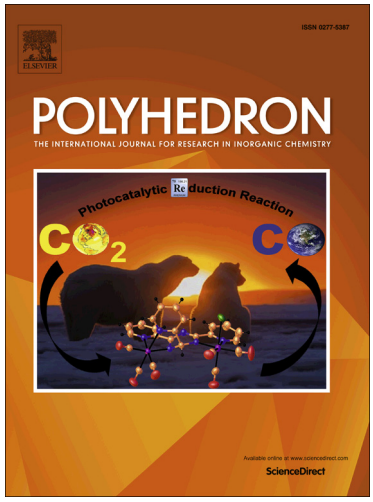
Accepted Manuscript



New ruthenium(II) complexes of 2,2':6',2'' -terpyridine derivatives as supramolecular building blocks

Chao Shen, Pi Wang, Jonathon E. Beves

PII: S0277-5387(15)00351-4
DOI: http://dx.doi.org/10.1016/j.poly.2015.06.035
Reference: POLY 11382

To appear in: *Polyhedron*

Received Date: 6 January 2015
Accepted Date: 29 June 2015

Please cite this article as: C. Shen, P. Wang, J.E. Beves, New ruthenium(II) complexes of 2,2':6',2'' -terpyridine derivatives as supramolecular building blocks, *Polyhedron* (2015), doi: http://dx.doi.org/10.1016/j.poly.2015.06.035

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

ACCEPTED MANUSCRIPT

New ruthenium(II) complexes of 2,2':6',2''-terpyridine derivatives as supramolecular building blocks

Chao Shen,[a] Pi Wang,[a,b] and Jonathon E. Beves*[,a,c]

[a] School of Chemistry, UNSW Australia, Sydney 2052, Australia,

[b] State Key Laboratory of Chemical Engineering, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

[c] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China.

Email: j.beves@unsw.edu.au, T: +61 29385 4673

Keywords: ruthenium, coordination, terpyridine, supramolecular, Suzuki

Dedication: This paper is dedicated to Prof Catherine Housecroft, a devoted mentor and chemical educator, on the occasion of her 60th birthday.

Abstract

Eight new heteroleptic ruthenium(II) complexes of 2,2':6',2''-terpyridine derivatives are reported and characterized by multinuclear NMR and electrospray mass spectrometry. Complexes featuring pendant aryl bromide or pyridyl groups in the 4' position of terpyridine are suitable for palladium(0) coupling reactions to form large metallo-supramolecular ligands. Aryl boronic ester derivatives were found to be unstable with respect to hydroxylation.

1 Introduction

Ruthenium(II) complexes of 2,2':6',2''-terpyridine are substitution-inert complexes with redox- and photo-properties suitable for applications as photosensitizers.[1] This class of complexes is also suitable as building blocks[2] for large supramolecular assemblies, such as coordination polymers,[3] coordination networks,[4] metallo macrocycles[5] or large cage structures[6] and other metallosupramolecular structures.[7] In order to assemble larger structures additional metal ion binding groups are appended to form 'expanded ligands'[8] which can be combined with labile metal ions to self-assemble into the desired architectures. With this goal in mind, our approach was to use Pd(0)-mediated cross-coupling reactions on inert ruthenium(II) complexes[9] to prepare large bridging units which feature metal ion binding groups on the periphery. Pyridyl donor groups are particularly appealing due to their ability to coordinate to a wide range of metal ions, including to square planar Pd(II) centers[10] and are the basis of this work. Herein we report eight new heteroleptic ruthenium(II) complexes of 4'-substituted 2,2':6',2''-terpyridine ligands featuring either pendant pyridyl units, aryl bromides or aryl boronic acids which can act as supramolecular building blocks.[9, 11]

ACCEPTED MANUSCRIPT

2 Experimental

2.1 *General*

The numbering scheme adopted for ligands **1**-**7** is shown in Figure 1. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III-300; Avance III-400 or Avance III-600 spectrometer. The chemical shifts for the ^{1}H and ^{13}C NMR spectra are referenced to residual solvent resonance. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad, ddd = doublet of double doublets. ^{1}H and ^{13}C NMR assignments were made using 2D-NMR methods (COSY, ROESY, NOCSY, HSQC, HMBC) and are unambiguous unless stated otherwise. Ligands **1**,[12] **2**,[13] **3**,[14] **4**,[15] **5a**,[16] **5b**,[6c] **6a**,[11b] **6b**[17] and **7**[12] have been previously reported.

2.2 *Ru(**1**)Cl_3*

Ligand **1** (0.33 g, 0.85 mmol) and $RuCl_3 \cdot xH_2O$ (0.18 g, 0.85 mmol) was suspended in EtOH 95% (30 mL) and heated at reflux for 4h. After cooling to r.t., the precipitate was collected, washed with CH_3CN (2 x 5 mL), EtOH (5 mL) then Et_2O (5 mL) and dried in air to afford Ru(**2**)Cl_3 as a brown solid. Yield 0.42 g, 0.70 mmol, 82%.

2.3 *Ru(**2**)Cl_3*

Same scale and conditions as for Ru(**1**)Cl_3. Yield: brown solid, 0.38 g, 0.64 mmol, 75%.

2.4 *Ru(**5a**)Cl_3*

Ligand **5a** (0.20 g, 0.47 mmol) and $RuCl_3 \cdot xH_2O$ (97 mg, 0.47 mmol) were suspended in *n*-butanol (15 mL) and heated at reflux for 6h. After cooling to r.t., the precipitate was collected, washed CH_3CN (2 × 5 mL), EtOH (5 mL) then Et_2O (5 mL) and dried in air to afford Ru(**5a**)Cl_3 as a brown solid. Yield 0.20 g, 0.32 mmol, 69%. Due to difficulties characterizing this intermediate, it is unclear whether the boronic ester remains intact, or is hydrolyzed to form the boronic acid. *Anal.* Found: C, 47.77; H, 3.83; N, 6.54 %. *Calc*. for $C_{26}H_{24}BCl_3N_3O_2Ru \cdot 1.1H_2O$: C, 48.45; H, 4.07; N, 6.48 %.

2.5 *Ru(**6a**)Cl_3*

Same scale and conditions as for Ru(**5a**)Cl_3. Yield: brown solid, 0.21 g, 0.33 mmol, 71%. Due to difficulties characterizing this intermediate, it is unclear whether the boronic ester remains intact, or is hydrolyzed to form the boronic acid. *Anal.* found: C, 46.24; H, 3.63; N, 6.38%. Calc. for $C_{26}H_{24}BCl_3N_3O_2Ru \cdot 2.2H_2O$: C, 46.72; H, 4.08; N, 6.29 %.

ACCEPTED MANUSCRIPT

2.6 *[Ru(**1**)(**3**)](PF$_6$)$_2$*

Ru(**1**)Cl$_3$ (0.10 g, 0.17 mmol) and ligand **3** (0.05 g, 0.17 mmol) was suspended in ethane-1, 2-diol (8 cm^3). The suspension heated at 150 ℃ for 2 h. The deep red solution was poured into excess aqueous KPF_6 (20 mL). A red precipitate formed and was collected on Celite, washed with H_2O (5 mL), EtOH (2 mL), Et_2O (5 mL), and dissolved in CH_3CN. The product was purified by chromatography (SiO_2, CH_3CN: H_2O: saturated aqueous KNO_3 14: 1.2: 0.5). Addition of excess aqueous saturated KPF_6 solution and removal of CH_3CN under reduced pressure gave a red precipitate which was collected on Celite, washed with H_2O (5 mL), EtOH (2 mL), Et_2O (5 mL) and dissolved in CH_3CN. Removal of solvent gave [Ru(**1**)(**3**)](PF$_6$)$_2$ as a red solid (74 mg, 68 μmol, 40%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.39 (dd, *J* = 2.5, 0.9 Hz, 1H, H^{C2}), 9.04 (s, 2H, H^{B3}), 9.01 (s, 2H, $H^{B3'}$), 8.86 (dd, *J* = 4.8, 1.6 Hz, 1H, H^{C6}), 8.65 (m, 4H, $H^{A3+A3'}$), 8.53 (ddd, *J* = 8.0, 2.5, 1.6 Hz, 1H, H^{C4}), 8.43 (t, *J* = 1.8 Hz, 1H, $H^{C2'}$), 8.19 (ddd, *J* = 7.8, 1.9, 1.0 Hz, 1H, $H^{C4'}$), 8.02-7.94 (m, 4H, $H^{A4+A4'}$), 7.86 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H, $H^{C6'}$), δ 7.75 (dd, *J* = 8.0, 4.8 Hz, 1H, H^{C5}), 7.69 (t, *J* = 7.9 Hz, 1H, $H^{C5'}$), 7.46 – 7.38 (m, 4H, $H^{A6+A6'}$), 7.25 – 7.14 (m, 4H, $H^{A5+A5'}$). ^{13}C NMR (101 MHz, CD_3CN) δ 159.0 ($C^{A2/A2'}$), 159.0 ($C^{A2/A2'}$), 156.6 ($C^{B2/B2'}$), 156.5 ($C^{B2/B2'}$), 153.5 ($C^{A6+A6'}$), 152.0 (C^{C6}), 149.6 (C^{C2}), 147. 7 ($C^{C3'}$), 146.3 (C^{B4}), 140.0 ($C^{B4'}$), 139.15 ($C^{A4/A4'}$), 139.12 ($C^{A4/A4}$), 136.4 (C^{C4}), 134.1 ($C^{C6'}$), 133.8 (C^{C3}), 132.5 ($C^{C5'}$), 131.7 ($C^{C2'}$), 128.6 ($C^{A5/A5'}$), 128.6 ($C^{A5/A5'}$), 127.7 ($C^{C4'}$), 125.64 ($C^{A3/A3'}$), 125.62 ($C^{A3/A3'}$), 125.4 (C^{C5}), 124.1 ($C^{C1'}$), 122.8 ($C^{B3/B3'}$), 122.8 ($C^{B3/B3'}$). LR-ESI-MS (in CH_3CN): *m/z* 945.98 [M-PF$_6$]$^+$ requires 946.03; 400.64 [M-2PF$_6$]$^{2+}$ requires 400.53. *Anal.* found: C, 45.51; H, 3.70; N, 9.95 %. Calc. for $C_{41}H_{28}F_{12}N_7P_2Ru{\cdot}4.5H_2O{\cdot}1CH_3CN$: C, 45.63; H, 3.56; N, 9.90.

2.7 *[Ru(**1**)(**4**)](PF$_6$)$_2$*

The preparation of [Ru(**1**)(**4**)](PF6)$_2$ was the same as for [Ru(**1**)(**3**)](PF$_6$)$_2$, starting with Ru(**1**)Cl$_3$ (0.10 g, 0.17 mmol) and ligand **4** (0.05 g, 0.17 mmol). [Ru(**1**)(**4**)](PF$_6$)$_2$ was isolated as a red solid (76 mg, 70 μmol, 41%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.05 (s, 2H, H^{B3}), 9.01 (s, 2H, $H^{B3'}$), 8.97 (d, *J* = 5.4 Hz, 2H, H^{C2}),), 8.70 – 8.65 (d, *J* = 8.1 Hz, 4H, $H^{A3+A3'}$), 8.43 (t, *J* = 1.8 Hz, 1H, $H^{C2'}$), 8.19 (d, *J* = 8.2 Hz, 1H, $H^{C4'}$), 8.13 (d, *J* = 5.4 Hz, 2H, H^{C3}), 8.02 – 7.94 (m, 4H, $H^{A4+A4'}$), 7.86 (d, *J* = 6.5 Hz, 1H, $H^{C6'}$), 7.69 (t, *J* = 7.9 Hz, 1H, $H^{C5'}$), 7.48 – 7.42 (m, 4H, $H^{A6+A6'}$), 7.25 – 7.17 (m, 4H, $H^{A5+A5'}$). ^{13}C NMR (101 MHz, CD_3CN) δ 159.0 ($C^{A2/A2'}$), 158.9 ($C^{A2/A2'}$), 156.9 ($C^{B2/B2'}$), 156.4 ($C^{B2/B2'}$), 153.5 ($C^{A6/A6'}$), 153.5 ($C^{A6/A6'}$), 151.1 (C^{C2}), 147.9 ($C^{C3'}$), 146.2 (C^{C4}), 145.9 (C^{B4}), 140.0 ($C^{B4'}$), 139.2 ($C^{A4+A4'}$), 134.1 ($C^{C6'}$), 132.5 ($C^{C5'}$), 131.7 ($C^{C2'}$), 128.7 ($C^{A5/A5'}$), 128.6 ($C^{A5/A5'}$), 127.74 (C^{C4}), 125.7 ($C^{A4/A4'}$), 125.6 ($C^{A4/A4'}$), 124.1 (C^{C1}), 123.4 (C^{C3}), 122.8 ($C^{B3+B3'}$). LR-ESI-MS (in CH_3CN): *m/z* 945.98 [M-PF$_6$]$^+$ requires 946.03; 400.62 [M-2PF$_6$]$^{2+}$ requires 400.53. *Anal.* found: C, 40.62; H, 3.7; N, 8.49%. Calc. for $C_{41}H_{28}F_{12}N_7P_2Ru{\cdot}1.5H_2O$: C, 41.08; H, 4.12; N, 8.18.

2.8 *[Ru(**2**)(**3**)](PF$_6$)$_2$*

The preparation of [Ru(**2**)(**3**)](PF$_6$)$_2$ was the same as for [Ru(**1**)(**3**)](PF$_6$)$_2$, starting with Ru(**2**)Cl$_3$ (0.10 g, 0.17 mmol) and ligand **3** (0.05 g, 0.17 mmol). [Ru(**2**)(**3**)](PF$_6$)$_2$ was isolated as a red solid (72 mg, 66 μmol, 39%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.39 (dd, *J* = 2.5, 0.9 Hz, 1H, H^{C2}), 9.04 (s, 2H, H^{B3}), 8.99 (s, 2H, $H^{B3'}$), 8.86 (dd, *J* = 4.8, 1.6 Hz, 1H, H^{C6}), 8.64 (d, *J* = 8.0 Hz, 4H, $H^{A3+A3'}$), 8.53 (dt, *J* = 8.1, 1.9 Hz, 1H, H^{C4}), 8.12 (d, *J* = 8.1 Hz, 2H,

ACCEPTED MANUSCRIPT

$H^{C3'}$), 8.00 – 7.91 (m, 6H, $2H^{C2'}$ + $4H^{A4+A4'}$), 7.74 (dd, *J* = 8.0, 4.8 Hz, 1H, H^{C5}), 7.46 – 7.40 (m, 4H, $H^{A6+A6'}$), 7.23 – 7.17 (m, 4H, $H^{A5+A5'}$). ^{13}C NMR (101 MHz, CD_3CN) δ 159.1 ($C^{A2/A2'}$), 159.0 ($C^{A2/A2'}$), 156.6 ($^{CB2/B2'}$), 156.5 ($C^{B2/B2'}$), 153.5 ($C^{A6+A6'}$), 152.2 (C^{C6}), 149.7 (C^{C2}), 148.1 ($C^{C4'}$), 146.3 (C^{B4}), 139.14 ($C^{A4/A4'}$), 139.12 ($C^{A4/A4'}$),137.0 ($C^{B4'}$), 136.2 (C^{C4}), 133.7 ($C^{C2'}$), 130.6 ($C^{C3'}$), 128.6 ($C^{A5/A5'}$), 128.5 ($C^{A5/A5'}$), 125.6 ($C^{A3+A3'}$), 125.4 ($C^{C1'}$), 125.3 (C^{C5}), 122.8 (C^{B3}), 122.6 ($C^{B3'}$). LR-ESI-MS (in CH_3CN): *m/z* 945.98 $[M\text{-}PF_6]^+$ requires 946.03; *m/z* 400.64 $[M\text{-}2PF_6]^{2+}$ requires 400.53. *Anal*. found: C, 43.19; H, 3.30; N, 8.6 5%. Calc. for $C_{41}H_{28}F_{12}N_7P_2Ru\cdot 6.5H_2O$: C, 43.70; H, 3.67; N, 8.70.

2.9 *Ru(**2**)(**4**)](PF$_6$)$_2$*

The preparation of [Ru(**2**)(**4**)](PF$_6$)$_2$ was the same as for [Ru(**1**)(**3**)](PF$_6$)$_2$, starting with Ru(**2**)Cl$_3$ (0.10 g, 0.17 mmol) and ligand **4** (0.05 g, 0.17 mmol) to give [Ru(**2**)(**4**)](PF$_6$)$_2$ as a red solid (76 mg, 73 μmol, 43%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.05 (s, 2H, H^{B3}), 9.00 (s, 2H, $H^{B3'}$), 8.97 (d, *J* = 5.6 Hz, 2H, H^{C2}), 8.65 (m, 4H, $H^{A3+A3'}$), 8.18 – 8.07 (m, 4H, $H^{C3+C3'}$), 8.02 – 7.90 (m, 6H, $4H^{A4+A4'}$ + $2H^{C2'}$), 7.49 – 7.36 (m, 4H, $H^{A6+A6'}$), 7.25 – 7.13 (m, 4H, $H^{A5+A5'}$). ^{13}C NMR (101 MHz, CD_3CN) δ 159.0 ($C^{A2/A2'}$), 158.9 ($C^{A2/A2}$), 156.8 ($C^{B2/B2'}$), 156.4 ($C^{B2/B2'}$), 153.50 ($C^{A6/A6'}$), 153.46 ($C^{A6/A6'}$), 152.1 (C^{C2}), 148.3 ($C^{C4'}$), 146.3 (C^{C4}), 145.1 (C^{B4}), 139.2 ($C^{A4+A4'}$), 137.0 ($C^{B4'}$), 133.7 ($C^{C2'}$), 130.6 ($C^{C3'}$), 128.6 ($C^{A5/A5'}$), 128.5 ($C^{A5/A5'}$), 125.7 ($C^{A3/A3'}$), 125.6 ($^{CA3/A3'}$), 125.5 ($C^{C1'}$), 122.9 (C^{C3}), 122.8 (C^{B3}), 122.6 ($C^{B3'}$). LR-ESI-MS (in CH_3CN): *m/z* 945.98 $[M\text{-}PF_6]^+$ requires 946.03; 400.62 $[M\text{-}2PF_6]^{2+}$ requires 400.53. *Anal*. found: C, 46.79; H, 3.29; N, 9.67%. Calc. for $C_{41}H_{28}F_{12}N_7P_2Ru\cdot 2H_2O$: C, 47.09; H, 3.08; N, 9.38.

2.10 *Ru(**5b**)(**3**)](PF$_6$)$_2$*

The preparation of [Ru(**5b**)(**3**)](PF$_6$)$_2$ was the same as for [Ru(**1**)(**3**)](PF$_6$)$_2$, starting with Ru(**5a**)Cl$_3$ (0.10 g, 0.16 mmol) and ligand **3** (0.05 g, 0.17 mmol). [Ru(**5b**)(**3**)](PF$_6$)$_2$ was isolated as a red solid (50 mg, 46 μmol, 29%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.39 (d, *J* = 2.1 Hz, 1H, H^{C2}), 9.06 (s, 2H, H^{B3}), 9.03 (s, 2H, $H^{B3'}$), 8.86 (dd, *J* = 4.8, 1.5 Hz, 1H, H^{C6}), 8.72 – 8.62 (m, 4H, $H^{A3+A3'}$), 8.59 (s, 1H, $H^{C2'}$), 8.53 (d, *J* = 8.1 Hz, 1H, H^{C4}), 8.26 (d, *J* = 8.1 Hz, 1H, $H^{C4'}$), 8.07 (d, *J* = 7.4 Hz, 1H, $H^{C6'}$), 8.00 – 7.90 (m, 4H, $H^{A4+A4'}$), 7.82 – 7.69 (m, 2H, $H^{C5+C5'}$), 7.51 – 7.39 (m, 4H, $H^{A6+A6'}$), 7.23 – 7.14 (m, 4H, $H^{A5+A5'}$), 6.42 (s, 2H, $B(OH)_2$). ^{13}C NMR (75 MHz, CD_3CN) δ 159.2 ($C^{A2/A2'}$), 159.1 ($C^{CA2/A2'}$), 156.7 ($C^{CB2/B2'}$), 156.4 ($C^{B2/B2'}$), 153.50 ($C^{A6/A6'}$), 153.45 ($C^{A6/A6'}$), 152.1 (C^{C6}), 149.9 ($C^{B4'}$), 149.7 (C^{C2}), 146.2 (C^{B4}), 139.1 ($C^{A4+CA4'}$), 137.2 ($C^{C3'}$), 136. 9 ($C^{C6'}$), 136.2 (C^{C4}), 134.5 ($C^{C2'}$), 133.8 (C^{C3}), 133.1 ($C^{C1'}$), 130.8 ($C^{C4'}$), 130.0 ($C^{C5'}$), 128.6 ($C^{A5/A5'}$), 128.4 ($C^{A5/A5'}$), 125.6 ($C^{A3/A3'}$), 125.3 (C^{C5}), 122.83 ($C^{B3/B3'}$), 122.78 ($C^{B3/B3'}$). LR-ESI-MS (in MeOH): *m/z* 938.10 [(MeOBOMe)PF_6 adduct]$^+$ requires 938.16; 924.16 [(MeOBOH)PF_6 adduct]$^+$ requires 924.15; 396.72 [(MeOBOMe) adduct]$^{2+}$ requires 396.60; 389.74 [(MeOBOH) adduct]$^{2+}$ requires 389.59. HR-ESI-MS (in MeOH): *m/z* 938.1621 [(MeOBOMe)PF_6 adduct]$^+$ requires 938.1488; 924.1337 [(MeOBOH)PF_6 adduct]$^+$ requires 924.1464; 396.5927 [(MeOBOMe) adduct]$^{2+}$ requires 396.5989; 389.5859 [(MeOBOH) adduct]$^{2+}$ requires 389.5911.

ACCEPTED MANUSCRIPT

2.11 *[Ru(**5b**)(**4**)](PF$_6$)$_2$*

The preparation of [Ru(**5b**)(**4**)](PF$_6$)$_2$ was the same as for [Ru(**1**)(**3**)](PF$_6$)$_2$, starting with Ru(**5a**)Cl$_3$ (0.10 g, 0.16 mmol) and ligand **4** (0.05 g, 0.17 mmol). [Ru(**5b**)(**4**)](PF$_6$)$_2$ was isolated as a red solid (59 mg, 56 μmol, 35%). ^{1}H NMR (400 MHz, CD$_3$CN) δ 9.05 (s, 2H, H^{B3}), 9.04 (s, 2H, H$^{B3'}$), 8.97 (d, *J* = 5.2 Hz, 2H, H^{C2}), 8.70 – 8.62 (m, 4H, H $^{A3+A3'}$), 8.58 (s, 1H, H$^{C2'}$), 8.26 (d, *J* = 7.8 Hz, 1H, H$^{C4'}$), 8.13 (d, *J* = 5.3 Hz, 2H, H^{C3}), 8.07 (d, *J* = 7.4 Hz, 1H, H$^{C6'}$), 8.01 – 7.90 (m, 4H, H$^{A4+A4'}$), 7.78 (t, *J* = 7.6 Hz, 1H, H$^{C5'}$), 7.52 – 7.35 (m, 4H, H$^{A6+A6'}$), 7.25 – 7.14 (m, 4H, H$^{A5+A5'}$), 6.42 (s, 2H, B(OH)$_2$). ^{13}C NMR (75 MHz, CD$_3$CN) δ 159.2 (C$^{A2/A2'}$), 159.0 (C$^{A2/A2'}$), 156.9 (C$^{B2/B2'}$), 156.3 (C$^{B2/B2'}$), 153.5 (C$^{A6+A6'}$), 152.1 (C^{C2}), 150.0 (C$^{C3'}$), 146.2 (C^{C4}), 145.1 (C^{B4}), 139.2 (C$^{A4/A4'}$), 139.1 (C$^{A4/A4'}$), 137.2 (C$^{B4'}$), 136.9 (C$^{C6'}$), 134.5 (C$^{C2'}$), 132.9 (C$^{C1'}$), 130.8 (C$^{C4'}$), 130.0 (C$^{C5'}$), 128.6 (C$^{A5/A5'}$), 128.4 (C$^{A5/A5'}$), 125.7 (C$^{A3/A3'}$), 125.6 (C$^{A3/A3'}$), 122.9 (C^{C3}), 122.9 (C^{B3}), 122.8 (C$^{B3'}$). LR-ESI-MS (in MeOH): *m/z* 938.12 [(MeOBOMe)PF$_6$ adduct]$^+$ requires 938.16; 924.16 [(MeOBOH)PF$_6$ adduct]$^+$ requires 924.15; 396.70 [(MeOBOMe) adduct]$^{2+}$ requires 396.60; 389.74 [(MeOBOH) adduct]$^{2+}$ requires 389.59. *Anal.* found: C, 44.81; H, 2.70; N, 8.84 %. Calc. for C$_{41}$H$_{30}$F$_{12}$N$_7$O$_2$P$_2$Ru·2.4H$_2$O: C, 45.30; H, 3.23; N, 9.02.

2.12 *[Ru(**6b**)(**3**)](PF$_6$)$_2$*

The preparation of [Ru(**6b**)(**3**)](PF$_6$)$_2$ was the same as for [Ru(**1**)(**3**)](PF$_6$)$_2$, starting with Ru(**6a**)Cl$_3$ (0.10 g, 0.16 mmol) and ligand **3** (0.05 g, 0.17 mmol). [Ru(**6b**)(**3**)](PF$_6$)$_2$ was isolated as a red solid (62 mg, 59 μmol, 37%). ^{1}H NMR (400 MHz, CD$_3$CN) δ 9.39 (d, *J* = 2.6 Hz, 1H, H^{C2}), 9.04 (s, 2H, H^{B3}), 9.04 (s, 2H, H$^{B3'}$), 8.86 (dd, *J* = 4.8, 1.6 Hz, 1H, H^{C6}), 8.70 – 8.60 (m, 4H, H$^{A3+A3'}$), 8.53 (ddd, *J* = 8.0, 2.5, 1.6 Hz, 1H, H^{C4}), 8.21 (d, *J* = 7.8 Hz, 1H, H$^{C3'}$), 8.14 (d, *J* = 7.7 Hz, 1H, H$^{C2'}$), 8.00 – 7.91 (m, 4H, H$^{A4+A4'}$), 7.74 (dd, *J* = 7.9, 4.8 Hz, 1H, H^{C5}), 7.50 – 7.37 (m, 4H,H$^{A6+A6'}$), 7.24 – 7.15 (m, 4H, H$^{A5+A5'}$), 6.52 (s, 2H, B(OH)$_2$). ^{13}C NMR (101 MHz, CD$_3$CN) δ 159.2 (C$^{A2/A2'}$), 159.0 (C$^{A2/A2'}$), 156.7 (C$^{B2/B2'}$), 156.4 (C$^{B2/B2'}$), 153.48 (C$^{A6/A6'}$), 153.45 (C$^{A6/A6'}$), 152.2 (C$^{C1'}$), 149.7 (C^{C2}), 149.3 (C$^{C4'}$), 146.3 (C^{B4}), 139.6 (C$^{B4'}$), 139.1 (C$^{A4/A4'}$), 139.1 (C$^{A4/A4'}$), 136.2 (C$^{C4/C2'}$), 133.7 (C^{C3}), 128.6 (C$^{A5/A5'}$), 128.5 (C$^{A5/A5'}$), 128.0 (C$^{C3'}$), 125.6 (C$^{A3+A3'}$), 125.3 (C^{C5}), 122.8 (C$^{B3/B3'}$), 122.7 (C$^{B3/B3'}$). LR-ESI-MS (in MeOH): *m/z* found 938.14 [(MeOBOMe)PF$_6$ adduct]$^+$ requires 938.16; 924.14 [(MeOBOH)PF$_6$ adduct]$^+$ requires 924.15; 396.72 [(MeOBOMe) adduct]$^{2+}$ requires 396.60; 389.72 [(MeOBOH) adduct]$^{2+}$ requires 389.59. *Anal.* found: C, 45.55; H, 2.75; N, 9.11 %. Calc. for C$_{41}$H$_{30}$F$_{12}$N$_7$O$_2$P$_2$Ru·2.5H$_2$O: C, 45.23; H, 3.24; N, 9.01.

2.13 *[Ru(**6b**)(**4**)](PF$_6$)$_2$*

The preparation of [Ru(**6b**)(**4**)](PF$_6$)$_2$ was the same as for [Ru(**1**)(**3**)](PF$_6$)$_2$, starting with Ru(**6a**)Cl$_3$ (0.10 g, 0.16 mmol) and ligand **4** (0.05 g, 0.17 mmol). [Ru(**6b**)(**4**)](PF$_6$)$_2$ was isolated as a red solid (71 mg, 67 μmol, 42%). ^{1}H NMR (400 MHz, CD$_3$CN) δ 9.05 (s, 2H, H^{B3}), 9.04 (s, 2H, H$^{B3'}$), 8.97 (d, *J* = 5.2 Hz, 2H, H^{C2}), 8.70 – 8.62 (m, 4H, H$^{A3+A3'}$), 8.24 – 8.10 (m, 6H, 2H^{C3}+ 4H$^{C2'+C3'}$), 8.01 – 7.91 (m, 4H, H$^{A4+A4'}$), 7.50 – 7.37 (m, 4H, H$^{A6+A6'}$), 7.24 – 7.14 (m, 4H, H$^{A5+A5'}$), 6.23 (s, 2H, B(OH)$_2$). ^{13}C NMR (151 MHz, CD$_3$CN) δ 159.1 (C$^{A2/A2'}$), 158.9 (C$^{A2/A2'}$), 156.9 (C$^{B2/B2'}$), 156.4 (C$^{B2/B2'}$), 154.3 (C$^{C1'}$), 153.5 (C$^{A6+A6'}$), 152.1 (C^{C2}), 149.5 (C$^{C4'}$), 146.2 (C^{C4}), 145.1 (C^{B4}), 139.5 (C$^{B4'}$), 139.2 (C$^{A4/A4'}$), 139.1 (C$^{A4/A4'}$), 136.2 (C$^{C2'}$), 128.6 (C$^{A5/A5'}$), 128.5 (C$^{A5/A5'}$), 128.0 (C$^{C3'}$), 125.7 (C$^{A3/A3'}$), 125.6 (C$^{A3/A3'}$), 122.9 (C$^{B3/B3'}$), 122.8 (C$^{B3/B3'}$). LR-ESI-MS (in MeOH): *m/z* 938.12 [(MeOBOMe)PF$_6$

ACCEPTED MANUSCRIPT

adduct]$^{+}$ requires 938.16; 924.16 [(MeOBOH)PF_6 adduct]$^{+}$ requires 924.15; 396.72 [(MeOBOMe) adduct]$^{2+}$ requires 396.60; 389.72 [(MeOBOH) adduct]$^{2+}$ requires 389.59. HR-ESI-MS (in MeOH): *m/z* 938.1621 [(MeOBOMe)PF_6 adduct]$^{+}$ requires 938.1488; 924.1337 [(MeOBOH)PF_6 adduct]$^{+}$ requires 924.1464; 396.5927 [(MeOBOMe) adduct]$^{2+}$ requires 396.5989; 389.5859 [(MeOBOH) adduct]$^{2+}$ requires 389.5911.

3 Results and Discussion

The ligands used in this study are shown in Figure 1, and have all been reported previously.

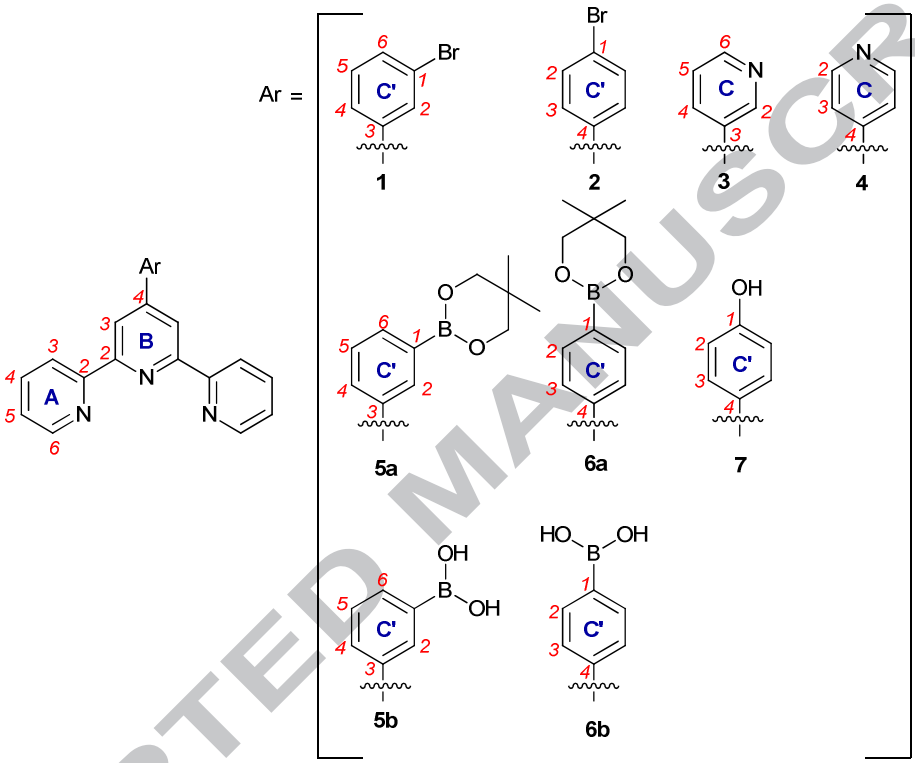


Figure 1 Ligands used in this study and the numbering scheme adopted. Ligands **1**,[12] **2**,[13] **3**,[14] **4**,[15] **5a**,[16] **5b**,[6c] **6a**,[11b] **6b**[17] and **7**[12] have been previously reported.

3.1 *Ligand synthesis*

The 2,2':6',2" terpyridine ligands (**1**-**4**) were prepared using the one-pot method reported by Hanan (Figure 2).[18] Specifically, reaction of 2-acetyl pyridine, the appropriate aryl aldehyde, aqueous ammonia and potassium hydroxide in ethanol gave ligands **1**-**4** as pure white microcrystalline solids in isolated yields of 33-43%.

ACCEPTED MANUSCRIPT

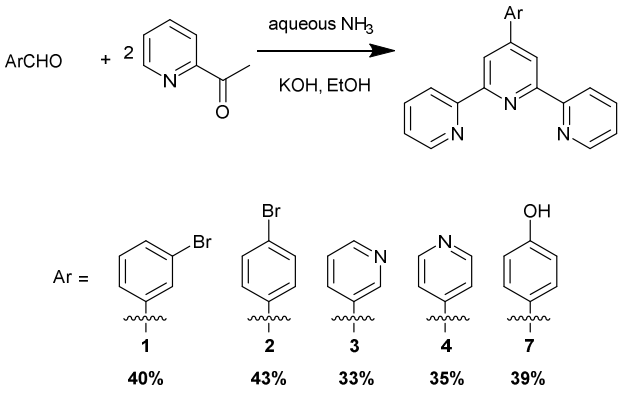


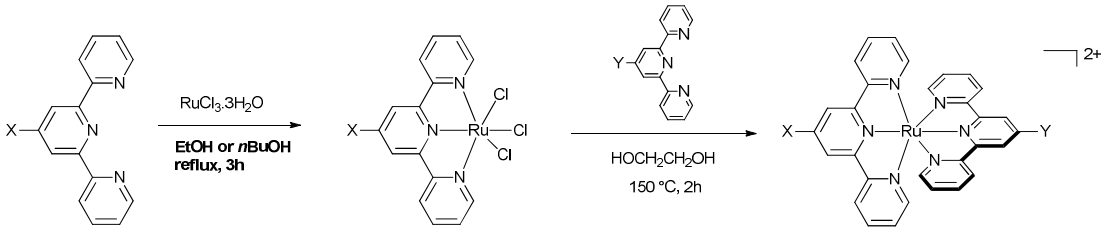
Figure 2 Ligands **1-4** and **7** were prepared using the one-pot method reported by Hanan.[18]

The boronic esters **5a** and **6a**[11b] were prepared from the corresponding 3-bromophenyl (**1**) or 4-bromophenyl (**2**) functionalized terpyridine ligands following reported procedures.[11b] Specifically, 3- or 4-bromophenyl terpyridine (ligands **1** or **2**) was treated with potassium acetate, bis(neopentyl glycolato)diboron and Pd(dppf)Cl_2 in DMSO at 80 ℃ for 5.5 h under argon to yield white solids in 55% and 60% yield respectively.[11b] Bis(neopentyl glycolato)diboron was used in preference to bis(pinacolato)diboron as it has been reported to readily hydrolyze to the boronic acid,[11b] increasing the reactivity of this functional group.

3.2 *Ruthenium(II) complex synthesis and characterization*

The reaction of $RuCl_3.3H_2O$, a starting material of ill-defined composition,[19a] and one equivalent of a terpyridine ligand (Xtpy = a tpy derivative) in refluxing alcohols (ethanol, *n*-butanol etc.) typically results in complexes of the type Ru(Xtpy)Cl_3 as insoluble brown/black solids (Figure 3a). Although recent progress has allowed these types of complexes to be prepared and characterized in detail[19b], characterization of the complexes prepared in this study was difficult due to solubility problems, and therefore these were used in subsequent steps without further purification or analysis, as reported in previous studies.[20] Where ligands **5a** or **6a** where used, microanalysis and FTIR spectroscopy supports the formation of Ru(Xtpy)Cl_3 salts as their boronic esters, with no evidence for hydrolysis to form boronic acids (see SI for details). The reaction of a suspension of Ru(Xtpy)Cl_3 and one equivalent of a second terpyridine derivative (Ytpy) in ethylene glycol at 150 ℃ for 2h gave intensely colored red solutions. Anion exchange with potassium hexafluorophosphate, followed by column chromatography and work up gave pure ruthenium complexes of the type [Ru(Xtpy)(Ytpy)]$(PF_6)_2$ in yields of 20-33% over two steps (Figure 3b).

ACCEPTED MANUSCRIPT



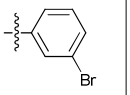
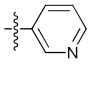
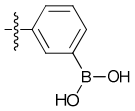
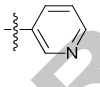
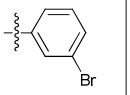
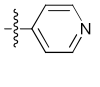
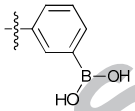
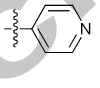
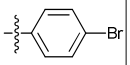
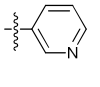
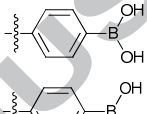
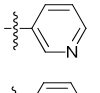
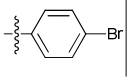
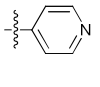
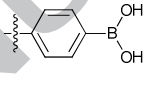
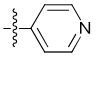
Complex	X =	Y =	Yield*	Complex	X =	Y =	Yield*
[Ru(**1**)(**3**)](PF$_6$)$_2$			33%	[Ru(**5b**)(**3**)](PF$_6$)$_2$			20%
[Ru(**1**)(**4**)](PF$_6$)$_2$			34%	[Ru(**5b**)(**4**)](PF$_6$)$_2$			24%
[Ru(**2**)(**3**)](PF$_6$)$_2$			29%	[Ru(**6b**)(**3**)](PF$_6$)$_2$			26%
[Ru(**2**)(**4**)](PF$_6$)$_2$			32%	[Ru(**6b**)(**4**)](PF$_6$)$_2$			30%

Figure 3 Synthetic route to heteroleptic Ru(II) complexes prepared in this study. *Yields are given over 2 steps.

In the case of complexes prepared from ligands **5a** or **6a**, which feature boronic ester groups, ^{1}H NMR and electrospray ionization mass spectrometry (ESI-MS) confirmed the hydrolysis of the ester groups to form boronic acids. Similar behavior has been reported previously.[11b] The addition of the reducing agent 4-ethylmorpholine to the second complexation reaction, as is commonly performed,[21] was found to result poor yields in the cases of boronic ester substituted terpyridine ligands. In all cases short reaction times proved important for the isolation of the desired heteroleptic complexes. The ruthenium(II) complexes were characterized by ^{1}H and ^{13}C NMR, ESI-MS and elemental analysis.

3.3 *Mass Spectrometry characterization*

Electrospray ionization mass spectrometry (ESI-MS) was used to identify charged ions for each complex. For complexes not containing boronic ester groups, peaks corresponding to $[M–PF_6]^+$ and $[M–2PF_6]^{2+}$ were observed when ionized from acetonitrile solutions, with isotope patterns matching that for the calculated ions (see Supplementary Information for details). By comparison, complexes containing boronic acids were only found to show meaningful signals when methanol was used as the solvent for ESI-MS, with the adducts corresponding to $[M\text{-B(OMe)}_2 + PF_6]^+$, $[M\text{-B(OH)(OMe)} + PF_6]^+$, $[M\text{-B(OMe)}_2]^{2+}$, $[M\text{-B(OH)(OMe)}]^{2+}$ being observed, where M = the complex in question. For example, for [Ru(**6b**)(**4**)](PF$_6$)$_2$ the series of peaks were observed (calc.) at *m/z* 938.12 (938.16), 924.16 (924.15), 396.72 (396.60) and 389.72 (389.59) *m/z* with isotope distributions and peak separations consistent with the theoretical values (see Supplementary Information for details).

ACCEPTED MANUSCRIPT

3.4 *Nuclear Magnetic Resonance (NMR) characterization*

NMR spectra of all new compounds were assigned using ^{1}H NMR, ^{13}C NMR, COSY, HSQC, HMBC and NOESY techniques in CD_3CN. The ^{1}H NMR spectra of all complexes are shown in Figure 4.

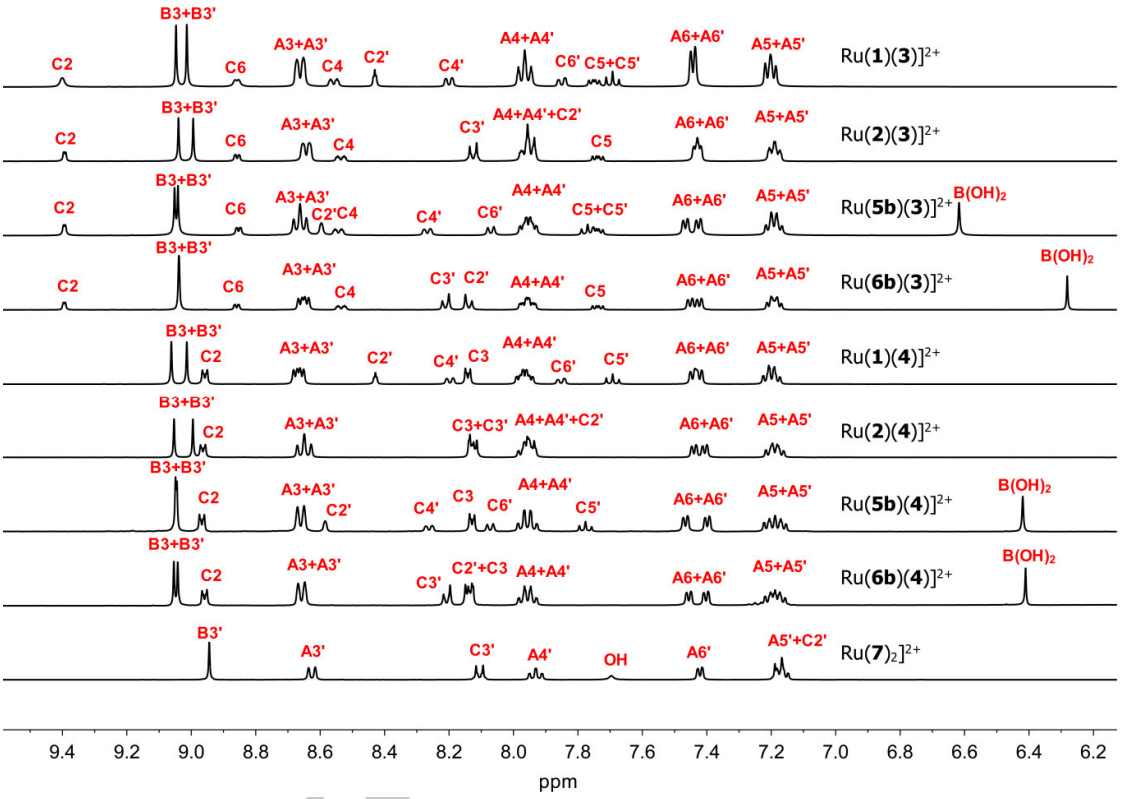


Figure 4 ^{1}H NMR spectra (400 MHz, CD_3CN, 298K) for Ru(II) complexes synthesized in this study. Top to bottom: [Ru(**1**)(**3**)]$(PF_6)_2$; [Ru(**2**)(**3**)]$(PF_6)_2$; [Ru(**5b**)(**3**)]$(PF_6)_2$; [Ru(**6b**)(**3**)]$(PF_6)_2$; [Ru(**1**)(**4**)]$(PF_6)_2$; [Ru(**2**)(**4**)]$(PF_6)_2$; [Ru(**5b**)(**4**)]$(PF_6)_2$; [Ru(**6b**)(**4**)]$(PF_6)_2$ and [Ru(**7**)$_2$]$(PF_6)_2$. See Figure 1 for labelling scheme adopted.

The proton NMR signals for the metal binding terpyridine units show a very similar pattern across all complexes studied. Due to closely overlapping multiplets, the assignment of signals corresponding to the terminal pyridyl rings of the terpyridine units (H^{A3}, H^{A4}, H^{A5} and H^{A6}) to each ligand was generally not feasible. The H^{B3} signals, which are expected to be more influenced by substituents in the B4 position, show greater variation and could be assigned for the 3-bromophenyl- or 4-bromophenyl- ligands (**1** and **2**). However for the boronic acid analogues (ligands **5b**, **6b**), these H^{B3} signals invariably occurred very close to the H^{B3} of the 3-pyridyl or 4-pyridyl functionalized terpyridine on the other side of the Ru(II) center. Ligands **3** and **4** both have two coordination domains: the pendant pyridyl group and the terpyridine domain. In each example containing the 3-pyridyl functionalized ligand **3** the ^{1}H NMR signals (δ/ppm: H^{C2} 9.39; H^{C6} 8.86; H^{C4} 8.53; H^{C5} 7.69) are effectively independent of the other terpyridine ligand coordinated to the Ru(II) center. Similarly, the ^{1}H NMR signals

ACCEPTED MANUSCRIPT

corresponding to the pendant 4-pyridyl group of ligand **4** are constant for each complex containing this ligand (δ/ppm: H^{C2} 8.97; H^{C3} 8.13). ^{13}C NMR also confirmed that both of these pyridyl units are independent of the other ligand coordinated to the metal center. For complexes containing the 4-bromophenyl functionalized ligand **2**, signals corresponding to $H^{C2'}$ and $H^{C3'}$ were distinguished by the appearance in the NOESY spectrum of a cross peak between $H^{B3'}$ and $H^{C3'}$. Similar analysis can also distinguish the signals for $H^{C4'}$and $H^{C6'}$ of the 3-bromophenyl functionalized ligand **1**, which appear at 8.19 ppm and 7.86 ppm. For the 3- or 4-boronic acid functionalized phenyl rings of ligands **5b** and **6b**, the signals around the phenyl ring were identified based on chemical shift and coupling patterns, and NOESY cross peaks similar to those discussed above. The $B(OH)_2$ protons of this complexes, which are pH dependent, appear in the ^1H NMR as a sharp singlet in the range from 6.2 ppm and 6.6 ppm.

3.5 *Electronic spectroscopy and Electrochemical Characterization*

The UV-visible absorption spectra of all complexes were recorded in acetonitrile. The complexes each exhibit an intense MLCT absorption around 490 nm, typical of Ru(4'-Artpy)$_2^{2+}$ (Ar = aromatic) complexes, as well as higher energy ligand centred transitions. As is well established for homoleptic complexes containing ligand **4**,[15b, 21, 22] the absorption spectra of all the complexes reported here are sensitive to protonation. The spectra of those complexes with bromophenyl-functionalised ligands (i.e. Ru(**1**)(**3**)$^{2+}$, Ru(**1**)(**4**)$^{2+}$, Ru(**2**)(**3**)$^{2+}$, Ru(**2**)(**4**)$^{2+}$) have effectively identical absorption spectra, in close agreement with the homoleptic complexes (see Table 1). Those complexes featuring boronic acid groups (i.e. Ru(**5b**)(**3**)$^{2+}$, Ru(**5b**)(**4**)$^{2+}$, Ru(**6b**)(**3**)$^{2+}$, Ru(**6b**)(**4**)$^{2+}$) showed concentration dependent spectra, with the emergence of shoulder at higher energy (455 nm) upon dilution. This band is significantly and reproducibly more intense for the 4-pyridyl derivatives than the 3-pyridyl derivatives. While it is not clear the origin of this band, it may be due to deprotonation of the boronic acid groups at low concentrations, or photodecomposition due to the relatively high flux of light within the spectrometer.

The cyclic voltammograms of each complex were recorded in acetonitrile and the data is presented in Table 1. As data for the homoleptic complexes of the 3-bromophenyl- and 4-bromophenyl ligands do not appear to be reported, we recorded these as references. For the bromophenyl derivatives (Ru(**1**)$_2^{2+}$ and Ru(**2**)$_2^{2+}$) the $Ru^{II/III}$ redox potential were +0.88 (*vs* Fc/Fc^+) in both cases, essentially identical to that of Ru(tpyPh)$_2^{2+}$ (tpyPh = 4'-phenyl-2,2':6',2''-terpyridine) and significantly lower potential than for the homoleptic 3-pyridyl and 4-pyridyl analogues (Ru(**3**)$_2^{2+}$ and Ru(**4**)$_2^{2+}$ +0.95 and +0.96 V respectively).[15b]

ACCEPTED MANUSCRIPT

Table 1 Electrochemical[a] and absorption data[b]

	$M^{2+/3+}$ (V *vs* Fc/Fc^+)	Ligand reductions[c] (V *vs* Fc/Fc^+)			MLCT λ_{max} /nm (ε / $10^3 dm^3\ mol^{-1}\ cm^{-1}$)	Ref.
$[Ru(tpy)_2](PF_6)_2$[d]	+0.92	-1.67	-1.92		475 (10.4)	[15b, 20]
$[Ru(tpyPh)_2](PF_6)_2$[d]	+0.90	-1.66	-1.92		487 (26.2)	[15b, 20]
$[Ru(\mathbf{1})_2](PF_6)_2$	+0.88	-1.58	-1.81	-2.35	489 (24.0)	This work
$[Ru(\mathbf{2})_2)](PF_6)_2$	+0.88	-1.59	-1.80		489 (24.6)	[31]
$[Ru(\mathbf{3})_2)](PF_6)_2$	+0.96	-1.25	-1.73		489 (30.8)	[21]
$[Ru(\mathbf{4})_2)](PF_6)_2$	+0.95	-1.54	-1.80		488 (30.9)	[15b]
$[Ru(\mathbf{2})(\mathbf{4})](PF_6)_2$	+0.88	-1.59	-1.82	-2.21	490 (26.2)	This work
$[Ru(\mathbf{2})(\mathbf{3})]\ (PF_6)_2$	+0.89	-1.61	-1.84	-2.31	490 (24.4)	This work
$[Ru(\mathbf{1})(\mathbf{4})]\ (PF_6)_2$	+0.88	-1.59	-1.81	-2.23	490 (23.6)	This work
$[Ru(\mathbf{1})(\mathbf{3})]\ (PF_6)_2$	+0.89	-1.60	-1.78	-2.40[irr]	490 (22.3)	This work
$[Ru(\mathbf{6b})(\mathbf{4})]\ (PF_6)_2$	+0.90	-1.59	-1.81	-2.30	490 (23.1)	This work
$[Ru(\mathbf{6b})(\mathbf{3})]\ (PF_6)_2$	+0.90	-1.61	-1.86	-2.38[irr,e]	490 (21.7)	This work
$[Ru(\mathbf{5b})(\mathbf{4})]\ (PF_6)_2$	+0.89	-1.60	-1.75	-2.29	490 (23.1)	This work
$[Ru(\mathbf{5b})(\mathbf{3})]\ (PF_6)_2$	+0.89	-1.60	-1.81	-2.23	490 (23.3)	This work

[a]All measurements in MeCN [*n*BuN]PF_6, with a glassy carbon working electrode, platinum counter electrode and silver wire reference. [b] All data recorded in MeCN at concentrations below 3.4 x 10^{-6} mol.L^{-1} [c]All processes are reversibly, except where noted irr = irreversible. [d] tpy = 2,2':6',2''-terpyridine; tpyPh = 4'-phenyl-2,2':6',2''-terpyridine. [e] Two irreversible processes at -2.38 and -2.40V

3.6 *Stability of Ru(II) complexes*

All new compounds were found to be stable during the workup (column chromatography with silica gel, washing with water, ethanol and ether) at room temperature. Aryl bromo functionalized complexes were stable in air, at room temperature for months. The synthesis of boronic acid functionalized ruthenium(II) complexes was repeated reliably many times in our hands. However, anion exchange using ammonium hexafluorophosphate appeared to result in decomposition of the boronic acid groups, confirmed by the disappearance of the ^1H NMR signals for $B(OH)_2$ and the appearance of new aromatic signals, which do not correspond to the hydroxylated product (see below), and could not be identified (See Fig S34). No such decomposition products were observed when potassium hexafluorophosphate was used for anion exchange. Complexes with boronic acid groups were routinely collected as red solids which could not be dissolved in acetonitrile. Attempts to dissolve these materials by addition of dilute hydrochloric acid or trifluoroacetic acid also led to decomposition of the boronic acid group. Most importantly, the boronic acid functionalized complexes were found to be unstable when stored for weeks, even in the fridge. Previous reports show that the oxidative hydroxylation of aryl boronic acids to form phenols can be photocatalyzed by $Ru(bpy)_3Cl_2$ (bpy = 2,2'-bipyridine) and visible light,[24] as well as by $CuCl_2$,[25]

ACCEPTED MANUSCRIPT

palladium(II) phosphine complexes,[26] or non-metal oxidants such as hydrogen peroxide,[27] Oxone,[28] *N*-oxides[29] or hydroxylamine.[30] Similar reactions appear to occur to the Ru(II) complexes presented here which feature boronic acid groups, although the exact mechanism remains unclear. Due to the hydroxylation, the result of elemental analysis was not always satisfactory, but NMR spectra are consistent with the assigned structures.

To confirm that the isolated complexes were indeed the boronic acid derivatives, and not the phenol decomposition products, 4'-(4-phenol)-2,2':6',2''-terpyridine (**7**) was synthesized according the literature[18] and the homoleptic compound $[Ru(\mathbf{7})_2](PF_6)_2$ was prepared as a reference using the same method as for the other complexes reported here. The spectroscopic data was consistent with the literature,[31] except for the pH sensitive OH peak. The ^{1}H NMR signals of the $H^{C2'}$ protons of $[Ru(\mathbf{6b})(\mathbf{3})]^{2+}$ and $[Ru(\mathbf{6b})(\mathbf{4})]^{2+}$ both occur at 8.14 ppm, whereas the equivalent peak for $[Ru(\mathbf{7})_2]^{2+}$ appears at 7.17 ppm, overlapping with the signal of $H^{A5'}$. The broad peak which integrates as 1H at 7.70 ppm corresponding to the OH group is significantly different to the signal integrating as 2H for $B(OH)_2$ which is observed between 6.6 – 6.2 ppm and provides additional evidence for the isolation of the boronic acid functionalized complexes.

3.7 *Conclusions*

Eight new heteroleptic Ru(II) complexes of terpyridine ligands are reported. Those terpyridine ligands featuring boronic esters were hydrolyzed to form boronic acids upon coordination to Ru(II) center. Furthermore, the resulting boronic acid functionalized complexes were unstable with respect to hydroxylation to form the corresponding phenols. The complexes reported here are suitable for Suzuki cross coupling reactions[9, 11] to form dimetallic expanded ligands,[8] provided they are reacted soon after preparation. The bromo-functionalized complexes are stable and also suitable for other Pd(0) catalyzed cross coupling reactions.[9, 11b] The construction of large supramolecular structures from these building blocks is currently under investigation.

Acknowledgements

This work was supported by a National Science Foundation of China (NSFC) Research Fund for International Young Scientists Project (No. 21450110060) and the University of New South Wales (UNSW Australia).

[1]. For recent examples of $[Ru(tpy)_2]^{2+}$ as a photosensitizer, see a) D. Hvasanov, J. R. Peterson and P. Thordarson, Chem. Sci., 2013, **4**, 3833-3838; b) A. Breivogel, C. Kreitner and K. Heinze, Eur. J. Inorg. Chem., 2014, **2014**, 5468-5490.

[2]. For recent examples of $[Ru(tpy)_2]^{2+}$ units as potential building blocks, see a) J. Veliks, O. Blacque and J. S. Siegel, Inorg. Chem., 2014, **53**, 12122-12126; b) J. Veliks, J.-C. Tseng, K. I. Arias, F. Weisshar, A. Linden and J. S. Siegel, Chem. Sci., 2014, **5**, 4317-4327; c) A. K. Pal, B. Laramee-Milette, G. S. Hanan, RSC Advances **2014**, *4*, 21262-21266.

[3]. For examples of coordination polymers containing $[Ru(tpy)_2]^{2+}$ units, see a) J. E.

ACCEPTED MANUSCRIPT

Beves, E. C. Constable, C. E. Housecroft, C. J. Kepert and D. J. Price, CrystEngComm, 2007, **9**, 456-459; b) J. E. Beves, E. C. Constable, C. E. Housecroft, C. J. Kepert, M. Neuburger, D. J. Price, S. Schaffner and J. A. Zampese, Dalton Trans., 2008, 6742-6751; c) J. E. Beves, E. C. Constable, S. Decurtins, E. L. Dunphy, C. E. Housecroft, T. D. Keene, M. Neuburger and S. Schaffner, CrystEngComm, 2008, **10**, 986-990; d) J. E. Beves, D. J. Bray, J. K. Clegg, E. C. Constable, C. E. Housecroft, K. A. Jolliffe, C. J. Kepert, L. F. Lindoy, M. Neuburger, D. J. Price, S. Schaffner and F. Schaper, Inorg. Chim. Acta, 2008, **361**, 2582-2590.

[4]. For examples of coordination networks incorporating $[Ru(tpy)_2]^{2+}$ units, see ref 3c and I. Eryazici, O. K. Farha, O. C. Compton, C. Stern, J. T. Hupp and S. T. Nguyen, Dalton Trans., 2011, **40**, 9189-9193.

[5]. For examples of macrocycles formed with $[Ru(tpy)_2]^{2+}$ units, see Ref 2c and a) G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, R. Cush and P. S. Russo, Angew. Chem., Int. Ed., 1999, **38**, 3717-3721; b) S.-H. Hwang, C. N. Moorefield, F. R. Fronczek, O. Lukoyanova, L. Echegoyen and G. R. Newkome, Chem. Commun., 2005, 713-715; c) S.-H. Hwang, P. Wang, C. N. Moorefield, L. A. Godinez, J. Manriquez, E. Bustos and G. R. Newkome, Chem. Commun., 2005, 4672-4674.

[6]. For discrete molecular cages containing Ru(II) polypyridyl complexes, see a) A. J. Metherell and M. D. Ward, Chem. Commun., 2014, **50**, 10979-10982; b) A. J. Metherell and M. D. Ward, Chem. Commun., 2014, **50**, 6330-6332; c) T.-Z. Xie, S.-Y. Liao, K. Guo, X. Lu, X. Dong, M. Huang, C. N. Moorefield, S. Z. D. Cheng, X. Liu, C. Wesdemiotis and G. R. Newkome, J. Am. Chem. Soc., 2014, **136**, 8165-8168.

[7]. For a review of self-assembled discrete metallosupramolecular luminophores see a) M. W. Cooke, D. Chartrand and G. S. Hanan, Coord. Chem. Rev., 2008, **252**, 903-921. For a review of the photophysical properties of $Ru(tpy)_2^{2+}$ and related complexes, see b) A. K. Pal and G. S. Hanan, Chem. Soc. Rev., 2014, **43**, 6184-6197. For recent examples of other polynuclear assemblies containing Ru(II) polypyridyl complexes, c) G. R. Newkome, T. J. Cho, C. N. Moorefield, R. Cush, P. S. Russo, L. A. Godínez, M. J. Saunders and P. Mohapatra, Chem.- Eur. J., 2002, **8**, 2946-2954; d) G. R. Newkome, T. J. Cho, C. N. Moorefield, P. P. Mohapatra and L. A. Godínez, Chem.- Eur. J., 2004, **10**, 1493-1500; e) I. Eryazici and G. R. Newkome, New J. Chem., 2009, **33**, 345 - 357; f) A. Schultz, X. Li, B. Barkakaty, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, J. Am. Chem. Soc., 2012, **134**, 7672-7675; g) Lu, X.; Li, X.; Guo, K.; Xie, T.-Z.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. J. Am. Chem. Soc. **2014**, *136*, 18149..

[8]. E. C. Constable, Coord. Chem. Rev., 2008, **252**, 842-855.

[9]. J. Yang, J. K. Clegg, Q. Jiang, X. Lui, H. Yan, W. Zhong and J. E. Beves, Dalton Trans., 2013, **42**, 15625-15636.

[10]. For examples of self-assembly using Pd(II) centers with pyridine ligands, see a) M. Fujita, M. Tominaga, A. Hori and B. Therrien, Acc. Chem. Res., 2005, **38**, 369-378; b) Y. Inokuma, M. Kawano and M. Fujita, Nature Chem., 2011, **3**, 349-358; c) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, Chem. Rev., 2011, **111**, 6810-6918.

[11]. For examples of Pd(0) mediated couplings on metal complexes, see a) C. Patoux, J.-P. Launay, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, S. James and J.-P. Sauvage, J. Am. Chem. Soc., 1998, **120**, 3717-3725; b) C. J. Aspley and J. A. G. Williams, New J. Chem., 2001, **25**, 1136-1147; c) K. J. Arm and J. A. G. Williams, Dalton Trans., 2006, 2172-2174; d) Y.-W. Zhong, N. Vila, J. C. Henderson, S. Flores-Torres and H. D. Abruna, Inorg. Chem., 2007, **46**, 10470-10472; e) O. Johansson and R. Lomoth, Inorg. Chem., 2008, **47**, 5531-5533; f) W. Leslie, A. S. Batsanov, J. A. K. Howard and J. A. G. Williams, Dalton Trans., 2004, 623-631; g) V. L. Whittle and J. A. G.

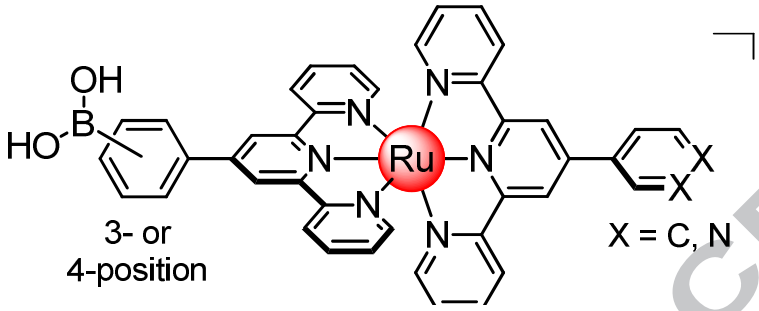
ACCEPTED MANUSCRIPT

Williams, Inorg. Chem., 2008, **47**, 6596-6607; h) V. L. Whittle and J. A. G. Williams, Dalton Trans., 2009, 3929-3940.
[12]. W. Spahni and G. Calzagerri, Helv. Chim. Acta, 1984, **67**, 450-454.
[13]. S. Bonnet, J.-P. Collin and J.-P. Sauvage, Chem. Commun., 2005, 3195-3197.
[14]. W. Goodall and J. A. G. Williams, J. Chem. Soc., Dalton Trans., 2000, 2893-2895.
[15]. a) E. C. Constable and A. M. W. C. Thompson, J. Chem. Soc., Dalton Trans., 1992, 2947-2950; b)E. C. Constable and A. M. W. C. Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 1409-1418.
[16]. F. Wehmeier and J. Mattay, Beilstein Journal of Organic Chemistry, 2010, **6**, 53.
[17]. M. Vrábel, M. Hocek, L. Havran, M. Fojta, I. Votruba, B. Klepetářová, R. Pohl, L. Rulíšek, L. Zendlová, P. Hobza, I. h. Shih, E. Mabery and R. Mackman, Eur. J. Inorg. Chem., 2007, 1752-1769.
[18]. J. Wang and G. S. Hanan, Synlett, **2005**, 1251-1254.
[19]. a) H.-J. Cantow, H. Hillebrecht, S. N. Magonov, H. W. Rotter, M. Drechsler and G. Thiele, Angew. Chem., Int. Ed. Engl., 1990, **29**, 537-541. For a detailed report on the selective synthesis and characterization of $Ru(tpy)Cl_3$ complexes, see b) M.-P. Santoni, A. K. Pal, G. S. Hanan, A. Proust and B. Hasenknopf, *Inorg. Chem. Commun.*, 2011, **14**, 399-402.
[20]. M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. C. Thompson, Inorg. Chem., 1995, **34**, 2759-2767.
[21]. J. E. Beves, E. L. Dunphy, E. C. Constable, C. E. Housecroft, C. J. Kepert, M. Neuburger, D. J. Price and S. Schaffner, Dalton Trans., 2008, 386-396.
[22]. E. C. Constable, C. E. Housecroft, A. C. Thompson, P. Passaniti, S. Silvi, M. Maestri and A. Credi, Inorg. Chim. Acta, 2007, **360**, 1102-1110.
[23]. V. Duprez, M. Biancardo, H. Spanggaard and F. C. Krebs, Macromolecules, 2005, **38**, 10436-10448.
[24]. Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R. L. Davis, K. A. Jørgensen and W.-J. Xiao, Angew. Chem., Int. Ed., 2012, **51**, 784-788.
[25]. K. Inamoto, K. Nozawa, M. Yonemoto and Y. Kondo, Chem. Commun., 2011, **47**, 11775-11777.
[26]. A. D. Chowdhury, S. M. Mobin, S. Mukherjee, S. Bhaduri and G. K. Lahiri, Eur. J. Inorg. Chem., **2011**, 3232-3239.
[27]. a) N. Mulakayala, Ismail, K. M. Kumar, R. K. Rapolu, B. Kandagatla, P. Rao, S. Oruganti and M. Pal, Tetrahedron Lett., 2012, **53**, 6004-6007; b) M. Gohain, M. du Plessis, J. H. van Tonder and B. C. B. Bezuidenhoudt, Tetrahedron Lett., 2014, **55**, 2082-2084.
[28]. R. E. Maleczka, F. Shi, D. Holmes and M. R. Smith, J. Am. Chem. Soc., 2003, **125**, 7792-7793.
[29]. C. Zhu, R. Wang and J. R. Falck, Org. Lett., 2012, **14**, 3494-3497.
[30]. E. Kianmehr, M. Yahyaee and K. Tabatabai, Tetrahedron Lett., 2007, **48**, 2713-2715.
[31]. V. Duprez, M. Biancardo, H. Spanggaard, F. C. Krebs, *Macromolecules* **2005**, *38*, 10436-10448.

ACCEPTED MANUSCRIPT

Graphical Abstract

Eight new heteroleptic Ru(II) complexes of 2,2':6',2''-terpyridine which could act as supramolecular building blocks are reported and characterized by NMR and MS.



ACCEPTED MANUSCRIPT