Journal of Organometallic Chemistry, 289 (1985) 117–131
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

INDENYL COMPLEXES OF RUTHENIUM(II). CRYSTAL STRUCTURE OF $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4 \cdot \frac{1}{2}CH_2Cl_2$

LUIS A. ORO, MIGUEL A. CIRIANO, MARINA CAMPO

Departamento de Química Inorgánica, Universidad de Zaragoza, 50009 Zaragoza (Spain)

CONCEPCION FOCES-FOCES and FELIX H. CANO

Departamento de Rayos-X, Instituto Rocasolano C.S.I.C., Serrano 119, Madrid-6 (Spain)

(Received January 18th, 1985)

Summary

The compound $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (I) has been made in high yield by reaction of $[RuCl_2(PPh_3)_3]$ with indene and potassium hydroxide in ethanol and its reactions have been examined. Complex I reacts with appropriate nucleophiles to give the complexes $[RuX(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ ($X = H$, CH_3, I, $SnCl_3$, C_2Ph) and $[RuCl(dppe)(\eta^5\text{-}C_9H_7)]$. Heating of complex I with methanol in a sealed tube leads to the elimination of the indenyl group and decarbonylation of methanol. Cationic complexes of formulae $[RuL(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ ($L = CH_3CN$, $2\text{-}ClC_6H_4CN$, $CH_2{=}CHCN$, $1,2\text{-}(CN)_2C_6H_4$, $C_2H_4(CN)_2$, N_2H_4, $CNBu^t$, CO, $C{=}CHPh$, and C_2H_4) and $[Ru(L\text{-}L)PPh_3(\eta^5\text{-}C_9H_7)]ClO_4$ (L–L = 2,5-norbornadiene (nbd), tetrafluorobenzobarrelene (tfb), ethylenediamine (en), propylenediamine (pn), biimidazole (Hbim), 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen)) are obtained by treatment of complex I with the appropriate ligand and sodium perchlorate in methanol. Reaction of the vinylideneruthenium complex $[Ru(\eta^1\text{-}C{=}CHPh)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ with oxygen gives $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$.

The structure of $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4 \cdot \frac{1}{2}CH_2Cl_2$ has been determined by X-ray diffraction. The space group is $P\bar{1}$ with lattice constants a 18.5513(14), b 12.9165(5), and c 9.6898(5) Å, and α 80.942(5), β 104.998(7) and γ 111.130(4)°. Final R and R_w factors are 0.039 and 0.043, respectively, for the 6836 observed data ($3\sigma(I)$ criterion). The metal is bonded to an indenyl group through the five-membered ring, and hexacoordination of the ruthenium atom is completed by two triphenylphosphine ligands and a carbonyl group.

Introduction

An extensive chemistry based on the readily available complex $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ has been developed, mainly by Stone and Bruce [1]. In contrast, the

0022-328X/85/$03.30

analogous indenyl derivative [RuCl$(PPh_3)_2(\eta^5$-$C_9H_7)$] is still unknown, and indenyl ruthenium complexes are generally scarce; those known are: [Ru$(\eta^5$-$C_9H_7)_2$], [Ru$(CO)_2(\eta^5$-$C_9H_7)]_2$ (which was obtained in low yield [2]), the air-sensitive [Ru(CO)$(\eta^3$-$C_3H_5)(\eta^5$-$C_9H_7)$] [3], and the cluster species [Ru$_4$(CO)$_9$(η^2,η^5,η^2-C_9H_7)(η^5-C_9H_7)] [4].

Kinetic studies of substitution reactions of [Rh$(CO)_2(\eta^5$-$C_9H_7)$] [5] and [Mn$(CO)_3(\eta^5$-$C_9H_7)$] [6] and the corresponding cyclopentadienyl complexes have shown the much greater reactivity of the former, which is due to operation of an associative (S_N2) pathway when the indenyl group is present. The ability of the indenyl ligand to undergo a η^5 to η^3 migration, allowing nucleophilic attack on the metal centre [7], has been used recently in preparative studies of complexes of rhodium [8,9].

We now describe the preparation of the stable complex [RuCl$(PPh_3)_2(\eta^5$-$C_9H_7)$] (in high yield) and some neutral and cationic derivatives, and present the structure of [Ru(CO)$(PPh_3)_2(\eta^5$-$C_9H_7)$] ClO_4 as determined by X-ray diffraction.

Results and discussion

Synthesis of [RuCl$(PPh_3)_2(\eta^5$-$C_9H_7)$] and related neutral complexes

Bruce has described a high-yield synthesis of the complex [RuCl$(PPh_3)_2(\eta^5$-$C_5H_5)$] from ruthenium trichloride, triphenylphosphine and cyclopentadiene in refluxing ethanol [10a], but [Ru$Cl_2(PPh_3)_3$] is obtained if indene is used in place of cyclopentadiene [10b]. Nevertheless if potassium hydroxide is added to a brown ethanolic suspension of [Ru$Cl_2(PPh_3)_3$] and indene under reflux the colour changes to yellow and a red-brown solid [RuCl$(PPh_3)_2(\eta^5$-$C_9H_7)$] (I), is gradually formed in high yield. The complex [RuH_2(CO)$(PPh_3)_3$] is a by-product in this reaction and is formed by decarbonylation of the solvent by [Ru$Cl_2(PPh_3)_3$] in the basic medium, as previously described [11]. However if methanol is used as solvent the decarbonylation competes strongly with the formation of I, which is obtained in lower yield (ca. 30%). These facts suggest that an alkoxyruthenium complex is a common intermediate in both rections, since [Ru$Cl_2(PPh_3)_3$] does not react with pure indene in either ethanol or methanol under reflux in the absence of potassium hydroxide.

The pentahapto coordination of the indenyl group in complex I is evident from the NMR spectra. Resonances due to H^1 and H^2 appear as a triplet and a doublet, respectively, shifted from the aromatic region towards high field. The resonances of the benzene protons overlap with those from the triphenylphosphine ligands to give a broad multiplet. A singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum, in accord with the proposed structure (see Fig. 1).

Reaction of [RuCl$(PPh_3)_2(\eta^5$-$C_9H_7)$] with methanol in a Carius tube at 85°C for several hours gives a deep-red solution from which a white solid crystallizes out slowly. Prolonged heating affords a yellow solution of a mixture of ruthenium carbonyl complexes which has not been resolved. The IR spectrum of the white crystals reveals the presence of methanol (3340m and 1065m cm^{-1}) and hydride (ν(RuH) 2050w cm^{-1}) and carbonyl (ν(CO) 1930s cm^{-1}) groups. No terminal ν(RuCl) bands are present in the 350–250 cm^{-1} region. The solid analyzes for RuClH(CO)$(PPh_3)_2$MeOH but its insolubility precludes further characterization.

This reaction involves the removal of the indenyl group in a reversal of the formation of complex I and also the decarbonylation of methanol. In contrast, the

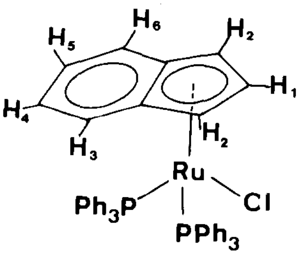

Fig. 1. Proposed structure for $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$.

related compound $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ is recovered unchanged after similar treatment.

The complex $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ reacts with a variety of nucleophiles to give the complexes $[RuX(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (X = H, CH_3, I, $SnCl_3$, C_2Ph) (see Table 1).

The hydridoruthenium complex II is readily formed by reaction of complex I with sodium methoxide in methanol, and is isolated as a microcrystalline air-stable solid in good yield. β-Disubstituted alkoxides, such as isopropoxide, give II in low yield, suggesting that the nucleophilic attack on the metal is hindered by bulky groups. The ruthenium-alkoxide intermediate undergoes β-elimination to give complex II. Alkoxy groups without hydrogen in the β-position do not react with complex I to give complex II: thus complex I was recovered unchanged after 1 h of reflux with potassium t-butoxide in t-butanol. Complex II was characterized by IR and NMR spectroscopy (see Experimental); it reacts rapidly with hydrogen chloride in the NMR tube to re-form complex I.

Methylmagnesium iodide reacts with complex I in diethyl ether to give initially a dark red suspension, which slowly changes to an orange solution of the methyl-

TABLE 1

COLOURS, YIELDS, ANALYTICAL DATA, AND MOLECULAR WEIGHTS FOR THE NEUTRAL COMPLEXES

Complex	Colour	Yield (%)	Analyses (Found (calcd.)(%))			Mol.wt. ($CHCl_3$) (Found(calcd.))
			C	H	Cl	
$[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (I)	red-brown	85	69.05	4.80	4.70	760
			(69.65)	(4.80)	(4.60)	(776)
$[RuH(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (II)	orange	61	72.00	5.15		–
			(72.85)	(5.15)		
$[Ru(CH_3)(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (III)	orange	47	71.10	5.45		732
			(73.10)	(5.35)		(756)
$[RuI(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (IV)	dark red	63	62.20	4.40		800
			(62.30)	(4.30)		(868)
$[Ru(SnCl_3)(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (V)	orange	88	55.60	3.80		951
			(55.95)	(3.85)		(966)
$[Ru(\eta^1\text{-}C_2Ph)(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (VI)	orange	70	74.65	5.25		–
			(75.60)	(5.05)		
$[RuCl(dppe)(\eta^5\text{-}C_9H_7)]$ (VII)	orange	40	64.30	5.10		650
			(64.65)	(4.80)		(650)

ruthenium complex III. Complex III is an air-stable solid, very soluble in organic solvents. Its ^1H NMR spectrum shows a singlet for the methyl group along with a doublet (H^2), a triplet (H^1) and an AA'BB' system (H^3,H^4,H^5,H^6) due to the protons of the indenyl ring, as well as complex multiplets centered at δ 7.1 from the triphenylphosphine ligands. The dark-red suspension was presumably of the iodoruthenium complex IV which is readily formed upon reaction of complex I with hydrogen iodide in methanol. On the other hand complex I reacts with $SnCl_2$ in refluxing chloroform to give complex V. Complex V was isolated as a microcrystalline solid showing characteristic ν(SnCl) bands of the trichlorostannate group at 325s and 295 s,br cm^{-1}.

Reaction of phenylacetylene with complex I in refluxing methanol gives a red solution of the complex $[Ru(\eta^1\text{-C=CHPh})(PPh_3)_2(\eta^5\text{-}C_9H_7)]Cl$. Potassium hydroxide in methanol and alumina in dichloromethane both abstract the vinylidene proton to give the acetylideruthenium complex VI, which is an air-stable solid. This rection is reversed if a strong acid such as perchloric is added to the acetylide complex. Protonation occurs at the β-acetylide carbon as described for the related $[Ru(\eta^1\text{-}C_2Ph)(PPh_3)_2(\eta^5\text{-}C_5H_5)]$, and $[Ru(\eta^1\text{-}C_2Ph)(PMe_3)_2(\eta^5\text{-}C_5H_5)]$ complexes [12] and predicted by Fenske [13]. Complex VI shows the characteristic sharp strong band of the η^1-coordinated acetylide at 2080 cm^{-1}, and resonances due to the indenyl protons, the triphenylphosphine and the phenyl group (see Experimental).

Replacement of both triphenylphosphine ligands in complex I can be achieved by reaction with 1,2-bis(diphenylphosphino)ethane in toluene under reflux. The isolated complex $[RuCl(dppe)(\eta^5\text{-}C_9H_7)]$ (VII) is an air-stable solid, and was characterized by analytical and spectroscopic methods.

Cationic complexes

Reaction of complex I with the appropriate neutral ligand L and sodium perchlorate in methanol gives cationic complexes of formula $[RuL(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (complexes VIII–XVII, Table 2). All of them are 1 : 1 electrolytes in acetone solution and were characterized by analysis and IR spectrocopy. They show typical bands of the uncoordinated perchlorate anion (ca. 1100s and 620s cm^{-1}) along with the expected bands of the triphenylphosphine and the corresponding L ligand. The nitrile complexes present significant shifts of the ν(CN) vibration to higher frequency, confirming the coordination of the nitrile ligands. Two ν(CN) bands are observed in the IR spectra of the dinitrile complexes, corresponding to free and coordinated CN groups. The hydrazine complex XIII shows ν(NH) at 3350w, 3290w and 3240w cm^{-1}, while the t-butylisocyanide complex XIV has a single ν(CN) band at 2140s cm^{-1}, and the carbonyl derivative XV displays a ν(CO) band at 1970s cm^{-1}. An X-ray structure determination on this complex is described below.

Interestingly, complex I reacts with phenylacetylene and sodium perchlorate in methanol to give the vinylidene complex $[Ru(\eta^1\text{-C=CHPh})(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (XVI), which was isolated as a red crystalline solid. The ^1H NMR spectrum of complex XVI shows a characteristic resonance of the vinylidenic proton at δ 5.21, and also those of the indenyl and triphenylphosphine groups. The IR spectrum has broad bands in the 1650–1600 cm^{-1} region associated with the vinylidene group. A methanolic solution of this complex in air deposits yellow crystals of $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ during several days, but the reaction is complete in about 3 h if oxygen is bubbled through the solution. Such a reaction represents an oxidative cleavage of multiple carbon–carbon bonds by oxygen, and has been briefly described by Bruce for the related $[Ru(\eta^1\text{-C=CHPh})(PPh_3)_2(\eta^5\text{-}C_5H_5)]^+$ complex [14]. The reaction in $CDCl_3$ was monitored by ^1H NMR spectroscopy for four days, and only the resonances of the starting material and the final product were observed.

It is of interest that the ethylene complex XVII is obtained by direct reaction of complex I with ethylene and sodium perchlorate in methanol while the cyclopentadiene derivative $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ does not react under similar conditions [15], although the complex $[Ru(C_2H_4)(dppe)(\eta^5\text{-}C_5H_5)]PF_6$ has been described [16].

Complex XVII can probably be isolated because of its insolubility in methanol, since it decomposes readily in solution with loss of ethylene. The ^1H NMR spectrum of a freshly prepared solution of complex XVII in acetone-d_6 shows a triplet at 2.46 (J 2.9 Hz) corresponding to ethylene.

Chelating nitrogen ligands (2,2′-bipyridine, 1,10-phenantroline, ethylenediamine, propylenediamine or biimidazole) and diolefins (tetrafluorobenzobarrelene or 2,5-norbornadiene) react with complex I and sodium perchlorate in methanol to give $[Ru(L\text{–}L)(PPh_3)(\eta^5\text{-}C_9H_7)]ClO_4$ complexes (XVIII–XXIV), chelation taking place by replacement of one triphenylphosphine ligand. The products are 1 : 1 electrolytes in acetone and show bands of the uncoordinated perchlorate anion at ca. 1100s and 620s cm^{-1} which are split in the complexes XX–XXII, probably because of a $O_3ClO \cdots HN$ interaction [17].

The structure of $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4 \cdot \frac{1}{2}CH_2Cl_2$

The crystal structure consists of mononuclear cations $[Ru(CO)(PPh_3)(\eta^5\text{-}C_9H_7)]^+$, perchlorate anions, and dichloromethane of crystallization. A view of the cation with

(continued on p. 124)

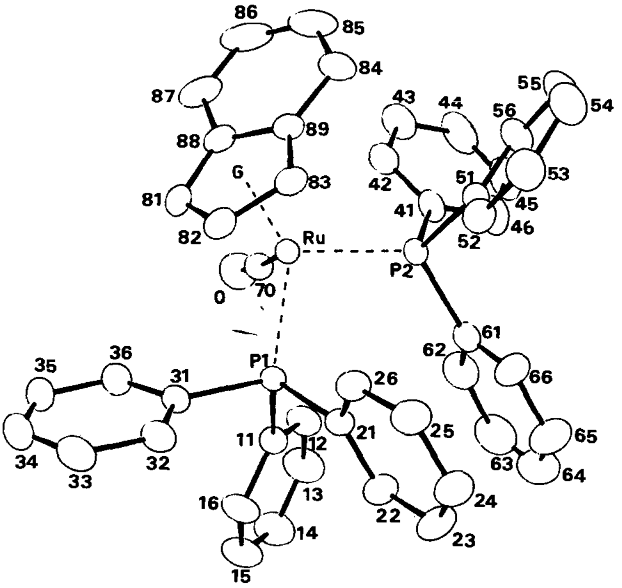

Fig. 2. A view of the cation $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]^+$, showing the coordination and the numbering system. The symbols of the carbon atoms are omitted for clarity.

TABLE 2

COLOURS, YIELDS, ANALYTICAL DATA, AND MOLAR CONDUCTIVITIES FOR THE CATIONIC COMPLEXES

Complex	Colour	Yield (%)	Analyses (Found(calcd.)(%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	ν(CN) (cm^{-1})
			C	H	N		
$[Ru(CH_3CN)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (VIII)	yellow	79	63.45 (64.05)	4.25 (4.55)	1.70 (1.60)	120	2285
$[Ru(2\text{-}ClC_6H_4CN)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (IX)	orange	56	63.75 (63.85)	4.15 (4.25)	1.50 (1.45)	121	2230
$[Ru(CH_2{=}CHCN)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (X)	yellow	77	63.80 (64.55)	4.55 (4.50)	1.55 (1.55)	119	2255
$[Ru\{1,2\text{-}(CN)_2C_6H_4\}(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (XI)	orange	89	64.75 (65.75)	4.70 (4.25)	2.85 (2.90)	112	2220,2230
$[Ru\{C_2H_4(CN)_2\}(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (XII)	orange	72	63.05 (63.95)	4.60 (4.50)	2.95 (3.05)	112	2240,2260
$[Ru(N_2H_4)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (XIII)	orange	88	61.30 (61.95)	4.80 (4.75)	3.35 (3.20)	111	
$[Ru(CNBu^t)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (XIV)	orange	78	64.70 (65.05)	4.95 (5.00)	1.50 (1.50)	117	
$[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4 \cdot \frac{1}{2}CH_2Cl_2$ (XV)	yellow	80	61.15 (61.30)	4.55 (4.20)	- -	107	

[Ru{C=CHPh}(PPh$_3$)$_2$(η^5-C$_9$H$_7$)]ClO$_4$ (XVI)	red	74	67.40	4.75	–	112
			(67.55)	(4.60)	–	
[Ru(C$_2$H$_4$)(PPh$_3$)$_2$(η^5-C$_9$H$_7$)]ClO$_4$ (XVII)	yellow	68	63.80	4.65	–	110
			(65.00)	(4.75)		
[Ru(nbd)(PPh$_3$)(η^5-C$_9$H$_7$)]ClO$_4$ (XVIII)	orange	78	61.30	4.35	–	125
			(60.95)	(4.50)		
[Ru(tfb)(PPh$_3$)(η^5-C$_9$H$_7$)]ClO$_4$ (XIX)	orange	38	58.35	3.35	–	115
			(58.25)	(3.50)	–	
[Ru(en)(PPh$_3$)(η^5-C$_9$H$_7$)]ClO$_4$ (XX)	orange	62	54.40	4.70	4.60	114
			(54.60)	(4.75)	(4.40)	
[Ru(pn)(PPh$_3$)(η^5-C$_9$H$_7$)]ClO$_4$ (XXI)	orange	45	55.55	5.00	4.50	111
			(55.25)	(4.95)	(4.30)	
[Ru(Hbim)(PPh$_3$)(η^5-C$_9$H$_7$)]ClO$_4$ (XXII)	orange	69	54.90	4.25	7.85	99
			(55.65)	(3.95)	(7.85)	
[Ru(bipy)(PPh$_3$)(η^5-C$_9$H$_7$)]ClO$_4$ (XXIII)	red	45	60.25	4.10	3.90	115
			(60.55)	(4.10)	(3.80)	
[Ru(phen)(PPh$_3$)(η^5-C$_9$H$_7$)]ClO$_4$ (XXIV)	red	60	60.75	4.35	3.60	111
			(61.80)	(4.00)	(3.70)	

the atomic numbering scheme is shown in Fig. 2. Selected bond distances and angles are listed in Table 3.

The ruthenium atom is bonded to a carbonyl, to two triphenylphosphine ligands,

TABLE 3

SELECTED GEOMETRICAL PARAMETERS [a]

Interatomic distances (Å)			
Ru–P(1)	2.322(1)	P(2)–C(61)	1.837(5)
Ru–P(2)	2.389(1)	C(81)–C(82)	1.420(6)
Ru–C(81)	2.239(5)	C(81)–C(88)	1.438(4)
Ru–C(82)	2.246(4)	C(82)–C(83)	1.407(5)
Ru–C(83)	2.265(3)	C(83)–C(89)	1.447(4)
Ru–C(88)	2.356(4)	C(84)–C(85)	1.364(8)
Ru–C(89)	2.352(3)	C(84)–C(89)	1.426(4)
Ru–C(70)	1.863(3)	C(85)–C(86)	1.403(10)
P(1)–C(11)	1.833(3)	C(86)–C(87)	1.360(7)
P(1)–C(21)	1.827(4)	C(87)–C(88)	1.429(6)
P(1)–C(31)	1.829(3)	C(88)–C(89)	1.416(6)
P(2)–C(41)	1.829(3)	Ru–G	1.945(3)
P(2)–C(51)	1.831(3)	C(70)–O	1.145(4)
Bond angles (°)			
G–Ru–P(1)	120.85(6)	C(81)–C(82)–C(83)	109.6(3)
G–Ru–P(2)	123.11(5)	C(82)–C(83)–C(89)	107.2(3)
G–Ru–C(70)	121.7(1)	C(85)–C(84)–C(89)	117.8(4)
C(70)–Ru–P(1)	90.6(1)	C(84)–C(85)–C(86)	121.8(4)
C(70)–Ru–P(2)	94.2(1)	C(85)–C(86)–C(87)	122.4(5)
P(1)–Ru–P(2)	98.80(2)	C(86)–C(87)–C(88)	117.5(5)
Ru–P(1)–C(31)	110.0(1)	C(81)–C(88)–C(87)	131.3(4)
Ru–P(1)–C(21)	115.2(1)	C(87)–C(88)–C(89)	120.2(3)
Ru–P(1)–C(11)	120.7(1)	C(81)–C(88)–C(89)	108.3(3)
Ru–P(2)–C(61)	121.5(1)	C(84)–C(89)–C(88)	120.2(3)
Ru–P(2)–C(51)	111.6(1)	C(83)–C(89)–C(88)	107.7(3)
Ru–P(2)–C(41)	113.8(1)	C(83)–C(89)–C(84)	131.8(3)
C(21)–P(1)–C(31)	104.4(2)	C(51)–P(2)–C(61)	103.2(2)
C(11)–P(1)–C(31)	99.4(2)	C(41)–P(2)–C(61)	102.7(2)
C(11)–P(1)–C(21)	104.9(2)	C(41)–P(2)–C(51)	101.8(2)
C(82)–C(81)–C(88)	106.8(3)	Ru–C(70)–O	174.4(4)
Torsion angles (°)			
C(81)–G–Ru–P(1)	−64.3(2)	C(70)–Ru–P(1)–C(11)	20.8(2)
C(81)–G–Ru–P(2)	168.7(2)	C(70)–Ru–P(1)–C(21)	148.4(2)
C(82)–G–Ru–P(1)	7.8(2)	C(70)–Ru–P(1)–C(31)	−93.9(2)
C(82)–G–Ru–P(2)	−119.3(2)	C(70)–Ru–P(2)–C(41)	40.1(2)
C(83)–G–Ru–P(1)	79.0(2)	C(70)–Ru–P(2)–C(51)	154.5(1)
C(83)–G–Ru–P(2)	−48.0(2)	C(70)–Ru–P(2)–C(61)	−83.4(2)
C(88)–G–Ru–P(1)	−136.5(2)	C(81)–C(82)–C(83)–C(89)	4.9(4)
C(88)–G–Ru–P(2)	96.4(2)	C(82)–C(83)–C(89)–C(88)	−1.8(4)
C(89)–G–Ru–P(1)	151.9(2)	C(83)–C(89)–C(88)–C(81)	−1.9(4)
C(89)–G–Ru–P(2)	24.9(2)	C(89)–C(88)–C(81)–C(82)	4.8(2)
Ru–P(1)–C(11)–C(12)	22.0(4)	C(88)–C(81)–C(82)–C(83)	−6.0(4)
Ru–P(1)–C(21)–C(22)	−132.8(3)	Ru–P(2)–C(41)–C(42)	21.2(4)
Ru–P(1)–C(31)–C(32)	−119.8(3)	Ru–P(2)–C(51)–C(52)	56.9(3)
		Ru–P(2)–C(61)–C(62)	84.2(4)

[a] G stands for the centroid of the five-membered ring.

and to an indenyl group through the five-membered ring. The geometry about the metal atom can be regarded as distorted octahedral if the η^5-indenyl group is assumed to occupy three facial coordination positions.

The indenyl function is clearly pentahapto bonded to the metal, and displays the asymmetric coordination generally observed with this ligand [18]. Thus three of the Ru–C bond lengths, those involving the C(81), C(82), and C(83) atoms, are significantly shorter than the two to the bridging, C(88) and C(89), carbon atoms. The former three Ru–C bond lengths fall within the range of individual Ru–C distances (2.16–2.26 Å) found for structures of cyclopentadienylruthenium complexes [17,19,20] while the last two are outside this range. Slipping of the metal across the η^5-bonded face towards a η^3-coordination has been invoked to describe this asymmetry, but the parameters ψ and Δ [18] which can be used as a measure of this do not differ from zero after allowance for the experimental uncertainty: Ru–G 1.945(3) Å versus Ru–(η^5-least-squares plane) 1.941(3) Å. The five-membered ring is not a regular pentagon, as observed in the complexes $[Mo(CO)(PEt_3)(MeC_2Me)(\eta^5\text{-}C_9H_7)]BF_4$ and $[Mo(PMe_3)_2(MeC_2Me)(\eta^5\text{-}C_9H_7)]BF_4$ [21], the bonds C(83)–C(89) and C(81)–C(88) being longer than the others. This ring is not planar within the experimental precision, showing a slight puckering to give a half chair conformation [22] with a pseudobinary axis through C(89). The benzene ring, being planar, shows significant localization of the double bonds at C(84)–C(85) and C(86)–C(87), as previously found for other indenyl complexes [18]. The two rings form a dihedral angle of 7.0(1)°.

The two Ru–P bonds are unequal, but both bond distances fall within the usual range (2.206–2.426 Å) [23], as does the P–C distances [17]. There is an asymmetry in the P–C–C angles in all but one of the phenyl groups, (117.6(3)–120.0(3)°) versus (120.1(3)–123.5(3)°), which display the usual regular hexagon geometry.

The carbonyl group has a terminal geometry, with the Ru–C–O angle (174.4(4)°) and the Ru–C and C–O bond distances (1.863(3) and 1.145(4) Å, respectively) close to previously reported values [24].

Experimental

All reactions were carried out in degassed solvents under oxygen-free nitrogen. $[RuCl_2(PPh_3)_3]$ [25], tetrafluorobenzobarrelene [26], and biimidazole [27] were prepared by published methods. Indene was purified by vacuum-distillation and was satisfactory for syntheses, but pure indene was obtained as described in ref. 28.

Microanalyses were carried out on a Perkin–Elmer 240B microanalyzer. IR spectra were recorded on a Perkin–Elmer 599 spectrometer using Nujol suspensions between polyethylene sheets. Conductivities were measured for ca. 5×10^{-4} M acetone solutions with a Philips PW 9501/01 conductimeter. The ^1H and ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer at room temperature; $CDCl_3$ was used as solvent unless otherwise stated, and $SiMe_4$ and 85% H_3PO_4 were used as internal and external standards, respectively. Molecular weights were measured in chloroform by use of a Perkin–Elmer 115 osmometer.

Typical preparations are given below, and the yields are listed in Tables 1 and 2.

Preparation of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ *(I)*

A solution of potassium hydroxide (9.3 ml, 0.11 M in ethanol, 1.04 mmol) was rapidly added to a refluxing suspension of $[RuCl_2\ (PPh_3)_3]$ (1.00 g, 1.04 mmol) and indene (2 ml) in ethanol (10 ml) to give, after a brief period, a red-brown suspension. The mixture was refluxed for 4 h then cooled and filtered. The crude red-brown solid was extracted with dichloromethane (8 ml). The extract was filtered and then methanol (30 ml) was added to give crystals of the product. After 30 min the solid was separated by filtration, washed with methanol, then with diethyl ether, and dried under vacuum.

In some preparations the recrystallized solid contained an impurity which gave rise to IR absorptions at 2020m and 1930s cm^{-1}. This was removed by extraction of the solid with acetone (ca. 500 ml), evaporation of the extract to dryness, and recrystallization of the residue from dichloromethane/diethyl ether. Ruby red crystals of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)] \cdot 0.5CH_2Cl_2$ (Found: C, 66.96; H, 4.51. $C_{45}H_{37}ClP_2Ru \cdot 0.5CH_2Cl_2$ calcd.: C, 66.75; H, 4.68%) or $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)] \cdot 0.5C_2H_4Cl_2$ (Found: C, 67.25; H, 4.71. $C_{46}H_{39}Cl_2P_2Ru$ calcd.: C, 66.91; H, 4.71%) were obtained by slow addition of methanol to dilute solutions of the compound in dichloromethane or 1,2-dichloroethane. $^{31}P\{^1H\}$ NMR spectrum: δ (ppm) 46.5(s); ^1H NMR spectrum: δ(ppm) 7.0 (complex m, 34H, PPh_3 and benzene ring); 4.60(t, 1H, J 3 Hz); 3.90(d, 2H, J 3 Hz).

Preparation of the neutral complexes $[RuX(PPh_3)_2(\eta^5\text{-}C_9H_7)]$

(a) $[RuH(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ *(II).* Solid $[RhCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (78 mg, 0.1 mmol) was added to a solution of sodium methoxide (prepared by reaction of sodium (2.4 mg, 0.1 mmol) with methanol (5 ml)). The red suspension was stirred at room temperature for 2 h to give an orange-yellow solid, which was separated by filtration, washed with methanol, and air-dried. $^{31}P\{^1H\}$ NMR spectrum: δ (ppm) 63.8(s). ^1H NMR spectrum: δ (ppm) 7.1. (complex, m, 30H, PPh_3); 6.75(m, 2H); 5.75(m, 2H); 4.70(t, 1H, J 2.4 Hz); 3.98(d, 2H, J 2.4 Hz); -15.40(t, 1H, ^2J(PH) 31.6 Hz); IR spectrum: ν(Ru–H) 2055 cm^{-1}.

(b) $[Ru(CH_3)(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ *(III).* A suspension of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (50.7 mg, 0.088 mmol) in a solution of methylmagnesium iodide (0.4 ml of a 0.22 *M* solution in diethyl ether; i.e. 0.88 mmol) in diethyl ether (10 ml) was stirred for 48 h at room temperature. The suspension was hydrolyzed with saturated aqueous ammonium chloride and the ethereal layer was separated and evaporated to ca. 0.5 ml. The product was precipitated by dropwise addition of cold methanol, filtered off, and air-dried. ^1H NMR spectrum: δ(ppm) 7.10 (complex m, 30H, PPh_3); 6.70(m, 2H); 5.76(m, 2H); 5.00(t, 1H); 4.55(d, 2H); 1.55(s, 3H).

(c) $[RuI(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ *(IV).* A mixture of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (50 mg, 0.065 mmol), hydroiodic acid (0.5 ml, 7.57 *M* in water, 3.52 mmol) and methanol (10 ml) was refluxed for 20 min to give a dark-red suspension. The solid was filtered off, washed with methanol, and air-dried.

(d) $[Ru(SnCl_3)(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ *(V).* A mixture of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (50.3 mg, 0.065 mmol), and $SnCl_2 \cdot 2H_2O$ (39 mg, 0.17 mmol) in chloroform (10 ml) was refluxed for 2 h to give an orange solution. Evaporation of this solution under vacuum to dryness and stirring of the residue with methanol (5 ml) gave the product as an orange solid, which was filtered off, IR spectrum: ν(SnCl) 325, 295 cm^{-1}.

(e) $[Ru(\eta^1\text{-}C{\equiv}CPh)(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ *(VI).* A solution of potassium hydroxide (1.46 ml, 0.11 *M* in methanol, 0.161 mmol) was added to a red solution prepared by brief refluxing of a mixture of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (125 mg, 0.161 mmol) and

phenylacetylene (0.1 ml, 0.92 mmol)) in methanol (10 ml). A yellow-orange suspension was formed. The solvent was pumped-off and the residue chromatographed on alumina (15 × 1 cm column) with dichloromethane as eluent. Evaporation of the orange band and addition of hexane gives the compound as orange crystals. ^{1}H NMR spectrum: δ(ppm) 7.2 (complex m, 35H, PPh_3 and Ph), 6.73(m, 2H), 6.20(m, 2H); 5.37(t, 1H, *J* 2.50 Hz); 4.56(d, 2H, *J* 2.50 Hz). IR spectrum ν(C≡C) 2080s cm^{-1}.

(f) $[RuCl(dppe)(\eta^5\text{-}C_9H_7)]$ (VII). A solution of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (100 mg, 0.13 mmol) and 1,2-bis(diphenylphosphino)ethane (52 mg, 0.13 mmol) in toluene (15 ml) was refluxed for 24 h. The solution was evaporated under vacuum to dryness and the residue was washed with diethyl ether then extracted with dichloromethane (5 ml). Hexane was slowly added to the extract until a yellow floculent solid separated. Evaporation of the solution to ca. 1 ml and addition of hexane gave the product as a deep orange solid. ^{1}H NMR spectrum: δ(ppm) 7.3(complex m, 24H,dppe and benzene ring); 4.90 (t, 1H); 4.50(d, 2H); 2.4 (complex m, 4H, dppe).

Preparation of the complexes $[Ru(nitrile)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (nitrile = CH_3CN, 2-ClC_6H_4CN, $CH_2{=}CHCN$) (VIII–X)

A red suspension of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (78 mg, 0.1 mmol) $NaClO_4 \cdot H_2O$ (70 mg, 0.5 mmol) and the appropriate nitrile (1.5 mmol) in methanol (10 ml) was stirred at room temperature for 1 h, orange suspensions being formed. The solids were filtered off, washed with methanol and then with diethyl ether, and vacuum-dried.

Preparation of the complexes $[Ru(dinitrile)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (dinitrile = 1,2-$(CN)_2C_6H_4$, $C_2H_4(CN)_2$) (XI–XII)

A mixture of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (78 mg, 0.1 mmol), $NaClO_4 \cdot H_2O$ (43 mg, 0.30 mmol) and phthalonitrile or succinonitrile (0.3 mmol) in methanol (5 ml) was stirred for 6 h at room temperature to give orange-yellow suspensions. The solvent was removed under vacuum and the residue extracted with dichloromethane, filtered, and concentrated to ca. 0.5 ml. Addition of diethyl ether to the extract gave the products as solids, which were filtered off and vacuum-dried.

Preparation of $[Ru(N_2H_4)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (XIII)

Stirring of a mixture of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (78 mg, 0.1 mmol), $NaClO_4 \cdot H_2O$ (43 mg, 0.30 mmol) and $N_2H_4 \cdot H_2O$ (25 μl, 0.5 mmol) in methanol (5 ml) for 4 h gave an orange suspension. Working up was as described for the dinitrile complexes.

Preparation of $[Ru(CNBu^t)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ (XIV)

A mixture of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (78 mg, 0.1 mmol), $NaClO_4 \cdot H_2O$ (29 mg, 0.21 mmol) and t-butylisocyanide (0.027 ml, 0.25 mmol) in methanol (10 ml) was stirred for 3 h at room temperature to give an orange-yellow suspension. The solid was filtered off and washed with methanol and then diethyl ether. ν(CN) 2140s cm^{-1}.

Preparation of $[Ru(CO)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4 \cdot \frac{1}{2}CH_2Cl_2$

Dry carbon monoxide was bubbled through a suspension of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (47 mg, 0.06 mmol) and $NaClO_4 \cdot H_2O$ (14 mg, 0.1 mmol) in methanol (10 ml) for 1.5 h to give a yellow suspension. The solvent was pumped-off and the residue recrystallized from dichloromethane/diethyl ether. ^{1}H NMR spectrum: δ(ppm) 7.3 (complex m, 18H, PPh_3); 7.09(m, 2H, benzene ring) 6.90 (complex, m, 12H, PPh_3); 6.53(m, 2H, benzene ring); 5.46(t, 1H, J 2.6 Hz); 5.28(d, 2H, J 2.6 Hz); 5.30(s,CH_2Cl_2). IR spectrum: ν(CO) 1970s cm^{-1}.

Preparation of $[Ru(\eta^1\text{-}C{=}CHPh)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ *(XVI)*

A suspension of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (346 mg, 0.45 mmol), $NaClO_4 \cdot H_2O$ (74 mg, 0.53 mmol) and phenylacetylene (0.10 ml, 0.89 mmol) in methanol (10 ml) was briefly refluxed (ca. 10 min) to give a red solution. This solution was kept in a refrigerator overnight to give the product as red crystals, which were filtered off and washed with cold methanol. ^{1}H NMR spectrum: δ(ppm) 7.4(m), 7.2(m), 6.8(m)

TABLE 4

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	$C_{46}H_{37}OP_2Ru \cdot ClO_4 \cdot \frac{1}{2}CH_2Cl_2$
Crystal habit	Yellow, plate hexagonal prism
Crystal size (mm)	0.32×0.29×0.26×0.13
Symmetry	Triclinic, $P\bar{1}$
Unit cell determination	
Leasts-squares fit	48 reflexions up to θ(Cu-K_α) < 45°
Unit cell dimensions (Å)	a 18.5513(14), b 12.9165(5); c 9.6898(5) α 80.942(5); β 104.998(7); γ 111.130(4)°
Packing: V (Å^3), Z	2086.7(2), 2
D_x (g cm^{-3}), M, F(000)	1.449, 910.733, 933
Experimental data	
Radiation and technique	Cu-K_α. PW1100 Philips diffractometer, bisecting geometry, graphite monochromated.
Collection mode	$\omega/2\theta$. 1×1 detector. θ < 65°. 1 min/reflex. 1.5 scan width. Sample stable.
Total independent data	7055
Observed data: $I > 3\sigma(I)$	6836
μ (cm^{-1}). Min-max transmission	54.25, 0.262–0.585
Solution and refinement	
Solution mode	Patterson (X-RAY 76 System [29]. Vax 11/750)
Refinement mode	Least-squares on F's. Observed reflexions only. 3 blocks in the final cycles.
Parameters:	
Final shift/error	0.25
Degrees of freedom	6135
No. variables	701 (H(90a) and H(90b) fixed)
Weighting scheme	Empirical as to give no trends on $\langle \omega\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ and $\langle \sin\theta/\lambda \rangle$
Max. thermal values (Å^2)	$U_{33}(07) = 0.50(5)$
Final F peaks (e Å^{-3})	0.79 near the Ru atom
Final R, R_ω	0.039, 0.043
Atomic factors	International Tables for X-Ray Crystallography [30]

TABLE 5

FINAL ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Ru	0.30035(1)	0.05156(2)	0.35793(2)
P(1)	0.37330(4)	0.23740(6)	0.39384(7)
P(2)	0.18027(4)	0.04529(6)	0.41219(8)
C(81)	0.3917(2)	−0.0196(3)	0.3442(4)
C(82)	0.4055(2)	0.0066(3)	0.4878(4)
C(83)	0.3399(2)	−0.0583(3)	0.5465(3)
C(84)	0.2154(2)	−0.2268(3)	0.4482(5)
C(85)	0.1826(3)	−0.2925(3)	0.3353(8)
C(86)	0.2154(4)	−0.2698(4)	0.2141(7)
C(87)	0.2817(3)	−0.1815(4)	0.2015(4)
C(88)	0.3188(2)	−0.1117(3)	0.3185(4)
C(89)	0.2858(2)	−0.1345(3)	0.4410(3)
C(11)	0.3517(2)	0.3477(3)	0.2640(3)
C(12)	0.2790(2)	0.3310(3)	0.1704(5)
C(13)	0.2633(3)	0.4161(5)	0.0746(6)
C(14)	0.3209(3)	0.5193(4)	0.0721(6)
C(15)	0.3941(3)	0.5365(3)	0.1620(5)
C(16)	0.4096(2)	0.4518(3)	0.2574(4)
C(21)	0.3800(2)	0.2816(3)	0.5681(3)
C(22)	0.3670(3)	0.3776(3)	0.5844(4)
C(23)	0.3713(3)	0.4056(4)	0.7199(5)
C(24)	0.3881(3)	0.3389(4)	0.8395(5)
C(25)	0.4016(3)	0.2429(3)	0.8256(4)
C(26)	0.3978(2)	0.2150(3)	0.6910(4)
C(31)	0.4761(2)	0.2657(3)	0.3859(4)
C(32)	0.5402(2)	0.3044(3)	0.4993(4)
C(33)	0.6173(2)	0.3269(3)	0.4814(6)
C(34)	0.6300(2)	0.3121(3)	0.3544(6)
C(35)	0.5670(3)	0.2731(3)	0.2423(6)
C(36)	0.4904(2)	0.2501(3)	0.2578(4)
C(41)	0.0914(2)	−0.0200(3)	0.2785(3)
C(42)	0.0930(2)	−0.0910(3)	0.1874(4)
C(43)	0.0236(3)	−0.1515(4)	0.0970(5)
C(44)	−0.0474(3)	−0.1381(5)	0.0981(5)
C(45)	−0.0492(2)	−0.0658(6)	0.1851(5)
C(46)	0.0191(2)	−0.0076(4)	0.2778(5)
C(51)	0.1609(2)	−0.0446(3)	0.5739(3)
C(52)	0.2181(2)	−0.0222(3)	0.7024(4)
C(53)	0.2073(3)	−0.0913(4)	0.8247(4)
C(54)	0.1399(3)	−0.1842(5)	0.8219(5)
C(55)	0.0836(3)	−0.2061(4)	0.6971(6)
C(56)	0.0934(2)	−0.1373(3)	0.5734(4)
C(61)	0.1649(2)	0.1722(3)	0.4414(5)
C(62)	0.1379(3)	0.2366(5)	0.3256(7)
C(63)	0.1300(5)	0.3374(6)	0.3463(13)
C(64)	0.1456(5)	0.3699(5)	0.4775(16)
C(65)	0.1717(5)	0.3079(6)	0.5957(12)
C(66)	0.1822(3)	0.2090(4)	0.5771(7)
C(70)	0.2688(2)	0.0868(3)	0.1629(3)
O	0.2517(2)	0.1019(3)	0.0410(3)
Cl(1)	0.5000	0.0000	0.0000
O(1) [a]	0.4760(19)	0.0508(14)	0.0690(21)
O(2) [a]	0.4710(10)	−0.0018(14)	−0.1426(12)

TABLE 5 (continued)

Atom	x/a	y/b	z/c
O(3) [a]	0.4523(11)	−0.1360(12)	0.0619(19)
O(4) [a]	0.5782(9)	−0.0045(16)	0.0246(30)
O(5) [a]	−0.0104(13)	0.4945(16)	0.8173(17)
O(6)	0.0236(8)	0.5982(6)	0.9894(13)
O(7) [a]	0.1039(11)	0.5146(22)	0.9766(45)
Cl(2) [a]	0.0261(2)	0.4899(2)	0.9568(3)
Cl(3) [a]	0.8411(3)	0.4569(4)	0.2467(5)
Cl(4)	1.0000	0.5000	0.5000
C(90) [a]	0.9433(14)	0.5248(30)	0.3178(32)

[a] Means population parameter = 0.50.

(37H, PPh_3 and Ph); 6.12(m, 2H, benzene ring); 5.87(t, 1H, J 2.6 Hz); 5.64(d, 2H, J 2.6 Hz); 5.21(t, $^4J(PH) < 1$ Hz, 1H, vinylidene). IR spectrum: ν(C=C) 1637m and 1620m cm^{-1}.

Preparation of $[Ru(\eta^2\text{-}C_2H_4)(PPh_3)_2(\eta^5\text{-}C_9H_7)]ClO_4$ *(XVII)*

To a solution of $NaClO_4 \cdot H_2O$ (237 mg, 1.70 mmol) in methanol (15 ml) saturated with ethylene was added $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (80 mg, 0.1 mmol). The mixture was stirred for 15 h at room temperature under an atmosphere of ethylene to give a yellow suspension. The solid was filtered off, washed with methanol, and air-dried.

Preparation of the complexes $[Ru(chel)(PPh_3)(\eta^5\text{-}C_9H_7)]ClO_4$ *(chel = nbd, tfb, en, pn, Hbim, bipy, phen) (XVIII–XXIV)*

A mixture of $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (78 mg, 0.1 mmol) $NaClO_4 \cdot H_2O$ (63 mg, 0.45 mmol) and the relevant ligand * in methanol (10 ml) was refluxed for several hours to give orange or red suspensions. The solvent was pumped-off and the residue was extracted with dichloromethane. The extract was filtered and concentrated to ca. 1 ml under vacuum. Addition of diethyl ether gave microcrystalline solids, which were filtered off. Complexes XX, XXI, XXII and XXIV were recrystallized from acetone/diethyl ether, and complex XXIII was washed with cold acetone.

X-Ray analysis

Yellow hexagonal prisms of complex XV were grown by gaseous diffusion of diethyl ether into a concentrated solution of the complex in dichloromethane.

Details of the procedure are given in Table 4. There are two independent ClO_4 groups, each with population 0.5. One has the Cl atom at a centre of symmetry and the other has another centre of symmetry midway between two oxygen atoms. There is also half a molecule of CH_2Cl_2 per unit of complex, and this has a Cl atom at another centre of symmetry. Tables 3 and 5 show the main geometrical features and the final fractional coordinates, the numbering in both cases corresponding to that in Fig. 2, which presents a view of the cation. Lists of hydrogen parameters, thermal

---

* Amounts and reaction times were: 2 ml, 17 h for nbd; 115 mg, 48 h for tfb; 13 μl, 20 h for en; 10 μl, 20 h for pn; 14 mg, 16 h for Hbim; 32 mg, 24 h for bipy; 15 mg, 24 h for phen.

factors, and observed and calculated structure factors can be obtained from the author on request.

Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica (C.A.I.C.Y.T.) for financial support (Project 1790/82).

References

1 M.I. Bruce in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Oxford, 1982.

2 P. McArdle and R. Manning, J. Chem. Soc., Dalton Trans., (1970) 2128.

3 E.W. Abel and S. Moorhouse, J. Chem. Soc., Dalton Trans., (1973) 1706; J.W. Faller and B.V. Johnson and T.P. Dryja, J. Organomet. Chem., 65 (1974) 395.

4 A. Eisenstadt, F. Frolow and A. Efrati, J. Chem. Soc., Chem. Commun., (1982) 642.

5 M.E. Rerek, L.N. Ji and F. Basolo, J. Chem. Soc., Chem. Commun., (1983) 1208.

6 L.N. Ji, M.E. Rerek and F. Basolo, Organometallics, 3 (1984) 740.

7 A.J. Hart-Davis and R.J. Mawby, J. Chem. Soc. A, (1969) 2403.

8 P. Caddy, M. Green, E. O'Brien, L.E. Smart and P. Woodward, J. Chem. Soc., Dalton Trans., (1980) 962.

9 P. Caddy, M. Green, J.A.K. Howard, J.M. Squire and N.J. Pugh, J. Chem. Soc., Dalton Trans., (1981) 400.

10 (a) M.I. Bruce, C. Hameister, A.G. Swincer and R.C. Wallis, Inorg. Synth., 21 (1982) 78; (b) M.I. Bruce and N.J. Windsor, Aust. J. Chem., 30 (1977) 1601.

11 B.N. Chaudret, D.J. Cole-Hamilton, R.S. Nohr and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1977) 1546; P.S. Hallman, B.R. McGarvey and G. Wilkinson, J. Chem. Soc. A, (1968) 3143.

12 M.I. Bruce and R.C. Wallis, Aust. J. Chem., 32 (1979) 1471; M.I. Bruce, F.S. Wong, B.M. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1982) 2203; S. Abbott, S.G. Davies and P. Warner, J. Organomet. Chem., 246 (1983) C65.

13 N.M. Kostić and R.F. Fenske, Organometallics, 1 (1982) 974.

14 M.I. Bruce, A.G. Swincer and R.C. Wallis, J. Organomet. Chem., 178 (1978) C5.

15 M.I. Bruce and F.S. Wong, J. Organomet. Chem., 210 (1981) C5.

16 S.G. Davies and F. Scott, J. Organomet. Chem., 188 (1980) C41.

17 R. Usón, L.A. Oro, M.A. Ciriano, M.M. Naval, M.C. Apreda, C. Foces-Foces, F.H. Cano and S. García-Blanco, J. Organomet. Chem., 256 (1983) 331.

18 S.R. Allen, P.K. Baker, S.G. Barnes, M. Botrill, M. Green, A.G. Orpen, I.D. Williams and A.J. Welch, J. Chem. Soc., Dalton Trans., (1983) 927 and references therein.

19 M.I. Bruce, F.S. Wong, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1981) 1398 and references therein.

20 H. Adams, N.A. Bayley and C. White, Inorg. Chem., 22 (1983) 1155.

21 S.R. Allen, P.K. Baker, S.G. Barnes, M. Green, L. Trollope, L. Manojlović-Muir and K.W. Muir, J. Chem. Soc., Dalton Trans., (1981) 873.

22 D. Cremer and J.A. Pople, J. Am. Chem. Soc., 97 (1975) 1354.

23 L.J. Guggenberger, Inorg. Chem., 12 (1973) 1317.

24 J.M. Clear, J.M. Kelly, C.M. O'Connell, J.G. Vos, C.J. Cardin, S.R. Costa and A.J. Edwards, J. Chem. Soc., Chem. Commun., (1980) 750.

25 P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12 (1970) 237.

26 D.M. Roe and A.G. Massey, J. Organomet. Chem., 28 (1971) 273.

27 B.F. Fieselman, D.N. Hendrickson and G.D. Stucky, Inorg. Chem., 17 (1978) 2078.

28 D.D. Perrin, W.L.F. Armarego and D.R. Perrin in Purification of Laboratory Chemicals, 2nd Ed., Pergamon Press, Oxford, 1980, p. 296.

29 J.M. Stewart, P.A. Machin, C.W. Dickinson, H.L. Ammon, H. Heck and H. Flack, "The X-Ray System", Univ. of Maryland. USA, 1976.

30 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4.