Synthesis and characterization of palladium(II) complexes $[PdX_2(p-diben)]$ (X = Cl, Br, I, N₃, or NCO; *p*-diben = *N*,*N*'-bis(4-dimethylaminobenzylidene)ethane-1,2-diamine): crystal structure of $[Pd(N_3)_2(p-diben)]$

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Abstract Five new complexes of general formula $[PdX_2(p-diben)]$, where *p*-diben = *N*,*N'*-bis(4-dimethylaminobenzy-lidene)ethane-1,2-diamine) (1) and X = Cl (2), Br (3), I (4), N₃ (5), or CNO (6), were synthesized and characterized by physicochemical and spectroscopic methods. The crystal structure of compound (5) was determined by single-crystal X-ray diffraction. Complexes 2–6 were characterized as *N*,*N*-chelated products. The crystal structure confirmed this formulation for $[Pd(N_3)_2(p-diben)]$, besides showing the isomerism inversion of one of the C=N bonds, caused by Pd(II) coordination.

Introduction

Schiff bases have been widely used as chelating ligands in the field of coordination chemistry [1–4]. These compounds are easily prepared by the condensation reactions of aldehydes and imines [5, 6]. Over the last few decades, a great deal of interest in the chemistry of transition metal Schiff base chelates has resulted from their biologic activity as antifungal, antibacterial, and antitumor agents [1, 7–11], and also their catalytic activity in reactions, such as oxidation, epoxidation, and hydrolysis [12–16]. In this context, the complexes of palladium(II) with Schiff base ligands are of particular interest. Such palladium(II) complexes have various applications, in addition to those already mentioned, including photoluminescence [17] and materials science (liquid crystals) [18]. The aim of this work was the synthesis

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Instituto de Química, Universidade Federal de Alfenas-UNIFAL-MG, Alfenas, MG 37130-000, Brazil e-mail: tonon@unifal-mg.edu.br and characterization of new palladium(II) complexes of the N,N'-bis(4-dimethylaminobenzylidene)ethane-1,2-diamine (*p*-diben) ligand [19, 20], including halides (Cl⁻, Br⁻, and I⁻) and pseudohalides (N₃⁻ and NCO⁻), synthesized by a regiospecific substitution [21] of the chloride complex. Substitution of chloride by other halides or pseudohalides is generally highly stereospecific [22].

Experimental

All syntheses were carried out at room temperature. All reagents were obtained from commercial suppliers and used without further purification. Elemental analysis of carbon, nitrogen, and hydrogen was performed using a Leco Instruments Ltd—TruSpec CHNS-O instrument. Infrared spectra were recorded as KBr pellets on a Shimadzu—Prestige-21 spectrophotometer in the spectral range 400–4,000 cm⁻¹. NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz (¹H) and 75 MHz (¹³C), using CDCl₃ as solvent.

An orange parallelepiped single crystal of $[Pd(N_3)_2(p-diben)]$ with dimensions equal to $0.37 \times 0.27 \times 0.04$ mm was obtained from slow evaporation of a chloroform solution of the complex. The single-crystal X-ray diffraction measurements were performed at 295 K on a Gemini A-Ultra diffractometer equipped with an Atlas CCD detector using graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). The program CrysAlisPRO [23] was used for data collection, cell refinement, and data reduction. The structure was solved by direct methods using the software Sir92 [24] and refined by full-matrix least squares on F^2 using the software SHELXL-2013 [25]. The non-hydrogen atoms were refined with least squares of full matrix on F^2 with anisotropic parameters considered.

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Table 1 Crystallographic data obtained for [Pd(N₃)₂(p-diben)]

Parameters	Data
Chem formula	$C_{20}H_{26}N_{10}Pd$
Fw	512.91
Space group	P2 ₁ /n
a (Å)	13.9552(4)
<i>b</i> (Å)	8.2896(2)
<i>c</i> (Å)	20.0633(7)
β (°)	106.738(4)
$V(\text{\AA}^3)$	2222.65(11)
Ζ	4
$\mu \text{ (mm}^{-1}\text{)}$	0.86
ρ calcd (Mg m ⁻¹)	1.533
θ -Range for data collection	2.1–29.5°
Refl. collected/unique	17,233/5,544
Data/parameter/restraints	5,544/280/0
<i>R</i> indices $[I > 2\delta(I)]$	R1 = 0.0425 / wR2 = 0.1097
GooF on F^2	1.068
Residual density (e $Å^{-3}$)	0.56 and -0.65

Aromatic H atoms were observed in a difference Fourier synthesis but were refined using a riding model. C–H atoms were positioned and refined with individual parameters Uiso(H) = 1,2Ueq (C). The main crystallographic data are given in Table 1. These were generated with WingX [26], and the figures were prepared with mercury [27]. Conformation and molecular geometry were analyzed with the software MOGUL [28].

Synthesis of *p*-diben (1)

The title imine was synthesized according to previously described methods [19, 20]. To a solution of 4-(dimethylamino)benzaldehyde (13.4 mmol) in absolute ethanol (50 mL) was added over for 1 h a solution of ethylenediamine (6.7 mmol) in absolute ethanol (5 mL). The mixture was stirred at room temperature (approximately 25 °C) for 2 h. The white precipitate was separated by filtration, washed with water, ethyl ether, and dried in vacuum. Yield: 97 %. Elemental analysis: % calculated (found) for C₂₄H₂₄N₂: C: 74.5 (74.4); H: 6.1 (6.0); and N: 17.4 (17.1). FTIR (KBr cm⁻¹): 1,639 (s), 1,604 (vs), 1,526 (s), 1,443 (m), 1,430 (m), 1,363 (s), 1,340 (m), 1,308 (m), 1,229 (m), 1,187 (vs), 1,106 (w), 1,037 (w), (s), 1,005 (w), 939 (vw), 919 (vw), 862 (w), 809 (vw), 788 (m), 747 (vs), 711 (w), 653 (vw), 625 (vw), 580 (w), 563 (w), 514 (m), 474 (vw), 457 (vw), 445 (vw), and 425 (m). ¹H NMR (CDCl₃, δ (ppm)): 2.96 (s, 12H), 3.87 (s, 4H), 6.65 (d, 4H, J = 8 Hz), 7.57 (d, 4H, J = 8.33), and 8.15 (s, 2H). 13 C NMR (CDCl₃, δ (ppm)): 40.20, 62.11, 111.57, 124.53, 129.50, 151.97, and 162.36.

Synthesis of $[PdCl_2(p-diben)]$ (2)

To a solution of lithium tetrachloropalladate(II), Li₂[PdCl₄], prepared from a one-pot synthesis by reaction of PdCl₂ and LiCl (PdCl₂, 5.6 mmol) in methanol (70 mL), was added the Schiff base (1). (p-diben, 5.6 mmol). The reaction mixture was stirred for 8 h at room temperature. The orange precipitate was filtered off, washed with water and ethyl ether, and dried in vacuum. Yield: 93 %. Elemental analysis: % calculated (found) for C24H24N2-PdCl₂C: 48.1 (48.1); H: 5.2 (5.1); and N: 11.2 (11.4). FTIR (KBr cm^{-1}) : 1,595 (vs), 1,535 (s), 1,483 (vw), 1,444 (m), 1,408 (vw), 1,377 (s), 1,328 (w), 1,251 (w), 1,230 (w), 1,190 (s), 1,105 (vw), 1,168 (vw), 1,033 (w), 972 (vw), 945 (m), 813 (m), 792 (w), 734 (vw), 576 (vw), 516 (w), and 449 (vw). ¹H NMR (CDCl₃, δ (ppm)): 3.08 (s, 12H), 3.80 (t, 2H, J = 6.63 Hz), 4.26 (t, 2H, J = 9.43 Hz), 6.70 (m, 4H. J = 9.28 Hz), 7.46 (dd, H, J = 28.87 and 8.76 Hz). 7.77 (d, H, J = 25.04 and 8.62 Hz), 8.63 (m, 2H, J = 24.61 and 9.65 Hz), and 9.73 (s, 2H). ¹³C (CDCl₃, δ (ppm)): 39.95, 57.60, 66.14, 111.00, 117.74, 133.26, 134.81, 167.40, 169.54, and 190.29.

Synthesis of [PdBr₂(p-diben)] (3)

To a suspension of $[PdCl_2(p-diben)]$ (1.00 mmol) in acetone (30 mL), was added a solution of KBr (2.1 mmol) in distilled water (5 mL). The reaction mixture was stirred for 2 h at room temperature. The yellowish precipitate was filtered off, washed with water and ethyl ether, and dried in vacuum. Yield: 80 %. Elemental analysis: % calculated (found) for C₂₄H₂₄N₂PdBr₂C: 40.8 (40.7); H: 4.4 (4.4); and N: 9.5 (9.6). FTIR (KBr cm⁻¹): 1,597 (vs), 1,534 (m), 1,465 (w), 1,437 (w), 1,409 (w), 1,376 (m), 1,254 (w), 1,231 (w), 1,190 (w), 1,166 (s), 1,057 (m), 943 (w), 815 (m), 729 (m), 596 (w), 554 (w), and 515 (w).¹H NMR (CDCl₃, δ (ppm)): 3.07 (s, 12H), 4.56 (s, 4H), 6.70 (d, 4H, J = 8.89 Hz), 7.74 (d, 4H, J = 9.06 Hz), and 9.74 (s, 2H). ¹³C (CDCl₃, δ (ppm)): 40.09, 111.00, 125.21, 132.00, 154.35, and 190.33.

Synthesis of $[PdI_2(p-diben)]$ (4)

The synthesis of compound (4) followed the same method as for compound (3). However, the salt used was KI (2.1 mmol). The brown precipitate was filtered off, washed with water and ethyl ether, and dried in vacuum. Yield: 72 %. Elemental analysis: % calculated (found) for C₂₄. H₂₄N₂PdI₂C: 35.2 (35.1); H: 3.8 (3.9); and N: 8.2 (8.3). FTIR (KBr cm⁻¹): 1,591 (vs), 1,529 (s), 1,481 (vw), 1,438 (m), 1,409 (w), 1,375 (w), 1,325 (w), 1,247 (vw), 1,228 (w), 1,188 (s), 1,170 (s), 1,141 (vw), 1,124 (vw), 1,060 (w), 1,001 (vw), 945 (w), 813 (m), and 518 (w). ¹H NMR (CDCl₃, δ (ppm)): 3.08 (s, 12H), 4.18 (m, 4H, J = 3.09 Hz), 6.73 (d, 4H, J = 8.91 Hz), 7.84 (d, 4H, J = 9.36 Hz), and 9.52 (s, 2H). ¹³C (CDCl₃, δ (ppm)): 40.24, 65.19, 111.15, 130.22, 157.49, and 189.90.

Synthesis of $[Pd (N_3)_2(p-diben)]$ (5)

The synthesis of compound (5) followed the same method as for compound (3). However, the salt used was NaN_3 (2.3 mmol). The orange precipitate was filtered off, washed with water and ethyl ether, and dried in vacuum. Yield: 86 %. Elemental analysis: % calculated (found) for C_{24} H₂₄N₈PdC: 46.8 (46.6); H: 5.1 (5.2); and N: 27.3 (27.5). FTIR (KBr cm⁻¹): 2,021 (vs), 1,587 (vs), 1,529 (s), 1,481 (vw), 1,438 (m), 1,411 (w), 1,377 (s), 1,325 (m), 1,284 (w), 1,234 (w), 1,190 (s), 1,174 (s), 1,128 (vw), 1,067 (w), 1,028 (vw), 945 (m), 812 (m), 756 (w), and 524 (m). ¹H NMR $(CDCl_3, \delta (ppm))$: 3.02 (s, 12H), 3.72 (t, 2H, J = 4.2 Hz), 4.08 (t, 2H, J = 5.89 Hz), 6.78 (m, 4H, J = 7.14 Hz), 7.58 (d, 2H, J = 9.13 Hz), 7.79 (d, H, J = 9.13 Hz), 8.24 (s, H), 8.31 (d, 2H, J = 8.98 Hz), and 9.63 (s, 2H). ¹³C (CDCl₃, δ (ppm)): 39.86, 57.21, 65.78, 111.00, 118.41, 133.56, 134.15, 152.51, 154.27, 169.93, and 189.93.

Synthesis of [Pd (NCO)₂(p-diben)] (6)

The synthesis of compound (**6**) followed the same method as for compound (**3**). However, the salt used was KCNO (2.2 mmol). The yellowish precipitate was filtered off, washed with water and ethyl ether, and dried in vacuum. Yield: 68 %. Elemental analysis: % calculated (found) for $C_{26}H_{24}N_4O_2Pd$ C: 51.5 (51.5); H: 5.1 (5.2); and N: 16.4 (16.3). FTIR (KBr cm⁻¹): 2,196 (vs), 1,593 (vs), 1,533 (s), 1,483 (vw), 1,444 (m), 1,409 (w), 1,377 (s), 1,328 (m), 1,251 (w), 1,218 (w), 1,190 (s), 1,144 (vw), 1,066 (w), 1,033 (w), 1,002 (w), 945 (m), 813 (s), 792 (vw), 736 (w), and 516 (m). ¹H NMR (CDCl₃, δ (ppm)): 3.09 (s, 12H), 4.15 (s, 4H), 6.79 (d, 4H, J = 8.52 Hz), 7.72 (d, 4H, J = 8.91 Hz), and 9.68 (s, 2H). ¹³C (CDCl₃, δ (ppm)): 39.95, 110.74, 115.62, 121.87, 131.57, 150.21, and 190.64.

Results and discussion

Spectroscopic characterization

The IR spectrum of the free Schiff base (1) exhibits the v(N=C) band at 1,639 cm⁻¹, indicating formation of the imine linkage as expected. Compared with the spectrum of the starting primary amine, the absence of bands corresponding to the characteristic asymmetric (~3,300 cm⁻¹) and symmetric (~3,200 cm⁻¹) stretching (N–H) bond is noticeable. Moreover, when compared with the spectrum



Fig. 1 Structure of *N*,*N*'-bis(4-dimethylaminobenzylidene)ethane-1,2-diamine) [19, 20]

of the aldehyde precursor, the intense stretching band of the v(C=O) bond characteristic of aromatic aldehyde ($\sim 1,700 \text{ cm}^{-1}$) is absent. These data indicate the formation of a Schiff base from the starting reagents.

The ¹H and ¹³C NMR spectra of the Schiff base show a symmetric structure [19, 20], with the formation of two imine bonds as shown in Fig. 1.

In the IR spectra of the complexes 2–6, a shift in the v(N=C) band to lower frequencies can be observed, overlapping a v(C=C) aromatic band (~1,597 cm⁻¹). This shift can be explained by coordination of the imine nitrogen to the metal, such that an electronic relocation occurs in this bond. The replacement of halide Cl⁻ by Br⁻ (3) and l⁻ (4) cannot be discerned from the IR spectra; however, terminal coordination of the azide group in complex (5) is suggested by the $v_{as}NNN$ band at 2,021 cm⁻¹ [29–31]. In the IR spectrum of complex (6), the presence of the v_{as} -NCO absorption at 2,196 cm⁻¹ indicated the *N*-terminally coordinated cyanate ligands [29].

The ¹H and ¹³C NMR spectra of complexes 2-6 also indicate the formation of N,N-chelated products. Thus, there is a displacement of the (-HC=N-) signal [δ (ppm) = 9.73, 9.74, 9.52, 9.84, and 9.68, respectively]when compared with the free ligand [δ (ppm) = 8.15], indicating the coordination of the nitrogen atom to palladium(II). This coordination deshields the imine hydrogen, resulting in a higher chemical shift value. Furthermore, all of the major signals can be observed in the spectra of the complexes, indicating that the structure of the Schiff base ligand is preserved in the complexes. On further analysis, the spectra of complexes (2) and (5), one can note a significant change in the aromatic region involving a complicated series of signals observed at 6.70, 7.46, and 7.77 ppm for complex (2), and 6.82, 7.43, 7.74, and 7.86 ppm for complex (5). This can be explained by E/Zisomerization [26-31] of one of the imines of the ligand. Conjugation of the imine with the aromatic ring causes a decrease in the double bond character of the C=N bond, facilitating rotation to minimize the steric hindrance. The ¹H NMR spectra of complexes (3), (4), and (6) show relatively little change in the aromatic region (6.70 and

Fig. 2 Representation of the asymmetric unit of the complex 5 with ellipsoids with 50 % of probability. The hydrogen atoms have been omitted for better view of the structure



7.74 ppm for (3); 6.73 and 7.84 ppm for (4); 6.79 and 7.72 ppm for (6)) when compared with the imine ligand (6.65 and 7.57 ppm). This suggests that the two C=N bonds are presented as the same isomers. As the ions Br^- , I^- , and NCO⁻ are bulky, the E/Z isomerization is favored.

The ¹³C NMR spectra of the complexes show a shift of the imine carbon signal [δ (ppm) = 190.29 (2), 190.33 (3), 189.90 (4), 189.93(5), and 190.64 (6)] when compared with the free ligand (δ = 162.36 ppm). In the ¹³C NMR spectra of complexes (2) and (5), the aromatic region shows a series of signals (110–170 ppm), indicating a difference in aromatic ring carbons caused by different forms of the two imines. The ¹³C NMR spectra of the compounds (3), (4), and (6) show the expected signals in the aromatic region (111.00, 125.21, 132.00, and 154.35 ppm for (3); 111.15, 130.22, and 157.49 ppm for (4); 110.74, 121.87, 131.57 and 150.721 ppm for (6)) when compared with the imine ligand (111.57, 124.53, 129.50, and 151.97 ppm).

X-ray crystallographic determination

The crystal structure of complex (5) was studied by singlecrystal X-ray diffraction, and the data show that it consists with a neutral molecule of $[Pd(N_3)_2(p-diben)]$, as shown by the representation given in Fig. 2.

The palladium(II) is four-coordinated with a characteristic square-planar geometry, in which the nitrogen atoms form a basal plane with the metal atom (RMSD of 0.067). The Pd–N bond lengths are in the range of 2.033–2.110 Å, and the angles around the metal center are all very close to 90°, as shown in Table 2. The variations in the angles can be explained in terms of steric effects and presence of intermolecular interactions. Thus, the reduced N2–Pd1–N3 angle can be attributed to the C10–C11 bond that forces the angle to lower values, whereas the N3–Pd1–N8 and N5– Pd1–N8 angles can be explained by the steric effect

Table 2 Distance (Å) andangles (°) around the metallicion for the complex

	Compound 5
Pd1–N2	2.033(3)
Pd1–N3	2.050(2)
Pd1–N5	2.110(3)
Pd1–N8	2.067(3)
N2-Pd1-N3	81.76(11)
N2-Pd1-N5	90.84(11)
N3-Pd1-N8	93.42(11)
N5-Pd1-N8	93.83(12)

between ring B and N8 atom and between the azide groups, respectively. The increase in the N5–Pd1–N8 angle may also be attributed to participation of the azide groups in nonclassical intermolecular hydrogen bonds, which tends to cause a slight deviation in this parameter.

The molecular structure was analyzed with the software MOGUL, which showed that all bond lengths and angles were in agreement with the expected statistical values for a good X-ray diffraction structure refinement and do not reveal any deviations when compared with fragments of structures deposited in the CSD. Comparing a selected bond length of the parent ligand (polymorphs A and B) with the coordinated one, it is possible to observe a slight lengthening of the C9–N2, N2–C10, C11–N3, and N3–C12 bonds (Table 3). This is expected due to the electronic relocation caused during the metal coordination. The molecular structure clearly revealed a change in the conformation of the ligand upon metal coordination, as predicted by the NMR data, in which the ligands have an E/E configuration and the complex has an E/Z one, as discussed above.

The analysis of the crystal structure of the complex revealed the absence of classical intermolecular hydrogen bonds, since the potential donors and acceptors are coordinated to the metal atom. However, the structure is stabilized

Table 3	Distance (A) and	angles (°) of	nonclassical	hydrogen	bonds
Table 3	Distance (F	() anu	angies) 01	nonciassical	nyurogen	bonus

	D–H	НА	DA	<d-ha< th=""></d-ha<>
System A ¹	0.930	2.656	3.567	166.39
System B ²	0.960	2.722	3.398	128.04
System C ³	0.970	2.733	3.425	128.85

D donor, A acceptor

Symmetry code: (1) -0.5 + x, 0.5 - y, -0.5 + z; (2) 0.5 + x, 0.5 - y, -0.5 + z; and (3) 0.5 - x, 0.5 + y, 0.5 - z

by nonclassical intermolecular hydrogen bonds, involving the systems C17–H17...N7 (system A), C2–H2c...N10 (system B), and C10–H10b...N8 (system C) (Table 3). These interactions arrange system A in an infinite chain along the plane (101) and system B along the plane (10–1), while system B is arranged in an infinite chain, with a headto-tail network along the [010] direction.

Conclusion

In summary, we have described in this paper the synthesis of a Schiff base ligand and five of its palladium(II) complexes. Elemental analysis and IR, ¹H, and ¹³C NMR data of the complexes all indicate the formation of *N*,*N*-chelated products. The IR spectra of complexes (**5**) and (**6**) indicate *N*-terminal coordination of both pseudohalides (N₃ and NCO). Single-crystal X-ray diffraction revealed that in the complex (**5**), there is a slightly distorted square-planar geometry around the palladium atom, caused by repulsion between the azide group and the Schiff base aromatic ring, while the Pd–N distances are within the expected ranges.

Supplementary data

CCDC 984033 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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