# Synthesis, crystal, molecular, and electronic structures of hydride carbonyl ruthenium(II) complexes with pseudohalide ligands

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Received: 15 January 2013/Accepted: 18 February 2013/Published online: 28 February 2013 © Springer Science+Business Media Dordrecht 2013

**Abstract** Two pseudohalide hydride carbonyl ruthenium(II) complexes with formulae:  $[RuH(N_3)(CO)(PPh_3)_3]$ (1) and  $[RuH(NCO)(CO)(PPh_3)_3]$  (2) have been synthesized by the reactions of  $[RuHCl(CO)(PPh_3)_3]$  with sodium azide or sodium cyanate, respectively, and are compared with the previously described thiocyanate analog  $[RuH(NCS)(CO)-(PPh_3)_3]$ . The molecular structures of the new compounds were determined by X-ray crystallography and their spectroscopic properties have been studied. Based on the crystal structures, computational investigations have been carried out in order to determine the electronic structures of the complexes. The electronic spectra were calculated with the use of time-dependent DFT methods, and the electronic spectra of the transitions were correlated with the molecular orbitals of the complexes.

#### Introduction

Hydride carbonyl ruthenium(II) complexes containing triphenylphosphine ligand are of growing interest for their potential applications [1–5]. The hydride ligand, a powerful  $\sigma$ -donor, is found to be very efficient for the compensation of electron deficiency at the central metal in such complexes. The "trans effect" of the H<sup>-</sup> ligand and the interaction between CO and N-donor ligands in mutually trans positions are factors which help to explain the stability of the complexes [6]. Hence, the synthesis and spectral characterization of new hydride carbonyl ruthenium(II) complexes derived from the parent complex

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Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland e-mail: ank806@wp.pl [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] is very interesting. To date, the greatest attention has been paid to chloride analogs with heteroaromatic ligands in contrast to pseudohalide derivatives. The introduction of thiocyanate, cyanate, or azide groups to the ruthenium coordination sphere modifies the electronic structures of the resulting complexes sufficiently to allow for tuning their spectroscopic and redox properties, as in the case of heteroaromatic ligands. It is well known that pseudohalide ligands tune the spectral and redox properties of ruthenium(II) complexes by destabilizing the metal  $t_{2g}$  orbital. Thus, understanding of the differences in crystal, molecular, and electronic structures of such complexes is of interest.

In this paper, we report the synthesis, crystal, molecular, and electronic structures of new azide and cyanate analogs of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>], their spectroscopic characterization, and discussion of their properties with respect to [RuH(SCN)(CO)(PPh<sub>3</sub>)<sub>3</sub>], which was described in a recent publication [7]. Based on the crystal structures, computational studies were carried out in order to determine the electronic structures of the complexes by analysis of their optimized molecular geometries and their electronic populations using the natural bond orbitals scheme. In addition, time-dependent density functional theory (TD-DFT) was used to calculate the electronic absorption spectra. These results allowed for the interpretation of the experimental UV–Vis spectra. The luminescence properties of the complexes are also reported.

#### **Experimental**

The  $[RuHCl(CO)(PPh_3)_3]$  was synthesized by the literature method [8]. All other reagents were commercial materials and have been used without further purification.

Synthesis of the complexes  $[RuH(N_3)(CO)(PPh_3)_3]$  (1),  $[RuH(NCO)(CO)(PPh_3)_3]$  (2)

The complexes  $[RuH(N_3)(CO)(PPh_3)_3]$  (1) and  $[RuH(NCO)-(CO)(PPh_3)_3]$  (2) were synthesized by the reactions of  $[RuHCl(CO)(PPh_3)_3]$  (0.2 g; 2.0 × 10<sup>-4</sup> mol) and sodium azide or sodium cyanate (0.020 g; 2.2 × 10<sup>-4</sup> mol). The reaction mixtures were refluxed in methanol (60 mL) for 4 h, then were cooled and filtered. Crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the reaction mixtures.

 $\begin{array}{l} Complex \ I \ IR \ (KBr): \ 3,054 \ v_{ArH}, \ 2,053 \ v_{N3}; \ 1,924 \ v_{(CO/Ru-H)}; \\ 1,583, \ 1,570; \ 1,479 \ \delta_{(C-CH \ in \ the \ plane)}; \ 1,433 \ v_{Ph(P-Ph)}; \ 1,090 \\ \delta_{(C-CH \ in \ the \ plane)}; \ 742 \ \delta_{(C-C \ out \ of \ the \ plane)}; \ 696 \ \delta_{(C-C \ in \ the \ plane)}; \\ 517 \ \delta_{(Ru-(H)CO)}. \end{array}$ 

UV–Vis (methanol; logɛ): 342 (1.26), 259 (sh), 201 (4.92). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.87–6.01 (m, PPh<sub>3</sub>), -4.44 (t, *J* = 19.3 Hz, H<sub>(Ru)</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$ : 40.11 (d, *J* = 15.9 Hz, PPh<sub>3</sub>), 39.13 (s, PPh<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 206.88 (s, C=O); 134.12, 133.12, 132.16, 132.07, 131.94, 131.92, 128.57, 128.44, 128.14 (PPh<sub>3</sub>).

*Complex 2* IR (KBr): 3,055 v<sub>ArH</sub>; 2,235 v<sub>(CN from NCO)</sub>; 1,991 v<sub>(Ru-H)</sub>; 1,928 v<sub>(CO)</sub>; 1,585, 1,570, 1,478  $\delta_{(C-CH in the plane)}$ ; 1,432 v<sub>Ph(P-Ph)</sub>; 1,330 v<sub>(CO from NCO)</sub>1,091  $\delta_{(C-CH in the plane)}$ ; 741  $\delta_{(C-C)}$  out of the plane); 692  $\delta_{(C-C in the plane)}$ ; 601  $\delta_{(NCS)}$ ; 518  $\delta_{(Ru-(H)CO)}$ . UV–Vis (methanol; logɛ): 327 (1.54), 274 (3.77), 253 (3.87), 227 (4.18), 206 (4.65). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.77–6.94 (m, PPh<sub>3</sub>), -7.23, -6.97 (dt, J = 24.7 Hz, 24.6 Hz, H<sub>(Ru)</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$ : 40.48 (s, PPh<sub>3</sub>), 40.28 (d, J = 15.5 Hz, PPh<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 206.92 (C = O), 135.81, 135.44, 135.32, 135.12, 134.04, (PPh<sub>3</sub>), 133.11 (NCO), 132.02, 129.37, 129.05, 128.48, 127.80 (PPh<sub>3</sub>).

### Physical measurements

Infrared spectra were recorded on a Perkin–Elmer spectrophotometer in the range 4,000–450 cm<sup>-1</sup> using KBr pellets. Electronic spectra were measured on a Lab Alliance UV–VIS 8500 spectrophotometer in the range of 600–180 nm in methanol solution. The <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were obtained at room temperature in CDCl<sub>3</sub> using a Bruker Avance 400 MHz spectrometer. Luminescence measurements were made in ethanolic solutions on an F-7000 FL spectrophotometer at room temperature.

# Computational methods

All calculations were carried out using the Gaussian09 [9] program. Molecular geometries of the singlet ground states of both complexes were fully optimized in the gas phase using the B3LYP functional [10, 11]. For each compound, a frequency calculation was carried out, verifying that the obtained optimized molecular structure corresponded to an

energy minimum, and thus, only positive frequencies were expected. The DZVP basis set [12] with f-functions with exponents 1.94722036 and 0.748930908 was used to describe the ruthenium atom, and the basis set used for the lighter atoms (C, N, O, S, P, H) was 6-31G with a set of d and p polarization functions. TD-DFT [13] was employed to calculate the electronic absorption spectra of the complexes. The solvent effect of methanol was included with the polarizable continuum model. In this work, 100 singlet excited states were calculated as vertical transitions for the complexes. A natural bond orbital (NBO) analysis was also made for all the complexes using the NBO 5.0 package [14] included in Gaussian 09. NBO are orbitals localized on one or two atomic centers that describe molecular bonding in a manner similar to a Lewis electron pair structure, and they correspond to an orthonormal set of localized orbitals of maximum occupancy. NBO analysis provides the contribution of atomic orbitals (s, p, d) to the NBO  $\sigma$  and  $\pi$  hybrid orbitals for bonded atom pairs. In this scheme, three NBO hybrid orbitals are defined, specifically bonding orbital, lone pair, and core. These were analyzed on the atoms directly bonded to or presenting some kind of interaction with the ruthenium atom. The contribution of each group (ligands, central metal) to a given molecular orbital was calculated using Mulliken population analysis. GaussSum 2.2 [15] was used to calculate group contributions to the molecular orbitals and to prepare the partial density-of-states (DOS) spectra. The DOS spectra were created by convoluting the molecular orbital information with Gaussian curves of unit height and FWHM of 0.3 eV.

Crystal structure determination and refinement

The crystals of  $[RuH(N_3)(CO)(PPh_3)_3]$  (1), [RuH(NCO)- $(CO)(PPh_3)_3$  (2) were mounted in turn on an Xcalibur, Atlas, Gemini Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector. X-ray intensity data were collected with graphite monochromated  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at temperature 295.0(2) K, with  $\omega$ scan mode. Ewald sphere reflections were collected up to  $(2\theta = 50.10)$ . The unit cell parameters were determined from least-squares refinement of the setting angles of 11,968 and 7,825 strongest reflections for complexes (1) and (2), respectively. Details concerning crystal data and refinement are gathered in Table 1. Lorentz, polarization and empirical absorption corrections using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm [16] were applied. The structures were solved by the Patterson method and subsequently completed by difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. Bearing in mind the limits of Fourier synthesis and the problems in recognizing artifacts in the immediate neighborhood of heavy atoms, it is doubtful whether a reliable position for the hydrogen atom bound to the Ru atom can be found in the difference Fourier map while avoiding the danger of mistaking the effects of the series termination errors for a true atomic position. In both complexes, the Ru–H bond length close to 1.60 Å is normal. The Olex2 [17] and SHELXS97, SHELXL97 [18] programs were used for all the calculations. Atomic scattering factors were incorporated in the computer programs.

#### **Results and discussion**

#### Spectroscopic characterization of the complexes

The experimental and calculated IR spectra of complexes (1) and (2) are presented in Fig. 1, and calculated and experimental IR transitions with their assignments are

Table 1Crystal data andstructure refinement details of[RuH(N\_3)(CO)(PPh\_3)\_3] (1),[RuH(NCO)(CO)(PPh\_3)\_3] (2)complexes

given in Table 2. The differences in calculated and
experimental spectra mainly result from the neglect of
intermolecular interactions for the gas phase. The IR
spectrum of complex (2) shows a strong $C \equiv O$ band and
the Ru-H stretching band at 1,928 and 1,991 cm <sup>-1</sup> ,
respectively. In the case of complex (1), these bands are
combined and they are observed at 1,924 cm <sup>-1</sup> . Mean-
while, the calculations predict $v_{Ru-H}$ and $v_{CO}$ at 2,073
(2,063) and $1,994$ $(2,004)$ cm <sup>-1</sup> , respectively, for complex
(1), with the values for complex (2) given in parenthesis. In
contrast to [RuH(NCS)(CO)(PPh <sub>3</sub> ) <sub>3</sub> ] for which the shift of
$v_{CO}$ (from 1,922 to 1,947 cm <sup>-1</sup> ) is clearly visible, the
experimental values of this stretching band for complexes
(1) and (2) are comparable with the position of this band
for the parent complex [RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub> ], which shows
$v_{CO}$ and $v_{Ru-H}$ at 1,922 and 2,020 cm <sup>-1</sup> . In the spectrum of
complex (2), three characteristic bands are observed at
2,235, 1,330, and 601 cm <sup><math>-1</math></sup> assigned, respectively, as the
<b>C</b> 1 <b>V</b>

	(1)	(2)
Empirical formula	C55H46N3OP3Ru	$C_{56}H_{46}NO_2P_3Ru$
Formula weight	958.93	958.92
Temperature (K)	295.0(2)	295.0(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /c
Unit cell dimensions		
a (Å)	26.5946(8)	12.7705(3)
b (Å)	12.6847(4)	14.8409(4)
c (Å)	27.5047(11)	25.0460(8)
α (°)	90.00	90.00
β (°)	94.681(3)	91.478(3)
γ (°)	90.00	90.00
Volume (Å <sup>3</sup> )	9,247.6(6)	4,745.3(2)
Z	8	4
Calculated density (Mg/m <sup>3</sup> )	1.378	1.342
Absorption coefficient (mm <sup>-1</sup> )	0.486	0.474
F(000)	3,952	1,976
Crystal dimensions (mm)	$0.14\times0.09\times0.07$	$0.17\times0.11\times0.07$
$\theta$ range for data collection (°)	3.27-25.05	3.47-25.05
Index ranges	$-31 \le h \le 31,$	$-15 \le h \le 12,$
	$-12 \le k \le 15,$	$-17 \le k \le 17,$
	$-31 \le 1 \le 32$	$-29 \le 1 \le 29$
Reflections collected	39,799	22,764
Independent reflections	16,321 [R(int) = 0.0430]	8,381 [R(int) = 0.0335]
Data/restraints/parameters	16,321/0/1,143	8,381/0/572
Goodness-of-fit on F <sup>2</sup>	1.006	1.048
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0456,$	$R_1 = 0.0471,$
	$wR_2 = 0.0925$	$wR_2 = 0.0842$
R indices (all data)	$R_1 = 0.0768,$	$R_1 = 0.0711,$
	$wR_2 = 0.1015$	$wR_2 = 0.0909$
Largest diff. peak and hole	1.007/-0.509	0.542/-0.364

 $v_{(CN)}$ ,  $v_{(CO)}$ , and  $\delta_{(NCO)}$  modes of the isocyanate ligand. The same  $v_{(CN)}$  vibration was detected for [RuH(NCS) (CO)(PPh<sub>3</sub>)<sub>3</sub>] but with decreased wavenumber characteristic of N-bonded isothiocyanate ligand. The strong band at 2,053 cm<sup>-1</sup> indicates the presence of an azide ligand in complex (1). The calculated vibrational band at 2,184 cm<sup>-1</sup> corresponds to this stretching mode. The stretching modes of the Ar–H are observed at 3,054 and 3,055 cm<sup>-1</sup>, for complexes (1) and (2), respectively.

The <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra of the complexes were obtained at room temperature in CDCl<sub>3</sub> (see in the "Experimental" section). The expected signals of the

Fig. 1 The experimental and calculated IR spectra of [RuH(N<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (1), [RuH(NCO)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (2) complexes

triphenylphosphine ligands are observed in the <sup>1</sup>H NMR spectra of the complexes. Moreover, a doublet of triplets at -7.23, -6.97 ppm for complex (2) indicates the presence of a hydride ligand. In the spectrum of complex (1), the hydride ligand gives a triplet at -4.44 ppm. In general, the NMR spectra of complexes containing both hydride and triphenylphosphine ligands give rise to a doublet of triplets due to coupling with the phosphorus atoms. However, in practice, many of these complexes show only a triplet, as is in the case for complex (1). The <sup>31</sup>P NMR spectra show doublets and singlets close to 40 ppm, arising from non-equivalent phosphorus atoms. The <sup>13</sup>C NMR spectra of the complexes



**Table 2** Experimental and calculated IR transitions for  $[RuH(N_3)-(CO)(PPh_3)_3]$  (1),  $[RuH(NCO)(CO)(PPh_3)_3]$  (2) complexes

Vibrational	1		2			
assignments	Wavenumbers (cm <sup>-1</sup> )					
	Exp	Calc	Exp	Calc		
V <sub>ArH</sub>	3,054	3,180	3,055	3,182		
V <sub>N3/CN</sub> from NCO	2,053	2,184	2,235	2,325		
V <sub>RuH</sub>	1,924	2,073	1,991	2,063		
ν <sub>CO</sub>		1,994	1,928	2,004		
$\delta_{C-CH}$ in the plane	1,583	1,535	1,585	1,529		
VPh(P-Ph)	1,433	1,479	1,432	1,478		
VCO from NCO	-	-	1,330	1,368		
$\delta_{C-CH}$ in the plane	1,090	1,110	1,091	1,110		
$\delta_{C-C}$ out of the plane	742	759	741	766		
$\delta_{C-C}$ in the plane	696	711	692	710		
δ <sub>NCS</sub>	-	_	601	608		
δ <sub>Ru-(H)CO</sub>	517	528	518	516		

show signals attributed to both the PPh<sub>3</sub> and CO ligands. Additionally, the spectrum of complex (2) shows a signal at 133.11 ppm ascribed to cyanate carbon.

### Molecular structures

Complex (1) crystallizes in monoclinic  $P2_1/n$  space group and complex (2) in monoclinic  $P2_1/c$  space group. In the molecular structure of complex (1), two independent molecules exist in the asymmetric unit. The molecular structures of the complexes are shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. In both of the complexes, the ruthenium centers have an octahedral environment with distortion arising from steric hindrance of the PPh<sub>3</sub> ligands. The angles between the phosphine ligands depart from the expected values of 180° and 90° by an average of 11.4 % for complex (1) and 13.2 % for complex (2). This deviation was also visible in the same range in the thiocyanate analog [7].

Complexes (1) and (2), like [RuH(NCS)(CO)(PPh<sub>3</sub>)<sub>3</sub>], are analogs of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] in which a chloride ligand is replaced by one of the bulkier pseudohalide ligands. In these complexes, the hydride ligand is *trans* to the equatorial triphenylphosphine. The trans effect of the hydride ligand is reflected in a slight elongation of the Ru(1)–P(3) bond lengths in relation to the bonds Ru(1)–P(1), Ru(1)–P(2) in all of the studied complexes by an average of 0.12 Å. The N– N–Ru angles in the azide complex significantly deviate from linearity, as observed previously for the other ruthenium(II) azide complexes [19, 20]. The Ru–N–C angles for cyanate analogs range between 150° and 170°, which indicates that the mode of coordination is via nitrogen for these ambidentate ligands [21]. Thus, the similarity in values of these angles for the isothiocyanate and isocyanate complexes results from the same mode of coordination. Taking into account the fact that N and O atoms have very similar sizes and electronic conditions, the N-coordination mode of cyanate ion was tested and verified, as this model refined to a significantly lower R-value than the model with O-coordination. The azide and isocyanate groups are almost linear, with angles near to 178°. The Ru–N distances are comparable to those in other ruthenium complexes containing pseudohalide N-donor ligands reported in the literature [7, 19–26]. The conformations of the complexes are stabilized by intra- and intermolecular hydrogen bonds, details of which are collected in Table 4.

# DFT calculations

To get an insight in the electronic structures and bonding properties of these complexes, DFT calculations were carried out. Initially, their geometries were optimized in singlet states using the B3LYP functional. In general, the predicted bond lengths and angles are in agreement with the values from the X-ray crystal structure data, and the general trends observed in the experimental data are reproduced in the calculations (Table 3). The largest differences between the experimental and calculated bond lengths are found in the Ru(1)-P(3) distances, being 0.12 and 0.16 Å. The experimental and calculated angles between ruthenium and the azide ligand in complex (1)or isocyanate ligand in complex (2) differ by about 10°. Based on the optimized geometries of the complexes, a NBO analysis was performed in order to reveal the nature of coordination between ruthenium and the various donor atoms of the ligands. This analysis showed that the pseudohalide donor ligands do not show covalent bonding with ruthenium; the Coulomb-type interactions between the ruthenium center and these ligands are clearly visible in the calculated Wiberg bond indexes, which are considerably lower than one (0.55). The Ru-P bond orders are also less than 1 and close to 0.70 for the PPh<sub>3</sub> ligands in mutually *trans* conformation and 0.55 for the triphenylphosphines in cis positions. This low value is connected with the *trans* effect exerted by the hydride ligand. The NBO analysis (Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis) also shows that the contributions from the azide and isocyanate ligands to the ruthenium centers have similar values close to 250 kcal/mol, while the back donations are equal to 42.9 and 40.5 kcal/mol in complexes (1) and (2), respectively. There are no significant differences in these energy values compared to those calculated for the thiocyanate analog.

**Fig. 2** Molecular structures of [RuH(N<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (1), [RuH(NCO)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (2) complexes. Hydrogen atoms (bonding with carbons) are omitted for clarity





**Table 3** Selected bond lengths (Å) and angles (°) for  $[RuH(N_3)(CO)(PPh_3)_3]$  (1),  $[RuH(NCO)(CO)(PPh_3)_3]$  (2) complexes with the optimized geometry values

$\operatorname{RuH}(N_3)(\operatorname{CO})(\operatorname{PPh}_3)_3]$			[RuH(NCO)(CO)(PPh <sub>3</sub> ) <sub>3</sub> ]				
	Exp		Exp	Calc		Exp	Calc
Bond lenghts (Å)							
Ru(1)–C(1)	1.855(4)	Ru(2)–C(61)	1.896(4)	1.868	Ru(1)–C(1)	1.834(4)	1.862
Ru(1)–N(1)	2.124(3)	Ru(2)–N(61)	2.079(3)	2.168	Ru(1)–N(1)	2.099(3)	2.140
Ru(1)–P(1)	2.3868(9)	Ru(2)–P(61)	2.3538(10)	2.464	Ru(1)–P(1)	2.3970(9)	2.457
Ru(1)–P(2)	2.3605(9)	Ru(2)–P(62)	2.4020(10)	2.456	Ru(1)–P(2)	2.3516(10)	2.442
Ru(1)–P(3)	2.5073(9)	Ru(2)–P(63)	2.4950(10)	2.622	Ru(1)–P(3)	2.4857(9)	2.646
Ru(1)–H(1)	1.48(3)	Ru(2)–H(2)	1.63(3)	1.597	Ru(1)–H(1)	1.57(3)	1.597
O(1)–C(1)	1.146(4)	O(61)–C(61)	1.127(4)	1.167	O(1)–C(1)	1.161(4)	1.166
N(1)–N(2)	1.187(4)	N(61)–N(62)	1.101(5)	1.209	N(1)–C(2)	1.140(5)	1.198
N(2)–N(3)	1.161(4)	N(62)–N(63)	1.248(7)	1.161	O(2)–C(2)	1.208(5)	1.202
Angles							
O(1)-C(1)-Ru(1)	171.9(3)	O(61)-C(61)-Ru(2)	160.0(4)	176.06	O(1)-C(1)-Ru(1)	176.9(3)	178.04
C(1)-Ru(1)-N(1)	172.63(13)	C(61)-Ru(2)-N(61)	174.04(17)	176.53	C(1)-Ru(1)-N(1)	174.33(14)	175.57
C(1)-Ru(1)-P(1)	85.08(11)	C(61)-Ru(2)-P(61)	92.10(13)	85.40	C(1)-Ru(1)-P(1)	98.66(11)	97.63
C(1)-Ru(1)-P(2)	86.10(11)	C(61)-Ru(2)-P(62)	100.05(12)	88.08	C(1)-Ru(1)-P(2)	93.76(11)	94.65
C(1)-Ru(1)-P(3)	100.89(11)	C(61)-Ru(2)-P(63)	88.07(14)	99.97	C(1)-Ru(1)-P(3)	89.47(11)	88.97
N(1)-Ru(1)-P(1)	95.56(8)	N(61)-Ru(2)-P(61)	85.22(10)	93.99	N(1)-Ru(1)-P(1)	81.66(9)	82.22
N(1)-Ru(1)-P(2)	90.76(8)	N(61)-Ru(2)-P(62)	80.71(10)	91.18	N(1)-Ru(1)-P(2)	83.52(9)	83.82
N(1)-Ru(1)-P(3)	86.25(8)	N(61)-Ru(2)-P(63)	97.67(9)	83.50	N(1)-Ru(1)-P(3)	95.96(9)	95.40
P(2)-Ru(1)-P(1)	158.43(3)	P(61)-Ru(2)-P(62)	156.60(3)	156.74	P(2)-Ru(1)-P(1)	151.18(3)	154.33
P(1)-Ru(1)-P(3)	99.82(3)	P(61)-Ru(2)-P(63)	101.37(3)	101.78	P(1)-Ru(1)-P(3)	103.87(3)	101.32
P(2)-Ru(1)-P(3)	101.16(3)	P(62)-Ru(2)-P(63)	98.97(3)	101.33	P(2)-Ru(1)-P(3)	102.14(3)	101.36
C(1)-Ru(1)-H(1)	90.9(11)	C(61)-Ru(2)-H(2)	86.6(11)	90.40	C(1)-Ru(1)-H(1)	88.8(12)	86.39
N(1)-Ru(1)-H(1)	81.9(11)	N(61)-Ru(2)-H(2)	87.7(11)	86.13	N(1)-Ru(1)-H(1)	85.7(12)	89.23
P(1)-Ru(1)-H(1)	82.6(12)	P(61)-Ru(2)-H(2)	80.5(11)	79.27	P(1)-Ru(1)-H(1)	78.8(12)	79.71
P(2)-Ru(1)-H(1)	77.9(12)	P(62)-Ru(2)-H(2)	80.3(11)	78.49	P(2)-Ru(1)-H(1)	75.5(12)	78.66
P(3)-Ru(1)-H(1)	168.1(11)	P(63)-Ru(2)-H(2)	174.4(11)	169.62	P(3)-Ru(1)-H(1)	177.0(12)	175.35
N(2)-N(1)-Ru(1)	123.2(2)	N(62)–N(61)–Ru(2)	143.2(4)	122.30	C(2)-N(1)-Ru(1)	167.3(3)	158.31
N(3)-N(2)-N(1)	178.6(4)	N(61)-N(62)-N(63)	167.0(6)	177.07	N(1)-C(2)-O(2)	178.4(6)	177.58

Table 4 Hydrogen bonds for  $[RuH(N_3)(CO)(PPh_3)_3]$  (1),  $[RuH(N-CO)(CO)(PPh_3)_3]$  (2) complexes (Å and °)

D-HA	d(D–H)	d(HA)	d(DA)	<(DHA)
[RuH(N <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>3</sub> ]				
C(7)-H(7)N(2)	0.93	2.49	3.241(5)	137.6
C(43)-H(43)N(1)	0.93	2.36	3.191(5)	148.1
C(79)-H(79)-N(61)	0.93	2.49	3.223(5)	135.4
C(111)–H(111)N(61)	0.93	2.49	3.228(5)	136.0
[RuH(NCO)(CO)(PPh <sub>3</sub> ) <sub>3</sub> ]				
C(4)-H(4)N(1)	0.93	2.58	3.278(5)	132.7
C(34)-H(34)N(1)	0.93	2.53	3.316(5)	142.9
C(37)-H(37)O(2)#1	0.93	2.49	3.154(6)	128.4
C(50)-H(50)N(1)	0.93	2.57	3.212(5)	126.5

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

The interactions between the ligands and central metal can be characterized by the calculated natural charges on the metal, whose values are significantly lower than the formal oxidation state. These natural charges are equal to -1.070(1) and -1.076 (2), indicating that the donations from the ligands to the metal are greater than the back donations from the metal to ligands. The same situation was observed in the case of [RuH(SCN)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (natural charge on the ruthenium was -1.088). The calculated natural charges of the hydride ligands are both +0.09, and the Wiberg indices of the Ru-H bonds are close to 0.75. The charges on the carbonyl group, calculated by summing the individual charges on the carbon and oxygen, are +0.16 and +0.19 for complexes (1) and (2), respectively. The Wiberg indexes of the CO bonds in the complexes are reduced by about 0.23 with respect to free CO ( $W_{CO} = 2.23$ ).

Analysis of the frontier molecular orbitals is useful for understanding the spectroscopic properties such as electronic absorption and emission spectra. The DOS and overlap population density-of-states (OPDOS) in term of Mulliken population analysis were calculated using the GaussSum program, and Fig. 3 presents the compositions of the fragment orbitals contributing to the molecular orbitals of the complexes. In the HOMO's, the azide or isocyanate ligands play a significant role, contributing with 73 and 51 %, respectively, and the contribution from the  $d_{\rm Ru}$  orbitals is 18 and 29 % in complexes (1) and (2), respectively. For the thiocyanate analog, a greater share of thiocyanate ligand with a decline in contribution of  $d_{\rm Ru}$ orbitals was found in the HOMO. For complexes (1) and (2), the LUMOs are localized on the triphenylphosphine ligands (84, 79 %) with antibonding participation of 13–18 %  $d_{Ru}$  orbitals. In the case of the azide complex, the contribution of the PPh<sub>3</sub> orbitals to the LUMO is higher compared to the isocyanate analog and the recently reported complex [RuH(NCS)(CO)(PPh<sub>3</sub>)<sub>3</sub>]. At higher unoccupied orbitals LUMO + 18—LUMO + 21 (0.38–1.18 eV for complex (1) and 0.51–1.44 eV for complex (2)), the participation of ruthenium *d* orbitals is in the range of 16–29 and 12–23 % for complexes (1) and (2), respectively. The  $\pi^*$  orbitals of the carbonyl groups have significant contributions to LUMO + 18—LUMO + 21, in the range of 11–49 and 24–68 % for complexes (1) and (2), respectively. In the OPDOS plots of the complexes, the antibonding interactions between the pseudohalide ligands and ruthenium(II) center in the HOMO and HOMO-1 orbitals are visible. The



Fig. 3 The density-of-states diagrams and overlap partial DOS for interactions between ruthenium central ions and ligands in the complex  $[RuH(N_3)(CO)(PPh_3)_3]$  (1),  $[RuH(NCO)(CO)(PPh_3)_3]$  (2)

Table 5 The electronic transitions for the complexes calculated with B3LYP functional by the TD-DFT method

Wavelength (nm)	f	Transitions	Exp (nm)
1			
377.15	0.1125	HOMO $\rightarrow$ LUMO (62 %), HOMO $\rightarrow$ L + 1 (26 %)	
336.63	0.0346	H-2 $\rightarrow$ LUMO (44 %), H-1 $\rightarrow$ LUMO (14 %), HOMO $\rightarrow$ L + 1 (10 %)	342
292.09	0.0037	HOMO $\rightarrow$ L + 8 (88 %)	
262.03	0.0191	HOMO $\rightarrow$ L + 15 (41 %), HOMO $\rightarrow$ L + 18 (25 %)	
256.74	0.0191	$H-2 \rightarrow L + 8 (59 \%)$	259
250.72	0.0024	$H-1 \rightarrow L + 9 \ (64 \ \%)$	
245.69	0.0138	$H-2 \rightarrow L + 10 (54 \%)$	
2			
356.95	0.1214	H-1 $\rightarrow$ LUMO (70 %)	
347.01	0.0019	HOMO $\rightarrow$ LUMO (82 %)	
331.60	0.0012	H-2 → LUMO (73 %)	327
271.88	0.1127	H-3 $\rightarrow$ LUMO (43 %), H-2 $\rightarrow$ L + 2 (11 %), H-2 $\rightarrow$ L + 3 (13 %)	274
248.15	0.0146	HOMO $\rightarrow$ L + 16 (42 %)	253
232.24	0.0064	$H-2 \rightarrow L + 13 (11 \%), H-2 \rightarrow L + 14 (29 \%)$	



Fig. 4 Experimental and calculated electronic absorption spectra and oscillator strength of calculated transitions for complex  $[RuH(N-CO)(CO)(PPh_3)_3]$  (2)

combination of the carbonyl ligands and ruthenium d orbitals to the HOMO orbitals has positive value indicating the bonding character of these interactions.

#### Experimental and theoretical electronic spectra

The theoretical absorption spectra of the complexes were obtained from the calculations of the singlet excited states by TD-DFT. Computation of 100 excited states allowed for the interpretation of the experimental spectra. The selected excited states assigned to the absorption bands are shown in Table 5. Complex (1) shows experimental maxima at 342, 259, and 201 nm, while complex (2) has maxima at 327, 274, 253, 227, and 206 nm. The experimental and calculated spectra of complex (2) with the oscillator

strengths of the calculated transitions are presented in Fig. 4. From the calculated electronic structures, it appears that the HOMOs are localized on pseudohalide ligand  $\pi$  orbitals with admixture of the ruthenium *d* orbitals. However, the phosphine ligands are the main contributors to the LUMOs with addition of ruthenium orbitals. Taking into account the electronic structures of the complexes, the bands at 342 for complex (1) and at 327 nm for complex (2) have been attributed to MLLCT with admixture of *d*-*d* character. The bands observed at 259 and 274, 253 nm have been assigned to intra- and interligand  $(\pi^b_{C6H6} \rightarrow 3d_{phosphorus} and \pi \rightarrow \pi_{C=C})$  transitions with admixture of MLCT transitions  $(d_{Ru} \rightarrow \pi^*_{N-ligand} and d_{Ru} \rightarrow \pi^*_{Ph})$ . The highest experimental bands close to 210 nm may result from transitions in the PPh<sub>3</sub> ligands.

Fluorescence spectra of the complexes have been measured at room temperature in ethanolic solutions with the concentration of  $1 \times 10^{-3}$  mol/dm<sup>3</sup>. The solutions of the complexes were excited at wavelengths corresponding to the first transitions of the complexes. The complexes do not show emission properties, in contrast to the isothiocyanate analog. The lack of emissions in the isocyanate and azide complexes is probably connected with the smaller impact of NCO<sup>-</sup> and N<sub>3</sub><sup>-</sup> on the frontier HOMOs than was found for the isothiocyanate.

# Conclusions

Two new complexes of ruthenium with azide and isocyanate ligands were synthesized and characterized as a continuation of previous studies on pseudohalide hydride carbonyl ruthenium(II) complexes. Electronic structures of the complexes have been determined by DFT, allowing analysis of the UV–Vis spectra. We conclude that the differences in the electronic structures of the present complexes and the previously reported isothiocyanate analog have major influences on their spectroscopic properties and determine their ability of fluorescence. Hence, variation of the pseudohalide ligands may allow for intentional modification of the spectroscopic properties of such complexes.

# Supplementary data

CCDC 871975 and CCDC 910264 contain the supplementary crystallographic data for the complexes  $[RuH(N_3)(-CO)(PPh_3)_3]$  (1),  $[RuH(NCO)(CO)(PPh_3)_3]$  (2). These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or e-mail: deposit@ccdc.cam. ac.uk.

Acknowledgments The GAUSSIAN-09 calculations were carried out in the Wrocław Centre for Networking and Supercomputing, WCSS, Wrocław, Poland, http://www.wcss.wroc.pl, under calculational Grant No. 18.

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