Versatile coordination modes of benzothiazole hydrazone derivatives towards Ru(II), Rh(III) and Ir(III) complexes and their reactivity studies with azides and activated alkynes

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ABSTRACT

Metal precursors of the type [(p-cymene)RuCl2]2 and [Cp*MCl2]2 (M = Rh/Ir) on reacting with benzothiazole hydrazones ligands (L1 = benzylidenehydrazinyl benzothiazole, L2 = 4-flourobenzylidenehydrazinyl benzothiazole and L3 = 4-methylbenzylidenehydrazinyl benzothiazole) in the ratio of 1:2 (M:L), leads to the formation of range of complexes. In the case of ruthenium precursor with ligand L1, a cationic complex [(p-cymene)Ru(k-N=N-L1)Cl] (1) is formed whereas with L2 and L3 neutral complexes [(p-cymene)Ru(k-N=N-L2/L3)Cl]2 (4 and 7) are obtained. Rhodium precursor with L1 and L2 forms mono denta te neutral complexes [Cp*Rh(x-N=N-L1/L2)Cl]2 (2 and 5) while with L3 bidentate NN’ bonding complex [Cp*Ir(k-N=N-L3)Cl]2 (8) is obtained. However, iridium precursor with these ligands yielded neutral bidentate complexes (3, 6 and 9) having the general formula [Cp*Ir(k-N=N-L)Cl] (L = L1, L2 and L3 respectively. Some of these complexes have been treated with sodium azide to yield azido compounds. Conformational switching of the benzothiazole hydrazone derivatives of complexes 2 and 5 from trans (E) to cis (Z) are observed on treatment with sodium azide. These azido complexes obtained, have been treated with activated acetylenes of dimethyl and diethyl acetylene carbonates, which undergo [3 + 2] cycloadditions to form arene ruthenium triazolato complexes. All these complexes have been characterized by analytical, spectroscopic and single crystal x-ray diffraction studies. These complexes have also been carried out for antibacterial studies, but unfortunately none of these compounds or ligands exhibits antibacterial activity towards gram-positive and gram-negative bacteria.

1. Introduction

Half-sandwich complexes of some platinum group metals (ruthenium, rhodium and iridium) have occupied a significant position in organometallic chemistry due to their readiness to form stable complexes with a variety of ligands [1,2]. The dimeric chlor bridged complexes [[(arene)M(μ-Cl)]2] where arene = benzene, p-cymene, hexamethylbenzene and M = Ru and [(Cp*M)(μ-Cl)]2 where M = Rh or Ir have been the subject of exploration by many research groups as they are useful starting materials [3]. These half sandwich complexes have unique properties; the mild reaction conditions required for synthesis, high yields and a wide range of stability under aqueous conditions have enabled them to occupy a respectable position in organometallic chemistry. Their complexes have found application as good catalysts in water oxidation [4], hydrogen activation [5], transfer hydrogenation [6] and aerobic alcohol oxidation [7]. In addition, their complexes are also found to be biologically active against cancer and bacteria [8].

Vast number of researchers has paid considerable interest in the development of new compounds with activities such as anticancer, anti-malarial, antimicrobial etc. Hydrazones derivative constitute an important class of compounds for development of such new drugs. Therefore, many researchers have synthesized a variety of these compounds as target structures and evaluated their biological activities. Although benzothiazole hydrazones itself displayed wide range of biological activities yet only few reports on the chemistry of ruthenium, rhodium and iridium complexes containing these hydrazone derivatives. Souvik and co-worker [9] have studied the
antimalarial activity of these related benzothiazole hydrazones. Priyanka and co-worker [10] have developed a series of novel 2-substituted hydrazino-6-fluoro-1,3-benzothiazole derivatives that show antimicrobial activity. Felipe and co-worker [11] reported that these small benzothiazole molecule were able to induce apoptosis and prevent metastasis through DNA interaction and c-MYC gene suppression in diffuse-type gastric adenocarcinoma cell line. Hence, the choice of ligand plays a crucial role in determining the application of these complexes. Hydrazone functional group in addition to its biological application, displayed interesting structural properties. The presence of nucleophilic imine and amino type nitrogen’s, an imine carbon that has both electrophilic and nucleophilic character, configurational isomerism of the C=N group and in most cases an acidic N–H proton enables them to display varieties of bonding with other metals [12].

Keeping in mind the biological activity of benzothiazole hydrazone derivatives we are interested to explore this possibility and also to study the reactivity of p-cymene ruthenium and Cp* rhodium complexes containing these derivatives towards NaN₃ and with acetylene carboxylates {dimethylacetylenedicarboxylate (DMAD) and diethylacetylenedicarboxylate (DEAD)}. These azido with acetylene carboxylates pellets in the range of 400–800 nm at room temperature in acetonitrile. Mass spectra were recorded using HRMS model Xevo XS QT of mass spectrometer, Waters ACQUITY UHPLC and Waters ZQ 4000 MS instrument by ESI method using acetonitrile as solvent. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. All these mononuclear metal complexes were synthesized and characterized by using FT-IR, ¹H NMR, UV–Vis and Single-crystal X-ray diffraction techniques.

2.2. Single-crystal X-ray structures analyses

Single crystal X-ray diffraction data for some of the complexes were collected on an Oxford Diffraction Xcalibur Eos Gemini diffractometer at 293 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Suitable crystals were selected and each mounted on a glass fiber. The strategy for the data collection was evaluated using the CrysAlisPro CCD software [16]. Crystal data were collected by standard “phi–omega scan” techniques and were scaled and reduced using CrysAlisPro RED software. Using Olex2 [17] the structures were solved with ShelXT [18] solution program using direct method and refined with olex2.refine [19] refinement package using Gauss-Newton minimization. Crystallographic and structure refinement details for the complexes are summarized in Table S1 and selected bond lengths and bond angles are presented in Table 1. Figs. 1–4 were drawn with ORTEP3 program [20].

2.3. New procedure for synthesis of rhodium and iridium dimer

In a sample test tube of size 10 ml 500 mg of Rh/IrCl₃.nH₂O, 0.4 ml of Cp* and 2 ml of dry methanol was added and mix thoroughly. A small size Teflon coated magnetic stirrer was inserted for stirring purpose. The mixture was sealed tightly and placed into an Anton Paar Mono-Wave 50 instrument. The reaction condition was adjusted by setting the temperature to 110 °C and pressure will reach around 20 bars for 45 min. The instrument takes about 2–3 min to heat up to the set temperature and the reaction proceeds smoothly for 45 min. On completion, the reaction cools down to a temperature of 60 °C. A red-orange crystalline solid was obtained. The solvent was decanted, washed several times with diethyl ether and dry in vacuum.

Yield: 87% for Rhodium dimer and 90% for Iridium dimer.

2.4. General procedure for synthesis of cationic and neutral complexes (1–9)

A mixture of starting metal precursor (0.05 mmol) and appropriate ligand (L) (0.1 mmol) were dissolved in dry methanol (10 ml) and stirred at room temperature for 8 h (Scheme 1). The solvent was evaporated using rotavapor, the residue was dissolved in DMSO-d₆ and CDCl₃ as solvents. Absorption spectra were recorded on a Perkin-Elmer Lambda 25 UV/Visible spectrophotometer in the range of 200–800 nm at room temperature in acetonitrile. Mass spectra were recorded using HRMS model Xevo XS QT of mass spectrometer, Waters ACQUITY UHPLC and Waters ZQ 4000 MS instrument by ESI method using acetonitrile as solvent. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. All these mononuclear metal complexes were synthesized and characterized by using FT-IR, ¹H NMR, UV–Vis and Single-crystal X-ray diffraction techniques.
dichloromethane and filtered through Celite, the filtrate was concentrated to 1 ml and excess diethyl ether was added to precipitate the compound. The precipitate was collected and dried in vacuum.

2.4.1. [(p-cymene)Ru(μ²-N=N=1)Cl]Cl (1)
Yield: 82%, Color: Orange; IR (KBr, cm⁻¹): 3412 ν(N=N)ₕ, 3054 ν(C=H) (sp²), 1596-1561 ν(C≡N), 1509-1449 ν(C=O), 759 ν(C≡S).

1H NMR (400 MHz, Chloroform-d) δ 8.76 (s, 1H), 8.14 (d, J = 8 Hz, 2H), 7.63-7.42 (m, 6H), 7.23 (t, J = 8 Hz, 1H), 5.46 (s, 2H), 5.26 (d, J = 8 Hz, 1H), 4.74 (s, 1H), 4.49 (d, J = 8 Hz, 1.2H), 2.46 (sept, 1H), 2.22 (s, 3H), 1.40 (d, J = 8 Hz, 3H), 0.87 (d, J = 4 Hz, 3H).

ESI-MS (m/z): 524.02 [M-Cl]-, 488.05 [M-Cl₂]-; UV–Vis (Acetonitrile, λmax nm (ε/10⁻⁴ M⁻¹ cm⁻¹)):
1.273 and 1.339
212 (7.275), 297 (2.340), 340 (2.174), 386
Fig. 2. ORTEP generated molecular structure of complexes 3 and 4 with 50% thermal ellipsoid probability.

Fig. 3. ORTEP generated molecular structure of complexes 5 and 6 with 50% thermal ellipsoid probability.

Fig. 4. ORTEP generated molecular structure of complexes 8 and 11 with 50% thermal ellipsoid probability. Complex 11 shows interesting chemical disorder with one set containing two azides, the other an azide group and a chloride group. Because of low theta value, the crystal structure of complexes 8 is presented just to show its solid-state composition.

2.4.2. [Cp*Rh(k-1,N-L1)Cl] (2)
Yield: 85%, Color: Orange; IR (KBr, cm⁻¹): 3060 (ν(C-H) (sp²)), 1602-1560 (ν(C=C)), 1489-1452 (ν(C≡C)), 759 (ν(C-S)). ¹H NMR (400 MHz, DMSO-d₆) δ 8.08 (s, 1H), 7.69 (d, J = 8 Hz, 2H), 7.63 (d, J = 4 Hz, 1H), 7.59–7.54 (m, 1H), 7.49 (d, J = 8 Hz, 1H), 7.39 (m, 3H), 7.28 (t, J = 8 Hz, 1H), 7.10 (t, J = 8 Hz, 1H), 1.75 (s, 15H). UV–Vis {Acetonitrile, λ_max nm (ε/10⁻⁴ M⁻¹ cm⁻¹)}: 225 (8.803), 333 (7.641), 395 (0.891).

2.4.3. [Cp*Ir(k-1,N,N)-L1]Cl (3)
Yield: 83%, Color: Yellow; IR (KBr, cm⁻¹): 3060 (ν(C-H) (sp²)), 1599-1561 (ν(C≡C)), 1489-1453 (ν(C≡C)), 759 (ν(C-S)). ¹H NMR (400 MHz, chloroform-d) δ 7.96 (s, 1H), 7.60 (d, J = 8 Hz, 3H), 7.44 (d, J = 8 Hz, 1H), 7.36–7.19 (m, 5H), 7.04 (t, J = 8 Hz, 1H), 1.67 (s, 15H). ESI-MS (m/z): 616.18 [M]¹, 580.16 [M-Cl]¹; UV–Vis {Acetonitrile, λ_max nm (ε/10⁻⁴ M⁻¹ cm⁻¹)}: 222 (6.101), 332 (5.555), 403 (0.443).

2.4.4. [(p-cymene)Ru(k-2,N,N)-L2]Cl (4)
Yield: 87%, Color: Yellow; IR (KBr, cm⁻¹): 3060 (ν(C-H) (sp²)), 1601-1562 (ν(C≡C)), 1506-1452 (ν(C≡C)), 754 (ν(C-S)). ¹H NMR (400 MHz, Chloroform-d) δ 8.76 (s, 1H), 8.26 (dd, d J = 8 Hz, 4 Hz, 2H), 7.63 (d, J = 8 Hz, 1H), 7.52–7.44 (m, 2H), 7.25 (m, 3H), 5.46 (s, 2H), 5.32 (d, J = 4 Hz, 1H), 4.61 (d, J = 8 Hz, 1H), 2.55–2.45 (sept, 1H), 2.24 (s, 3H), 1.07 (d, J = 8 Hz, 3H), 0.88 (d, J = 8 Hz, 3H). ESI-MS (m/z): 542.01 [M-Cl]¹, 506.04 [M-Cl₂]¹; UV–Vis {Acetonitrile, λ_max nm (ε/10⁻⁴ M⁻¹ cm⁻¹)}: 213 (7.908), 273 (2.598), 302 (2.593), 336 (2.638).

2.4.5. [Cp*Rh(k-1,N,N)-L2]Cl₂ (5)
Yield: 85%, Color: Orange; IR (KBr, cm⁻¹): 3432 (ν(C≡C)), 3032 (ν(C-H) (sp²)), 1601-1562 (ν(C≡C)), 1507-1452 (ν(C≡C)), 757 (ν(C-S)). ¹H NMR (400 MHz, DMSO-d₆) δ 8.00 (s, 1H), 7.62 (d, J = 8 Hz, 2H), 7.54 (d, 1H), 7.34–7.28 (m, 3H), 7.22 (t, J = 8 Hz, 1H), 7.04 (t, J = 8 Hz, 1H), 1.66 (s, 15H); UV–Vis {Acetonitrile, λ_max nm (ε/10⁻⁴ M⁻¹ cm⁻¹)}: 223 (6.892), 331 (5.118), 392 (0.988).

2.4.6. [(p-cymene)Ru(k-2,N,N)-L2]Cl₂ (6)
Yield: 82%, Color: Yellow; IR (KBr, cm⁻¹): 3430 (ν(C≡C)), 3054 (ν(C-H) (sp²)), 1601-1563 (ν(C≡C)), 1508-1453 (ν(C≡C)), 756 (ν(C-S)). ¹H NMR (400 MHz, DMSO-d₆) δ 8.09 (s, 1H), 7.73–7.66 (m, 3H), 7.41 (d, J = 4 Hz, 1H), 7.25 (t, J = 8 Hz, 1H), 7.18 (t, J = 8 Hz, 2H), 7.07 (t, J = 8 Hz, 1H), 1.65 (s, 15H). ESI-MS (m/z): 598.14 [M-Cl]¹; UV–Vis {Acetonitrile, λ_max nm (ε/10⁻⁴ M⁻¹ cm⁻¹)}: 220 (7.904), 239 (5.585), 332 (7.090) 399 (0.296).
2.4.7. [(p-cymene)Ru(κ^2(NN-L3)]Cl] (7)

Yield: 84%, Color: Yellow; IR (KBr, cm⁻¹): 3430 ν(N-H), 3054 ν(C=C) (sp²), 1601-1562 ν(C=C=O), 1508-1453 ν(C=C), 756 ν(C-S). ¹H NMR (400 MHz, Chloroform-d) δ 8.78 (s, 1H), 8.13 (d, J = 8 Hz, 2H), 7.68 (d, J = 8 Hz, 1H), 7.69-7.51 (m, 2H), 7.39 (d, J = 8 Hz, 2H), 7.32 (t, J = 8 Hz, 1H), 5.52 (d, J = 4 Hz, 2H), 5.31 (d, J = 8 Hz, 1H), 4.71 (d, J = 4 Hz, 1H), 2.59-2.50 (m, 4H), 2.33 (s, 3H), 1.13 (d, J = 8 Hz, 3H), 0.97 (d, J = 8 Hz, 3H). UV-Vis (Acetonitrile, λmax nm (ε/10⁻⁴ M⁻¹ cm⁻¹)): 211 (9.537), 267 (3.779) 299 (3.435) 351 (3.322) 393 (2.975).

2.4.8. [Cp*Rh(κ^2(NN-L3)]Cl] (8)

Yield: 83%, Color: Orange; IR (KBr, cm⁻¹): 3432 ν(N-H), 3032 ν(C=C) (sp²), 1601-1562 ν(C=C=O), 1507-1452 ν(C=C), 757 ν(C-S). ¹H NMR (400 MHz, DMSO-d₆) δ 8.08 (s, 1H), 7.74 (d, J = 4 Hz, 1H), 7.57 (d, J = 8 Hz, 2H), 7.42 (s, 1H), 7.29-7.24 (m, 3H), 7.09 (t, J = 8 Hz, 1H), 2.33 (s, 3H), 1.61 (s, 15H); UV-Vis (Acetonitrile, λmax nm (ε/10⁻⁴ M⁻¹ cm⁻¹)): 225 (8.228), 243 (5.849), 333 (7.0002), 391 (0.958).

2.4.9. [Cp*Ir(κ^2(NN-L3)]Cl] (9)

Yield: 81%, Color: Yellow; IR (KBr, cm⁻¹): 3430 ν(N-H), 3054 ν(C=C) (sp²), 1601-1563 ν(C=C=O), 1508-1453 ν(C=C), 756 ν(C-S). ¹H NMR (400 MHz, DMSO-d₆) δ 8.08 (s, 1H), 7.75 (d, J = 4 Hz, 1H), 7.57 (d, J = 8 Hz, 2H), 7.42 (s, 1H), 7.29-7.24 (m, 3H), 7.09 (t, J = 8 Hz, 1H), 2.32 (s, 3H), 1.61 (s, 15H); ESI-MS (m/z): 598.14 [M-Cl]⁺; UV-Vis (Acetonitrile, λmax nm (ε/10⁻⁴ M⁻¹ cm⁻¹)): 221 (8.614), 244 (5.953), 333 (8.555), 398 (0.712).

2.5. General procedure for synthesis of azido complexes (10–15)

The corresponding starting complexes of 1, 2, 4, 6, 7 and NaN₃ in 1:4 M ratio was suspended in dry methanol (15 ml) and stirred at room temperature for 6 h (Scheme 2). The solvent was removed to dryness using rotary evaporator. The residue was extracted with dichloromethane, filtered and precipitated with hexane.

2.5.1. [(p-cymene) Ru(κ^2(NN-L3)]N₃] (10)

Yield: 68%, Color: Yellow; IR (KBr, cm⁻¹): 3058 ν(C=H) (sp²), 2026 ν(N₃), 1634-1577 ν(C=C=O), 1484-1450 ν(C=C), 748 ν(C-S). ¹H NMR (400 MHz, Chloroform-d) δ 8.30 (d, J = 8 Hz, 2H), 8.00 (s, 1H), 7.49-7.44 (m, 3H), 7.42 (d, J = 4 Hz, 1H), 7.36 (d, J = 8 Hz, 2H), 7.04 (t, J = 4 Hz, 1H), 5.79 (d, J = 4 Hz, 1H), 5.65 (d, J = 8 Hz, 1H), 5.54 (d, J = 4 Hz, 1H), 5.29 (d, J = 8 Hz, 1H), 2.49 (sept, 1H), 2.33 (s, 3H), 1.09 (d, J = 8 Hz, 3H), 1.02 (d, J = 8 Hz, 3H).

2.5.2. [Cp*Rh(κ^2(NN-L3)]N₃] (11)

Yield: 75%, Color: Orange; IR (KBr, cm⁻¹): 3060 ν(C=H) (sp²), 2019 ν(N₃), 1635 ν(C=C=O), 1497-1450 ν(C=C), 782 ν(C-S). ¹H NMR (400 MHz, chloroform-d) δ 8.76 (s, 1H), 8.09 (d, J = 8 Hz, 2H), 7.49 (t, J = 8 Hz, 2H), 7.43 (t, J = 8 Hz, 2H), 7.27-7.19 (m, 2H), 6.96 (t, J = 8 Hz, 1H), 1.39 (s, 15H).

2.5.3. [(p-cymene)Ru(κ^2(NN-L3)]N₂] (12)

Yield: 71%, Color: Orange; IR (KBr, cm⁻¹): 3060 ν(C=H) (sp²), 2027 ν(N₃), 1645-1597 ν(C=C=O), 1488-1452 ν(C=C), 748 ν(C-S). ¹H NMR (400 MHz, Chloroform-d) δ 8.72 (s, 1H), 8.18 (dd, J = 4 Hz, 4 Hz, 2H), 7.43 (d, J = 8 Hz, 1H), 7.29-7.20 (m, 4H), 6.99 (t, J = 8 Hz, 1H), 5.54 (d, J = 8 Hz, 1H), 5.37 (d, J = 4 Hz, 1H), 5.03 (d, J = 4 Hz, 1H), 4.50 (d, J = 4 Hz, 1H), 2.43-2.30 (m, 4H), 1.08 (d, J = 4 Hz, 3H), 0.99 (d, J = 8 Hz, 3H).

2.5.4. [Cp*Rh(κ^2(NN-L3)]N₂] (13)

Yield: 68.3%, Color: Orange; IR (KBr, cm⁻¹): 3032 ν(C=H) (sp²), 2019 ν(N₃), 1635-1562 ν(C=C=O), 1497-1450 ν(C=C), 758 ν(C-S). ¹H NMR (400 MHz, Chloroform-d) δ 8.79 (s, 1H), 8.13 (dd, J = 8 Hz, 8 Hz, 2H), 8.04 (d, J = 8 Hz, 1H), 7.52 (d, J = 4 Hz, 1H), 7.20 (t, J = 8 Hz, 3H), 6.97 (t, J = 8 Hz, 1H), 1.47 (s, 15H).

2.6.2. [(p-cymene)Ru(\(J\text{d},\text{hexane} (2\text{ml})\) this solution, 30 ml of hexane was added whereby the compound diethylacetylene dicarboxylate and dichloromethane (20 ml) was added, whereby the compound formed a microcrystalline yellow precipitate.

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2.6.5. [(p-cymene)Ru(\(J\text{d},\text{hexane} (2\text{ml})\) this solution, 30 ml of hexane was added whereby the compound diethylacetylene dicarboxylate and dichloromethane (20 ml) was added, whereby the compound formed a microcrystalline yellow precipitate.

2.6.6. [(p-cymene)Ru(\(J\text{d},\text{hexane} (2\text{ml})\) this solution, 30 ml of hexane was added whereby the compound diethylacetylene dicarboxylate and dichloromethane (20 ml) was added, whereby the compound formed a microcrystalline yellow precipitate.

3. Results and discussion

3.1. Synthesis of metal complexes

In the present work we have carried out the synthesis and reactivity studies of metal complexes of ruthenium, rhodium and
Cationic complex 8 were then treated with sodium azide to yield azido compounds. The analytical data of these compounds are consistent with the formulations. All complexes are characterized by \( ^1 \)H NMR, IR and mass spectroscopy. The molecular structure of the complexes determined by single crystal X-ray diffraction method, revealed the different modes of binding of the metals to the ligands L1, L2 and L3 that differs only at para position of the phenyl group.

### 3.2. Spectral studies of the complexes

#### 3.2.1. IR studies of metal complexes

Complexes 1–9 exhibit characteristic stretching frequencies for \( \nu(N^\equiv H) \), \( \nu(C=C=N) \) and \( \nu(C=\equiv S) \). The IR spectra of the complexes were compared with that of the free ligand. The free ligands show a characteristic stretching frequency at 3434–3412 cm\(^{-1} \) for \( \nu(N^\equiv H) \) and stretching frequency at 1630 and 1619 cm\(^{-1} \) for \( \nu(C=\equiv N) \). On formation of complexes the C=\equiv N stretching frequency decreases and is observed between 1602 and 1561 cm\(^{-1} \) and N–H stretching frequency was observed only for complexes 2 and 5 which suggest that coordination occurs only through the benzothiazole nitrogen forming a mono-dentate neutral complexes. The absence of N–H stretching frequency for complexes 3, 4, 6, 7, 8 and 9 indicates the formation of bidentate neutral complexes which coordinates through the benzothiazole and imine nitrogen’s.

Azido complexes 10–15 were confirmed from their IR spectra by the presence of a strong absorption band at around 2018–2027 cm\(^{-1} \) which corresponds to terminal \( \nu(N_3) \). The formation of triazole complexes 16–18 were also confirmed from their IR spectra. The absence of a sharp band at 2018–2027 cm\(^{-1} \) and the appearance of a strong band at around 1720–1734 cm\(^{-1} \) which corresponds to the stretching frequency of the carbonyl group of esters confirmed the formation of triazole compounds. The IR spectra of some complexes were given in supplementary data (Figure S15 to S18).

#### 3.2.2. \( ^1 \)H NMR studies of the complexes

To further reveal the coordination behavior of the ligands to metal and the formation of triazole complexes, \( ^1 \)H NMR analyses of all these complexes were recorded in deuterated solvent at room temperature. The ligand protons of complex 1 displayed one singlet for NH proton at 4.74 ppm whereas the NH proton signal of complexes 2 and 5, which were recorded in CHCl\(_3\)-d\(_1\) and DMSO-d\(_6\), mixture in (3:1) ratio was not observed due to solvent exchange. The disappearance of NH proton signal in complexes 3, 4, 6, 7, 8 and 9 indicates the deprotonation of NH proton of the hydrazine group. The imine proton of all the complexes displayed one singlet at around 7.96–8.76 ppm. Upon co-ordination to the metal center the aromatic proton signals of the ligand are shifted downfield which is due to the donation of lone pairs of electron from the nitrogen atom.
of the benzothiazole (N) and the imine nitrogen (N') to the metal center. In all the complexes several multiplets were observed in the range of 7.44–7.60 ppm due to overlap of the protons of phenyl and benzothiazole rings. All ruthenium complexes (1, 4 and 7) displayed one singlet with two protons at 5.46 ppm and two doublets with one proton each at 5.33–4.48 ppm which corresponds to the aromatic protons of the p-cymene ring and the methyl protons of the isopropyl group of the p-cymene ring displayed two doublets in the range of 0.86–1.08 ppm. This unusual splitting of the aromatic and isopropyl protons may be attributed to the diastropic methyl protons of isopropyl group and chiral nature of the metal center [21,22]. The methine proton of the p-cymene ring exhibits a septet in the range of 2.41–2.55 ppm. In addition, complex 7 displayed one singlet at 2.23 ppm for 3 protons of the methyl group in para position of the aldehyde derivative. The methyl singlet of fifteen protons for rhodium and iridium complexes (2, 3, 5, 6, 8 and 9) was observed in the range of 1.65–1.75 ppm. The 1H NMR of all these complexes was given in supplementary data (Figure S1 to S9).

From the 1H NMR spectra of azido complexes 10–15, there is not much different in the splitting pattern of their protons except that their chemical shift value has shifted slightly to the downfield region for all the ruthenium azido complexes. The aromatic protons of the p-cymene N(1) ring displayed four doublets in the range of 5.89 to 4.49 ppm instead of one singlet and two doublets, which clearly indicate the formation of different complexes due to the attachment of N3 group to form azido complexes. The diastropic methyl protons of isopropyl group displayed the same two doublets in the range of 1.30 to 0.98 ppm and the methine protons of the p-cymene ring of all the ruthenium azido complexes displayed a septet in the range of 2.74 to 2.34 ppm. In the case of rhodium azido complexes the ligand protons shifted towards the downfield region while the Cp* protons shifted towards the upfield region 1.3–1.4 ppm as compared to their relative complexes where the Cp* protons displayed in region of 1.6–1.7 ppm. The deprotonation of NH proton for mono-dentate rhodium complexes 2 and 5 to form bidentate neutral azido complexes 11 and 13 could not be explained from their NMR spectra due to the absence of NH protons signal in the spectra of the former. However, this is being confirmed from their solid-state structure obtained by single crystal X-ray diffraction (SXRD) method, which indicates the formation of azido complexes along with the conversion of mono-dentate to bidentate complexes, which is similar to the complexes reported by our group [12,13].

The 1H NMR of triazolato complexes based from previous reported articles the triazole anion can coordinate to the metal center via N(1) or N(2) nitrogen atoms [23,24] forming two types of isomers which are isoequivalent as confirmed by molecular calculation [24,25]. However, these isomers can be easily differentiated from their 1H NMR spectra as they displayed different splitting pattern. Based on the evidence obtained from previous articles, these two isomers can either be formed simultaneously [23–26] or in some cases N(2) bound isomer being formed exclusively [23,26–28]. Both of these evidence were true depending on the overall stability of the complexes either kinetically N(1) and thermodynamically N(2) as our group have reported in previous article [29]. Other factors that determined the formation of N(1) or N(2) bound isomers are electronic factor such as nucelophilicity of the triazole anion which favor N(1) bound isomer or steric factor which arises upon coordination of the ligands to the metal center which favor N(2) bound isomer [30]. In this present work, we obtained exclusively only the N(2) bound isomers for both alkoxy substituted acetylenes. The 1H NMR spectra of triazolato complexes 16–21 displayed characteristic peaks corresponding to the ligands (L1, L2 and L3) and the p-cymene moiety. In addition, the 1H NMR of complexes 16, 18 and 20 displayed a singlet in the range of 3.67–3.74 ppm, which corresponds to the six protons of the methoxy carbonyl group. Also, from the 1H NMR of complexes 17, 19 and 21 the ethoxy carbonyl group displayed a quartet in the range of 4.17–4.23 ppm, which corresponds to the four protons of the methylene group and a triplet in the range of 1.18–1.23 ppm which corresponds to the six protons of the methyl group. These splitting pattern clearly suggest the formation of N(2) bound isomer as reported by our group [13,14,29]. The 1H NMR spectra of some of these triazolato complexes were given in supplementary data (Figure S10 to S14).

3.2.3. Mass studies of the complexes

The mass spectra of some of the complexes 1, 3 and 4 are presented in supplementary data (Figure S19 to S21). Complex 1 displayed its predominant molecular ion peak at m/z: 488.05 which corresponds to [M-Cl]þ ion peak whereas complexes 3 and 4 display their predominant molecular ion peaks at m/z: 580.16 and m/z: 506.04 respectively which corresponds to [M-Cl]þ ion. In cationic complex 1, fragmentation of the counter ion and the chloride was observed while in neutral complexes 3 and 4 fragmentation of chloride attached to the metal center takes place. The mass spectra values of all these complexes strongly support the formation of the desired product.

3.2.4. UV—visible description of metal complexes

The absorption spectra of ligands and complexes 1–9 were recorded in acetonitrile of 10–4 M cm−1 at room temperature and the UV plot of these complexes along with the ligands is provided in supplementary information Figure S22. The ligand exhibited medium intensity band at 245 nm and a high intensity band at 332 nm corresponding to ligand center π–π* and n–π* transitions [31,32]. An absorption bands in the visible region around 400–450 nm are attributed as charge transfer band. Because of low molar absorptivity values these band maybe assigned as d–d transition.

3.3. Single crystal X-ray structure determination of complexes

Single crystals suitable for X-ray diffraction analysis were obtained for complexes 1, 2, 3, 4, 5, 6, 8 and 11. These crystals are orange, yellow and red in colors and were obtained by solvent diffusion method for all the complexes except complex 4 which was crystallized from methanol by slow evaporation method. The molecular structures of these complexes have been established by single crystal X-ray structure analysis. Because of low theta value, the molecular structure of complexes 1, 8 and 11 were given only to confirm their structural composition and binding mode of the ligand towards metal. ORTEP diagrams of these complexes are presented in Figs. 1–4 and their X-ray data collection parameters, selected bond lengths, and selected bond angles are presented in Tables 1 and 2 respectively. Complex 1 crystalize in triclinic with PT space group whereas complexes 2, 5, 6 and 11 crystalizes in monoclinic with P21/n space group and complexes 3 and 4 crystalizes in monoclinic with P21/c space group. Complex 8 crystalize in orthorhombic with Pna21 space group. In complexes 1, 4 and 7 metal is coordinated to a p-cymene and in complexes 2, 3, 5, 6, 8 and 9 the metal is coordinated to a Cp* ligand as seat. From the molecular structure of complexes the metal (Ru/Rh/Ir) binds to one chloride and two nitrogen donor atoms of the chelating ligand forming half-sandwich three-legged piano stool structure around each metal center. The complexes are mononuclear neutral and cationic only in the case of ruthenium complex 1 in which the ligand with hydrogen (H) substituent at para position of the phenyl ring acts as N=N donor. However, ruthenium complex 4 with fluorene (F) at para position of the phenyl ring formed neutral bidentate complex (Fig. 2). Complexes of rhodium 2 and 5 with H
and F substituents respectively at para position of the phenyl ring binds to one nitrogen donor atom of the benzothiazole ring and two terminal chlorides forming neutral mono-dentate complexes. The molecular structure of these complexes (Figs. 1 and 3) clearly shows the trans conformation of the benzothiazole hydrazone derivatives. Interestingly when these trans conformers mono coordinated rhodium complexes were treated with sodium azide (chemical activation) [12] in methanol the benzothiazole derivatives undergo conformational switching from trans (E) to cis (Z) conformers. The formed azido complexes clearly justified the conformational switching of the benzothiazole derivatives as seen from the molecular structure of complex 11 (Fig. 4). This in turn changes the binding modes of the ligands from neutral monodentate to neutral bidentate complexes with the deprotonation of acidic NH proton. Molecular structure of complex 11 shows interesting chemical disorder with one set containing two azides, the other an azide group and a chloride group. In contrast, rhodium complex 8 with methyl group as substituent at para position of the phenyl ring binds to both the nitrogen forming neutral bidentate complex as seen from the molecular structure of the complex (Fig. 4). Hence, the variations in the binding modes of the benzothiazole hydrazone derivatives may also be contributed by the substituents at the para position of the phenyl ring (H, F, CH₃). However, in the case of iridium complexes 3 and 6 (Figs. 2 and 3) the mode of bonding of the benzothiazole hydrazone derivatives does not change even when the substituents at para position of the phenyl ring were different. Thus, the variation of bonding of the same ligand towards different metal happen which is not unusual where similar bonding behaviors has been reported by our group with pyridyl azine ligands [33,34].

The distance between the metal center to the centroid of the arene ring in complexes 1–6 and 11 are 1.705 Å, 1.773 Å, 1.797 Å, 1.692 Å, 1.769 Å, 1.794 Å and 1.805 Å respectively (Table 2). The M(1)-N(1) bond distances in complexes 1–6 and 11 are 2.12(2) Å, 2.167(3) Å, 2.083(5) Å, 2.083(3) Å, 2.161(3) Å, 2.126(4) Å, 2.063(9) Å and M(1)-N(3) bond distances in complexes 1, 3, 4, 6 and 11 are 2.10(2), 2.113(6), 2.140(3), 2.126(4) and 2.103(8) Å respectively. The M(1)-N(4) bond distance in complex 11 is 2.131(9) Å. The M(1)-Cl(1 or 2) bond distance in these complexes are found to be in the range of 2.3983 Å to 2.4387 Å which is comparable with earlier reported complexes [35,36]. The bond angle values of N(1)-M(1)-(N3) for bidentate complexes are found to be in the range of 75.1°–76.15° and N-M-Cl bond angle values are in the range of 83.1°–92.80° for both mono-dentate and bidentate complexes. The bond angle values of N(1)-M(1)-N(4) and N(3)-M(1)-N(4) in azido complex 11 are in the range of 86.2°–86.5° which is close to that of an octahedral bond angle. This deviation from the octahedral bond angle is the evidence for attaining “piano stool” geometry. In Complex 1, the N(1)–C(17) bond length is 1.231 Å which is close to that of double bond character indicating the presence of NH proton which does not deprotonate in solution and also confirming the formation of a cationic complex. Also in complexes 2 and 5 the N(1)–C(17) bond length is close to that of a double bond character i.e., 1.310–1.315 Å and the C(17)–N(2) bond length is around 1.347–1.349 Å which is close to a single bond character. This indicates the presence of NH proton, nevertheless the absence of counter ion in their molecular structure confirmed the formation of neutral monodentate complexes. In bidentate complexes 3, 4, 6 and 11 the bond length of C(17)–N(2) were found to be in the range of 1.298–1.308 Å which is close to that of a double bond character. This suggest the absent of acidic NH proton which deprotonate in solution forming a double bond C(17)–N(2) while the C(17)–N(1) bond length increases to 1.325–1.340 Å indicating the shifting of electron density towards N(1) where the C(17)–N(1) bond length is now converted to a single bond. The deprotonation of NH proton assists the benzothiazole ring to coordinate to the metal center as anionic ligands forming neutral bidentate complexes. The molecular structure of these complexes obtained clearly explicit the mode of bonding between the ligands and metals. From the crystal-packing diagram (Figure S23), the presence of hydrogen bonding interaction such as N–H–Cl and non-covalent interaction such as C–Cl between molecules in complexes 3 contribute to the overall stability of the complex. DCM which is the solvent of crystallization crystalized along with the complex and involved in two types of interaction. One of distance 2.609 Å involving interaction between nitrogen of the imine group of the ligand with one of the hydrogen atom of DCM. The other of distance 3.397 Å involving the carbon of the phenyl ring with one of the chlorine of DCM. Unfortunately, we could not obtain single crystal for triazolato complexes required for X-ray diffraction studies.

**4. Conclusion**

All together 21 new complexes have been synthesized. The ligands and complexes were characterized by spectroscopic techniques. Anti-bacterial studies for all the compounds have been carried out but none of them show any significant inhibition towards gram-positive and gram-negative bacteria. Versatility of benzothiazole hydrazone derivatives maybe attributed due to the presence of acidic NH proton. Substituents at para position of phenyl ring (H, F, CH₃) may also contribute to the versatility in the bonding modes of the benzothiazole hydrazone derivatives.
towards the metal centers especially in the case of rhodium complexes. Azido complexes of ruthenium and rhodium were found to be stable while triazolato complexes of rhodium were found to be unstable and depurate during separation. However triazolato complexes of ruthenium were found to be stable and their ¹H NMR clearly justified the formation of N(2) bound isomer. The single crystal X-ray diffraction study reveals the usual pseudo-octahedral “piano-stool” geometry of the complexes. Complexes of rhodium 2 and 5 bind preferentially through the benzothiazole nitrogen forming neutral mono-dentate complexes whereas their azido complexes bind to one azide anion and two nitrogen donor atoms of the chelating ligand forming neutral bidentate complex. In this complex the benzothiazole hydrazone derivatives undergo conformational switching from E to Z conformers. Thus, the introduction of sodium azide plays a vital role for the changes in conformation of the benzothiazole derivatives of monodentate rhodium complexes.

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Appendix A. Supplementary data

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References