

**Synthesis of Mononuclear Complexes of Ru and Os and Heterobimetallic M–M' (M = Ru or Os; M' = Rh, Ir, or Au) Compounds with Pyrazolate or Imidazolate Type Ligands. X-Ray Crystal Structure of [(Ph<sub>3</sub>P)<sub>2</sub>(OC)HRu(μ-bim)Rh(cod)] (bim = dianion of 2,2'-bi-imidazole, cod = cyclo-octa-1,5-diene) \***

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The synthesis and characterization of several mono- and poly- (di-, tri-, or tetra)-nuclear compounds are reported. The mononuclear compounds are of the type [MH(CO)(HL)(PPh<sub>3</sub>)<sub>2</sub>] [M = Ru or Os; HL = Hbim (monoanion of 2,2'-bi-imidazole), Hbbzim (monoanion of 2,2'-bibenzi-imidazole)], or [RuH(pz)(CO)(Hpz)(PPh<sub>3</sub>)<sub>2</sub>] [Hpz (pyrazole)]. They react with [{M'(μ-OMe)(diolefin)}<sub>2</sub>] {M' = Rh or Ir; diolefin = cyclo-octa-1,5-diene (cod) or tetrafluorobenzobarrelene (tetrafluorobenzo-[5,6]bicyclo[2.2.2]octa-2,5,7-triene) (tfbb)}, giving the heterodinuclear complexes [(Ph<sub>3</sub>P)<sub>2</sub>(OC)HMLM'(diolefin)]. In some of these compounds the diolefin can easily be displaced by carbon monoxide yielding [(Ph<sub>3</sub>P)<sub>2</sub>(OC)HRuL<sub>2</sub>M'(CO)<sub>2</sub>] [L<sub>2</sub> = bbzim, M' = Rh; L<sub>2</sub> = (pz)<sub>2</sub>, M' = Rh or Ir]. The structure of [(Ph<sub>3</sub>P)<sub>2</sub>(OC)HRu(μ-bim)Rh(cod)] was established by X-ray crystallography: the crystals are monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 16.209 1(7), *b* = 14.437 1(5), *c* = 18.960(1) Å, β = 93.700(4)°, and *Z* = 4. The molecule is binuclear with a 2,2'-bi-imidazolate ligand bridging, as a tetradentate bichelating group, two different metallic centres, a square-planar rhodium(I) and a slightly distorted octahedral ruthenium(II). In this molecule, the rhodium co-ordination sphere, the bridging anion, and the carbonyl and hydride ligands are planar. The Ru–N bond distances are markedly asymmetric [2.283(5) and 2.180(5) Å, to N(1) and N(2)] reflecting their different *trans* groups: a hydride and a carbonyl. The compound [RuH(CO)(Hbim)(PPh<sub>3</sub>)<sub>2</sub>] reacts with [Au(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> in different proportions affording heteropolynuclear Ru(μ-H)Au complexes of formula [(Ph<sub>3</sub>P)<sub>2</sub>(OC)HRu(μ-bim){Au(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]BF<sub>4</sub>, [(Ph<sub>3</sub>P)Au(μ-H)(Ph<sub>3</sub>P)<sub>2</sub>(OC)Ru(μ-bim){Au(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]BF<sub>4</sub>, and [(Ph<sub>3</sub>P)Au(μ-H)(Ph<sub>3</sub>P)<sub>2</sub>(OC)Ru(μ-Hbim){Au(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]BF<sub>4</sub>.

Heterobinuclear transition-metal complexes have received much attention in recent years;<sup>1</sup> many types of binuclear complexes with bridging ligands have been synthesized and used in studies of electron-transfer processes and metal–metal interactions.<sup>2</sup> Bridging ligands can change the nature of metal–metal interactions. For example studies on binuclear complexes with bridging imidazolate ligands suggest that imidazolate is particularly efficient in promoting electron transfer.<sup>3</sup>

Our interest in catalytic processes involving binuclear complexes<sup>4</sup> prompted us to prepare heterobinuclear complexes in which the bridging ligands between the two metals were azolate-type ligands. We chose 2,2'-bi-imidazole (H<sub>2</sub>bim) which can act in its doubly deprotonated form as a bridging bis-bidentate ligand in binuclear complexes;<sup>5</sup> this ligand does not allow close proximity of both metals but it probably favours electronic communication between the non-adjacent metal centres. We have recently shown<sup>6</sup> that the heterobinuclear complexes [(Ph<sub>3</sub>P)<sub>2</sub>(OC)HRu(μ-bim)M(cod)] (M = Rh or Ir, cod = cyclo-octa-1,5-diene) are more active catalysts than the mononuclear parent (ruthenium, rhodium, or iridium) compounds for the hydrogenation of cyclohexene with molecular hydrogen and hydrogen transfer from propan-2-ol to cyclohexanone, styrene, or benzylideneacetophenone. We now report their synthesis, the X-ray crystal structure of the rhodium derivative, and the preparation of some other heterobinuclear complexes with bi-imidazolate (bim), bibenzi-imidazolate (bbzim), or pyrazolate (pz) bridges.

It is now well established that many transition-metal hydrides are capable of combining with electron-deficient species to afford bimetallic complexes containing M(μ-H)M' linkages.

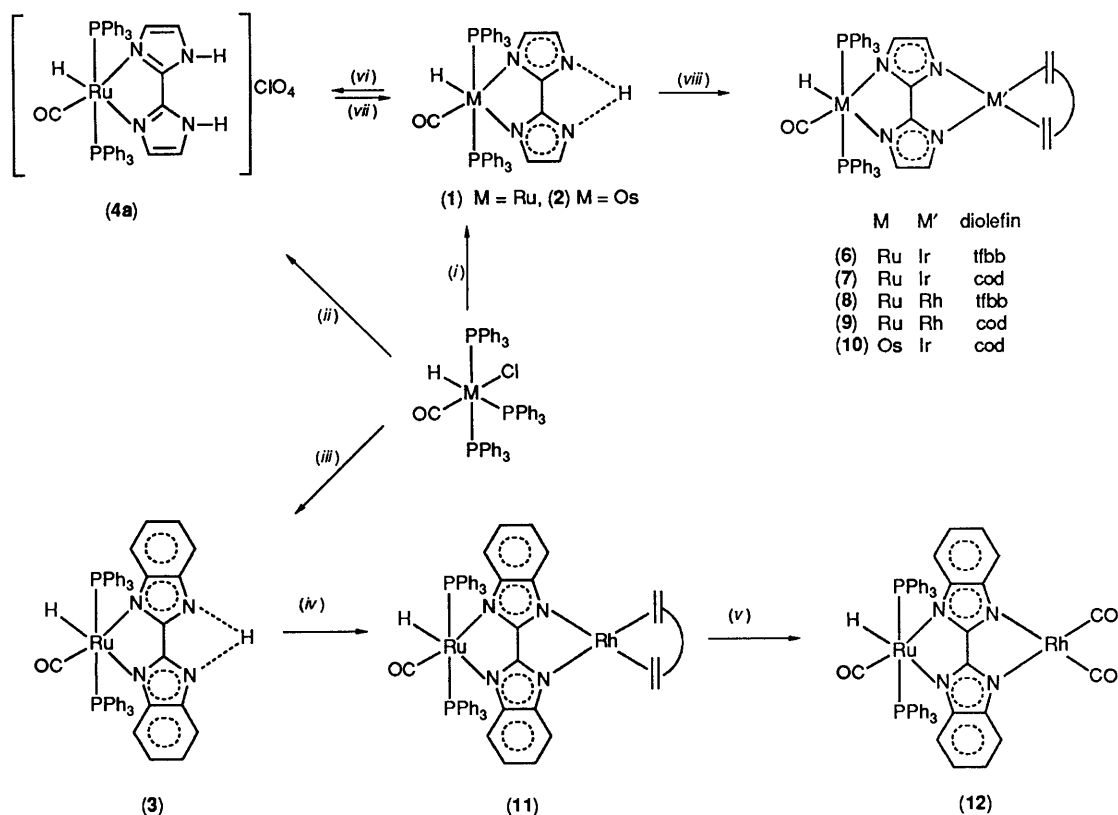
The interest in the synthesis and characterization of polynuclear hydridogold complexes<sup>7</sup> is due to their intrinsically novel structures as well as their properties because each metal centre may be involved separately in the activation of other molecules. For these reasons we have also studied the reaction of [RuH(CO)(Hbim)(PPh<sub>3</sub>)<sub>2</sub>] with [Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in different proportions.

## Results and Discussion

*Compounds with the Ligands H<sub>2</sub>bim or H<sub>2</sub>bbzim.—Mononuclear complexes.* In complexes of the type [MH(Cl)(CO)(PPh<sub>3</sub>)<sub>3</sub>] (M = Ru or Os) the phosphine *trans* to the hydride ligand is very labile and can easily be displaced;<sup>8</sup> when these complexes react with anionic ligands such as Hbim<sup>−</sup> or Hbbzim<sup>−</sup>, which can act as bidentate chelate ligands, the chlorine atom is also removed. Thus treatment of [MH(Cl)(CO)(PPh<sub>3</sub>)<sub>3</sub>] with 1 mol of H<sub>2</sub>bim or H<sub>2</sub>bbzim in the presence of 1 mol of a strong base (KOH in methanol) affords in high yield the neutral complexes [MH(CO)(HL)(PPh<sub>3</sub>)<sub>2</sub>] [HL = Hbim, M = Ru, (1), or Os, (2); HL = Hbbzim, M = Ru, (3)] (see Scheme 1). The reactions are slow and it is necessary to keep the suspensions stirring during 4 h to obtain the

\* μ-2,2'-Bi-imidazolato-1:2κ<sup>4</sup> N<sup>1</sup>,N<sup>1'</sup>:N<sup>3</sup>,N<sup>3'</sup>-carbonyl-1κC-2(η<sup>4</sup>)-cyclo-octadiene(hydrido-1κH)bis(triphenylphosphine-1κP)ruthenium-rhodium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.



**Scheme 1.** (i)  $\text{H}_2\text{bim}$ ,  $\text{KOH}-\text{MeOH}$ ; (ii)  $\text{H}_2\text{bim}$ ,  $\text{NaClO}_4$ ; (iii)  $\text{H}_2\text{bbzim}$ ,  $\text{KOH}-\text{MeOH}$ ; (iv)  $\frac{1}{2}[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ ; (v)  $\text{CO}$ ; (vi)  $\text{HClO}_4$ ; (vii)  $\text{KOH}-\text{MeOH}$ ; (viii)  $\frac{1}{2}[\{\text{M}'(\mu\text{-OMe})(\text{diolefin})\}_2]$

**Table 1.** Analytical data for the new complexes

| Compound   | Colour        | Yield (%) | Analysis (%) <sup>*</sup> |             |             |
|--|---------------|-----------|---------------------------|-------------|-------------|
|  |               |           | C                         | H           | N           |
| (1) $[\text{RuH}(\text{CO})(\text{Hbim})(\text{PPh}_3)_2]$   | White         | 95        | 65.55 (65.55)             | 4.50 (4.60) | 7.20 (7.10) |
| (2) $[\text{OsH}(\text{CO})(\text{Hbim})(\text{PPh}_3)_2]$   | White         | 90        | 59.25 (58.90)             | 4.60 (4.15) | 6.40 (6.40) |
| (3) $[\text{RuH}(\text{CO})(\text{Hbbzim})(\text{PPh}_3)_2]$   | Yellow        | 68        | 68.95 (69.00)             | 4.75 (4.55) | 5.90 (6.30) |
| (4a) $[\text{RuH}(\text{CO})(\text{H}_2\text{bim})(\text{PPh}_3)_2]\text{ClO}_4$   | White         | 75        | 58.10 (58.15)             | 4.15 (4.20) | 6.50 (6.30) |
| (5) $[\{\text{RuH}(\text{CO})(\text{PPh}_3)_2\}_2(\mu\text{-bim})]$  | White         | 60        | 66.65 (66.15)             | 5.10 (4.70) | 3.90 (3.90) |
| (6) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Ir}(\text{tfbb})]$   | Orange        | 77        | 54.90 (54.80)             | 3.60 (3.45) | 4.75 (4.65) |
| (7) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Ir}(\text{cod})]$  | Bright yellow | 89        | 56.30 (56.35)             | 4.80 (4.35) | 5.25 (5.15) |
| (8) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Rh}(\text{tfbb})]$   | Yellow        | 65        | 58.75 (59.20)             | 3.75 (3.70) | 4.90 (5.00) |
| (9) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Rh}(\text{cod})]$  | Pale yellow   | 87        | 61.45 (61.40)             | 4.80 (4.70) | 5.65 (5.60) |
| (10) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HOs}(\mu\text{-bim})\text{Ir}(\text{cod})]$   | Yellow        | 89        | 52.35 (52.05)             | 4.25 (4.05) | 4.75 (4.75) |
| (11) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bbzim})\text{Rh}(\text{cod})]$   | Yellow        | 76        | 63.80 (64.55)             | 4.90 (4.70) | 4.90 (5.10) |
| (12) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bbzim})\text{Rh}(\text{CO})_2]\cdot\text{CH}_2\text{Cl}_2$                                   | Yellow        | 62        | 57.60 (57.35)             | 4.10 (3.65) | 5.00 (4.95) |
| (13) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\{\text{Au}(\text{PPh}_3)_2\}_2]\text{BF}_4$  | White         |           | 52.30 (52.90)             | 3.60 (3.65) | 3.25 (3.10) |
| (14) $[(\text{Ph}_3\text{P})\text{Au}(\mu\text{-H})(\text{Ph}_3\text{P})_2(\text{OC})\text{Ru}(\mu\text{-bim})\{\text{Au}(\text{PPh}_3)_2\}_2]\text{BF}_4$ | White         | 73        | 49.70 (49.80)             | 3.35 (3.45) | 2.50 (2.40) |
| (17) $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$  | White         | 89        | 65.35 (65.40)             | 5.05 (4.85) | 7.10 (7.10) |
| (18) $[\text{RuH}(\text{CO})(\text{Hpz})_2(\text{PPh}_3)_2]\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2$  | White         | 84        | 55.50 (56.00)             | 4.50 (4.20) | 5.90 (6.00) |
| (19) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Ir}(\text{tfbb})]$   | Yellow        | 69        | 54.75 (54.72)             | 3.95 (3.60) | 4.60 (4.65) |
| (20) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Rh}(\text{tfbb})]$   | Yellow        | 65        | 59.25 (59.10)             | 4.20 (3.90) | 4.95 (5.00) |
| (21) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Ir}(\text{CO})_2]$   | Yellow        | 66        | 52.25 (52.10)             | 3.80 (3.60) | 5.25 (5.40) |
| (22) $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Rh}(\text{CO})_2]$   | Pale yellow   | 60        | 56.45 (57.05)             | 4.05 (3.95) | 5.90 (5.90) |

\* Calculated values are given in parentheses.

compounds, which were characterized by the data given in Tables 1–3.

The spectroscopic data are consistent with compounds (1)–(3) containing  $\text{Hbim}^-$  or  $\text{Hbbzim}^-$  co-ordinated as bidentate ligands. The broad structure in the i.r. spectra, from 3 000 to 2 300  $\text{cm}^{-1}$  indicates the presence of a N–H bond remaining in

these co-ordinated monoanions.<sup>9</sup> Their high-field  $^1\text{H}$  n.m.r. spectra (20 °C,  $\text{CDCl}_3$ ) show a triplet due to the terminal hydride in a *cis*-position to both phosphorus atoms; this atom disposition occurs in all the compounds described.

Treating a dichloromethane suspension of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$  with excess of  $\text{H}_2\text{bim}$  gave a cationic species

**Table 2.** I.r. data (cm<sup>-1</sup>) for the new complexes

| Complex | v(CO) <sup>a</sup>  | v(M-H) <sup>b</sup> | v(N-H) <sup>b</sup> |
|---------|---------------------|---------------------|---------------------|
| (1)     | 1 915               | 2 010w              | 2 300—3 000         |
| (2)     | 1 895               | 2 110w              | 2 300—3 000         |
| (3)     | 1 925               | 2 060w              | 2 300—3 000         |
| (4a)    | 1 935               | 2 020w              | 3 100—3 400         |
| (5)     | 1 925 <sup>b</sup>  | 2 060m              |                     |
| (6)     | 1 930               | 2 015m              |                     |
| (7)     | 1 930               | 2 020m              |                     |
| (8)     | 1 925               | 2 000m              |                     |
| (9)     | 1 920               | 2 015m              |                     |
| (10)    | 1 905               | 2 120m              |                     |
| (11)    | 1 925               | 1 975m              |                     |
| (12)    | 1 927, 2 000, 2 070 |                     |                     |
| (13)    | 1 930               |                     |                     |
| (14)    | 1 970               |                     |                     |
| (17)    | 1 925               | 1 980s              |                     |
| (18)    | 1 945               | 2 035w              | 3 220—3 470         |
| (19)    | 1 912               | 1 970s              |                     |
| (20)    | 1 925               | 1 962s              |                     |
| (21)    | 1 930, 1 980, 2 060 |                     |                     |
| (22)    | 1 925, 2 000, 2 070 |                     |                     |

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>b</sup> In Nujol mull. All v(CO) absorptions collected are very strong.

[RuH(CO)(H<sub>2</sub>bim)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> which can be crystallized as the ClO<sub>4</sub><sup>-</sup>, (4a), or BF<sub>4</sub><sup>-</sup>, (4b), salts by simple metathetical reaction. Compound (4a) can also be obtained by treating (1) with a protonic acid, such as HClO<sub>4</sub>. This reaction is reversible, so treatment of (4a) with 1 equivalent of KOH (methanolic solution) in dichloromethane again gives compound (1).

*Binuclear compounds:* (a) *homobinuclear.* The addition of 0.5 equivalent of 2,2'-bi-imidazole and KOH (methanolic solution) to [RuH(Cl)(CO)(PPh<sub>3</sub>)<sub>3</sub>], in toluene solution, leads to a white solid whose analytical and i.r. data (Tables 1 and 2) agree with the formulation of [{RuH(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-bim)] (5) as a binuclear compound with the bi-imidazole dianion coordinated, in a tetradentate manner, to two ruthenium atoms. Its i.r. spectrum (Nujol mull) shows absorptions due to v(CO) at 1 925 cm<sup>-1</sup> and v(Ru-H) at 2 060 cm<sup>-1</sup>, but no bands assignable to v(N-H). The low solubility of this compound, in most solvents, prevented recording of its n.m.r. spectra and determination of its molecular weight.

(b) *Heterodinuclear.* The mononuclear complexes (1)–(3) retain one nitrogen atom and an acidic N-H group capable of co-ordination; thus they react with [M'(μ-OMe)(diolefin)]<sub>2</sub> yielding the heterobinuclear neutral compounds (6)–(11) (Scheme 1)

By bubbling carbon monoxide through a dichloromethane solution of (11) the diolefin cyclo-octadiene is displaced and a new heterobimetallic complex [(Ph<sub>3</sub>P)<sub>2</sub>(OC)HRu(μ-bbzim)-Rh(CO)<sub>2</sub>] (12) is formed. However, similar treatment of

**Table 3.** Proton and <sup>31</sup>P-{<sup>1</sup>H} n.m.r. data for the new complexes<sup>a</sup> (in CDCl<sub>3</sub>)

| Compound                   | <sup>1</sup> H (δ)   | <sup>31</sup> P (δ) <sup>b</sup>                      |
|----------------------------|--|---|
| (1)                        | 9.0 (1 H, br, NH), 6.87 (1 H, s), 6.61 (1 H, s), 6.34 (1 H, s), 5.85 (1 H, s) (=CH, bim), -11.45 [1 H, t, J(HP) 20.5]  | 47.98   |
| (2)                        | 6.13 (1 H, br, NH), 6.85 (1 H, s), 6.59 (1 H, s), 6.28 (1 H, s), 5.80 (1 H, s) (=CH, bim), -12.49 [1 H, t, J(HP) 19.0]   | 19.56   |
| (3)                        | -10.97 [1 H, t, J(HP) 20.7]  | 46.75   |
| (4a)                       | 11.0 (2 H, br, NH), 7.04 (1 H, s), 6.81 (1 H, s), 6.41 (1 H, s), 6.03 (1 H, s) (=CH, bim), -11.93 [1 H, t, J(HP) 19.4]   | 47.51   |
| (6)                        | 6.67 (1 H, s), 6.04 (1 H, s), 5.73 (1 H, s), 5.70 (1 H, s) (=CH, bim), 5.6 (2 H, m, CH, tfbb), 2.8 (m, 4 H, =CH, tfbb), -13.39 [1 H, t, J(HP) 19.5]  | 48.31   |
| (7)                        | 6.70 (1 H, s), 6.22 (1 H, s), 5.93 (1 H, s), 5.75 (1 H, s) (=CH, bim), 3.8 (m, 4 H, =CH, cod), 2.2 (m, 4 H, CH <sub>2</sub> , cod), 1.4 (m, 4 H, CH <sub>2</sub> , cod), -13.28 [1 H, t, J(HP) 19.5]   | 48.33   |
| (8)                        | 6.70 (1 H, s), 6.00 (1 H, s), 5.73 (1 H, s), 5.69 (1 H, s) (=CH, bim), 5.6 (2 H, m, CH, tfbb), 3.6 (4 H, m, =CH, tfbb), -12.94 [1 H, t, J(HP) 19.8]  | 48.47   |
| (9)                        | 6.71 (1 H, s), 6.10 (1 H, s), 5.80 (1 H, s), 5.78 (1 H, s) (=CH, bim), 4.1 (4 H, m, =CH, cod), 2.4 (4 H, m, CH <sub>2</sub> , cod), 1.7 (4 H, m, CH <sub>2</sub> , cod), -12.89 [1 H, t, J(HP) 19.5]   | 48.50   |
| (10)                       | 6.65 (1 H, s), 6.17 (1 H, s), 5.86 (1 H, s), 5.66 (1 H, s) (=CH, bim), 3.9 (4 H, m, =CH, cod), 2.2 (4 H, m, CH <sub>2</sub> , cod), 1.4 (4 H, m, CH <sub>2</sub> , cod), -14.44 [1 H, t, J(HP) 16.8]   | 19.51   |
| (11)                       | 4.84 (4 H, m, =CH, cod), 2.51 (4 H, m, CH <sub>2</sub> , cod), 1.87 (4 H, m, =CH, cod), -12.55 [1 H, t, J(HP) 20.0]  | 48.72   |
| (12)                       | 5.29 (2 H, s, CH <sub>2</sub> Cl <sub>2</sub> ), -12.93 [1 H, t, J(HP) 19.6]   | 48.24   |
| (13)                       | 6.82 (1 H, s), 6.52 (1 H, s), 6.23 (1 H, s) (=CH, bim), <sup>c</sup> -11.44 [1 H, t, J(HP) 19.7]   | 47.58 (2 P, Ru), 31.14 (1 P), 30.76 (1 P)             |
| (14) <sup>d</sup>          | -6.24 [1 H, dt, J(HP) <sub>trans</sub> 74.1, J(HP) <sub>cis</sub> 12.9]  | 45.4 (1 P), 34.18 (2 P, Ru), 31.76 (1 P), 31.63 (1 P) |
| (15) and (16) <sup>d</sup> | 11.4 (br, NH), -6.20 [dt, J(HP) <sub>trans</sub> 73, J(HP) <sub>cis</sub> 13], -6.01 [dt, J(HP) <sub>trans</sub> 73, J(HP) <sub>cis</sub> 13]  | 46.1, 45.6, 36.1, 35.7, 35.4, 32.9                    |
| (17)                       | 7.11 (1 H, d), 7.09 (1 H, d), 7.05 (1 H, d), 6.61 (1 H, d) (H <sup>3</sup> , H <sup>3'</sup> , H <sup>5</sup> , H <sup>5'</sup> , pz), 5.96 (1 H, t), 5.53 (1 H, t) (H <sup>4</sup> , H <sup>4'</sup> , pz), -11.65 (1 H, t, J(HP) 20.2]   | 45.64   |
| (18)                       | 10.0 (2 H, s, 2NH), 7.54 (1 H, s), 6.96 (1 H, s), 6.69 (1 H, s), 6.12 (1 H, s), 5.57 (1 H, s) (pz), <sup>c</sup> 5.29 (1 H, s, CH <sub>2</sub> Cl <sub>2</sub> ), -12.67 [1 H, t, J(HP) 20.1]  | 45.89   |
| (19)                       | 6.84 (1 H, d), 6.65 (1 H, d), 6.54 (1 H, d), 6.25 (1 H, d), (H <sup>3</sup> , H <sup>3'</sup> , H <sup>5</sup> , H <sup>5'</sup> , pz), 5.76 (1 H, t), 5.23 (1 H, t) (H <sup>4</sup> , H <sup>4'</sup> , pz), 5.1 (2 H, m, CH, tfbb), 2.3 (4 H, m, =CH, tfbb), -11.77 [1 H, t, J(HP) 20.1] | 45.86   |
| (20)                       | 6.90 (1 H, d), 6.59 (1 H, d), 6.57 (1 H, d), 6.15 (1 H, d), (H <sup>3</sup> , H <sup>3'</sup> , H <sup>5</sup> , H <sup>5'</sup> , pz), 5.79 (1 H, t), 5.28 (1 H, t) (H <sup>4</sup> , H <sup>4'</sup> , pz), 5.2 (2 H, m, CH, tfbb), 3.1 (4 H, m, =CH, tfbb), -11.70 [1 H, t, J(HP) 21.1] | 45.91   |
| (21)                       | 7.65 (1 H, d), 7.15 (1 H, d), 6.96 (1 H, d), 6.62 (1 H, d), (H <sup>3</sup> , H <sup>3'</sup> , H <sup>5</sup> , H <sup>5'</sup> , pz), 5.39 (1 H, t), 5.38 (1 H, t) (H <sup>4</sup> , H <sup>4'</sup> , pz), -11.74 [1 H, t, J(HP) 21.6]  | 44.30   |
| (22)                       | 7.65 (1 H, d), 6.97 (1 H, d), 6.63 (1 H, d), (H <sup>3</sup> , H <sup>3'</sup> , H <sup>5</sup> , H <sup>5'</sup> , pz), <sup>c</sup> 5.90 (1 H, t), 5.39 (1 H, t) (H <sup>4</sup> , H <sup>4'</sup> , pz), -11.68 [1 H, t, J(HP) 22.0]  | 44.23   |

<sup>a</sup> Chemical shifts (δ) in p.p.m., coupling constants in Hz; s = singlet, d = doublet, t = triplet, and m = multiplet. <sup>b</sup> All resonances are singlets. <sup>c</sup> One of the =CH signals is overlapped with the PPh<sub>3</sub> protons. <sup>d</sup> In [2H<sub>6</sub>] acetone.

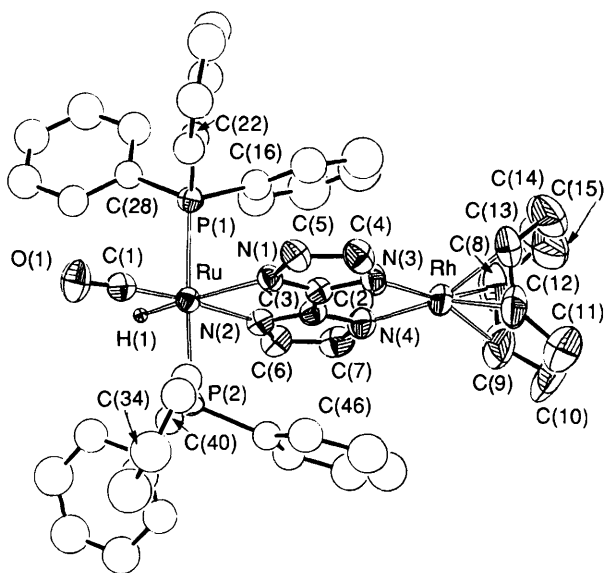


Figure 1. The molecular structure of  $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Rh}(\text{cod})]$  (**9**) showing the crystallographic numbering scheme

Table 4. Selected bond distances (Å) and angles (°) for compound (**9**)

|                |           |                |           |
|----------------|-----------|----------------|-----------|
| Ru-P(1)        | 2.367(3)  | Rh-N(3)        | 2.127(5)  |
| Ru-P(2)        | 2.358(3)  | Rh-N(4)        | 2.134(5)  |
| Ru-N(1)        | 2.283(5)  | Rh-C(8)        | 2.103(9)  |
| Ru-N(2)        | 2.180(5)  | Rh-C(9)        | 2.102(10) |
| Ru-C(1)        | 1.829(6)  | Rh-C(12)       | 2.110(8)  |
| Ru-H(1)        | 1.51(5)   | Rh-C(13)       | 2.118(8)  |
| N(1)-C(2)      | 1.332(7)  | N(3)-C(2)      | 1.329(7)  |
| N(1)-C(5)      | 1.375(7)  | N(3)-C(4)      | 1.370(8)  |
| N(2)-C(3)      | 1.322(7)  | N(4)-C(3)      | 1.339(7)  |
| N(2)-C(6)      | 1.380(8)  | N(4)-C(7)      | 1.383(8)  |
| C(1)-O(1)      | 1.154(7)  | C(4)-C(5)      | 1.367(8)  |
| C(2)-C(3)      | 1.412(7)  | C(6)-C(7)      | 1.358(8)  |
| C(8)-C(9)      | 1.367(14) | C(11)-C(12)    | 1.506(13) |
| C(8)-C(15)     | 1.505(13) | C(12)-C(13)    | 1.384(12) |
| C(9)-C(10)     | 1.547(15) | C(13)-C(14)    | 1.512(11) |
| C(10)-C(11)    | 1.440(18) | C(14)-C(15)    | 1.455(16) |
| P(1)-Ru-P(2)   | 175.7(1)  | P(2)-Ru-H(1)   | 90(2)     |
| P(1)-Ru-N(1)   | 89.2(1)   | N(1)-Ru-N(2)   | 79.2(2)   |
| P(1)-Ru-N(2)   | 88.9(1)   | N(1)-Ru-C(1)   | 106.1(2)  |
| P(1)-Ru-C(1)   | 93.7(2)   | N(1)-Ru-H(1)   | 172(2)    |
| P(1)-Ru-H(1)   | 89(2)     | N(2)-Ru-C(1)   | 174.2(2)  |
| P(2)-Ru-N(1)   | 90.9(1)   | N(2)-Ru-H(1)   | 93(2)     |
| P(2)-Ru-N(2)   | 86.9(1)   | C(1)-Ru-H(1)   | 82(2)     |
| P(2)-Ru-C(1)   | 90.4(2)   | Ru-C(1)-O(1)   | 174.9(5)  |
| N(3)-Rh-N(4)   | 82.2(2)   | N(4)-Rh-M(1)*  | 94.3(3)   |
| N(3)-Rh-M(1)*  | 175.8(3)  | N(4)-Rh-M(2)*  | 176.4(3)  |
| N(3)-Rh-M(2)*  | 94.2(3)   | M(1)-Rh-M(2)*  | 89.3(3)   |
| Ru-N(1)-C(2)   | 106.3(3)  | Rh-N(3)-C(2)   | 107.6(3)  |
| Ru-N(1)-C(5)   | 150.7(4)  | Rh-N(3)-C(4)   | 149.4(4)  |
| C(2)-N(1)-C(5) | 103.0(4)  | C(2)-N(3)-C(4) | 102.9(4)  |
| Ru-N(2)-C(3)   | 109.2(3)  | Rh-N(4)-C(3)   | 107.4(3)  |
| Ru-N(2)-C(6)   | 146.8(4)  | Rh-N(4)-C(7)   | 150.0(4)  |
| C(3)-N(2)-C(6) | 104.0(4)  | C(3)-N(4)-C(7) | 102.5(4)  |
| N(1)-C(2)-N(3) | 116.2(5)  | N(2)-C(3)-N(4) | 115.7(5)  |

\* M(1) and M(2) represent the midpoints of the olefinic C(8)-C(9) and C(12)-C(13) bonds.

complexes (**6**)—(**9**) leads to mixtures of compounds which cannot be totally identified.

All the new binuclear complexes (**6**)—(**12**) are isolated in good yield as microcrystalline solids. They were characterized

by the data given in Tables 1—3. The i.r. spectra (in  $\text{CH}_2\text{Cl}_2$  solution and Nujol mulls) confirm the presence of terminal carbonyls and terminal hydride ligands. The high-field  $^1\text{H}$  n.m.r. spectra show a triplet for the hydride ligands indicating that this ligand retains the *cis* position to the two phosphorus atoms. As expected, the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra contain only one peak for both equivalent phosphine groups.

In order to get further structural information about these systems, the crystal structure of compound (**9**) was determined.

*Description of the Structure of  $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Rh}(\text{cod})]$  (**9**).*—The molecular geometry of the heterodinuclear complex (**9**) is shown in Figure 1. The bi-imidazole dianion co-ordinates as a planar ligand in a symmetrical tetradentate manner to the rhodium(I) and ruthenium(II). Selected bond distances and angles are in Table 4.

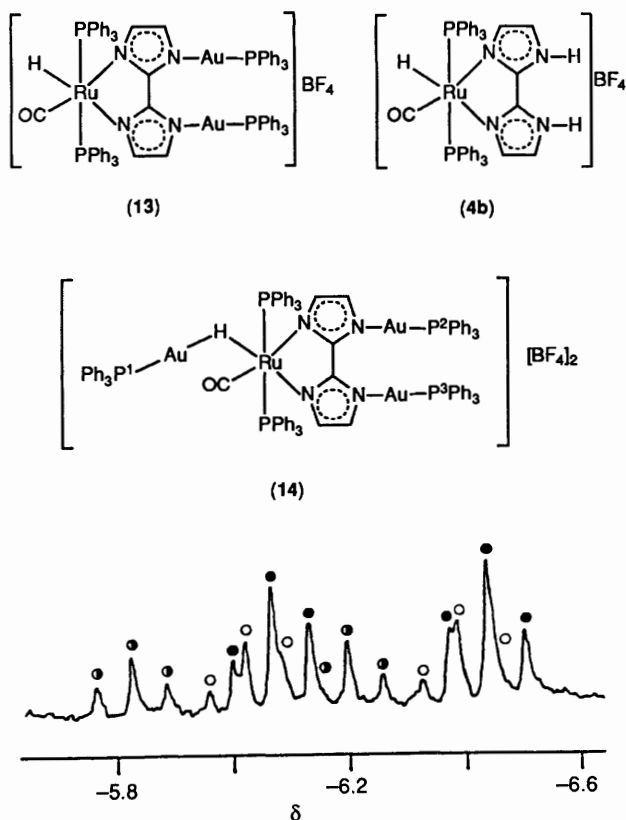
The co-ordination sphere around the rhodium atom is approximately square planar with the co-ordination polyhedron defined by two nitrogen atoms from the bi-imidazole ligand and the midpoints of the two olefinic bonds from the cyclo-octadiene ring. If M(1) and M(2) are the midpoints of the C(8)-C(9) and C(12)-C(13) bonds, the deviations of M(1), M(2), N(3), and N(4) from the mean plane passing through them are  $-0.058(9)$ ,  $0.039(8)$ ,  $-0.010(4)$ , and  $0.010(4)$  Å respectively with the rhodium atom deviating from this plane by  $0.010(2)$  Å. The Rh-N(3) and Rh-N(4) bond distances,  $2.127(5)$  and  $2.134(5)$  Å, are in the range found in related rhodium(I) bi-imidazolate or imidazolate complexes.<sup>9,10</sup> The cyclo-octa-1,5-diene ligand takes its customary 'tub' conformation. The co-ordinated double bonds, C(8)-C(9) and C(12)-C(13), have lengths of  $1.367(14)$  and  $1.384(12)$  Å respectively, greater than those in the free cod molecule ( $1.34$  Å), as expected.

The ruthenium atom shows a distorted-octahedral environment formed by the other two nitrogen atoms of the bridging ligand, two triphenylphosphine groups in relative *trans*-disposition and a carbonyl and a hydride ligand both in the plane of the bi-imidazole dianion. The very significant difference between Ru-N(1) and Ru-N(2),  $2.283(5)$  and  $2.180(5)$  Å respectively, is indicative of a significant *trans*-effect lengthening by the hydride ligand opposite to atom N(1). A similar observation has been made for related complexes.<sup>11</sup> The hydride was clearly located in the final Fourier difference map; the distance from the metal,  $1.51(5)$  Å, is shorter than that found for related mononuclear complexes,<sup>11a,12</sup> but compares well with the dinuclear compound  $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-Cl})(\mu\text{-pz})\text{Ir}(\text{tfbb})]\{\text{tfbb} = \text{tetrafluorobenzobarrelene (tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene)}\}$ .<sup>4c</sup>

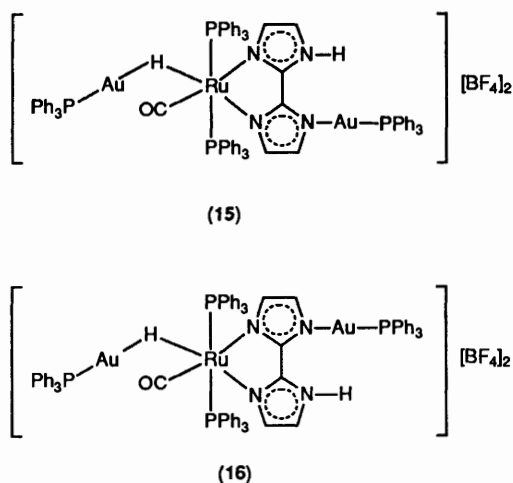
Each imidazolate ring of the bi-imidazole ligand is strictly planar and both are slightly twisted making a dihedral angle of  $2.6(2)^\circ$ . A similar angle ( $4.0^\circ$ ) has been reported for the tetranuclear  $[\text{Rh}_4(\text{CO})_8(\text{bim})_2]$ ,<sup>10b</sup> whereas the two rings have been found to be perfectly coplanar in  $[\text{Rh}_2(\text{cod})_2(\text{bim})_2]$ <sup>10a</sup> where the  $\text{bim}^{2-}$  behaves as a symmetrical bichelating ligand, as in compound (**9**).

The two metal centres, Ru and Rh, are separated by a distance of  $5.579(2)$  Å.

*Reactivity of Compound (1) with  $[\text{Au}(\text{PPh}_3)]^+$ .*—The addition of 1 equivalent of  $[\text{Au}(\text{PPh}_3)]\text{BF}_4$  to compound (**1**) in acetone or tetrahydrofuran solution gave the cationic mixed-metal  $\text{RuAu}_2$  complex (**13**) together with (**4b**); (**13**) and (**4b**) can be separated because their different solubility in dichloromethane-diethyl ether. Both were characterized by i.r. and  $^{31}\text{P}$  and  $^1\text{H}$  n.m.r. spectroscopy. The i.r. spectrum of compound (**13**) around  $\approx 2000$   $\text{cm}^{-1}$  has only a broad band, assignable to  $\nu(\text{CO})$ , at  $1930$   $\text{cm}^{-1}$ ; the terminal stretch Ru-H is absent or overlapped by  $\nu(\text{CO})$ . The presence of the hydride ligand was

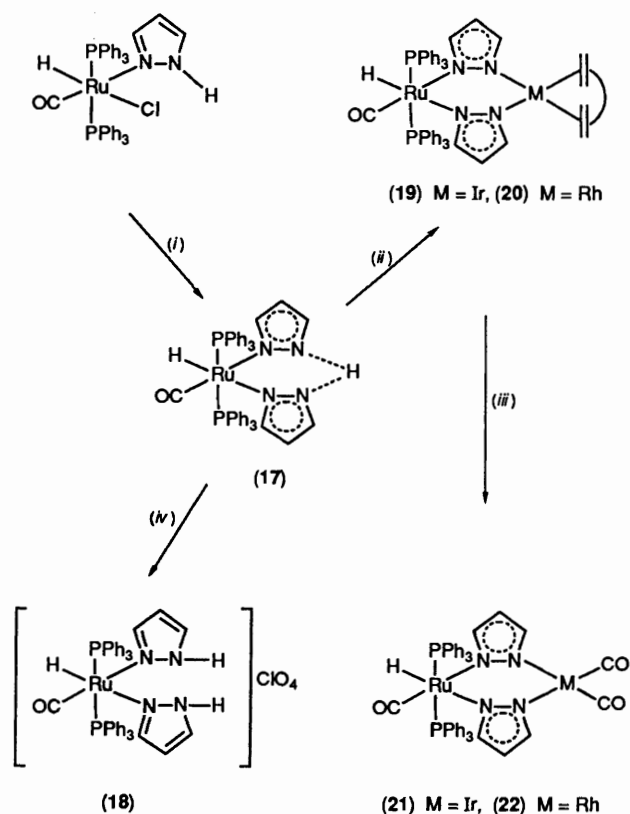


**Figure 2.** High-field proton n.m.r. spectrum of the mixture of compounds obtained by reaction of complex (1) and 2 mol of  $[\text{Au}(\text{PPh}_3)]^+$ . The signals marked with ● correspond to compound (14) and those with ⊙ and ○ to (15) and (16)



confirmed by the observation of a triplet resonance at  $\delta -11.4$  [ $J(\text{HP}) = 19.7$  Hz] in the  $^1\text{H}$  n.m.r. spectrum at room temperature. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum in  $\text{CDCl}_3$  as solvent consists of three singlets with relative intensities of 2:1:1 at  $\delta$  47.6 (s, PRu), 31.1 (s, PAu), and 30.8 p.p.m. (s, PAu), respectively.

When 3 equivalents of  $[\text{Au}(\text{PPh}_3)]^+$  were added to compound (1), in acetone solution, a tetranuclear RuAu complex (14) was obtained as a white solid. Recrystallization from acetone-diethyl ether gave colourless needles. The i.r. spectrum of compound (14) shows a broad band attributed to  $\nu(\text{CO})$  at  $1970\text{ cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ). The  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectra show unambiguously that this complex is tetranuclear and that



**Scheme 2.** (i) Hpz, KOH-MeOH; (ii)  $\frac{1}{2}[\text{M}(\mu\text{-OMe})(\text{tfbb})_2]$ ; (iii) CO; (iv)  $\text{HClO}_4$

the bridging hydride is bonded to two metal atoms. The high-field  $^1\text{H}$  n.m.r. spectrum (20 °C,  $[\text{H}_6]$ acetone) consists of a doublet of triplets centred at  $\delta -6.24$  [1 H,  $J(\text{HP})_{\text{trans}} = 74.1$ ,  $J(\text{HP})_{\text{cis}} = 12.9$  Hz]. The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum (20 °C,  $[\text{H}_6]$ acetone) contains four singlet resonances with relative intensities of 1:2:1:1; at  $\delta$  45.4 (s,  $\text{P}^1$ ), 34.2 (s, PRu), 31.8 and 31.6 p.p.m. (singlets,  $\text{P}^2$  or  $\text{P}^3$ ).

The reaction of compound (1) with 2 equivalents of  $[\text{Au}(\text{PPh}_3)]^+$  in acetone or tetrahydrofuran solution led to a white solid which is a mixture of three compounds identified by the  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectra. The high-field  $^1\text{H}$  n.m.r. spectrum of the solid, in  $[\text{H}_6]$ acetone at 20 °C, consists of three doublets of triplets (Figure 2); one is assignable to compound (14); the other two [ $\delta -6.0$  and  $-6.2$ ,  $J(\text{HP})_{\text{trans}} = 73$ ,  $J(\text{HP})_{\text{cis}} = 13$  Hz] are probably due to the trinuclear isomeric compounds (15) and (16). There is also a broad signal at  $\delta$  11.4 due to the imino hydrogen resonances.

The  $^{31}\text{P}\{-^1\text{H}\}$  spectrum of the reaction product in  $[\text{H}_6]$ acetone at 20 °C is in agreement with the existence of these three species: there are ten signals, four singlets corresponding to compound (14) and other six, at  $\delta$  46.1, 45.6, 36.1, 35.7, 35.4, and 32.9, which can be assigned to compounds (15) and (16).

Recrystallization of the mixture in acetone-diethyl ether gives pure compound (14). The structure proposed for complexes (14)–(16) is based on the X-ray crystal structures of related 'M( $\mu\text{-H}$ )Au-PPh $_3$ ' complexes,<sup>7c,13</sup> it should be noted that in all cases the M, Au, and P atoms are not linear. To assert the correct bonding picture an X-ray structure determination would be necessary.

*Complexes with the Pyrazolate Ligand.*—Using  $[\text{RuH}(\text{Cl})\text{CO}(\text{Hpz})(\text{PPh}_3)_2]$  (Hpz = pyrazole) as starting reagent a

**Table 5.** Atom co-ordinates ( $\times 10^4$ ) for the non-hydrogen atoms of  $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\text{bim})\text{Rh}(\text{cod})]$  (**9**)

| Atom  | X/a      | Y/b       | Z/c       | Atom  | X/a      | Y/b      | Z/c       |
|-------|----------|-----------|-----------|-------|----------|----------|-----------|
| Ru    | 2 752(1) | 3 189(1)  | 675(1)    | C(22) | 2 030(3) | 2 314(4) | 2 300(3)  |
| Rh    | 2 451(1) | -397(1)   | -407(1)   | C(23) | 1 279(3) | 2 650(4) | 2 052(3)  |
| P(1)  | 2 961(1) | 2 522(1)  | 1 813(1)  | C(24) | 562(4)   | 2 455(4) | 2 398(3)  |
| P(2)  | 2 621(1) | 3 778(1)  | -487(1)   | C(25) | 624(5)   | 1 938(5) | 2 999(4)  |
| N(1)  | 1 754(3) | 2 108(3)  | 403(2)    | C(26) | 1 361(5) | 1 609(5) | 3 262(4)  |
| N(2)  | 3 490(3) | 2 077(3)  | 259(2)    | C(27) | 2 072(4) | 1 791(4) | 2 915(3)  |
| N(3)  | 1 667(3) | 656(3)    | -40(2)    | C(28) | 3 632(3) | 3 128(4) | 2 472(3)  |
| N(4)  | 3 374(3) | 638(3)    | -197(2)   | C(29) | 4 053(4) | 2 672(5) | 3 040(3)  |
| O(1)  | 1 927(3) | 4 880(3)  | 1 192(2)  | C(30) | 4 535(5) | 3 179(5) | 3 539(4)  |
| C(1)  | 2 214(3) | 4 203(4)  | 997(3)    | C(31) | 4 596(4) | 4 119(5) | 3 487(4)  |
| C(2)  | 2 138(3) | 1 384(4)  | 137(3)    | C(32) | 4 181(4) | 4 580(5) | 2 937(3)  |
| C(3)  | 3 000(3) | 1 377(4)  | 66(3)     | C(33) | 3 706(4) | 4 079(4) | 2 424(3)  |
| C(4)  | 898(4)   | 936(4)    | 132(3)    | C(34) | 3 415(4) | 4 583(4) | -752(3)   |
| C(5)  | 947(3)   | 1 814(4)  | 401(3)    | C(35) | 3 792(4) | 5 157(4) | -248(4)   |
| C(6)  | 4 267(4) | 1 775(4)  | 109(3)    | C(36) | 4 385(5) | 5 821(5) | -446(4)   |
| C(7)  | 4 194(4) | 909(4)    | -168(3)   | C(37) | 4 573(5) | 5 863(5) | -1 133(4) |
| C(8)  | 3 285(6) | -1 514(5) | -359(5)   | C(38) | 4 220(4) | 5 309(5) | -1 638(4) |
| C(9)  | 3 210(6) | -1 185(6) | -1 036(6) | C(39) | 3 632(4) | 4 650(4) | -1 456(3) |
| C(10) | 2 672(8) | -1 620(8) | -1 653(6) | C(40) | 1 659(3) | 4 393(4) | -745(3)   |
| C(11) | 1 801(8) | -1 696(7) | -1 554(5) | C(41) | 1 644(4) | 5 140(5) | -1 218(4) |
| C(12) | 1 492(5) | -1 154(5) | -946(4)   | C(42) | 883(5)   | 5 523(6) | -1 462(5) |
| C(13) | 1 573(5) | -1 452(5) | -251(5)   | C(43) | 153(5)   | 5 159(5) | -1 244(4) |
| C(14) | 2 005(7) | -2 331(5) | 1(5)      | C(44) | 169(4)   | 4 451(4) | -760(3)   |
| C(15) | 2 878(7) | -2 391(6) | -129(6)   | C(45) | 922(3)   | 4 087(4) | -502(3)   |
| C(16) | 3 402(4) | 1 354(4)  | 1 788(3)  | C(46) | 2 609(3) | 2 861(4) | -1 162(3) |
| C(17) | 2 867(4) | 607(5)    | 1 686(4)  | C(47) | 3 351(4) | 2 480(4) | -1 346(3) |
| C(18) | 3 187(5) | -302(6)   | 1 604(4)  | C(48) | 3 349(5) | 1 708(5) | -1 797(4) |
| C(19) | 4 013(5) | -411(6)   | 1 638(5)  | C(49) | 2 619(5) | 1 349(5) | -2 046(4) |
| C(20) | 4 560(6) | 298(6)    | 1 742(4)  | C(50) | 1 885(5) | 1 708(5) | -1 879(4) |
| C(21) | 4 244(5) | 1 219(5)  | 1 805(4)  | C(51) | 1 879(4) | 2 481(4) | -1 429(3) |

series of new mono- and bi-nuclear complexes containing two pyrazole groups can be prepared (see Scheme 2). Thus treatment of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$  with the stoichiometric amount of KOH (methanolic solution) and pyrazole affords in high yield the neutral complex  $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$  (**17**). A cationic species, crystallized as its perchlorate salt,  $[\text{RuH}(\text{CO})(\text{Hpz})_2(\text{PPh}_3)_2]\text{ClO}_4$  (**18**), can be obtained by reaction of (**17**) with perchloric acid. Compound (**17**) also reacts with  $[\{\text{M}(\mu\text{-OMe})(\text{tfbb})\}_2]$  in a similar synthesis to that described for complexes (**6**)–(**9**), yielding the binuclear compounds  $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{M}(\text{tfbb})]$  [ $\text{M} = \text{Ir}$ , (**19**); or  $\text{Rh}$ , (**20**)]. While for complexes (**6**)–(**9**) the reaction goes to completion in 2 h at room temperature, for (**18**) and (**19**) it is necessary to stir the solution in acetone at reflux temperature for 24 h. The diolefin tfbb, in compounds (**19**) and (**20**) can easily be displaced by carbon monoxide giving  $[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{M}(\text{CO})_2]$  [ $\text{M} = \text{Ir}$ , (**21**); or  $\text{Rh}$ , (**22**)]. Data characterizing complexes (**17**)–(**22**) are listed in Tables 1–3.

The  $^1\text{H}$  n.m.r. spectra of these compounds show a triplet for the hydride ligand which is in *cis* position to the phosphorus atoms; signals for both inequivalent pyrazolate groups were also observed. The  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. spectra consist of a singlet for both equivalent phosphine groups.

### Experimental

All solvents were distilled and dried by standard methods.<sup>14</sup> All reactions were carried out under a nitrogen atmosphere by standard Schlenk techniques. Proton and  $^{31}\text{P}$  n.m.r. spectra were recorded on a Varian XL-200 spectrophotometer operating at 200.057 and 80.984 MHz respectively; chemical shifts are relative to  $\text{SiMe}_4$  and 85%  $\text{H}_3\text{PO}_4$  as external references. I.r. spectra ( $4\,000$ – $200\text{ cm}^{-1}$ ) were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls between polyethylene

sheets, or dichloromethane solutions in NaCl cells. Elemental analyses were carried out with a Perkin-Elmer 240 B micro-analyser.

The precursors  $\text{H}_2\text{bim}$ ,  $\text{H}_2\text{bbzim}$ ,<sup>15</sup>  $[\text{MH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$  ( $\text{M} = \text{Ru}$  or  $\text{Os}$ ),<sup>16</sup>  $[\text{RuH}(\text{Cl})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$ ,<sup>4c</sup>  $[\{\text{M}(\mu\text{-OMe})(\text{diolefin})\}_2]$  (diolefin = cod,  $\text{M} = \text{Ir}$ ,  $\text{Rh}$ ; diolefin = tfbb,  $\text{M} = \text{Rh}$ )<sup>17</sup> and  $[\{\text{Ir}(\mu\text{-OMe})(\text{tfbb})\}_2]$ <sup>18</sup> were prepared by published methods.

$[\text{RuH}(\text{CO})(\text{Hbim})(\text{PPh}_3)_2]$  (**1**).—To a solution of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$  (286 mg, 0.3 mmol) in dichloromethane ( $30\text{ cm}^3$ ) were added solid  $\text{H}_2\text{bim}$  (40.3 mg, 0.3 mmol) and KOH in methanol (0.3 mmol). After stirring for 4 h the solution was partially concentrated under reduced pressure. Addition of methanol ( $15\text{ cm}^3$ ) led to the precipitation of the complex as a white solid (225 mg).

$[\text{OsH}(\text{CO})(\text{Hbim})(\text{PPh}_3)_2]$  (**2**).—The procedure described for (**1**), but starting from  $[\text{OsH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$  (312.5 mg, 0.3 mmol), gave a white solid (236 mg).

$[\text{RuH}(\text{CO})(\text{Hbbzim})(\text{PPh}_3)_2]$  (**3**).—The procedure described for (**1**), but starting from  $\text{H}_2\text{bbzim}$  (70.3 mg, 0.3 mmol), gave the complex as a yellow solid (181.1 mg).

$[\text{RuH}(\text{CO})(\text{H}_2\text{bim})(\text{PPh}_3)_2]\text{ClO}_4$  (**4**).—A mixture of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$  (286 mg, 0.3 mmol) and an excess of  $\text{H}_2\text{bim}$  (60 mg, 0.45 mmol) in dichloromethane ( $30\text{ cm}^3$ ) was stirred for 3 h. The resulting suspension was filtered to remove the excess of  $\text{H}_2\text{bim}$ , the solution was concentrated to ca.  $3\text{ cm}^3$ , and  $\text{NaClO}_4$  (42 mg, 0.3 mmol) dissolved in methanol ( $20\text{ cm}^3$ ) was added. The solution was stirred for 2 h. Partial evaporation led to the precipitation of compound (**4**) as a white solid (200 mg).

$[\{\text{RuH}(\text{CO})(\text{PPh}_3)_2\}_2(\mu\text{-bim})]$  (**5**).—The ligand  $\text{H}_2\text{bim}$  (20 mg, 0.15 mmol) and  $\text{KOH}$  ( $\text{MeOH}$ ) (0.3 mmol) were added to a suspension of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$  (286 mg, 0.3 mmol) in toluene (30  $\text{cm}^3$ ). The resulting solution was stirred for 8 h with the formation of a white solid which was collected by filtration (130 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Ir}(\text{tfbb})]$  (**6**).—A solution of compound (**1**) (236.3 mg, 0.3 mmol) in  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ) was treated with  $[\{\text{Ir}(\mu\text{-OMe})(\text{tfbb})\}_2]$  (134 mg, 0.15 mmol) and the mixture was stirred for 2 h at room temperature. The solution was partially concentrated under reduced pressure and addition of methanol gave the complex as an orange solid (278.5 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Ir}(\text{cod})]$  (**7**).—The procedure described for compound (**6**), but starting from  $[\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2]$  (100 mg, 0.15 mmol), gave a bright yellow microcrystalline solid (291 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Rh}(\text{tfbb})]$  (**8**).—The procedure described for compound (**6**), but starting from  $[\{\text{Rh}(\mu\text{-OMe})(\text{tfbb})\}_2]$  (108 mg, 0.15 mmol), gave a yellow solid (217 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\text{Rh}(\text{cod})]$  (**9**).—The procedure described for compound (**6**), but starting from  $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$  (73 mg, 0.15 mmol), gave the complex as a pale yellow microcrystalline solid (260 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HOs}(\mu\text{-bim})\text{Ir}(\text{cod})]$  (**10**).—The procedure described for compound (**7**), but starting from (**2**) (263.1 mg, 0.3 mmol), gave a yellow microcrystalline solid (314 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bbzim})\text{Rh}(\text{cod})]$  (**11**).—A suspension of compound (**3**) (133.2 mg, 0.15 mmol) in dichloromethane (20  $\text{cm}^3$ ) was treated with  $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$  (36.3 mg, 0.075 mmol) and the resulting 'green-yellow' solution was stirred for 90 min at room temperature. The solution was partially concentrated under reduced pressure and the addition of methanol gave a lemon-yellow microcrystalline solid which was filtered off, washed with methanol, and vacuum dried (125 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bbzim})\text{Rh}(\text{CO})_2]$  (**12**).—Carbon monoxide was bubbled through a suspension of compound (**11**) (109.8 mg, 0.1 mmol) in dichloromethane for 30 min. The resulting solution was concentrated under reduced pressure, and methanol was added; a yellow solid was formed, which was filtered off, washed with methanol, and vacuum dried (70 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-bim})\{\text{Au}(\text{PPh}_3)_2\}_2]\text{BF}_4$  (**13**).—A tetrahydrofuran solution (15  $\text{cm}^3$ ) of  $[\text{Au}(\text{PPh}_3)(\text{thf})_x]\text{BF}_4$ , prepared by treating  $[\text{AuCl}(\text{PPh}_3)]$  (79.6 mg, 0.16 mmol) with  $\text{Ag}[\text{BF}_4]$  (31.1 mg, 0.16 mmol) for 30 min in the absence of light and removing the  $\text{AgCl}$  by filtration, was added to a solution of compound (**1**) (126 mg, 0.16 mmol) in  $\text{thf}$  (7  $\text{cm}^3$ ) and stirred for 3 h. The solution was vacuum concentrated to ca. 2  $\text{cm}^3$  and addition of diethyl ether (12  $\text{cm}^3$ ) led to the precipitation of a white solid mixture of (**13**) and (**4b**); this was dissolved in dichloromethane and addition of diethyl ether afforded pure compound (**13**) as a solid while complex (**4b**) remained in solution.

$[(\text{Ph}_3\text{P})\text{Au}(\mu\text{-H})(\text{Ph}_3\text{P})_2(\text{OC})\text{Ru}(\mu\text{-bim})\{\text{Au}(\text{PPh}_3)_2\}_2]\text{BF}_4$  (**14**).—A mixture of compound (**1**) (63 mg, 0.08 mmol),  $[\text{AuCl}(\text{PPh}_3)]$  (119.5 mg, 0.24 mmol), and  $\text{Ag}[\text{BF}_4]$  (46.7 mg, 0.24 mmol) (1:3:3 mol ratio) in the absence of light was stirred in acetone (15  $\text{cm}^3$ ) for 2 h and the  $\text{AgCl}$  was removed by filtration. Concentration of the filtrate to ca. 2  $\text{cm}^3$  and addition

of diethyl ether (15  $\text{cm}^3$ ) gave rise to precipitation of a white solid (**14**) (136 mg).

$[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$  (**17**).—A solution of  $[\text{RuH}(\text{Cl})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$  (303.2 mg, 0.4 mmol) in dichloromethane (20  $\text{cm}^3$ ) was treated with the stoichiometric amounts of  $\text{KOH}$  in methanol (0.4 mmol) and pyrazole (27.2 mg, 0.4 mmol). The reaction mixture was stirred for 4 h at room temperature and filtered through Kieselguhr. The solution was concentrated until a white solid precipitated, methanol was added to complete the precipitation (281 mg).

$[\text{RuH}(\text{CO})(\text{Hpz})_2(\text{PPh}_3)_2]\text{ClO}_4$  (**18**).—A solution of compound (**17**) (158 mg, 0.2 mmol) in dichloromethane was treated with a stoichiometric amount of  $\text{HClO}_4$  (60%) (22  $\mu\text{l}$ , 0.2 mmol) and stirred for 90 min. The solvent was partially evaporated and addition of diethyl ether led to precipitation of the complex as a white solid (157 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Ir}(\text{tfbb})]$  (**19**).—A stoichiometric amount of  $[\{\text{Ir}(\mu\text{-OMe})(\text{tfbb})\}_2]$  (89.3 mg, 0.1 mmol) was added to a suspension of compound (**17**) (158 mg, 0.2 mmol) in acetone (25  $\text{cm}^3$ ) and the mixture stirred for 24 h at reflux temperature. The resulting suspension was cooled to room temperature, the solvent was partially evaporated, and the yellow solid formed was filtered off, washed with acetone and hexane, and vacuum dried (166 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Rh}(\text{tfbb})]$  (**20**).—The procedure described for compound (**19**), but starting with  $[\{\text{Rh}(\mu\text{-OMe})(\text{tfbb})\}_2]$  (72 mg, 0.1 mmol), gave a pale yellow solid (183 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Ir}(\text{CO})_2]$  (**21**).—The procedure described for compound (**12**), but starting with (**19**) (120.7 mg, 0.1 mmol), gave a yellow solid (68.3 mg).

$[(\text{Ph}_3\text{P})_2(\text{OC})\text{HRu}(\mu\text{-pz})_2\text{Rh}(\text{CO})_2]$  (**22**).—The procedure described for compound (**12**), but starting with (**20**) (120.7 mg, 0.1 mmol), gave a pale yellow solid (57.1 mg).

*X-Ray Structure Determination of Complex (9)*.—Suitable yellow crystals of compound (**9**) were obtained by slow diffusion of ethanol into a dichloromethane solution of the complex at room temperature.

*Crystal data*.  $\text{C}_{51}\text{H}_{47}\text{N}_4\text{OP}_2\text{RhRu}$ ,  $M = 997.88$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 16.209$  (7),  $b = 14.437$  (5),  $c = 18.960$  (1) Å,  $\beta = 93.700$  (4)°,  $U = 4427.6$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.497$  g  $\text{cm}^{-3}$ ,  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.710$  69 Å), crystal size  $0.403 \times 0.403 \times 0.407$  mm,  $\mu = 8.14$   $\text{cm}^{-1}$ ,  $F(000) = 2032$ .

*Data collection and processing*. Stoe-Siemens AED-2 four-circle diffractometer (graphite-monochromated  $\text{Mo-K}\alpha$  radiation),  $2\theta_{\text{max}}$ . 45°, 12 084 reflections measured, 5 728 unique ( $R_{\text{int}}$  0.018), 5 057 with  $F \geq 6\sigma(F)$  used for calculations. Absorption correction based on  $\psi$ -scan method (minimum and maximum transmission factors 0.7318 and 0.7884).<sup>19</sup> Cell constants refined from  $2\theta$  values of 68 reflections in the range 20–32°.

*Structure solution and refinement*. Patterson and Fourier methods, refinement by full-matrix least squares on  $F$  using the SHELX system<sup>20</sup> with initial isotropic and subsequent anisotropic thermal parameters for all non-hydrogen atoms, except the carbons of the phenyl groups. Eleven hydrogen atoms (including the hydride ligand) were clearly found in Fourier difference maps; the others were placed in calculated positions. The hydride was refined freely as an isotropic atom and the remaining hydrogens were included in the structure-factor calculations riding on their carbon atoms with a common thermal parameter ( $U = 0.107$  Å<sup>2</sup>); weighting scheme

$w = 10.4784/(\sigma^2 F_o + 0.000\ 013 F_o^2)$ . The model reached convergence with  $R = 0.044$  and  $R' = 0.047$ . Analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref. 21. All calculations were performed on the VAX 11/780 computer at the Centro de Cálculo de la Universidad de Zaragoza. The final atomic co-ordinates for the non-hydrogen atoms are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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