In the past few years, the cyclopalladated chemistry have undergone spectacular advances mainly due to their potential uses as technologically relevant materials (e.g. liquid crystals) [1], catalysts [2, 3], and antitumoral drugs [4]. Despite the increased attention on the cyclopalladated compounds, less attention appears to have been paid to their derivatives containing linear pyridyl-donor ligands. Of particular interest is to use pyrazine, 4,4'-bipyridine, and trans-1,2-bis(4-pyridyl)ethylene as bridges between metals, yielding binuclear species as well supramolecular architectures [5, 6]. We reasoned that unusual bimetallic compounds could be generated by the cleavage of ortho-palladated compounds of the type \([\text{Pd(dmba)(})_{2}\mu-X\text{]_2}(X=\text{bridging anionic group; dmba=}\text{N,N-dimethylbenzylamine})\) by the desired linear exobidentate ligands such as trans-1,2-bis(4-pyridyl)ethylene (bpe). In the framework of our current research on cyclometallated compounds [7–12] as well in the coordination and supramolecular chemistry of pseudohalides [13, 14], we report herein the synthesis, characterization and thermal study of novel binuclear cyclopalladated species of general formulae \([\text{Pd}_2(\text{dmba})_2X_2(\mu-bpe)]\) \((X=\text{Cl}^-, \text{N}_3^-, \text{NCO}^-, \text{NCS}^-; \text{bpe=trans-1,2-bis(4-pyridyl)ethylene})\) (1). The synthesis, characterization and thermal analysis of the novel cyclometallated compounds \([\text{Pd}_2(\text{dmba})_2\mu-X\text{]_2}(\mu-bpe))\) \((2), [\text{Pd}_2(\text{dmba})_2(\text{NCO})_2(\mu-bpe)](3), [\text{Pd}_2(\text{dmba})_2(\text{SCN})_2(\mu-bpe)](4), [\text{Pd}_2(\text{dmba})_2(\text{NO}_3)_2(\mu-bpe)](5)\) (bpe=trans-1,2-bis(4-pyridyl)ethylene; dmba=\text{N,N-dimethylbenzylamine}) are described. The thermal stability of \([\text{Pd}_2(\text{dmba})_2X_2(\mu-bpe)]\) complexes varies in the sequence \(1>4>3>2>5\). The final residues of the thermal decompositions were characterized as metallic palladium by X-ray powder diffraction.

**Keywords:** cyclopalladated complexes, DTA, pseudohalides, TG

### Experimental

#### Preparation of the complexes

The complexes \([\text{Pd(dmba)}(\mu-X)]_2\) \((X=\text{Cl}^-, \text{N}_3^-, \text{NCO}^-, \text{NCS}^-)\) and \([\text{Pd(dmba)}(\text{CH}_3\text{CN})_2(\text{NO}_3)]\) were prepared as previously described [4, 7, 8]. \([\text{Pd}_2(\text{dmba})_2X_2(\mu-bpe)]\) \((X=\text{Cl}^-, \text{N}_3^-, \text{NCO}^-, \text{NCS}^-)\) were synthesized for the first time by adding a solution containing 0.354 mmol of trans-1,2-bis(4-pyridyl)ethylene in \(\text{CH}_2\text{Cl}_2\) to the respective \([\text{Pd}_2(\text{dmba})(\mu-X)]_2\) precursors (0.354 mmol) dissolved in 15 mL of \(\text{CH}_2\text{Cl}_2\). \([\text{Pd}_2(\text{dmba})_2(\text{NO}_3)_2(\mu-bpe)]\) was prepared as mentioned above but using the \([\text{Pd}_2(\text{dmba})(\text{CH}_3\text{CN})_2(\text{NO}_3)]\) precursor. The resulting clear suspensions were stirred for 1 h and filtered off. The pale yellow powders obtained were washed with \(\text{CH}_2\text{Cl}_2\) and pentane and dried in vacuum. All compounds showed poor solubility in most common solvents. Yields: 80–90%.

#### Instrumentation

Melting points were determined on a Mettler FP-2 microscope. Elemental analyses of carbon, nitrogen, and hydrogen were performed on a microanalyser CE Instruments, model EA 1110 – CHNS-O. Infrared spectra were recorded as KBr pellets on a Nicolet FTIR-Impact 400 spectrophotometer in the spectral range 4000–400 cm\(^{-1}\). Simultaneous thermal analysis (TG-DTA) were carried out using a TA system model SDT 2960, under flow of dry synthetic air.
(100 mL min\(^{-1}\)), temperature up to 1000°C and heating rate of 10°C min\(^{-1}\), in α-alumina sample holders. The reference substance was pure α-alumina in DTA measurements. X-ray powder patterns of the residues were obtained with a Zeiss HGZ4/B horizontal diffractometer (G.D.R.) equipped with a proportional counter and pulse height discriminator. The Bragg–Brentano scheme was adopted using CuK\(_{\alpha}\) radiation (\(\lambda=1.541\) Å) and setting of 34 kV and 20 mA. The residues (Pd, PdO) were identified using ICDD bases [15].

**Results and discussion**

The elemental analyses results and thermogravimetric data, together with IR spectroscopy data, confirmed the proposed binuclear formulae for the synthesized compounds. The results of the analyses and melting points are presented in Table 1.

**Infrared spectra**

The most important bands frequencies observed in the IR spectra of the complexes along with their assignments are presented in Table 2.

Comparison of the IR spectra of the precursors [4, 7, 8] and 1–5 allowed us to gain some insight about the molecular structures of these novel species. The characteristic bands of the cyclometallated ring (dmba) at 3045–3050 cm\(^{-1}\) (vCH), 2885–2912 cm\(^{-1}\) (vCH\(_{3}\)), and 2792–2844 cm\(^{-1}\) (vCH\(_{2}\)) in IR spectra of 1–5 were found unchanged when compared to those observed for the precursors. Therefore, the interaction between bpe ligand and the precursors did not affect the integrity of orthometallated ring. Concerning to the anionic ligands (X), the presence of terminal azide in (2) was evidenced by the v\(_{\text{asNNN}}\) band at 2036 cm\(^{-1}\) [13] whereas the terminal N-bonded cyanato ligand in (3) was inferred on basis of the v\(_{\text{asNCO}}\) absorption at 2203 cm\(^{-1}\) [16]. Compounds (4) and (5) are characterized by the existence of terminal S-bonded thiocyanate (2134 cm\(^{-1}\), v\(_{\text{asSCN}}\)) [13] and unidentate O-nitrato groups (1369 cm\(^{-1}\), v\(_{\text{sNO2}}\)) [8], respectively. The bidentate coordination of trans-1,2-bis(4-pyridyl)ethylene (bpe) in 1–5 was clearly evidenced by the appearance of additional IR bands at 2978–2999 cm\(^{-1}\) (vCH), and 1573–1606 cm\(^{-1}\) (v\(_{\text{ring}}\)) taking into account the discussion of the IR data, the adjacent coordination sites of the resulting cis-protected fragment (dmba)Pd are occupied by one terminal anionic group (X) and one 4-pyridyl ring from the bidentate bpe ligand which acts as a bridge between two metallic centers. The proposed molecular structure for compounds 1–5 is shown in Fig. 1.

**Thermogravimetric analysis**

TG and DTA curves for the compounds 1–5 are depicted in Fig. 2. Table 3 presents the results of the thermal studies of these complexes together with the assignments of each decomposition step. In the range 165–459°C, the compounds 1–4 lose their organic (i.e. bpe and dmba) and inorganic (X) lig-