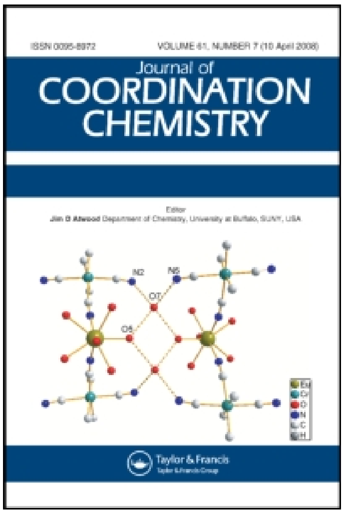


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF DICHLOROBIS (1-PHENYL-3-METHYLPYRAZOLE) PALLADIUM(II) AND DIAZIDOBIS (1-PHENYL-3-METHYLPYRAZOLE) PALLADIUM(II)

A. V. Godoy Netto[a]; A. E. Mauro[a]; R. C. G. Frem[a]; A. M. Santana[a]; R. H. A. Santos[b]; J. R. Zoia[b]
[a] Instituto de Química de Araraquara, Araraquara, S.P., Brazil [b] Instituto de Química de São Carlos, São Carlos, S.P., Brazil

To cite this Article Netto, A. V. Godoy , Mauro, A. E. , Frem, R. C. G. , Santana, A. M. , Santos, R. H. A. and Zoia, J. R.(2001) 'SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF DICHLOROBIS (1-PHENYL-3-METHYLPYRAZOLE) PALLADIUM(II) AND DIAZIDOBIS (1-PHENYL-3-METHYLPYRAZOLE) PALLADIUM(II)', Journal of Coordination Chemistry, 54: 2, 129 — 141

To link to this Article: DOI: 10.1080/00958970108027149

URL: http://dx.doi.org/10.1080/00958970108027149

J. Coord. Chem., 2001, Vol. 54, pp. 129–141
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.
Printed in Malaysia.

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF DICHLOROBIS (1-PHENYL-3-METHYLPYRAZOLE) PALLADIUM(II) AND DIAZIDOBIS (1-PHENYL-3-METHYLPYRAZOLE) PALLADIUM(II)

A. V. GODOY NETTO[a], A. E. MAURO[a,*], R. C. G. FREM[a],
A. M. SANTANA[a], R. H. A. SANTOS[b] and J. R. ZOIA[b]

[a]*Instituto de Química de Araraquara, UNESP, C.P. 355, 14801-970, Araraquara-S.P., Brazil;* [b]*Instituto de Química de São Carlos, USP, C.P. 780, 13560-970, São Carlos-S.P., Brazil*

(Received 19 June 2000; In final form 20 September 2000)

Mononuclear pyrazolyl Pd(II) complexes of the type $[PdX_2(phmPz)_2]$ ($X = Cl^-, N_3^-$) have been prepared. The 1-phenyl-3-methylpyrazole displaces acetonitrile from $[PdCl_2(CH_3CN)_2]$ to form $[PdCl_2(phmPz)_2]$ (phmPz = 1-phenyl-3-methylpyrazole) (1). $[Pd(N_3)_2(phmPz)_2]$ (2) could be obtained by metathesis from $[PdCl_2(CH_3CN)_2]$ or by substitution of the chloride in (1) by the azide ion. Both complexes were characterized by elemental analysis, infrared spectroscopy, ^1H and ^{13}C NMR and by single crystal X-ray diffraction. The coordination geometry around Pd(II) in these complexes is nearly square-planar, with the ligands in a *trans* configuration.

Keywords: Pyrazole; Palladium(II); Azide; Infrared spectroscopy; NMR spectroscopy; X-ray diffraction

INTRODUCTION

Pyrazole-type heterocycles represent an important class of ligands in coordination chemistry [1]. They can act either as neutral monodentate

---

*Corresponding author. Tel.: 550162322022, Fax: 550162227932, e-mail: mauro@iq.unesp.br

(pyrazole-*N*), anionic monodentate (pyrazolato-*N*), or exo-bidentate anionic ligands (pyrazolato-*N*,*N'*) coordinating to metal centers. The study of this family of palladium (II) complexes has attracted considerable interest in recent years owing to their wide range of reactivity and catalytic properties. Major research has been concentrated on binuclear complexes containing pyrazolato bridges [2]. Despite the extensive work, very few mononuclear pyrazolyl complexes of palladium (II) with *pseudo*halides have been reported [3]. This is surprising, since *pseudo*halides are well known to exhibit different bonding modes, 1,3-cycloaddition reactions [4] and many other reactions on the coordinated *pseudo*halide [5].

One of our major research interests has been the synthesis, reactivity and solid state structural characterization of compounds with *pseudo*halides and nitrogen based ligands [6]. In the present study we describe the preparation of new mononuclear palladium(II) complexes containing 1-phenyl-3-methylpyrazole (phmPz) along with chloro and azido ligands. The complexes containing unsymmetrical *N*-substituted pyrazoles have received special attention due to their potential ability as anti-tumor drugs [7] and for the possibility of cyclometallation reactions [8].

EXPERIMENTAL

General Comments

The materials used in the syntheses were all commercially available and were used without purification. All solvents were dried and kept over molecular sieves prior to use. Literature procedures were followed for the synthesis of $[PdCl_2(MeCN)_2]$ [9]. Central Analítica of IQ-USP (Brazil) performed the elemental analyses.

Synthesis of *trans*-$[PdCl_2(phmPz)_2]$ (1)

1-phenyl-3-methylpyrazole (103 mg; 0.65 mmols) in 2 mL of $CHCl_3$ was added to a deep orange solution of $[PdCl_2(MeCN)_2]$ (80 mg; 0.31 mmols) in 10 mL of $CHCl_3$. After stirring the orange solution for 5 min., the mother liquid was concentrated and the addition of pentane afforded a pale orange solid which was filtered, washed with pentane and dried under vacuum. Yield 75%. M.p. = 205.7–206.9°C. *Anal.* Calcd. for $C_{20}H_{20}N_4Cl_2Pd$(%): C, 48.65; N, 11.35; H, 4.08. Found: C, 48.51; N, 11.39; H, 3.37.

Synthesis of *trans*-[Pd$(N_3)_2$(phmPz)$_2$] (2)

Method a

1-phenyl-3-methylpyrazole (103 mg; 0.65 mmols) in 2 mL of $CHCl_3$ was added to the deep orange solution of [$PdCl_2(MeCN)_2$] (80 mg; 0.31 mmols) in 10 mL of $CHCl_3$. After stirring the orange solution for 5 min., NaN_3 (42 mg; 0.65 mmols) in 2 mL of CH_3OH/H_2O (1 : 1) was added and the solution became red. The mother liquor was filtered and the addition of pentane afforded a red-brown solid, which after the normal workup yielded a solid identified as (2) in 80% yield.

Method b

To an orange solution of [$PdCl_2$(phmPz)$_2$] (100 mg; 0.20 mmols) in 10 mL of $CHCl_3$ was added 28 mg of NaN_3 (0.42 mmols) dissolved in 2 mL of CH_3OH/H_2O (1 : 1). The entire mixture became red. After stirring for 5 min., the mixture was filtered and addition of pentane to the filtrate afforded a red-brown solid. Yield 70%. M.p. = 121.0–121.9°C. *Anal.* Calcd. for $C_{20}H_{20}N_{10}Pd$(%): C, 47.39; N, 27.63; H, 3.98. Found: C, 47.29; N, 27.27; H, 3.95.

Instrumentation

Infrared spectra were recorded as KBr pellets on a Nicolet FTIR-Impact 400 spectrophotometer (range 4000–400 cm^{-1}). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at room temperature on a Brucker AC-200 spectrophotometer working at 200 MHz for hydrogen and 50 MHz for carbon, using $SiMe_4$ as an internal standard. Melting points were determined on a Mettler FP-2 apparatus.

Crystal and Molecular Structure Determination of [Pd$(X)_2$(phmPz)$_2$] ($X = Cl^-, N_3^-$)

Single crystals of the compounds (1) and (2) were 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 the refinement conditions. The intensity data were collected to F_o values and corrected by absorption factors ($\mu(MoK_\alpha) = 11.4$ and 8.7 cm^{-1} for (1) and (2), respectively). The

TABLE I Summary of data collection and refinement conditions for palladium(II) complexes

Formula	$[PdCl_2(phmPz)_2]$	$[Pd(N_3)_2(phmPz)_2]$
Crystal system	orthorhombic	monoclinic
Space Group	Pbac	$P2_1/n$
a(Å)	7.279(3)	10.685(2)
b(Å)	14.788(5)	7.3791(8)
c(Å)	19.475(6)	14.175(1)
Z	4	2
V(Å^3)	2096.2(1.3)	1080.5(3)
Molecular weight	493.715	506.85
D_c(g · cm^{-3})	1.564	1.558
Crystal size(mm)	0.13 × 0.15 × 0.05	0.15 × 0.15 × 0.10
Crystal colour	orange	red
μ(cm^{-1})	11.4	8.7
K_α *Mo*, λ (Å)	0.71073	0.71073
Scan mode	ω-2θ	ω-2θ
Temperature (K)	298	298
Speed scan(°/min)-max.	16.48	16.48
Speed scan(°/min)-min.	1.65	1.49
θ range (°)	2.1-30.0	2.0-28.0
Reflections collected	3480	3269
Unique reflections	1507	2075
Reflections observed	1267	1678($I = 2\sigma(I)$)
R	0.026	0.040
R_w	0.034	0.047
R_{all}	0.119	0.088
GOF	1.07	1.07
No. of parameters refined	124	142
Max. density in diff. map (e/Å^3)	0.263(5)	0.76(6)
Min. Density in diff. map(e/Å^3)	-0.219(5)	-0.21(6)

TABLE II Fractional atomic coordinates and isotropic equivalent temperature factor with e.s.d.'s in parentheses for the $[PdCl_2(phmPz)_2]$ complex

Atom	*x*	*y*	*z*	*B*(*Å*^{2})
Pd	0.000	0.000	0.000	2.553(5)
Cl	-0.00547(6)	0.2520(2)	0.07149(5)	3.85(2)
N1	-0.1853(2)	-0.0731(5)	0.0577(2)	3.43(7)
N2	-0.1361(2)	-0.0191(4)	0.0020(2)	3.20(6)
C3	-0.1947(3)	0.0302(5)	-0.0464(2)	3.55(9)
C4	-0.2824(3)	0.0073(6)	-0.0224(2)	4.7(1)
C5	-0.2743(3)	-0.0568(6)	0.0429(3)	4.6(1)
C6	-0.1455(3)	-0.1349(5)	0.1198(2)	3.69(9)
C7	-0.0798(3)	-0.2703(6)	0.1177(2)	4.21(9)
C8	-0.0442(4)	-0.3363(8)	0.1787(3)	5.8(1)
C9	-0.0742(4)	-0.2629(9)	0.2406(2)	7.3(2)
C10	-0.1382(4)	-0.1294(9)	0.2409(2)	7.6(2)
C11	-0.1764(4)	-0.0622(7)	0.1814(3)	6.0(1)
C12	-0.1646(3)	0.0961(8)	-0.1141(2)	5.7(1)

structures were solved by Patterson function and difference Fourier synthesis, and refined by full matrix least squares, using the MoLEN [10] system. The hydrogen atoms were located in their ideal positions and not

TABLE III Fractional atomic coordinates and isotropic equivalent temperature factor with e.s.d.'s in parentheses for the $[Pd(N_3)_2(phmPz)_2]$ complex

Atom	*x*	*y*	*z*	*Beq*(*Å* ^{2})
Pd	0.000	0.000	0.000	2.770(7)
N1	−0.1586(3)	0.1000(5)	−0.2034(2)	3.49(8)
N2	−0.1587(3)	0.0506(5)	−0.1105(2)	3.28(7)
N3	−0.0336(4)	0.2232(5)	0.0737(3)	4.39(9)
N4	−0.1106(3)	0.3336(5)	0.0342(2)	3.62(8)
N5	−0.1853(5)	0.4459(7)	0.0018(3)	5.9(1)
C3	−0.2837(4)	0.0358(6)	−0.1093(3)	3.7(1)
C4	−0.3617(4)	0.0811(8)	−0.2016(4)	4.4(1)
C5	−0.2802(4)	0.1184(7)	−0.2589(3)	4.4(1)
C6	−0.0419(4)	0.1351(6)	−0.2326(3)	3.39(9)
C7	−0.0331(5)	0.0726(8)	−0.3223(3)	4.6(1)
C8	0.0764(5)	0.1162(9)	−0.3529(4)	5.6(1)
C9	0.1746(5)	0.2135(9)	−0.2949(4)	5.5(1)
C10	0.1654(5)	0.2754(8)	−0.2044(4)	5.0(1)
C11	0.0551(4)	0.2363(7)	−0.1732(3)	4.1(1)
C12	−0.3202(5)	−0.0252(9)	−0.0208(4)	5.8(1)

refined, using d(C—H) = 0.96 Å, 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 Mann [11] with anomalous dispersion from Cromer and Liberman [12] and for the hydrogen atoms from Stewart *et al.* [13]. The atomic coordinates of the heavy atoms for (**1**) and (**2**) are shown in Tables II and III, respectively. The anisotropic thermal parameters, observed and calculated structure factors, hydrogen coordinates, complete angles and distance tables are available from A.E.M. as supplementary material.

RESULTS AND DISCUSSION

The syntheses have been carried out at room temperature under constant magnetic stirring and the complexes obtained are crystalline and stable in atmospheric conditions. The elemental analyses were in agreement with the proposed formulas. Two methods were used for the synthesis of $[Pd(N_3)_2(phmPz)_2]$, as described in the Experimental Section.

$$[PdCl_2(MeCN)_2] \xrightarrow[(-\,2\ MeCN)]{2\ phmPz} [PdCl_2(phmPz)_2] \xrightarrow[(-\,2\ Cl^-)]{2\ NaN_3} [Pd(N_3)_2(phmPz)_2]$$

SCHEME 1

Infrared Spectroscopy

The infrared spectrum of [$PdCl_2(phmPz)_2$] (**1**) showed the coordination of 1-phenyl-3-methylpyrazole to the palladium atom for its characteristic bands at 3128 (νCH); 1598, 1526, 1504, 1375 (νCC); 1088 (δCH); 777, 701 (γCH) cm^{-1}, and the disappearance of the νCN stretching of the coordinated CH_3CN in [$PdCl_2(CH_3CN)_2$], which was previously observed as a strong band at 2329 cm^{-1}. The displacement of the chloro from (**1**) by the azido ligand was proved by the presence of a new, strong band at 2016 cm^{-1} and another band at 1276 cm^{-1} observed in the IR spectrum of (**2**), assigned to $\nu_{as}N_3$ and ν_sN_3 stretching modes, respectively, which are characteristic for terminally coordinated azides [14].

^{1}H NMR Spectra

The ^{1}H NMR results are given in Table IV. Although the overall pattern of the spectrum of complex (**1**) resembles[1] the free ligand,[2] all the signals have been shifted. The H-4 and H-5 protons in the ^{1}H NMR spectrum of (**1**) gave an AM spin system (see Scheme 2) and their resonances, confirmed by homonuclear decoupling experiments, appeared as doublets at 6.21 and 7.52 ppm (^3J(HH) = 2.5 Hz), respectively. The most significative shifts of the signals of the coordinated ligand compared to the free pyrazole were those

TABLE IV ^{1}H-NMR data (ppm) for phmPz and Pd(II) complexes (200 MHz) at 298 K, in $CDCl_3$, given as δ (^{1}H) (ppm), multiplicity, assignment, J (Hz), [integration]

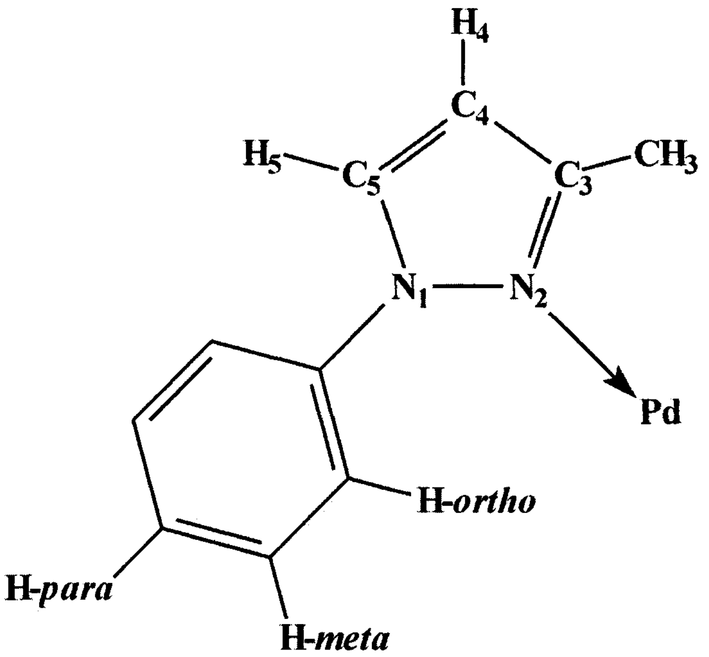
	^{1}H NMR	
Compounds	*Pyrazole ring*	*Phenyl ring*
phmPz	2.30 *s*, CH_3, [3H] 6.13 *d*, H-4, $J = 2.4 =$ Hz, [1H] 7.69 *d*, H-5, $J = 2.4$ Hz, [1H]	7.13 *pseudotriplet*, H-*para*; 7.31 *t*, H-*meta*, $J = 8$ Hz, 7.56 *dd*, H-*ortho*, $J = 8$ Hz, [5H]
(**1**)	2.47 *s*, CH_3, [3H] 6.21 *d*, H-4, $J = 2.5$ Hz, [1H] 7.52 *d*, H-5, $J = 2.5$ Hz	7.81 – 7.57 *m*, H-*para*/H-*meta* [4H + H-5] 8.02 *dd*, H-*ortho*, $J = 8$ Hz, [2H]
(**2**)	2.37 *s*, CH_3, (**2b**), 2.47 *s*, CH_3, (**2a**), [3H] 6.24 *d*, H-4, $J = 2.3$ Hz (**2b**), 6.27 *d*, H-4, $J = 2.5$ Hz, (**2a**), [1H] 7.59 *d*, H-5, $J = 2.5$ Hz, (**2a**), 7.80 *d*, H-5, $J = 2.3$ Hz, (**2b**)	7.25 *pseudotriplet*, H-*para*, (**2b**), 7.42 *t*, H-*meta*, $J = 6$ Hz, (**2b**), 7.77 – 7.61 *m*, H-*para*/H-*meta*, (**2a**), 7.94 *dd*, H-*ortho*, $J = 8$ Hz, (**2a**), [6H + H-5]

Abbrevations: *s* = singlet; *d* = doublet; *t* = triplet; *pseudot* = pseudotriplet; *dd* = double doublet; *m* = multiplet.

---

[1] To that of.

[2] It was verified that upon coordination.



SCHEME 2

of the phenyl substituent. For instance, the hydrogens of the *ortho*-carbon of that ring changed from 7.56 ppm in the free ligand to 8.04 ppm in the complex. Also, the resonances of the *meta* and *para* hydrogens of the phenyl ring, which appeared in the range of 7.0 to 7.4 ppm as an apparent doublet of doublets and a triplet, respectively, for the free pyrazole, were compacted in an almost symmetrical multiplet centered at 7.64 ppm in (**1**). A singlet at 2.47 ppm was assigned to the methyl group of the coordinated pyrazole.

The ^{1}H NMR spectrum of a crude sample of (**2**) clearly indicated the presence of two isomers in solution (**2a – b**) at room temperature, with two methyl signals at 2.47 and 2.37 ppm, respectively, in a 2 : 1 ratio. Moreover, in addition to the signals for the phenyl substituent of the pyrazole coordinated as in (**1**), a series of signals appeared that are similar to the free pyrazole, but shifted to lower field. Thus, two sets of signals for the new H-4/H-5 groups were also found. In order to obtain an unambiguous assignment for the H-4 and H-5 doublets, homonuclear decoupling was carried out that showed the doublets at 6.27 (H-4) and 7.59 ppm (H-5) (^3J(HH) = 2.5 Hz) for (**2a**), whereas isomer (**2b**) exhibited doublets at 6.24 ppm (H-4) and 7.80 ppm (H-5) (^3J(HH) = 2.3 Hz).

Comparison of the H-4/H-5 coupling constants in the ^{1}H NMR spectra of (**1**) and (**2a**–**b**) allowed some insight about the geometry of the isomers (**2a**) and (**2b**). As mentioned for complex (**1**), only one isomer which exhibited two doublets in its ^{1}H NMR spectrum (^3J(HH) = 2.5 Hz), separated by $\Delta\delta = 1.31$ ppm was seen in solution. For the mixture (**2a**–**b**), the doublets separated by $\Delta\delta = 1.32$ ppm (^3J(HH) = 2.5 Hz) were assigned for (**2a**) and for (**2b**), those separated by $\Delta\delta = 1.56$ ppm and with a coupling ^3J(HH) of 2.3 Hz. Therefore, the NMR data indicated that the geometry of the complexes (**1**) and (**2a**) was very similar. The possible spatial arrangements of the ligand 1-phenyl-3-methylpyrazole, or different modes of transition-metal complexation can be determined by ^{1}H NMR by observation of the AA'BB'C spin system of phenyl protons. As in isomer (**2b**), the *meta* and *para* hydrogens signals appeared as a triplet at 7.42 ppm ($J = 6$ Hz) and a *pseudo*triplet centered at 7.25 ppm, showing shifts of 0.11 and 0.13 ppm relative to the free ligand, respectively. According to Alonso *et al.* [8], palladium(II) complexes derived from 1-methyl-3-substituted pyrazoles are found as a *cis-trans* mixture in solution. A similar proposal was made by Verstuyft *et al.* [15], whose work showed that compounds of the type $[PdX_2(PR_3)_2]$, where X represents a monodentate uninegative anion (N_3^-, Cl^-) and PR_3 a tertiary phosphine, are found as *cis-trans* isomers. In addition, Redfield *et al.* [16], considered that $[PdCl_2(PR_3)_2]$ complexes are essentially *trans* in solution whereas the analogous azido complexes showed a higher percentage of the *cis* isomer in solution due to the lesser steric interactions of the azide ion as compared to the chloro ion. On the basis of these assumptions, it appeared that (**1**, **2a**) and (**2b**) could also be isomers of *cis/trans* configurations.

Displacement of the chloro by the azido ligand in the coordination sphere of the palladium(II) did not significantly change the ^{13}C NMR spectrum of the complexes (see Tab. V). A tentative assignment of the ^{13}C NMR signals of the second isomer in solution was unsuccessful due to their low intensities.

TABLE V ^{13}C-NMR data (ppm) for phmPz and Pd(II) complexes, (50 MHz) at 298 K, in $CDCl_3$

Compounds	*phmPz*	*[PdCl$_2$(phmPz)$_2$]*	*[Pd(N$_3$)$_2$(phmPz)$_2$]*
C-3	140.00	139.04	139.17
C-4	107.29	108.42	108.93
C-5	127.09	134.37	134.93
C-methyl	13.51	14.50	13.60
C-phenyl	150.25; 129.12; 125.65; 118.51	152.39; 129.28; 126.61	152.06; 129.52; 126.13; 118.72

In order to identify the possible *cis*/*trans* isomerism of complexes (**1**), (**2a**–**b**) and relate the structures to the obtained NMR data, the X-ray structural determination of complexes (**1**) and (**2a**) was undertaken.

X-ray Diffraction Studies

The monomeric nature of these compounds and the important structural features suggested by IR and NMR spectroscopies were definitely proved by the crystal and molecular structure X-ray analysis. The molecular structures of the complexes (**1**) and (**2**) with the labeling scheme are depicted in Figures 1 and 2, respectively.

trans-[PdCl$_2$(phmPz)$_2$]

The X-ray single crystal structure of complex (**1**) revealed that the palladium atom is on the inversion center, coordinated to two Cl and two N atoms

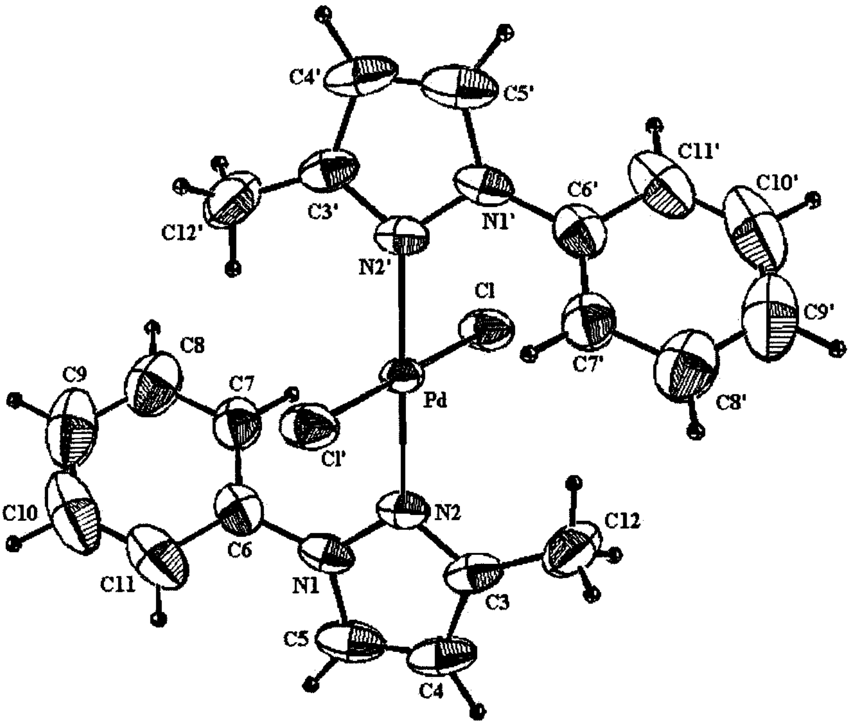


FIGURE 1 ORTEP representation of *trans*-[PdCl$_2$(phmPz)$_2$] showing the labeling of the atoms.

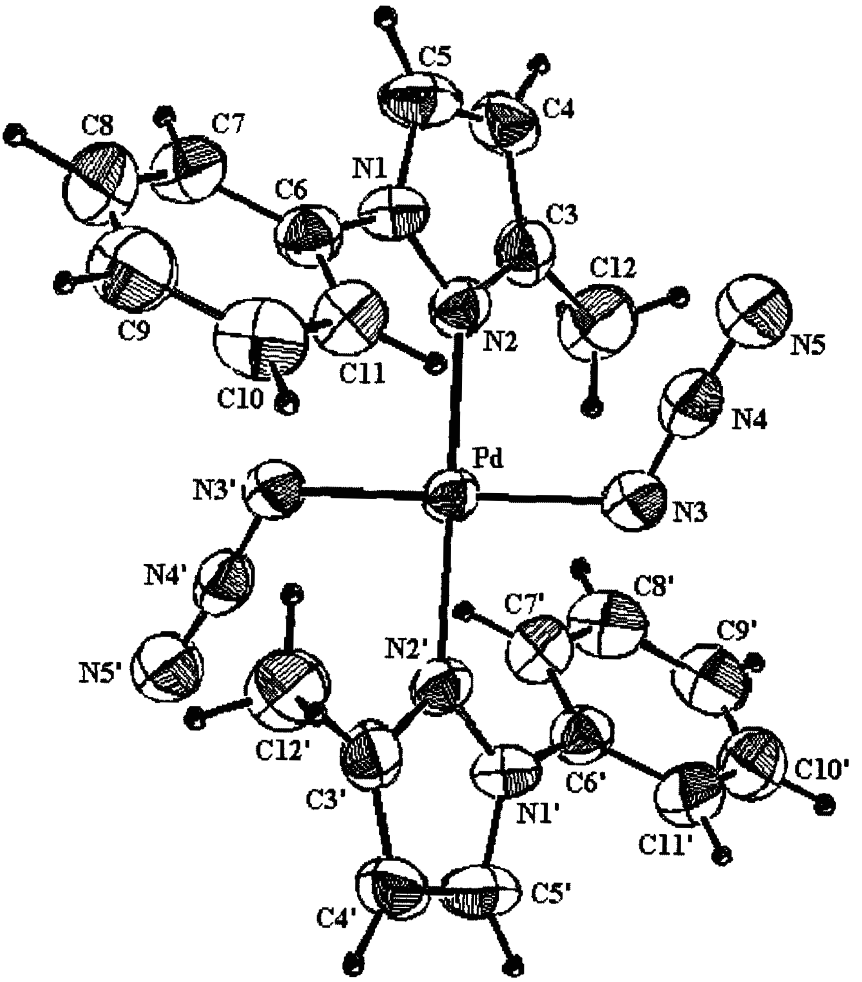


FIGURE 2 ORTEP representation of *trans*-[Pd$(N_3)_2$(phmPz)$_2$] showing the labeling of the atoms.

(from the phmPz ligand) in a *trans* configuration. Selected bond lengths and bond angles are given in Table VI. The geometry around the Pd(II) is essentially square planar in which the Cl—Pd—N angles lie in the range 89.52(9)–90.48(9)°, and due to the strict $\bar{1}$ symmetry the Cl—Pd—Cl′/N2—Pd—N2′ angles are 180.0°. The Pd—N bond length of 2.018(3) Å compares well with the values found for [PdCl$_2$(1-benzyl-2,5-dipropyl-4-ethylpyrazole)$_2$] (2.014 Å) [17], [Pd(3,5-dimethylpyrazole)$_2$ (3,5-dimethylpyrazolate)$_2$]$_2$ (2.008–2.015 Å) [18] and [PdCl$_2${bis(1-pyrazolyl)methane}] (2.018–2.030 Å) [19]. There are no significant differences among the Pd—Cl distance for complex (1), 2.304(1) Å and those found

TABLE VI Selected bond lengths (Å) and bond angles (°) for the complex *trans*-$[PdCl_2(phmPz)_2]$

Pd—Cl	2.304(1)	Cl—Pd—N(2)	90.48(9)
Pd—N(2)	2.018(3)	Cl—Pd—N(2)′	89.52(9)
N(1)—N(2)	1.364(4)	Cl—Pd—Cl′	180.0
C(5)—C(4)	1.359(7)	N(2)—Pd—N(2)′	180.0
C(4)—C(3)	1.388(6)	Pd—N(2)—N(1)	124.5(2)

in $[PdCl_2(3,5\text{-dimethylpyrazole})_2]_2$ [20] (2.293 – 2.304 Å) and $[Pd_3Cl_6\{1,2\text{-bis}(3,5\text{-dimethylpyrazol-1-yl})\text{ethane}\}_3]$ [21] (2.289(1) – 2.305(1) Å). The mean square plane of the pyrazolyl ring forms a dihedral angle of 65.5(1)° with the plane of the palladium coordination, whereas the angle between the pyrazolyl and the phenyl rings is 130.3(2)°. It is interesting to note that the Pd—N1—N2 angle of 124.5(2)° is almost ideal for the sp^2-hybridized nitrogen atom.

trans-[Pd(N$_3$)$_2$(phmPz)$_2$]

The structure of complex (**2**) showed that the palladium atom is also on the crystallographic $\bar{1}$ center. The coordination is square planar, with four nitrogen atoms, two from azide and two from phmPz ligands in a *trans* configuration, with interatomic bond angles that deviate slightly from 90° (N3—Pd—N2 = 91.4(1)° and N3—Pd—N2′ = 88.6(1)°). Selected bond lengths and bond angles are given in Table VII. The bond distance Pd—N(azide), 2.031(4) Å, is significantly longer than those found in the $[Pd_2(N_3)_6]^{2-}$ anion (mean value of 2.004 Å) [22] or $[Pd(N_3)(CH_2Ph)(2,2'\text{-bipyridine})]$ (2.003(8) Å) [23], however it is significantly shorter than that in $[Pd(N_3)(\text{tetraethyldiethylenetriamine})]NO_3$ (2.08(1) Å) [24] or *trans*-$[Pd(N_3)_2(\text{tribenzylphosphine})_2]$ (2.045(6) Å) [25]. The Pd-N(azide) bond length of 2.031(4) Å is indicative of a single-bond character [14], although the asymmetry observed for the N—N distances in the azido group (N3—N4 = 1.191(5) Å and N4—N5 = 1.161(6) Å) could suggest some π interaction between the *p* orbital on N3 and the *d* orbitals on the Pd(II) atom [14]. The Pd—N(pyrazole ring) distances of 2.026(3) Å falls within the range observed for similar pyrazolyl complexes of palladium(II)

TABLE VII Selected bond lengths (Å) and bond angles (°) for the complex *trans*-$[Pd(N_3)_2(phmPz)_2]$

Pd—N(3)	2.031(4)	N(3)—Pd—N(3)′	180.0(0)
Pd—N(2)	2.026(3)	N(3)—Pd—N(2)	91.4(1)
N(3)—N(4)	1.191(5)	Pd—N(3)—N(4)	120.4(3)
N(4)—N(5)	1.161(6)	N(2)—Pd—N(2)′	180.0(0)
N(1)—N(2)	1.366(5)	N(3)—Pd—N(2)′	88.6(1)
C(5)—C(4)	1.364(8)	N(3)—N4—N(5)	175.5(5)

[17–21]. Another structural parameter of interest is the Pd—N_3 bond angle. For complex (**2**), the Pd—N3—N4 angle of 120.4(3)° agrees well with the expected value for a trigonally hybridized nitrogen. The azido group was found to be nearly linear (N3—N4—N5 = 175.5(5)°). The dihedral angles formed between the mean square plane of the palladium coordination and the planes of the pyrazolyl and phenyl rings are, respectively, 111.16(5)° and 65.02(5)°. The angle between the planes defined by pyrazolyl and phenyl rings is 135.8(1)°.

Comparing the molecular structures of (**1**) and (**2**) complexes allows to evaluate the relative *cis*-influence of the azido and chloro ligands. The Pd—N(pyrazole ring) distance of 2.018(3) Å in (**1**) is slightly shorter than the 2.026(3) Å distance in (**2**), suggesting that azido exerts a greater *cis*-influence to the Pd—N(pyrazole ring) distance than chloro ligand. The difference in *cis* influence could be assigned to the larger σ-contribution from an azido rather than from a chloro ligand.

CONCLUSIONS

The synthesis and structural properties of the complexes $[PdCl_2(phmPz)_2]$ (**1**) and $[Pd(N_3)_2(phmPz)_2]$ (**2**) have been described. X-ray structure determinations revealed a square-planar coordination at palladium(II) in which the ligands are *trans* for both complexes. The complex containing chloro is prepared as a pure species, whereas that containing the azido ligand exists as a *cis*/*trans* mixture, from which the *trans* form can be separated. ^1H NMR data can be used to identify both forms in solution, the *trans* configuration being that which shows the smallest H4—H5 $\Delta\delta$.

Further studies involving Pd(II) pyrazolyl complexes containing *pseudo*halide ligands, especially their tendency to react with small molecules as such CO, CO_2 and CS_2, are currently underway in our laboratories. Studies of the thermal behaviour of complexes (**1**) and (**2**) are also underway. Our first thermogravimetric analysis (TG) obtained under dynamic flow of dry synthetic air clearly indicated that (**1**) has a higher thermal stability than (**2**).

Acknowledgement

This work was sponsored by grants from CNPq, FAPESP, FINEP and CAPES. We thank Dr. S. I. Klein for discussion of the NMR data.

References

[1] S. Trofimenko, *Chem. Rev.* **72**, 497 (1972); S. Trofimenko, *Prog. Inorg. Chem.* **34**, 115 (1986).
[2] A. P. Sadimenko and S. S. Basson, *Coord. Chem. Rev.* **147**, 247 (1996).
[3] M. Hvastijová and J. Kohout, *Z. Anorg. Allg. Chem.* **600**, 177 (1991).
[4] H. W. Fruhauf, *Chem. Rev.* **97**, 523 (1997); A. E. Mauro, A. C. F. Caires, R. H. A. Santos and M. T. P. Gambardella, *J. Coord. Chem.* **48**, 521 (1999).
[5] M. Hvastijová, J. Kohout, A. Adamíková and P. Fodran, *J. Coord. Chem.* **14**, 259 (1986).
[6] O. L. Casagrande, S. I. Klein, A. E. Mauro and K. Tomita, *Transition Metal Chem.* **14**, 45 (1989); A. C. F. Caires, A. E. Mauro, R. H. A. Santos, M. T. P. Gambardella and J. R. Lechat, *Gazz. Chim. Ital.* **123**, 495 (1993); A. E. Mauro, C. C. Porta, S. R. Ananias, V. Sargentelli, R. H. A. Santos and M. T. P. Gambardella, *J. Coord. Chem.* **49**, 9 (1999); V. A. de Lucca Neto, A. E. Mauro, A. C. F. Caires, S. R. Ananias and E. T. De Almeida, *Polyhedron* **18**, 413 (1998).
[7] N. Saha, A. Saha and A. Misra, *Polyhedron* **13**, 2025 (1994).
[8] M. T. Alonso, O. Juanes, J. Mendoza and J. C. Rodrígues-Ubis, *J. Organomet. Chem.* **430**, 335 (1992).
[9] R. F. Heck, *Palladium Reagents in Organic Synthesis: Best Synthetic Methods* (Academic Press, 1985), p. 17.
[10] C. K. Fair, *Molecular Structure System* (Enraf-Nonius, Holland, 1990), I.
[11] D. T. Cromer and J. B. Mann, *Acta Cryst.* **A24**, 321 (1968).
[12] D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
[13] R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.* **42**, 3175 (1965).
[14] Z. Dori and R. F. Ziolo, *Chem. Rev.* **73**, 247 (1973); W. Beck, W. P. Fehlhammer, P. Pollman and R. S. Tobias, *Inorg. Chim. Acta* **2**, 467 (1968); K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (4th edn., John Wiley & Sons, New York, N.Y., 1986), p. 290; A. M. Golub, H. Kohler and V. V. Skopenko, *Chemistry of Pseudohalides* (Elsevier-Amsterdam, 1986), p. 34.
[15] A. W. Verstuyft, D. A. Redfield, L. W. Cary and J. H. Nelson, *Inorg. Chem.* **16**(11), 2776, (1977) and references therein.
[16] D. A. Redfield and J. H. Nelson, *Inorg. Nucl. Chem. Letters* **10**, 931 (1974).
[17] V. Agre, N. P. Kozlova, V. K. Trunov, L. G. Makarevich and O. V. Ivanov, *Koord. Khim.* **5**(9), 1413 (1979).
[18] G. A. Ardizzoia, G. L. Monica, S. Cenini, M. Moret and N. Masciocchi, *J. Chem. Soc. Dalton Trans.* p. 1351 (1996).
[19] G. Minghetti, M. A. Cinellu, A. L. Bandini, G. Banditelli, F. Demartin and M. Manassero, *J. Organomet. Chem.* **315**, 387 (1986).
[20] C. H. Cheng, J. S. Lain, Y. J. Wu and S. L. Wang, *Acta Cryst.* **C46**, 208 (1990).
[21] A. T. Baker, J. K. Crass, M. Maniska and D. C. Craig, *Inorg. Chim. Acta* **230**, 225 (1995).
[22] W. P. Fehlhammer and L. F. Dahl, *J. Amer. Chem. Soc.* **94**(10), 3377 (1972).
[23] A. J. Canty, P. R. Traill, B. W. Skelton and A. H. White, *J. Organomet. Chem.* **402**, C33-C36 (1991).
[24] N. B. Pahor, M. Calligaris and L. Randaccio, *J. Chem. Soc. Dalton Trans.* **8**, 725 (1976).
[25] B. Bendiksen, W. C. Riley, M. W. Babich, J. H. Nelson and R. A. Jacobson, *Inorg. Chim. Acta* **57**, 29 (1982).