

X-ray structure of (η^5 -cyclopentadienyl)bis-(triphenylphosphine) (*p*-nitro-benzoato)ruthenium (II)

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The structure of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)$ (**1**) is determined by single crystal X-ray studies. The crystal belongs to the monoclinic space group $\text{P2}_1/\text{n}$ with the following unit cell dimensions for the $\text{C}_{48}\text{H}_{39}\text{NO}_4\text{P}_2\text{Ru}$ ($M_r = 856.55$): $a = 11.960(5)$ Å; $b = 19.129(4)$ Å; $c = 18.123(2)$ Å; $\beta = 102.86(2)^\circ$, $V = 4042.6$ Å³, $Z = 4$, $D_c = 1.40$ g cm⁻³, $\text{MoK}_\alpha = 0.7107$ Å, $\mu = 4.11$ cm⁻¹, $F(000) = 1748$, $T = 293$ K, $R = 0.077$ ($R_w = 0.069$) for 2325 [$I \geq 3 \sigma(I)$] reflections. The structure consists of discrete molecules. The symmetry about the ruthenium atom is essentially octahedral showing the presence of a $\eta^5\text{-C}_5\text{H}_5$ and a η^1 -carboxylato ligands in the coordination sphere besides two coordinated PPh_3 groups.

While the electron-rich nature of the $\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\}^+$ moiety has led to the synthesis of a wide range of compounds¹ with π -acceptor ligands, similar compounds with ligands having hard-base binding sites are relatively unknown². Recently, we have reported³ the synthesis and properties of a series of a carboxylato compounds, $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{O}_2\text{CR})$. Herein we present the results obtained from a single crystal X-ray study done on a representative complex, $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)$ (**1**), of the series.

Materials and Methods

Method for the synthesis of **1** is given in our earlier report³. Compound **1** was obtained in the crystalline state by dissolving the solid in benzene followed by layering with *n*-hexane in a Schlenk tube under dinitrogen atmosphere.

X-ray crystallographic procedures

An irregular shaped red coloured crystal (approx. dimension: $0.30 \times 0.20 \times 0.15$ mm) of $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)$ was mounted on a glass fibre with epoxy cement. The initial cell parameters were obtained from oscillation and Weissenberg photographs. The final cell parameters were obtained by indexing 25 reflections in the range of $16^\circ < 2\theta < 29^\circ$, using an automated four-circle Enraf-Nonius CAD-4 diffractometer. Data collection was done by ω - 2θ scan technique in the limit of $4^\circ \leq 2\theta \leq 50^\circ$, using graphite monochromated MoK_α radiation ($\lambda_\alpha = 0.7107$ Å). Lo-

Table 1 – Positional parameters ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) and their e.s.d.'s

Atom	x	y	z	$U_{\text{iso}}(\text{eq})^a$
Ru	2207(1)	465(1)	3956(1)	39(1)*
P1	2345(4)	1587(2)	3500(2)	44(2)*
P2	737(4)	27(2)	2994(2)	42(2)*
O1	3497(8)	269(5)	3363(5)	50(4)*
O2	4256(10)	-731(6)	3897(6)	68(5)*
C1	3284(17)	209(12)	5105(9)	61(8)*
C2	2420(19)	-318(10)	4865(8)	65(8)*
C3	1267(17)	-11(10)	4744(8)	54(7)*
C4	1475(18)	714(9)	4912(8)	57(8)*
C5	2710(17)	837(11)	5144(8)	57(8)*
C11	1632(13)	2255(8)	3978(8)	44(4)
C12	464(15)	2228(9)	3858(9)	58(5)
C13	-150(16)	2683(10)	4245(10)	75(6)
C14	499(15)	3186(9)	4762(9)	65(5)
C15	1686(15)	3188(9)	4897(9)	62(5)
C16	2306(14)	2710(9)	4505(9)	57(5)
C21	1840(13)	1780(8)	2493(8)	46(4)
C22	1216(15)	2375(9)	2222(9)	65(5)
C23	805(16)	2461(11)	1412(11)	78(6)
C24	1154(16)	1966(10)	932(9)	73(6)
C25	1815(15)	1380(9)	1223(9)	61(5)
C26	2158(13)	1303(8)	2002(8)	44(4)
C31	3813(13)	1908(8)	3650(8)	47(4)
C32	4070(15)	2497(9)	3253(9)	60(5)
C33	5208(15)	2748(9)	3402(9)	57(5)
C34	6053(15)	2483(9)	3952(9)	62(5)
C35	5820(16)	1906(10)	4365(10)	72(6)
C36	4683(15)	1622(9)	4208(9)	55(5)
C41	-537(11)	596(7)	2829(7)	36(4)
C42	-1192(13)	613(8)	3376(8)	48(4)
C43	-2116(15)	1111(9)	3298(10)	66(5)
C44	-2368(15)	1570(9)	2678(10)	66(5)
C45	-1690(15)	1520(9)	2139(9)	65(5)

(contd.)

Table 1 – Positional parameters ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) and their e.s.d.'s – *Contd.*

C46	-755(15)	1056(9)	2188(9)	57(5)
C51	219(14)	-834(8)	3252(8)	48(4)
C52	1106(13)	-1349(8)	3470(8)	50(5)
C53	768(15)	-2033(10)	3657(9)	68(5)
C54	-354(16)	-2174(9)	3608(9)	66(5)
C55	-1230(17)	-1707(11)	3376(10)	78(6)
C56	-898(14)	-1002(9)	3172(9)	58(5)
C61	837(13)	-225(8)	2021(8)	44(4)
C62	1895(13)	-394(9)	1891(8)	55(5)
C63	1988(15)	-654(9)	1167(9)	66(5)
C64	992(15)	-714(9)	586(9)	60(5)
C65	-53(14)	-584(9)	736(9)	60(5)
C66	-178(13)	-319(8)	1457(8)	50(4)
C71	4200(13)	-260(8)	3428(8)	41(4)
C72	4947(13)	-280(8)	2872(8)	45(4)
C73	5476(15)	-906(9)	2727(9)	61(5)
C74	6069(16)	-938(10)	2133(10)	72(6)
C75	6101(15)	-342(11)	1721(10)	71(6)
C76	5610(17)	269(11)	1804(10)	86(6)
C77	4996(16)	306(10)	2427(10)	81(6)
N1	6708(17)	-421(13)	1056(11)	121(7)
O3	6691(16)	101(11)	690(10)	159(7)
O4	7117(15)	-980(10)	979(9)	140(6)

^aStarred atoms are refined anisotropically. The expression for isotropic (equivalent) thermal parameter is $U_{iso} (eq) = [\Sigma_i \Sigma_j U_{ij} a_i^* a_j^*] / 3$.

rentz and polarization corrections were made on the data but not the absorption correction. Systematic absences uniquely defined the space group as $P2_1/n$. There were 7081 unique reflections with 2325 having $I \geq 3\sigma(I)$ collected with $0 < h < 14$, $0 < k < 22$, $-21 < l < 21$. Three intensity standards, checked every hour of exposure time, showed no significant decay during data collection. The structure was solved by conventional heavy-atom methods. The position of ruthenium was obtained from the Patterson function and the remaining atoms were located by Fourier method. The ruthenium and the atoms in the coordination sphere and the carboxylato oxygen were refined anisotropically leaving the remaining atoms at the isotropic stage. The structure was refined to $R = 0.077$ and $R_w = 0.069$ using 2325 data ($I \leq 3\sigma(I)$) and 275 parameters to an overall scale factor of 1.49 and the largest shift/esd of 0.059. The highest peak in the final difference Fourier map was of $0.87 \text{ e}\text{\AA}^{-3}$. $[R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|]$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2(F_o) + gF_o^2]$, $g = 0.00000$. Calculations were carried out using SHELX 76 program⁴ at the Indian Institute of Science Computer Centre. The

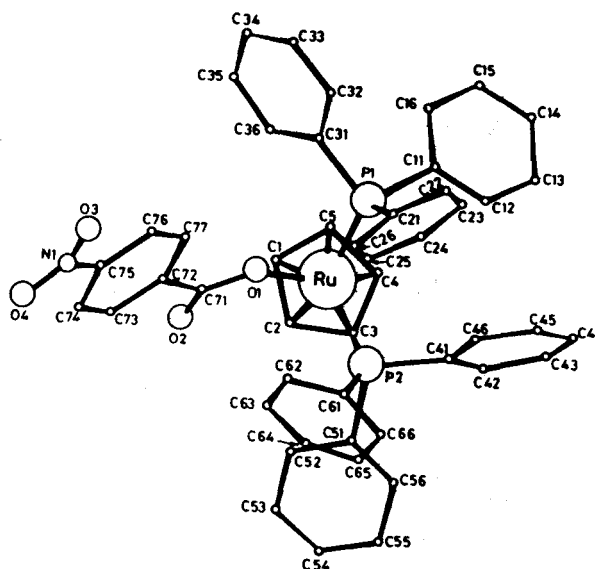


Fig. 1 – A PLUTO diagram of the $[Ru(\eta^5-C_5H_5)(PPh_3)_2(O_2CC_6H_4-p-NO_2)]$ (1) molecule along with the atom labelling scheme

perspective view of the molecule was obtained using PLUTO program⁵.

Results and Discussion

The cell constants and crystallographic data are: mol. formula, $C_{48}H_{39}NO_4P_2Ru$; molecular wt, 856.55; monoclinic; $a = 11.960(5) \text{ \AA}$; $b = 19.129(4) \text{ \AA}$; $c = 18.123(2) \text{ \AA}$; $\beta = 102.86(2)^\circ$; $V = 4042.6 \text{ \AA}^3$; space group $P2_1/n$; $Z = 4$; $D_c = 1.40 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 4.11 \text{ cm}^{-1}$; $F(000) = 1748$. The positional parameters along with equivalent isotropic thermal parameters are presented in Table 1†. Tables 2 and 3 list the bond distances and angles, respectively. A PLUTO drawing of the molecule is shown in Fig. 1, together with the numbering scheme used. The list of structure factors can be obtained from the author on request.

The structure consists of discrete mononuclear molecules in which the geometry around ruthenium is essentially octahedral. The interesting feature in the structure is the unidentate mode of coordination of the *p*-nitrobenzoate ligand. The C–O distances are found to vary considerably. The presence of two bulky PPh_3 groups makes the $P1-Ru-P2$ angle obtuse. The difference in the two $P-Ru-O1$ angles could be due to crystal

†The anisotropic thermal parameters of the metal and the atoms in the coordination sphere can be had from authors on request.

Table 2 – Bond distances (Å) for $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)$

Atom A	Atom B	Distance	Atom A	Atom B	Distance
Ru	P(1)	2.320(4)	C(1)	C(2)	1.440(22)
Ru	P(2)	2.338(4)	C(1)	C(5)	1.393(23)
Ru	O(1)	2.099(10)	C(3)	C(2)	1.470(22)
Ru	C(1)	2.245(16)	C(4)	C(3)	1.431(22)
Ru	C(2)	2.199(14)	C(5)	C(4)	1.461(23)
Ru	C(3)	2.203(16)	C(11)	C(12)	1.366(19)
Ru	C(4)	2.162(16)	C(11)	C(16)	1.406(19)
Ru	C(5)	2.221(14)	C(12)	C(13)	1.420(22)
P(1)	C(11)	1.854(15)	C(13)	C(14)	1.444(22)
P(1)	C(21)	1.827(15)	C(14)	C(15)	1.386(21)
P(1)	C(31)	1.823(16)	C(15)	C(16)	1.457(21)
P(2)	C(41)	1.843(14)	C(21)	C(22)	1.387(21)
P(2)	C(51)	1.856(16)	C(22)	C(23)	1.449(21)
P(2)	C(61)	1.856(14)	C(23)	C(24)	1.412(23)
O(1)	C(71)	1.304(16)	C(24)	C(25)	1.405(22)
O(2)	C(71)	1.231(16)	C(25)	C(26)	1.387(19)
C(21)	C(27)	1.386(18)	C(31)	C(32)	1.407(20)
C(32)	C(33)	1.413(20)	C(33)	C(34)	1.350(20)
C(34)	C(35)	1.396(21)	C(35)	C(36)	1.432(22)
C(36)	C(31)	1.392(20)	C(41)	C(42)	1.394(17)
C(42)	C(43)	1.443(21)	C(43)	C(44)	1.404(21)
C(44)	C(45)	1.405(21)	C(45)	C(46)	1.415(21)
C(46)	C(41)	1.434(18)	C(51)	C(52)	1.437(20)
C(52)	C(53)	1.433(21)	C(53)	C(54)	1.353(21)
C(54)	C(55)	1.369(22)	C(55)	C(56)	1.476(23)
C(56)	C(51)	1.351(20)	C(61)	C(62)	1.376(19)
C(62)	C(63)	1.431(19)	C(63)	C(64)	1.409(21)
C(64)	C(65)	1.360(20)	C(65)	C(66)	1.441(19)
C(66)	C(61)	1.413(18)	C(71)	C(72)	1.489(19)
C(72)	C(73)	1.406(20)	C(73)	C(74)	1.432(21)
C(74)	C(75)	1.357(23)	C(75)	C(76)	1.333(23)
C(76)	C(77)	1.478(23)	C(77)	C(72)	1.391(21)
C(75)	N(1)	1.546(23)	N(1)	O(3)	1.196(23)
N(1)	O(4)	1.198(23)			

Table 3 – Bond angles (deg) for Ru(η^5 -C₅H₅)(PPh₃)₂(O₂CC₆H₄-*p*-NO₂)

Atom A	Atom B	Atom C	Angle	Atom A	Atom B	Atom C	Angle
P(1)	Ru	P(2)	99.6(2)	C(12)	C(13)	C(14)	117.8(17)
P(1)	Ru	O(1)	82.2(3)	C(13)	C(14)	C(15)	119.8(16)
P(2)	Ru	O(1)	94.1(3)	C(14)	C(15)	C(16)	121.7(16)
P(1)	Ru	C(1)	117.4(6)	C(11)	C(16)	C(15)	116.3(14)
P(2)	Ru	C(1)	142.6(5)	P(1)	C(21)	C(22)	123.5(12)
P(1)	Ru	C(2)	153.1(5)	P(1)	C(21)	C(26)	115.6(12)
P(2)	Ru	C(2)	104.9(6)	C(22)	C(21)	C(26)	120.9(14)
O(1)	Ru	C(2)	106.6(6)	C(21)	C(22)	C(23)	119.1(16)
C(1)	Ru	C(2)	37.8(6)	C(22)	C(23)	C(24)	107.9(17)
P(1)	Ru	C(3)	134.5(5)	C(23)	C(24)	C(25)	121.5(17)
P(2)	Ru	C(3)	85.9(5)	C(24)	C(25)	C(26)	118.7(16)
O(1)	Ru	C(3)	142.9(6)	C(21)	C(26)	C(25)	121.6(15)
C(1)	Ru	C(3)	65.0(7)	P(1)	C(31)	C(32)	120.4(13)
C(2)	Ru	C(3)	39.0(6)	P(1)	C(31)	C(36)	121.1(12)
P(1)	Ru	C(4)	98.9(5)	C(32)	C(31)	C(36)	118.3(15)
P(2)	Ru	C(4)	107.8(6)	C(31)	C(32)	C(33)	119.0(15)
O(1)	Ru	C(4)	157.5(6)	C(32)	C(33)	C(34)	123.0(17)
C(1)	Ru	C(4)	63.6(7)	C(33)	C(34)	C(35)	119.1(17)
C(2)	Ru	C(4)	63.3(6)	C(34)	C(35)	C(36)	119.2(17)
C(3)	Ru	C(4)	38.3(6)	C(31)	C(36)	C(35)	121.2(16)
P(1)	Ru	C(5)	91.3(6)	P(2)	C(41)	C(42)	118.3(10)
P(2)	Ru	C(5)	146.5(5)	P(2)	C(41)	C(46)	119.2(11)
O(1)	Ru	C(5)	118.8(6)	C(42)	C(41)	C(46)	122.2(14)
C(1)	Ru	C(5)	36.3(6)	C(41)	C(42)	C(43)	119.0(14)
C(2)	Ru	C(5)	62.0(7)	C(42)	C(43)	C(44)	120.9(16)
C(3)	Ru	C(5)	64.5(6)	C(43)	C(44)	C(45)	117.4(17)
C(4)	Ru	C(5)	38.9(6)	C(44)	C(45)	C(46)	124.7(16)
Ru	P(1)	C(11)	113.3(5)	C(41)	C(46)	C(45)	115.7(15)
Ru	P(1)	C(21)	120.6(5)	P(2)	C(51)	C(52)	114.2(12)
C(11)	P(1)	C(21)	104.1(7)	P(2)	C(51)	C(56)	124.1(13)
Ru	P(1)	C(31)	113.6(5)	C(52)	C(51)	C(56)	121.3(16)
C(11)	P(1)	C(31)	103.1(7)	C(51)	C(52)	C(53)	117.4(15)
C(21)	P(1)	C(31)	100.0(7)	C(52)	C(53)	C(54)	119.7(17)
Ru	P(2)	C(41)	111.5(4)	C(53)	C(54)	C(55)	124.8(18)
Ru	P(2)	C(51)	111.5(5)	C(54)	C(55)	C(56)	116.3(17)
Ru	P(2)	C(61)	127.2(5)	C(51)	C(56)	C(55)	120.3(16)
C(41)	P(2)	C(51)	104.7(7)	P(2)	C(61)	C(62)	118.6(11)
C(41)	P(2)	C(61)	103.0(6)	P(2)	C(61)	C(66)	119.5(11)
C(51)	P(2)	C(61)	96.0(7)	C(62)	C(61)	C(66)	121.4(14)
Ru	O(1)	C(71)	128.6(9)	C(61)	C(62)	C(63)	120.0(14)
O(1)	C(71)	O(2)	124.4(14)	C(62)	C(63)	C(64)	119.3(16)

(contd.)

Table 3 – Bond angles (deg) for $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-NO}_2)$ – *Contd.*

Atom A	Atom B	Atom C	Angles	Atom A	Atom B	Atom C	Angle
Ru	C(1)	C(2)	69.4(8)	C(63)	C(64)	C(65)	119.8(16)
Ru	C(1)	C(5)	70.9(9)	C(64)	C(65)	C(66)	122.1(15)
C(2)	C(1)	C(5)	106.9(17)	C(61)	C(66)	C(65)	117.0(14)
Ru	C(2)	C(1)	72.8(9)	O(1)	C(71)	C(72)	115.5(14)
Ru	C(2)	C(3)	70.6(8)	O(2)	C(71)	C(72)	120.0(15)
C(1)	C(2)	C(3)	110.5(17)	C(71)	C(72)	C(73)	120.8(15)
Ru	C(3)	C(2)	70.4(9)	C(71)	C(72)	C(77)	118.8(15)
Ru	C(3)	C(4)	69.3(10)	C(73)	C(72)	C(77)	119.9(15)
C(2)	C(3)	C(4)	104.1(17)	C(72)	C(73)	C(74)	120.0(16)
Ru	C(4)	C(3)	72.4(9)	C(73)	C(74)	C(75)	116.9(18)
Ru	C(4)	C(5)	72.7(9)	C(74)	C(75)	C(76)	127.6(20)
C(3)	C(4)	C(5)	109.5(16)	N(1)	C(75)	C(74)	114.3(19)
Ru	C(5)	C(1)	72.8(10)	N(1)	C(75)	C(76)	118.0(20)
Ru	C(5)	C(4)	68.4(8)	C(75)	C(76)	C(77)	115.8(18)
C(1)	C(5)	C(4)	109.0(16)	C(72)	C(77)	C(76)	119.8(17)
P(1)	C(11)	C(12)	117.4(12)	O(3)	N(1)	C(75)	113.5(23)
C(12)	C(11)	C(16)	122.8(15)	O(4)	N(1)	C(75)	116.9(22)
C(11)	C(12)	C(13)	121.4(16)	O(4)	N(1)	O(3)	129.6(25)

packing. Although, the η^1 -mode of bonding of S-thioformato complexes are known⁶, the present structure exemplifies the first structural report on the η^1 -carboxylato compounds containing the $\{\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\}^+$ moiety.

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