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CYCLOADDITION REACTION OF THE AZIDO-BRIDGED CYCLOMETALLATED COMPLEX $[Pd(dmba)N_3]_2$ WITH CS_2 . CRYSTAL AND MOLECULAR STRUCTURE OF $DI(\mu, N, S-1,2,3,4$ -THIATRIAZOLE-5-THIOLATE)BIS[(N, N -DIMETHYLBENZYL-AMINE- C^2, N)PALLADIUM(II)]

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**CYCLOADDITION REACTION OF THE
AZIDO-BRIDGED CYCLOMETALLATED
COMPLEX [Pd(dmba)N₃]₂ WITH CS₂.
CRYSTAL AND MOLECULAR STRUCTURE
OF DI(μ, N,S-1,2,3,4-THIATRIAZOLE-5-
THIOLATE) BIS[(N,N-DIMETHYLBENZYL-
AMINE-C²,N)PALLADIUM(II)]**

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The 1,3-dipolar cycloaddition of carbon disulfide to the coordinated azide in the cyclometalated compound [Pd(dmba)(N₃)]₂ (1), dmba = N,N-dimethylbenzylamine, was investigated. The compound obtained di(μ, N,S-1,2,3,4-thiatriazole-5-thiolate)-bis[(N,N-dimethylbenzylamine-C²,N)palladium(II)] (2), was characterized by IR spectroscopy and X-ray diffraction. Complex (2) is dimeric with the two [Pd(N,N-dimethylbenzylamine)] moieties being connected by the two vicinal bridging N,S-1,2,3,4-thiatriazole-5-thiolate anions in a square-planar coordination for the palladium atoms.

Keywords: Cycloaddition; palladium; azido; carbon disulfide; infrared spectroscopy; X-ray diffraction

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INTRODUCTION

The last decade has shown an increasing interest for cyclometallated compounds as a result of their applications. The first research in this field was motivated by using these compounds as new pathways for organic synthesis.¹ Later, it was verified that they are very important in other areas such as catalysis,² in the design of metallomesogens³ and as anti-tumor drugs.⁴ A plethora of halide-bridged cyclopalladated complexes have been described⁵ and their chemistry is well known. We have prepared similar species containing *pseudo*-halides bridging the palladium atoms. The reason is that, in this way, we enlarge the applications for the resulting cyclopalladate since the coordinated *pseudo*-halide group has, itself, interesting reactivity. For example, the 1,3-dipolar cycloaddition of multiply-bonded molecules to coordinated azide, in metal complexes, is an effective method for obtaining metal-bonded heterocycles, many of which are otherwise inaccessible.⁶

As a part of our ongoing studies on both cyclopalladated^{7,8} and complexes containing azide⁹ we have examined the reaction of the dimeric species $[\text{Pd}(\text{dmba})(\text{N}_3)]_2$ (**1**), *dmba* = *N,N*-dimethylbenzylamine, with CS_2 . The compound obtained $[\text{Pd}(\text{dmba})(\mu\text{-N, S-}\overline{\text{CN}_3\text{S}_2})]_2$ (**2**) was subjected to full IR and X-ray crystallographic characterization.

To the best of our knowledge this paper describes for the first time a crystal structure determination by X-ray diffraction of a compound containing the heterocyclic anion 1,2,3,4-thiazotriazole-5-thiolate coordinated to a metallic center.

EXPERIMENTAL

General Comments

The synthesis of $[\text{Pd}(\text{dmba})(\mu\text{-N, S-}\overline{\text{CN}_3\text{S}_2})]_2$ (**2**) was carried out under purified nitrogen in a Schlenk apparatus. Solvents were distilled under nitrogen from an appropriate drying agent (dichloromethane first over phosphorous pentoxide and then over calcium hydride; acetone over calcium chloride). $[\text{Pd}(\text{dmba})(\text{N}_3)]_2$ (**1**) was prepared according to the literature.⁷ Central Analitica of IQ-USP (Brazil) performed elemental analyses. The IR spectrum of the title complex was recorded as *CsI* pellets on a Nicolet FTIR-Impact 400 spectrophotometer.

Synthesis of $[\text{Pd}(\text{dmba})(\mu\text{-N}, \text{S}-\overline{\text{CN}_3\text{S}_2})_2]$ (2)

To a solution of 0.113 g (0.2 mmol) of $[\text{Pd}(\text{dmba})(\text{N}_3)_2]$ in 30 mL of dichloromethane was added 0.5 mL (8.3 mmol) of carbon disulfide. The solution was stirred for 8 h, the solvent was partially removed and the yellow solid obtained was filtered off, washed thoroughly with acetone, diethylether and dried in vacuum. Recrystallization from a mixture of toluene/acetone (1 : 1) gave yellow crystals suitable for X-ray analysis. Yield: 0.119 g. Anal. Calcd. for $\text{PdS}_2\text{N}_4\text{C}_{10}\text{H}_{12}$ (%): C, 42.9; H, 4.5; N, 20.9. Found: C, 42.5; H, 4.7; N, 20.5.

Crystal Structure Determination of $[\text{Pd}(\text{dmba})(\mu\text{-N}, \text{S}-\overline{\text{CN}_3\text{S}_2})_2]$ (2)

A crystal of the title compound was mounted in the Enraf-Nonius CAD4 diffractometer, at room temperature and using 25 reflections automatically centered the cell parameters were obtained and refined. Table I shows the data collection and refinement conditions. The intensity data were reduced to F_o values and corrected by absorption factors [$\mu(\text{Mo-K}\alpha) = 9.48 \text{ cm}^{-1}$]. The structure was solved by Patterson function and difference Fourier synthesis, and refined by full matrix least squares, using the MoLEN system.¹⁰ The hydrogen atoms were located in their ideal positions and not refined, using $d(\text{C-H}) = 0.96 \text{ \AA}$, and with thermal vibration equal to 1.3 times the isotropic equivalent B of the attached carbon. All non-hydrogen atoms were refined anisotropically, and the atomic scattering factors were those from Cromer and Mann¹¹ with anomalous dispersion from Cromer and Liberman¹² and for the hydrogen atoms from Stewart *et al.*¹³ The atomic coordinates of the heavy atoms are shown in Table II. The anisotropic thermal parameters, observed and calculated structure factors, hydrogen coordinates, complete angles and distances tables have been deposited with the Editor as supplementary material.

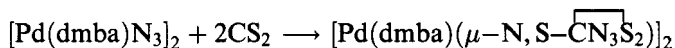
RESULTS AND DISCUSSION

The compound $[\text{Pd}(\text{dmba})\text{N}_3]_2$ (1) is an interesting species as it can be cleaved by nucleophiles like phosphines (L) or tertiary amines (L) to give mononuclear complexes of the type $[\text{Pd}(\text{dmba})\text{N}_3(\text{L})]$.¹⁴ Furthermore it must be pointed out that an azido group coordinated to metals may react with unsaturated molecules, in analogy to other metal-induced organic syntheses. A 1,3-dipolar addition of the azido bridging group of (1) to CS_2 ,

TABLE I Summary of data collection and refinement for [Pd(dmba)(μ -N, S- $\overline{\text{CN}_3\text{S}_2}$)]₂

Molecular formula	PdS ₂ N ₄ C ₁₀ H ₁₂
Molecular weight	358.762
Crystal system	monoclinic
Space group	C2/c
Z (molec/unit cell)	8
Dc (g · cm ⁻³)	1.868
a (Å)	16.697(2)
b (Å)	9.507(1)
c (Å)	17.078(2)
β (°)	109.77(1)
V (Å ³)	2551(1)
F(000)	1424
Crystal size (mm)	0.12 × 0.10 × 0.07
λ (Å)	0.71073
Scan mode	ω - 2θ
Scan rate (° min ⁻¹)	2 - 10
Scan range (°)	0.80
Check reflection	802, $\bar{9}\bar{1}\bar{2}$
θ range (°)	2 - 24.97
Range in hkl:	
min	-19, 0, 0
max	18, 11, 20
Unique reflections	2244
Reflections used ($I \geq 3\sigma(I)$)	1982
No. of variables	154
Goodness of fit	0.92
R, R _w	0.0328, 0.0352
Rall	0.0960
Max. shift/e.s.d.	0.01
Max. density in diff. map (e · Å ⁻³)	0.801
Min. density in diff. map (e · Å ⁻³)	-0.444
Minimized function	$\Sigma W(F_o - F_c)^2$
weight system (w) for:	
observed	pivot point
unobserved	0

in dichloromethane was observed in this work, affording [Pd(dmba)(μ -N, S- $\overline{\text{CN}_3\text{S}_2}$)]₂ (**2**), accordingly to the following equation:



The yellow compound (**2**) is insoluble in the reaction medium and its formula is based on elemental analysis, IR spectroscopy and X-ray diffraction of single crystals. Some important points have emerged from the analysis of the IR spectrum of this complex. First, it showed no band assigned to the azide asymmetric stretching vibration, $\nu_{\text{as}}\text{N}_3$, which was observed as a very strong band at 2059 cm⁻¹ in the IR spectrum of (**1**).^{1,15} Secondly, new bands

TABLE II Fractional atomic coordinates and isotropic equivalent temperature factor with e.s.d.'s in parentheses for the $[\text{Pd}(\text{dmba})(\mu\text{-N, S-CN}_3\text{S}_2)]_2$

Atom	x	y	z	Beq (\AA^2)
Pd	0.40243(2)	0.55051(4)	0.20543(2)	2.316(6)
S(1)	0.60781(8)	0.6947(2)	0.19029(8)	3.32(3)
S(2)	0.4982(1)	0.9114(2)	0.0811(1)	4.98(4)
N(1)	0.3847(2)	0.4172(4)	0.1018(2)	2.52(9)
N(2)	0.4355(3)	0.7278(5)	0.1454(2)	2.77(9)
N(3)	0.3710(3)	0.8089(5)	0.0963(3)	3.6(1)
N(4)	0.3906(3)	0.9078(6)	0.0578(3)	4.6(1)
C(1)	0.3693(3)	0.3770(6)	0.2517(3)	2.7(1)
C(2)	0.3403(3)	0.3638(6)	0.3196(3)	3.3(1)
C(3)	0.3198(4)	0.2320(8)	0.3422(4)	4.4(1)
C(4)	0.3252(4)	0.1145(7)	0.2987(4)	4.6(2)
C(5)	0.3513(4)	0.1255(7)	0.2316(4)	4.0(1)
C(6)	0.3729(3)	0.2548(6)	0.2082(4)	3.2(1)
C(7)	0.4038(3)	0.2735(6)	0.1355(3)	3.3(1)
C(8)	0.4367(4)	0.4495(8)	0.0500(3)	4.0(1)
C(9)	0.2928(4)	0.4287(7)	0.0497(3)	3.9(1)
C(10)	0.5114(3)	0.7662(6)	0.1438(3)	2.9(1)

appeared in the IR spectrum of (2), which can be assigned¹⁶ to the five-membered heterocyclic anion, as follows: 1247, $\nu\text{C}=\text{S}$; 1101, $\nu\text{CN} + \nu\text{CS}$, 908, δNCS , cm^{-1} .

Moreover this anion is of considerable interest since it has several coordination possibilities. Thus, it can be coordinated to the metallic center as a monodentate N- or S-bonded ion, as an N, S-donor chelate or, finally, as an N, S-bridging anion.¹⁷ From the IR spectrum of (2) it was not possible to decide the bonding of the heterocyclic anion to the palladium atoms. In order to elucidate the bonding and provide more detailed knowledge of the structural features of (2) we undertook a full X-ray crystallographic analysis.

The X-ray diffraction study confirmed that the title compound is in fact dimeric. The structure of the molecule with the atom-numbering scheme is shown in Figure 1. Selected bond lengths and bond angles are given in Table III. The two $[\text{Pd}(\text{dmba})]$ moieties are connected by two vicinal bridging N,S-1,2,3,4-thiatriazole-5-thiolate anions and the coordination geometry around each of the palladium atoms is slightly distorted square planar. The overall dimeric molecular structure has C_2 crystallographic symmetry. In addition, it is observed that the sulfur atom of CN_3S_2^- is oriented *trans* to the dmba nitrogen.

The long Pd-Pd' distance of 3.094(4) \AA excludes any metal-metal bonding. On the other hand, the Pd-C(1) distance of 1.987(6) \AA reflects multiple bond character, since it is shorter than the sum of covalent radii for the

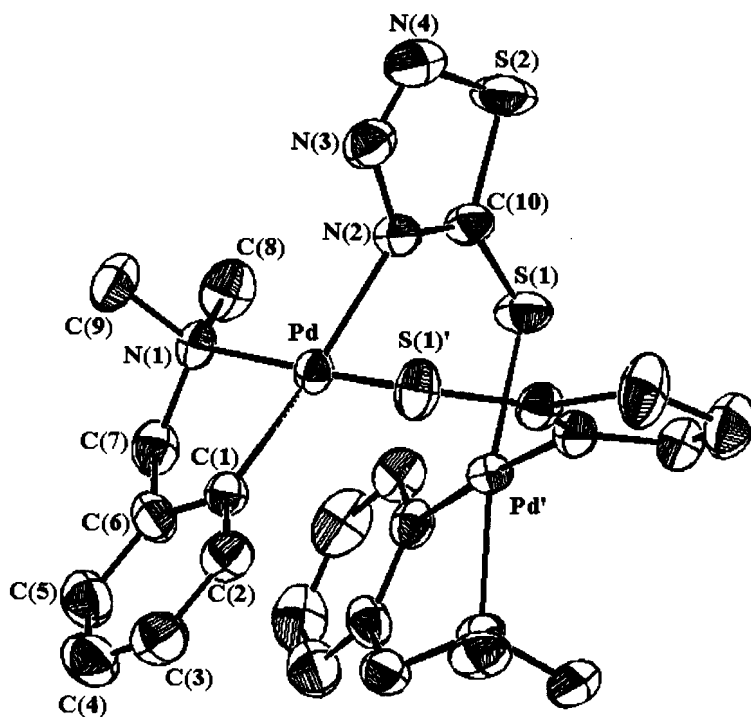


FIGURE 1 ORTEP drawing of $[\text{Pd}(\text{dmba})(\mu\text{-N,S-CN}_3\text{S}_2)]_2$ showing the labeling of atoms.

TABLE III Selected distances (Å) and angles (°) for $[\text{Pd}(\text{dmba})(\mu\text{-N,S-CN}_3\text{S}_2)]_2$

Pd-C(1)	1.987(6)	N(1)-Pd-S(1)'	168.4(1)
Pd-N(1)	2.114(4)	N(1)-Pd-N(2)	93.2(2)
Pd-S(1)'	2.300(2)	N(1)-Pd-C(1)	81.7(2)
Pd-N(2)	2.140(5)	N(2)-Pd-S(1)'	90.0(1)
N(2)-N(3)	1.359(6)	C(1)-Pd-S(1)'	94.8(2)
N(3)-N(4)	1.252(8)	N(2)-Pd-C(1)	174.9(2)
C(10)-S(1)	1.678(5)	N(2)-N(3)-N(4)	117.2(5)
C(10)-S(2)	1.715(6)	N(3)-N(4)-S(2)	109.5(4)
S(2)-N(4)	1.705(6)	N(4)-S(2)-C(10)	91.9(3)
N(2)-C(10)	1.328(7)	S(2)-C(10)-N(2)	108.2(4)
Pd-Pd'	3.094(4)	N(3)-N(2)-C(10)	113.2(4)

¹1-x, y, 1/2-z.

atoms of palladium and carbon, 1.31 and 0.771 Å respectively.¹⁸ The value for the Pd-C(1) distance agrees well with the Pd-C bond length of 2.002(8) Å observed¹⁹ in the palladocycle $[\{\text{Pd}[2,4\text{-Me}_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{NCy}]\}(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2(\mu\text{-Cl}))]$. Another interesting feature emerges from the

Pd–N(1) bond length of 2.114(4) Å which is longer than the single bond distance of 2.01 Å obtained from the covalent radius of nitrogen (sp^2), 0.70 Å, and palladium, 1.31 Å.¹⁸ This increase in Pd–N distance is, probably, of electronic origin and reflects the *trans*-influence of the sulfur atom of the anion $\overline{CN_3S_2}^-$, and is in accordance to the Pd–N distance of 2.084 Å observed²⁰ for $[Pd(8-mq)(CO)(SPPPh_3)]^+$ (8-mq = 8-quinolylmethyl). The Pd–S(1)' distance of 2.300(2) Å agrees well with the value of 2.297(1) Å found in $[Pd(dmba)(qns)]_2$, which has the heterocyclic anion 2-quinoline-thiolate (qns) coordinated to the Pd atoms.⁷ The bond angles at palladium do not deviate greatly from 90°, the only noteworthy deviation is the reduced N(1)–Pd–C(1) angle of 81.7(2)° as a consequence of chelation. The five-membered heterocycle shows two distinct nitrogen–nitrogen bond distances, N(2)–N(3) of 1.359(6) Å and N(3)–N(4) of 1.252(8) Å, clearly suggesting the multiple bond character of N(3)–N(4). The carbon–sulfur bonds are also of different strength, the C(10)–S(1) of 1.678(5) Å being stronger than C(10)–S(2) of 1.715(6) Å.

Current studies involving cyclopalladated complexes containing *pseudo*-halide ligands are underway in order to exploit the interesting reactivity of these species toward small molecules such as CO and CO₂.

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