Benzamidinatorhodium Complexes. *X*-Ray Structures of $[Rh\{CPh(NPh)_2\}(cod)]$ and $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(tfbb)_2]$†

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Complexes $[\{MCl(diolefin)\}_2]$ (M = Rh or Ir) react with *N,N'*-diphenylbenzamidinate to yield binuclear $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(diolefin)_2]$ [diolefin = norbornadiene (nbd) or tetrafluorobarrelene (tfbb)] or mononuclear $[M\{CPh(NPh)_2\}(cod)]$ (cod = cyclo-octa-1,5-diene) complexes. The rhodium complexes react with carbon monoxide to give $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(CO)_4]$. The latter complex undergoes a two-centre oxidative addition with iodine yielding the rhodium(II) complex $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2I_2(CO)_4]$. An A-frame compound of formula $[Rh_2\{\mu\text{-}CPh(NPh)_2\}(\mu\text{-}dppm)_2(CO)_2]ClO_4$ (dppm = $Ph_2PCH_2PPh_2$) has been isolated. Some related mononuclear complexes containing a unidentate benzamidine ligand have also been prepared. The crystal structures of the complexes $[Rh\{CPh(NPh)_2\}(cod)]$ (**1**) and $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(tfbb)_2]$ (**4**) have been determined by *X*-ray diffraction methods. Complex (**1**) crystallizes in the monoclinic space group $P2_1/n$, with a = 10.315(2), b = 19.507(3), c = 11.429(3) Å, β = 103.62(1)°, and Z = 4. Crystals of compound (**4**) are monoclinic, space group $P2_1/c$, with Z = 4 and a unit cell of dimensions a = 21.692(2), b = 12.512(2), c = 19.969(2) Å, and β = 107.90(1)°. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares to R 0.040 and 0.047, respectively. The structure of (**1**) is mononuclear with the *N,N'*-diphenylbenzamidinate acting as a chelating ligand, through the nitrogen atoms. In contrast, complex (**4**) is binuclear with the benzamidinate ligand bridging two rhodium atoms [Rh ··· Rh 2.982(3) Å].

Several nitrogen-donor ligands containing  units such as naphthyridine,[1] azaindole,[2] acetamidine,[3] or formamidines[4—6] have proved to be versatile ligands towards rhodium. They can attach to the metals in a unidentate, chelating, or bridging mode. In some cases, the co-ordination mode depends on the auxiliary ligands; thus, while $[Rh(cod)(2Me\text{-}napy)]^+$ is mononuclear, binuclear complexes of formula $[Rh_2(\mu\text{-}2Me\text{-}napy)_2L_4]^{2+}$ are formed when L_2 = norborna-2,5-diene (nbd), tetrafluorobarrelene, or L = CO (cod = cyclo-octa-1,5-diene, 2Me-napy = 2-methyl-1,8-naphthyridine).[1] We now report some new binuclear and mononuclear benzamidinate and benzamidine rhodium complexes and the determination of the crystal structures of $[Rh\{CPh(NPh)_2\}(cod)]$ and $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(tfbb)_2]$,† that, as far as we know, are the first reported crystal structures of amidinatorhodium(I) complexes.

Results and Discussion

The reaction of $[\{MCl(diolefin)\}_2]$ complexes (M = Rh or Ir, diolefin = cod;[7,8] M = Rh, diolefin = tfbb[9] or nbd[10]) with potassium *N,N'*-diphenylbenzamidinate (prepared *in situ* from *N,N'*-diphenylbenzamidine[11] and potassium hydroxide) results in the isolation in good yields of $[\{M[CPh(NPh)_2](diolefin)\}_x]$ complexes. Molecular-weight measurements in $CHCl_3$ show that the cyclo-octadiene complexes $[M\{CPh(NPh)_2\}(cod)]$ are mononuclear, but binuclear rhodium complexes of formula $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(diolefin)_2]$ are obtained for diolefin = nbd or tfbb. The combination of the higher steric hindrance and lower π-acceptor of the cod ligand in comparison with other diolefins (nbd, tfbb) seems to determine the nuclearity of the isolated complexes. In order to confirm the chelating or binucleating ability of this ligand and to determine the rhodium–rhodium distance in the binuclear complexes, the structures of $[Rh\{CPh(NPh)_2\}(cod)]$ (**1**) and $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(tfbb)_2]$ (**4**) were solved by *X*-ray methods (see below). In contrast, binuclear di-μ-formamidinato-bis(diolefinrhodium) complexes are obtained for cod and nbd, when the related di-*p*-tolylformamidinate ligand was used.[5] Furthermore, a monomer–dimer equilibrium has been detected for the $[Rh\{N(NC_6H_4F)_2\}(cod)]$ complex by n.m.r. spectroscopy.[12]

Interestingly, bubbling of carbon monoxide through a dichloromethane solution of $[Rh\{CPh(NPh)_2\}(cod)]$ gives rise to the tetracarbonyl derivative $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(CO)_4]$ (**5**). As expected, this complex is also obtained by carbonylation of $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(diolefin)_2]$ derivatives. The i.r. spectrum shows three absorptions at 2 070, 2 045, and 2 000 cm^{-1} in accord with a C_{2v} symmetry, as proposed for related $[Rh_2\{\mu\text{-}X(NR)_2\}_2(CO)_4]$ (X = N or CR'; R = aryl, R' = H or Me) complexes.[3,4] The last complexes readily undergo carbonyl-substitution reactions with triphenylphosphine at room temperature in hexane giving $[Rh_2\{\mu\text{-}X(NR)_2\}_2(CO)_2(PPh_3)_2]$. In contrast, complex (**5**) is rather inert and no reaction was observed after 24 h, by addition of PPh_3 or bis(diphenylphosphino)methane (dppm), at room temperature, to a hexane solution of $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(CO)_4]$. However, the A-frame complex $[Rh_2\{\mu\text{-}CPh(NPh)_2\}(\mu\text{-}dppm)_2(CO)_2]ClO_4$ (**6**), related to some $[Rh_2(\mu\text{-}pz)(\mu\text{-}dppm)_2(CO)_2]^+$ derivatives (pz = pyrazolate-type ligand) recently prepared and character-

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† (η-Cyclo-octa-1,5-diene)(*N,N'*-diphenylbenzamidinato-*NN'*)-rhodium and di-μ-(*N,N'*-diphenylbenzamidinato-*NN'*)-bis{(2—3:7—8-η-tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene)rhodium}.

Supplementary data available: (No. SUP 56204, 7 pp.): H-atom coordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

* tfbb = Tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tetrafluorobenzobarrelene).

Table 1. Analytical data for the compounds

	Analysis[a] (%)			M[a]		
Complex	C	H	N	($CHCl_3$)	Colour	Yield
(**1**) $[Rh\{CPh(NPh)_2\}(cod)]$	67.05	5.55	5.80	464	Yellow	78
	(67.2)	(5.65)	(5.80)	(482)		
(**2**) $[Ir\{CPh(NPh)_2\}(cod)]$	55.85	4.50	4.50	624	Orange	65
	(56.7)	(4.75)	(4.90)	(572)		
(**3**) $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(nbd)_2]$	66.0	5.05	5.85	983	Red	70
	(66.95)	(4.95)	(6.00)	(932)		
(**4**) $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(tfbb)_2]$	61.8	3.75	5.15	1 125	Red	85
	(62.0)	(3.55)	(4.65)	(1 200)		
(**5**) $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(CO)_4]$	58.25	4.20	6.25	802	Red	87
	(58.6)	(3.75)	(6.50)	(860)		
(**6**) $[Rh_2\{\mu\text{-}CPh(NPh)_2\}(\mu\text{-}dppm)_2(CO)_2]ClO_4$	61.1	4.75	1.90	b	Red	65
	(60.85)	(4.05)	(2.00)			
(**7**) $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2I_2(CO)_4]$	45.05	2.70	5.05	1 116	Violet	75
	(45.25)	(2.70)	(5.05)	(1 114)		
(**8**) $[RhCl(PhN{=}CPh{-}NHPh)(cod)]$	61.85	5.70	5.15		Yellow	90
	(62.5)	(5.45)	(5.40)			
(**9**) $[RhCl(PhN{=}CPh{-}NHPh)(tfbb)]$	58.2	3.65	4.10		Yellow	80
	(58.45)	(3.50)	(4.40)			
(**10**) $[IrCl(PhN{=}CPh{-}NHPh)(cod)]$	53.3	4.65	4.60		Yellow	85
	(52.75)	(4.80)	(4.55)			
(**11**) $[Rh(PhN{=}CPh{-}NHPh)(cod)(PPh_3)]ClO_4$	62.85	5.65	3.05	c	Yellow	70
	(63.95)	(5.05)	(3.30)			
(**12**) $[Rh(PhN{=}CPh{-}NHPh)(tfbb)(PPh_3)]ClO_4$	59.65	3.75	2.50	d	Yellow	62
	(61.1)	(3.85)	(2.90)			

[a] Calculated values are given in parentheses. [b] Λ_M = 120 ohm^{-1} cm^2 mol^{-1}. [c] Λ_M = 115 ohm^{-1} cm^2 mol^{-1}. [d] Λ_M = 100 ohm^{-1} cm^2 mol^{-1}.

ized in our laboratory,[13] was isolated by addition of benzamidinate anion to the solvated dication $[Rh_2(\mu\text{-}dppm)_2(CO)_2(Me_2CO)_2]^{2+}$, prepared by adding silver perchlorate to *trans*-$[Rh_2Cl_2(\mu\text{-}dppm)_2(CO)_2]$.[14]

The addition of 1 equivalent of iodine to hexane solutions of the tetracarbonyl complex (**5**) results in the precipitation of a violet complex of formula $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2I_2(CO)_4]$ (**7**). The carbonyl i.r. spectrum has bands at 2 100, 2 080, and 2 060 cm^{-1}, with a pattern similar to that of the parent compound (**5**), suggesting a related structure. Furthermore, the observed shift to higher wavenumber of the ν(CO) bands of (**7**) relative to (**5**) suggests a two-centre oxidative addition with concurrent metal–metal bond formation, as previously observed in related binuclear complexes containing rhodium atoms in close proximity.[15,16]

Neutral complexes of formula $[MCl(PhN{=}CPh{-}NHPh)(diolefin)]$ (**8**)—(**10**) containing the benzamidine ligand can be prepared by interaction of the ligand with the corresponding binuclear chloro-complexes $[\{MCl(diolefin)\}_2]$ (M = Rh or Ir). Bubbling of carbon monoxide through a dichloromethane solution of $[RhCl(PhN{=}CPh{-}NHPh)(cod)]$ gives rise to the tetracarbonyl complex (**5**). The formation of the latter was also observed upon treatment of $[RhCl(PhN{=}CPh{-}NHPh)(cod)]$ with $[Rh(acac)(CO)_2]$ (acac = acetylacetonate), in an unsuccessful attempt to prepare an unsymmetrical binuclear complex.

Addition of perchloric acid to an equimolecular dichloromethane solution of $[Rh\{CPh(NPh)_2\}(cod)]$ and PPh_3 leads to protonation of the benzamidinate ligand and formation of the compound $[Rh(PhN{=}CPh{-}NHPh)(cod)(PPh_3)]ClO_4$ (**11**). Attempts to prepare the related cationic complex with tfbb diolefin ligand using the same synthetic method were unsuccessful, but the expected compound $[Rh(PhN{=}CPh{-}NHPh)(tfbb)(PPh_3)]ClO_4$ (**12**) was prepared by addition of silver perchlorate and PPh_3 to the neutral complex $[RhCl(PhN{=}CPh{-}NHPh)(tfbb)]$ (**9**).

All the above mentioned complexes exhibit strong bands due to ν(N$\overset{..}{-}$C$\overset{..}{-}$N) at *ca.* 1 600 cm^{-1}. In addition, a ν(N–H) band at *ca.* 3 200 cm^{-1} is observed for the benzamidine derivatives, together with the characteristic bands of the co-ordinated diolefin, carbonyl, or triphenylphosphine ligands. Table 1 collects analytical and physical data for the isolated complexes.

Description of the Crystal Structures.—$[Rh\{CPh(NPh)_2\}(cod)]$ (**1**). The solid state structure of complex (**1**) is shown in Figure 1 together with the atomic numbering scheme. Selected bond distances and angles are given in Table 2. The structure consists of a *N*,*N'*-diphenylbenzamidinate ligand bonded to the rhodium atom through its nitrogen atoms; the co-ordination around the metal is completed by a cyclo-octa-1,5-diene molecule interacting through the two olefinic bonds. The rhodium atom has a square-planar environment, the deviations of m(1), m(2), N(1), and N(2) [m(1) and m(2) being the midpoints of the olefinic C(20)–C(21) and C(24)–C(25) bonds] from the mean plane passing through them being 0.001, −0.001, −0.026, and 0.026 Å with the rhodium atom out of this plane by 0.032 Å. The bite angle of the chelating benzamidinate ligand, N(1)–Rh–N(2) 63.2(2)°, is very narrow but close to the values found for chelating amidinate ligands[17] or for related isoelectronic triazenido-ligands.[18,19]

Complex (**1**) has no crystallographically imposed symmetry, but shows a pseudo-C_2 symmetry with the two-fold axis passing through the Rh, C(1), and C(8) atoms. The four-membered chelate ring is strictly planar [deviations of Rh, N(1), N(2), and C(1): −0.001, 0.003, 0.003, and −0.005 Å], with the C(2), C(8), and C(14) atoms deviating from this plane by −0.262, 0.005, and 0.219 Å. The chelation plane is practically coincident with the co-ordination plane, the dihedral angle between the two planes being 1.8.°

It is noteworthy that in the benzamidinate ligand the N(1)–C(1) and N(2)–C(1) bond distances are almost equal [1.356(9) and 1.331(9) Å] and intermediate between the expected values for a single and double bond. This is indicative of extensive π-electronic delocalization along the N–C–N

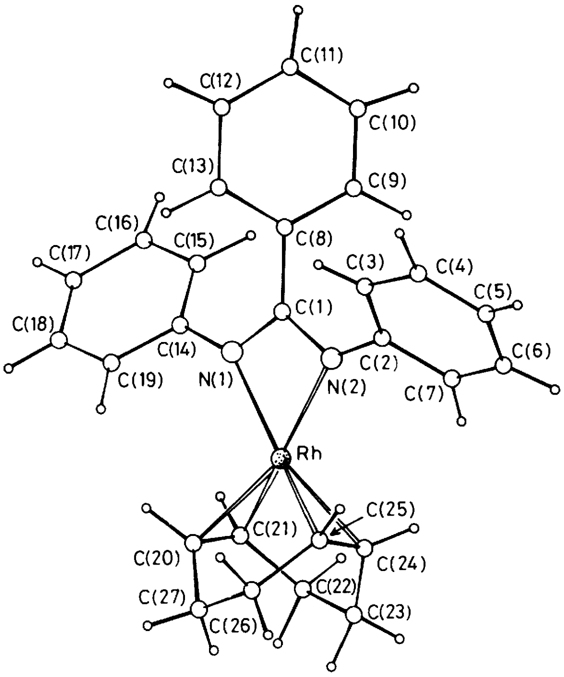

Figure 1. View of the mononuclear complex [Rh{CPh(NPh)$_2$}(cod)] with the atomic numbering scheme

Table 2. Selected bond distances (Å) and angles (°) for monomeric complex (**1**)

Co-ordination around the Rh atom

Rh–N(1)	2.106(6)	Rh–N(2)	2.095(6)
Rh–C(20)	2.151(7)	Rh–C(21)	2.133(8)
Rh–C(24)	2.151(8)	Rh–C(25)	2.127(9)
N(1)–Rh–N(2)	63.2(2)	N(2)–Rh–C(25)	100.0(3)
N(1)–Rh–C(20)	105.0(3)	C(20)–Rh–C(21)	39.2(3)
N(1)–Rh–C(21)	102.1(3)	C(20)–Rh–C(24)	90.2(3)
N(1)–Rh–C(24)	160.9(3)	C(20)–Rh–C(25)	82.7(3)
N(1)–Rh–C(25)	153.2(3)	C(21)–Rh–C(24)	82.3(3)
N(2)–Rh–C(20)	157.3(3)	C(21)–Rh–C(25)	99.8(3)
N(2)–Rh–C(21)	156.6(3)	C(24)–Rh–C(25)	38.5(3)
N(2)–Rh–C(24)	106.0(3)		

Cyclo-octa-1,5-diene ligand

C(20)–C(21)	1.438(10)	C(23)–C(24)	1.554(13)
C(20)–C(27)	1.511(12)	C(24)–C(25)	1.412(12)
C(21)–C(22)	1.515(11)	C(25)–C(26)	1.535(11)
C(22)–C(23)	1.566(14)	C(26)–C(27)	1.574(14)
Rh–C(20)–C(21)	69.7(4)	Rh–C(24)–C(23)	112.4(5)
Rh–C(20)–C(27)	113.0(5)	Rh–C(24)–C(25)	69.8(5)
C(21)–C(20)–C(27)	124.3(7)	C(23)–C(24)–C(25)	124.1(7)
Rh–C(21)–C(20)	71.1(4)	Rh–C(25)–C(24)	71.7(5)
Rh–C(21)–C(22)	110.3(5)	Rh–C(25)–C(26)	108.9(6)
C(20)–C(21)–C(22)	126.2(7)	C(24)–C(25)–C(26)	126.2(7)
C(21)–C(22)–C(23)	111.8(7)	C(25)–C(26)–C(27)	111.7(7)
C(22)–C(23)–C(24)	110.8(7)	C(20)–C(27)–C(26)	111.2(7)

N,N'-Diphenylbenzamidinate ligand

N(1)–C(1)	1.356(9)	N(2)–C(1)	1.331(9)
N(1)–C(14)	1.415(11)	N(2)–C(2)	1.411(10)
C(1)–C(8)	1.490(8)		
Rh–N(1)–C(1)	92.8(4)	C(1)–N(2)–C(2)	126.8(6)
Rh–N(1)–C(14)	139.7(5)	N(1)–C(1)–N(2)	110.0(6)
C(1)–N(1)–C(14)	126.3(6)	N(1)–C(1)–C(8)	125.7(6)
Rh–N(2)–C(1)	94.0(4)	N(2)–C(1)–C(8)	124.3(6)
Rh–N(2)–C(2)	137.1(5)		

moiety, also in accord with the presence in the i.r. spectrum of the complex of the N$\dot{-}$C$\dot{-}$N stretching vibration in the region of 1 600 cm^{-1}, as reported before.[5,6]

The phenyl groups are so disposed as to minimize steric hindrance. The dihedral angles between the mean planes of the phenyl groups [bonded to N(1), C(1), and N(2) respectively] and the chelation plane are 41.8, 54.9, and 44.6°.

The Rh–N bond distances [2.106(6) and 2.095(6) Å] are comparable with those reported for rhodium(I) complexes with related N-containing ligands (*e.g.* naphthyridine,[1] pyrazolate,[20] or azaindolate[2]). Also the Rh–C bond distances (2.12—2.15 Å) are quite regular when compared with other bond distances involving the cod ligand[21,22] or ligands exhibiting similar behaviour such as norborna-2,5-diene.[1,2] Both co-ordinated double bonds, C(20)–C(21) and C(24)–C(25), have lengths [1.438(10) and 1.412(12) Å] longer than in free cod (1.34 Å),[23] as expected. The carbon atoms of cod involved in co-ordination are only approximately coplanar, the deviations of C(20), C(21), C(24), and C(25) from the mean plane passing through them (−0.071, 0.072, −0.074, and 0.076 Å respectively) denoting a slight tetrahedral distortion. This plane is almost perpendicular to the co-ordination plane (the dihedral angle being 88.6°).

[Rh$_2${μ-CPh(NPh)$_2$}$_2$(tfbb)$_2$] (**4**). A perspective view of the structure of complex (**4**) with the atom labelling is shown in Figure 2. Selected bond distances and angles are given in Table 3.

In contrast with complex (**1**) this compound is binuclear with two *N,N'*-diphenylbenzamidinate ligands bridging two rhodium atoms. This behaviour of the benzamidinate, or in general of amidinate groups, as a bridging ligand between metal atoms has been previously reported for Re, Mo, and Cr.[24—26]

The co-ordination at each Rh centre, besides the two N atoms from the benzamidinate ligands, involves also a tfbb molecule interacting through its two olefinic bonds. Taking into account the midpoints of the two double bonds and the two N atoms, each rhodium atom is in a slightly distorted square-planar environment. The deviations of N(1), N(2), m(1), and m(2) [m(1) and m(2) being the midpoints of the C(53)–C(54) and C(51)–C(56) double bonds] from the mean plane passing through them are −0.271, 0.269, −0.002, and 0.002 Å respectively with Rh(1) out of this plane by 0.171 Å. The deviations of N(3), N(4), m(3), and m(4) [m(3) and m(4) are the midpoints of the C(41)–C(42) and C(39)–C(44) double bonds] from the mean plane passing through them are 0.320, −0.324, 0.004, and −0.004 Å with Rh(2) out of this plane by −0.170 Å. The large dihedral angle (52.2°) between the two co-ordination planes is probably determined by the steric requirements of the tetrafluorobarrelene ligands. The two rhodium co-ordination planes are usually parallel in most of the complexes with metal–metal multiple bonds studied by Cotton and co-workers.[24—26] The complex as whole shows, as for (**1**), a pseudo-C_2 symmetry with the two-fold axis passing through the middle of the Rh–Rh and C(1)–C(2) segments.

As in complex (**1**) the N–C bond distances are almost equal in both benzamidinate ligands [1.317(9) and 1.339(7) Å for C(2)–N(2) and C(2)–N(3); 1.350(7) and 1.346(7) Å for C(1)–N(1) and C(1)–N(4)] confirming the π-electronic delocalization along the N–C–N moiety. The two five-membered Rh–N–C–N–Rh rings are not planar as found also in the reported structures of heterometallic complexes Cu(Ag)–Rh(Ir) with isoelectronic triazenido-ligands.[27,28] In these rings the torsion angles are comparable: Rh(1)–N(1)–C(1)–N(4) 25.8, Rh(1)–N(2)–C(2)–N(3) 28.0; Rh(2)–N(3)–C(2)–N(2) 17.2, and Rh(2)–N(4)–C(1)–N(1) 17.6°. Atoms Rh(1), Rh(2), N(2), C(2), and N(3) are out of the mean plane passing through them by −0.051, 0.049,

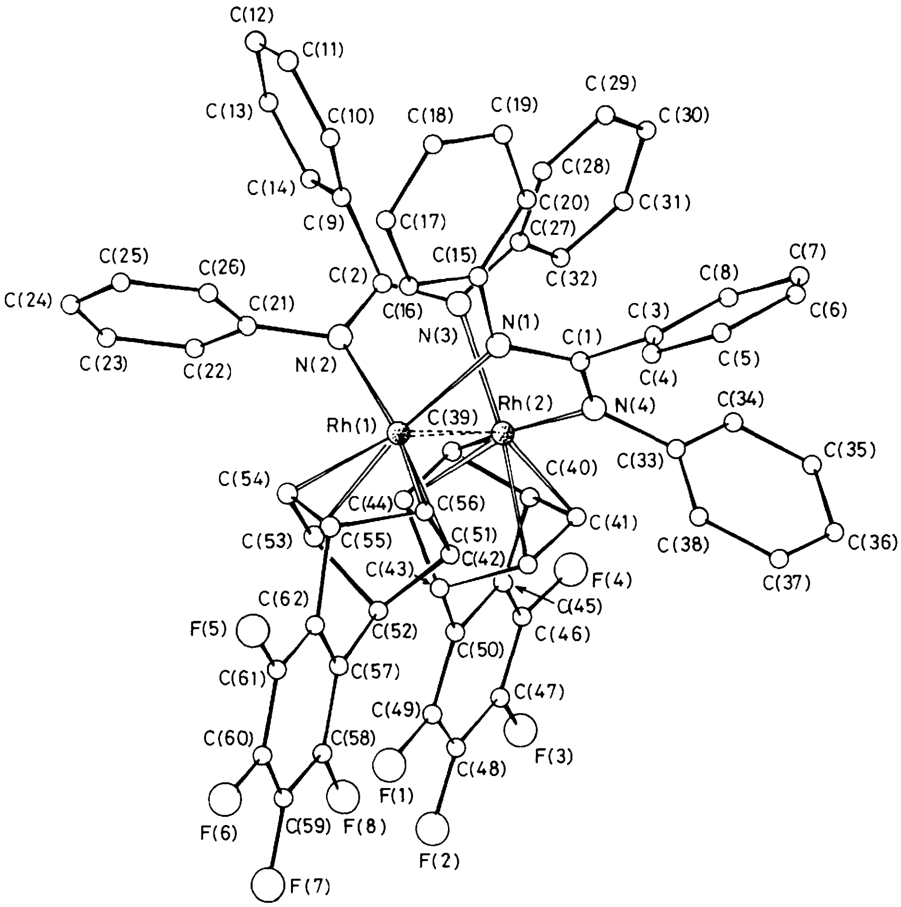

Figure 2. View of the binuclear complex $[Rh_2\{\mu\text{-}CPh(NPh)_2\}_2(tfbb)_2]$ with the atomic numbering scheme

0.475, −0.007, and −0.453 Å respectively; Rh(1), Rh(2), N(1), C(1), and N(4) are out of the mean plane through them by −0.043, 0.045, 0.569, 0.029, and −0.430 Å respectively, with a dihedral angle between the two planes of 94.2°.

The distance between the bridged rhodium atoms is short [2.982(3) Å]. Shorter distances ranging from 2.612 to 2.841 Å have been found in some binuclear complexes with carbonyl or dppm bridges;[29,30] these distances were considered indicative of the presence of a metal–metal bond. Separations of 2.916 and 2.975 Å have been found in some related rhodium(I) complexes[1,22] and the presence of a metal–metal interaction was postulated. In our case the presence of some Rh–Rh interaction is suggested by the deviation of the metal atoms from a square co-ordination plane towards the other rhodium atom, 0.171 Å for Rh(1) and 0.170 Å for Rh(2).

The Rh–N bond distances, 2.086—2.138 Å, are comparable with those observed for complex (**1**) and with those reported for complexes with ligands containing two nitrogen atoms bridging two Rh atoms (pyrazolate,[20] imidazolate,[31] bi-imidazolate,[22] and 7-azaindolate[2]). The tfbb ligand presents no peculiar structural features, including the Rh–C bond distances compared with other complexes of tfbb.[32] In the two tfbb molecules the carbon atoms involved in co-ordination to the metals are strictly planar. The plane passing through C(51), C(53), C(54), and C(56) forms a dihedral angle of 83.3° with the co-ordination mean plane of Rh(1); the plane through C(39), C(41), C(42), and C(44) forms a dihedral angle of 83.2° with the co-ordination mean plane of Rh(2). The two planes form a dihedral angle of 110.8°. It is noteworthy that the two substituted phenyl rings of the two tfbb molecules are nearly parallel, the dihedral angle being only 9.3°.

Experimental

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Infrared spectra (range 4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets or dichloromethane solutions and NaCl windows. Conductivities were measured for *ca.* 5×10^{-4} mol dm^{-3} acetone solutions using a Philips 9509 conductimeter. Molecular weights were determined with a Perkin-Elmer 115 osmometer using chloroform solutions.

Preparations.—$[Rh\{CPh(NPh)_2\}(cod)]$ (**1**). To a solution of $K[CPh(NPh)_2]$ in methanol (25 cm^3), prepared from PhN=CPh–NHPh (166 mg, 0.61 mmol) and KOH (0.60 mmol), was added $[\{RhCl(cod)\}_2]$ (150 mg, 0.30 mmol). The suspension was heated under reflux, with stirring, for *ca.* 1 h. Then the yellow solution was evaporated to dryness. Extraction of the residue into dichloromethane, evaporation to low volume, and addition of methanol gave the complex as yellow crystals.

$[Ir\{CPh(NPh)_2\}(cod)]$ (**2**). To a stirred suspension of $[\{IrCl(cod)\}_2]$ (200 mg, 0.30 mmol) in deoxygenated methanol was added PhN=CPh–NHPh (163 mg, 0.60 mmol) and NEt_3 (83.3 µl, 0.60 mmol). The suspension immediately turned into an

Table 3. Selected bond distances (Å) and angles (°) for binuclear complex (**4**)

Co-ordination sphere of the metals

Rh(1)–N(1)	2.125(4)	Rh(2)–N(3)	2.138(4)
Rh(1)–N(2)	2.086(6)	Rh(2)–N(4)	2.093(5)
Rh(1)–C(51)	2.141(7)	Rh(2)–C(39)	2.138(6)
Rh(1)–C(53)	2.130(6)	Rh(2)–C(41)	2.114(6)
Rh(1)–C(54)	2.110(7)	Rh(2)–C(42)	2.126(6)
Rh(1)–C(56)	2.141(7)	Rh(2)–C(44)	2.150(6)

N(1)–Rh(1)–N(2)	89.4(2)	N(3)–Rh(2)–N(4)	90.8(2)
N(1)–Rh(1)–Rh(2)	78.1(1)	N(3)–Rh(2)–Rh(1)	77.7(1)
N(1)–Rh(1)–C(51)	103.2(2)	N(3)–Rh(2)–C(39)	92.1(2)
N(1)–Rh(1)–C(53)	169.5(2)	N(3)–Rh(2)–C(41)	141.8(2)
N(1)–Rh(1)–C(54)	143.0(2)	N(3)–Rh(2)–C(42)	169.7(2)
N(1)–Rh(1)–C(56)	92.1(2)	N(3)–Rh(2)–C(44)	104.2(2)
N(2)–Rh(1)–Rh(2)	77.5(1)	N(4)–Rh(2)–Rh(1)	76.5(2)
N(2)–Rh(1)–C(51)	160.9(2)	N(4)–Rh(2)–C(39)	159.1(2)
N(2)–Rh(1)–C(53)	100.8(2)	N(4)–Rh(2)–C(41)	99.4(2)
N(2)–Rh(1)–C(54)	99.7(2)	N(4)–Rh(2)–C(42)	99.4(2)
N(2)–Rh(1)–C(56)	158.2(2)	N(4)–Rh(2)–C(44)	158.5(2)
Rh(2)–Rh(1)–C(51)	90.8(2)	Rh(1)–Rh(2)–C(39)	124.4(2)
Rh(2)–Rh(1)–C(53)	101.2(2)	Rh(1)–Rh(2)–C(41)	140.5(2)
Rh(2)–Rh(1)–C(54)	138.8(2)	Rh(1)–Rh(2)–C(42)	102.9(2)
Rh(2)–Rh(1)–C(56)	124.0(2)	Rh(1)–Rh(2)–C(44)	91.6(2)
C(51)–Rh(1)–C(53)	66.3(3)	C(39)–Rh(2)–C(41)	66.4(2)
C(51)–Rh(1)–C(54)	79.0(3)	C(39)–Rh(2)–C(42)	79.0(2)
C(51)–Rh(1)–C(56)	37.6(2)	C(39)–Rh(2)–C(44)	37.8(3)
C(53)–Rh(1)–C(54)	38.2(3)	C(41)–Rh(2)–C(42)	38.2(2)
C(53)–Rh(1)–C(56)	79.5(3)	C(41)–Rh(2)–C(44)	78.4(2)
C(54)–Rh(1)–C(56)	66.9(3)	C(42)–Rh(2)–C(44)	65.5(2)

Tetrafluorobenzobarrelene ligands

C(51)–C(52)	1.559(8)	C(39)–C(40)	1.527(9)
C(51)–C(56)	1.381(9)	C(39)–C(44)	1.388(10)
C(52)–C(53)	1.544(9)	C(40)–C(41)	1.550(9)
C(52)–C(57)	1.542(10)	C(40)–C(45)	1.532(8)
C(53)–C(54)	1.387(9)	C(41)–C(42)	1.389(10)
C(54)–C(55)	1.559(11)	C(42)–C(43)	1.530(8)
C(55)–C(56)	1.531(9)	C(43)–C(44)	1.516(9)
C(55)–C(62)	1.542(9)	C(43)–C(50)	1.512(9)
C–F[a]	1.355(5)	C–F[b]	1.356(5)

Rh(1)–C(51)–C(52)	96.6(4)	Rh(2)–C(39)–C(40)	96.2(4)
Rh(1)–C(51)–C(56)	71.2(4)	Rh(2)–C(39)–C(44)	71.6(4)
C(52)–C(51)–C(56)	114.4(6)	C(40)–C(39)–C(44)	113.8(6)
C(51)–C(52)–C(53)	97.6(5)	C(39)–C(40)–C(41)	98.3(5)
C(51)–C(52)–C(57)	107.8(5)	C(39)–C(40)–C(45)	109.9(5)
C(53)–C(52)–C(57)	106.9(5)	C(41)–C(40)–C(45)	106.8(5)
Rh(1)–C(53)–C(52)	97.5(4)	Rh(2)–C(41)–C(40)	96.4(4)
Rh(1)–C(53)–C(54)	70.1(4)	Rh(2)–C(41)–C(42)	71.4(4)
C(52)–C(53)–C(54)	113.5(5)	C(40)–C(41)–C(42)	114.4(5)
Rh(1)–C(54)–C(53)	71.7(4)	Rh(2)–C(42)–C(41)	70.4(3)
Rh(1)–C(54)–C(55)	96.3(4)	Rh(2)–C(42)–C(43)	97.5(4)
C(53)–C(54)–C(55)	113.6(5)	C(41)–C(42)–C(43)	111.4(5)
C(54)–C(55)–C(56)	98.6(5)	C(42)–C(43)–C(44)	98.9(5)
C(54)–C(55)–C(62)	108.0(6)	C(42)–C(43)–C(50)	108.8(5)
C(56)–C(55)–C(62)	108.4(5)	C(44)–C(43)–C(50)	111.6(5)
Rh(1)–C(56)–C(51)	71.2(4)	Rh(2)–C(44)–C(39)	70.7(4)
Rh(1)–C(56)–C(55)	96.0(4)	Rh(2)–C(44)–C(43)	96.9(4)
C(51)–C(56)–C(55)	113.1(6)	C(39)–C(44)–C(43)	112.6(6)
C(52)–C(57)–C(62)	115.6(6)	C(40)–C(45)–C(50)	112.3(5)
C(55)–C(62)–C(57)	113.3(6)	C(43)–C(50)–C(45)	113.0(5)

N,*N*′-Diphenylbenzamidinate ligands

N(1)–C(1)	1.350(7)	N(2)–C(2)	1.317(9)	Rh(1)–N(1)–C(1)	120.8(4)	Rh(1)–N(2)–C(2)	124.2(4)
N(1)–C(15)	1.442(6)	N(2)–C(21)	1.445(6)	Rh(1)–N(1)–C(15)	118.2(3)	Rh(1)–N(2)–C(21)	119.1(3)
N(4)–C(1)	1.346(7)	N(3)–C(2)	1.339(7)	C(1)–N(1)–C(15)	120.5(5)	C(2)–N(2)–C(21)	116.7(5)
N(4)–C(33)	1.429(5)	N(3)–C(27)	1.431(7)	Rh(2)–N(4)–C(1)	126.2(4)	Rh(2)–N(3)–C(2)	122.4(4)
C(1)–C(3)	1.501(6)	C(2)–C(9)	1.502(7)	Rh(2)–N(4)–C(33)	116.4(3)	Rh(2)–N(3)–C(27)	113.9(3)
				C(1)–N(4)–C(33)	117.3(5)	C(2)–N(3)–C(27)	123.7(4)
				N(1)–C(1)–N(4)	118.1(5)	N(2)–C(2)–N(3)	120.4(5)
				N(1)–C(1)–C(3)	121.1(5)	N(2)–C(2)–C(9)	118.7(5)
				N(4)–C(1)–C(3)	120.5(4)	N(3)–C(2)–C(9)	120.9(5)

[a] Average value in tfbb bonded to Rh(1). [b] Average value in tfbb bonded to Rh(2).

orange solution, then an orange solid was formed. This was filtered off, washed with methanol, and vacuum dried.

[$Rh_2\{\mu$-$CPh(NPh)_2\}_2(nbd)_2$] (**3**). To a solution of K[$CPh(NPh)_2$] in methanol (25 cm^3), prepared from PhN=CPh–NHPh (225 mg, 0.83 mmol) and KOH (0.82 mmol), was added [$\{RhCl(nbd)\}_2$] (200 mg, 0.43 mmol), and the mixture was stirred for *ca.* 1 h at room temperature. The red suspension formed was evaporated to dryness and the residue extracted with dichloromethane. Evaporation to low volume and addition of methanol gave the product as red crystals.

[$Rh_2\{\mu$-$CPh(NPh)_2\}_2(tfbb)_2$] (**4**). To a solution of K[$CPh(NPh)_2$] in methanol (25 cm^3) prepared from PhN=CPh–NHPh (225 mg, 0.83 mmol) and KOH (0.82 mmol) was added [$\{RhCl(tfbb)\}_2$] (300 mg, 0.41 mmol). The suspension was heated under reflux for *ca.* 1 h. The yellow-orange solution was evaporated to dryness. Extraction of the residue into dichloromethane gave a red solution. Evaporation to low volume and addition of methanol led to the precipitation of the complex as red crystals.

[$Rh_2\{\mu$-$CPh(NPh)_2\}_2(CO)_4$] (**5**). Bubbling of carbon monoxide through a yellow solution of [$Rh\{CPh(NPh)_2\}(cod)$] (200 mg, 0.41 mmol) in dichloromethane (20 cm^3), for 30 min, gave a red solution. This solution was evaporated to dryness and the addition of methanol–water (1:1) caused the precipitation of a red complex. The product was dissolved in hexane (5 cm^3) and cooled to 0 °C to give the complex as red crystals.

[$Rh_2\{\mu$-$CPh(NPh)_2\}(\mu$-$dppm)_2(CO)_2]ClO_4$ (**6**). A mixture of [$Rh_2Cl_2(\mu$-$dppm)_2(CO)_2$] (60 mg, 0.05 mmol) and $AgClO_4$ (23 mg, 0.11 mmol) was stirred for 30 min, the AgCl formed was filtered off through Kieselguhr, and the orange solution was added to a solution of K[$CPh(NPh)_2$] (0.05 mmol) in methanol. The mixture was stirred for 30 min and then the orange-red solution was evaporated to dryness. Extraction of the residue into dichloromethane gave a red solution. Evaporation to low volume and addition of diethyl ether led to the precipitation of the complex as red crystals.

[$Rh_2\{\mu$-$CPh(NPh)_2\}_2I_2(CO)_4$] (**7**). To a solution of [$Rh_2\{\mu$-$CPh(NPh)_2\}_2(CO)_4$] (150 mg, 0.35 mmol) in hexane (20 cm^3) was added iodine (88.5 mg, 0.35 mmol). After stirring for 5 min, the complex precipitated as a violet solid. The suspension was stirred for 1 h, then the solvent was evaporated to small volume and the product filtered off and washed with cold hexane.

[RhCl(PhN=CPh–NHPh)(cod)] (**8**). Benzamidine (44.2 mg, 0.16 mmol) was added to a solution of [$\{RhCl(cod)\}_2$] (40 mg,

Table 4. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of the complex [Rh{CPh(NPh)$_2$}(cod)]

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh	915(1)	1 237(1)	2 723(1)	C(13)	248(8)	−1 247(4)	2 847(8)
N(1)	1 154(5)	221(3)	2 187(6)	C(14)	1 930(7)	−159(4)	1 546(7)
N(2)	−578(5)	537(3)	2 872(6)	C(15)	1 377(8)	−593(4)	586(7)
C(1)	7(6)	11(3)	2 460(7)	C(16)	2 211(9)	−931(4)	−42(8)
C(2)	−1 632(6)	504(4)	3 464(7)	C(17)	3 601(9)	−817(5)	285(9)
C(3)	−1 762(7)	−11(4)	4 270(7)	C(18)	4 136(8)	−382(5)	1 225(10)
C(4)	−2 804(8)	18(5)	4 866(8)	C(19)	3 317(7)	−53(4)	1 890(9)
C(5)	−3 685(8)	570(5)	4 703(9)	C(20)	2 883(7)	1 675(4)	3 081(7)
C(6)	−3 556(8)	1 089(4)	3 906(9)	C(21)	2 202(7)	1 788(4)	1 846(7)
C(7)	−2 535(7)	1 060(4)	3 271(8)	C(22)	1 546(8)	2 450(4)	1 319(8)
C(8)	−548(7)	−697(3)	2 304(7)	C(23)	737(9)	2 792(4)	2 163(8)
C(9)	−1 864(8)	−792(4)	1 604(8)	C(24)	72(7)	2 239(4)	2 808(8)
C(10)	−2 399(9)	−1 451(5)	1 456(9)	C(25)	627(8)	1 992(4)	3 980(8)
C(11)	−1 607(10)	−2 010(4)	1 998(10)	C(26)	1 989(9)	2 190(5)	4 782(8)
C(12)	−280(10)	−1 911(4)	2 713(10)	C(27)	3 101(8)	2 220(5)	4 047(8)

Table 5. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of the complex [Rh$_2${CPh(NPh)$_2$}$_2$(tfbb)$_2$]

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	2 007(1)	1 883(1)	1 482(1)	C(61)	115(4)	1 232(6)	2 549(4)
Rh(2)	2 658(1)	570(1)	650(1)	C(62)	571(3)	1 150(5)	2 192(4)
F(1)	425(2)	−2 023(3)	−631(2)	C(3)	3 945(2)	1 060(3)	2 855(2)
F(2)	404(2)	−3 440(3)	−1 676(3)	C(4)	3 818(2)	1 200(3)	3 493(2)
F(3)	1 416(3)	−3 557(4)	−2 185(2)	C(5)	4 308(2)	1 034(3)	4 127(2)
F(4)	2 476(2)	−2 297(3)	−1 659(2)	C(6)	4 925(2)	728(3)	4 122(2)
F(5)	145(3)	2 032(4)	3 020(3)	C(7)	5 052(2)	588(3)	3 484(2)
F(6)	−825(2)	607(4)	2 766(3)	C(8)	4 562(2)	754(3)	2 850(2)
F(7)	−948(2)	−968(4)	1 809(3)	C(9)	2 853(2)	4 063(3)	295(2)
F(8)	−61(2)	−1 148(4)	1 102(3)	C(10)	3 055(2)	4 914(3)	762(2)
N(1)	2 999(2)	2 043(4)	2 080(3)	C(11)	3 186(2)	5 906(3)	516(2)
N(2)	2 147(2)	2 986(4)	759(3)	C(12)	3 114(2)	6 046(3)	−197(2)
N(3)	3 020(2)	2 137(3)	566(3)	C(13)	2 912(2)	5 194(3)	−664(2)
N(4)	3 276(2)	432(3)	1 683(3)	C(14)	2 781(2)	4 203(3)	−418(2)
C(1)	3 406(3)	1 201(4)	2 178(3)	C(15)	3 207(2)	3 031(3)	2 453(2)
C(2)	2 666(3)	3 019(4)	549(3)	C(16)	2 738(2)	3 642(3)	2 623(2)
C(39)	2 309(3)	387(5)	−468(3)	C(17)	2 908(2)	4 611(3)	2 977(2)
C(40)	2 550(3)	−757(5)	−483(3)	C(18)	3 547(2)	4 970(3)	3 161(2)
C(41)	2 698(3)	−1 021(5)	309(3)	C(19)	4 016(2)	4 359(3)	2 991(2)
C(42)	2 170(3)	−922(4)	559(3)	C(20)	3 846(2)	3 390(3)	2 638(2)
C(43)	1 558(3)	−605(5)	−29(3)	C(21)	1 669(2)	3 813(3)	495(2)
C(44)	1 780(3)	470(5)	−219(3)	C(22)	1 279(2)	3 771(3)	−205(2)
C(45)	1 987(3)	−1 479(5)	−884(3)	C(23)	810(2)	4 554(3)	−470(2)
C(46)	1 958(4)	−2 195(5)	−1 406(3)	C(24)	731(2)	5 380(3)	−34(2)
C(47)	1 440(4)	−2 852(5)	−1 678(4)	C(25)	1 121(2)	5 423(3)	666(2)
C(48)	933(4)	−2 791(6)	−1 415(4)	C(26)	1 590(2)	4 639(3)	931(2)
C(49)	931(3)	−2 059(5)	−891(4)	C(27)	3 675(2)	2 152(4)	550(2)
C(50)	1 451(3)	−1 397(5)	−626(3)	C(28)	4 137(2)	2 805(4)	1 009(2)
C(51)	1 714(3)	469(5)	1 906(3)	C(29)	4 782(2)	2 756(4)	1 019(2)
C(52)	1 039(3)	355(5)	1 338(3)	C(30)	4 966(2)	2 054(4)	572(2)
C(53)	1 018(3)	1 467(5)	996(3)	C(31)	4 503(2)	1 401(4)	114(2)
C(54)	1 060(3)	2 306(5)	1 462(4)	C(32)	3 858(2)	1 450(4)	103(2)
C(55)	1 127(3)	1 937(5)	2 227(4)	C(33)	3 558(2)	−596(2)	1 888(2)
C(56)	1 757(3)	1 300(5)	2 373(3)	C(34)	4 027(2)	−979(2)	1 602(2)
C(57)	520(3)	358(5)	1 720(3)	C(35)	4 283(2)	−2 001(2)	1 773(2)
C(58)	11(4)	−358(6)	1 582(4)	C(36)	4 071(2)	−2 641(2)	2 230(2)
C(59)	−442(3)	−269(6)	1 944(4)	C(37)	3 602(2)	−2 259(2)	2 516(2)
C(60)	−381(4)	529(7)	2 425(5)	C(38)	3 346(2)	−1 237(2)	2 345(2)

0.08 mmol) in dichloromethane. The resulting yellow solution was stirred for 30 min. Addition of hexane to the concentrated solution gave a yellow solid.

[RhCl(PhN=CPh–NHPh)(tfbb)] (**9**). To a solution of [{RhCl(tfbb)}$_2$] (50 mg, 0.07 mmol) in dichloromethane was added PhN=CPh–NHPh (37.4 mg, 0.14 mmol). After stirring for 30 min the solvent was evaporated and hexane was added to give a yellow compound.

[IrCl(PhN=CPh–NHPh)(cod)] (**10**). To a solution of [{IrCl(cod)}$_2$] (50 mg, 0.07 mmol) in deoxygenated dichloromethane was added PhN=CPh–NHPh (40.5 mg, 0.15 mmol). The yellow-orange solution was stirred for 30 min and then evaporated to low volume. Addition of hexane caused the precipitation of a yellow-orange compound.

[Rh(PhN=CPh–NHPh)(cod)(PPh_3)]ClO_4 (**11**). To a solution of [Rh{CPh(NPh)$_2$}(cod)] (50 mg, 0.1 mmol) in dichloromethane was added PPh_3 (26.2 mg, 0.1 mmol) and $HClO_4$ (11.3 µl, 0.1 mmol). The solution was stirred for 30 min and then evaporated to low volume. Addition of ether led to the precipitation of the complex as a yellow solid.

$[Rh(PhN{=}CPh{-}NHPh)(tfbb)(PPh_3)]ClO_4$ (**12**). A solution of $[RhCl(PhN{=}CPh{-}NHPh)(tfbb)]$ (50 mg, 0.08 mmol) in acetone (20 cm^3) was treated with $AgClO_4$ (16.3 mg, 0.08 mmol) and PPh_3 (20.6 mg, 0.08 mmol). After stirring for 30 min and filtration through Kieselguhr (to remove the AgCl formed) the yellow filtrate was concentrated and the complex precipitated with ether.

Crystallography.—Crystal data. A yellow prismatic crystal of complex (**1**), with approximate dimensions 0.22 × 0.25 × 0.56 mm, was used for the data collection.

$C_{27}H_{27}N_2Rh$, M = 482.43, monoclinic, a = 10.315(2), b = 19.507(3), c = 11.429(3) Å, β = 103.62(1)°, U = 2 235(1) $Å^3$ (by least-squares refinement of the θ values of 28 reflections accurately measured, λ = 1.541 78 Å), space group $P2_1/n$, Z = 4, D_c = 1.434 g cm^{-3}, $F(000)$ = 992, $\mu(Cu\text{-}K_\alpha)$ = 64.06 cm^{-1}.

Crystals of complex (**4**) suitable for the *X*-ray analysis were obtained by slow diffusion of methanol (precipitant) in a solution of the complex in dichloromethane. A red prismatic crystal, with approximate dimensions 0.25 × 0.34 × 0.63 mm, was used for the data collection.

$C_{62}H_{42}F_8N_4Rh_2$, M = 1 200.84, monoclinic, a = 21.692(2), b = 12.512(2), c = 19.969(2) Å, β = 107.90(1)°, U = 5 157(1) $Å^3$ (by least-squares refinement of the θ values of 22 reflections accurately measured, λ = 1.541 78 Å), space group $P2_1/c$, Z = 4, D_c = 1.546 g cm^{-3}, $F(000)$ = 2 416, $\mu(Cu\text{-}K_\alpha)$ = 59.16 cm^{-1}.

Data collection and processing. Complex (**1**): Siemens AED diffractometer, θ—2θ mode, nickel-filtered $Cu\text{-}K_\alpha$ radiation; 4 446 reflections measured ($3 \leqslant \theta \leqslant 70°$, $\pm h,k,l$), 4 234 unique (merging R = 0.056) giving 3 507 with $I \geqslant 2\sigma(I)$. Usual Lorentz and polarization reduction, absorption ignored. Complex (**4**): as above, except 8 992 reflections measured ($3 \leqslant \theta \leqslant 65°$, $\pm h,k,l$), 8 729 unique (merging R = 0.026) giving 7 118 with $I \geqslant 2\sigma(I)$.

Structure analysis and refinement. Complex (**1**): Patterson and Fourier methods, full-matrix least-squares refinement, all non-hydrogen atoms refined anisotropically; hydrogen atoms clearly found from a ΔF map were included in the final calculations, but not refined; unit weights gave satisfactory agreement analysis. Final R and R' values 0.040 and 0.050. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4. Complex (**4**): Patterson and Fourier methods, full-matrix least-squares refinement, all non-hydrogen atoms (except those of the phenyl rings, refined as rigid groups with D_{6h} geometry) refined anisotropically. Hydrogen atoms of both tfbb ligands found from a ΔF map, those of the phenyl rings placed in their calculated positions (C–H 1.08 Å); all included in the final calculations, but not refined. Weighting scheme used: $w = 1.7598/[\sigma^2(F_o) + 0.005F_o^2]$. Final R and R' values 0.047 and 0.060. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 5.

The atomic scattering factors (corrected for anomalous dispersion of Rh) were taken from ref. 33. All calculations were carried out using the SHELX system of computer programs[34] on the CYBER-76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

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