CHAPTER 3

Ruthenium half-sandwich complexes with tautomerized pyrazolyl pyridazine ligands: Syntheses, spectroscopic and molecular structural studies
Ruthenium half-sandwich complexes with tautomerized pyrazolyl pyridazine ligands: Syntheses, spectroscopic and molecular structural studies*

3.1 Abstract
Condensation of 1,4-dichloropyridazine with pyrazole, 3,5-dimethylpyrazole and 3-methylpyrazole yielded two types of pyrazolyl pyridazine ligands, viz., (i) products of substitution on one side of the pyridazine as 3-chloro-6-(pyrazolyl)pyridazine (Cl-L1), 3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine (Cl-L2) and 3-chloro-6-(3-methylpyrazolyl)pyridazine (Cl-L3), and (ii) products of substitution on both sides such as 3,6-bis(pyrazolyl)pyridazine (L1), 3,6-bis(3,5-dimethylpyrazolyl)pyridazine (L2) and tautomers of 3,6-bis(3-methylpyrazolyl)pyridazine (L3). The reactions of η⁶-arene ruthenium complexes in methanol with the above mentioned pyrazolyl pyridazine ligands form mononuclear complexes of the type [(η⁶-arene)Ru(Cl-L)(Cl)]⁺ and [(η⁶-arene)Ru(L)(Cl)]⁺; (arene = benzene and p-cymene; Cl-L = Cl-L1, Cl-L2, Cl-L3; L = L1, L2, L3). All these complexes are characterized by IR, NMR, mass spectrometry and UV/visible spectroscopy. The structures of some representative complexes are established by single crystal X-ray diffraction studies.

3.2 Introduction

Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 40 years. In particular, \( \eta^6 \)-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1, 2]. Coordination of a metal fragment to an arene ring dramatically facilitates electrophilic aromatic addition and substitution, arene deprotonation and benzylic deprotonation. Arene metal complexes have been utilized as homogeneous catalysts or catalyst precursors in numerous transformations such as hydrogenation, esterification, olefin metathesis and Diels-Alder cycloaddition [3-6]. In recent years, we have been carrying out reactions of arene ruthenium dimers with a variety of nitrogen-based ligands [7-12] including pyridyl-pyridazine and pyrazolyl-pyradazine ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to oxygen [13, 14]. Although extensive studies have been made on ruthenium complexes containing polypyridyl ligands, complexes containing annular tautomerized pyrazolyl-pyradazine ligands have not yet been investigated.

Herein, we describe the synthesis of pyrazole-based ligands in which the starting 3-methylpyrazole moiety tautomerizes to a 5-methylpyrazole moiety [15]; the existence of both tautomers in a single compound is reported here. The syntheses of 12 mononuclear arene ruthenium complexes incorporating these as well as some other pyrazolyl-pyridazine ligands are also reported. Given below are the structures of the ligands used in this study. All these complexes are characterized by IR, NMR, mass spectrometry and UV/visible spectroscopy. The molecular structures of the ligand (L3) and four representative complexes are also presented in this chapter.
3. Complexes of pyrazolyl ligands

![Chemical structures of pyrazolyl ligands]

| R=R'=H,        | Cl-L1            | (3-chloro-6-(pyrazolyl)pyridazine) |
| R=R'=CH₃,      | Cl-L2            | (3-chloro-6-(3,5-dimethylpyrazolyl)pyridazine) |
| R=CH₃, R'=H,   | Cl-L3            | (3-chloro-6-(3-methylpyrazolyl)pyridazine) |

| R=R'=H,        | L1               | (3,6-Bis(pyrazolyl)pyridazine) |
| R=R'=CH₃,      | L2               | (3,6-Bis(3,5-dimethylpyrazolyl)pyridazine) |
| R=CH₃, R'=H,   | L3               | (3,6-Bis(3-methylpyrazolyl)pyridazine) |

**Ligands used in this study**

### 3.3 Experimental

All solvents were dried and distilled prior to use. Ruthenium trichloride trihydrate (Arora Matthey Ltd.), pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole and 3,6-dichloropyridazine (Aldrich) were purchased and used as received. The ligands were prepared by following a literature procedure [16]. The precursor complexes [(η⁶-arene)Ru(µ-Cl)Cl]₂ (arene = benzene and p-cymene) were prepared by following the literature methods [17-19]. NMR spectra were recorded on an AMX 400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. Mass spectra were obtained from a Waters ZQ 4000 mass spectrometer by the ESI method. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 UV-visible spectrophotometer. All the new complexes gave satisfactory CHN results.
3. Complexes of pyrazolyl ligands

3.3.1 Single-crystal X-ray structures analyses

Crystals suitable for X-ray diffraction study for complexes [1]PF₆, [3]PF₆, [10]PF₆ and [11]ClO₄ were grown by slow diffusion of diethylether into dichloromethane solution of the respective complexes. For the ligand L₃, crystals were grown by slow evaporation of chloroform solution of L₃. The intensity data of the white crystal of L₃, the bright orange crystal of [1]PF₆, the red color crystal of [10]PF₆ and the yellow crystals of compound [3]PF₆ and [11]ClO₄ were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoKα radiation (λ = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with the SAINT and XPREP software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS. Structures were solved by direct methods using SHELXS-97 [20] and refined with full-matrix least squares on F² using SHELXL-97 [21]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [22] for Windows. The ORTEP presentations of the representative complexes are shown in Figures 3.5 to 3.9 respectively. The bond lengths and angles and data collection parameters are presented in Tables 3.2 and 3.3.


3.3.2.1 Synthesis of [(η⁶- p-cymene)Ru(µ-Cl)Ll]Cl/PF₆ ([1]PF₆)

A mixture of [(η⁶- p-cymene)Ru(µ-Cl)Cl]₂ (50 mg, 0.08 mmol), Cl-L₁ (28 mg, 0.16 mmol) and 2.5 equivalents of NH₄PF₆ in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a color change from light red to deep red. The solvents were removed using a rotary evaporator under reduced pressure, the residue dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 69 mg, 70.9%
Elemental Anal (%) Calc. for C_{17}H_{19}N_{4}RuCl_{2}PF_{6}: C 34.24; H 3.21; N 9.40; found: C 33.92; H 3.33; N 9.49

$^1$H NMR (400MHz, CDCl₃, 25 °C, TMS): δ = 8.02 (d, $^3$J_{H,H} = 9.6 Hz, 2H), 7.85 (d, $^3$J_{H,H} = 9.6 Hz, 2H), 6.39 (t, $^3$J_{H,H} = 8.0 Hz, 1H), 5.90 (d, $^3$J_{H,H} = 6.4 Hz, 1H, Ar_{p-cy}), 5.84 (d, $^3$J_{H,H} = 6.4 Hz, 1H, Ar_{p-cy}), 5.76 (d, $^3$J_{H,H} = 6.0 Hz, 1H, Ar_{p-cy}), 5.69 (d, $^3$J_{H,H} = 6.0 Hz, 1H, Ar_{p-cy}), 2.99 (sep, $^3$J_{H,H} = 6.8 Hz, 1H), 2.19 (s, 3H), 1.32 (d, $^3$J_{H,H} = 7.2 Hz, 3H), 1.29 (d, $^3$J_{H,H} = 6.8 Hz, 3H). ESI-MS (m/z): 451.2 [M- PF₆], 415.1 [M-PF₆-Cl].

3.3.2.2 Synthesis of [(η⁶-C₆H₆)Ru(Cl-L1)]ClPF₆ ([2]PF₆)

A mixture of [(η⁶-C₆H₆)Ru(µ-Cl)Cl]₂ (50 mg, 0.10 mmol), Cl-L1 (36 mg, 0.020 mmol) and 2.5 equivalents of NH₄PF₆ in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 65 mg, 60.2%

Elemental Anal (%) Calc. for C_{13}H_{11}N_{4}RuCl_{2}PF_{6}: C 28.90; H 2.05; N 10.37; found: C 29.05; H 1.98; N 10.55

$^1$H NMR (400MHz, CD₃CN, 25 °C, TMS): δ = 8.20 (d, $^3$J_{H,H} = 9.6 Hz, 2H), 7.91 (d, $^3$J_{H,H} = 9.6 Hz, 2H), 6.44 (t, $^3$J_{H,H} = 8.0 Hz, 1H), 6.12 (s, 6H, C₆H₆). ESI-MS (m/z): 395.1 [M- PF₆].

3.3.2.3 Synthesis of [(η⁶-p-cymene)Ru(Cl-L2)]ClPF₆ ([3]PF₆)

A mixture of [(η⁶-p-cymene)Ru(µ-Cl)Cl]₂ (50 mg, 0.08 mmol), Cl-L2 (34 mg, 0.16 mmol) and 2.5 equivalents of NH₄PF₆ in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvents were reduced using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 65 mg, 63.9%

Elemental Anal (%) Calc. for C_{19}H_{23}N_{4}RuCl_{2}PF_{6}: C 36.55; H 3.71; N 8.97; found: C 36.43; H 3.79; N 9.01
3. Complexes of pyrazolyl ligands

$^1$H NMR (400MHz, CDCl$_3$, 25 °C, TMS): δ = 8.05 (d, $^3$J$_{H,H}$ = 9.6 Hz, 1H), 7.85 (d, $^3$J$_{H,H}$ = 9.6 Hz, 1H), 6.40 (s, 1H), 5.96 (d, $^3$J$_{H,H}$ = 6.4 Hz, 1H, Arp-cy), 5.85 (d, $^3$J$_{H,H}$ = 6.4 Hz, 1H, Arp-cy), 5.80 (d, $^3$J$_{H,H}$ = 6.0 Hz, 1H, Arp-cy), 5.75 (d, $^3$J$_{H,H}$ = 6.0 Hz, 1H, Arp-cy), 2.91 (sep, $^3$J$_{H,H}$ = 6.8 Hz, 1H), 2.20 (s, 6H, CH$_3$), 2.1 (s, 3H), 1.35 (d, $^3$J$_{H,H}$ = 7.2 Hz, 3H), 1.29 (d, $^3$J$_{H,H}$ = 6.8 Hz, 3H).

ESI-MS (m/z): 479.2 [M- PF$_6$].

3.3.2.4 Synthesis of [(η$^6$-C$_6$H$_6$)Ru(Cl-L2)Cl]PF$_6$ ([4]PF$_6$)

A mixture of [(η$^6$-C$_6$H$_6$)Ru(µ-Cl)Cl]$_2$ (50 mg, 0.10 mmol), Cl-L2 (41 mg, 0.20 mmol) and 2.5 equivalents of NH$_4$PF$_6$ in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 67 mg, 59.0%.

Elemental Anal (%) Calc. for C$_{15}$H$_{15}$N$_4$RuCl$_2$PF$_6$: C 31.70; H 2.66; N 9.86; found: C 32.37; H 2.45; N 9.72.

$^1$H NMR (400 MHz, DMSO-d$_6$, 25 °C, TMS): δ = 8.44 (d, $^3$J$_{H,H}$ = 9.6 Hz, 1H), 8.22 (d, $^3$J$_{H,H}$ = 9.6 Hz, 1H), 6.53 (s, 1H), 6.04 (s, 6H, C$_6$H$_6$), 2.71 (s, 6H.CH$_3$).

ESI-MS (m/z): 422.7 [M-PF$_6$].

3.3.2.5 Synthesis of [(η$^6$-p-cymene)Ru(Cl-L3)Cl]PF$_6$ ([5]PF$_6$)

A mixture of [(η$^6$-p-cymene)Ru(µ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), Cl-L3 (31 mg, 0.16 mmol) and 2.5 equivalents of NH$_4$PF$_6$ in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 66 mg, 66.3%.

Elemental Anal (%) Calc. for C$_{18}$H$_{21}$N$_4$RuCl$_2$PF$_6$: C 35.42; H 3.47; N 9.18; found: C 35.61; H 3.11; N 9.34

$^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 8.58 (d, $^3$J$_{H,H}$ = 5.6 Hz, 1H), 8.32 (d, $^3$J$_{H,H}$ = 6.4 Hz, 1H), 8.21 (d, $^3$J$_{H,H}$ = 5.6 Hz, 1H), 7.92 (d, $^3$J$_{H,H}$ = 6.0 Hz, 1H), 6.12 (d, $^3$J$_{H,H}$ = 6.4 Hz,
3. Complexes of pyrazolyl ligands

1H, Arₚ-cy), 5.98 (d, 3Jₜtₜ = 6.4 Hz, 1H, Arₚ-cy), 5.86 (d, 3Jₜtₜ = 5.6 Hz, 1H, Arₚ-cy), 5.79 (d, 3Jₜtₜ = 5.6 Hz, 1H, Arₚ-cy), 3.22 (sep, 3Jₜtₜ = 6.8 Hz, 1H), 2.41 (s, 3H, CH₃), 2.31 (s, 3H), 1.53 (d, 3Jₜtₜ = 7.2 Hz, 3H), 1.49 (d, 3Jₜtₜ = 5.6 Hz, 3H). ESI-MS (m/z): 465.2 [M- PF₆], 430.1 [M- PF₆-Cl].

3.3.2.6 Synthesis of [(η⁶-C₆H₆)Ru(Cl-L3)Cl]PF₆ ([6]PF₆)

A mixture of [(η⁶-C₆H₆)Ru(µ-Cl)Cl] (50 mg, 0.10 mmol), Cl-L3 (39 mg, 0.20 mmol) and 2.5 equivalents of NH₄PF₆ in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 70 mg, 63.3%.

Elemental Anal (%) Calc. for C₁₄H₁₃N₄RuCl₂PF₆: C 30.34; H 2.36; N 10.11; found: C 29.97; H 2.55; N 10.32.

1H NMR (400 MHz, CD₃CN, 25 °C, TMS): δ = 8.52 (d, 3Jₜtₜ = 2.0 Hz, 1H), 8.39 (d, 3Jₜtₜ = 3.6 Hz, 1H), 8.19 (d, 3Jₜtₜ = 4.8 Hz, 1H), 7.98 (d, 3Jₜtₜ = 7.2 Hz, 1H), 6.25 (s, 6H, C₆H₆), 2.65 (s, 3H, CH₃). ESI-MS (m/z): 408.9 [M- PF₆].


3.3.3.1 Synthesis of [(η⁶-p-cymene)Ru(L1)Cl]PF₆ ([7]PF₆)

A mixture of [(η⁶-p-cymene)Ru(µ-Cl)Cl] (50 mg, 0.08 mmol), L1 (35 mg, 0.16 mmol) and 2.5 equivalents of NH₄PF₆ in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a light red to deep red color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 65 mg, 63.4%

Elemental Anal (%) Calc. for C₂₀H₂₂N₆RuClPF₆: C 38.26; H 3.53; N 13.38; found: C 37.92; H 3.77; N 12.95.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.61 (d, 3Jₜtₜ = 2.4 Hz, 1H), 8.59 (d, 3Jₜtₜ = 2.4 Hz, 1H), 8.55 (d, 3Jₜtₜ = 7.6 Hz, 1H), 8.23 (d, 3Jₜtₜ = 6.4 Hz, 1H), 7.90 (d, 3Jₜtₜ = 6.4 Hz,
3. Complexes of pyrazolyl ligands

1H), 7.72 (d, \(^3J_{HH} = 8.0 \text{ Hz}, 1\text{H}\)), 6.87 (t, \(^3J_{HH} = 6.0 \text{ Hz}, 1\text{H}\)), 6.48 (t, \(^3J_{HH} = 5.6 \text{ Hz}, 1\text{H}\)), 6.20 (d, \(^3J_{HH} = 6.4 \text{ Hz}, 1\text{H}, \text{Ar}_{p-cy}\)), 6.07 (d, \(^3J_{HH} = 6.4 \text{ Hz}, 1\text{H}, \text{Ar}_{p-cy}\)), 5.91 (d, \(^3J_{HH} = 6.0 \text{ Hz}, 1\text{H}, \text{Ar}_{p-cy}\)), 5.82 (d, \(^3J_{HH} = 6.0 \text{ Hz}, 1\text{H}, \text{Ar}_{p-cy}\)), 5.91 (d, \(^3J_{HH} = 6.0 \text{ Hz}, 1\text{H}, \text{Ar}_{p-cy}\)), 2.72 (sep, \(^3J_{HH} = 6.2 \text{ Hz}, 1\text{H}\)), 2.20 (s, 3H), 1.22 (d, \(^3J_{HH} = 7.2 \text{ Hz}, 3\text{H}\)), 1.18 (d, \(^3J_{HH} = 7.6 \text{ Hz}, 3\text{H}\)).

ESI-MS (m/z): 483.1 [M- PF\(_6\)].

3.3.3.2 Synthesis of [(η\(^6\)-C\(_6\)H\(_6\))Ru(L\(_1\))Cl\(_2\)]PF\(_6\) (8PF\(_6\))

A mixture of [(η\(^6\)-C\(_6\)H\(_6\))Ru(µ-Cl)Cl\(_2\)] (50 mg, 0.10 mmol), L\(_1\) (42 mg, 0.20 mmol) and 2.5 equivalents of NH\(_4\)PF\(_6\) in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 66 mg, 57.8%

Elemental Anal (%) Calc. for C\(_{16}\)H\(_{14}\)N\(_6\)RuClPF\(_6\): C 33.61; H 2.47; N 14.70; found: C 33.73; H 2.65; N 13.98.

\(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 8.72\) (d, \(^3J_{HH} = 2.4 \text{ Hz}, 1\text{H}\)), 8.63 (d, \(^3J_{HH} = 2.4 \text{ Hz}, 1\text{H}\)), 8.54 (d, \(^3J_{HH} = 7.6 \text{ Hz}, 1\text{H}\)), 8.44 (d, \(^3J_{HH} = 7.6 \text{ Hz}, 1\text{H}\)), 8.02 (d, \(^3J_{HH} = 6.4 \text{ Hz}, 1\text{H}\)), 7.91 (d, \(^3J_{HH} = 6.0 \text{ Hz}, 1\text{H}\)), 6.92 (t, \(^3J_{HH} = 8.0 \text{ Hz}, 1\text{H}\)), 6.53 (t, \(^3J_{HH} = 6.4 \text{ Hz}, 1\text{H}\)), 5.90 (s, 6H, C\(_6\)H\(_6\)).

ESI-MS (m/z): 427.2 [M- PF\(_6\)].

3.3.3.3 Synthesis of [(η\(^6\)-p-cymene)Ru(L\(_2\))Cl\(_2\)]PF\(_6\) (9PF\(_6\))

A mixture of [(η\(^6\)-p-cymene)Ru(µ-Cl)Cl\(_2\)] (50 mg, 0.08 mmol), L\(_2\) (43 mg, 0.16 mmol) and 2.5 equivalents of NH\(_4\)PF\(_6\) in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvent was reduced using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml) and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 67 mg, 65.6%

Elemental Anal (%) Calc. for C\(_{24}\)H\(_{30}\)N\(_6\)RuClPF\(_6\): C 46.06; H 4.83; N 13.43; found: C 46.73; H 4.25; N 13.07

\(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 8.36\) (d, \(^3J_{HH} = 9.6 \text{ Hz}, 1\text{H}\)), 8.11 (d, \(^3J_{HH} = 9.2 \text{ Hz}, 1\text{H}\)), 6.54 (s, 2H), 6.05 (d, \(^3J_{HH} = 6.0 \text{ Hz}, 1\text{H}, \text{Ar}_{p-cy}\)), 5.92 (d, \(^3J_{HH} = 6.4 \text{ Hz}, 1\text{H}, \text{Ar}_{p-}\).
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cy), 5.84 (d, \(3J_{H,H} = 6.4\) Hz, 1H, Ar-p-cy), 5.77 (d, \(3J_{H,H} = 6.4\) Hz, H, Ar-p-cy), 2.71 (s, 12H, CH3), 2.69 (sep, \(3J_{H,H} = 6.0\) Hz, 1H), 2.18 (s, 3H), 1.09 (d, \(3J_{H,H} = 7.2\) Hz, 3H), 1.06 (d, \(3J_{H,H} = 6.8\) Hz, H). ESI-MS (m/z): 538.8 [M- PF6].

3.3.3.4 Synthesis of \([(\eta^6-C_6H_6)Ru(L2)Cl]PF_6 ([10]PF_6)]

A mixture of \([(\eta^6-C_6H_6)Ru(\mu-Cl)Cl]_2 (50 mg, 0.10 mmol), L2 (53 mg, 0.20 mmol) and 2.5 equivalents of NaPF_6 in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethylether and dried under vacuum.

Yield: 64 mg, 56.3%.

Elemental Anal (%): Calc. for C_{20}H_{22}N_{6}RuClPF_6: C 42.16; H 3.89; N 14.75; found: C 41.90; H 4.05; N 14.33.

\(^1\)H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): \(\delta = 8.50\) (d, \(3J_{H,H} = 9.6\) Hz, H), 8.48 (d, \(3J_{H,H} = 9.6\) Hz, 1H), 7.76 (s, 2H), 5.87 (s, 6H, C_6H_6), 2.78 (s, 12H, CH3).

ESI-MS (m/z): 483.3 [M- PF_6].

3.3.3.5 Synthesis of \([(\eta^6-p-cymene)Ru(L3)Cl]ClO_4 ([11]ClO_4)]

A mixture of \([(\eta^6-p-cymene)Ru(\mu-Cl)Cl]_2 (50 mg, 0.08 mmol), L3 (39 mg, 0.16 mmol) and 2.5 equivalents of NaClO_4 in 15 ml of dry methanol was stirred at room temperature for 4 hours producing a red to yellow color change. The solvents were removed using a rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml), and the solution was filtered to remove ammonium chloride. The solution was concentrated to 5 ml, when addition of excess diethylether gave the yellow complex, which was separated and dried under vacuum.

Yield: 73 mg, 73.4%.

Elemental Anal (%): Calc. for C_{22}H_{26}N_{6}RuCl_2O_4: C 43.28; H 4.29; N 13.77; found: C 43.78; H 3.94; N 13.92

\(^1\)H NMR (400 MHz, CDCl_3, 25 °C, TMS): \(\delta = 8.53\) (d, \(3J_{H,H} = 10.0\) Hz, 1H), 8.45 (d, \(3J_{H,H} = 2.4\) Hz, 1H), 8.27 (s, 1H), 8.19 (d, \(3J_{H,H} = 9.6\) Hz, H), 6.44 (d, \(3J_{H,H} = 3.9\) Hz, 1H), 6.34 (d, \(3J_{H,H} = 2.4\) Hz, 1H), 5.93 (d, \(3J_{H,H} = 6.0\) Hz, 1H, Ar-p-cy), 5.87 (d, \(3J_{H,H} = 6.4\) Hz, 1H, Ar-p-cy), 5.76 (d, \(3J_{H,H} = 6.0\) Hz, 1H, Ar-p-cy), 5.68 (d, \(3J_{H,H} = 6.0\) Hz, 1H, Ar-p-cy), 5.31 (sep, \(3J_{H,H} = 6.8\) Hz, H).
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3.3.3.6 Synthesis of [(η⁶-C₆H₆)Ru(L3)Cl]PF₆ ([I2]PF₆)

A mixture of [(η⁶-C₆H₆)Ru(µ-Cl)Cl]₂ (50 mg, 0.10 mmol), L3 (48 mg, 0.20 mmol) and 2.5 equivalents of NH₄PF₆ in 15 ml of dry methanol was stirred at room temperature for 4 hours. The brown compound which formed was filtered, washed with methanol and diethyl ether and dried under vacuum.

Yield: 56 mg, 51.78%.

Elemental Anal (%): Calcd. for C₁₈H₁₆N₆RuClPF₆: C 39.91; H 3.35; N 15.51; found: C 40.22; H 3.08; N 14.92

¹H NMR (400 MHz, CD₃CN, 25 °C, TMS): δ = 8.53 (d, ³Jₓₓₓ,H = 9.6 Hz, 1H), 8.46 (d, ³Jₓₓₓ,H = 10.4 Hz, H), 8.42 (s, 1H), 8.31 (d, ³Jₓₓₓ,H = 9.6 Hz, 1H), 8.21 (d, ³Jₓₓₓ,H = 9.6 Hz, H), 6.76 (d, ³Jₓₓₓ,H = 2.8 Hz, 1H), 6.09 (s, 6H, C₆H₆), 2.76 (s, 6H, CH₃). ESI-MS (m/z): 455.2 [M- PF₆], 419.2 [M-PF₆-Cl].

3.4 Results and Discussion

3.4.1 Pyrazolyl pyridazine ligands

The ligands were synthesized by a known procedure [16] involving the condensation of 3,6-dichloropyridazine with substituted pyrazoles by refluxing in THF for around 8 hours. These starting materials in 1:1 ratio yielded one-side condensation products viz. pyrazolylchloropyridazines, while in 1:2 ratios they yielded both-side condensation products such as bis-pyrazolylpyridazines. In the case of both-side condensation, a small fraction of the one-side condensed product is also formed which is easily separated. An interesting phenomenon observed here is that, in the preparation of the ligand 3,6-bis(3-methylpyrazolyl)pyridazine (L3), a 1:1 mixture of two isomers, viz., 3,6-bis(3-methylpyrazolyl)pyridazine and 6-(3-methylpyrazolyl)-3-(5-methylpyrazolyl) -pyridazine is formed. The presence of both isomers was confirmed by ¹³C NMR spectroscopy. Apparently the starting 3-methylpyrazole under the reaction conditions undergoes tautomerization as shown in Scheme 3.1.
3. Complexes of pyrazolyl ligands

The existence of the two annular tautomers is reported herein. The numbering of the pyrazole carbons depends on the concerned tautomer, since the protonated nitrogen (N-H) is always N1. In the tautomer A (Scheme 3.1) [23], C3 is the carbon bearing the methyl substituent, while in B it is C5. The isomer ratios are determined tentatively by taking the $^{13}$C NMR spectrum of a concentrated solution of the synthesized ligand (L3) in CDCl$_3$ (see Figure 3.1). The isomers are not easily separable by TLC or column chromatography. Crystallization yielded single crystals of the 3,3-isomer of the pyrazolyl pyridazine ligand (L3) whose crystal structure is presented herein. However, after metallation, the presence of both the 3,3- and 3,5-pyrazolyl pyridazine tautomers is confirmed from the combination of single crystal X-ray structure of the complex [11]ClO$_4$, as well as from the $^{13}$C NMR spectrum of the ligand and the complex. We were able to isolate single crystals of the 3,3 isomer of the ligand and of the complex containing the 3,5-isomer of the ligand, indicating both isomers exist in the pure ligand as well as in the complex. The $^{13}$C NMR spectrum of the ligand in CDCl$_3$ reveals that the signal at 13.8 ppm corresponds to 3-methylpyrazole ($\approx$50%), whereas the signal at 14.8 ppm is for 5-methylpyrazole ($\approx$50%) (Figure 3.1). Although the formation of another isomer, viz., 3,6-bis(5-methylpyrazolyl)-pyridazine is also hypothetically possible (C in Scheme 3.1), its formation here was not observed from these NMR studies.
3. Complexes of pyrazolyl ligands

3.4.2 Arene ruthenium complexes

The dinuclear arene ruthenium complexes \([(\eta^6\text{-arene})\text{Ru}(\mu-\text{Cl})\text{Cl} )_2\] (arene = C₆H₆, p-cymene) reacted in methanol with the ligands (Cl-L1), (Cl-L2), (Cl-L3), L1, L2 and L3 to give the mononuclear cationic complexes \([(\eta^6\text{-p-cymene})\text{Ru}(\text{L})\text{Cl} )^+\] \((L = \text{Cl-L1 ([1]PF₆ ); Cl-L2 ([3]PF₆ ); Cl-L3 ([5]PF₆ ); L1 ([7]PF₆ ); L2 ([9]PF₆ ); L3 ([11]ClO₄ ); Cl-L1 ([2]PF₆ ); Cl-L2 ([4]PF₆ ); Cl-L3 ([6]PF₆ ); L1 ([8]PF₆ ); L2 ([10]PF₆ ); L3 ([12]PF₆ ))\) (Schemes 3.2 and 3.3). The cationic ruthenium complexes ([1]PF₆ ) to ([10]PF₆ ) and ([12]PF₆ ) are obtained as their hexafluorophosphate salts, while complex ([11]ClO₄ ) is obtained as its perchlorate salt.

soluble in acetonitrile and partially soluble in dichloromethane, chloroform, methanol and acetone.

The infrared spectra of these complexes exhibit a strong $\nu_{C=N}$ band in the range of 1543 to 1583 cm$^{-1}$ and a $\nu_{C=C}$ band in the range of 1437 to 1450 cm$^{-1}$ which are the characteristic bands of the ligands. Besides these, the complexes ([1]PF$_6$ to [10]PF$_6$ and [12]PF$_6$) also exhibit a strong band at around 836-845 cm$^{-1}$ due to the stretching $\nu_{P-F}$ mode of the counter ion of these complexes. However, in the case of the complex [11]ClO$_4$, a strong absorption at 1100 cm$^{-1}$ is observed due to the perchlorate ion [24]. The $m/z$ values of all these complexes and their stable ion peaks obtained from the ZQ mass spectra, as listed in the experimental section, are in good agreement with the theoretically expected values.
3. Complexes of pyrazolyl ligands

3.4.3 NMR spectroscopy

The $^1$H NMR spectra of the $p$-cymene and benzene derivatives which have Cl-L1, Cl-L2, Cl-L3, L1, L2 and L3 as ligands exhibit three resonances in the region $\delta = 8.02-6.39$ for Cl-L1 ([1]PF$_6$, [2]PF$_6$), three resonances in the region $\delta = 8.05-6.40$ for Cl-L2 ([3]PF$_6$, [4]PF$_6$), four resonances in the region $\delta = 8.58-7.92$ for Cl-L3 ([5]PF$_6$, [6]PF$_6$), eight resonances at around $\delta = 8.72-6.48$ for L1 ([7]PF$_6$, [8]PF$_6$), three resonances at around $\delta = 8.50-6.54$ for L2 ([9]PF$_6$, [10]PF$_6$) and six resonances in the region $\delta = 8.53-6.34$ for L3 ([11]ClO$_4$, [12]PF$_6$) in the aromatic region corresponding to the pyrazole and pyridazine protons which are clearly assigned as shown later. Besides these, all ligands other than Cl-L1 and L1 show a singlet in the region $\delta = 2.70 - 2.20$ which corresponds to the methyl protons of these ligands.
The $^{13}$C NMR spectrum of the complex [11]ClO$_4$ (Figure 3.3) indicates a mixture of the two tautomers of the ligand. We were unable to separate these isomers. However, we were able to provide assignments of the resonances for both isomers. Crystallization yields the tautomer of the 3,5 complex (see molecular structure). The peaks assigned at around 13.6 and 14.3 ppm correspond respectively to the methyl carbons of the 3,3-isomer and of the 3,5-isomer of the ligand, which are also in accordance with the methyl peaks of the isomers as shown in $^{13}$C NMR spectrum of the free ligands (Figure 3.1). This also confirms the presence of both the tautomers in the complex as well.

![Figure 3.2: Mass spectra of complexes 11 and 12](image-url)
3. Complexes of pyrazolyl ligands

Figure 3.3: $^{13}$C NMR spectrum of the complex mixture of 3,3 and 3,5 [11]ClO$_4$ in CDCl$_3$+CD$_3$CN.

In addition to these signals, complexes [2]PF$_6$, [4]PF$_6$, [6]PF$_6$, [8]PF$_6$, [10]PF$_6$, [12]PF$_6$ exhibit a singlet for the benzene ring protons at $\delta = 6.25$–6.04. The complexes [1]PF$_6$, [3]PF$_6$, [5]PF$_6$, [7]PF$_6$, [9]PF$_6$ and [11]ClO$_4$ exhibit an unusual pattern of resonances for the $p$-cymene ligand. For instance, the methyl protons of the isopropyl group display two doublets at ca. $\delta = 1.53$–1.08 instead of one doublet as in the starting precursor. The aromatic protons of the $p$-cymene ligand for these complexes also display four doublets at ca. $\delta = 6.20$–5.68, instead of two doublets as in the starting precursor. This pattern is due to the diastereotopic nature of the methyl protons of the isopropyl group and the aromatic protons of the $p$-cymene ligand. It may also be attributed to the behavior of the ruthenium atom which is stereogenic when coordinated with four different ligand atoms [25]. In other words we can say the different signals are entirely due to the chiral nature of the metal [26, 27].

3.5 UV-visible spectroscopy

of representative complexes are depicted in Figure 3.4. The low spin $d^6$ configuration of these mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II) centers which can interact with the low lying $\pi^*$ orbital of the ligands. One should therefore expect a band attributable to the metal-to-ligand charge transfer (MLCT) $t_{2g} \rightarrow \pi^*$ transition in their electronic spectra [28-33]. The electronic spectra of these complexes display a medium intensity band in the UV-visible region. The lowest energy absorption bands in the electronic spectra of these complexes in the visible region ~ 420–410 and ~ 368–335 nm have been tentatively assigned on the basis of their intensity and position to $\pi \rightarrow \pi^*$ MLCT transitions. The bands on the high energy side at ~ 305–292 nm for the complexes [2]PF$_6$, [3]PF$_6$, [9]PF$_6$, [11]ClO$_4$ and [12]PF$_6$, have been assigned to ligand-centered $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions [34, 35]. In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based $\pi \rightarrow \pi^*$ transition for pyrazolyl pyridazine ligands in the UV region and metal-to-ligand charge transfer transitions in the visible region.

Table 3.1: UV-Vis absorption data in acetonitrile at 298 K

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<td>412(0.14)</td>
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<tr>
<td>[2]PF$_6$</td>
<td>302(0.20)</td>
<td>340(0.07) 410(0.04)</td>
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<tr>
<td>[3]PF$_6$</td>
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<td>365(0.17) 420(0.14)</td>
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<td>415(0.06)</td>
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<td>[9]PF$_6$</td>
<td>305(0.90)</td>
<td>368(0.14) 418(0.07)</td>
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<tr>
<td>[11]ClO$_4$</td>
<td>293(0.99)</td>
<td>366(0.05) 413(0.04)</td>
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<td>[12]PF$_6$</td>
<td>302(0.46)</td>
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3.6 Molecular structures

The crystal structures of the ligand L3 and the complexes [1]PF₆, [3]PF₆, [10]PF₆ and [11]ClO₄ are shown in Figures 3.5 to 3.9 respectively. Selected inter-atomic distances and angles are listed in Table 3.2. The overall geometry of all these structures [except L3] corresponds to the characteristic piano-stool configuration. For all these compounds, the aromatic ring is planar as observed in related structures [36, 37]. The aromatic C-H bonds are bent umbrella-like towards the metal. We also observe a significant alternation in the aromatic C-C distances. The N1-Ru bond length in complex [11]ClO₄ is shorter by 0.029 Å than the N1-Ru average bond distance in complexes [1]PF₆ and [3]PF₆. The Ru-Cl bond distance of all these complexes are almost similar to those of other Ru-Cl complexes reported [38-46]. The N-N bond distances in all the complexes and in the ligand are comparable to each other, i.e., not much variation is observed. The average P-F bond distance is 1.553(4) Å. The average metal-centroid distance is 1.685 Å, which appears to be close to the average distance of 1.69 Å in other Ru(II)-Cl complexes [47].
Figure 3.5: Molecular structure of the ligand L3 with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Figure 3.6: Molecular structure of complex [(η⁶-C₁₀H₁₄)Ru(Cl-L1)Cl]PF₆ [I]PF₆ with 50% probability thermal ellipsoids.
Values of the angle N1-Ru-N3 in the p-cymene complexes [3]PF₆, [10]PF₆ and [11]ClO₄ are respectively 75.38(14), 75.50(9) and 75.9(2)°, while in the benzene complex [1]PF₆ the value is 76.09(14)°, larger than for the p-cymene complexes. In contrast, the angle Ru-N(1)-N(2) for the benzene complex [1]PF₆ is smaller than for the p-cymene complexes [3]PF₆, [10]PF₆ and [11]ClO₄. The p-cymene hydrogens and the pyrazole hydrogen of one molecule and the pyrazole hydrogens of another molecule are involved in an intermolecular C-H...O interaction with oxygen atoms of the ClO₄ counter ion (Figure 3.10). The matrices for these interactions are as follows: H1....O2 (2.503 Å), H4A....O4 (2.594 Å), H22A....O2 (2.705 Å), and \(\angle H1-O2-H22A \) (76.25°).
3. Complexes of pyrazoly ligands

Figure 3.8: Molecular structure of complex \([\eta^6-\text{C}_{6}\text{H}_{6}]\text{Ru(1,2)Cl}]\text{PF}_6 [10]\text{PF}_6 \) with 50% probability thermal ellipsoids.

Figure 3.9: Molecular structure of complex \([\eta^6-\text{C}_{10}\text{H}_{14}]\text{Ru(3)Cl}]\text{ClO}_4 [11]\text{ClO}_4 \) with 50% probability thermal ellipsoids.
3. Complexes of pyrazolyl ligands

Figure 3.10: Diagram showing hydrogen bonding between two adjacent molecular units in [11]ClO₄.

3.7 Conclusion

In summary, a series of η⁶-arene ruthenium pyrazolyl pyridazine complexes which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. The titled complexes represent a new structural moiety related to the existence of two tautomers in the same compound which are not easily separable by TLC or column chromatography but are easily confirmed by ¹³C NMR and single crystal X ray diffraction studies.

Supplementary material

CCDC- 710387 (L3), 710388 [1](PF₆), 710389 [3](PF₆), 710390 [10](PF₆) and 710391 [11](ClO₄) contain the supplementary crystallographic data for this chapter.

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3. Complexes of pyrazolyl ligands

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3. Complexes of pyrazoyl ligands

References

3. Complexes of pyrazolyl ligands

3. Complexes of pyrazolyl ligands


