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# Synthesis, spectroscopic and structural characterization of new complex of ruthenium(II) with Hmtpo ligand

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# ABSTRACT

The [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)] complex has been prepared and studied by IR, NMR, UV–VIS spectroscopy and X-ray crystallography. The complex was prepared in reactions of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] with 7-hydroxy-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine in methanol. The electronic structure and UV–Vis spectrum of the obtained compound have been calculated using the TD–DFT method.

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# 1. Introduction

In the chemistry of ruthenium, the coordination chemistry of complexes containing *N*-heterocyclic derivatives is one of the most studied aspects. The wide interest is this field originates form very rich redox chemistry and photophysics of these compounds. Even small changes in coordination environment around ruthenium plays a key role in altering the redox properties of its complexes and thus complexation of ruthenium by different ligands is very interesting and been widely studied [1–7].

The ruthenium carbonyl and hydride complexes are very interesting due to their catalytic and structural properties. On the other hand the triazolopyrimidine derivatives are examples of purine mimics and 7-hydroxy-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (Hmtpo) is a good sample among these derivatives. The studied compound merge the benefits of ruthenium coordination compounds and complexes containing Hmtpo and carbonyl group, thus their synthesis and determination of properties was undertaken. In the paper, we present the synthesis, crystal, molecular and electronic structures and the spectroscopy characterization of the new carbonyl ruthenium(II) complex.

# 2. Experimental

## 2.1. Physical measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range of 4000–400 cm<sup>1</sup> with the sample in the form of KBr pellet. Electronic spectra were measured on a Lab Alliance UV–VIS 8500 spectrophotometer in the range of 800–200 nm in dichloromethane solution. Elemental analyses (C, H, N) were performed on a Perkin–Elemer CHN-2400 analyzer. The <sup>1</sup>H NMR spectrum was obtained at room temperature in CDCl<sub>3</sub> using INOVA 300 spectrometer.

All reagents used for the synthesis of the complex are commercially available and were used without further purification. The [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] complex was synthesized using a literature method [8].

# 2.2. Synthesis of [RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(Hmtpo)]

A suspension of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.95 g;  $1 \times 10^{-3}$  mol) and 7hydroxy-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (Hmtpo) (0.30 g;  $2 \times 10^{-3}$  mol) in methanol (100 cm<sup>-3</sup>) was refluxed until the solid dissolved, cooled and filtered. The crystals suitable for X-ray crystal analysis were obtained by slow evaporation the reaction mixture. Yield 79%.

*Anal.* Calc. for C<sub>44</sub>H<sub>40</sub>ClN<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 61.79; H, 4.71; Cl, 4.15; N, 6.55; O, 3.74; P, 7.24; Ru, 11.82. Found: C, 62.01; H, 4.63; N, 6.66%.



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<sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): -10.74 (t, Ru-H); 7.05-7.71 (m, PPh<sub>3</sub>); 8.42 (Hmtpo); 6.92 (Hmtpo); 2.01 (Hmtpo). <sup>31</sup>P NMR (δ, CDCl<sub>3</sub>): 43.87 (s, PPh<sub>3</sub>).

UV-VIS (nm) in acetonitrile: 267.5; 209.0.

#### 2.3. DFT calculations

GAUSSIAN-03 program [9] was used for the calculations. The geometry optimization was carried out using the DFT method with the B3LYP functional [10,11]. The electronic transitions were calculated with the PCM model [12] in the acetonitrile solution as the solvent. The calculation was performed using the DZVP basis set [13] with f functions with exponents 1.94722036 and 0.748930908 on ruthenium atom, and polarization functions for all other atoms: 6-31 g(2d,p) – chlorine,  $6-31 \text{ g}^{**}$  – carbon, nitrogen, oxygen, and 6-31 g(d,p) – hydrogen. Natural bond orbital (NBO) calculations were performed using the NBO code [14] included in GAUSSIAN-03.

#### 2.4. Crystal structure determination and refinement

A yellow prism of [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)] was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo  $K\alpha$  radiation  $(\lambda = 0.71073 \text{ Å})$  at temperature 291.0(3) K, with  $\omega$  scan mode. The full Ewald sphere reflections were collected up to  $2\theta = 50.0^{\circ}$ . The unit cell parameters have been determined basing on leastsquares refinement of the setting angles of 7026 strongest reflections. Details concerning crystal data and refinement are given in Table 1. During the data reduction a decay correction coefficient has been taken into account. Lorentz, polarization, and numerical absorption [15] corrections have been applied. The structure has been solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on  $F^2$ . The carbon bonded hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement,

#### Table 1

Crystal data and structure refinement details of [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)].

	1
Empirical formula	C43H37ClN4O2P2Ru
Formula weight	840.23
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	18.0095(7)
b (Å)	20.3436(7)
c (Å)	10.9748(4)
β	102.388(4)
Volume (Å <sup>3</sup> )	3927.3(3)
Ζ	4
Calculated density (Mg/m <sup>3</sup> )	1.431
Absorption coefficient (mm <sup>-1</sup> )	0.591
F (0 0 0)	1744
Crystal dimensions (mm)	$0.16 \times 0.16 \times 0.16$
$\theta$ Range for data collection (°)	2.84-25.00
Index ranges	$-21\leqslant h\leqslant 20$
	$-22\leqslant k\leqslant 24$
	$-13 \leqslant l \leqslant 10$
Reflections collected	6880
Independent reflections	4919 ( $R_{int} = 0.0277$ )
Data/restraints/parameters	4919/0/480
Goodness-of-fit (GOF) on F <sup>2</sup>	0.911
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0277$
	$wR_2 = 0.0658$
R indices (all data)	$R_1 = 0.0470$
	$wR_2 = 0.0687$
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.556 and -0.388

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. The H(1R) atom has been placed in calculated position (Ru–H distance 1.6 Å) according to similar structures. SHELXS97, SHELXL97 [16] and SHELXTL [17] programs have been used for all calculations. Atomic scattering factors had values incorporated in the computer programs.

#### 3. Results and discussion

The reactions of the ruthenium(II) carbonyl hydride complex [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] with 7-hydroxy-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (Hmtpo) has been performed. Refluxing the [RuHCl(-CO)(PPh<sub>3</sub>)<sub>3</sub>] complex with the ligand in methanol leads to [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)] complex with good yields. Elemental analysis of the compound is in a good agreement with their formula. Infrared spectrum of the complex exhibit characteristic bands due to ligand rings vibrations. The  $v_{C=N}$  band appears around 1611 cm<sup>-1</sup>. The  $v_{Ru-H}$  with  $v_{C=O}$  band in this compound appears around 1967 cm<sup>-1</sup>. More details are given in Table 2. The  $v_{CO}$  and  $v_{Ru-H}$  stretching vibration in the [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] complex are at 2020 and 1903 cm<sup>-1</sup>, respectively. The positions of the  $v_{CO}$  and  $v_{Ru-H}$  bands in the IR spectrum of the studied complex indicate a decrease of the metal – carbonyl carbon interaction and an increase of the Ru–H bond order.

The <sup>1</sup>H NMR contains a triplet at -10.736 ppm, resulting from hydrido ligand coordinated to ruthenium. The Hmtpo and triphenylphosphine ligands have given the signals at 8.418, 6.921, 2,005 and 7.049–7.710 ppm, respectively. The singlet at 43.871 ppm in the <sup>31</sup>P NMR spectrum indicated both the triphenylphosphoine ligands in the studied complex are equivalent and are mutually *trans* disposed.

Studied compound crystallize in monoclinic  $P_{2,1}/c$  space group. The molecular structure of the complex is shown in Fig. 1 (structural drawing is presented in Fig. 2). The selected bond lengths and angles with the calculated values are listed in Table 3. The ruthenium atom has a distorted octahedral environment with the *trans* triphenylphosphine ligands (angle P–Ru–P 170.05(2)°). The N donor atom of 7-hydroxy-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine is in *trans* positions to carbonyl (C(27)–Ru(1)–O(1) 175.94(9)°) and *cis* to hydride (N(1)–Ru(1)–H(1Ru) 85.7°) ligands. The Ru–Cl distance (2.557(6) Å) is longer than the typical ruthenium–chloride distances are normal and comparable with distances in other ruthenium complexes containing the heterocyclic ligands.

The two intermolecular hydrogen bond [18–20] linking the OH group of 7-hydroxy-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine and

Table 2			
The vibrational	spectrum	of studied	compound.

Assignment	
O–H str	3278
Alkyl group C–H str	3058
Ru–H str + C=O str	1967
Phenyl ring C=C str + C=N str	1611, 1521
Phenyl ring C–H bend	1481
Alkyl group C–H bend	1434, 1027
Phenyl ring C–H bend	1344
All C–H bend	1090
Phenyl ring C=C str	899
Phenyl ring C–H twist	848, 828
Phenyl ring C=C str	743
Phenyl ring C-H twist	695
Skeleton deformation	619



Fig. 1. ORTEP drawing of [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)] with 50% probability thermal ellipsoids.



Fig. 2. Structural drawing of [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)].

# Table 3 Selected bond lengths (Å) and angles (°) for [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)].

	Experimental	Calculated
Bond lengths (Å)		
Ru(1)-C(43)	1.818(3)	1.815
Ru(1)-Cl(1)	2.557(6)	2.557
Ru(1)-N(1)	2.177(19)	2.177
Ru(1)-P(2)	2.348(7)	2.344
Ru(1)–P(1)	2.376(6)	2.372
Ru(1)–H1(Ru)	1.588	1.368
C(43)-O(1)	1.155(3)	1.155
Angles (°)		
C(43)-Ru(1)-P(2)	88.40(8)	89.4
C(43)-Ru(1)-N(1)	175.94(9)	168.0
N(1)-Ru(1)-P(2)	91.18(5)	91.0
C(43)-Ru(1)-P(1)	93.80(8)	90.6
N(1)-Ru(1)-P(1)	85.94(5)	89.0
P(2)-Ru(1)-P(1)	170.05(2)	180.0
C(43)-Ru(1)-Cl(1)	90.32(8)	99.6
N(1)-Ru(1)-Cl(1)	93.73(5)	92.3
P(2)-Ru(1)-Cl(1)	96.37(2)	92.8
P(1)-Ru(1)-Cl(1)	93.33(2)	87.2
C(43)-Ru(1)-H(1Ru)	90.2	99.6
Cl(1)-Ru(1)-H(1Ru)	179.0	174.1
N(1)-Ru(1)-H(1Ru)	85.7	85.9
P(2)-Ru(1)-H(1Ru)	84.4	89.5
P(1)-Ru(1)-H(1Ru)	85.8	90.5

Table 4

Hyc	drogen	bonds in	$[(PPh_3)_2]$	RuHCl	CO)(Hm	itpo)]. l	Distances	are in	(A) an	id ang	les a	ire in
(°).												

D−H···A	<i>d</i> (D–H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	<(DHA)
$\begin{array}{c} C(5)-H(5)\cdots O(2)\#1\\ C(29)-H(29)\cdots O(2)\#2\\ C(39)-H(39)\cdots O(1)\#3 \end{array}$	0.93	2.48	3.377(4)	161.4
	0.93	2.33	3.181(4)	152.6
	0.93	2.51	3.125(3)	124.3

Symmetry operators used to generate equivalent atoms: **#1** x, 5/2 - y, 1/2 + z; **#2** 2 - x, 2 - y, -z; **#3** x, y, -1 + z.

phenyl from triphenylophosphine ligands and one between carbonyl and pyrimidine ligand are being observed (see Table 4).

### 3.1. Optimized geometries

The geometry of the studied complex has been optimized in singlet states using the DFT method with the B3LYP functional. The optimized geometric parameters of the singlet state of the complex are gathered in Table 3. In general, the predicted bond lengths and angles are in good agreement with the values based on the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations. The largest differences are observed in the Ru–H distance 0.22 Å. Maximum deviation between the calculated angles and the observed ones is close to 9.95° (carbonyl–ruthenium–chloride).

#### 3.2. Electronic structure and NBO analysis

After geometry optimization the contributions from various groups of the molecule in molecular orbitals were described. The occupancies of the ruthenium d orbitals, obtained from NBO analysis, are as follows:  $d_{xy} - 1.74$ ;  $d_{xz} - 1.93$ ;  $d_{yz} - 1.67$ ;  $d_{Z_2} - 1.29$ ;  $d_{x_2-y_2} - 1.07$ . The Homo orbital of studied compound is composed of the  $d_{xz}$  metal orbital with antibonding contribution of  $\pi$  chlorine orbital. The Lumo orbital is mainly localized on the Hmtpo ligand. The Homo–Lumo gap is 4.18 eV in B3LYP functional and 3.61 eV in

Generalized Gradient Approximation (GGA) term which is more "realistic". The following orientation of the axes has been used for determination of the MO characters: the *z* axis goes along H(1Ru)-Re-Cl(1) linkage and *x* goes through the P(1)-Re-P(2) bonds. More details of atomic contributions to the lowest unoccupied and highest occupied molecular orbitals are given in Supplementary Data in Table S1. Moreover the isodensity plots of the several Homo and Lumo orbitals of studied complex are shown in Fig. 3. Wiberg bond order for Ru-Cl and Ru-P are close to 0.59 (0.54)<sup>1</sup> and 0.70 (0.45), respectively.

In the frontier region, neighboring orbitals are being often closely spaced. In such cases, consideration of only the Homo and Lumo may not yield a realistic description of the frontier orbitals. For this reason, the density-of-states (DOS) and overlap population density-of-states (OPDOS) in terms of Mulliken population analysis were calculated using the GAUSSSUM program [21]. They provide a pictorial representation of MOs compositions and their contributions to chemical bonding. The DOS and OPDOS diagrams are shown in Fig. 4. The DOS plots mainly present the composition of the fragment orbitals contributing to the molecular orbitals. The OPDOS can enable us to ascertain the bonding, non-bonding and antibonding characteristics with respect to the particular fragments. A positive value in OPDOS plots means a bonding interaction; while a negative value represents antibonding interaction and a value near zero indicates a non-bonding interaction.

As can be seen from the OPDOS plot in the Homo and Homo-1 molecular orbitals the chloride ligand has significant antibonding character and bonding character in the Homo-4 and Homo-5. The interactions of phosphine and Hmtpo ligands with Ru(II) d orbitals have negative values in the frontier occupied molecular orbitals (antibonding character of the interactions). The covalent bond character of Ru-CO and Ru-H is displayed by positive values of the interactions in OPDOS plot. Wiberg bond order for Ru-C is close to 1.33 (1.37) and for Ru-H 0.79 (0.79). The lowest virtual orbitals are mainly localized on the Hmtpo and phosphine ligands. In the Lumo+1 the antibonding interaction of ruthenium d orbital (29%) with PPh<sub>2</sub> ligand is visible. The interactions between metal and phosphine. Hmtpo ligands are antibonding in the frontier virtual orbitals but in this energy region Ru and H ligand has bonding interaction. In the Lumo orbitals composed with more Hmtpo contributions the Ru(II) proportion is small (Lumo, Lumo+3, Lumo+5) which indicates the ligand as a weak  $\pi$ -acceptor. Wiberg bond order for Ru-N(7) is close to 0.37 (0.29) which indicate the stronger ionic character of Ru-N bond comparing with other ruthenium ligand interaction in studied compound.

Basing on the NBO theory [22], occupancy and hybridization of the calculated natural bond orbital between the ruthenium and the hydrido ligand in the complex is 1.861 and  $0.721(sd)_{Ru} + 0.693(s)_{H}$ , respectively; occupancy of the antibonding orbital of Ru–H is 0.131. The occupancy and hybridization of Ru–CO bond is as follows: 1.938 (antibonding 0.142) and  $0.586(sd^{2.52})_{Ru} + 0.810(sp^{0.50})_{C}$ .

The stabilization energy<sup>2</sup> which has been calculated in this analysis has shown that the lone pairs localized on the ruthenium atom in the compound donate the charge to ruthenium carbonyl bond, and the stabilization energy ( $\Delta E_{ij}$ ) is 105.79 kcal/mol. The interaction between antibonding parts of Ru–C and Ru–H has the energy close to 80.89 kcal/mol. The stabilization energy calculated in this analysis for the complex has shown that the lone pairs localized on the chlorine and Hmtpo's

<sup>&</sup>lt;sup>2</sup>  $\Delta E_{ij}$  (kcal/mol) associated with delocalization is estimated by the second-order perturbative as:  $\Delta E_{ij} = q_i (F(i,j)^2)/(\varepsilon_j - \varepsilon_i)$  where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$ ,  $\varepsilon_j$  are diagonal elements (orbital energies) and F(i,j) is the off-diagonal NBO Fock or Kohn-Sham matrix element.



Fig. 3. The contours of several Homo and Lumo molecular orbitals.

nitrogen ligands donate the charge to ruthenium d orbital, and the stabilization energy ( $\Delta E_{ii}$ ) is 218.33 and 79.03 kcal/mol, respectively.

<sup>&</sup>lt;sup>1</sup> In parenthesis are given values from Nalewajski-Mrozek bond-order analysis (A. Michalak, R.L. DeKock, T. Ziegler, Bond Multiplicity in Transition-Metal Complexes: Applications of Two-Electron Valence Indices, J. Phys. Chem. A 112 (2008) 7256.



**Fig. 4.** Partial density-of-states and overlap population density-of-states diagrams for [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)] complex.

In studied complex, ruthenium is formally +2 but the calculated natural charge on the ruthenium atom is -0.928. The charges of hydride and chloride ligands are close to 0.04 and -0.516, respectively. The charge on the carbon atom of the carbonyl ligand is positive (0.709), whereas the oxygen atom is negatively charged (-0.491). The atomic charge calculations can give a feature for the relocation of the electron density of the compounds. Because the electron distribution is not apparent from the partial atomic charges in Fig. 5 are given the plot of the electrostatic potentials for the studied compound. The isoelectronic contours are plotted at 0.005 a.u. (3.1 kcal/mol). The color code of these maps is in the range of 0.05 a.u. (deepest red) to -0.005 a.u. (deepest blue),



**Fig. 5.** Electrostatic potential (ESP) surface of [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)] complex. ESP surface is shown both in space (with positive and negative regions shown in blue and red, respectively) and mapped on electron densities (isovalue = 0.004) of the molecule (ESP color scale is such that  $\delta^+ \rightarrow \delta^-$  in the direction red  $\rightarrow$  blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where blue indicates the strongest attraction and red indicates the strongest repulsion. Regions of negative V(r) are usually associated with the lone pair of electronegative atoms. The negative potential in the studied compound wraps the heteroaromatic nitrogen, hydroxyl, carbonyl oxygen and chloride atoms.

The energy decomposition analysis of the studied complex based on the work of Morokuma [23] and the extended transition state (ETS) partitioning scheme of Ziegler [24] has been carried out using ADF program (Release 2008) at the level of B3LYP/TZP has been performed. The binding energy of the compound was calculated as the difference between the energy of complex with the optimized geometry and the energies of the optimized ligand Hmtpo and fragment [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)]. General theoretical background on the bond energy decomposition scheme can be found in the review paper [25]. In Table 5 are listed the result of energy decomposition analysis calculated for the complex in gas phase and more realistic in methanol solvent. As could be seen the Coulomb (steric and orbital interaction) energy plays a important role for the [(PPh<sub>3</sub>)<sub>3</sub>RuHCl(CO)]–Hmtpo binding.

## 3.3. Electronic spectra

Several transitions, with the oscillator strength above 0.01, have been collected in Table S2 in Supplementary Data. In the studied complex, 140 electronic transitions have been calculated using the TDDFT method and they do not comprise all the experimental

Table 5

Energy decomposition analysis for complex [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)] in the [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)] fragment and the Hmtpo ligand (energies in kcal mol<sup>-1</sup>).

Energy (kcal/mol)	[(PPh <sub>3</sub> ) <sub>2</sub> RuHCl(CO)(Hmtpo)] gas phase	[(PPh <sub>3</sub> ) <sub>2</sub> RuHCl(CO)(Hmtpo)] CH <sub>3</sub> OH solvent
$\Delta E_{ m elstat}$	-69.65	-60.60
$\Delta E_{ m kinetic}$	-2985.63	-91.66
$\Delta E_{\text{Coulomb (steric+orbInt)}}$	2728.31	193.26
$\Delta E_{\rm XC}$	249.60	-48.79
$\Delta E_{ m solvation}$		-25.04
$\Delta E$	-77.37	-32.83

absorption bands. The UV–Vis spectra have been calculated up to  $\sim$ 215 nm, so considering that the solution spectra of PPh<sub>3</sub> and *N*-heterocyclic ligands exhibit intense absorption bands in about 210 nm region, some intraligand and interligand transitions are expected to be found at higher energies in the calculations.

The experimental spectrum of studied complex exhibit broad band with the maximum at 267.5 nm. Basing on the calculated transitions the band is of *Metal–Ligand Charge Transfer* type with the d  $\rightarrow$  d (Ligand Field) contribution. The intra- and interligand transitions are calculated in the region of high energies and attributed to the experimental band with maximum at 209.0 nm. As it was pointed out in the literature, the TDDFT method gives such transitions at too small energies [26–34] and we may expect also that this is the case in our calculations.

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#### Appendix A. Supplementary data

CCDC 740627 contains the supplementary crystallographic data for [(PPh<sub>3</sub>)<sub>2</sub>RuHCl(CO)(Hmtpo)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2009.12.007.

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