

# Sterically promoted $N^2$ bound tetrazolate complex formation in the 1,3-dipolar cycloaddition of $p\text{-OMeC}_6\text{H}_4\text{CN}$ to the coordinated azide in the palladium complex $[\text{Pd}(\text{N-N-S})(\text{N}_3)]$ . X-ray crystal structure of $[\text{Pd}(\text{N-N-S})(\text{N}_4\text{C-}p\text{-OMeC}_6\text{H}_4)]$

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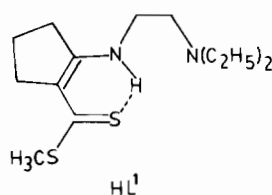
## Abstract

The 1,3-dipolar cycloaddition of  $p\text{-OMeC}_6\text{H}_4\text{CN}$  to the coordinated azide in the  $[\text{PdL}(\text{N}_3)]$  complex (HL = methyl 2-(((2-diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate) has been studied. The tetrazolate complex  $[\text{PdL}(\text{N}_4\text{C-}p\text{-OMeC}_6\text{H}_4)]$  (**1**) thus produced has been characterized from its IR and  $^1\text{H}$  NMR spectra, and X-ray crystal structure. Complex **1** crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 8.922(1)$ ,  $b = 17.041(1)$ ,  $c = 8.043(1)$  Å,  $\alpha = 90.26(1)$ ,  $\beta = 101.68(1)$ ,  $\gamma = 82.81(1)^\circ$ ,  $V = 1187.8(4)$  Å<sup>3</sup> and  $D_{\text{calc}} = 1.546$  g cm<sup>-3</sup> for  $Z = 2$ . The structure was solved by the heavy-atom technique and refined by the block-diagonal least squares method to converge at  $R = 0.057$  and  $R_w = 0.051$  for 3669 observed ( $|F_o| > 3\sigma|F_o|$ ) reflections. The tetrazole in **1** is bound to Pd through its  $N^2$  nitrogen atom.

## Introduction

1,3-Dipolar cycloaddition reactions of multiple bonded molecules to coordinated azide in metal complexes have received considerable attention [1–18]. The reaction between a nitrile and an azido complex is of special interest because the tetrazolate complex thus formed can be either a  $N^1$  or  $N^2$  bound species, or a mixture of both the isomers. In the majority of cases the stereochemistry of the tetrazolate complexes has been ascertained from their  $^1\text{H}$  NMR spectra, although in a few cases X-ray crystal structures have been determined [4, 9, 15, 19, 20]. We have shown [17, 18] that the reactions of  $[\text{ML}(\text{N}_3)]$  complexes (where  $\text{M(II)} = \text{Ni, Pd}$ ; HL = methyl 2-(((2-amino/dialkylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate) with nitriles give rise to *syn*- $N^1$ , *anti*- $N^1$  and  $N^2$  bound tetrazolates whose relative abundances as well as rates of formation are strongly influenced by the electronic and steric factors of the reactants. The relative abundance of the  $N^2$  isomer decreases with concomitant increase of the  $N^1$  isomer when the nitrile contains an electron-releasing substituent. On

the other hand, while steric interactions between the substituents in L and RCN impede the formation of  $N^1$  bound tetrazolates, formation of the  $N^2$  bound isomer, however, is far less affected. We have been interested in knowing about the stereochemistry of the cycloaddition product when these two opposing factors become operative. To this end we report here the synthesis and X-ray crystal structure of the tetrazolate complex obtained by reacting  $[\text{PdL}^1(\text{N}_3)]$  (HL<sup>1</sup> = methyl 2-(((2-diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate) with  $p\text{-OMeC}_6\text{H}_4\text{CN}$ .



## Experimental

*Preparation of the complex  $[\text{PdL}^1(\text{N}_4\text{C-}p\text{-OMeC}_6\text{H}_4)]$  (**1**)*

$[\text{PdL}^1(\text{N}_3)]$  (0.42 g, 1 mmol) was dissolved in hot nitromethane (25 cm<sup>3</sup>) and  $p\text{-OMeC}_6\text{H}_4\text{CN}$  (0.53 g,

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TABLE 1. Summary of crystallographic data

Chemical formula	C <sub>21</sub> H <sub>30</sub> N <sub>6</sub> OS <sub>2</sub> Pd
Formula weight	552.5
Space group	<i>P</i> $\bar{1}$ (triclinic)
<i>a</i> (Å)	8.922(1)
<i>b</i> (Å)	17.041(1)
<i>c</i> (Å)	8.043(1)
$\alpha$ (°)	90.26(1)
$\beta$ (°)	101.68(1)
$\gamma$ (°)	82.81(1)
<i>V</i> (Å <sup>3</sup> )	1187.8(4)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.546
$\mu$ (cm <sup>-1</sup> )	9.636
Crystal dimension (mm)	0.22 × 0.17 × 0.38
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71069
Temperature (K)	293
Reflections collected	4185
Reflections used in refinement	3669
Parameters refined	280
$R = \sum( F_o  -  F_c ) / \sum  F_o $	0.057
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w  F_o ^2]^{1/2}$	0.051

4 mmol) was added. The solution was heated on a steam bath for 50 h. During this period the solution was twice filtered to remove the small amount of solid material deposited. Orange crystals of the product were obtained (70%) on concentration of the solution on a rotary evaporator. X-ray diffraction quality crystals were obtained by slow evaporation

of a nitromethane solution on a hot plate. *Anal.* Calc. for C<sub>21</sub>H<sub>30</sub>N<sub>6</sub>OS<sub>2</sub>Pd: C, 45.62; H, 5.43; N, 15.21; Pd, 19.26. Found: C, 45.5; H, 5.55; N, 15.1; Pd, 19.4%.

#### Physical measurements

<sup>1</sup>H NMR spectra were recorded on CDCl<sub>3</sub> solutions on a Jeol FX-100 spectrometer using Me<sub>4</sub>Si ( $\delta=0$  ppm) as the internal reference. IR spectra were carried out as KBr pellets using a Perkin-Elmer model 783 spectrophotometer. C, H and N analyses were performed on a Perkin-Elmer model 240 C elemental analyzer.

#### Crystallographic studies

X-ray diffraction data of **1** were collected on a Enraf-Nonius CAD-4 diffractometer. Cell dimensions were accurately determined using 25 arbitrarily chosen higher order reflections and are listed in Table 1 along with relevant parameters for data collection and structure solution. The structure was solved by the heavy-atom method and refined using the SDP package of programs for the PDP-11/73 [21]. Refinement by the block-diagonal least-squares method converged at  $R=0.057$  and  $R_w=0.051$  for all non-hydrogen atoms refined with anisotropic thermal parameters. Hydrogen atoms were held fixed at positions obtained in the difference map after a complete convergence of anisotropic refinement and

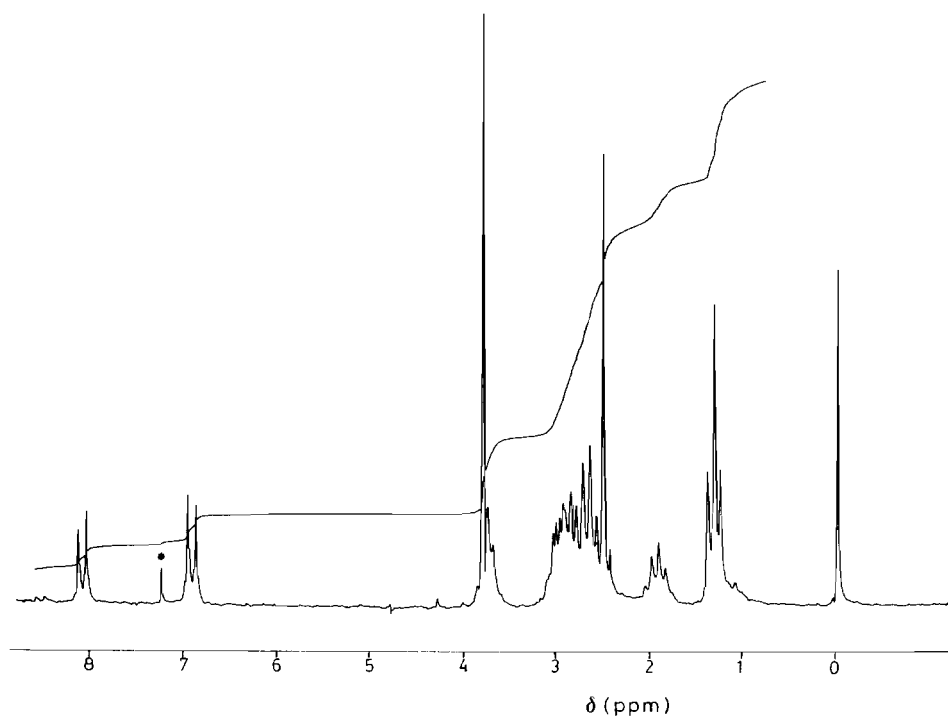


Fig. 1. 100 MHz <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub>.

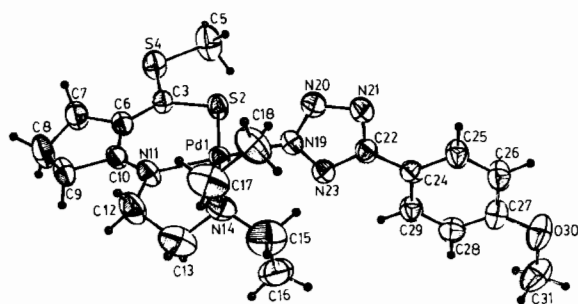


Fig. 2. ORTEP view of **1** with atom-labelling scheme.

TABLE 2. Positional parameters and their e.s.d.s

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Pd1	0.40133(3)	0.16198(2)	0.19760(4)	2.932(4)
S2	0.2756(1)	0.05615(6)	0.1352(1)	3.51(2)
S4	0.3203(2)	-0.11869(7)	0.1746(2)	4.54(2)
O30	-0.2701(8)	0.4852(3)	-0.6524(6)	6.0(1)
N11	0.6059(4)	0.1020(3)	0.3007(6)	3.97(7)
N14	0.5202(5)	0.2638(3)	0.2603(6)	4.19(7)
N19	0.1952(4)	0.2259(2)	0.0925(5)	3.43(6)
N20	0.0813(5)	0.2481(3)	0.1729(5)	4.22(7)
N21	-0.0281(4)	0.2935(3)	0.0643(6)	4.15(7)
N23	0.1626(4)	0.2542(2)	-0.0663(5)	3.64(6)
C3	0.3979(4)	-0.0280(2)	0.2035(5)	3.13(6)
C5	0.1228(7)	-0.0935(4)	0.073(1)	6.3(1)
C6	0.5517(4)	-0.0357(3)	0.2802(5)	3.37(6)
C7	0.6458(6)	-0.1146(4)	0.3334(9)	4.7(1)
C8	0.8108(6)	-0.0979(4)	0.385(1)	5.7(1)
C9	0.8064(5)	-0.0104(4)	0.4071(8)	4.47(9)
C10	0.6447(4)	0.0271(3)	0.3225(5)	3.34(6)
C12	0.7247(6)	0.1546(4)	0.365(1)	5.6(1)
C13	0.685(1)	0.2312(6)	0.257(1)	7.0(2)
C15	0.473(2)	0.3321(7)	0.144(2)	7.8(2)
C16	0.500(1)	0.3177(5)	-0.037(1)	6.4(1)
C17	0.515(1)	0.2849(8)	0.435(2)	7.7(2)
C18	0.3539(8)	0.3243(5)	0.4583(9)	6.0(1)
C22	0.0242(5)	0.2964(2)	-0.0792(6)	3.36(6)
C24	-0.0554(4)	0.3422(3)	-0.2326(6)	3.38(6)
C25	-0.1881(6)	0.3960(3)	-0.2329(6)	4.03(8)
C26	-0.2567(7)	0.4424(3)	-0.3743(8)	4.64(9)
C27	-0.1936(6)	0.4362(3)	-0.5204(7)	4.21(8)
C28	-0.0650(6)	0.3812(3)	-0.5233(6)	4.23(8)
C29	0.0014(5)	0.3349(3)	-0.3812(6)	3.85(7)
C31	-0.194(1)	0.4881(5)	-0.7918(9)	6.6(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

were given isotropic thermal parameters, based upon the non-hydrogen atoms to which they are bonded. A unit-weighting scheme was used along with the Dunitz–Seiler factor [22]. Absorption corrections were made according to North *et al.* [23]. The final difference map was essentially featureless ( $0.3 \text{ e } \text{Å}^{-3}$ ) except for the positions of the ethyl groups connected

to nitrogen wherein peaks of around  $1.2 \text{ e } \text{Å}^{-3}$  were found. Attempts to refine these positions by means of a disordered model were not successful. Hence these peaks were ignored and the atoms refined with positions of higher electron density. The scattering factors for Pd, S, O, N and C were taken from ref. 24, and those of hydrogen atoms from Stewart *et al.* [25].

## Results and discussion

The cycloaddition reaction between  $[\text{PdL}^1(\text{N}_3)]$  and *p*-OMeC<sub>6</sub>H<sub>4</sub>CN to produce complex **1** takes place very slowly at 100 °C in nitromethane. On the other hand, considerable decomposition of the product occurs when the reaction is carried out at 150 °C in nitrobenzene. Monitoring of the reaction mixture by observing the disappearance of  $\nu_{\text{as}}[\text{N}_3^-]$  at  $2030 \text{ cm}^{-1}$  of the azido complex showed that at 100 °C the reaction is complete in *c.* 48 h. The tetrazolate complex exhibits several new bands in the range  $1650\text{--}450 \text{ cm}^{-1}$ , viz. at 1600, 1525, 1295, 1245, 1170, 1000, 840, 640, 620 and  $535 \text{ cm}^{-1}$ , in addition to those observed in the azido complex.

The <sup>1</sup>H NMR spectrum of **1** (Fig. 1) shows a triplet due to the methyl group of the N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> moiety at  $\delta$  1.30, a singlet at 2.52 due to SCH<sub>3</sub>, another singlet at 3.80 due to OCH<sub>3</sub> (which is flanked by a CH<sub>2</sub> group of the ethylene bridge of L), and two doublets at 6.90 and 8.06 due to the *meta* and *ortho* protons of the phenyl ring, respectively. The observation of these resonances gives a clear indication of the formation of a single isomer in the cycloaddition reaction. However, it is not obvious from the NMR spectrum whether the complex is a N<sup>1</sup> or N<sup>2</sup> bound tetrazolate species.

In order to establish the stereochemistry of the product definitely the X-ray crystal structure of **1** was determined. The molecular structure of **1** is shown in Fig. 2, with the numbering scheme. Although the hydrogen atoms are shown in the Figure, these are not included in the numbering scheme for the sake of clarity. Positional parameters, refined displacement parameters, bond lengths and bond angles are given in Tables 2, 3, 4 and 5, respectively. The crystal structure consists of discrete molecules separated by van der Waals distances. The stereoscopic projection of the molecules in the unit cell is shown in Fig. 3.

The molecular structure shows that the Pd atom is in a distorted square planar environment provided by the N<sub>2</sub>S donor set of L<sup>-</sup> and the N<sup>2</sup> nitrogen of the tetrazole. The deviations of the atoms to the square plane consisting of S(2), N(14), N(11), N(19), and Pd(1) are as follows: S(2),  $-0.011 \text{ Å}$ ; N(14),

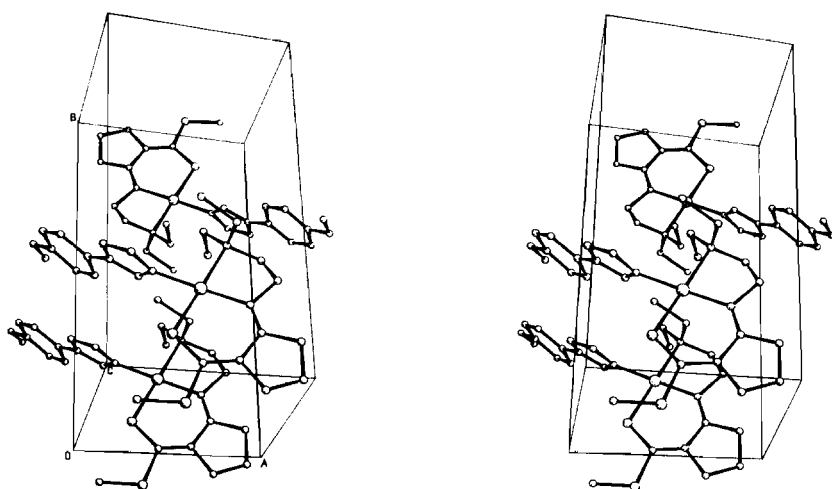
Fig. 3. Stereoscopic projection of **1** in the unit cell.

TABLE 3. Refined displacement parameters with e.s.d.s

	<i>B</i> (1,1)	<i>B</i> (2,2)	<i>B</i> (3,3)	<i>B</i> (1,2)	<i>B</i> (1,3)	<i>B</i> (2,3)
Pd1	0.00867(2)	0.00253(1)	0.01314(3)	−0.00165(2)	0.00309(5)	−0.00074(3)
S2	0.00917(9)	0.00262(3)	0.0178(2)	−0.00154(8)	−0.0014(2)	−0.0004(1)
S4	0.0142(1)	0.00266(3)	0.0239(2)	−0.0020(1)	0.0004(3)	−0.0009(1)
O30	0.0253(8)	0.0045(2)	0.0168(6)	0.0035(6)	−0.001(1)	0.0023(5)
N11	0.0082(3)	0.0040(1)	0.0189(6)	−0.0019(3)	0.0017(7)	−0.0011(5)
N14	0.0133(4)	0.0034(1)	0.0201(6)	−0.0053(3)	0.0081(8)	−0.0035(4)
N19	0.0098(3)	0.0031(1)	0.0152(5)	−0.002(3)	0.0062(6)	−0.0004(4)
N20	0.0129(4)	0.0042(1)	0.0163(5)	0.0013(4)	0.0111(7)	0.0024(5)
N21	0.0113(4)	0.0041(1)	0.0178(5)	0.0017(4)	0.0100(7)	0.0019(5)
N23	0.0113(4)	0.0033(1)	0.0154(5)	−0.0001(3)	0.0073(7)	0.0004(4)
C3	0.0096(4)	0.0027(1)	0.0129(5)	−0.0008(3)	0.0013(7)	−0.0000(4)
C5	0.0154(6)	0.0036(2)	0.037(2)	−0.0047(5)	−0.010(2)	−0.0038(8)
C6	0.0100(4)	0.0034(1)	0.0124(5)	−0.0002(4)	0.0035(7)	−0.0010(4)
C7	0.0123(5)	0.0040(2)	0.0224(9)	0.0000(5)	0.002(1)	0.0013(6)
C8	0.0111(5)	0.0047(2)	0.030(1)	0.0024(6)	−0.002(1)	0.0005(9)
C9	0.0093(4)	0.0046(2)	0.0197(7)	0.0006(5)	−0.000(1)	0.0006(6)
C10	0.0084(3)	0.0035(1)	0.0138(5)	−0.0007(4)	0.0040(7)	−0.0000(4)
C12	0.0105(5)	0.0043(2)	0.033(1)	−0.0034(5)	−0.003(1)	−0.0013(8)
C13	0.0193(8)	0.0065(3)	0.034(2)	−0.0075(8)	0.017(2)	−0.004(1)
C15	0.030(1)	0.0059(3)	0.034(2)	−0.005(1)	0.020(3)	−0.004(1)
C16	0.0232(9)	0.0058(3)	0.025(1)	−0.0059(7)	0.017(1)	0.0035(8)
C17	0.023(1)	0.0074(4)	0.034(2)	−0.008(1)	0.018(2)	−0.005(1)
C18	0.0165(6)	0.0057(2)	0.0266(9)	−0.0010(7)	0.015(1)	−0.0102(7)
C22	0.0108(4)	0.0024(1)	0.0162(5)	−0.0010(3)	0.0053(8)	−0.0003(4)
C24	0.0103(4)	0.0027(1)	0.0164(5)	−0.0015(3)	0.0074(7)	−0.0013(4)
C25	0.0133(5)	0.0037(1)	0.0143(5)	0.0024(4)	0.0059(8)	−0.0005(5)
C26	0.0149(5)	0.0037(2)	0.0194(7)	0.0030(5)	0.006(1)	0.0004(6)
C27	0.0155(6)	0.0031(1)	0.0157(6)	0.0002(5)	−0.001(1)	−0.0003(5)
C28	0.0149(5)	0.0039(2)	0.0154(6)	−0.0022(5)	0.0075(9)	−0.0009(5)
C29	0.0125(4)	0.0033(1)	0.0155(6)	0.0004(4)	0.0059(8)	−0.0006(5)
C31	0.032(1)	0.0049(2)	0.0183(8)	−0.002(1)	0.011(2)	0.0048(7)

The form of the anisotropic displacement is  $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$ .

TABLE 4. Bond distances (Å) with e.s.d.s

Pd1–S2	2.244(2)	N23–C22	1.333(5)
Pd1–N11	1.998(3)	C3–C6	1.376(5)
Pd1–N14	2.151(4)	C6–C7	1.507(7)
Pd1–N19	2.040(3)	C6–C10	1.434(6)
S2–C3	1.710(4)	C7–C8	1.509(9)
S4–C3	1.766(4)	C8–C9	1.50(1)
S4–C5	1.786(6)	C9–C10	1.526(6)
O30–C27	1.364(7)	C12–C13	1.53(1)
O30–C31	1.43(1)	C15–C16	1.54(2)
N11–C10	1.283(6)	C17–C18	1.55(1)
N11–C12	1.484(8)	C22–C24	1.467(6)
N14–C13	1.51(1)	C24–C25	1.403(6)
N14–C15	1.46(1)	C24–C29	1.390(7)
N14–C17	1.46(1)	C25–C26	1.378(7)
N19–N20	1.326(6)	C26–C27	1.400(9)
N19–N23	1.330(5)	C27–C28	1.392(7)
N20–N21	1.337(6)	C28–C29	1.377(7)
N21–C22	1.333(7)		

–0.011 Å; N(11), 0.009 Å; N(19), 0.009 Å; Pd(1), 0.004 Å. The Pd(1)–N(11) and Pd(1)–N(19) distances, which are 1.998 and 2.040 Å, respectively, are within  $\pm 0.02$  Å of the sum of the covalent radii (1.32 + 0.70 = 2.02 Å) [26]. The Pd(1)–S(2) distance, 2.244 Å, is considerably shorter than the sum of the covalent radii (2.36 Å). However, the Pd(1)–N(14) separation, 2.151 Å, is much longer than the other two Pd–N bonds. This is expected because the strongly *trans*-directing S(2) atom causes the N(14) nitrogen atom to be weakly bonded and therefore longer than normal Pd–N bonds. While the angles S(2)Pd(1)N(11) (96.5°) and N(14)Pd(1)N(19) (94.8°) are wider than 90°, the remaining two angles N(11)Pd(1)N(14) (83.7°) and S(2)Pd(1)N(19) (85.0°) are closer than the theoretical value.

The six-membered chelate ring formed by Pd(1)S(2)C(3)N(11)C(10)C(6) atoms is almost planar. The maximum deviation of the constituent atoms from the mean plane does not exceed 0.016 Å. Strong electron delocalization in this chelate ring is evident from the considerable shortening of the S(2)–C(3) (1.710 Å), C(3)–C(6) (1.376 Å), C(6)–C(10) (1.434 Å) and C(10)–N(11) (1.283 Å) bonds. A similar  $\pi$ -delocalization effect has been reported [27] in *N,N'*-ethanebis(methyl 2-aminocyclopent-1-enedithiocarboxylato)copper(II) chelate [28].

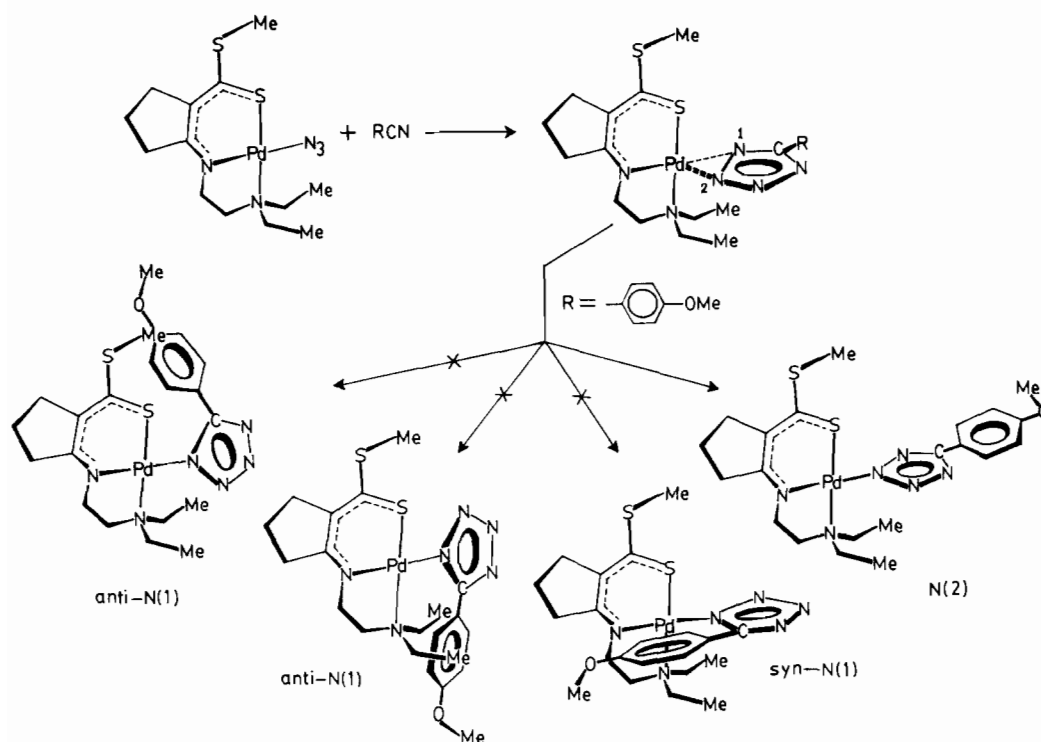
The tetrazole ring coordinated through N(19) (that is, N<sup>2</sup>) is perfectly planar. No ring atoms deviate from the mean plane by more than 0.006 Å. Bond lengths are almost equal and lie in the narrow range 1.326–1.337 Å. There is practically no difference between C–N and N–N bonds, which indicates strong  $\pi$ -electron delocalization in the tetrazole ring. The angles between adjacent atoms in the ring lie in the range 103.6–111.8° and close to that expected for a regular pentagon, 108°.

The dihedral angle between the planes S(2)N(14)N(11)N(19)Pd(1) (plane 1) and the six-membered chelate ring is  $1.17 \pm 2.70^\circ$ , while the angle between plane 1 and the tetrazole ring is  $83.44 \pm 0.15^\circ$ . The planes of the phenyl ring and tetrazole ring create an angle of  $10.43 \pm 0.76^\circ$ . The C(22)–C(24) distance between the two rings, 1.467 Å, is considerably shorter than the value (1.54 Å) expected for a paraffinic single bond. This indicates that there is an extended conjugation of double bonds in the two rings.

The probable mechanism of 1,3-dipolar cycloaddition reaction between [PdL<sup>1</sup>(N<sub>3</sub>)] and *p*-OMe-

TABLE 5. Bond angles (°) with e.s.d.s

S2–Pd1–N11	96.5(1)	Pd1–N19–20	125.5(3)	N11–C12–C13	108.0(6)
S2–Pd1–N14	179.2(1)	Pd1–N19–N23	122.8(3)	N14–C13–C12	107.9(7)
S2–Pd1–N19	85.0(1)	N20–N19–N23	111.5(3)	N14–C15–C16	115.0(9)
N11–Pd1–N14	83.7(2)	N19–N20–N21	107.1(4)	N14–C17–C18	113.7(7)
N11–Pd1–N19	178.5(2)	N20–N21–C22	105.9(4)	N21–C22–N23	111.8(4)
N14–Pd1–N19	94.8(2)	N19–N23–C22	103.6(4)	N21–C22–C24	125.3(4)
Pd1–S2–C3	109.5(1)	S2–C3–S4	117.1(2)	N23–C22–C24	122.9(4)
C3–S4–C5	105.6(2)	S2–C3–C6	128.9(3)	C22–C24–C25	121.4(4)
C27–O30–C31	115.2(6)	S4–C3–C6	114.0(4)	C22–C24–C29	120.6(4)
Pd1–N11–C10	129.5(3)	C3–C6–C7	122.9(4)	C25–C24–C29	118.0(4)
Pd1–N11–C12	112.7(3)	C3–C6–C10	126.6(4)	C24–C25–C26	121.0(5)
C10–N11–C12	117.8(4)	C7–C6–C10	110.5(4)	C25–C26–C27	119.8(5)
Pd1–N14–C13	102.2(5)	C6–C7–C8	105.7(5)	O30–C27–C26	114.9(6)
Pd1–N14–C15	116.8(6)	C7–C8–C9	107.1(5)	O30–C27–C28	125.5(5)
Pd1–N14–C17	108.8(6)	C8–C9–C10	107.0(4)	C26–C27–C28	119.6(5)
C13–N14–C15	109.2(8)	N11–C10–C6	129.0(3)	C27–C28–C29	119.7(5)
C13–N14–C17	107.4(6)	N11–C10–C9	123.5(4)	C24–C29–C28	121.7(4)
C15–N14–C17	111.9(8)	C6–C10–C9	107.4(4)		



Scheme 1.

$C_6H_4CN$  is shown in Scheme 1. The formation of a three-centred activated complex has been suggested [12, 18]. The breaking of the Pd–N<sup>2</sup> bond in the activated state will be preferred on electronic grounds because the N<sup>1</sup> nitrogen is electron-rich due to the electron releasing OMe group. However, as shown in the Scheme, the breaking of the Pd–N<sup>1</sup> bond will be sterically promoted due to severe steric interactions between the N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> or SCH<sub>3</sub> group and the phenyl ring. As a result neither *syn*-N<sup>1</sup>, nor *anti*-N<sup>1</sup> bound tetrazolate will be free from steric interactions. Thus, although a strongly electron-releasing substituent in the reacting nitrile will favour the formation of a N<sup>1</sup> bound tetrazolate, steric factors will play a more dominating role in deciding the stereochemistry of the product. Alternatively one can argue that no matter the transition state, this reaction will be under thermodynamic control, especially because it is run at 100 °C. The outcome of the reaction, therefore, can be explained by considering the relative stabilities of the isomers alone.

#### Supplementary material

Listings of positional parameters for hydrogen atoms, bond distances and angles involving hydrogen atoms, torsional angles, least-squares planes and

dihedral angles may be obtained from author K.N. on request.

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