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Polyhedron 26 (2007) 5120-5130

The reactions between $[RuHCl(CO)(PPh_3)_3]$ and quinoline carboxylic acids

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Revised 11 July 2007; accepted 12 July 2007 Available online 24 August 2007

Abstract

The reactions of [RuHCl(CO)(PPh₃)₃] with 8-hydroxy-2-methyl-quinoline-7-carboxylic acid and quinoline-2-carboxylic acid have been examined, and two novel ruthenium(II) complexes $-[(PPh_3)_2RuH(CO)(C_{10}H_8NO_3)]$ and $[(PPh_3)_2RuCl(CO)(C_9H_6O_2)]$ have been obtained. The compounds have been studied by IR and UV-Vis spectroscopy, and X-ray crystallography. The molecular orbital diagrams of the complexes have been calculated with the density functional theory (DFT) method. The spin-allowed singlet-singlet electronic transitions of the compounds have been calculated with the time-dependent DFT method, and the UV-Vis spectra of the compounds have been discussed on this basis.

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Keywords: Ruthenium; Quinoline carboxylic acid; Hydride and carboxyl complexes; X-ray structure; TDDFT method

1. Introduction

The quinoline moiety is present in many classes of biologically active compounds. A number of them have been clinically used as antifungal, antibacterial and antiprotozoic drugs [1,2] as well as antituberculotic agents [3,4]. Some quinoline-based compounds show antineoplastic activity [5]. Quinoline derivatives reveal also antiasthmatic and antiplatelet activity [6-10] and due to acetylcholinesterase inhibition, these compounds are potential drugs for treatment of nervous diseases [11]. Recently strong attention has been focused on styrylquinoline derivatives because of their activity as prospective HIV integrase inhibitors [12–16]. The study dealing with styrylquinoline derivatives showed that they could also possess strong antifungal activity [17], thus the compounds containing 8-hydroxyquinoline pharmacophore seem especially interesting. According to the results reported recently, some new 8-hydroxyquinoline derivatives possess interesting antifungal and herbicidal activities [18-20].

On the other hand ruthenium carbonyl and hydride complexes are very interesting due to their catalytic and structural properties. As it was shown for the complex with quinoline 2-carboxylic acid, the formation of cis-coordinated metal complexes is often a leading step in the cytostatic processes involving metal based drugs [21].

In this paper we present the synthesis and characterisations of two novel ruthenium(II) complexes containing the quinoline moiety.

2. Experimental

2.1. Physical measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range $4000-400 \text{ cm}^{-1}$

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^{0277-5387/\$ -} see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.07.023

Table 1

 $Crystal \ data \ and \ structure \ refinement \ details \ of \ [(PPh_3)_2 RuH(CO)(C_{10}H_8NO_3)] \cdot 0.5 CH_3OH \ (1) \ and \ [(PPh_3)_2 RuCl(CO)(C_9H_6O_2)] \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ (2) \ ($

	1	2
Empirical formula	$C_{49.50}H_{45}NO_{5.50}P_2Ru$	C47H36ClNO3P2Ru
Formula weight	904.88	861.23
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
<i>a</i> (Å)	12.3516(5)	10.9441(5)
b (Å)	15.1962(5)	21.2302(11)
c (Å)	22.7646(9)	16.8572(8)
β	97.205(4)	92.153(4)
Volume (Å ³)	4239.1(3)	3913.9(3)
Ζ	4	4
D_{calc} (Mg/m ³)	1.418	1.462
Absorption coefficient (mm ⁻¹)	0.496	0.595
<i>F</i> (000)	1868	1760
Crystal dimensions (mm)	$0.08 \times 0.08 \times 0.28$	$0.04 \times 0.12 \times 0.38$
θ Range for data collection (°)	2.83-25.00	2.91-25.00
Index ranges	$-14 \leq h \leq 14, -8 \leq k \leq 18, -27 \leq l \leq 26$	$-7 \leq h \leq 13, -25 \leq k \leq 25, -20 \leq l \leq 20$
Reflections collected	26145	24198
Independent reflections $[R_{int}]$	7333 [0.0371]	6860 [0.0467]
Data/restraints/parameters	7333/0/543	6860/0/496
Goodness-of-fit on F^2	0.915	0.977
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0338$ $R_1 = 0.0267$	
	$wR_2 = 0.0746$	$wR_2 = 0.0627$
R indices (all data)	$R_1 = 0.0669, wR_2 = 0.0793$	$R_1 = 0.0467, wR_2 = 0.0652$
Largest difference in peak and hole ($e \text{ Å}^{-3}$)	0.857 and -0.508	0.516 and -0.357



Fig. 1. Drawing of $[(PPh_3)_2RuH(CO)(C_{10}H_8NO_3)] \cdot 0.5CH_3OH$ with 50% probability displacement ellipsoids. The hydrogen atoms except H(1Ru) are omitted.



Fig. 2. Drawing of [(PPh₃)₂RuCl(CO)(C₃H₆O₂)] with 50% probability displacement ellipsoids. The hydrogen atoms are omitted for clarity.

with the samples in the form of KBr pellets. Electronic spectra were measured on a Lab Alliance UV–Vis 8500 spectrophotometer in the range 800–200 nm in dichloromethane solution. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN–2400 analyzer.

All reagents, except the 8-hydroxy-2-methylquinoline-7carboxylic acid, used for the synthesis of the complexes are commercially available and were used without further purification. The [RuHCl(CO)(PPh₃)₃] complex was synthesised using a literature method [22]. The 8-hydroxy-2methylquinoline-7-carboxylic acid was synthesised as described in the literature [13].

2.2. Synthesis of $[(PPh_3)_2RuH(CO)(C_{10}H_8NO_3)]$ (1) and $[(PPh_3)_2RuCl(CO)(C_9H_6O_2)]$ (2)

A suspension of $[RuHCl(CO)(PPh_3)_3]$ (0.95 g, 1×10^{-3} mol) and 8-hydroxy-2-methyl-quinoline-7-carboxylic acid (0.21 g) or quinoline-2-carboxylic acid (0.18 g) in



methanol (100 cm^{-3}) was refluxed until the solid dissolved, then the solution was cooled and filtered. Crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the reaction mixture. Yield 78% (1) and 82% (2).

Anal. Calc. for 1: C₄₇H₃₆ClNO₃P₂Ru: C, 63.94; H, 4.58; N, 3.64. Found: C, 64.01; H, 4.53; N, 3.66%.

2: $C_{50}H_{42}CINO_3P_2Ru$: C, 66.48; H, 4.69; N, 1.55. Found: C, 66.28; H, 4.59; N, 1.51%.

IR (KBr, cm⁻¹): 1: 3055 v_{CH} ; 2925 $v_{CH-phenyl}$; 1945 v_{Ru-H} ; v_{CO} ; 1610 v_{CN} ; 1590 as v_{COO} ; 1482 $\delta_{(C-CH in the plane)}$; $v_{Ph(P-Ph)}$; 1378 s v_{COO} ; 1121 $\delta_{(C-CH in the plane)}$; $\delta_{(C-C \text{ out of the plane)}}$; 756 $\delta_{(C-C \text{ out of the plane})}$; 697 $\delta_{(C-C \text{ in the plane})}$.

2: 3060 v_{CH} ; 1938 v_{CO} ; 1650 v_{CN} ; 1596 as v_{COO} ; 1482 $\delta_{(C-CH \text{ in the plane})}$; 1434 $v_{Ph(P-Ph)}$; 1348 s v_{COO} ; 1089 $\delta_{(C-CH \text{ in the plane})}$; 750 $\delta_{(C-C \text{ out of the plane})}$; 696 $\delta_{(C-C \text{ in the plane})}$.

UV-Vis [nm] in CH₃OH (log ε): 1: 400 (3.48); 357 sh (3.59); 332 (3.77); 281 (4.31); 210 (4.40).

2: 350 (3.01); 283 (3.38); 238 (4.20); 206 (4.32).



Fig. 3. Structural drawing of [(PPh₃)₂RuH(CO)(C₁₀H₈NO₃)].

Fig. 4. Structural drawing of [(PPh₃)₂RuCl(CO)(C₉H₆O₂)].



Fig. 5. Part of the molecular packing of [(PPh₃)₂RuH(CO)(C₁₀H₈NO₃)].

2.3. DFT calculations

The GAUSSIAN-03 program [23] was used for the calculations. The geometry optimisation was carried out using the DFT method with the B3LYP functional [24,25]. The electronic transitions were calculated with the PCM model [26] with dichloromethane as the solvent. The calculation was performed using the DZVP basis set [27] with f functions and with exponents 1.94722036 and 0.748930908 on the ruthenium atom and polarisation functions for all other atoms: 6-31g(2d,p) – chlorine, $6-31g^{**}$ – carbon, nitrogen, oxygen, and 6-31g(d,p) – hydrogen. Natural bond orbital (NBO) calculations were performed using the NBO code [28] included in GAUSSIAN-03.

2.4. Crystal structure determination and refinement

A green prism of complex 1 and a white prism of 2 were mounted in turn on a KM-4-CCD automatic diffractometer equipped with a CCD detector, and were used for data



Fig. 6. Part of the molecular packing [(PPh₃)₂RuCl(CO)(C₉H₆O₂)].

collection. X-ray intensity data were collected with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at the temperature 295.0(3) K, with the ω scan mode. The Ewald sphere reflections were collected up to $2\theta = 50.0^{\circ}$ for both complexes. The unit cell parameters were determined from least-squares refinement of the setting angles of 7333 and 6860 strongest reflections for complexes 1 and 2, respectively. Details concerning the crystal data and refinement are gathered in Table 1. The reference frames, monitored every 40 measurement frames, show 1.01% decay for the crystal of compound 1 and no decay for the crystal of compound 2. During the data reduction of compound 1 a decay correction was taken into account. Lorentz, polarisation and numerical absorption [29] corrections were applied. The structures were solved using the Patterson method combined with a partial structure expansion procedure. All the non-hydrogen atoms were refined anisotropically using the full-matrix, least-squares technique on F^2 . The hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with an individual isotropic temperature factor equal to 1.2 times the value of the equivalent temperature factor of the parent atom. The H(1Ru) atom in complex 1 was placed in a calculated position (Ru–H distance 1.6 Å) according to similar compounds [30–36]. SHELXS97 [37], SHELXL97 [38] and SHELXTL [39] programs were used for all calculations. Atomic scattering factors had values incorporated in the computer programs.

3. Results and discussion

The reaction between the [RuHCl(CO)(PPh₃)₃] complex and 8-hydroxy-2-methyl-quinoline-7-carboxylic acid or quinoline-2-carboxylic acid in methanolic solution gives the mononuclear ruthenium(II) compounds [(PPh₃)₂RuH- $(CO)(C_{10}H_8NO_3)]$ (green, air-stable, crystalline solid) and $[(PPh_3)_2RuCl(CO)(C_9H_6O_2)]$ (white solid). Infrared spectra of the complexes exhibit characteristic bands of coordinated ligands – quinoline carboxylic acid, CO, PPh₃ and the hydride group.

The strong bands at 1938 and 1918 cm⁻¹ for complex 1 and 2, respectively, are assigned to the v_{CO} stretching vibrations of the ruthenium bonded carbonyl group, and the band at 1945 cm⁻¹ corresponds to v_{Ru-H} of the hydride ligand (complex 1). The v_{CO} and v_{Ru-H} stretching vibrations in the [RuHCl(CO)(PPh₃)₃] complex are at 2020 and 1903 cm⁻¹, respectively. The bands at 1610 and 1650 cm⁻¹ are attributed to the CN stretching vibration of the quinoline ligand. The asymmetric and symmetric v_{COO} stretching bands are at 1590, 1596 cm⁻¹ and 1378, 1348 cm⁻¹ for compounds 1 and 2, respectively.

The positions of the v_{CO} and v_{Ru-H} bands in the IR spectrum of complex 1 indicate a decrease of the metal–carbonyl carbon interaction and an increase of the Ru–H bond order. Taking into account the IR spectra of both complexes, the quinoline type ligand is a σ -donor that induces a large Ru–CO back-bonding.

3.1. Crystal structure

Both obtained complexes crystallise in the monoclinic space group $P2_1/n$. The crystal data of complexes 1 and 2 are given in Table 1. The molecular structures of 1 and 2 are presented in Figs. 1 and 2 (see Figs. 3, 4), respectively,

and molecular packing is depicted, receptively, in Figs. 5 and 6. The ruthenium atom in the complex $[(PPh_3)_2RuH-(CO)(C_{10}H_8NO_3)]$ is in a distorted octahedral environment with *trans*-triphenylphosphine ligands (angle P(1)–Ru(1)– P(2) 172.19(3)°). The carbonyl ligand is in a *trans*-position to the O donor atom (C(1)–Ru(1)–O(4) 178.12(11)°) and the hydrido ion lies *trans* to the coordinated nitrogen from the quinoline ligand – with an angle of 170.0°. The Ru–N bond distance is longer in complex 1 than in complex 2 due to the *trans* effect of the hydride ligand. The interatomic distances in the carbonyl and triphenylphosphine ligands are normal.

In the structure of compound **1** one very weak intramolecular O(4)–HO(3) hydrogen bond (D···A distance 2.554(3) Å and D–H···A angle 151.7°) and one very weak intermolecular C(40)–H(40)O(98) hydrogen bond (D···A distance 3.290(10) Å and D–H···A angle 139.5°) can be found.

The ruthenium atom of complex **2**, $[(PPh_3)_2RuCl(CO)-(C_9H_6O_2)]$, is also in a distorted octahedral environment with *cis*-triphenylphosphine ligands (angle P–Ru–P 99.28(2)°). The carbonyl ligand is in a *trans* position to the carboxylic O donor atom (O(2)–Ru–C(19) 174.95(9)°) and the chloride ion is *trans* to the P(2) atom -166.11(2)°. All Ru–ligand distances, namely Ru–Cl 2.4250(6), Ru–P 2.3763(7), 2.3861(7), Ru–N 2.169(2), Ru–C 1.826(3) and Ru–O 2.1035(16) Å, are normal and comparable with distances in other ruthenium complexes containing heterocyclic ligands.

Table 2

Selected bond lengths (Å) and angles (°) for $[(PPh_3)_2RuH(CO)(C_{10}H_8NO_3)]$ (1) and $[(PPh_3)_2RuCl(CO)(C_9H_6O_2)]$ (2)

	1			2	
	Experimental	Calculated		Experimental	Calculated
Bond lengths (Å)					
Ru(1)–C(1)	1.805(4)	1.806	Ru(1) - C(19)	1.826(3)	1.865
Ru(1)–O(4)	2.127(19)	2.126	Ru(1)-O(2)	2.1035(16)	2.108
Ru(1) - N(1)	2.221(3)	2.225	Ru(1) - N(1)	2.169(2)	2.243
Ru(1)–P(2)	2.355(8)	2.354	Ru(1) - P(2)	2.3861(7)	2.456
Ru(1) - P(1)	2.360(8)	2.361	Ru(1) - P(1)	2.3763(7)	2.438
Ru(1)-H(1Ru)	1.6042	1.604	Ru(1)-Cl(3)	2.4250(6)	2.458
C(1)–O(1)	1.231(4)	1.159	C(19)–O(1)	1.155(3)	1.164
Angles (°)					
C(1)-Ru(1)-O(4)	178.12(11)	178.14	C(19)-Ru(1)-O(2)	174.95(9)	178.18
C(1)-Ru(1)-N(1)	103.76(12)	103.67	N(1)-Ru(1)-C(19)	98.15(10)	101.67
O(4) - Ru(1) - N(1)	75.66(9)	75.83	O(2)-Ru(1)-N(1)	77.43(7)	76.57
C(1)-Ru(1)-P(2)	92.83(10)	92.87	P(1)-Ru(1)-C(19)	84.89(8)	87.79
O(4) - Ru(1) - P(2)	89.02(6)	88.97	P(1)-Ru(1)-O(2)	99.05(5)	94.03
N(1)-Ru(1)-P(2)	97.25(6)	97.33	N(1)-Ru(1)-P(1)	169.76(6)	163.87
C(1)-Ru(1)-P(1)	86.66(10)	86.68	C(19)-Ru(1)-P(2)	99.86(8)	97.02
O(4) - Ru(1) - P(1)	91.55(6)	91.53	O(2) - Ru(1) - P(2)	82.70(5)	82.57
N(1)-Ru(1)-P(1)	90.44(6)	90.44	N(1)-Ru(1)-P(2)	89.87(6)	90.77
P(2)-Ru(1)-P(1)	172.19(3)	172.10	P(2)-Ru(1)-P(1)	99.28(2)	101.11
C(1)-Ru(1)-H(1Ru)	85.4	85.30	C(19)-Ru(1)-Cl(3)	92.45(8)	93.27
O(4) - Ru(1) - H(1Ru)	95.1	95.09	O(2)-Ru(1)-Cl(3)	84.56(5)	86.92
N(1)-Ru(1)-H(1Ru)	170.0	170.21	N(1)-Ru(1)-Cl(3)	81.98(6)	80.28
P(2)-Ru(1)-H(1Ru)	86.1	85.99	P(1)-Ru(1)-Cl(3)	88.14(2)	86.21
P(1)-Ru(1)-H(1Ru)	86.1	86.12	P(2)-Ru(1)-Cl(3)	166.11(2)	167.56

The molecules in the crystal are connected by four very weak C–H···O intramolecular hydrogen bonds: C(12)– H(12)···O(2) (D···A distance 3.059(3) Å, D–H···A angle 120.0°), C(21)–H(21)···O(2) (D···A distance 3.074(3) Å, D–H···A 145.6°), C(6)–H(6)···Cl(3) (D···A distance 3.208(3) Å, D–H···A angle 108.90°) and C(43)– H(43)···O(1) (D···A distance 3.267(4) Å, D–H···A angle 132.6°).

3.2. Geometry optimisation

The geometries of the studied complexes were optimised by the DFT method with the B3LYP functional. The geometry parameters for the optimised complexes are gathered in Table 2. In general, the predicted bond lengths and angles are in agreement with the X-ray structural data. The largest difference is found for the C(1)–O(1) bond (~0.072 Å) (compound 1). The maximum differences between the optimised and experimental geometry of compound 2 are exhibited in the Ru(1)–N(1) distance (0.074 Å) and N(1)–Ru(1)–P(1) angle (5.9°).

3.3. Charge distribution and NBO analysis

The calculated charges on the ruthenium atom in the studied complexes are considerable lower than the formal charge of +2 and are close to -0.01 and 0.26 for 1 and 2, respectively. The charges on the P atoms are positive and close to 1.15 (1.20); the charge on the chloride ligand in [(PPh₃)₂RuCl(CO)(C₉H₆O₂)] is larger than -1 (-0.55), the charge on the quinoline carboxylic acid ligands is close to -0.64 for 1 and -0.52 for 2. The occupancies of the ruthenium d orbitals, obtained from the NBO analysis, are as follow: $d_{xy} - 1.73$; $d_{xz} - 1.84$; $d_{yz} - 1.21$; $d_{x^2-y^2} - 1.23$; $d_{z^2} - 1.61$ for [(PPh₃)₂RuH-(CO)(C₁₀H₈NO₃)] and $d_{xy} - 1.80$; $d_{xz} - 1.74$; $d_{yz} - 1.75$; $d_{x^2-y^2} - 1.13$; $d_{z^2} - 0.96$ for [(PPh₃)₂RuCl(CO)(C₉H₆O₂)].

The Ru–C bond orbitals in the two studied complexes are polarised towards the carbon atom, and the C \equiv O bond orbitals are polarised towards the oxygen end. The oxygen atoms of the carbonyl ligands have one lone pair (LP) orbital. The occupancies of the Ru–C bonds are (*anti*-bonding NBOs are given in round brackets)

Table 3

The energy and character of selected occupied and virtual MOs for $[(PPh_3)_2RuH(CO)(C_{10}H_8NO_3)]$ (1) and $[(PPh_3)_2RuCl(CO)(C_9H_6O_2)]$ (2)

	[(PPh ₃) ₂ RuH(CO)($[(PPh_3)_2RuH(CO)(C_{10}H_8NO_3)]$ (1)		$[(PPh_3)_2RuCl(CO)(C_9H_6O_2)]$ (2)	
	E (eV)	Character	E (eV)	Character	
HOMO – 20	-7.902	$\pi_{qu} + n_P$	-7.728	$\pi_{\rm Cl} + n_{\rm P}$	
HOMO - 19	-7.788	π_{qu}	-7.510	π_{Cl}	
HOMO - 18	-7.393	$\pi_{ m qu} + \sigma_{ m H}$	-7.282	π_{Ph}	
HOMO - 17	-7.306	$\pi_{\rm phosphine}$	-7.219	π_{Ph}	
HOMO - 16	-7.249	$\pi_{\text{phosphine}}$	-7.203	$\pi_{qu} + \pi_{Cl}$	
HOMO - 15	-7.200	π _{COOH}	-7.099	$\pi_{\rm Ph} + \pi_{\rm COO}$	
HOMO - 14	-7.067	π_{Ph}	-7.061	$\pi_{ m Cl} + \pi_{ m Ph}$	
HOMO - 13	-6.999	$\pi_{ m Ph}$	-7.040	$\pi_{COO} + d$	
HOMO - 12	-6.983	π_{Ph}	-6.949	π_{Ph}	
HOMO - 11	-6.966	π_{Ph}	-6.931	π_{Ph}	
HOMO - 10	-6.893	$\pi_{\rm Ph}$	-6.865	π_{Ph}	
HOMO – 9	-6.860	$\pi_{\rm Ph}$	-6.838	$\pi_{\rm Ph}$	
HOMO – 8	-6.787	$\pi_{\rm Ph}$	-6.819	$\pi_{\rm Ph}$	
HOMO - 7	-6.776	$\pi_{\rm Ph} + d + \pi_{\rm CO}$	-6.770	$\pi_{\rm Ph}$	
HOMO – 6	-6.708	$\pi_{\rm Ph} + d + \pi_{\rm CO}$	-6.721	π_{Ph}	
HOMO – 5	-6.669	$\pi_{\rm Ph} + d$	-6.675	$\pi_{\rm Ph} + d + \pi_{\rm CO}$	
HOMO – 4	-6.615	$\pi_{\rm Ph}$	-6.596	$\pi_{\rm Ph}$	
HOMO – 3	-6.400	$d + \pi_{CO} + n_P$	-6.588	$\pi_{\rm Ph} + d + \pi_{\rm CO}$	
HOMO - 2	-6.313	$d + \pi^*_{CO}$	-6.487	$\pi_{\rm Cl} + \pi_{\rm qu}$	
HOMO – 1	-5.886	$d + n_P$	-6.248	$d + \pi_{Cl}^* \pi_{Co}$	
НОМО	-5.255	$d + \pi^*_{au}$	-6.119	$d + \pi^*_{Cl}$	
LUMO	-1.567	π^*_{au}	-2.025	$\pi^*_{ m cm}$	
LUMO + 1	-0.838	$d_{z^2} + \pi^*_{au}$	-1.518	$d - \sigma_{Cl} - n_p$	
LUMO + 2	-0.759	$\pi_{au}^{+} + \pi_{Ph}^{+}$	-0.999	π^*_{au}	
LUMO + 3	-0.631	$d + \pi^*_{Ph}$	-0.882	$d + \pi^*_{au}$	
LUMO+4	-0.571	$d + \pi^*_{Ph}$	-0.811	$d + \pi_{Ph}^*$	
LUMO + 5	-0.484	π^*_{Ph}	-0.713	π^*_{Ph}	
LUMO + 6	-0.272	π^*_{Ph}	-0.555	π^*_{Ph}	
LUMO + 7	-0.179	π^*_{Ph}	-0.539	π^*_{Ph}	
LUMO + 8	-0.160	π^*_{Pb}	-0.433	$d + \pi^*_{CO} + \pi^*_{Ph}$	
LUMO + 9	-0.098	$\pi^*_{ m Ph}$	-0.248	$\mathrm{d}+\pi^*_\mathrm{CO}+\pi^*_\mathrm{Ph}$	
LUMO + 10	0.041	π^*_{Ph}	-0.218	$\pi^*_{ m Ph}+\pi^*_{ m CO}$	
LUMO + 11	0.065	π^*_{Ph}	-0.174	$\mathrm{d}+\pi^*_{\mathrm{CO}}+\pi^*_{\mathrm{Ph}}$	
LUMO + 12	0.201	$\mathrm{d}+\pi^*_{\mathrm{CO}}+\pi^*_{\mathrm{Ph}}$	-0.063	π^*_{Ph}	
LUMO + 13	0.234	$d+\pi^*_{CO}+\pi^*_{Ph}$	-0.052	π^*_{Ph}	

for complex 1: 1.976 (0.398) and for complex 2: 1.938 (0.272).

3.4. Electronic structure

The energies and characters of several highest occupied and lowest unoccupied molecular orbitals of the studied complexes are presented in Table 3. The HOMO-LUMO gaps of complexes 1 and 2 are 3.69 and 4.09 eV, respectively. In both cases, the ruthenium atom possesses a d⁶ configuration. The highest MO is d_{xz} with a contribution of the p_{π} antibonding orbitals from the quinoline ligand in the case of complex 1 and from the chlorine ligands of compound 2. The π_{Ru-CO} bonding interaction contribute in the H-2 and H-3 orbitals of compounds 1 and 2. The π_{Ru-CO}^* orbitals are also distributed among several unoccupied molecular orbitals. They contribute in L + 12, L + 13 (complex 1) and L + 9, L + 11 for 2. The LUMO orbitals are localised on the quinoline ring. The d_{z^2} orbital of the Ru atom



Fig. 7. The UV–Vis spectra of [(PPh₃)₂RuH(CO)(C₁₀H₈NO₃)]: (a) experimental; (b) calculated.

makes the largest contribution into L + 3, whereas the L + 4 molecular orbital has $d_{x^2-y^2}$ character in the studied complexes.

3.5. Electronic spectrum

The experimental and calculated electronic spectra of allowed singlet transitions, calculated with the TDDFT

method, are presented in Figs. 7 and 8, respectively, for complexes 1 and 2. The contour of the calculated spectrum was broadening by the Lorentzian function, calculated by the equation:

$$I = \frac{I_0}{1 + \left(\frac{\nu - \nu_0}{\gamma}\right)^2}; \text{ where }$$

 $\gamma = 1/2$ the spectral width at 1/2 height.



Fig. 8. The UV-Vis spectra of [(PPh₃)₂RuCl(CO)(C₉H₆O₂)]: (a) experimental; (b) calculated.

Hundred electronic transitions were calculated for the studied complexes using the DZVP with the f functions basis set on the ruthenium atom, and they do not comprise all the experimental absorption bands. The UV–Vis spectra were calculated up to ~ 225 nm, so the shortest wavelength experimental bands cannot be assigned to calculated transitions. However, considering that the solution spectra of PPh₃ and quinoline type ligands exhibit intense absorption bands in the 260–200 nm region, some additional intraligand and interligand transitions are expected to be found at higher energies in the calculations.

The assignments of the calculated transitions to the experimental bands are based on the criterion of the energy and oscillator strength of the calculated transitions. In the description of the electronic transitions only the main components of the molecular orbitals are taken into consideration.

The first experimental bands at 400 and 357 nm in $[(PPh_3)_2RuH(CO)(C_{10}H_8NO_3)]$ (1) and at 350.0 nm in $[(PPh_3)_2RuCl(CO)(C_9H_6O_2)]$ (2) consist of $d \rightarrow \pi^*_{qu}$ MLCT (Metal-Ligand Charge Transfer) transitions (HOMO/H-1 \rightarrow LUMO). The next bands with maxima at 332 and 280 nm for complex 1 and 283 nm for 2 were calculated as the $d \rightarrow d$ LF (Ligand Field) transitions with contributions of MLCT excitation between *d* ruthenium and $\pi^*_{phosphine/qu}$ orbitals. For the higher energy band (maximum at 238 nm) of complex 2, mainly intra- and interligand transitions are observed ($\pi_{qu} \rightarrow \pi^*_{Ph}$; $\pi_{qu} \rightarrow \pi^*_{qu}$; $\pi_{CI} \rightarrow \pi^*_{Ph}$; $\pi_{CO} \rightarrow \pi^*_{Ph}$; $\pi_{CO} \rightarrow \pi^*_{Ph}$; $\pi_{CO} \rightarrow \pi^*_{Ph}$; $\pi_{CO} \rightarrow \pi^*_{Ph}$, were not calculated but in the energy region some additional intraligand and interligand transitions are expected.

Acknowledgement

The crystallographic part was financed by funds allocated by the Ministry of Science and Higher Education to the Department of X-ray Crystallography and Crystal Chemistry, Institute of General and Ecological Chemistry, Technical University of Łódź.

Appendix A. Supplementary material

CCDC 649418 and 649903 contain the supplementary crystallographic data for **1** and **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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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