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Journal of Organometallic Chemistry 658 (2002) 43–49

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthetic, spectral and structural aspects of some Rh(III) pentamethylcyclopentadiene complexes containing *N*,*N′*-donor bridging ligands

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Received 8 January 2002; accepted 21 May 2002

Abstract

Reactions of the chloro-bridged dimeric rhodium complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$ with the *N*,*N′*-donor bridging ligands pyridine-2-carbaldehyde azine (paa), *p*-phenylene-bis(picoline)aldamine (pbp) or *p*-biphenylene-bis(picoline)aldamine (bbp) in 1:1 molar ratio in methanol led in the formation of cationic binuclear complexes $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-}L)RhCl(\eta^5\text{-}C_5Me_5)]^{2+}$ (L = paa, pbp or bbp) in high yield. It was further observed that reactions of the chloro-bridged dimeric rhodium complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$, with an excess of the above mentioned ligands also, resulted in binuclear complexes. The reaction products have been characterized by microanalyses and spectroscopic studies (IR, ^{1}H-, ^{13}C-NMR, ESMS/FAB mass and electronic spectra). Molecular structure of the representative binuclear complex $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-}paa)RhCl(\eta^5\text{-}C_5Me_5)](BF_4)_2$ has been confirmed by single crystal X-ray analysis. Crystal data: monoclinic, $P2_1/n$, $a = 10.2050(7)$, $b = 15.4470(7)$, $c = 24.959(2)$ Å, $\beta = 97.904(6)°$, $V = 3897.1(5)$ Å^3, $Z = 4$, $R = 0.0609$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium pentamethylcyclopentadiene complexes; Pyridine-2-carbaldehyde azine; *p*-Phenylene-bis(picoline)aldamine; *p*-Biphenylene-bis(picoline)aldamine; Bridged complexes

1. Introduction

For many years, there has been great interest in binuclear and polynuclear poly–pyridyl complexes because of their interesting photophysical and photochemical properties, their possible use as potential catalysts, as multi-electron storage systems and in designing new materials and molecular devices [1a–d]. The photophysical and -chemical properties of the complexes largely depend upon the nature of the bridging ligand mediating the metal–metal interactions. The specific role of the bridging ligands is influenced by the acceptor and donor properties of the coordination sites, the length and rigidity of the spacers, presence or absence of the conjugated bonds, orientation of the substituents and scope of manipulating the ligand charge. In this regard, α-diimine and α-azoimine bridging poly–pyridyl ligands, viz. 2,2′-bipyrimidine (bpym); 2,3-bis(2-pyridyl)pyrazine (bppz); 2,5-bis(2-pyridyl)-pyrazine; 3,5-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz); azo-2,2′-bipyridine (abpy), 2,4,6-tris(2-pyridyl)-1,3,5-triazine etc. have received special attention [2a–g]. Closely related bridging ligands having immine–azine hybrid-chelating systems viz. pyridine-2-carbaldehyde azine (paa), *p*-phenylene-bis(picoline)aldamine (pbp), *p*-biphenylene-bis(picoline)aldamine (bbp) (Fig. 1) have relatively been less studied [3a–g].

These ligands possess low lying π* orbitals which, can back accept electron density from filled metal d_π orbitals. As a consequence, they exhibit reversible reduction processes and intense charge transfer bands in the visible region. The N_2 diazine linkage in the ligand pyridine-2-carbaldehyde azine (paa) offers several possible mononucleating and binucleating modes due to flexibility of the ligand around the N–N single bond and can give rise to the complexes having different geometries [4a–f]. Literature survey further reveals that most

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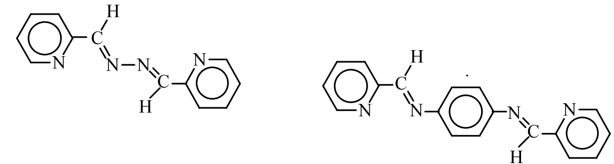
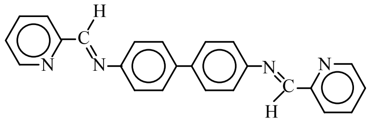
PII: S0022-328X(02)01598-X



pyridine-2-carbaldehyde azine (paa) *p*-phenylene-bis(picoline)-aldamine (pbp)



p-biphenylene-bis(picoline)-aldamine (bbp)

Fig. 1. Structure of the bridging ligands.

of the work reported with these ligands is mainly on the complexes of the first series transition metal ions, Mo and reactivity of the Ir nitrosyl complexes. Reactivity of these ligands with the chloro-bridged rhodium complex [{Rh(η^5-C_5Me_5)(μ-Cl)Cl}$_2$] and related species has not yet been studied.

Because of current interests in the co-ordinatively unsaturated Cp*M (α-diimine) complexes (M = Rh or Ir) [5a–e] and our continuing interests in designing *metallo-ligands* or *synthon* based on organometallic systems [6a,b], we have made a detailed study on reactivity of the dimeric chloro-bridged complex [{Rh(η^5-C_5Me_5)(μ-Cl)Cl}$_2$] with pyridine-2-carbaldehyde azine. Such a reaction, in methanol at room temperature led in the formation of highly stable paa bridged cationic binuclear complex [(η^5-C_5Me_5)ClRh(μ-paa)RhCl(η^5-C_5Me_5)]$^{2+}$. Further, in order to look into effect on the separated distance and π conjugation between the two metal centers bridged by diazine ligands, we have also carried out reactions of [{Rh(η^5-C_5Me_5)(μ-Cl)Cl}$_2$] with pbp and bbp under similar reaction conditions. In this paper, we report reproducible synthesis and spectral properties of some stable cationic Rh(III) binuclear complexes with the general formulation [(η^5-C_5Me_5)ClRh(μ-paa)RhCl(η^5-C_5Me_5)]$^{2+}$ in which two Rh(III) centres are bridged by diazine ligands. We also, present herein single crystal X-ray structure of the complex [(η^5-C_5Me_5)ClRh(μ-paa)RhCl(η^5-C_5Me_5)](BF$_4$)$_2$.

2. Experimental

The chemicals used for the reaction were Analar or chemically pure grade. Solvents were dried and distilled prior to use following the standard literature procedures. The ligands paa, pbp and bbp [3b,4b] and the precursor complex [{Rh(η^5-C_5Me_5)(μ-Cl)Cl}$_2$] were prepared and purified following the literature procedure [7]. The elemental analyses were performed by microanalytical laboratory of the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. IR spectra in Nujol mulls were recorded on a Perkin–Elmer-881 spectrophotometer. NMR spectra were taken on a Brucker DRX-300 MHz NMR instrument. The chemical shifts are given in ppm relative to Me_4Si (^{1}H, ^{13}C{^{1}H}). Electronic spectra in C_3H_6O were obtained on a Shimadzu UV-160 spectrophotometer. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature (r.t.) with m-NBA as the matrix Electrospray mass spectra were recorded on a Micromass Quattro-II triple quadrupole mass spectrometer. Samples were introduced into the ESI source through a syringe pump at 4.0 ml h^{-1}. The ESI capillary was 3.5 kV and cone voltage 20–50 V. The spectra were collected in 4 s scans and the print outs are averaged spectra of 5–10 scans.

2.1. Procedure

2.1.1. Preparation of [(η^5-C_5Me_5)ClRh(μ-paa)Rh(η^5-C_5Me_5)Cl](BF$_4$)$_2$ (**1**)

To a suspension of the dimeric chloro-bridged rhodium complex [{Rh(η^5-C_5Me_5)Cl$_2$}$_2$] (618 mg, 1.0 mmol) in MeOH (25 ml), paa (210 mg,1.0 mmol) was added and stirred at r.t. The precursor complex slowly dissolved and led to a yellow solution, which was further stirred at r.t. for ca. 4 h. It was filtered through celite to remove any solid impurities. The filtrate was treated with saturated solution of NH_4BF_4 dissolved in MeOH (10 ml) and left for slow crystallization. After 2–3 days yellow crystalline product separated. It was separated by filtration washed a couple of times with MeOH, Et_2O and dried under in vacuo. Yield: 74%. Anal. Found: C, 41.12; H, 5.98; N, 4.35; Calc. for $C_{32}H_{40}B_2Cl_2F_8N_4Rh_2$: C, 41.24; H, 6.01; N, 4.29%. ESMS (*m/z*): Obs. (Calc.): 843.1 (844), 585 (586), 483.1 (483), 447.1 (447), 312.9 (312). ^{1}H-NMR (CDCl$_3$, δ ppm): 9.21 (d), 9.06 (d), 9.003 (s), 8.49 (t), 8.28 (m), 7.94 (m), 1.68 (s). ^{13}C{^{1}H}-NMR (CDCl$_3$, δ ppm): 162.9 (C–H), 153.7, 140.4, 129.5, 127.1, 122.8, 98.7 (C_5Me$_5$), 8.8 (CH$_3$). UV–vis (nm): $\lambda_{\max}$ (ε) 335 (14,500), 420 (10,000) and 694 (9800).

2.1.2. Preparation of [(η^5-C_5Me_5)ClRh(μ-pbp)Rh(η^5-C_5Me_5)Cl](BF$_4$)$_2$ (**2**)

This complex was prepared following the above procedure except that pbp was used in place of paa. It gave orange red crystalline solid and was separated by filtration washed a couple of times with MeOH, Et_2O and dried under *vacuum*. Yield: 68%. ESMS (*m/z*): Obs. (Calc.): 919.1 (920), 562.1 (563), 523.1 (527). Anal. Found: C, 45.44; H, 4.42; N, 5.71. Calc. for $C_{38}H_{44}B_2Cl_2F_8N_4Rh_2$: C, 45.28; H, 4.36; N, 5.67%. ^{1}H-NMR (CDCl$_3$, δ ppm): 9.23 (d), 8.72 (d), 8.33 (m), 8.11 (s), 7.55 (m), 6.8 (dd), 1.81 (s). ^{13}C{^{1}H}-NMR (CDCl$_3$, δ ppm): 169.3 (C–H), 154.6, 140, 130.8–129.4, 124, 97.6 (C_5Me_5), 8.8 (CH_3). UV–vis (nm): λ_{max} (ε) 329.6 (17,720), 377.6 (28,190) and 579.2 (3900).

2.1.3. Preparation of $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-bbp})Rh(\eta^5\text{-}C_5Me_5)Cl](BF_4)_2$ (3)

It was prepared following the above procedure except that bbp was used in place of paa. It separated as brownish red crystalline solid and was washed a couple of times with MeOH, Et_2O and dried under *vacuum*. Yield: 70%. FAB mass (*m*/*z*): Obs. (Calc.) 998 (996), 908 (909), 873 (872), 635 (634), 600 (598). Anal. Found: C, 48.72; H, 4.48; N, 5.22. Calc. for $C_{44}H_{48}B_2Cl_2F_8N_4Rh_2$: C, 48.75; H, 4.43; N, 5.17%. ^{1}H-NMR ($CDCl_3$, δ ppm): 9.10 (d), 9.05 (m), 8.35 (s), 8.04(m), 7.89 (d), 7.51(m), 1.50 (s). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 167.6 (C–H), 153.9, 148.2, 140.5, 133–132, 97.4 (C_5Me_5), 8.3 (CH_3). UV–vis (nm): λ_{max} (ε) 324.6 (30,040), 377.6 (30,000) and 689.6 (9500).

2.1.4. Single crystal X-ray analyses

Crystals suitable for single crystal X-ray analyses for the complex $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-paa})Rh(\eta^5\text{-}C_5Me_5)Cl](BF_4)_2$ (**1**) were grown from CH_2Cl_2–petroleum ether at r.t. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on Enraf–Nonius MACH3 diffractometer using graphite monochromatized Mo–K_α radiation. The crystal orientation, cell refinement and intensity measurements were made using the program CAD-4 PC. Absorption correction was done by performing psi-scan measurement. The data reduction was done by using MAXUS and structure solution and refinement using the programs SHELXS-97 and SHELXL-97 [8a–c] methods respectively. The structure was refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

3. Results and discussion

The ligand pyridine-2-carboxaldehyde azine, which is derived from hydrazine and contain a single N–N bond offers several mononucleating and binucleating coordination modes and also the potential for free rotation about N–N bond. Treatment of the chloro-bridged dimeric rhodium complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$ with the ligands paa, pbp or bbp in methanol, in 1:1 molar ratio, led in the formation of stable cationic binuclear complexes with the formulation $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-L})Rh(\eta^5\text{-}C_5Me_5)Cl]^{2+}$ (L = paa, pbp or bbp) in high yield which, were isolated as BF_4–PF_6 salts (Scheme 1). In these reactions no intermediates could be isolated, it is supposed that these reactions proceed through the intermediacy of the complexes derived by chloro-bridge cleavage and coordination of the ligands through immine–azine nitrogen.

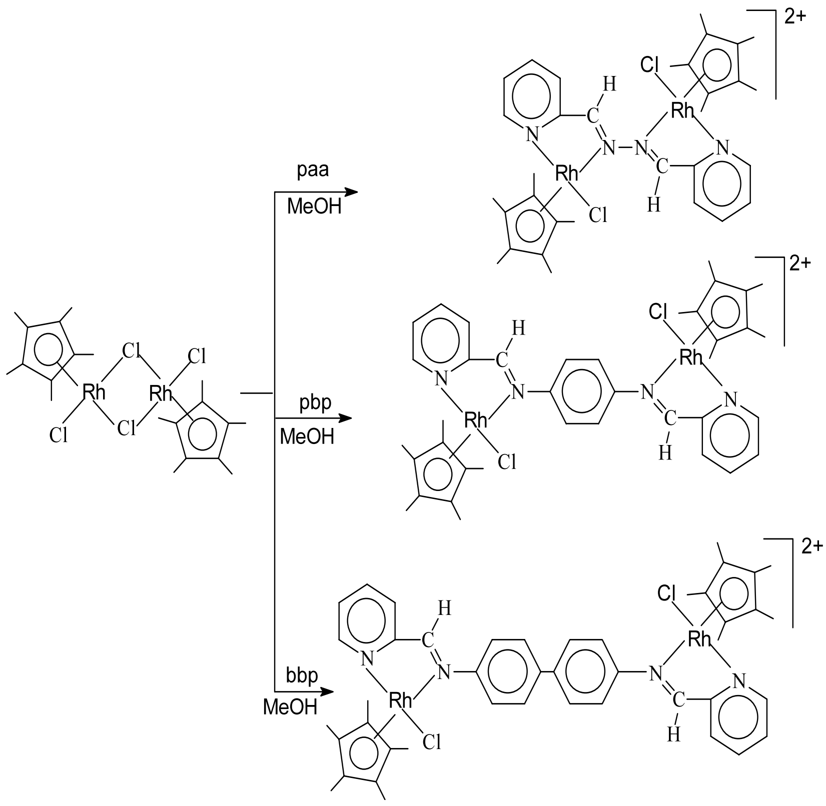
The pale yellow to orange red complexes are air stable, non-hygroscopic, microcrystalline solid. These are soluble in water, acetone, acetonitrile, dichloromethane, chloroform, dimethylsulfoxide, dimethylformamide and insoluble in diethyl ether and petroleum ether. Corresponding pbp and bbp complexes are highly insoluble in most of the common organic solvents.

Analytical data of the complexes conformed well to our formulations. Further information about composition of the complexes has been obtained from ESMS/FAB Mass spectral studies. ESMS/FAB mass spectra of the complexes **1**, **2** or **3** exhibited intense peaks at *m*/*z* 843.1, 919.1 and 998 corresponding to the cationic species $\{[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-paa})Rh(\eta^5\text{-}C_5Me_5)Cl]BF_4\}^+$, $\{[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-pbp})Rh(\eta^5\text{-}C_5Me_5)Cl]BF_4\}^+$ and $\{[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-bbp})Rh(\eta^5\text{-}C_5Me_5)Cl]BF_4\}^+$, respectively. The presence of these peaks and overall fragmentation pattern of the complexes strongly supported formation of the binuclear complexes.

Infra red spectra of the complexes exhibited characteristic bands due to pyridyl ring of the ligands along with the characteristic bands corresponding to counter anions. The ν_{C-N} band in the complexes shifted towards lower wave numbers and appeared around 1595 cm^{-1} as compared to that in the free ligand (1640 cm^{-1}). The band associated with pyridyl ring breathing mode appeared at about 1020 cm^{-1}. The shift in the position of ν_{C-N} and pyridine ring breathing mode suggested coordination of the metal ion through pyridyl and diazine nitrogen. Broad bands in the region 1145 cm^{-1} have been assigned to counter ion BF_4^-.

The complexes can exist as diastereomers, but all efforts to separate the diastereomers were unsuccessful at our hands. However, it has been supported by ill-resolved NMR data. In the respective spectra, signals for the minor diastereomer are hidden or not well resolved, therefore, we are unable to make precise interpretation of the different signals. In the present manuscript, we have taken into account major isomer, in which pentamethylcyclopentadiene rings are almost *trans* disposed with respect to the ligand.

^{1}H-NMR spectrum of the binuclear complex $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-paa})Rh(\eta^5\text{-}C_5Me_5)Cl](BF_4)_2$ (**1**) displayed signals at δ 9.21(d), 9.06 (d), 8.49 (t), 8.28 (m), 7.94 (m), corresponding to pyridyl protons, δ 9.003(s) ppm corresponding to N=CH proton and δ 1.68 ppm corresponding to η^5-C_5Me_5 protons. The paa protons exhibited a downfield shift as compared to that in the free ligand upon coordination with the metal centre [9a,b]. Presence of only five well resolved signals in the ^{1}H-NMR corresponding to paa ligand strongly suggested coordination of both the pyridyl and diazine moieties of the ligand bis-chelating two $[(\eta^5\text{-}$



Scheme 1.

C_5Me_5)ClRh] moieties. It is in good agreement for a symmetrically bridged complex in which two Rh(III) centres are coordinated by the ligand paa. The η^5-C_5Me_5 protons also exhibited a downfield shift as compared to that in the precursor complex [9b] and resonated as a sharp singlet at δ 1.68 ppm. The $^{13}C\{^1H\}$ spectrum of the complex **1** in $CDCl_3$ exhibited resonance at δ 162.9 (N=*C*H), 153.7, 140.4, 129.5, 127.1, 122.8 (pyridyl carbons) 98.7 (*C*$_5$Me$_5$) and 8.8 (*C*H$_3$) ppm. It is in good agreement with the conclusions drawn from ^{1}H-NMR spectral studies. The ^{1}H-NMR spectra of the complexes **2** and **3** followed the general trends observed in the ^{1}H-NMR spectra of the complex **1** except that, it showed additional resonances at 6.8 (dd) and 6.4–6.8 (m) ppm corresponding to phenyl protons of the ligand pbp, bbp. The η^5-C_5Me_5 protons in these complexes also resonated in the same range as that observed in ^{1}H-NMR spectra of the complex **1**. The position and integrated intensity of different signals corroborated well to the formulation of the complexes **2** and **3**. The $^{13}C\{^1H\}$ -NMR spectra of the complexes **2** and **3** followed the trends observed in the ^{1}H-NMR spectra of these complexes.

Electronic spectral data along with their assignments for the binuclear complexes are compiled with the selected data of the complexes. In the electronic spectra of these complexes, intense π–π^* transitions are exhibited in the UV region and ligand to metal charge transfer bands in the visible region. The same general trend is observable in the electronic spectra of all the complexes. For example, the electronic spectra of the representative complex **1** displayed bands in the region ca. 694, 420 and 335 nm. The band and ca. 694 and 420 nm have been assigned to LMCT transitions while the bands around 335 nm has been assigned to intra-ligand π–π^* transitions.

The above analytical and spectral data are consistent with our formulation of the complexes. Finally structure of the representative complex $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-}paa)Rh(\eta^5\text{-}C_5Me_5)Cl](BF_4)_2$ (**1**) has been confirmed by single crystal X-ray diffraction studies (Table 1). An ORTEP view of the complex cation is shown in Fig. 1 and selected bond lengths (Fig. 2), bond angles and torsion angles are recorded in Table 2. The metal centre Rh(1) is coordinated through the pyridyl nitrogen N(3), diazine nitrogen N(2) the chloro ligand Cl(2) and η^5—pentamethylcyclopentadiene ring represented by C(13), C(14), C(15), C(16), C(17) while Rh(2) through the pyridyl nitrogen N(4), diazine nitrogen N(1) the chloro ligand Cl(1) and pentamethylcyclopentadiene ring represented by C(18), C(19), C(20), C(21), C(22). Considering coordination of the pentamethylcyclopentadiene ring as a single coordination site bonded in η^5 manner through its centroid, coordination geometry about both of the metal centres Rh(1) and Rh(2) might be regarded as typical 'piano-stool' geometry. Both the η^5-

Table 1
Crystal data and structure refinement parameters for $C_{32}H_{40}B_2Cl_2F_8N_4ORh_2$

Empirical formula	$C_{32}H_{40}B_2Cl_2F_8N_4ORh_2$
Formula weight	947.02
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	10.205(7)
b (Å)	15.447(7)
c (Å)	24.959(2)
α (°)	90.000(5)
β (°)	97.904(6)
γ (°)	90.000(5)
V (Å^3)	3897.1(5)
Z	4
D_{calc} (mg m^{-3})	1.614
Absorption coefficient (mm^{-1})	1.054
$F(000)$	1896
Crystal size (mm)	0.4 × 0.35 × 0.35
θ Range for data collection (°)	1.55–24.93
Index ranges	$0 \le h \le 12$, $0 \le k \le 18$, $-29 \le l \le 28$
Reflections collected/unique	5923/5923 [$R_{int} = 0.0000$]
Completeness to 2θ	24.93, 83.2%
Absorption correction	ψ-Scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5923/0/464
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0609$, $wR_2 = 0.1621$
R indices (all data)	$R_1 = 0.0708$, $wR_2 = 0.1723$
Goodness-of-fit on F^2	1.059
Largest difference peak and hole (e Å^{-3})	3.212 and −1.283

Table 2
Selected bond lengths (Å), angles (°) and torsion angles (°)

Bond lengths	
Rh(1)–N(3)	2.110(6)
Rh(1)–N(2)	2.154(6)
Rh(2)–N(4)	2.099(6)
Rh(2)–N(1)	2.131(5)
Rh(2)–Cl(1)	2.3840(18)
N(1)–C(7)	1.265(9)
N(1)–N(2)	1.404(8)
N(2)–C(1)	1.269(9)
Bond angles	
N(3)–Rh(1)–N(2)	75.7(2)
N(3)–Rh(1)–Cl(2)	86.29(16)
N(2)–Rh(1)–Cl(2)	85.91(15)
N(4)–Rh(2)–N(1)	75.8(2)
N(4)–Rh(2)–Cl(1)	86.12(17)
N(1)–Rh(2)–Cl(1)	86.28(15)
C(7)–N(1)–N(2)	115.4(6)
C(7)–N(1)–Rh(2)	116.1(5)
N(2)–N(1)–Rh(2)	127.9(4)
C(1)–N(2)–N(1)	114.5(6)
C(1)–N(2)–Rh(1)	115.3(5)
N(1)–N(2)–Rh(1)	129.8(4)
C(6)–N(3)–Rh(1)	125.7(6)
C(8)–N(4)–Rh(2)	115.8(4)
N(3)–C(2)–C(1)	114.0(6)
N(4)–C(8)–C(9)	123.3(7)
N(4)–C(8)–C(7)	114.2(6)
N(1)–C(7)–C(8)	117.9(6)
N(2)–C(1)–C(2)	118.7(7)
Torsion angles	
N(4)–Rh(2)–N(1)–C(7)	−1.4(5)
N(4)–Rh(2)–N(1)–N(2)	−172.7(5)
C(7)–N(1)–N(2)–C(1)	−131.8(7)
N(3)–Rh(1)–N(2)–C(1)	−4.0(5)
Rh(2)–N(1)–N(2)–Rh(1)	−148.4(3)

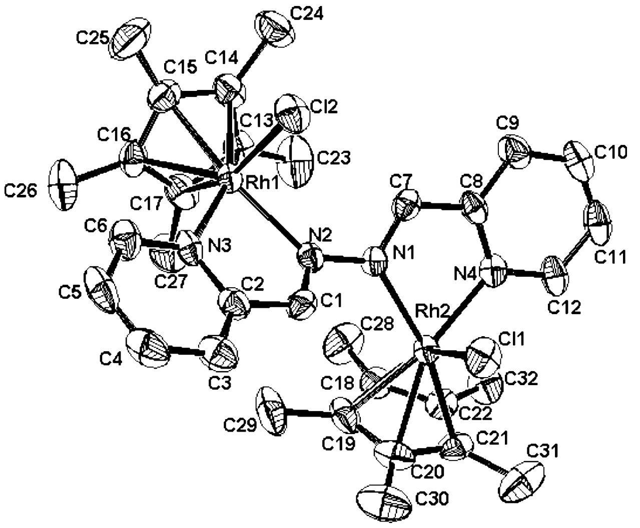


Fig. 2. ORTEP view of the complex cation [(η^5-C_5Me_5)ClRh(μ-paa)Rh(η^5-C_5Me_5)Cl]$(BF_4)_2$ (**1**).

C_5Me_5 rings are planar and methyl substituents on each of the rings are normal. The inter rhodium distance Rh(1)–Rh(2) is 5.1948 Å.

The average Rh(1)–C distance is 2.152(7) Å [range 2.118(8)–2.177(7)] and Rh(2)–C distance is 2.156(7) Å [range 2.122(7)–2.176 Å (7)]. The distance between Rh(1), Rh(2) and centroids of the respective η^5-C_5Me_5 rings are 1.780 and 1.784 Å, respectively. These are comparable to those observed in the other Rh(III) complexes [10a–g]. The C–C bond lengths within the η^5-C_5Me_5 rings and C–CH_3 are 1.423,1.482 Å, respectively. Rh(1)–Cl(2) and Rh(2)–Cl(1) bond lengths are 2.408(18) and 2.38(18) Å. These are comparable to the distances in other related complexes [11a,b].

The ligand paa is not planar and the C(1) N(2) N(1) C(7) torsion angle is −137.8(7)°. The Rh(2)–N(1)–N(2)–Rh(1) torsion angle is −148.4(3)° and it is closer to *trans* than to the *cis* configuration. The Rh to pyridyl nitrogen bond distances Rh(1)–N(3) and Rh(2)–N(4) are 2.110(6) and 2.099(5) Å, respectively and these are slightly lower than rhodium diazine bond lengths Rh(1)–N(2) and Rh(2)–N(1) which are, 2.154(6) and 2.131(5) Å, respectively. These are comparable to those observed in other Rh(III) complexes [12a–e]. The N(1)–N(2) bond distance is 1.404(8) Å, it can be defined as single bond and it is comparable with N–N bond length in hydrazine (1.47 Å) [14]. The C=N bond lengths C(1)–N(2) and C(7)–N(2) are essentially equal and are 1.269(9) and 1.265(9) Å respectively and can be considered to have double bond character. The sum of the angles at N(1) and N(2) are 359.4 and 355°, respectively and indicate that there is no pyramidal distortion.

4. Conclusions

In the present study, we observed that reactions of the ligands paa, pbp or bbp with the chloro-bridged rhodium complex $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$ under 1:1 or 1:2 molar ratios gave binuclear complexes. We could not isolate monomeric complexes even in presence of an excess of the ligands. In related studies, we have isolated and structurally characterized paa containing complexes $[RuH(CO)(PPh_3)_2(paa)]BF_4$ and $[(\eta^6\text{-}C_6Me_6)RuCl(paa)]BF_4$ by reactions of $[RuH(CO)Cl(PPh_3)_3]$ and $[\{(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl\}_2]$ with paa in methanol. It is supposed that these reactions proceed through the intermediacy of the complexes derived by chloro-bridge cleavage and coordination of the ligands through immine–azine nitrogen. The coordination geometry about both the metal centres in these complexes is a typical 'piano stool' geometry. We have structurally characterized the representative complex in which two $(\eta^5\text{-}C_5Me_5)RhCl$ units are bridged by paa. It is the first representative of the structurally characterized rhodium complex containing paa and $[(\eta^5\text{-}C_5Me_5)RhCl]$ moiety. Due to presence of a labile chloro group in these complexes, these could find wide application as homogeneous catalyst. More detailed work in this direction is in progress in our laboratory.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 175310 for the compound $[(\eta^5\text{-}C_5Me_5)ClRh(\mu\text{-}paa)Rh(\eta^5\text{-}C_5Me_5)Cl](BF_4)_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for providing financial assistance through the scheme [HRDG 01(1587)/99/EMR-II], for awarding SRA to A.N.S. and National Diffraction Facility, X-ray Division, IIT Mumbai for single crystal data collection. We also thank to The Head, RSIC, Central Drug Research Institute, Lucknow, for providing analytical and spectral facilities and The Head, Department of Chemistry, A.P.S. University, Rewa for extending laboratory facilities. Special thanks are due to Professor P.M., Department of Chemistry, Indian Institute of Technology, Mumbai for providing single crystal X-ray facility.

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