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Synthesis, molecular, crystal and electronic structure of [RuCl₃(NO)(PPh₃)(HPz)]

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Abstract

The reaction of $[RuCl_3(NO)(PPh_3)_2]$ complex with pyrazole has been examined. The new ruthenium complex – $[RuCl_3(NO)(PPh_3)(C_3 H_4N_2)]$ has been obtained and characterised by IR and UV–Vis measurements. Crystal, molecular and electronic structures of the complexes have been determined. The electronic spectrum of the complex was calculated by the TDDFT method. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Ruthenium nitrosyl complexes; Pyrazole; X-ray structure; TDDFT method

1. Introduction

The chemistry of ruthenium nitrosyls is a recent renewed interest in particular in the field of medicinal inorganic chemistry [1–10]. The complexes are investigated as controlled NO-releasing agents for medicinal applications, in particular for the control of high blood pressure (vasodilatation), and as antitumor agents which might perform the release of cytotoxic NO within tumor cells, thus leading to cell death. In other hand the nitrosyl ruthenium complexes have been studied due to their importance as potential catalysts in homogeneous processes [11–16].

In this paper we report the synthesis of the new ruthenium nitrosyl complex with pyrazole ligand. The molecular and crystal structures of the obtained complex are presented. The electronic structure was calculated with the DFT method by using the GAUSSIAN03 program package.

2. Experimental

All reagents used to the synthesis of the complex are commercially available and were used without further purification. The [RuCl₃(NO)(PPh₃)₂] complex was synthesized by publishing procedure [17] from RuCl₃NO, which was prepared by passing NO through a solution of RuCl₃ in dichloromethane until the solution become red followed by evaporation to dryness. The dried solid obtained was kept in a vacuum desiccator for at least three days before used. Gaseous NO, obtained in the reaction: $2NaNO_2 + 3H_2SO_4 + FeSO_4 \rightarrow 2NO + 2NaH$ $SO_4 + Fe_2(SO_4)_3 + 2H_2O$, was purified by passing through the washers with concentrated KOH solution and over solid NaOH.

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2.1. Synthesis of $[RuCl_3(NO)(PPh_3)(C_3H_4N_2)]$

A mixture of $[\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2]$ (0.76 g; 1×10^{-3} mol) and pyrazole (0.42 g; 6×10^{-3} mol) in acetone (100 cm⁻³) was refluxed for 4 h, cooled and filtered. The yellow-orange crystals suitable for X-ray crystal analysis grew after the reaction mixture was left overnight.

Yield 92%. IR (KBr): 3137 $v_{\rm NH}$; 3058 $v_{\rm CH-pyrazole}$; 3021, $v_{\rm CH-phenyl}$; 1879 $v_{\rm NO}$; 1572 $v_{\rm CN}$, $v_{\rm C=C}$; 1487 $\delta_{\rm (C-CH \ in \ the \ plane)}$; 1436 $v_{\rm Ph(P-Ph)}$; 1320 $\delta_{\rm (NH; \ CH)}$; 1095 $\delta_{\rm (C-CH \ in \ the \ plane)}$; 994 $\delta_{\rm (C-C \ out \ of \ the \ plane)}$; 749 $\delta_{\rm (C-C \ out \ of \ the \ plane)}$; 687 $\delta_{\rm (C-C \ in \ the \ plane)}$; 598 $v_{\rm P-Ph}$. *Anal*. Calc. for C₂₁H₁₉Cl₃N₃OPRu: C, 44.42%; H, 3.37%; Cl, 18.73%; N, 7.40%; O, 2.28%; P, 5.46%; Ru, 17.80%. Found: C, 44.12%; H, 3.35%; N, 7.29%.

2.2. Physical measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm^{-1} with the sample in the form of KBr pellet. Electronic spectra were measured on a spectrophotometer Lab Alliance UV–Vis 8500 in the range 800–200 nm in dichloromethane solution. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN–2400 analyzer.

2.3. DFT calculations

GAUSSIAN03 program [18] was used in the calculations. The geometry optimization was carried out with the DFT method with the use of B3LYP functional [19,20]. The electronic spectrum was calculated with the TDDFT method [21].

Two basis set were used in the calculation. LANL2DZ basis set [22] was used on the ruthenium atom, 6-31G(d) on the chlorine, nitrogen, oxygen and carbon atoms and 6-31G basis on the hydrogen atoms in the first calculations the second one was performed using the SSD basis set on ruthenium atom. The obtained results of calculation were compared.

Natural bond orbital (NBO) analyses was performed using the NBO program as implemented in the GAUSS-IAN03 program.

2.4. Crystal structures determination and refinement

A orange crystal of [RuCl₃(NO)(PPh₃)(C₃H₄N₂)] was mounted on a KM–4–CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at temperature 293.0(2) K, with ω scan mode. The 21-s exposure time was used and a full Ewald sphere was collected up to $2\theta = 50.28^{\circ}$. The unit cell parameters were determined from least-squares refinement of the setting angles of 16,950 strongest reflections. Details concerning crystal data and refinement are given in Table 1. During the data reduction above decay correction coefficient was taken into account. Lorentz, polarization, and numerical absorption [23] corrections were applied. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2 . All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent atom. SHELXS97 [24], SHELXL97 [25] and SHELXTL [26] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

3. Results and discussion

Refluxing of the $[RuCl_3(NO)(PPh_3)_2]$ complex with an excess of pyrazole in acetone leads to the new ruthenium nitrosyl $[RuCl_3(NO)(PPh_3)(C_3H_4N_2)]$ complex in high yield. The elemental analysis of the complex is in

Table 1 Crystal data and structure refinement for [RuCl₃(NO)(PPh₃) (C₂H,N₂)]

$(C_3H_4N_2)]$	
Empirical formula	C ₂₁ H ₁₉ Cl ₃ N ₃ OPRu
Formula weight	567.78
Crystal system,	orthorhombic
space group	Pca2/1 (No. 29)
Unit cell dimensions	
a (Å)	22.2395(9)
b (Å)	11.8466(5)
<i>c</i> (Å)	17.6351(6)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	4646.2(3)
Ζ	8
D_{calc} (Mg/m ³)	1.623
Absorption coefficient (mm ⁻¹)	1.107
F(000)	2272
Crystal size (mm)	$0.249 \times 0.281 \times 0.286$
Theta range for data collection (°)	3.02-25.14
Index ranges	$-26 \leqslant h \leqslant 26, -14 \leqslant k \leqslant 13,$
	$20 \leqslant l \leqslant 20$
Reflections collected/unique	47,979/8274
	$[R_{(int)} = 0.0289]$
Completeness to $2\theta = 25.11$	99.6%
Maximum and minimum transmission	0.789 and 0.722
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	8274/1/542
Goodness-of-fit on F^2	1.019
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0206, wR_2 = 0.0485$
R indices (all data)	$R_1 = 0.0223, wR_2 = 0.0490$
Largest difference between peak and hole ($e \text{ Å}^{-3}$)	0.318 and -0.453

good agreement with its formulation. The characteristic bands of the pyrazole ligand v(NH) at 3137 cm⁻¹ and v(CN), v(C=C) at 1572 cm⁻¹ are present in the IR spectrum of the obtained complex. The spectrum of the complex shows v (NO) at 1879 cm⁻¹, what is consistent with the linear NO range of Haymore and Ibers (v(NO) above 1620–1610 cm⁻¹ were assigned to linear M–N–O systems, while v(NO) below 1610 cm⁻¹ were assigned to bent M–N–O systems) [27].

3.1. Crystal structure

The [RuCl₃(NO)(PPh₃)(C₃H₄N₂)] complex crystallises in the orthorhombic space group Pca2/1 The relative orientation of molecules is depicted in Fig. 1 which also shows the displacement vibration ellipsoids (structural drawing of the complex is presented in Fig. 2.). The selected bond lengths and angles are listed in Table 2. The two crystallographically independent molecules are structurally nearly identical (I and II hereafter for molecules containing Ru(1) and Ru(51), respectively). The most different distances are Ru(1)-Cl(1)2.396(7) Å and Ru(51)-Cl(51) 2.372(7) Å. The most different angles are N(1)-Ru(1)-N(2) 94.68(10)° and N(51)-Ru(51)-N(52) 91.16(10)°. The ruthenium atom is in a distorted octahedral environment with linear N-O group trans to one of Cl ligands, two mutually cis Cl ligands and the PPh₃ and pyrazole molecules in trans. The short bond distances Ru-N (1.735(3) Å), N–O (1.134(3) Å) and particularly the Ru–N–O $(176.4(3)^{\circ})$ angle (average values) strongly indicate the nitrosonium character of the NO group, in accordance with the similar data observed for the other ruthenium nitrosyl complexes [28]. The Ru-Cl bond distances (2.372(7)-2.396(7) Å) fall in the range reported in the literature for Ru^{II} complexes, with the exception of the



Fig. 1. Relative orientation of the two molecules of the [RuCl₃-(NO)(PPh₃)($C_3H_4N_2$)] complex in the asymmetric unit. Thermal vibration ellipsoids scaled to include 50% probability.



Fig. 2. Structural drawing of [RuCl₃(NO)(PPh₃)(C₃H₄N₂)].

chlorine *trans* to the nitrosyl group (2.342 Å average value). The NO bond length (1.135(3), 1.133(3) Å) is a little longer than the distance 1.06 Å of the free NO⁺ group [29]. The pyrazole and triphenylphosphine ligands display Ru–N and Ru–P distances which are in the range of these reported in the literature.

The bond valences were computed as $v_{ij} = \exp i \theta$ $[(R_{ij} - d_{ij})/0.37]$ [30–33], where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single-bond length between *i* and *j* atoms) [22]. The R_{Ru-N} , R_{Ru-P} , R_{Ru-Cl} were taken as 1.656 [34], 1.985 [35] and 1.932 [34], respectively. The computed bond valences of the ruthenium are $v_{Ru-N(nitrosyl)} = 0.817$, $v_{Ru-N(pyrazole)} =$ 0.262, $v_{Ru-P} = 0.334$; $v_{Ru-Cl} = 0.285$, 0.335, 0.300 v.u. (valence units) for molecule I and $v_{Ru-N(nitrosyl)} = 0.801$, $v_{\text{Ru-N(pyrazole)}} = 0.265, \quad v_{\text{Ru-P}} = 0.325; \quad v_{\text{Ru-Cl}} = 0.304,$ 0.327, 0.300 v.u. which means that Ru-N(nitrosyl) bonds are almost three times stronger than other bonds, and the Ru–N(pyrazole) bonds are the weakest ones. The valence sum rule states that the sum of the valences of the bonds formed by an atom is equal to the valence of the atom. Computed total valence of the Ru atom is 2.332 and 2.323 v.u. for molecules I and II, respectively. Which means that differences in coordination sphere arrangement are local in character and do not influence the molecule.

The three intermolecular hydrogen bond [36-38] linking the Cl ligand and pyrazole ring N(53)- $H(53N) \cdots Cl(1)$ (D···A distance 3.368(2) A, D-H···A angle 128.0°), C(53)–H(53)···Cl(2) (#1 x + 1/2, -y - 3,z) (D···A distance 3.316(3) Å, D–H···A angle 116.7°) and NO with pyrazole C(71)–H(71)···O(1) (#2 x, y - 1, z) (D···A distance 3.208(4) Å, D-H···A angle 126.0°) atoms are observed (Table 3). Other intramolecular hydrogen bonds are presented in the structure of the complex: between pyrazole N(3)–H(3A) and Cl(2) $(D \cdots A \text{ distance } 3.092(3) \text{ A}, D - H \cdots A \text{ angle } 115.4^{\circ}),$ N(53)–H(53N) and Cl(51) (D···A distance 3.160(2) Å, D-H···A angle 122.6°), between phenyl C(14)-H(14) and Cl(2) (D···A distance 3.372(3) Å, D–H···A angle 140.3°), C(58)-H(58) and Cl(51) (D···A distance 3.268(3) Å, D-H···A angle 112.8°), C(64)-H(64) and

Table 2

Bond lengths (Å) and angles (°) for [RuCl₃(NO)(PPh₃)(C₃H₄N₂)]

Bond lengths (Å)	
Ru(1)-Cl(1)	2.396(7)
Ru(1)-Cl(2)	2.337(6)
Ru(1)-Cl(3)	2.378(7)
Ru(1)-N(1)	1.731(2)
Ru(1)–N(2)	2.151(2)
Ru(1)-P(1)	2.391(7)
N(1)–O(1)	1.135(3)
Ru(51)–Cl(51)	2.372(7)
Ru(51)–Cl(52)	2.346(8)
Ru(51)–Cl(53)	2.377(7)
Ru(51)–N(51)	1.738(3)
Ru(51)–N(52)	2.147(2)
Ru(51)–P(51)	2.401(8)
N(51)–O(51)	1.133(3)
Bond angles (°)	
Cl(1)-Ru(1)-Cl(2)	85.68(2)
Cl(1)-Ru(1)-N(1)	88.44(9)
Cl(3)-Ru(1)-N(1)	93.00(9)
Cl(2)-Ru(1)-Cl(3)	93.04(3)
N(1)–Ru(1)–N(2)	94.68(10)
Cl(1)-Ru(1)-N(2)	87.09(6)
Cl(2)-Ru(1)-N(2)	86.89(7)
Cl(3)-Ru(1)-N(2)	87.33(7)
Cl(1)-Ru(1)-P(1)	95.58(2)
Cl(2)-Ru(1)-P(1)	86.16(2)
Cl(3)-Ru(1)-P(1)	89.83(3)
N(1)-Ru(1)-P(1)	92.58(8)
N(2)-Ru(1)-P(1)	172.34(7)
Cl(1)-Ru(1)-Cl(3)	174.33(3)
N(1)-Ru(1)-Cl(2)	173.83(10)
Ru(1)-N(1)-O(1)	176.6(3)
Cl(51)-Ru(51)-Cl(52)	87.31(3)
Cl(51)-Ru(51)-N(51)	89.73(10)
Cl(53)-Ru(51)-N(51)	90.78(9)
Cl(52)-Ru(51)-Cl(53)	92.04(3)
N(51)-Ru(51)-N(52)	91.16(10)
Cl(51)-Ru(51)-N(52)	87.80(6)
Cl(52)-Ru(51)-N(52)	86.70(6)
Cl(53)-Ru(51)-N(52)	88.47(6)
Cl(51)-Ru(51)-P(51)	92.68(3)
Cl(52)-Ru(51)-P(51)	87.47(3)
CI(53) - Ru(51) - P(51)	90.99(3)
N(51)-Ru(51)-P(51)	94.69(8)
N(52)-Ru(51)-P(51)	174.13(7)
CI(51)-Ru(51)-CI(53)	176.24(3)
N(51)-Ru(51)-Cl(52)	176.41(9)
Ku(51)–N(51)–O(51)	176.1(2)

Cl(52) (D···A distance 3.501(3) Å, D–H···A angle
147.1°) and between phenyl C(52)-H(52) and N _{NO} (51)
$(D \cdots A \text{ distance } 3.035(4) \text{ Å}, D-H \cdots A \text{ angle } 109.0^{\circ})$. In
this way infinite three-dimensional hydrogen-bonded
net has been created.

3.2. Geometry and electronic structure

The optimized geometry parameters for the complex are given in Table 4. In Table 5 the energies of several HOMO and LUMO orbitals are gathered. The calculated bond lengths agree well with the experiment. The largest difference were found for the ruthenium–chlorine bonds (0.152 Å, 0.056 Å, 0.084 Å – LANL2DZ basis and 0.114 Å, 0.028 Å, 0.045 Å – SSD for Ru–Cl(1), Ru–Cl(2) and Ru–Cl(3), respectively), but the relative differences in these bond lengths are reproduced in the calculations. The N–O distance calculated by using both basis sets are comparable (the difference is 0.005 Å). The SSD basis set has given better Ru–N_(NO) and Ru–P distances.

In Table 6 the atomic charges from natural population analysis (NPA) are shown. The formal charge of ruthenium is +2 in this complex. The calculated charge, obtained from NPA, on the ruthenium is close 0.342. This is a result from a charge donation from chloride ions and triphenylphosphine group. There are large positive charges on the phosphorus atom (1.268, total charge on PPh_3 is 1.18), and the charges on the chloride ions are significantly smaller than -1 (Cl1 -0.491, Cl2 -0.409 and Cl3 -0.462). The charge on the pyrazole nitrogen atom bonded with ruthenium is negative (-0.318) – the pyrazole ligands act as electron acceptors (total charge on pyrazole ligand is -0.14). The total charge on the NO group is 0.217 (the charge of $N_{(NO)}$) is 0.370). The π -acceptor nature of NO⁺ enhances π -donation by *trans* chlorine ligand, and according to the structural *trans* effect the Ru–Cl(2) distance is shorter than the other ruthenium chlorine ones. The trans effect of NO ligand in the complex is presented in Fig. 3.

The linear unit M–NO is usually deemed to coordinate as NO^+ to the metal. In the valence-bond treatment the resulting NO^+ group is considered to involve sp hybridization at the N and O atoms. The following resonance forms may present the linear bonding mode:

$$M \stackrel{\bullet}{\leftarrow} N \equiv O;^{\dagger} \stackrel{\bullet}{\longleftrightarrow} M \stackrel{\bullet}{=} N \stackrel{=}{=} O; \stackrel{\bullet}{\longleftrightarrow} M \stackrel{=}{=} N^{\dagger} = O; \stackrel{\bullet}{\longleftrightarrow} M \stackrel{=}{=} N^{\dagger} = O;$$

Taking into consideration the electron population in the Ru–N and N–O bonds, from NBO analysis, (Ru–N/ (BD + BD*) = 5.099, N–O/BD = 1.991 and N–O/ BD* = 0.018) the resonance structure D becomes more important for the investigated complex.

Table 3		
Hydrogen bonds for	[RuCl ₃ (NO)(PPh ₃)(C ₃ H ₄ N ₂)] (Å	and °)

, , ,	- /		-/ - (/
D–H···A	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(\mathbf{D} \cdot \cdot \cdot \mathbf{A})$	∠(DHA)
$N(3)-H(3A)\cdots Cl(2)$	0.86	2.62	3.092(3)	115.4
$N(53)-H(53N)\cdots Cl(51)$	0.94	2.55	3.160(2)	122.6
$N(53)-H(53N)\cdots Cl(1)$	0.94	2.71	3.368(2)	128.0
$C(14)-H(14)\cdots Cl(2)$	0.93	2.60	3.372(3)	140.3
$C(52)-H(52)\cdots N(51)$	0.93	2.60	3.035(4)	109.0
C(53)–H(53)···Cl(2)#1	0.93	2.79	3.316(3)	116.7
$C(58)-H(58)\cdots Cl(51)$	0.93	2.79	3.268(3)	112.8
$C(64)-H(64)\cdots Cl(52)$	0.93	2.68	3.501(3)	147.1
C(71)–H(71)···O(1)#2	0.93	2.57	3.208(4)	126.0

Symmetry transformations used to generate equivalent atoms: #1 x + 1/2, -y - 3, z; #2 x, y - 1, z.

Table 5

The energy and character

[RuCl₃(NO)(PPh₃)(C₃H₄N₂)]

Table 4 Optimized geometry parameters for [RuCl₃(NO)(PPh₃)(C₃H₄N₂)]

	LANL2DZ	SSD	Experimental
Bond lengths (Å)			
Ru–N1 _(NO)	1.766	1.742	1.734
Ru–N2 _(HPz)	2.174	2.176	2.149
Ru–Cl1	2.500	2.462	2.384
Ru–Cl2	2.398	2.370	2.342
Ru–Cl3	2.462	2.423	2.378
Ru–P	2.459	2.443	2.396
N–O	1.150	1.155	1.134
Bond angles (°)			
Cl(1)–Ru(1)–Cl(2)	87.40	87.32	86.50
Cl(1)-Ru(1)-N(1)	86.79	87.94	89.09
Cl(3)-Ru(1)-N(1)	92.30	92.45	91.89
Cl(2)–Ru(1)–Cl(3)	93.49	92.15	92.54
N(1)-Ru(1)-N(2)	94.57	93.03	92.92
Cl(1)-Ru(1)-N(2)	87.28	87.18	87.45
Cl(2)-Ru(1)-N(2)	85.20	85.15	86.80
Cl(3)-Ru(1)-N(2)	88.53	88.28	87.90
Cl(1)-Ru(1)-P(1)	94.56	94.60	94.13
Cl(2)-Ru(1)-P(1)	85.34	86.86	86.82
Cl(3)-Ru(1)-P(1)	89.79	89.88	90.41
N(1)-Ru(1)-P(1)	95.07	95.11	93.64
N(2)-Ru(1)-P(1)	170.28	171.73	173.24
Cl(1)-Ru(1)-Cl(3)	175.62	175.46	175.29
N(1)-Ru(1)-Cl(2)	174.19	175.00	175.12
Ru(1)-N(1)-O(1)	174.58	175.15	176.35

The structure of the M–NO bond is composed of a σ bond, using the nitrogen lone pair and two π -interactions involving the filled d_{xz} and d_{yz} orbitals on ruthenium atom and the π^* orbitals of the NO (in this complex LUMO and LUMO + 1) [39]. The LUMO and LUMO + 1 orbitals are composed mainly of π_{NO}^* orbitals (about 63%). In the occupied orbitals the π_{NO}^* are distributed among several MOs, but their participation do not excess 15%. On the basis of the molecular orbital composition and the small charge on the NO group (Table 6) the NO⁺ character of nitrosyl in this complex can be confirmed.

The HOMO orbital is d_{xy} metal orbital with the admixture of chlorine π orbitals. HOMO – 1, HOMO – 2 and HOMO – 3 are π orbitals of phenyl groups with a contribution from the π Cl atoms. LUMO + 2 and LUMO + 3 are d_z^2 and $d_{x^2-y^2}$ orbitals with an antibonding admixture of the chlorine, phosphorus and pyrazole nitrogen lone pairs orbitals The HOMO - 4, HOMO - 5 and HOMO - 6 orbitals are π type (phenyl and Cl) with a substantial contribution from the appropriate d ruthenium orbitals. The participation of d_{xy} , d_{xz} and d_{yz} orbitals is visible in the lowest HOMO orbitals (H - 15, H - 16, H - 18, H - 19,H – 20, H – 21, H – 22) which are mainly π orbitals of phenyl with contribution of π Cl. The pyrazole ligand participates in lower HOMO orbitals (H - 8, H - 12)and H – 13) with contribution from π phenyl and Cl orbitals. The character of the HOMO and LUMO orbitals calculated by using the SSD basis set on ruthenium

valence

	MO	E (eV)	Character
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	LANI2DZ		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H = 21	-9.55	$d + \sigma_{\rm Pl} + \sigma_{\rm P} + \pi_{\rm VIO}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H = 20	_9.45	$d_{xz} + \sigma_{Ph} + \sigma_{P} + \pi_{NO}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	H = 19	-9.31	$d_{yz} + \sigma_{Ph} + \sigma_{P} + \sigma_{NO}$
	H = 18	_9.15	$d_{xz} + \sigma_{ph} + \sigma_{p}$
	H = 17	_8.96	$\sigma_{yz} + \sigma_{Ph} + \sigma_{P}$
	Н 16	8.83	$d + \pi + \sigma + \sigma + \sigma + \sigma$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H = 10 H = 15	-8.83	$d_{xz} + \pi c_1 + \sigma_2 + \sigma_N + \sigma_C_1$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	н = 15 Н 14	8 20	$d_{yz} + n_{\rm Cl} + 0$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	н 13	7 73	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	н 15 Н 12	7 57	$\pi_{\rm Cl} + \pi_{\rm HPz}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H = 12 H = 11	-7.57	π _{HPz}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H = 10	-7.32	$\pi_{\rm Cl}$ = $\pi_{\rm cr}$ = $\pi_{\rm cr}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H = 0	_7.40	$\pi_{\rm Ph}$ ' $\pi_{\rm HPz}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	н 9 Н 8	7.51	π _{Ph}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	н - 8 H - 7	7 17	$\pi_{\rm HPz}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	П = /	7.07	π _{Ph} · π _{Cl}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H 5	6.07	$d + \pi_{-1} + \pi_{-1}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		6.05	$u_{yz} + hp_h + hCl$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		6.00	TCI T
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Pi = 3$ $\Pi = 2$	-0.90	TCI T
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Pi = 2$ $\Pi = 1$	-0.84	$n_{\rm Ph}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	П — 1 Ц	-0.73	$h_{\rm Ph} + h_{\rm Cl} + h_{\rm P}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	II I	-0.01	$d_{xy} + h_{Cl}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L I ± 1	-3.08	$d_{xz} + \pi_{NO}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L + 1 L + 2	-3.03	$d_{yz}^2 + n_{NO}$ $d^2 + \sigma$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L + 2 L + 2	-2.49	$d_z + O_{Cl}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L + 3 $I \pm 4$	-1.93	$d_{x^2-y^2} + O_{Cl} + O_{Pl}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L + 4 L + 5	-0.99	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-0.78	$n_{\rm Ph} + n_{\rm P}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L + 0 L + 7	-0.01	$n_{\rm Ph} + n_{\rm P}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	L + /	-0.55	$n_{\rm Ph} + n_{\rm P}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SSD		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H - 18	-9.10	$d_{yz} + \sigma_{Ph} + \sigma_{P}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 17	-8.93	$d_{xz} + \pi_{Cl} + \sigma_P + \sigma_N$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H - 16	-8.74	$d_{yz} + \pi_{Cl} + \sigma_P$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H – 15	-8.60	$\pi_{\rm Ph} + \pi_{\rm Cl}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 14	-8.21	σ_{Cl}
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 13	-7.64	π_{HPz}
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 12	-7.53	$\pi_{\rm Ph} + \pi_{\rm HPz}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 11	-7.38	$\pi_{\rm Ph} + \pi_{\rm Cl}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H - 10	-7.31	$\pi_{\rm Cl}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 9	-7.27	$\pi_{\rm Ph} + \pi_{\rm HPz}$
$\begin{array}{cccccccc} H-7 & -7.07 & \pi_{Ph}+\pi_{Cl} \\ H-6 & -6.99 & d_{yz}+\pi_{Ph}+\pi_{Cl} \\ H-5 & -6.93 & \pi_{Ph} \\ H-3 & -6.76 & \pi_{Cl} \\ H-2 & -6.70 & \pi_{Cl}+\pi_{Ph} \\ H-1 & -6.69 & \pi_{Ph}+\pi_{Cl}+n_{P} \\ H & -6.36 & d_{xy}+\pi_{Cl} \\ L & -2.68 & d_{xz}+\pi_{NO}^{*} \\ L+1 & -2.65 & d_{yz}+\pi_{NO}^{*} \\ L+2 & -2.05 & d_{z}^{2}+\sigma_{Cl} \\ L+3 & -1.61 & d_{x^{2}-y^{2}}+\sigma_{Cl}+\sigma_{P} \\ L+4 & -0.91 & \pi_{Ph}+\pi_{N}(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph}+\pi_{P} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \\ \end{array}$	H - 8	-7.22	π_{HPz}
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H - 7	-7.07	$\pi_{\rm Ph} + \pi_{\rm Cl}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 6	-6.99	$d_{yz} + \pi_{Ph} + \pi_{Cl}$
$\begin{array}{ccccccc} H-4 & -6.87 & \pi_{Ph} \\ H-3 & -6.76 & \pi_{Cl} \\ H-2 & -6.70 & \pi_{Cl} + \pi_{Ph} \\ H-1 & -6.69 & \pi_{Ph} + \pi_{Cl} + n_{P} \\ H & -6.36 & d_{xy} + \pi_{Cl} \\ L & -2.68 & d_{xz} + \pi_{NO}^{*} \\ L+1 & -2.65 & d_{z}^{2} + \sigma_{Cl} \\ L+2 & -2.05 & d_{z}^{2} + \sigma_{Cl} \\ L+3 & -1.61 & d_{x^{2}-y^{2}} + \sigma_{Cl} + \sigma_{P} \\ L+4 & -0.91 & \pi_{Ph} + \pi_{N}(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph} + \pi_{P} \\ L+8 & -0.20 & \pi_{Ph} + \pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	H – 5	-6.93	π_{Ph}
$\begin{array}{ccccccc} H-3 & -6.76 & \pi_{Cl} \\ H-2 & -6.70 & \pi_{Cl} + \pi_{Ph} \\ H-1 & -6.69 & \pi_{Ph} + \pi_{Cl} + n_P \\ H & -6.36 & d_{xy} + \pi_{Cl} \\ L & -2.68 & d_{xz} + \pi_{NO}^* \\ L+1 & -2.65 & d_{yz} + \pi_{NO}^* \\ L+2 & -2.05 & d_{z}^2 + \sigma_{Cl} \\ L+3 & -1.61 & d_{x^2-y^2} + \sigma_{Cl} + \sigma_P \\ L+4 & -0.91 & \pi_{Ph} + \pi_{N}(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph} + \pi_P \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph} + \pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	H – 4	-6.87	π_{Ph}
$\begin{array}{cccccc} H-2 & -6.70 & \pi_{Cl}+\pi_{Ph} \\ H-1 & -6.69 & \pi_{Ph}+\pi_{Cl}+n_P \\ H & -6.36 & d_{xy}+\pi_{Cl} \\ L & -2.68 & d_{xz}+\pi_{NO}^* \\ L+1 & -2.65 & d_{yz}^2+\sigma_{Cl} \\ L+2 & -2.05 & d_z^2+\sigma_{Cl} \\ L+3 & -1.61 & d_{x^2-y^2}+\sigma_{Cl}+\sigma_P \\ L+4 & -0.91 & \pi_{Ph}+\pi_N(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph}+\pi_P \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	H - 3	-6.76	$\pi_{\rm Cl}$
$\begin{array}{ccccc} H-1 & -6.69 & \pi_{Ph}+\pi_{Cl}+n_P \\ H & -6.36 & d_{xy}+\pi_{Cl} \\ L & -2.68 & d_{xz}+\pi_{NO}^* \\ L+1 & -2.65 & d_{yz}+\pi_{NO}^* \\ L+2 & -2.05 & d_z^2+\sigma_{Cl} \\ L+3 & -1.61 & d_{x^2-y^2}+\sigma_{Cl}+\sigma_P \\ L+4 & -0.91 & \pi_{Ph}+\pi_{N}(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph}+\pi_P \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	H - 2	-6.70	$\pi_{\rm Cl} + \pi_{\rm Ph}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H – 1	-6.69	$\pi_{\rm Ph} + \pi_{\rm Cl} + n_{\rm P}$
$ \begin{array}{cccccc} L & & -2.68 & & d_{xz} + \pi^*_{NO} \\ L + 1 & & -2.65 & & d_{1z} + \pi^*_{NO} \\ L + 2 & & -2.05 & & d_z^2 + \sigma_{Cl} \\ L + 3 & & -1.61 & & d_{x^2-y^2} + \sigma_{Cl} + \sigma_P \\ L + 4 & & -0.91 & & \pi_{Ph} + \pi_N(HPz) \\ L + 5 & & -0.73 & & \pi_{Ph} \\ L + 6 & & -0.57 & & \pi_{Ph} + \pi_P \\ L + 7 & & -0.31 & & \pi_{Ph} \\ L + 8 & & -0.20 & & \pi_{Ph} + \pi_{Cl} \\ L + 9 & & -0.13 & & \pi_{Ph} + \pi_{HPz} \\ L + 10 & & 0.00 & & \pi_{Ph} \\ L + 11 & & 0.36 & & \pi_{Ph} \end{array} $	Н	-6.36	$d_{xy} + \pi_{Cl}$
$ \begin{array}{cccccc} L+1 & -2.65 & d_{zz}+\pi_{NO}^{*} \\ L+2 & -2.05 & d_{z}^{2}+\sigma_{Cl} \\ L+3 & -1.61 & d_{x^{2}-y^{2}}+\sigma_{Cl}+\sigma_{P} \\ L+4 & -0.91 & \pi_{Ph}+\pi_{N}(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph}+\pi_{P} \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array} $	L	-2.68	$d_{xz} + \pi^*_{NO}$
$ \begin{array}{cccccc} L+2 & -2.05 & d_z^2 + \sigma_{Cl} \\ L+3 & -1.61 & d_{\chi^2-y^2} + \sigma_{Cl} + \sigma_P \\ L+4 & -0.91 & \pi_{Ph} + \pi_N(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph} + \pi_P \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph} + \pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph} + \pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array} $	L + 1	-2.65	$d_{yz} + \pi^*_{NO}$
$\begin{array}{ccccc} L+3 & -1.61 & d_{x^2-y^2}+\sigma_{C1}+\sigma_P \\ L+4 & -0.91 & \pi_{Ph}+\pi_N(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph}+\pi_P \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{C1} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	L + 2	-2.05	$d_z^2 + \sigma_{Cl}$
$\begin{array}{ccccc} L+4 & -0.91 & \pi_{Ph}+\pi_N(HPz) \\ L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph}+\pi_P \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	L + 3	-1.61	$d_{x^2-y^2} + \sigma_{Cl} + \sigma_P$
$\begin{array}{cccccc} L+5 & -0.73 & \pi_{Ph} \\ L+6 & -0.57 & \pi_{Ph}+\pi_{P} \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	L + 4	-0.91	$\pi_{\rm Ph} + \pi_{\rm N}({\rm HPz})$
$\begin{array}{ccccc} L+6 & -0.57 & \pi_{Ph}+\pi_{P} \\ L+7 & -0.31 & \pi_{Ph} \\ L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	L + 5	-0.73	π_{Ph}
$\begin{array}{ccccc} L+7 & & -0.31 & & \pi_{Ph} \\ L+8 & & -0.20 & & \pi_{Ph}+\pi_{Cl} \\ L+9 & & -0.13 & & \pi_{Ph}+\pi_{HPz} \\ L+10 & & 0.00 & & \pi_{Ph} \\ L+11 & & 0.36 & & \pi_{Ph} \end{array}$	L + 6	-0.57	$\pi_{\mathrm{Ph}} + \pi_{\mathrm{P}}$
$\begin{array}{cccc} L+8 & -0.20 & \pi_{Ph}+\pi_{Cl} \\ L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	L + 7	-0.31	π_{Ph}
$\begin{array}{cccc} L+9 & -0.13 & \pi_{Ph}+\pi_{HPz} \\ L+10 & 0.00 & \pi_{Ph} \\ L+11 & 0.36 & \pi_{Ph} \end{array}$	L + 8	-0.20	$\pi_{\rm Ph} + \pi_{\rm Cl}$
$ \begin{array}{cccc} L + 10 & 0.00 & \pi_{\rm Ph} \\ L + 11 & 0.36 & \pi_{\rm Ph} \end{array} $	L + 9	-0.13	$\pi_{Ph} + \pi_{HPz}$
$L + 11$ 0.36 π_{Ph}	L + 10	0.00	π_{Ph}
	L + 11	0.36	π_{Ph}

H denotes HOMO and L denotes LUMO.

are close to these obtained from calculation with LANL2DZ basis. The energy of appropriate HOMO and LUMO orbitals calculated with SSD basis set is

for

MO

Table 6 Atomic charges from the natural population analysis (NPA) of $[RuCl_3(NO)(PPh_3)(C_3H_4N_2)]$

Rul	0.342
Cl1	-0.491
C12	-0.409
C13	-0.462
P1	1.268
N1 _(NO)	0.370
N2 _(HPz)	-0.301
01	-0.153



Fig. 3. The structural trans effect of NO ligand in $[RuCl_3(NO)-(PPh_3)(C_3H_4N_2)]$.

lower than obtained from calculation with LANL2DZ basis on Ru atom (maximum difference is about 0.4 eV). The HOMO–LUMO gap in both calculations are similar (the difference is 0.15 eV).

3.3. Electronic spectrum

The experimental spectrum of $[RuCl_3(NO)-(PPh_3)(C_3H_4N_2)]$ shows bands at 534.6, 468.4, 438.6, 330.8 300.0, 228.8 and 216.8 nm. There is also a shoulder at about 270 nm. The measured electronic spectrum is shown in Fig. 4.

With the use of the TDDFT method 80 electronic transitions were calculated for $[RuCl_3(NO)(PPh_3)(C_3 H_4N_2)]$ using the LANL2DZ basis set and 90 transitions with SSD basis set. The calculated electronic transitions are gathered in Tables 7 and 8. Both LANL2DZ and SSD calculation predict the experimental spectra of the complex with similar accuracy. Except for the low energy part of the spectrum, only transitions with oscillator strengths larger than 0.01 are listed. The calculated spectra obtained by both calculations are depicted in Fig. 5. Each calculated transition in Fig. 5 was represented by a gaussian function with the height equal to the oscillator strength and width equal to 0.05.

We ascribe the first experimental bans at 534 nm to the calculated transitions at 517 and 513 nm with small oscillator strengths. These are $d \rightarrow \pi^*_{NO}$ transitions. The transition calculated with SSD basis set is at 502.1 nm. The experimental band at 468 nm is assigned to the transitions calculated between 461 and 429 nm in the case of



Fig. 4. UV-Vis spectrum of [RuCl₃(NO)(PPh₃)(C₃H₄N₂)].

Most important configurations			<i>E</i> (V)	λ (nm)	f		Exp. λ (nm) (E (eV)) ε
$H(d) \rightarrow L(\pi^*_{NO})$			2.39	517.1	0.0001	ì	534.6(2.32)21
$H(d) \rightarrow L + I(\pi_{NO}^*)$			2.41	513.4	0.0003	}	
$H(d) \rightarrow L + 2(d)$			2.68	461.3	0.0001	٦	468.4(2.65)67
$H - 4(\pi_{Cl}) \rightarrow L(\pi^*_{NO})$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(\pi_{NO}^*)$		2.85	434.7	0.0001	}	
$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi_{NO}^*)$			2.88	429.3	0.0003	Ś	
$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi^*_{NO})$			2.96	418.3	0.0004		438.6(2.83)120
$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi^*_{NO})$	$H - 2(\pi_{Ph}) \rightarrow L(+1\pi^*_{NO})$		2.99	414.3	0.0005	6	
$H - 8(\pi_{HPz}) \rightarrow L(\pi^*_{NO})$	$H - 5(d + \pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi_{NO}^*)$	$H - 3(\pi_{Cl}) \rightarrow L(\pi^*_{NO})$	3.05	406.3	0.0012	J	
$H - 5(d + \pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi^*_{NO})$	$H - 4(\pi_{Cl}) \rightarrow L + 1(\pi^*_{NO})$		3.09	400.8	0.0031	-	
$H - 7(\pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi_{NO}^*)$			3.41	362.9	0.0092)	
$H - 11(\pi_{Cl}) \rightarrow L(\pi^*_{NO})$	$H - 3(\pi_{Cl}) \rightarrow L + 2(d)$	$H - 2(\pi_{Ph}) \rightarrow L + 2(d)$	3.47	356.9	0.0111	1	330.8(3.75)8660
$H - 5(d + \pi_{Ph} + \pi_{Cl}) \rightarrow L + 2(d)$	$H - 3(\pi_{Cl}) \rightarrow L + 2(d)$		3.67	337.4	0.0 110	~	
$H - 10(\pi_{Ph} + \pi_{Cl} + \pi_{HPz}) \rightarrow L + 1(\pi^*_{NO})$	$H - 8(\pi_{HPz}) \rightarrow L + 1(\pi^*_{NO})$	$H - 2(\pi_{Ph}) \rightarrow L + 2(d)$	3.75	329.9	0.0137		
$H - 6(\pi_{Ph}) \rightarrow L + 3(d)$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 3(d)$		3.97	312.2	0.0372		
$H - 5(d + \pi_{Ph} + \pi_{Cl}) \rightarrow L + 3(d)$	$H - 3(\pi_{Cl}) \rightarrow L + 3(d)$	$H-2(\pi_{Ph}) \rightarrow L+3(d)$	4.28	289.0	0.0395	ſ	300.0(4.13)5523
$H - 8(\pi_{HPz}) \rightarrow L + 3(d)$	$H - 6(\pi_{Ph}) \rightarrow L + 3(d)$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 3(d)$	4.30	287.6	0.0249	Ş	
$H - 13(\pi_{Cl} + \pi_{HPz}) \rightarrow L + 2(d)$	$H-4(\pi_{Cl}) \to L+3(d)$	$H-2(\pi_{Ph}) \rightarrow L+3(d)$	4.32	286.4	0.0411	J	
$H - 13(\pi_{Cl} + \pi_{HPz}) \rightarrow L + 2(d)$	$H - 12(\pi_{HPz}) \rightarrow L + 2(d)$		4.34	285.1	0.0283	ſ	270sh(4.59)
$H - 8(\pi_{HPz}) \rightarrow L + 3(d)$	$H - 7(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 3(d)$		4.47	277.1	0.0667	Ş	
$H - 11(\pi_{Cl}) \rightarrow L + 3(d)$	$H-9(\pi_{Ph}) \rightarrow L+3(d)$		4.69	263.9	0.0107	J	
$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 4(\pi_{Ph}^* + \sigma_P)$	$H(d) \rightarrow L + 5(\pi_{Ph}^* + \pi_P)$		5.15	240.5	0.0245		228.8(5.42)11089
$H - 18(d + \sigma_P + \sigma_{Ph}) \rightarrow L(\pi^*_{NO})$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 4(\pi_{Ph}^* + \sigma_P)$	$H(d) \rightarrow L + 5(\pi^*_{Ph} + \pi_P)$	5.18	238.9	0.0120		
$H - 16(d + \sigma_P + \sigma_N + \sigma_{Cl}) \rightarrow L + 2(d)$			5.26	235.6	0.0122		
$H-3(\pi_{Cl}) \rightarrow L+4(\pi_{Ph}^*+\sigma_P)$			5.27	235.0	0.0183	(
$H - 4(\pi_{Cl}) \rightarrow L + 4(\pi_{Ph}^* + \sigma_P)$	$H - 3(\pi_{Cl}) \rightarrow L + 4(\pi^*_{Ph} + \sigma_P)$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 5(\pi_{Ph}^* + \pi_P)$	5.31	233.4	0.0113		
$H - 14(\sigma_{Cl}) \rightarrow L + 3(d)$	$\mathrm{H}-4(\pi_{\mathrm{Cl}}) \rightarrow \mathrm{L}+4(\pi^*_{\mathrm{Ph}}+\sigma_{\mathrm{P}})$		5.34	231.8	0.0225	ノ	
							216.8(5.72)9903

Table 7	
Calculated electronic transitions for [RuCl ₃ (NO)(PPh ₃)(C ₃ H ₄ N ₂)] with the TDDFT method (LANL2DZ basis set)

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Table 8 Calculated electronic transitions for $[RuCl_3(NO)(PPh_3)(C_3H_4N_2)]$ with the TDDFT method (SSD basis set)

Most important configurations			$E(\mathbf{V})$	λ (nm)	f	Exp. λ (nm) (E (eV)) ε
$\overline{H(d) ightarrow L(\pi^*_{N\Omega})}$			2.47	502.1	0.0004	534.6(2.32)21
$H(d) \rightarrow L + l(\pi_{NO}^*)$			2.49	498.3	0.0002	468.4(2.65)67
$H(d) \rightarrow L + 2(d)$	$H - 3(\pi_{Cl}) \rightarrow L(\pi^*_{NO})$		2.80	442.6	0.0001	438.6(2.83)120
$H-4(\pi_{Ph}) \rightarrow L(\pi_{NO}^*)$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(\pi_{NO}^*)$		2.85	434.7	0.0001	}
$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(\pi_{NO}^*)$	$H - 3(\pi_{Cl}) \rightarrow L + 1(\pi^*_{NO})$		3.04	407.3	0.0002	J
$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi^*_{NO})$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(\pi_{NO}^*)$		3.21	385.9	0.0007	
$H - 5(\pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi^*_{NO})$	$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L(\pi^*_{NO})$		3.38	366.3	0.0037	`
$H - 5(\pi_{C1}) \rightarrow L + 1(\pi_{NO}^*)$	$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(d)$		3.44	360.8	0.0024	330.8(3.75)8660
$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 2(d)$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 2(d)$		3.47	357.7	0.0016	
$H - 5(\pi_{C1}) \rightarrow L + 1(\pi_{NO}^*)$	$H - 7(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(d)$		3.53	351.0	0.0011	(
$H - 6(d + \pi_{Ph} + \pi_{Cl}) \rightarrow L(d)$	$H-4(\pi_{Ph})\to L(d)$		3.72	333.5	0.0092	
$H - 10(\pi_{Ph} + \pi_{Cl} + \pi_{HPz}) \rightarrow L + 1(\pi_{NO}^{*})$	$H - 8(\pi_{HPz}) \rightarrow L(\pi^*_{NO})$	$H - 3(\pi_{Cl}) \rightarrow L + 2(d)$	3.77	329.0	0.0133	
$H - 2(\pi_{Ph}) \rightarrow L + 3(d)$	$H - 3(\pi_{Cl}) \rightarrow L + 3(d)$		3.99	311.0	0.0051	300.0(4.13)5523
$H - 11(d + \pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(d)$	$H - 10(\pi_{Cl}) \rightarrow L + 1(d)$	$H - 14(\sigma_{Cl}) \rightarrow L + 1(d)$	4.07	304.4	0.0121	
$H - 12(\pi_{HPz}) \rightarrow L(d)$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 3(d)$		4.14	299.3	0.0269	\langle
$H-13(\pi_{Cl}+\pi_{HPz})\rightarrow L(d)$	$H - 12(\pi_{Ph} + \pi_{HPz}) \rightarrow L(d)$	$H-2(\pi_{Ph}+\pi_{Cl})\rightarrow L+2(d)$	4.16	298.3	0.0249	J
$H - 13(\pi_{Cl} + \pi_{HPz}) \rightarrow L(d)$	$H - 12(\pi_{Ph} + \pi_{HPz}) \rightarrow L(d)$	$H - 1(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 3(d)$	4.18	296.9	0.0102	270sh(4.59)
$H - 8(\pi_{HPz}) \rightarrow L + 2(d)$	$H - 7(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 2(d)$		4.34	285.4	0.0096	}
$H - 7(\pi_{Cl}) \rightarrow L + 3(d)$	$H - 6(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 3(d)$		4.59	269.9	0.0697	J
$H - 15(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 1(\pi_{Ph}^* + \sigma_P)$	$H - 3(\pi_{Cl}) \rightarrow L + 2(d + \sigma_{Cl})$		4.77	259.8	0.0258	228.8(5.42)11089
$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 4(\pi_{NO}^*)$	$H-3(\pi_{C1})\rightarrow L+4(\pi^*_{Ph}+\pi_{HPz})$		5.19	239.1	0.0188	
$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 5(\pi_{Ph})$	$H(d) \rightarrow L + 7(\pi_{Ph})$		5.34	232.3	0.0203	>
$H - 2(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 6(\pi_{Ph}^* + \sigma_P)$			5.51	225.0	0.0229	(
$H - 7(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 4(\pi_{Ph}^* + \pi_{HPz})$	$H(d) \rightarrow L + 6(\pi_{Ph}^* + \sigma_P)$	$H-6(\pi_{Ph}+\pi_{Cl})\rightarrow L+4(\pi_{Ph}^*+\pi_{HPz})$	5.57	223.2	0.0117	J
$H - 16(d + \sigma_P + \sigma_{Cl}) \rightarrow L + 2(d)$	$H - 7(\pi_{Ph} + \pi_{Cl}) \rightarrow L + 4(\pi_{Ph}^* + \pi_{HPz})$		5.58	222.2	0.0044	
						216.8(5.72)9903



Fig. 5. Calculated electronic spectrum of [RuCl₃(NO)(PPh₃)(HPz)] (solid line – LANL2DZ, dashed line – SSD).

calculation with LANL2DZ basis and with SSD basis set the band we ascribe to the calculated transition at 498.3 nm. These transitions are of d \rightarrow d and $\pi_{CI} \rightarrow \pi^*_{NO}$ type (LLCT). In these range of energy transitions the prediction of experimental values with LANL2DZ basis set is better than with using the ECP basis (SSD). The transitions calculated between 418 and 400 nm (442–407 nm SSD) are ascribed to the band at 438 nm. These transitions are again of LCT type and occur from the chlorine, phenyl and pyrazole orbitals to the π^*_{NO} orbitals.

The experimental band at 330 nm is ascribed to the transitions calculated between 356 and 312 nm with medium oscillator strengths and to transitions between 366.3 and 311.0 nm while the SSD basis set was using. These are mainly transitions from the pyrazole, phenyl and chlorine ligands orbitals to the metal d orbitals (LMCT). The transitions 289 and 263 nm (304.4 to 269.9 - SSD) are assigned to the band at 300 nm and shoulder at about 270 nm. These are again transitions of LMCT character.

The transitions between 240 and 231 nm and 259.8 to 222.2 nm in calculation with SSD, respectively, are assigned to the band at 228 nm. They are of LLCT type (interligand transitions) and intraligand $(\pi_{Ph} \rightarrow \pi_{Ph}^*)$ (transitions). The experimental band at 216 nm could not be assigned on the basis of the calculated transitions. This band probably corresponds also to $\pi_{Ph} \rightarrow \pi_{Ph}^*$ transitions in the PPh₃ ligand.

As it can be seen from Tables 7 and 8 the UV–Vis spectrum calculated with the SSD basis set on the ruthenium atom gave better results in the higher energy and the LANL2DZ basis set in the lower energy range of the spectrum.

4. Supplementary material

Crystallographic data for the structure of the complex have been deposited at Cambridge Crystallographic Data Center (CCDC 239378). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or at www: http://www.ccdc.cam.ac.uk).

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