

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:541.49

CRYSTAL STRUCTURE OF CARBONYL TRICHLORO BIS(TRIPHENYL PHOSPHINE) RUTHENIUM(III) COMPLEX

M. Gowri¹, T. Srinivasan², D. Velmurugan²¹Department of Chemistry, Avinashilingam University for Women, Tamilnadu, India

E-mail: sriadit.gowrisuresh@gmail.com

²CAS in Crystallography and Biophysics, University of Madras, Tamilnadu, India

E-mail: srini771@gmail.com, shirai2011@gmail.com

Received April, 18, 2014

Revised — May, 23, 2014

The title complex is synthesized and analyzed using single crystal X-ray diffraction studies. The asymmetric unit $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$ of the title complex contains one half of the molecule. The molecular structure is stabilized by C3—H3...C11 and C9—H9...C12 intramolecular halogen interactions which result in two S(6) ring motifs. The crystal packing features are the C—H...Cg1 interactions, where Cg1 is the center of gravity of the phenyl ring (C14—C19). No classical hydrogen bond is found in the complex.

DOI: 10.15372/JSC20150628

Keywords: Ru(III) complex, triphenyl phosphine (PPh₃), chloride, carbonyl, single crystal XRD.

Organometallic complexes with bonds that have characters in-between ionic and covalent are very important in industry since they are relatively stable in solutions and relatively ionic to undergo reactions. This is the case of complexes having CO as one of their ligands $[\text{M}=\text{C}=\text{O} \leftrightarrow \text{M}^+ \equiv \text{C} - \text{O}^-]$. Phosphines are used as ligands for many metal complexes. The most popular phosphine ligand used is triphenyl phosphine: a shelf-stable solid that relatively slowly undergoes oxidation in air. Unlike most metal ammine complexes, metal phosphine complexes tend to be lipophilic, displaying good solubility in organic solvents. They are found to be compatible with metals in multiple oxidation states. Because of these two features, metal phosphine complexes are important in homogeneous catalysis [1]. Being bonded to the Ru(III) metal atom in the complexes, the ligands such as triphenyl phosphine, carbonyl, and chloride have characteristic biological activities and they have extensively been studied. Aryl phosphines are much stronger π acceptors than alkyl phosphines, which are poor π acceptors or possibly π donors. Phosphine with the strongest π acidity is trifluorophosphine (PF₃); its π acidity approaches that of the carbonyl ligand [2]. Phosphine ligands are usually "spectator" rather than "actor" ligands. They generally do not participate in reactions, except the dissociation from the metal center. At a certain high temperature hydroformylation reactions, the scission of P—C bonds is observed, however, in few cases [3]. The thermal stability of phosphine ligands is enhanced when they are incorporated into pincer complexes [4].

Based on the views and approaches to the complexes with triphenyl phosphine, carbonyl, and chloride as ligands, we herein investigate the crystal structure of a novel Ru(III) complex $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$ by X-ray diffraction studies.

Experimental. Synthesis. The dibasic tridentate Schiff base ligand, viz., (Z)-4-(((2-hydroxy phenyl)amino)phenyl) methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (H₂L) (370 mg, 1 mmol)

T a b l e 1

Crystal Data and Structure Refinement of the [RuCl₃(CO)(PPh₃)₂] Complex

Empirical formula	C ₃₇ H ₃₀ Cl ₃ OP ₂ Ru
Formula weight	759.97
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system, space group	Monoclinic, <i>C</i> 2/ <i>c</i>
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å	24.2912(7), 9.5543(3), 15.9568(4)
β, deg.	116.3420(10)
<i>V</i> , Å ³	3318.79(16)
<i>Z</i> , calculated density, g/cm ³	4, 1.521
Absorption coefficient, mm ⁻¹	0.840
<i>F</i> (000)	1540
Crystal size, mm	0.20×0.20×0.20
θ range for data collection, deg	1.87 to 28.44
Limiting indices <i>h</i> , <i>k</i> , <i>l</i>	-32 ≤ <i>h</i> ≤ 32, -12 ≤ <i>k</i> ≤ 11, -21 ≤ <i>l</i> ≤ 21
Reflections collected / unique	15081 / 4168 [<i>R</i> (int) = 0.0219]
Completeness to θ = 28.44°, %	99.6
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4168 / 0 / 201
Goodness-of-fit on <i>F</i> ²	1.041
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0538, <i>wR</i> ₂ = 0.1321
Largest diff. peak and hole, e ⁻ Å ⁻³	1.338 and -2.041
CCDC No.	892627

[5] was added to a [Ru(H)(Cl)(CO)(PPh₃)₃] solution (950 mg, 1 mmol) in equal volume mixtures of chloroform and ethyl acetate, and the mixture was refluxed for about 4 h. The expected product [Ru(CO)(PPh₃)₂L] was obtained as a green precipitate which was filtered off. The filtrate showed the presence of another product which was found to be different from any of the starting complexes and the expected product. The filtrate resulted in the formation of reddish brown colored transparent crystals on standing. These crystals were subjected to various spectroscopic and X-ray diffraction studies.

FT-IR spectrum. The FT-IR spectrum of the complex was recorded in KBr pellets using a Perkin Elmer spectrophotometer of the RXI model in the range 400–4000 cm⁻¹.

Single crystal X-ray diffraction. The single crystal X-ray diffraction of the title complex was carried out at the Madras University, Chennai. On the attempt to prepare a ruthenium(II) complex with the pyrazole Schiff base, the title complex [RuCl₃(CO)(PPh₃)₂], which was obtained accidentally as reddish brown crystals, was subjected to single crystal X-ray diffraction and its structure was solved by the direct method using the SHELXS-97 program [6] and refined by the full-matrix least squares method using SHELXL-97 [6–9] programs.

The main details of the X-ray diffraction study are given in Table 1. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 892627) deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The FT-IR spectrum of the [RuCl₃(CO)(PPh₃)₂] complex gives an indication of the coordination mode of the metal ion with the ligands. The characteristic frequencies of the aromatic C–H stretching (3053 cm⁻¹) and bending (856 cm⁻¹) are found in the expected regions. A characteristic band was observed at 1435 cm⁻¹, which was attributed to the triphenyl phosphine

Bond Lengths (Å) and Angles (deg.) for the [RuCl₃(CO)(PPh₃)₂] Complex

Bond lengths					
Ru(1)—C(1)	2.008(5)	C(14)—C(19)	1.393(5)	C(5)—H(5)	0.9300
Ru(1)—Cl(1)#1	2.3930(12)	C(15)—C(16)	1.400(6)	C(11)—C(10)	1.363(6)
Ru(1)—Cl(1)	2.3930(12)	C(15)—H(15)	0.9300	C(11)—H(11)	0.9300
Ru(1)—Cl(2)	2.413(4)	C(4)—C(5)	1.366(6)	C(3)—H(3)	0.9300
Ru(1)—P(1)	2.4194(8)	C(4)—C(3)	1.389(5)	C(7)—H(7)	0.9300
Ru(1)—P(1)#1	2.4194(8)	C(4)—H(4)	0.9300	C(18)—C(17)	1.368(8)
P(1)—C(2)	1.824(3)	C(19)—C(18)	1.383(6)	C(18)—H(18)	0.9300
P(1)—C(8)	1.826(3)	C(19)—H(19)	0.9300	C(9)—C(10)	1.388(6)
P(1)—C(14)	1.827(3)	C(16)—C(17)	1.366(8)	C(9)—H(9)	0.9300
C(1)—O(1)	0.834(13)	C(16)—H(16)	0.9300	C(10)—H(10)	0.9300
C(8)—C(9)	1.381(5)	C(12)—C(11)	1.357(7)	C(13)—H(13)	0.9300
C(8)—C(13)	1.382(5)	C(12)—H(12)	0.9300	C(17)—H(17)	0.9300
C(2)—C(3)	1.387(5)	C(6)—C(5)	1.367(7)		
C(2)—C(7)	1.389(5)	C(6)—C(7)	1.387(6)		
C(14)—C(15)	1.383(5)	C(6)—H(6)	0.9300		
Bond angles					
C(1)—Ru(1)—Cl(1)#1	84.81(3)	C(3)—C(2)—P(1)	122.1(3)	C(12)—C(11)—C(10)	119.2(4)
C(1)—Ru(1)—Cl(1)	84.81(3)	C(7)—C(2)—P(1)	119.7(3)	C(12)—C(11)—H(11)	120.4
Cl(1)#1—Ru(1)—Cl(1)	169.61(7)	C(15)—C(14)—C(19)	118.7(4)	C(10)—C(11)—H(11)	120.4
C(1)—Ru(1)—Cl(2)	180.000(1)	C(15)—C(14)—P(1)	121.7(3)	C(2)—C(3)—C(4)	120.5(3)
Cl(1)#1—Ru(1)—Cl(2)	95.19(3)	C(19)—C(14)—P(1)	119.2(3)	C(2)—C(3)—H(3)	119.8
Cl(1)—Ru(1)—Cl(2)	95.19(3)	C(14)—C(15)—C(16)	120.0(4)	C(4)—C(3)—H(3)	119.8
C(1)—Ru(1)—P(1)	89.35(2)	C(14)—C(15)—H(15)	120.0	C(6)—C(7)—C(2)	120.6(4)
Cl(1)#1—Ru(1)—P(1)	92.49(3)	C(16)—C(15)—H(15)	120.0	C(6)—C(7)—H(7)	119.7
Cl(1)—Ru(1)—P(1)	87.39(3)	C(5)—C(4)—C(3)	120.5(4)	C(2)—C(7)—H(7)	119.7
Cl(2)—Ru(1)—P(1)	90.65(2)	C(5)—C(4)—H(4)	119.8	C(17)—C(18)—C(19)	120.5(5)
C(1)—Ru(1)—P(1)#1	89.35(2)	C(3)—C(4)—H(4)	119.8	C(17)—C(18)—H(18)	119.8
Cl(1)#1—Ru(1)—P(1)#1	87.39(3)	C(18)—C(19)—C(14)	120.4(4)	C(19)—C(18)—H(18)	119.8
Cl(1)—Ru(1)—P(1)#1	92.49(3)	C(18)—C(19)—H(19)	119.8	C(8)—C(9)—C(10)	120.5(4)
Cl(2)—Ru(1)—P(1)#1	90.65(2)	C(14)—C(19)—H(19)	119.8	C(8)—C(9)—H(9)	119.7
P(1)—Ru(1)—P(1)#1	178.70(4)	C(17)—C(16)—C(15)	120.4(5)	C(10)—C(9)—H(9)	119.7
C(2)—P(1)—C(8)	100.13(15)	C(17)—C(16)—H(16)	119.8	C(11)—C(10)—C(9)	120.8(4)
C(2)—P(1)—C(14)	105.36(16)	C(15)—C(16)—H(16)	119.8	C(11)—C(10)—H(10)	119.6
C(8)—P(1)—C(14)	104.62(15)	C(11)—C(12)—C(13)	120.9(4)	C(9)—C(10)—H(10)	119.6
C(2)—P(1)—Ru(1)	118.52(11)	C(11)—C(12)—H(12)	119.6	C(8)—C(13)—C(12)	120.6(4)
C(8)—P(1)—Ru(1)	117.48(11)	C(13)—C(12)—H(12)	119.6	C(8)—C(13)—H(13)	119.7
C(14)—P(1)—Ru(1)	109.23(10)	C(5)—C(6)—C(7)	120.5(4)	C(12)—C(13)—H(13)	119.7
O(1)—C(1)—Ru(1)	180.000(2)	C(5)—C(6)—H(6)	119.8	C(16)—C(17)—C(18)	120.0(4)
C(9)—C(8)—C(13)	118.0(3)	C(7)—C(6)—H(6)	119.8	C(16)—C(17)—H(17)	120.0
C(9)—C(8)—P(1)	118.5(3)	C(4)—C(5)—C(6)	119.8(4)	C(18)—C(17)—H(17)	120.0
C(13)—C(8)—P(1)	123.5(3)	C(4)—C(5)—H(5)	120.1		
C(3)—C(2)—C(7)	118.2(3)	C(6)—C(5)—H(5)	120.1		

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

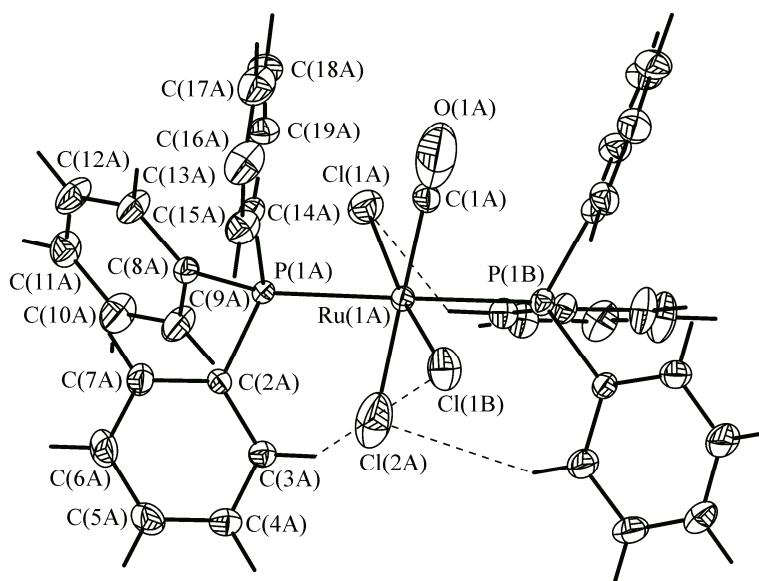


Fig. 1. The molecular structure of $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$ complex, showing displacement ellipsoids drawn at the 30 % probability level. H atoms are removed for structure clarity

group [10]. The presence of carbon monoxide as a ligand terminally coordinated to the metal is evident from the presence of a high-intensity sharp peak at 1945 cm^{-1} [11].

The title complex crystallizes in the monoclinic space group $C2/c$ with the cell parameters $a = 24.2912(7)\text{ \AA}$, $b = 9.5543(3)\text{ \AA}$, $c = 15.9568(4)\text{ \AA}$, $\alpha = 90.00(0)^\circ$, $\beta = 116.342(1)^\circ$, $\gamma = 90.00(0)^\circ$, $Z = 4$, $M_r = 759.97$, and $V = 3318.79(17)\text{ \AA}^3$. The structure was solved by direct methods using SHELXS-97 and refined by the full-matrix least squares method using SHELXL-97 programs [6]. The final R -factor value is 0.0471 with a GOOF value of 1.041 for 4168 independent reflections. The asymmetric unit of the title complex $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$ contains one half of the molecule, the complete molecule being generated by the operation with the crystallographic rotation axis (symmetry code: (i) $-x+2, y, -z+1/2$). The angles around the P1 atom ($\text{C}2\text{—P}1\text{—C}8 = 100.13(15)^\circ$, $\text{C}2\text{—P}1\text{—C}14 = 105.36(16)^\circ$ and $\text{C}8\text{—P}1\text{—C}14 = 104.62(15)^\circ$) deviate from the ideal tetrahedral values, which may be due to a steric interaction between benzene rings and the Ru atom. The molecular structure of the $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$ complex with displacement ellipsoids drawn at the 30 % probability level is shown in Fig. 1. No classical hydrogen bond was found in this complex.

Out of the three chloride ligands, two of them are found to be involved in intramolecular halogen interactions with the phenyl ring hydrogen atoms because of their proximity and the inclination angle, and this explains the increased stability of the complex. The intramolecular halogen interactions are given by $\text{C}3\text{—H}3\cdots\text{C}11$ ($\text{H}\cdots\text{Cl} = 2.64$ and the angle $\text{C}3\text{—H}3\cdots\text{C}11 = 132^\circ$ with the symmetry code of $2-x, y, 1/2-z$) and $\text{C}9\text{—H}9\cdots\text{C}12$ ($\text{H}\cdots\text{Cl} = 2.82$ and the angle $\text{C}9\text{—H}9\cdots\text{C}12 = 145^\circ$), which results in two pseudo six-membered ring structures. The crystal packing of the title complex viewed down the c axis with all hydrogen atoms is shown in Fig. 2.

Conclusions. We have reported the FT-IR and single crystal X-ray diffraction analyzes of the novel Ru(III) complex $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$. We have explained the structure of the ruthenium complex with the intramolecular halogen interactions. Based on all the above results, it may be further concluded that these by-product crystals are formed by the catalytic behavior of the expected product obtained in the same reaction of carrying out the oxidation of Ru(II) to Ru(III). The synthesis of various metal complexes and the evaluation of their catalytic activities are the ongoing project in our laboratory and the results will be published in due course.

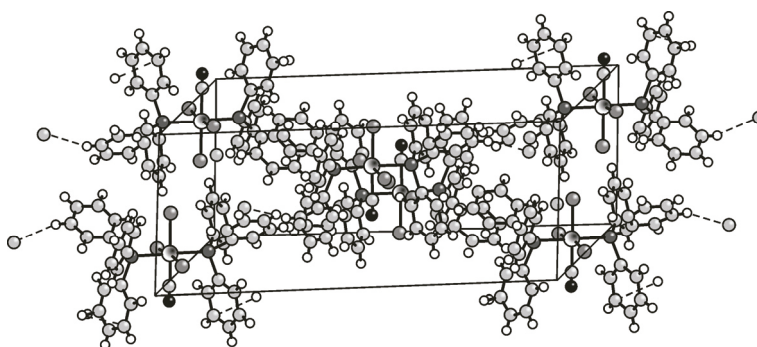


Fig. 2. The crystal packing of $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$ complex viewed down c axis

Table 3

Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for the $[\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]$ Complex. $U(\text{eq})$ is Defined as One Third of the Trace of the Orthogonalized U_{ij} Tensor

Atom	x	y	z	$U(\text{eq})$	Atom	x	y	z	$U(\text{eq})$
Ru(1)	10000	1721(1)	2500	27(1)	C(12)	8959(3)	2127(5)	5184(3)	59(1)
P(1)	9066(1)	1692(1)	2692(1)	26(1)	C(6)	7363(2)	3463(6)	1360(4)	67(2)
Cl(1)	10552(1)	1495(1)	4163(1)	61(1)	C(5)	7392(2)	4233(5)	659(3)	54(1)
Cl(2)	10000	4247(4)	2500	98(1)	C(11)	9132(2)	3477(5)	5421(3)	53(1)
C(1)	10000	-381(6)	2500	44(1)	C(3)	8431(2)	3487(4)	1162(2)	36(1)
C(8)	9111(2)	2337(4)	3798(2)	31(1)	C(7)	7865(2)	2689(6)	1965(3)	56(1)
C(2)	8406(2)	2686(4)	1870(2)	32(1)	C(18)	8991(2)	-2472(5)	3197(4)	59(1)
C(14)	8796(2)	-109(3)	2609(2)	32(1)	C(9)	9296(3)	3701(5)	4054(3)	4054(3)
C(15)	8286(2)	-586(5)	1834(3)	48(1)	C(10)	9299(3)	4265(5)	4858(4)	66(1)
C(4)	7924(2)	4262(4)	565(3)	46(1)	C(13)	8946(2)	1549(4)	4377(3)	49(1)
C(19)	9147(2)	-1069(4)	3296(3)	45(1)	C(17)	8491(3)	-2937(5)	2423(4)	70(2)
C(16)	8137(3)	-2011(6)	1745(4)	67(1)	O(1)	10000	-1254(14)	2500	151(4)

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