Cyclometallation of bis-benzimidazole derivatives with rhodium(III) halides

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Abstract

Treatment of rhodium(III) halides with the N-heterocycles (LH), 1,3-bis(benzimidazolyl)benzene (bBzlH$_2$bzH; **Ia**) and its N-methyl derivative (bBzlMe$_2$bzH; **Ib**) in methanol gave halobridged binuclear cyclometallated products of the composition [RhX$_2$L]$_2$ (X=Cl, Br or I). The chloro complex undergoes halobridge cleavage reactions to yield several new mononuclear complexes of the types RhCl$_2$(bBzlH$_2$bz)(AsPh$_3$), RhCl(bBzlH$_2$bz)(OClO$_3$)(L′/N-N) (L′=AsPh$_3$; N-N=2,2′-bipyridine or 1,10-phenanthroline) and the heterocycle bridged binuclear complexes of the composition [RhCl$_2$(bBzlH$_2$bz)]$_2$(μ-N-N) (N-N=pyrazine or 4,4′-bipyridine). Passage of CO through [RhCl$_2$(bBzlH$_2$bz)]$_2$ in DMF yielded mononuclear carbonyl complex RhCl$_2$(CO)(bBzlH$_2$bz)·2H$_2$O. Treatment of carbonylated solution of rhodium trichloride with **Ia** produced non-cyclometallated mononuclear complex of the type [Rh(CO)$_2$(bBzlH$_2$bzH)]Cl. The complexes are characterised by ^{1}H, ^{13}C NMR, IR, Far-IR, electronic and FAB-mass spectral studies. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclometallation; Rhodium; 1,3-Bis(benzimidazolyl)benzene; 1,3-Bis(*N*-methylbenzimidazolyl)benzene; Binuclear complexes; Multidentate N-heterocycles

1. Introduction

The chemistry of a variety of organorhodium complexes of several N-heterocycles and their derivatives has been widely investigated in recent years [1–8]. However, a relatively small number of N-heterocycles are observed to undergo cyclometallation to give five-membered metal-locycles (**II**) [9–16]. Furthermore, the chemistry of cyclometallated complexes is gaining importance as such complexes have been successively used in organic synthesis, asymmetric synthesis, homogeneous catalysis, liquid crystals and photochemistry [17].

Cyclometallation of the N-heterocycles **Ia** and **Ib** could give rise to products corresponding to (i) mononuclear closed metallo-bicycle (**IIIa**; 2-metallation), (ii) mononuclear open metallo-monocycle (**IIIb**; 4- or 6-metallation), or (iii) binuclear open metallo-bicycle (**IIIc**; 4- and 6-metallation, or **IIId**, 2 and 4-, or 2 and 6-metallation), the coordination being symmetrical (**IIIa, c**) or unsymmetrical (**IIIb, d**).

Williams et al. [18] have synthesised a trimer of the 6-metallated acetato palladium(II) complex (**IIIb**, R= CH$_3$; M=Pd) whose crystal structure has been established by X-ray crystallography, the pendant benzimidazole group serving as a donor to another cyclometallated palladium(II). In continuation of our recent publication [19] on the reactions of rhodium and iridium salts with multidentate N-heterocycles, herein we report cyclometallation reactions of rhodium(III) with bis(benzimidazole) derivatives (**I**).
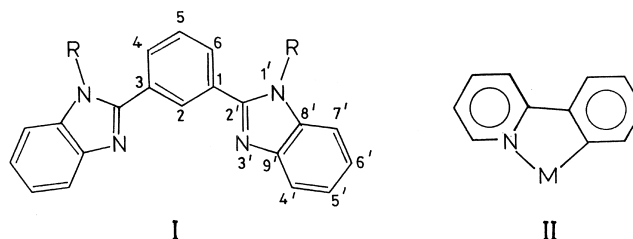
R	Abbreviation
(a) H	bBzlH$_2$bzH
(b) CH$_3$	bBzlMe$_2$bzH

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Symmetrical

Unsymmetrical

(a)

(b)

(c)

(d)
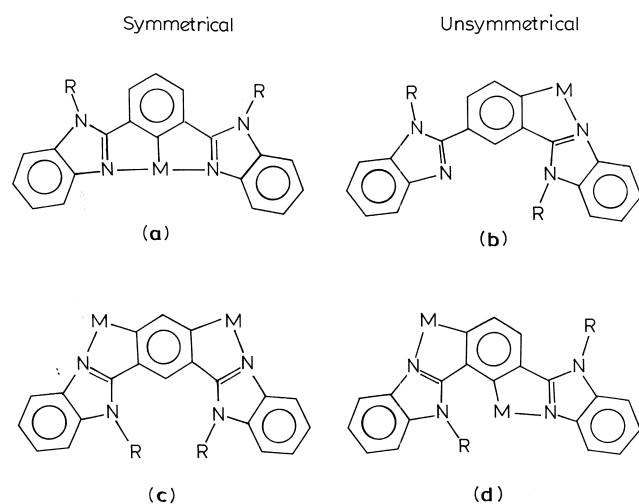
III

2. Experimental

2.1. Materials

The N-heterocycles bBzlH$_2$bzH and bBzlMe$_2$bzH were prepared according to a previously published report [20]. Rhodium trichloride was purchased from Arora-Matthey, India. Hydrated rhodium tribromide was prepared as described elsewhere [21].

2.2. Physical measurement

The IR spectra were recorded on a Carl-Zeiss SPECORD 75-IR and Nicolet FT-IR spectrometer. The electronic spectra were recorded on a Hitachi 150-20 spectrophotometer. The Far-IR spectra were recorded in polyethylene powder on a Bruker IFS 113V spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded at ambient temperatures on a Bruker WH-270 and AMX-400 spectrometer with TMS as the internal reference. Rotating frame Overhauser effect spectroscopy (ROESY) experiments [22,23] were performed in DMSO-d_6. A spin-lock mixing time of 250 ms was used. Nearly 512 FIDs were collected (each of 1024 complex data points) with t_1 incrementation. The resulting data were Fourier transformed along F_1 and F_2 dimensions with zero filling the t_1 data points to 1024. The data were multiplied by squared sinebell window function shifted by 90° on both t_2 and t_1 dimensions prior to Fourier transformation. ^{1}H and ^{13}C spin lattice (T_1) relaxation measurements were performed using inversion recovery method. The FAB-mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer (using Xenon as the FAB gas and *m*-nitrobenzyl alcohol as the matrix) at CDRI, Lucknow, India. Microanalyses were obtained from 240B Perkin Elmer elemental analyser. The molar conductivities were determined using an Elico model CM-82T conductivity bridge with a conventional dip type conductivity cell.

2.3. Preparation of the complexes

2.3.1. [RhX$_2$(bBzlH$_2$bz)]$_2$ and [RhX$_2$(bBzlMe$_2$bz)]$_2$ (X= Cl, Br or I)

Rhodium trichloride/bromide (1 mmol) dissolved in methanol (5 cm^3) was treated with a methanolic solution (5 cm^3) of the N-heterocycle (3 mmol). The mixture was heated under reflux for about 5 h during which a yellow or brown solid was separated. The solid was washed with methanol and dried in vacuo. Yield: 60–80%.

Metathesis reaction of the chloro complexes with 15-fold excess of sodium iodide on prolonged refluxing in methanol (24 h) gave yellowish-brown iodo complexes. Yield: 80%.

2.3.2. RhCl$_2$(bBzlH$_2$bz)(AsPh$_3$)

[RhCl$_2$(bBzlH$_2$bz)]$_2$ (0.5 mmol) was treated with triphenyl arsine (1 mmol) in methanol (50 cm^3) and the mixture was refluxed for 2 days when a yellow solid got separated. It was washed with methanol and dried in vacuo. Yield: 50%.

2.3.3. RhCl(bBzlH$_2$bz)(L′/N-N)(OClO$_3$) (L′=AsPh$_3$; N-N=bipy or phen)

To a suspension of [RhCl$_2$(bBzlH$_2$bz)]$_2$ (1 mmol) in methanol (50 cm^3), triphenyl arsine or 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) (2 mmol) and sodium perchlorate (10 mmol) were added and the mixture was refluxed for 24 h when a yellow solid got separated. It was washed with methanol and water and dried in vacuo. Yield: 60%.

2.3.4. [RhCl$_2$(bBzlH$_2$bz)]$_2$(μ-N-N) (N-N=pyz or bpy)

[RhCl$_2$(bBzlH$_2$bz)]$_2$ (1 mmol) and pyrazine (pyz) or 4,4′-bipyridine (bpy) (1 mmol) in methanol (100 cm^3) were refluxed for 24 h when a yellow solid got separated. It was washed with methanol and dried in vacuo. Yield: 80%.

2.3.5. RhCl$_2$(CO)(bBzlH$_2$bz)·2H$_2$O

CO was bubbled through [RhCl$_2$(bBzlH$_2$bz)]$_2$ (1 mmol) suspended in dimethyl formamide (10 cm^3) and heated to refluxing temperature. Gradually the complex dissolved to give a yellow solution. Passage of CO was continued for 6 h and the resultant solution was evaporated to dryness under reduced pressure when a yellow solid was obtained. It was washed with acetone and dried in vacuo. Yield: 60%.

2.3.6. [Rh(CO)$_2$(bBzlH$_2$bzH)]Cl

CO was bubbled through an ethanolic solution (10 cm^3) of rhodium trichloride (1 mmol) at refluxing temperature

until yellow. To this an ethanolic solution (5 cm^3) of the heterocycle (1 mmol) was added. Passage of CO was continued for about 2 h and the resultant solution was evaporated under CO atmosphere to a small volume when a light yellow solid got separated. The solid was washed quickly with acetone and dried in vacuo. Yield: 60%.

2.3.7. [Rh(CO)₂(bBzlH₂bzH)]ClO₄

[Rh(CO)$_2$(bBzlH$_2$bzH)]Cl (1 mmol) was suspended in methanol (20 cm^3) and to this sodium perchlorate (2 mmol) was added. CO was passed through the mixture at refluxing temperature for 4 h. The complex gradually dissolved to give a yellow solution. It was evaporated to dryness under reduced pressure to obtain a yellow solid. The resultant solid was washed with acetone followed by water and dried in vacuo. Yield: 60%.

3. Results and discussion

The reaction of rhodium(III) halides with the multidentate N-heterocycles (**I**, LH) in methanol resulted in yellow dimeric complexes of the composition [RhX$_2$L]$_2$ (X=Cl or Br). Metathesis reaction of the chloro complex with sodium iodide in methanol produced the iodo analogues in a low state of purity. The complexes are diamagnetic and are insoluble in common organic solvents except for [RhX$_2$(bBzlH$_2$bz)]$_2$ (X=Cl, Br or I) when dissolved in dimethyl formamide and dimethyl sulfoxide, result in solutions being non-conducting.

The solid state IR spectra of the complexes (Table 1) are comparable with those of the uncoordinated N-heterocycles barring minor shifts in the positions of the ligand bands. The NH stretching and N-Me deformation vibrations are observed around 3150 and 1415 cm^{-1}, respec-

Table 1
Analytical and IR data of the complexes

Complex	Analytical data (%) found (calc.)			IR spectral data (cm^{-1})						
	C	H	N	νNH/ δN-Me	νC=N & νC=C	νRh–X$_t$	νRh–X$_b$	νRh–C	νCO	νClO$_4$
[RhCl$_2$(bBzlH$_2$bz)]$_2$	49.5 (49.6)	3.1 (2.9)	11.0 (11.6)	3167	1620 1585	354	301	354		
[RhBr$_2$(bBzlH$_2$bz)]$_2$	42.2 (41.9)	2.1 (2.5)	9.6 (9.8)	3157	1614 1587	264	215	334		
[RhI$_2$(bBzlH$_2$bz)]$_2$	37.2 (36.0)	2.2 (2.1)	8.3 (8.4)	3153	1613 1592	205	150	327		
[RhCl$_2$(bBzlMe$_2$bz)]$_2$	51.9 (51.9)	3.4 (3.5)	10.9 (10.9)	1416	1604 1580	356	316	356		
[RhBr$_2$(bBzlMe$_2$bz)]$_2$	43.7 (44.0)	2.9 (3.0)	8.7 (9.3)	1413	1602 1577	281	223	304		
[RhI$_2$(bBzlMe$_2$bz)]$_2$	37.0 (38.1)	2.4 (2.5)	7.3 (8.1)	1413	1603 1580	212	152	315		
RhCl$_2$(bBzlH$_2$bz)(AsPh$_3$)	57.8 (57.8)	3.8 (3.6)	8.3 (7.1)	3167	1626 1595	322, 332, 337	275[a]	372		
RhCl(bBzlH$_2$bz)(AsPh$_3$)(OClO$_3$)	53.7 (53.5)	3.6 (3.3)	6.5 (6.6)	3155	1636 1610	317, 334	275[a]	340		1180, 1103, 628
RhCl(bBzlH$_2$bz)(bipy)(OClO$_3$)	51.5 (51.2)	3.0 (3.0)	12.0 (12.0)	3200	1624 1590	317, 352	–	369		1114, 1054, 628
RhCl(bBzlH$_2$bz)(phen)(OClO$_3$)	52.5 (52.8)	2.9 (2.9)	11.4 (11.6)	3181	1621 1586	316, 363	–	363		1105, 1057, 628
[RhCl$_2$(bBzlH$_2$bz)]$_2$(pyz)	49.8 (50.5)	3.1 (2.9)	13.0 (13.4)	3193	1625 1594	298, 351	–	366		
[RhCl$_2$(bBzlH$_2$bz)]$_2$(bpy)	53.5 (53.5)	3.3 (3.1)	12.4 (12.5)	3103	1594 1580	300, 358		358		
RhCl$_2$(CO)(bBzlH$_2$bz).2H$_2$O	45.7 (46.1)	3.9 (3.1)	9.9 (10.2)	3172	1629, 1603	321 (*trans*), 303, 336 (*cis*)	–	336	2019, 2091	
[Rh(CO)$_2$(bBzlH$_2$bzH)]Cl	52.1 (51.9)	3.3 (2.8)	10.9 (11.1)	3140	1620	–	–		2000, 2080	
[Rh(CO)$_2$(bBzlH$_2$bzH)]ClO$_4$	46.6 (46.5)	2.8 (2.3)	9.1 (9.9)	3181	1620, 1600	–	–	–	2029, 2091	1098, 628

[a] νRh–As.

Table 2
^{1}H NMR spectral data in DMSO-d_6 (δ in ppm)[a,b]

Complex	4′	5′	6′	7′	2	4,6	5	NH					
bBzlH$_2$bzH	7.65m	7.25m	7.25m	7.65m	9.07s	8.28d	7.75t	13.14s					
[RhCl$_2$(bBzlH$_2$bz)]$_2$	7.71d	7.41m	7.41m	8.01d	–	8.66d	7.51t	14.28s					
	(0.06)	(0.16)	(0.16)	(0.36)		(0.38)	(−0.24)	(1.14)					
[RhBr$_2$(bBzlH$_2$bz)]$_2$	7.73m	7.42m	7.42m	8.01d	–	8.84m	7.52t	14.28s					
	(0.08)	(0.17)	(0.17)	(0.36)		(0.56)	(−0.23)	(1.14)					
[RhI$_2$(bBzlH$_2$bz)]$_2$	7.71m	7.40m	7.40m	8.04d	–	9.09m	7.52t	14.29s					
	(0.06)	(0.15)	(0.15)	(0.39)		(0.81)	(−0.23)	(1.15)					
[Rh(CO)$_2$(bBzlH$_2$bzH)]Cl	7.82m	7.50m	7.50m	7.82m	9.20s	8.49d	8.00t	–					
	(0.17)	(0.25)	(0.25)	(0.17)	(0.13)	(0.21)	(0.25)						
RhCl$_2$(AsPh$_3$)(bBzlH$_2$bz)	6.37d	7.68m	7.68m	7.81d	–	8.57d	7.42m	14.24s	AsPh$_3$ (7.37 to 7.47m)				
	(−1.28)	(0.43)	(0.43)	(0.16)		(0.29)	(−0.33)	(1.10)					
									aa′	bb′	cc′	dd′	ee′
bipy									8.68d	7.93t	7.44t	8.39d	
RhCl(bipy)(bBzlH$_2$bz)(OClO$_3$)	6.00d	7.06t	7.26t	7.65d	–	8.23d	7.78t	14.44s	7.39d	7.31t	8.00t	8.70d	
	(−1.65)	(−0.19)	(0.01)			(−0.05)	(0.03)	(1.30)	(−1.29)	(−0.62)	(0.56)	(0.31)	
									10.24d	8.48t	8.83t	9.12d	
									(1.56)	(0.55)	(1.39)	(0.73)	
phen									9.10m	8.48m	7.77m		7.97s
RhCl(phen)(bBzlH$_2$bz)(OClO$_3$)	5.73d	6.88t	7.17t	7.59d	–	8.26m	7.82t	14.45s	7.71d	7.63t	8.62d		8.26m
	(−1.92)	(−0.37)	(−0.08)	(−0.06)		(−0.02)	(0.07)	(1.31)	(−1.39)	(−0.85)	(0.85)		(0.29)
									10.50d	8.81m	9.45m		8.57d
									(1.4)	(0.33)	(1.68)		(0.60)

[a] Values in parentheses are coordination induced shifts (c.i.s.=δ complex – δ ligand).
[b] s=singlet, d=doublet, t=triplet, m=multiplet.

Table 3
^{13}C NMR spectral data in DMSO-d_6 (δ in ppm)[a]

Complex	2′	4′	5′	6′	7′	8′	9′	1,3	2	4,6	5						
bBzlH$_2$bzH	150.85	119.04	122.04	122.95	111.67	135.21	143.84	131.03	124.84	127.65	129.82						
[RhCl$_2$(bBzlH$_2$bz)]$_2$	158.08	117.73	123.57	123.80	112.77	133.10	140.77	132.77	181.63[b],	124.62	124.31						
	(7.23)	(−1.31)	(1.53)	(0.85)	(1.10)	(−2.11)	(−3.07)	(1.74)	23.91[c]	(−3.03)	(−5.51)						
									(56.79)								
[RhBr$_2$(bBzlH$_2$bz)]$_2$	158.34	118.30	123.45	123.80	112.60	133.11	141.14	132.73	181.97[b]	124.70	124.36						
	(7.49)	(−0.74)	(1.41)	(0.85)	(0.93)	(−2.10)	(−2.7)	(1.70)	24.45[c]	(−2.95)	(−5.46)						
									(57.13)								
RhCl$_2$(CO)(bBzlH$_2$bz).2H$_2$O	150.65	115.18	122.96	122.96	115.18	138.78	138.78	133.37	184.10[b]	129.97	130.30				(CO) 181.51[b],		
	(−0.2)	(−3.86)	(0.92)	(0.01)	(3.51)	(3.57)	(−5.06)	(2.34)	20.0[c]	(2.32)	(0.48)				79.9[c]		
									(59.26)								
[Rh(CO)$_2$(bBzlH$_2$bzH)]Cl	148.95	114.67	124.86	124.86	114.67	135.01	135.01	127.30	130.56	130.22	126.72				(CO) 181.80[b],		
	(−1.9)	(−4.37)	(2.82)	(1.91)	(3.0)	(−0.2)	(−8.83)	(−3.73)	(5.72)	(2.57)	(1.88)				72.62[c]		
												aa′	bb′	cc′	dd′	ee′	ff′
bipy												149.07	137.03	120.29	123.93	155.18	
RhCl(bipy)(bBzlH$_2$bz)(OClO$_3$)	158.15	113.31	124.07	124.07	113.31	132.70	139.42	133.52	184.94[b]	125.21	125.59	151.68	128.04	139.96	124.07	156.46	
	(7.30)	(−5.73)	(2.03)	(1.12)	(1.64)	(−2.51)	(−4.42)	(2.49)	22.28[c]	(−2.44)	(−4.23)	(2.61)	(−8.99)	(19.67)	(0.14)	(1.28)	
									(60.1)			150.63	128.34	141.34		154.59	
												(1.56)	(−8.69)	(21.05)		(−0.59)	
phen												149.94	136.19	126.66	128.45	123.30	145.54
RhCl(phen)(bBzlH$_2$bz)(OClO$_3$)	158.29	113.34	123.75	123.75	113.18	132.75	139.64	133.91	184.93[b]	125.34	125.49	152.64	126.69	139.02	130.22	127.80	146.77
	(7.44)	(−5.7)	(1.71)	(0.8)	(1.51)	(−2.46)	(−4.20)	(2.88)	22.71[c]	(−2.31)	(−4.33)	(2.7)	(−9.5)	(12.36)	(1.77)	(4.5)	(1.23)
									(60.09)			151.64	127.19	139.99	130.50	128.31	145.49
												(1.7)	(−9.0)	(13.33)	(2.05)	(5.0)	(−0.05)

[a] Values in parentheses are coordination induced shifts (c.i.s.=δ complex − δ ligand).

[b] Doublet.

[c] J_{Rh-C} in Hz.

tively and are suggestive of the coordination of the N-heterocycles to the metal ion via the tertiary nitrogens. The Far-IR spectra of the complexes displayed peaks corresponding to rhodium–halogen stretches and are indicative of the presence of both terminal and bridged types of halides [24]. The spectra also displayed a peak due to νRh–C in the range 300–360 cm^{-1}; the result pointing to cyclometallation [25] of the bis-benzimidazole derivative. Cyclometallation is further supported by the ^{1}H and ^{13}C NMR spectra of the complexes and also the FAB-mass spectra.

The PMR spectra of bBzlH$_2$bzH and [RhX$_2$L]$_2$ in DMSO-d_6 (Table 2) exhibited resonances due to the central benzene and the benzimidazole ring protons. The resonance due to the imine proton is observed around 14 δ. The resonance at 9.07 δ arising from the proton on carbon-2 of the central benzene/phenylene ring of the un-coordinated heterocycle bBzlH$_2$bzH is absent in the spectra of the complexed species. Furthermore, the ^{13}C resonance of C-2 which appeared as a singlet at 129.82 δ for the free heterocycle is split into a doublet [26–28] and has shifted downfield by nearly 50 δ on complexation (Table 3). The splitting is due to the interaction of ^{13}C with ^{103}Rh (100%, $I=1/2$) the coupling constant being 24 Hz is diagnostic of rhodium–carbon direct linkage. The resonances due to C-4′ and C-9′ of bBzlH$_2$bz unit have undergone an upfield shift on complexation.

The FAB-MS of [RhCl$_2$L]$_2$ (LH=bBzlH$_2$bzH) has confirmed the dinuclear nature of the complex. The spectrum showed a parent ion peak at m/z 966 [M$^+$+2H]. The parent ion loses Cl, HCl or [HCl+H] to give peaks at m/z 931, 930 and 929, respectively. These further lose (HCl+H), HCl or Cl, respectively to give a peak at m/z 894 due to Rh$_2$Cl$_2$L$_2$. Subsequent fragmentation produced the mononuclear species RhL$_2$ (by loss of RhCl+Cl) and RhClL (due to loss of RhClL). These molecular ions lose L or Cl, respectively, to give RhL (m/z 412), which in turn loses (Rh+2H) to give a peak (L $-$2H) at m/z 307. The fragmentation reactions are summarised in Scheme 1.

The electronic spectra of [RhX$_2$L]$_2$ exhibited weak absorption bands in the range 400–500 nm (Table 4) and are ascribed to d–d transitions of octahedral spin paired d^6 system [29]. An intense peak at 370 nm is attributed to metal-to-ligand charge transfer transition.

The N-heterocycles can serve as bidentate or tridentate ligands. Earlier, it has been observed that the heterocycles have displayed a bidentate non-cyclometallated behaviour [20] in CoX$_2$(LH) (X=Cl, Br or I; LH=Ia or Ib) and Co(LH)$_2$(ClO$_4$)$_2$ complexes and a bridging tridentate cyclometallated behaviour in [PdL(OOCCH$_3$)]$_3$·9CH$_3$CN complex [18]. In the present investigation a tridentate behaviour of the N-heterocycles (N–C–N) leading to non-bridging cyclometallation but dihalobridged binuclear nature has been observed. Considering the N-heterocycles as planar and by taking the N–C–N skeleton, two structures can be conceived for such complexes, the one being
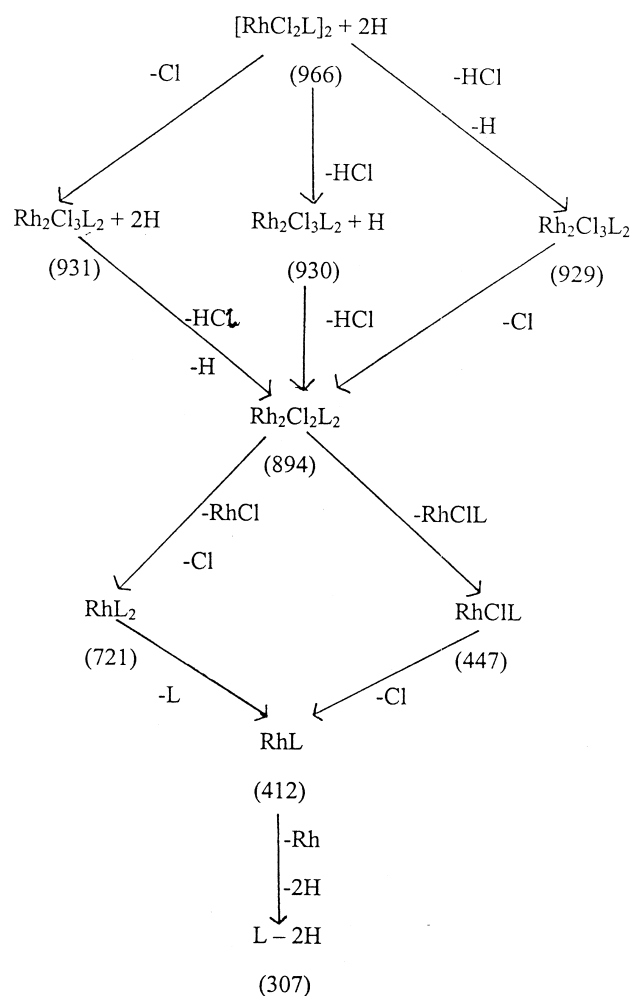
Scheme 1. Fragmentation pathway of [RhCl$_2$L]$_2$.

centrosymmetric (*trans*, **IVa**) and the other being non-centrosymmetric (*cis*, **IVb**). Molecular models favour the former (**IVa**) which has less steric hindrance than the latter. Further with both in the ^{1}H and ^{13}C NMR spectra, only one set of resonances have been observed implying the chemical equivalence of the corresponding protons as well as the carbons of the two heterocycles in each of the binuclear complexes.

The complex [RhCl$_2$(bBzlH$_2$bz)]$_2$ undergoes halobridge cleavage reaction. It reacts with AsPh$_3$ in methanol at refluxing temperature to give a monomeric complex RhCl$_2$(bBzlH$_2$bz)(AsPh$_3$) (**V**). In the presence of excess of sodium perchlorate, complex of the type RhCl(bBzlH$_2$bz)(AsPh$_3$)(OClO$_3$) has been isolated. The dimer [RhCl$_2$(bBzlH$_2$bz)]$_2$ reacts with chelating bidentate ligands like 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) in the presence of excess of sodium perchlorate to form yellow crystalline monomeric complexes of the type RhCl(bBzlH$_2$bz)(N-N)(OClO$_3$) (**VI**) (N-N=bipy or phen). On the other hand with bridging bidentate ligands, [RhCl$_2$(bBzlH$_2$bz)]$_2$ in methanol yielded complexes of the type [RhCl$_2$(bBzlH$_2$bz)]$_2$(μ-N-N) (**VII**) (N-N=pyrazine

Table 4
Electronic spectral data in DMF (nm)

Complex	Electronic transitions[a]		
	Ligand bands	M→L Charge transfer Transition	d→d transitions
bBzlH$_2$bzH	300 (44231)		
	309 (51442)		
	324 (35817)		
	335 (2599)		
[RhCl$_2$(bBzlH$_2$bz)]$_2$	299 (29170)		
	309 (31340)	370(9434)	
	336 (16585)	384(7774)	443(98), 469(34), 517(5)
[RhBr$_2$(bBzlH$_2$bz)]$_2$	304 (37409)	367(12863)	
	339 (15855)	384(11593)	405(737),434(208), 475(83), 548(18)
[RhI$_2$(bBzlH$_2$bz)]$_2$	299(28333)	373(11391)	
	310(29925)	386(8358)	459(266), 591(27)
	325(22895)		
	340(16855)		
RhCl$_2$(bBzlH$_2$bz)(AsPh$_3$)	309(36509)	376(10816)	
	345(22209)	386(8899)	
		395(4763)	440(140), 468(64)
RhCl(bBzlH$_2$bz)(AsPh$_3$)(OClO$_3$)	308(43478)	396(4512)	
	338(28225)	388(7406)	439(58), 469(71)
	343(24792)		
RhCl(bBzlH$_2$bz)(bipy)(OClO$_3$)	297(30027)	388(9835)	
	360(18283)	398(3004)	418(905), 466(42)
RhCl(bBzlH$_2$bz)(phen)(OClO$_3$)	278(30425)	389(9162)	
	292(29621)	397(3759)	447(66), 466(31)
	358(18703)		
[RhCl$_2$(bBzlH$_2$bz)]$_2$(pyz)	304(53888)	386(23056)	
	367(24078)	392(1200)	
		394sh(11341)	439(258), 471(94)
[RhCl$_2$(bBzlH$_2$bz)]$_2$(bpy)	294(47525)	382(29670)	
	300(39142)	393(13894)	440(207), 474(119)
RhCl$_2$(CO)(bBzlH$_2$bz).2H$_2$O	305(35605)	375(2288)	
		395(809)	422(244), 450(74)

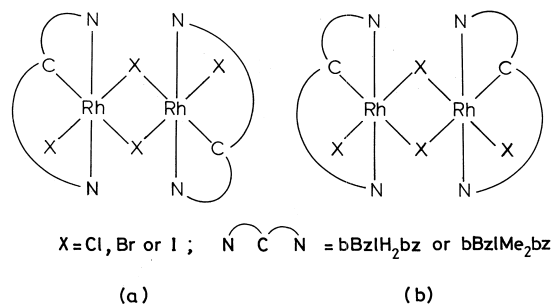[a] ϵ values are in parentheses.

(pyz) or 4,4′-bipyridyl (bpy)). A similar reaction with phenazine also produced a binuclear complex, though in a low state of purity. Reaction of CO with [RhCl$_2$(bBzlH$_2$bz)]$_2$ in dimethylformamide at refluxing temperature gave monomeric yellow rhodium(III) carbonyl complex of the composition RhCl$_2$(CO)(bBzlH$_2$bz)·2H$_2$O (**VIII**).
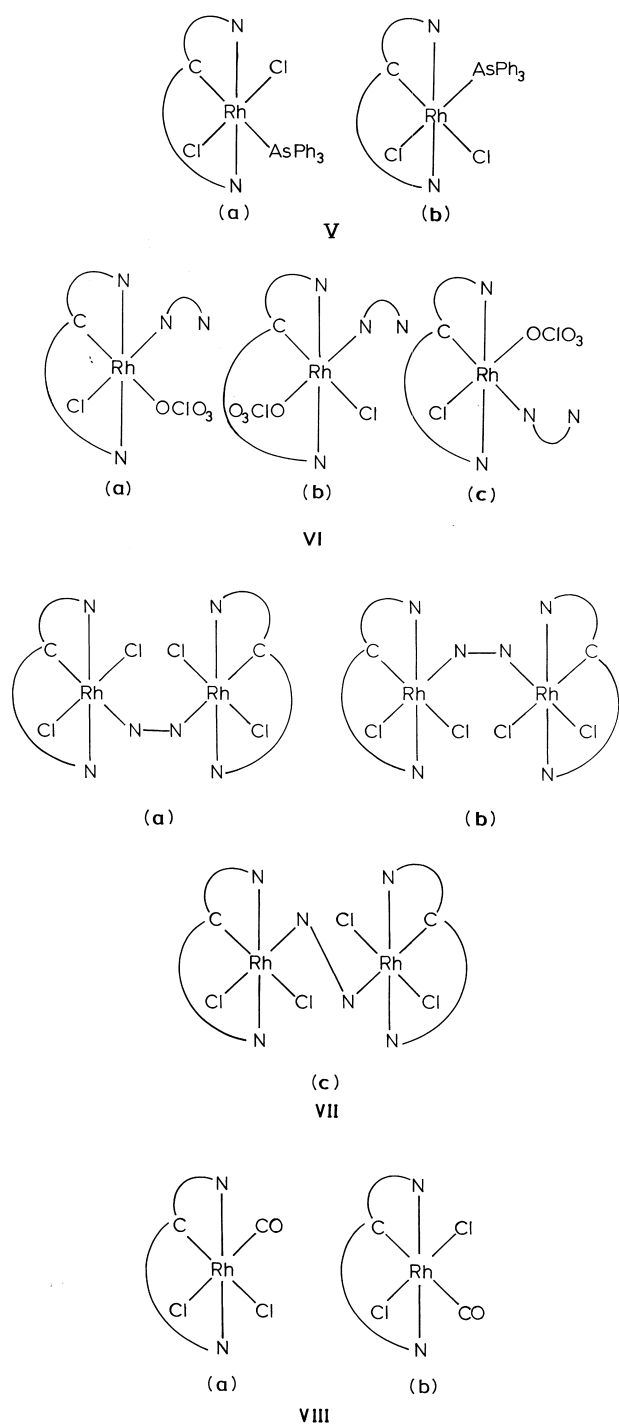
The complexes are insoluble in common organic solvents but soluble in dimethyl formamide or dimethyl sulfoxide in which the solutions are non-conducting. The physical properties and analytical data of the complexes are listed in Table 1.

The complexes exhibit νNH in the range 3100–3200 cm^{-1} as a broad peak. The perchlorate complexes (being non-electrolytes in DMSO/DMF) in addition to the heterocycle bands exhibit peaks around 1100 and 628 cm^{-1}, the former peak is split indicating the coordination of perchlorate to the metal ion [30]. In view of the above, it is likely that the heterocycle bipy or phen is behaving as a monodentate rather than bidentate ligand. This is sup-

ported by ^{1}H and ^{13}C NMR spectra of the complexes. The carbonyl complex exhibits two intense νCO peaks at 2019 and 2091 cm^{-1} indicating the presence of two isomers (**VIII**; CO *trans* to Cl and *trans* to C). The Far-IR spectra of the complexes exhibit peaks corresponding to νM-Cl, νM-N and νM-C, and are diagnostic of terminal halides.

The ^{1}H NMR spectra of the complexes displayed peaks

X = Cl, Br or I ;   N⌒C⌒N = bBzlH$_2$bz or bBzlMe$_2$bz

(a)   (b)

IV

V (a) (b)

VI (a) (b) (c)

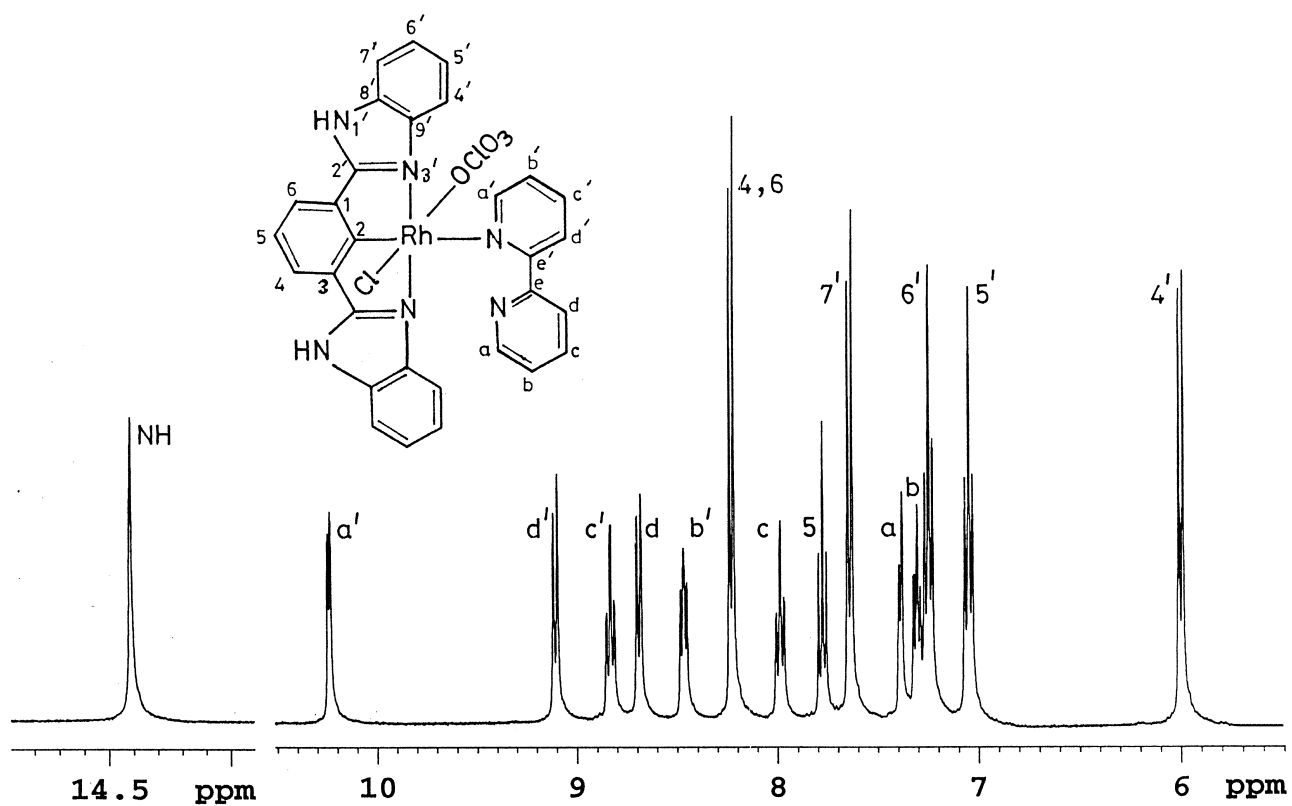**VII** (a) (b) (c)

VIII (a) (b)

due to bBzlH$_2$bz and the substituted ligands. The resonance due to the imine proton is observed around 14 δ. The resonance of H-4′ of bBzlH$_2$bz has undergone an upfield shift as compared to that of the parent complex. A negative c.i.s. has been observed and this is probably due to metal-to-ligand π-back donation [31]. Interestingly the ^{1}H and ^{13}C NMR spectra of the complexes RhCl(bBzlH$_2$bz)(N-N)(OClO$_3$) (N-N=bipy or phen) exhibited two sets of resonances due to bipy or phen (Figs. 1 and 2). One set of proton resonances in the upfield region assignable to the

uncoordinated part of the heterocycle and the other set in the downfield region to the coordinated part. Surprisingly, the heterocycle, bipy or phen is neither chelating nor bridging bidentate in the complexes. Such a coordination with pendant nitrogen is rather unusual in organometallic chemistry. The monodentate behaviour of bipy or phen in the complexes is also supported by ROESY measurements. The ROESY spectra of the complexes have revealed the interaction of all the protons (a′ to d′) of the coordinated part of bipy or phen with H-4′ of bBzlH$_2$bz as evidenced by the interligand NOE measurements. The H-4′ shows NOE to a′, b′, c′ and d′ in the bipy complex and a′, b′ and c′ in the phen complex. The results indicate that the coordinated part of the bipy or phen is much closer to bBzlH$_2$bz than the uncoordinated part. The spin lattice relaxation times of the protons and carbons of the coordinated part of the bipy in RhCl(bBzlH$_2$bz)(bipy)(OClO$_3$) are observed to be lower compared to those of the uncoordinated part implying more flexibility of the latter unit. Detailed 2D NMR studies on the complexes are in progress. The monodentate behaviour of the ligand may be attributed to the electronic factor rather than the steric hindrance around the metal ion. The complexes exhibit negative c.i.s. values for C-4′ and C-9′ of bBzlH$_2$bz. The ^{13}C NMR spectrum of the carbonyl complex displayed two doublets one at 182 and the other at 184 δ. The ^{103}Rh – ^{13}C coupling constant of the former is 80 Hz (due to Rh–CO) whereas that of the latter is 20 Hz (due to Rh–C-2 of bBzlH$_2$bz).

The FAB-MS of RhClL(N-N)(OClO$_3$) (LH= bBzlH$_2$bzH) have confirmed the mononuclear nature of the complexes. The spectra consist of molecular ion peaks at m/z 702 (N-N=bipy) and 726 (N-N=phen). Both the complexes first lose perchlorate to produce RhClL(N-N) and then Cl to give RhL(N-N). Subsequent loss of N-N gives RhL (m/z 412). Both RhL(N-N) and RhL lose Rh+2H to give a ligand peak at m/z 307. In the case of the FAB-MS of [RhCl$_2$(bBzlH$_2$bz)]$_2$(μ-bpy) the molecular ion peak corresponding to the dimer (m/z 1120) was not observed, but the peaks due to the fragmentation products RhClL$_2$ (m/z 757), RhL$_2$ (m/z 712), RhClL (m/z 447) and Rh(bBzlH$_2$bz) (m/z 412) were observed.

A dicarbonyl complex of rhodium(I) RhCl(CO)$_2$(bBzlH$_2$bzH) as a light yellow solid was isolated by treating an alcoholic carbonylated solution of rhodium trichloride with bBzlH$_2$bzH. In the case of bBzlMe$_2$bzH, a blue coloured dicarbonyl (νCO, 1993 and 2068 cm^{-1}) of low state of purity was obtained. The chloro carbonyl is insoluble in nitrobenzene and acetonitrile but soluble in dimethyl formamide and alcohol in which its electrolytic behaviour is uni-univalent.

The IR spectrum of the chloro carbonyl in addition to the ligand peaks exhibited two intense peaks around 2000 and 2080 cm^{-1} due to νCO. The νNH of the coordinated heterocycle is observed at 3140 cm^{-1}. The complex has not undergone metallation reaction as evidenced by its ^{1}H and ^{13}C NMR spectra. The PMR spectrum has displayed a

Fig. 1. ^{1}H NMR spectrum of RhCl(bBzlH$_2$bz)(bipy)(OClO$_3$).
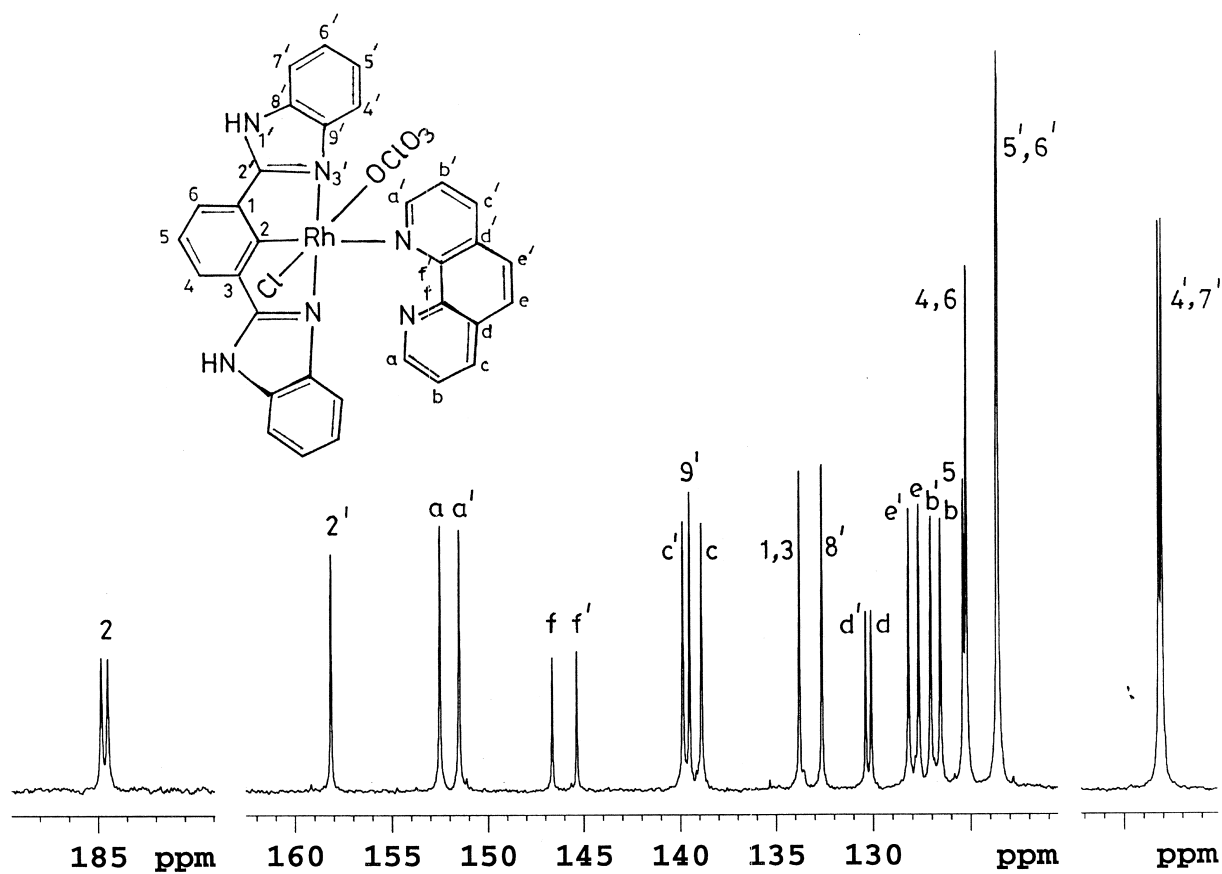
Fig. 2. ^{13}C NMR spectrum of RhCl(bBzlH$_2$bz)(phen)(OClO$_3$).

$N \underset{H}{\overset{C}{\frown}} N = bBzlH_2bzH$

IX
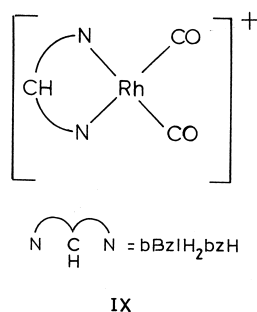
singlet at 9.20 δ corresponding to the proton on carbon-2. The imine proton resonance is not observed and is probably too broad owing to rapid exchange of this proton with those of water in the solvent. In the ^{13}C NMR spectrum a peak due to C-2 of bBzlH$_2$bzH is observed at 126.7 δ. This has not shifted appreciably as compared to that of the free heterocycle. Furthermore the peak is not split implying non-metallation. However, a doublet resonance at 181 δ due to the carbonyl with a Rh–C coupling constant of 73 Hz has been observed. The FAB-MS of RhCl(CO)$_2$(bBzlH$_2$bzH) has revealed mononuclear nature of the complex. The spectrum displayed a parent ion peak at m/z 505 (M$^+$+H). Loss of the carbonyl groups and HCl produced Rh(LH) (m/z 413). Further loss of Rh occurs to give L+H (m/z 311).

The carbonyl complex is cationic in nature. The ionic chloride can be replaced by perchlorate by suspending the complex in alcohol in the presence of sodium perchlorate in CO atmosphere. The IR spectrum of the resultant complex [Rh(CO)$_2$(bBzlH$_2$bzH)]ClO$_4$ exhibited two νCO peaks (2029 and 2091 cm^{-1}) and also peaks due to ionic perchlorate [30] (1098 and 628 cm^{-1}). Based on the above results a square planar structure (**IX**) wherein the heterocycle would function as bidentate has been proposed for the complex cation.

Acknowledgements

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