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MONO AND DINUCLEAR Pd(II) COMPLEXES WITH PYRAZOLE AND IMIDAZOLE-TYPE LIGANDS

Synthesis, characterization and thermal behaviour

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The cyanate-bridged cyclopalladated compound [Pd(C^2,N-dmba)(μ-NCO)]$_2$ (dmba=N,N-dimethylbenzylamine) reacts in acetone with pyrazole (pz), 3,5-dimethylpyrazole (dmpz), imidazole (imz) and 2-methylimidazole (mimz) to give [Pd$_2$(C^2,N-dmba)$_2$(μ-NCO)(μ-pz)] (**1**), [Pd$_2$(C^2,N-dmba)$_2$(μ-NCO)(μ-dmpz)] (**2**), [Pd(C^2,N-dmba)(NCO)(imz)] (**3**) and [Pd(C^2,N-dmba)(NCO)(mimz)] (**4**), respectively. The compounds were characterized by elemental analysis, IR spectroscopy and TG. The thermal decomposition of the compounds occurs in three consecutive steps and the final decomposition products were identified as Pd(0) by X-ray powder diffraction. The thermal stability order of the complexes is **2**>**3**>**1**>**4**.

Keywords: *cyclopalladated compounds, imidazoles, pyrazoles, spectroscopy, thermal analysis*

Introduction

In the past few years, the cyclopalladated compounds have undergone spectacular advances mainly due to their important applications in fields such as organic synthesis [1], new materials (e.g., metallomesogens) [2], catalysis [3] and medical science (e.g., antitumor drugs) [4]. The pseudohalide-bridged cyclopalladated dimers are also good starting materials for reactions with nucleophiles like pyridines or quinolinethiols affording new mono or dinuclear compounds, respectively [5, 6]. We have also described the molecular structures, obtained by X-ray crystal diffraction of cyclopalladated species, which were prepared from 1,3-dipolar cycloaddition reaction of CS$_2$ on azido bridge groups. These insertions reactions are important working tools because the complexes obtained are inaccessible through other synthetic routes [7].

On the other hand, pyrazoles and imidazoles are well known versatile ligands which can interact with metallic centre in neutral monodentate, anionic monodentate, or exo/endo-bidentate anionic fashions [8]. Thus, these ligands represent a good choice for designing new structures sustained by coordinate and/or hydrogen bonds [9]. In addition, compounds containing pyrazole or imidazole ligands [8, 10, 11] have been successfully employed in catalysis, chemotherapy, electrochemical reduction of carbon dioxide, as metallomesogens, and as models of active sites in metalloenzymes. As a part of our research program in this area, we report in the present study the synthesis, characterization and thermal behaviour of the compounds [Pd$_2$(C^2,N-dmba)$_2$(μ-NCO)(μ-pz)] (**1**), [Pd$_2$(C^2,N-dmba)$_2$(μ-NCO)(μ-dmpz)] (**2**), [Pd(C^2,N-dmba)(NCO)(imz)] (**3**) and [Pd(C^2,N-dmba)(NCO)(mimz)] (**4**).

Experimental

Preparation of the complexes

All the syntheses were carried out at room temperature. All reagents were obtained from commercial suppliers and employed without further purification. The starting material [Pd$_2$(C^2,N-dmba)(μ-NCO)]$_2$ was prepared as previously described [12].

[Pd$_2$(C^2,N-dmba)$_2$(μ-NCO)(m-pz)] (**1**), [Pd$_2$(C^2,N-dmba)$_2$(μ-NCO)(μ-dmpz)] (**2**), [Pd(C^2,N-dmba)(NCO)(imz)] (**3**) and [Pd(C^2,N-dmba)(NCO)(mimz)] (**4**). To a suspension of 0.10 g (0.18 mmol) of [Pd(C^2,N-dmba)(μ-NCO)]$_2$ in 20 mL of acetone was added 0.35 mmol of ligand (0.024 g of pz; 0.034 g of dmpz; 0.024 g of imz; 0.029 g of mimz). After stirring the resulting colourless solutions for 0.5 h, the solvent was removed under reduced pressure and the white solids obtained were washed with pentane and then dried in vacuum. The yield was 85% in each case.

Instrumentation

Elemental analyses of carbon, nitrogen and hydrogen were performed on a microanalyzer CE Instruments,

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model EA1110–CHNS-O. Melting points were determined on a Mettler FP-2 microscope. Infrared spectra (IR) were recorded on a Nicolet Impact 400 spectrophotometer in the spectral range 4000–400 cm^{-1}, with a resolution of 4 cm^{-1}, in KBr pellets. Thermal analyses (TG) were carried out using a SDT 2960 system from TA Instruments, under dynamic flow of dry synthetic air (50 mL min^{-1}) at a heating rate of 20°C min^{-1} using α-alumina open crucibles for sample and reference. The X-ray powder diffractograms were obtained in a Siemens D5000 diffractometer, using CuK_α radiation (λ=1.541 Å) and setting of 40 kV and 30 mA. The residues (Pd, PdO) were identified using ICDD bases [13].

Results and discussion

The reactions of the cyclopalladated compound $[Pd(C^2,N\text{-dmba})(\mu\text{-NCO})]_2$ and pz, dmpz, imz and mimz in the molar ratio 1:2 occur readily, leading to the species $[Pd_2(C^2,N\text{-dmba})_2(\mu\text{-NCO})(\mu\text{-pz})]$ (**1**), $[Pd_2(C^2,N\text{-dmba})_2(\mu\text{-NCO})(\mu\text{-dmpz})]$ (**2**), $[Pd(C^2,N\text{-dmba})(NCO)(imz)]$ (**3**) and $[Pd(C^2,N\text{-dmba})(NCO)(mimz)]$ (**4**). The elemental analyses for the synthesized compounds were in agreement with the proposed formula, Table 1. The complexes were characterized by IR spectroscopy and thermogravimetric analysis. The data given by these techniques are present as follows.

Infrared spectra

The characteristic bands of the cyclometallated ring at 3045–3054 cm^{-1} (ν_{CHring}), 2909–2917 cm^{-1} (ν_{CH3}) and 2853–2886 cm^{-1} (ν_{CH2}) in the infrared spectra of compounds **1**–**4** were found unchanged when compared to those observed for the starting compound [12]. Therefore, the interaction between pz, dmpz, imz and mimz ligands and $[Pd(C^2,N\text{-dmba})(\mu\text{-NCO})]_2$ did not affect the integrity of the orthometallatted ring, as observed in other cyclopalladated compounds [14]. Concerning the NCO ligand, the presence of the N-bridging cyanato group in **1** and **2** was evidenced by the ν_{CN} band at 2172 and 2177 cm^{-1}, respectively [6, 15]. For the species **3** and **4**, the presence of ν_{CN} bands at 2215 and 2206 cm^{-1}, respectively, is consistent with terminal N-bonded cyanate [15]. The bidentate coordination of pz and dmpz between [Pd(dmba)] moieties in **1** and **2** was clearly evidenced by the appearance of additional IR bands at 3131–3177 cm^{-1} (ν_{CH}), and 1525–1711 cm^{-1} (ν_{ring}), as well as by the disappearance of the bands at 3480–3540 and 1120–1140 cm^{-1} (ν_{NH} and δ_{NH}, respectively), characteristics of the neutral ligands [9]. Regarding to the IR spectra of **3** and **4**, the monodentate coordination of the imz and mimz ligands was detected by the appearance of the bands at 3134–3205 and 3069–3131 cm^{-1}, attributed to the vibrational modes ν_{NH} and ν_{CH}, respectively, of these molecules. The proposed molecular structures for compounds **1**–**4** are shown in Fig. 1.

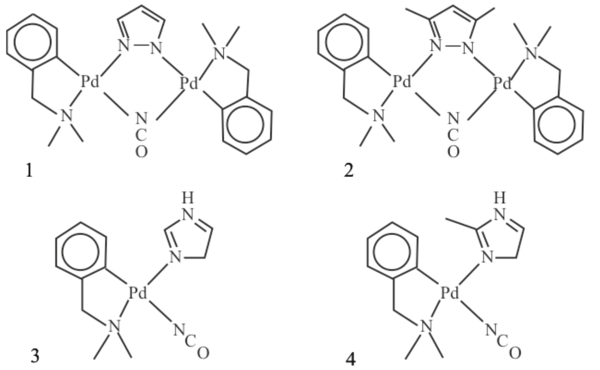

Fig. 1 Suggested structures for compounds **1**–**4**

Thermogravimetric analysis

In the present paper, the main objectives of the thermogravimetry (TG) is to enlight the influence of the pyrazole and imidazole-type ligands in the initial decomposition temperature of the complexes, as well as to propose decomposition steps. The TG curves for the dinuclear (**1** and **2**) and mononuclear compounds (**3** and **4**) are shown in Figs 2 and 3, respectively. Table 2 presents the thermal studies data of complexes **1**–**4**, together with the assignment for each decomposition step.

In the range 185–371°C, compounds **1** and **2** lose the organic (dmba, pz and dmpz) and inorganic (NCO) ligands, with uptake of O_2, yielding a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515) [13].

Table 1 Elemental analyses and melting points for complexes **1**–**4**

Complex	Melting point/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
		found	calc.	found	calc.	found	calc.
1	195.2 (dec.)	45.24	44.76	4.75	4.61	11.22	11.86
2	230.0 (dec.)	46.42	46.62	4.89	5.05	11.22	11.32
3	178.6 (dec.)	43.80	44.52	4.41	4.60	15.42	15.98
4	193.4 (dec.)	46.06	46.10	4.98	4.97	14.21	15.36

Table 2 Thermal analysis data for the compounds **1**–**4**

Complex	Step	ΔT/°C	Δm/mg		
			calc.	found	Assignment
1	1	185–318	–4.66	–4.69	–2dmba, –pz, –NCO, +0.5O_2
	2	318–801	+0.21	+0.33	+0.5O_2,
(m_i=7.61 mg)	3	801–843	–0.42	–0.40	–1.0O_2
	residue		2.74	2.85	Pd
2	1	234–371	–3.26	–3.24	–2dmba, –dmpz, –NCO, +0.5O_2
	2	371–801	+0.14	+0.21	+0.5O_2
(m_i=5.17 mg)	3	801–843	–0.27	–0.29	–1.0O_2
	residue		1.78	1.85	Pd
3	1	189–441	–3.66	–3.65	–1dmba, –imz, –NCO, +0.25O_2
	2	441–809	+0.12	+0.15	+0.25O_2
(m_i=5.44 mg)	3	809–847	–0.25	–0.27	–0.5O_2
	residue		1.65	1.67	Pd
4	1	167–450	–5.17	–5.10	–1dmba, –mimz, –NCO, +0.25O_2
	2	450–809	+0.16	+0.15	+0.25O_2
(m_i=7.54 mg)	3	809–847	–0.33	–0.33	–0.5O_2
	residue		2.20	2.24	Pd

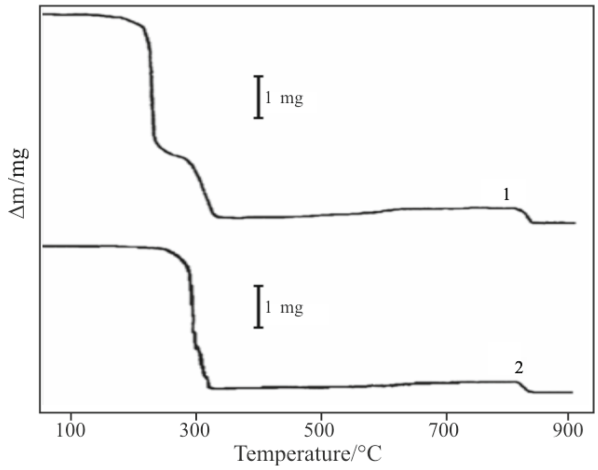

Fig. 2 TG curves for the complexes **1** and **2**

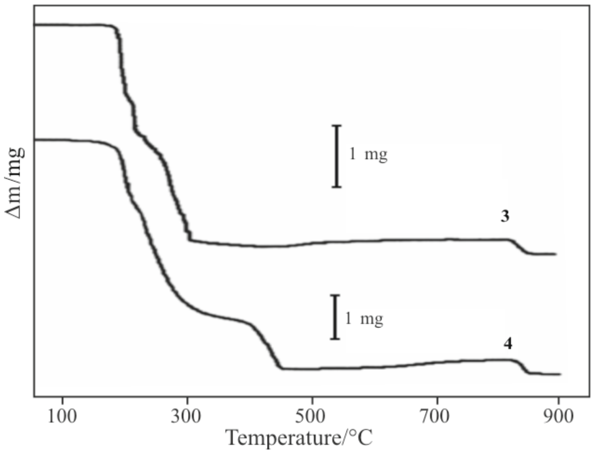

Fig. 3 TG curves for the complexes **3** and **4**

Afterwards, the TG curves also exhibit a progressive mass gain up to 801°C due to the partial oxidation of the Pd to PdO. The last mass loss is characterized by the decomposition of the remaining PdO to Pd (ASTM 05-0681) at 843°C. Regarding to the TG curves of the compounds **3** and **4**, the ligands are eliminated in the range 167–450°C, with uptake of O_2, affording a mixture of Pd (ASTM 05-0681) and PdO (ASTM 06-0515). In the range 450–809°C the partial oxidation of Pd to PdO is observed. The last step corresponds to the decomposition of the remaining PdO to Pd (ASTM 05-0681) at 809–847°C.

Thus, taking into account the initial decomposition temperatures, the following thermal stability order can be established: **2**>**3**>**1**>**4**. It is suggested that the lower thermal stability of **1** in comparison with that observed in **2** can be the result of the more strained metallocycle formed by the metal and the ligands (NCO and pz). Finally, compound **4** is less stable than **3**, probably due to molecular distortions arising from the presence of the mimz ligand.

Conclusions

The results of the present investigation showed that the compound $[Pd(C^2,N\text{-dmba})(\mu\text{-NCO})]_2$ reacts with the nitrogen donor ligands giving products that are easily isolated. For the cyclopalladated species $[Pd_2(C^2,N\text{-dmba})_2(\mu\text{-NCO})(m\text{-pz})]$ (**1**) and $[Pd_2(C^2,N\text{-dmba})_2(\mu\text{-NCO})(\mu\text{-dmpz})]$ (**2**), both NCO and pyrazole groups act as bridging ligands between two [Pd(dmba)] moieties. For compounds $[Pd(C^2,N\text{-dmba})(NCO)(imz)]$ (**3**) and $[Pd(C^2,N\text{-dmba})(NCO)(mimz)]$ (**4**), the cyanate and imidazole ligands are coordinated to the palladium atom in the monodentate coordination mode. The thermoanalytical data showed that the thermal stability of compounds **1**–**4** varies in the sequence **2**>**3**>**1**>**4**.

The high stability of **2** can be explained by the less tensioned metallocycle formed between the metallic centres and bridging ligands (dmpz and NCO). Compound **4** is less stable than **3**, probably due to molecular distortions arising from the presence of the 2-methylimidazole ligand.

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