Di- and Tetra-nuclear Mixed-valence Complexes of Rhodium(III,I) and Rhodium(III)–Iridium(I) with the 2,2′-Bi-imidazolate(2−) Anion (bim) as Bridging Ligand. Crystal Structure of $[\{(\eta\text{-}C_5Me_5)[P(OEt)_3]Rh(bim)Rh(nbd)\}_2][ClO_4]_2$[†]

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The reaction of the new mononuclear species $[Rh^{III}(\eta\text{-}C_5Me_5)Cl(Hbim)]$ (H_2bim = 2,2′-bi-imidazole) and $[Rh^{III}(\eta\text{-}C_5Me_5)(Hbim)L'][ClO_4]$ [L′ = pyridine (py), $NCBu^t$, PPh_3, or $P(OEt)_3$] with the corresponding acetylacetonate (acac) complexes of formulae $[M^I(acac)L_2]$ [M = Rh; L = CO, L_2 = tetrafluorobenzobarrelene (tfb) (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) or norborna-2,5-diene (nbd). M = Ir, L_2 = tfb] yields di- and tetra-nuclear mixed-valence compounds of the types $[\{(\eta\text{-}C_5Me_5)ClRh^{III}(bim)Rh^IL_2\}_2]$ [L = CO or L_2 = tfb], $[\{(\eta\text{-}C_5Me_5)L'Rh^{III}(bim)Rh^IL_2\}_n][ClO_4]_n$ [L′ = py; L_2 = tfb (n = 1). L′ = py; L = CO or L_2 = nbd (n = 2). L′ = $NCBu^t$, PPh_3, or $P(OEt)_3$; L = CO, L_2 = tfb or nbd (n = 2)] and $[\{(\eta\text{-}C_5Me_5)L'Rh^{III}(bim)Ir^I(tfb)\}_n][ClO_4]_n$ [L′ = py (n = 1), L′ = PPh_3 or $P(OEt)_3$ (n = 2)]. The structure of $[\{(\eta\text{-}C_5Me_5)[P(OEt)_3]Rh^{III}(bim)Rh^I(nbd)\}_2][ClO_4]_2$ has been determined by X-ray diffraction methods. Crystals are orthorhombic, space group F_{ddd} with Z = 16 in a unit cell of dimensions a = 21.337(3), b = 41.943(5), and c = 31.815(7) Å. The structure was solved by direct and Fourier methods and refined by full-matrix least squares to R = 0.075 for 2 984 observed reflections. The complex cation $[\{(\eta\text{-}C_5Me_5)[P(OEt)_3]Rh^{III}(bim)Rh^I(nbd)\}_2]^{2+}$, having imposed C_2 symmetry, is tetranuclear with two bim^{2-} ligands bridging the metal atoms. Each bim^{2-} anion co-ordinates to the Rh metals in an unsymmetrical tetradentate manner through its four nitrogen atoms of the two imidazolate rings, being chelated to one formally six-co-ordinated Rh atom [Rh(1)] through two N atoms and being bonded in an unidentate manner to two four-co-ordinated Rh atoms [Rh(2)], through the other two N atoms. The co-ordination around Rh(1) is completed by an $\eta\text{-}C_5Me_5$ group and by a $P(OEt)_3$ ligand, that around Rh(2) by a nbd molecule interacting through the two double bonds. A short non-bonding Rh(2)–Rh(2′) distance [3.250(5) Å] is present in the cation.

Di- and tetra-nuclear metal complexes have received much attention due to their importance in the study of electrical and catalytic co-operative effects between adjacent metal centres.[1,2] Synthetic pathways to the formation of these complexes, which allow systematic syntheses of a series of di- or tetra-nuclear species, are of interest. 2,2′-Bi-imidazole (H_2bim) is an acidic ligand that readily binds metal ions in its anionic forms ($Hbim^-$, bim^{2-}), displaying different types of co-ordination.[3] In order to extend earlier work on 2,2′-bi-imidazole–rhodium chemistry,[4–7] we report herein a synthetic strategy that allows the preparation of new di- and tetra-nuclear mixed-valence rhodium compounds. As far as we know, no rhodium(III) complexes with 2,2′-bi-imidazole or its anionic derivatives have been reported previously.

In order to confirm the tetranuclear nature of some of the mixed-valence complexes prepared and to ascertain the relative disposition of the rhodium(I) and rhodium(III) atoms, the X-ray crystal structure of $[\{(\eta\text{-}C_5Me_5)[P(OEt)_3]Rh(bim)Rh(nbd)\}_2][ClO_4]_2$ (nbd = norborna-2,5-diene) has been determined.

Results and Discussion

Mononuclear Complexes.—The complex $[Rh(\eta\text{-}C_5Me_5)Cl(acac)]$ (acac = acetylacetonate)[8] reacts with H_2bim to give the neutral complex $[Rh(\eta\text{-}C_5Me_5)Cl(Hbim)]$ (**1**). Similarly, the cationic mononuclear complexes $[Rh(\eta\text{-}C_5Me_5)(Hbim)L'][ClO_4]$ [L′ = pyridine (**2a**), $NCBu^t$ (**2b**), PPh_3 (**2c**), or $P(OEt)_3$ (**2d**)] are prepared by reacting the corresponding complex $[Rh(\eta\text{-}C_5Me_5)(acac)L'][ClO_4]$[8] with H_2bim. Long times of reaction are necessary to achieve high yields, especially in the case of (**2d**) (6 d), probably due to the co-ordinative saturation of the parent rhodium(III) complexes. The i.r. spectra, in the solid state, of these complexes show a strong and very broad absorption in the region 3 000—2 100 cm^{-1} and no bands were observed at >3 000 cm^{-1}. These observations indicate the presence of the N–H bond remaining in the co-ordinated monoanion $Hbim^-$ and suggest that a strong association of the type N–H ··· N is operating.[3,4,6] Accordingly, conductivity measurements on (**2c**) (the only product soluble enough to allow solution measurements) give a value of the slope for the Onsager equation of −839, confirming the dinuclear nature of the cation of this complex in acetone solution.[9] Attempts to prepare mononuclear neutral compounds of the type $[Rh(\eta\text{-}C_5Me_5)(bim)L]$ (L = unidentate neutral ligand), from the reaction of the corresponding $[Rh(\eta\text{-}C_5Me_5)Cl_2L]$[10] complex with H_2bim in the presence of two moles of potassium hydroxide, failed. Nevertheless, mononuclear complexes in which the dianion bim^{2-} displays a bidentate chelate co-ordination are known for neutral palladium(II) and platinum(II) derivatives.[11] Futhermore, Rasmussen *et al.*[12] have recently described mononuclear anionic derivatives of rhodium(I) in which the related ligand 4,4′,5,5′-tetracyano-2,2′-bi-imidazole

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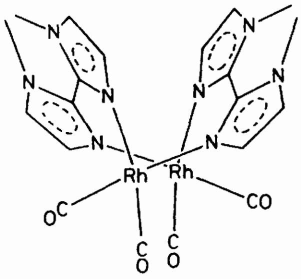
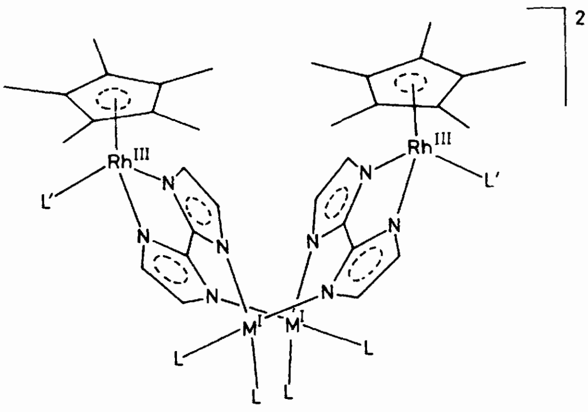
[†] *Supplementary data available* (No. SUP 56321, 4 pp.); H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

(H_2tcbim), in its dianionic form, is co-ordinated as described above.

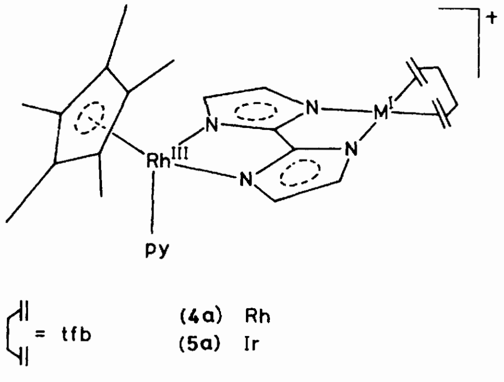
Tetranuclear Complexes.—The mononuclear complexes prepared retain one nitrogen atom and an acidic N–H group which are capable of co-ordination. Thus, (**1**) reacts with [Rh(acac)L_2] (L = CO[13] or L_2 = tfb[14])* yielding the tetranuclear neutral complexes [{(η-C_5Me_5)ClRh(bim)RhL_2}$_2$] [L = CO (**3a**) or L_2 = tfb (**3b**)]. In a similar way (**2a**)—(**2d**) react with [Rh(acac)L_2] (L = CO, L_2 = tfb or nbd[15]) yielding the cationic polynuclear complexes [{(η-C_5Me_5)L′Rh(bim)RhL_2}$_n$][ClO_4]$_n$ [L′ = pyridine (py); L_2 = tfb (**4a**), L = CO (**4b**), or L_2 = nbd (**4c**). L′ = NCBu^t; L = CO (**4d**), L_2 = tfb (**4e**) or nbd (**4f**). L′ = PPh_3; L = CO (**4g**), L_2 = tfb (**4h**) or nbd (**4i**). L′ = P(OEt)$_3$; L = (CO) (**4j**), L_2 = tfb (**4k**) or nbd (**4l**)]. Analytical data are reported in Table 1. Molecular weight measurements on complex (**3a**) confirm the proposed tetranuclear formulation. Furthermore, the i.r. spectrum, in the solid state or in dichloromethane solution, of this complex shows three strong absorptions, due to ν(CO), at 2 080, 2 060 and 2 010 cm^{-1}, which are consistent with the arrangement of the four CO groups as shown below.[5]



Complex (**3b**) shows, in acetone solution, a moderate electrical conductivity (Λ_M = 46 cm^2 Ω^{-1} mol^{-1}) which we assign to an ionic dissociation of the chloride ion present in the molecule. Consequently, molecular weight measurements on (**3b**) give smaller values than that calculated for a tetranuclear formulation[6] (Table 1). Although conductivity studies at different concentrations cannot be considered conclusive, the measurements performed in acetone solution for the cationic complexes (**4a**)—(**4l**) seem to suggest that compounds (**4b**)—(**4l**) are tetranuclear (n = 2). Nevertheless, the value of A, in Onsager's equation, for complex (**4a**) is −448. This value suggests a dinuclear formulation for this complex (n = 1). Unfortunately, all attempts to prepare suitable crystals to carry out an *X*-ray characterization have been unsuccessful. The factors that govern the nuclearity in bi-imidazolate complexes are still unknown. Thus, although [Rh_2(bim)(cod)$_2$] (cod = cyclo-octa-1,5-diene) is a dinuclear complex,[4] the [Rh_4(bim)$_2$(CO)$_8$] derivative, prepared by carbonylation of the former, displays a tetranuclear structure.[5] In a similar way, the carbonylation product of the dinuclear complex [Rh_2(tcbim)(cod)$_2$] is the tetranuclear species [Rh_4(tcbim)$_2$(CO)$_8$]. In this last case, it has been pointed out that the formation of the tetrameric species results from the need for the metals to increase their limited electron density by sharing.[16] The i.r. spectra of complexes (**4a**)—(**4l**) show, along with the two characteristic bands of the perchlorate ion (T_d; *ca.* 1 100 and 620 cm^{-1}),[17] bands assignable to the ancillary ligand L (or L_2) and L′. In addition, all these complexes exhibit two intense bands in the region 1 405—1 125 cm^{-1} attributable to the four-co-ordinate bi-imidazolate anion[5,6] (Table 1). In particular, the carbonylated derivatives (**4b**), (**4d**), (**4g**), and (**4j**) show the three-band pattern characteristic of an arrangement of carbonyl groups as shown above.[5] An *X*-ray molecular structure determination confirms the tetranuclear nature of (**4l**) (see below).



	M	L	L′
(**4b**)	Rh	CO	py
(**4c**)	Rh	½ nbd	py
(**4d**)	Rh	CO	NCBu^t
(**4e**)	Rh	½ tfb	NCBu^t
(**4f**)	Rh	½ nbd	NCBu^t
(**4g**)	Rh	CO	PPh_3
(**4h**)	Rh	½ tfb	PPh_3
(**4i**)	Rh	½ nbd	PPh_3
(**4j**)	Rh	CO	P(OEt)$_3$
(**4k**)	Rh	½ tfb	P(OEt)$_3$
(**4l**)	Rh	½ nbd	P(OEt)$_3$
(**5c**)	Ir	½ tfb	PPh_3
(**5d**)	Ir	½ tfb	P(OEt)$_3$



(4a) Rh
(5a) Ir

Attempts to prepare the related complex [{(η-C_5Me_5)(PPh_3)Rh(bim)Rh(CO)(PPh_3)}$_n$][ClO_4]$_n$ from the reaction of (**2c**) with [Rh(acac)(CO)(PPh_3)],[18] or of (**4g**) with PPh_3, have been unsuccessful. In the former reaction, mixtures of complexes containing some unreacted material and ill defined products are recovered from the reaction medium after work-up. In the latter, a monocarbonylated species is detected, in solution and in the solid state, but the reaction does not go to completion, even using excess of PPh_3. When [Rh(acac)(cod)] is used as a reagent towards cationic Hbim$^-$ complexes of type (**2**), a different reactivity is found. In particular, with the complex (**2a**), a redistribution reaction takes place; thus, the isolated products are the previously described complexes [(cod)Rh(bim)Rh(cod)][4] and [Rh(η-C_5Me_5)(acac)(py)][ClO_4].[8] Redistribution reactions have been previously observed in our laboratory for related bi-imidazolate- and pyrazolate-rhodium(I) complexes.[6,19]

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* tfb = tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene).

Table 1. Analytical, conductance, and i.r. data and molecular weights and yields for the new complexes

	Analysis[a] (%)						
Complex	C	H	N	M[a]	A[b]	I.r.[c] (cm^{-1})	Yield (%)
(3a)	39.2 (38.3)	3.7 (3.4)	10.4 (10.0)	1 108 (1 129)	—	1 405s,[d] 1 138s[e] (2 080vs, 2 060vs, 2 010vs)[f]	65
(3b)	45.4 (45.8)	4.2 (3.4)	7.1 (7.6)	956 (1 470)	—	1 405s,[d] 1 130s[e] 1 490vs[g]	74
(4a)	44.8 (45.1)	4.1 (3.4)	7.6 (8.0)	—	−448	1 405s,[d] 1 130s[e] 1 490vs[g] 1 605m[h]	78
(4b)	38.1 (39.0)	3.3 (3.4)	9.7 (9.9)	—	−1 403	1 400s,[d] 1 140s[e] (2 085vs, 2 056vs, 2 015vs)[f] 1 600m[h]	63
(4c)	45.2 (45.2)	4.1 (4.3)	9.7 (9.4)	—	−1 221	1 405s,[d] 1 135s[e] 1 305w[i] 1 605m[h]	74
(4d)	38.8 (38.8)	3.8 (4.0)	9.7 (9.8)	—	−1 166	1 405s,[d] 1 128s[e] (2 085vs, 2 065vs, 2 015vs)[f] 2 200vs[j]	65
(4e)	44.2 (44.9)	4.5 (3.9)	7.9 (7.9)	—	−1 038	1 405s,[d] 1 130s[e] 1 490vs[g] 2 195vs[j]	71
(4f)	43.9 (45.0)	4.8 (4.8)	9.2 (9.4)	—	−1 363	1 405s,[d] 1 130s[e] 1 305w[i] 2 198vs[j]	80
(4g)	47.7 (48.5)	4.6 (3.9)	6.3 (6.3)	—	−1 289	1 400s,[d] 1 135s[e] (2 090vs, 2 070vs, 2 020vs)[f] 520s[k]	78
(4h)	52.1 (52.1)	4.6 (3.8)	5.4 (5.3)	—	−1 181	1 400s,[d] 1 125s[e] 1 490vs[g] 520s[k]	73
(4i)	52.6 (53.1)	4.9 (4.6)	5.9 (6.0)	—	−1 008	1 398s,[d] 1 125s[e] 1 310w[i] 520s[k]	76
(4j)	35.2 (36.3)	4.3 (4.3)	6.5 (7.0)	—	−1 400	1 400s,[d] 1 140s[e] (2 085vs, 2 065vs, 2 015vs)[f] (1 000—1 040vs, 960vs)[l]	78
(4k)	42.6 (42.3)	4.5 (4.2)	5.6 (5.8)	—	−1 048	1 405s,[d] 1 130s[e] 1 490vs[g] (1 000—1 040vs, 960vs)[l]	52
(4l)	41.7 (41.9)	5.4 (5.1)	6.6 (6.7)	—	−934	1 405s,[d] 1 125s[e] 1 305w[i] (1 000—1 040vs, 960vs)[l]	81
(5a)	40.8 (41.0)	3.9 (3.1)	7.7 (7.2)	—	−571	1 405s,[d] 1 130s[e] 1 490vs[g] 1 605m[h]	70
(5c)	47.3 (48.0)	4.0 (3.5)	4.8 (4.9)	—	−1 180	1 400s,[d] 1 130s[e] 1 490vs[g] 520s[k]	55
(5d)	39.0 (38.7)	4.0 (3.8)	5.6 (5.3)	—	−975	1 410s,[d] 1 135s[e] 1 490vs[g] (1 000—1 040vs, 960vs)[l]	60

[a] Calculated values are given in parentheses. [b] Value of A in Onsager's equation $\Lambda_e = \Lambda_\infty + A\sqrt{c}$. [c] Nujol mulls. [d] Ring stretching for the bi-imidazolate group. [e] In-plane C–H bending in the bi-imidazolate group. [f] ν(CO). [g] tfb. [h] py. [i] nbd. [j] NCBu^t. [k] PPh$_3$. [l] P(OEt)$_3$.

Interestingly, the synthesis described for polynuclear complexes is not limited to the preparation of rhodium(III)–rhodium(I) derivatives, but it is more general. Thus, the reaction of **(2a)**, **(2c)**, or **(2d)** with [Ir(acac)(tfb)][20] led to the isolation of the related rhodium(III)–iridium(I) derivatives [{(η-C$_5$Me$_5$)-L′Rh(bim)Ir(tfb)}$_n$][ClO$_4$]$_n$ [L′ = py **(5a)**, PPh$_3$ **(5c)**, or P(OEt)$_3$ **(5d)**]. Analytical data and electrical conductivity measurements at different concentrations, in acetone solution, confirm the formulation of the cations in complexes **(5c)** and **(5d)** as tetranuclear (n = 2) (Table 1). The value of A in Onsager's equation for complex **(5a)** is −571, suggesting a dinuclear formulation (n = 1) as observed for the related rhodium derivative **(4a)**. The i.r. spectra of complexes **(5)** are nearly identical with those of complexes **(4)**. The most representative absorptions for the rhodium(III)–iridium(I) complexes are given in Table 1.

It is noteworthy that the cations in complexes **(5)** contain, simultaneously, rhodium and iridium atoms in formal oxidation states of III and I, respectively, bonded through the bi-imidazolate anion. This combination of oxidation states is unusual because iridium has a greater tendency than rhodium to be in oxidation state III. The synthetic strategy reported in this paper may have wider implications for the generation of heteropolynuclear complexes, by using other transition metals and a large variety of ancillary ligands. Further work in this area is in progress.

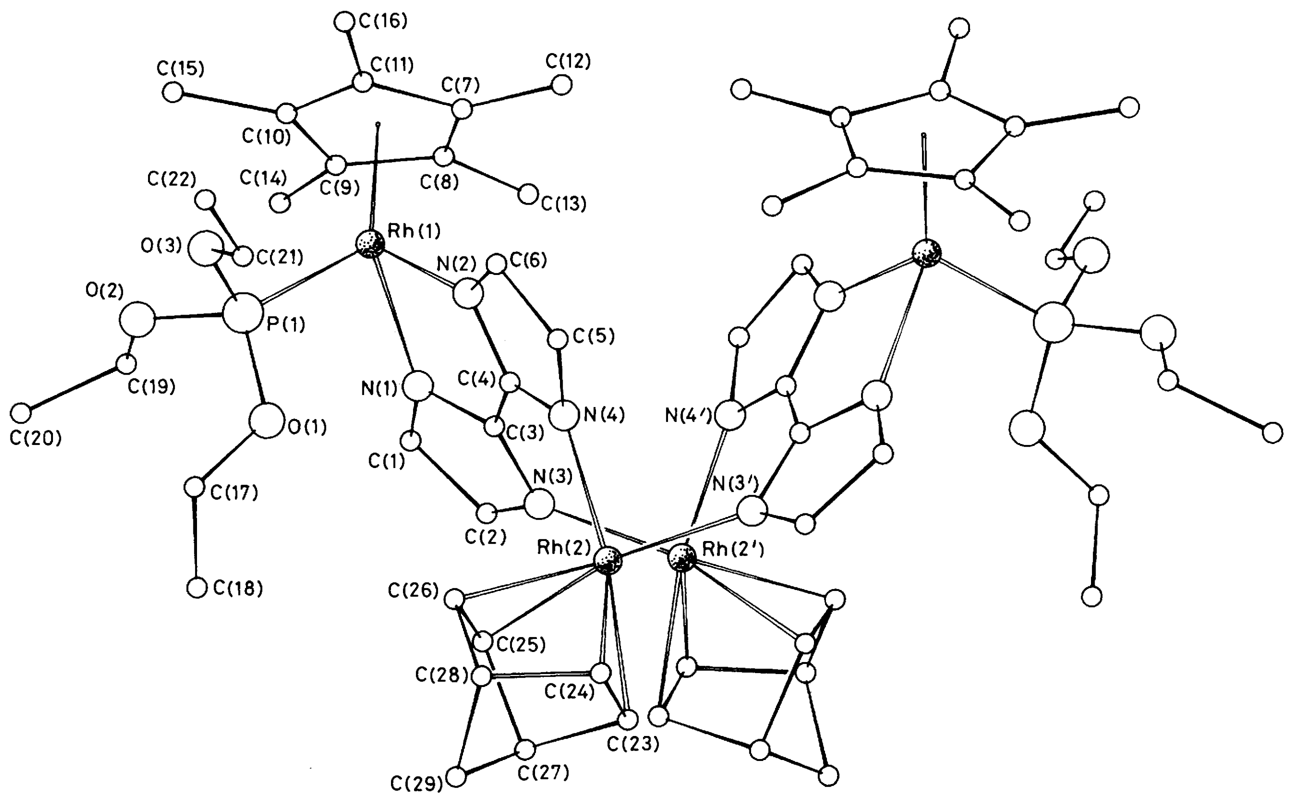

Figure. View of the cationic complex $[\{(\eta\text{-}C_5Me_5)[P(OEt)_3]Rh(bim)Rh(nbd)\}_2]^{2+}$ with the atomic numbering scheme

Molecular Structure of $[\{(\eta\text{-}C_5Me_5)[P(OEt)_3]Rh(bim)Rh(nbd)\}_2][ClO_4]_2$ (**4l**).—Crystals of (**4l**) consist of tetranuclear cations and perchlorate anions. A view of the cation with the atomic numbering scheme is given in the Figure. Selected bond distances and angles are given in Table 2.

The cation consists of two $(\eta\text{-}C_5Me_5)[P(OEt)_3]Rh(bim)Rh(nbd)$ units and has precise (*i.e.* crystallographically required) C_2 symmetry. As shown in Figure 1, atoms in the basic asymmetric unit are labelled normally, while atoms in the 'other half' of the cation, which is related to the basic unit by the transformation $(x',y',z') = (\frac{1}{4} - x, y, \frac{1}{4} - z)$, are primed. Each bim^{2-} anion co-ordinates to the metals (in different oxidation states) in an unsymmetrical quadridentate manner through the four nitrogen atoms of the two imidazole rings, chelating to one Rh^{III} atom [Rh(1)] through two nitrogens and bonding in a unidentate manner to the two Rh^{I} atoms [Rh(2) and the symmetrically related Rh(2′)] through the other two nitrogen atoms. The atom Rh(1), as well as through the two nitrogen atoms [N(1) and N(2)], achieves the expected 'noble-gas configuration' by the donation of six electrons from a $\eta\text{-}C_5Me_5^-$ group and two electrons from the $P(OEt)_3$ neutral ligand. The co-ordination geometry of Rh(1) can be loosely referred to as a 'three-legged piano stool'. Angles between the non-carbon atoms bonded to Rh(1) are: P(1)–Rh(1)–N(1) 90.8(4), P(1)–Rh(1)–N(2) 88.4(4), and N(1)–Rh(1)–N(2) 77.4(6)°. This last value compares well with those found in other related tetranuclear bi-imidazolate complexes of Rh^{I} and Pd^{II}, in which the bim^{2-} ligand acts as chelate.[5,6] Individual rhodium–carbon distances involving the C_5Me_5 ligand show significant variations [ranging from Rh(1)–C(11) 2.14(2) to Rh(1)–C(8) 2.26(2) Å], probably reflecting the asymmetry of ligand arrangements on the other side of the metal. The average value, 2.20 Å, is slightly longer than those previously reported for $Rh^{III}(C_5Me_5)$ complexes (*ca.* 2.15 Å).[21] The Rh(1) atom lies −1.822(4) Å from the least-squares plane through the five-membered carbocyclic ring; no atom deviates more than 0.05(2) Å from this plane, the methyl substituents bending away from the rhodium atom; displacements for C(12), C(13), C(14), C(15), and C(16) are 0.01(2), 0.06(2), 0.08(2), 0.16(2), and 0.12(2) Å respectively. Both Rh(1)–N bonds involving the bim^{2-} ligands, 2.09(1) and 2.08(1) Å, are in good agreement with those found in other $Rh^{III}(C_5Me_5)$ pyrazolate complexes.[22] The Rh(1)–P(1) bond distance, 2.248(7) Å, is longer than those found in the rhodium(I) pyrazolate complex $[\{Rh(pz)(CO)[P(OPh)_3]\}_2]$, with triphenyl phosphite ligands [2.188(6) and 2.191(6) Å].[23]

The co-ordination of the Rh^{I} atom, besides the two N atoms [N(4) and N(3′)] from the two bim^{2-} ligands, also involves a nbd molecule interacting through the two double bonds. The geometry around the Rh atom is approximately square planar with the plane defined by the two N atoms and the midpoints of the two olefinic bonds of the norborna-2,5-diene ligand. If M(1) and M(2) are the midpoints of the C(23)–C(24) and C(25)–C(26) bonds, the deviations of M(1), M(2), N(3′), and N(4) from the mean plane passing through them are −0.11(1), 0.11(1), 0.09(1), and −0.09(1) Å respectively, with the rhodium out of this plane by 0.170(4) Å. This slight deviation of the metal from square-planar co-ordination towards the other metal could suggest, as has been proposed for $[Rh_2(\mu\text{-}napy)_2(nbd)_2]^{2+}$ (napy = 1,8-naphthyridine),[24] some interaction between the two Rh^{I} atoms, in spite of the relatively long separation between the Rh atoms [3.250(5) Å]. The Rh(2)–N bond distances [2.09(1) and 2.10(1) Å] are in the range found in related rhodium(I) bi-imidazolate complexes,[4,5] and of the same order as those observed for Rh^{III}–N bonds (see above), although slightly longer bond lengths might be anticipated for Rh^{I}–N due to the larger Rh^{I} ionic radius. Each of the two parts of

Table 2. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses *

(*a*) Co-ordination sphere of the metals							
Rh(1)–P(1)	2.248(7)	Rh(1)–C(8)	2.26(2)	Rh(2)–N(3′)	2.09(1)	Rh(2)–C(24)	2.13(2)
Rh(1)–N(1)	2.09(1)	Rh(1)–C(9)	2.18(2)	Rh(2)–N(4)	2.10(1)	Rh(2)–C(25)	2.12(2)
Rh(1)–N(2)	2.08(1)	Rh(1)–C(10)	2.21(2)	Rh(2)–C(23)	2.15(2)	Rh(2)–C(26)	2.15(2)
Rh(1)–C(7)	2.20(2)	Rh(1)–C(11)	2.14(2)				
P(1)–Rh(1)–N(1)	90.8(4)	N(3′)–Rh(2)–C(24)	98.3(6)	N(4)–Rh(2)–C(24)	144.7(6)	C(23)–Rh(2)–C(26)	81.3(7)
P(1)–Rh(1)–N(2)	88.4(4)	N(3′)–Rh(2)–C(25)	162.9(7)	N(4)–Rh(2)–C(25)	99.1(6)	C(24)–Rh(2)–C(25)	82.2(7)
N(1)–Rh(1)–N(2)	77.4(6)	N(3′)–Rh(2)–C(26)	156.8(6)	N(4)–Rh(2)–C(26)	89.4(6)	C(24)–Rh(2)–C(26)	69.6(7)
N(3′)–Rh(2)–N(4)	90.4(5)	N(4)–Rh(2)–C(23)	168.0(6)	C(23)–Rh(2)–C(24)	37.2(7)	C(25)–Rh(2)–C(26)	38.5(7)
N(3′)–Rh(2)–C(23)	101.2(6)			C(23)–Rh(2)–C(25)	68.9(8)		
(*b*) 2,2′-Bi-imidazolate ligand							
N(1)–C(1)	1.42(2)	N(3)–C(3)	1.34(2)	N(2)–C(4)	1.33(2)	N(4)–C(5)	1.40(2)
N(1)–C(3)	1.35(2)	C(1)–C(2)	1.42(3)	N(2)–C(6)	1.38(2)	C(5)–C(6)	1.41(3)
N(3)–C(2)	1.37(2)	C(3)–C(4)	1.44(2)	N(4)–C(4)	1.37(2)		
Rh(1)–N(1)–C(1)	137(1)	N(1)–C(1)–C(2)	105(2)	Rh(1)–N(2)–C(6)	138(1)	N(2)–C(4)–N(4)	113(1)
Rh(1)–N(1)–C(3)	115(1)	N(3)–C(2)–C(1)	110(1)	Rh(1)–N(2)–C(4)	115(1)	N(2)–C(4)–C(3)	117(1)
C(1)–N(1)–C(3)	105(1)	N(1)–C(3)–N(3)	114(1)	C(4)–N(2)–C(6)	107(1)	N(4)–C(4)–C(3)	130(1)
Rh(2′)–N(3)–C(2)	126(1)	N(1)–C(3)–C(4)	113(1)	Rh(2)–N(4)–C(4)	130(1)	N(4)–C(5)–C(6)	106(1)
Rh(2′)–N(3)–C(3)	126(1)	N(3)–C(3)–C(4)	132(1)	Rh(2)–N(4)–C(5)	121(1)	N(2)–C(6)–C(5)	109(1)
C(2)–N(3)–C(3)	105(1)			C(4)–N(4)–C(5)	106(1)		
(*c*) Pentamethylcyclopentadienyl ligand							
C(7)–C(8)	1.45(2)	C(9)–C(10)	1.42(2)	C(7)–C(12)	1.48(3)	C(10)–C(15)	1.51(3)
C(7)–C(11)	1.45(3)	C(10)–C(11)	1.45(3)	C(8)–C(13)	1.50(3)	C(11)–C(16)	1.50(3)
C(8)–C(9)	1.47(3)			C(9)–C(14)	1.51(3)		
(*d*) Triethyl phosphite ligand							
P(1)–O(1)	1.55(1)	O(1)–C(17)	1.48(4)			C(17)–C(18)	1.55(6)
P(1)–O(2)	1.55(2)	O(2)–C(19)	1.29(4)			C(19)–C(20)	1.63(5)
P(1)–O(3)	1.62(2)	O(3)–C(21)	1.48(4)			C(21)–C(22)	1.34(5)
Rh(1)–P(1)–O(1)	114(1)	Rh(1)–P(1)–O(3)	116(1)	O(1)–P(1)–O(3)	106(1)		
Rh(1)–P(1)–O(2)	118(1)	O(1)–P(1)–O(2)	105(1)	O(2)–P(1)–O(3)	96(1)		
(*e*) Norborna-2,5-diene ligand							
C(23)–C(24)	1.37(3)	C(24)–C(28)	1.56(3)	C(25)–C(27)	1.60(3)	C(27)–C(29)	1.59(3)
C(23)–C(27)	1.57(3)	C(25)–C(26)	1.41(3)	C(26)–C(28)	1.61(3)	C(28)–C(29)	1.56(3)
(*f*) Perchlorate anions							
Cl(1)–O(4)	1.41(3)	Cl(2)–O(61)	1.37(4)	Cl(2)–O(71)	1.43(4)		
Cl(1)–O(5)	1.40(3)	Cl(2)–O(62)	1.41(6)	Cl(2)–O(72)	1.37(7)		

* Primed atoms are related to those unprimed by the transformation $\frac{1}{4} - x, y, \frac{1}{4} - z$.

the bim^{2-} ligand is perfectly planar these being slightly twisted and making a dihedral angle of 15.8° with each other; this fact is probably due to the demands of behaving as both a chelating and bridging ligand.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets, or in dichloromethane solutions between NaCl plates. Conductivities were measured in acetone solutions with a Philips 9501/01 conductimeter at concentrations of 10^{-3} to 10^{-4} mol dm^{-3}. Molecular weights were measured in $CHCl_3$ with a Perkin-Elmer 115 osmometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. All reactions were carried out at room temperature and solvents were dried and distilled before use.

Preparation of the Complex (**2c**).—A mixture of [Rh(η-C_5Me_5)(acac)(PPh_3)][ClO_4] (69.9 mg, 0.10 mmol) and H_2bim (13.4 mg, 0.10 mmol) in methanol (30 cm^3) was stirred for 24 h. The resulting solution was partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow microcrystalline solid which was filtered off, washed with diethyl ether, and air-dried. Yield 85% (Found: C, 56.1; H, 5.3; N, 7.5. $C_{34}H_{35}ClN_4O_4PRh$ requires C, 55.7; H, 4.8; N, 7.6%). Complexes (**1**), (**2a**), (**2b**), and (**2d**) were prepared similarly.

Preparation of the Complexes (**3a**) *and* (**3b**).—Under nitrogen, a mixture of (**1**) (49.0 mg, 0.12 mmol) and [Rh(acac)(tfb)] (51.3 mg, 0.12 mmol) or, respectively, [Rh(acac)$(CO)_2$] (31.1 mg, 0.12 mmol), in methanol (20 cm^3) was stirred for 15 min. The resulting solutions were evaporated to dryness. The orange residues were dissolved in acetone (5 cm^3) and the addition of hexane gave orange solids, which were filtered off, washed with hexane, and air-dried.

Preparation of the Complexes (**4a**)—(**4l**).—Under nitrogen, a mixture of (**2a**) (72.5 mg, 0.13 mmol), (**2b**) (70.7 mg, 0.13 mmol), (**2c**) (100.0 mg, 0.14 mmol), or (**2d**) (95.6 mg, 0.15 mmol) and

Table 3. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	9 423(1)	262(1)	1 411(1)
Rh(2)	11 391(1)	−731(1)	1 752(1)
P(1)	8 980(3)	41(1)	1 982(2)
O(1)	9 229(7)	−297(3)	2 088(5)
O(2)	8 256(8)	8(4)	1 995(5)
O(3)	9 040(8)	245(4)	2 412(5)
N(1)	9 532(7)	−187(3)	1 136(4)
N(2)	10 293(7)	116(3)	1 639(4)
N(3)	10 222(7)	−561(3)	919(4)
N(4)	11 018(6)	−269(3)	1 696(4)
C(1)	9 235(9)	−367(4)	816(6)
C(2)	9 683(9)	−598(4)	693(5)
C(3)	10 110(7)	−316(4)	1 179(5)
C(4)	10 477(8)	−170(4)	1 507(5)
C(5)	11 187(9)	−26(4)	1 978(5)
C(6)	10 727(9)	214(4)	1 933(6)
C(23)	11 570(9)	−1 233(4)	1 806(6)
C(24)	11 683(9)	−1 090(4)	2 184(6)
C(25)	10 541(9)	−994(5)	1 771(6)
C(26)	10 637(8)	−854(4)	2 168(6)
C(27)	10 863(10)	−1 339(4)	1 791(6)
C(28)	11 053(9)	−1 105(4)	2 431(6)
C(29)	10 767(10)	−1 425(5)	2 272(7)
C(7)	9 808(8)	697(4)	1 122(5)
C(8)	9 440(9)	538(4)	801(6)
C(9)	8 800(9)	500(4)	968(5)
C(10)	8 771(8)	669(4)	1 353(5)
C(11)	9 397(9)	771(4)	1 470(6)
C(12)	10 483(10)	775(5)	1 101(6)
C(13)	9 693(9)	421(5)	388(6)
C(14)	8 250(11)	373(5)	721(7)
C(15)	8 191(10)	728(5)	1 616(7)
C(16)	9 524(9)	973(5)	1 848(6)
C(17)	9 008(18)	−485(10)	2 453(12)
C(18)	8 868(16)	−808(9)	2 239(11)
C(19)	7 971(17)	−137(8)	1 691(11)
C(20)	7 323(15)	−293(7)	1 870(9)
C(21)	9 561(18)	228(8)	2 719(12)
C(22)	9 567(17)	412(8)	3 063(12)
Cl(1)	1 250	5 486(5)	1 250
Cl(2)	1 250	1 250	13(5)
O(4)	1 811(12)	5 363(6)	1 082(8)
O(5)	983(12)	5 657(6)	919(8)
O(61)*	1 719(20)	1 157(10)	−253(13)
O(62)*	1 326(30)	1 563(15)	163(20)
O(71)*	1 866(20)	1 377(10)	64(13)
O(72)*	1 436(33)	1 035(16)	314(21)

* Atom with occupancy factor of 0.5.

stoicheiometric amounts of the corresponding complexes [Rh(acac)L_2] (L = CO, L_2 = tfb or nbd) in methanol (30 cm^3) was stirred for 1 h [(**2a**), (**2c**), and (**2d**) (L = CO)], 2 h [(**2b**)], or 7 h [(**2d**) (L_2 = tfb or nbd)]. The mixture was filtered to remove some unreacted solids in some cases. The resulting orange solutions were partially concentrated under reduced pressure and the slow addition of diethyl ether gave orange microcrystalline solids which were filtered off, washed with diethyl ether, and air-dried.

Preparation of the Complexes (**5a**), (**5c**) *and* (**5d**).—Under nitrogen, a mixture of [Ir(acac)(tfb)] (57.2 mg, 0.11 mmol) and (**2a**), (**2c**), or (**2d**) (0.11 mmol) in methanol (30 cm^3) was stirred for 16 h [(**2c**)], or for 6 h [(**2a**), (**2d**)]. The red solutions were partially concentrated under reduced pressure and the slow addition of diethyl ether gave red microcrystalline solids, which were filtered off, washed with diethyl ether, and air-dried.

X-*Ray Crystal Structure Analysis of Complex* (**4l**).—Single crystals suitable for *X*-ray diffraction studies were grown by slow diffusion of diethyl ether into a concentrated dichloromethane solution of the complex. An orange crystal having approximate dimensions 0.14 × 0.18 × 0.55 mm was used for the *X*-ray analysis.

Crystal data. $C_{58}H_{84}Cl_2N_8O_{14}P_2Rh_4$, M = 1 661.82, orthorhombic, a = 21.337(3), b = 41.943(5), c = 31.815(7) Å, U = 28 472(8) Å^3 (by least-squares refinement from the θ values of 28 accurately measured reflections), space group F_{ddd}, Z = 16, D_c = 1.551 g cm^{-3}, μ(Cu-K_α) = 92.08 cm^{-1}, $F(000)$ = 13 504.

Data collection and processing. Siemens AED diffractometer, nickel-filtered Cu-K_α radiation (λ = 1.541 78 Å), θ/2θ scan mode, 6 069 independent reflections measured ($3 \leqslant \theta \leqslant 65°$), 2 984 observed [$I \geqslant 2\sigma(I)$], data corrected for absorption following ref. 25 (max. and min. transmission factors: 1.1338 and 0.8641) using the program ASSORB (F. Ugozzoli, University of Parma).

Structure analysis and refinement. Direct and Fourier methods were used, with full-matrix least-squares refinement with anisotropic thermal parameters for Rh, P, N, O(1)—O(3), C(1)—C(6), and C(23)—C(29) atoms in the last cycles. One perchlorate anion was found disordered and distributed in two positions of equivalent occupancy. The hydrogen atoms were placed at their geometrically calculated positions and included in the final structure factor calculations. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$. The weighting scheme used in the last cycles was $w = 0.6387/[\sigma^2(F_o) + 0.0066F_o]$. Final R and R' values were 0.075 and 0.083. Programs used are given in ref. 26. Atomic scattering factors (corrected for anomalous dispersion) for Rh, P, and Cl were from ref. 27. 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. Final atomic coordinates for non-hydrogen atoms are given in Table 3.

References

1 E. L. Muetterties, *Bull. Soc. Chim. Belg.*, 1975, **84**, 959.

2 K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, J. L. Atwood, and J. Zaworotko, *J. Am. Chem. Soc.*, 1982, **104**, 920.

3 R. Uson, L. A. Oro, J. Gimeno, M. A. Ciriano, J. A. Cabeza, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, 1983, 323 and refs. therein.

4 S. W. Kaiser, R. B. Saillant, W. M. Butler, and P. G. Rasmussen, *Inorg. Chem.*, 1976, **15**, 2681.

5 S. W. Kaiser, R. B. Saillant, W. M. Butler, and P. G. Rasmussen, *Inorg. Chem.*, 1976, **15**, 2688.

6 R. Usón, J. Gimeno, L. A. Oro, J. M. Martínez de Ilarduya, J. A. Cabeza, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, 1983, 1729.

7 R. Usón, J. Gimeno, L. A. Oro, M. Valderrama, R. Sariego, and E. Martínez, *Transition Met. Chem.*, 1981, **6**, 103.

8 W. Rigby, H.-B. Lee, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 387.

9 L. A. Oro, D. Carmona, and J. Reedijk, *Inorg. Chim. Acta*, 1983, **71**, 115; R. Usón, J. Gimeno, J. Forniés, and F. Martínez, *ibid.*, 1981, **50**, 173.

10 J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

11 R. Usón, J. Gimeno, L. A. Oro, M. A. Aznar, and J. A. Cabeza, *Polyhedron*, 1983, **2**, 163.

12 P. G. Rasmussen, O. H. Bailey, J. C. Bayón, and W. M. Butler, *Inorg. Chem.*, 1984, **23**, 343.

13 Yu. S. Varshavskii and T. G. Cherkasova, *Russ. J. Inorg. Chem.*, 1967, 599.

14 D. M. Roe and A. G. Massey, *J. Organomet. Chem.*, 1971, **28**, 273.

15 S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 4997.

16 P. G. Rasmussen, O. H. Bailey, and J. C. Bayón, *Inorg. Chem.*, 1984, **23**, 338.

17 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091; J. Peone, jun., and L. Vaska, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 511; *Angew. Chem.*, 1971, **83**, 497; R. Usón P. Lahuerta, D. Carmona, and L. A. Oro, *Transition Met. Chem.*, 1980, **5**, 327.

18 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.

19 R. Uson, L. A. Oro, M. A. Ciriano, M. T. Pinillos, and J. A. Cabeza, *J. Organomet. Chem.*, 1981, **221**, 249.

20 R. Uson, L. A. Oro, D. Carmona, and M. A. Esteruelas, *J. Organomet. Chem.*, 1984, **263**, 109.

21 P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.

22 L. A. Oro, D. Carmona, M. P. Lamata, M. C. Apreda, C. Foces-Foces, F. H. Cano, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1823.

23 R. Uson, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1981, **205**, 247.

24 A. Tiripicchio, M. Tiripicchio Camellini, R. Usón, L. A. Oro, M. A. Ciriano, and F. Viguri, *J. Chem. Soc., Dalton Trans.*, 1984, 125.

25 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

26 G. M. Sheldrick, SHELX System of Computing Programs, University of Cambridge, 1976.

27 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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