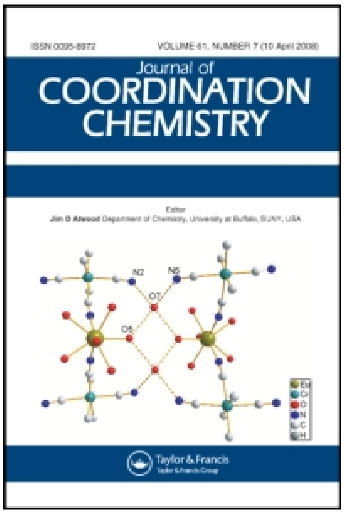

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# A new ruthenium(II) hydride carbonyl complex with pyrimidine ligand

J. G. MaŁecki[a]; R. Kruszynski[b]; Z. Mazurak[c]
[a] Department of Inorganic and Coordination Chemistry, Institute of Chemistry, University of Silesia, Katowice, Poland [b] X-Ray Crystallography Laboratory, Institute of General and Ecological Chemistry, Technical University of Łódź, Łódź, Poland [c] Polish Academy of Sciences, Centre of Polymer Chemistry, Zabrze, 41-819, Poland

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# A new ruthenium(II) hydride carbonyl complex with pyrimidine ligand

J. G. MAŁECKI*†, R. KRUSZYNSKI‡ and Z. MAZURAK§

†Department of Inorganic and Coordination Chemistry, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006, Katowice, Poland
‡X-Ray Crystallography Laboratory, Institute of General and Ecological Chemistry, Technical University of Łódź, 116 Żeromski St., 90-924, Łódź, Poland
§Polish Academy of Sciences, Centre of Polymer Chemistry, M. Sklodowskiej-Curie 34, Zabrze, 41-819, Poland

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The reaction of [RuHCl(CO)(PPh$_3$)$_3$] with pyrimidine gives [RuHCl(CO)(PPh$_3$)$_2$(C$_4$H$_4$N$_2$)]. The compound has been studied by IR, UV-Vis and X-ray crystallography. The molecular orbital diagram of the complex has been calculated with density functional theory (DFT). The spin-allowed singlet-singlet electronic transitions of the complex have been calculated with time-dependent DFT method, and the UV-Vis spectrum of the compound has been discussed on this basis. Emission of the compound was studied.

*Keywords*: Ruthenium hydride carbonyl complexes; Pyrimidine; X-ray structure; UV-Vis spectrum; Luminescence, DFT calculations

## 1. Introduction

Coordination chemistry of ruthenium complexes containing N-heterocyclic derivatives generates wide interest from rich redox chemistry and photophysics. Even small changes in coordination environment around ruthenium play a key role in altering the redox properties of its complexes such that complexation of ruthenium by different ligands is widely studied [1].

Ruthenium complexes containing N-heteroaromatic ligands have applications in conversion of solar energy to electrical energy [2], in long-range electron transfer and energy translocation [3], molecular electronic devices [4], supramolecular self-assembly processes [5] and as DNA photoprobes [6]. These compounds contain a delocalized $\pi$-electron system important in luminescent and redox-active compounds [7]. Ruthenium compounds containing pyridine derivatives and carbonyl groups have been extensively studied because of their high activity in the water–gas shift reaction

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*Corresponding author. Email: gmalecki@us.edu.pl

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and in the reduction of carbon dioxide [8]. Thus, exploration of such complexes as model species has importance [9].

In this paper we present the synthesis, molecular and electronic structure of a new hydridocarbonyl ruthenium(II) complex with pyrimidine and triphenylphosphine ligands. The molecular orbital diagram of the examined complex has been calculated with density functional theory (DFT). Density functional theory (DFT) is commonly used to examine the electronic structure of transition metal complexes, being accurate, easy to use and fast enough to allow the study of relatively large transition metal complexes [10]. The spin-allowed singlet-singlet electronic transitions of $[RuHCl(CO)(PPh_3)_2(C_4H_4N_2)]$ have been calculated with time-dependent DFT method (TDDFT method), and agreement with the experimental spectrum has been observed.

## 2. Experimental

All reagents used in the synthesis of the complex are commercially available and were used without further purification.

Table 1. Crystal data and structure refinement details of $[RuHCl(CO)(C_4H_4N_2)(PPh_3)_2]$.

| | |
|---|---|
| Empirical formula | $C_{41}H_{35}C_lN_2OP_2Ru$ |
| Formula weight | 770.17 |
| Temperature (K) | 291.0(3) |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions (Å, °) | |
| $a$ (Å) | 15.800(2) |
| $b$ (Å) | 13.921(10) |
| $c$ (Å) | 16.221(2) |
| $\beta$ (Å) | 96.638(12) |
| Volume (Å$^3$) | 3566.20(7) |
| $Z$ | 4 |
| Calculated density (Mg m$^{-3}$) | 1.434 |
| Absorption coefficient (mm$^{-1}$) | 0.640 |
| $F(000)$ | 1576 |
| Crystal dimensions (mm$^3$) | $0.211 \times 0.203 \times 0.030$ |
| $\theta$ range for data collection (°) | 1.70 to 25.05 |
| Index ranges | $-18 \leq h \leq 18$<br>$-14 \leq k \leq 16$<br>$-19 \leq l \leq 19$ |
| Reflections collected | 35444 |
| Independent reflections | 6317 ($R_{(int)} = 0.0200$) |
| Data/restraints/parameters | 6317/0/433 |
| Goodness-of-fit on $F^2$ | 1.154 |
| Final $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.0223$<br>$wR_2 = 0.0674$ |
| $R$ indices (all data) | $R_1 = 0.0337$<br>$wR_2 = 0.0808$ |
| Largest diff. Peak and hole (e Å$^{-3}$) | 0.312 and $-0.435$ |

### 2.1. *Physical measurements*

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 $\mathrm{cm^{-1}}$ on KBr pellets. Electronic spectra were measured on a spectrophotometer Lab Alliance UV-Vis 8500 in the range 800–200 nm in dichloromethane. Elemental analyses (C, H, N) were performed on a Perkin-Elmer CHN–2400 analyzer. Luminescence measurements were made on a Jobin-Yvon (SPEX) FLUOROLOG-3.12 spectrofluorometer at room temperature.

### 2.2. *Synthesis of [RuHCl(CO)(PPh$_3$)$_2$(C$_4$H$_4$N$_2$)]*

A suspension of [RuHCl(CO)(PPh$_3$)$_3$] (0.95 g; $1 \times 10^{-3}$ mol) and pyrimidine (0.16 g; $2 \times 10^{-3}$ mol) in methanol (100 $\mathrm{cm^3}$) was refluxed until the solid dissolved, cooled and filtered. Orange crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the filtrate. Yield 83%.

Anal. Calcd for $C_{41}H_{35}ClN_2OP_2Ru$: C, 63.94%; H, 4.58%; N, 3.64%. Found: C, 64.04%; H, 4.51%; N, 3.69%.

IR (KBr) [$\mathrm{cm^{-1}}$]: 3053 $\nu_{\mathrm{CH-pyrimidine}}$; 2027 $\nu_{\mathrm{Ru-H}}$; 1921 $\nu_{\mathrm{CO}}$; 1581 $\nu_{\mathrm{CN}}$; 1479 $\delta_{(\mathrm{C-CH\ in\ the\ plane})}$; 1432 $\nu_{\mathrm{Ph(P-Ph)}}$; 1093 $\delta_{(\mathrm{C-CH\ in\ the\ plane})}$; 1000 $\delta_{(\mathrm{C-C\ out\ of\ the\ plane})}$; 746 $\delta_{(\mathrm{C-C\ out\ of\ the\ plane})}$; 696 $\delta_{(\mathrm{C-C\ in\ the\ plane})}$; 604 $\nu_{\mathrm{P-Ph}}$.

UV-Vis (dichloromethane) [nm] (log $\varepsilon$): 332.1 (1.71), 282.0 (sh), 265.7 (sh), 235.4 (3.01), 210.7 (3.59).

### 2.3. *Crystal structure determination and refinement*

A dark yellow plate of the complex was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector used for data collection. X-ray intensity data were collected with graphite monochromated Mo-K$\alpha$ ($\lambda = 0.71073$ Å) at 291.0(3) K, with $\omega$ scan mode. All the reflections inside Ewald sphere were collected up to $2\theta = 50.10°$. Unit cell parameters were determined from least-squares refinement of the setting angles of the 9227 strongest reflections. Details concerning crystal data and refinement are given in table 1. Monitoring of 18 reflection intensities on two reference frames measured every 40 frames show 0.03% decay of intensity. During the data reduction above decay correction coefficient was taken into account. Lorentz, polarization, and numerical absorption [11] corrections were applied. The structure was solved by the Patterson method combined with partial structure expansion procedure. All the non-hydrogen atoms were refined anisotropically using 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 individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent atom with geometry idealization after each cycle. SHELXS97 [12], SHELXL97 [13] and SHELXTL [14] were used for all calculations. Atomic scattering factors were those incorporated in the computer programs.

## 3. Results and discussion

Refluxing $[RuHCl(CO)(PPh_3)_3]$ with pyrimidine in methanol leads to $[RuHCl(CO)(PPh_3)_2(C_4H_4N_2)]$ in good yield. Elemental analysis of the complex is in good agreement with its formulation. IR spectra of the complexes are consistent with its structure. The C≡O and C=N stretching bands are observed at 1921 and $1581\,cm^{-1}$, respectively. The $\nu_{Ph(P-Ph)}$ absorption at $1432\,cm^{-1}$ indicates triphenylphosphine ligands. The Ru–H stretching mode is visible at $2027\,cm^{-1}$. The values $\nu_{Ru-H}$ and $\nu_{CO}$ are close to the parent $[RuHCl(CO)(PPh_3)_3]$ complex – 2020 and $1903\,cm^{-1}$, respectively. The changing of the position of $\nu_{Ru-H}$ and $\nu_{Ru-CO}$ indicates small decrease in the metal-carbonyl carbon interaction and an increase in the Ru–H bond order.

### 3.1. *Crystal structures*

$[RuHCl(CO)(PPh_3)_2(C_4H_4N_2)]$ crystallizes in the monoclinic $P2_1/n$ group. The crystal data of the complex are given in table 1 and the molecular structure is presented in figure 1. The most important angles and bond lengths are reported in table 2.

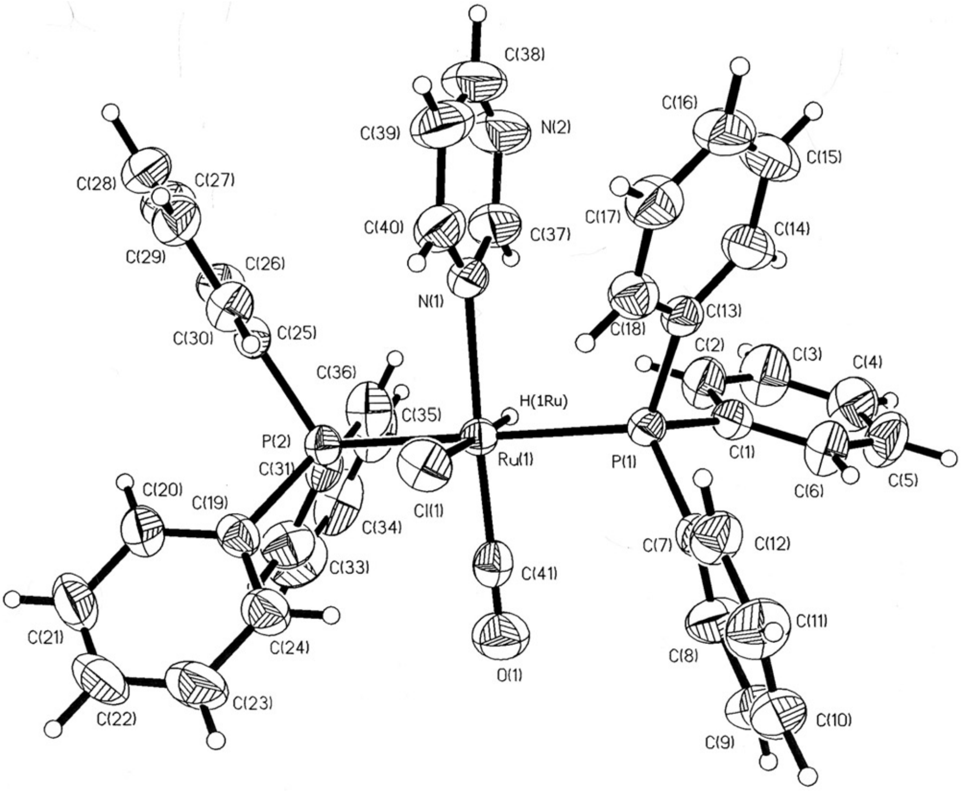

Figure 1. The ORTEP plot of $[RuHCl(CO)(C_4H_4N_2)(PPh_3)_2]$. The displacement ellipsoids are drawn with 50% probability.

The ruthenium is in a distorted octahedral environment with *trans* triphenylphosphines (angle P–Ru–P 175.60(2)°). The carbonyl is *trans* to pyrimidine (C–Ru–N 171.36(8)°) and the chloride ion lies *trans* to hydride (178.3°). The Ru–Cl distance (2.532(6) Å) is longer than the typical ruthenium-chloride distance due to the *trans* effect of hydride. The Ru–C bond distance (1.866(3) Å) is normal for a monomeric Ru(II) carbonyl complex (the distances generally range from 1.74 to 1.98 Å) [16]. The Ru–P, Ru–N and Ru–C distances are normal and comparable with distances in other ruthenium complexes containing heterocyclic ligands. The C(41)–O(1) bond show some shortening in comparison with typical distances in CO substituents, but similar distances can be found in several compounds [17–28]. The conformation of the molecule is stabilized by three weak intramolecular hydrogen bonds, linking phenyl phosphine CH and Cl ligand.

### 3.2. *Geometry optimization*

The geometry was optimized by DFT with the B3LYP functional. The optimized geometry parameters are given in table 2 and the relative orientation of the optimized and experimental molecules are presented in figure 2. 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 well reproduced in the calculations. The calculated bond lengths and angles for [$RuCl(CO)(PPh_3)_2(C_4H_4N_2)$] agree with the experimental, the largest difference found for the Ru(1)–H(Ru1) bond (0.12 Å). The maximum difference between the calculated and experimental angles is for Cl(1)–Ru(1)–H(1Ru), close to 4.7°.

Table 2. Selected bond lengths (Å) and angles (°) for [$RuHCl(CO)(C_4H_4N_2)(PPh_3)_2$].

| | Emperimental | Calculated |
|---|---|---|
| Ru(1)–C(41) | 1.866(3) | 1.854 |
| Ru(1)–N(1) | 2.212(19) | 2.271 |
| Ru(1)–P(1) | 2.372(6) | 2.439 |
| Ru(1)–P(2) | 2.351(6) | 2.426 |
| Ru(1)–Cl(1) | 2.532(6) | 2.594 |
| Ru(1)–H(1Ru) | 1.718 | 1.606 |
| C(41)–O(1) | 1.095(3) | 1.164 |
| C(41)–Ru(1)–N(1) | 171.36(8) | 169.82 |
| C(41)–Ru(1)–P(1) | 91.36(8) | 90.37 |
| N(1)–Ru(1)–P(1) | 88.61(5) | 90.71 |
| C(41)–Ru(1)–P(2) | 87.78(8) | 87.85 |
| N(1)–Ru(1)–P(2) | 91.59(5) | 90.89 |
| P(1)–Ru(1)–P(2) | 175.60(2) | 178.01 |
| C(41)–Ru(1)–Cl(1) | 97.97(7) | 101.45 |
| N(1)–Ru(1)–Cl(1) | 90.67(5) | 88.68 |
| P(1)–Ru(1)–Cl(1) | 90.68(2) | 89.60 |
| P(2)–Ru(1)–Cl(1) | 93.71(2) | 91.63 |
| C(41)–Ru(1)–H(1Ru) | 83.4 | 84.93 |
| P(1)–Ru(1)–H(1Ru) | 90.2 | 91.08 |
| P(2)–Ru(1)–H(1Ru) | 85.4 | 87.88 |
| N(1)–Ru(1)–H(1Ru) | 87.9 | 84.93 |
| Cl(1)–Ru(1)–H(1Ru) | 178.3 | 173.58 |

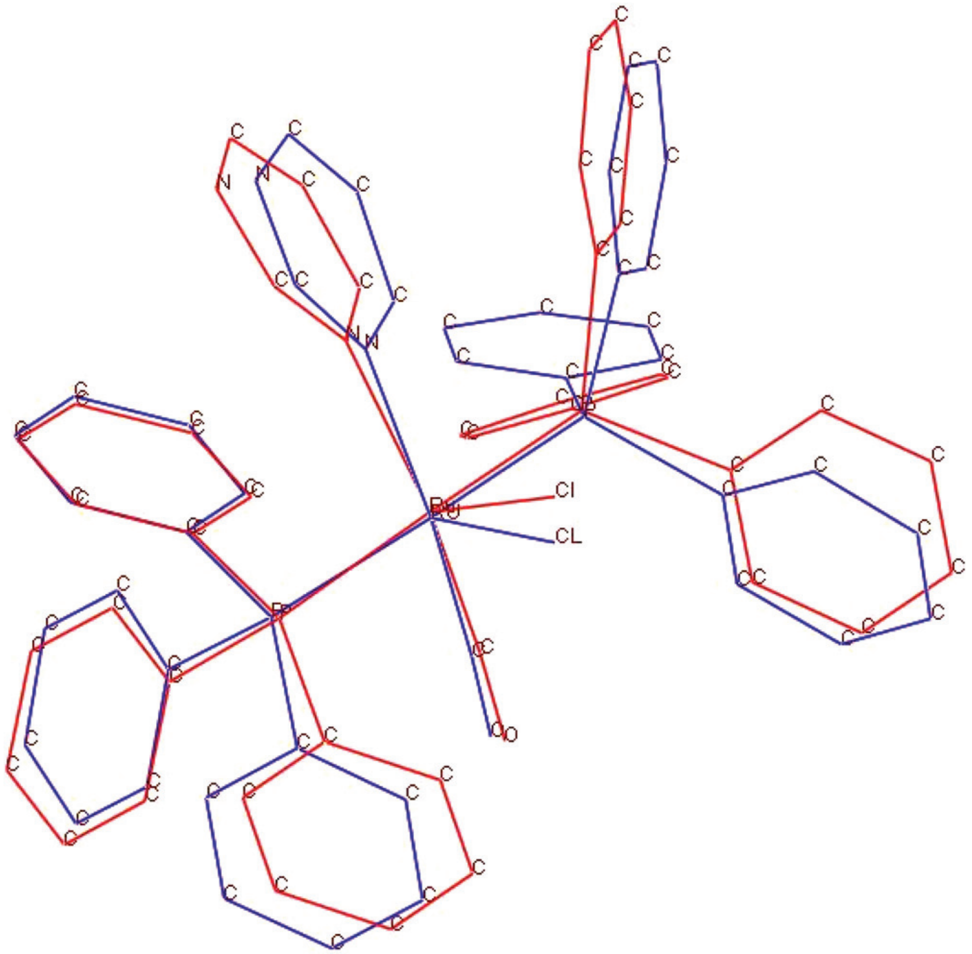

Figure 2. Relative orientation of the experimental (blue) and optimized (red) molecules of $[RuHCl(CO)(C_4H_4N_2)(PPh_3)_2]$.

### 3.3. *Charge distribution and electronic structure*

The calculated charges on the ruthenium atom in the $[RuHCl(CO)(PPh_3)_2(C_4H_4N_2)]$ complex is considerably lower than the formal charge of +2, close to 0 (−0.09). Charges on the P atoms are positive (~1.15); the charge on the chloride is −0.7; the charge on the pyrimidine is 0.12. The occupancy of the ruthenium *d* orbitals, obtained from NBO analysis, is $d_{xy}$ (1.73), $d_{xz}$ (1.93), $d_{yz}$ (1.77), $d_{x^2-y^2}$ (1.05) and $d_{z^2}$ (1.22).

The occupied $d_{xy}$ and $d_{xz}$ ruthenium orbitals participate in backdonation from Ru to the carbonyl. The largest contribution of the $\pi_{Ru-CO}$ bonding interaction is from H-1. The $\pi^*_{Ru-CO}$ orbitals are distributed among several unoccupied molecular orbitals, L+7, L+10 and L+14. The HOMO of $[RuHCl(CO)(PPh_3)_2(C_4H_4N_2)]$ is composed of the $d_{xz}$ metal orbital with the antibonding contribution of the $\pi$ orbital of chloride ligand. The LUMO is localized on the pyrimidine ring. The $d_{z^2}$ orbital of Ru makes the largest contribution into L+2, and L+5, L+10 have $d_{x^2-y^2}$ character.

Table 3. Energy and character of selected MOs of $[RuHCl(CO)(C_4H_4N_2)(PPh_3)_2]$.

| MO | Energy | Character |
|---|---|---|
| H-14 | −7,10495 | $\pi_{\text{phosphine}} + \pi_{\text{Cl}}$ |
| H-13 | −7,0342 | $\pi_{\text{phosphine}} + \pi_{\text{Cl}}$ |
| H-12 | −6,97978 | $\pi_{\text{phosphine}} + \pi_{\text{Cl}}$ |
| H-11 | −6,92535 | $\pi_{\text{phosphine}} + \pi_{\text{Cl}}$ |
| H-10 | −6,86277 | $\pi_{\text{phosphine}}$ |
| H-9 | −6,84644 | $\pi_{\text{phosphine}}$ |
| H-8 | −6,83828 | $\pi_{\text{phosphine}}$ |
| H-7 | −6,78657 | $\pi_{\text{phosphine}}$ |
| H-6 | −6,75936 | $\pi_{\text{phosphine}}$ |
| H-5 | −6,7131 | $\pi_{\text{phosphine}} + \sigma_{\text{H}}$ |
| H-4 | −6,63691 | $\pi_{\text{phosphine}}$ |
| H-3 | −6,50085 | $d_{xy} + n_{\text{P}} + \pi^*{}_{\text{Cl}}$ |
| H-2 | −6,15799 | $d_{xz} + n_{\text{P}} + \pi^*{}_{\text{Cl}}$ |
| H-1 | −5,91308 | $d_{xz} + \pi_{\text{CO}} + \pi^*{}_{\text{Cl}}$ |
| H | −5,66273 | $d_{xz} + \pi^*{}_{\text{Cl}}$ |
| L | −1,46398 | $\pi^*{}_{\text{pyrimidine}}$ |
| L+1 | −1,1184 | $\pi^*{}_{\text{pyrimidine}}$ |
| L+2 | −0,93336 | $d_z^2 + \pi^*{}_{\text{pyrimidine}} + \pi^*{}_{\text{phosphine}}$ |
| L+3 | −0,73743 | $\pi^*{}_{\text{phosphine}}$ |
| L+4 | −0,65308 | $\pi^*{}_{\text{phosphine}}$ |
| L+5 | −0,53607 | $\pi^*{}_{\text{phosphine}} + d_{x^2-y^2}$ |
| L+6 | −0,45715 | $\pi^*{}_{\text{phosphine}}$ |
| L+7 | −0,35103 | $\pi^*{}_{\text{phosphine}} + \pi^*{}_{\text{CO}}$ |
| L+8 | −0,283 | $\pi^*{}_{\text{phosphine}}$ |
| L+9 | −0,2313 | $\pi^*{}_{\text{phosphine}}$ |
| L+10 | −0,11701 | $d_{x^2-y^2} + \pi^*{}_{\text{phosphine}} + \pi^*{}_{\text{CO}}$ |
| L+11 | 0,013606 | $\pi^*{}_{\text{phosphine}}$ |
| L+12 | 0,048981 | $\pi^*{}_{\text{phosphine}}$ |
| L+13 | 0,108846 | $\pi^*{}_{\text{phosphine}} + \pi^*{}_{\text{pyrimidine}}$ |
| L+14 | 0,144221 | $d_{x^2-y^2} + \pi^*{}_{\text{phosphine}} + \pi^*{}_{\text{CO}}$ |

In some of the lowest unoccupied molecular orbitals of $[RuHCl(CO)(PPh_3)_2(C_4H_4N_2)]$, the contribution of the phosphorus orbitals is visible (L+3, L+4, L+5). In classical concepts empty phosphorus 3d orbitals are used in $\pi$-back bonding between metal center and phosphine ligand. It is generally recognized that d orbitals have very high energy and play only a minor role in $\pi_{\text{M–PR3}}$ bond formation [29]. In the $\pi$-back bonding between metal center and phosphine ligand, the $\sigma^*$(P–C) orbitals are involved. The HOMO–LUMO gap is 4.20 eV. The energy and character of the selected frontier molecular orbitals are given in table 3.

### 3.4. *Electronic spectrum*

The experimental and calculated electronic spectra of $[RuHCl(CO)(PPh_3)_2(C_4H_4N_2)]$ are presented in figure 3. The contour of the calculated spectrum was broadened by Lorentzian function calculated by:

$$I = \frac{I_0}{1 + ((\nu - \nu_0)/\gamma)^2}$$

where $\gamma = 1/2$ of spectral width on 1/2 height.

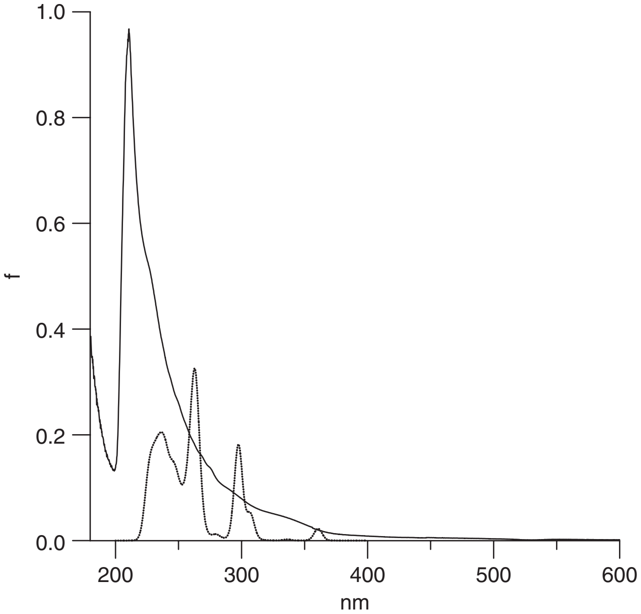

Figure 3. The UV-Vis spectra of [$RuHCl(CO)(C_4H_4N_2)(PPh_3)_2$] solid line – experimental; dashed line – calculated.

One hundred electronic transitions were calculated using the TDDFT method (PCM model with dichloromethane as the solvent was used in the calculations) and they do not comprise all the experimental absorption bands. The UV-Vis spectrum was calculated up to 220 nm, so the shortest wavelength experimental bands cannot be assigned to the calculated transitions. However, considering that the solution spectra of $PPh_3$ and pyrimidine 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 electronic transitions only the main components of the molecular orbital are taken into consideration. The first calculated transition was at 361.3 nm. The experimental bands start at this wavelength. The transition is HOMO to LUMO, and as the LUMO is composed of the $\pi^*$ orbitals of the pyrimidine the transition is *Metal–Ligand Charge Transfer*.

The shoulders at 282.0 and 265.7 nm are ascribed to the metal-ligand charge transfer transitions ($d \rightarrow \pi^*_{PPh3}$ and $d \rightarrow \pi^*_{pyrimidine}$). In this region transitions between HOMO, HOMO-2 and HOMO-3 to LUMO+1, LUMO+2 and LUMO+3 were calculated. Because the LUMO+2 is composed from ruthenium d orbital with an antibonding admixture of $\pi$ phosphine and pyrimidine orbitals in these shoulders the $d \rightarrow d$ transitions participate.

The last calculated transition attributed to the experimental one at 235.4 nm proceeds mainly from the d ruthenium orbitals with admixture of $\pi$ chloride $\pi^*_{Ph}$ and $\pi^*_{pyrimidine}$ giving *Ligand–ligand Charge Transfer* transitions ($\pi_{PPh3} \rightarrow \pi^*_{pyrimidine}$) and the

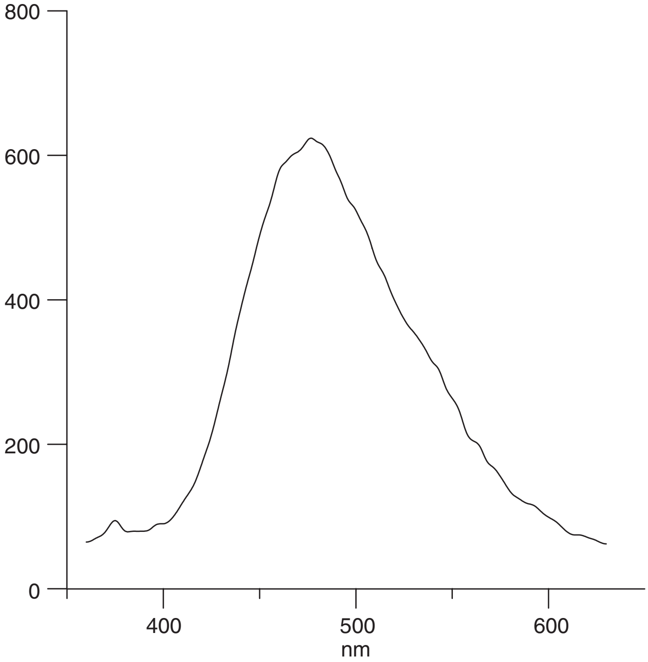

Figure 4. The emission spectrum of [RuHCl(CO)($C_4H_4N_2$)($PPh_3$)$_2$].

intraligand transitions $\pi_{PPh3} \rightarrow \pi^*_{PPh3}$. The experimental band at 210.7 nm could not be assigned on the basis of the calculated transitions; it can be assumed that the band results from transitions in the $PPh_3$ ligands and from $\pi \rightarrow \pi^*$ excitations in the pyrimidine ligand.

The differences between experimental and calculated UV-Vis spectra of the complex follow from the known failure (only the transitions of energies smaller than the energy of HOMO orbital are well reproduced by this method) of the TDDFT method to describe CT transitions [30–34].

Emission of the studied complex has been examined in dichloromethane at room temperature. The luminescence spectrum was presented in figure 4. On excitation at 385 nm the emission peak was observed at 476 nm, independent of concentration of the solution. The emission originates from the lowest energy metal to ligand charge transfer (MLCT) state, derived from the excitation involving a $d_\pi \rightarrow \pi^*_{pyrimidine}$ transition.

## 4. Conclusions

The new hydrido carbonyl ruthenium complex with pyrimidine ligand has been synthesized and characterized by IR and UV-Vis spectra. The complex crystallizes in the monoclinic space $P2_1/n$ group. The electronic spectrum of [RuHCl(CO)($PPh_3$)$_2$($C_4H_4N_2$)] was calculated by the TDDFT method. Luminescence of the complex was examined with emission at 476 nm observed.

## Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request quoting deposition number CCDC 648744.

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