Synthesis and thermal behavior study of complexes of the type $[Pd(\mu-X)(4-eb-p-phen)]_2$ (X = Cl, Br, I, N₃, NCO, SCN) and 4-eb*p*-phen [bis(4-ethylbenzyl)*p*-phenylenediimine]

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Abstract The Schiff base bis(4-ethylbenzyl) *p*-phenylenediimine, 4-eb-*p*-phen (1), and six new dimeric Pd(II) complexes of the type $[Pd(\mu-X)(4-eb-p-phen)]_2 \{X = Cl (2),$ Br (3), I (4), N₃ (5), NCO (6), SCN (7)} have been synthesized and characterized by elemental analysis, IR spectroscopy, and ¹H and ¹³C{¹H}-NMR experiments. The thermal behavior of the complexes 2–7 has been investigated by means of thermogravimetry and differential thermal analysis. From the final decomposition temperatures, the thermal stability of the complexes can be ordered in the following sequence: $3 > 4 > 7 > 2 \approx 5 > 6$. The final products of the thermal decompositions were characterized as metallic palladium by X-ray powder diffraction (XRD).

Keywords Cyclopalladated · Iminic ligands · IR and NMR spectroscopy · TG–DTA

Introduction

Cyclometalated compounds have been the subject of many studies over the last decades because of their numerous applications in organic synthesis and catalysis of metallomesogens in liquid crystals, synthesis of supramolecules, and as biologically active compounds [1].

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UNESP - Univ Estadual Paulista, Instituto de Química, CEP, Araraquara, SP 14801-970, Brazil Cyclometalated complexes of palladium(II) have often been considered to be interesting organometallic molecules because they show properties that may have useful applications in several domains of Chemistry, Physics, or Biology. Studies have demonstrated that palladium derivatives exhibit a noticeable cytotoxic activity, similar to standard platinum-based drugs used as a reference, and show fewer side effects relative to other heavy metal anticancer compounds [2].

Palladium(II) compounds show ligand-exchange kinetics 10⁵ times greater than the platinum(II) analogs, which may facilitate the hydrolysis of the leaving groups that dissociate readily in solution, before the complex reaches the pharmacological target. To overcome their high lability, chelating ligands have been used to afford high thermodynamically stable and kinetically inert Pd(II) complexes [3].

In particular, palladacycles result in an interesting biological activity because of their possible capacity to inhibit the replication of DNA by single or simultaneous interactions, such as insertion and/or coordination with DNA structure by its metallic center [4].

Schiff bases are compounds characterized by the presence of at least one imine functional group. These compounds are obtained by the condensation of primary amines and aldehydes or ketones. These bases play an important role in coordination chemistry because the C=N group is suitable for many coordinated reactions. Also the bidentate imines are an important class of chelating ligands [5–7].

As a part of our research program in this area, we report in the present study the synthesis, characterization, and thermal behavior of the compounds 4-eb-*p*-phen (1), $[Pd(\mu-Cl)(4-eb-p-phen)]_2$ (2), $[Pd(\mu-Br)(4-eb-p-phen)]_2$ (3), $[Pd(\mu-I)(4-eb-p-phen)]_2$ (4), $[Pd(\mu-(N_3))(4-eb-p-phen)]_2$ (5), $[Pd(\mu-(NCO)(4-eb-p-phen)]_2$ (6), and $[Pd(\mu-(SCN))(4-eb-p-phen)]_2$ (7).

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Experimental

All syntheses were carried out at room temperature. All reagents were obtained from commercial suppliers and used without further purification.

Preparation of Schiff base (1)

To a solution of *p*-phenylenediamine (2.77 mmol) in ethanol (100 mL), a solution of 4-ethyl-benzaldehyde (5.54 mmol) in ethanol (5 mL) was added slowly for 3 h. The yellow solid formed was filtered off and dried in vacuum, obtaining a reaction yield of 97 %. The proposed structure for the ligand is shown in Fig. 1.

Preparation of the complexes 2–7

For the synthesis of the compound $[Pd(\mu-Cl)(4-eb-p-phen)]_2$ (2), the following methodology has been employed: Firstly, 1.00 g (5.65 mmol) of palladium chloride was partially solubilized in 100.00 mL of methanol at 50 °C. To this solution, 0.50 g (11.77 mmol) of lithium chloride was added. After that the mixture was left under stirring at 50 °C until the solution turned reddish brown. The mixture was cooled and filtered off. Then, 1.92 g (5.76 mmol) of the ligand 4-eb-*p*-phen was added, followed by the slow addition of 0.82 mL (5.82 mmol) of triethylamine in 8.00 mL of methanol. Lastly, the mixture was stirred for 8 h, forming an orange solid. The yellow suspension was filtered off, and the obtained solid was



Fig. 1 Proposed structure for the ligand 4-eb-p-phen

Fig. 2 Proposed structure for the compounds $[Pd(\mu-X)(4-eb$ *p*-phen)]₂ (X = Cl (2); Br (3); I (4); N₃ (5), NCO (6), SCN (7) washed with distilled water and ethyl ether, and vacuum dried, obtaining a yield of 91 %.

Compounds 3–7 were readily obtained by metathetical reactions of $[Pd(\mu-Cl)(4-eb-p-phen)]_2$ (2) (0.35 g; 0.364 mmol) with 0.728 mmol of the appropriate salts (KBr, KI, NaN₃, KNCO, and KSCN, respectively) in 50 mL of acetone under constant stirring for 2 h. The resulting suspensions were filtered off, and the obtained solids were washed with distilled water and ethyl ether, and vacuum dried. The yields of the compounds are as follows: 85 % (3), 81 % (4), 77 % (5), 83 % (6), and 68 % (7). The proposed structure for the complexes 3–7 is shown in Fig. 2.

Instrumentation

Elemental analysis of carbon, hydrogen, and nitrogen was performed on Elemental Analyzer, Leco Instruments LTD-TruSpec model CHNS-O. The absorption spectra in the infrared region were recorded on spectrophotometer, Thermo Scientific-IS-Nicolet FT-IR 50, in the $4000-400 \text{ cm}^{-1}$ spectral range. The spectra of nuclear magnetic resonance of ¹H and ¹³C were recorded on Bruker AC-200 spectrometer working at 300 MHz for ¹H and 75 MHz for ${}^{13}C{}^{1}H$, using CDCl₃ for (1) and (2) or DMSO- d_6 for 3–7 for dissolution of samples. The melting or decomposition points were obtained using the MARTE (PFM II) equipment. Simultaneously, thermal analyses (TG-DTA) were carried out using a thermobalance, TA Instruments-SDT Q600, under flow of dry synthetic air $(100 \text{ mL min}^{-1})$, temperature up to 1,100 °C, and heating rate of 20 °C min⁻¹, in α -alumina sample holders, using sample masses of about 10 mg. The reference was pure α alumina in DTA measurements. The patterns of powder X-ray diffraction were obtained by Rigaku Ultima IX equipment using K_{\alpha}Cu wavelength ($\lambda = 1.5418$ Å) setting of 34 kV and 20 mA.



Table 1 Results of the elemental analyses and melting or decomposition point of the compounds 1–7

Compound	m.p./°C	Carbon/%		Nitrogen/%		Hydrogen/%	
		Calc.	Obt.	Calc.	Obt.	Calc.	Obt.
1	153	86.67	83.98	8.23	8.66	6.66	7.11
2	271 (dec.)	59.89	59.18	5.82	6.11	4.82	5.07
3	315 (dec.)	54.82	53.67	5.33	5.86	4.41	4.17
4	260 (dec.)	50.33	49.19	4.89	5.16	4.05	3.98
5	198 (dec.)	59.08	58.98	14.35	13.87	4.75	4.97
6	210 (dec.)	61.54	59.98	8.61	8.47	4.75	4.23
7	170 (dec.)	59.58	58.38	8.34	9.38	4.60	4.91

Results and discussion

The results of elemental analysis supported the proposal for the compounds 1-7 (Table 1).

Spectroscopy

The IR absorption spectrum of the ligand 4-eb-*p*-phen (1), in Fig. 3, presented an intense band at 1623 cm⁻¹ assigned to the stretching mode of the characteristic imine C=N bond, confirming its formation [8]. Compared with the spectrum of the starting primary amine, the disappearance of the bands corresponding to the characteristic asymmetric (\sim 3300 cm⁻¹) and symmetric (\sim 3200 cm⁻¹) stretching NH bond is observed. Moreover, when compared with the spectrum of the precursor aldehyde, there is a disappearance of the intense stretching band characteristic of the C=O bond of the aromatic aldehyde (\sim 1700 cm⁻¹). These spectral data indicated the formation of a new compound from the starting materials.

For the regiospecific substitutions, the replacement of the chloro ligand in (2) by Br (3) and I (4) was not observed in the spectrum in the analyzed IR region, in Fig. 3. For the pseudohalides, the IR spectrum of the azido complex $[Pd(\mu-(N_3))(4-eb-p-phen)]_2$ (5) exhibited a characteristic $v_{\rm as}N_3$ band at 2062 cm⁻¹, consistent with *end-on* azido groups [9]. The pseudohalides NCO and SCN are also versatile ligands that can bind as monodentate ligands or bridging groups. The IR spectrum of the compound [Pd(µ- $(NCO)(4-eb-p-phen)]_2$ (6) showed an intense band at 2175 cm⁻¹ assigned to the asymmetric stretching vibrational mode of NCO group, indicating that the NCO is coordinated in an end-on fashion [8]. With regard to the IR spectrum of complex $[Pd(\mu-(SCN))(4-eb-p-phen)]_2$ (7), the presence of an absorption band was noticed between the 2146 and 2114 cm⁻¹ region which may suggest the *end-to*end coordination mode of the SCN group [10].

Analyzing the ¹H NMR spectrum of the Schiff base (1), in Fig. 4, a triplet was observed at 1.28 ppm (H_3C -CH₂-),



Fig. 3 IR spectra for compounds 1-7

a quadruplet at 2.72 ppm ($H_3C-C\underline{H}_2-$), a singlet at 8.48 ppm ($-\underline{H}C=N-$), and the typical multiplets associated with the symmetrical aromatic rings between 7.25 and 8.50 ppm. The ¹³C NMR spectrum of (1) showed the major signals in 15.39 ppm ($H_3\underline{C}-CH_2-$), 28.98 ppm ($H_3C-\underline{C}H_2-$), 159.65 ppm ($-\underline{H}\underline{C}=N-$), and between 121 and 150 ppm (symmetrical aromatic rings).

The formulation of (2) and (4) as $[Pd(\mu-X)(4-eb-p-phen)]_2$ due to the appearance of two signals at ca. 9.94 and ~8.48 ppm in 1:1 ratio indicates the presence of distinct –**H**C=N– groups in their molecular structures. The signal at 8.48 ppm remains unchanged at the same position in both ¹H NMR spectra of the 4-eb-*p*-phen ligand and complexes (2) and (4). This fact strongly supports that one imino group does not participate in coordination. On the other hand, the downfield shift of the –**H**C=N– proton from



Fig. 4 1 H NMR spectra for compounds (1) and (2) in CDCl₃ and (4) in DMSO- d_6

8.48 ppm (free ligand) to ca. 9.94 ppm strongly supports the coordination to the Pd atom through the iminic nitrogen. This deshielding is attributed to the removal of the electron density from the ligand to the palladium center via σ-charge donation from the imine-like N-donor atom. The existence of different distinct $-\underline{H}C=N-$ groups was also evidenced by ¹³C{¹H} NMR spectra; in Fig. 5 the ¹³C signal at ~160 ppm is associated with the non-coordinated imine group, whereas the low field resonance at 192.05 ppm (2)/193.17 ppm (4) is related to the coordinated $-\underline{H}C=N-$ groups. The presence of a complicated series of multiplets in the aromatic region of both ¹H NMR spectra has hindered their assignment. NMR spectra of compounds (3), (5), (6), and (7) could not be recorded due to their low solubility in common deuterated solvents.

Thermal analysis

The ranges of temperature (°C), mass loss (%), and the DTA peak for each of the steps proposed for the decomposition of compounds 2–7, and assignment related to mass loss are presented in Table 2. These assignments (Δm – Calc.) are based on the structural fragments from the theoretical formulae of the compounds 2–7, Fig. 2. This implies that the groups proposed in the right column of Table 2 are not necessarily the gaseous decomposition products generated. The final residues were analyzed by X-ray powder diffraction (XRD), and peaks were identified on the basis of ICDD to Pd⁰ (05-0681) and PdO (06-0515) [11].



 $[Pd(\mu-I)(4-eb-p-phen)]_2$ (4)

[Pd(µ-C1)(4-eb-p-phen)]₂ (2)

Fig. 5 ${}^{13}C{}^{1}H$ NMR spectra for compounds (1) and (2) in CDCl₃ and (4) in DMSO- d_6

TG and DTA curves of the organic compound 4-eb-pphen are shown in Fig. 6. TG curve shows that the compound is thermally stable up to 260 °C. Then three steps of mass loss are observed: the first one occurs over the temperature range of 260–468 °C, followed by two consecutive steps up to 716 °C. These events are also indicated in the DTA curve through exothermic peaks at 450 and 665 °C with shoulder at 590 °C. Furthermore, the DTA curve also shows an endothermic peak at 160 °C before decomposition, corresponding to the melting of the compound, which was confirmed by melting point analysis. The residual mass obtained was 0.41 %, indicating complete decomposition.

TG and DTA curves of the compound $[Pd(\mu-Cl)(4-eb-p$ phen)]₂ (2) are shown in Fig. 7. TG curve shows that the compound is thermally stable up to 110 °C. The mass-loss steps occurring in the range of 110–553 °C can be assigned to the removal of ligands 4-eb-p-phen and Cl, in addition to 0.66 O₂ uptake, corresponding to a mass loss of 73.95 % (calc. 75.69 %). Exothermic peaks appear at 249 and 508 °C, and an endothermic at 321 °C, in the DTA curve, corresponding to these successive decomposition steps. Between 553 and 793 °C, a mass gain of 1.06 % was observed, which can be attributed to oxidation of the remainder of Pd^0 to PdO with 0.34 O₂ uptake. The decomposition of PdO to Pd⁰ is observed between 793 and 821 °C with a mass loss of 3.13 % (calc. 3.32 %), corroborated by an endothermic peak in the DTA curve at 809 °C. The residual mass obtained was 23.18 % (calc. 22.11 %).

Table 2 Thermal analysis data of compounds $[Pd(\mu-X)(4-eb-p-phen)]_2 \{X = Cl (2), Br (3), I (4), N_3 (5), NCO (6), SCN (7)\}$

Compounds	Step	<i>ΔT</i> /°C	$\Delta m / \%$		Peaks DTA/°C		Assignment	
			Obt.	Calc.	Endo	Exo		
2	1	110-553	-73.96	-75.69	321	249/508	$-2Cl^{-}$. $-2(4-eb-p-phen)$. $+0.66O_2$	
	2	553-796	+1.06	+1.12	-	_	+0.34O ₂	
	3	793-821	-3.13	-3.32	809	_	$-O_{2}$	
	Residue		23.18	22.11			Pd ⁰	
3	1	130-693	-76.87	-76.71	386	263/636	$-2Br^{-}$. $-2(4-eb-p-phen)$. $+O_2$	
	2	797–834	-2.42	-3.04	818	_	$-O_{2}$	
	Residue		20.79	20.24			Pd ⁰	
4	1	114-666	-80.46	-81.2	-	251/636	$-2I^{-}2(4\text{-eb-}p\text{-phen}). +0.39O_{2}$	
	2	666–792	+1.22	+1.8	-	_	$+0.61O_{2}$	
	3	792-825	-2.01	-2.79	807	_	$-O_{2}$	
5	Residue		18.61	18.58			Pd^0	
	1	118-551	-74.91	-74.9	-	164/508	$-2N_3^{-}$. $-2(4-eb-p-phen)$. $+O_2$	
	2	796–831	-3.08	-3.28	826	_	$-O_{2}$	
	Residue		21.82	21.81			Pd^0	
6	1	115-535	-74.68	-76.55	-	271/471	$-2(\text{NCO})^{-}$. $-2(4\text{-eb-}p\text{-phen})$. $+0.47\text{O}_2$	
	2	598–794	+1.71	+1.75	-	_	+0.53O ₂	
	3	794–814	-3.21	-3.28	816	_	$-O_{2}$	
	Residue		22.14	21.81			Pd^0	
7	1	116–598	-75.31	-77.06	-	271/541	$-2(SCN)^{-}$. $-2(4-eb-p-phen)$. $+0.57O_2$	
	2	598–794	+1.33	+1.35	-	_	+0.43O ₂	
	3	794-819	-3.13	-3.17	809	-	$-O_{2}$	
	Residue		21.3	21.12			Pd^0	



Fig. 6 TG and DTA curves of the ligand 4-eb-p-phen



Fig. 7 TG and DTA curves of the complex [Pd(µ-Cl)(4-eb-p-phen)]₂

Figure 8 presents the TG and DTA curves of the complex $[Pd(\mu-Br)(4-eb-p-phen)]_2$ (3). This compound is thermally stable up to 130 °C. Between 130 and 693 °C, successive stages of decomposition can be observed in the TG curve, resulting in a mass loss of 76.87 % (calc. 77.23 %), and the DTA curve presented exothermic, at 263 and 636 °C, and endothermic, at 386 °C, peaks. This mass loss is related to the elimination of Br ligands and 4-eb-pphen. Simultaneously with the end of the elimination of the ligands, there is an O₂ uptake resulting in the oxidation of Pd⁰ to PdO. The decomposition of PdO to Pd⁰, between 797 and 834 °C, resulting in a decrease of 2.42 % of mass



Fig. 8 TG and DTA curves of the complex $[Pd(\mu-Br)(4-eb-p-phen)]_2$



Fig. 9 TG and DTA curves of the complex $[Pd(\mu-I)(4-eb-p-phen)]_2$



Fig. 10 TG and DTA curves of the complex $[\text{Pd}(\mu\text{-}(N_3))(4\text{-eb-}p\text{-}p\text{-}hen)]_2$



Fig. 11 TG and DTA curves of the complex $[Pd(\mu\text{-}(NCO))(4\text{-}eb\text{-}p\text{-}phen)]_2$



Fig. 12 TG and DTA curves of the complex $[Pd(\mu\text{-}(SCN))(4\text{-}eb\text{-}p\text{-}phen)]_2$

(calc. 3.94 %) is in agreement with the endothermic peak at 818 °C in the DTA curve. The residual mass of Pd^{0} obtained was 20.79 % (calc. 20.24 %).

TG and DTA of the compound $[Pd(\mu-I)(4-eb-p-phen)]_2$ (4) resulted in the curves presented in Fig. 9. This compound is considered to be thermally stable at temperatures up to 114 °C. Consecutive mass-loss steps can be observed between 115 and 666 °C, resulting in 80.46 % of mass loss (calc. 81.20 %). These steps are in agreement with DTA curve which presented two exothermic peaks at 251 and 636 °C, assigned to the removal of iodides and 4-eb-*p*-phen ligand, in addition to 0.39 O₂ uptake, between 666 and 792 °C; a mass gain of 1.22 % occurs due to the oxidation of the remainder of Pd⁰ to PdO with 0.61 O₂. The decomposition of PdO to Pd⁰ between 792 and 825 °C, with a mass loss of 3.08 % (calc. 3.28 %), is corroborated

Fig. 13 Thermogravimetric curves for the thermal decomposition of compounds 2–7, highlighting the final temperatures of step 1

by an endothermic peak in the DTA curve at 807 °C. The residual mass obtained was 18.61 % (calc. 18.58 %).

Figure 10 shows TG and DTA curves of $[Pd(\mu-N_3)(4$ $eb-p-phen)]_2$ complex (5). Being thermally stable up to 118 °C, the compound exhibits successive decomposition steps up to 551 °C to form PdO. These steps result in a mass loss of 74.91 % (calc. 74.90 %), equivalent to the elimination of N₃ ions, the 4-eb-p-phen ligands, and reaction with O_2 . In this temperature range, by DTA curve, the existence of exothermic peaks at 164 and 508 °C has been observed. The reduction of PdO to Pd occurs between 796 and 831 °C, and is confirmed by an endothermic peak at 826 °C and a mass loss of 3.08 % (calc. 3.28 %). The mass residue of Pd⁰ obtained was 21.72 % (calc. 21.81 %). It is important to note that the thermal behavior of (5) is similar to that observed for other Pd(II) compounds containing coordinated azide, which exhibit inherent tendency of highly exothermic decomposition, yielding Pd and/or PdO and gaseous products, such as N2. In some cases, these compounds are potential explosives [12–14].

TG and DTA curves of the compound $[Pd(\mu-(NCO))(4$ $eb-p-phen)]_2$ (6) are illustrated in Fig. 11. This complex presents thermal stability at temperatures up to 115 °C; above this temperature, it undergoes several stages of mass loss up to 535 °C, resulting in a total mass loss of 74.68 % (calc. 76.55 %). This mass loss is equivalent to the elimination of two NCO pseudohalides and two 4-eb-p-phen ligands, in addition to $0.47 O_2$ uptake. In this temperature range, DTA curve shows two exothermic peaks at 271 and 471 °C. In the second step (535-795 °C), a mass gain of 1.71 % occurs due to the oxidation of the remaining Pd^{0} to PdO with 0.53 O₂. The final step, between 795 and 831 °C, corresponds to the reduction of PdO to Pd⁰, characterized by a mass loss of 3.21 % (calc. 3.28 %) and to the existence of an endothermic peak at 816 °C. The final mass after total decomposition was 22.14 % (calc. 21.81 %).

Figure 12 shows TG and DTA curves of the $[Pd(\mu -$ (SCN))(4-eb-*p*-phen)]₂ compound (7). This complex starts its thermal decomposition at 116 °C and subsequently consecutive mass loss steps, up to 598 °C, can be observed in the TG curve, with a 75.31 % (calc. 77.06 %) mass loss, which are in agreement with the exothermic peaks, at 271 and 541 °C, presented in the DTA curve. This mass loss is equivalent to the elimination of SCN and 4-eb-p-phen ligands, and to the $0.57 O_2$ uptake. The next step extends to 785 °C and is characterized by a slight increase of 1.33 % mass, as well as the compounds (2), (4), and (6). This effect occurs by oxidation of the remaining Pd⁰ to PdO. The last step is due to the reducing of PdO to Pd^{0} , with a 3.13 % mass loss (calc. 3.17 %) and final residue of 21.30 % (calc. 21.12 %). This last step is corroborated by an endothermic peak in the DTA curve at 807 °C.

On analyzing the TG and DTA curves of all synthesized complexes, it is possible to note that there are no significant differences in various steps. Overall, the TG curves presented characteristic thermal behavior of palladium coordination compounds [15]. The oxidation of Pd^0 to PdO and subsequent decomposition events, most visible in the TG curves of compounds (2), (4), (6), and (7), are also characteristic of these types of compounds [16, 17].

The substitution of Cl ions by other halides (Br and I) and pseudohalides (N₃, NCO and SCN) has not significantly altered the initial decomposition temperatures of the compounds. On the other hand, an interesting trend can be observed from the inspection of final decomposition temperatures (Table 2): **3** (693 °C) > **4** (666 °C) > 7 (598 °C) > **2** (553 °C) \approx **5**(551 °C) > **6** (535 °C)

Compounds **3** (693 °C), **4** (666 °C), and **7** (598 °C) showed higher final temperatures, when compared with the others, in Fig. 13. This can be explained by the fact that the ions Br, I, and SCN have higher affinity with Pd(II), according to the theory of acidity and basicity of Pearson



[18], resulting in a greater bond stability, thereby increasing the final temperature of the decomposition step.

The residual mass of Pd⁰ has also changed with the substitution of the chloride in the compounds, in the following order: $2 > 5 \approx 6 > 7 > 3 > 4$. This order is explained because the palladium content of the compounds is inversely proportional to the mass of the substituent ions.

Conclusions

The thermal behavior of the complexes of general formula $[Pd(\mu-X)(4-eb-p-phen)]_2$ was described satisfactorily. From the final decomposition temperatures, the thermal stability of the complexes can be ordered in the following sequence: $3 > 4 > 7 > 2 \approx 5 > 6$. The difference in the temperatures in some stages of decomposition and mainly the residual masses of Pd⁰ evidences that the substitution reactions occurred. The combination of TG and DTA with other techniques such as FT-IR, NMR, and CHN elemental analysis, enabled the characterization of the compounds formed.

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