J. Braz. Chem. Soc., Vol. 14, No. 5, 764-770, 2003.
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0103 - 5053 $6.00+0.00

Article

Thermal Behavior and Spectroscopic Study of Neutral and Cationic Mononuclear Cyclopalladated Compounds

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As reações do ciclopaladado catiônico [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) (dmba = *N,N*-dimetilbenzilamina), como os pré-ligantes 3,5-dimetilpirazol (Hdmpz); 2-quinolinatiol (qnSH) e 1,1'-bis(difenilfosfina)ferroceno (dppf) levaram à formação dos compostos, respectivamente, [Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**2**), [Pd(N,C-dmba)(qnSH)(ONO$_2$)] 0.5CH$_2$Cl$_2$ (**3**) e [Pd(N,C-dmba)(dppf)](NO$_3$) (**4**). As novas espécies mononucleares **2**, **3** e **4** foram caracterizadas através de análise elementar, espectroscopia de absorção na região do infravermelho, espectroscopia de ressonância magnética nuclear e análise termogravimétrica. Os dados da espectroscopia no IV mostram bandas consistentes com o grupo nitrato monodentado nos casos dos compostos **2** e **3** e nitrato iônico no da espécie **4**. Os dados de RMN de ^{13}C e ^{1}H confirmam que os respectivos ligantes encontram-se coordenados ao átomo de paládio e o RMN de ^{31}P{^{1}H} de **4** evidencia claramente a ocorrência de três espécies ciclopaladadas em solução, com o dppf atuando como ligante ponte em duas e como um quelato em uma. O comportamento térmico dos compostos **1-4** sugere que o composto **2** é o mais estável. Os resultados da difratometria de raios X, método do pó, confirmam a formação dos seguintes resíduos finais de termodecomposição: PdO para as espécies **1** e **2**, uma mistura de PdO e Fe$_2$(PO$_4$)$_3$ para **4** e, Pd$_2$OSO$_4$ para o composto **3**.

The reactions of the precursor [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) (dmba = *N,N*-dimethylbenzylamine), with the proligands 3,5-dimethylpyrazole (Hdmpz), 2-quinolinethiol (qnSH) and 1,1'-bis(diphenylphosphine)ferrocene (dppf) afforded the compounds [Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**2**), [Pd(N,C-dmba)(qnSH)(ONO$_2$)] 0.5CH$_2$Cl$_2$ (**3**) and [Pd(N,C-dmba)(dppf)](NO$_3$) (**4**), respectively. The mononuclear species **2**, **3** and **4** were characterized by elemental analysis, infrared spectroscopy, NMR and thermogravimetric analysis. The IR spectra show bands which are consistent with terminal monodentate nitrate group for **2**-**3** and ionic nitrate for **4**. The ^{1}H and ^{13}C NMR data confirm that coordination of the organic ligands has occurred and the ^{31}P{^{1}H} NMR data for **4** clearly evidences the occurrence in solution of three cyclopalladated species with the dppf acting as a bridging ligand in two cases and as a chelate in one. The thermal behavior of compounds **1**-**4** suggests that complex **2** is the most stable. The X-ray diffractometry results show the formation of PdO from **1** and **2**, Pd$_2$OSO$_4$ from **3**, and of a mixture of PdO and Fe$_2$(PO$_4$)$_3$ from **4**, as final decomposition products.

Keywords: cyclopalladated species, IR and NMR spectroscopy, thermogravimetric analysis

Introduction

The intramolecular C-H activation, or cyclometallation reaction, which is a major achievement of organometallic chemistry,[1] provides access to metalacyclic derivatives of the transition metals.[2] Many papers dealing with this subject were reported in the literature during the last decade[3] demonstrating the enormous interest suscitated particularly by the cyclopalladated compounds. These complexes have provided a stimulating area of research and they can be found in interesting uses such as in organic synthesis,[4] liquid crystals,[5] photochemistry,[6] catalysis[7] and as anti-tumor agents.[8]

We have recently described the synthesis, reactivity and application as anti-tumor agents of palladium cyclometallated compounds[9] and in the framework of our current research on this class of compounds we report in the present paper the reactivity of the compound [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) (dmba = *N,N*-dimethylbenzylamine) towards the proligands 3,5-dimethylpyrazole (Hdmpz), 2-quinolinethiol (qnSH) and 1,1'-bis(diphenyl-

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phosphine)ferrocene (dppf). The choice of these molecules was due to their versatility as ligands,[10] since they exhibit various modes of bonding to metallic centres and also to the biological and catalytic importance of their complexes. All the new compounds obtained, namely [Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**2**), [Pd(N,C-dmba)(qnSH)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**3**) and [Pd(N,C-dmba)(dppf)](NO$_3$) (**4**) are mononuclear species. These compounds were characterized by elemental analysis, IR and NMR spectroscopy. In addition they were investigated by thermogravimetric analysis and the final decomposition products were identified by X-ray powder diffractometry.

Experimental

Materials

All the syntheses were carried out at room temperature and the reagents were employed without further purification. [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) was prepared as described in the literature.[11]

Syntheses

[Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5 CH$_2$Cl$_2$ (2). To a solution of 0.10g (0.26 mmol) of [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) in 10 mL of dichloromethane were added 0.049g (0.52 mmol) of 3,5-dimethylpyrazole (Hdmpz) in 5 mL of dichloromethane. The resulting colorless solution was stirred for 1h; it was then concentrated under reduced pressure and the addition of a mixture of diethyl ether/pentane (1:1) afforded a white solid. The compound was filtered off, washed thoroughly with pentane and dried *in vacuo*. Recrystallization from a mixture of dichloromethane/ acetone (1:1) gave a white solid. Yield: 0.087g, 90%. (Found: C, 42.9; H, 4.5; N, 14.8. $C_{14,5}H_{21}N_4O_3ClPd$ calcd.: C, 42.8; H, 4.8; N, 14.7%).

*[Pd(N,C-dmba)(qnSH)(ONO$_2$)]0.5 CH$_2$Cl$_2$ (3).*To a solution of [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) (0.10g, 0.26 mmol) in 5 mL of dichloromethane were added 0.042g (0.26 mmol) of 2-quinolinethiol (qnSH) in 5 mL of dichloromethane. The solution was stirred for 1h; the solvent was then partially removed under reduced pressure and a dark orange solid was obtained by addition of pentane. The compound was filtered off, washed thoroughly with pentane and dried *in vacuo*. Recrystallization from a mixture of dichloromethane/ pentane (1:1) afforded a dark orange solid. Yield: 0.12g, 90%. (Found.: C, 43.8; H, 3.45; N, 8.4. $C_{18,5}H_{20}N_3O_3SClPd$ calcd.: C, 43.9; H, 3.7; N, 8.30%).

[Pd(N,C-dmba)(dppf)](NO$_3$) (4). To a solution of 0.10g (0.26 mmol) of [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) in 15 mL of dichloromethane were added 0.14g (0.26 mmol) of 1,1'-bis(diphenylphosphine)ferrocene (dppf) in 10 mL of dichloromethane. The mixture was stirred for 1h; the solvent was then partially removed under reduced pressure and addition of pentane afforded an orange solid. The solid was filtered off, washed thoroughly with pentane and dried *in vacuo*. Recrystallization from a mixture of dichloromethane/pentane (1:1) afforded an orange solid. Yield: 0.21g, 90%. (Found C, 56.2; H, 4.5; N, 4.7. $C_{43}H_{40}N_2O_3P_2FePd$ calcd.: C, 56.2; H, 4.4; N, 4.5%).

Instrumental

IR spectra were recorded on a NICOLET IMPACT 400 spectrophotometer in the 4000-400 cm^{-1} range with the samples in the form of KBr pellets. ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra were obtained in CDCl$_3$ solutions using SiMe$_4$ as the reference for the ^{1}H and ^{13}C NMR spectra and 85% H$_3$PO$_4$ for the ^{31}P{^{1}H} NMR spectra. Thermogravimetric analyses (**TG**) were carried out under dynamic flow of dry synthetic air (25 mL min^{-1}) and at a heating rate of 20 °C min^{-1}, using a TGS-2 Perkin-Elmer Thermoanalyser. The X-ray diffractograms were obtained with an HGZ 4/B horizontal diffractometer (G.D.R) equipped with a proportional counter and pulse height discriminator. The Bragg-Bretano arrangement was adopted using CuK$_\alpha$ radiation (λ = 1.541 Å) and settings of 34 KV and 20 mA. The peaks were identified using ASTM data files.

Results and Discussion

IR and NMR spectra

Taking into account that cationic palladium(II) complexes containing weakly coordinated ligands such as MeCN are excellent precursors for further synthesis, we were motivated to perform the reactions of [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**) with 3,5-dimethylpyrazole (Hdmpz), 2-quinolinethiol (qnSH) and 1,1'-bis(diphenylphosphine)ferrocene (dppf) which afforded, respectively, [Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**2**), [Pd(N,C-dmba)(qnSH)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**3**) and [Pd(N,C-dmba)(dppf)](NO$_3$)] (**4**), according to Scheme 1. The most important bands (cm^{-1}) observed in the IR spectra of **1-4** are given in Table 1. The IR spectra show no ν_{CN} bands due to the acetonitrile molecules, which are observed at 2308 and 2249 cm^{-1} in the IR spectrum of **1**, indicating clearly their displacement by the Hdmpz, qnSH and dppf ligands. The presence of ν_{NO} bands at 1406 and 1315 cm^{-1} for **2** and at 1426 and 1334 cm^{-1} for **3** are characteristic of terminal monodentate nitrate group.[12] On the other hand the IR spectrum of **4** shows ν_{NO} and δ_{ONO} bands at 1354 and 833 cm^{-1}, respectively, which are consistent with an ionic nitrate group.[12] Other important features that emerged from the analysis of the IR spectrum of **3** are the absence of a band near 2500 cm^{-1}, typical[13] of ν_{SH}, and the presence of bands at 3100, ν_{NH}, 1618, ν_{CC}/ν_{CN}; 1301, $\nu_{C=S} + \nu_{C=N} + \nu_{CH}$; 1148, $\nu_{C=S}$; 1505, ν_{CN}, cm^{-1}. This data strongly suggests that qnSH is acting as a S-unidentate ligand which is in accordance with the soft character of both palladium and sulphur atoms.

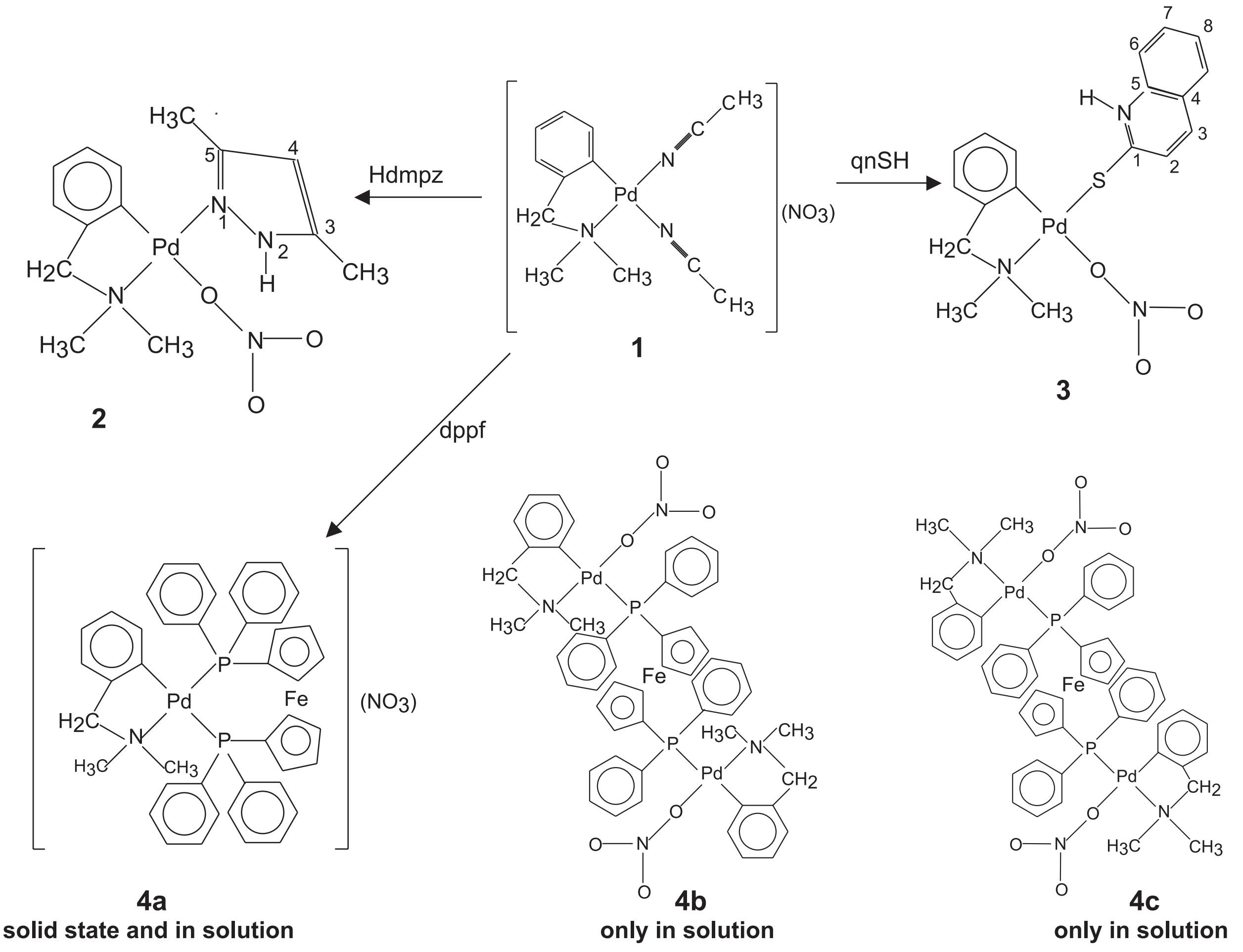
Moreover, on the basis of the aforementioned discussion and considering that the coordination geometry around the palladium atom is square planar we suggest for complexes **2**, **3** and **4** the structures shown in Scheme 1.

The ^{1}H and ^{13}C NMR spectra of the compounds **2**, **3** and **4**, Table 2, give further evidence for the structural proposals outlined above. The ^{1}H NMR spectra reveal, in addition to the proton resonances of the dmba moiety, other signals characteristic of Hdmpz, qnSH and dppf coordinated to the palladium atom.[14] Although the overall pattern of the spectra is similar to that of the free ligands,

Table 1. IR spectral data (cm^{-1}) for compounds **1**-**4**

Compound	ν CN	ν NO	δ NO	ν PC	ν CC$_{Cp}$
[Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**)	2308^{a}w, 2249^{a}w	1387vs	852m		
[Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**2**)	1580^{b}m ,1472^{b}m	1406vs, 1315vs	841m, 801m		
[Pd(N,C-dmba)(qnSH)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**3**)	1584^{b}m ,1505^{b}m	1426vs, 1334s	841m, 801m		
[Pd(N,C-dmba)(dppf)](NO$_3$) (**4**)		1354vs	833m	1164m	1093m

^{a} nitrile; ^{b} nitrogen ligand.



Scheme 1.

upon coordination all the signals shift to higher frequencies.[14] Thus, for complex **2** the H(4), (3-CH_3) and (5-CH_3) resonances appear as singlets at δ 5.69, 2.97 and 2.74, respectively, whereas for the free Hdmpz the signals are observed at δ 5.74 [H(4)] and 2.40 (3-CH_3 and 5-CH_3). The ^{13}C NMR spectrum of **2** exhibits the C(3) and C(5) signals at δ 14.0 and 15.0, respectively, whereas these nuclei appear at δ 11.3 and 12.9 in the spectrum of free Hdmpz.

The ^{13}C NMR spectrum of compound **3** exhibits the resonances of the quaternary carbon atoms of the qnSH ligand, namely C(4) and C(5), at δ 141.0 and 122.0, respectively. In the case of complex **3** the two NMe groups appear to be diastereotopic as a result of a slow rotation around the Pd-S bond.

The ^{1}H NMR spectrum of **4** presents signals assigned to the Cp ring protons in the δ 5.27-3.96 range. The dmba (-N-CH_2-) resonance was shifted to higher frequency, being in this way hidden by the Cp protons resonances, and hence was not assigned. The ^{13}C NMR spectrum shows Cp ring resonances in the δ 76.5-72.3 range, and also in this case the (-N-CH_2-) group resonance is hidden by those of the Cp ring.

Surprisingly the ^{31}P{^{1}H} NMR spectrum of **4** exhibits two singlets at δ 27.6 and 27.1, and two doublets at δ 31.9 and 12.7, of approximate relative intensities 1:2:2 thus suggesting the presence of three species in solution. The singlets are assigned to two structures in which the dppf acts as a bridging ligand, the compounds **4b** and **4c**, while the two doublets are ascribed to another structure containing a chelating dppf molecule, the monomer **4a**, as shown in Scheme 1. The two dinuclear structures **4b** and **4c** differ with respect to the disposal of the ligands around the palladium atom: in **4b**, the dppf ligand is *trans* to the metallated carbon of dmba and the nitrate is *trans* to the nitrogen atom, whereas in **4c** the dppf ligand is *trans* to the nitrogen atom of dmba and the nitrate is *trans* to the metallated carbon. Interestingly, the IR and microanalytical data, indicate the existence of only one species, [Pd(N,C-dmba)(dppf)](NO_3)] (**4a**), in the solid state.

Thermogravimetric analyses

The thermogravimetric analysis has been extensively employed in the study of coordination compounds but few papers have been published dealing with its use for the investigation of cyclopalladated compounds. In the present paper we used this technique to evidence the influence of the ligands coordinated to the palladium atom on the initial decomposition temperatures and on the thermal decomposition steps. The steps, initial and final temperatures (°C), partial and total weight losses (%) for the decomposition of compounds **1-4** in dry air atmosphere, are given in Table 3 and in Figure 1.

The thermal degradation of **1** occurs in three steps. The first mass loss occurs between 85-180 °C and corresponds to, by mass calculation, the loss of two MeCN molecules. This fact is confirmed by the IR spectrum of the residue isolated at this stage that shows no bands assignable to the nitrile group. In the 180-336 °C range the mass loss is attributed to the elimination of the dmba group. The last step, in the 336-893 °C range, suggests the elimination of the nitrate group and the uptake of O_2. The final residue was identified as PdO [ASTM card file 6-0515].[15] The IR spectra of the residues of each step confirmed the mass losses suggested. The TG curve of **2** indicates that its decomposition occurs in three steps. The first step, between 30-201 °C, evidences the loss of a dichloromethane molecule, due to the peak at 61 °C in the dTG curve; the second step in the 201-282 °C range, suggests the loss of the dmba group. The third step, in the 282-894 °C range, is due to the elimination of the pyrazole ligand, a nitrate group and the uptake of O_2. The final residue was identified as Pd(0) [ASTM card file 5-0681].[15] These data were

Table 2. NMR spectral data for compounds **1**-**4**

Compound			^{13}C NMR			^{1}H NMR		^{31}P{^{1}H} NMR
	C-Pd	-N-CH_2-	[-N(CH_3)$_2$]	C$_{arom.}$	H$_{arom.}$	-N-CH_2-	[-N(CH_3)$_2$]	
[Pd(N,C-dmba)(MeCN)$_2$](NO_3) (**1**)	146.9	72.9	51.6	140.4-121.9	7.08-6.94m	3.91s	2.78s	
[Pd(N,C-dmba)(Hdmpz)(ONO_2)] 0.5CH_2Cl_2 (**2**)	147.4	73.5	51.8	143.3-105.0	7.18-6.08m	5.76d	2,70s	
[Pd(N,C-dmba)(qnSH)(ONO_2)] 0.5CH_2Cl_2 (**3**)	147.9	72.7	52.0,51.5	141.0-117.0	8.48-6.58m	3.92s	2.97s, 2.67s	
[Pd(N,C-dmba)(dppf)](NO_3) (**4**)	147.9		49.8	137.2-123.2	7.64-6.33m		2.69s, 2.31s	27.6s, 27,1s; 31.9,12.7d, J_{pp} 30 Hz

δ 120.0 and 51.6, -$NCCH_3$ (^{13}C NMR) and δ 2.78 and 2.36, -$NCCH_3$ (^{1}H NMR) for [Pd(N,C-dmba)(MeCN)$_2$](NO_3) (**1**); δ 141.0 and 122.0 for C(4) and C(5), respectively, for [Pd(N,C-dmba)(qnSH)(ONO_2)]0.5CH_2Cl_2 (**3**).

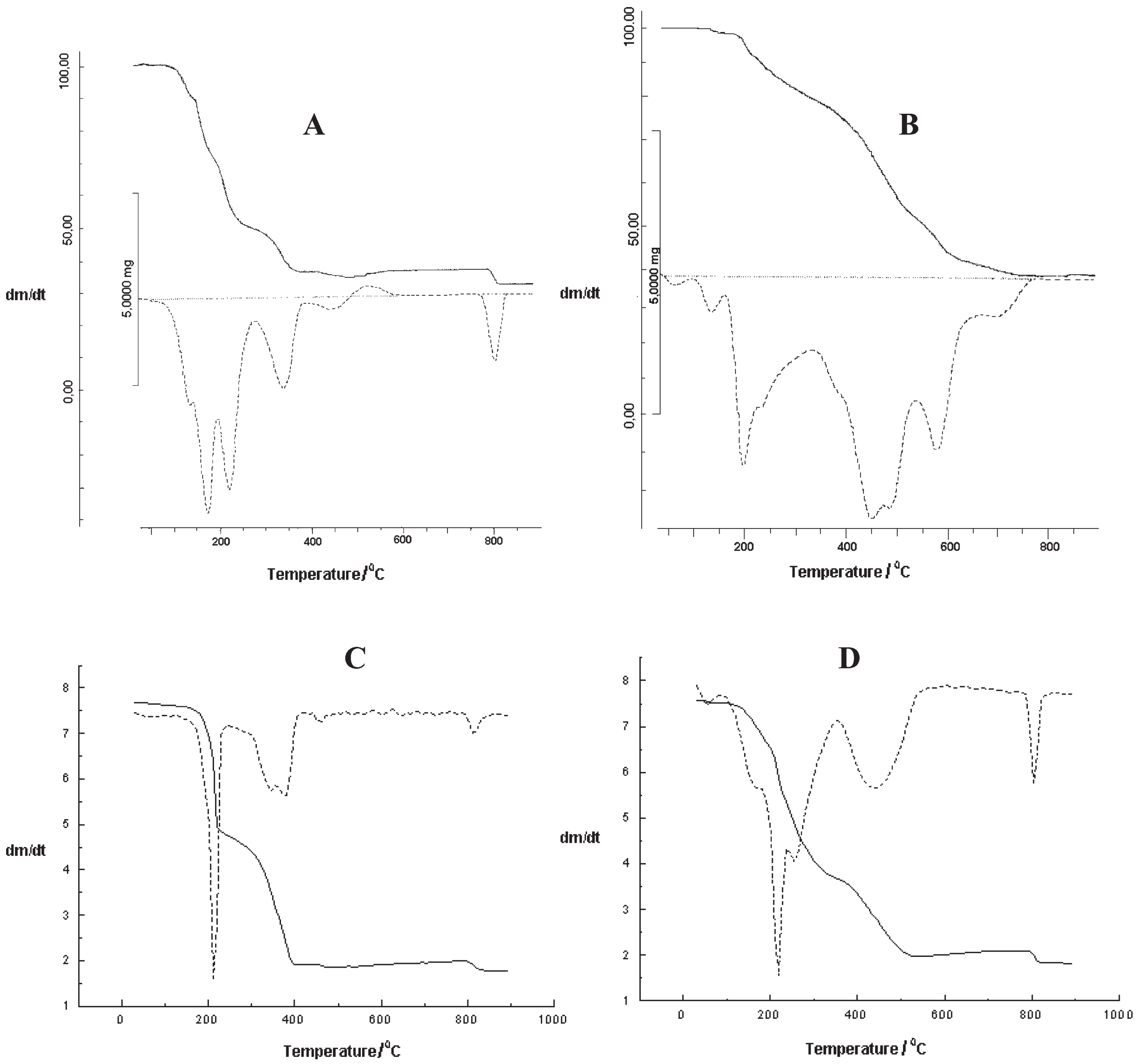


Figure 1. TG(—) and dTG(- - -) curves of compounds: (A) [Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**); (B) [Pd(N,C-dmba)(dppf)](NO$_3$) (**4**); (C) [Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**2**) and (D) [Pd(N,C-dmba)(qnSH)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**3**).

Table 3. Thermal analysis for compounds **1**-**4**

Compound	Step	T$_i$ /°C	T$_f$ /°C	Δm / %
[Pd(N,C-dmba)(MeCN)$_2$](NO$_3$) (**1**)	1	85	180	21.81
	2	180	336	35.00
	3	336	893	12.33
				(69.14)
[Pd(N,C-dmba)(Hdmpz)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**2**)	1	30	201	13.75
	2	201	282	28.93
	3	282	894	34.25
				(76.93)
[Pd(N,C-dmba)(qnSH)(ONO$_2$)]0.5CH$_2$Cl$_2$ (**3**)	1	30	170	8.09
	2	170	255	26.79
	3	255	462	31.60
	4	462	894	9.48
				(75.96)
[Pd(N,C-dmba)(dppf)](NO$_3$) (**4**)	1	108	292	6.32
	2	292	900	55.94
				(62.10)

confirmed by the IR spectra of the residues of each step. The thermal decomposition of **3** shows that the degradation occurs in four steps. The first step, in the 30-170 °C range, is assigned to loss of a dichloromethane molecule. The second step, 170-255 °C, comprises the elimination of the dmba group and the third step, 255-462 °C, suggests the elimination of aromatic rings of the qnSH ligand. Finally, the last step, 462-894 °C, corresponds to the elimination of the nitrate group and the uptake of O_2. The final residue is suggested to be Pd_2OSO_4. The X-ray diffractogram of this residue showed the following interplanar distance values d(hkl)(%): 9.64(35); 7.37(33); 5.26(32); 5.07(34); 3.91(40); 3.53(41); 3.03(43); 2.84(45); 2.65(64); 2.57(32); 2.54(32); 2.25(100); 1.95(80); 1.56(32); 1.49(39); 1.46(50); 1.45(32) e 1.39(37) Å. The TG curve of **4** shows that its decomposition occurs in two consecutive steps. The first step, in the 108-292 °C range, is assigned to the elimination of the dmba group and the second step, in the 292-900 °C range, comprises the elimination of the dppf and nitrate groups, and the uptake of O_2. The residue was identified as a mixture of PdO and $Fe_2(PO_4)_3$ [ASTM card file 14-337].[15] The IR spectra of the residues of each step confirm the mechanism proposed. Considering the initial temperature of the thermal decomposition processes, it is possible to establish the following relative thermal stability order: **2 > 3 > 4 > 1**. The lower stability of **1** can be explained by the presence of weakly coordinated acetonitrile ligands.

Conclusions

The acetonitrile molecules of **1** are easily displaced by ligands such as 3,5-dimethylpyrazole (Hdmpz), 2-quinolinethiol (qnSH), 1,1'-bis(diphenylphosphine) ferrocene (dppf) affording mononuclear products. The solid state IR spectra clearly indicate the presence of a monodentate nitrate ligand in compounds **2** and **3** and of an ionic nitrate in **4**. In solution, however, $^{31}P\{H\}$ NMR spectroscopy indicates that compound **4** exists in three forms: **4a**, in which the dppf ligand acts as a chelate, and **4b** and **4c**, in which it acts as a bridging ligand.

The thermal analysis data will be of great importance notably for further applications of these complexes in homogeneous catalysis processes such as in the carbonylation of amines to ureas or carbamates, currently under investigation in our laboratory.

Acknowledgements

The authors wish to acknowledge CNPq, FAPESP and CAPES for partial financial support.

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Received: September 17, 2002
Published on the web: August 12, 2003

FAPESP helped in meeting the publication costs of this article.