estimated standard deviations are listed in Table 4.

The crystal structure comprises a centrosymmetric dinuclear cation (half of the cation per asymmetric



Scheme 1. Treatment of the semicarbazone ligands **a**, **b** or **c** with $Li_2[PdCl_4]$ in methanol (i) gave compounds **1a–c**, which were further reacted (ii) to give **2–7** or (iii) **8**, **9** followed by (iv) resulting in **2–7**.

unit), and two perchlorate anions. Each four-coordinated palladium(II) is bonded to a terdentate semicarbazone system through the aryl C(1) carbon, the imine N(1) nitrogen and the amide O oxygen atoms, and to a phosphorus atom of a 1,3-bis(diphenylphosphine)propane, which bridges a crystallographic inversion center between the two metal atoms.

The Pd–N(1) bond length of 1.98(2) Å is within the expected value based on the sum of the covalent radii [16] for palladium (1.31 Å) and nitrogen (sp^2) (0.7 Å) and similar to others reported [13]. The Pd–C(1), 2.00(2), and Pd–P, 2.246(7) Å, bond lengths are somewhat shorter than the values predicted from their covalent radii [16], and they are similar to values found earlier [13]. The Pd–O length, 2.15 Å, is longer then the expected value of 1.97 Å, and shows the *trans* influence of the aryl carbon atom. The sum of angles about the palladium atom is 360.4°, with the only noteworthy deviation being the somewhat reduced [N(1)–Pd–C(1)] bond angle consequent upon chelation, which is reflected in the the value of the Pd–C(1)–C(6), 130.8°, angle.

The geometry around the palladium atom is planar (r.m.s. = 0.0692 Å; plane 1). The metallated ring [Pd, C(1), C(2), C(7), N(1)] and the coordination ring [Pd,N(1), N(2), C(8), O(1)] are also planar (r.m.s. = 0.0189 Å; plane 2) and (r.m.s. = 0.0289 Å; plane 3), respectively. Angles between planes are as follows: plane 1/plane 2, 5.5°; plane 1/plane 3, 6.7°; plane 2/plane 3, 3.8°.

3. Experimental details

3.1. Materials and instrumentation

Solvents were purified by standard methods [17]. Chemicals were reagent grade. Palladium(II) chloride was a generous loan by Johnson Matthey. The phosphines $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb) were purchased from Aldrich-Chemie; $Ph_2PC(=CH_2)PPh_2$ (vdpp) and *trans*-$Ph_2PCH=CHPPh_2$ (*trans*-dppe) were prepared according to procedures described elsewhere [18]. 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 $CDCl_3$ DMSO-d_6 or $(CD_3)_2CO$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C) 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.

The synthesis of the semicarbazones 4-$MeC_6H_4C(Me)=NN(H)C(=O)NH_2$ (**a**), 3,4-$Me_2C_6H_3C$-

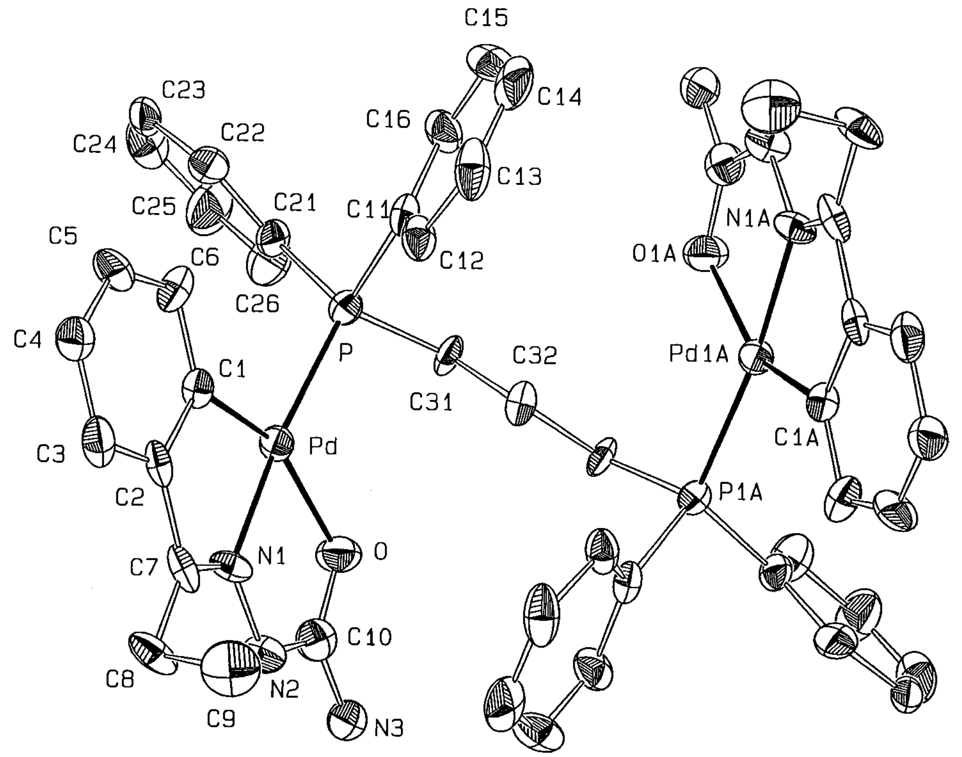


Fig. 1. Molecular structure of $[\{Pd[C_6H_4C(Et){=}NN(H)C({=}O)NH_2]\}2(\mu\text{-}Ph_2P{-}(CH_2)_3PPh_2)][ClO_4]_2$.

(Me)=NN(H)C(=O)NH_2 (**b**) and $C_6H_5C(Et){=}NN(H)C$-(=O)NH_2 (**c**) was performed according to methods described in the literature [19]. ^{13}C-{1H}NMR (75.48 MHz DMSO-d_6): **a,** δ 157.8 (C=O); δ 144.5 (C=N); δ 135.9 (C4); δ 129.1 (C3, C5); δ 126.2 (C2, C6); δ 21.1, 13.6 (Me); **b,** δ 157.7 (C=O); δ 144.5 (C=N); δ 127.24 (C6); δ 137.0, 136.3, 136.2 (C1, C3, C4); δ 123.8 (C2); δ 129.6 (C5); δ 19.5, 19.7, 13.6 (Me); **c,** δ 157.7 (C=O); δ 148.5 (C=N); δ 137.2 (C1); δ 128.5, 128.4, 126.1 (C2, C3, C4, C5, C6); δ 18.9 (CH_2CH_3); δ 10.5 (CH_2CH_3).

3.2. Preparations

3.2.1. [Pd{4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)NH$_2$}(Cl)] 1a

To a stirred solution of lithium tetrachloropalladate in 50 ml of methanol, prepared in situ from 200 mg (1.13 mmol) of palladium(II) chloride and 100 mg (2.33 mmol) of lithium chloride, 100 mg (1.22 mmol) of sodium acetate and 240 mg (1.25 mmol) of the semicarbazone $4\text{-}MeC_6H_4C(Me){=}NN(H)C({=}O)NH_2$ (**a**) were added. The mixture was stirred for 48 h at room temperature. The precipitate was filtered off and washed with methanol. The solid was added to 50 ml of ethanol and heated to reflux. The hot mixture was filtered and the pale-yellow solid resulting dried in air. Yield 80%. Anal. Found: C, 36.4; H, 3.7; N, 12.4. $C_{10}H_{12}N_3OClPd$ Calc.: C, 36.2; H, 3.6; N, 12.6%. IR: ν(C=O) 1670s, ν(C=N) 1620s, ν(Pd–Cl) 340w cm^{-1}. ^{13}C-{^1H}NMR (62.46 MHz DMSO-d_6): δ 166.0 (C=O); δ 159.8 (C=N); δ 149.7 (C6); δ 144.6 (C1); δ 139.3 (C4); δ 137.8 (C5); δ 129.14, 126.2 (C2, C3): δ 21.9, 14.2 (Me).

Compounds **1b** and **1c** were obtained following a similar procedure as yellow solids.

3.2.2. [Pd{3,4-Me$_2$C$_6$H$_2$C(Me)=NN(H)C(=O)NH$_2$}(Cl)] 1b

Yield 85%. Anal. Found: C, 38.0; H, 4.0; N, 11.8. $C_{11}H_{14}N_3OClPd$ Calc.: C, 38.2; H, 4.1; N, 12.1%. IR: ν(C=O) 1649s, ν(C=N) 1628s, ν(Pd–Cl) 332w cm − 1. ^{13}C-{^1H}NMR (62.46 MHz DMSO-d_6): δ (C=O); δ (C=N); δ (C6); δ 145.2 (C1); δ 137.7, 135.9, 132.7, 131.9, 122.0 (C2, C3, C4, C5); δ 20.13, 11.17 (Me).

3.2.3. [Pd{C$_6$H$_4$C(Et)=NN(H)C(=O)NH$_2$}(Cl)] 1c

Yield 73%. Anal. Found: C, 36.1; H, 3.8; N, 12.6. $C_{10}H_{12}N_3OClPd$ Calc.: C, 36.2; H, 3.6; N, 12.6%. IR: ν(C=O) 1645s, ν(C=N) 1616s, ν(Pd–Cl) 347w cm^{-1}. ^{13}C-{^1H}NMR (62.46 MHz DMSO-d_6): δ (C=O); δ (C=N); δ 150.0 (C6); δ 146.7 (C1);δ 135.0 (C5); δ 129.4, 126.9, 124.7 (C2, C3, C4); δ 20.13 (CH_2CH_3); δ 11.2 (CH_2CH_3).

3.2.4. [{Pd[4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)-NH$_2$]}$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)][ClO$_4$]$_2$ 2a

A suspension of **1a** (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. $Ph_2P(CH_2)_4PPh_2$ (32 mg, 0.08 mmol) was added to the filtrate and the solution stirred for 4 h, the solvent removed and the product recrystallized from dichloromethane/hexane to give the desired complex as a white solid. Yield 82%. Anal. Found: C, 47.6; H, 4.3; N, 7.1. $C_{48}H_{52}N_6O_{10}Cl_2Pd_2P_2$ Calc.: C, 47.3; H, 4.3; N, 6.9%. IR: ν(C=O) 1651m, ν(C=N) 1631sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 250\ ohm^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

Compounds **3a**–**7a**, **2b**–**7b** and **2c**–**7c**,were synthesized following a similar procedure as white or yellow solids.

3.2.5. [{Pd[4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)-NH$_2$]}$_2$(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)][ClO$_4$]$_2$ ***3a***

Yield 90%. Anal. Found: C, 46.8; H, 4.1; N, 6.8. $C_{47}H_{50}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.8; H, 4.2; N, 7.0%. IR: ν(C=O) 1651s, ν(C=N) 1637sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 300\ ohm^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

Table 2
Crystal data for 3c

Empirical formula	$C_{47}H_{50}Cl_2N_6O_{10}P_2Pd_2$
Formula weight	1204.6
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	25.044(7)
b (Å)	10.847(1)
c (Å)	24.034(7)
β (°)	121.83(3)
Volume	5547(5) $Å^3$
Z	4
$D_{calc.}$ ($g\ cm^{-3}$)	1.442
Absorption coefficient (cm^{-1})	8.477
F(000)	2440
Crystal size (mm)	0.40 × 0.25 × 0.30
Minimum, Maximum, absorption correction	0.430/1.126
Maximum value of (sin θ)/λ reached in intensity mesurement ($Å^{-1}$)	0.660
Total no. of reflections measured, θ range	14 359, 3–28°
No. of unique reflections; R_{int}	13 725, 0.045
No. of observed reflections	1738
Criterion for observed reflections	$I > 3\sigma(I)$
Weighting scheme	$1/\sigma^2(F)$
Parameters refined	219
Value of *R*	0.086
Value of *wR*	0.099
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.02
Max. $\Delta\rho$ in final difference electron density map (e $Å^{-3}$)	1.342
Error in an observation of unit weight	13.467

Table 3
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **3c**

	x	*y*	*z*	B_{iso}
Pd	0.35502(7)	0.6949(2)	0.11584(7)	2.68(3)
Cl	0.0631(3)	0.2399(7)	0.6070(3)	5.8(2)
P	0.3763(2)	0.6142(5)	0.2115(2)	2.5(1)
O	0.4051(6)	0.567(1)	0.0920(6)	4.1(4)
O(1)	0.0833(9)	0.271(2)	0.672(1)	9.3(7)
O(2)	0.043(2)	0.126(4)	0.584(2)	21(2)
O(3)	0.024(2)	0.324(5)	0.559(2)	24(2)
O(4)	0.110(2)	0.271(4)	0.599(2)	19(1)
N(1)	0.3473(7)	0.771(2)	0.0375(7)	4.0(5)
N(2)	0.3781(7)	0.710(2)	0.0111(7)	3.8(4)
N(3)	0.4356(8)	0.538(2)	0.0200(8)	4.8(6)
C(1)	0.2996(7)	0.839(2)	0.1034(9)	2.2(5)
C(2)	0.2903(8)	0.911(2)	0.0505(9)	3.0(5)
C(3)	0.2508(9)	1.015(2)	0.033(1)	4.2(6)
C(4)	0.2247(9)	1.048(2)	0.069(1)	4.9(7)
C(5)	0.235(1)	0.976(2)	0.120(1)	4.6(7)
C(6)	0.2729(9)	0.873(2)	0.138(1)	3.7(5)
C(7)	0.3176(9)	0.874(2)	0.014(1)	3.8(6)
C(8)	0.317(1)	0.946(2)	−0.040(1)	4.8(7)
C(9)	0.367(1)	1.043(3)	−0.013(1)	8.1(9)
C(10)	0.4051(8)	0.604(2)	0.043(1)	4.2(6)
C(11)	0.4037(7)	0.716(2)	0.2828(8)	2.3(4)
C(12)	0.4189(9)	0.833(2)	0.281(1)	4.1(5)
C(13)	0.445(1)	0.903(3)	0.340(1)	5.5(7)
C(14)	0.456(1)	0.850(3)	0.396(1)	5.3(6)
C(15)	0.438(1)	0.740(2)	0.396(1)	4.6(6)
C(16)	0.414(1)	0.664(2)	0.341(1)	4.5(6)
C(21)	0.3162(8)	0.517(2)	0.2094(9)	3.1(4)
C(22)	0.267(1)	0.573(2)	0.213(1)	4.3(6)
C(23)	0.218(1)	0.497(3)	0.204(1)	4.9(6)
C(24)	0.219(1)	0.374(2)	0.195(1)	4.7(6)
C(25)	0.263(1)	0.318(3)	0.188(1)	6.4(7)
C(26)	0.314(1)	0.393(2)	0.196(1)	4.7(6)
C(31)	0.4430(9)	0.515(2)	0.2343(9)	3.5(5)
C(32)	0.500	0.590(3)	0.250	2.0(5)

3.2.6. [{Pd[4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)-NH$_2$]}$_2$(μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$)][ClO$_4$]$_2$ ***4a***

Yield 74%. Anal. Found: C, 46.3; H, 4.3; N, 7.0. $C_{46}H_{48}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.4; H, 4.1; N, 7.1%. IR: ν(C=O) 1649s, ν(C=N) 1635sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 308\ ohm^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.7. [{Pd[4-MeC$_6$H$_3$C(Me)=NN(H)C(=O)-NH$_2$]}$_2$(μ-trans-Ph$_2$PCH=CHPPh$_2$)][ClO$_4$]$_2$ ***5a***

Yield 68%. Anal. Found: C, 46.6; H, 3.6; N, 7.1. $C_{46}H_{46}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.5; H, 3.9; N, 7.1%. IR: ν(C=O) 1641s, ν(C=N) 1585m cm^{-1}. Specific molar conductivity, $\Lambda_m = 315\ ohm^{-1}\ cm^2\ mol^{-1}$ (in acetonitrile).

3.2.8. $[\{Pd[4\text{-}MeC_6H_3C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2PC(=CH_2)PPh_2)][ClO_4]_2$ **6a**

Yield 81%. Anal. Found: C, 46.2; H, 3.8; N, 7.3. $C_{46}H_{46}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.5; H, 3.9; N, 7.1%. IR: ν(C=O) 1649s, ν(C=N) 1634sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 320$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.9. $[\{Pd[4\text{-}MeC_6H_3C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2PCH_2PPh_2)][ClO_4]_2$ **7a**

Yield 80%. Anal. Found: C, 45.2; H, 3.7; N, 7.0. $C_{45}H_{46}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 45.9; H, 3.9; N, 7.1%. IR: ν(C=O) 1651s, ν(C=N) 1631sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 290$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.10. $[\{Pd[3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)][ClO_4]_2$ **2b**

Yield 77%. Anal. Found: C, 48.2; H, 4.5; N, 6.7. $C_{50}H_{56}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 48.2; H, 4.5; N, 6.7%. IR: ν(C=O) 1649m, ν(C=N) 1630sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 325$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.11. $[\{Pd\{3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)][ClO_4]_2$ **3b**

Yield 85%. Anal. Found: C, 47.6; H, 4.3; N, 6.7. $C_{49}H_{54}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 47.7; H, 4.4; N, 6.8%. IR: ν(C=O) 1651s, ν(C=N) 1630sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 310$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

Table 4
Selected bond lengths [Å] and angles [°] for **3c**

Bond lengths (Å)			
Pd–C(1)	2.00(2)	Pd–N(1)	1.98(2)
Pd–O	2.15(2)	Pd–P	2.246(7)
O–C(10)	1.25(3)	N(1)–N(2)	1.40(3)
P–C(11)	1.84(2)	P–C(21)	1.81(2)
P–C(31)	1.81(2)	N(1)–C(7)	1.29(3)
N(2)–C(10)	1.35(3)	N(3)–C(10)	1.35(4)
C(1)–C(2)	1.41(3)	C(2)–C(7)	1.43(4)
Bond angles (°)			
P–Pd–O	99.5(4)	O–Pd–N(1)	78.2(7)
N1–Pd–C(1)	79.6(9)	P–Pd–C(1)	103.1(7)
O–Pd–C(1)	157.3(7)	P–Pd–N(1)	173.1(5)
C(1)–C(2)–C(7)	120(2)	N(1)–C(7)–C(2)	108(2)
N(1)–C(7)–C(8)	125(3)	N(2)–N(1)–C(7)	122(3)
C(3)–C(2)–C(7)	122(2)	C(2)–C(7)–C(8)	126(2)
N(2)–C(10)–N(3)	116(2)	N(1)–N(2)–C(10)	113(2)
O–C(10)N(2)	124(2)	O–C(10)–N(3)	120(2)
C(11)–P–C(21)	106(2)	C(11)–P–C(31)	104.1(8)
C(21)–P–C(31)	106(2)	P–C(31)–C(32)	111(2)

3.2.12. $[\{Pd\{3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2P(CH_2)_2PPh_2)][ClO_4]_2$ **4b**

Yield 89%. Anal. Found: C, 42.8; H, 4.5; N, 6.6. $C_{48}H_{52}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 47.3; H, 4.3; N, 6.9%. IR: ν(C=O) 1643m, ν(C=N) 1630sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 340$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.13. $[\{Pd[3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}trans\text{-}Ph_2PCH=CHPPh_2)][ClO_4]_2$ **5b**

Yield 76%. Anal. Found: C, 47.7; H, 4.1; N, 6.7. $C_{48}H_{50}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 47.4; H, 4.1; N, 6.9%. IR: ν(C=O) 1647m, ν(C=N) 1628sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 333$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.14. $[\{Pd[3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2PC(=CH_2)PPh_2)][ClO_4]_2$ **6b**

Yield 78%. Anal. Found: C, 47.1; H, 4.1; N, 6.8. $C_{48}H_{50}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 47.4; H, 4.1; N, 6.9%. IR: ν(C=O) 1647s, ν(C=N) 1631sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 300$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.15. $[\{Pd[3,4\text{-}Me_2C_6H_2C(Me)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2PCH_2PPh_2)][ClO_4]_2$ **7b**

Yield 62%. Anal. Found: C, 46.9; H, 4.0; N, 7.1. $C_{47}H_{50}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.9; H, 4.2; N, 7.0%. IR: ν(C=O) 1660s, ν(C=N) 1643s cm^{-1}. Specific molar conductivity, $\Lambda_m = 342$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.16. $[\{Pd[C_6H_4C(Et)=NN(H)C(=O)NH_2]\}_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)][ClO_4]_2$ **2c**

Yield 77%. Anal. Found: C, 47.5; H, 4.2; N, 6.6. $C_{48}H_{52}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 47.3; H, 4.3; N, 6.9%. IR: ν(C=O) 1649m, ν(C=N) 1631w cm^{-1}. Specific molar conductivity, $\Lambda_m = 250$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.17. $[\{Pd[C_6H_4C(Et)=NN(H)C(=O)NH_2\}(Cl)]\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)][ClO_4]_2$ **3c**

Yield 69%. Anal. Found: C, 46.8; H, 4.0; N, 7.1. $C_{47}H_{50}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.8; H, 4.2; N, 7.0%. IR: ν(C=O) 1649s, ν(C=N) 1631s cm^{-1}. Specific molar conductivity, $\Lambda_m = 312$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.18. $[\{Pd[C_6H_4C(Et)=NN(H)C(=O)NH_2\}(Cl)]\}_2(\mu\text{-}Ph_2P(CH_2)_2PPh_2)][ClO_4]_2$ **4c**

Yield 85%. Anal. Found: C, 46.3; H, 4.2; N, 6.6. $C_{46}H_{48}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.4; H, 4.1; N, 7.1%. IR: ν(C=O) 1649m, ν(C=N) 1646sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 235$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.19. *[{Pd[$C_6H_4C(Et)$=NN(H)C(=O)-NH_2}(Cl)]}$_2$(μ-trans-Ph_2PCH=CH–PPh_2)][ClO_4]$_2$* **5c**

Yield 85%. Anal. Found: C, 46.6; H, 3.9; N, 6.9. $C_{46}H_{46}N_6O_{10}Cl_2Pd_2P_2$.Calc.: C, 46.5; H, 3.9; N, 7.1%. IR: ν(C=O) 1651s, ν(C=N) 1626sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 290$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.20. *[{Pd[$C_6H_4C(Et)$=NN(H)C(=O)-NH_2}(Cl)]}$_2$(μ-Ph_2PC(=CH_2)PPh_2)][ClO_4]$_2$* **6c**

Yield 85%. Anal. Found: C, 46.7; H, 3.8; N, 7.2. $C_{46}H_{46}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 46.5; H, 3.9; N, 7.1%. IR: ν(C=O) 1649s, ν(C=N) 1626sh cm^{-1}. Specific molar conductivity, $\Lambda_m = 316$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.21. *[{Pd[$C_6H_4C(Et)$=NN(H)C(=O)-NH_2}(Cl)]}$_2$(μ-$Ph_2PCH_2PPh_2$)][ClO_4]$_2$* **7c**

Yield 86%. Anal. Found: C, 45.5; H, 3.8; N, 7.1. $C_{45}H_{46}N_6O_{10}Cl_2Pd_2P_2$. Calc.: C, 45.9; H, 3.9; N, 7.1%. IR: ν(C=O) 1655s, ν(C=N) 1628m cm^{-1}. Specific molar conductivity, $\Lambda_m = 284$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3.2.22. *[{Pd[4-$MeC_6H_3C(Me)$=NN(H)C(=O)-NH_2](Cl)}$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)]* **8a**

$Ph_2P(CH_2)_4PPh_2$ (32 mg, 0.08 mmol) was added to a suspension of **1a** (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 90%. Anal. Found: C, 52.8; H, 4.8; N, 7.8. $C_{48}H_{52}N_6O_2Cl_2Pd_2P_2$. Calc.: C, 52.9; H, 4.8; N, 7.7%. IR: ν(C=O) 1720s, ν(C=N) 1620m, ν(Pd–Cl) 285w cm^{-1}. Compounds **9a**, **8c** and **9c** were obtained following a similar procedure.

3.2.23. *[{Pd[4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2]-(Cl)}$_2$(μ-$Ph_2P(CH_2)_2PPh_2$)]* **9a**

Yield 79%. Anal. Found: C, 52.2; H, 4.3; N, 7.7. $C_{46}H_{48}N_6O_2Cl_2Pd_2P_2$. Calc.: C, 52.0; H, 4.5; N, 7.9%. IR: ν(C=O) 1720s, ν(C=N) 1620m, ν(Pd–Cl) 265w cm^{-1}.

3.2.23.1. [{Pd[4-$MeC_6H_3C(Me)$=NN(H)C(=O)NH_2]-(Cl)}$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] **8c**. Yield 79%. Anal. Found: C, 53.0; H, 5.0; N, 7.8. $C_{48}H_{52}N_6O_2Cl_2Pd_2P_2$. Calc.: C, 52.9; H, 4.8; N, 7.7%. IR: ν(C=O) 1712s, ν(C=N) 1627s, ν(Pd–Cl) 280w cm^{-1}.

3.2.24. *[{Pd[$C_6H_4C(Et)$=NN(H)C(=O)NH_2]-(Cl)}$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)]* **9c**

Yield 85%. Anal. Found: C, 52.4; H, 4.9; N, 7.7. $C_{47}H_{50}N_6O_2Cl_2Pd_2P_2$. Calc.: C, 52.0; H, 4.7; N, 7.8%. IR: ν(C=O) 1710s, ν(C=N) 1629s, ν(Pd–Cl) 280w cm^{-1}.

An alternative route for the synthesis of **2a** was performed as follows:To a suspension of **8a** (50 mg, 0.05 mmol) in acetone (15 cm^3) $AgClO_4$ (10 mg, 0.05 mmol) was added. The resulting suspension was stirred for 4 h and filtered trough Celite to remove the AgCl. The solvent was removed and the product recrystallized from dichloromethane/hexane to give **2a**. **4a**, **2c** and **3c** could be synthesized following a similar procedure by reacting **9a**, **8c** and **9c** with $AgClO_4$, respectively.

3.3. *Single-crystal diffraction analysis*

A yellow prismatic crystal of [{Pd[$C_6H_4C(Et)$=NN(H)C(=O)NH_2]}$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)][ClO_4]$_2$ **3c** was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range $6.23° < \theta < 13.16°$ in a ENRAF-NONIUS CAD4 automatic diffractometer [20]. Data were collected at 293 K using Mo–K_α radiation ($\lambda = 0.70930$ Å) and the $\omega/2\theta$ scan technique. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was made [21]. A summary of the crystal data, experimental details and refinement results are listed in Table 2.

The structure was solved by direct methods [22] which revealed the position of all non-H atoms, and refined on F by full-matrix least-squares procedure using anisotropic displacement parameters for all non-H atoms except the phenyl groups and perchlorate anions. The H atoms were calculated at idealized positions and added to the structure factor calculations as fixed contributions ($B_{iso} = 5.0$ Å) but their positional parameters were not refined. After all shift/e.s.d. ratios were < 0.03, the refinement convereged to the agreement factors listed in Table 2. Atomic scattering factors from International Tables for X-ray crystallography [23]. Molecular graphics from ORTEP [24].

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