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Reactions of rhodium and iridium salts with multidentate *N*-heterocycles

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Abstract—Complexes of rhodium and iridium of the types MX_3L, $MX(CO)_2L$ and $MX_3(CO)L$ (X = halide) containing multidentate *N*-heterocycles (L), 2,6-bis(benzimidazolyl)pyridine ($bBzlH_2py$) and 2,6-bis(*N*-methylbenzimidazolyl)pyridine ($bBzlMe_2py$) have been prepared and characterized by IR, electronic and ^1H and ^{13}C NMR spectral data. $RhX(CO)_2L$, on treatment with alcoholic solvents or DMF undergoes reversible decarbonylation to produce $RhXL \cdot 2H_2O$. Passage of NO or O_2 through the carbonyl suspended in hot 2-methoxyethanol releases CO_2. Copyright © 1997 Elsevier Science Ltd

Keywords: rhodium; iridium; multidentate *N*-heterocycles; carbon monoxide; 2,6-bis(benzimidazolyl) pyridine; 2,6-bis(*N*-methylbenzimidazolyl)pyridine.

Development of new multidentate *N*-heterocycles, which produce organised supramolecules upon coordination to metal ions is of interest in the recent past [1]. They are quite promising in the design of stable light conversion devices and in the production of triple stranded helicates [2]. Further a wide variety of complexes associated with *N*-donor ligands are being actively considered for their catalytic activity [3]. We have been investigating metal complexes containing *N*-heterocycles as they are of potential relevance in such studies. Here, we describe the syntheses and characterization of complexes of rhodium and iridium containing polydentate benzimidazole derivatives (I), 2,6-bis(benzimidazolyl/*N*-methylbenzimidazolyl) pyridine ($bBzlH_2py$/$bBzlMe_2py$).

I

R	L
H	$bBzlH_2py$
CH_3	$bBzlMe_2py$
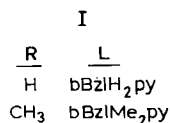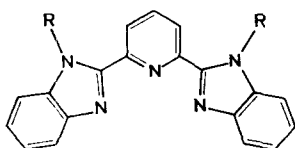
EXPERIMENTAL

Hydrated rhodium trichloride and sodium hexahaloiridates were obtained from Arora Matthey, India and Johnson Matthey, England. Hydrated rhodium tribromide and rhodium(III) perchlorate were prepared as described elsewhere [4]. Polydentate *N*-heterocycles-2,6-bis(benzimidazolyl)pyridine and its *N*-methylated derivative were prepared according to literature methods [5–7]. The IR (nujol mull and KBr) and electronic (Nujol mull and DMF solution) spectra were recorded on Carl–Zeiss SPECORD 75-IR and Hitachi 150-20 spectrophotometers, respectively. The ^1H and ^{13}C NMR spectra in DMSO-d_6 were recorded at ambient temperatures on Bruker 270 and 400 MHz spectrometers with TMS as the internal reference. Conductivity measurements were carried out using a Toshniwal conductivity bridge type CL 01.02.

Preparation of the complexes

$RhX_3(bBzlH_2py/bBzlMe_2py)$ (X = Cl, Br *or* I). An ethanolic solution (10 cm³) of rhodium trichloride/bromide (1 mmol) was treated with the *N*-heterocycle (1 mmol) dissolved in ethanol (10 cm³) and the mixture was refluxed on a steam bath for 4 h during which yellow or orange solid separated. It was washed with alcohol and dried *in vacuo*.

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Metathesis reaction of the chloro complex in ethanol with 15-fold excess of sodium iodide gave the iodo complex as a brown solid. Yield: 80–90%.

[Rh(bBzlH$_2$py)$_2$(OClO$_3$)](ClO$_4$)$_2$ *and* [Rh(bBzlMe$_2$py)](ClO$_4$)$_3$. The perchlorate complexes were prepared using the procedure described above by taking rhodium perchlorate and the heterocycle in the mole ratio 1:2. Yield: 65%.

IrX$_3$(bBzlH$_2$py/bBzlMe$_2$py) (X = Cl *or* Br). The complexes were prepared in the same way (preceding method) starting from sodium hexahalo iridate(IV) using 2-methoxy ethanol as the solvent. Yield: 55–60%.

RhX(CO)$_2$L · nH$_2$O (X = Cl *or* Br, L = bBzlH$_2$py, n = 1.5; X = Cl, L = bBzlMe$_2$py, n = 1). CO was bubbled through an ethanolic solution (10 cm^3) of hydrated rhodium trihalide (1 mmol) at refluxing temperature until it turned yellow. To this was added the N-heterocycle (1 mmol) in ethanol (10 cm^3) and the passage of CO was continued for about half an hour when an amorphous green solid separated. The solid was washed with ether and dried *in vacuo*. Yield: 60–70%.

Rh(bBzlH$_2$py)(CO)$_2$(OClO$_3$) *and* [Rh(bBzlMe$_2$py)(CO)$_2$]ClO$_4$. The complexes were prepared starting from the carbonylated rhodium perchlorate solution using the procedure described above. Yield: 60%.

[RhX$_2$(CO)(bBzlH$_2$py)]X (X = Cl *or* Br). RhX(CO)$_2$(bBzlH$_2$py) · 1.5H$_2$O (1 mmol) was suspended in CCl$_4$ (10 cm^3) and to this was added the corresponding halogen in CCl$_4$ (2 mmol) followed by ethanol (5 cm^3). The mixture was stirred, when the green dicarbonyl gradually dissolved simultaneously precipitating yellow/orange solid. It was washed with CCl$_4$ followed by ether and dried *in vacuo*. Yield: 60%.

IrX(CO)$_2$ (bBzlH$_2$py) · nH$_2$O (X = Cl, n = 1; X = Br, n = 1.5). CO was bubbled through sodium hexahalo iridate (1 mmol) in 2-methoxy ethanol (10 cm^3) at refluxing temperature until the solution turned yellow. The solution was cooled to room temperature and the N-heterocycle (1 mmol) dissolved in 10 cm^3 of 2-methoxyethanol was added and the passage of CO was continued for 2 h. The solvent was evaporated under CO atmosphere to nearly 5 cm^3 and cooled to ice temperature when a green or red solid separated. It was washed with ether and dried *in vacuo*. Yield: 55%.

RESULTS AND DISCUSSION

Reaction of rhodium trihalide or sodium hexahalo iridate with the N-heterocycle, bBzlH$_2$py/bBzlMe$_2$py (I) in 1:1 mole ratio in alcohol/2-methoxyethanol produced yellow, orange and red complexes whose elemental analyses correspond to the formula MX$_3$L (M = Rh or Ir, X = Cl or Br, L = bBzlH$_2$py or bBzlMe$_2$py). In the case of rhodium, the iodo analogs

are prepared by stirring a mixture of rhodium trichloride with 15-fold excess of sodium iodide and the N-heterocycle in 1:1 mole ratio in methanol. The complexes are insoluble in common organic solvents, but dissolve in DMF in which they behave as non-electrolytes. The complexes containing bBzlMe$_2$py are sparingly soluble in DMF.

Rhodium(III) perchlorate reacts with bBzlH$_2$py and bBzlMe$_2$py in the mole ratio 1:2 in methanol refluxing temperature to give yellow crystalline solids. The elemental analyses of the complexes correspond to the formula RhL$_2$(ClO$_4$)$_3$. While the bBzlH$_2$py complex behaves as a 1:2 electrolyte in MeCN or DMF, the bBzlMe$_2$py analog is a 1:3 electrolyte in the same solvents. However, the former displayed 1:3 electrolytic behavior in DMSO. Some physical properties and analytical data of the complexes are listed in Table 1.

Treatment of a carbonylated solution of rhodium trihalide/perchlorate with the multidentate N-heterocycles produced green solids of the composition MX(CO)$_2$L · nH$_2$O (M = Rh, X = Cl or Br, n = 1.5, L = bBzlH$_2$py; X = ClO$_4$, n = 0, L = bBzlH$_2$py or bBzlMe$_2$py; X = Cl, n = 1, L = bBzlMe$_2$py). The halocarbonyl complexes are also obtained by the (i) carbonylation of RhX$_3$L in DMF (ii) halobridge cleavage of the carbonyl dimers, [RhX(CO)$_2$]$_2$ (X = Cl or Br) with the N-heterocycle. The bromocarbonyl complex containing bBzlMe$_2$py is obtained in a low state of purity. Carbonylation reactions with sodium hexahalo iridate and the N-heterocycle yielded green/orange solids of the composition IrX(CO)$_2$ (bBzlH$_2$py). The bBzlMe$_2$py analogs are yet to be properly characterized.

The chloro- and bromocarbonyl complexes of rhodium are diamagnetic and undergo decarbonylation on treatment with solvents like alcohol, 2-methoxy ethanol and DMF to produce yellow solids whose elemental analyses correspond to the formula RhX(L) · 2H$_2$O. Carbonylation of the latter suspended in the same solvents produced the parent carbonyls. Further the passage of NO or O$_2$ through alcoholic (2-methoxy or 2-ethoxy ethanol) suspension of RhX(CO)$_2$L or RhXL · 2H$_2$O around 100°C produced carbon dioxide. Thus, these complexes seem to be good candidates for the design of three-way catalysts for automobile exhaust emissions. This is in view of the fact that among platinum group metals, rhodium has displayed the best catalytic activity [8]. This work is being pursued.

The dicarbonyl RhX(CO)$_2$(bBzlH$_2$py) · 1.5H$_2$O (X = Cl or Br) on oxidative addition with the corresponding halogen in CCl$_4$ undergoes the loss of a CO ligand and affords yellow or orange products of the formula [RhX$_2$(CO)(bBzlH$_2$py)]X. Such an oxidative addition reaction did not proceed in the case of RhCl(CO)$_2$(bBzlMe$_2$py) · H$_2$O.

The Nujol mull IR spectra of the complexes are similar to those of the uncoordinated N-heterocycles, except for the minor shifts in the positions of the

Table 1. Physical properties and analytical data of the complexes

Complex	Color	m.p. d.p. (°C)	IR spectral data (cm^{-1}) v_{CO}	v_{ClO_4}	Analytical data (%) Found (Calc) C	H	N
RhCl$_3$(bBzlH$_2$py)	Yellow	>250			43.9 (43.8)	2.2 (2.5)	13.4 (13.5)
RhBr$_3$(bBzlH$_2$py)	Orange	>250			34.6 (34.9)	2.2 (2.0)	10.3 (10.7)
RhI$_3$(bBzlH$_2$py)	Brown	>250			28.2 (28.7)	1.7 (1.7)	8.5 (8.8)
[Rh(bBzlH$_2$py)$_2$(OClO$_3$)](ClO$_4$)$_2$	Yellow	180		1143 1120 623	46.8 (44.6)	2.6 (2.6)	13.6 (13.7)
RhCl(CO)$_2$(bBzlH$_2$py)·1.5H$_2$O	Green	225	2021, 1987		47.4 (47.3)	3.0 (3.0)	13.9 (13.2)
RhBr(CO)$_2$(bBzlH$_2$py)·1.5H$_2$O	Green	180	2027 1193		43.1 (43.7)	2.6 (2.8)	12.6 (12.1)
Rh(CO)$_2$(bBzlH$_2$py)(OClO$_3$)	Green	200–210	2047, 1987	1141, 1113, 1100, 627	45.3 (44.3)	2.8 (2.3)	12.4 (12.3)
RhCl(bBzlH$_2$py)·2H$_2$O	Yellow	>250			46.9 (47.0)	3.3 (3.5)	13.7 (13.7)
RhBr(bBzlH$_2$py)·2H$_2$O	Yellow	>250			42.2 (43.0)	3.3 (3.2)	12.5 (13.2)
[RhCl$_2$(CO)(bBzlH$_2$py)]Cl	Yellow	>250	2119w 2068s		43.8 (43.8)	2.5 (2.4)	12.8 (12.7)
[RhBr$_2$(CO)(bBzlH$_2$py)]Br	Orange	>250	2100w/ 2100s 2058s/	35.0	2.1 (35.2)	9.7 (1.9)	(10.3)
RhCl$_3$(bBzlMe$_2$py)	Yellow	>250	2060w		46.3 (46.0)	2.9 (3.1)	13.3 (12.8)
RhBr$_3$(bBzlMe$_2$py)	Orange	>250			36.9 (37.0)	2.4 (2.5)	11.1 (10.3)
RhI$_3$(bBzlMe$_2$py)	Brown	>250			29.8 (30.7)	2.0 (2.1)	8.3 (8.5)
[Rh(bBzlMe$_2$py)$_2$](ClO$_4$)$_3$	Yellow	>250		1052 630	46.4 (46.7)	3.2 (3.2)	13.1 (12.9)
RhCl(CO)$_2$(bBzlMe$_2$py)·H$_2$O	Green	255–260	2060 1977		50.6 (50.1)	3.2 (3.5)	13.5 (12.7)
[Rh(CO)$_2$(bBzlMe$_2$py)]ClO$_4$	Green	235–240	1973	1093 627	46.6 (46.2)	3.1 (2.9)	12.6 (11.7)
IrCl$_3$(bBzlH$_2$py)	Orange	>250			37.1 (37.4)	2.6 (2.2)	10.9 (11.5)
IrBr$_3$(bBzlH$_2$py)	Orange	>250			30.8 (30.7)	2.0 (1.8)	9.5 (9.4)
IrCl(CO)$_2$(bBzlH$_2$py)·H$_2$O	Brown	>250	2003 (2010 in KBr)		41.3 (41.1)	3.0 (2.5)	11.5 (11.4)
IrBr(CO)$_2$(bBzlH$_2$py)·1.5H$_2$O	Red	>250	2020 (2020 in KBr)		37.9 (37.8)	2.5 (2.4)	10.5 (10.5)
IrCl$_3$(bBzlMe$_2$py)	Red	>250			39.4 (39.5)	2.7 (2.7)	10.1 (11.0)
IrBr$_3$(bBzlMe$_2$py)	Orange	>250			32.5 (32.7)	2.1 (2.2)	8.2 (9.1)

peaks. The spectra of MX$_3$(bBzlH$_2$py) exhibited a ν_{NH} band in the range 3150–3180 cm^{-1}, indicating the coordination of the heterocycle through the tertiary nitrogens. This is further supported by the shift of the $\nu_{C=N}$ band by 20 cm^{-1} to lower/higher wave-number in the complexed species. A band at 1412 cm^{-1} noticed in the spectra of MX$_3$(bBzlMe$_2$py) complexes is assigned to the N—Me stretch [7,9].

The IR spectra of the complexes RhL$_2$(ClO$_4$)$_3$, in addition to the peaks due to *N*-heterocycle, displayed bands due to perchlorate groups around 1100 (ν_3) and 620 cm^{-1} (ν_4). In the spectrum of Rh(bBzlH$_2$py)$_2$(ClO$_4$)$_3$, the former band is split (1083, 1010 cm^{-1}), implying the coordination of at least one of the perchlorates. This is supported by 1:2 electrolytic behavior of the complex in MeCN/DMF. In the case of Rh(bBzlMe$_2$py)$_2$(ClO$_4$)$_3$, both the IR spectral and conductivity data indicate the ionic nature of the perchlorates [10].

The IR spectra of Rh^I halocarbonyl complexes in KBr displayed a split peak at 1990 and 2030 cm^{-1} due to ν_{CO} and the intensities of the two peaks have been found to fluctuate with different preparations despite the elemental analysis being satisfactory. The IR spec-

tra of Rh(CO)$_2$(bBzlH$_2$py)(ClO$_4$) (ν_{CO}, 2047, 1987 cm^{-1}) and its bBzlMe$_2$py analog (ν_{CO}, 1973 cm^{-1}), in addition to ν_{CO} peaks, displayed bands characteristic of coordinated (1113, 1110, 627 cm^{-1}) and ionic (1093, 627 cm^{-1}) perchlorates, respectively. The KBr pellet spectra of the monocarbonyls [RhX$_2$(CO)(bBzlH$_2$py)]X (X = Cl or Br) exhibited two peaks, one around 2060 cm^{-1} and the other at 2100 cm^{-1} due to ν_{CO}, suggesting the presence of isomeric forms. For the chloro complex, the former band is more intense than the latter, whereas for the bromo analog the intensities of the two peaks varied with different preparations. The dicarbonyl complex of iridium IrX(CO)$_2$(bBzlH$_2$py) (X = Cl or Br) displayed a strong IR peak around 2000 cm^{-1}, indicating a *trans* disposition of the carbonyl groups.

The ^{1}H NMR spectra of bBzlH$_2$py and bBzlMe$_2$py in DMSO-d$_6$ exhibited resonances due to phenylene and pyridine ring protons (Table 2) and the assignments are in consonance with those reported by Addison and coworkers [11]. The spectra of the complexes illustrated both positive and negative coordination induced shifts (c.i.s = $\delta_{complex}$-δ_{ligand}), the appreciable one being for H-4′. The resonance due

Table 2. Proton chemical shifts for the free ligands and their rhodium and iridium complexes in DMSO-d$_6^a$

| Compound | Benzimidazole ring protons | | | | Pyridine ring protons | | NH |
	4′	5′	6′	7′	3,5	4	N—Me
bBzlH$_2$py	7.8m	7.3m	7.3m	7.8m	8.4d	8.2t	13.0s
RhCl$_3$(bBzlH$_2$py)	8.6d	7.5qn	7.5qn	7.8d	8.4d	8.5t	10.2s
	(0.8)	(0.2)	(0.2)			(0.3)	(−2.8)
Rh(bBzlH$_2$py)$_2$(ClO$_4$)$_3$	6.1d	7.2t	7.3t	8.8d	9.0d	9.3t	7.9br
	(−1.7)	(−0.1)		(1.0)	(0.6)	(1.1)	(−5.1)
IrCl$_3$(bBzlH$_2$py)	8.4d	7.5t	7.6t	7.8d	8.7d	8.2t	15.0s
	(0.6)	(0.2)	(0.3)		(0.3)		(2.0)
RhCl(CO)$_2$(bBzlH$_2$py)	7.6m	7.3m	7.3m	7.8m	8.4m	8.2t	
	(0.2)						
RhBr(CO)$_2$(bBzlH$_2$py)	7.7d	7.4m	7.4m	7.8m	8.4m	8.3t	
	(−0.1)	(0.1)	(0.1)			(0.1)	
[RhCl$_2$(CO)(bBzlH$_2$py)]Cl	8.4m	7.6t	7.5m	7.5m	8.7m	8.7m	15.4s
	(0.6)	(0.3)	(0.2)	(−0.3)	(0.3)	(0.5)	(2.4)
[RhBr$_2$(CO)(bBzlH$_2$py)]Br	8.7m	7.6t	7.6m	7.6m	8.8m	8.8m	15.3s
	(0.9)	(0.3)	(0.3)	(−0.2)	(0.4)	(0.6)	(2.3)
bBzlMe$_2$py	7.8d	7.4t	7.3t	7.7d	8.4d	8.2t	4.3s
Rh(bBzlMe$_2$py)$_2$(ClO$_4$)$_3$	6.1d	7.5t	7.3t	7.9d	9.4d	9.3t	4.6s
	(−1.7)	(0.1)		(0.2)	(1.0)	(1.1)	(0.3)

^{a}Values in parentheses are coordination induced shifts:

(c.i.s.) $= \delta_{complex} - \delta_{ligand}$.
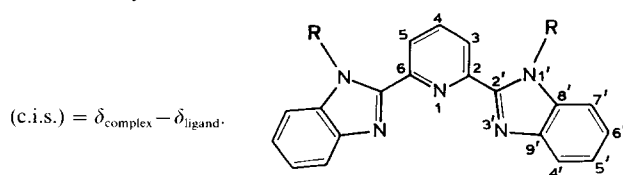
R = H or Me
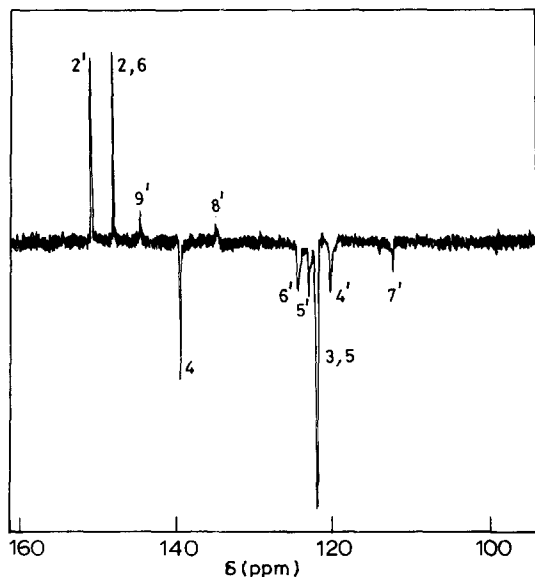
Fig. 1. ^{13}C SEFT NMR spectrum of bBzlH$_2$py

to the imine proton observed in the range 7–16 is concentration dependant. In the spectra of some of the complexes, the imine proton resonance is not observed, and probably it is too broad owing to rapid exchange with water protons present in the solvent. For the cationic complexes [Rh(bBzlH$_2$py)$_2$ (OClO$_3$)](ClO$_4$)$_2$ and [Rh(bBzlMe$_2$py)$_2$](ClO$_4$)$_3$ only one set of proton resonances have been observed implying the magnetic equivalence of the cor-

responding protons in both the coordinated N-heterocycles. In the former complex, it is likely that the coordinated perchlorate becomes displaced by the uncoordinated N atom of the heterocycle. The spectra revealed c.i.s. and H-4′ has experienced a shielding effect.

The ^{13}C NMR spectra of the uncoordinated N-heterocycles in DMSO-d$_6$ displayed 10 resonances as against eight signals reported by Addison and coworkers [11], and the assignments are given in Table 3. An additional resonance at δ 32.5 is observed for the N—Me group of bBzlMe$_2$py. According to the earlier report on bBzlMe$_2$py, the phenylene carbons 7′ and 4′ are magnetically equivalent, so also are the quaternary carbons 8′ and 9′. Thus, two resonances, one at δ 115.72 for C-7′,4′ and another at δ 139.23 for C-8′,9′, have been reported [11]. A similar finding has been made for bBzlMe$_2$py. Surprisingly in the present investigation, the four carbons 7′, 4′, 8′ and 9′ are seen to be magnetically nonequivalent in the same solvent and thus four resonances at δ 112.1, 119.9, 134.5 and 144.2, respectively, have been observed (Fig. 1). On complexation, the carbons have displayed both positive and negative c.i.s. The resonances have been identified by Spin Echo Fourier Transformation experiments (Fig. 2).

The electronic spectra of MX$_3$L (L = bBzlH$_2$py or bBzlMe$_2$py, X = Cl, Br or I for M = Rh and X = Cl or Br for M = Ir), RhL$_2$(ClO$_4$)$_3$ (L = BzlH$_2$py or bBzlMe$_2$py) and RhX$_3$(CO)(bBzlH$_2$py) (X = Cl or Br) complexes in Nujol mull have exhibited an intense band in the range 400–450 nm and is assigned to metal-to-ligand charge transfer transition. Two more

Table 3. ^{13}C NMR chemical shifts for the free ligands and their complexes in DMSO-d$_6^a$

Compound	Benzimidazole ring							Pyridine ring			N—Me
	2′	4′	5′	6′	7′	8′	9′	2,6	3,5	4	
bBzlH$_2$py	150.7	119.9	122.6	124.1	112.1	134.5	144.2	147.9	121.7	139.4	
RhCl$_3$(bBzlH$_2$py)	151.3	119.0	121.8	124.9	114.2	134.9	141.5	149.4	124.0	140.8	
	(0.6)	(−0.9)	(−0.8)	(0.8)	(2.1)	(0.4)	(−2.7)	(1.5)	(2.3)	(1.4)	
Rh(bBzlH$_2$py)$_2$(ClO$_4$)$_3$	151.5	116.3	124.8	125.8	113.4	135.3	138.4	149.0	126.3	145.7	
	(0.8)	(−3.6)	(2.2)	(1.7)	(1.3)	(0.8)	(−5.8)	(1.1)	(4.6)	(6.3)	
IrCl$_3$(bBzlH$_2$py)	153.6	118.4	121.6	125.2	113.8	132.5	141.5	150.5	125.6	140.4	
	(2.9)	(−1.5)	(−1.0)	(1.1)	(1.7)	(−2.0)	(−2.7)	(2.6)	(3.9)	(1.0)	
bBzlMe$_2$py	150.2	120.2	123.7	125.3	110.0	137.3	142.7	149.7	122.9	138.0	32.5
Rh(bBzlMe$_2$py)$_2$(ClO$_4$)$_3$	149.5	114.9	126.8	128.2	113.5	134.9	136.5	148.4	127.1	144.8	33.7
	(−0.7)	(−5.3)	(3.1)	(2.9)	(3.5)	(−2.4)	(−6.2)	(−1.3)	(4.2)	(6.8)	(1.2)

^{a} Values in parentheses are coordination-induced shifts: c.i.s. $= \delta_{complex} - \delta_{ligand}$.
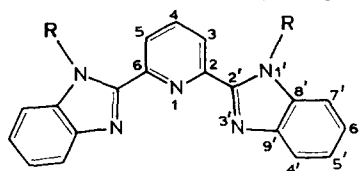
R = H or Me

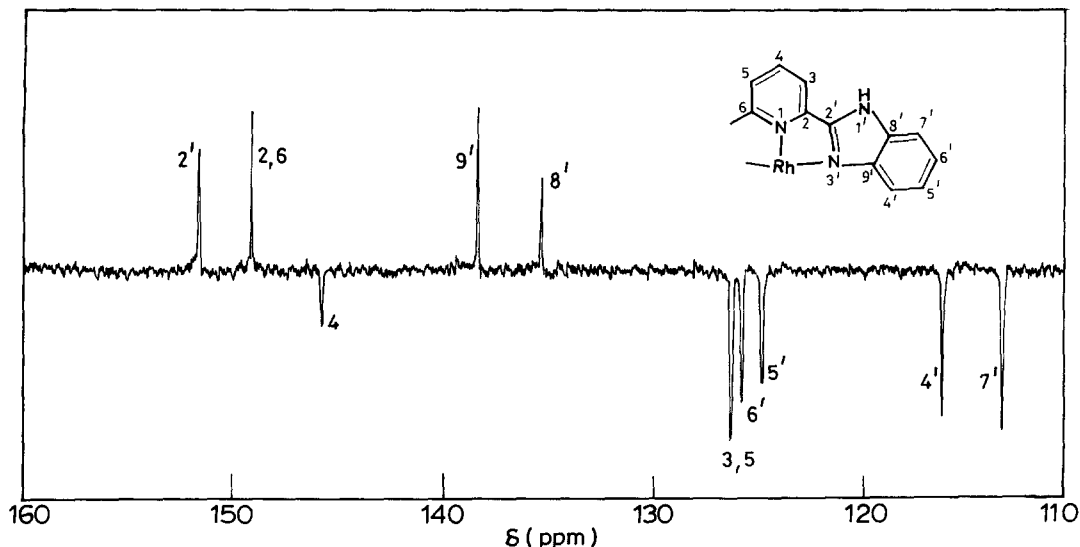Fig. 2. ^{13}C SEFT NMR spectrum of [Rh(bBzlH$_2$py)$_2$](ClO$_4$)$_3$

peaks are observed around 500 (weak) and 550 nm (very weak) and are respectively assigned to the $^1A_{1g} \to {}^1T_{1g}$ and $^1A_{1g} \to {}^3T_{2g}$ transition of an octahedral low-spin d^6 system [12,13]. The $^1A_{1g} \to {}^1T_{2g}$ transition is probably obscured in the M → L charge transfer band. The electronic spectra of MX$_3$(bBzlH$_2$py), RhL$_2$(ClO$_4$)$_3$ and [RhX$_2$(CO)(bBzlH$_2$py)]X complexes in DMF are compiled in Table 4. In the case of carbonyl complexes of rhodium(I) and iridium(I) the metal ions have strong reducing character and hence their d–d transitions are probably obscured in the intense metal-to-ligand charge-transfer band in the range 400–450 nm [13].
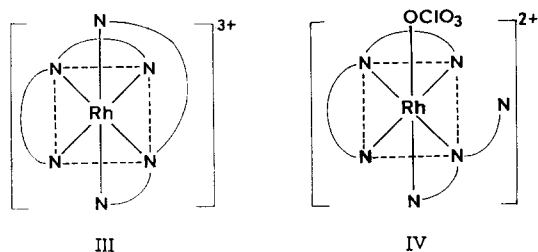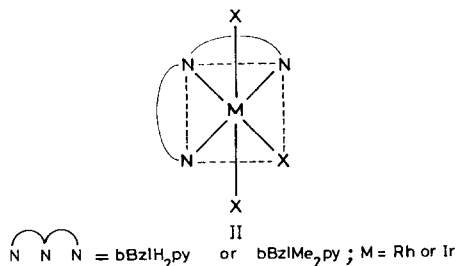
Stereochemistry

The *N*-heterocycles (L) are planar and each would function as chelating tridentate *via* the tertiary nitrogens. Hence, MX$_3$L complexes possess an octahedral meridional structure **II**. For the complex [Rh(bBzlMe$_2$py)$_2$](ClO$_4$)$_3$ an octahedral structure **III**, wherein each of the planar *N*-heterocycle would function as tridentate, is proposed, the two heterocycles' planes being mutually perpendicular [14]. In the case of [Rh(bBzlH$_2$py)$_2$(OClO$_3$)](ClO$_4$)$_2$ the solid-state IR spectrum indicated the presence of coordinated and ionic perchlorate and hence structure **IV** for the

Table 4. Electronic spectral data in DMF (nm)

Compound	Observed electronic transitions[a]
bBzlH$_2$py	312(33058), 330(37645), 342(32686).
RhCl$_3$(bBzlH$_2$py)	325(49470), 346(48987), 364(44960), 430(5670).
RhBr$_3$(bBzlH$_2$py)	329(28590), 345(29496), 367(26990), 425(5071).
RhI$_3$(bBzlH$_2$py)	342(32540), 370(31230), 426(8975).
[Rh(bBzlH$_2$py)$_2$(OClO$_3$)](ClO$_4$)$_2$	336(50981), 357(44846), 374(45429), 414(10613), 435(6074), 450(1786).
[Rh(CO)Cl$_2$(bBzlH$_2$py)]Cl	322(26452), 343(27590), 363(24972), 419(5586).
[Rh(CO)Br$_2$(bBzlH$_2$py)]Br	329(26634), 344(25899), 366(20629), 424(3738)
IrCl$_3$(bBzlH$_2$py)	315(37960), 331(44060), 343(42910), 364(31740), 430(5647), 514(1091), 565(503).
IrBr$_3$(bBzlH$_2$py)	333(51810), 439(7980), 515(614), 571(288).
bBzlMe$_2$py	306(51495), 323(61747).
[Rh(bBzlMe$_2$py)$_2$](ClO$_4$)$_3$	326(41724), 368(31517), 401(14879), 421(10310), 441(2569), 484(65), 516(53), 577(15).

[a] ε values are in parentheses.

complex, wherein one of the N-heterocycles is tridentate and the other is bidentate with a pendant nitrogen. Such varied coordination behavior for the multidentate N-heterocycles have been observed in [Cu(bBzlMe₂py)₂]ClO₄·2H₂O [14], [Co(bBzlH₂py)₂ (OClO₃)]ClO₄ and [Co(bBzlMe₂py)₂](ClO₄)₂ [7,15].

$$X$$

II

N N N = bBzlH₂py   or   bBzlMe₂py ; M = Rh or Ir

III

IV

The halo/perchlorate dicarbonyl complexes of rhodium(I) are expected to be five-coordinate with the N-heterocycle behaving as chelating tridentate. Five-coordinate complexes of rhodium(I) generally conceive trigonal-bipyramidal (tbp) or square-pyramidal (sp) (V–VIII) configuration [16].

V

VI

VII
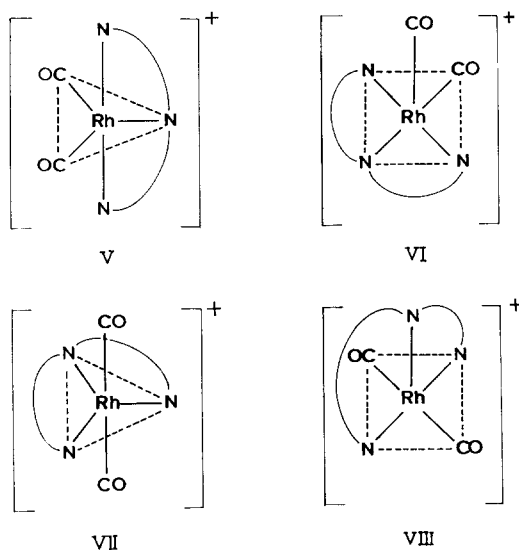
VIII

For the complex [Rh(CO)₂(bBzlMe₂py)]ClO₄ the 1 : 1 electrolytic behavior in nitrobenzene and a single v_{CO} peak in the IR region suggest trans disposition of the carbonyls and hence structure VII or VIII for the cation. The trihalo carbonyl cations may be proposed

to have configuration IX or X, wherein the N-heterocycle would serve as a chelating tridentate ligand. Here again it is likely that the complexes exhibit isomerism as the intensities of the two v_{CO} peaks varied with different preparations.

IX

X
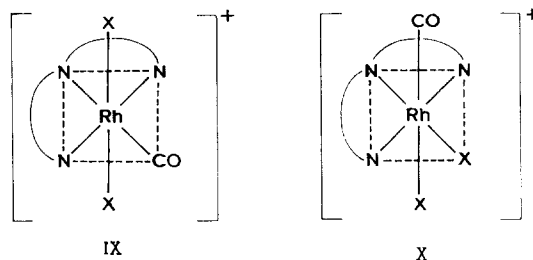
The halodicarbonyls [IrX(CO)₂(bBzlH₂py)] exhibit a single v_{CO} peak and hence five-coordinate square pyramidal/trigonal bipyramidal trans-COs structures (XI or XII) with the N-heterocycle as chelating bidentate are proposed.
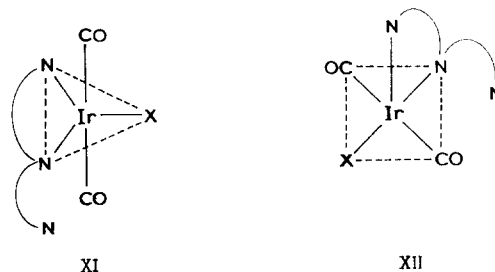
XI

XII

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