

Synthesis of rhodium(III) complexes with tris/tetrakis-benzimidazoles and benzothiazoles – quick identification of cyclometallation by nuclear magnetic resonance spectroscopy

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Reactions of rhodium(III) halides with multidentate *N,S*-heterocycles, (LH₃) 1,3,5-tris(benzimidazolyl)benzene (L¹H₃; 1), 1,3,5-tris(*N*-methylbenzimidazolyl) benzene (L²H₃; 2) and 1,3,5-tris(benzothiazolyl)benzene (L³H₃; 3), in the molar ratio 1 : 1 in methanol–chloroform produced mononuclear cyclometallated products of the composition [RhX₂(LH₂)(H₂O)] (X = Cl, Br, I; LH₂ = L¹H₂, L²H₂, L³H₂). When the metal to ligand (1–3 or 1,2,4,5-tetrakis(benzothiazolyl)benzene [L⁴H₂; 4]) molar ratio was 2 : 1, the reactions yielded binuclear complexes of the compositions [Rh₂Cl₅(LH₂)(H₂O)₃] (LH₂ = L¹H₂, L²H₂, L³H₂) and [Rh₂X₄(L⁴)(H₂O)₂] (X = Cl, Br, I). Elemental analysis, IR and ¹H nuclear magnetic resonance (NMR) chemical shifts supported the binuclear nature of the complexes. Cyclometallation was detected by conventional ¹³C NMR spectra that showed a doublet around ~190 ppm. Cyclometallation was also detected by gradient-enhanced heteronuclear multiple bond correlation (g-HMBC) experiment that showed cross-peaks between the cyclometallated carbon and the central benzene ring protons of 1–3. Cyclometallation was substantiated by two-dimensional ¹H–¹H correlated experiments (gradient-correlation spectroscopy and rotating frame Overhauser effect spectroscopy) and ¹H–¹³C single bond correlated two-dimensional NMR experiments (gradient-enhanced heteronuclear single quantum coherence). The ¹H–¹⁵N g-HMBC experiment suggested the coordination of the heterocycles to the metal ion via tertiary nitrogen. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: ¹H NMR; ¹³C NMR; rhodium; cyclometallation; g-HMBC

Introduction

Cyclometallated complexes are gaining much importance owing to their extensive utilization in organic synthesis, asymmetric synthesis, homogeneous catalysis, liquid crystals and photochemistry.^[1] Lonnon *et al.*^[2] have reported the X-ray crystal structure and NMR study of the catalytically active rhodium(III) complex with N₄-tripodal ligand, tris(2-benzimidazolylmethyl)amine. Other studies have illustrated how tripodal (*N*-heterocyclic alkyl)amine ligand design influences the geometry of the complexes and the internal exchange processes between isomers.^[3,4] Gayathri *et al.*^[5,6] prepared a series of cyclometallated rhodium complexes with 1,3-bis(benzimidazolyl)benzene. The conventional ¹³C NMR experiment takes longer time to detect the cyclometallated carbon because of sensitivity problem and also due to poor solubility of metal complexes in the desired solvents. Here, we describe the detection of cyclometallation by gradient-enhanced heteronuclear multiple bond correlation (g-HMBC) technique.

Experimental

Materials

Polydentate *N*-heterocycles 1,3,5-tris(benzimidazolyl)/*N*-methylbenzimidazolyl/benzothiazole)benzene and 1,2,4,5-tetrakis

(benzothiazolyl)benzene were prepared according to literature methods.^[7–9] Hydrated rhodium trichloride was purchased from Arora-Matthey, India. Rhodium tribromide was prepared as described elsewhere.^[10] Deuterated dimethyl sulphoxide (DMSO) used as a solvent for NMR studies was obtained from Aldrich chemicals.

Physical measurements

The infrared (IR) and electronic spectra (nujol mull) were recorded on Nicolet impact 400 D spectrometer and Hitachi 150-20 spectrophotometer, respectively. Microanalyses were obtained on Vario El III and Carlo Erba-1108. The fast atom bombardment (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 Central Drug Research Institute (CDRI), Lucknow, India. The molar conductivities were determined using a digital conductivity meter.

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Table 1. Analytical and IR spectral data of rhodium(III) complexes

Complex	Color	Analytical data (%) ^a			Infrared bands (cm ⁻¹)	
		C	H	N	$\nu_{\text{N-H}}/\nu_{\text{N-CH}_3}/\nu_{\text{C-S}}$	Ring vibrations
RhCl ₂ (L ¹ H ₂)(H ₂ O)	Yellow	52.14 (52.53)	2.63 (3.10)	13.39 (13.61)	3210	1372, 1212, 662
RhBr ₂ (L ¹ H ₂)(H ₂ O)	Brown	45.11 (45.92)	2.12 (2.71)	11.22 (11.90)	3195	1383, 1160, 659
RhI ₂ (L ¹ H ₂)(H ₂ O)	Dark brown	39.95 (40.53)	2.32 (2.39)	10.15 (10.50)	3185	1379, 1216, 662
RhCl ₂ (L ² H ₂)(H ₂ O)	Yellow	54.75 (54.65)	3.75 (3.82)	12.93 (12.75)	1471	1380, 1150, 668
RhBr ₂ (L ² H ₂)(H ₂ O)	Brown	47.65 (48.15)	3.27 (3.37)	11.13 (11.23)	1466	1374, 1225, 669
RhI ₂ (L ² H ₂)(H ₂ O)	Dark brown	42.32 (42.78)	3.10 (2.87)	10.01 (9.98)	1462	1379, 1224, 669
RhCl ₂ (L ³ H ₂)(H ₂ O)	Brown	47.83 (48.51)	2.38 (2.41)	5.79 (6.29)	1321	1368, 1218, 673
RhBr ₂ (L ³ H ₂)(H ₂ O)	Brown	42.53 (42.76)	1.95 (2.13)	5.72 (5.54)	1319	1376, 1226, 663
RhI ₂ (L ³ H ₂)(H ₂ O)	Dark brown	36.84 (37.28)	2.24 (2.09)	5.13 (4.83)	1313	1373, 1150, 661
Rh ₂ Cl ₅ (L ¹ H ₂)(H ₂ O) ₃	Brown	38.14 (37.59)	3.05 (2.69)	9.99 (9.74)	3240	1379, 1218, 667
Rh ₂ Cl ₅ (L ² H ₂)(H ₂ O) ₃	Brown	39.14 (39.82)	3.12 (3.23)	9.45 (9.29)	1479	1188, 1159, 672
Rh ₂ Cl ₅ (L ³ H ₂)(H ₂ O) ₃	Brown	35.98 (35.49)	2.13 (1.99)	4.71 (4.60)	1326	1379, 1224, 676
Rh ₂ Cl ₄ (L ⁴)(H ₂ O) ₂	Brown	40.76 (41.15)	1.78 (2.03)	8.32 (8.47)	1320	1378, 1219, 664
Rh ₂ Br ₄ (L ⁴)(H ₂ O) ₂	Brown	35.05 (34.89)	1.85 (1.72)	4.95 (4.79)	1315	1389, 1158, 662
Rh ₂ I ₄ (L ⁴)(H ₂ O) ₂	Dark brown	29.98 (30.06)	1.68 (1.48)	4.02 (4.12)	1314	1378, 1212, 665

^a Calculated values are in parentheses.

The ¹H and ¹³C NMR spectra in DMSO-d₆ were recorded at ambient temperatures on Bruker AMX 400 and DRX 500 MHz spectrometers with tetra methyl silane (TMS) as the internal reference. The ¹H–¹H gradient-correlation spectroscopy (g-COSY),^[11] rotating frame Overhauser effect spectra (ROESY),^[12,13] ¹H and ¹³C gradient-enhanced heteronuclear single quantum coherence (g-HSQC) spectra with improved sensitivity by preservation of equivalent pathways^[14–16] and g-HMBC^[17,18] spectra were obtained on a Bruker DRX 500 spectrometer. For g-COSY and ROESY experiments, $\pi/2$ pulse length 9.3 μ s, acquisition time 0.1 s and a spectral width of 5000 Hz in both dimensions were used. About 256 free induction decays (FIDs) with t_1 increments each of 1024 complex data points were collected with a relaxation delay of 1.5 s. About 2 and 32 transients were obtained and co-added for g-COSY and ROESY, respectively. Data were collected in the magnitude mode for g-COSY, whereas phase-sensitive data were obtained by the two phase pulse increment (TPPI) method^[19] for ROESY experiments. A spin-lock mixing time of 200 ms was used for the ROESY spectra. The resulting data were multiplied by a squared sine-bell window function shifted by $\pi/2$ along both dimensions prior to Fourier transformation. The resulting data were double Fourier transformed after multiplying by a squared sine-bell window function shifted by $\pi/2$ along the t_2 and t_1 dimensions.

For g-HSQC and g-HMBC experiments, the proton and carbon $\pi/2$ pulse lengths were 9.3 and 11.2 μ s, respectively. Spectral widths of 5000 and 27 000 Hz in the ¹H and ¹³C dimensions were used, respectively. In g-HSQC experiment, 256 FIDs were collected with t_1 increments each with 1024 points. Two transients were collected with a recycle delay of 1.5 s and an acquisition time of 0.08 s. In the case of g-HMBC experiment, 128 FIDs were collected each with 4096 complex data points. About 16 transients were collected with a recycle delay of 2 s and an acquisition time of 0.35 s. Phase-sensitive data were obtained for g-HSQC using the echo anti-echo method, and the data for the g-HMBC experiment were obtained in the magnitude mode. The resulting data were double Fourier transformed after multiplying by a squared sine-bell window function shifted by $\pi/2$ along the t_2 dimension and a sine-bell window function shifted by $\pi/2$ along the t_1 dimension.

Preparation of the complexes

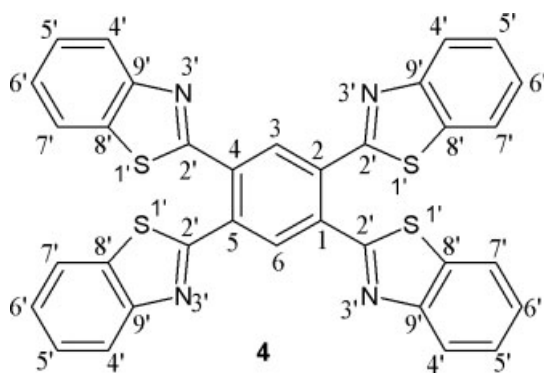
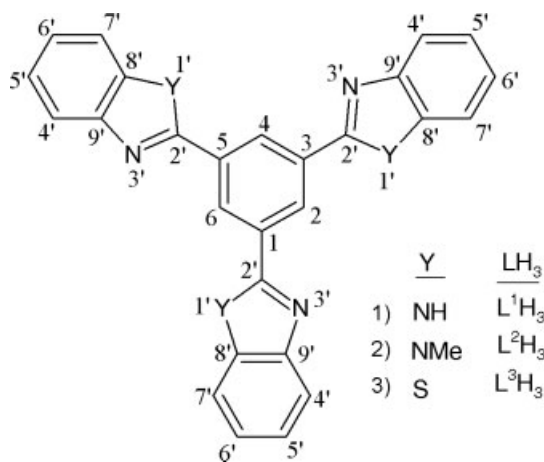
[RhX₂(LH₂)(H₂O)], (LH₂ = L¹H₂, L²H₂, L³H₂; X = Cl, Br or I) [Rh₂Cl₅(LH₂)(H₂O)₃] (LH₂ = L¹H₂, L²H₂, L³H₂) and [Rh₂X₄(L⁴H₂)(H₂O)₂] (X = Cl, Br or I)

Rhodium trichloride (1.0 or 2.0 mm) dissolved in methanol (5 cm³) was treated with chloroform–methanolic solution (5 cm³) of the *N*-heterocycle, LH₃ or L⁴H₂ (1 mm). The mixture was heated under reflux for about 8 h during which a yellow, yellowish brown or brown solid separated. The solid was washed with methanol and dried *in vacuo*. Yield: 60–80%. The corresponding bromo complexes were prepared starting from rhodium tribromide, whereas the iodo complexes were produced by the metathesis reaction of the chloro complexes with sodium iodide.

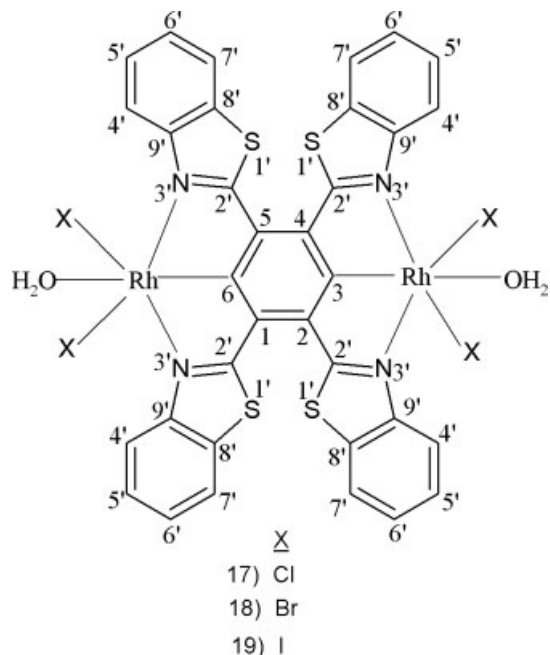
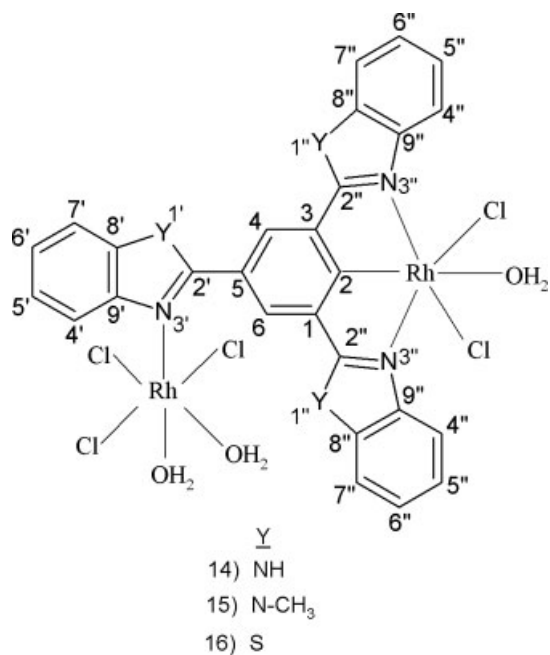
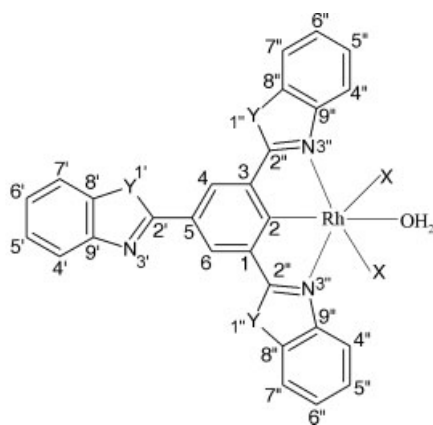
Results and Discussion

Treatment of rhodium(III) trichloride/bromide with multidentate *N,S*-heterocycles, LH₃ **1–3**, in the molar ratio 1:1 in methanol–chloroform gave cyclometallated complexes of the type [RhCl₂(LH₂)(H₂O)] (**5–13**; LH₂ = L¹H₂, L²H₂, L³H₂). The reaction of rhodium(III) chloride with *N,S*-heterocycle **1–3** or **4** in the molar ratio 2:1 in methanol–chloroform produced binuclear complexes of the compositions [Rh₂Cl₅(LH₂)(H₂O)₃] (**14–16**; LH₂ = L¹H₂, L²H₂, L³H₂) and [Rh₂Cl₄(L⁴H₂)(H₂O)₂] (**17**). The bromo analogue, **18** of the latter was prepared starting from rhodium tribromide, whereas the iodo one, **19** was obtained from the metathesis reaction of the chloro complex. The complexes are diamagnetic and are insoluble in common organic solvents but dissolve in dimethyl formamide and DMSO, the solutions being non-conducting. The nujol mull 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 3200 and 1470 cm⁻¹, respectively. The IR spectra displayed a peak around 1600 cm⁻¹ due to $\nu_{\text{C=N}}$ for the uncoordinated heterocycles and this has shifted to around 1620 cm⁻¹ in the complexes and the data are suggestive of the coordination of

the 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 only terminal halides.^[20] The spectra also displayed a peak due to $\nu_{\text{Rh-C}}$ in the range 300–360 cm^{-1} ; the result pointing to cyclometallation^[21] of the tris/tetrakis-benzimidazole derivatives. Cyclometallation is further supported by the ^1H and ^{13}C NMR spectra of the complexes. The thermo gravimetric analysis (TGA) experiments on the complexes indicated the presence of coordinated water molecule(s). The TGA plots show that the complexes loose water molecule(s) above 250 °C. For instance, the weight loss in $[\text{RhCl}_2(\text{L}^1\text{H}_2)(\text{H}_2\text{O})]$ due to elimination of one water molecule occurred at 280 °C implying the latter as coordinately bound.



- | | |
|------------------------|------------------------|
| $\underline{\text{Y}}$ | $\underline{\text{X}}$ |
| 5) NH | Cl |
| 6) NH | Br |
| 7) NH | I |
| 8) N-CH ₃ | Cl |
| 9) N-CH ₃ | Br |
| 10) N-CH ₃ | I |
| 11) S | Cl |
| 12) S | Br |
| 13) S | I |



The ^1H and ^{13}C NMR spectra of the complexes showed both positive and negative coordination-induced shifts (CIS; Tables 2–6). Appreciable CIS was observed for proton at 4' that is in the vicinity of the coordinated tertiary nitrogen of the heterocycle. In the same way, quaternary carbon 9' also exhibited significant CIS. In the ^{13}C NMR spectra of uncoordinated heterocycles, the resonance due to carbon-2 was observed in the range 125–131 ppm (Table 6) as a singlet. The resonance in the spectrum of complex was split into a doublet and shifted to high frequency by nearly 60 ppm. The magnitude of the coupling, around 25 Hz, is typical of one-bond ^{13}C – ^{103}Rh coupling.^[22–24] This observation clearly indicated cyclometallation of the tris/tetrakis-benzimidazole derivatives. Furthermore, the resonances due to protons 2 of LH_3 and 3 and 6 of L^4H_2 were absent substantiating cyclometallation. Furthermore, the ^1H – ^{15}N g-HMBC experiment suggested the coordination of the

Table 2. ^1H nuclear magnetic resonance chemical shifts (δ in ppm) for heterocycle **1** and complexes **5–7** and **14**

Proton number	1	5	6	7	14
2	9.12s	–	–	–	–
4	9.12s	8.68s (–0.44)	8.79s (–0.33)	8.98s (–0.14)	8.68s (–0.44)
6	9.12s	8.68s (–0.44)	8.79s (–0.33)	8.98s (–0.14)	8.68s (–0.44)
1''N–H	13.30b	9.31b (–3.99)	9.34b (–3.96)	9.28b (–4.02)	9.26b (–4.04)
4'	7.65b	7.77–7.80m (0.12–0.15)	7.79–7.82m (0.14–0.17)	7.77–7.80m (0.12–0.15)	7.89–7.91m (0.24–0.26)
5'	7.28m	7.39–7.44m (0.11–0.16)	7.40–7.45m (0.12–0.17)	7.38–7.43m (0.10–0.15)	7.57–7.59m (0.29–0.31)
6'	7.28m	7.39–7.44m (0.11–0.16)	7.40–7.45m (0.12–0.17)	7.38–7.43m (0.10–0.15)	7.57–7.59m (0.29–0.31)
7'	7.65b	7.77–7.80m (0.12–0.15)	7.79–7.82m (0.14–0.17)	7.77–7.80m (0.12–0.15)	7.89–7.91m (0.24–0.26)
1''N–H	13.30b	14.62b (1.32)	14.72b (1.42)	14.82b (1.52)	14.90b (1.60)
4''	7.65b	8.69d (1.04)	8.71d (1.06)	8.68d (1.03)	8.70d (1.05)
5''	7.28m	7.45–7.49m (0.17–0.21)	7.46–7.50m (0.18–0.22)	7.44–7.48m (0.16–0.20)	7.45–7.50m (0.17–0.22)
6''	7.28m	7.45–7.49m (0.17–0.21)	7.46–7.50m (0.18–0.22)	7.44–7.48m (0.16–0.20)	7.45–7.50m (0.17–0.22)
7''	7.65b	7.77–7.80m (0.12–0.15)	7.79–7.82m (0.14–0.17)	7.77–7.80m (0.12–0.15)	7.80d (0.15)

Note: Coordination-induced shifts are given in parentheses; s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

Table 3. ^1H nuclear magnetic resonance chemical shifts (δ in ppm) for heterocycle **2** and complexes **8–10** and **15**

Proton number	2	8	9	10	15
2	8.50s	–	–	–	–
4	8.50s	8.65s (0.15)	8.85s (0.35)	8.95s (0.45)	8.67s (0.17)
6	8.50s	8.65s (0.15)	8.85s (0.35)	8.95s (0.45)	8.67s (0.17)
1'N–CH ₃	4.05s	4.17s (0.12)	4.27s (0.22)	4.29s (0.24)	4.18s (0.13)
4'	7.75d	7.89–7.97m (0.14–0.22)	7.91–7.99m (0.16–0.24)	7.90–7.98m (0.15–0.23)	7.92–7.94m (0.27–0.29)
5'	7.28t	7.49–7.59m (0.21–0.31)	7.51–7.61m (0.23–0.33)	7.48–7.58m (0.20–0.30)	7.57–7.63m (0.29–0.35)
6'	7.35t	7.49–7.59m (0.14–0.24)	7.51–7.61m (0.16–0.26)	7.48–7.58m (0.13–0.23)	7.57–7.63m (0.22–0.28)
7'	7.67d	7.89–7.97m (0.22–0.32)	7.91–7.99m (0.24–0.32)	7.90–7.98m (0.23–0.31)	8.02d (0.35)
1''N–CH ₃	4.05s	4.49s (0.44)	4.53s (0.48)	4.57s (0.52)	4.49s (0.44)
4''	7.75d	8.84–8.86m (1.09–1.11)	8.86–8.88m (1.11–1.13)	8.85–8.87m (1.10–1.12)	8.84–8.86m (1.09–1.11)
5''	7.28t	7.49–7.59m (0.21–0.31)	7.51–7.61m (0.23–0.33)	7.48–7.58m (0.20–0.30)	7.50–7.52m (0.22–0.24)
6''	7.35t	7.49–7.59m (0.28–0.38)	7.51–7.61m (0.30–0.40)	7.48–7.58m (0.27–0.37)	7.50–7.52m (0.29–0.31)
7''	7.67d	7.89–7.97m (0.22–0.30)	7.91–7.99m (0.24–0.32)	7.90–7.98m (0.23–0.31)	7.92–7.94m (0.25–0.27)

Note: Coordination-induced shifts are given in parentheses; s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

heterocycles through metal ion via tertiary nitrogen. The ^1H – ^{15}N g-HMBC spectrum (Fig. 1) of complex $[\text{RhCl}_2(\text{L}^2\text{H}_2)(\text{H}_2\text{O})]$ (**8**) the resonance at 8.85 ppm due to proton 4'' displayed a cross peak with that at 240 ppm due to nitrogen-3''. Furthermore, the resonances due to protons 7'', 1'N–Me and 1''N–Me displayed cross-peaks with nitrogens at 225, 230 and 225 ppm, respectively suggesting

the coordination of the heterocycle to rhodium via tertiary nitrogen. The ^1H and ^{13}C NMR spectra of the uncoordinated *N,S*-heterocycles **1–3** displayed only one set of resonances, implying magnetic equivalence of the corresponding protons and the carbons of the three benzimidazole rings. In the case of the spectra of complexes **5–16**, two sets of resonances with intensity

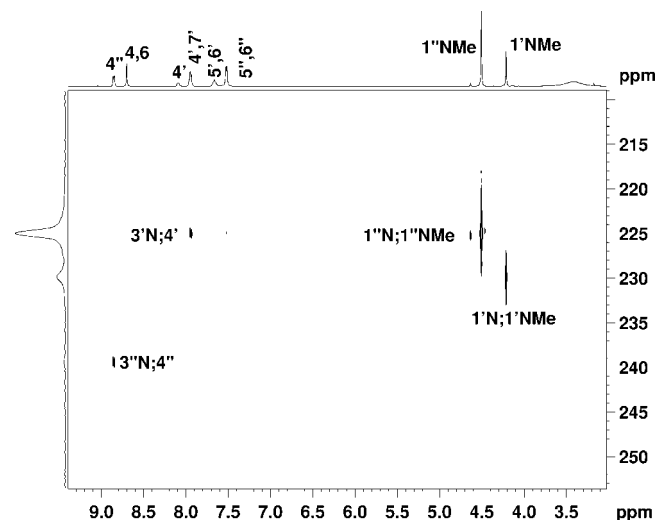


Figure 1. Two-dimensional ^1H - ^{15}N gradient-enhanced heteronuclear multiple bond correlation spectrum of complex **15** recorded on Bruker 500 MHz DRX spectrometer. The cross-peaks correlate protons and the nitrogens that are connected through multiple bonds. The spectrum on the F1 dimension is two-dimensional projection. The cross-peaks marked are separated by a semi-colon, the first prior to semi-colon denotes the nitrogen and the second after semi-colon denotes the proton. Assignments of the resonances of protons are marked on the one-dimensional trace corresponding to ^1H spectrum.

Table 4. ^1H nuclear magnetic resonance chemical shifts (δ in ppm) for heterocycle **3** and complexes **11–13** and **16**

No.	3	11	12	13	16
2	8.79s	–	–	–	–
4	8.79s	8.83s (0.04)	8.92s (0.13)	8.89s (0.10)	8.84s (0.05)
6	8.79s	8.83s (0.04)	8.92s (0.13)	8.89s (0.10)	8.84s (0.05)
4'	8.08d	8.10–8.35m (0.02–0.27)	8.12–8.37m (0.04–0.29)	8.09–8.34m (0.01–0.26)	8.26t (0.18)
5'	7.45t	7.43–7.52m (–0.02–0.07)	7.44–7.53m (–0.01–0.08)	7.42–7.51m (–0.03–0.06)	7.55t (0.10)
6'	7.35t	7.43–7.52m (0.08–0.17)	7.44–7.53m (0.09–0.18)	7.42–7.51m (0.07–0.16)	7.64t (0.29)
7'	7.88d	8.10–8.35m (0.22–0.47)	8.12–8.37m (0.24–0.49)	8.09–8.34m (0.21–0.46)	8.21d (0.33)
4''	8.08d	9.92d (1.84)	9.90d (1.82)	9.91d (1.83)	9.93d (1.85)
5''	7.45t	7.66–7.71m (0.21–0.26)	7.67–7.72m (0.22–0.27)	7.65–7.70m (0.20–0.25)	7.78t (0.33)
6''	7.35t	7.66–7.71m (0.31–0.36)	7.67–7.72m (0.32–0.37)	7.65–7.70m (0.30–0.35)	7.67t (0.32)
7''	7.88d	8.10–8.35m (0.22–0.47)	8.12–8.37m (0.24–0.49)	8.09–8.34m (0.21–0.46)	8.38d (0.50)

Note: Coordination-induced shifts are given in parentheses; s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

ratio 2 : 1 were observed as expected. The proton resonance due to coordinated H_2O molecule(s) was not observed. It is likely that it becomes labile and undergoes exchange with free molecules in the solvent.

Generally, ^{13}C NMR experiment requires a longer time to detect the presence of cyclometallated carbon. The poor solubility of the metal complexes produces a sensitivity problem. For instance, the experimental time involved for recording the conventional ^{13}C NMR spectrum (Fig. 2) of complex **15** was 15 h but still the intensity of the cyclometallated carbon doublet at 189.5 ppm was not satisfactory. This was overcome by HMBC experiment and this was quick in detecting the cyclometallated carbon. The experimental time required to record HMBC spectrum of complex **15** (Fig. 3) was only 30 min. A similar observation was made while recording the spectrum of complex **16** (Fig. 4). The cross-peaks displayed at 189.5 ppm along the carbon dimension and

8.67 ppm along the proton dimension were adequate in intensity for detection.

The ^1H NMR spectrum (Fig. 5a) of **2** exhibited a single resonance at 4.05 ppm (Table 3) due to the three methyl groups. In the case of complex **15**, two resonances (Fig. 5b) were observed for the protons of the methyl groups, one at 4.49 and the other at 4.17 ppm of intensity ratio 2 : 1, implying their non-equivalence. Furthermore, the protons of the benzimidazole benzene ring of free heterocycle showed one set of peaks at 7.28, 7.35, 7.67 and 7.75 implying their equivalence in the corresponding groups. But they are non-equivalent in the complex as two sets of resonances of intensity ratio 2 : 1 were observed. The resonances corresponding to protons 4', 5', 6' and 7' of **14–16** are shifted more towards downfield as compared with those of chloro complexes of **5–7**, indicating binuclear nature of former complexes. In the ^1H and ^{13}C NMR spectra of complexes, two sets of resonances were observed for the *N,S*-heterocycles as compared with those of

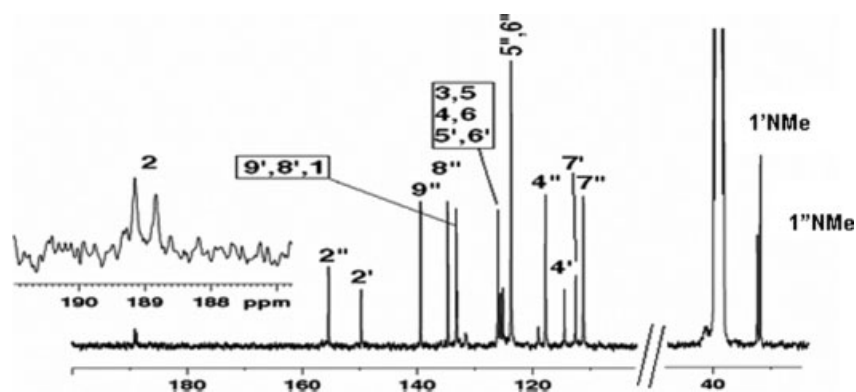


Figure 2. ^{13}C nuclear magnetic resonance spectrum of the complex **15** in $(\text{CD}_3)_2\text{SO}$ recorded on 400 MHz Bruker AMX spectrometer at 300 K. In the inset showed carbon resonance at 189 ppm and has split into a doublet due to one bond ^{13}C - ^{103}Rh spin-spin coupling. The coupling constant 25 Hz is a typical of one bond ^{13}C - ^{103}Rh coupling. Assignments of the resonances of carbons are marked.

Table 5. ^1H nuclear magnetic resonance chemical shifts (δ in ppm) for heterocycle **4** and complexes **17–19**

Proton number	4	17	18	19
3	8.61s	–	–	–
6	8.61s	–	–	–
4'	8.08d	8.10–8.33m (0.02–0.25)	8.12–8.35m (0.04–0.27)	8.11–8.32m (0.03–0.24)
5'	7.42t	7.42–7.73m (0.00–0.31)	7.43–7.76m (0.01–0.34)	7.41–7.72m (–0.01–0.30)
6'	7.52t	7.42–7.73m (–0.10–0.21)	7.43–7.76m (–0.09–0.24)	7.41–7.72m (–0.11–0.20)
7'	7.85d	8.10–8.33m (0.25–0.48)	8.12–8.35m (0.27–0.50)	8.11–8.32m (0.26–0.47)
4''	8.08d	8.10–8.33m (0.02–0.25)	8.12–8.35m (0.04–0.27)	8.11–8.32m (0.03–0.24)
5''	7.42t	7.42–7.73m (0.00–0.31)	7.43–7.76m (0.01–0.34)	7.41–7.72m (–0.01–0.30)
6''	7.52t	7.42–7.73m (–0.10–0.21)	7.43–7.76m (–0.09–0.24)	7.41–7.72m (–0.11–0.20)
7''	7.85d	8.10–8.33m (0.25–0.48)	8.12–8.35m (0.27–0.50)	8.11–8.32m (0.26–0.47)

Note: Coordination-induced shifts are given in parentheses; s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

Table 6. ^{13}C nuclear magnetic resonance chemical shifts (δ in ppm) for heterocycle **1–3** and complexes **14–16**

Carbon number	1	14	2	15	3	16
1	131.8	133.3 (1.5)	130.9	133.5 (2.6)	134.6	138.6 (4.0)
2	125.5	188.8d (63.3) (25) ^a	130.5	189.5d (59.0) (24) ^a	127.4	187.6d (60.2) (24) ^a
3	131.8	133.3 (1.5)	130.9	133.5 (2.6)	134.6	138.6 (4.0)
4	125.5	124.1 (–1.4)	130.5	126.4 (–4.1)	127.4	125.6 (–1.8)
5	131.8	123.9 (–7.9)	130.9	126.0 (–4.9)	134.6	126.2 (–8.4)
6	125.5	124.1 (–1.4)	130.5	126.4 (–4.1)	127.4	125.6 (–1.8)
	–	–	31.4	32.6 (1.2)	–	–
1'Y	Y = NH	Y = NH	Y = N–CH ₃	Y = N–CH ₃	Y = S	Y = S
2'	150.3	150.8 (0.5)	151.4	150.3 (–1.1)	165.1	166.4 (1.3)
4'	111.8	114.4 (2.6)	119.5	115.0 (–4.5)	122.9	122.6 (–0.3)
5'	122.5	125.3 (–0.2)	121.9	125.5 (3.6)	126.0	125.8 (–0.2)
6'	122.5	125.3 (–0.2)	122.5	125.5 (0.0)	125.1	126.9 (1.8)
7'	118.6	114.4 (–4.2)	110.5	112.8 (2.3)	121.2	123.0 (1.8)
8'	135.4	124.3 (–11.1)	136.2	133.7 (–2.5)	134.7	134.8 (0.1)
9'	143.6	133.4 (–10.2)	142.2	133.8 (–8.4)	153.8	153.4 (–0.4)
	–	–	31.4	32.3 (0.9)	–	–
1''Y	Y = NH	Y = NH	Y = N–CH ₃	Y = N–CH ₃	Y = S	Y = S
2''	150.3	157.0 (6.7)	151.4	156.0 (4.6)	165.1	174.8 (9.7)
4''	111.8	117.8 (6.0)	119.5	118.2 (–1.3)	122.9	122.8 (–0.1)
5''	122.5	124.3 (1.8)	121.9	124.1 (2.2)	126.0	127.9 (1.9)
6''	122.5	124.3 (1.8)	122.5	124.1 (1.6)	125.1	126.7 (1.6)
7''	118.6	113.2 (–5.4)	110.5	111.6 (1.1)	121.2	123.8 (2.6)
8''	135.4	133.7 (–1.7)	136.2	135.2 (–1.0)	134.7	132.0 (–2.7)
9''	143.6	140.6 (–3.0)	142.2	139.9 (–2.3)	153.8	149.9 (–3.9)

Note: Coordination-induced shifts in parentheses; d, doublet.

^a $^1J_{\text{Rh-C}}$

the free heterocycles **1–3**, indicating the loss of symmetry on coordination. Of these two sets of resonances, one set has shifted considerably to high frequency. Unambiguous assignment of the various ^1H and ^{13}C resonances for the complexes and for the *N*-heterocycles was made using a combination of g-COSY, g-HSQC and g-HMBC experimental data.

The g-COSY spectrum of complex **14** displayed cross-peaks for the pairs of protons 4', 5'; 6', 7'; 4'', 5'' and 6'', 7''. It was not possible to distinguish among the resonances due to pairs of protons 4', 7' and 4'', 7'' with the help of g-COSY owing to similar cross-peaks arising from protons 5', 6' and 5'', 6'', respectively. To support the

assignments, g-HMBC experiment was conducted on complex **15** (Fig. 3), and this exhibited the resonances due to carbons 8' and 8'' at 133.7 and 135.2 ppm, respectively. The spectrum consisted of cross-peaks arising from carbon-8' due to interaction with methyl protons on 1'N–Me and proton at 7', carbon-8'' with methyl protons on 1''N–Me and proton 7''. The spectrum also exhibited resonances due to quaternary carbons 5, 1, 3, 9', 9'', 2', 2'' and 2 at 126.0, 133.5, 133.5, 133.8, 139.9, 150.3, 156.0 and 189.5(d) ppm, respectively. The g-HSQC experiment of complex **15** showed resonances at 32.3, 32.6, 111.6, 112.8, 115.0, 118.2, 124.1, 124.1, 125.5, 125.5, 126.4 and 126.4 ppm due to carbons 1'N–CH₃, 1'N–

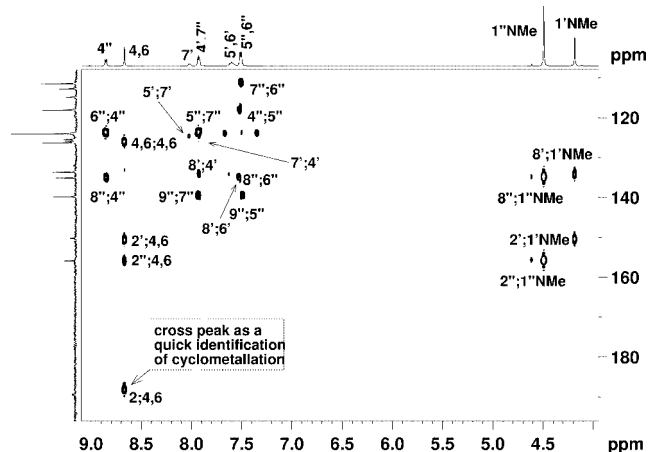


Figure 3. Two-dimensional ^1H - ^{13}C gradient-enhanced heteronuclear multiple bond correlation spectrum of complex **15** recorded on Bruker 500 MHz DRX spectrometer. The cross-peaks correlate protons and the carbons that are connected through multiple bonds. Cross-peaks due to one-bond proton-carbon are also seen, although they are weak in intensity. Two cross-peaks are seen due to one-bond coupling since the spectrum is recorded without decoupling in the F2 dimension. The cross-peaks marked are separated by a semi-colon, the first prior to semi-colon denotes the carbon and the second after semi-colon denotes the proton. Assignments of the resonances of protons are marked on the one-dimensional traces corresponding to ^1H and ^{13}C NMR spectra.

CH_3 , $7''$, $7'$, $4'$, $4''$, $5''$, $6''$, $5'$, $6'$, 4 and 6 , respectively. The g-COSY spectrum of the complex displayed cross-peaks due to protons $4''$ and $5''$ and $6''$ and $7''$. Similarly, the spectrum showed cross-peaks arising from protons $4'$ and $5''$ and $6'$ and $7'$.

To substantiate the above findings, nuclear Overhauser effect (NOE) measurements were carried out on complex **15**. The two-dimensional NOESY experiments did not show cross-peaks in the spectra possibly due to $\omega\tau_c \approx 1$ (ω = frequency of the instrument, τ_c = correlation time of the molecule). Therefore, two-dimensional ROESY experiments were carried out. In the ROESY spectrum (Fig. 6) of complex **15**, NOE enhancement of resonances due to protons on $1''\text{N-Me}$ with 4 , 6 and $7'$ was observed supporting the resonance of $7'$ at 8.02 ppm as a doublet ($J = 7.6$ Hz). Similarly, NOE

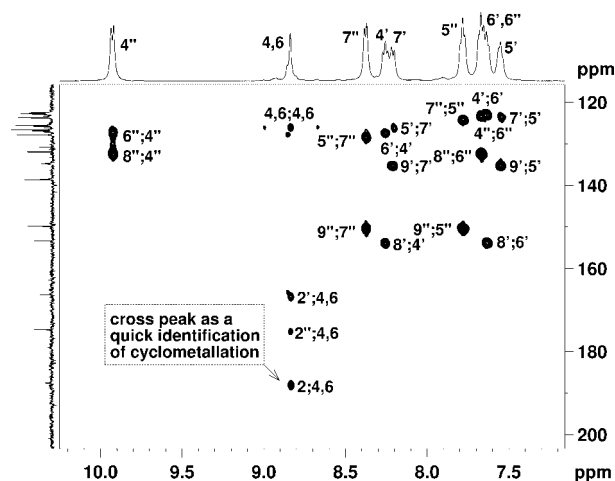


Figure 4. Two-dimensional ^1H - ^{13}C gradient-enhanced heteronuclear multiple bond correlation spectrum of complex **16** recorded on Bruker 500 MHz DRX spectrometer displaying the cross-peak between the proton and the cyclometallated carbon for detection of cyclometallation. Cross-peaks numbered are similar to those numbered in Fig. 3.

enhancement of the resonance of protons on $1''\text{N-Me}$ coupling with 4 , 6 and $7''$ substantiated the resonance of $7''$ as a multiplet in the range 7.92 – 7.94 ppm. The resonance arising from proton $4''$ has shifted to a higher frequency and this is obvious due to the nearby rhodium.

Conclusions

Cyclometallation of the complexes was evidenced by IR and NMR spectral methods. Although the far-IR spectra revealed primary information about the cyclometallation, the NMR method was almost confirmatory. The g-HMBC experiment was principally used to detect cyclometallation, and this was useful for complexes **5–16** but not for **17–19**. The results suggest that the technique demanded the presence of a proton in the vicinity of the cyclometallated carbon for the detection of cyclometallation. The structure of complex **15** was analysed on the basis of one- and

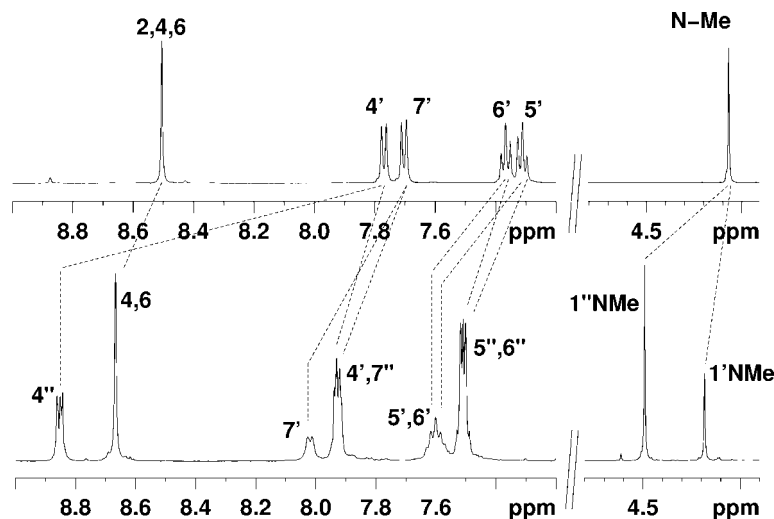


Figure 5. A correlation of proton resonances of free heterocycle **2** (a) and complex **15** (b) recorded on Bruker AMX 400MHz spectrometer. Assignments of the resonances of protons are marked.

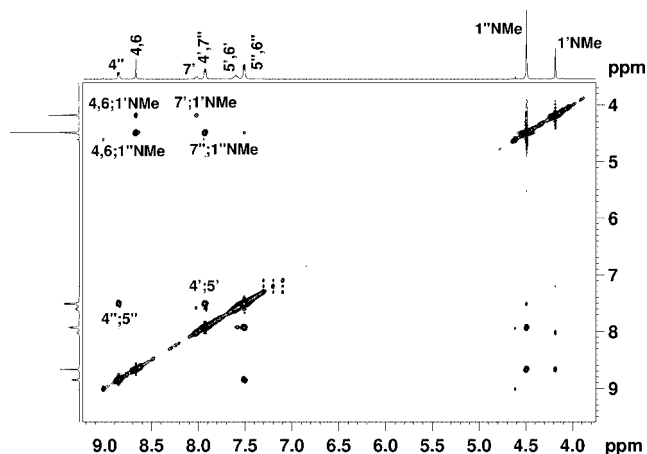


Figure 6. Rotating frame Overhauser effect spectrum of complex **15** recorded with a spin-lock mixing time of 200 ms on a Bruker DRX500 spectrometer at 300 K in deuterated dimethyl sulphoxide solvent. Assignments of the protons are marked on the one-dimensional trace of the spectrum. The nuclear Overhauser effect cross-peaks {4,6;1''(N-Me)}, (4,6;1''N-Me), (7'';1''N-Me), (7'';1''N-Me), (4'';5'') and (4'';5'') are labeled.

two-dimensional techniques. Although the g-HMBC experiment was primarily used for the detection of cyclometallation, it was also useful in unambiguous assignments.

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