Bi-imidazole (H_2bim) and Bibenzimidazole η^3-Allylic Complexes of Palladium(II). Mono- and Tetra-nuclear Palladium(II) and Heteronuclear Palladium(II)–Rhodium(I) Complexes. Crystal Structure of $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mu\text{-bim})_2]\cdot CH_2Cl_2$ †

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Novel cationic η^3-allylic palladium(II) complexes of the type $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(H_2L)]^+$ [R = H or Me; H_2L = 2,2′-bi-imidazole (H_2bim) or 2,2′-bibenzimidazole (H_2bzim)] have been obtained by reaction of $[\{Pd(\eta^3\text{-}2\text{-}RC_3H_4)(\mu\text{-}Cl)\}_2]$ with $AgClO_4$ and subsequent addition of H_2L. Treatment of the complex $[\{Pd(\eta^3\text{-}2\text{-}RC_3H_4)(\mu\text{-}Cl)\}_2]$ with H_2L (1 : 2 mol ratio) in the presence of KOH leads to neutral mononuclear η^3-allylic palladium(II) complexes of general formula $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(HL)]$ (R = H or Me; HL^- = $Hbim^-$ or $Hbzim^-$). The use of a 1 : 1 mol ratio affords tetranuclear complexes of the type $[Pd_4(\eta^3\text{-}2\text{-}RC_3H_4)_4(\mu\text{-}L)_2]$. The neutral mono- and tetra-nuclear complexes have also been prepared by reaction of $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(acac)]$ (Hacac = acetylacetone) with H_2bim or H_2bzim in 1 : 1 or 2 : 1 mol ratios, respectively. Reactions of acac complexes with bi-imidazolate or bibenzimidazolate derivatives containing the anion HL^- render similar heterotetranuclear η^3-allylic palladium(II)–rhodium(I) compounds. The reported molecular weights, i.r. spectra, and ^{1}H n.m.r. studies support the tetranuclearity of the compounds, in which the bi-imidazolate or bibenzimidazolate anions are acting as tetradentate bridging ligands. The crystal structure of the compound $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mu\text{-bim})_2]\cdot CH_2Cl_2$ has been determined by *X*-ray methods; it crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$, $a = 13.081(8)$, $b = 20.843(13)$, $c = 12.722(7)$ Å, $\alpha = 106.78(4)$, $\beta = 108.56(4)$, $\gamma = 84.98(3)°$. The structure has been solved by direct and Fourier methods and refined by full-matrix least squares to $R = 0.084$ for 4 667 observed reflections. The crystals consist of two essentially identical, but crystallographically independent, complexes of $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mu\text{-bim})_2]$ and dichloromethane molecules of crystallization. In each complex each bim^{2-} anion co-ordinates to the Pd metals in an unsymmetrical tetradentate manner through its four nitrogen atoms of the two imidazolate rings; chelating to one Pd atom through two N atoms and being bonded in a unidentate manner to two Pd atoms through the other two N atoms. The co-ordination at all four Pd atoms also involves an allyl ligand bonded through an η^3-interaction with the three carbon atoms.

In previous papers [1,2] we have reported on the ability of the bibenzimidazolate anion to act as a bridging ligand, thus giving rise to the formation of bi-, tri- and tetra-nuclear gold(I), gold(I)–palladium(II), or gold(I)–rhodium(I) complexes. Moreover, the *X*-ray crystal structure [2] of $[(cod)Rh(\mu\text{-bzim})Au_2(PPh_3)_2][ClO_4]$ (H_2bzim = 2,2′-bibenzimidazole, cod = cyclo-octa-1,5-diene) evidences the behaviour of $bzim^{2-}$ as a tetradentate bridging ligand.

In this paper we describe the synthesis and characterization of new homo- and hetero-nuclear 2,2′-bi-imidazole (H_2bim) or 2,2′-bibenzimidazole complexes of two different types: (*a*) mononuclear η^3-allylic palladium(II) complexes, which can either be neutral [complexes (1)—(4)], containing the anions $Hbim^-$ or $Hbzim^-$ or cationic [complexes (5)—(8)], containing H_2bim or H_2bzim with the heterocyclic ligands acting as bidentate chelates; and (*b*) neutral tetranuclear η^3-allylic palladium(II) [complexes (9)—(12)] and palladium(II)–rhodium(I) [complexes (13)—(18)] complexes, where bim^{2-} or $bzim^{2-}$ anions act as tetradentate bridging ligands. The crystal and molecular structure of $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mu\text{-bim})_2]$, determined by single-crystal *X*-ray diffraction, is also reported.

Results and Discussion

Mononuclear Palladium(II) *Derivatives*.—(*a*) *Neutral complexes*. The complexes $[\{Pd(\eta^3\text{-}2\text{-}RC_3H_4)(\mu\text{-}Cl)\}_2]$ (R = H [3] or Me [4]) react in 1 : 2 mol ratio with H_2L (H_2L = H_2bim [5] or H_2bzim [5]) in the presence of potassium hydroxide and in methanol solution to give the white complexes (1)—(4). The reactions only give rise to the dissociation of one of the aminic hydrogens of H_2L, thus preventing the formation of the expected anionic complexes $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)L]^-$ (L^{2-} = bim^{2-} or $bzim^{2-}$). Complexes (1)—(4) can also be obtained by reaction of $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(acac)]$ [6] (Hacac = acetylacetone) with equimolar amounts of H_2L. The absorption band at 3 000—2 300 cm^{-1} can be assigned to the N–H bond, though the low-energy points are assigned to intermolecular association in the solid state due to hydrogen bonds (see below). Moreover, the molecular weights, determined osmometrically in chloroform (see Table 1) are higher than the calculated ones.

(*b*) *Cationic complexes*. Treatment of acetone solutions of $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(Me_2CO)_x][ClO_4]$ (prepared *in situ* by reacting $[\{Pd(\eta^3\text{-}2\text{-}RC_3H_4)(\mu\text{-}Cl)\}_2]$ with silver perchlorate and filtering

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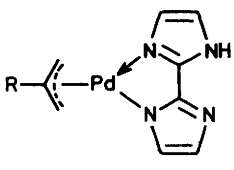
† Bis{μ-[*NN*′-(1—3-η-allyl)palladio(2,2′-bi-imidazolato-*N*″*N*‴)]}-bis(1—3-η-allylpalladium).

Supplementary data available (No. SUP 23599, 31 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

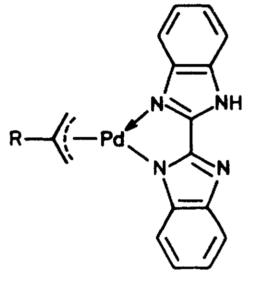
Table 1. Analytical [a] and physical data

Compound	C (%)	H (%)	N (%)	*M*	Λ_M [b]	M.p. [c] (°C)
(1)	38.75 (38.50)	3.80 (3.60)	19.25 (19.95)	*d*	—	147
(2)	41.10 (40.75)	4.10 (4.10)	19.20 (19.00)	361 (295)	—	150
(3)	52.95 (53.65)	3.65 (3.70)	14.75 (14.70)	500 (381)	—	235
(4)	53.80 (54.75)	4.20 (4.10)	13.75 (14.20)	540 (395)	—	240
(5)	28.25 (28.35)	2.90 (2.90)	14.55 (14.70)	—	79.1 [e,f]	230
(6)	30.35 (30.40)	3.25 (3.30)	14.15 (14.20)	—	73.5 [e,f]	190
(7)	42.25 (42.45)	3.25 (3.15)	11.00 (11.65)	—	127.5 [g]	300
(8)	43.45 (43.65)	3.25 (3.45)	11.40 (11.30)	—	122 [g]	300
(9)	34.70 (33.75)	3.50 (3.30)	12.75 (13.10)	809 (854)	—	187
(10)	36.50 (36.95)	4.00 (4.00)	12.35 (12.30)	940 (910)	—	199
(11)	45.85 (45.55)	3.65 (3.45)	11.00 (10.65)	1 014 (1 054)	—	219
(12)	47.25 (47.60)	4.15 (4.00)	10.00 (10.10)	946 (1 110)	—	180
(13)	41.95 (41.60)	4.45 (4.30)	11.15 (11.40)	930 (981)	—	214
(14)	42.60 (42.85)	4.75 (4.60)	11.45 (11.10)	965 (1 009)	—	219
(15)	50.70 (50.80)	4.35 (4.25)	9.30 (9.50)	897 (1 182)	—	212
(16)	52.05 (51.65)	4.65 (4.50)	8.90 (9.25)	982 (1 210)	—	220
(17)	30.30 (30.15)	2.20 (2.05)	13.05 (12.80)	864 (877)	—	162
(18)	32.30 (31.85)	2.60 (2.45)	12.75 (12.40)	915 (905)	—	173

[a] Calculated values are in parentheses. [b] Units are Ω^{-1} cm^2 mol^{-1}. [c] Decomposition points. [d] Not soluble enough for determination. [e] In nitromethane. [f] Onsager's equation slope: 217.8 for (5) and 288.6 for (6). K. O. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587; W. J. Geary, *Coord. Chem. Rev.*, 1971, **71**, 81; K. J. Bagnall, D. Brown, P. J. Jones, and J. G. H. Du Preez, *J. Chem. Soc.*, 1965, 3594. [g] In acetone.

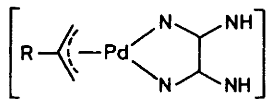


(1; R = H)
(2; R = Me)



(3 ; R = H)
(4 ; R = Me)

off the formed AgCl) with H_2L leads to solutions from which the white complexes (5) and (6) can be crystallized, or to the instantaneous precipitation of the pale yellow complexes (7) and (8). The bonding in [Pd(η^3-2-RC_3H_4)(H_2L)][ClO_4] (5)—(8) is shown below. The i.r. spectra of the solids show a broad absorption band (at 3 310—3 130 cm^{-1}) assignable to the ν(N–H) stretching vibration. This band is shifted towards higher energies relative to its location in the free ligands, thus pointing to their co-ordination as bidentate chelates.[7] The absorptions

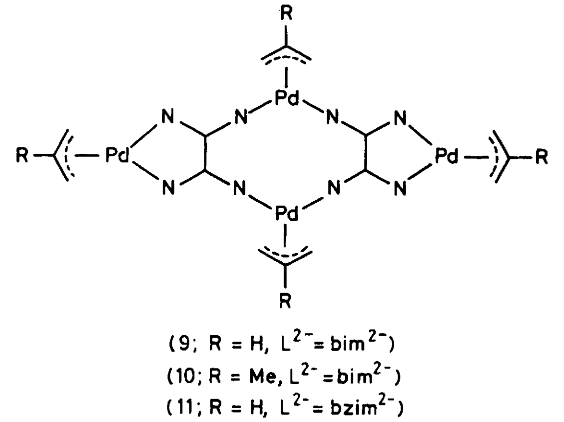


(5 ; R = H, H_2L = H_2bim)
(6 ; R = Me, H_2L = H_2bim)
(7 ; R = H, H_2L = H_2bzim)
(8 ; R = H, H_2L = H_2bzim)

expected for the perchlorate anion (T_d)[8] at *ca.* 1 100 and 620 cm^{-1} are split (see Experimental section) probably because of hydrogen bridging *via* NH···$OClO_3$, which gives rise to a distortion of the T_d symmetry. As we have recently shown[2] the same distortion is also observed for similar rhodium(I) complexes. This association seems to disappear in solution as the recorded spectra obtained are the expected ones. Conductance data (acetone or nitromethane solutions) show that they are 1 : 1 electrolytes (Table 1).

The ^1H n.m.r. spectra in deuterioacetone of (5) and (6) [(7) and (8) are not soluble enough] show two singlet resonances of equal integrated area (δ 7.57, 7.41 and 7.56, 7.36 p.p.m. respectively) assigned to chemically inequivalent H_2bim ring protons. The resonance patterns observed for the allyl groups are similar to those shown for η^3-allyl co-ordination.[9]

Homo- and Hetero-polynuclear Derivatives.—(*a*) *Homonuclear palladium*(II) *complexes*. Tetranuclear palladium(II) complexes can be obtained by two different methods: (*i*) by reaction of $[\{Pd(\eta^3\text{-}2\text{-}RC_3H_4)(\mu\text{-}Cl)\}_2]$ with an equimolecular amount of H_2L in the presence of an excess of potassium hydroxide in methanol (with $[\{Mn(CO)_4(\mu\text{-}Br)\}_2]$ in the same mol ratio only binuclear Mn^I derivatives are obtained [10]); or (*ii*) by treatment of a methanol solution of $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(acac)]$ with H_2L in 2 : 1 mol ratio. Partial evaporation of the solvent affords white (9) and (10) or pale yellow (12) crystalline complexes. Complex (11) precipitates spontaneously as a pale yellow compound. The bonding in $[Pd_4(\eta^3\text{-}2\text{-}RC_3H_4)_4(\mu_3\text{-}L)_2]$ (9)—(12) is shown below. Molecular weight determinations (osmometrically in chloroform) indicate the tetranuclear structure of these complexes (see Table 1). Their i.r. spectra in Nujol mulls exhibit the absorption bands which are characteristic of the η^3-allyl group along with those due to L^{2-}.[11] Thus, the spectra of the bi-imidazolate derivatives (9) and (10) show absorptions at 1 398, 1 137, and 1 126 or at 1 400, 1 138, and 1 128 cm^{-1} respectively, which are displaced towards lower energies relative to those of the corresponding binuclear bi-imidazolate palladium(II) complexes.[11] This seems to point to a tetranuclear structure, in accordance with Rasmussen and co-workers,[12] who reported a similar shift for tetranuclear bi-imidazolate rhodium(I) complexes.



(9; R = H, L^{2-} = bim^{2-})
(10; R = Me, L^{2-} = bim^{2-})
(11; R = H, L^{2-} = bzim^{2-})
(12; R = Me, L^{2-} = bzim^{2-})

The ^1H n.m.r. spectra at room temperature in deuteriochloroform [only (9), (10), and (12) are soluble enough] are consistent with the tetranuclear structures, showing the expected resonances for the two types of chemically equivalent allyl groups. Thus, the spectra of the methylallyl derivatives (10) and (12) (Figure 1) show in the allyl region three groups of two single resonances, corresponding to the two inequivalent types of methyl (highest field resonances), the H_{anti}, and the H_{syn} protons (the latter tentatively assigned to the lowest field resonances). The spectrum of (10) displays two singlet resonances for the H_{exo} and H_{endo} protons of the bi-imidazolate rings (δ 6.82 and 6.57 p.p.m.) whilst the spectrum of (12) shows a multiplet for the bibenzimidazolate aromatic protons (δ 7.16 p.p.m.). The spectrum of (9), which is more complicated due to the coupling of H_{syn} and H_{anti} with the respective allyl H^2 proton (R group) [H^2, δ 5.25 (m, 4 H); H_{syn}, 3.85 (d, 4 H), 3.60 (d, 4 H); H_{anti}, 2.80 (m, 8 H)], is also consistent with the proposed structure. The molecular structure of compound (9) has unambiguously been established by *X*-ray diffraction methods (see below).

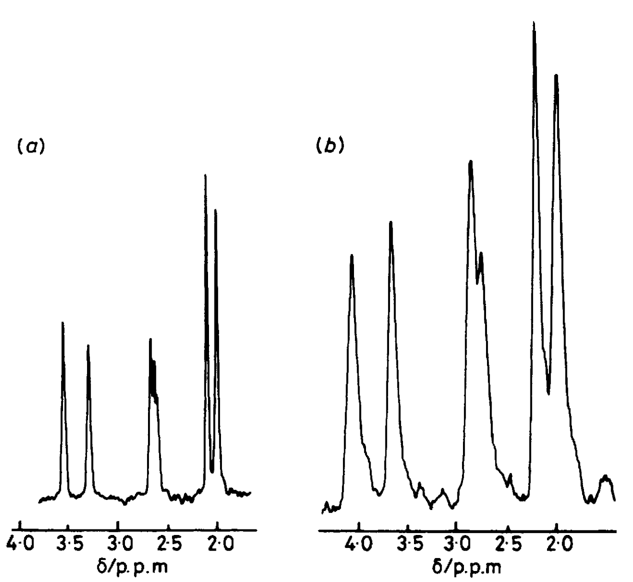
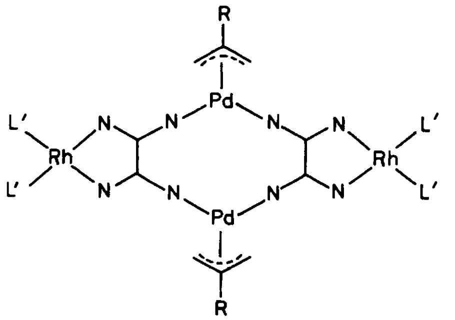


Figure 1. ^1H N.m.r. spectra in the allyl region of complexes (10) (*a*) and (12) (*b*)

(*b*) *Heteronuclear palladium*(II)*-rhodium*(I) *complexes*. The slightly acid character of the aminic portion in complexes which contain the anion HL^- allows reaction with acac derivatives, giving rise to the elimination of Hacac and to the formation of heteronuclear complexes. Thus, [Rh(Hbim)(cod)] [12] in dichloromethane reacts readily with $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(acac)]$ (1 : 1 mol ratio) to give the yellow microcrystalline complexes (13) and (14). Similarly, $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(Hbzim)]$ (3) and (4) react with [Rh(acac)(cod)] [13] to give (15) and (16). Bubbling of carbon monoxide (at normal pressure) through dichloromethane solutions of (13) and (14) leads to displacement of cod and to the formation of the corresponding carbonyl derivatives as orange (17) or deep red (18) microcrystalline solids. The bonding in $[Pd_2Rh_2(\eta^3\text{-}2\text{-}RC_3H_4)_2(\mu_3\text{-}L)_2(L')_4]$ (13)—(18) is shown above.



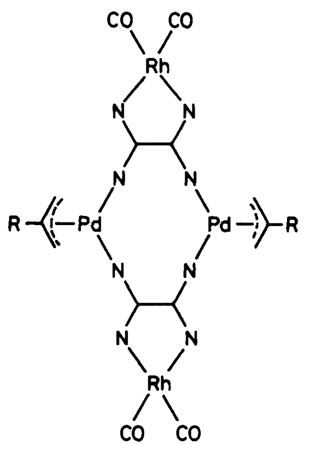
(13; L'_2 = cod, R = H, L^{2-} = bim^{2-})
(14; L'_2 = cod, R = Me, L^{2-} = bim^{2-})
(15; L'_2 = cod, R = H, L^{2-} = bzim^{2-})
(16; L'_2 = cod, R = Me, L^{2-} = bzim^{2-})
(17; L' = CO, R = H, L^{2-} = bim^{2-})
(18; L' = CO, R = Me, L^{2-} = bim^{2-})

Similar reactions of complexes (15) and (16) give rise to rearrangements and to the formation of homonuclear palladium(II) and rhodium(I) derivatives, according to the following reaction.

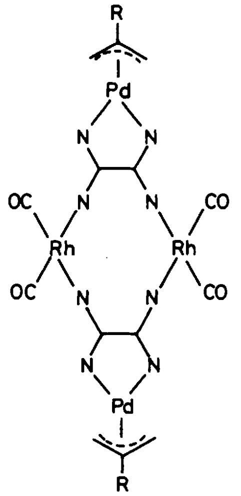
$$2\ (15)\ [\text{or } 2\ (16)] + 8\ \text{CO} \longrightarrow [Pd_4(\eta^3\text{-}2\text{-}RC_3H_4)_4(\mu\text{-bzim})_2] + [Rh_4(CO)_8(\mu\text{-bzim})_2] + 4\ \text{cod}$$

The compound $[Rh_4(CO)_8(\mu\text{-bzim})_2]$ has previously been described.[14] All the complexes are tetranuclear, although the molecular weights of (15) and (16) point to some dissociation in solution. The 1 400—1 130 cm^{-1} range of the i.r. spectra of the bi-imidazolate derivatives in the solid state (see Experimental section) show absorptions which, as above, indicate their tetranuclear character. The i.r. spectra in dichloromethane solution of the carbonyl derivatives (17) and (18) show two CO stretching bands at 2 078, 2 022 and 2 084, 2 016 cm^{-1} respectively, which are consistent with the arrangement of the four CO groups as shown in structure (I),[14] since for structure (II) three ν(CO) stretching bands should be expected as has been found for the related compound $[Rh_4(cod)_2(CO)_4(\mu\text{-bim})_2]$.[12]

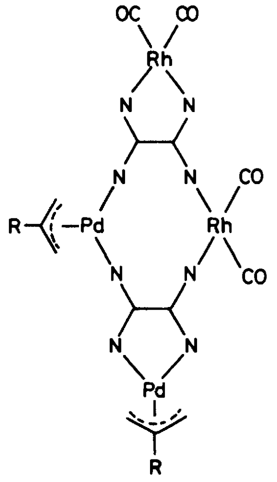
The ^1H n.m.r. spectrum of (18) shows three singlet resonances at δ 2.17 (6 H), 2.77 (4 H), and 3.48 (4 H) p.p.m. assigned respectively to Me, H_{anti}, and H_{syn} protons of two chemically equivalent allyl groups as expected for structure (I). This rules out the assignment of structure (III). The ^1H n.m.r.



(I)



(II)



(III)

Table 2. Selected bond distances (Å) and angles (°)

(*a*) Pd environment

Pd(11)–N(11)	2.09(3)	Pd(12)–N(12)	2.09(2)
Pd(11)–N(61)	2.08(2)	Pd(12)–N(62)	2.08(2)
Pd(11)–C(131)	2.17(4)	Pd(12)–C(132)	2.14(3)
Pd(11)–C(141)	2.12(4)	Pd(12)–C(142)	7.14(4)
Pd(11)–C(151)	2.14(4)	Pd(12)–C(152)	2.12(3)
Pd(21)–N(21)	2.08(2)	Pd(22)–N(22)	2.06(2)
Pd(21)–N(51)	2.05(3)	Pd(22)–N(52)	2.02(2)
Pd(21)–C(161)	2.13(4)	Pd(22)–C(162)	2.16(3)
Pd(21)–C(171)	2.11(4)	Pd(22)–C(172)	2.11(4)
Pd(21)–C(181)	2.14(4)	Pd(22)–C(182)	2.14(3)
Pd(31)–N(31)	2.06(3)	Pd(32)–N(32)	2.01(2)
Pd(31)–N(41)	2.10(3)	Pd(32)–N(42)	2.05(2)
Pd(31)–C(191)	2.11(4)	Pd(32)–C(192)	2.19(4)
Pd(31)–C(201)	2.17(4)	Pd(32)–C(202)	2.12(4)
Pd(31)–C(211)	2.12(5)	Pd(32)–C(212)	2.06(4)
Pd(41)–N(71)	2.03(2)	Pd(42)–N(72)	2.03(2)
Pd(41)–N(81)	2.09(3)	Pd(42)–N(82)	2.09(2)
Pd(41)–C(221)	2.17(3)	Pd(42)–C(222)	2.09(3)
Pd(41)–C(231)	2.10(4)	Pd(42)–C(232)	2.08(4)
Pd(41)–C(241)	2.15(4)	Pd(42)–C(242)	2.10(3)

N(11)–Pd(11)–N(61)	93(1)	N(12)–Pd(12)–N(62)	93(1)
N(11)–Pd(11)–C(131)	102(1)	N(12)–Pd(12)–C(132)	167(1)
N(11)–Pd(11)–C(141)	133(1)	N(12)–Pd(12)–C(142)	135(1)
N(11)–Pd(11)–C(151)	170(1)	N(12)–Pd(12)–C(152)	98(1)
N(61)–Pd(11)–C(131)	163(1)	N(62)–Pd(12)–C(132)	95(1)
N(61)–Pd(11)–C(141)	124(1)	N(62)–Pd(12)–C(142)	132(1)
N(61)–Pd(11)–C(151)	96(1)	N(62)–Pd(12)–C(152)	158(1)
C(131)–Pd(11)–C(141)	39(1)	C(132)–Pd(12)–C(142)	37(1)
C(131)–Pd(11)–C(151)	69(2)	C(132)–Pd(12)–C(152)	71(1)
C(141)–Pd(11)–C(151)	37(2)	C(142)–Pd(12)–C(152)	40(1)
N(21)–Pd(21)–N(51)	92(1)	N(22)–Pd(22)–N(52)	90(1)
N(21)–Pd(21)–C(161)	96(1)	N(22)–Pd(22)–C(162)	167(1)
N(21)–Pd(21)–C(171)	129(1)	N(22)–Pd(22)–C(172)	133(1)
N(21)–Pd(21)–C(181)	166(1)	N(22)–Pd(22)–C(182)	96(1)
N(51)–Pd(21)–C(161)	169(1)	N(52)–Pd(22)–C(162)	100(1)
N(51)–Pd(21)–C(171)	133(1)	N(52)–Pd(22)–C(172)	137(1)
N(51)–Pd(21)–C(181)	99(1)	N(52)–Pd(22)–C(182)	172(1)
C(161)–Pd(21)–C(171)	36(2)	C(162)–Pd(22)–C(172)	37(1)
C(161)–Pd(21)–C(181)	72(1)	C(162)–Pd(22)–C(182)	73(1)
C(171)–Pd(21)–C(181)	37(2)	C(172)–Pd(22)–C(182)	38(1)
N(31)–Pd(31)–N(41)	79(1)	N(32)–Pd(32)–N(42)	78(1)
N(31)–Pd(31)–C(191)	110(1)	N(32)–Pd(32)–C(192)	178(1)
N(31)–Pd(31)–C(201)	137(1)	N(32)–Pd(32)–C(202)	144(1)
N(31)–Pd(31)–C(211)	171(2)	N(32)–Pd(32)–C(212)	112(1)
N(41)–Pd(31)–C(191)	170(1)	N(42)–Pd(32)–C(192)	102(1)
N(41)–Pd(31)–C(201)	133(1)	N(42)–Pd(32)–C(202)	131(1)
N(41)–Pd(31)–C(211)	109(2)	N(42)–Pd(32)–C(212)	169(1)
C(191)–Pd(31)–C(201)	38(1)	C(192)–Pd(32)–C(202)	37(2)
C(191)–Pd(31)–C(211)	61(2)	C(192)–Pd(32)–C(212)	68(2)
C(201)–Pd(31)–C(211)	38(2)	C(202)–Pd(32)–C(212)	42(2)
N(71)–Pd(41)–N(81)	79(1)	N(72)–Pd(42)–N(82)	80(1)
N(71)–Pd(41)–C(221)	177(1)	N(72)–Pd(42)–C(222)	109(1)
N(71)–Pd(41)–C(231)	140(1)	N(72)–Pd(42)–C(232)	143(1)
N(71)–Pd(41)–C(241)	104(1)	N(72)–Pd(42)–C(242)	177(1)
N(81)–Pd(41)–C(221)	103(1)	N(82)–Pd(42)–C(222)	171(1)
N(81)–Pd(41)–C(231)	140(1)	N(82)–Pd(42)–C(232)	133(1)
N(81)–Pd(41)–C(241)	175(1)	N(82)–Pd(42)–C(242)	100(1)
C(221)–Pd(41)–C(231)	38(1)	C(222)–Pd(42)–C(232)	39(1)
C(221)–Pd(41)–C(241)	74(2)	C(222)–Pd(42)–C(242)	71(1)
C(231)–Pd(41)–C(241)	37(2)	C(232)–Pd(42)–C(242)	38(1)

(*b*) Organic ligands

N(11)–C(11)	1.35(4)	N(12)–C(12)	1.38(3)
N(11)–C(31)	1.30(4)	N(12)–C(32)	1.36(3)
N(21)–C(41)	1.37(4)	N(22)–C(42)	1.39(4)
N(21)–C(51)	1.37(4)	N(22)–C(52)	1.50(4)
N(31)–C(21)	1.40(6)	N(32)–C(22)	1.45(3)
N(31)–C(31)	1.43(4)	N(32)–C(32)	1.34(3)

Table 2 (*continued*)

N(41)–C(41)	1.41(5)	N(42)–C(42)	1.39(4)
N(41)–C(61)	1.39(5)	N(42)–C(62)	1.40(5)
N(51)–C(71)	1.35(5)	N(52)–C(72)	1.45(4)
N(51)–C(91)	1.36(4)	N(52)–C(92)	1.37(4)
N(61)–C(101)	1.35(4)	N(62)–C(102)	1.46(4)
N(61)–C(111)	1.36(4)	N(62)–C(112)	1.40(4)
N(71)–C(81)	1.49(5)	N(72)–C(82)	1.46(4)
N(71)–C(91)	1.34(5)	N(72)–C(92)	1.32(3)
N(81)–C(101)	1.33(4)	N(82)–C(102)	1.41(4)
N(81)–C(121)	1.41(5)	N(82)–C(122)	1.32(4)
C(11)–C(21)	1.34(6)	C(12)–C(22)	1.34(4)
C(31)–C(41)	1.40(5)	C(32)–C(42)	1.35(4)
C(51)–C(61)	1.23(6)	C(52)–C(62)	1.37(5)
C(71)–C(81)	1.35(6)	C(72)–C(82)	1.33(5)
C(91)–C(101)	1.50(5)	C(92)–C(102)	1.38(4)
C(111)–C(121)	1.38(5)	C(112)–C(122)	1.28(5)
C(131)–C(141)	1.42(6)	C(132)–C(142)	1.36(5)
C(141)–C(151)	1.34(6)	C(142)–C(152)	1.44(5)
C(161)–C(171)	1.33(6)	C(162)–C(172)	1.36(5)
C(171)–C(181)	1.37(6)	C(172)–C(182)	1.38(5)
C(191)–C(201)	1.41(6)	C(192)–C(202)	1.36(6)
C(201)–C(211)	1.39(6)	C(202)–C(212)	1.50(6)
C(221)–C(231)	1.40(6)	C(222)–C(232)	1.39(5)
C(231)–C(241)	1.34(6)	C(232)–C(242)	1.37(5)

C(11)–N(11)–C(31)	107(3)	C(12)–N(12)–C(32)	105(2)
C(11)–N(11)–Pd(11)	125(2)	C(12)–N(12)–Pd(12)	123(2)
C(31)–N(11)–Pd(11)	127(2)	C(32)–N(12)–Pd(12)	131(2)
C(41)–N(21)–C(51)	105(3)	C(42)–N(22)–C(52)	106(2)
C(41)–N(21)–Pd(21)	129(2)	C(42)–N(22)–Pd(22)	133(2)
C(51)–N(21)–Pd(21)	121(2)	C(52)–N(22)–Pd(22)	118(2)
C(21)–N(31)–C(31)	101(3)	C(22)–N(32)–C(32)	103(3)
C(21)–N(31)–Pd(31)	139(3)	C(22)–N(32)–Pd(32)	139(2)
C(31)–N(31)–Pd(31)	116(2)	C(32)–N(32)–Pd(32)	117(2)
C(41)–N(41)–C(61)	103(3)	C(42)–N(42)–C(62)	103(3)
C(41)–N(41)–Pd(31)	111(2)	C(42)–N(42)–Pd(32)	112(2)
C(61)–N(41)–Pd(31)	146(3)	C(62)–N(42)–Pd(32)	144(2)
C(71)–N(51)–C(91)	103(3)	C(72)–N(52)–C(92)	104(2)
C(71)–N(51)–Pd(21)	124(2)	C(72)–N(52)–Pd(22)	123(2)
C(91)–N(51)–Pd(21)	129(2)	C(92)–N(52)–Pd(22)	130(2)
C(101)–N(61)–C(111)	105(3)	C(102)–N(62)–C(112)	107(2)
C(101)–N(61)–Pd(11)	133(2)	C(102)–N(62)–Pd(12)	129(2)
C(111)–N(61)–Pd(11)	119(2)	C(112)–N(62)–Pd(12)	122(2)
C(81)–N(71)–C(91)	101(3)	C(82)–N(72)–C(92)	100(2)
C(81)–N(71)–Pd(41)	141(2)	C(82)–N(72)–Pd(42)	142(2)
C(91)–N(71)–Pd(41)	118(2)	C(92)–N(72)–Pd(42)	117(2)
C(101)–N(81)–C(121)	107(3)	C(102)–N(82)–C(122)	109(2)
C(101)–N(81)–Pd(41)	113(2)	C(102)–N(82)–Pd(42)	107(2)
C(121)–N(81)–Pd(41)	140(2)	C(122)–N(82)–Pd(42)	144(2)
C(21)–C(11)–N(11)	110(3)	C(22)–C(12)–N(12)	109(2)
N(31)–C(21)–C(11)	109(4)	N(32)–C(22)–C(12)	108(2)
C(41)–C(31)–N(11)	136(3)	C(42)–C(32)–N(12)	131(2)
C(41)–C(31)–N(31)	111(3)	C(42)–C(32)–N(32)	114(2)
N(11)–C(31)–N(31)	112(3)	N(12)–C(32)–N(32)	114(2)
N(21)–C(41)–N(41)	108(3)	N(22)–C(42)–N(42)	112(2)
N(21)–C(41)–C(31)	131(3)	N(22)–C(42)–C(32)	130(3)
N(41)–C(41)–C(31)	121(3)	N(42)–C(42)–C(32)	118(3)
C(61)–C(51)–N(21)	111(3)	C(62)–C(52)–N(22)	103(3)
N(41)–C(61)–C(51)	112(4)	N(42)–C(62)–C(52)	115(3)
C(81)–C(71)–N(51)	112(3)	C(82)–C(72)–N(52)	105(3)
N(71)–C(81)–C(71)	106(3)	N(72)–C(82)–C(72)	113(3)
C(101)–C(91)–N(51)	131(3)	C(102)–C(92)–N(52)	131(3)
C(101)–C(91)–N(71)	112(3)	C(102)–C(92)–N(72)	112(2)
N(51)–C(91)–N(71)	116(3)	N(52)–C(92)–N(72)	117(2)
N(61)–C(101)–N(81)	112(3)	N(62)–C(102)–N(82)	103(2)
N(61)–C(101)–C(91)	130(3)	N(62)–C(102)–C(92)	134(3)
N(81)–C(101)–C(91)	117(3)	N(82)–C(102)–C(92)	123(3)
C(121)–C(111)–N(61)	111(3)	C(122)–C(112)–N(62)	108(3)
N(81)–C(121)–C(111)	105(3)	N(82)–C(122)–C(112)	113(3)
C(151)–C(141)–C(131)	124(4)	C(152)–C(142)–C(132)	124(3)
C(161)–C(171)–C(181)	137(4)	C(162)–C(172)–C(182)	139(3)
C(191)–C(201)–C(211)	101(3)	C(192)–C(202)–C(212)	112(4)
C(221)–C(231)–C(241)	144(4)	C(222)–C(232)–C(242)	124(3)

Table 2 (*continued*)

(*c*) Torsion angles

Pd(11)–N(11)–C(31)–C(41)	8.3
Pd(12)–N(12)–C(32)–C(42)	4.2
N(11)–C(31)–C(41)–N(21)	9.6
N(12)–C(32)–C(42)–N(22)	16.0
C(31)–C(41)–N(21)–Pd(21)	27.4
C(32)–C(42)–N(22)–Pd(22)	22.8
C(41)–N(21)–Pd(21)–N(51)	−136.1
C(42)–N(22)–Pd(22)–N(52)	−137.9
N(21)–Pd(21)–N(51)–C(91)	45.2
N(22)–Pd(22)–N(52)–C(92)	49.0
Pd(21)–N(51)–C(91)–C(101)	18.5
Pd(22)–N(52)–C(92)–C(102)	17.8
N(51)–C(91)–C(101)–N(61)	9.2
N(52)–C(92)–C(102)–N(62)	3.9
C(91)–C(101)–N(61)–Pd(11)	16.0
C(92)–C(102)–N(62)–Pd(12)	17.7
C(101)–N(61)–Pd(11)–N(11)	−126.4
C(102)–N(62)–Pd(12)–N(12)	−122.3
N(61)–Pd(11)–N(11)–C(31)	53.1
N(62)–Pd(12)–N(12)–C(32)	55.3

spectra of the cod derivatives are also consistent with the proposed arrangements of the metal atoms (see Experimental section). They also display the expected resonances for the inequivalent bi-imidazolate ring protons; nevertheless an unexplained singlet resonance has been found for the aromatic ring protons in bibenzimidazolate derivatives.

Table 1 lists the analytical data, conductivities in nitromethane (or in acetone), molecular weights, and decomposition points for all the isolated complexes. Further information on the i.r. and ^{1}H n.m.r. spectra is collected in the Experimental section.

X-Ray Structure of [Pd$_4$(η^3-C$_3$H$_5$)$_4$(μ-bim)$_2$]·CH$_2$Cl$_2$.—The crystal structure of [Pd$_4$(η^3-C$_3$H$_5$)$_4$(μ-bim)$_2$]·CH$_2$Cl$_2$ consists of tetranuclear Pd complexes and dichloromethane molecules of crystallization. The crystals consist of two essentially identical, but crystallographically independent, complexes and dichloromethane molecules (hereafter indicated as 1 and 2). A view of one of the two independent complexes with the atomic numbering system is shown in Figure 2. Selected bond distances and angles in the complexes 1 and 2 are given in Table 2.

Each complex, possessing an idealized C_2 symmetry, has a ' butterfly ' shape (Figure 3). The two bi-imidazolate anions each act as an unsymmetrical tetradentate ligand through the four N atoms from two imidazolate rings. Bonding occurs in a unidentate manner through two N atoms to two Pd atoms which are in a hinge position [Pd(1) and Pd(2)], forming the wings, and through the other two N atoms by chelation with another Pd atom [Pd(3) and Pd(4) respectively] on the wing-tip. The Pd(1) · · · Pd(2) hinge separation [3.128(4) and 3.101(4) Å in complexes 1 and 2] is rather short and can indicate a weak metal–metal interaction. The co-ordination of all four Pd atoms is completed by an allyl ligand, η^3-interacting through the three carbon atoms.

Both Pd–N (involving the bim^{2-} ligands) and Pd–C (involving the allyl ligands) bonds (in the range 2.01—2.10 and 2.06—2.19 Å respectively) are in good agreement with those found in other complexes with these ligands.

The Pd tetranuclear complex studied here is strictly comparable with [Rh$_4$(CO)$_8$(bim)$_2$] [12] where the bim^{2-} anions behave in the same manner and two carbonyl groups substitute an allyl ligand on each metal atom. Nevertheless the Rh–Rh separation is much shorter [2.975(1) Å].

Each bim^{2-} ligand consists of two imidazolate rings bonded through two carbon atoms [C(3) and C(4), C(9) and C(10)

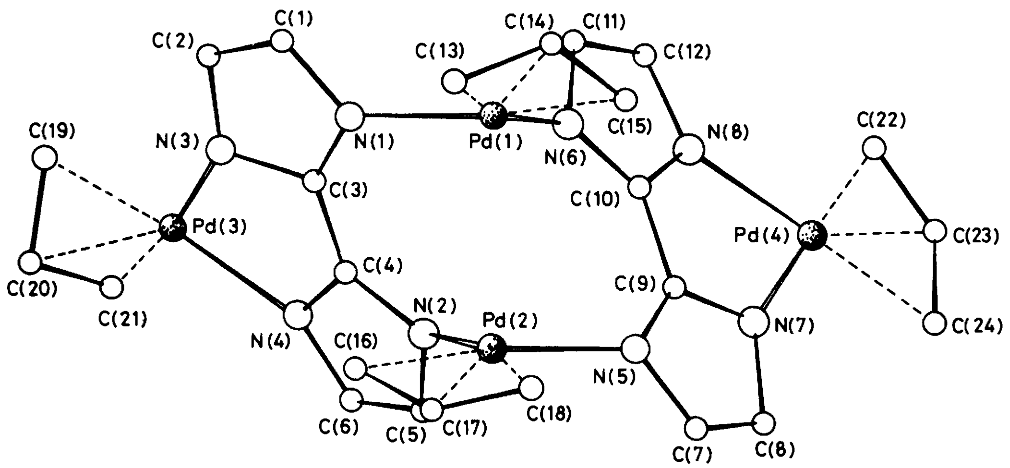


Figure 2. View, along the idealized two-fold axis, of one of the two independent complexes $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mu\text{-bim})_2]$ (9) with the atomic numbering scheme

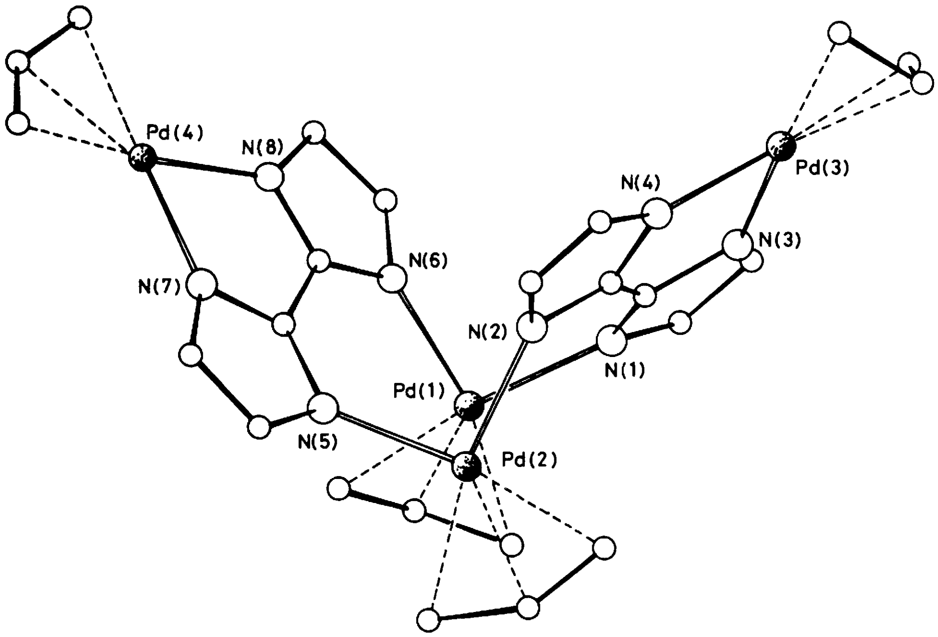


Figure 3. View of the complex $[Pd_4(\eta^3\text{-}C_3H_5)_4(\mu\text{-bim})_2]$ (9) showing its ' butterfly ' shape

respectively]. Each ring is planar with no atom deviating more than σ from the best five-atom least-squares plane. The two rings of each ligand are slightly twisted making dihedral angles of 9.7 and 5.1 in the complex 1 and 11.6 and 5.7° in the complex 2. A narrower angle (4.0°) has been found in $[Rh_4(CO)_8(bim)_2]$,[12] whereas the two rings have been found perfectly coplanar in $[Rh_2(cod)_2(bim)]$ [12] where the bim^{2-} dianion behaves as a symmetrical bichelating ligand. The separation between the chelating N(3), N(4), and N(7), N(8) atoms (2.65, 2.62 in complex 1 and 2.56, 2.65 Å in complex 2) is shorter than the separation between the N(1), N(2) and N(5), N(6) atoms (3.23, 3.28 in complex 1 and 3.15, 3.31 Å in complex 2); this trend is also observed in $[Rh_4(CO)_8(bim)_2]$ [2.625 and 3.218 Å respectively] [12] whereas the separations are equal [2.818 and 2.807 Å] in $[Rh_2(cod)_2(bim)]$ [12] with the ligand symmetrically bonded.

The two Pd(1) and Pd(2) atoms bridging the two bim^{2-} ligands form a ten-membered ring; the torsion angles are given in Table 2.

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 *ca.* 5×10^{-4} mol dm^{-3} acetone or nitromethane solutions with a Philips PW 9501/01 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. Molecular weights were determined with a Hitachi Perkin-Elmer 115 osmometer. ^{1}H N.m.r. spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ solutions at room temperature on a Varian FT-80A spectrophotometer (80 MHz) using $SiMe_4$ as internal standard. Decomposition points were measured in a Buchi apparatus.

Palladium(II) and rhodium(I) starting materials were obtained as described elsewhere: $[\{Pd(\eta^3\text{-}2\text{-}RC_3H_4)(\mu\text{-}Cl)\}_2]$ (R = H [3] or Me [4]), $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(acac)]$,[6] [Rh(Hbim)(cod)],[14] [Rh(acac)(cod)].[15] 2,2′-Bi-imidazole and 2,2′-bibenzimidazole were prepared according to the literature methods.[5] All reactions were carried out at room temperature under nitrogen and solvents were dried and distilled before use.

Preparation of [Pd(η^3-2-RC$_3$H$_4$)(HL)] [HL = Hbim, R = H (1) *or* Me (2); HL = Hbzim, R = H (3) *or* Me (4)].—*Method A*. A mixture of H$_2$L (1 mmol) and KOH (2 mmol) in 30 cm^3 of methanol–dichloromethane (1 : 1) was stirred for 2 h and [{Pd(η^3-2-RC$_3$H$_4$)(μ-Cl)}$_2$] (0.5 mmol) in dichloromethane (10 cm^3) was added. After stirring for 6 h the solution was filtered and the filtrate evaporated to dryness. The residue was washed with water (until no chloride anion could be detected in the washing liquid) and finally vacuum dried. Yields (%): (1), 63; (2), 60; (3), 48; (4), 33. I.r.: ν(N–H) *ca.* 3 000—2 300 cm^{-1}.

Method B. An equimolar mixture (0.8 mmol) of H$_2$L and [Pd(η^3-2-RC$_3$H$_4$)(acac)] (prepared *in situ* by treating [{Pd(η^3-2-RC$_3$H$_4$)(μ-Cl)}$_2$] with Tl(acac) in methanol, and removing the formed TlCl by filtration) was stirred with methanol (30 cm^3) for 3 h [(1) and (2)] or 15 h [(3) and (4)]. The complexes were isolated by partial vacuum evaporation [(3) and (4)] and subsequent addition of ether [(1) and (2)]. Yields (%): (1), 79, (2), 45; (3), 70; (4), 10.

Preparation of [Pd(η^3-2-RC$_3$H$_4$)(H$_2$L)][ClO$_4$] [H$_2$L = H$_2$bim, R = H (5) *or* Me (6); H$_2$L = H$_2$bzim, R = H (7) *or* Me (8)].—Silver perchlorate (0.58 mmol) was added to a solution of [{Pd(η^3-2-RC$_3$H$_4$)(μ-Cl)$_2$}] (0.29 mmol) in acetone (30 cm^3) and stirred for 1 h. The solution was filtered and H$_2$bim (0.58 mmol) added. After stirring for a further 4 h the suspension was filtered and the filtrate was vacuum evaporated to dryness. The solid (R = H) or oily (R = Me) residue was stirred with hexane to isolate the white complexes (5) and (6). For the off-white complexes (7) and (8), after addition of H$_2$bzim (0.58 mmol) the solution was stirred for 24 h. Yields (%): (5), 67; (6), 75; (7), 72; (8), 55. ^{1}H N.m.r. [(CD$_3$)$_2$CO]: (5) δ 7.57 (s, 2 H, bim), 7.41 (s, 2 H, bim), 5.76 (m, 1 H, H^2), 4.51 [d, 2 H, H$_{syn}$, J(H$_{syn}$H^2) = 6.9], 3.31 [d, 2 H, H$_{anti}$, J(H$_{anti}$H^2) = 12.3 Hz]; (6) δ 7.56 (s, 2 H, bim), 7.36 (s, 2 H, bim), 4.29 (s, 2 H, H$_{syn}$), 3.12 (s, 2 H, H$_{anti}$), 2.17 (s, 3 H, Me) p.p.m. I.r.: ν(N–H) 3 310—3 130; ν(ClO$_4$) ν_3, 1 140—1 040 (complex band); ν_4, 612—625 cm^{-1} (two bands).

Preparation of [Pd$_4$(η^3-2-RC$_3$H$_4$)$_4$(μ-L)$_2$] [L^{2-} = bim^{2-}, R = H (9) *or* Me (10); L^{2-} = bzim^{2-}, R = H (11) *or* Me (12)].—*Method A*. A mixture of [{Pd(η^3-2-RC$_3$H$_4$)(μ-Cl)}$_2$] (1 mmol) and K$_2$L [obtained by stirring H$_2$L (1 mmol) with KOH (2 mmol) in methanol (40 cm^3) (for H$_2$bim) or dichloromethane–methanol (1 : 1) (for H$_2$bzim)] was stirred for 2 h. Partial evaporation led to solids which were washed with water (until no chloride anion could be detected in the washing liquids) and vacuum-dried. Yields (%): (9), 80; (10), 74; (11), 90; (12), 65. Dichloromethane solutions lead to crystals which contain molecules of the solvent.

Method B. A mixture of H$_2$L (0.4 mmol) and [Pd(η^3-2-RC$_3$H$_4$)(acac)] (0.8 mmol) [prepared *in situ* in methanol (40 cm^3) (for H$_2$bim) or dichloromethane–methanol (1 : 1) (for H$_2$bzim)] was stirred for 4 h [(9), (10), (12)] or 16 h [(11)]. Complex (11) precipitated spontaneously, whilst complexes (9), (10), and (12) were isolated after partial evaporation and subsequent addition of diethyl ether. Yields (%): (9), 77; (10), 66; (11), 65; (12), 66. ^{1}H N.m.r. (CDCl$_3$): (9) δ 6.65 (m, 8 H, bim), 5.25 (m, 4 H, H^2 + H$^{2\prime}$), 3.85 [d, 4 H, H$_{syn}$, J(H$_{syn}$H^2) = 6.8], 3.60 [d, 4 H, H$_{syn}'$, J(H$_{syn}$H^2)$'$ = 6.8 Hz], 2.80 (m, 8 H, H$_{anti}$ + H$_{anti}'$): (10) δ 6.82 (s, 4 H, bim), 6.57 (s, 4 H, bim), 3.63 (s, 4 H, H$_{syn}$), 3.36 (s, 4 H, H$_{syn}'$), 2.71 (4 H, H$_{anti}$), 2.68 (s, 4 H, H$_{anti}'$), 2.12 (s, 6 H, Me), 2.01 (s, 6 H, Me$'$): (12) δ 7.16 (16 H, bzim), 4.16 (s, 4 H, H$_{syn}$), 3.75 (s, 4 H, H$_{syn}'$), 2.90 (s, 4 H, H$_{anti}$), 2.80 (s, 4 H, H$_{anti}'$), 2.22 (s, 6 H, Me), 1.99 (s, 6 H, Me$'$) p.p.m.

Preparation of Complexes (13) *and* (14).—The complexes [Pd(η^3-2-RC$_3$H$_4$)(acac)] (0.726 mmol) and [Rh(Hbim)(cod)] (0.726 mmol) in dichloromethane (20 cm^3) were stirred for 90 min. Addition of hexane to the yellow solution and partial concentration *in vacuo* led to the precipitation of yellow microcrystalline solids. Yields (%): (13), 78; (14), 87. Selected i.r. absorptions (Nujol mulls) for bim^{2-}: (13), 1 408s, 1 148, 1 132m; (14) 1 405s, 1 148m, 1 133m cm^{-1}. ^{1}H N.m.r. (CDCl$_3$): (13) δ 6.77 (4 H, bim), 6.44 (4 H, bim), 5.42 (m, 2 H, H^2), 4.38 (s, br, 8 H, cod vinyl protons), 3.60 (m, 4 H, H$_{syn}$), 2.83 (m, 4 H, H$_{anti}$), 2.46 (m, 8 H, cod methylene), 1.90 (m, 8 H, cod methylene); (14) δ 6.52 (s, 4 H, bim), 6.44 (s, 4 H, bim), 4.38 (s, br, 8 H, cod vinyl protons), 3.42 (s, 4 H, H$_{syn}$), 2.67 (s, 4 H, H$_{anti}$), 2.44 (m, 8 H, cod methylene), 2.15 (s, 6 H, Me), 1.96 (m, 8 H, cod methylene) p.p.m.

Preparation of Complexes (15) *and* (16).—The complexes [Pd(η^3-2-RC$_3$H$_4$)(Hbzim)] (0.22 mmol) and [Rh(acac)(cod)] (0.22 mmol) in dichloromethane (20 cm^3) were stirred for 1 h. Addition of hexane to the yellow solution and partial concentration under reduced pressure led to the precipitation of the yellow microcrystalline solids. Yields (%): (15), 85; (16), 83. ^{1}H N.m.r. (CDCl$_3$): (15) δ 7.10 (s, br, 16 H, bzim), 5.92 (m, 2 H, H^2), 5.05 (m, 8 H, cod vinyl protons), 4.05 [d, 4 H, H$_{syn}$, J(H$_{syn}$H^2) = 7.1], 3.03 [d, 4 H, H$_{anti}$, J(H$_{anti}$H^2) = 11.4 Hz], 2.47 (m, 8 H, cod methylene), 1.88 (m, 8 H, cod methylene); (16) δ 7.13 (s br, 16 H, bzim), 5.02 (s br, 8 H, cod vinyl protons), 2.99 (s, 4 H, H$_{anti}$), 2.84 (s, 4 H, H$_{syn}$), 2.50 (m, 8 H, cod methylene), 2.29 (s, 6 H, Me), 1.98 (m, 8 H, cod methylene) p.p.m.

Preparation of Complexes (17) *and* (18).—Dry carbon monoxide was bubbled for 20 min through a solution of complex (13) or (14) (0.07 mmol) in dichloromethane (25 cm^3). Addition of hexane and partial evaporation under reduced pressure led to the precipitation of the orange-red (17) or deep red (18) microcrystalline complexes. Yields (%): (17), 72; (18), 62. Selected i.r. absorptions (Nujol mulls) for bim^{2-}: (17) 1 403s, 1 147m, 1 134m; (18) 1 403s, 1 148m, 1 135m cm^{-1}. Carbonyl absorption (CH$_2$Cl$_2$): (17) 2 087s, 2 022s; (18) 2 084s, 2 016s cm^{-1}. ^{1}H N.m.r. (CDCl$_3$): (17) δ 6.94 (m, 4 H, bim), 6.75 (m, 4 H, bim), 5.52 (m, 2 H, H^2), 3.87 (m, 4 H, H$_{syn}$), 3.13 (m, 4 H, H$_{anti}$); (18) δ 6.80 (s, 4 H, bim), 6.54 (s, 4 H, bim), 3.48 (s, 4 H, H$_{syn}$), 2.77 (s, 4 H, H$_{anti}$), 2.17 (s, 6 H, Me) p.p.m.

Reactions of (15) *and* (16) *with Carbon Monoxide*.—Dry carbon monoxide was bubbled for 20 min through a solution of complex (15) or (16) (0.1 mmol) in dichloromethane (20 cm^3). An orange-coloured microcrystalline solid was collected by filtration and identified by analyses and i.r. as [Rh$_4$(CO)$_8$(μ-bzim)$_2$] (Found: C, 38.80; H, 1.30; N, 10.65. C$_{36}$H$_{16}$N$_8$O$_8$Rh$_4$ requires C, 39.30; H, 1.45; N, 10.2%). I.r., ν(CO) (Nujol mulls): 2 089s, 2 083 (sh), 2 049 (sh), 2 036s, 2 020 (sh) cm^{-1}.[14] Addition of hexane to the filtrate and partial evaporation under reduced pressure yielded yellow solids which were identified as a mixture of (11) or (12) with [Rh$_4$(CO)$_8$(μ-bzim)$_2$].

X-Ray Data Collection: Structure Determination and Refinement of the Complex [Pd$_4$(η^3-C$_3$H$_5$)$_4$(μ-bim)$_2$]·CH$_2$Cl$_2$.—A yellow plate-like crystal having approximate dimensions 0.07 × 0.30 × 0.45 mm was used for data collection. The unit-cell parameters were obtained from a least-squares refinement of

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

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd(11)	10 487(2)	8 614(1)	3 203(2)	C(121)	10 890(27)	8 667(16)	6 645(30)
Pd(21)	8 987(2)	7 358(1)	1 886(2)	C(131)	10 330(32)	9 094(18)	1 853(30)
Pd(31)	13 392(2)	6 258(1)	3 638(2)	C(141)	9 968(32)	9 520(17)	2 756(35)
Pd(41)	8 593(2)	8 138(1)	6 636(2)	C(151)	9 222(28)	9 338(18)	3 139(36)
Pd(12)	3 424(2)	7 398(1)	−104(2)	C(161)	9 519(28)	7 057(18)	399(29)
Pd(22)	3 440(2)	6 975(1)	−2 648(2)	C(171)	8 475(33)	7 203(24)	79(31)
Pd(32)	7 099(2)	5 464(1)	−231(2)	C(181)	7 799(29)	7 666(18)	519(30)
Pd(42)	6 112(2)	9 460(1)	−542(3)	C(191)	15 065(27)	6 076(19)	4 045(38)
Cl(1)	2 770(10)	−6(6)	5 176(11)	C(201)	14 541(28)	5 450(16)	3 461(32)
Cl(2)	4 203(11)	836(7)	4 913(12)	C(211)	14 030(38)	5 396(21)	4 235(39)
Cl(3)	573(9)	3 780(6)	2 933(10)	C(221)	9 213(31)	8 464(21)	8 509(29)
Cl(4)	1 743(10)	4 397(6)	5 292(11)	C(231)	8 133(31)	8 260(21)	8 122(30)
N(11)	11 825(20)	8 000(12)	3 112(22)	C(241)	7 378(30)	7 873(21)	7 247(36)
N(21)	10 183(18)	6 863(11)	2 887(20)	C(12)	4 507(20)	6 308(12)	1 075(22)
N(31)	13 019(20)	7 150(12)	3 255(22)	C(22)	5 312(19)	5 860(11)	1 134(21)
N(41)	11 716(23)	6 285(14)	3 371(25)	C(32)	5 181(19)	6 272(11)	−302(21)
N(51)	8 193(21)	7 620(12)	3 103(23)	C(42)	5 510(24)	6 375(14)	−1 147(26)
N(61)	10 446(18)	8 429(10)	4 710(19)	C(52)	5 775(24)	6 685(14)	−2 639(26)
N(71)	7 996(20)	7 792(12)	4 894(21)	C(62)	6 600(31)	6 302(19)	−2 171(33)
N(81)	9 876(21)	8 349(13)	6 146(24)	C(72)	3 850(27)	8 128(16)	−3 519(29)
N(12)	4 412(16)	6 578(10)	174(18)	C(82)	4 498(26)	8 663(15)	−3 103(28)
N(22)	5 015(18)	6 720(11)	−1 959(20)	C(92)	4 615(21)	8 345(12)	−1 613(23)
N(32)	5 791(17)	5 843(10)	243(18)	C(102)	4 967(22)	8 390(13)	−450(24)
N(42)	6 478(19)	6 084(11)	−1 278(20)	C(112)	5 362(24)	8 309(14)	1 398(25)
N(52)	3 930(17)	7 895(10)	−2 527(19)	C(122)	5 913(26)	8 784(16)	1 397(29)
N(62)	4 727(19)	8 022(11)	267(20)	C(132)	2 243(25)	8 177(14)	−158(30)
N(72)	5 001(15)	8 833(9)	−1 853(17)	C(142)	1 726(25)	7 576(17)	−547(35)
N(82)	5 751(18)	8 856(11)	355(20)	C(152)	2 002(23)	7 056(15)	37(27)
C(11)	12 802(25)	8 214(15)	3 194(28)	C(162)	1 752(20)	7 015(13)	−3 600(24)
C(21)	13 537(37)	7 736(23)	3 361(40)	C(172)	1 958(25)	6 454(16)	−3 229(34)
C(31)	11 939(25)	7 381(15)	3 140(28)	C(182)	2 782(26)	6 001(14)	−3 022(31)
C(41)	11 276(26)	6 882(16)	3 110(28)	C(192)	8 559(28)	5 085(19)	−687(34)
C(51)	9 978(27)	6 263(16)	3 029(30)	C(202)	8 100(36)	4 610(19)	−433(38)
C(61)	10 815(32)	5 942(19)	3 275(34)	C(212)	7 979(32)	4 853(19)	749(33)
C(71)	7 226(33)	7 365(19)	2 960(35)	C(222)	6 609(23)	10 163(14)	−1 171(25)
C(81)	7 080(29)	7 392(17)	3 979(32)	C(232)	7 391(26)	10 102(18)	−170(29)
C(91)	8 603(28)	7 874(17)	4 267(31)	C(242)	7 182(28)	10 141(17)	837(27)
C(101)	9 661(25)	8 211(15)	5 006(28)	C(25)	3 028(26)	769(15)	5 162(38)
C(111)	11 179(29)	8 734(17)	5 726(32)	C(26)	919(29)	3 735(16)	4 368(21)

the θ values of 29 reflections accurately measured on a Siemens AED single-crystal diffractometer.

Crystal data. $C_{25}H_{30}Cl_2N_8Pd_4$, $M = 939.07$, Triclinic, $a = 13.081(8)$, $b = 20.843(13)$, $c = 12.722(7)$ Å, $\alpha = 106.78(4)$, $\beta = 108.56(4)$, $\gamma = 84.98(3)^\circ$, $U = 3\,148(3)$ Å^3, $Z = 4$, $D_c = 1.981$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $F(000) = 1\,816$, μ(Mo-K_α) $= 24.22$ cm^{-1}, space group $P\bar{1}$ from structure determination.

A total of 8 767 independent reflections, with θ in the range 3—24°, were collected on the same diffractometer using niobium-filtered Mo-K_α radiation and the θ/2θ scan technique. 4 667 Reflections having $I \geqslant 2\sigma(I)$ were considered observed and employed in the analysis. One reflection was remeasured after 20 reflections as a check on crystal and instrument stability; no significant change in the measured intensity of this reflection was observed during the data collection. 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.

The structure was solved by direct and Fourier methods. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs[16] with first isotropic thermal parameters and then anisotropic thermal parameters for the Pd atoms only. No attempt was made to localize hydrogen atoms. The final *R* value was 0.084 (observed reflections only). The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used in the first cycles of refinement, the weight calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$ (where $K = 0.4416$ and $g = 0.0483$) was chosen in the final cycles. The atomic scattering factors used, corrected for the anomalous dispersion of Pd and Cl, were taken from ref. 17. Final atomic co-ordinates of the non-hydrogen atoms are given in Table 3. All calculations were carried out 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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