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Asymmetric and symmetric triazenido cyclopalladated complexes: Synthesis, structural analysis and DFT calculations

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HIGHLIGHTS

- Two new cyclopalladated complexes containing triazenido ligands were obtained.
- Compounds were characterized by IR techniques and single crystal XRD.
- C—H···C interactions are relevant for molecular assembly during the crystallization.

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ABSTRACT

The reaction of [Pd{*dmba*}(μ-N_3)]$_2$ (*dmba* = *N*,*N*-dimethylbenzylamine) with 1-(2-fluorophenyl)-3-(4-nitrophenyl)triazenido (*L*^{1}) or 1,3-*bis*(4-nitrophenyl)triazenido (*L*^{2}) anions, in methanol, and subsequent treatment with pyridine (py) allows the preparation of the corresponding cyclopalladated compounds *[Pd(dmba)(L*^{1}*)(py)]* (**1**) and *[Pd(dmba)(L*^{2}*)(py)]·py* (**2**). The acentric mononuclear entities of (**1**) and (**2**) are connected by weak intermolecular non-classical C—H···C hydrogen bonds, which results in 2-D arrangements by translation, along the [100] and [001] crystallographic directions, respectively.

Introduction

Cyclometallation reaction can be defined as the formation of a bond between a transition metal and a carbon atom of one of its ligands, affording a metallocycle [1–4]. Particularly, spectacular progress has been made in this rich and active area of organometallic chemistry by using palladium as metal center due to the importance of cyclopalladated compounds in catalysis [5,6], organic synthesis [7,8], medicinal chemistry [9–12] and nanotechnology [13–14].

One of the most important reactions of cyclometallated compounds is the cleavage of halide bridged dimers by neutral or anionic ligands [1–4]. A phlethora of new ortho palladated derivatives with distinct structures and physico-chemical properties may be obtained from these reactions due to the large and diverse number of ligands available. For many years, we have been interested in the reactivity of pseudohalido-bridged cyclopalladated dimeric complexes [15–21]. Particularly, the cyclometallated [Pd(*dmba*)(μ-N_3)]$_2$ (*dmba* = *N*,*N*-dimethylbenzylamine) is a versatile precursor in azido-bridge splitting reactions and dipolar cycloaddition of unsaturated molecules (such as CS_2) to a coordinated azido ligand [22,23]. As an example, we reported the synthesis and characterization of [Pd(*dmba*)(μ-N,S—CN_3S_2)]$_2$ [22], which was the first X-ray crystal structure of an ortho metallated complex bearing the heterocyclic anion [CN_3S_2]$^-$. It was a result of the 1,3-dipolar cycloaddition of carbon disulfide to the azide bridge in [Pd(*dmba*)(μ-N_3)]$_2$. In addition, another advantage on using [Pd(*dmba*)(μ-N_3)]$_2$ as precursor is that the formation of the

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products from is readily confirmed by monitoring the strong $\nu_{as}(N_3)$ bandat 2059 cm^{-1} [24].

However, apart from bridge cleavage reactions of azido-bridged dimers with various phosphines and other ligands [15–21], studies involving such reactions with triazenido have not been carried out so far. In particular, it seemed interesting to us to investigate the reactions of cyclopalladated compounds with triazenido ligands for the reasons that follow. Firstly, due to the ability of these ligands to coordinate with metal atoms in a variety of modes, as it is well documented in the literature [25–27], and secondly, due to their chemotherapeutic properties [28,29] which can be enhanced by coordination with palladium ions.

As part of our ongoing studies of both cyclopalladated and triazenido ligands [15–24], the reaction of the dimeric compound [Pd(*dmba*)(μ-N_3)]$_2$ with the deprotonated 1-(2-fluorophenyl)-3-(4-nitrophenyl)triazene (L^1) or 1,3-*bis*(4-nitrophenyl)triazene (L^2) has been carried out in the presence of pyridine. The single-crystal structural analysis of triazenido complexes, including [Pd(II)(*dmba*)(Py)] cations bearing a one-dimensional arrangement via secondary hydrogen bonding, is reported.

Experimental

X-ray crystallography

The Xray data of both compounds were collected at room temperature on an Enraf-Nonius CAD4 diffractometer, using Mo$K\alpha$ radiation (λ = 0.70930 Å) and a graphite monochromator. The unit cell dimensions were obtained from a least-squares fit of the setting angles of 25 reflections. Lorenz and polarization corrections were also applied [30]. The structures were solved using direct methods and refined on F^2 by full-matrix least-squares methods with anisotropic displacement factors for all non-hydrogen atoms [31]. The H atoms of the phenyl groups were geometrically positioned (C—H = 0.93 Å for Csp^2 atoms) and were considered to be dependent on their respective C atoms, with U_{iso}(H) values set at 1.2U_{eq}Csp^2. Molecular graphs were obtained using the program *DIAMOND* 3.1 afor Windows [32]. Details of the structure refinement and the final reliability factors are given in Table 1.

Table 1
Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Molecular formula	$C_{26}H_{25}FN_6O_2Pd$	$C_{28.50}H_{28}N_{7.50}O_4Pd$
Molecular weight	578.92	645.98
Radiation, wavelength	Mo K_α, 0.71073 Å	Mo Kα, 0.71073 Å
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P(-1)$
a (Å)	*a* = 8.557(5) Å	*a* = 11.2962(10) Å
b (Å)	*b* = 13.539(5) Å	*b* = 11.9100(10) Å
c (Å)	*c* = 21.832(5) Å	*c* = 12.217(10) Å
	$\alpha = \beta = \gamma = 90°$	α = 72.529(5)°
		β = 76.444(5)°
		γ = 66.451(4)°
Z (mol/unit cell)	4	2
V (Å^3)	2529.3(18) Å^3	1424.87(17) Å^3
D_c (g cm^{-3})	1.520 mg/m^3	1.506 mg/m^3
Crystal size (mm)	0.243 × 0.156 × 0.11 mm	0.25 × 0.2 × 0.15 mm
μ (cm^{-1})	0.776 mm^{-1}	0.699 mm^{-1}
Temperature (K)	293	293
F (000)	1176	659
θ range for data collection	2.40–27.66°	2.35–25.09°
Index range	$-11 \leqslant h \leqslant 0$	$-13 \leqslant h \leqslant 13$
	$-17 \leqslant k \leqslant 0$	$-13 \leqslant k \leqslant 14$
	$-28 \leqslant l \leqslant 0$	$0 \leqslant l \leqslant 14$
Reflections collected	3317	5276
Independent reflections	3317 [*R*(int) = 0.0208]	5019/ [*R*(int) = 0.0157]
Data/restraints/ parameters	3317/0/325	5019/0/370
Goodness-of-fit on F^2	1.045	1.031
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0380	R_1 = 0.0272
	wR_2 = 0.0748	wR_2 = 0.0681
R indices (all data)	R_1 = 0.0964	R_1 = 0.0390
	wR_2 = 0.0883	wR_2 = 0.0723
Absolute structure parameter	−0.02(5)	–
Largest diff. peak and hole	0.539 and −0.646 eÅ^{-3}	0.381 and −0.402 eÅ^{-3}

Instruments

KBr pellets of the free ligands and complexes were prepared in order to acquire the IR spectra using a Bruker TENSOR27 FTIR-Spectrometer in the 4000–400 cm^{-1} spectral range. For determination of the melting points, single crystals of complexes **1** and **2** inserted into a glass capillary, were adapted on a MEL-TEMP II instrument.

Synthesis

The ligand 1,3-*bis*(4-nitrophenyl)triazene (L^2) and the precursor complex [Pd(*dmba*)(μ-N_3)]$_2$ were prepared as reported in the literature [24,33].

Synthesis of 1-(2-fluorophenyl)-3-(4-nitrophenyl)triazene (L^1)

2-Fluoroaniline (0.303 g, 2.76 mmol) was dissolved in a mixture of 15 mL of CH_3COOH and 5 mL of distilled water and the system was cooled to 0 °C. Under constant stirring, sodium nitrite (0.190 g, 2.76 mmol) was also added. After 30 min of stirring slowly added 4-nitroaniline (0.380 g, 2.76 mmol) previously dissolved in 20 ml of glacial acetic acid, 20 min after the addition of the amine the solution was neutralized to pH 6.0 with sodium acetate. The yellow precipitate obtained was filtered under vacuum and washed several times with cold water. The product was dried in vacuum. Yield: 53%. Melting point: 182 °C. Anal. Calc. for $C_{12}H_9NO_2F$ (218): C, 66.05; H, 4.12; N, 6.42. Found: C, 66.12; H, 4.09; N, 6.77. IR (KBr/cm^{-1}): 3200–3100 [s,ν(N—H)]; 1498[ν_{as}(-NO_2)]; 1397[ν(N=N)]; 1319 [vs,$\nu_s(NO_2)$]; 1184 [vs,ν_s(N—N)]; 1256 [(ν(F—C_{ar})].

*Synthesis of [Pd(dmba)(L^1)(py)] (**1**)*

The cyclopalladated complex **1** was obtained from a solution (0.210 g, 0.348 mmol) of [Pd(*dmba*)(μ-N_3)]$_2$ in 10 mL of methanol, which was slowly added to a mixture of 1-(2-fluorophenyl)-3-(4-nitrophenyl)triazene (0.200 g, 0.768 mmol) in 10 mL of methanol/KOH. After 1 h of continuous stirring at room temperature, 1 mL of pyridine was added to the deep red reaction mixture which was then stirred for a further 24 h. Red-prism-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent mixture at room temperature. Yield of the crystallized complex: 47%, based on $FC_6H_4NNN(H)C_6H_4NO_2$. Anal. Calc. for $C_{26}H_{25}FN_6O_2Pd$ (578.92 g/mol): C, 53.89; H, 4.31; N, 14.50%. Found: C, 52.51; H, 4.03; N, 14.51%. Melting point: 185 °C (decomposition). See Scheme 1. IR (KBr/cm^{-1}): the νN—H band is absent. 1503 [s,$\nu_{as}(NO_2)$], 1317 [s,$\nu_s(NO_2)$], and1292 cm^{-1} [vs,ν_{as}(NNN)].

Synthesis of [Pd(dmba)(L^2)(py)]·py (2)

In the same way, the cyclopalladated complex (**2**) was obtained from a solution (0.187 g, 0.349 mmol) of [Pd(*dmba*)(μ-N_3)]$_2$ in 10 mL of methanol, which was slowly added to a solution of 1,3-*bis*(4-nitrophenyl)triazene (0.200 g, 0.697 mmol) in 20 mL of methanol/KOH. After 1 h of continuous stirring at room temperature, 1 mL of pyridine was added to the deep red reaction mixture,

which was then stirred for a further 24 h. After slow evaporation of the solvents, red prism-shaped crystals suitable for X-ray analysis were obtained. Yield of the crystallized complex: 50%, based on free ligand. Anal. Calc. for $C_{28}H_{27}N_8O_4Pd$ (645.98 g/mol): C,53.01; H,4.17; N,17.33%. Found: C,52.8; H,4.11; N, 17.1%. Melting point: 208–212 °C (decomposition). IR (KBr/cm^{-1}) of the free ligand $O_2NC_6H_4NNN(H)C_6H_4NO_2$: 3282 [s,$\nu$(N—H)]; 1518 [vs,$\nu_{as}(NO_2)$];1405 [m, ν(N=N)]; 1326 [vs,$\nu_s(NO_2)$]; and 1170 cm^{-1} [vs,ν_s(N—N)]; *[Pd(dmba)(L^1)(py)]* (**2**): the νN—H band is absent. 1475 [s,$\nu_{as}(NO_2)$], 1322 [s,$\nu_s(NO_2)$], and 1275 cm^{-1} [vs,ν_{as}(NNN)].

Computational details

Density functional theory (DFT) calculations have been performed to study the electronic structure and to determine the reactivity indices (Fukui function) using the Gaussian 09 package [34]. The correlation and exchange functional was described by the hybrid B3LYP functional [35–36]. The molecular orbitals of the H, C, N, O, and F atoms were represented by the 6-31G basis set augmented by *p* and *d* polarization functions. The Pd orbitals were described by the compact effective potential with split valence basis set (CEP-31G) [37]. Geometry optimizations were performed and the obtained geometries were verified to exhibit only real infrared frequencies. Local softness maps [38] have been obtained as differences between calculated electronic densities of the relevant charge states of each studied systems. The resulting 3D maps were generated through the ChemCraft package [39].

Results and discussion

The dimeric precursor [Pd(*dmba*)(μ-N_3)]$_2$ readily undergoes bridge cleavage reactions with deprotonated 1-(2-fluorophenyl)-3-(4-nitrophenyl)triazene or 1,3-*bis*(4-nitrophenyl)triazene, in the presence of pyridine, to afford the monomeric, neutral complexes *[Pd(dmba)(L^1)(py)]* (**1**) and *[Pd(dmba)(L^2)(py)]·py* (**2**), respectively, as yellow colored solids (Scheme 1).

The IR spectra (KBr pellets) of **(1)** and **(2)** show the absence of the absorption assigned to $\nu_{as}(N_3)$, which is observed as a very strong band at 2059 cm^{-1} in the IR spectrum of [Pd(*dmba*)(μ-N_3)]$_2$ [24]. The absence of the νN—H band in the 3100–3200 cm^{-1} region demonstrates the coordination of the triazenido anions originated by deprotonation of the respective free triazenes, and this is characterized by strong ν_{as}NNN bands at 1292 cm^{-1} for (**1**) and 1275 cm^{-1} for (**2**), respectively.

Crystal data and experimental parameters are given in Table 1. Selected bond distances and angles of the title complexes are listed in Table 2. Fig. 1 shows the molecular structure of the entities of *[Pd(dmba)(L^1)(py)]* (**1**) in a thermal ellipsoid representation [25–27].

The molecular structure of (**1**) is depicted in Fig. 1. The X-ray structure analysis shows that, in the monomeric complex, the coordination geometry around the Pd^{2+} ion is nearly square-planar (*r.m.s.* deviation of 0.1237 Å). The metal center is surrounded by the C and N atoms of the *ortho* metallated *dmba* ligand, a deprotonated 1-(2-fluorophenyl)-3-(4-nitrophenyl)triazenido ion $[FC_6H_4NNNC_6H_4NO_2]^-$ acts as a monodentate (two-electron donor), and a neutral pyridine molecule is in a *trans* position to the carbon atom of the *dmba*. The elevation of Pd from the plane formed by the atoms C31, N13, N5, and N6, is 0.026(3) Å.

Table 2
Selected bond lengths (Å) and angles (°) for *[Pd(dmba)(L^1)(py)]* (**1**) and *[Pd(dmba)(L^2)(py)]·py* (**2**).

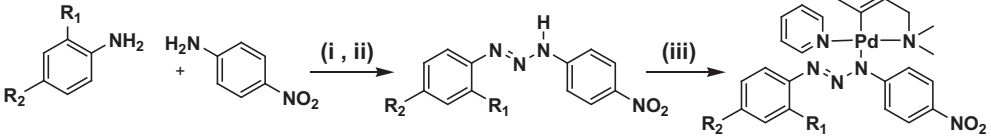
Complex (**1**)		Complex (**2**)	
Bond lengths		Bond lengths	
Pd—C(31)	1.981(6)	Pd—C(41)	1.987(4)
Pd—N(13)	2.047(5)	Pd—N(6)	2.036(3)
Pd—N(6)	2.094(5)	Pd—N(7)	2.083(3)
Pd—N(5)	2.180(6)	Pd—N(11)	2.149(3)
F—C(12)	1.363(8)	N(11)—N(12)	1.313(4)
N(13)—N(12)	1.334(6)	Bond angles	
N(11)—N(12)	1.282(6)	C(41)—Pd—N(6)	93.68(14)
Bond angles		C(41)—Pd—N(7)	82.48(15)
C(31)—Pd—N(13)	93.3(2)	N(6)—Pd—N(7)	174.98(13)
C(31)—Pd—N(6)	82.8(2)	C(41)—Pd—N(11)	176.47(15)
N(13)—Pd—N(6)	170.62(19)	N(6)—Pd—N(11)	88.27(13)
C(31)—Pd—N(5)	174.6(2)	N(7)—Pd—N(11)	95.73(13)
N(13)—Pd—N(5)	86.5(2)	C(35)—N(6)—Pd	117.6(3)
N(6)—Pd—N(5)	98.2(2)	N(12)—N(11)—Pd	122.9(3)

The structural parameters of the Pd(*dmba*) fragment are similar to those found in other complexes containing this ligand. The Pd—C31 bond distance [1.980(6) Å] and the Pd—N6 bond distance [2.093(5) Å] are in good agreement with the distances found in other palladium-*dmba* complexes [22,24,40].

The Pd—$N5_{py}$ bond distance [2.181 Å], which is *trans* to the σ-bonded aryl group, is longer than the sum of the covalent radii which is 2.08 Å [41]. The pyridine ring (N5—C45) is planar within experimental accuracy (*r.m.s.* = 0.0105 Å). The Pd—N5 bond distance of 2.181(6) Å is longer than the sum of the covalent radii, which totals 2.08 Å [42], and is in good agreement with values found in the compounds [Pd—N_{Py} = 2.03 Å] [43] and [Pd(*dmba*)-Py(Cl)] [Pd—N_{Py} = 2.042 Å] [42].

The Pd—N11 bond length of 2.047(5) Å between the metallic center and the nitrogen atom of the triazenido chain agrees well with the Pd-N bond length of 2.034(7) Å observed in the palladacycle [Pd($C_6H_4NHN{=}C(CH_3)C_5H_4N$)(*p*-tolNNN*p*-tol)] [44].

If we take into account the triazenido ligand, we can observe that it shows a strong deviation from planarity, with the largest interplanar angle of 26.0(6)° occurring between the phenyl ring of the *ortho*-fluorophenyl group and the plane defined by the NNN moiety. Due to the delocalization of the π electrons over the nitro group, and the C11—C16 phenyl ring extended over the N11—N12=N13 chain, in this part of the triazenido ligand the deviation from planarity is less accentuated, with interplanar angles of



R1 = F - complex **1**
R2 = NO_2 - complex **2**

(i) $NaNO_2$, HAc, 0-5°C; (ii) H_2O, $NaCOOCH_3$; (iii) [Pd(*dmba*)(N_3)]$_2$, KOH, MeOH, pyridine

Scheme 1.

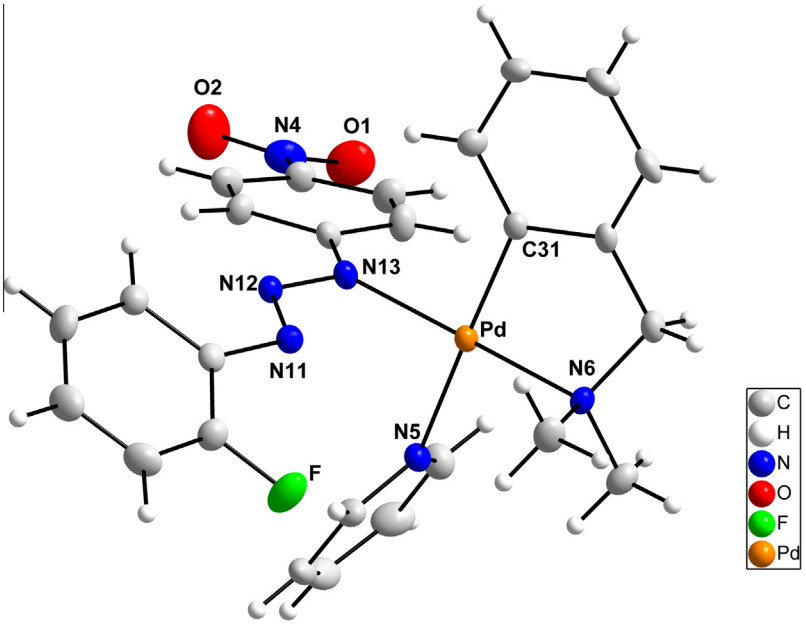


Fig. 1. Displacement ellipsoids are drawn at the 40% probability level.

8.7(1)° for O1N4O2/C21—C26 and 16.6(7)° for C21—C26/N11—N12=N13. The delocalization of the π electrons over the NNN chain and the *para*-nitrophenyl substituent is also underlined by the deviation from the normal N—N bond lengths. The N12—N13 bond length of 1.334(7) Å is longer than the characteristic value for a double bond (1.24 Å), whereas N11—N12 [1.282(6) Å] is shorter than the expected value of 1.44 Å for a single bond, and N13—C21 [1.388(3) Å] is shorter than what is expected for a C_{aryl}—N single bond [40]. Note that the deviation of the planarity of the N11=N12—N13 chain can also be explained by a hydrogen bond between the atoms N12 and C39#—H39# in a bonding order of 2.744(8) Å [H39#···N12]. Symmetry code: (#) $1-x$, $0.5+y$, $1.5-z$. Other details can be seen in Table 3. Fig. 2 shows the interactions between the atoms.

On the other hand, the stark deviation from the *ortho*-fluorophenyl group can be attributed to a weak intramolecular hydrogen bond between a H atom (see Fig. 2) from the pyridine ligand and the F atom, C45—H45···F [H45···F = 2.661(9) Å]—for more information, see Table 3.

Finally, it can be observed in Fig. 2 that there are also weak contacts between adjacent molecules as a result of C—H···C_{aryl} intermolecular hydrogen bonding. The related molecules of (**2**) are connected by weak C44—H44···C34#, C35#, and C36# interactions {2.843(7) Å [H44···C34#]; 2.835(9) Å [H44—C35#]; 2.865(10) Å and [H44—C36#] symmetry code: (#) $1-x$, $0.5+y$, $1.5-z$}, giving rise to an extended trifurcated hydrogen bond [45–47] along the [1 0 0] crystallographic direction (Fig. 2).

Structure of [Pd(dmba)(L^2)(py)]·py (2)

An illustration of the structure of complex (**2**) is shown in Fig. 3. The X-ray analysis of the monomeric complex shows that the nearly square planar coordinated Pd^{2+} ion is surrounded by the C and N atoms of an *ortho*–metallated *dmba* ligand, a monodentate 1,3-*bis*(4-nitrophenyl)triazenido ion $[O_2NC_6H_4N{=}N{-}NC_6H_4NO_2]^-$, and a pyridine molecule. Differently to complex (**1**), in the structure of (**2**) the *trans*-position for the carbon atom of *dmba* is occupied by the N atom from the triazenido anion (Fig. 3).

The structural parameters of the Pd(*dmba*) fragment are similar to those found in complex (**1**). The Pd-C41 bond distance [1.987(6) Å] and the Pd—N7 bond distance [2.082(6) Å] are very similar to that found in complex (**2**) and other related palladium-*dmba* complexes [22,24,40].

Table 3
Secondary interactions: lengths (Å) and angles (°) for complexes (**1**) and (**2**).

D—H···A[a]	D—H	H···A	D···A	D—H···A
Complex (1)				
C39#—H39#···N12	0.960(8)	2.774(8)	3.471(11)	133.01(41)
C45—H45··· F	0.930(7)	2.661(9)	3.588(13)	174.55(43)
C44—H44···C34#	0.930(9)	2.843(7)	3.753(11)	166.32(55)
C44—H44···C35#	0.930(9)	2.835(9)	3.718(13)	159.11(55)
C44—H44···C36#	0.930(9)	2.865(10)	3.652(14)	143.22(54)
Complex (2)				
C48#—H48#···O1[b]	0.861(3)	2.185(1)	2.957(2)	149.15(11)

[a] D = donor and A = acceptor. Symmetry operations used to generate equivalent atoms: (#) $1-x$, $0.5+y$, $1.5-z$.
[b] Complex **2**. Symmetry operations(#) $1-x$, $-y$, $-z$.

In the structure of (**2**), the pyridine ring N6—C35 is *cis*-oriented to the C atom of the *dmba* fragment, and the Pd1—N6 bond length [2.036(6) Å] is typical for a Pd—N(sp^2) [41].

The *trans* position for the σ-bonded aryl group in (**2**) is occupied by the triazenido ligand. The observed Pd—N11 bond length [2.149(4) Å] is longer than the sum of the covalent radii of Pd and N [41], which may be a result of the *trans* influence of the aryl group on the *dmba* ligand.

Due to the delocalization of the π electrons in both nitro groups and the phenyl rings, which extends over the triazenide chain, the whole triazenido ligand shows little deviation from planarity. The two terminal 4-nitrophenyl substituents show interplanar angles with the N—N=N chain of 15.9(1)° and 5.2(1)°, respectively, which confirms the small deviation from planarity for the whole molecule.

The analysis of the secondary crystal structure of (**2**) also reveals that the individual molecules are ordered as *synthons* [45–48] by C48—H48···O1# and C48#—H48#···O1 intermolecular hydrogen bonding [H48···O1# = 2.453(9) Å; C48···O1# = 3.254(12) Å; and symmetry code (#) $1-x$, $-y$, $-z$] along the [1 0 1] crystallographic direction. The occurrence of this hydrogen bonding can also explain the small deviation from planarity for the triazenido ligand. The

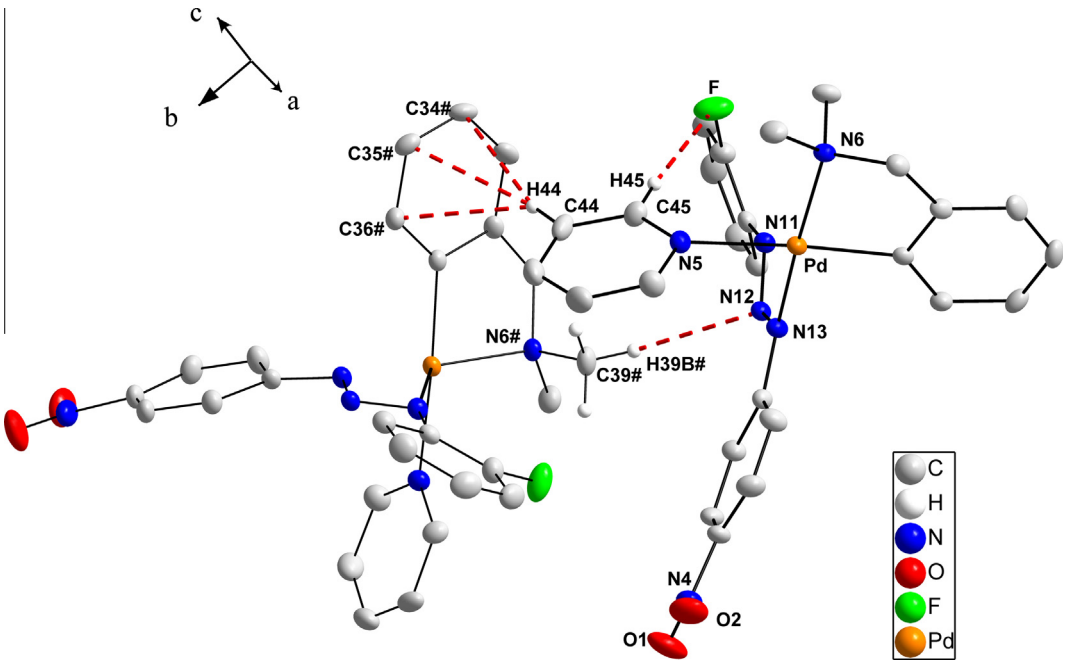


Fig. 2. The packing in complex **1** shows multiple hydrogen-bonding. Symmetry operations used to generate equivalent atoms: (#) $1 - x$, $0.5 + y$, $1.5 - z$.

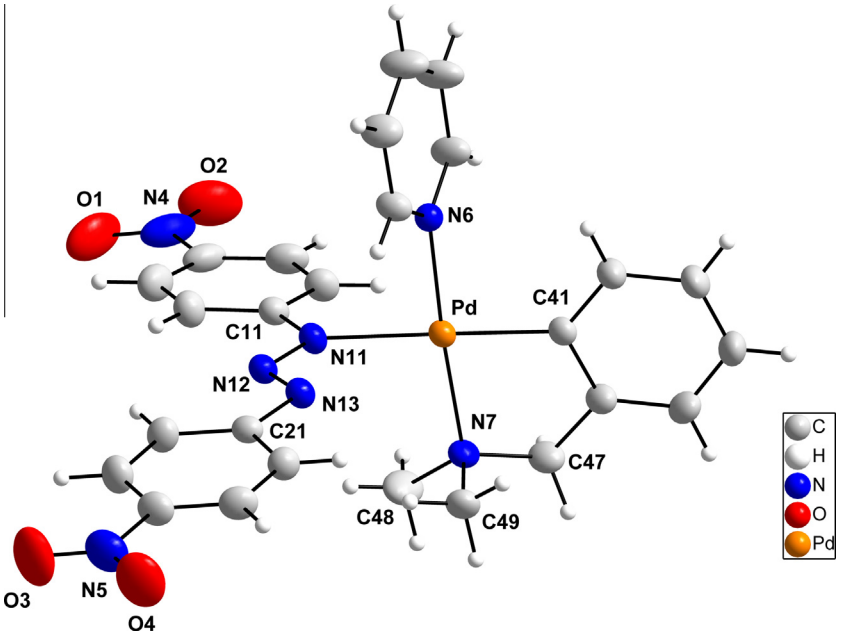


Fig. 3. Displacement ellipsoids are drawn at the 40% probability level. Disorder pyridine solvate has been omitted for clarity.

hydrogen-bonding scheme can be seen in the extended crystal-lattice structure (Fig. 4).

Frontier orbitals and Fukui functions

In order to analyse the influence of different ligands on the chemical activity of compounds (**1**) and (**2**), we have determined their frontier orbitals (HOMO and LUMO), and their Fukui functions related to nucleophilic and electrophilic attacks [38]. These quantities give almost the same information, since compounds under electrophilic (nucleophilic) attacks are expected to lose (gain) charge through their frontier orbitals. Fig. 5 shows the frontier orbitals for compounds (**1**) and (**2**).

As can be seen from this Figure the frontier orbitals from compounds (**1**) and (**2**) reveal a great similarity, with the electronic distributions forming π-like orbitals delocalized along the triazene. A distinctive feature of these orbitals is that in the HOMO there is an electron concentration on the N11 atoms but not on N12, while for the LUMO the opposite is observed (see Figs. 1, 3 and 5).

The Fukui functions for nucleophilic, $f^{+}(r)$, and electrophilic, $f^{-}(r)$, attacks were estimated as the differences between total electronic densities of appropriate charge states, according to the following formulas:

$$f^{+}(r) = \rho_{N}(r) - \rho_{N-1}(r),$$

$$f^{-}(r) = \rho_{N+1}(r) - \rho_{N}(r),$$

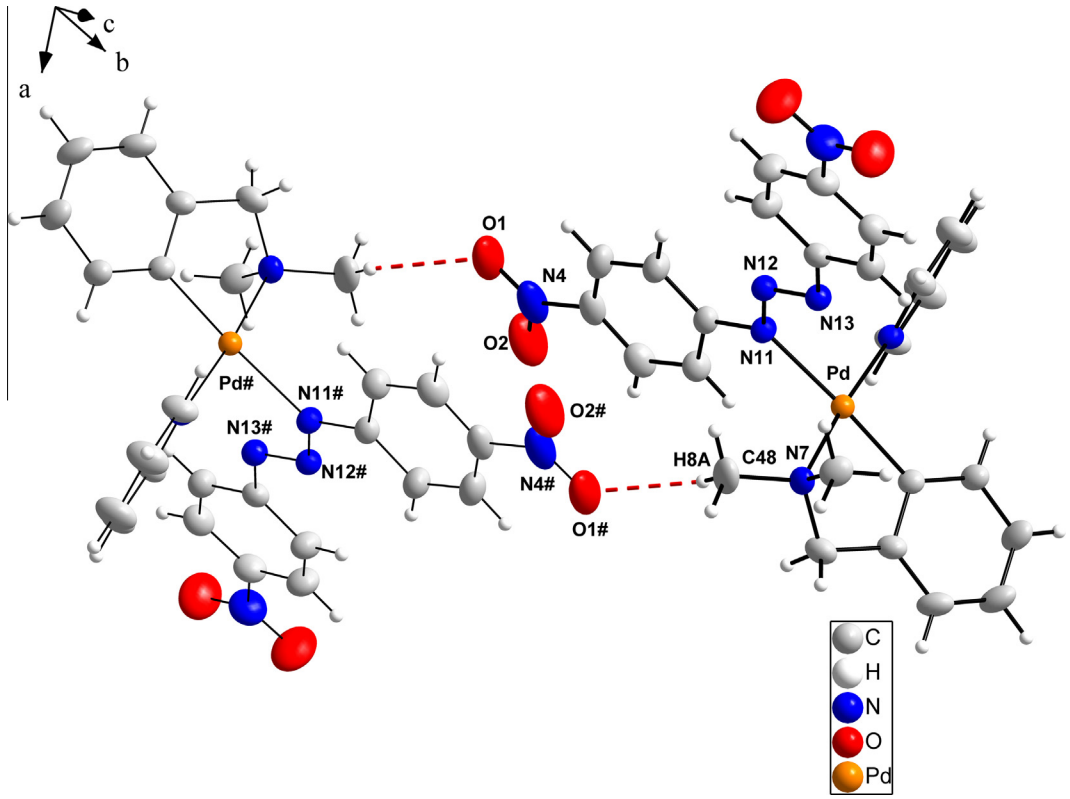


Fig. 4. The hydrogen-bonding scheme in the structure of (**2**). Symmetry transformations to generate equivalent atoms:(#) $1-x, -y, -z$.

where $\rho_X(r)$ represents the total electronic density at position r of a system with X electrons.

The Fukui functions for compounds (**1**) and (**2**) are shown in Fig. 6. For compound (**1**), the active sites for nucleophilic attacks are centered on the nitrogen atoms N12 and N13 of triazene, with contributions from the nitro group and the pyridine. For electrophilic attacks, on the other hand, the reactive sites of compound (**1**) are the N11 and N13 atoms of triazene. No contribution from the fluorine atom is observed for both cases.

For compound (**2**), the reactive sites for electrophilic attacks follow the same pattern as for compound (**1**). For nucleophilic attacks, however, some differences can be noted. The N12 and nitro groups remain as active sites. The presence of a second nitro group and the absence of the fluorine atom change the reactive sites from the

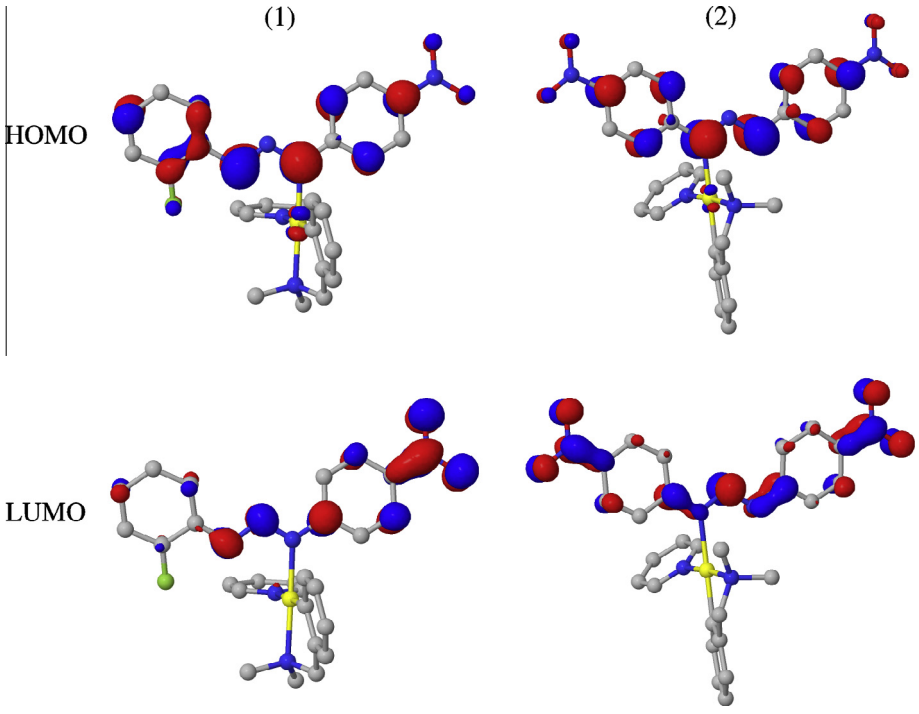


Fig. 5. Illustrative pictures of the frontier orbitals HOMO and LUMO for compounds (**1**) and (**2**).

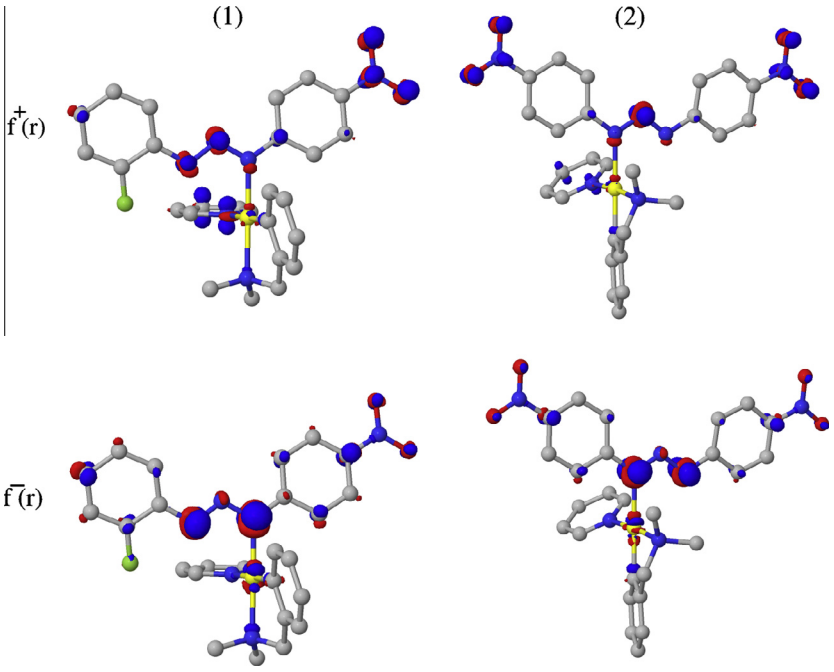


Fig. 6. Illustrative pictures of the Fukui functions for nucleophilic, $f^{+}(r)$, and electrophilic, $f^{-}(r)$, attacks calculated for compounds (**1**) and (**2**).

N13 atom and pyridine, in compound (**1**), to the additional nitro group of compound (**2**).

The discussed differences between compounds (**1**) and (**2**) against nucleophilic attacks do not prevail, however, over the general behavior of the Fukui functions, which show a great similarity for the two compounds, despite the asymmetry of compound (**1**) introduced by the fluorine atom. In this respect, it is interesting to note the apparent chemical inactivity of the fluorine atom against nucleophilic and electrophilic attacks.

Conclusions

The synthesis of organometallics containing diazoamino fragments proved to be very effective, both in the methodology and in the yields obtained. The complexes obtained have been characterized by X-ray diffraction, showing a great potential for the formation of non-classical hydrogen interactions. This situation was crucial in detecting interesting supramolecular trends in crystal structures of cyclopalladated compounds. Moreover, theoretical calculations show no significant change when the change in the position and nature of the substituent. This evidence allows us to plan carefully new synthesis and choose for symmetrical complexes for use as catalysts.

Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 987440 and 987441). Further details of the crystal structure investigations are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.htmlor from CCDC at 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; and e-maildeposit@ccdc.cam.ac.uk.

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