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SYNTHESIS AND REACTIONS OF BINUCLEAR DIOLEFIN RHODIUM(I) COMPOUNDS BRIDGED BY NITROGEN HETEROCYCLES. CRYSTAL STRUCTURE OF DICHLORO-DI-1,5-CYCLOOCTADIENE(μ-PYRAZINE)-DIRHODIUM(I) $[\{Rh(1,5\text{-}C_8H_{12})Cl\}_2(\mu\text{-}C_4H_4N_2)]$

R. HALESHA, G.K.N.REDDY *
Department of Chemistry, Bangalore University, Bangalore-560001 (India)

S.P. SUDHAKAR RAO and H. MANOHAR
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012 (India)

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Summary

Binuclear complexes of rhodium(I) of the type [(dien)(X)Rh(μ-N–N)Rh(X)(dien)] (dien = 1,5-cyclooctadiene or norbornadiene; N–N = pyrazine, 4,4′-bipyridine or Phenazine and X = Cl or Br) with bridging heterocycles have been isolated and their reactions with carbon monoxide, 2,2′-bipyridine and 1,10-phenanthroline investigated. The crystal structure of [(COD)(Cl)Rh(μ-pyrazine)Rh(Cl)(COD)] has been determined.

Introduction

Complexes of rhodium with nitrogen heterocycles have been extensively examined for catalytic activity, especially for hydrogenations. In this connection binuclear complexes would possibly be of special interest as they can be expected to show superior activity. A few binuclear complexes of rhodium with bridging nitrogen heterocycles have been reported earlier. Usón et al. have isolated complexes of rhodium with pyrazolate, imidazolate and indazolate(Y–Y) bridges of the type $[(COD)Rh(\mu\text{-}Y\text{-}Y)]_2$ [1,2]. Recently they have also reported the isolation of several polynuclear cationic species [3] of rhodium(I) containing diolefins and nitrogen heterocycles. The mixed ligand complex $[(NC)_5Fe(\mu\text{-pyz})Rh(NH_3)_5]$ [4] with pyrazine as the bridging ligand has been reported by Haim et al. The binuclear species [(COD)Rh(μ-BiIm)Rh(COD)] [5] with biimidazolate as the bridging ligand has been isolated by Rassmussen and coworkers, and its crystal structure determined. The isolation of the complex ion $[(PPh_3)_2(CO)Rh(\mu\text{-}4,4'\text{-bipy})Rh(CO)(PPh_3)_2]^{2+}$ [6] as

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its perchlorate has been reported from our laboratory. We now describe the isolation of new binuclear complexes of rhodium with the nitrogen heterocycles, pyrazine, 4,4′-bipyridine and phenazine(N–N) as bridging ligands and the results of a crystal structure analysis of [(COD)(Cl)Rh(μ-pyz)Rh(Cl)(COD)].

Results and discussion

Synthesis and characterisation

The halogeno-bridged binuclear complexes $[RhX(COD)]_2$ [7] (X = Cl or Br, COD = 1,5-cyclooctadiene) react with the nitrogen donor heterocycles, pyrazine, 4,4′-bipyridine and phenazine to give crystalline compounds which behave as non-electrolytes in nitrobenzene and show bands assignable to 1,5-cyclooctadiene and the nitrogen heterocycles in their infrared spectra. These results taken together with the analysis data indicate that the compounds should be formulated as binuclear species of rhodium(I) with bridging heterocycle of the type [(COD)(X)Rh(μ-N–N)Rh(X)(COD)]. Osmometric molecular weight determinations support this formulation (Tab. 1).

The proton magnetic resonance spectra of the complexes further support the assigned structures. All the compounds show three resonances around 1.9, 2.5 and 4.3 δ assignable to the diene ligands of the molecules. The signal pattern for the nitrogen donor ligands (Table 2) indicate their symmetrical location in the molecules. The pyrazine compounds show a single resonance around 8.7 δ, all four protons being equivalent. The 4,4′-bipyridine and phenazine compounds show two multiplets from two sets of equivalent protons (For example, in the bridging 4,4′-bipyridine ligand the two sets of equivalent protons are 3,3′, 5,5′ and 2,2′, 6,6′).

The dichloro-bridged dinuclear complexes of rhodium $[RhCl(NBD)]_2$ [8] containing norbornadiene (NBD) reacts with pyrazine and 4,4′-bipyridine in the same way as its COD analogue to give complexes of the formula [(NBD)(Cl)Rh(μ-N–N)Rh(Cl)(NBD)].

In order to confirm unequivocally the presence of bridging nitrogen heterocycles in the molecules an X-ray crystal structure analysis of the compound [(COD)(Cl)Rh(μ-pyrazine)Rh(Cl)(COD)] was carried out.

Crystallographic study

The molecular geometry of the binuclear complex is shown in Fig. 1. The asymmetric unit consists of half of the $[\{Rh(COD)Cl\}_2(C_4H_4N_2)]$ molecule, with the centre of inversion located at the center of the pyrazine ring. Consequently the two chlorine atoms on the two metal atoms are *trans* to each other.

Each of the rhodium atoms is coordinated in a slightly distorted square planar geometry to one chlorine, one nitrogen of pyrazine, and two double bonds of COD. A mean plane (coordination plane) through rhodium, chlorine, nitrogen, M(1) (mid-point between C(3) and C(4)) and M(2) (mid-point between C(7) and C(8)) reveals deviations of Rh −0.022, Cl 0.053, N −0.045, M(1) 0.061 and M(2) −0.047 Å. The dihedral angles between the diagonally opposite planes Cl–Rh–M(2) and N–Rh–M(1), and Cl–Rh–N and M(1)–Rh–M(2) are 4.3 and 4.5°, respectively, indicating slight deviation from square geometry.

The pyrazine ring is virtually planar (deviations ~ 0.005 Å). This plane of the pyrazine ring makes an angle of 56.9° with the coordination plane, as expected from

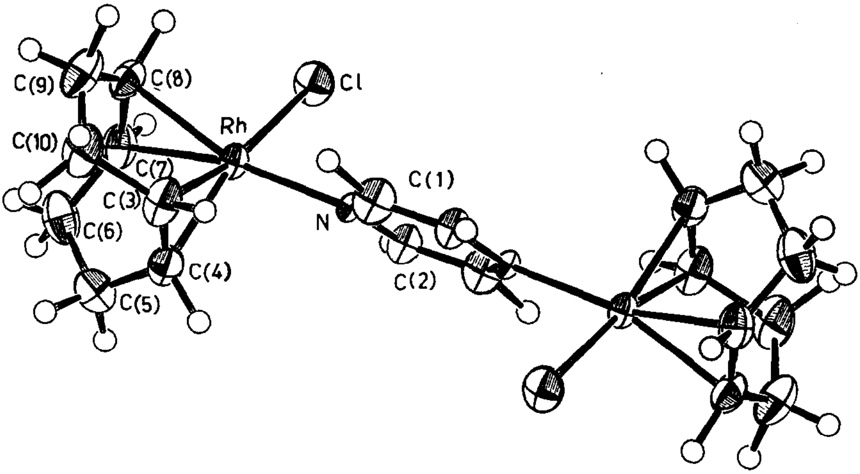


Fig. 1. Molecular geometry of the binuclear complex dichloro-di-1,5-cyclooctadiene(μ-pyrazine)dirhodium(I).

steric considerations arising from bulky chlorine atom. The bond lengths and bond angles of pyrazine ring are consistent with the previous structural studies of pyrazine containing compounds [9,10].

The COD ligand takes its customary skewed conformation as observed in the free molecule [11] and also when coordinated to other metals [12]. The coordinated double bonds C(3)–C(4) and C(7)–C(8) have lengths of 1.38 and 1.39 Å, respectively, compared to uncoordinated olefinic distance of 1.34 Å. The C–C single bond distances range from 1.48 to 1.54 Å, results typical for COD bonded to a heavy metal [12]. The C(3)–C(4) and C(7)–C(8) double bonds of COD are nearly normal to the line joining rhodium to the respective double bond centers (Rh–M(1)–C(3) 90.5°; Rh–M(2)–C(7) 90.1°). However the planes defined by Rh, C(3) and C(4), and Rh, C(7) and C(8) deviate very slightly, by 3.8 and 2.9°, respectively, from normality in the same direction with respect to coordination plane.

The Rh–C (olefinic carbon) bond lengths are in the range 2.099(6)–2.145(6) Å. Both smaller and greater metal–olefin distances have been reported for related rhodium(I) complexes, and the nature of the other ligand can have an appreciable effect on the strength of the Rh–olefin bond [12]. The distances between Rh and the double bond centers M(1) and M(2) are 1.989 and 2.028 Å, respectively, and are on the short end of the range 2.00–2.14 Å found in heavy metal complexes with COD [12,13,15]. This shortening may be due to strong π-back-bonding resulting from the presence of the relatively poorer π-bonding pyrazine and chlorine. The distance between the mid-points of the double bonds can be regarded as an indication of the strength of the metal–olefin bond. The distance M(1)–M(2) is 3.05 Å in the free molecule, 2.91 Å in (COD)(duroquinone)Ni complex [14] (in which it is suggested that COD is only weakly bonded), 2.74 Å in (COD)(acac)Rh [15] (in which olefin is bonded strongly to rhodium), and 2.79 Å in the title compound, indicating a strong Rh–olefin bond. However the small difference between the two Rh–olefin distances (Δ 0.049 Å) may be due to the difference between the *trans*-effects of the diagonally opposite atoms chlorine and nitrogen. The Rh–Cl bond length (2.357(1) Å) agrees

(Continued on p. 237)

TABLE 1

PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF THE ISOLATED COMPLEXES

Compound		Colour	M.p. or D.p. (°C)	Mol.Wt. [a]	Analyses [a] (%)		
					C	H	N
[(COD)(Cl)Rh(μ-pyz)Rh(Cl)(COD)]	(I)	Orange-yellow	135	586 (573)	41.91 (41.79)	4.89 (4.91)	4.89 (4.77)
[(COD)(Br)Rh(μ-pyz)Rh(Br)COD)]	(II)	Orange-yellow	142	649 (662)	36.27 (36.42)	4.23 (4.08)	4.23 (4.29)
[(COD)(Cl)Rh(μ-4,4′-bipy)Rh(Cl)(COD)]	(III)	Yellow	> 250	671 (649)	48.15 (48.15)	4.93 (4.96)	4.31 (4.38)
[(COD)(Br)Rh(μ-4,4′-bipy)Rh(Br)(COD)]	(IV)	Yellow	> 250	740 (738)	42.29 (42.31)	4.33 (4.20)	3.79 (3.86)
[(COD)(Cl)Rh(μ-phenz)Rh(Cl)(COD)]	(V)	Reddish-brown	243–244	–	50.41 (49.94)	4.24 (4.74)	4.09 (4.16)
[(COD)(Br)Rh(μ-phenz)Rh(Br)(COD)]	(VI)	Reddish-brown	249–251	–	44.30 (44.12)	4.40 (4.23)	3.90 (3.67)
[(NBD)(Cl)Rh(μ-pyz)Rh(Cl)(NBD)]	(VII)	Orange-yellow	128	–	39.30 (39.95)	3.34 (3.70)	5.35 (5.18)
[(NBD)(Cl)Rh(μ-4,4′-bipy)Rh(Cl)(NBD)]	(VIII)	Yellow	> 200	–	46.83 (46.68)	3.69 (3.89)	4.31 (4.52)

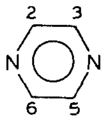
$[(CO)_2(Cl)Rh(\mu\text{-pyz})Rh(Cl)(CO)_2]$	(IX)	Metallic-red	133	–	20.69	0.63	5.47
					(20.48)	(0.83)	(5.97)
$[(CO)_2(Br)Rh(\mu\text{-pyz})Rh(Br)(CO)_2]$	(X)	Metallic-red	Unstable	–	–	–	–
$[(CO)_2(Cl)Rh(\mu\text{-}4,4'\text{-bipy})Rh(Cl)(CO)_2]$	(XI)	Orange-yellow	160	–	31.01	1.27	5.07
					(30.85)	(1.47)	(5.15)
$[(CO)_2(Br)Rh(\mu\text{-}4,4'\text{-bipy})Rh(Br)(CO)_2]$	(XII)	Orange-yellow	142	–	26.25	1.42	4.49
					(26.51)	(1.26)	(4.42)
$[(CO)_2(Br)Rh(\mu\text{-phenz})Rh(Br)(CO)_2]$	(XIII)	Red	155	–	29.70	1.05	4.70
					(29.20)	(1.25)	(4.25)
$[(COD)Rh(phen)][(CO)_2RhCl_2]$	(XIV)	Red	186–188	–	42.50	3.29	4.53
					(42.54)	(3.24)	(4.51)
$[(COD)Rh(bipy)][(COD)RhCl_2]$	(XV)	Orange-yellow	155	–	47.67	4.97	4.12
					(48.08)	(4.93)	(4.31)
$[(COD)Rh(bipy)]Br$	(XVI)	Orange-yellow	227–230	–	48.83	4.55	6.43
					(48.35)	(4.47)	(6.26)
$[(COD)Rh(phen)]Cl$	(XVII)	Orange-yellow	> 200	–	56.25	4.73	6.63
					(56.26)	(4.67)	(6.56)
$[(COD)Rh(phen)]Br$	(XVIII)	Orange-yellow	> 200	–	50.05	3.94	6.31
					(50.95)	(4.24)	(5.94)

[a] Calculated values are in parentheses.

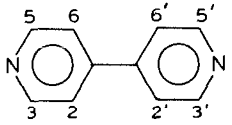
TABLE 2

^{1}H NMR SPECTRA (δ in ppm; m = multiplet; d = doublet; s = singlet)

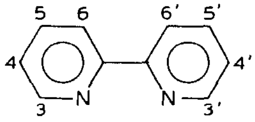
Pyrazine (pyz)



4,4′-bipyridine



2,2′-bipyridine



Compound	diene		pyz	4,4′-bipy		2,2′-bipy			
	CH_2	CH	2,3,6,5	2,2′ 6,6′	3,3′ 5,5′	3,3′	4,4′	5,5′	6,6′
I	1.80m,2.49m	4.21s	8.67s	–	–	–	–	–	–
II	1.80m,2.49m	4.21s	8.69s	–	–	–	–	–	–
III	1.86m,2.53m	4.21s	–	7.46m	8.86m	–	–	–	–
IV	1.83m,2.48m	4.25s	–	7.44m	8.86m	–	–	–	–
VIII	1.33s	3.87s,4.02s	–	7.50m	8.59m	–	–	–	–
IX	– –	– –	8.82s	–	–	–	–	–	
XV	1.70m,2.15m 2.44m,2.58m	4.24s,4.53s	–	–	–	7.60m	7.77d	8.36m	9.19d
XVI	2.12m,2.61m	4.44m	–	–	–	7.60m	7.83d	8.23m	9.95d

well with terminal Rh–Cl distances in other rhodium(I) compounds [16].

The observation that the two halogen atoms on the two metal centers are *trans* to each other can be extended to the other analogous compounds described in this paper. That the compounds containing the bulkier bridging ligands such as phenazine and substituted pyrazine may show more tilting with respect to the coordination plane can also be expected.

Reactions of the compounds [(dien)(X)Rh(μ-N–N)Rh(X)(dien)]

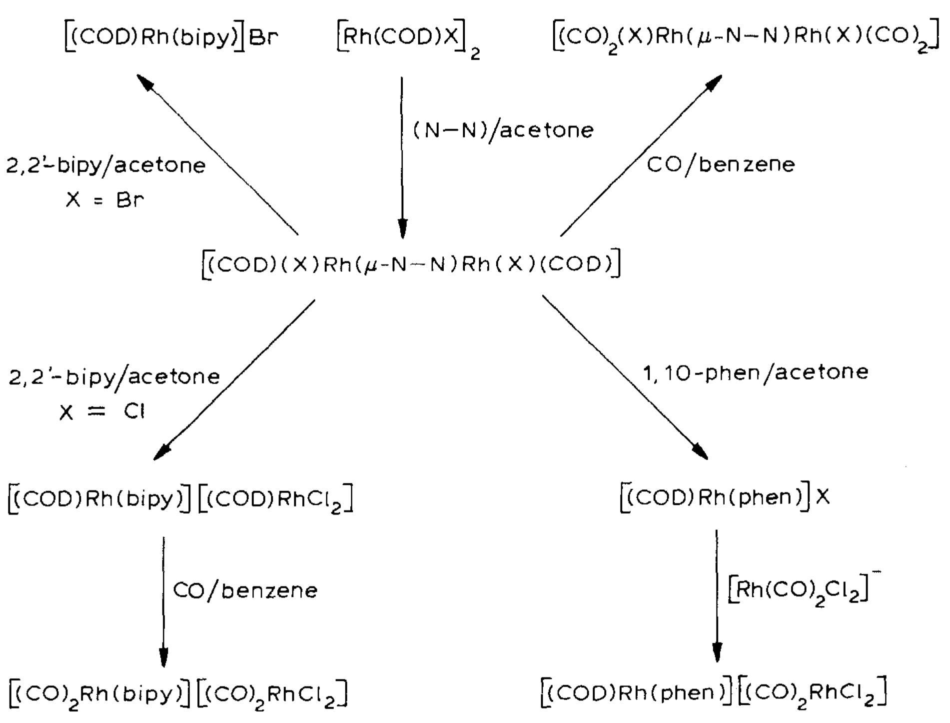
The π-bonding diene ligands of the binuclear compounds can be readily displaced by other π-bonding ligands such as carbon monoxide. Thus bubbling carbon monoxide through benzene solutions of the complexes produces carbonyl complexes of the formula $[(CO)_2(X)Rh(\mu\text{-}N{-}N)Rh(X)(CO)_2]$, with the $Rh(\mu\text{-}N{-}N)Rh$ unit remaining intact. Each of these compounds show two carbonyl stretches in the 2000 cm^{-1} region of the infrared indicating the presence of *cis* carbonyl groups on each of the metal atoms. The PMR spectra of the molecules show only peaks due to the protons of the bridging nitrogen heterocycles. The compounds are non-electrolytes in nitrobenzene. The NBD containing dinuclear complexes react with carbon monoxide in the same way as their COD analogues and give identical compounds. The compounds IX and XI were isolated earlier by other routes [17,18]. The pyrazine-bridged carbonyl chloro compound (IX) slowly decomposes when exposed to the atmosphere, and reacts with ethanol to give a solid product which does not contain carbon monoxide. The bromo analogue (X) is highly unstable and could not be analysed. A Nujol mull for the IR spectra was, however, satisfactorily made under an atmosphere of nitrogen (Tab. 3).

Reaction of the COD-containing dinuclear compounds with 2,2′-bipyridine results in bridge-breaking and elimination of the bridging heterocycle; thus treatment of compounds I and III with 2,2′-bipyridine gives the ionic complex $[Rh(COD)(bipy)][Rh(COD)Cl_2]$ [7]. The compound is a 1/1-electrolyte in nitrobenzene, and its PMR spectrum shows two sets of resonances due to the protons of the two dienes (located in different environments) in addition to peaks due to the bipyridine protons. Carbon monoxide again displaces both the dienes from the molecule to give $[Rh(CO)_2(bipy)][Rh(CO)_2Cl_2]$ [19]. The COD-containing binuclear bromo complexes II and IV react with 2,2′-bipyridine to give the simple compound [Rh(COD)(bipy)]Br. 1,10-Phenanthroline similarly gives compounds of the formula [Rh(COD)(phen)]X [7,19] with both the binuclear chloro and bromo complexes (I–IV). The compounds [Rh(COD)(phen)] X react with a carbonylated alcoholic

TABLE 3

INFRARED DATA FOR CARBONYL COMPLEXES (cm^{-1})

Compound		ν(CO)
$[(CO)_2(Cl)Rh(\mu\text{-pyz})Rh(Cl)(CO)_2]$	(IX)	2015s, 2105s
$[(CO)_2(Br)Rh(\mu\text{-pyz})Rh(Br)(CO)_2]$	(X)	2016s, 2095s
$[(CO)_2(Cl)Rh(\mu\text{-}4,4'\text{-bipy})(Cl)(CO)_2]$	(XI)	2000s, 2090s
$[(CO)_2(Br)Rh(\mu\text{-}4,4'\text{-bipy})(Br)(CO)_2]$	(XII)	1980sh, 2020s, 2066sh, 2080s
$[(CO)_2(Br)Rh(\mu\text{-phenz})Rh(Br)(CO)_2]$	(XIII)	2005s, 2085s
$[(COD)Rh(phen)][(CO)_2RhCl_2]$	(XIV)	1982s, 2071s



(N—N = pyrazine, 4,4'-bipyridine or phenazine; X = Cl or Br)

SCHEME 1. Synthesis and reactions of binuclear complexes of rhodium(I).

solution of rhodium trichloride, which would contain the anion $[Rh(CO)_2Cl_2]^-$, to give the complex $[Rh(COD)(phen)][Rh(CO)_2Cl_2]$. The observed reactions are summarised in Scheme 1.

Experimental

Preparation

The compounds $[RhX(COD)]_2$ and $[RhCl(NBD)]_2$ [7,8] and $[Rh(CO)_2X]_2$ [20] were prepared by published methods.

Infrared and proton NMR spectra were recorded on a Specord 75 IR spectrophotometer and a Bruker WH 270 spectrometer, respectively. Molecular weights were determined with a KNAUER vapour pressure osmometer. Conductivity measurements were carried out with a Toshniwal conductivity bridge.

Dihalo-di-1,5-cyclooctadiene (μ-4,4'-bipyridine or pyrazine or phenazine)dirhodium(I) [(COD)(X)Rh(μ-N–N)Rh(X)(COD)]. The nitrogen heterocycle (0.5 mmol) was added to a hot solution of $[RhX(COD)]_2$ (0.5 mmol) in acetone (50 ml). The resulting yellow to reddish brown solution was refluxed for 3 h, after which shining crystals of the desired product had separated. The crystals were filtered off, washed with acetone, and dried under vacuum.

Dichloro-di-norbornadiene(μ-4,4′-bipyridine or pyrazine)dirhodium(I) [(NBD)(Cl)-Rh(μ-N–N)Rh(Cl)(NBD)]. To a benzene solution of 0.5 mmol of $[RhCl(NBD)]_2$ was added 0.5 mmol of the nitrogen heterocycle in benzene. The solution was stirred for 2 h and evaporated to a small volume if necessary. The product separated as a yellow or orange microcrystalline solid and was filtered off, washed with benzene, and dried in vacuum.

Dihalo-tetracarbonyl(μ-4,4′-bipyridine or pyrazine or phenazine)dirhodium(I) $[(CO)_2(X)Rh(\mu\text{-}N–N)Rh(X)(CO)_2]$. Carbon monoxide was bubbled through benzene solutions of compounds I–VI for 2–3 h. The crystals of the tetracarbonyl were separated, washed with benzene, and dried in vacuum.

The phenazine-bridged compounds $[(CO)_2(X)Rh(\mu\text{-phenazine})Rh(X)(CO)_2]$ were also isolated by stirring benzene solutions of $[Rh(CO)_2X]_2$ and phenazine in 1/1 mol ratio.

The pyrazine-bridged bromo compound $[(CO)_2(Br)Rh(\mu\text{-pyrazine})Rh(Br)CO)_2]$ unlike its chloro analogue was very unstable, and could not be analysed. The 4,4′-bipyridine bridged tetracarbonyl compound $[(CO)_2(Cl)Rh(\mu\text{-4,4'-bipyridine})Rh(Cl)(CO)_2]$ was also isolated by adding 4,4′-bipyridine to the yellow solution (containing carbonylated rhodium(I) species) obtained by bubbling carbon monoxide through an alcoholic solution of rhodium trichloride.

1,5-Cyclooctadiene-phenanthroline-rhodium(I) dichloro-dicarbonyl-rhodate(I) $[COD)Rh(phen)][(CO)_2RhCl_2]$. Carbon monoxide was bubbled through a hot alcoholic solution of rhodium trichloride (0.25 mmol) until the solution turned yellow. A methanol solution of [Rh(COD)(phen)]Cl (0.25 mmol) was added with stirring, and the orange yellow microcrystals which separated were filtered off, washed with methanol, and dried in vacuum.

1,5-Cyclooctadiene(phenanthroline or bipyridyl)rhodium(I)halide [(COD)-Rh(Z–Z)]X (X = Cl or Br; Z–Z = phen or bipy). To an acetone solution of the compounds I–VI (0.25 mmol) 0.5 mmol of the ligand (Z–Z) was added with stirring. If necessary the mixture was refluxed for 2 h. The resulting orange microcrystals were washed with acetone and dried in vacuum.

However, 2,2′-bipyridine reacted with [(COD)(Cl)Rh(μ-N–N)Rh(Cl)(COD)] to give $[(COD)Rh(bipy)][(COD)RhCl_2]$.

Crystal and intensity data

$C_{20}Cl_2H_{28}N_2Rh_2$, $M = 573.0$, triclinic, space group $P\bar{1}$, a 6.945(2), b 8.231(2), c 9.928(1) Å, α 111.16(2), β 94.17(3), γ 101.31(3)°, V 512.5 Å^3, $Z = 1$, D 1.85 kg dm^{-3}, Mo-K_α radiation, λ 0.7107 Å, μ 17.9 cm^{-1}.

An orange-yellow coloured needle-shaped crystal (ca. 0.08 × 0.05 × 0.25 mm) was used for data collection on an Enraf-Nonius CAD-4 diffractometer. Data were measured using graphite monochromated Mo-K_α radiation up to a maximum Bragg angle of 23° by $\omega/2\theta$ scan with a scan width of $\Delta\theta = (0.75 + 0.45 \tan\theta)$.

The intensities of two standard reflections monitored every 50 min varied by less than 4% during data collection. The data were corrected for Lorentz and polarisation effects but not for absorption. Out of 1443 unique reflections, 1344 reflections with $I > 3\sigma(I)$ were used for the structure analysis.

Structure solution and refinement

The position of the rhodium atom was located from a three-dimensional Patter-

TABLE 4

FINAL POSITIONAL (FRACTIONAL) PARAMETERS $(\times 10^4)$ AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS $(\times 10^3)$ FOR NONHYDROGEN ATOMS; e.s.d.'s are given in parentheses

Atom	x	y	z	U_{eq} (Å^2)
Rh	2626(1)	3248(1)	2340(0)	24.60(0.20)
Cl	882(2)	5525(2)	2748(2)	41.40(0.60)
N	4082(7)	4267(6)	929(5)	14.90(1.70)
C(1)	6071(9)	4802(8)	1077(6)	48.20(2.40)
C(2)	3038(8)	4457(8)	−166(6)	29.60(2.20)
C(3)	4664(10)	1699(9)	2483(7)	43.20(2.80)
C(4)	3181(10)	706(9)	1302(7)	39.60(2.60)
C(5)	1476(12)	−781(9)	1251(8)	55.00(3.00)
C(6)	300(11)	−197(9)	2518(9)	55.50(3.10)
C(7)	492(9)	1767(9)	3186(7)	37.90(2.50)
C(8)	1964(10)	2952(11)	4325(8)	38.70(2.40)
C(9)	3699(12)	2475(11)	4988(8)	55.90(3.20)
C(10)	4769(11)	1346(10)	3900(8)	53.30(3.20)

son-map. With this position the structure refined to $R = 0.31$. The subsequent difference Fourier maps revealed all the nonhydrogen atoms. The atomic positions were refined by full-matrix least-squares methods. The thermal parameters of all the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located

TABLE 5

INTERATOMIC DISTANCES (Å) AND ANGLES (°) [a], with e.s.d.'s in parentheses

Atoms	Distance	Atoms	Angle
Rh–Cl	2.357(1)	Cl–Rh–N	86.8(1)
Rh–N	2.100(4)	Cl–Rh–M(2)	91.6(2)
Rh–C(3)	2.111(6)	N–Rh–M(1)	93.9(2)
Rh–C(4)	2.099(6)	M(1)–Rh–M(2)	87.8(2)
Rh–C(7)	2.145(6)	C(1)–N–C(2)	116.1(5)
Rh–C(8)	2.142(6)	N–C(1)–C(2′)	121.5(5)
Rh–M(1)	1.989	N–C(2)–C(1′)	122.4(5)
Rh–M(2)	2.028	C(3)–C(4)–C(5)	125.3(6)
N–C(1)	1.345(7)	C(4)–C(5)–C(6)	112.9(5)
N–C(2)	1.336(7)	C(5)–C(6)–C(7)	114.1(5)
C(1)–C(2′)	1.380(7)	C(6)–C(7)–C(8)	124.3(6)
C(3)–C(4)	1.38(1)	C(7)–C(8)–C(9)	125.6(6)
C(4)–C(5)	1.51(1)	C(8)–C(9)–C(10)	114.8(5)
C(5)–C(6)	1.53(1)	C(9)–C(10)–C(3)	111.7(5)
C(6)–C(7)	1.48(1)	C(10)–C(3)–C(4)	122.2(6)
C(7)–C(8)	1.39(1)		
C(8)–C(9)	1.52(1)		
C(9)–C(10)	1.50(1)		
C(10)–C(3)	1.54(1)		

[a] All C–H distances are in the range 0.85–1.15 Å. Primed atoms are related to respective unprimed atoms by center of symmetry.

from the difference Fourier map and were included in the final structure factor calculations. The structure was refined to a final R value of 0.038 and R_w of 0.046 *. The successful refinement of the structure in centrosymmetric space group confirms the space group $P\bar{1}$. A final difference Fourier map was featureless (0.24 e/Å^3). The quantity minimised during refinement was $\Sigma w[|F_o| - |F_c|]^2$ where $w = 0.7022/(\sigma|F_o|^2 + 0.0012|F_o|^2)$ based on counting statistics.

Scattering factors for all the atoms were taken from International Tables [21]. The SHELX-76 programm was used for structure solution and refinement [22]. Final positional parameters with equivalent isotropic thermal parameters are given in Table 4. Bond distances and bond angles are summarized in Table 5. A full list of observed and calculated structure factors is available from authors.

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* The agreement indices are defined as: $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.