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Six-coordinate ruthenium(II) complexes containing both formate and alkenyl ligands. Crystal structure of $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$

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Abstract

The formate complexes $Ru(O_2CH)(CO)(RC{=}CHR')(PPh_3)_2$ have been obtained in qantitative yield from the reaction of the unsaturated complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ with sodium formate in CH_2Cl_2/MeOH mixtures. The synthesized complexes contain the formate ligand η^2-coordinated to metal. The structure of the complex $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$ has been established by an X-ray diffraction study. The molecule consist of an distorted octahedral ruthenium atom coordinated by two PPh_3 ligands in the axial positions and the other ligands in the equatorial plane. The η^2-coordinated formate ligand is not symmetric, and has C–O distances of 1.21(2) and 1.43(2) Å.

Introduction

The unsaturated 16-electron complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ obtained by reaction of $RuH(CO)Cl(PPh_3)_3$ and alkynes [1–3] are very reactive toward alkynes [1], CO [4], CN^tBu [5], CS_2 [6], 3.5-dimethylpyrazole [7] and carboxylates [8] to give six-coordinated ruthenium(II) complexes. The reaction with alkynes, CO, CN^tBu and CS_2 leads to coupling with the alkenyl group through C–C bond formation. The various complexes obtained from these reactions have been structurally characterized by X-ray diffraction studies, which have revealed that most of them have a *trans* disposition of the two phosphines except in the case of the products of the reaction with CS_2.

The carboxylate complexes of ruthenium(II) are very interesting because of their recently reported catalytic activity in hydrogenation and hydroformylation of alkenes [9], and so some modification of the alkenyl ligand was expected when the chloride ligand was substituted by a carboxylate group in the $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes. Unfortunately, the complexes $Ru(O_2CR'')(CO)(CR{=}CHR')(PPh_3)_2$ formed had the carboxylate group η^2-symmetrically coordinated to metal and the alkenyl ligand unchanged. The easy substitution of the chlorine by carboxylates in Ru(CO)Cl(RC=CHR')$(PPh_3)_2$ complexes prompted us to examine their reactions with the formate anion. The formate complexes are of importance because of their relevance to the carbon dioxide chemistry, and yet have been little studied [10]. Furthermore, the acidic nature of the formate hydrogen offers another reaction site in the molecule toward the alkenyl ligand and alkynes. We describe have the reactions of the Ru(CO)Cl(RC=CHR')$(PPh_3)_2$ complexes with the formate anion, And the reactions of some formate derivative with terminal alkynes HC≡CR" (R" = ^{t}Bu and Ph).

Results and discussion

When a CH_2Cl_2 solution of the Ru(CO)Cl(RC=CHR')$(PPh_3)_2$ complexes is treated with a MeOH solution of sodium formate new yellow crystalline products are obtained in a quantitative yield. These products are stable to air and soluble in CH_2Cl_2 but insoluble in petroleum ether and alcohols. Suitable crystals for X-ray diffraction studies were grown from in CH_2Cl_2/MeOH solutions of mixtures of products. All the complexes were identified by IR and ^{1}H NMR spectroscopy and from their, C and H elemental analyses, which reveal that there has been introduction of a formate ligand into the complexes with loss of a chlorine atom.

The IR spectra of complexes recorded with KBr pellets show strong absorptions at 1529–1555 cm^{-1} and 1352–13689 cm^{-1} corresponding to ν(OCO) vibrations. The difference between the positions of the two ν(OCO) bands in the IR spectra has a value of ≈ 185 cm^{-1} and is indicative of a η^2-coordination through the oxygens of the formate ligand to ruthenium [11]. The ν(C≡O) band appears at 1906–1934 cm^{-1}. The higher ν(C≡O) values are observed for complexes with an alkenyl ligand bearing electron-withdrawing groups which lower the electron density at ruthenium centre. Lower ν(C≡O) bands arise from complexes containing an alkenyl ligand bearing inductive groups (Me, ^{t}Bu and $SiMe_3$). The positions of the ν(C≡O) band in the new complexes is very similar to those for the acetate and 3,3-dimethylacrylate complexes previously described [8]. The ν(C=C) absorption is often obscured by the formate bands, but is observed at 1508–1595 cm^{-1} in some complexes.

The ^{1}H NMR of complexes show the signals of the coordinated ligands. The formate hydrogen appears at ≈ 7 ppm as a singlet for all the complexes [12]. The spectra of complexes containing a terminal alkenyl group display the –CH= proton at 6.2–9.6 ppm and the =CHR hydrogen at 4.6–5.7 ppm as a doublet with J(H–H) = 12–18 Hz characteristic of a *trans* disposition of hydrogens. as in the related acetate and 3,3-dimethylacrylate derivatives [8]. The signals of the alkenylic protons are large, hindering the exact determination of the J(H–P) values. The approximate H–P coupling constants for the alkenylic hydrogens in the formate complexes are: $J(H_\alpha–P) = 2$ Hz and $J(H_\beta–P) = 1.3$ Hz. The formate complexes show an upfield shift of the –C= protons and a downfield shift of the =CHR hydrogens relative to the corresponding position signals in the ^{1}H NMR spectra of Ru(CO)Cl(RC=CHR')$(PPh_3)_2$ compounds. The signals of the alkenyl hydrogens in the complexes containing a disubstituted alkenyl ligand are appear between 4.3 and 5.3 ppm. The spectroscopic similarity of the formate derivatives to other carboxylate complexes containing an alkenyl ligands are indicative of a similar electronic effect in the molecules. The geometry of the alkenyl ligands in the formate complexes is also similar to that in the starting complexes.

All analytical and spectroscopic data suggest that the structure of the synthesized

Table 1

IR and ^{1}H NMR data for complexes $Ru(O_2CH)(CO)(RC{=}CHR')(PPh_3)_2$

RC=CHR′	IR (cm^{-1})			^{1}H NMR (δ) [a]	
	CO	C=C	OCO		
$HC{=}CH_2$	1921	1566	1549	4.58	d, $J=16$, 1H
(1)			1352	4.92	3, $J=6$, 1H
				6.99	s, 1H
				7.2–7.73	m, 31H, 6Ph+1H
$HC{=}CHCMe_3$	1909	1573	1546	0.77	2, 9H
(2)			1354	4.89	d, $J=15$, 1H
				6.22	s, $J=15$, 1H
				7.00	s, 1H
				7.3–7.5	m, 30H
$HC{=}CHSiMe_3$	1915	1508	1544	−0.5	2, 9H
(3)			1368	5.56	d, $J=16$, 1H
				7.40	s, 1H
				7.45–7.6	m, 30H
				7.75	d, $J=16$, 1H
HC=CHPh	1925	1595	1555	5.75	d, $J=16$, 1H
(4)			1358	6.4–7.5	m, 35H
				7.60	s, 1H
				7.70	d, $J=16$, 1H
MeC=CHMe	1906		1553	1.93	s, 3H
(5)			1366	2.31	s, 3H
				4.28	s, 1H
				7.3–7.8	m, 31H
PhC=CHPh	1922		1551	5.35	s, 1H
(6)			1369	6.4–7.5	m, 40H
				7.95	s, 1H
$HC{=}CHCO_2Me$	1924		1541	3.38	s, 3H
(7)	1690		1354	5.40	d, $J=12$, 1H
				7.09	s, 1H
				7.2–7.55	m, 30H
				9.51	d, $J=12$, 1H
$HC{=}CHCO_2Et$	1922		1539	1.10	tr, $J=8$, 3H
(8)	1683		1353	3.85	q, $J=8$, 2H
				5.39	d, $J=18$, 1H
				7.02	s, 1H
				7.2–7.76	m, 30H
				9.57	d, $J=18$H, 1H
$MeO_2CC{=}CHCO_2Me$	1934	1568	1548	3.39	s, 3H, 3H
(9)	1706		1372	3.61	s, 3H, 3H
				4.89	s, 1H
				7.11	s, 1H
				7.26–7.7	m, 30H

[a] J in Hz.

Table 2

Selected bond lengths (Å) and angles (°) for $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$

Ru–P1	2.414(5)	Ru–P2	2.395(5)
Ru–O2	2.278(7)	Ru–O3	2.370(7)
Ru–C1	1.753(11)	Ru–C3	2.036(8)
O1–C1	1.13(2)	O2–C2	1.21(2)
O3–C3	1.43(2)	C3–C4	1.35(1)
C4–C5	1.51(2)	P1–C100	1.92(2)
P1–C106	1.84(1)	P1–C112	1.89(2)
P2–C200	1.82(1)	P2–C206	1.75(2)
P2–C212	1.83(1)		
C1–Ru–C3	118.3(4)	O3–RuC3	127.2(3)
O3–Ru–C1	114.4(4)	O2–Ru–C3	70.8(3)
O2–Ru–C1	170.8(4)	O2–Ru–O3	56.4(3)
P2–Ru–C3	92.9(3)	P2–Ru–C1	88.0(4)
P2–Ru–O3	85.4(2)	P2–Ru–O2	91.0(2)
P1–Ru–C3	91.8(3)	P1–Ru–C1	90.2(4)
P1–Ru–O3	91.4(2)	P1–Ru–O2	90.1(2)
P1–Ru–P2	175.3(1)	Ru–O2–C2	100.8(8)
Ru–O3–C2	90.3(6)	Ru–C1–O1	179.2(1)
O2–C2–O3	112.4(2)	Ru–C3–C4	124.4(7)
C3–C4–C5	123.4(1)		

complexes consist of a ruthenium atom coordinated to an η^2-formate, an η^1-alkenyl, CO and two PPh_3 ligands. Table 1 shows the spectroscopic data for the new complexes. The crystal structures of related carboxylate complexes have shown that the two PPh_3 ligands are in a *trans* position and the remaining ligands in an equatorial pseudoplane. Because of the structural interest of the formate ligand and the limited data on their ruthenium derivatives [13] and X-ray diffraction of $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$ was undertaken.

The structure of $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$

Table 2 lists selected bond lengths and angles. The structure of the molecule of $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$ is depicted in the Fig. 1. The atom coordinates are listed in Table 3. The crystal consists of discrete $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$ molecules held together by Van der Waals forces. The molecule can be described as consisting of a distorted octahedral ruthenium atom coordinated by two PPh_3 in a *trans* position and by one molecule of CO, an η^1-2-phenylethenyl, and an η^2-formate ligand in an equatorial plane. The angle formed by the two phosphines and the ruthenium is 175.3(1)°. The ruthenium–phosphorus distances are slightly different (Ru–P1; 2.414(5) Å and Ru–P2: 2.395(5) Å) and comparable to such bonds in related complexes [8]. The formate ligand is assymetrically η^2-coordinated to ruthenium, with Ru–O2 and Ru–O3 distances of 2.278(7) and 2.370(7) Å respectively. The shorter distance corresponds to the Ru–O2 bond *trans* ligand is that the two C–O distances are different. The O2–C2 bond has a length of 1.21(2) Å and the O3–C2 bond are of 1.43(2) Å. From these values is seems that the electronic density is not symmetrically distributed over the coordinated ligand. Thus, the O2–C2 bond can be considered as double, whereas the O3–C2 bond has a

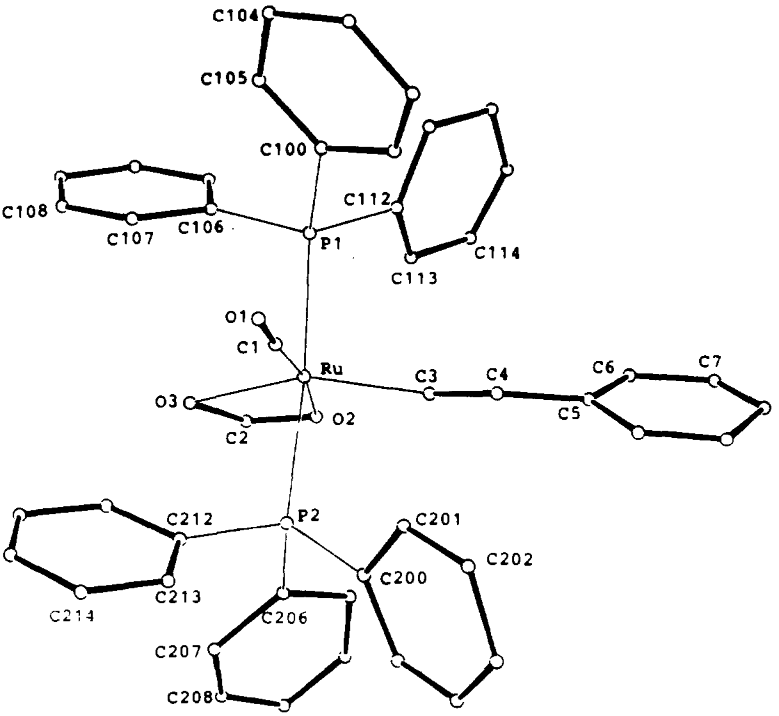
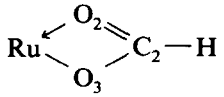


Fig. 1. The molecular structure of $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$.

length expected for a single C–O bond. The coordination of the formate ligand to ruthenium can be represented as:



The slight difference in length between the Ru–O bonds is probably caused by *trans* position of the π-acceptor CO ligand to the Ru–O2 bond inducing π-interactions between the p_π system of the carboxylate and a filled metal d_π orbital, as suggested previously [14]. The O2–C2–O3 angle is 112.4(1)°, as, in other η^2-carboxylate complexes. This angle gives rise to the small O2–Ru–O3 angle of 56.64(3)°, which modifies the remaining equatorial angles around the ruthenium atom (O2–Ru–C3: 70.8(3)°, C3–Ru–C1: 118.3(4)° and C1–Ru–O3: 118.3(4)°). The C1–O1 distance is 1.13(2) Å, and is found for related ruthenium complexes [8]. The 2-phenylethenyl ligand is η^1 bonded to metal with a C3–Ru distance of 2.036(8) Å, identical to the corresponding distance in the $Ru(O_2CMe)(CO)(CH{=}CHPh)(PPh_3)_2$ [8]. The phenylethenyl ligand lies in a plane, and the C3–C4 double bond length is 1.35(1) Å.

Reaction of $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$ complexes with $HC{\equiv}CR$ alkynes

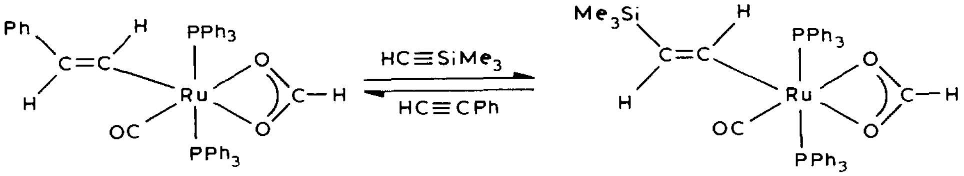
The complex $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$ reacts with an excess of HC=CR (R = ^{t}Bu and $SiMe_3$) alkynes in an equimolar mixture of CH_2Cl_2 and MeOH at room temperature, and within 4 hours the –CH=CHPh group has been completely replaced by a –CH=CHR (R = ^{t}Bu and $SiMe_3$) ligand but the formate

Table 3

Atomic coordinates for $C_{46}H_{38}O_3P_2Ru$

Atom	*x*	*y*	*z*
Ru	0.17850(0)	0.20735(3)	0.13040(0)
P1	0.0771(3)	0.2146(3)	0.0234(2)
P2	0.2803(3)	0.2139(3)	0.2351(2)
O1	0.3341(11)	0.2620(15)	0.0634(8)
O2	0.0524(5)	0.1887(5)	0.1859(4)
O3	0.0992(5)	0.3353(5)	0.1742(3)
C1	0.2734(7)	0.2412(7)	0.0900(5)
C2	0.0347(13)	0.2705(9)	0.1974(8)
C3	0.1530(6)	0.0664(6)	0.1403(5)
C4	0.2114(7)	−0.0032(7)	0.1267(5)
C5	0.1877(27)	−0.1071(6)	0.1291(17)
C6	0.0945(13)	−0.1588(14)	0.1202(10)
C7	0.0957(14)	−0.2574(13)	0.1188(13)
C8	0.1706(29)	−0.3053(7)	0.1288(25)
C9	0.2615(16)	−0.2544(18)	0.1404(9)
C10	0.2620(20)	−0.1585(19)	0.1394(14)
C100	0.1402(13)	0.2094(11)	−0.0542(10)
C101	0.1910(7)	0.1299(7)	−0.0614(5)
C102	0.2391(7)	0.1174(9)	−0.1119(6)
C103	0.2296(22)	0.1903(22)	−0.1616(13)
C104	0.1702(18)	0.2756(18)	−0.1582(13)
C105	0.1308(13)	0.2822(13)	−0.1030(11)
C106	0.0147(5)	0.3285(6)	0.0185(4)
C107	0.0709(9)	0.4144(7)	0.0260(5)
C108	0.0144(10)	0.5006(7)	0.0269(6)
C109	−0.0745(9)	0.5101(6)	0.0125(5)
C110	−0.1247(7)	0.4257(8)	0.0036(5)
C111	−0.0828(6)	0.3362(8)	0.0048(5)
C112	−0.0126(12)	0.1170(13)	0.0071(11)
C113	−0.0617(13)	0.0937(16)	0.0559(10)
C114	−0.1334(15)	0.0249(12)	0.0443(11)
C115	−0.1556(12)	−0.0120(12)	−0.0179(10)
C116	−0.1095(11)	0.0150(13)	−0.0712(10)
C117	−0.0412(15)	0.0880(13)	−0.0597(10)
C200	0.3741(10)	0.1279(9)	0.2540(6)
C201	0.4237(14)	0.0926(12)	0.2012(10)
C202	0.4958(16)	0.0257(19)	0.2147(12)
C203	0.5155(16)	−0.0123(17)	0.2825(12)
C204	0.4644(16)	0.0211(15)	0.3312(8)
C205	0.3936(12)	0.0829(14)	0.3180(9)
C206	0.2238(11)	0.2117(11)	0.3070(10)
C207	0.2337(15)	0.2830(14)	0.3500(10)
C208	0.1775(24)	0.2738(23)	0.2738(23)
C209	0.1291(20)	0.1984(19)	0.4296(14)
C210	0.1200(9)	0.1338(9)	0.3829(6)
C211	0.1620(7)	0.1358(9)	0.3190(5)
C212	0.3435(6)	0.3264(7)	0.2437(4)
C213	0.4411(6)	0.3331(7)	0.2575(5)
C214	0.4893(10)	0.4209(9)	0.2616(7)
C215	0.4359(10)	0.4999(10)	0.2478(6)
C216	0.3292(90)	0.5022(8)	0.2370(6)
C217	0.2981(5)	0.4109(6)	0.2294(4)

ligand has been maintained. Thus, after the reaction of $Ru(O_2CH)(CO)(HC{=}CHPh)(PPh_3)_2$ with $HC{\equiv}CSiMe_3$ the complex $Ru(O_2CH)(CO)(HC{=}CHSiMe_3)(PPh_3)_2$ was identified by IR and ^1H NMR spectroscopy and was isolated in a quantitative yield. The reaction of the same complex with $HC{\equiv}C^tBu$ produced a compound with an IR spectrum very similar to that of $Ru(O_2CH)(CO)(HC{=}CH^tBu)(PPh_3)_2$ but the ^1H NMR spectrum showed two paris of doublets at 6.35 ($J = 16$ Hz), 6.30 ($J = 16$ Hz), 5.03 ($J = 16$ Hz) and 4.98 ($J = 16$ Hz) ppm. Two of these sets of signals are coincident with those for the complex $Ru(O_2CH)(CO)(HC{=}CH^tBu)(PPh_3)_2$ (6.30 and 4.97 ppm). The other two doublets must be attributed to an isomeric form of complex $Ru(O_2CH)(CO)(HC{=}CH^tBu)(PPh_3)_2$, probably that with the two PPh_3 ligands *cis* to one another if it is assumed that the J(H–H) is 16 Hz for all the signals, a value indicative of a *trans* disposition of the alkenyl hydrogens [1,2]. The $^{31}P\{^1H\}$ NMR of the mixture displays two signals, at 37.6 and 37.1 ppm, supporting our suggestion of the presence of two isomers with equivalent phosphines. The displacement of the alkenyl group in these reactions is reversible, and can be depicted as follows:



Experimental

The ^1H NMR spectra were recorded on a Bruker AM 400 spectrometer at room temperature in $CDCl_3$ solutions and are referenced to $SiMe_4$. The ^1H decoupled ^{31}P NMR spectra were recorded on the same instrument in $CDCl_3$ solutions with aqueous 85% H_3PO_4 as external reference. The IR spectra were recorded on a Perkin–Elmer 1710-FT spectrometer with KBr pellets. The C and H elemental analyses were carried out with a Perkin–Elmer 240B analyzer.

All reactions were performed under a nitrogen atmosphere using Schlenk techniques. The complex $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ were prepared by published methods [1–3].

Preparation of complexes

To a 10 ml of a CH_2Cl_2 solution of 0.2 g of $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ was added a small excess of sodium formate in 5 ml of MeOH. The solution turned rapidly yellow. Stirring was maintained for 2 hours and solution was then evaporated to dryness and the residue dissolved in CH_2Cl_2. The precipitate was filtered off, concentrated to a few ml, and petroleum ether added to precipitate the product. The products can be recrystallized from CH_2Cl_2/MeOH mixtures.

$Ru(O_2CH)(CO)(HC{=}CH_2)(PPh_3)_2$ (1). Found: C, 66.30; H, 4.60. $C_{40}H_{34}O_3P_2Ru$ calc.: C, 66.20; H, 4.73%.

$Ru(O_2CH)(CO)(HC{=}CHCMe_3)(PPh_3)_2$ (2). Found: C, 67.70; H, 5.40. $C_{44}H_{42}O_3P_2Ru$ calc.: C, 67.59; H, 5.43%. ^{31}P NMR (ppm): 37.6(s).

$Ru(O_2CH)(CO)(HC{=}CHSiMe_3)(PPh_3)_2$ (3). Found: C, 64.15; H, 5.60. $C_{43}H_{42}O_3P_2SiRu$ calc.: C, 64.72; H, 5.32%.

$Ru(O_2CH)(CO)(HC=CHPh)(PPh_3)_2$ (4). Found: C, 69.00; H, 4.80. $C_{46}H_{38}O_3P_2Ru$ calc.: C, 68.90; H, 4.79%. ^{31}P NMR (ppm): 37.5 (s).

$Ru(O_2CH)(CO)(MeC=CHMe)(PPh_3)_2$ (5). Found: C, 66.95; H, 5.90. $C_{42}H_{38}O_3P_2Ru$ calc.: C, 66.92; H, 5.09%.

$Ru(O_2CH)(CO)(PhC=CHPh)(PPh_3)_2$ (6). Found: C, 71.19; H, 4.80. $C_{52}H_{42}O_3P_2Ru$ calc.: C, 71.19; H, 4.83%.

$Ru(O_2CH)(CO)(HC=CHCO_2Me)(PPh_3)_2$ (7). Found: C, 64.30; H, 4.71. $C_{42}H_{36}O_5P_2Ru$ calc.: C, 64.35, H, 4.64%.

$Ru(O_2CH)(CO)(HC=CHCO_2Et)(PPh_3)_2$ (8). Found: C, 64.72; H, 4.79. $C_{43}H_{38}O_5P_2Ru$ calc.: C, 64.74; H, 4.77%.

$Ru(O_2CH)(CO)(MeO_2CC=CHCO_2Me)(PPh_3)_2$ (9). Found: C, 62.80; H, 4.78. $C_{44}H_{38}O_7P_2Ru$ calc.: C, 62.78; H, 4.56%.

X-ray structure determination

The crystal data and experimental details for the structure determination, solution and refinement are given in Table 4. Accurate cell dimensions were determined by least-square analysis of setting angles of 26 automatically centered reflections in the range ($10 < \theta < 26°$) using graphite monochromated Mo-K_α radiation Enraf–

Table 4

Crystal data, data collection and structure refinement

Crystal data	
Formula	$C_{46}H_{38}O_3P_2Ru$
Crystal dimensions (mm)	0.20×0.27×0.30.
Symmetry	Monoclinic, *Cc*
Unit cell dimensions	
a, b, c (Å)	14.486(6), 14.101(7), 20.007(3)
α, β, γ (°)	90.00, 97.807(3), 90.00
Packing	
V (Å^3), Z	4048.9(3.1), 4
D_c (g cm^{-3}), M, $F(000)$	1.3154, 801, 1648
μ (cm^{-1}) (Mo-K_α)	4.936
Experimental data	
Technique	Four circle Enraf–Nonius CAD-4 diffractometer
Scanning range for θ	$10 < \theta < 26°$
Number of reflexions:	
measured	4700
observed	3720 ($I > 2\sigma(I)$ criterion)
Solution and refinement	
Number of variables	467
Ratio of freedom	7.96
Degrees of freedom	3253
Final R and R_w	5.0, 5.5%
Weighting scheme	empirical as to give no trends in $\langle w\lambda^2F\rangle$ vs. $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$ [16]
Computer and programs	VAX 11/750, XRAY-76 [17]
Scattering and programs	Ref. 18

Nonius on a CAD-4 diffractometer. Systematic absences were consistent with space group *Cc* and *C*2/*c*. Intensity data were collected with Mo-K_α radiation on an Enraf–Nonius CAD-4 diffractometer, two reflections were measured every hour to check crystal stability, and no significant variations were observed. Lorentz, polarization, and empirical absorption corrections were applied.

The structure was solved by direct methods (MULTAN80 [15]) and the positions of the Ru and P atoms deduced from the electron density map. Successive difference Fourier synthesis and least squares refinement revealed the positions of the light atoms except H, and allowed exclusion of the alternative non-centrosymmetric space group *Cc*. H-atoms attached to C2, C3 and C4 were located from difference electron densities, but the protons on the aromatic rings were placed in calculated positions (C–H: 1.00 Å). All H-atoms were included with fixed-atom contributions with each given the isotropic temperature factor of its associated non-H atom.

A table of thermal parameters, a complete list of bond lengths and angles, and lists of structure factors are available from the authors

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References

1 M.R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 326 (1987) 413.
2 M.R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 309 (1986) 169.
3 M.R. Torres, A. Santos, J. Ros and X. Solans, Organometallics, 6 (1987) 1091.
4 M.R. Torres, A. Perales, H. Loumrhari and J. Ros, J. Organomet. Chem., 384 (1990) C61.
5 J. Montoya, A. Santos, A.M. Echavarren and J. Ros, J. Organomet. Chem., 390 (1990) C57.
6 M.R. Torres, A. Perales and J. Ros, Organometallics, 7 (1988) 1223.
7 M.R. Torres, A. Santos, A. Perales and J. Ros, J. Organomet. Chem., 353 (1988) 221.
8 (a) M.R. Torres, A. Perales, H. Loumrhari and J. Ros, J. Organomet. Chem., 385 (1990) 379. (b) H. Loumrhari, J. Ros, M.R. Torres and A. Perales, Polyhedron, 9 (1990) 907.
9 (a) A.J. Lindsay, G. McDermott and G. Wilkinson, Polyhedron, 7 (1988) 1239; (b) J. Jenck, P. Kalck, E. Pinelli, M. Siani and A. Thorez, J. Chem. Soc., Chem. Commun., (1988) 1428.
10 R.P.A. Sneeden, in G. Wilkinson, F.G.A. Stone and E. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, Oxford, England, 1982, Chap. 50.4.
11 S.D. Robinson and F. Uttley, J. Chem. Soc., Dalton Trans., (1973) 1912.
12 G.L. Hillhouse and B.L. Barrimore, Inorg. Chem., 26 (1987) 1876.
13 M.A. Bennett, M.I. Bruce and T.W. Matheson, in G. Wilkinson, F.G.A. Stone and E. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon, Oxford, England, 1982, Chap. 32.3.
14 D.C. Brower, P.B. Winston, T.L. Tonker and J.L. Templeton, Inorg. Chem., 25 (1986) 2883
15 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq and M.M. Woolfson. MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, 1980, Univs. of York, England, and Louvain, Belgium.
16 M. Martinez-Ripoll and F.H. Cano, PESOS. A computer Program for the Automatic Treatment of Weighting Schemes. Instituto Rocasolano C.S.I.C. Madrid.
17 J.M. Stewart, F.A. Kundell and J.C. Baldwin, The XRAY70 System. Computer Science Center, University of Maryland, College Park, MD, 1974.
18 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.