

THERMAL AND SPECTROSCOPY INVESTIGATION OF CYCLOPALLADATED COMPOUNDS OF THE TYPE $[\text{Pd}(\text{C}_{13}\text{H}_{10}\text{N})(\mu\text{-X})_2]$, ($\text{X}=\text{H}_3\text{CCOO}$, NCO , SCN , CN)

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Abstract

The dimeric compound $[\text{Pd}(\text{bzan})(\mu\text{-OOCCH}_3)_2]$ (1) (*bzan*=N-benzylideneaniline) reacts with KX , in methanol/acetone (2:1), affording the analogous dimeric pseudohalogen-bridged species $[\text{Pd}(\text{bzan})(\mu\text{-X})_2]$ [$\text{X}=\text{NCO}$ (2), SCN (3), CN (4)]. The compounds were characterized by elemental analysis, infrared spectroscopy, NMR and thermogravimetric analysis. IR data for 2–4 showed bands typical of coordinated pseudohalogen ligands clearly indicating the occurrence of the exchange reaction. Their thermal behaviour was investigated and suggested that their stability is influenced by the bridging ligand. The thermal stability decreased in the order $[\text{Pd}(\text{bzan})(\mu\text{-CN})_2] > [\text{Pd}(\text{bzan})(\mu\text{-SCN})_2] > [\text{Pd}(\text{bzan})(\mu\text{-OOCCH}_3)_2] > [\text{Pd}(\text{bzan})(\mu\text{-NCO})_2]$. X-ray results showed the formation of Pd° as final decomposition product.

Keywords: cyclopalladated, IR spectroscopy, pseudohalogens, thermal analysis, X-ray diffraction

Introduction

Cyclometallated compounds constitute an important class of organometallic chemistry, nowadays largely investigated in many important laboratories. Particularly, there has been a great interest in cyclopalladated with nitrogen donors due to their application in a variety of fields such as synthesis of supramolecules [1], organic synthesis [2], as anti-tumor drugs [3], for the design of new metalomesogens [4], catalysis [5] and photochemistry [6]. Furthermore, we have recently shown that pseudohalogen-bridged cyclopalladated complexes are also good starting materials for reactions with CS_2 giving new heterocycles coordinated to the palladium atoms [7].

Although many palladium(II) coordination compounds have been studied by thermoanalytical techniques, it is fact that cyclopalladated species, as such, have been scarcely investigated so far [8]. So, we decided to synthesize new cyclopalladated from $[\text{Pd}(\text{bzan})(\mu\text{-OOCCH}_3)_2]$ [9] by an anion exchange reaction. The compounds

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prepared have the general formula $[\text{Pd}(\text{bzan})(\mu\text{-X})]_2$ [$\text{bzan}=\text{N-benzylideneaniline}$, $\text{X}=\text{NCO}(2)$, $\text{SCN}(3)$, $\text{CN}(4)$] and were characterized by elemental analysis, infrared and NMR spectroscopies and thermal analysis, simultaneous TG and DTA. All final decomposition products were characterized by X-ray powder diffractometry. To the best of our knowledge, this present study is one of the first ones dealing with a systematic thermal behaviour in a series of cyclopalladated-pseudohalogen complexes.

Experimental

Preparation of the complexes

$[\text{Pd}(\text{bzan})(\mu\text{-X})]_2$ ($\text{X}=\text{NCO}$, SCN , CN). To a solution of 0.1000 g (0.145 mmol) of $[\text{Pd}(\text{bzan})(\mu\text{-OOCCH}_3)]_2$ in 45 cm³ of methanol/acetone (2:1) was added 0.290 mmol of KX (0.0235 g of KNCO ; 0.0282 g of KSCN or 0.0189 g of KCN). The mixtures were stirred for 1 h and the yellow solids formed were filtered off, washed carefully with water and diethyl ether. The compounds were recrystallized from dichloromethane/hexane (1:1) and then dried in vacuum. The yields were 90, 75 and 72% respectively for $[\text{Pd}(\text{bzan})(\mu\text{-NCO})]_2$, $[\text{Pd}(\text{bzan})(\mu\text{-SCN})]_2$ and $[\text{Pd}(\text{bzan})(\mu\text{-CN})]_2$.

Instrumentation

Elemental analysis of carbon, nitrogen and hydrogen were performed at Instituto de Química de Araraquara on an analyser CE Instruments, model EA 1110 – CHNS-O.

The infrared spectra (IR) were recorded on a Nicolet FTIR-400 spectrophotometer in the spectral range 4000–400 cm⁻¹, with the samples in the form of potassium bromide pellets.

NMR of ¹H and ¹³C spectra were obtained as DMSO-d₆ solutions and referred to the high field SiMe₄ signal, on a Bruker AC-200 spectrometer.

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a TA system model SDT 2960, under flow of dry synthetic air (100 cm³ min⁻¹), temperature up to 900°C and at heating rate of 5°C min⁻¹, in α-alumina sample holders. The reference substance was pure α-alumina in DTA measurements.

The X-ray powder patterns were obtained with a Zeiss HZG HGZ4/B horizontal diffractometer (G.D.R.). The Bragg–Brentano arrangement was adopted using CuK_α radiation ($\lambda=1.541 \text{ \AA}$) and setting of 34 kV and 20 mA. The peaks were identified using ICDD data bases [10].

Results and discussion

The reactions of the cyclopalladated compound $[\text{Pd}(\text{bzan})(\mu\text{-OOCCH}_3)]_2$ and KX ($\text{X}=\text{NCO}$, SCN , CN) in a molar ratio 1:2 occurred readily, leading to the species $[\text{Pd}(\text{bzan})(\mu\text{-X})]_2$ (Scheme 1).

Elemental analysis for the synthesized compounds were in agreement with the proposed formula and the results are present in Table 1.

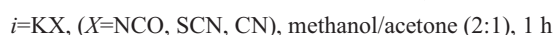
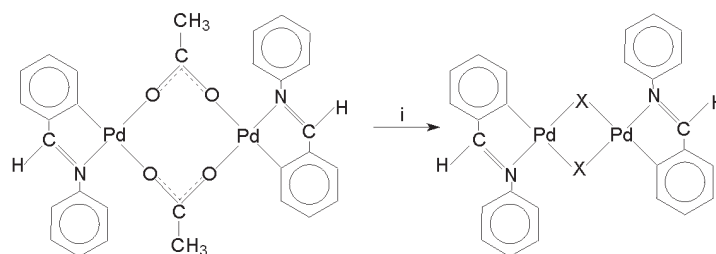


Table 1 Elemental analysis data of compounds 1–4

Compound	C		H		N	
	found	calc.	found	calc.	found	calc.
[Pd(bzan)(μ -OOCCH ₃)] ₂	51.00	51.52	3.57	3.75	4.11	4.12
[Pd(bzan)(μ -NCO)] ₂	51.31	51.16	3.02	3.07	8.48	8.52
[Pd(bzan)(μ -SCN)] ₂	48.38	48.78	2.90	2.92	8.02	8.12
[Pd(bzan)(μ -CN)] ₂	57.27	57.78	3.20	3.22	8.91	8.96

The complexes were characterized by IR and NMR spectroscopies and thermogravimetric analysis. The data given by those techniques are present as follows.

The pseudohalogen groups NCO, SCN and CN are versatile ligands which can function as terminal monodentate or bridging groups. In this way, pseudohalogen metal complexes have a remarkable structural diversity. In general, the vibrational modes of pseudohalogen ligands are very characteristic and allow a clear identification of their mode of coordination to the metallic centers. It is worthy to note that, for the complex 2, the bands at 2170, ν CN; 1330, ν CO; 613 δ NCO, cm^{-1} [11] are consistent with bridging N-bonded cyanate. For the compound 3 the presence of bands at 2141, ν CN; 840, ν CS, 436, δ NCS, cm^{-1} [11] shows that the thiocyanate is acting as a bridging group and coordinated simultaneously through nitrogen and sulphur to Pd atoms. Finally, the IR spectrum of 4 shows a band at 2153 cm^{-1} , assigned to ν CN which gives evidence of cyanide bridging to Pd centers via carbon atom [8, 11].

¹H as well as ¹³C spectra unambiguously showed the formation of the products. In the ¹H NMR the (–N=CH–), imine group appears, respectively, as a singlet, at δ =7.61 for 1, 8.39 for 2, 8.46 for 3 and 8.39 for 4. In the same way, ¹³C spectra confirm the proposed structure showing the resonance signals for [Pd–C] at 147.2 for 1, 146.5 for 2, 147.6 for 3 and 147.7 for 4, which are characteristic of ortho-metallation of the aromatic ring [8]. The ¹³C spectra also showed signals assigned to imine group (–N=CH–) respectively, at 172.7 for 1, 176.1 for 2, 177.6 for 3 and 176.1 for 4 [12].

In order to get more information about these cyclopalladated complexes in the solid state, we utilized thermal analysis and the results obtained are discussed below.

Thermal behaviour

Nowadays, it must be pointed out that thermogravimetry has become an important technique for studies of organometallic compounds, like the cyclopalladated species [8]. Particularly in the series $[\text{Pd}(\text{bzan})(\mu\text{-X})_2]$ ($\text{X}=\text{OOCCH}_3$ (1), NCO (2), SCN (3), CN (4)) the application of thermogravimetry has its main goals in revealing the influence of bridging group X on the initial decomposition temperature and on the thermal decomposition mechanisms. The steps, initial and final temperatures ($^{\circ}\text{C}$), partial mass losses (%) for the thermal decompositions of all compounds in dry synthetic air, are given in Table 2.

The TG curves for these compounds are shown in Fig. 1. As proved in accordance with X-ray powder diagrams with final products with ICDD data bases, all compounds decompose giving Pd, card 05-0681 [10].

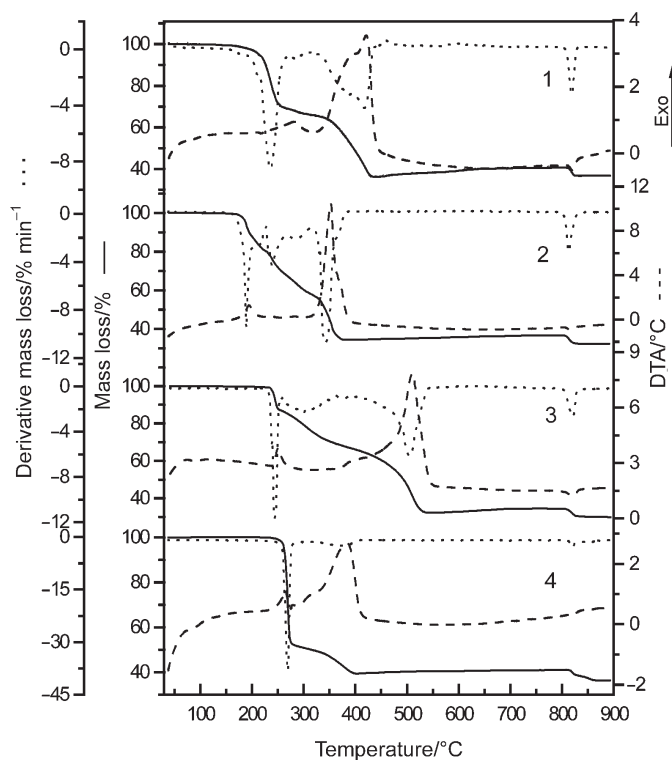


Fig. 1 TG (—), DTG (····) and DTA (- - -) curves for compounds 1-4

We observed that compounds 1, 2, 3 and 4 decompose in two steps, the first one being concerned with acetate or pseudohalogen elimination, followed by pyrolysis of bzan. The first mass loss of 1 occurs between 123–290 $^{\circ}\text{C}$, corresponding to, by mass calculation, two acetate groups and 0.6 bzan mol. The second step, 290–438 $^{\circ}\text{C}$, suggests a mass loss which was attributed to the final elimination of bzan, and uptake of O_2 . It was noted a mass gain in the temperature range 438–807 $^{\circ}\text{C}$, attributed to PdO formation, which de-

composed above 807°C affording Pd° [13]. The first mass loss of 2 observed between 106–228°C, suggests elimination of two NCO groups and 0.26 bzan mol. The second step, in the range 228–372°C, is due to the final elimination of bzan molecules and uptake of O₂, giving a mixture of Pd° and PdO. There is a mass gain between 372–800°C, attributed to the formation of PdO, which decomposed above 800°C giving Pd° [13]. The first mass loss of 3, in the temperature range 144–251°C, is due to elimination of 1.5 SCN mol. The second step, between 251–542°C, corresponds, by mass calculation, to the loss of two bzan mols and of 0.5 SCN mol, as well as gain of O₂. It was observed between 542–800°C an uptake of O₂, assigned to the oxidation of Pd° to PdO. As before, there is a decomposition of PdO into Pd° above 800°C [13]. The first decomposition step of 4, between 231–278°C, suggests mass loss attributed to elimination of two CN groups and 1.36 bzan mol. The second step, 278–401°C, is assigned to the elimination of 0.64 bzan mol, and gain of O₂, giving a mixture of Pd° and PdO. In the last event, between 401–817°C, occurs a mass gain forming PdO, that decomposes to Pd°, as before [13].

The thermal decomposition steps proposed are supported by IR spectra of the residues corresponding to the first mass losses of 1, 2 and 4, which show no absorption bands corresponding to the vibrational modes of bridging groups. In addition, the presence of both Pd° and PdO in the residue of the second step was clearly demonstrated by X-ray diffraction data.

Table 2 Thermogravimetric analysis (TG) and differential thermal analysis (DTA) data for compounds 1–4

Compound <i>m_i</i> /mg	Δm /mg	$\Delta T / T_i - T_f$ / °C	Found/	Calc./	Peaks/°C	
			%	%	exo	endo
[Pd(bzan)(μ -OOCCH ₃) ₂] 3.96	-1.30	123–290	32.83	32.82	280	–
	-1.23	290–438	33.99	33.99	420	–
	+0.18	438–807	4.54	4.63	–	–
	-0.16	807–824	4.04	4.63	–	802
[Pd(bzan)(μ -NCO)] ₂ 5.03	-1.00	106–228	19.88	19.94	196	–
	-2.30	228–372	47.72	47.71	352	–
	+0.12	372–800	2.39	2.43	–	–
	-0.22	800–834	4.34	4.38	–	818
[Pd(bzan)(μ -SCN)] ₂ 6.53	-0.82	144–251	12.56	12.64	250	–
	-3.60	251–542	55.13	56.50	510	–
	+0.14	542–800	2.14	2.32	–	–
	-0.28	800–893	4.29	4.64	–	820
[Pd(bzan)(μ -CN)] ₂ 3.72	-1.77	231–278	47.58	47.57	264	–
	-0.49	278–401	18.29	18.45	385	–
	+0.04	401–817	1.08	1.54	–	–
	-0.19	817–892	5.11	5.12	–	822

m_i – initial mass, *T_i* – initial temperature, *T_f* – final temperature, ΔT – variation of temperature, Δm – variation of mass, found/% – experimental percentage, calc./% – calculated percentage

DTA curves of 1, 2, 3, and 4 are given in Fig. 1 with DTA data summarized in Table 2. Two exothermic peaks are observed in DTA curves of all compounds, besides a weak endothermic peak observed at 216°C in DTA curve of 1, indicative of partial melting of this compound, which is in agreement with its melting range of 210–220°C [9]. The first exothermic peak is strongly associated with the loss of the bridging ligand and the second is strongly associated with the loss of bzan ligand, in accordance with the TG data of the compounds 1–4. In addition, all DTA curves show an endothermic peak corresponding to thermal decomposition of PdO to Pd° in the range of 800–850°C [13].

Conclusions

Summarizing the previous results, it was observed that all species decompose in two steps. For all them the first step is concerned with the total or partial elimination of the bridging groups, followed by thermal decomposition of bzan. Furthermore, taking into account the initial temperature of the decomposition process, it is possible to establish the following thermal stability order: $[\text{Pd}(\text{bzan})(\mu\text{-CN})]_2 > [\text{Pd}(\text{bzan})(\mu\text{-SCN})]_2 > [\text{Pd}(\text{bzan})(\mu\text{-OOCCH}_3)]_2 > [\text{Pd}(\text{bzan})(\mu\text{-NCO})]_2$. The greater thermal stability of $[\text{Pd}(\text{bzan})(\mu\text{-CN})]_2$ relies on the basis of electronic grounds as strong Pd–CN bonds may result from the back-bonding of appropriate full metal orbitals to empty π^* -CN orbitals. The thermal data obtained in the present work will be extremely valuable for further studies involving the application of the compounds 1, 2, 3 and 4 in homogeneous catalysis, such as in the carbonilation of amines.

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