2,2'-Bibenzimidazolate Anions as Bridging Ligands in Cationic Heteronuclear Gold(I)–Rhodium(I) Complexes. Crystal Structure of $[(Ph_3P)_2Au_2(\mu-bbzim)Rh(cod)][ClO_4]$ ·CHCl₃ †

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Heterobinuclear complexes of the general formula $[LAu(\mu-Hbbzim)RhR][ClO_4]$ [L = P(OMe)₃ or PPh₃; R = cyclo-octa-1,5-diene (cod) or norborna-2,5-diene (nbd)] have been prepared by treatment of [Rh(Hbbzim)R] with Ag[ClO₄] and [AuClL]. Binuclear 2,2'-bibenzimidazolate gold(1) (bbzim = dianion of 2,2'-bibenzimidazole) complexes of the type $[Au_2(bbzim)L_2] [L = P(OMe)_3$ or PPh₃; L₂ = bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe)] react with $[Rh(cod)(OCMe_2)_*][ClO_4]$ to give new heterotrinuclear complexes of general formula $[L_2Au_2(\mu-bbzim)Rh(cod)][ClO_4]$. Bubbling of carbon monoxide through solutions of the complexes generally leads to the formation of the corresponding dicarbonylrhodium species. Nonetheless, $[(Ph_3P)Au(\mu-Hbbzim)Rh(cod)][ClO_4]$ reacts with carbon monoxide to yield $[(Ph_3P)_2Au_2(\mu-bbzim)Rh (CO)_2$ [CIO₄] and [Rh(H₂bbzim)(CO)₂][CIO₄]. Other related monocarbonyls are also described. The structure of the chloroform solvate of the compound $[(Ph_3P)_2Au_2(\mu-bbzim)Rh(cod)][CIO_4]$ has been determined by X-ray methods; it crystallizes in the triclinic space group $P\overline{1}$ with a = 20.972(14), b = 11.324(9), c = 14.425(10) Å, $\alpha = 64.00(7)$, $\beta = 85.84(6)$, $\gamma = 91.18(6)$ °, and Z = 2. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.078 for 2 460 observed reflections. The bbzim dianion co-ordinates to the metal atoms in an unsymmetrical tetradentate manner: it chelates to one Rh atom through two N atoms from both imidazole rings and is bonded to two Au atoms through the other two N atoms of the imidazole rings. The co-ordination at the Rh atom also involves a cod molecule interacting through the two double bonds. The co-ordination at the Au atoms is completed by a PPh₃ ligand and is essentially linear. A short intramolecular Au · · · Au contact [3.134(4) Å] is observed in the complex.

In a recent paper ¹ we reported that compounds of type $[PtL_2(dppe)][dppe = 1,2-bis(diphenylphosphino)ethane, L = pyrazolate (pz) or imidazolate (im) anions] can act as bidentate ligands in cationic rhodium(1) complexes, using for co-ordination all the nitrogen atoms of their azolate groups. Attempts to employ the complex <math>[Au(pz)(PPh_3)]^{1,2}$ as a potential unidentate ligand in rhodium(1) derivatives generally gives rise to rearrangements leading to the formation of homonuclear complexes, whilst the use of $[Au(im)(PPh_3)]^1$ frequently allows the preparation of heteronuclear gold(1)-rhodium(1) complexes, which do not undergo any further rearrangement.¹

The formation of heterometallic complexes can be favourably influenced by the use of appropriate ligands to hinder any subsequent rearrangement. In this paper we present a study on the capacity of anionic 2,2'-bibenzimidazole (H₂bbzim) derivatives to act as bridging ligands in heteronuclear gold(I)-rhodium(I) complexes.

2,2'-Bi-imidazole, 2,2'-bibenzimidazole (both containing the unit A), and their anionic derivatives can display different types of co-ordination. Examples of the following have already been described: B (M = Rh^{1,3} Cu^{11,4} Co^{11,4,5} Fe^{11,4} Fe^{11,5} Ni^{11,4-6} Mo^{11,7} Ru^{11,8} and Au¹¹¹⁹); C (M = Rh^{1 10} and Ir¹¹⁰); D (M = Rh^{1,10,11} Ir^{1,10,11} Mo^{11,7} Ti^{111,12} Cu^{11,13} Au^{111,9} Pd^{11,14} Ru^{11,8} and Mn^{1 15}); E (M = Au¹¹⁶); F (M = Au¹¹⁶); G (M = Au¹¹⁶); and H (M = M' = Rh^{1 11} and M = Pd¹¹, M' = Au¹¹⁶).



Herein we communicate the synthesis of new rhodium(I) 2,2 -bibenzimidazolate complexes of the types C and H along with a novel type of co-ordination, I. These polymetallic complexes may be of interest in relation to electrical or catalytic co-operative effects between adjacent metal centres.¹⁷

In order to confirm the ability of the 2,2'-bibenzimidazolate group to act as a tetradentate bridging ligand between different metals and to know the relative disposition of the gold atoms, the X-ray crystal structure of $[(Ph_3P)_2Au_2(\mu-bbzim)Rh(cod)]$ -[CIO₄]·CHCl₃ is also described.

 $t_{1,1'-Bis(triphenylphosphineaurio)-2,2'-bibenzimidazolato(1-)-N^3N^3'](η-cyclo-octa-1,5-diene)rhodium perchlorate-chloroform (1/1).$

Supplementary data available (No. SUP 23450, 19 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, J. Chem. Soc., Dalton Trans., 1981, Index issue.



(1)(11) C(21) C(22) C(18) C(17) C/19 (15) C(20) Ć(16) Rh C(11) C(7) N(4) C(2) C(12) C(6) Ć(10) C(1) C(3) C (13) Č(8) (9) C(5) Č(4) N(1) N(3) C(14) Au(1) C(57) C(25) Au(2) C(24) C(58) C(37) C(36) P(1) P(2 , C(23)_{C(26)} C(56) C(42) C(53) (38) Č(43 C(48) C(55) α_{29} Č(54) Ć(27) Č(28) Č(30) C(39) C(49) C(34) C(52) C(31)

Results and Discussion

Synthesis and Properties.—The complex [Rh(acac)R]¹⁸ (acac = acetylacetonate, R = diolefin) reacts with H₂bbzim¹² to give [Rh(Hbbzim)R] [R = cyclo-octa-1,5-diene (cod) (1a), or norborna-2,5-diene (nbd) (1b)]. These complexes still have one nitrogen atom capable of co-ordination. Thus, their reaction with [AuClL]¹⁹ and Ag[ClO₄] gives rise to the formation of the heterobinuclear complexes [LAu(μ -Hbbzim)Rh(cod)][ClO₄] [L = P(OMe)₃ (2a) or PPh₃ (2b)] and [LAu(μ -Hbbzim)Rh(nbd)][ClO₄] [L = P(OMe)₃ (3a) or PPh₃ (3b)].

On the other hand, the complexes $[Au_2(bbzim)L_2]^{16}$ prepared by reacting $M_2(bbzim)$ (M = K or Tl) with [AuClL] $[L = P(OMe)_3$ or PPh₃] or $[(AuCl)_2L_2]$ [$L_2 = bis(diphenyl-phosphino)methane (dppm) or dppe], which have two uncoordinated nitrogen atoms, can also be considered as Lewis bases. Their reaction with [Rh(cod)(OCMe_2)_x][ClO_4] ²⁰ renders heterotrinuclear complexes of the general formula [<math>L_2Au_2(\mu-bbzim)Rh(cod)$][ClO₄] [$L = P(OMe)_3$ (4a) or PPh₃ (4b); $L_2 = dppm$ (4c) or dppe (4d)].

Bubbling carbon monoxide through dichloromethane solutions or suspensions of the complexes (1a) or (1b), (2a) or (3a), and (4a) or (4b) leads only to the displacement of the coordinated diolefin and formation of [Rh(Hbbzim)(CO)₂] (5), [{(MeO)₃P}Au(μ -Hbbzim)Rh(CO)₂][ClO₄] (6) or, respectively, [L₂Au₂(μ -bbzim)Rh(CO)₂][ClO₄] [L = P(OMe)₃ (7a) or PPh₃ (7b)].

It seems noteworthy that all attempts to prepare [(Ph₃P)Au- $(\mu$ -Hbbzim)Rh(CO)₂[ClO₄] either by treating (2b) or (3b) with carbon monoxide or by reacting complex (5) with [AuCl(PPh₃)] and Ag[ClO₄] have proved unsuccessful. In both cases an equimolar mixture of [(Ph₃P)₂Au₂(µ-bbzim)Rh- $(CO)_2$ [CIO₄] (7b) and of the recently described ³ complex $[Rh(H_2bbzim)(CO)_2][ClO_4]$ is obtained. In the solid state the absorptions expected for the perchlorate anion $(T_d)^{21}$ in the complex [Rh(H₂bbzim)(CO)₂][ClO₄] and in the analogous $[Rh(H_2bbzim)(cod)][ClO_4]$ are split (v_3 = 1 165 and 1 050 cm^{-1} , $v_4 = 630$ and $622 cm^{-1}$). As far as we know no five-coordinate rhodium(I) complexes with the perchlorate anion as ligand have been reported, although some square-planar rhodium(1) complexes with Rh-OClO3 bonds have been previously described.²¹ Accordingly, the observed splitting of the perchlorate absorptions could probably arise from an interaction NH \cdots OClO₃.

Addition of stoicheiometric amounts of $P(OMe)_3$ or PPh_3 to solutions of (5) or (6) leads to the substitution of one mole of carbon monoxide by the phosphorus donor ligand and to the formation of complexes of the types [Rh(Hbbzim)(CO)-L], (8a) and (8b), or $[\{(MeO)_3P\}Au(\mu-Hbbzim)Rh(CO)L]-[CIO_4]$, (9a) and (9b), respectively. The analogous complexes $[(Ph_3P)Au(\mu-Hbbzim)Rh(CO)L][CIO_4]$, (10a) and (10b), have been obtained by reacting (8a) and (8b) with $[AuCl(PPh_3)]$ and $Ag[CIO_4]$. Furthermore, complexes of type $[L_2Au_2(\mu-Hbbzim)Rh(CO)L]$

Figure 1. View of the cation $[(Ph_3P)_2Au_2(\mu-bbzim)Rh(cod)]^+$ with the atomic numbering scheme

C(33)

OC(32)

C(50)

C(51)

bbzim)Rh(CO)(PPh₃)][CIO₄] [L = P(OMe)₃ (11a) or PPh₃ (11b); $L_2 = dppm (11c) or dppe (11d)$] have been synthesized either by treating (7a)—(7d) with stoicheiometric amounts of PPh₃ or by reacting the solvated complex [Rh(CO)(PPh₃)-(OCMe₂)_x][CIO₄]²² with [Au₂(bbzim)L₂].

The i.r. spectra in the solid state or in dichloromethane or chloroform solutions of the dicarbonyl complexes (5)-(7) show two strong absorptions due to v(CO) in the 2 100-2 000 cm⁻¹ region which confirm the *cis* co-ordination of the two CO groups,²³ whilst the monocarbonyl derivatives (8)-(11) exhibit a single absorption band due to v(CO) in the 2 020-1 980 cm⁻¹ range.^{23,24} In particular, the X-ray diffraction studies on compound (4b) and the presence of these absorption bands for all the carbonyl derivatives support the formulation of the compounds as derived from structure (I). The structure (II) could be ruled out since a three-band spectrum for the pair of bridging dicarbonylrhodium units should be expected as in the analogous compound $[Rh_4(\mu-bim)_2(cod)_2(CO)_4]$ $(H_2 bim = 2,2'-bi-imidazole).^{11}$ The ionic character of the new complexes is supported by two strong bands at ca. 1 095 and 623 cm⁻¹ (Nujol), characteristic of the perchlorate ion (T_d) ²¹ as well as by their molar conductivities in acetone.^{23,25} The v(NH) stretching (Nujol mulls) in the neutral rhodium(1) complexes (1a), (1b), (5), (8a), and (8b) appears as a strong and

(a) Co-ordination sphe	ere of the met	als		C(8)-C(1)-N(1)	120(3)	N(3)-C(8)-N(4)	117(3)
Au(1)-P(1)	2.23(1)	Rh-N(4)	2.11(3)	C(8) - C(1) - N(2)	114(3)	N(3)-C(8)-C(1)	125(3)
Au(1) - N(1)	1.96(3)	Rh-C(15)	2.05(4)	N(1)-C(1)-N(2)	125(3)	N(4)-C(8)-C(1)	117(3)
Au(2) - P(2)	2.22(1)	Rh-C(16)	2.02(4)	C(3) - C(2) - C(7)	117(3)	C(10) - C(9) - C(14)	129(4)
Au(2) - N(3)	1.98(3)	Rh-C(19)	2.10(4)	C(3) - C(2) - N(2)	109(3)	C(10)-C(9)-N(3)	106(3)
Rh-N(2)	2.08(3)	Rh - C(20)	2.13(5)	C(7)-C(2)-N(2)	133(3)	C(14) - C(9) - N(3)	126(3)
	1 .00(0)			C(4) - C(3) - N(1)	129(3)	C(11)-C(10)-N(4)	129(3)
P(1)-Au(1)-N(1)	177(1)	N(4)-Rh-C(19)	94(2)	C(4)-C(3)-C(2)	123(4)	C(11)-C(10)-C(9)	118(3)
P(2) - Au(2) - N(3)	173(1)	N(4)-Rh-C(20)	100(2)	N(1)-C(3)-C(2)	108(3)	N(4)-C(10)-C(9)	112(3)
N(2)-Rh-N(4)	80(1)	C(15)-Rh-C(16)	43(2)	C(5)-C(4)-C(3)	118(4)	C(12)-C(11)-C(10)	114(3)
N(2)-Rh-C(15)	95(2)	C(15)-Rh-C(19)	98(2)	C(6)-C(5)-C(4)	122(4)	C(13)-C(12)-C(11)	121(4)
N(2) - Rh - C(16)	92(2)	C(15)-Rh- $C(20)$	80(2)	C(7) - C(6) - C(5)	117(3)	C(14) - C(13) - C(12)	127(4)
N(2) - Rh - C(19)	158(1)	C(16)-Rh-C(19)	84(2)	C(2) - C(7) - C(6)	123(3)	C(9) - C(14) - C(13)	110(3)
N(2) - Rh - C(20)	165(2)	C(16) - Rh - C(20)	93(2)	C(1)-N(1)-C(3)	96(4)	C(8) - N(3) - C(9)	102(4)
N(4) - Rh - C(15)	161(2)	C(19) - Rh - C(20)	37(2)	C(1) - N(1) - Au(1)	134(4)	C(8) - N(3) - Au(2)	128(4)
N(4) - Rh - C(16)	154(2)	0(17) 101 0(20)		C(3) - N(1) - Au(1)	124(3)	C(9) - N(3) - Au(2)	125(3)
	101(4)			C(1) - N(2) - C(2)	100(4)	C(8) - N(4) - C(10)	102(4)
(b) Cyclo-octa-1,5-die	ne ligand			C(1) - N(2) - Rh	115(3)	C(8) - N(4) - Rh	112(4)
C(15) - C(16)	1 49(5)	C(18) - C(19)	1 54(6)	C(2) - N(2) - Rh	142(3)	C(10) - N(4) - Rh	144(4)
C(15) = C(22)	1.59(6)	C(10) - C(20)	1 34(5)	C(2) $R(2)$ $R(1)$	142(5)	C(10) IN(4) INI	144(4)
C(15) - C(17)	1.60(6)	C(20) - C(21)	1.34(5)	(d) Triphenylphosph	ine ligand		
C(17) = C(18)	1.52(6)	C(21) - C(22)	1.40(0)	P(1) - C(23)	1 83(2)	$P(2) \sim C(41)$	1.81(2)
	1.52(0)	C(21) $C(22)$	1.54(0)	P(1) - C(29)	1.03(2)	P(2) = C(47)	1.01(2) 1.77(2)
C(16) - C(15) - C(22)	124(3)	C(20)~C(19)~Rh	73(3)	P(1) - C(25)	1.00(2) 1.83(2)	P(2) = C(47)	1.83(2)
C(16) - C(15) - Rh	67(3)	C(20) - C(19) - C(18)	123(4)	$\Gamma(1) C(33)$	1.05(2)	$\Gamma(2) C(33)$	1.65(2)
C(22) - C(15) - Rh	119(3)	Rh-C(19)-C(18)	113(3)	C(23)-P(1)-C(29)	104(1)	C(41) - P(2) - C(47)	107(1)
C(17) - C(16) - Rh	114(3)	C(21) - C(20) - Rh	114(3)	C(23) - P(1) - C(35)	108(1)	C(41) - P(2) - C(53)	105(2)
$\hat{\mathbf{C}}(17) - \hat{\mathbf{C}}(16) - \hat{\mathbf{C}}(15)$	120(3)	C(21) - C(20) - C(19)	135(4)	C(23) - P(1) - Au(1)	112(1)	C(41) - P(2) - Au(2)	114(1)
Rh-C(16)-C(15)	69(3)	Rh - C(20) - C(19)	70(3)	C(29) - P(1) - C(35)	107(1)	C(47) - P(2) - C(53)	105(2)
C(18) - C(17) - C(16)	113(3)	C(22)-C(21)-C(20)	118(4)	C(29) - P(1) - Au(1)	112(1)	C(47) - P(2) - Au(2)	112(1)
C(19) - C(18) - C(17)	112(3)	C(15)-C(22)-C(21)	107(4)	C(35) - P(1) - Au(1)	112(1)	C(53) - P(2) - Au(2)	113(1)
	112(3)	0(15) 0(22) 0(21)	10/(1)	() D 11			
(c) 2,2°-Bibenzimidazo			(e) Perchlorate anior	1			
N(1)-C(1)	1.29(4)	N(3)-C(8)	1.37(4)	Cl(1)-O(1)	1.34(4)	Cl(1)-O(3)	1.42(4)
N(1)-C(3)	1.51(4)	N(3)-C(9)	1.50(4)	Cl(1)-O(2)	1.40(4)	Cl(1)-O(4)	1.34(4)
N(2)-C(1)	1.31(4)	N(4)-C(8)	1.34(4)	O(2) $O(1)$ $O(1)$	100(0)	O(2) $O(1)$ $O(2)$	111/0
N(2)-C(2)	1.41(4)	N(4)-C(10)	1.41(4)	O(2) - CI(1) - O(1)	108(2)	O(3) - CI(1) - O(2)	111(2)
C(1) - C(8)	1.53(5)	C(9)-C(10)	1.36(4)	O(3) - C(1) - O(1)	111(3)	O(4) - CI(1) - O(2)	112(3)
C(2) - C(3)	1.37(4)	C(9) - C(14)	1.32(4)	O(4) - CI(1) - O(1)	105(3)	O(4) - CI(1) - O(3)	109(3)
C(2) - C(7)	1.32(5)	C(10) - C(11)	1.49(5)	(f) Chloroform mole	cula		
C(3) - C(4)	1.43(5)	C(11) - C(12)	1.34(5)				
C(4) - C(5)	1.33(5)	C(12) - C(13)	1.32(5)	C(59)-Cl(2)	1.76(5)	C(59)-Cl(4)	1.63(5)
C(5)-C(6)	1.39(5)	C(13) - C(14)	1.42(5)	C(59)-Cl(3)	1.77(5)		
C(6)-C(7)	1.44(5)			$C_{1}(2) = C_{1}(2) = C_{1}(2)$	107(2)	$C^{1}(3) = C^{1}(5) = C^{1}(4)$	111(2)
				C(2) = C(37) = C(3) C(2) = C(50) = C(4)	107(2) 111(2)	CI(3) C(39) CI(4)	111(2)
				$U(2)^{-}U(39)^{-}U(4)$	111(2)		

broad band in the 3 000–2 300 cm^{-1} range pointing to a strong intermolecular association. In the spectra of the gold(1)–rhodium(1) heterobinuclear complexes (2), (3), (6), (9), and (10) this absorption is to be found in a higher range, at 3 000–2 800 cm⁻¹, indicating that the gold substituent at the nitrogen atom hinders association.

Description of the Structure of $[(Ph_3P)_2Au_2(\mu$ -bbzim)Rh-(cod)][ClO₄]·CHCl₃.—The crystal structure consists of a heterotrinuclear cation $[(Ph_3P)_2Au_2(\mu$ -bbzim)Rh(cod)]⁺, perchlorate anion, and chloroform molecule of crystallization. A view of the cationic complex with the atomic numbering scheme is given in Figure 1. Selected bond distances and angles in the cation, the anion, and chloroform molecule are given in Table 1. In the cation, having an approximate C_2 symmetry, the bbzim ligand co-ordinates to the metals in an unsymmetrical tetradentate manner through the four nitrogen atoms of the two imidazole rings, chelating to one Rh atom through two nitrogen atoms and being bonded in a unidentate manner to the gold atoms through the other two nitrogen atoms.

The two Au atoms approach each other quite closely [Au(1) \cdots Au(2) = 3.134(4) Å]. The co-ordination at each Au atom,

also involving a P atom from the PPh₃ ligand, is essentially linear [P-Au-N 177(1) and 173(1)°]. Because of the small tendency of gold to form complexes with N-donor ligands, a small number of these complexes have been structurally investigated to give few values for the Au¹-N bond reported in the literature. In the present complex the values for these bonds [1.96(3) and 1.98(3) Å] are comparable with those found in the structure of sodium bis(1-methylhydantoinato-N³)aurate-(1) tetrahydrate (av. value = 1.94 Å),²⁶ whereas much longer values are reported for the other N-donor ligand complexes (2.02-2.10 Å).²⁷ Values of the Au-P bonds [2.23(1) and 2.22(1) Å] fall in the expected range for two-co-ordinate Au with tertiary phosphine ligands.²⁷

The co-ordination at the Rh atom, besides the two N atoms from the bbzim ligand, also involves a cod molecule interacting through the two double bonds. The geometry around the Rh atom is approximately square planar with the polyhedron defined by the two N atoms and the midpoints of the two double bonds of the cyclo-octa-1,5-diene ring. The axes of the double bonds are normal to the co-ordination plane. The cod molecule exhibits the usual tub conformation, with the C(15), C(16), C(19), and C(20) atoms nearly coplanar; devi-

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Figure 2. Projection along b of the structure showing the packing of the cation, perchlorate anion, and chloroform molecule

ations of these atoms from the mean plane passing through them are -0.03(6), 0.03(6), -0.03(6), and 0.04(7) Å respectively, deviations of the other C(17), C(18), C(21), and C(22) atoms from this plane being 1.25(7), 1.06(6), 1.01(6), and 1.11(7) Å respectively. Even if much less accurate, the values of the Rh-N [2.08(3) and 2.11(3) Å] and Rh-C bonds [in the range 2.02-2.13 Å] are comparable with those reported for the complex [Rh₂(cod)₂(bim)]¹⁰ where the bonding of the 2,2'bi-imidazolate and of the cod ligands to each Rh atom is quite similar.

The bbzim dianion consists of two moieties bonded through the C(1) and C(8) atoms. Each moiety is planar, with no atom deviating more than 1.2σ from the nine-atom planes. The two moieties are slightly twisted and make a dihedral angle of 17.6° with each other. In the similar bim dianion, the two imidazole rings were found nearly coplanar in [Rh₄(CO)₈- $(bim)_2$ ¹¹ (dihedral angle 4.0°) and perfectly coplanar in [Rh₂(cod)₂(bim)].¹⁰ The separation between the chelating N(2) and N(4) atoms [2.69(6) Å] is shorter than the separation between the N(1) and N(3) atoms [3.01(6) Å]; this trend is also observed in [Rh₄(CO)₈(bim)₂] [the values of the separations are 2.625(7) and 3.218(7)Å], in which the four N atoms of the bim ligand co-ordinate to the Rh atoms in a similar way, whereas the separations are equal [2.818(7) and 2.807(7) Å] in [Rh₂(cod)₂(bim)] as the same ligand acts as a symmetrical bichelating ligand.

In the present complex the short intramolecular Au · · · Au distance, 3.134(4) Å, is noteworthy. Short Au · · · Au contacts (in the range 2.7-3.4 Å) are a common structural feature of Au¹ compounds and are ascribed to weak metal-metal interactions, although the nature of them has not clearly been defined. These contacts concern simple linear complexes in which the Au atoms are unexpectedly close to one another and compounds with bidentate ligands or with two Au atoms bonded to a common atom. In the complexes [ClAu(Ph2PCH2-PPh₂)AuCl]²⁸ and [ClAu(Ph₂PCHCHPPh₂)AuCl]²⁹ with bidentate phosphine ligands, short Au · · · Au contacts [3.341 and 3.05 Å respectively] can be indicative of weak metalmetal attraction as on the basis of the purely steric grounds the metals are not forced to a close approach. In the compound [(Ph₃P)Au(µ-Cl)Au(PPh₃)][ClO₄],³⁰ although the bridging Cl could force the Au atoms relatively near each other, the very short Au · · · Au distances (3.035 and 3.085 Å in two independent cations) and the Au-Cl-Au angles much narrower than 90° (80.7 and 82.7°) indicate a weak bonding interaction.

In the present complex the geometry of the bbzim ligand constrains the Au atoms to be very close, but both the N(1)-N(3)separation and the twist of the two moieties of the ligand seem to contradict a better approach and a stronger attraction of the Au atoms, perhaps because of the steric hindrance of the triphenylphosphine ligands. So presumably in this case a balance is obtained between the $Au \cdots Au$ attractions and the steric hindrances in the complex.

The packing in the crystals of the heteronuclear complexes, perchlorate anions, and chloroform molecules is represented in Figure 2.

Experimental

Measurements.—Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. Infrared spectra (range 4 000—200 cm⁻¹) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets, or dichloromethane or chloroform solutions in NaCl windows. Conductivities were measured at room temperature in ca. 5×10^{-4} mol dm⁻³ acetone solutions using a Philips 9501/01 conductimeter.

Syntheses.—The reactions were generally carried out at room temperature with 0.1—0.3 mmol of starting materials. Prior to use solvents were purified by standard methods.³¹ The compounds H₂bbzim,¹² [Rh(acac)R] (R = diolefin),¹⁸ [Au-ClL],¹⁹ [Au₂(bbzim)L₂],¹⁶ and [Rh(cod)(OCMe₂)_x][ClO₄]²⁰ were prepared as previously described. Table 2 gives the yields and colours, and analytical, spectroscopic, and conductance data for all the new complexes.

Compounds (1a) and (1b). The compound [Rh(acac)R](R = diolefin) and H_2bbzim (1 : 1 mol ratio) were refluxed for 10 h in dichloromethane-methanol (3 : 1) (20 cm³) whereupon the insoluble residue was filtered off. The addition of diethyl ether (15 cm³) to the filtrate gave rise to the precipitation of yellow solids which were filtered off, washed with diethyl ether, and vacuum-dried.

Compounds (2a), (2b), (3a), and (3b). Under argon and in absence of light (1a) or (1b), [AuClL], and Ag[ClO₄] (1:1:1 mol ratio) were stirred in acetone (15 cm³) for 20 min and the AgCl was removed by filtration. Concentration of the filtrate to ca. 1 cm³ and addition of diethyl ether (10 cm³) gave rise to the precipitation of the required complexes which were recrystallized from dichloromethane-diethyl ether (1:8).

Compounds (4a)—(4d). The compound $[Au_2(bbzim)L_2]$ was added to an acetone solution (15 cm³) of $[Rh(cod)(OCMe_2)_x]$ - $[ClO_4]$ (1 : 1 mol ratio) and stirred for 4 h. The solution was vacuum evaporated to dryness, the residue extracted with dichloromethane (10 cm³), and filtered. Concentration of the filtrate to ca. 1 cm³ and addition of diethyl ether (8 cm³) led to the precipitation of microcrystalline solids, which were filtered off, washed with diethyl ether, and vacuum-dried. When they are recrystallized from chloroform they crystallize with one molecule of the solvent.

Compounds (5), (6), and (7a)—(7d). Dry carbon monoxide was bubbled for 20 min through dichloromethane solutions (20 cm³) of (1), (2a), (3a), or (4a)—(4d). Addition of hexane (15 cm³) and concentration to *ca*. 5 cm³ led to the precipitation of the required products, which were filtered off, washed with diethyl ether and hexane, and vacuum-dried.

Reaction of (2b) or (3b) with carbon monoxide. Dry carbon monoxide was bubbled for 20 min through a dichloromethane solution (20 cm³) of (2b) or (3b). The colour of the yellow solution turned to deep orange and yellow crystals precipitated. They were filtered off, washed with diethyl ether, vacuum-dried, and identified by elemental analyses, conductance studies, and i.r. spectroscopy as $[Rh(H_2bbzim)(CO)_2]$ - $[ClO_4]$.³ The filtrate was vacuum-concentrated until the precipitation of a brownish red solid was observed. The precipitation was completed upon addition of diethyl ether. The solid was recrystallized from chloroform-diethyl ether (1 : 8) and identified as (7b).

Reaction of (5) with $[Au(PPh_3)(OCMe_2)_x][ClO_4]$. An acetone solution (15 cm³) of $[Au(PPh_3)(OCMe_2)_x][ClO_4]$ {prepared by

reacting $[AuCl(PPh_3)]$ with Ag $[ClO_4]$ (20 min in acetone) was added to a suspension of (5) in acetone (10 cm³) (1 : 1 mol ratio), and stirred for 3 h until the presence of yellow crystals could be observed. The work-up was continued as above, leading to the same results (see above).

Compounds (8a), (8b), (9a), and (9b). Either $P(OMe)_3$ or PPh_3 was added to a suspension of (5) or, respectively, a solution of (6) (1 : 1 mol ratio) in dichloromethane (20 cm³) and stirred for 1 h. Addition of hexane (10 cm³) and concentration led to the precipitation of the required compounds, which were filtered off, washed with hexane, and vacuum-dried.

Compounds (10a) and (10b). An acetone solution (15 cm^3) of $[Au(PPh_3)(OCMe_2)_x][ClO_4]$ was added to a suspension of (8a) or (8b) in the same solvent (10 cm³). After stirring for 2 h the insoluble residue was removed by filtration. The filtrate was evaporated to dryness and the residue extracted with the minimum amount of dichloromethane. Addition of diethyl ether led to the precipitation of the required compounds, which were filtered off, washed with diethyl ether, and vacuum-dried.

Compounds (11a)—(11d). These can be prepared by two different methods. Method 1. A stoicheiometric amount of PPh₃ was added to a dichloromethane solution (20 cm³) of (7a)— (7d) and stirred for 2 h. The solution was concentrated to ca. 2 cm³ and the required compounds were precipitated upon addition of diethyl ether. They were filtered off, washed with diethyl ether, and vacuum-dried.

Method 2. An acetone solution (8 cm^3) $[L = P(OMe)_3 \text{ or } PPh_3]$ or suspension (L = dppm or dppe) of $[Au_2(bbzim)L_2]$ was added to a solution of $[Rh(CO)(PPh_3)(OCMe_2)_x][ClO_4]^{22}$ in the same solvent (10 cm³) (1 : 1 mol ratio). After stirring for 4 h the solution was concentrated to dryness, whereupon the residue was extracted with dichloromethane (20 cm³). The insoluble solids were removed by filtration and the filtrate was concentrated to *ca*. 3 cm³. Addition of diethyl ether led to the precipitation of the required compounds which were filtered off, washed with diethyl ether, and vacuum-dried.

X-Ray Data Collection of (4b).—Red crystals of (4b) were obtained at the interface of a concentrated chloroform hexane-solution in a 8 mm diameter glass tube. A roughly flat crystal with approximate dimensions $0.03 \times 0.15 \times 0.25$ mm was used for data collection. The unit-cell dimensions were determined first from rotation and Weissenberg photographs and then refined by least squares using the θ values of 29 reflections accurately measured on a Siemens AED single-crystal diffractometer.

Crystal data. $C_{58}H_{50}Au_2ClN_4O_4P_2Rh$ ·CHCl₃, M = 1 580.67, Triclinic, a = 20.972(14), b = 11.324(9), c = 14.425(10) Å, $\alpha = 64.00(7)$, $\beta = 85.84(6)$, $\gamma = 91.18(6)^\circ$, U = 3 066(4) Å³, Z = 2, $D_c = 1.712$ g cm⁻³, Mo- K_{α} radiation ($\lambda = 0.710$ 69 Å), F(000) = 1 532, $\mu(Mo-K_{\alpha}) = 53.00$ cm⁻¹, space group PI from structure determination.

A total of 7 068 independent reflections (with θ in the range 3-22°) were collected on the same diffractometer using niobium-filtered Mo- K_{α} radiation and the θ -2 θ scan technique; 2 460 of them, for which $I \ge 2\sigma(I)$, were considered observed and employed in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established first by Wilson's method and then by least-squares refinement. No correction for absorption was applied because of the irregular shape of the crystal and of the low value of μr (linear absorption coefficient \times thickness of crystal).

Structure determination and refinement. The structure was solved by Patterson and Fourier methods localizing first the Au and Rh atoms from the Patterson map and then the remaining non-hydrogen atoms from successive Fourier maps.

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Table 2. Colours and yields, and analytical, spectroscopic, and conductance data for the new complexes

				Analys	is (%)					
		l	U.		H		Z			Viald/
Compound	Colour	Calc.	Found	Calc.	Found	Calc.	Found	v(CO) ^a /cm ⁻¹	^م MA	
(1a) [Rh(Hbbzim)(cod)]	Yellow	59.45	59.10	4.75	4.45	12.60	12.45	I	I	72
(1b) [Rh(Hbbzim)(nbd)]	Yellow	58.90	58.25	4.00	3.90	13.10	13.35	1	1	82
(5) [Rh(Hbbzim)(CO) ₂]	Orange	49.00	48.35	2.30	2.40	14.30	14.50	2 090, 2 024	I	82
(8a) [Rh(Hbbzim)(CO){P(OMe) ₃ }]	Yellow	44.30	44.85	3.70	3.95	11.45	11.85	2 010	I	35
(8b) [Rh(Hbbzim)(CO)(PPh ₃)]	Yellow	63.30	63.15	3.85	3.70	8.95	9.25	1 983 °	1	80
(2a) [{(MeO) ₃ P}Au(µ-Hbbzim)Rh(cod)][CIO ₄]	Yellow	34.70	34.45	3.50	3.65	6.50	6.45	ł	114	87
(2b) [(Ph3P)Au(µ-Hbbzim)Rh(cod)][CIO4]	Yellow	47.90	47.75	3.60	3.55	5.60	5.75	ł	139	83
(3a) [{(MeO) ₃ P}Au(μ-Hbbzim)Rh(nbd)][CIO ₄]	Yellow	33.95	33.75	3.10	3.05	6.60	6.40	1	133	11
(3b) [(Ph ₃ P)Au(μ-Hbbzim)Rh(nbd)][ClO ₄]	Yellow	47.45	47.05	3.25	3.40	5.70	5.95	ł	113	75
(6) [{(MeO) ₃ P}Au(μ-Hbbzim)Rh(CO) ₂][ClO ₄]	Dark	28.10	28.00	2.25	2.35	6.90	6.95	2 097, 2 034	142	8
	green									
(9a) [{(MeO) ₃ P}Au(µ-Hbbzim)Rh(CO){P(OMe) ₃ }][ClO ₄]	Cream	27.75	27.10	3.00	3.05	6.15	5.90	2 019	125	87
(9b) [{(MeO) ₃ P}Au(μ-Hbbzim)Rh(CO)(PPh ₃)][ClO ₄]	Salmon	41.30	41.25	3.20	3.05	5.35	5.05	2 012	1 4 0	82
(10a) [(Ph ₃ P)Au(μ-Hbbzim)Rh(CO){P(OMe) ₃ }][ClO ₄]	Yellow	41.30	41.65	3.20	3.30	5.35	5.10	2 016	128	2
(10b) [(Ph ₃ P)Au(μ-Hbbzim)Rh(CO)(PPh ₃)][ClO ₄]	Yellow	51.70	52.05	3.30	3.50	4.75	4.55	1 988	124	73
(4a) [{(MeO) ₃ P} ₂ Au ₂ (μ-bbzim)Rh(cod)][CIO ₄]	Orange	31.10	31.10	3.55	3.60	5.20	5.15	١	110	91
(4b) [(Ph ₃ P) ₂ Au ₂ (μ-bbzim)Rh(cod)][CIO ₄]	Red	47.65	47.90	3.45	3.55	3.85	4.05	ł	120	86
(4c) [(dppm)Au ₂ (μ-bbzim)Rh(cod)][ClO ₄]	Yellow	42.75	42.30	3.20	3.20	4.25	4.25	I	129	83
(4d) [(dppe)Au ₂ (μ-bbzim)Rh(cod)][ClO ₄]	Orange	43.20	42.70	3:30	3.40	4.40	4.15	1	115	85
(7a) [{(MeO) ₃ P} ₂ Au ₂ (µ-bbzim)Rh(CO) ₂][CIO ₄]	Dark	23.35	23.35	2.30	2.15	4.95	5.15	2 088, 2 022	130	8
(7h) I(Ph,P),A11,(11-bhzim)Rh(CO),11CJO,1	violet Red-brown	44.30	44.25	2.70	2.80	4.00	4.25	2 083, 2 018	116	94
(7c) [(dopm)Au,(u-bbzim)Rh(CO),][ClO ₄]	Orange	38.80	39.00	2.40	2.55	4.40	4.60	2 081, 2 018	139	6
(7d) [(dppe)Au ₂ (μ -bbzim)Rh(CO) ₂][CIO ₄]	Dark	39.30	39.40	2.50	2.70	4.35	4.20	2 090, 2 023	139	92
	violet									
(11a) [{(MeO) ₃ P} ₂ Au ₂ (µ-bbzim)Rh(CO)(PPh ₃)][ClO ₄]	Red-brown	34.25	35.05	3.00	2.80	4.10	3.80	2013	129	45 ª
(11b) [(Ph ₃ P) ₂ Au ₂ (μ-bbzim)Rh(CO)(PPh ₃)][CIO ₄]	Brown	50.45	49.05	3.25	3.50	3.40	3.30	1 990 °	132	37 e
(11c) [(dppm)Au ₂ (μ-bbzim)Rh(CO)(PPh ₃)][ClO ₄]	Pale	46.35	46.55	3.00	3.20	3.75	3.45	1 993	116	و0 <i>و</i>
	brown									
(11d) [(dppe)Au ₂ (µ-bbzim)Rh(CO)(PPh ₃)][ClO ₄]	Brown	46.70	46.60	3.10	3.10	3.70	3.75	1 995 °	127	40 e
" In dichloromethane unless otherwise stated. " Ω^{-1} cm2 mol-1, i	acetone solutions	. ^e In chlo	roform. ⁴ Ob	tained by	method 1. °	Obtained	by method	2.		

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Table 3. Fractional atomic co-ordinates (\times 10⁴) with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z c	Atom	X/a	Y/b	Z c
Au(1)	2 309(1)	2 045(2)	1 636(2)	C(22)	-1 790(36)	1 936(71)	1 495(59)
Au(2)	1 886(1)	-191(2)	3 853(2)	C(23)	3 495(18)	4 451(28)	715(26)
Rh	-395(2)	2 370(4)	1 999(4)	C(24)	3 083(18)	5 110(28)	-42(26)
Cl(1)	3 241(8)	907(17)	7 981(14)	C(25)	3 279(18)	6 332(28)	-857(26)
Cl(2)	4 270(11)	4 894(22)	7 886(18)	C(26)	3 887(18)	6 895(28)	-915(26)
Cl(3)	4 382(10)	4 650(21)	6 006(17)	C(27)	4 300(18)	6 236(28)	-158(26)
Cl(4)	5 204(11)	3 353(21)	7 554(18)	C(28)	4 103(18)	5 014(28)	657(26)
P(1)	3 268(7)	2 823(14)	1 770(11)	C(29)	3 902(14)	1 825(31)	1 666(29)
P(2)	2 572(7)	-1769(14)	4 217(12)	C(30)	4 061(14)	1 867(31)	696(29)
O(1)	2 730(26)	1 153(51)	7 431(42)	C(31)	4 549(14)	1 118(31)	568(29)
O(2)	3 186(23)	-424(49)	8 697(39)	C(32)	4 878(14)	328(31)	1 410(29)
O(3)	3 819(23)	1 220(45)	7 319(37)	C(33)	4 719(14)	287(31)	2 380(29)
O(4)	3 208(25)	1 713(53)	8 439(42)	C(34)	4 231(14)	1 035(31)	2 508(29)
N(1)	1 454(21)	1 468(41)	1 485(35)	C(35)	3 307(20)	2 916(38)	3 002(25)
N(2)	359(19)	1 659(37)	1 408(32)	C(36)	2 731(20)	2 822(38)	3 584(25)
N(3)	1 205(19)	1 059(38)	3 691(32)	C(37)	2 734(20)	2 931(38)	4 511(25)
N(4)	234(22)	1 929(43)	3 172(37)	C(38)	3 313(20)	3 133(38)	4 855(25)
C(1)	885(24)	1 496(46)	1 882(39)	C(39)	3 889(20)	3 226(38)	4 272(25)
C(2)	602(22)	1 579(43)	498(37)	C(40)	3 886(20)	3 118(38)	3 346(25)
C(3)	1 251(25)	1 470(49)	501(42)	C(41)	2 861(20)	-2 017(44)	3 108(27)
C(4)	1 632(33)	1 354(65)	-312(57)	C(42)	2 925(20)	-965(44)	2 120(27)
C(5)	1 342(28)	1 347(54)	-1102(46)	C(43)	3 122(20)	-1 176(44)	1 262(27)
C(6)	683(34)	1 431(66)	-1142(55)	C(44)	3 255(20)	-2 439(44)	1 393(27)
C(7)	330(25)	1 555(50)	-296(43)	C(45)	3 191(20)	-3 491(44)	2 382(27)
C(8)	793(26)	1 531(50)	2 935(43)	C(46)	2 994(20)	-3 280(44)	3 239(27)
C(9)	852(26)	1 241(51)	4 554(43)	C(47)	3 254(16)	-1448(37)	4 742(29)
C(10)	274(26)	1 675(51)	4 217(44)	C(48)	3 192(16)	-763(37)	5 342(29)
C(11)	-181(28)	1 971(57)	4 917(49)	C(49)	3 714(16)	- 583(37)	5 823(29)
C(12)	4(32)	1 596(62)	5 874(53)	C(50)	4 298(16)	-1 089(37)	5 704(29)
C(13)	582(30)	1 190(59)	6 103(48)	C(51)	4 361(16)	-1 775(37)	5 104(29)
C(14)	1 060(26)	958(52)	5 464(45)	C(52)	3 839(16)	-1 954(37)	4 623(29)
C(15)	-1 051(31)	2 137(62)	1 094(50)	C(53)	2 232(21)	-3 382(32)	5 184(32)
C(16)	-688(31)	3 445(63)	575(50)	C(54)	2 537(21)	-4 206(32)	6 046(32)
C(17)	-1 035(31)	4 737(62)	465(51)	C(55)	2 260(21)	-5 452(32)	6 708(32)
C(18)	-1 038(34)	4 953(69)	1 432(57)	C(56)	1 679(21)	-5 876(32)	6 509(32)
C(19)	886(29)	3 703(61)	2 392(47)	C(57)	1 374(21)	-5 052(32)	5 648(32)
C(20)	-1 256(37)	2 585(73)	2 781(58)	C(58)	1 651(21)	-3 805(32)	4 986(32)
C(21)	-1 844(36)	2 144(71)	2 485(59)	C(59)	4 477(31)	3 814(64)	7 348(52)

The refinement was carried out by means of full-matrix least squares using the SHELX system of computer programs ³² with initially isotropic and then anisotropic thermal parameters only for the Au and Rh atoms. The carbon atoms of the phenyl groups were treated as rigid groups of D_{6h} symmetry with C-C distances of 1.395 Å. The hydrogen atoms were placed at their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The final R value was 0.078 for the observed reflections only. The atomic scattering factors used, corrected for the anomalous dispersion of Au and Rh, were taken from ref. 33. The function minimized in the leastsquares calculations was $\Sigma w |\Delta F|^2$; unit weights were chosen at each stage of the refinement after analysing the variation of $|\Delta F|$ with respect to F_0 . Final atomic co-ordinates for nonhydrogen atoms are given in Table 3. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

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