

**CYCLOPENTADIENYL RUTHENIUM COMPLEXES WITH CHELATING DIAMINES AND DIOLEFINS. CRYSTAL STRUCTURES OF  $[\text{Ru}(\text{nbd})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  AND  $[\text{Ru}((\eta^6\text{-C}_6\text{H}_5)\text{Ph}_2\text{PO})(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$ . A NEW MODE OF COORDINATION OF TRIPHENYLPHOSPHINE OXIDE**

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**Summary**

Complexes of the general formulae  $[\text{Ru}(\text{diamine})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  and  $[\text{Ru}(\text{diolefin})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  (diamine = ethylenediamine (en), propylenediamine (pn), 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), biimidazole ( $\text{H}_2\text{bim}$ ), bibenzimidazole ( $\text{H}_2\text{bbzim}$ ) and 2-(2'-pyridyl)benzimidazole ( $\text{Hpybzim}$ ); diolefin = 2,5-norbornadiene (nb), tetrafluorobenzobarrelene (tfb)) have been made by reaction of the complex  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  with the diamine or diolefin in the presence of sodium perchlorate. A single-crystal X-ray diffraction study of  $[\text{Ru}(\text{nb})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  has been carried out. Crystals of the complex are monoclinic, space group  $P2_1/n$ , with  $a$  18.0576(5),  $b$  14.5070(3),  $c$  10.3186(3) Å;  $\beta$  103.20(6)°. The structure was solved by Patterson synthesis using 4209 observed reflections ( $2\sigma(I)$  criterion) and refined to a  $R$  factor of 0.040. Reaction of  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  with oxygen in the presence of sodium perchlorate leads to oxidation of the coordinated triphenylphosphine ligands giving the complex  $[\text{Ru}((\eta^6\text{-C}_6\text{H}_5)\text{Ph}_2\text{PO})(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$ . In order to establish the structural identity of this compound a single-crystal X-ray diffraction study has been made. Crystals of this complex are monoclinic, space group  $P2_1/c$ , with  $a$  10.8182(5),  $b$  9.4480(3),  $c$  21.0036(19) Å;  $\beta$  90.246(6)°. The structure was solved by Patterson synthesis using 3819 observed reflections ( $3\sigma(I)$  criterion) and refined to a  $R$  factor of 0.036. The ruthenium atom is coordinated in a sandwich fashion by the cyclopentadienyl group and a phenyl ring of the triphenylphosphine oxide ligand. The synthesis of new heteronuclear ruthenium(II)-rhodium(I) complexes of formulae  $[(\eta\text{-C}_5\text{H}_5)(\text{Ph}_3\text{P})\text{-Ru}(\mu\text{-bim})\text{RhY}_2]_x$  ( $x = 2$  or 1) and  $(\eta\text{-C}_5\text{H}_5)(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-bbzim})\text{RhY}_2$  ( $\text{Y} = \text{CO}$ ,  $\text{Y}_2 = \text{diolefin}$ ) is also described.

## Introduction

There has been a recent increase in the amount of work on cyclopentadienyl-ruthenium complexes [1]. In particular, some cationic complexes with monoolefins and nitriles have been reported [2-4], but as far as we know no related cationic cyclopentadienylruthenium complexes with chelating diolefins or diamines have been described. We describe in this paper mononuclear complexes of the type  $[\text{Ru}(\text{diamine})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$ ,  $[\text{Ru}(\text{diolefin})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  and  $[\text{Ru}((\eta^6\text{-C}_6\text{H}_5)\text{Ph}_2\text{PO})(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$ , and some heteropolynuclear ruthenium(II)-rhodium(I) complexes; these confirm that the 2,2'-biimidazolate or 2,2'-bibenzimidazolate anions can act as tetradentate bridging ligands between different metals [5].

## Results and discussion

Reaction of the compound  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  with an excess of pyridine takes place readily in refluxing methanol in the presence of a poor coordinating anion such as perchlorate. Pyridine displaces the methanol in the species  $[\text{Ru}(\text{HOMe})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$  present in these solutions [1c] to give the complex  $[\text{Ru}(\text{py})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$ , which has been isolated as a yellow air-sensitive solid. No displacement of triphenylphosphine is observed even after prolonged refluxing and in this feature pyridine behaves like nitriles [2]. However, under similar conditions, the compound  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  reacts with equimolecular amounts of chelating diamines with displacement of methanol and a molecule of triphenylphosphine, affording the complexes of the type  $[\text{Ru}(\text{diamine})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  (diamine = en (I), pn (II), bipy (III), phen (IV),  $\text{H}_2\text{bim}$  (V),  $\text{H}_2\text{bbzim}$  (VI),  $\text{Hpybzim}$  (VII), which were isolated as air-stable crystalline solids.

The solid state IR spectra of the complexes III and IV show the characteristic bands of the uncoordinated perchlorate anion, but those of the complexes I, II, V-VII, in which the ligand contains primary or secondary amine groups, display very broad and split perchlorate bands, probably arising from an interaction  $\text{NH} \cdots \text{OClO}_3$  in the solid state similar to that found in the complex  $[\text{Rh}(\text{H}_2\text{bbzim})(\text{cod})]\text{ClO}_4$  [5], since they behave as 1:1 electrolytes in acetone. Among the bands from the ancillary ligands the IR spectra display a characteristic pattern of three bands decreasing in intensity between 535 and 495  $\text{cm}^{-1}$  associated with the triphenylphosphine ligand, which we have used to detect the substitution of one molecule of phosphine.

The diolefins, 2,5-norbornadiene and tetrafluorobenzobarrelene, react with  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  in refluxing methanol in the presence of sodium perchlorate giving complexes of the formula  $[\text{Ru}(\text{diolefin})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  (diolefin = nbd (VIII), tfb (IX) which were isolated as air-stable crystalline solids in good yields. They are quite unreactive, and are recovered after 2 h of refluxing with either hydrogen chloride in chloroform or sodium hydroxide in methanol. The IR spectra of complexes VIII and IX show characteristic bands of the uncoordinated perchlorate anion at ca. 1100 and 620  $\text{cm}^{-1}$ , the diolefins (at 1310  $\text{cm}^{-1}$  for nbd and 1500s, 1040s, 885  $\text{cm}^{-1}$  for tfb) and the pattern mentioned above associated with one molecule of coordinated triphenylphosphine between 535 and 495  $\text{cm}^{-1}$ . Complexes VIII and IX are 1:1 electrolytes in acetone and accordingly must be 18-electron complexes in which the diolefin is coordinated through both olefinic bonds.

The  $^{31}\text{P}$  NMR spectrum of complex VIII exhibits the expected single resonance at  $\delta 51.5$  ppm, but its  $^1\text{H}$  NMR spectrum shows complex multiplets for the 2,5-norbornadiene protons. On the other hand, its  $^{13}\text{C}$  NMR spectrum in dimethyl sulfoxide- $d_6$  shows resonances at  $\delta 134.4$  (d,  $J(\text{PC})$  10 Hz), 134.3 (d,  $^1J(\text{PC})$  47 Hz), 130.9 (d,  $^4J(\text{PC})$  3 Hz) and 128.6 (d,  $J(\text{PC})$  10 Hz) ( $\text{C}_6\text{H}_5$ ); 85.9(s) ( $\text{C}_5\text{H}_5$ ); 62.3(s) and 62.1(s) ( $\text{C}=\text{C}$ ); 49.1(s), 47.3(s) and 45.8(s) ( $>\text{CH}$  and  $>\text{CH}_2$ ), which indicates that the olefinic carbons and the  $>\text{CH}$  units of the 2,5-norbornadiene are in different magnetic environments. The magnetic inequivalence of the olefinic protons is also rather significant. In order to verify the formulation and to ascertain the detailed geometry, an X-ray structural determination of complex VIII was undertaken.

The complex  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  apparently reacts with the diolefins 1,5-cyclooctadiene, trimethyltetrafluorobenzobarrelene or 1,1,4,4-tetraphenyl-1,3-butadiene in the presence of sodium perchlorate during several days in methanol under reflux. An amber, crystalline solid identified as  $[\text{Ru}(\text{Ph}_3\text{PO})(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$  (X), and free triphenylphosphine oxide can be isolated in variable yield, which reaches 75% when 1,1,4,4-tetraphenyl-1,3-butadiene is used. The oxidation of the coordinated phosphine is caused by traces of oxygen. Complex X is obtained in shorter times by slowly bubbling oxygen through a suspension of  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  and sodium perchlorate in refluxing methanol\*, but it is not formed if the reaction is carried out under anaerobic conditions in a sealed tube. This complex is also formed in the reaction of  $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  with  $\text{H}_2\text{O}_2$  in methanol in the presence of  $\text{NaClO}_4$ . The complex X is a 1 : 1 electrolyte in acetone and displays a single resonance on its  $^{31}\text{P}$  NMR spectrum at  $\delta 25.5$  ppm. Its IR spectrum shows characteristic bands  $[6] \nu(\text{PO})$  and  $\delta(\text{PO})$  at 1200 and  $850\text{ cm}^{-1}$ , respectively, due to the triphenylphosphine oxide not coordinated through the oxygen atom. In addition bands at 1588w, 1503w, 1485m, 1416m and 1395m suggest the coordination of a phenyl ring [7]. The  $^1\text{H}$  NMR spectrum of complex X is indicative again of this type of coordination. Two broad multiplets centered at  $\delta 7.5$  and  $6.5$  due to the phenyl protons along with a triplet resonance at  $\delta 5.30$  ( $J(\text{PC})$  6 Hz) due to the cyclopentadienyl protons, of relative intensity 10/5/5 is evidence for the different way of bonding of one of the phenyl rings, as occurs in the complexes  $\text{Ru}((\eta^6\text{-C}_6\text{H}_5)_3\text{P})_2(\eta\text{-C}_5\text{H}_5)$  [1c],  $\text{RuH}((\eta^6\text{-C}_6\text{H}_5)_2\text{P})(\text{PPh}_3)_2$  [8,9] and  $\text{RuH}(\text{BPh}_4)_2\text{L}_2$  [10]. In complex X the ruthenium atom must be coordinated in a sandwich fashion by the cyclopentadienyl ligand and a phenyl ring of the triphenylphosphine oxide ligand. We confirmed this by determining the crystal structure of complex X by X-ray methods.

#### *The structure of $[\text{Ru}(\text{nb})](\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$*

Figure 1 shows the molecular structure and atom numbering, the phenyl rings following the sequence  $\text{X}1, \dots, \text{X}5$  ( $\text{X} = 1, 2, 3$ ). Table 1 presents the coordinates for the non-hydrogen atoms and Table 2 shows the main geometrical characteristics.

Taking account of the angles (Table 2) around the Ru atom formed with P, C(0), C(2-3) and C(5-6) ((C(2-3) and C(5-6) being the mid point of the olefinic bonds and C(0) the center of the cyclopentadienyl ring), and considering C(0) as representative of either a tetrahedral site or the center of three *fac* octahedral sites, the fit of the

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\* Under these conditions  $\text{RhCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  is a catalyst for the oxidation of free  $\text{PPh}_3$  to  $\text{OPPh}_3$ .

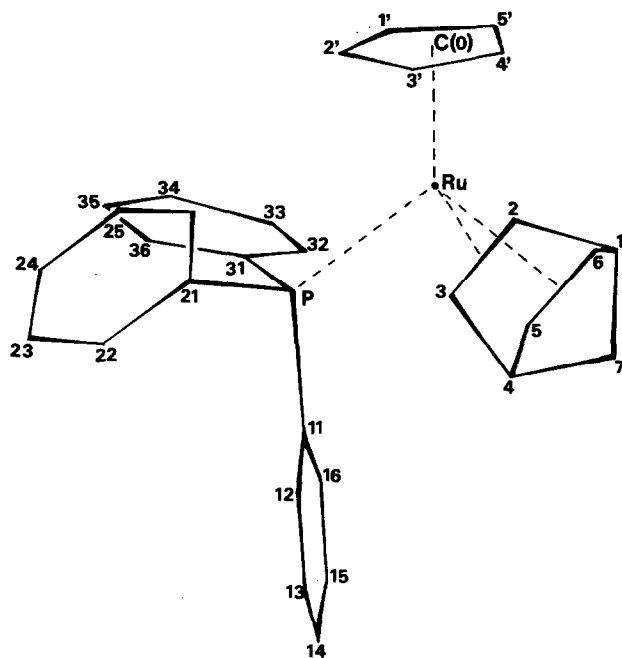


Fig. 1. Molecular structure and atom numbering of  $[\text{Ru}(\text{nbd})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{ClO}_4$ .

TABLE 1

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) FOR THE NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES <sup>a</sup>

| Atom                 | $x/a$       | $y/b$       | $z/c$       | $U_{eq}(\times 10^4)$ |
|----------------------|-------------|-------------|-------------|-----------------------|
| <i>Compound VIII</i> |             |             |             |                       |
| Ru                   | 0.57822(1)  | 0.18914(2)  | 0.34327(2)  | 352(1)                |
| C(1)                 | 0.41710(27) | 0.16504(40) | 0.27068(56) | 683(17)               |
| C(2)                 | 0.46947(24) | 0.18558(36) | 0.40626(49) | 601(15)               |
| C(3)                 | 0.49020(22) | 0.27816(33) | 0.40301(46) | 529(13)               |
| C(4)                 | 0.45018(23) | 0.31417(35) | 0.26593(47) | 569(15)               |
| C(5)                 | 0.49458(22) | 0.26302(29) | 0.17870(39) | 480(12)               |
| C(6)                 | 0.47372(23) | 0.17114(31) | 0.18254(42) | 518(13)               |
| C(7)                 | 0.37579(27) | 0.25687(47) | 0.24002(78) | 771(21)               |
| C(1')                | 0.63051(47) | 0.08429(45) | 0.49120(59) | 891(27)               |
| C(2')                | 0.68870(29) | 0.12618(33) | 0.43679(79) | 839(24)               |
| C(3')                | 0.67261(39) | 0.10320(37) | 0.30232(71) | 805(24)               |
| C(4')                | 0.61067(43) | 0.05088(34) | 0.27386(66) | 814(23)               |
| C(5')                | 0.58276(36) | 0.03824(32) | 0.38419(76) | 808(24)               |
| P                    | 0.64389(4)  | 0.33248(5)  | 0.36560(8)  | 331(2)                |
| C(11)                | 0.60255(20) | 0.43860(23) | 0.28280(35) | 400(10)               |
| C(12)                | 0.55678(30) | 0.49419(32) | 0.34230(48) | 618(16)               |
| C(13)                | 0.52410(40) | 0.57405(37) | 0.27932(61) | 812(21)               |
| C(14)                | 0.53799(41) | 0.60054(36) | 0.16033(63) | 843(23)               |
| C(15)                | 0.58341(40) | 0.54641(41) | 0.10046(60) | 811(22)               |

TABLE 1 (continued)

| Atom              | $x/a$        | $y/b$        | $z/c$        | $U_{eq} (\times 10^4)$ |
|-------------------|--------------|--------------|--------------|------------------------|
| C(16)             | 0.61457(29)  | 0.46562(34)  | 0.16059(46)  | 593(15)                |
| C(21)             | 0.67310(19)  | 0.37240(24)  | 0.53839(33)  | 396(10)                |
| C(22)             | 0.70669(24)  | 0.45916(29)  | 0.56895(41)  | 504(13)                |
| C(23)             | 0.72595(28)  | 0.48943(37)  | 0.69972(49)  | 628(16)                |
| C(24)             | 0.71267(27)  | 0.43539(40)  | 0.80093(45)  | 648(16)                |
| C(25)             | 0.68001(27)  | 0.34990(37)  | 0.77297(41)  | 594(15)                |
| C(26)             | 0.66019(21)  | 0.31809(29)  | 0.64201(37)  | 459(12)                |
| C(31)             | 0.73136(19)  | 0.32276(23)  | 0.30600(35)  | 382(10)                |
| C(32)             | 0.72627(22)  | 0.28714(29)  | 0.17843(38)  | 471(12)                |
| C(33)             | 0.79046(26)  | 0.27766(35)  | 0.12819(45)  | 576(15)                |
| C(34)             | 0.86108(24)  | 0.30242(34)  | 0.20510(49)  | 587(15)                |
| C(35)             | 0.86676(23)  | 0.33658(33)  | 0.33113(46)  | 551(14)                |
| C(36)             | 0.80257(20)  | 0.34770(28)  | 0.38200(38)  | 449(11)                |
| Cl                | 0.09059(5)   | 0.37798(7)   | 0.37932(10)  | 533(3)                 |
| O(1)              | 0.06404(28)  | 0.29979(34)  | 0.43563(62)  | 1007(20)               |
| O(2)              | 0.06384(57)  | 0.45472(39)  | 0.43744(67)  | 1518(38)               |
| O(3)              | 0.16831(28)  | 0.36671(49)  | 0.40379(116) | 1765(48)               |
| O(4)              | 0.06029(53)  | 0.38113(75)  | 0.24487(49)  | 1711(44)               |
| <i>Compound X</i> |              |              |              |                        |
| Ru                | 0.13711(3)   | 0.21705(3)   | 0.10928(1)   | 429(1)                 |
| C(1)              | 0.22765(52)  | 0.10487(79)  | 0.18609(27)  | 837(22)                |
| C(2)              | 0.29560(61)  | 0.22328(102) | 0.17169(42)  | 1060(31)               |
| C(3)              | 0.33600(53)  | 0.20633(117) | 0.10525(52)  | 1163(38)               |
| C(4)              | 0.28973(66)  | 0.07837(101) | 0.08641(34)  | 938(28)                |
| C(5)              | 0.22266(60)  | 0.01602(73)  | 0.13490(33)  | 849(22)                |
| P                 | -0.13633(8)  | 0.12780(10)  | 0.19449(4)   | 402(3)                 |
| O(1)              | -0.05229(28) | 0.09380(34)  | 0.24849(13)  | 545(9)                 |
| C(11)             | -0.19862(38) | -0.02695(42) | 0.15573(18)  | 466(12)                |
| C(12)             | -0.14183(52) | -0.15660(49) | 0.16568(24)  | 616(16)                |
| C(13)             | -0.19148(67) | 0.27595(52)  | 0.13479(31)  | 775(20)                |
| C(14)             | -0.29221(65) | -0.26605(64) | 0.09658(29)  | 788(21)                |
| C(15)             | -0.34659(50) | -0.13743(66) | 0.08630(25)  | 726(19)                |
| C(16)             | -0.30131(43) | -0.01646(54) | 0.11583(22)  | 554(14)                |
| C(21)             | -0.06063(30) | 0.22695(40)  | 0.13136(16)  | 376(10)                |
| C(22)             | -0.00580(35) | 0.35878(41)  | 0.14642(21)  | 442(12)                |
| C(23)             | 0.06229(41)  | 0.43377(50)  | 0.10066(26)  | 563(15)                |
| C(24)             | 0.07786(41)  | 0.37731(53)  | 0.03916(23)  | 581(15)                |
| C(25)             | 0.02238(40)  | 0.24892(54)  | 0.02356(21)  | 541(14)                |
| C(26)             | -0.04795(35) | 0.17277(45)  | 0.06850(18)  | 453(11)                |
| C(31)             | -0.26523(33) | 0.23758(39)  | 0.21679(17)  | 395(10)                |
| C(32)             | -0.31547(40) | 0.21601(51)  | 0.27690(20)  | 505(13)                |
| C(33)             | -0.41537(41) | 0.29589(58)  | 0.29637(22)  | 598(15)                |
| C(34)             | -0.46479(40) | 0.39689(57)  | 0.25708(24)  | 591(15)                |
| C(35)             | -0.41724(41) | 0.41777(54)  | 0.19712(24)  | 575(15)                |
| C(36)             | -0.31644(38) | 0.33789(47)  | 0.17689(20)  | 494(13)                |
| Cl                | -0.32623(10) | 0.16756(12)  | 0.47582(5)   | 577(3)                 |
| O(2)              | -0.39559(56) | 0.28017(62)  | 0.50015(28)  | 1180(22)               |
| O(3)              | -0.39452(64) | 0.08785(70)  | 0.43202(27)  | 1291(26)               |
| O(4)              | -0.27864(46) | 0.08303(48)  | 0.52600(17)  | 893(16)                |
| O(5)              | -0.22105(44) | 0.22169(56)  | 0.44096(24)  | 985(18)                |

<sup>a</sup> The last column  $U_{eq}$  is the isotropical equivalent thermal factor ( $\text{\AA}^2$ ),  $1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos(a_i a_j)$ .

TABLE 2

SELECTED GEOMETRICAL PARAMETERS (WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES) FOR COMPOUND VIII

| <i>Interatomic distances (Å)</i> |           |                   |           |
|----------------------------------|-----------|-------------------|-----------|
| Ru—C(1')                         | 2.208(6)  | C(1')—C(2')       | 1.435(11) |
| Ru—C(2')                         | 2.206(5)  | C(1')—C(5')       | 1.405(9)  |
| Ru—C(3')                         | 2.229(7)  | C(2')—C(3')       | 1.392(11) |
| Ru—C(5')                         | 2.227(5)  | C(5')—C(4')       | 1.359(11) |
| Ru—C(4')                         | 2.252(6)  | C(3')—C(4')       | 1.328(9)  |
| Ru—C(0)                          | 1.888(7)  | C(2)—C(3)         | 1.397(7)  |
| Ru—Q(1'-5')                      | 1.886(8)  | C(5)—C(6)         | 1.388(6)  |
| Ru—P                             | 2.379(1)  | C(1)—C(2)         | 1.528(7)  |
| Ru—C(2)                          | 2.206(5)  | C(1)—C(6)         | 1.518(8)  |
| Ru—C(6)                          | 2.225(4)  | C(4)—C(5)         | 1.528(7)  |
| Ru—C(3)                          | 2.241(5)  | C(4)—C(3)         | 1.526(6)  |
| Ru—C(5)                          | 2.268(4)  | C(4)—C(7)         | 1.550(7)  |
| Ru—C(23)                         | 2.114(5)  | C(1)—C(7)         | 1.524(9)  |
| Ru—C(56)                         | 2.130(4)  | Cl—O(1)           | 1.408(6)  |
| P—C(11)                          | 1.835(3)  | Cl—O(2)           | 1.402(7)  |
| P—C(21)                          | 1.834(3)  | Cl—O(3)           | 1.378(5)  |
| P—C(31)                          | 1.827(4)  | Cl—O(4)           | 1.371(5)  |
| <i>Interatomic angles (°)</i>    |           |                   |           |
| P—Ru—C(0)                        | 117.7(2)  | C(4')—C(3')—C(2') | 109.3(6)  |
| P—Ru—C(2-3)                      | 98.6(1)   | C(5')—C(1')—C(2') | 105.5(6)  |
| P—Ru—C(5-6)                      | 101.6(1)  | C(3')—C(2')—C(1') | 106.5(6)  |
| C(0)—Ru—C(2-3)                   | 131.8(3)  | C(6)—C(1)—C(2)    | 100.2(4)  |
| C(0)—Ru—C(5-6)                   | 128.3(3)  | C(3)—C(4)—C(5)    | 100.3(4)  |
| C(2-3)—Ru—C(5-6)                 | 66.5(2)   | C(6)—C(1)—C(7)    | 100.9(4)  |
| Ru—P—C(11)                       | 123.2(1)  | C(2)—C(1)—C(7)    | 101.0(4)  |
| Ru—P—C(21)                       | 113.4(1)  | C(3)—C(4)—C(7)    | 100.6(4)  |
| Ru—P—C(31)                       | 110.5(1)  | C(5)—C(4)—C(7)    | 100.9(4)  |
| C(11)—P—C(21)                    | 100.6(2)  | C(4)—C(7)—C(1)    | 94.0(5)   |
| C(11)—P—C(31)                    | 101.5(2)  | C(1)—C(2)—C(3)    | 106.2(4)  |
| C(21)—P—C(31)                    | 105.8(2)  | C(2)—C(3)—C(4)    | 106.2(4)  |
| P—C(21)—C(22)                    | 121.1(3)  | C(4)—C(5)—C(6)    | 105.5(4)  |
| P—C(21)—C(26)                    | 120.5(3)  | C(5)—C(6)—C(1)    | 107.3(4)  |
| P—C(11)—C(12)                    | 120.0(3)  | O(1)—Cl—O(3)      | 104.9(4)  |
| P—C(11)—C(16)                    | 122.0(3)  | O(1)—Cl—O(2)      | 106.3(4)  |
| P—C(31)—C(32)                    | 118.0(3)  | O(2)—Cl—O(4)      | 108.0(5)  |
| P—C(31)—C(36)                    | 123.3(3)  | O(3)—Cl—O(4)      | 110.1(5)  |
| C(5')—C(4')—C(3')                | 110.3(6)  | O(1)—Cl—O(4)      | 110.5(4)  |
| C(4')—C(5')—C(1')                | 108.4(6)  | O(2)—Cl—O(3)      | 116.9(5)  |
| <i>Torsion angles (°)</i>        |           |                   |           |
| Ru—P—C(11)—C(12)                 | 85.4(3)   |                   |           |
| Ru—P—C(11)—C(16)                 | −93.8(3)  |                   |           |
| Ru—P—C(21)—C(22)                 | −174.6(3) |                   |           |
| Ru—P—C(21)—C(26)                 | 3.5(3)    |                   |           |
| Ru—P—C(31)—C(32)                 | 52.5(3)   |                   |           |
| Ru—P—C(31)—C(36)                 | −126.5(3) |                   |           |
| C(1)—C(2)—C(3)—C(4)              | 0.3(5)    |                   |           |
| C(2)—C(3)—C(4)—C(5)              | −70.0(4)  |                   |           |
| C(3)—C(4)—C(5)—C(6)              | 69.7(4)   |                   |           |
| C(4)—C(5)—C(6)—C(1)              | 0.1(5)    |                   |           |

TABLE 2 (continued)

*Torsion angles (°)*

|                     |           |
|---------------------|-----------|
| C(5)–C(6)–C(1)–C(2) | – 69.5(5) |
| C(6)–C(1)–C(2)–C(3) | 68.9(5)   |
| C(7)–C(1)–C(6)–C(5) | 33.8(5)   |
| C(6)–C(5)–C(4)–C(7) | – 33.3(5) |
| C(5)–C(4)–C(7)–C(1) | 51.3(5)   |
| C(4)–C(7)–C(1)–C(6) | – 51.0(5) |
| C(7)–C(1)–C(2)–C(3) | – 34.4(5) |
| C(2)–C(3)–C(4)–C(7) | 33.3(5)   |
| C(3)–C(4)–C(7)–C(1) | – 51.5(5) |
| C(4)–C(7)–C(1)–C(2) | 51.8(5)   |

angle values is better for the octahedral (90 and 125.3°) than for the tetrahedral configuration (109.5°) [11]. The Ru–P distance is within the normal range [11,12] and those with the olefinic bonds show some asymmetry similar to that found in related complexes [13–15]. Distances relating to the  $\eta$ -coordination of Ru with the cyclopentadienyl ring are within the normal range [11,16] (Table 2). The variations, in these distances together with the slight puckering of the ring, allow definition of their relative situations: The least squares plane through the ring leaves the C(3') and C(5') atoms towards the Ru atom, while C(4') is away from it. The normal to the plane through the Ru intersects it at Q, near the C(1')–C(2') part, while the center of the ring C(0) is near to C(4'), in such a way that the angle C(0)–Ru–Q is 2.6° (see Fig. 3). This leaves the Ru atom nearer to the C(1')–C(2') part of the ring.

The P–C distances in the triphenylphosphine ligand have values similar to those in some analogous compounds [11,12,16]. One of the Ru–P–C angles is higher than the others, as was reported for RuCl(PPh<sub>3</sub>)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>) [11], but all three are larger than any of the C–P–C angles (see Table 2), which reach a lowest value of 100.6(2)°.

In the phenyl rings the shorter bonds corresponding to atoms with the highest thermal factors, C(X3)–C(X4), C(X4)–C(X5); X = 1,2,3 can be distinguished from the rest of the bonds, the respective ranges being (1.363(10)–1.387(6) Å) and (1.381(7)–1.402(5) Å), respectively. Similarly, the angles on C(X1) and C(X4), ranging from 118.0(4) to 119.8(5)°, are significantly lower than the other bond angles which range, 120.0(4) to 121.1(5)°.

Although bond distances and angles (Table 2) in the cyclopentadienyl ring are within reported ranges [11,16], the variations are consistent with the deformation of the ring described above. It retains almost a *m*-symmetry, but in such a way that C(5')–C(4') and C(4')–C(3'), being shortened, the angle at C(4') is enlarged, while the shortening of the angles at C(2') and C(1') is associated with lengthening of the C(1')–C(2') bond (see Table 2). It is worth noting that the larger C–C bonds in the ring correspond to the shorter Ru–C coordination distances. The puckering of the ring is very small (see Fig. 3). Cremer and Pople's parameters [17] define it as an almost perfect envelope at C(4') ( $q$  0.008 Å,  $\phi$  284.5° compared with a perfect envelope at  $\phi$  288°).

In the nbd ligand, the C–C distances in the two olefinic bonds are similar (Table 2), both are greater than the value of 1.343(3) Å reported for free nbd [11]; but in

TABLE 3

C–H BOND DISTANCES AND NON-BONDING CONTACTS INVOLVING THE HYDROGEN ATOMS OF THE nbd MOIETY IN COMPOUND VIII

| Atom         | Symmetry code <sup>a</sup> | Distance (Å) (e.s.d.) |
|--------------|----------------------------|-----------------------|
| C(1)–H(1)    | i                          | 1.00(8)               |
| C(2)–H(2)    | i                          | 1.04(9)               |
| C(3)–H(3)    | i                          | 0.81(5)               |
| C(4)–H(4)    | i                          | 0.89(6)               |
| C(5)–H(5)    | i                          | 0.91(8)               |
| C(6)–H(6)    | i                          | 0.91(6)               |
| H(3)···P     | i                          | 2.93(6)               |
| H(5)···P     | i                          | 3.03(6)               |
| H(3)···H(13) | ii                         | 2.49(11)              |
| H(5)···O(1)  | iii                        | 2.60(7)               |
| H(4)···C(12) | i                          | 2.59(5)               |
| H(6)···H(4') | i                          | 2.42(9)               |
| H(6)–O(2)    | iv                         | 2.64(6)               |

<sup>a</sup> i:  $x, y, z$ ; ii:  $1 - x, 1 - y, 1 - z$ ; iii:  $x - 1/2, 1/2 - y, 1/2 + z$ ; iv:  $1/2 - x, 1/2 + y, 1/2 - z$ .

agreement with the values in related structures [18,19,20]. The conformation of the ligand is quite symmetric, with both five-membered rings forming envelopes (Cremer and Pople's [17] values of  $q$  0.560 Å,  $\phi$  324.3° and  $q$  0.555 Å,  $\phi$  324.3° compared with perfect envelopes at  $\phi = 36 \times n$ ;  $n$  integer), and the six-membered ring having almost a perfect boat shape (Cremer and Pople's parameters of  $\theta$  89.8°,  $q_2$  1.016 Å and  $\phi_2$  180.1° compared with a perfect boat at  $\theta$  90° and  $\phi_2 = 60 \times n$ ).

An examination of the non-bonding distances (see Table 3) shows that the olefinic protons are involved in different contact schemes, mainly due to the proximity of the P atom to the protons bonded to the C(3) and C(5) atoms (see Fig. 1).

The magnetic inequivalence of the olefinic protons, as detected by NMR spectroscopy is probably due to asymmetry in the molecule caused by the triphenylphosphine ligand and the cyclopentadienyl ring.

#### *The structure of [Ru{( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>)Ph<sub>2</sub>PO}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]ClO<sub>4</sub>*

The molecular structure of the compound is shown in Fig. 2 along with the atom numbering. Table 1 lists the coordinates for the non-hydrogen atoms and Table 4 shows the main geometrical characteristics.

The ruthenium atom is coordinated in a sandwich fashion between the cyclopentadienyl ring and a phenyl ring C(21)···C(26) of the OPPh<sub>3</sub> group. The coordination distances between the ruthenium and the cyclopentadienyl ring range between 2.155(8) and 2.179(7) Å these being values different from those of compound VIII: 2.206(5) to 2.252(6) Å. The distances between the ruthenium and the phenyl carbons C(21)···C(26) range from 2.191(4) to 2.214(4) Å. The distance C(2)–C(3) is the longest, 1.473(14) Å, and the coordination distances (Ru–C(2) and Ru–C(3)) are the shortest (2.155(8) and 2.156(6) Å). Similar features are present in compound VIII.

The rings which are coordinated with the ruthenium are almost parallel, as in the complex Ru{( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>)Ph<sub>3</sub>B}( $\eta$ -C<sub>5</sub>H<sub>5</sub>) [21], the angle between them being 2.1°. The



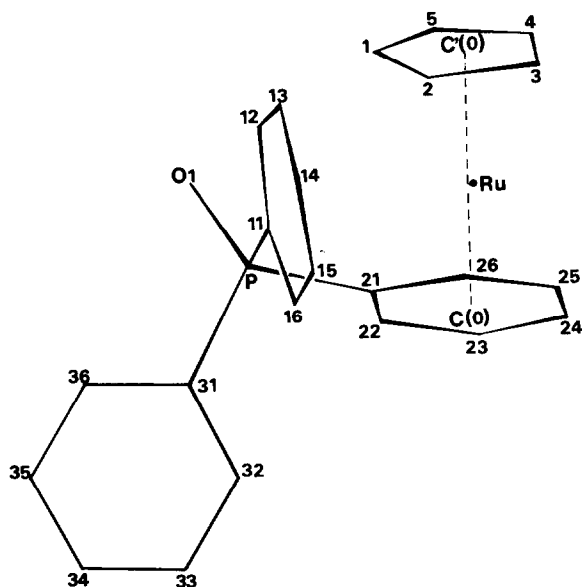


Fig. 2. Molecular structure and atom numbering of  $[\text{Ru}((\eta^6\text{-C}_6\text{H}_5)\text{Ph}_2\text{PO})(\eta^5\text{-C}_5\text{H}_5)]\text{ClO}_4$ .

ruthenium is practically on the line through the centroids of the phenyl  $\text{C}(21) \cdots \text{C}(26)$  ( $\text{C}(0)$ ) and the cyclopentadienyl rings ( $\text{C}'(0)$ ). The angle between the lines  $\text{Ru}-\text{C}(0)$  and  $\text{Ru}-\text{C}'(0)$  is  $178.9(3)^\circ$  (see Fig. 3).

The ruthenium is nearer to the phenyl ring than to the cyclopentadienyl ring (see Table 4). The former ring deviates from planarity, in contrast with the other two, to a conformation of twist-boat. The values of the conformational parameters [17] are:  $q = 0.022 \text{ \AA}$ ,  $\theta 84.8^\circ$  and  $\phi 333.6^\circ$  compared to  $\theta 90^\circ$  and  $\phi 330^\circ$  for a perfect twist.

The distance between the phosphorus atom and the carbon  $\text{C}(21)$  ( $1.821(4) \text{ \AA}$ ) is longer than the  $\text{P}-\text{C}(11)$  and  $\text{P}-\text{C}(31)$  distances ( $1.803(4)$  and  $1.802(4) \text{ \AA}$  respectively). The mean distance for the phenyl  $\text{C}(11) \cdots \text{C}(16)$  and  $\text{C}(31) \cdots \text{C}(36)$  is  $1.382(7)$ , and  $1.409(6) \text{ \AA}$  for the phenyl  $\text{C}(21) \cdots \text{C}(26)$ . As for compound VIII, the lengths of the  $\text{C}(X3)-\text{C}(X4)$  and  $\text{C}(X4)-\text{C}(X5)$  bonds ( $X = 1, 3$ ) are different from the rest; the respective ranges are:  $(1.354(10)-1.377(7) \text{ \AA})$  and  $(1.380(6)-1.406(8) \text{ \AA})$ . The angles range over both phenyl rings from  $118.1(5)$  to  $121.5(6)^\circ$ . In the five-membered ring the mean distance is  $1.392(12) \text{ \AA}$ . All the  $\text{H}-\text{H}$  contact distances are all larger than  $2.60 \text{ \AA}$ .

The perchlorate anions show the usual high thermal factors, with two bonds of similar length which is different from that of the other two which are also of similar length.

#### Heteronuclear complexes

Attempts to employ the potentially bidentate ligand  $(\text{dpe})\text{Pt}(\text{pz})_2$  [22], which has two uncoordinated nitrogen atoms available as donor sites, to prepare the heterobinuclear complex  $[(\text{dpe})\text{Pt}(\mu\text{-pz})_2\text{Ru}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{BPh}_4$  were unsuccessful. Thus, on mixing  $(\text{dpe})\text{Pt}(\text{pz})_2$  with the species  $[\text{Ru}(\text{HOME})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$  [1c] in methanol, an immediate rearrangement reaction takes place with precipitation of the previously reported  $[\text{Pt}_2(\mu\text{-pz})_2(\text{dpe})_2]^{2+}$  derivative [22] and a yellow very air-sensi-

TABLE 4

SELECTED GEOMETRICAL PARAMETERS (WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES) FOR COMPOUND X

*Interatomic distances (Å)*

|                   |           |             |           |
|-------------------|-----------|-------------|-----------|
| Ru–C(1)           | 2.161(6)  | P–C(31)     | 1.802(4)  |
| Ru–C(2)           | 2.155(8)  | C(1)–C(2)   | 1.373(1)  |
| Ru–C(3)           | 2.156(6)  | C(2)–C(3)   | 1.473(14) |
| Ru–C(4)           | 2.163(8)  | C(3)–C(4)   | 1.366(14) |
| Ru–C(5)           | 2.179(7)  | C(4)–C(5)   | 1.385(10) |
| Ru–C(21)          | 2.193(3)  | C(5)–C(1)   | 1.365(9)  |
| Ru–C(22)          | 2.191(4)  | C(21)–C(22) | 1.415(5)  |
| Ru–C(23)          | 2.209(5)  | C(22)–C(23) | 1.405(6)  |
| Ru–C(24)          | 2.206(5)  | C(23)–C(24) | 1.408(7)  |
| Ru–C(25)          | 2.203(4)  | C(24)–C(25) | 1.392(7)  |
| Ru–C(26)          | 2.214(4)  | C(25)–C(26) | 1.412(6)  |
| Ru– $\pi$ (21–26) | 1.692(6)  | C(26)–C(21) | 1.423(5)  |
| Ru– $\pi$ (1–5)   | 1.809(12) | Cl–O(2)     | 1.400(6)  |
| P–O(1)            | 1.486(3)  | Cl–O(3)     | 1.398(6)  |
| P–C(11)           | 1.803(4)  | Cl–O(4)     | 1.417(4)  |
| P–C(21)           | 1.821(4)  | Cl–O(5)     | 1.449(5)  |

*Interatomic angles (°)*

|                |          |                   |          |
|----------------|----------|-------------------|----------|
| C(0)–Ru–C'(0)  | 178.9(3) | C(2)–C(3)–C(4)    | 105.1(8) |
| C(11)–P–O(1)   | 113.3(2) | C(3)–C(4)–C(5)    | 110.9(7) |
| C(21)–P–O(1)   | 113.1(2) | C(4)–C(5)–C(1)    | 107.4(6) |
| C(31)–P–O(1)   | 113.5(2) | C(22)–C(21)–C(26) | 118.8(3) |
| C(11)–P–C(21)  | 104.9(2) | C(21)–C(22)–C(23) | 120.8(4) |
| C(21)–P–C(31)  | 104.1(2) | C(22)–C(23)–C(24) | 120.1(4) |
| C(31)–P–C(11)  | 107.2(2) | C(23)–C(24)–C(25) | 119.5(4) |
| C(22)–C(21)–P  | 118.7(3) | C(24)–C(25)–C(26) | 121.3(4) |
| C(26)–C(21)–P  | 122.4(3) | C(25)–C(26)–C(21) | 119.4(4) |
| C(12)–C(11)–P  | 119.0(3) | O(2)–Cl–O(5)      | 109.9(3) |
| C(16)–C(11)–P  | 120.7(3) | O(2)–Cl–O(3)      | 111.5(4) |
| C(32)–C(31)–P  | 117.2(3) | O(3)–Cl–O(4)      | 112.0(3) |
| C(36)–C(31)–P  | 123.2(3) | O(4)–Cl–O(5)      | 106.9(3) |
| C(5)–C(1)–C(2) | 110.3(6) | O(5)–Cl–O(3)      | 105.8(3) |
| C(1)–C(2)–C(3) | 106.3(8) | O(4)–Cl–O(2)      | 110.5(3) |

*Torsion angles (°)*

|                     |           |
|---------------------|-----------|
| C(32)–C(31)–P–C(21) | –158.6(3) |
| C(36)–C(31)–P–C(21) | 22.8(3)   |
| C(12)–C(11)–P–C(21) | 106.5(4)  |
| C(16)–C(11)–P–C(21) | –72.8(4)  |

tive solution, presumably of  $\text{Ru}(\text{pz})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ . In contrast, heterobinuclear rhodium-platinum complexes of formula  $[(\text{dpe})\text{Pt}(\mu\text{-pz})_2\text{RhY}_2]^+$  ( $\text{Y} = \text{CO}$ ,  $\text{Y}_2 = \text{cod}$ ) have been reported [23].

Heteropolynuclear ruthenium-rhodium complexes can be obtained when the neutral complexes  $\text{Ru}(\text{Hbim})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  (XI), and  $\text{Ru}(\text{Hbbzim})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  (XII), (prepared by treatment of compounds V or VI with KOH) are used as ligands. The binding of the imidazol rings in the 2,2'-biimidazolate or 2,2'-bibenzimidazolate anions hinders rearrangements. Thus, complexes XI and XII react with  $\text{Rh}(\text{acac})\text{Y}_2$

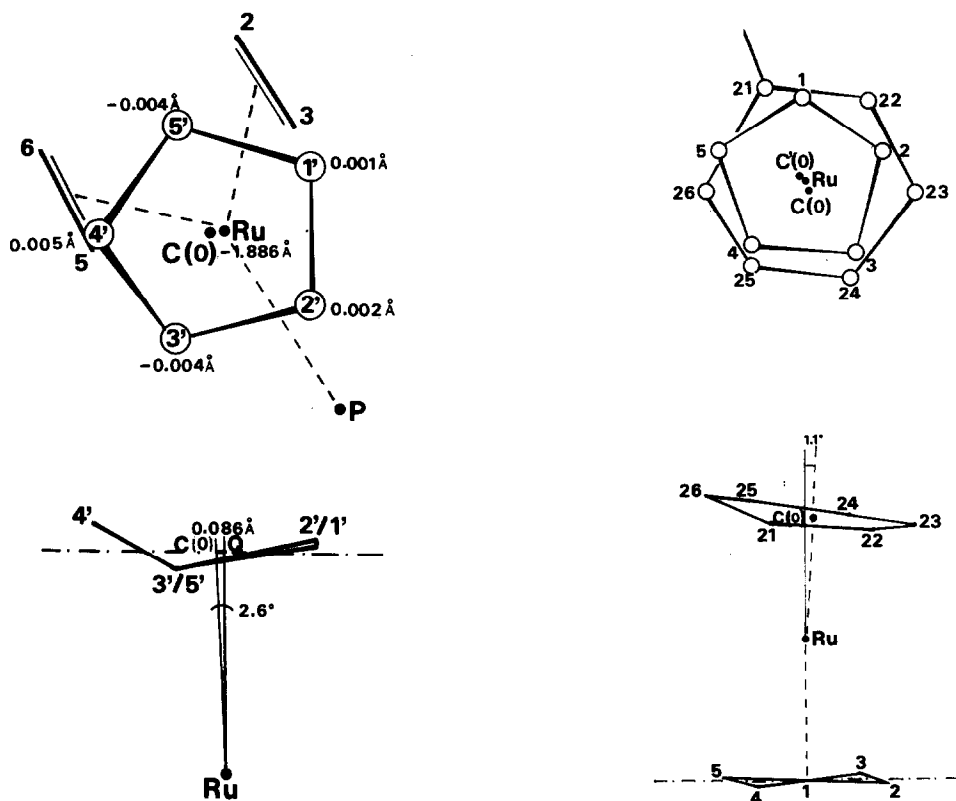
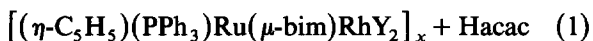
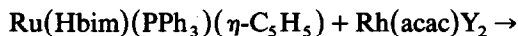
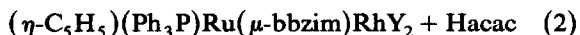
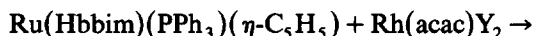


Fig. 3. The coordination of the Ru atoms in compounds VIII and X as projected normal to the cyclopentadienyl rings.

(Y = CO [24]; Y<sub>2</sub> = cod, nbd or tfb [25]) to form neutral heteropolynuclear complexes containing the biimidazolate anion as a bridging ligand between ruthenium and rhodium (eqs. 1 and 2)



(x = 2, Y = CO (XIII), Y<sub>2</sub> = nbd (XIV); x = 1, Y<sub>2</sub> = tfb (XV))



(Y = CO (XVI), Y<sub>2</sub> = cod (XVII), nbd (XVIII), tfb (XIX))

While the tetranuclear 2,2'-biimidazolato complexes (XIII, XIV) are formed with the Rh(CO)<sub>2</sub> or Rh(nbd) moieties, the binuclear derivative XV is isolated in the case of the Rh(tfb) moiety. Nevertheless, carbonylation of compound XV gives the tetranuclear complex XIII. In this line, previous studies [26] on [Rh<sub>2</sub>(μ-bim)(Y<sub>2</sub>)<sub>2</sub>]<sub>x</sub> derivatives show x = 2 for Y = CO but x = 1 for Y<sub>2</sub> = cod.

On the other hand, only binuclear ruthenium-rhodium complexes, (XVI–XIX) are formed when the 2,2'-bibenzimidazolate anion is acting as a bridging ligand. The



TABLE 5

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, IR DATA, COLOUR AND YIELDS FOR THE CATIONIC COMPLEXES

| Complex | (Found Analyses (calcd.) (%)) |                |                | $\Delta_M$<br>(ohm <sup>-1</sup><br>cm <sup>2</sup> mol <sup>-1</sup> ) | IR (cm <sup>-1</sup> )     |                              | Colour | Yield (%) |
|---------|-------------------------------|----------------|----------------|-------------------------------------------------------------------------|----------------------------|------------------------------|--------|-----------|
|         | C                             | H              | N              |                                                                         | $\nu$ (NH)                 | $\nu$ (ClO <sub>4</sub> )    |        |           |
| I       | 51.80<br>(51.05)              | 5.00<br>(4.80) | 4.75<br>(4.75) | 115                                                                     | 3320s,3280s                | 1090s,1045s,1030s,br,625s    | yellow | 78        |
| II      | 52.45<br>(51.85)              | 5.00<br>(5.00) | 4.70<br>(4.65) | 127                                                                     | 3340s,3320s<br>3295s,3275s | 1110s,1070s,630s             | yellow | 86        |
| III     | 57.55<br>(57.95)              | 4.40<br>(4.15) | 4.05<br>(4.10) | 126                                                                     |                            | 1090s,620s                   | orange | 68        |
| IV      | 59.60<br>(59.40)              | 4.60<br>(4.00) | 4.05<br>(3.95) | 137                                                                     |                            | 1090s,625s                   | orange | 51        |
| V       | 52.95<br>(52.60)              | 4.10<br>(3.95) | 8.25<br>(8.45) | 137                                                                     | 3200s,br                   | 1150s,1100s,1030s,625s       | yellow | 83        |
| VI      | 58.50<br>(58.30)              | 4.65<br>(3.95) | 6.85<br>(7.35) | 119                                                                     | 3200s,br                   | 1140s,1095s,1043s,640sh,625s | orange | 73        |
| VII     | 58.40<br>(58.15)              | 4.60<br>(4.05) | 5.60<br>(5.80) | 127                                                                     | 3200s,br                   | 1130s,1100s,1060s,623s       | orange | 65        |
| VIII    | 58.40<br>(58.10)              | 4.70<br>(4.55) | —              | 121                                                                     |                            | 1090s,625s                   | yellow | 82        |
| IX      | 56.15<br>(55.75)              | 3.75<br>(3.50) | —              | 133                                                                     |                            | 1100s,625s                   | yellow | 62        |
| X       | 50.45<br>(50.80)              | 3.95<br>(3.70) | —              | 128                                                                     |                            | 1090s,625s                   | amber  | 56        |

TABLE 6

ANALYTICAL RESULTS, MOLECULAR WEIGHTS, COLOUR AND YIELDS FOR THE NEUTRAL COMPLEXES

| Complex | (Found Analyses (calcd.) (%)) |                |                  | Mol.wt.<br>(CHCl <sub>3</sub> )<br>Found<br>(calcd.) | Colour | Yield (%) |
|---------|-------------------------------|----------------|------------------|------------------------------------------------------|--------|-----------|
|         | C                             | H              | N                |                                                      |        |           |
| XI      | 62.20<br>(62.00)              | 4.95<br>(4.50) | 10.10<br>(10.00) | 568<br>(562)                                         | yellow | 88        |
| XII     | 67.50<br>(67.20)              | 4.65<br>(4.40) | 8.40<br>(8.45)   | 624<br>(662)                                         | yellow | 86        |
| XIII    | 52.10<br>(51.80)              | 3.70<br>(3.35) | 7.80<br>(7.80)   | 1393<br>(1439)                                       | orange | 86        |
| XIV     | 57.60<br>(57.25)              | 5.00<br>(5.25) | 7.60<br>(7.40)   | 1421<br>(1511)                                       | orange | 60        |
| XV      | 54.80<br>(55.40)              | 3.95<br>(3.40) | 5.85<br>(6.30)   | 977<br>(890)                                         | orange | 62        |
| XVI     | 57.00<br>(57.15)              | 3.40<br>(3.45) | 6.80<br>(6.85)   | 912<br>(820)                                         | yellow | 83        |
| XVII    | 61.75<br>(62.00)              | 5.80<br>(4.65) | 6.65<br>(6.45)   | 895<br>(872)                                         | yellow | 91        |
| XVIII   | 62.90<br>(61.80)              | 5.00<br>(4.25) | 6.45<br>(6.55)   | 865<br>(856)                                         | yellow | 77        |
| XIX     | 59.95<br>(59.45)              | 4.35<br>(3.45) | 5.65<br>(5.65)   | 912<br>(990)                                         | yellow | 79        |

several hours \*. The solvent was pumped off, the residue was extracted with dichloromethane (20 ml) and the solution was filtered through Celite. Evaporation of the filtrate to a volume of ca. 2 ml and careful addition of diethyl ether (20 ml) gave the products (complexes I–VII) as crystals. These were filtered off, washed with diethyl ether, and air-dried.

The complexes I–VII were obtained analytically pure, but they can be recrystallized from dichloromethane/diethyl ether or methanol/diethyl ether if required.

#### *Preparation of $[Ru(\text{diolefin})(PPh_3)(\eta\text{-}C_5H_5)]ClO_4$*

A mixture of  $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$  (0.218 g, 0.3 mmol), sodium perchlorate hydrate (0.043 g, 0.3 mmol), and an excess of diolefin (6 ml of 2,5-norbornadiene or 0.750 g of tetrafluorobenzobarrelene) was refluxed in methanol for 24 h. The resulting yellow solution was evaporated to dryness, and the residue was extracted with dichloromethane (25 ml). The extract was filtered through Celite, then evaporated to a volume of ca. 2 ml. Slow addition of diethyl ether (20 ml) gave the complexes VIII and IX as crystals, which were filtered off, washed with diethyl ether, and air-dried.

#### *Preparation of $[Ru(\eta^6\text{-}C_6H_5)Ph_2PO)(\eta\text{-}C_5H_5)]ClO_4$*

Oxygen was slowly bubbled through a suspension of  $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$  (0.358 g, 0.49 mmol) and  $NaClO_4 \cdot H_2O$  (0.070 g, 0.5 mmol) in degassed methanol (30 ml) for 45 min, and the resulting solution was refluxed for 30 min to give a yellow-green solution. The solvent was pumped off and the residue was extracted with dichloromethane (20 ml). The extract was filtered and concentrated to ca. 3 ml and diethyl ether (40 ml) was added to give brown crystals, which were filtered off. Evaporation of the filtrate to dryness and recrystallization of the residue from dichloromethane (1 ml)/hexane (20 ml) gave triphenylphosphine oxide.

Filtration of a warm methanolic solution (20 ml) of the crude product through a pad (1 cm) of alumina deactivated with methanol, evaporation of the solution to ca. 1 ml and addition of diethyl ether gave the pure product.

#### *Oxidation of triphenylphosphine*

A refluxing solution of  $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$  (0.037 g, 0.05 mmol),  $NaClO_4 \cdot H_2O$  (0.010 g, 0.07 mmol) and  $PPh_3$  (2.33 g, 8.88 mmol) in methanol (40 ml) was stirred in the presence of oxygen. After 11 h 33% of  $OPPh_3$  was formed.

#### *Reaction of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ with $(dpe)Pt(pz)_2$*

Solid  $(dpe)Pt(pz)_2$  (0.145 g, 0.2 mmol) and  $NaBPh_4$  (0.035 g, 0.2 mmol) were added to a suspension of  $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$  (0.073 g, 0.1 mmol) in refluxing methanol (15 ml) to give a white precipitate and a yellow solution. The mixture was refluxed for 2 h and then the white solid was filtered off and identified, as  $[Pt_2(\mu\text{-}pz)_2(dpe)_2](BPh_4)_2$ . (Found: C, 65.54; H, 5.02; N, 3.18.  $C_{106}H_{94}N_4B_2P_4Pt_2$  calcd.: C, 64.97; H, 4.83; N, 2.86%).

\* Reaction times were 3 h for complex I; 7 h for III; 13 h for V; 15 h for VI; 22 h for II; 24 h for VII and 30 h for IV. Longer times are necessary for larger scale reactions.

*Preparation of Ru(Hbim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>) (XI) and Ru(Hbbzim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>) (XII)*

A suspension of either [Ru(H<sub>2</sub>bim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]ClO<sub>4</sub> (0.661 g, 1 mmol) or [Ru(H<sub>2</sub>bbzim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]ClO<sub>4</sub> (0.381 g, 0.5 mmol) in methanol (20 ml) was vigorously stirred with an equimolar amount of potassium hydroxide in water (20 ml) for 1 h. The resulting yellow solid was filtered off, washed with methanol/water (1/1), and air dried. Complex XII was washed with a small volume of acetone to remove a green impurity.

*Preparation of [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(Ph<sub>3</sub>P)Ru( $\mu$ -bim)Rh(CO)<sub>2</sub>]<sub>2</sub> (XIII) and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(Ph<sub>3</sub>P)-Ru( $\mu$ -bbzim)Rh(CO)<sub>2</sub> (XVI)*

A suspension of either Ru(Hbim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>) or Ru(Hbbzim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>) (0.1 mmol) and Rh(acac)(CO)<sub>2</sub> (0.026 g, 0.1 mmol) in methanol (15 ml) was vigorously stirred for 1 h. The resulting solid was filtered off, washed with cold methanol, and air-dried.

*Preparation of [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(Ph<sub>3</sub>P)Ru( $\mu$ -bim)Rh(diolefin)]<sub>x</sub> (XIV,XV) and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)-(Ph<sub>3</sub>P)Ru( $\mu$ -bbzim)Rh(diolefin), (XVII–XIX)*

To a solution of either Ru(Hbim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>) or Ru(Hbbzim)(PPh<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>5</sub>) (0.1 mmol) in dichloromethane (15 ml) was added the Rh(acac)(diolefin) appropriate complex (0.1 mmol). The mixture was kept at room temperature for 3 h then the solvent was pumped-off and the oily residue crystallized by addition of cold methanol (5 ml). (Scratching the walls of the flask was often necessary to induce crystallization.) The solid was filtered off, washed with cold methanol and air-dried.

*Crystallography*

Suitable single crystals of complexes VIII and X were grown by slow diffusion of diethyl ether into dichloromethane solutions.

*Crystal data*

**Compound VIII.** C<sub>30</sub>H<sub>28</sub>ClO<sub>4</sub>PRu, *M* = 620.1, monoclinic, space group *P*2<sub>1</sub>/*n* *a* 18.0576(5), *b* 14.5070(3), *c* 10.3186(3) Å,  $\beta$  103.20(6)°, *V* 2631.6(1) Å<sup>3</sup>, *D<sub>m</sub>* 1.564 g cm<sup>-3</sup>, *Z* = 4, *F*(000) = 1264,  $\mu_{Cu}$  68.1 cm<sup>-1</sup>. Sample: yellow, transparent hexahedral prism limited by faces  $\pm(210)$ ,  $\pm(010)$ ,  $\pm(210)$  and with the  $\pm(01\bar{1})$  and  $\pm(011)$  faces placed capping the basis, respective dimensions between opposite faces; 0.24, 0.21, 0.24, 0.29, 0.29 mm.

**Compound X.** C<sub>23</sub>H<sub>20</sub>ClO<sub>5</sub>PRu, *M* = 543.9, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* 10.8182(5), *b* 9.4480(3), *c* 21.0036(19) Å,  $\beta$  90.246(6)°, *V* 2146.8(2) Å<sup>3</sup>, *D<sub>m</sub>* 1.683 g cm<sup>-3</sup>, *Z* = 4, *F*(000) = 1096,  $\mu_{Cu}$  82.3 cm<sup>-1</sup>. Sample: rectangular prism of dimensions 0.27 × 0.06 × 0.27 mm between opposite faces  $\pm(0\ 1\ 10)$ ,  $\pm(10\ 1\ \bar{1})$ ,  $\pm(0\ 5\ 1)$ , respectively.

*Intensity data*

Data were collected with Cu-K $\alpha$  radiation on a Philips PW 1100 four-circle diffractometer with a graphite oriented monochromator. Unique data set were measured up to  $2\theta_{max}$  of 65° (at a rate of 1 reflection/min), with a scan amplitude of 1.4°. A total of 4456 (for VIII), 3819 (for X) reflections were measured; of these 4209 with *I* > 2 $\sigma$ (*I*) (for VIII), 3373 with *I* > 3 $\sigma$ (*I*) (for X) were considered observed. Two reflections monitored every 90 min, showed no variation. Data were

corrected for absorption (min. and max. transmission factors 0.248 and 0.386 (for VIII) and 0.170 and 0.605 (for X) and transformed to relative structure factors.

#### *Structures solution and refinement*

Both structures were solved by Patterson methods and refined by least squares and Fourier syntheses, using the observed reflections and a 5 (for VIII), 4 (for X) diagonal block matrix for the final stages where the shift/errors were 0.18 for the 446 (for VIII), 0.07 for the 352 (for X) variables involved. Hydrogen atoms, located in the Fourier map, were included in these last cycles, where an empirical weighting scheme, to give no trends on  $w\Delta^2F$  versus either  $F_{\text{obs}}$  or  $\sin\theta/\lambda$ , was used. Final disagreement factors were  $R = 0.040$  (for VIII),  $R = 0.036$  (for X) with  $R_w = 0.042$  (for VIII),  $R_w = 0.040$  (for X) for the observed data. The final differences synthesis showed no peaks outside  $\pm 0.48 \text{ e } \text{\AA}^{-3}$  (for VIII),  $\pm 0.29 \text{ e } \text{\AA}^{-3}$  (for X), and the maximum thermal parameter were  $U_{33}(\text{O}(3)) 0.35(1) \text{ \AA}^2$  (for VIII),  $U_{33}(\text{C}(31)) 0.16(5) \text{ \AA}^2$  (for X).

Computations were carried out using the X-RAY 70 SYSTEM [30] on a UNIVAC 1108. Neutral atomic scattering factors were used from International Tables [31], including real parts of anomalous scattering for Ru, P and Cl atoms for both compounds. Lists of hydrogen-atom parameters, thermal factors for all atoms, and structure-factor amplitudes can be obtained from the authors on request.

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