Supporting Information

Substituted Pyridazines As Ligands In Homoleptic (fac and mer) and Heteroleptic Ru(II) Complexes

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Experimental Details

Unless otherwise stated all reactions were carried out in air. Solvents were dried as required according to standard techniques. Flash chromatography was performed using silica gel or activated alumina (Aldrich Chemicals) as the stationary phase. All chemicals were purchased from Aldrich Chemical Co. Ltd. and were used without further purification unless otherwise stated. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer. Nuclear magnetic resonance spectra were recorded in deuterated acetonitrile or chloroform on a Bruker Avance DPX-600 MHz, AV-400 MHz, or AV-600 MHz spectrometers, the signals referenced to a TMS standard. UV-vis absorption spectra were recorded on a Shimadzu UV-2401PC UV-Vis recording spectrometer. The emission spectra were not corrected and were recorded at room temperature on a Varian Fluorescence Cary Eclipse spectrophotometer. IR spectra were obtained using a Perkin Elmer Diffuse Reflectance spectrometer in solid form in a KBr mixture. Elemental analyses were carried out using a Carlo Erba 1006 automatic analyser. Melting points are given uncorrected and were on a Griffin melting point apparatus. Single crystal analyses were carried out on a Brüker SMART APEX CCD diffractometer using graphite monochromised Mo-Kα (λ = 0.71073Å) radiation at the temperatures given following data. Data reduction was performed using SAINT. Intensities were corrected for Lorentz and polarization effects and for absorption by SADABS. The structures were solved by direct methods using SHELXS and refined on F^{2} using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons.

Note: The following abbreviations are used to distinguish resonances in NMR analyses. Py = pyridine, ph = phenyl, pz = pyridazine, pm = pyrimidine, pr = pyrazine, bpy = bipyridine, C^{4} = quaternary carbon, s = singlet, d = doublet, t = triplet, Ψt = pseudo triplet (unresolved dd).

3,4,6-tri (2-pyridyl) pyridazine (1a)

The reaction was carried out in air by adding a 2.5% methanolic solution of KOH (1 mL) to a THF solution (5 mL) containing bptz (0.50 g, 2.116 mmol) and 2-acetyl pyridine (400 μL, 3.567 mmol) at 40°C. The mixture was stirred for 5 mins, allowed to cool, washed with water, and extracted into dichloromethane. The solvent was then reduced under vacuum, and the resulting mixture was run through a silica column (10% methanol in ethyl acetate) to give the product (0.530 g, 1.702 mmol). This was further purified by recrystallisation from a mixture of ethyl acetate and petroleum ether (yield 80%).

IR (KBr): vbar 3081m, 3066m, 3004m, 1578s, 1546s, 1482s, 1466s, 1460s, 1419m, 1366s, 1242s, 1192s, 1165s, 1129s, 1050m, 993s, 757m, 701m, 697s.

H NMR: (400 MHz, CDCl_{3}): δ 8.82 (s, 1H, H^{A}), 8.75 (d, 1H, H^{B} J = 8.0 Hz ), 8.69 (d, 1H, H^{D} J = 4.5 Hz), 8.51 (d, 1H, H^{B'}, J = 4.5 Hz), 8.31 (d, 1H, H^{C}, J = 4.5 Hz), 8.13 (d, 1H, H^{B''} J = 8.0 Hz), 7.88 (Ψtd, 1H, H^{B''}, J = 3.5, 1.5 Hz ), 7.82 (Ψtd, 1H, H^{D}, J = 7.5, 1.5 Hz ), 7.63 (Ψtd, 1H, H^{A}, J = 7.5, 1.5 Hz), 7.36 (m, 1H, H^{C}, J = 8.0 Hz ), 7.22 ppm (m, 2H, H^{B', B''}).

^{13}C NMR (100 MHz, CDCl_{3}): δ 157.7 (C^{D1}), 157.5 (C^{D2}), 155.3 (C^{B'}, 155.1 (C^{B}), 152.8 (C^{A}), 149.0 (C^{A}), 141.8 (C^{C}), 138.9 (C^{B}), 136.8 (C^{B'}, 136.4 (C^{A}), 135.8 (C^{C}), 125.3 (C^{A}), 124.4 (C^{A}), 124.2 (C^{C}), 123.6 (C^{C}), 123.0 (C^{B}), 122.4 (C^{C}), 121.4 ppm (C^{C}).

HRMS: (CH_{3}CN): calculated [MH]^{+} m/z 312.1250, found: 312.1252

Anal. Calcd. for C_{18}H_{14}N_{5}: C 73.30, H 4.21; N 22.49. Found: C 72.87, H 4.32, N 22.33. m.p. 165°-166°C.

Synthesis of 3,6-di-(2-pyridyl) 4-pyrimidyl pyridazine (2a)

The reaction was carried out in air by refluxing bptz (0.102 g, 0.433 mmol) and 5-ethynylpyrimidine (0.047 g, 0.451 mmol) in toluene (2.5 mL) for 24 hrs. The solvent was removed by rotary evaporation, and the reaction mixture purified on a silica column (ethyl acetate, 20% methanol). The product was recovered as a light yellow solid (0.087 g, 0.279 mmol, 65%).
I.R. vbar 3093m, 3065m, 3039m, 3022m, 1582s, 1571s, 1555s, 1477s, 1419s, 1393s, 991s, 793s, 773s, 724m, 656m, 629m, 620m, 588w, 531w cm⁻³.

1H NMR (400 MHz, CDCl3): δ 9.21 (s, 1H, H15), 8.81 (d, 1H, H6, J = 8.0 Hz), 8.73 (d, 1H, H5, J = 4.0 Hz), 8.68 (s, 2H, H8, 8.67 (s, 1H, H13), 8.36 (d, 1H, H9, J = 4.5 Hz), 8.32 (d, 1H, H1, J = 8.0 Hz), 7.94 (ψtotal, 1H, H8, J = 8.0, 2.0 Hz), 7.90 (ψtotal, 1H, H4, J = 6.5 Hz), 7.70 (dd, 1H, H5, J = 7.5, 5.0, 1.0 Hz), 7.31 ppm (dd, 1H, H1, J = 7.5, 5.0, 1.0 Hz).

13C NMR (100 MHz, CDCl3): δ 157.9 (C10), 157.7 (C14), 157.1 (C1), 156.0 (C8, 8'), 154.2 (C5), 152.5 (C7), 149.5 (C6), 148.7 (C4), 137.3 (C3), 137.2 (C6), 134.1 (C13), 132.0 (C2), 126.0 (C15), 125.2 (C5), 124.7 (C3), 124.2 (C4), 121.8 ppm (C3).

HRMS: (CH2CN): calculated [MHI⁺] m/z 355.1021, found: 355.1081

Anal. Calc. For C18H12N2; C, 69.22; H, 3.87; N, 26.91. Found: C, 68.93; H, 3.85; N, 26.71. m.p. 170º-172ºC.

3.6-di(2-pyridyl)-4,5-diphenyl pyridazine (3a)

Bptz (0.600 g, 2.540 mmol) and trans-stilbene (0.469 g, 2.600 mmol) were refluxed in toluene (20 mL) for 24 hrs. The colour of the solution changed from dark pink to a bright yellow. The solvent was removed in vacuo, and the reaction mixture was run through a silica column (10% diethyl ether in dichloromethane) to furnish the product as a light yellow solid (0.9370 g, 2.210 mmol, 95%).

1H NMR (400 MHz, CDCl3): δ 9.43 (s, 1H, H15), 8.67 (d, 1H, H6, J = 3.8 Hz), 8.61 (d, 1H, H5, J = 4.4 Hz), 8.10 (d, 1H, H4, J = 7.9 Hz), 7.63 (ψtotal, 1H, H8, J = 7.8, 1.8 Hz), 7.57 (ψtotal, 1H, H13, J = 7.8, 1.5 Hz), 7.30-7.17 (m, 11H, H1, H5, 5', 5', 9', 10, 9', 10', 6', 6', 6').

13C NMR (100 MHz, CDCl3): δ 154.2 (C11), 151.6 (C14), 149.0 (C6), 148.3 (C5), 141.9 (C0), 138.9 (C0), 136.1 (C4), 135.9 (C3), 135.1 (C9), 129.9 (2C0), 128.5 (2C), 128.3 (4C), 128.3 (1C), 127.2 (1C), 126.7 (1C), 125.5 (1C), 123.0 (1C), 122.7 (1C), 121.5 (1C), 108.2 (C13), 41.5 ppm (C13).

HRMS: (CH2CN): calculated [MHI⁺] m/z 389.1766, found: 389.1782.


3.6-di(2-pyridyl)-4,5-diphenyl pyridazine

A solution of NaNO₂ (6 M, 20 mL) was added dropwise to a concentrated HCl (12 mL). The gas evolved was passed through a dichloromethane solution (40 mL) of 3.6-di(2-pyridyl)-4,5-diphenyl-1,4-dihydropyridazine which was maintained at 0ºC until all the sodium nitrite had been added. The dihydropyridazine solution was then allowed to return to room temperature, with constant N₂ bubbling to remove excess nitrous gas. The solvent was removed under vacuum and the reaction mixture dissolved in water and neutralized by the addition of 10% ammonia solution. The mixture was extracted into CH₂Cl₂, dried over MgSO₄ and purified using a silica column (10% methanol in ethyl acetate). The product was recovered as a white solid (0.598 g, 1.6 mmol, 74%).

I.R. vbar 3078m, 3054m, 3024m, 3003m, 1587s, 1569s, 1474s, 1377s, 1155s, 991s, 793s, 782s, 771s, 746s, 636s, 624s, 531m, 486m cm⁻³.

1H-NMR (400 MHz, CH₃CN): δ 8.42 (d, 2H, H8, J = 4.5 Hz), 7.64 (m, 4H, H3, 4) 7.17 (ψtotal, 2H, H4, J = 6.5, 1.5 Hz), 7.05 (m, 6H, H6, H8, 8'), 6.87 ppm (m, 2H, H9).

13C NMR (100 MHz, CDCl3): δ 158.5 (C11), 155.6 (C5), 148.4 (C6), 138.7 (C13), 135.7 (C4), 134.2 (C7), 129.7 (C0), 127.1 (C6), 126.9 (C10), 124.6 (C4), 122.5 ppm (C5).

HRMS: (CH₂CN): calculated [MHI⁺] m/z 387.1596 found: 387.1610.

Anal. Calc. For C26H14N2: C, 80.81; H, 4.69; N, 14.50. Found: C, 79.92; H, 4.64; N, 14.26. m.p. 190º-191 ºC.

3.6-di(2-pyridyl)-4,5-di(4-pyridyl) pyridazine (4a)

Bptz (0.500 g, 2.116 mmol) and (E)-1,2-di(4'-pyridyl)ethene (0.410 g 2.251 mmol) were added to toluene (10 mL) and heated in a sealed tube at 180ºC for 24 hrs. The solvent was removed in vacuo and the reaction mixture purified on a silica column (20% methanol in diethyl ether). The product was isolated as a bright yellow solid (0.619 g, 1.6 mmol, 75%).
1H-NMR (400 MHz, CDCl3): δ 9.50 (s, 1H, H6), 8.72 (d, 1H, H6, J = 5.0 Hz), 8.61 (d, 1H, H6, J = 6.0 Hz), 8.50 (d, 2H, H18, J = 6.5 Hz), 8.41 (d, 2H, H18, J = 6.0 Hz), 8.13 (d, 1H, H7, J = 8.0 Hz), 7.66 (Ψtd, 1H, H6, J = 7.8, 1.5 Hz), 7.55 (Ψtd, 1H, H7, J = 7.5, 1.5 Hz), 7.46 (d, 2H, H18, J = 6.0 Hz), 7.36 (d, 1H, H6, J = 6.0 Hz), 7.32 (d, 1H, H5, J = 2.0 Hz), 7.22 (m, 1H, H5, J = 2.0 Hz), 7.06 (d, 2H, H5, J = 6.0 Hz), 5.86 ppm (s, 1H, H18).

13C NMR (100 MHz, CDCl3): δ 153.4 (C2), 150.8 (C2), 150.1 (C9,9'), 150.0 (C9,9'), 150.0 (C6), 148.4 (C6), 146.3 (C7), 140.7 (C10), 138.7 (C13), 136.5 (C6), 136.2 (C5), 125.6 (C1), 124.1 (C1), 123.9 (C8,8'), 123.3 (C5), 123.1 (C8,8'), 121.5 (C3), 102.5 (C11), 39.5 ppm (C7).

HRMS: (CH3CN); calculated for C24H18N6; [MH]+ m/z 391.1671 found: 391.1667.

Anal. Calc. For C24H18N6; C: 73.83; H: 4.65; N: 21.52. Found: C: 73.85; H: 4.70; N: 20.93

3.6- di(2-pyridyl)-4,5-di(4-pyridyl) pyridazine

The same procedure was used as for 3a. Purification was carried out using column chromatography (SiO2, 50% ether, 50% methanol). The product was recovered as a white solid (0.308 g, 50 % yield).

I.R. vbar 3059m, 3039m, 3027m, 1596s, 1584s, 1568s, 1408s, 1382s, 1274s, 1218m, 991s, 813s, 808s, 796s, 786s, 750s, 648s, 624s, 538m, 489w cm⁻¹.

1H-NMR (400 MHz, CDCl3): δ 8.34 (d, 2H, H6, J = 5.5 Hz), 8.30 (d, 2H, H6, J = 4.5 Hz), 8.01 (d, 2H, H1, J = 7.6 Hz), 7.81 (Ψtd, 2H, H2, J = 7.5, 1.5 Hz), 7.23 (m, 2H, H5), 6.85 ppm (d, 2H, H8, J = 6.0 Hz).

13C NMR (100 MHz, CDCl3): δ 157.0 (C10), 154.2 (C2), 148.7 (C6), 148.3 (C6), 142.6 (C1), 136.3 (C4), 136.1 (C11), 124.5 (C1), 124.1 (C8), 123.2 ppm (C5).

HRMS: (CH3CN); calculated: [MH]+ m/z 387.1504 found: 387.1515.

Anal. Calcd. For C24H18N6: C, 74.21; H, 4.15; N, 21.64. Found: C, 75.23; H, 4.60; N, 20.88. m.p. 119 - 221 °C

3.6-di(2-pyridyl)-4,5-di-(3,5-dimethoxyphenyl)pyridazine (5a)

3.6-di(2-pyridyl)-4,5-di-(3,5-dimethoxyphenyl)-4,4-dihydropyridazine

The same procedure was used as for 3a, Purification was carried out using column chromatography (SiO2, 50% ether, 50% methanol). The product was recovered as a white solid (0.308 g, 50 % yield).

I.R. vbar 3059m, 3039m, 3027m, 1596s, 1584s, 1568s, 1408s, 1382s, 1274s, 1218m, 991s, 813s, 808s, 796s, 786s, 750s, 648s, 624s, 538m, 489w cm⁻¹.

1H-NMR (400 MHz, CDCl3): δ 9.37 (s, 1H, H15), 8.64 (d, 1H, H6, J =5.0 Hz), 8.60 (d, 1H, H6, J = 4.5 Hz), 8.16 (d, 1H, H7, J = 8.0 Hz), 7.61 (Ψtd, 1H, H6, J = 7.5, 1.8 Hz), 7.47 (Ψtd, 1H, H6, J = 7.5, 1.5 Hz), 7.37 (d, 1H, H13, J = 8.0 Hz), 7.18 (m, 2H, H5, J = 2.0 Hz), 6.80 (d, 2H, H8, J = 2.0 Hz), 6.41 (d, 2H, H8, J = 2.0 Hz), 6.35 ppm (s, 6H, H8, J =2.0 Hz).

13C NMR (100 MHz, CDCl3): 160.3 (C6), 159.9 (C6), 154.2 (C5), 151.5 (C1), 148.5 (C6), 147.8 (C6), 144.2 (C5), 140.9 (C5), 140.8 (C5), 135.4 (C5), 135.5 (C5), 125.2 (C3,3'), 122.6 (C5,5'), 122.2 (C5,5'), 121.0 (C3,3'), 107.7 (C5), 107.5 (C8,8'), 106.3 (C8,8'), 99.2 (C10,10'), 98.1 (C10,10'), 54.7 (-OMe), 54.7 (-OMe), 44.1 ppm (C12).

HRMS: (CH3CN); calculated for C30H23NO2; [MH]+ m/z 509.2189 found: 509.2211.

Anal. Calc. For C30H23NO2; C: 70.85; H: 5.55; N: 11.02. Found: C: 70.89; H: 5.60; N: 11.00.

3.6-di(2-pyridyl)-4,5-di-(3,5-dimethoxyphenyl)pyridazine

The same procedure was applied as for 3a using a dichloromethane solution (40 mL) containing 3,6-di(2-pyridyl)-4,5-di-(3,5-dimethoxyphenyl)-1,4-dihydropyridazine. The product was purified by column chromatography on silica (dichloromethane:ethanol, 5:1) and recovered as a yellow solid (0.855g, 1.68 mmol, 75 %).

I.R. (KBr) vbar 3052s, 3005s, 2941s, 2839s, 1592s, 1494s, 1462s, 1425s, 1363s, 1343s, 1204s, 1145s, 1064s, 842s, 805s, 830s, 749s, 693s cm⁻¹.

1H NMR (400 MHz, CDCl3) δ: 8.55 (d, 2H, H6, J = 5.0 Hz), 7.72 (Ψtd, 2H, H7, J = 7.5, 1.5 Hz), 7.61 (d, 2H, H7, J = 8.0 Hz), 7.23 (m, 2H, H5), 6.22 (t, 2H, H13, J = 2.0 Hz), 6.10 (d, 4H, H11, J = 2.0 Hz), 3.67 ppm (s, 12H, -OMe).

13C NMR (100 MHz, CDCl3) δ: 160.0 (C5), 158.9 (C6), 156.1 (C5), 149.1 (C6), 138.7 (C6), 136.4 (C5), 136.2 (C5), 124.8 (C1), 123.0 (C3), 108.4 (C4), 100.4 (C10), 55.3 ppm (CH3, -OMe).

HRMS: (PhMe) calculated for [MH]+ m/z: 507.2028, found: 507.2032.
3,6-di-(2-pyrazinyl)-4-(2-pyridyl)-pyridazine (1b)

The same procedure was used as for 1a using bpttz (0.310 g, 1.30 mmol) and (147 µL, 1.25 mmol) of 2-acetyl pyridine. The product was purified by column chromatography (ethyl acetate: methanol, 10:1) and isolated as an off-white solid.

I.R. vbar 3062s, 3016s, 1698m, 1586s, 1571s, 1477s, 1469s, 1387s, 1154s, 1149s, 1020, 861s, 805s, 785s, 752s, 621m, 585m, 503m, 411s cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 10.02 (d, 1H, H¹, J = 1.5 Hz), 9.42 (d, 1H, H³, J = 1.5 Hz), 8.81 (s, 1H, H⁴), 8.73 (d, 1H, H⁵, J = 2.5 Hz), 8.70 (d, 1H, H⁶, J = 1.5 Hz), 8.58 (d, 1H, H⁷, J = 2.4 Hz), 8.53 (d, 1H, H¹¹, J = 4.7 Hz), 8.32 (d, 1H, H⁷, J = 1.5 Hz), 7.75 (s (brd, 1H, H⁸, J = 8.0, 1.5 Hz), 7.45 (d, 1H, H⁸, J = 7.4 Hz), 7.29 ppm (ddd, 1H, H¹⁰, J = 7.5, 1.5, 0.9Hz).

¹³C-NMR (100 MHz, CDCl₃): δ 156.5 (C¹²/¹⁵), 155.9 (C¹²/¹⁵), 154.3 (C⁷), 150.7 (C²), 149.3 (C¹¹), 147.8 (C²), 145.4 (C⁶), 145.3 (C³), 144.0 (C⁵), 143.6 (C⁵), 143.4 (C⁵), 142.5 (C⁵), 139.6 (C¹³), 136.3 (C⁶), 125.5 (C¹⁴), 123.5 (C⁸), 123.0 ppm (C¹⁰).

HRMS: (CH₃CN): calculated for [MH]+ m/z: 314.1154, found: 314.1158.


3,6-di-(2-pyrazinyl)-4-(pyrimidyl) pyridazine (2b)

The same procedure was used as for 2a using bpttz (0.310 g, 1.30 mmol) and 5-ethynyl pyrimidine (0.140 g, 1.39 mmol). The product was obtained after column chromatography on silica (10:1 ethyl acetate:methanol) as an off-white solid (0.214 g, 49% yield).

I.R. vbar 3130m, 3098m, 3033s, 1575s, 1556s, 1434s, 1380s, 1161s, 1019s, 869s, 860s, 758m, 724s, 631s, 581m, 482m cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 10.02 (d, 1H, H¹, J = 1.4 Hz), 9.64 (d, 1H, H³, J = 1.4 Hz), 9.28 (s, 1H, H⁴), 8.79 (d, 1H, H⁶, J = 2.2 Hz), 8.73 (m, 3H, H⁶), 8.66 (m, 2H, H⁸), 8.36 (d, 1H, H⁵, J = 2.0 Hz), 7.75 (s (brd, 1H, H⁸, J = 8.0, 1.5 Hz), 7.45 (d, 1H, H⁸, J = 7.4 Hz), 7.29 ppm (ddd, 1H, H¹⁰, J = 7.5, 1.5, 0.9Hz).

¹³C-NMR (100 MHz, CDCl₃): δ 156.0 (C¹⁰), 156.4 (C¹¹), 155.4 (C⁷), 154.9 (C¹⁴), 149.1 (C²), 147.2 (C⁷), 145.8 (C⁶), 145.5 (C³), 144.80 (C⁵), 143.7 (C⁵), 143.4 (C⁵), 142.5 (C⁵), 134.6 (C²), 130.7 (C¹³), 126.09 ppm (IC, C¹³).

HRMS: (CH₃CN): calculated for [MH]+ m/z: 337.0926, found: 337.0899.

Anal. Calculated for C₁₅H₁₄N₈: C 61.14, H 3.21, N 35.65. Found: C 59.60, H; 3.17; N, 35.04. m.p. 226 – 228 ºC

3,6-di-(2-pyrazinyl)-4,5-diphenylpyridazine (3b)

3,6-di-(2-pyrazinyl)-4,5-diphenyl-1,4-dihydropyridazine

The same procedure was used as for 3,6 di(2-pyridyl) 4,5-diphenyl-1,4-dihydropyridazine (above) using trans-stilbene (0.240 g, 1.33 mmol) and bpttz (0.310 g 1.30 mmol). Purification by column chromatography (dichloromethane: diethyl ether, 10:1) gave the product as a yellow solid (0.390 g, 75% yield).

¹H-NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H, H¹), 9.43 (s, 1H, H³), 8.57 (d, 1H, H⁵), 8.51 (d, 1H, H⁷), 7.55 (m, 3H, H⁶), 7.72 (m, 3H, H⁷), 7.27 (m, 8H, H³, H²), 7.12 ppm (s, 1H, H¹).

HRMS: (CH₃CN): calculated for C₂₆H₂₀N₈: [MH]+ m/z 391.1701 found: 391.1700.


3,6-di-(2-pyrazinyl)-4,5-diphenylpyridazine

The same procedure was used as for 3a, using a dichloromethane (20 mL) suspension of 3,6-di(2-pyrazinyl) 4,5-diphenyl-1,4-dihydropyridazine. After recrystallisation from ethyl acetate/petroluem, the product was obtained as a beige solid (0.327 g, 49%).

I.R. vbar 3075s, 3049s, 2963s, 2927s, 1963m, 1737m, 1493s, 1471s, 1444s, 1371s, 1262s, 1145s, 1070s, 1064s, 1036s, 863s, 772s, 756s, 701s, 659s, 639s, 628s, 536m, 527m cm⁻¹.

¹H-NMR: (400 MHz, CDCl₃): δ 8.98 (s, 2H, H¹), 8.51 (d, 2H, H⁷, J = 2.0Hz), 8.43 (s, 2H, H³), 7.11 (m, 6H, H⁷), 6.89 ppm (dd, 4H, H², J = 6.3, 1.5 Hz).

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3,6-di(2-pyrazinyl)-4,5-di(4-pyridyl) pyridazine (4b)

The same procedure was used as for 4a using bpz (0.300 g, 1.26 mmol) and \(\text{E}-\text{1,2-di(4-pyridyl)ethene} (0.238 \text{ g}, 1.30 \text{ mmol}).\) Purification via silica column chromatography (diethyl ether:methanol, 1:1) yielded the product as a bright yellow solid (0.437 g, 0.76 mmol, 60%).

\[\text{H-NMR (400 MHz, CDCl}_3\): } \delta 9.37 (s, 2H, H1', J = 1.0 Hz), 8.56 (d, 2H, H2', J = 2.5 Hz), 8.40 (d, 4H, H3', J = 5.6 Hz), 8.29 (d, 2H, H2, J = 2.0 Hz), 6.88 (d, 4H, H3, J = 6.0 Hz).

HRMS: (CH₁CN) calculated for [MH⁺] m/z: 393.1576, found: 393.1592

Anal. Calcd. for C 67.68; H, 3.61; N, 28.70. Found: C, 66.21; H, 3.54; N, 28.70.

3,6-di(2-pyridyl)-4,5-di(4-pyridyl) pyridazine

The same procedure was used as for 3a using a dichloromethane (40 mL) solution containing 3,6-di(2-pyrazinyl)-4,5-di(4-pyridyl)-1,4-dihydropyridazine. Purification was carried out by column chromatography on silica using diethyl ether: methanol (3:1) as eluent. The product was recovered as a yellow solid (0.175 g, 0.30 mmol, 40%).

I.R. vθ 3069s, 3036s, 2987m, 1597s, 1409s, 1371s, 1154s, 1016s, 991m, 849s, 796s, 762s, 627s, 549m, 509m cm⁻¹.

\[\text{H-NMR (400 MHz, CDCl}_3\): } \delta 9.37 (s, 2H, H1', J = 1.0 Hz), 8.56 (d, 2H, H2', J = 2.5 Hz), 8.40 (d, 4H, H3', J = 5.6 Hz), 8.29 (d, 2H, H2, J = 2.0 Hz), 6.88 (d, 4H, H3, J = 6.0 Hz).

HRMS: (CH₁CN) calculated for [MH⁺] m/z: 393.1576, calculated for C₅₂H₃₈N₈: [MH⁺] = 393.1515.

Anal. Calculated for C, 67.68; H, 3.61; N, 28.70. Found: C, 66.86, H, 3.65, N, 28.41. m.p. 216-218 °C.

Ruthenium bis bipyridyl/ deuterated bis bipyridyl complexes

General Procedure:

Unless otherwise stated, ligand (1a, 2a, 3a, 4a, 5a, 6) and ruthenium(II) bisbipyridine dichloride were heated for 4 hrs at 80 °C in a mixture of ethylene glycol (5 mL) and water (5 mL). The reaction mixture was then diluted with water and washed with dichloromethane to remove excess ligand. The volume of the aqueous layer was reduced under vacuum and a saturated solution of KPF₆ was added. The mixture was filtered and the filtrate purified by column chromatography on silica, using the solvent systems outlined below.

\[\text{[Ru(bpy)}₂(1a)]PF₆²⁻\]

\[\text{[Ru(bpy)}₂(1a)]PF₆²⁻\] (1a) (0.100 g, 0.320 mmol) and ruthenium(II) bisbipyridine dichloride (0.156 g, 0.299 mmol). The compound was purified by column chromatography on silica (MeCN: KNO₃:H₂O 10: ½:1 ½).

Product obtained as red solid (0.222g, 0.218 mmol, 65%).

\[\text{H-NMR (600 MHz, CD₃CN): } \delta 8.99 (s, 1H, H10, J = 7.9 Hz), 8.64 (d, 2H, H4', J = 4.7 Hz), 8.20 (d, 1H, H3', J = 3.9 Hz), 8.57-8.50 (m, 2H, H1', J = 4.7 Hz), 7.99 (d, 1H, H3', J = 2.5 Hz), 7.92 (d, 1H, H4', J = 5.4 Hz), 7.82 (d, 1H, H3', J = 3.7 Hz), 7.80 (d, 1H, H3', J = 3.0 Hz), 7.79 (m, 2H, H1', J = 2.5 Hz), 7.73 (d, 1H, H3', J = 1.0 Hz), 7.71-7.46 (m, 2H, H1', J = 1.0 Hz), 7.38 (m, 1H, H3', J = 1.0 Hz), 7.35 (d, 1H, H3', J = 8.0 Hz), 7.32 (m, 1H, H3', J = 8.0 Hz), 7.27 ppm (d, 1H, H3', J = 8.0 Hz).

HRMS: (CH₃CN) m/z = 362.5786 [M-2PF₆]²⁻ Calculated for C₃₂H₂₄N₄Ru: 362.5795,
[Ru(bpyd8)2(1a)][PF₆]₂
1a (0.015 g, 0.049 mmol) and deuterated ruthenium bis bipyridine dichloride (0.0075 g, 0.014 mmol). The product was purified by column chromatography on silica (MeCN: KNO₃:H₂O 10:½:1 ½). Red solid (0.0092 g, 0.009 mmol, 64%).

**[Ru(bpy)]₂(2a)][PF₆]₂**
2a (0.105 g, 0.337 mmol) and ruthenium(II) bisbipyridine dichloride (0.157 g, 0.301 mmol). The product was purified by column chromatography on silica (MeCN: KNO₃:H₂O 10:½:1 ½). Red solid (0.222 g, 0.218 mmol, 73%).

**[Ru(bpyd8)₂(2a)][PF₆]₂**
2a (0.009 g, 0.028 mmol) and deuterated ruthenium (II) bisbipyridine dichloride were reacted as for [Ru(bpy)]₂(1a)][PF₆]₂. The product was purified by chromatography on silica (MeCN: KNO₃:H₂O 10:½:1 ½). Red solid (0.222 g, 0.218 mmol, 68%).

**[Ru(bpy)]₂(3a)][PF₆]₂**
3a (0.100 g, 0.258 mmol) and ruthenium(II) bisbipyridine dichloride (0.114 g, 0.222 mmol). Purification was carried out by column chromatography on silica (acetonitrile:water: sat. KNO₃ 10:1:5:1). (0.112 g, 0.1399 mmol, 63% yield)

**HRMS:** 
- 1H-NMR (600 MHz, CD₃CN): δ 8.76 (s, 1H, H⁹), 8.39 (d, 1H, H⁶, J = 8.0 Hz), 8.48 (d, 1H, H², J = 4.6 Hz), 8.24 (d, 1H, J = 7.9 Hz), 8.04 (s, 1H, H³, J = 8.3 Hz), 8.63 (d, 1H, H⁶, J = 4.6 Hz), 8.17 (dd, 1H, H⁴, J = 7.9, 1.4 Hz), 7.95 (d, 1H, H⁴, J = 5.4 Hz), 7.77 (dd, 1H, H⁴, J = 7.5, 1.1 Hz), 7.58 (m, 1H, H⁸), 7.38 (Ψtd, 1H, H³, J = 4.6, 0.8 Hz), 7.23 ppm (d, 1H, H³, J = 7.9 Hz).
- HRMS: (CH₃CN) m/z = 371.1400 [M-2PF₆]²⁺. Calculated for C₅H₁₂N₁₀Ru: 371.1265.

**[Ru(bpy)]₂(3a)][PF₆]₂**
3a (0.100 g, 0.258 mmol) and ruthenium(II) bisbipyridine dichloride (0.114 g, 0.222 mmol). Purification was carried out by column chromatography on silica (acetonitrile:water: sat. KNO₃ 10:1:5:1). (0.112 g, 0.1399 mmol, 63% yield)

**HRMS:** 
- 1H-NMR (600 MHz, CD₃CN): δ 8.76-8.52 (m, 3H), 8.44 (d, 1H, H³, J = 8.2 Hz), 8.19-8.11 (m, 5H), 7.95 (m, 2H), 7.90 (m, 2H), 7.69 (dd, 1H, H⁶, J = 5.5, 0.7 Hz), 7.68-7.56 (m, 4H), 7.53-7.30 (m, 7H), 7.20 (m, 1H), 7.09 (m, 5H ) 6.92 ppm (1H, H⁷, J = 7.9 Hz).
- HRMS: (CH₃CN) m/z = 300.0990 [M-2PF₆]²⁺. Calculated for C₄₃H₂₆N₁₀Ru: 400.0757.

**Anal. Calcd.:** C 46.16, H 2.88, N 12.42. Found C 46.40, H 2.99, N 12.40. m.p > 280 °C
[Ru(bpy\textsubscript{d8})\textsubscript{2}(3a)][PF\textsubscript{6}]\textsubscript{2}

3a (0.005g, 0.014 mmol) and deuterated ruthenium (II) bisbipyridine dichloride (0.007g, 0.014 mmol). Following ion exchange and filtration no further purification was required. Deep red solid (0.012 g, 0.0109 mmol, 78% yield).

1\textsuperscript{H}-NMR (600 MHz, CD\textsubscript{2}CN): \(\delta\) 8.16 (d, 1H, \(H^6\), J = 4.7 Hz), 7.95 (d, 1H, \(H^6\), J = 5.8 Hz), 7.66 (\(\Psi_{td}\), 1H, \(H^1\), J = 7.8, 0.8 Hz), 7.56 (\(\Psi_{td}\), 1H, \(H^1\), J = 7.5, 0.7 Hz), 7.47-7.33 (m, 5H, \(H^7-8,\)), 7.20 (m, 1H, \(H^5\)), 7.13-3.06 (m, 6H, \(H^{8,9,5}\)), 6.93 ppm (d, 1H, \(H^3\), J = 8.1 Hz).

HRMS: (CH\textsubscript{2}CN) \(m/z = 408.1601\) [M-2PF\textsubscript{6}]\textsuperscript{2+}. Calculated for C\textsubscript{46}H\textsubscript{36}D\textsubscript{2}N\textsubscript{4}Ru: 408.1601.


[Ru(bpy\textsubscript{2})(4a)][PF\textsubscript{6}]\textsubscript{2}

4a (0.102g, 0.264 mmol) and ruthenium(II) bisbipyridine dichloride (0.130g, 0.251 mmol). The product was purified by column chromatography on silica (acetone:ammonia:Sat. KNO\textsubscript{3}: 20:3:0.5).

Red solid (0.144 g, 0.136 mmol, 54 %).

1\textsuperscript{H}-NMR (600 MHz, CD\textsubscript{2}CN): \(\delta\) 8.67-8.55 (m, 4H, \(H^{4,pp}\), \(H^{pp}\)), 8.49 (d, 1H, \(H^{pp}\), J = 8.0 Hz), 8.41-8.08 (m, 6H), 8.04-8.00 (m, 2H), 7.92 (d, 1H, \(H^{pp}\), J = 5.4 Hz), 7.88 (d, 1H, \(H^{pp}\), J = 5.4 Hz), 7.71-7.67 (m, 3H), 7.59-7.52 (m, 3H), 7.46 (m, 1H), 7.43-7.35 (m, 2H), 7.25-7.14 (m, 5H), 6.82 ppm (s, 1H).

HRMS: (CH\textsubscript{2}CN) \(m/z = 401.0940\) [M-2PF\textsubscript{6}]\textsuperscript{2+}. Calculated for C\textsubscript{46}H\textsubscript{36}N\textsubscript{4}Ru: 401.0928.

Anal. Calcd.: C 65.91, H 4.02, N 17.47. Found C 66.10, H 4.20, N 17.56. m.p >280 °C

Ru(bpy\textsubscript{d8})\textsubscript{2}(4a)][PF\textsubscript{6}]\textsubscript{2}

4a (0.006 g, 0.015 mmol) and ruthenium(II) bisbipyridine dichloride (0.008 g, 0.015 mmol). The product was purified by chromatography on silica (acetone:ammonia:sat. KNO\textsubscript{3}: 20:3:0.5).

Red solid (0.012 g, 0.011 mmol, 75% yield).

1\textsuperscript{H}-NMR (600 MHz, CD\textsubscript{2}CN): \(\delta\) 8.67 (d, 1H, \(H^{pp}\), J = 4.4 Hz), 8.62 (d, 1H, \(H^{pp}\), J = 4.7 Hz), 8.29 (m, 2H, \(H^{pp}\)), 8.12 (d, 1H, \(H^{pp}\), J = 3.9 Hz), 7.98 (d, 1H, \(H^{pp}\), J = 5.5 Hz), 7.67 (m, 2H, \(H^{pp}\)), 7.40 (m, 2H, \(H^{pp}\)), 7.26 (dd, 1H, \(H^{pp}\), J = 5.0 Hz, 1.0 Hz), 7.13 (m, 3H, \(H^{pp}\), \(H^{pp}\)), 6.78 ppm (m, 1H, \(H^{pp}\)).

HRMS: (CH\textsubscript{2}CN) \(m/z = 409.1554\) [M-2PF\textsubscript{6}]\textsuperscript{2+}. Calculated for C\textsubscript{46}H\textsubscript{36}D\textsubscript{2}N\textsubscript{4}Ru: 409.1034.

Anal. Calcd.: C 64.61, H 5.91, N 17.12. Found C 64.80, H 5.98, N 17.10. m.p >280 °C

[Ru(bpy\textsubscript{2})(5a)][PF\textsubscript{6}]\textsubscript{2}

5a (0.020 g, 0.040 mmol) and ruthenium(II) bis bipyridine dichloride (0.021 g, 0.040 mmol) in mixture of ethylene glycol (3 mL) and water (3 mL). The product was purified by chromatography on silica (acetone:ammonia:sat. KNO\textsubscript{3}: 20:2:2). Red solid (0.027 g, 0.022 mmol, 56% yield).

1\textsuperscript{H}-NMR (600 MHz, CD\textsubscript{2}CN): \(\delta\) 8.60 (m, 2H, \(H^{pp}\)), 8.53 (d, 1H, \(H^{pp}\), J = 7.9 Hz), 8.43 (d, 1H, \(H^{pp}\), J = 8.1 Hz), 8.23 (d, 1H, \(H^{pp}\), J = 4.7, 1.0 Hz), 8.20 - 8.15 (m, 3H), 8.08 (dd, 1H, \(H^{pp}\), J = 5.5, 0.8 Hz), 7.97 (m, 3H), 7.89 (d, 1H, \(H^{pp}\), J = 5.0 Hz), 7.71 (m, 3H), 7.61-7.49 (m, 3H), 7.37 (\(\Psi_{td}\), 1H, \(H^{pp}\), J = 5.6, 1.2 Hz), 7.22 (m, 3H), 7.10 (d, 1H, \(H^{pp}\), J = 7.8 Hz), 6.58 (\(\Psi_{td}\), 2H, \(H^{pp}\), J = 1.5 Hz), 6.34 (m, 1H, \(H^{pp}\)), 6.24 (d, 1H, \(H^{pp}\), J = 2.3 Hz), 3.73 (s, 3H, \(H^{OMe}\)), 3.71 (s, 3H, \(H^{OMe}\)), 3.56 ppm (s, 6H, \(H^{OMe}\)).

HRMS: (CH\textsubscript{2}CN) \(m/z = 460.1170\) [M-2PF\textsubscript{6}]\textsuperscript{2+}. Calculated for C\textsubscript{50}H\textsubscript{42}N\textsubscript{6}O\textsubscript{4}Ru: 460.1185.

Anal. Calcd.: C 65.28, H 4.60, N 12.18. Found C 66.00, H 4.70, N 12.50. m.p >280 °C

[Ru(bpy\textsubscript{2})(6)][PF\textsubscript{6}]\textsubscript{2}

6 (0.046 g, 0.128 mmol) and ruthenium(II) bis bipyridine dichloride (0.066 g, 0.127 mmol) were heated for 5 hrs at 80 °C in a mixture of ethylene glycol (3 mL) and water (3 mL). The reaction was allowed to cool, further diluted with water (25 mL) and an excess of NH\textsubscript{4}PF\textsubscript{6} was added. The solution was extracted into dichloromethane (30 mL) and washed with water (3 x 15 mL). The solvent
was removed in vacuo to yield a red solid, which was recrystallised from acetone/hexane (0.074g, 0.097 mmol, 76%).

$^1$H NMR (600 MHz, CD$_3$CN) δ: 9.29 (d, 1H, H$^4$, J = 8.0 Hz), 8.92 (d, 1H, H$^5$, J = 7.4 Hz), 8.87 (d, 1H, H$^6$, J = 4.3 Hz), 8.63 (d, 1H, H$^7$, J = 7.3 Hz), 8.48 (d, 1H, H$^{99}$, J = 8.2 Hz), 8.46 (d, 1H, H$^{109}$, J = 7.6 Hz), 8.44 (d, 1H, H$^8$, J = 8.0 Hz), 8.37 (d, 1H, H$^2$, J = 8.2 Hz), 8.25 (Ψtd, 1H, H$^6$, J = 8.0, 1.4 Hz), 8.16 (Ψtd, 1H, H$^{109}$, J = 8.0, 1.4 Hz), 8.03 (m, 3H, 2H$^{109}$, 1H$^8$), 7.98 (m, 3H, 2H$^{99}$, 1H$^7$), 7.88 (Ψtd, 1H, H$^5$, J = 7.8, 1.3 Hz), 7.84 (Ψt, 1H, H$^8$, J = 7.8 Hz), 7.72 (d, 1H, H$^{99}$, J = 5.6 Hz), 7.62 (m, 2H, H$^{5.5}$), 7.52 (ddd, 1H, H$^{99}$ J = 7.6, 5.6, 1.1 Hz), 7.42 (m, 2H, 2H$^{109}$), 7.35 (ddd, 1H, H$^{109}$, J = 7.5, 5.7, 1.3 Hz), 7.22 ppm (d, 1H, H$^3$, J = 7.9 Hz).

HRMS: (CH$_3$CN) m/z = 386.0819 [M-2PF$_3$]$^{2+}$ Calculated for C$_{30}$H$_{30}$N$_4$Ru: 386.0819.

Analyt. Calcd.: C 68.47, H 3.92, N 14.52. Found C 69.04, H 4.00, N 14.90. m.p > 280 °C

**Ruthenium tris homoleptic complexes**

**General procedure:** Unless otherwise stated, the ligand (3a, 4a, 5a) was added to ruthenium(III) chloride hydrate in ethylene glycol (5 mL). N-Ethyl morpholine (6 drops) was added and the mixture was degassed by bubbling with argon for 30 mins. The mixture was then heated at 170°C for 72 hrs, cooled and extracted into CH$_2$Cl$_2$. The facial and meridional isomers were isolated as described.

[Ru(3a)$_3$][PF$_6$]$_2$

3a (0.0209g, 0.0542 mmol) was added to ruthenium(III) chloride hydrate (0.0029g, 0.0142 mmol). The facial isomer was separated using a preparative silica TLC plate (acetone:water:sat.KNO$_3$, 120:12:0.5) (2.70 mg, 12% yield, R$_f$ = 0.35). The residue remaining on the plate was collected and the meridional isomer was isolated from this mixture using a second preparative TLC plate (acetone:trile:ammonia:sat.KNO$_3$, 20:2:4). (6.45 mg, 29% yield, R$_f$ = 0.15).

**Mer isomer:**

$^1$H-NMR (600 MHz, CD$_3$CN): δ 8.64 (d, 1H, H$^9$, J = 5.0 Hz), 8.40 (d, 1H, H$^{109}$, J = 4.6 Hz), 8.34 (d, 1H, H$^{109}$, J = 5.1 Hz), 8.26 (d, 2H, J = 4.6 Hz), 8.18 (d, 1H, H$^8$, J = 4.2 Hz), 7.72 – 6.97 (m, 26H), 6.98 (1H, H$^7$, J = 7.4 Hz), 6.89 (1H, H$^9$, J = 7.9 Hz), 6.86 (1H, H$^{109}$, J = 7.9 Hz), 6.48 ppm (1H, H$^8$, J = 7.4 Hz).

HRMS: (CH$_3$CN) m/z = 630.1813 [M-2PF$_6$]$^{2+}$. Calculated for C$_{10}$H$_{30}$N$_4$Ru: 630.1819. m.p. > 280 °C

**Fac isomer:**

$^1$H-NMR (600 MHz, CD$_3$CN): δ 8.46 (d, 3H, H$^6$, J = 4.0 Hz), 8.43 (d, 3H, H$^6$, J = 6.0 Hz), 7.72 (d, 3H, H$^4$, J = 7.7 Hz), 7.71 (d, 3H, H$^5$, J = 8.0 Hz), 7.57 (Ψt, 3H, H$^5$, J = 6.3 Hz), 7.42 (m, 6H, H$_{7/8}^{7/8}$), 7.31 (m, 6H, H$^{5/7/8}^{5/7/8}$), 7.20 (d, 3H, H$^3$, J = 7.7 Hz), 7.09 (m, 9H, H$^{7/8/9}$), 6.98 (d, 3H, H$^5$, J = 8.6 Hz), 6.68 (m, 3H, H$_{7/8}^{7/8}$), 6.10 ppm (m, 6H, H$_{7/8}^{7/8}$).

$^{13}$C-NMR (100 MHz, CD$_3$CN): δ 159.4 (C$^5$), 157.1 (C$^6$), 155.4 (C$^8$), 154.4 (C$^9$), 155.8 (C$^{10}$), 149.1 (C$^{13}$), 143.1 (C$^{7}$), 139.3 (C$^{11}$), 137.4 (C$^{9}$), 136.6 (C$^{9}$), 133.4 (C$^{10}$), 132.7 (C$^{11}$), 129.4 (C$^{13}^{7/8}$), 129.2 (C$^{13}^{7/8}$), 129.1 (C$^{13}^{7/8}$), 128.5 (C$^{13}^{7/8}$), 128.3 (C$^{13}$), 127.6 (C$^{7/8}$), 127.2 (C$^{7/8}$), 124.3 (C$^{3}$), 123.7 ppm (C$^{3}$).

HRMS: (CH$_3$CN) m/z = 630.1809 [M-2PF$_6$]$^{2+}$. Calculated for C$_{10}$H$_{30}$N$_4$Ru: 630.1819. m.p. > 280 °C
4a (0.0212 g, 0.0546 mmol) and ruthenium(III) chloride hydrate (0.0032 g, 0.0156 mmol). The facial isomer was separated using a TLC plate (acetone:water:sat. KNO₃, 20:5:1) (2.5 mg 10% yield, Rₜ = 0.33). The residue from the previous plate was purified on a second plate (acetonitrile:ammonia:sat. KNO₃, 20:3:1) from which the meridional isomer was isolated. (3.4 mg, 14% yield, Rₜ = 0.70).

5 Mer isomer:

1H-NMR (CD₃CN): δ 8.73 (d, 1H, H⁴, J = 5.7 Hz), 8.68 (d, 1H, H⁶, J = 4.5 Hz), 8.67 (d, 1H, H⁶, J = 5.7 Hz), 8.60 (d, 1H, H⁴), J = 4.5 Hz), 8.56 (d, 1H, H⁴), J = 4.9 Hz), 8.52 (d, 1H, H⁶, J = 5.3 Hz), 8.41-8.26 (m, 5H), 8.17 (m, 1H), 7.81 (m, 2H, H⁵), 7.68 (m, 3H), 7.64 (m, 1H), 7.43 (m, 2H), 7.38 (m, 1H), 7.30 (m, 2H), 7.12 (m, 2H), 7.07 (d, 1H, H³, J = 8.0), 6.99 (m, 2H), 6.83 (m, 2H), 6.37 ppm (d, 1H, H², J = 4.9Hz).

HRMS: (CH₃CN) m/z = 633.17 [M-2PF₆]²⁺. Calculated for C₇₂H₄₈N₁₃Ru: 1266.3353, found: 1266.3354. m.p. > 280 °C

Fac isomer:

1H-NMR (600 MHz, CD₃CN): δ 8.65 (d, 3H, H⁸, J = 4.7 Hz), 8.53 (m, 3H, H⁶, 8.40 (m, 6H, H⁵⁻⁶), 8.28 (m, 6H, H⁶⁻⁷), 7.81 (m, 6H, H⁴⁻⁷), 7.64 (Ψt, 3H, H⁵, J = 6.5 Hz), 7.38 (Ψτd, 3H, H³, J = 4.5, 2.4 Hz), 7.29 (m, 6H, H⁵⁻⁷), 7.20 (d, 3H, H², J = 8.5 Hz), 6.69 (m, 3H, H²), 6.61 ppm (m, 6H, H²).

C-NMR (100 MHz, CD₃CN): δ 157.7 (C⁵), 156.2 (C⁴), 154.0 (C⁵), 152.7 (C⁶), 152.4 (C⁴), 150.8 (C²), 150.7 (C⁵), 149.1 (C⁶), 147.0 (2C¹), 140.5 (C⁵), 139.8 (C⁴), 138.3 (C⁶), 137.2 (C³), 128.6 (C⁵), 128.4 (C⁶), 124.6 (C⁴), 124.4 (C⁵), 123.9 (C⁴), 123.0 ppm (C⁵).

HRMS: (CH₃CN) m/z = 633.1663 [M-2PF₆]²⁺. Calculated for C₇₂H₄₈N₁₃Ru: 633.1677. m.p. > 280 °C

5a (0.100 g, 0.197 mmol) and ruthenium(III) chloride hydrate (0.0146 g, 0.0706 mmol). The facial isomer was isolated by column chromatography, (acetone:water:sat. KNO₃, 12:1:0.2) (0.012 g, 3% yield, Rₜ = 0.34). The meridional isomer was isolated by purifying the run-off from the column on a silica TLC plate (acetonitrile:ammonia:sat. KNO₃, 20:1:1.5) (0.0207g, 5% yield, Rₜ = 0.12).

Mer isomer:

1H-NMR (600 MHz, CD₃CN): δ 8.47 (d, 1H, H⁴, J = 4.9 Hz), 8.43 (d, 1H, H⁶, J = 3.7Hz), 8.27 (d, 1H, H⁴, J = 4.3 Hz), 8.26 (d, 1H, H⁶, J = 4.6 Hz), 8.23 (d, 1H, H⁴, J = 6.1 Hz), 8.17 (d, 1H, H⁶, J = 5.8 Hz), 7.81-7.62 (m, 8H), 7.38-7.11 (m, 11H), 6.60 (m, 3H, H⁷⁻⁸), 6.55 (m, 1H, H⁹), 6.52 (m, 1H, H⁹), 6.49 (m, 1H, H⁷⁻⁸), 6.40 (m, 1H, H⁷⁻⁸), 6.31 (m, 1H, H⁷⁻⁸), 6.36 (m, 1H, H⁴⁻⁷), 6.22 (m, 2H, H⁷⁻⁸), 3.15 (s, 6H, H²), 3.73 (s, 3H, H⁶), 3.70 (s, 3H, H⁸), 3.68 (s, 6H, H⁶), 3.55 ppm (m, 17H, H⁶).

HRMS: (CH₃CN) m/z = 810.2451 [M-2PF₆]²⁺. Calculated for C₇₂H₇₈N₁₂O₁₂Ru: 810.2453. m.p. > 280 °C

Fac isomer:

1H-NMR (600 MHz, CD₃CN): δ 8.47 (d, 3H, H⁶, J = 4.7 Hz), 8.40 (d, 3H, H⁶, J = 5.5 Hz), 8.71 (Ψtd, 3H, H⁴), J = 7.6, 1.5 Hz), 7.71 (Ψtd, 3H, H⁵, J = 7.8, 1.7 Hz), 7.60 (m, 3H, H⁶⁻⁷), 7.30 (m, 3H, H⁶⁻⁷), 7.27 (d, 3H, H³, J = 7.7 Hz), 7.15 (d, 3H, H⁵, J = 7.7 Hz), 6.56 (t, 4H, H⁶, J = 2.3 Hz), 6.43 (d, 3H, H⁵, J = 2.3 Hz), 6.24 (m, 4H, H⁸), 5.94 (m, 3H, H³), 3.70 (s, 9H, H⁶), 3.66 (s, 9H, H⁶), 3.55 (s, 18H, H²).
Iron(II) tris homoleptic complexes – General procedure:

Unless otherwise stated, the ligand (3a, 4a, 5a) was added to a solution of acetonitrile (5 mL) containing Fe(BF₄)₂. The solution was then heated at 60°C for two hrs. The solvent was removed in vacuo and water was added to the reaction mixture. A saturated solution of KPF₆ was added and the resulting precipitate extracted into dichloromethane and dried over MgSO₄. This was purified by silica column chromatography or on preparative TLC plates as outlined below.

\[
[\text{Fe(3a)$_3$}]_2[\text{PF}_6]_2
\]

3a (0.080 g, 0.21 mmol) and Fe(BF₄)₂ (0.112 g, 0.0355 mmol). Purification was by column chromatography on silica (acetone:water:sat. KNO₃, 100:10:1). Two purple products were isolated: mer isomer (0.069g, 24 % yield, Rₜ = 0.74), fac isomer (0.032g, 11 %, Rₜ = 0.26)

**Mer isomer**

\(^{1}H\)-NMR (600 MHz, CD₃CN): δ 8.58 (d, 1H, H\(^{P_3}\), J = 4.4 Hz), 8.38 (d, 1H, H\(^{P_3}\), J = 4.1 Hz), 8.26 (d, 1H, H\(^{P_3}\), J = 4.1 Hz), 8.17 (d, 1H, H\(^{P_3}\), J = 4.4 Hz), 8.10 (d, 1H, H\(^{P_3}\), J = 3.8 Hz), 7.76 (m, 4H), 7.63-6.94 (m, 42H), 6.90 (d, 1H, H\(^{P_3}\), J = 7.60 Hz), 6.81 (m, 2H), 6.42 (d, 1H, H\(^{P_3}\), J = 7.60 Hz).

HRMS: (CH₃CN) m/z = 607.1972 [M-2PF₆]⁺. Calculated for C\(_{78}H\(_{34}\)N\(_{12}\)O\(_{12}\)Fe: 607.1972.

Anal. Calculated for C\(_{78}H\(_{34}\)F\(_{12}\)N\(_{12}\)P\(_{2}\)Fe: C, 62.24; H, 3.62; N, 11.17. Found: C, 61.46, H, 4.61, N, 9.36. m.p. > 280 °C

**Fac isomer**

\(^{1}H\)-NMR (600 MHz, CD₃CN): δ 8.45 (d, 3H, H\(^{P_3}\), J = 5.0 Hz), 8.16 (d, 3H, H\(^{P_3}\), J = 5.6 Hz), 7.74 (m, 6H, 2 H\(^{P_3}\)), 7.57 (m, 3H, H\(^{P_3}\)), 7.43 (m, 6H, H\(^{P_3}\)), 7.33 (m, 6H, H\(^{P_3}\)), 7.21 (d, 3H, H\(^{P_3}\), J = 7.5 Hz), 7.01 (m, 12H, H\(^{P_3}\)), 6.94 (d, 3H, H\(^{P_3}\), J = 8.1 Hz), 6.65 (m, 3H, H\(^{P_3}\)), 6.08 (s, 3H, H\(^{P_3}\)).

HRMS: (CH₃CN) m/z = 607.1969 [M-2PF₆]⁺. Calculated for C\(_{78}H\(_{34}\)N\(_{12}\)Fe: 607.1969.

Anal. Calculated for C\(_{78}H\(_{34}\)F\(_{12}\)N\(_{12}\)P\(_{2}\)Fe: C, 62.24; H, 3.62; N, 11.17. Found: C, 59.74, H, 3.55, N, 10.17. m.p. > 280 °C
[Fe(4a)][PF₆]₂

4a (0.0201 g, 0.0515 mmol) and Fe(BF₄)₂ (0.0138 g, 0.06 mmol). The mixture was separated on a silica preparative TLC plate (acetone:ammonia:sat. KNO₃, 20:4:4). *Mer* isomer (3.35 mg, 16% yield, R₉ = 0.77), *fac* isomer (8.80 mg, 42% yield, R₉ = 0.63).

**Mer isomer**

1H-NMR (600 MHz, CD₃CN): δ 8.75 (d, 1H, H₄py, J = 5.3 Hz), 8.69 (d, 1H, H₄py, J = 4.5 Hz), 8.66 (d, 1H, H₄py, J = 5.0 Hz), 8.58 (d, 1H, H₄py, J = 5.0 Hz), 8.50 (d, 1H, H₄py, J = 5.2 Hz), 8.47 (d, 1H, H₄py, J = 5.2 Hz), 8.43 (d, 1H, H₄py, J = 5.2 Hz), 8.33 (m, 6H, H₃p), 8.16 (d, 1H, H₄py, J = 4.8 Hz), 8.03 (d, 1H, H₄py, J = 6.0 Hz), 7.87 (1H, H₄py, J = 7.6 Hz), 7.80 (1H, H₄py, J = 7.9 Hz), 7.76 (d, 1H, H₄py, J = 5.9 Hz), 7.67 (m, 4H), 7.63 (1H, H₄py, J = 6.9 Hz), 7.46 (d, 1H, H₄py, J = 4.8 Hz), 7.39 (m, 3H), 7.30 (m, 3H), 7.26 (d, 1H, H₄py, J = 5.0 Hz), 7.19 (d, 1H, H₄py), 7.12 (m, 2H), 7.06 (d, 1H, H₄py, J = 7.6 Hz), 6.99 (m, 3H), 6.88 (d, 1H, H₄py, J = 5.1 Hz), 6.35 (d, 1H, H₄py, J = 4.5 Hz).

HRMS: (CH₃CN) m/z = 610.1832 [M-2PF₆]²⁺. Calculated for C₇₂H₆₀N₁₃Fe: 610.1830. m.p. > 280 °C

**Fac isomer**

1H-NMR (600 MHz, CD₃CN): δ 8.67 (d, 3H, H₈, J = 5.2 Hz), 8.55 (d, 3H, H₈, J = 4.6 Hz), 8.40 (d, 3H, H₈, J = 4.3 Hz), 8.27 (br. s, 6H, H₈), 8.12 (d, 3H, H₈, J = 5.2 Hz), 7.88 (1H, H₄py, J = 8.2, 1.2 Hz), 7.82 (1H, H₄py, J = 7.4, 1.3 Hz), 7.63 (1H, H₄py, J = 6.4 Hz), 7.38 (m, 3H, H₈), 7.31 (dd, 3H, H₈), 7.26 (d, 3H, H₈, J=7.9 Hz), 7.21 (d, 3H, H₈, J = 7.6 Hz), 6.67 (m, 3H, H₈), 6.15 (s, 6H, H₈). m.p. > 280 °C

[Fe(5a)][PF₆]₂

5a (0.0916 g, 0.181 mmol) and Fe(BF₄)₂ (0.0674 g, 0.201 mmol). The meridional and facial isomers were separated by column chromatography on silica (1:1:0.1 of methanol:water:sat. KNO₃). *Mer* isomer (0.039g, 37% yield, R₉ = 0.51), *fac* isomer (0.021 g, 20% yield, R₉ = 0.14).
**Mer isomer**

$^1$H-NMR (600 MHz, CD$_3$CN): δ 8.42 (d, 1H, H$_{py}$, J = 4.2 Hz), 8.37 (d, 1H, H$_{py}$, J = 5.0 Hz), 8.30 (d, 1H, H$_{py}$, J = 4.4 Hz), 8.26 (d, 1H, H$_{py}$, J = 4.2 Hz), 7.89 (d, 1H, H$_{py}$, J = 8.0 Hz), 7.36 (m, 3H), 7.35 (m, 2H), 7.26 (d, 1H, H$_{py}$, J = 8.3 Hz), 7.10 (d, 1H, H$_{py}$, J = 8.0 Hz), 7.06 (d, 1H, H$_{py}$, J = 5.0 Hz), 6.64 (m, 3H), 6.55 (d, 1H, H$_{ph}$, J = 1.2 Hz), 6.53 (d, 1H, H$_{ph}$, J = 2.0 Hz), 6.50 (d, 1H, H$_{ph}$, J = 1.2 Hz), 6.37 (d, 1H, H$_{ph}$, J = 2.2 Hz), 6.29 (m, 3H, H$_{ph}$), 6.26 (m, 2H, H$_{ph}$), 5.75 (m, 1H, H$_{ph}$), 3.76 (m, 5H, H$_{OMe}$), 3.71 (s, 3H H$_{OMe}$), 3.67 (s, 3H, H$_{OMe}$), 3.64 (m, 4H, H$_{OMe}$), 3.57 (s, 7H, H$_{OMe}$), 3.54 (s, 7H, H$_{OMe}$).

HRMS: (CH$_3$CN) m/z = 787.2571 [M-2PF$_6$]$^{2+}$. Calculated for C$_{90}$H$_{78}$N$_{12}$O$_{12}$Fe: 787.2606. m.p. > 280 °C

**Fac isomer**

$^1$H-NMR (600 MHz, CD$_3$CN): δ 8.46 (d, 3H, H$_6$, J = 4.2 Hz), 8.12 (d, 3H, H$_6$, J = 5.6 Hz), 7.87 (Ψtd, 3H, H$_{4}$, J = 7.0, 1.7 Hz), 7.73 (d, 3H, H$_4$, J = 8.1, 1.4 Hz), 7.60 (d, 3H, H$_{5}$, J = 1.5 Hz), 7.31 (d, 3H, H$_{5}$, J = 1.3 Hz), 7.25 (d, 3H, H$_{4}$, J = 8.1 Hz), 7.17 (d, 3H, H$_5$, J = 7.8 Hz), 6.58 (s, 3H, H$_3$), 6.46 (s, 3H, H$_3$), 6.24 (s, 3H, H$_3$), 5.90 (s, 3H, H$_3$), 3.72 (s, 2H, H$_{OMe}$), 3.66 (s, 2H, H$_{OMe}$), 3.55 (s, 5H, H$_{OMe}$).

HRMS: (CH$_3$CN) m/z = 787.26 [M-2PF$_6$]$^2$. Calculated for C$_{90}$H$_{78}$N$_{12}$O$_{12}$Fe: 787.2606. m.p. > 280 °C
### Crystallographic Structural Data and Discussion

**Table S1: Data for compounds 1a, 2a, 3a, 6**

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<th>Compound reference</th>
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<th>2a</th>
<th>3a</th>
<th>6</th>
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Fig. S1 Asymmetric units (top) and representations of the lattice interactions in ligands 1a, 2a and 3a in molecular structure (centre) and schematic (bottom) forms.

Single crystals of 1a were grown from dichloromethane and had a P21/n centrosymmetric space group. One molecule is found in the asymmetric unit, as shown in Figure S1 (a). Rings A and B are almost coplanar, with a dihedral angle of 7.13° between them. The angle between the central pyridazine ring (B) and ring C is 55.04°, with an angle of 29.05° between rings B and D. The collective interactions of the pyridazine and the 2-pyridyl units leads to the formation of infinite chains giving a herringbone arrangement which is represented schematically in Figure S1 (a). In the three-dimensional arrangement, these chains are held by C–H⋯π (H⋯π, 2.83Å) interactions.

Colourless rod-like crystals of 2a were obtained from a dichloromethane-hexane solution. Single crystal X-ray analysis revealed that the compound crystallises in an orthorhombic crystal system with one molecule of 2a in the asymmetric unit. There is a small dihedral angle between the rings labelled A and B of 5.02°. The angles between B and C, and C and D, are 31.47° and 48.18° respectively. In the crystal lattice, the molecules are stabilised by C–H⋯N hydrogen bonds involving both pyridyl units (H⋯N, 2.64Å) as well as the pyrimidyl ring (H⋯N, 2.68Å). This interaction leads to the formation of an undulated layer as shown in Figure S1 (b) (bottom). Unlike 2a, the pyridazine ring plays no significant role in the hydrogen bond formation or stabilisation of the molecular assembly. The layers form an ABAB pattern and a zig-zag architecture.

Crystals of 3a were grown from a dichloromethane solution. The asymmetric unit (containing two independent molecules) and representations of the lattice packing are shown in Figure S1 (c). The dihedral angle between the central ring (B) and the two 2-pyridyl rings (A and C) is 45.19° and 43.06° respectively. The torsion angles between ring B and the two phenyl rings D and E are 55.60° and 68.01°. The molecules interact with each other through C–H⋯N Hydrogen bonds (2.5-2.6Å) and C–H⋯π interactions (3.0-3.2Å) to form linear chains with branches on one side. This interaction can be viewed pictorially as two interlocking branched chains as is represented in Figure S1 (c).
Crystals of 6 were obtained from a saturated dichloromethane solution. The compound crystallised in the orthorhombic Pbcn space group, the asymmetric unit consisting of half a molecule of 6 owing to the crystallographically imposed two-fold symmetry. The pyridazine ring forms intermolecular non-centrosymmetric hydrogen bonds (C-H-N, 3.466 Å) with the fluoranthene moiety, as shown in Figure S2. This, along with C-H-N interactions between neighbouring pyridyl rings (3.490 Å), results in the corrugated sheet structure observed in the lattice.