Journal of Organometallic Chemistry 655 (2002) 127–133

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Polynuclear cyclometallated palladium(II) complexes. Crystal and molecular structures of $[(PPh_3)(Cl)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Cl)(PPh_3)]$ and $[\{PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd\}\{Ph_2PC(H){=}C(H)PPh_2\text{-}P,P\}_2][ClO_4]_2$

Margarita López-Torres [a,*], Alberto Fernández [a], Jesús J. Fernández [a], Antonio Suárez [a], Samuel Castro-Juiz [a], M^a Teresa Pereira [b], José M. Vila [b,*]

[a] *Departamento de Química Fundamental, Universidad de La Coruña, E-15071 La Coruña, Spain*

[b] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain*

Received 22 February 2002; accepted 8 April 2002

Dedicated to Professor Joachim Strähle on the occasion of his 65th birthday

Abstract

Treatment of *N*,*N*-terephthalylidenebis(cyclohexylamine) (**L**) with palladium(II) acetate in toluene at room temperature gave the dicyclometallated acetato-bridged complex $[(OAc)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(OAc)]_n$ (**1**). Reaction of **1** with lithium chloride or bromide in acetone produced the chloro- or bromo-bridged complexes $[(Cl)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Cl)]_n$ (**2**) and $[(Br)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Br)]_n$ (**3**), respectively. Reaction of **2** with triphenylphosphine gave $[(PPh_3)(Cl)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Cl)(PPh_3)]$ (**4**). Treatment of **2** and **3** with bis(diphenylphosphino)methane and 1,5-bis(diphenylphosphino)pentane in a 1:1 molar ratio afforded $[\{(Cl)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Cl)\}_2\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ (**5**) and $[\{(Br)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Br)\}_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}_2]$ (**6**), respectively. Reaction of **2** and **3** with bis(diphenylphosphino)methane or *cis*-1,5-bis(diphenylphosphino)ethene, in a 1:2 molar ratio, and sodium perchlorate, gave dinuclear cyclometallated compounds with two chelated phosphine ligands $[\{PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd\}\{Ph_2PCH_2PPh_2\text{-}P,P\}_2][ClO_4]_2$ (**7**) and $[\{PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd\}\{Ph_2PC(H){=}C(H)PPh_2\text{-}P,P\}_2][ClO_4]_2$ (**8**). The compounds have been fully characterized by elemental analysis, mass spectrometry, IR and NMR spectroscopy, and complexes **4** and **8** by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyclometallation; Palladium(II); Phosphines; Schiff-base

1. Introduction

There has been a growing interest in the synthesis of cyclometallated compounds, due to their successful use in, e.g. organic [1] and asymmetric synthesis [2]; they are also very promising as photoluminiscent compounds [3] and potentially biologically active complexes [4].

Ligands bearing two donor atoms, which may undergo double metallation on the same phenyl ring have been studied by us and by others [5,6]. These ligands are capable of binding to two different metal centers simultaneously in a tetradentate fashion with formation of two σM–C bonds, and consequently give rise to two independent cyclometallated rings: one per each metal atom. More recently, we have been interested in the synthesis of doubly cyclometallated complexes derived from one of these ligands, namely *N*,*N*-terephthalylidenebis(cyclohexylamine), which was used in the preparation of new self-assembly supramolecular species [7] and in the synthesis of a novel pentacoordinated palladium(II) compound [8].

As a continuation of our work related to tetradentate [C, N, C, N] Schiff-base ligands, in the present paper we report the synthesis and characterization of new poly-

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* Corresponding author. Fax: +34-98-159-5012.
E-mail address: qideport@usc.es (José M. Vila).

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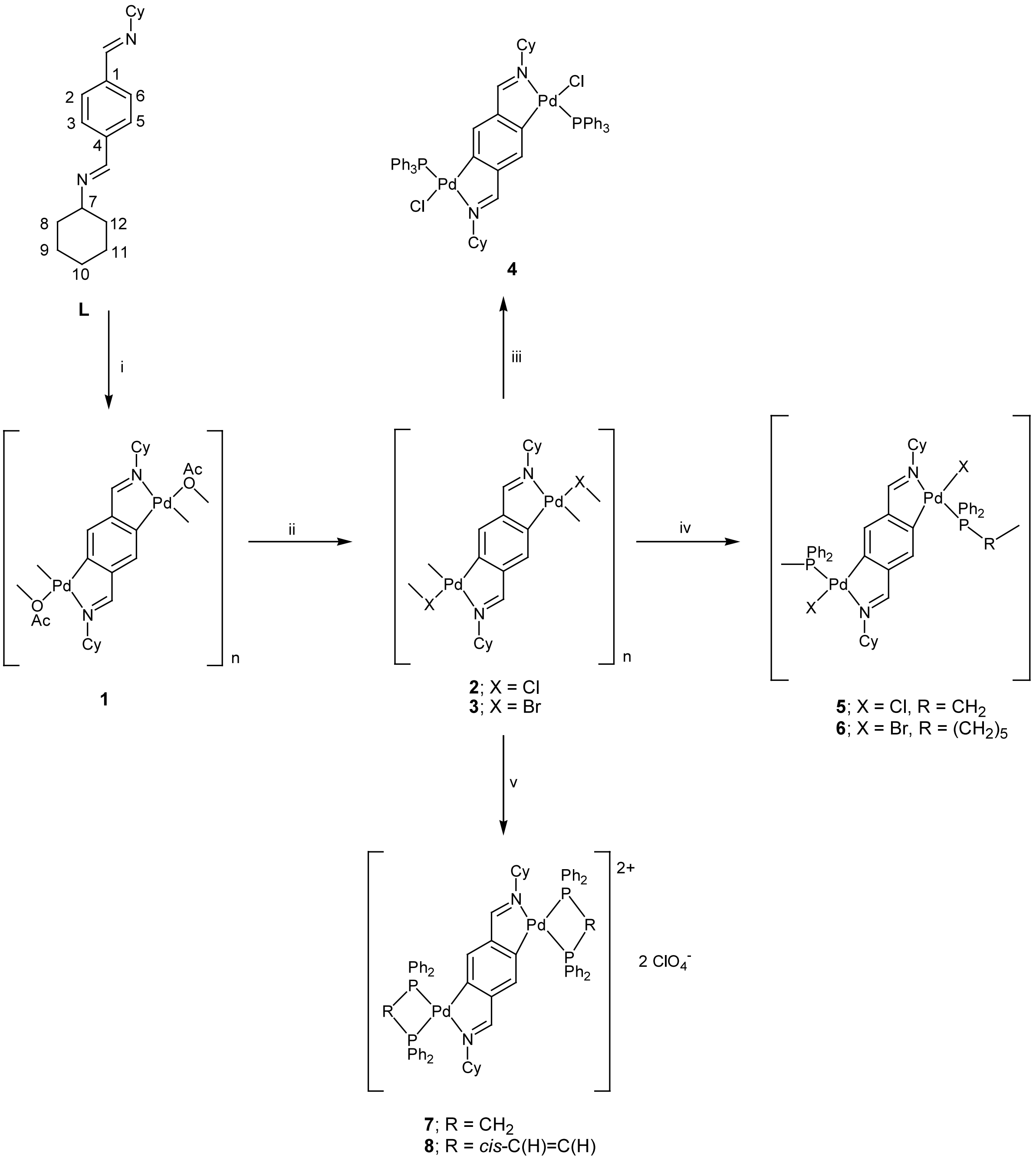
PII: S0022-328X(02)01468-7

nuclear cyclometallated palladium(II) complexes and their reactivity towards mono- and ditertiary phosphines. The crystal and molecular structures of compounds **4** and **8** are also given.

2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1. The compounds were air-stable solids and they were fully characterized by elemental analysis (C, H, N), mass spectrometry, IR and ^{1}H and ^{31}P-{^{1}H}-NMR spectroscopy, and compounds **4** and **8** by X-ray crystallography.

We have previously reported that the bidentate Schiff-base *N*,*N*-terephthalylidenebis(cyclohexylamine), **L**, reacts with palladium(II) acetate in boiling acetic acid to give a monocyclometallated dimer complex with a free formyl group on each phenyl ring [9]. Nevertheless, if the metallation process was varied by oxidative addition



Scheme 1. (i) Pd(OAc)$_2$, toluene, r.t.; (ii) LiX, acetone–H_2O; (iii) PPh$_3$ (1:1 molar ratio), dichlorometane; (iv) diphosphine (1:1 molar ratio), dichlorometane; (v) diphosphine (1:2 molar ratio), dichloromethane, NaClO$_4$ (ethanol).

reaction of the 2,5-dichloro derivative of **L** with [$Pd_2(dba)_3$], the dicyclometallated chloro-bridged complex, **2**, was obtained [10]. However, double metallation may also be achieved by electrophilic attack of the palladium atom on the organic ligand in a non-acidic media. Thus, treatment of **L** with palladium(II) acetate in toluene at room temperature gave the new dicyclometallated acetato-bridged complex, **1**.

The very low solubility of complex **1** did not allow its correct characterization and a polymeric structure was proposed for the complex, in spite that tetranuclear structures (which are usually more soluble) in the solid state are known for cyclometallated complexes derived from related Schiff-base ligands and that they have been previously reported [6,11]. Nevertheless, in view of the products obtained by the subsequent reactions of **1** with sodium halides we assume this supposition to be correct (vide infra). Thus, treatment of **1** with lithium chloride or bromide produced the chloro- or bromo-bridged complexes **2** and **3**, respectively, which were fully characterized. Complexes **2** and **3** were prepared by us earlier [10], although by oxidative addition of a palladium(0) compound to a dichloro Schiff-base ligand.

Reaction of **2** with tertiary phosphines in a 1:1 molar ratio gave compounds similar to **4**, i.e. dinuclear species in which the two Pd–C bonds remain and two new Pd–P bonds are present. We have reported this chemistry [10], but X-ray diffraction analysis remained outstanding; therefore, we now give the crystal structure of **4** which confirms the geometry predicted from spectroscopic data (vide infra).

Treatment of **2** and **3** with bis(diphenylphosphino)methane and 1,5-bis(diphenylphosphino)pentane in a 1:1 molar ratio gave complexes **5** and **6**, respectively. The shift of the ν(C=N) stretching vibration in the IR spectra towards lower wavenumbers [12] was indicative of palladium–nitrogen interaction. In the ^{1}H-NMR spectra a doublet at δ 6.94 (**5**) and 6.99 (**6**) was assigned to the HC=N resonance in each case, which was coupled to the ^{31}P nucleus [$^4J(PH) = 9.0$ (**5**), 8.8 Hz (**6**)]. A doublet resonance was observed for the two equivalents H2 and H5 protons at δ 5.57 (**5**) and 5.55 (**6**) [$^4J(PH) =$ 6.1 (**5**), 6.8 Hz(**6**)] which was shifted to lower frequency due to shielding by the phosphine phenyl rings [13]. As a result of double metallation the HC=N protons were also shielded by the phosphine phenyl rings, as we have shown before in related compounds [7]. The phosphorus resonances in the ^{31}P-{^{1}H}-NMR spectra of **5** and **6** were downfield shifted from their values in the free phosphine, suggesting coordination of both phosphorus atoms to a metal center. They showed a singlet resonance ca. δ 31, indicating the two phosphorus nuclei to be equivalent and *trans* to the nitrogen atom [14]. Electric conductivity measurements in dry acetonitrile showed they were non-electrolytes [15]. Although the FAB mass spectra showed peaks at $m/z = 1925$ (**5**) and 2215 (**6**), which point to tetranuclear complexes in which two dinuclear cyclometallated moieties are linked by two diphosphines acting as bridging ligands, as has been described before for related cyclometallated complexes [7], we can not definitely preclude a polymeric nature of the compounds, with the mentioned peaks assignable to a fragment of the polymeric structure.

Treatment of **2** or **3** with bis(diphenylphosphino)methane and *cis*-1,2-bis(diphenylphosphino)ethene, in a 1:2 molar ratio, and sodium perchlorate gave dinuclear cyclometallated compounds with two chelated phosphine ligands, **7** and **8**, respectively. They were 1:2 electrolytes as was shown by molar conductivity measurements in dry acetonitrile [15]. The ^{1}H-NMR spectra showed a doublet at δ 7.05 (**7**) and 8.20 (**8**) assigned to the HC=N resonance which was coupled only to the ^{31}P nucleus *trans* to nitrogen [$^4J(PH) = 8.3$ (**7**), 8.7 Hz (**8**)]. The H2 and H5 resonances appeared as a doublet of doublets as a result of coupling to both phosphorus nuclei [$^4J(P_{trans\text{-}C}H) = 9.5$, $^4J(P_{trans\text{-}N}H) = 7.5$, (**7**)]. The ^{31}P-{^{1}H}-NMR spectra showed two doublets confirming the two phosphorus atoms were non-equivalent, the resonance at lower frequency was assigned to the phosphorus *trans* to carbon, the ligand of greater *trans* influence [14]. The molecular structure of **8** is given below.

2.1. Molecular structure of [$(PPh_3)(Cl)PdN(Cy)=C(H)C_6H_2C(H)=N(Cy)Pd(Cl)(PPh_3)$] (4)

Suitable crystals of the title compound were grown by slowly evaporating a dichloromethane solution. The molecular structure is illustrated in Fig. 1. Crystal data and selected bond distances and angles are shown in Tables 1 and 2, respectively.

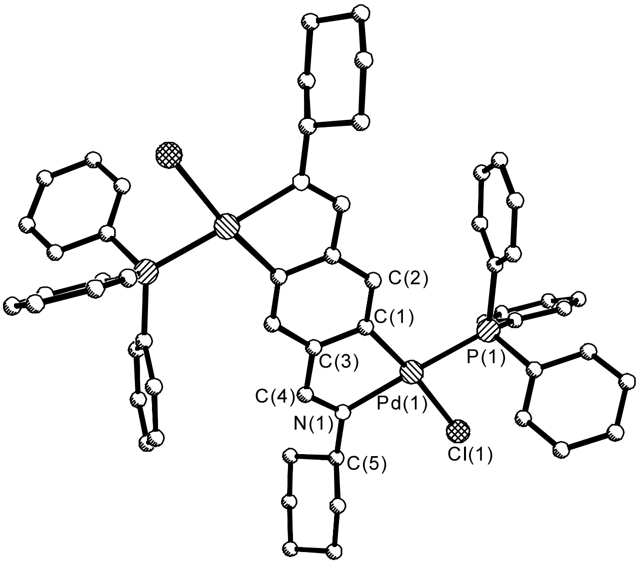


Fig. 1. Molecular structure of complex **4**. Hydrogen atoms have been omitted for clarity.

Table 1
Crystal data and structure refinement data

	4	**8**
Formula	$C_{56}H_{56}N_2P_2Cl_2Pd_2$	$C_{74}H_{70}N_2P_4Cl_8Pd_2O_8$
Formula weight	1102.67	1735.60
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	13.1205(3)	12.3179(1)
b (Å)	10.05210(10)	12.8886(2)
c (Å)	19.8418(5)	13.884
α (°)		106.1070(10)
β (°)	103.5034(4)	94.85
γ (°)		112.79
Volume (Å^3)	2544.56(9)	1905.96(3)
Z	2	1
μ (mm^{-1})	0.913	0.891
Crystal size (mm)	0.25 × 0.10 × 0.05	0.45 × 0.20 × 0.15
$2\theta_{max}$ (°)	56.5	56.5
Reflections collected	17772	12751
Reflections unique	6198 ($R_{int} = 0.0585$)	9123 ($R_{int} = 0.0232$)
Max/min transmissions	0.96, 0.80	0.87, 0.69
Number of parameters	335	497
R [F, $I > 2\sigma(I)$]	0.0554	0.0489
wR [F^2, all data]	0.1429	0.1284
max ρ (e Å^{-3})	0.630	1.051

Table 2
Bond lengths (Å) and angles (°)

4		**8**	
Bond lengths			
Pd(1)–C(1)	2.014(5)	Pd(1)–C(2)	2.071(4)
Pd(1)–N(1)	2.098(4)	Pd(1)–N(1)	2.122(3)
Pd(1)–P(1)	2.2690(14)	Pd(1)–P(1)	2.3518(10)
Pd(1)–Cl(1)	2.3901(13)	Pd(1)–P(2)	2.2457(10)
N(1)–C(4)	1.270(6)	N(1)–C(4)	1.289(5)
N(1)–C(5)	1.482(7)	N(1)–C(5)	1.487(5)
C(1)–C(3)	1.420(7)	C(1)–C(2)	1.416(5)
C(3)–C(4)	1.447(7)	C(1)–C(4)	1.461(5)
Bond angles			
C(1)–Pd(1)–N(1)	80.79(18)	C(2)–Pd(1)–N(1)	81.07(13)
N(1)–Pd(1)–Cl(1)	93.47(12)	N(1)–Pd(1)–P(1)	100.49(9)
P(1)–Pd(1)–Cl(1)	84.93(5)	P(2)–Pd(1)–P(1)	84.76(4)
C(1)–Pd(1)–P(1)	100.79(14)	C(2)–Pd(1)–P(2)	93.63(10)
N(1)–Pd(1)–P(1)	178.35(12)	C(11)–P(1)–Pd(1)	106.44(13)
C(1)–Pd(1)–Cl(1)	173.37(14)	C(12)–P(2)–Pd(1)	108.41(13)
C(2)–C(1)–Pd(1)	133.9(4)	C(3)–C(2)–Pd(1)	133.7(3)
C(4)–N(1)–C(5)	120.7(5)	C(5)–N(1)–Pd(1)	128.7(2)
C(3)–C(1)–Pd(1)	111.9(3)	C(4)–N(1)–Pd(1)	112.6(3)
C(1)–C(3)–C(4)	115.5(5)	N(1)–C(4)–C(1)	118.6(3)
N(1)–C(4)–C(3)	118.3(5)	C(2)–C(1)–C(4)	117.0(3)
C(4)–N(1)–Pd(1)	113.3(3)	C(1)–C(2)–Pd(1)	110.2(3)

The structure of **4** comprises a molecule of [$(PPh_3)(Cl)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Cl)(PPh_3)$] (one half molecule per asymmetric unit). Each palladium atom is bonded, in a slightly distorted square-planar geometry, to four different atoms: a nitrogen atom of the imine group, an *ortho* carbon atom of the phenyl ring, a chlorine atom and a phosphorus atom of triphenylphosphine ligand.

The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90 °, with the most noticeable distorsion being the C(1)–Pd(1)–N(1) angle of 80.79(18)°, consequent upon chelation. This is reflected in the value of the C(2)–C(1)–Pd(1) angle, 133.9(4)°. The sum of angles at palladium is 359.9°.

The Pd–C bond, 2.014(15) Å is shorter than the expected value of 2.081 Å based on the sum of the covalent radii of carbon and palladium. This is consistent with those found for related complexes where partial multiple-bond character of the Pd–C was assumed [16]. The Pd–N bond length, Pd(1)–N(1) 2.098(4) Å, is longer than the expected value of 2.01 Å calculated from the covalent radii of N(sp^2) and palladium (0.70 and 1.31 Å, respectively [17]), reflecting the strong *trans* influence of the phosphine ligand [18].

The Pd–P bond length, Pd(1)–P(1) 2.2690(14) Å, is shorter than the sum of the single bond radii for palladium and phosphorus, 2.41 Å suggesting some partial double bond between the palladium and phosphorus atoms may exist and is similar to others found earlier [19]. The Pd–Cl bond length, 2.3901(13) Å, is in accordance with the values found earlier in similar cyclometallated compounds [20]. The geometry around the palladium atom is planar (r.m.s. deviation of mean Pd(1), C(1), N(1), P(1), Cl(1) plane 0.0277 Å; plane 1) and this is nearly co-planar with the metallacycle (plane 2) and with the metallated phenyl ring (plane 3). Angles between planes are as follows: 1/2: 3.3°, 2/3: 1.5°, 1/3: 4.7°.

2.2. *Molecular structure of* [$\{PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd\}\{Ph_2PC(H){=}C(H)PPh_2\text{-}P,P\}_2$][$ClO_4$]$_2$ (**8**)

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 Table 1 and selected bond distances and angles are shown in Table 2.

The crystal structure comprises a dimetallic complex dication of [$\{PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd\}$-$\{Ph_2PC(H){=}C(H)PPh_2\text{-}P,P\}_2$][$ClO_4$]$_2$ (half dication per asymmetric unit) and two chloroform solvent molecules (one per asymmetric unit). Each four-coordinate palladium atom is bonded to one nitrogen atom and to the adjacent *ortho*-carbon atom of a tetradentate *N*,*N*-terephthalylidenebis(cyclohexylamine), and to two phosphorus atoms from a *cis*-1,2-bis(diphenylphosphino)ethene. The geometry around each metal atom is similar to that showed by complex **4**, with each palladium atom coordinated in a slightly distorted

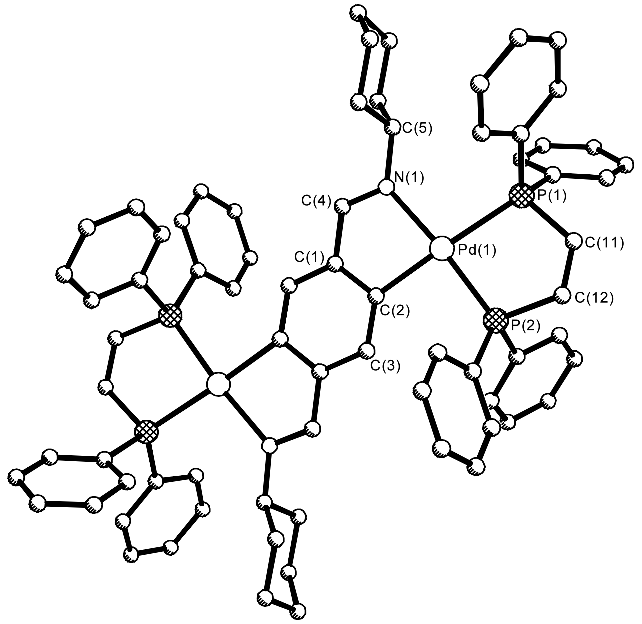


Fig. 2. The structure of the dication $[\{PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd\}\{Ph_2PC(H){=}C(H)PPh_2\text{-}P,P\}_2]^{2+}$ in complex **8**. Hydrogen atoms have been omitted for clarity.

square-planar environment, with the only noteworthy deviation being the somewhat reduced bond angle C(2)–Pd(1)–N(1) of 81.1(1)° consequent upon chelation, which is also reflected in the enlarged value of the C(3)–C(2)–Pd(1) of 133.7(3)°.

The bond distances and angles are within the expected values, with allowance for lengthening of the Pd–C bond due to the *trans* influence of the phosphine ligand [21]. The distinct Pd–P bond lengths [Pd–P(1) 2.3518(10) Å and Pd–P(2) 2.2457(10) Å] arise from the differing *trans* influence of the phenyl C_{sp^2} and nitrogen atoms of the organic ligand. The double bond length C(11)–C(12) of 1.323(6) Å is slightly shortened compared with the ideal double bond value of 1.337(6) Å, as has been observed before in several d^8 complexes containing chelated *cis*-1,2-bis(diphenylphosphino)ethene, probably due to the presence of π-bonding interactions throughout the coordination plane and the ethene bridge [22].

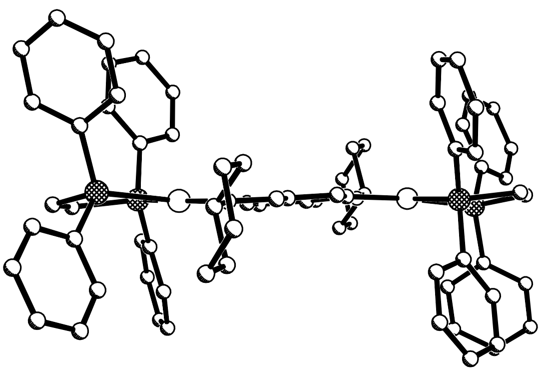


Fig. 3. Perspective view of complex **8**, showing the planarity of the dication except the phosphine phenyl and cyclohexyl rings.

The mean deviation from the least-squares planes determined by the five-membered phosphine chelate ring (plane 1), the cyclometallated ring (plane 2) and the metallated phenyl ring (plane 3) are 0.087, 0.0323 and 0.014 Å, respectively. The angles between planes are as follows: 1/2: 3.5°, 2/3: 3.7°, 1/3: 2.8°. Thus, apart from the phenyl phosphine and the cyclohexyl rings, the other five rings in the complex are nearly co-planar (see Fig. 3).

3. Experimental

Safety Note: 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.

Solvents were dried according to the standard methods [23]. Palladium(II) acetate was used as supplied from Johnson Matthey. Elemental analyses were carried out by the Servicios Generales de la Universidad de La Coruña using a Carlo–Erba elemental analyzer, Model 1108. IR spectra were recorded on a Perkin–Elmer 1330 spectrophotometer. NMR spectra were obtained as $CDCl_3$, DMSO or $(CD_3)_2CO$ solutions and referenced to $SiMe_4$ ((^1H) and $^{13}C\text{-}\{^1H\}$) or 85% H_3PO_4 ($^{31}P\text{-}\{^1H\}$) and were recorded on a Bruker AC 200F spectrometer.

The preparation of ligand **L** and complexes **2**, **3** and **4** were described in earlier papers [9,10]. Here we describe a new synthetic route for complexes **2** and **3**.

3.1. Synthesis of $[(OAc)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(OAc)]_n$ (*1*)

1,4-$(CyN{=}CH)_2C_6H_4$ (0.200 g, 0.674 mmol) and palladium(II) acetate (0.300 g, 1.336 mmol) were added to 25 cm^3 of toluene to give an orange solution. After stirring at room temperature (r.t.) for 2 days a red precipitate appeared. This was filtered off and used without further purification.

Yield: 80% Anal. Found: C, 46.0; H, 5.2; N, 4.6. Calc. for $C_{24}H_{32}Pd_2N_2O_4$: C, 46.1; H, 5.2; N, 4.5%. IR: ν(C=N) 1605s, ν_{as}(COO) 1578s; ν_s(COO) 1422s cm^{-1}.

3.2. Synthesis of $[(Cl)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Cl)]_n$ (*2*)

To a suspension of **1** (0.300 g, 0.480 mmol) in acetone (ca. 15 cm^3), LiCl was added (0.044 g, 1.056 mmol) and the mixture was stirred at r.t. for 1 h. Then water (ca. 15 cm^3) was added and stirring continued for another 3 h. The precipitate formed was filtered off, washed with water and dried in vacuo. Yield: 90%. Anal. Found: C, 41.3; H, 4.4; N, 4.7. Calc. for $C_{20}H_{26}Pd_2N_2Cl_2$: C, 41.6;

H, 4.5; N, 4.9%. IR: ν(C=N) 1603m; ν_{as}(Pd–Cl) 317, ν_s(Pd–Cl) 245 cm^{-1}.

A similar procedure was used to synthesize compound **3**.

3.3. [(Cl)PdN(Cy)=C(H)C$_6$H$_2$C(H)=N(Cy)Pd(Cl)]$_n$ (3)

Yield: 87%. Anal. Found: C, 36.1; H, 3.9; N, 4.2. Calc. for $C_{20}H_{26}Pd_2N_2Br_2$: C, 36.0; H, 3.8; N, 4.1%. IR: ν(C=N) 1606m cm^{-1}. ^{1}H-NMR (CD$_3$)$_2$CO: δ 8.15 [s, 2H, HC=N], 7.32 [s, 2H, H2, H5], 3.32 [m, 2H, C7], δ 1.8–0.5 [m, 20H, H8–H12].

3.4. Synthesis of [{(Cl)PdN(Cy)=C(H)C$_6$H$_2$C(H)=N(Cy)Pd(Cl)}$_2${μ-Ph$_2$PCH$_2$PPh$_2$}$_2$] (5)

To a suspension of **2** (0.050 g, 0.086 mmol) in dichloromethane (ca. 15 cm^3) Ph$_2$PCH$_2$PPh$_2$ (0.033 g, 0.086 mmol) was added and the mixture was stirred at r.t. for 24 h. The resulting solution was chromatographed on a column packed with silica gel. Elution with dichloromethane–ethanol 0.5% afforded the desired complex, which was recrystallized from dichloromethane–*n*-hexane to give a yellow solid.

Yield: 70%. Anal. Found: C, 56.3; H, 4.9; N, 2.8. Calc. for $C_{90}H_{96}Pd_4N_4P_4Cl_4$: C, 56.1; H, 5.0; N, 2.9%. IR: ν(C=N) 1619m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 8.5–7.1 [m, 40H, PPh$_2$], δ 6.94 [d, 4H, HC=N, ^4J(PH) = 9.0 Hz], δ 5.57 [d, 4H, H2, H5, ^4J(PH) = 6.1 Hz], δ 4.88 [t, 4H, PCH$_2$P, ^2J(PH) = 13.0 Hz], δ 3.91 [m, 4H, H7], δ 2.0–0.8 [m, 40H, H8–H12]. δ(P) = 31.3s.

Compound **6** was synthesized similarly.

3.5. [{(Br)PdN(Cy)=C(H)C$_6$H$_2$C(H)=N(Cy)Pd(Br)}$_2${μ-Ph$_2$P(CH$_2$)$_5$PPh$_2$}$_2$] (6)

Yield: 73% Anal. Found: C, 52.9; H, 5.3; N, 2.5. Calc. for $C_{98}H_{112}Pd_4N_4P_4Br_4$: C, 53.1; H, 5.1; N, 2.5%. IR: ν(C=N) 1621s cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.9–7.3 [m, 40H, PPh$_2$], δ 6.99 [d, 4H, HC=N, ^4J(PH) = 8.8 Hz], δ 5.55 [d, 4H, H2, H5, ^4J(PH) = 6.8 Hz], δ 4.49 [m, 4H, H7], δ 1.9–0.8 [m, 40H, H8–H12]. δ(P) = 31.1s.

3.6. Synthesis of [{(Cl)PdN(Cy)=C(H)C$_6$H$_2$C(H)=N(Cy)Pd(Cl)}{Ph$_2$PCH$_2$PPh$_2$-P,P}$_2$][ClO$_4$]$_2$ (7)

To a suspension of **2** (0.050 g, 0.086 mmol) in dichloromethane (ca. 15 cm^3) Ph$_2$PCH$_2$PPh$_2$ (0.066 g, 0.172 mmol) was added. The mixture was stirred at r.t. for 24 h; after which a solution of sodium perchlorate in MeOH was added and the resulting mixture was stirred for another 5 h; water was then added and stirring continued for 4 h. The precipitate formed was filtered off, dried in vacuo and recrystallized from dichloromethane–*n*-hexane.

Yield: 80% Anal. Found: C, 57.3; H, 4.9; N, 1.9. Calc. for $C_{70}H_{70}Pd_2N_2P_4Cl_2O_8$: C, 57.0; H, 4.8; N, 1.9%. IR: ν(C=N) 1618m cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 7.9–7.3 [m, 40H, PPh$_2$], δ 7.05 [d, 2H, HC=N, ^4J(PH) = 8.3 Hz], δ 6.62 [dd, 2H, H2, H5, ^4J(PH) = 7.5, 9.5 Hz], δ 3.90 [m, 2H, H7], δ 4.25 [dd, 4H, PCH$_2$P, ^2J(PH) = 7.8, 11.2 Hz], δ 1.9–0.7 [m, 20H, H8–H12]. ^{31}P-{^{1}H}-NMR (CDCl$_3$) = δ −4.4d, δ −28.0d, J(PP) = 36.5 Hz.

3.7. Synthesis of [PdN(Cy)=C(H)C$_6$H$_2$C(H)=N(Cy)Pd}{Ph$_2$PC(H)=C(H)PPh$_2$-P,P}$_2$][ClO$_4$]$_2$ (8)

To a suspension of **2** (0.050 g, 0.086 mmol) in dichloromethane (ca. 15 cm^3) *cis*-Ph$_2$PC(H)=C(H)PPh$_2$ (0.068 g, 0.172 mmol) was added. The mixture was stirred at r.t. for 24 h; after which sodium perchlorate in MeOH was added and the mixture was stirred for another 5 h. The reaction mixture was chromatographed on a column packed with silica gel. Elution with dichloromethane–ethanol 1% afforded the desired complex, which was recrystallized from chloroform–*n*-hexane to give a yellow solid.

Yield: 65% Anal. Found: C, 57.6; H, 4.6; N, 1.8. Calc. for $C_{72}H_{70}Pd_2N_2P_4Cl_2O_8$: C, 57.7; H, 4.7; N, 1.9%. IR: ν(C=N) 1620s cm^{-1}. ^{1}H-NMR (DMSO): δ 8.1–7.4 [m, 40H, PPh$_2$, δ 8.20 [d, 2H, HC=N, ^4J(PH) = 8.7 Hz], 7.00 [m, 2H, H2, H5], 3.90 [m, 2H, H7], δ 1.6–0.4 [m, 20H, H8–H12]. ^{31}P-{^{1}H}-NMR (DMSO):δ 63.4d, δ 55.5d, J(PP) = 7.4 Hz.

3.8. Single-crystal X-ray diffraction analysis. Crystal structure determination of complexes 4 and 8

Three-dimensional, r.t. X-ray data were collected, in the range $3.12 < 2\theta < 56.46°$ for **4** and $3.20 < 2\theta < 56.52°$ for **8** on a Siemens SMART CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. Of the 17772 (**4**) and 12751 (**8**) reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption using a semi-empirical correction based on symmetry-equivalent and repeated reflections (max, min transmissions 0.96, 0.80 (**4**) and 0.87, 0.69 for (**8**)), 3678 (**4**) and 7399 (**8**) 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 calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0554$ (**4**), 0.0489 (**8**) ($wR_2 =$ 0.1429 (**4**), 0.1284 (**8**) for all 6198 (**4**), 9123 (**8**) unique data, 335 (**4**), 497 (**8**) parameters), with allowance for the thermal anisotropy of all non hydrogen atoms.

For complex **4** the C(24) to C(28) carbon atoms of one of the phenyl rings of triphenylphosphine were found to be disordered over two positions with an angle between the two rings (C23 to C28) and (C23–C240 to C280) of 115.9°. The occupancies of the two pairs of positions were tied to give an overall value of 1.0 and then refined with each component having ca. 60/40% occupancies.

For complex **8** Cl(1), Cl(2), Cl(3) chlorine atoms of the chloroform molecule and the oxygen atoms of the perchlorate anion, O(1), O(2), O(4), were also found to be disordered in two different positions.

Minimum and maximum final electron density were -0.929 and 0.630 e $Å^{-3}$ for **4** and -1.215 and 1.051 e $Å^{-3}$ for **8**. The structure solution and refinement were carried out using the SHELX-97 program package [24].

4. Supplementary material

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 177799 for compound **4** and CCDC no. 177800 for compound **8**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Ministerio de Educación y Cultura (Proyecto PB98-0638-C02-01/02), the Xunta de Galicia (Proyecto PGIDT99PXI20907B) and the Universidad de la Coruña for financial support.

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