Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

trans-Bis[3-(2-fluorophenyl)-1-(4-nitrophenyl)triazenido-κN^3]-bis(pyridine-κN)palladium(II)

Manfredo Hörner,* Lorenzo do C. Visentin, Marisa Dahmer and Jairo Bordinhao

Departamento de Quimica, Universidade Federal de Santa Maria, Caixa Postal 5071, 97110-900 Santa Maria, RS, Brazil
Correspondence e-mail: hoerner@base.ufsm.br

Received 18 February 2002
Accepted 11 March 2002
Online 11 April 2002

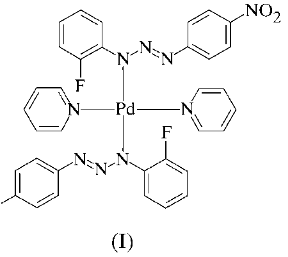
In the title complex, $[\mathrm{Pd}(\mathrm{C_{12}H_8FN_4O_2})_2(\mathrm{C_5H_5N})_2]$ or *trans*-$[\mathrm{Pd}(\mathrm{FC_6H_4N{=}N{-}NC_6H_4NO_2})(\mathrm{C_5H_5N})_2]$, the Pd atom lies on a centre of inversion in space group $P\overline{1}$. The coordination geometry about the Pd^{2+} ion is square planar, with two deprotonated 3-(2-fluorophenyl)-1-(4-nitrophenyl)triazenide ions, $\mathrm{FC_6H_4N{=}N{-}NC_6H_4NO_2}^-$, acting as monodentate ligands (two-electron donors), while two neutral pyridine molecules complete the metal coordination sphere. The whole triazenide ligand is not planar, with the largest interplanar angle being 16.8 (5)° between the phenyl ring of the 2-fluorophenyl group and the plane defined by the N=N—N moiety. The Pd—N(triazenide) and Pd—N(pyridine) distances are 2.021 (3) and 2.039 (3) Å, respectively.

Comment

Although palladium(II) complexes with nitrogen coordination spheres involving 1,3-diaryl-substituted triazenide ligands, $\mathrm{ArNNNAr}^-$, have been investigated over the last few decades, the structures of such compounds continue to attract interest (Moore & Robinson, 1986; Peregudov *et al.*, 1998; Cao *et al.*, 2000). In this work, we report the synthesis and structural characterization of the title complex, (I), a centrosymmetric mononuclear $\mathrm{Pd^{II}}$ complex with an asymmetric disubstituted 1,3-diaryltriazenide ion and pyridine (py) as ligands.

In the molecule of (I), with site symmetry $\overline{1}$, the square-planar-coordinated Pd^{2+} ion is situated on an inversion centre, with two 3-(2-fluorophenyl)-1-(4-nitrophenyl)triazenide ions, $\mathrm{FC_6H_4N{=}N{-}NC_6H_4NO_2}^-$, and two pyridine molecules coordinated *trans* to each other (Fig. 1).

The deviation observed in (I) from the normal N—N and $\mathrm{C_{ar}}$—N bonds makes evident the delocalization of the π electrons on the N11—N12=N13 group towards the terminal aryl substituents. The N12=N13 bond [1.283 (5) Å] is longer than the characteristic value for a double bond (1.24 Å), whereas N11—N12 [1.325 (5) Å] is shorter than the characteristic value for a single bond (1.44 Å; *International Tables for X-ray Crystallography*, 1985, Vol. III, p. 270), and both N11—C11 [1.403 (5) Å] and N13—C21 [1.413 (5) Å] are shorter than expected for a $\mathrm{C_{ar}}$—N single bond. The Pd—N11 bond distance of 2.021 (3) Å is close to the sum of the covalent radii (2.078 Å; Allen *et al.*, 1987; Teatum *et al.*, 1960) and corresponds to a covalent single bond. These values are in good agreement with the distances found in the related compound *trans*-[Pd(*R*N1—N2=N3*R*)Cl(PPh$_3$)$_2$] (*R* is *p*-tolyl; N2=N3 1.286, N1—N2 1.336 and Pd—N1 2.033 Å; Moore & Robinson, 1986; Bombieri *et al.*, 1975, 1976; Brown & Ibers, 1976).



(I)

Due to the delocalization of the π electrons over the nitro group and the C11–C16 phenyl ring towards the N11—N12=N13 chain, this part of the triazenide ligand is nearly planar [interplanar angles O1,N1,O2/C11–C16 3.0 (6)° and C11–C16/N11—N12=N13 4.2 (4)°]. On the other hand, the C21–C26 ring makes an angle of 16.8 (5)° with the plane defined by the N11—N12=N13 group, which accounts for the significant deviation from planarity of the whole 1,3-diaryltriazenide ligand. The C11–C16 phenyl ring and the 2-fluorophenyl substituent are almost planar (r.m.s. deviations 0.0064 and 0.0042 Å, respectively).

The pyridine ring (N31–C36) is planar within experimental accuracy (r.m.s. deviation 0.0062 Å), making a dihedral angle of 69.5 (2)° with the N11—Pd—N31$^{\mathrm{i}}$ moiety [symmetry code: (i) $-x$, $-y$, $-z$]. The Pd—N31 bond distance of 2.039 (3) Å is shorter than the sum of the covalent radii (2.08 Å; Sheldrick, 1997) and may be compared with the value found in $[\mathrm{Pd(py)_4}](\mathrm{I_3})_2$ (Pd—N$_{\mathrm{py}}$ 2.014 Å; Tebbe *et al.*, 1996).

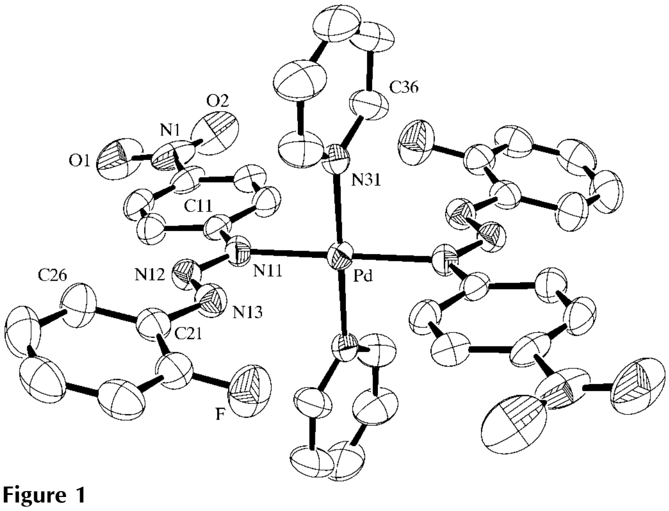


Figure 1
A perspective view of the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

DOI: 10.1107/S0108270102004602

Experimental

To a solution of $PdCl_2$ (17 mg, 0.1 mmol) in concentrated aqueous ammonium hydroxide (5 ml), a mixture of 3-(2-fluorophenyl)-1-(4-nitrophenyl)triazene (50 g, 0.2 mmol) in tetrahydrofuran (30 ml) and concentrated aqueous ammonium hydroxide (1 ml) was added slowly under continuous stirring. After stirring for 1 h at room temperature, pyridine (1 ml) was added to the deep-red reaction mixture, which was then stirred for a further 24 h. Red prism-shaped crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of the solvent mixture at room temperature (yield: 45 mg, 60%; m.p. 525–529 K).

Crystal data

$[Pd(C_{12}H_8FN_4O_2)_2(C_5H_5N)_2]$
$M_r = 783.07$
Triclinic, $P\overline{1}$
$a = 8.941$ (2) Å
$b = 9.732$ (2) Å
$c = 10.9449$ (10) Å
$\alpha = 110.058$ (14)°
$\beta = 93.437$ (13)°
$\gamma = 109.012$ (19)°
$V = 829.9$ (3) $Å^3$

$Z = 1$
$D_x = 1.567$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.6$–25.1°
$\mu = 0.63$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.20 × 0.13 × 0.07 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.885$, $T_{max} = 0.958$
3149 measured reflections
2947 independent reflections
2446 reflections with $I > 2\sigma(I)$

$R_{int} = 0.032$
$\theta_{max} = 25.1°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 10$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.105$
$S = 1.07$
2947 reflections
232 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e $Å^{-3}$
$\Delta\rho_{min} = -0.98$ e $Å^{-3}$

H atoms were treated as riding, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 1
Selected geometric parameters (Å, °).

Pd—N11	2.021 (3)	N11—C11	1.403 (5)
Pd—N31	2.039 (3)	N12—N13	1.283 (5)
Pd—N13	2.903 (4)	N13—C21	1.413 (5)
F—C22	1.353 (5)	N31—C36	1.317 (6)
O1—N1	1.231 (6)	N31—C32	1.326 (6)
O2—N1	1.229 (6)	N1—C14	1.460 (6)
N11—N12	1.325 (5)		
N11—Pd—N31	91.59 (14)	N13—N12—N11	111.0 (3)

This work received partial support from CNPq (Proc. 520424/94-8) and FAPERGS. MH and JB thank CNPq, and LCV and MD thank CAPES, for grants. The authors thank Professor Dr Ademir Neves and Professor Dr Ivo Vencato, Universidade Federal de Santa Catarina, Brazil, for the opportunity to use the diffractometer facility.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1195). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bombieri, G., Immirzi, A. & Toniolo, L. (1975). *Acta Cryst.* A**31**, S141–142.
Bombieri, G., Immirzi, A. & Toniolo, L. (1976). *Inorg. Chem.* **15**, 2428–2432.
Brown, L. D. & Ibers, J. A. (1976). *Inorg. Chem.* **15**, 2788–2793.
Cao, Q.-E., Zhao, Y., Yao, X., Hu, Z. & Xu, Q. (2000). *Spectrochim. Acta A*, **56**, 1319–1327.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Moore, D. S. & Robinson, S. D. (1986). *Adv. Inorg. Chem. Radiochem.* **30**, 1–68.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Peregudov, A. S., Kravtsov, D. N., Drogunova, G. I. & Godovikov, I. A. (1998). *Inorg. Chim. Acta*, **280**, 238–242.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Teatum, E., Gschneidner, K. & Waber, J. (1960). Report LA-2345. Los Alamos Scientific Laboratory, New Mexico, USA.
Tebbe, K.-F., Grafe-Kavoosian, A. & Freckmann, B. (1996). *Z. Naturforsch. Teil B*, **51**, 999–1006.