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Pyrazole cleavage of tris(3,5-dimethylpyrazolyl)borate with Ruthenium(II) complexes: Synthesis, structural characterization and DFT studies

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1. Introduction

Tris(3,5-dimethylpyrazolyl)borate (Tp*), a scorpionate ligand containing an alkyl-substituent of parent tris(pyrazolyl)borate (Tp) was introduced in 1966 by Trofimenko [1]. Since then, complexes formed by these versatile scorpionate ligands have been reported with almost every metal in the periodic table [2]. Many of these complexes have been investigated and are widely employed in various fields of chemistry such as catalysis, biomimetics, materials science and radiopharmaceutics [3,4]. Changing the nature of substituents on the pyrazolyl ring, especially those at the 3 position, leads to stabilization of the complexes by steric control of the interaction with the metal centres [5-7]. One interesting aspect of these ligands is that they show various modes of coordination which include ligand rearrangements or modifications [8,9]. Poly(pyrazolyl)borates undergo some transformations in which they give products containing pyrazole or pyrazolate derivatives, mainly due to B-N bond cleavage [10]. Because of this degradation, comparatively less work on the complexes containing well known Trofimenko scorpionate ligands has been reported.

ABSTRACT

The reaction of $[Ru(H)(Cl)(CO)(PPh_3)_3]$ (1) with KTp^* ($KTp^* =$ Potassium tris(3,5-dimethylpyrazolyl) borate) in a refluxing toluene yields a mixture of $[RuTp^*(H)(CO)(PPh_3)]$ (2), $[Ru(H)(Cl)(pz^*H)(CO)(PPh_3)_2]$ (3), and $[H(pz^*)B(\mu-pz^*)_2B(pz^*)H]$ (4) ($pz^*H = 3,5$ -dimethylpyrazole). The products (3) and (4) were obtained by the degradation of the scorpionate ligand, Tp*. These complexes were characterised by IR, ¹H NMR, UV, X-ray crystallography and DFT calculations.

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In this paper, we describe the synthesis of scorpionate complex $[RuTp^*(H)(CO)(PPh_3)]$ (2) and investigate the mechanistic pathways for the isolation of $[Ru(H)(Cl)(pz^*H)(CO)(PPh_3)_2]$ (3) and $[H(pz^*)B(\mu-pz^*)_2B(pz^*)H]$ (4) from the reaction mixtures. The analogous complex $[RuTp(H)(CO)(PPh_3)]$ reported in literature [11], provides the route of synthesizing the new complex $[RuTp^*(H)(-CO)(PPh_3)]$ (2).

2. Experimental section

2.1. Materials and methods

All chemicals were reagent grade, and solvents were dried and purified prior before use; toluene was distilled from sodium wire and acetophenone. The complex [Ru(H)(Cl)(CO)(PPh₃)₃] (1) [12] and KTp* ligand [13] were prepared according to literature methods. All the reactions were carried out in standard Schlenk technique under a dry and oxygen-free nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer using KBr pellets and the ¹H NMR spectra were recorded on Brucker AVENCE II 400 MHz spectrometer using tetramethylsilane as a reference. UV–Visible spectra were recorded on a Perkin-Elmer Lamda 25 UV–Visible spectrophotometer.







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2.2. Single crystal X-ray crystallography

Single crystals of the compounds were obtained by slow evaporation at room temperature. Single crystal X-ray data of the compounds were measured at 291.8 K, employing X calibur, Eos, Gemini diffractometer equipped with a monochromated Mo/K radiation (($\lambda = 0.71073$ Å) source. Crvs Alis PRO: Agilent. 2013 software packages were used for data collection and reduction. The structure of the complexes were solved by direct methods [14], and refined by a full matrix least squares procedure based on F^2 [14] minimizing $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$, $wR = [\Sigma [w (F_0^2 - F_c^2)^2] / \Sigma (F_0^2)^2]^{1/2}$ and $S = [\Sigma [(F_0^2 - F_c^2)^2/(n-p)]^{1/2}$. For structure solution and refinements SHELXT-2014 and SHELX-2014 [15] were used in all cases.

2.3. Computational methodology

All calculations were carried out using the Gaussian 09 package [16]. Full geometry optimizations of the complexes were performed using the density functional theory (DFT) based B3LYP [17] method along with the 6-31G(d,p) basis set for lighter atoms (H, B, C, N, P, Cl and O) and LANL2DZ for the heavier atom (Ru). The 6-31G(d,p) is a standard polarized basis set which adds d function on heavier atoms and p function on lighter atoms while LANL2DZ is pseudopotential basis set mainly used for post-third row atoms. The structures of the complexes (2, 3, and 4) were at the minima in the potential energy surface by ensuring the absence of imaginary frequencies. Natural Bond Orbital analysis (NBO) [18] has been carried out to obtain the natural electronic configurations, charges on the individual atoms and the d-orbital occupancies of the Ru metal atom present in the complexes. Time-dependent density functional theory (TDDFT) [19,20] with the B3LYP associated with the polarizable continuum solvent-effect model (PCM) [21] was performed to predict the UV spectra in dichloromethane solution. GaussSum 2.2 [22] was used for the analysis of UV–Vis spectra, oscillator-strengths, HOMO-LUMO energy-gap, transitions between various states and the fractional contributions of various groups to each molecular orbital. In addition, nucleus-independent chemical shift (NICS) was performed on product (4) using the gauge-invariant atomic orbital (GIAO) [23] approach. Since the ring current due to the cyclic π electron delocalization are induced by the external magnetic field which is applied perpendicular to the ring current, therefore the out of plane component of the NICS_{zz} tensor was evaluated using Multiwfn [24].

2.4. Synthesis of complexes (2), (3) and (4)

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A mixture of [Ru(H)(Cl)(CO)(PPh₃)₃] (1) (0.5 g, 0.524 mmol) and KTp* (0.17 g, 0.505 mmol) in toluene (40 ml) was refluxed for 24 h. The mixture was then allowed to cool to the room temperature, and

PPh₃

filtered to obtain the clear solution. The solvent was removed under reduced pressure to get a pale vellowish product. The product was washed well with diethylether and recrystallized from toluene leading to the deposition of pale yellowish crystals of (2), the orange blocks of (**3**) and the white crystalline products of (**4**). Small portion of samples were collected for spectroscopic analysis. A single crystal suitable for X-ray for all the complexes was obtained from toluene/ether solution. [RuTp*(H)(CO)(PPh₃)] (2):IR (KBr, pellet); 2518 cm⁻¹ (B–H), 2036 cm⁻¹ (Ru–H), 1912 cm⁻¹ (CO), ¹H NMR (CDCl₃, 400 MHz); δ –12.03 (d, *J*(PH) = 24 Hz, 1H, RuH), 1.36 (s, 3H, Tp*CH₃), 1.69 (s, 3H, Tp*CH₃), 1.85 (s, 3H, Tp*CH₃), 2.14 (s, 3H, Tp*CH₃), 2.19 (s, 3H, Tp*CH₃), 2.40 (s, 3H, Tp*CH₃), 5.01 (s, 1H, Tp*CH), 5.57 (s, 1H, Tp*CH), 5.61 (s, 1H, Tp*CH), 7.10-7.38 (m, 15H, PPh₃).

3. Results and discussion

3.1. General

The complex $[RuTp^*(H)(CO)(PPh_3)]$ (2) was synthesized by a similar procedure for the synthesis of the less steric KTp complex as reported by Ning-Yu Sun and Stephen J. Simpson [11]. Treatment of $[Ru(H)(Cl)(CO)(PPh_3)_3]$ (1) with 1 equivalent of KTp^{*} in toluene for 24 h leads to the formation of mixture of complexes (2), (3) and (4)(Scheme 1). These complexes have the same solubility in a range of solvents and were separated by recrystallization from the reaction mixture. The yellowish crystals of (2), orange blocks of complex (3)and the white crystalline product of complex (4) were collected manually which were sufficient for spectroscopic analysis. They were structurally identified by combination of spectroscopic analysis such as IR and ¹H NMR spectroscopy. In addition, the solid structures of (2), (3) and (4) were determined by single crystal Xray diffraction.

The IR spectrum of complex (2) shows the v_{B-H} band at 2518 cm⁻¹, indicating the presence of coordinated Tp* ligand when compared to the stretching frequency of free KTp* which was observed at 2437 cm⁻¹. Comparison of the v_{CO} and v_{Ru-H} stretching frequencies of complex (2) and its analogous complex (Table 1), shows that when Tp is replaced by a stronger electron donating Tp* ligand, both the metal-hydride σ -bond and metal-carbonyl bond are enhanced in the metal complex (2). Since, the σ and π type of interactions are mostly occurring between the metal and the ligands, a general conclusion can be drawn that "substitution by a stronger electron donating ligand to a transition metal complex enhances the inherent bonding of the ligands to the metal centre": and the reverse must be true.

The ¹H NMR spectrum of the complex (**2**) shows a doublet at $\delta - 12.03$ (J(PH) = 24 Hz) due to the hydride ligand and indicates the cis coupling with the phosphorus atom of the triphenylphosphine. The complex (2) exhibits three singlet peaks in the range of



K[HB(pz*)₃]

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Scheme 1. Reaction of [Ru(H)(Cl)(CO)(PPh₃)₃] (1) with KTp*.

Table 1

The ν_{CO} and ν_{Ru-H} stretching frequencies of Complex (2) with its analogue [RuTp (H)(CO)(PPh_3)].

Complex	$v_{CO} (cm^{-1})$	$\nu_{\text{Ru-H}}(cm^{-1})$
[RuTp(H)(CO)(PPh ₃)]	1922	1985
[RuTp*(H)(CO)(PPh ₃)] (2)	1912	2036

5.01–5.61 ppm for the three different chemical environments of the protons at 4-positions of the pyrazole rings, consistent with the rigid tridentate Tp* ligand. The IR and ¹H NMR spectra of products (**3**) and (**4**) are comparable to that of the reported values obtained by the different synthetic routes [25,26].

The main interest of our work was to obtain complex (**2**), but complex (**3**) formed by the usual pyrazole cleavage [27] was also obtained. However, the formation of (**3**) in which pz*H ligand is trans to CO (instead of H) may have a mechanistic significance because the phosphine ligand replaced by pz*H from [Ru(H)(Cl)(-CO)(PPh₃)₃] (**1**) was initially trans to H [28] (Scheme 1). Moreover, Romero and co-workers [25] kept on obtaining complex (**3**) when 1-hydroxymethyl-3,5-dimethylpyrazole was treated with different precursor complexes, such as, [RuCl₂(PPh₃)₃], [Ru(Cl)(H)(PPh₃)₃] and [Ru(H)(Cl)(CO)(PPh₃)₃]. The other two possible isomers of (**3**), namely, (**3a**) and (**3b**) (Fig. 1) were not reported in the literature. DFT based B3LYP calculations on (**3**), (**3a**) and (**3b**) were performed and support the formation of (**3**) as (**3a**) and (**3b**) are higher in energy by 3.77 and 23.83 kcal mol⁻¹ respectively.

The isolation of pyrazabole side product (4) was first reported by Blosch [26] when KTp* was treated with Tungsten (VI) complexes. The generation of pyrazabole from the poly(pyrazolyl)borate was also proposed by Hill and co-workers [29] when bis(pyrazolyl) borate was treated with [RuCl₂(PPh₃)₃]. The tris(pyrazolyl)borate ligand in the complex cleaves when there is one (i.e., bi-dentate κ^2 -*N*,*N* mode) or two (i.e., mono-dentate κ^{1} -*N*,*N* mode) pendant pyrazole nitrogen(s) left uncoordinated for sufficient amount of time to facilitate the nucleophilic attack [30]. Based on the above observations and the isolation of the products (3) and (4) from the reaction mixture, we are therefore tend to believe that the reaction proceeds by the mechanisms as shown in Scheme 2a and b in which exceptionally stable pyrazabole [31], is generated. The mechanism for the formation of (3) remains unclear, however the following scenarios are likely to happen: (i) Formation of an intermediate (A) activates the nucleophilic attack at the boron centre with either the free ligand (Scheme 2a) or with another intermediate (A) (Scheme 2b) to form the highly stable pyrazabole (4). (ii) Electronic and steric effects promote the transformation of (**B**) to (**3**) because the Ru(II) metal centre in (**B**) is bonded to relatively more π -acid and bulky phosphine ligands, hence replacing one PPh₃ by Cl⁻ to form (3) will be electronically and sterically favoured.

3.2. Molecular structure of complex (2)

The single crystal X-ray analysis shows that the complex is constructed from scorpionate ligand consisting of a tripodal



Fig. 1. The possible isomers of complex (3).

tris(3,5-dimethylpyrazolyl)borate, the monodentate ligands of triphenylphosphine, carbon monoxide and a hydride forming an octahedral geometry (Fig. 2). Table 2 shows the crystal data refinement of the complex (**2**) and Table 3 compiles the selected bond lengths, bond angles for the complexes and are comparable with the theoretical data.

3.3. Geometry optimization

The geometries of all the gas phase compounds (**2–4**) are optimized at B3LYP level and no geometrical constraints are applied during optimization. The input files of the complexes are prepared from the crystallographic coordinates obtained from X-ray measurements. The important bond-lengths and bond-angles of these complexes are tabulated in Table 3. The calculated bond-lengths and bond-angles are in good agreement with the experimental single crystal X-ray data measurements.

3.4. Atomic charge analysis

The atomic charge distributions on donor-acceptor atoms for the complexes under investigation are obtained from the NBO analysis and are tabulated in Table 4. Comparing the atomic charges in Table 4, it can be seen that the electron charge density on Ru(II) in their respective complexes is increased i.e., before complexation the charge on Ruthenium is +2, and after complexation the charge of Ru in complexes (2) and (3) are -0.803 and -1.158, respectively. This indicates that the ligands transfer their negative charges to the respective ruthenium metal ion during formation of complexes i.e., for complex (2) the electron charge density on hydride decreases from -1 to +0.081whereas for complex (3) the electron charge density on both hydride and chloride decreases from -1 to +0.104 and -0.544, respectively. The increase in electron charge density of the Ru metal ion in complexes (2) and (3) can also be understood from the natural electronic configuration obtained from NBO analysis. For instance, before complexation the natural electronic configuration for Ru(II) cation is 4d(6.00) but after complexation the natural electronic configurations for Ru metal ion in complexes (2) and (**3**) are 5s(0.36) 4d(7.73) 5p(0.72) 5d(0.02) and 5s(0.39) 4d(7.94) 5p(0.55) 5d(0.02) 6p(0.29), respectively. For Ru(II) metal ion in the free state, the valence d-orbitals occupancy in each of the d_{xy} , d_{yz} , and d_{xz} orbitals is 2.0, whereas d_{x-y}^{22} and d_z^2 orbitals remain unoccupied. This is because the energy of d_{x-y}^{22} and d_z^2 orbitals is 0.1126 a.u. higher than the d_{xy} , d_{yz} , and d_{xz} orbitals. On complexation the occupancy of d_{xy} , d_{yz} , and d_{xz} orbitals of Ru decreases (<2.0) and the d_{x-y}^{22} and d_z^2 orbitals get occupied as shown in Table 5.

The total hyperconjugation to $\sigma^*_{P1}-_{C16}$ and $\sigma^*_{P1}-_{C28}$ from the lone-pairs of N5 and N3 atoms and their respective N–C bond pairs of scorpionate ligand in complex (**2**) are 0.28 and 0.27 k cal mol⁻¹. Also in complex (**3**) the total hyperconjugation to $\sigma^*_{P1}-_{C12}$ and $\sigma^*_{P2}-_{C19}$ from the lone-pair of N1 atom and its respective N–C bond of pyrazole ligand are 0.58 kcal mol⁻¹. These observations suggest that in complexes (**2**) and (**3**) there are P···N interactions commonly known as pnicogen interactions.

3.5. Infrared, NICS_{zz} and electronic spectral analysis

The theoretical harmonic frequencies was scaled by a factor of 0.961 as obtained from CCCB database for B3LYP/6-31G(d,p) level of theory. Scaling of harmonic frequency is required to account for the anharmonicity of the fundamental frequencies which can aid in interpretation of experimental results from the theoretical calculated results. The theoretical IR vibrational frequencies are in



Scheme 2. Suggested mechanisms for the formation of $[Ru(H)(CI)(pz^*H)(CO)(PPh_3)_2]$ (3) and $[H(pz^*)B(\mu-pz^*)_2B(pz^*)H]$ (4).



Fig. 2. Molecular structures of the complexes (2) and (3).

reasonable agreement with the experimental IR spectra. The band observed at 2520 cm⁻¹(expt. value 2518 cm⁻¹) indicates the presence of v_{B-H} moiety in complex (**2**). For complex (**3**) the band at around 2520 cm⁻¹ was not observed which indicates the absence of B–H moiety. Strong bands observed around 1938 cm⁻¹(expt. value 1912 cm⁻¹) and 1963 cm⁻¹ (expt. value 1934 cm⁻¹) correspond to v_{CO} stretching frequencies and medium bands observed around

1978 cm⁻¹(expt. value 2036 cm⁻¹) and 2020 cm⁻¹(expt. value 2086 cm⁻¹) correspond to v_{Ru-H} stretching frequencies for complexes (**2**) and (**3**) respectively. NICS [32] is the computed value of the negative magnetic shielding at some selected point in space, generally at a ring or cage centre. Initially NICS(0)_{iso} was introduced by Paul Schleyer as a simple and efficient probe of aromaticity. But this index was not a pure measure of π -electron framework as σ

Table 2

Crystallographic and structure refinement for Complex (2).

Empirical formula	C34H38N6BPORu
Formula weight	689.55
Temperature/K	293.2(4)
Crystal system	Triclinic
Space group	P1
a/Å	10.1479(9)
b/Å	10.9974(8)
c/Å	16.3933(13)
a/°	74.118(6)
β/°	76.264(7)
$\gamma / ^{\circ}$	70.031(7)
Volume/Å ³	1632.8(2)
Z	2
μ/mm^{-1}	0.566
Radiation	MoK α ($\lambda = 0.71073$)
Reflections collected	12303
Data/restraints/parameters	7464/0/407
Goodness of fit on F2	1.050
Final R indexes $[I \ge 2\sigma(I)]$	R1 = 0.0322, wR2 = 0.0745
Final R indexes [all data]	R1 = 0.0420, $wR2 = 0.0797$

Table 3

Selected bond lengths and bond angles for complexes (2) an	d (3	3).
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Complex (2)			Complex(3)		
Distance (Å)	Expt.	Calc.	Distance (Å)	Expt.	Calc.
Ru1–P1	2.302(6)	2.398	Ru1–P1	2.361(13)	2.429
Ru1–N3	2.268(18)	2.342	Ru1–P2	2.359(13)	2.429
Ru1–N1	2.112(17)	2.154	Ru1–N1	2.172(4)	2.225
Ru1–N5	2.182(17)	2.217	Ru1–Cl1	2.565(17)	2.660
Ru1-C34	1.810(2)	1.855	Ru1-C37	1.967(7)	1.859
Ru1–H	1.546(2)	1.588	Ru1-H	1.935(3)	1.582
Angles (°)	Expt.	Calc.	Angles (°)	Expt.	Calc.
N3-Ru1-P1	101.63(5)	98.48	P1-Ru1-Cl1	90.35(5)	90.25
N1-Ru1-P1	174.96(5)	174.67	P2-Ru1-P1	177.35(5)	178.80
N1-Ru1-N3	81.91(7)	82.98	P2-Ru1-Cl1	92.25(5)	90.26
N3-Ru1-N5	90.04(6)	89.29	N1-Ru1-P1	91.43(12)	89.48
N5-Ru1-P1	95.18(5)	94.02	N1-Ru1-P2	88.26(12)	89.48
N3-Ru1-H	170.61(8)	171.43	N1-Ru1-Cl1	86.56(12)	85.74
C34-Ru1-P1	89.44(8)	91.48	N1-Ru1-H	85.64(10)	87.06
C34-Ru1-N3	96.36(8)	96.27	C37-Ru1-P1	90.23(17)	89.66
C34-Ru1-N1	93.75(9)	93.46	C37-Ru1-P2	89.72(17)	89.67
C34-Ru1-N5	171.21(9)	173.69	C37-Ru1-Cl1	101.5(2)	99.87
N1-Ru1-N5	81.89(7)	82.96	C37-Ru1-N1	171.8(2)	174.39
N1-Ru1-H	89.47(8)	89.27	C37-Ru1-H	86.10(10)	87.33
N5-Ru1-H	84.94(8)	85.91	P1-Ru1-H	89.28(10)	89.68
C34-Ru1-H	87.87(8)	87.76	P2-Ru1-H	88.09(10)	89.68
P1-Ru1-H	86.75(8)	88.94	Cl1-Ru1-H	172.42(10)	172.80

contributions also influences the magnetic environments which resulted in non-zero NICS(0)_{iso} for nonaromatic rings. Eventually NICS(1)_{iso} which referred to total isotropic shielding value at a point 1 Å above the ring centre was developed. NICS(1)_{iso} was therefore free from any σ contributions but it was still based on the total isotropic shielding values, rather than the contributions from the *zz*

Table 4

Calculated NBO charges (in e) of the central metal atom and atoms coordinated to the central metal atom in the complexes.

Complex (2)		Complex (3)	
q (Ru1)	-0.803	q (Ru1)	-1.158
q (N1)	-0.208	q (Cl1)	-0.544
q (N3)	-0.262	q (H)	+0.104
q (N5)	-0.240	q (P1)	+1.295
q (H)	+0.081	q (P2)	+1.295
q (C34)	+0.754	q (C37)	+0.239
q (P1)	+1.292	q (N1)	-0.239

Table 5

Calculated d orbital occupancy of the central metal atom in the complexes.

Complex (2)		Complex (3)	
d_{xy}	1.5758	d _{xy}	1.7755
d _{xz}	1.6090	d _{xz}	1.9456
d _{vz}	1.6832	d_{yz}	1.7554
d_{x-y}^{22}	1.3381	d_{x-y}^{22}	1.1413
d_z^2	1.5273	d_z^2	1.3212



Fig. 3. HOMO-LUMO energy gap of the complexes (2) and (3).

Table 6

Calculated individual energies (eV) along with the compositions (%) and character of virtual orbitals of the complexes.

Orbital	Energy (eV	')	Complex (2)				Character		
			Composition (%)						
			Ru	CO	Т	p*	Н	PPh_3	
H-6	-6.41		0	0	9	8	0	2	Tp*
H-4	-6.09		60	9	2	8	0	3	$Ru + Tp^*$
H-3	-6.01		14	2	8	1	0	2	Tp*
H-1	-5.55		46	9	4	3	1	2	$Ru + Tp^*$
HOMO (H)	-5.21		65	1	3	0	0	4	$Ru + Tp^*$
LUMO (L)	-0.73		2	0	1		0	96	PPh ₃
L+1	-0.53		7	1	3		1	88	PPh ₃
L+2	-0.49		5	0	2		0	93	PPh ₃
L+6	0.19		13	12	5	8	1	16	Tp*
L+12	1.24		4	3	9	1	0	2	Tp*
Orbital	Energy (eV)	Con	Complex(3)			Charac	ter		
		Con	Composition (%)						
		Ru	CO	pz*H	Н	PPh ₃	Cl		
H-4	-6.42	18	0	3	0	45	33	PPh ₃ +	- Cl
H-3	-6.21	22	4	6	0	67	0	PPh ₃ +	- Ru
H-2	-5.76	40	4	30	0	25	0	Ru + p	$z^*H + PPh_3$
H-1	-5.68	59	11	2	0	1	26	Ru + C	21
HOMO (H)	-5.35	58	0	0	0	11	30	Ru + C	21
LUMO (L)	-0.84	18	1	1	1	78	1	PPh ₃	
L+3	-0.35	3	1	3	0	93	0	PPh ₃	
L+8	-0.02	26	12	1	2	57	2	PPh ₃ +	- Ru

Table 7

Calculated major orbital excitation contributions (%), dominant excitation character, oscillator strength (f), energy difference (in eV), theoretical wavelengths (λ in nm) obtained from electronic transitions analysis with TDDFT(B3LYP) method.

Major orbital excitation contributions (%)	Dominant excitation character	Oscillator strength (f)	Energy gap (eV)	Calc. $\lambda(nm)$	Expt λ(nm)
Complex (2)					
$HOMO \rightarrow L + 1 (35\%)$	$Ru/Tp^* \rightarrow PPh_3 (MLCT/LLCT)$	0.0144	4.68	350	346
Homo \rightarrow Lumo (54%)	$Ru/Tp^* \rightarrow PPh_3 (MLCT/LLCT)$	0.0295	4.48	310	
$H-1 \rightarrow LUMO (35\%)$	$Ru/Tp^* \rightarrow PPh_3(MLCT/LLCT)$	0.0266	4.82	303	295
$H-1 \rightarrow L + 2 (20\%)$	$Ru/Tp^* \rightarrow PPh_3 (MLCT/LLCT)$	0.0238	5.06	263	
$H-4 \rightarrow LUMO (32\%)$	$Ru/Tp^* \rightarrow PPh_3 (MLCT/LLCT)$	0.0333	5.36	249	
H-6→LUMO (36%)	$Tp^* \rightarrow PPh_3 (LLCT)$	0.0248	5.68	243	
$H-6 \rightarrow L + 1 (39\%)$	$Tp^* \rightarrow PPh_3$ (LLCT)	0.0561	5.88	230	
$H-3 \rightarrow L + 6 (31\%)$	$Tp^* \rightarrow Tp^*$ (ILCT)	0.0257	6.20	216	218
$H-1 \rightarrow L + 12 (33\%)$	$Ru/Tp^* \rightarrow Tp^*MLCT/ILCT)$	0.1326	6.79	206	
Complex (3)					
$HOMO \rightarrow LUMO(78\%)$	$Ru/Cl \rightarrow PPh_3 (MLCT/LLCT)$	0.0319	4.51	358	340
$H-1 \rightarrow LUMO (79\%)$	$Ru/Cl \rightarrow PPh_3 (MLCT/LLCT)$	0.1174	4.84	314	
$H-3 \rightarrow LUMO (58\%)$	$PPh_3/Ru \rightarrow PPh_3 (ILCT/MLCT)$	0.2548	5.37	267	280
$H-4 \rightarrow L + 3 (35\%)$	$PPh_3/Cl \rightarrow PPh_3 (ILCT/LLCT)$	0.0577	6.07	222	
$H-3 \rightarrow L + 8 (34\%)$	$PPh_3/Ru \rightarrow PPh_3 (ILCT/MLCT)$	0.0536	6.19	217	212

component of the shielding tensor as ring current due to π electron delocalization which is induced by the external magnetic field applied perpendicular (*z* direction) to the ring. Therefore NICS(1)_{zz} is more popularly used for aromaticity evaluations. Negative NICS values denote aromaticity, positive NICS values denote antiaromaticity and small NICS value indicate non-aromaticity. For NICS(0)_{zz}, the ring critical point was selected for calculation. For product(**4**) the NICS(0)_{zz} and NICS(1)_{zz} are found to be 24.21 ppm and 5.52 ppm respectively, which indicate that complex (**4**) is antiaromatic in nature. The antiromaticity of (**4**) is attributed to the presence of electronegative nitrogen atoms in the ring which results in non-homogeneous electron distribution in the ring.

The HOMO-LUMO gap is the lowest energy electronic excitation possible in a molecule. The energy of the HOMO-LUMO gap reveal about what wavelengths the compound can absorb. The kinetic stability, chemical reactivity and the colour of the transition metal complexes in solution is governed by the HOMO-LUMO energy gap. The Frontier Molecular Orbital diagrams of both the complexes (2)



Fig. 4. The UV spectra of complexes (2) and (3) along with the TDDFT calculated UV spectra.

and (3) and their energy-gaps are shown in Fig. 3. The HOMO-LUMO energy gaps for the complexes (2) and (3) are 4.48 and 4.51 eV, respectively. The Mulliken population analysis used for calculating the percentage contributions of various groups to each molecular orbital (Table 6) suggests that for complex (2) the major percentage of HOMO is located over the metal atom Ru and Tp* whereas for complex (3), the major percentage of HOMO is located over the metal atom Ru and Cl ligand. The LUMO of both complexes (2) and (3) are located over the PPh₃ ligands. Some of the selected electronic transitions for complexes (2) and (3) based on oscillator strengths were tabulated in Table 7.

For complex (2), the calculated absorption bands in the range of 350-249 nm corresponds to MLCT/LLCT charge transfers and the dominant excitations leading to these charge transfers are HOMO \rightarrow L+1 (35%), HOMO \rightarrow LUMO (54%), H-1 \rightarrow LUMO (35%), H- $1 \rightarrow L+2$ (20%) and H-4 \rightarrow LUMO (32%). Other absorptions bands at around 243 nm and 230 nm corresponds to LLCT charge transfer whereas bands at 216 nm and 206 nm corresponds to ILCT and MLCT/ILCT charge transfers and the dominant excitations leading to these charge transfers are H-6 \rightarrow LUMO (36%), H-6 \rightarrow L+1 (39%), H- $3 \rightarrow L+6$ (31%) and $H-1 \rightarrow L+12$ (33%).

For complex (3), the calculated absorption bands at 358 and 314 correspond to MLCT/LLCT charge transfers whereas bands at 267 nm, 222 nm and 217 nm corresponds to ILCT/MLCT, ILCT/LLCT and ILCT/MLCT charge transfers and the dominant excitations leading to these charge transfers are HOMO→LUMO (78%), H- $1 \rightarrow LUMO$ (79%), H-3 $\rightarrow LUMO$ (58%), H-4 $\rightarrow L+3$ (35%) and H- $3 \rightarrow L+8$ (34%) respectively. The UV spectra of complexes (2) and (3) (Fig. 4) from TDDFT calculations show that main electronic transitions obtained are in good agreement with the experimental observations.

4. Conclusion

The synthesis of new complex $[RuTp^*(H)(CO)(PPh_3)]$ (2) was described and the side products (3) and (4) were obtained by pyrazole cleavage of KTp* ligand. There are several reasons that may lead to the cleavage of B-N bond in poly(pyrazolyl)borate ligands, such as polarity of solvents, the presence of Lewis acids or Bronsted acids, and the steric bulk of the peripheral ligands [33,34], but the formation of stable pyrazaboles must be the main driving force that leads to the degradation of the ligands. The substitution by a stronger electron donating ligand to a metal complex increases the inherent bonding of the ligands to the metal centre.

The experimental data of the complexes were in good agreements with theoretical DFT calculations. The theoretical calculations show that there are pnicogen interactions in the complexes (2) and (3).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.molstruc.2016.11.097.

References

- [1] (a) S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842–1844.
- [2] (a) S. Trofimenko, Scorpionates, the Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999; (b) S. Trofimenko, Chem. Rev. 93 (1993) 943–980;
 - (c) S. Trofimenko, Polyhedron 23 (2004) 197–203.
- [3] (a) N. Kitajima, W.B. Tolman, Prog. Inorg. Chem. 43 (1995) 419-531; (b) N.A. Foley, J.P. Lee, Z. Ke, T.B. Gunnoe, T.R. Cundari, Acc. Chem. Res. 42 (2009) 585-597.
- G. Parkin, Adv. Inorg. Chem. 42 (1995) 291-393. [4]
- H.D. Bari, M. Zimmer, Inorg. Chem. 43 (2004) 3344–3348. K. Niedenzu, S. Trofimenko, Top. Curr. Chem. 131 (1986) 1–37.
- [6]
- [7] A.L. Rheingold, R.L. Ostrander, B.S. Haggerty, S. Trofimenko, Inorg. Chem. 33 (1994) 3666-3676
- J.M. White, V.W.L. Ng, D.C. Clarke, P.D. Smith, M.K. Taylor, Charles G. Young, [8] Inorg. Chim. Acta. 362 (2009) 4570–4577.
- (a) J.S. Figueroa, J.G. Melnick, G. Parkin, Inorg. Chem. 45 (2006) 7056; [9] (b) K. Pang, J.M. Tanski, G. Parkin, Chem. Commun. (2008) 1008-1010.
- [10] S. Bieller, A. Haghiri, M. Bolte, J.W. Bats, M. Wagner, H. Lerner, Inorg. Chim. Acta 359 (2006) 1559–1572.
- [11] N.Y. Sun, S.J. Simpson, J. Organomet. Chem. 434 (1992) 341-349.
- [12] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45.
- S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288-6294. [13]
- [14] G.M. Sheldrick, Acta. Crystallogr. Sect. A Crystallogr. 64 (2008) 112.
- [15] G.M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinements, Uni-
- versity of Gottingen, Gottingen, Germany, 1996. [16] M.J. Frisch, et al., GAUSSIAN 09, Revision C.01, Gaussian Inc, Walling-ford CT, 2009.
- [17] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789.
- [18] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899-926.
- [19] M.E. Casida, J.M. Seminario (Eds.), Recent Developments and Applications in Modern Density Functional Theory, Theoretical and Computational Chemistry, vol. 4, Elsevier, 1996. Amsterdam.
- [20] N.N. Matsuzawa, A. Ishitani, D.A. Dixon, T. Uda, J. Phys. Chem. A 105 (2001) 4953-4962
- [21] V. Barone, M. Cossi, J. Tomasi, J. Chem. Phys. 107 (1997) 3210-3221.
- [22] N.M.O. Boyle, A.L. Tenderholt, K.M. Langner, J. Comput. Chem. 29 (2008) 839-845.
- [23] P. Pulay, J.F. Hinton, K. Wolinski, Mathematical and physical sciences, in: J.A. Tossel (Ed.), Nuclear Magnetic Shieldings and Molecular Structure, NATOASI Series C, vol. 386, 1993 (Amsterdam: Kluwer).
- [24] T. Lu, F. Chen, Multiwfn: a multifunctional wave function analyzer, J. Comp. Chem. 33 (2012) 580-592.
- [25] A. Romero, A. Vegas, A. Santos, A.M. Cuadro, J. Chem. Soc. Dalton Trans. (1987) 183-186.
- [26] L.L. Blosch, A.S. Gamble, K. Abboud, J.M. Boncella, Organometallics 11 (1992) 2342 - 2344
- [27] (a) L.M. Caldwell, Adv. Organomet. Chem. 56 (2008) 1; (b) M. Lail, K.A. Pittard, T.B. Gunnoe, Adv. Organomet. Chem. 56 (2008) 95; E. Becker, S. Pavlik, K. Kirchner, Adv. Organomet. Chem. 56 (2008) 155; (d) I.R. Crossley, Adv. Organomet. Chem. 56 (2008) 199;
 - (e) F.A. Jalon, A. Otero, A. Rodriguez, J. Chem. Soc. Dalton Trans. (1995) 1629-1633.
- [28] S.K. Seetharaman, M.C. Chung, U. Englich, K.R. Senge, M.B. Sponsler, Inorg. Chem. 46 (2007) 561-567.
- [29] R.J. Abernethy, A.F. Hill, M.K. Smith, A.C. Willis, Organometallics 28 (2009) 6152-6159.
- [30] G. Bellachioma, G. Cardaci, V. Gramlich, A. Macchioni, F. Pieroniand, L.M. Venanzi, J. Chem. Soc. Dalton Trans. (1998) 947-951.
- S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 4948.
- [32] H.F.B. Shaidaei, C.S. Wannere, C. Corminboeuf, R. Puchta, P.v.R. Schleyer, J. Org. Lett. 8 (2006) 863-866.
- [33] F. Yraola, F. Albericio, M. Corbella, M. Royo, Inorg. Chim. Acta 361 (2008) 2455-2461.
- [34] C.J. Jones, J.A. McClevetty, A.S. Rothin, J. Chem. Soc. Dalton Trans. (1986) 109-111.