# SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF [$Pd_2$ ($C^2$-dmba) ($\mu$-$SO_4$) $(SO_2)_2$]

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Recebido em 13/3/97; aceito em 17/12/97

**SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF [$Pd_2$ ($C^2$-dmba) ($\mu$-$SO_4$) $SO_2)_2$]. The bridged sulphate complex [$Pd_2$ ($C^2$,dmba) ($\mu$-$SO_4$) $(SO_2)_2$] has been obtained by reacting a saturated solution of $SO_2$ in methanol and the cyclometallated compound [Pd($C^2$,N-dmba)($\mu$-$N_3$)$]_2$; (dmba = N,N-dimethylbenzylamine), at room temperature for 24 h. Reaction product was characterized by elemental analysis, NMR comprising $^{13}C\{^1H\}$ and $^1H$ nuclei and I.R. spectrum's measurements. Thermal behavior has been investigated and residual products identified by X-ray powder diffraction.**

**Keywords: azido-cyclopalladated; sulphur dioxide; reactivity; thermal decomposition.**

## INTRODUCTION

Studies concerning the synthesis, structural characterization, reactivity and employment of new cyclopalladated compounds have been object of our researches[1-6], mainly of those containing coordinated azido group[1,2,4].

The particular interest in this class of compounds is because they have certain technological applications. Some of these compounds show mesomorfic properties[7-11], being able to be employed as liquid crystals. They also find direct application in synthetic organic chemistry by permitting for example, the addition of nucleofiles in halogen-palladium and carbon-palladium bonds, generating N-heterocyclic compounds[12-17]. Recently, these compounds have been used in the medical area as anti-cancerogeneous[18-19].They mainly combat leukemic and breast cancer cells. They still find applications in homogeneous catalysis, for example, in esthers hydrolytic processes[20-21].

This work presents the reactivity of the azido-cyclopalladated compound [$Pd_2$($C^2$,N-dmba)($\mu$-$N_3$)$]_2$; (dmba= N,N-dimethylbenzylamine), with sulphur dioxide, producing a novel organometallic compound, [$Pd_2$ ($C^2$-dmba) ($\mu$-$SO_4$) $(SO_2)_2$], which contains a $SO_2$ molecule and a sigma carbon-palladium bonding of dmba aromatic ring at each metallic center. These moieties are connected through a bridged sulphate ion.

After preparation, the title compound was characterized by elemental analysis, Nuclear Magnetic Resonance comprising $^{13}C\{^1H\}$ and $^1H$ nuclei, vibrational spectroscopy in the infrared region, and by the usage of TG/dTG curves. Finally, founded on analysis of these curves, a mechanism for its thermal decomposition has been proposed.

## EXPERIMENTAL

### Synthesis of [$Pd_2$($C^2$-dmba) ($\mu$-$SO_4$ ) ($SO_2$ $)_2$ ]

We added 0.113 g (0.2 mmol) of the [Pd($C^2$,N-dmba) ($\mu$-$N_3$)$]_2$, according to a method previously described[1], to 30 ml of a saturated $SO_2$ methanolic solution. This above oxide was generated by the addition of a sulphuric acid solution to solid sodium sulphite ($Na_2SO_3$) and stocked in methanol. The mixture, as a fine suspension, was placed to react under constant agitation during 24 h. After that, the formation of an intense yellow color homogeneous solution was observed. The solvent was evaporated under reduced pressure, and a pasty product was isolated. Under further freezing this compound solidified. The product, soluble in methanol only, was carefully washed with acetone and afterwards with pentane, for solvents elimination. Yield(0.13g-92%). Elemental analysis: calc.% (found): C:30,6(29,8); H:3,4(3,4); N:4,0(4,2) S:13,6(13,9).

### *Elemental Analysis*

The elemental analysis of C, H, N was performed at the Central Analitica- Instituto de Quimica-USP-São Paulo.

The elemental analysis for sulphur was performed by indirect barium determination by atomic absorption spectrophotometry on a $N_2O$/acetylene flame. For this, the sample was digested in diluted nitric acid and 130 V Hydrogen peroxide under heating. After digestion of the sample, the sulphur was precipitated as sulphate by addition of a standard solution of barium chloride. After having isolated the $BaSO_4$ by filtration, we analyzed the barium remaining at the filtrate. By difference, the content of sulphur in the sample was obtained.

### *Instrumental Methods Employed*

Thermogravimetric analysis was performed on *Perkin-Elmer* equipment, *mod. TGS-2*, endowed with a platinum heating oven and a compensation or null thermal scale. The contact is made through a platinum thermopar, destined to temperature measurements. The system is connected to a register X-Y *Hitachi, mod. 56.*

The TG/dTG curves were obtained simultaneously in a synthetic air atmosphere, with a heating rate of $20^oC.min^{-1}$, ranging from room temperature until $900^oC$.The register velocity was $5mm.min^{-1}$, with a measured flow of $5,0cm^3.m^{-1}$.

The I.R. absorption spectrum was measured on a Nicolet spectrophotometer *mod. 730 SX-FT*, ranging from 4000 to 400 $cm^{-1}$, employing liquid film thecniques with $4cm^{-1}$ resolution.

The NMR spectra were obtained in a multinuclear spectrometer *Bruker mod. AC-200*. Methanol-$d_4$ was employed for sample's dissolution. A frequency of 200 MHz was used for the $^1H$-NMR and 50 MHz for the $^{13}C\{^1H\}$ measurements. TMS was employed as internal standard.

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For the atomic absorption measurements a *Intralab mod. AA-1475* spectrophotometer was used.

The X-ray powder difratogram obtained from the residue formed after thermal decomposition was registered on a *Rigaku* difratometer, by using a sensible *Debye-Scherrer* camera. Radiation of the Cu-$K_\alpha$ was employed in the experiments. Difratograms were obtained on photographic films.

## RESULTS AND DISCUSSIONS

Isocyanide complexes of general formula $M(NCO)_2(R_3P)$,(M=Pd,Pt) react with $SO_2$, producing metoxisulfonil[22] complexes, as illustrated on the scheme(I).

$$(R_3P)_2M(NCO)_2 + 2SO_2 + 4MeOH \rightarrow (R_3OPO)_2M(SMe)_2 + H_2NCO_2Me \qquad (1)$$

The $Pd(NCO)_2(Ph_3P)_2$ complex reacts with $SO_2$ or with DMSO, in methanol, producing polynuclear complexes $[Pd(SO_2)(Ph_3P)]_3$ and [Pd(DMSO)($Ph_3P$)]n, respectively[22], with the total loss of the pseudohalogen. From this information we decided to investigate the reactivity of the cyclopalladated compound $[Pd(dmba)N_3]_2$[1] with sulphur dioxide, using methanol as solvent, because employing this compound there would be a possibility of an insertion reaction of $SO_2$ into the sigma palladium-carbon bond of metallocycle[5]. The reaction leads to the formation of the organometallic compound $[Pd_2(C_2\text{-dmba})_2(\mu\text{-}SO_4)(SO_2)_2]$, with rupture of the N $\rightarrow$ Pd coordination link.

The synthesized compound presents itself, at room temperature, as a pasty solid having an intense yellow color, becoming darker very fast when dried and exposed to the air. However, it shows a great stability when kept in the freezer in a methanol solution saturated with $SO_2$. This solid revealed itself completely insoluble in a very large number of organic solvents tested. A noticeable solubility was observed only in methanol.

The $^1H$-NMR spectrum of this compound in $CD_3OD$ presented a quartet of doublets between 7.46 and 7.51 ppm and another quartet of doublets between 7.54 and 7.59 ppm.Both sets of signals are attributed to the protons of the aromatic ring of the dimethylbenzylamine and constituting oneself an AMXY[23] type resonance system in which $^3J_{AX}$=8.1Hz, $^3J_{MY}$= 6.0Hz, $^4J_{AM}$=3.3Hz, $^4J_{XY}$=2.0Hz. The form of the signals of the protons set is an indication that the N-Pd coordination bond was broken, being the dmba now connected to the palladium atom only by the sigma Pd-C bond. The proton $^1H$-NMR spectrum also reveals the perfect equivalence between the (N-$CH_3$) groups of the molecule, presenting a signal in singlet form at 2.85 ppm. It also occurs with the (-$NCH_2$) protons, presenting a singlet in 3.38 ppm. The spectrum of cyclopalladated compound $[Pd(C^2,N\text{-dmba})(\mu\text{-}N_3)]_2$ in $CD_3OD$ shows the signal of protons (-$NCH_2$) at 4.42 ppm as a singlet and the signals assigned to (N-$CH_3$) protons groups in form of two singlets at 3.10 and 3.12 ppm.

The $^{13}C\{^1H\}$ spectrum of the synthesized compound in $CD_3OD$ presented the following chemical shifts (ppm); 43.16 (-$NCH_3$); 62.16 (-$NCH_2$ -); 130.40; 130.99; 131.14 and 132.21 (dmba ring), 139.95 (-*C-$CH_2$-N-); 151.98 (*C-Pd). For comparison sake, we will list here the NMR signals of $^{13}C\{^1H\}$ obtained by Garber and co- workers [24] for the cyclometallated $[Pd_2(dmba)Cl]_2$ and for the free dmba. The chemical shifts (ppm) obtained for this compound were: 146.7(C-Pd); 142.9 (-*C-$CH_2$-N-); 133.0; 125.0; 124.6; 121.0 (other carbon atoms of the dmba ring), 73.1 (-N-$CH_2$-); 52.6 (-$NCH_3$). The free ligand presents the following signals (ppm): 138.5 (-*C-$CH_2$-N); 128.4; 127.6, 126.4 (other carbons belonging to the aromatic ring); 63.9 (-$NCH_2$-), 44.7 (-$NCH_3$).

Although different solvents have been used for the measurements of the spectra it can be clearly observed that for the $[Pd_2(C^2,N\text{-dmba})\ (\mu\text{-}SO_4)\ (SO_2)_2]$ complex, we obtained signals of $^{13}C\{^1H\}$ - NMR very distinctive from the those found for the cyclopalladated compound and for the free ligand. It shows that in the synthesized compound there is some different way of binding dmba to palladium. The (-$NCH_3$) signal of $^{13}C\{^1H\}$ obtained for the synthesized complex, has a value very close to that found for the free ligand as well as the signal presented by the groups -$NCH_2$- and (*C-$CH_2$-N-). However, the signal at 151.98 ppm, assigned to the carbon atom bonded to the palladium atom (C-Pd), is located now in a field lower than the signal found on $[Pd(dmba)Cl]_2$ at 146.7 ppm. The remaining carbon atoms of the aromatic ring of the dmba on the $[Pd_2(C^2\text{-dmba})\ (\mu\text{-}SO_4)\ (SO_2)_2]$ complex also present signals in a field significantly lower than those of the cyclopalladated [Pd (dmba) Cl]$_2$ and the free ligand. These data confirm the rupture of the N-Pd coordination bond.

The absorption spectrum of synthesized complex in the infrared region does not exhibit a strong stretching relative to $\upsilon$as ($N_3$) at 2059 $cm^{-1}$, existent in the [Pd(dmba) $N_3]_2$[1]. It also shows four very intense absorption bands at 1158; 1063; 1048 and 925 $cm^{-1}$, highly characteristic of the normal vibrational modes of the bridged sulphate ion linking two metallic ions [25].

The IR spectrum of the compound also presented a band of very low intensity at 1250 $cm^{-1}$, assigned to the normal vibration mode $\upsilon$as ($SO_2$) coordinated to the metal[22]. As the coordination binding N-Pd was ruptured and the sulphate presents itself in a bridged bidentate form linking the two palladium moieties, the other two coordination positions of each palladium atom must contain a $SO_2$ molecule bonded in bidentate form to the metallic center. This is the way that charges balance and coordination number of the Pd (II) ion is satisfied.

A study on the thermal decomposition of the new synthesized compound was also performed. In figure 1 the simultaneous TG/dTG curves obtained in this study are presented. The attributions of the lost fragments in each step of the TG curves are presented in the table 1. By the observation of figure 1 we can confirm a practically continuous loss of mass. Even so, we could note a tendency for the formation of some landings. From 150 to 320 0C we have a loss of mass equivalent to two SO2 groups, followed by the loss of two $[C_6H_4 - CH_2 - (NCH_3)_2]$ fragments, with the rupture of the Pd-C sigma bond, which occurs between 230 and 300°C. The burning of the compound leaves metallic palladium as residue, probably due to the great reducing power of the $SO_2$, which should also contribute to the formation of Pd (I) species. The bridged sulphate group is probably decomposed, generating sulphur dioxide and oxygen.

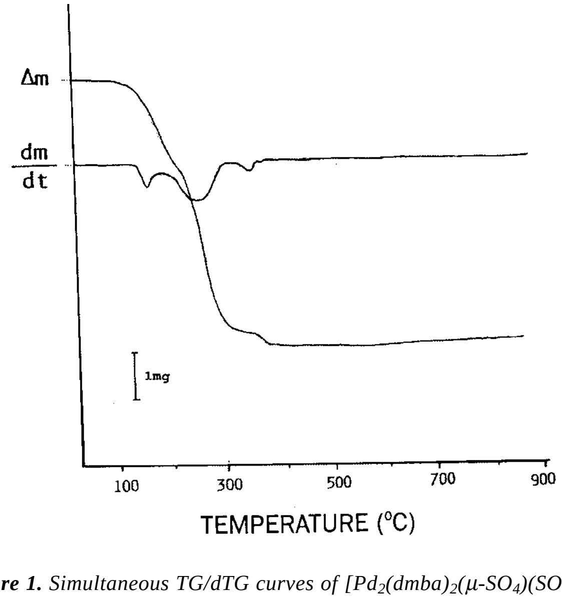

***Figure 1.*** *Simultaneous TG/dTG curves of* $[Pd_2(dmba)_2(\mu\text{-}SO_4)(SO_2)_2]$.

**Table 1.** Mass variations and temperature range corresponding to partial thermal decomposition of the compound $[Pd_2(C^2,N\text{-}dmba)(\mu\text{-}SO_4)(SO_2)_2]$.

| Compound | Δm(mg) | Δt(°C) | Partial Losses | %Exp. | %Calcd. |
|---|---|---|---|---|---|
| $[Pd_2(dmba)_2$ $(SO_{4)}(SO_2)_2]$ | 1,48 | 150-230 | $2SO_2$ | 18,20 | 18,16 |
| $[Pd_2(dmba)(SO_4)]$ | 3,00 | 230-300 | 2dmba | 38,10 | 38,01 |
| $[Pd_2(SO_4)_2]$ | 1,07 | 300-450 | $SO_2+O_2$ | 13,57 | 13,62 |
| $2Pd^0$ | 2,38* | | | 30,20 | 30,20 |

*Residual mass ($Pd^0$)

The probable mechanism of the thermal decomposition of this compound is shown on scheme (II).

$$[Pd_2\,(C^2\text{ - }dmba)_2\,(\mu\text{- }SO_4)\,(SO_2)_2] \rightarrow [Pd_2\,(C^2\text{-}dmba)_2\,(SO_4)] + 2SO_2$$

$$[Pd_2\,(C^2\text{ - }dmba)_2\,(SO_4)] \rightarrow [Pd_2\,(SO_4)] + 2\text{ dmba} \qquad (2)$$

$$[Pd_2\,(SO_4)] \rightarrow SO_2 + O_2 + 2\,Pd^0$$

The thermal decomposition residue was identified as metallic palladium. The following $d_{(h,k,l)}$ values were found, with the respective relative intensities estimated for each reflection (I%): 2.23 (100); 1.17 (90); 1.93 (80); 2.47 (60); 1.36 (50); 1.20 (20), which are very close to the values listed in the data banks for metallic palladium[26]. This analysis finally confirms the proposed structure for the compound, represented in figure 2.

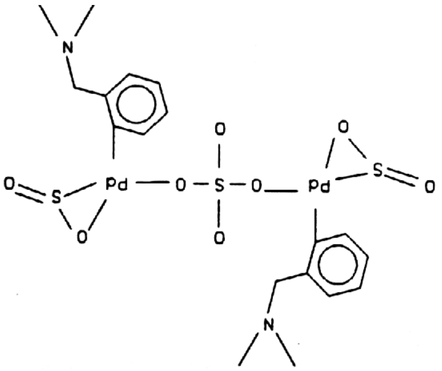

***Figure 2.*** *Schematic drawing of* $[Pd_2(dmba)_2(\mu\text{-}SO_4)(SO_2)_2]$

With all probability, this compound was generated by the formation of intermediary complexes containing ($-SO_3Me$) linked to the palladium[22]. This must have happened by the transfer of methanol's $H^+$ to the $N_3^-$, generating $HN_3$, with a posterior attack of (-OMe) over the $SO_2$, generating the species ($-SO_3Me$) coordinated to the palladium, which afterwards is oxidized to sulphate by the oxygen present.

## ACKNOWLEDGMENTS

The authors thank CNPq, FAPESP, FINEP and CAPES for financial support.

Antonio C. F. Caires thanks specially CNPq for the concession of the fellowship (Proc. N° 150140/95-9), allowing the development of this work and Dr. Petr Melnikov and Fernando Chahud by text revision.

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