Solid state conformational and theoretical study of complexes containing the (CxN)Pd moiety (CxN = 2-(phenylazo)phenyl-*C*,*N* and its derivatives)

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Palladium complexes having the 2-(phenylazo)phenyl-*C*,*N* ligand exhibit a planar chelating ring with N=N and N–C distances longer and shorter respectively than those found in *trans*-azobenzene. The ligand is not planar upon complexation, the mean angle between the phenyl ring and the chelating one found in the Cambridge Structural Database being of 45.6°. We have quantified and characterised the kind of distortion from planar coordination around metallic centers. The method employed makes use of two improper torsion angles, tetrahedral distortion being most frequently found in phenylazophenyl palladium complexes. Crystal structures of three succinimidate complexes having the title moiety are reported. The succinimidate ligand adopts a nearly perpendicular conformation to the metal coordination plane. A theoretical study using either Molecular Mechanical, Semiempirical and Density Functional Theory *ab initio* levels helps to grasp the main geometrical features.

Introduction

The *ortho*-palladated compounds have been widely studied, since they are successful starting materials for the synthesis of transition metal complexes[1,2] and reactive intermediates in organic synthesis.[3] Azobenzenes and heteroaromatic ligands such as 2-phenylpyridine can easily be *ortho*-metallated by Pd(II) salts *via* C(sp^2)–H bond cleavage[4,5] to give usually the corresponding acetato or halide-bridged dimers. These dinuclear complexes have been thoroughly studied[6] and employed as precursors of mononuclear cyclometallates of Pd or Pt. It should be noted that since a number of *ortho*-metallated complexes of the platinum group have been implicated as photosensitizers[7] and mononuclear palladium derivatives have been tested for nonlinear optical properties[6] there has been a growing interest in this kind of compound.

On the other hand, the conformational analysis of metallic complexes is an active research area,[8] the CSD being a powerful tool in this kind of study.[9] Despite the large amount of available structural data, a full understanding of the factors that determine the molecular structure of a particular compound has not been achieved yet. The manner in which a ligand controls the properties of the complex depends on a combination of steric and electronic factors. A detailed knowledge of these effects will afford a rational design of complexes with specific and predictable properties.[10]

In this paper we present the conformational study of palladium complexes with the phenylazophenyl ligand and its derivatives. We have performed a statistical analysis of Pd–C and Pd–N bond distances, the C–Pd–N bond angle and the conformation shown by the ligand from data retrieved in the CSD, together with those obtained from three new crystal structures that we report here. We have characterised numerically the kind of distortion from square planar coordination around metallic centers. With the aim of ascertaining the geometrical and electronic features of the title complexes, we describe the *ab initio* DFT results for one of them, as well as the conformational preferences of the phenylazophenyl palladium complexes by means of the intrinsic reaction coordinate generated by rotation of the free phenyl substituent for hypothetical $[Pd(CxN)(H)_2]^-$ and [Pd(CxN)(PH_3)(succinimide)] complexes at the PM3 level and for *trans*-azobenzene at MM level.

Experimental

Preparation of complexes

The complexes [Pd(CxN)(suc)(L)], (CxN = phenylazophenyl, suc = succinimidate, L = P(4–F–C_6H_4)$_3$ (**1**), P(4–MeO–C_6H_4)$_3$ (**2**), PPh_2Me (**3**) were prepared according to the published method.[11] To a dichloromethane (20 mL) solution of [{Pd(μ-suc)(CxN)}$_2$] (0.07 g, 0.091 mmol) was added the stoichiometric amount of the corresponding phosphine ligand (0.183 mmol). The solution was refluxed for 2 h, and then concentrated to *ca.* one fifth of the initial volume. Slow addition of hexane caused the precipitation of the complexes, which were filtered off, washed with *n*-hexane and air-dried. Crystals of these compounds suitable for X-ray diffraction studies were grown from acetone–*n*-hexane solution.

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Data collection, structure solution and refinement

Crystals suitable for a diffraction study (complexes **1**, **2** and **3**) were mounted on a glass fibre in a random orientation. Data collection was performed at 293 K on a Nonius Kappa-CCD single crystal diffractometer, using Mo Kα radiation (λ = 0.71073 Å). Crystal-detector distance was fixed at 35 mm for **1** and **2**, and 27 mm for **3**. The collected images were 102, 198 and 111 for **1**, **2** and **3** respectively, the oscillation was 2° in the three cases and the exposure time per image was 200 s, 110 s and 120 s for **1**, **2** and **3**, respectively. Data collection strategy was calculated with the program COLLECT,[12] data reduction and cell refinement were performed with the programs HKL DENZO and SCALEPACK.[13] Two molecules were found in the asymmetric unit for compound **2**. XABS2[14] absorption correction was applied in **3**. The structures were solved by direct methods and refined anisotropically on F^2.[15] Details of cell data, data collection and structure refinement are given in Table 1. Fig. 1 shows the molecular structure of complex **3**, with the atom-labelling scheme. Hydrogen atoms bonded to C atoms are omitted for clarity.†

Structural analysis

The Cambridge Structural Database (CSD)[16] v. 5.23 (April 2002 version containing 257 162 entries) was searched for all the structures containing the fragment shown in Fig. 2. A total of 27 refcodes matched the search, the Pd–C and Pd–N distances, the C–Pd–N angle, the N=N distance, the C–N distances, the angle between the chelating ring (Pd–C–C–N–N) and the phenyl ring (Fig. 2), and the intra-ring torsion angles in the chelating ring were tabulated (39 fragments) and transferred to Vista 2.1[16] for statistical and graphical analysis.

Computational details

The structural data in the CSD for *trans*-azobenzene[17] (pdb format) were transferred to Hyperchem v. 7.0 for the molecular mechanical analysis. Carbon and nitrogen atoms were set up as *aromatic* carbon and *azo* nitrogen respectively. The MM+ parameter set, an extension of MM2,[18] was used and the strain energy by the rotation of a phenyl group was calculated with a step of 5°. Conformational calculations were also run at the semiempirical PM3(d) level implemented in the Spartan '02 package[19] by performing relaxed PES scans.

In order to better understand the geometric features of the herein reported phenylazophenyl palladium complexes, one of the obtained structures has been compared with the calculated one. For simplicity we have chosen **3** for this study. These calculations were based on the Gaussian 98[20] program system and were performed at the *ab initio* DFT[21] level of theory, which has been proved to be remarkably successful in reproducing experimental ground-state geometries.[22,23] This method avoids the overestimation of some critical distances obtained at the Hartree–Fock level, due to neglecting the important effects of electron correlation, and it also prevents the overestimation of that correlation effect produced by the MP2 method which shortens those distances.[24] We used the B3LYP functional (Becke's three parameters hybrid functional[25] with the Lee–Yang–Parr correlation functional[26]) which has been proved to be suitable for palladium complexes[23] and the all-electron moderate-size 3-21G(d) basis set, unless otherwise stated. The use of Double Zeta all-electron basis set with polarisation function (DZVP) for all elements did not give better results although it is said to yield more realistic geometries and energies for palladium complexes.[23]

† CCDC reference numbers 210648–210650. See http://www.rsc.org/suppdata/nj/b3/b302653a/ for crystallographic data in .cif or other electronic format.

Values from the magnetic shielding tensor were obtained using the nonrelativistic DFT-GIAO approach. Bond orders were characterised by Wiberg bond indices[27] (WBI) and calculated with the Natural Bond Orbital (NBO) method as the sum of the squares of the off-diagonal density matrix elements between atoms, as formulated in terms of the natural atomic orbital (NAO) basis set. Interaction energies were calculated by second order perturbation analysis of Fock matrix in NBO basis.

Results and discussion

Conformation of palladium complexes with phenylazophenyl ligand and its derivatives

Phenylazophenyl ligand and its derivatives form through complexation five membered ring complexes. These show a planar chelating ring, therefore with the five torsion angles near zero. We have performed the statistical analysis of Pd–N, Pd–C distances, C–Pd–N angles, N=N and C–N distances, and the results are summarised in Table 2. The Pd–N distance exhibits a narrow range after removing the data with refcode NEPDIV, [(CxN)Pd(ppp)][ClO_4][28] (CxN = phenylazophenyl-*C*,*N*; ppp = bis(2-(diphenylphosphino)ethylphenylphosphine-*P*,*P*′,*P*″) which is a highly distorted five-coordinated palladium structure. The Pd–C distance is shorter than that found for Pd–N because of the negative charge on a deprotonated carbon atom, both distances (Pd–C and Pd–N) show a narrow range. The only structures clearly outside the range reported in Table 2 are PELTEF, [{(CxN)Pd(μ-Br)}$_2$][29] (CxN = 2′,6′-dimethylphenylazophenyl-*C*,*N*); NEPDIV and RUNDAF, [(CxN)Pd(dppm)][F_3CSO_3][30] (CxN = 4,4′-dimethylphenylazophenyl-*C*,*N*; dppm = bis(diphenylphosphino)methane). Regarding the C–Pd–N angle, it shows a narrow range (bite angle characteristic for phenylazophenyl ligand), nevertheless structures NEPDIV and AZFAPD11, [(F_6acac)Pd(CxN)][31] (F_6acac = hexafluoroacetylacetonate, CxN = phenylazophenyl-*C*,*N*) have values of 71.8° and 74.4°, which are considerably different from the mean (Table 2). The N=N distance is longer than that observed for the N=N bond in *trans*-azobenzene.[17] The C–N distances are different upon complexation, the distance involving the C in the chelating ring being shorter than that in *trans*-azobenzene.[17] We assume that, upon complexation, the observed elongation of the N=N distance and shortening of the N–C distance relative to those in *trans*-azobenzene,[17] could arise from the higher contribution of a resonance structure with charge separation, C_6H_4–N^+–N^-–C_6H_5, and the subsequent delocalization of the positive and negative formal charges over the phenylene and the N-phenyl rings, respectively, the latter being partially prevented by the ring rotation.

With the aim of completing our conformational study of complexes with the phenylazophenyl (or derivatives) ligand, we have performed the statistical analysis of the angle defined by the chelating ring and the phenyl group (Fig. 2). The histogram showing the values found for that angle is presented in Fig. 3. The structures with $\alpha \geq 70°$ (the "free" aromatic ring nearly perpendicular to the chelating ring) possess methyl groups in both *ortho* positions. The structures with α value about 15° (the aromatic ring not completely but nearly parallel to the chelating ring) show a small steric impediment; they correspond to [(Cp)Pd(CxN)] (refcode: VAFXEF[32]) with $\alpha = 14.06°$ and [(F_6acac)Pd(CxN)] (F_6acac = hexafluoroacetylacetonate) (refcode: AZFAPD11[31] with $\alpha = 13.21°$. Note that there has been reported another crystal structure for that compound with $\alpha = 40.54°$ and $\alpha = 45.50°$; two molecules in the asymmetric unit).

After removing the above structures with $15° \geq \alpha$ or $\alpha \geq 70°$ from the analysis, the mean value for this angle is 45.6° (the values ranging between 27° and 68°), see Fig. 3.

Table 1 Crystal data and structure refinement details for compounds **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	C_{34} H_{25} F_3 N_3 O_2 P Pd	C_{38} H_{36} Cl_2 N_3 O_5 Pd·1/8CH_2Cl_2	C_{29} H_{26} N_3 O_2 P Pd
Formula weight	701.94	748.66	585.90
Temperature/K	293(2)	293(2)	293(2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	$P\bar{1}$	*P*21/*c*
a/Å	32.6280(7)	15.0010(2)	14.2880(11)
b/Å	11.0790(3)	15.7410(2)	16.7260(15)
c/Å	17.3330(4)	18.1390(3)	12.104(2)
α/°	90	92.7670(6)	90
β/°	101.9690(10)	105.6230(7)	112.836(4)
γ/°	90	114.9541(5)	90
Volume/Å^3	6129.4(3)	3675.00(9)	2665.9(5)
Z	8	4	4
Density (calc.)/Mg m^{-3}	1.521	1.487	1.460
Absorption coefficient/mm^{-1}	0.712	0.741	0.787
F(000)	2832	1680	1192
Crystal size/mm^3	0.40 × 0.25 × 0.20	0.30 × 0.20 × 0.18	0.12 × 0.80 × 0.95
Reflections collected	17 757	45 274	10 109
Independent reflections	8114 [*R*(int) = 0.0500]	19544 [*R*(int) = 0.0476]	3169 [*R*(int) = 0.000]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.921	1.016	1.004
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0410$, $wR_2 = 0.0946$	$R_1 = 0.0531$, $wR_2 = 0.1503$	$R_1 = 0.0594$, $wR_2 = 0.1193$
R indices (all data)	$R_1 = 0.0925$, $wR_2 = 0.1213$	$R_1 = 0.1071$, $wR_2 = 0.1849$	$R_1 = 0.1385$, $wR_2 = 0.1475$

Deviation from planar coordination around metallic centers

The planar coordination around d^8 metallic centers appears often distorted in crystal structures. The distortion shows two "ideal" limiting cases: deviation towards tetrahedral coordination (Fig. 4, left) and distortion towards square pyramidal coordination (Fig. 4, right). In both cases the $L_4L_2L_1M$ and $L_3L_1L_2M$ improper torsion angles can be used to quantify the deviation from the planar coordination. In the tetrahedral distortion sign($L_4L_2L_1M$) = sign($L_3L_1L_2M$) and, assuming equal bond distances, both improper torsion angles show the same numerical value when the distances from L_3 and L_4 to the L_1ML_2 plane are identical (ideal tetrahedral distortion, Fig. 4). In the square pyramidal distortion sign($L_4L_2L_1M$) ≠ sign($L_3L_1L_2M$) and, assuming equal bond distances, both improper torsion angles show the same absolute value when the $L_1L_2L_3L_4$ atoms are on a plane and the metallic atom out of it (ideal square pyramidal distortion, Fig. 4).

The deviation from the planar coordination in palladium complexes bearing the phenylazophenyl ligand, retrieved from the CSD, has been quantified by the method described. We have employed L_4CNPd (ω_1), C and N being the donor atoms in the phenylazophenyl ligand, L_4 being the atom coordinated to palladium in position *cis* to C, and L_3NCPd (ω_2), L_3 being the atom *cis* to N. The scatter plot of ω_1 *vs.* ω_2 is shown in Fig. 5. Data on the diagonal of the first and third quadrants correspond to tetrahedral distortions, and data on the diagonal of the second and fourth quadrants correspond to square pyramidal distortions. Data on the axes correspond to structures with four atoms on a plane (Pd and three of the coordinated atoms). Ideal planar coordination shows a value of zero for both improper torsion angles. As can be seen in Fig. 5, the most frequent distortion in phenylazophenyl complexes is the tetrahedral one, which is usually larger than the pyramidal one with ω_1 and ω_2 values ranging up to −10°.

Structures of complexes 1, 2 and 3

As far as we are aware there are no entries in the CSD containing structures of 2-(phenylazo)phenyl-*C*,*N* palladium complexes having the succinimidate ligand. With the aim of investigating the possibility of extending the statistical results from the previous section to some new phenylazophenyl palladium complexes we report the structural features of three succinimidate-complexes adding those from the compound **4**: [Pd(2-(phenylazo)phenyl-*C*,*N*)(succinimide)(PPh_3)].[11] Moreover, the presence of the free-rotating succinimidate ligand

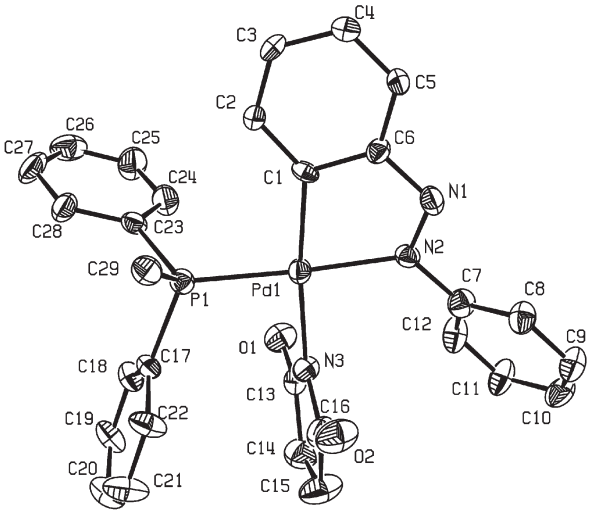

Fig. 1 Molecular structure of complex **3**. Displacement ellipsoids are drawn at the 50% probability level.

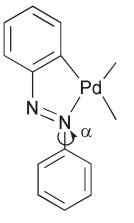

Fig. 2 Angle defined by the chelating ring and the rotating phenyl group.

Table 2 Statistical analysis of selected bond parameters in phenylazophenyl complexes

Parameter	Mean value	Range
Pd–N/Å	2.053(8)	1.987–2.133
Pd–C/Å	1.977(4)	1.932–2.013
C–Pd–N/°	78.9(1)	77.3–80.4
N=N/Å	1.267(2)	1.233–1.303
$C_{chelated\ ring}$–N/Å	1.397(3)	1.345–1.439
C–N/Å	1.439(2)	1.407–1.483

allows us to study the electronic and steric factors in the final geometry. In all of them, the coordination around palladium is approximately square-planar, the main distortion about the ideal geometry being the bite angle that involves the phenylazophenyl ligand. Table 3 lists the bond lengths and angles for complexes **1**–**4**.

Most of the geometrical parameters of these structures are similar to the mean values found for complexes containing the phenylazophenyl ligand in the CSD (Table 2). However the Pd–C distances are at the upper end of the range of distances found for this parameter. Tentatively, this can be explained by the considerable *trans*-influence of the succinimidate ligand, which has been claimed to behave as a pseudohalogen in terms of its σ-acceptor and π-donor properties.[33] Compound **1** shows a square pyramidal distortion from the ideal planar coordination around palladium with values for ω_1 and ω_2 of 4.05° and −4.43° respectively (Fig. 5). Compounds **2**, **3** and **4** show the metal and three coordinated atoms on a plane with the fourth coordinated atom out of that plane (data next to the axes in Fig. 5); compounds **2** and **3** have the P atom out of the plane while in compound **4** the succinimidate-N atom is the one placed out of plane. In all cases the succinimidate ligand is approximately perpendicular to the coordination plane, with angles between planes of 82.7(1)°, 85.9(1)°, 80.7(3)°, and 81.6(1)° for **1**, **2**, **3** and **4** respectively.

Calculations

Theoretical studies on the phenylazophenyl-succinimido complex **3** proved that the final geometry[34] is strongly subject to both electronic and steric control, and is in satisfactory agreement with the obtained X-ray structure. The main geometric features are related to parameters displayed in Table 3, for which a typical elongation in all distances (except that of the C(7)–N(2) bond) is observed. Of particular relevance are those elongations involving the central palladium atom, which arise from the employed all-electrons basis set, because of either its small size or the non-existence of relativistic core contraction for a second-row transition metal.[35] Also the ω_1 (7.64°) and ω_2 (−0.38°) calculated improper torsions are in satisfactory or perfect agreement with those observed (4.91° and −0.38° respectively).

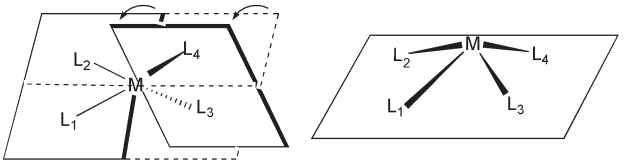

Fig. 4 Tetrahedral (left) and square pyramidal (right) distortions for square planar complexes.

It is noteworthy that the calculated torsion angle of the free phenyl ring turns out to be *ca.* 7° smaller than the experimental one (dihedral angle (Pd(1)–N(2)–C(7)–C(12) 41.4° *vs* 48.5°, respectively), the difference being mainly due to two factors. First, in the X-ray structure the phenyl substituent tends to become as much parallel as possible to the palladacycle (lower α) until H(12) reaches exactly a contact distance of 2.754 Å to succinimido N(3) atom (sum of van der Waals radii 2.75 Å). A lengthening of the calculated N(2)–Pd(1) and N(3)–Pd(1) distances, as described above, allows a more *periplanar* conformation until a H(12)–N(3) distance of 2.566 Å (lower than the contact distance). And second, it is also due to the crystal packing that determines the relative position of the phenyl ring and the succinimido ligand, so that the phenyl H(11) (2.552 Å) and the succinimidate H(14*cis*) (2.475 Å) are held close to each other by hydrogen bridge bonding to a carbonyl O(2) atom belonging to a second molecule in the crystal. Two other secondary close contacts are held by H(4) (2.633 Å) and one of the H(29) atoms (2.637 Å) to the O(1) atoms in two other neighbouring molecules.

In order to find a more general explanation to the high mean value of 45.6° for the phenyl torsion (Fig. 3), other than the

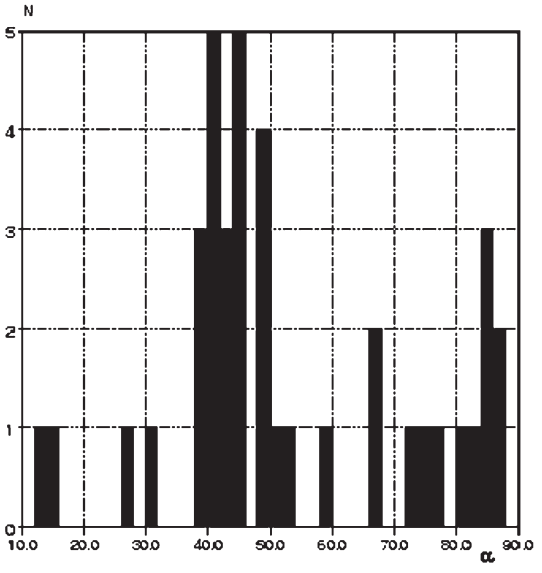

Fig. 3 Histogram showing the angle (α) defined by the chelating ring and the phenyl group in phenylazophenyl palladium complexes retrieved from the CSD.

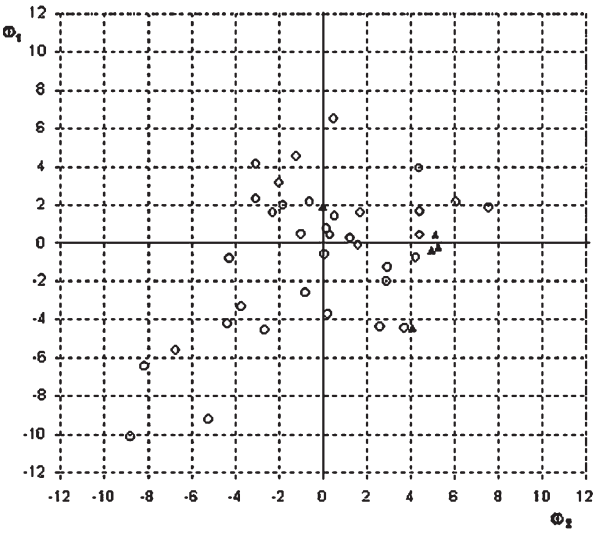

Fig. 5 Scatter plot of the improper torsion angles ω_1 *vs.* ω_2 for phenylazophenyl complexes in the CSD (circles) and for structures reported in this paper (triangles).

Table 3 Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

Bond(Å)/angle(°)	**1**	**2**[a]	**3**	**3**[b]	**4**
Pd(1)–P(1)	2.254(1)	2.258(1)	2.251(3)	2.310	2.258(1)
Pd(1)–C(1)	2.012(3)	2.011(4)	1.993(10)	2.048	2.008(2)
Pd(1)–N(2)	2.107(2)	2.091(3)	2.065(8)	2.150	2.100(2)
Pd(1)–(N3)	2.090(3)	2.086(3)	2.028(10)	2.098	2.097(2)
C(1)–Pd(1)–N(3)	171.75(11)	174.00(14)	173.8(4)	175.71	174.71(8)
C(1)–Pd(1)–N(2)	78.86(11)	78.38(15)	79.1(4)	78.40	78.45(8)
N(3)–Pd(1)–N(2)	96.19(10)	95.65(13)	94.7(4)	97.35	97.10(7)
C(1)–Pd(1)–P(1)	92.97(9)	94.87(12)	95.2(3)	93.52	93.28(6)
N(3)–Pd(1)–P(1)	91.26(8)	91.09(9)	90.9(3)	90.56	91.15(5)
N(2)–Pd(1)–P(1)	170.16(7)	170.18(10)	171.2(3)	166.86	171.74(5)
N(1)–N(2)	1.273(4)	1.268(5)	1.268(11)	1.297	1.269(2)
C(6)–N(1)	1.395(4)	1.394(6)	1.402(14)	1.403	1.402(3)
C(7)–N(2)	1.429(4)	1.465(6)	1.441(14)	1.429	1.436(3)
α	35.6(2)	51.3(2)	46.0(4)	41.4	44.7(1)

[a] Mean value for the two molecules in the asymmetric unit. [b] Calculated structure (B3LYP/3-21G*).

obviously invoked steric and crystal packing factors, we have investigated the effect of rotating the N(2)–C(7) exocyclic bond in model compounds ($[Pd(CxN)(H)_2]^-$ and $[Pd(CxN)(PH_3)(succ)]$) between periplanar (through the orthogonal) conformations of the phenyl substituent, at the semiempirical PM3(d) level.

At first sight, the equilibrium dihedral angle should arise from two opposite factors, named the widely accepted tendency to maximise extensive conjugation over all the unsaturated C_6H_4–N=N–C_6H_5 framework, which is achieved in *planar* conformations (α near 0°), and, on the other hand, the steric strain, if any, generated between the *ortho* H atoms and the metal ligands, being liberated upon rotation to *clinal* conformations although at the cost of steric inhibition of resonance.

trans-Azobenzene itself shows the expected conformational minimum for $\alpha = 0°$ and the rotational barrier of 2.2 kJ mol^{-1} at $\alpha = 90°$, with the absolute minimum located at *ca.* 13.5° (Fig. 6). The hypothetical sterically unhindered dihydridopalladate(II) exhibits a energetic profile with a global minimum at *ca.* 27.6°, and the expected rotational barriers, one of *ca.* 2.8 kJ mol^{-1} near the orthogonal conformation ($\alpha = 75°$), due to loss of conjugation, and a smaller one, of *ca.* 0.7 kJ mol^{-1}, at the *periplanar* conformation, due to steric strain as the *ortho* H12 and the *cis*-H ligand approach each other below the contact distance (sum of van der Waals radii 2.40 Å), that is at dihedral angles below 38° (Fig. 6).

The orthogonal conformations (α near 90°) could be slightly stabilised (less than 0.1 kJ mol^{-1}) by σ overlapping of the phenyl π system with the minor lobe of the sp^2 lone pair at N2, as well as by backbonding interaction from an occupied b_1 based MO on the phenyl group to a low lying unoccupied σ*-type Pd1–N2 MO, thus accounting for the observed local minimum, as well as the lengthening of the latter bond distance. Indeed, in an intermediate conformation, relevant N2–C8 and Pd1–C7 interactions ($WBI_{N2-C8} = 0.028$, $WBI_{Pd1-C7} = 0.010$) are observed for the target complex **3**.

On increasing the size of the two other ligands attached to palladium, as in the model succinimido-phosphino complex, the loss of conjugation at orthogonal conformations is energetically more favourable than the steric energy required to overcome the strain imposed by bringing H12 within contact distances to the succinimido N atom or carbonyl C atom (sum of van der Waals radii 2.75 and 2.72 Å, respectively),

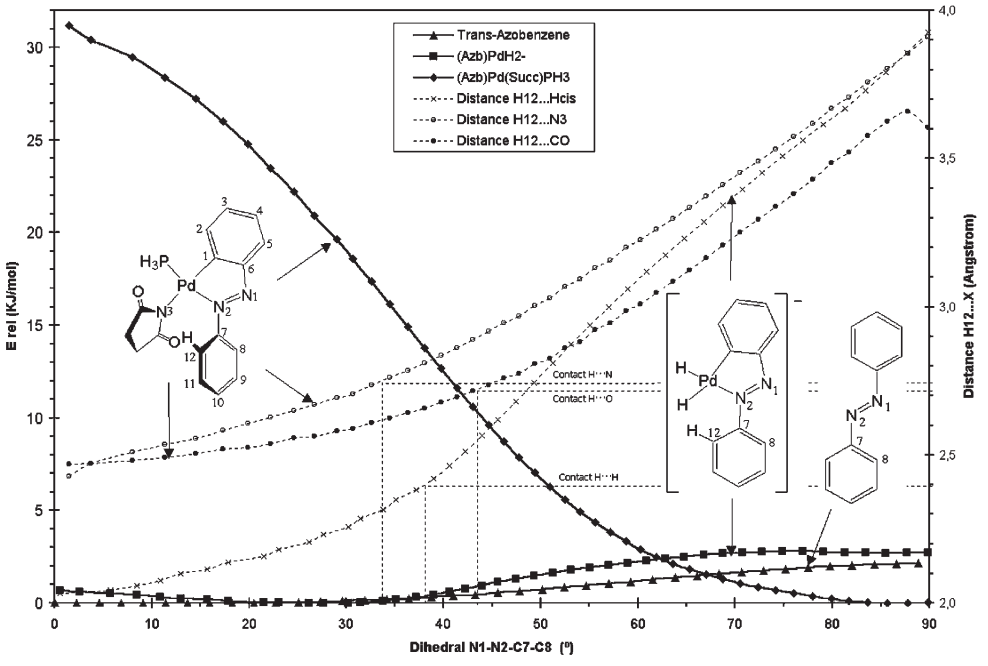

Fig. 6 Phenyl rotation in 2-(phenylazo)phenyl-*C*,*N* palladium(II) complexes and *trans*-azobenzene.

Table 4 Calculated NICS values (ppm) for rings in calculated and experimental **3** for the complete metal complex

Ring structure	Phenylene C(1)–C(6)	N-Phenyl C(7)–C(12)	P-Phenyl 1 C(17)–C(22)	P-Phenyl 2 C(23)–C(28)	Succinimido
Calculated	−5.96	−7.54	−7.81	−6.91	−2.08
Experimental	−5.75	−7.95	−7.57	−7.27	−2.24
Δ NICS$_{(exp-calc)}$	+0.21	−0.41	+0.24	−0.36	−0.16

attained at dihedral angles below 33° and 43° respectively, with an overall high energetic barrier of *ca.* 31.3 kJ mol^{-1} at the *periplanar* conformation.

The experimental dihedral angle found for the phenyl group rotation (Fig. 3), most of these complexes showing a phenyl rotating angle below 55°, can thus be explained in terms of steric hindrance of the palladium attached extra ligands. This angle is halfway between that predicted by semiempirical PM3(d) methods overestimating steric strain because of lower predicted Pd1–N2 bond distance, and that by DFT B3LYP/3-21G* (see above) overestimating palladium bond distances and hence underrating the aforementioned steric factors. Thus, *ortho*-substitution at the phenyl group leads to near orthogonal conformations ($\alpha \geq 70°$), while low hindered hexafluoroacetylacetonate and cyclopentadienyl phenyl-unsubstituted complexes show an almost *periplanar* conformation (α around 15°), the other complexes showing intermediate conformations with the phenyl group rotated enough to avoid contact.

The above results agree with the MM calculations on *trans*-azobenzene for which the strain energy profile shows two minima corresponding to planar conformations.

On the other hand, a reasonable electronic description of the aromatic rings is provided by Nuclear Independent Chemical Shifts (NICS, Table 4)[36] calculation as it points to the shielding effect of the diatropic ring current resulting from π-electron systems,[37] negative values corresponding to aromatic systems, and positive values to antiaromatics. For the sake of comparison, at the high theory level B3LYP/6-311+G(2d,p) the parent benzene displays a NICS value of −7.60[38] (in ppm), whereas NICS values for azobenzene and the free succinimido ligand are −6.78 and −0.34 ppm, respectively (−6.43 and −2.95 at 3-21-G*).

In the crystal structure, the P-phenyl ring which lies more parallel to the succinimidate ligand (P-phenyl 1) is slightly more aromatic than the other one (P-phenyl 2), and seems to donate electronic density to the weakly aromatic succinimido group.

It also should be pointed out that upon complexation, the phenyl ring acting as C-donor decreases its aromaticity, showing the lowest NICS value among all the phenyl rings, while the other free phenyl substituent exhibits an enhanced aromaticity. On moving from the calculated to the final experimental geometry, the aromaticity lowering experimented by the former is compensated by a rising for the latter.

Conclusions

In complexes containing the (CxN)Pd moiety (CxN = phenylazophenyl and its derivatives) the distortion from square planar coordination has been characterized by two improper torsion angles. The tetrahedral distortion is most frequent than the pyramidal one.

The phenylazophenyl ligand is not planar upon complexation. The angle between the "free" phenyl ring and the chelated one ranges mostly between 27° and 68°.

Theoretical studies on the [Pd(CxN)(succinimide)(PPh_2Me)], [Pd(CxN)(succinimide)(PH_3)] and [Pd(CxN)$(H)_2$]$^-$ proved that the final geometry is strongly subjected both to electronic and steric control. The results in [Pd(CxN)(succinimide)(PPh_2Me)], are in satisfactory agreement with the obtained X-ray structure.

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