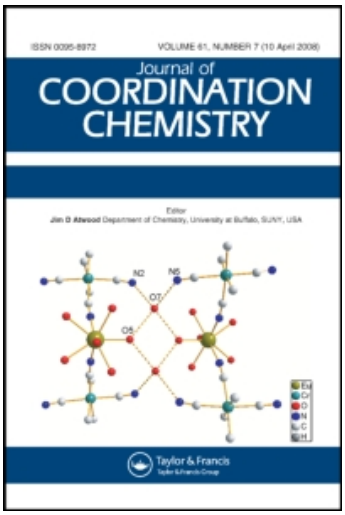

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Syntheses and characterization of ^{5}-pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes containing polypyridyls

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Syntheses and characterization of η^5-pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes containing polypyridyls

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Reaction of $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ {M = Rh (**1**), Ir (**2**)} and $[(\eta^5\text{-}C_5Me_5)MCl_2(DBT)]$ (DBT = dibenzothiophene) {M = Rh (**3**), Ir (**4**)} with polypyridyl ligands 2,3-bis(2-pyridyl)-pyrazine (bpp), 2,3-bis(2-pyridyl)quinoxaline (bpq), 1,3,5-tris(2-pyridyl)-2,4,6-triazine (tptz), 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) and 4′-pyridyl-2,2′:6′,2″-terpyridine (py-terpy) results in the formation of mononuclear cationic complexes, $[(\eta^5\text{-}C_5Me_5)MCl(poly\text{-}py)]^+$ (poly-py = polypyridyl ligand). The complexes were isolated as hexafluorophosphate salts and characterized by IR and NMR spectroscopy.

Keywords: Pentamethylcyclopentadienyl; Polypyridyl; Rhodium; Iridium; Synthesis

1. Introduction

For the past few decades, the coordination chemistry of the polypyridyl ligands 2,3-bis(2-pyridyl)pyrazine (bpp), 2,3-bis(2-pyridyl)quinoxaline (bpq), 1,3,5-tris (2-pyridyl)-2,4,6-triazine (tptz), 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) 4′-phenyl-2,2′: 6′2″-terpyridine (ph-terpy) and 4′-pyridyl-2,2′:6′,2″-terpyridine (py-terpy) has been an important focus of the inorganic community (see scheme 1) [1]. Transition metal complexes containing polypyridyl ligands are associated with interesting photochemical and electrochemical properties [2–6], can act as catalysts [7] and multi-electron storage systems [8], and are featured in the design of new materials [9] and molecular devices [10]. Complexes with these ligands are DNA intercalators with an ability to inhibit nucleic acid synthesis [11]. More recently, metal polypyridine complexes have been widely used as building blocks [12] in supramolecular systems. Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses and have attracted much attention [13]. In addition, their four-coordinate, pseudo-tetrahedral geometry makes them particularly suitable for

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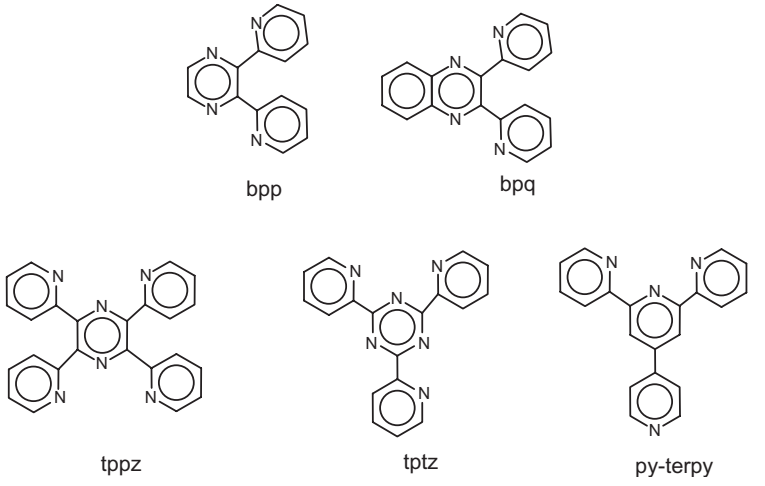


Scheme 1. Polypyridyl ligands used in this work.

investigation of the stereochemistry of reactions at metal centres [14]. Many studies of cyclopentadienyl- and areneruthenium(II) complexes with bidentate ligands have shown that substitution occurs predominantly with retention of configuration at the metal [15]. Very few studies had been carried out on pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes with polypyridyl ligands [16].

We have previously reported the syntheses of cyclopentadienyl- and areneruthenium complexes containing polypyridyl ligands [17] and areneruthenium(II) complexes with a variety of nitrogen-based ligands [18]. However, analogous pentamethylcyclopentadienyl rhodium(III) and iridium(III) polypyridyl complexes have not been explored to such an extent [19]. As a part of a continuing study in this area, we report the syntheses and characterization of new cationic pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes containing polypyridyl ligands (scheme 1).

2. Experimental

2.1. *Physical measurements*

Elemental analyses were performed on a Perkin–Elmer-2400 CHN/O instrument. IR spectra (KBr pellets) were recorded on a Perkin–Elmer 983 spectrophotometer and electronic spectra on a Hitachi 300 spectrophotometer. ^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR spectra were recorded in acetone-d_6 and $CDCl_3$ with TMS as internal standard on a Bruker ACF-300 (300 MHz) spectrometer.

2.2. *Materials and methods*

The ligands 2,3-bis(2-pyridyl)pyrazine (bpp), 2,3-bis(2-pyridyl)quinoxaline (bpq), 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) [20] and py-terpy [21] and the precursor complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ {M = Rh (**1**) and Ir (**2**)} and $[(\eta^5\text{-}C_5Me_5)M(DBT)Cl_2]$ {where M = Rh (**3**) and Ir (**4**); DBT = dibenzothiophene} [22] were synthesized

according to literature methods. 1,3,5-Tris(pyridyl)-2,4,6-triazine (tptz) was purchased from Loba Chemie Private Limited and used as received.

2.3. *[(η^5-C_5Me_5)MCl(L)]PF_6 (M = Rh or Ir; L = bpp (5, 6), bpq (7, 8), tptz (9, 10), tppz (11, 12), py-terpy (13, 14)*

The following general procedures were used for preparation of the complexes. To a solution of the complexes [(η^5-C_5Me_5)M(DBT)Cl_2] {M = Rh (**3**), Ir (**4**)} (0.172 mmol) in 30 cm^3 of dry methanol, the ligand L (0.344 mmol) and NH_4PF_6 (0.344 mmol) were added. The reaction mixture was stirred for 3 h, during which time the orange-yellow product separated out. The compound was filtered off, washed with diethylether and dried under vacuum.

For compounds **9**–**12** a slightly different procedure was adopted. To a solution of [(η^5-C_5Me_5)M(μ-Cl)Cl]$_2$ {M = Rh (**1**), Ir (**2**)} (0.162 mmol) in 20 cm^3 of dry methanol was added L (0.356 mmol) and NH_4PF_6 (0.356 mmol). The reaction mixture was stirred for 4 h at room temperature and solvent then removed under reduced pressure. The resulting solid mass was dissolved in dichloromethane and filtered. The solution was concentrated for 2 cm^3 and excess hexane added for precipitation. The orange-yellow product was filtered off, washed with diethylether and dried under vacuum.

[(η^5-C_5Me_5)RhCl(bpp)]PF_6, **5**: yield 110 mg (83%). IR (ν/cm^{-1}): 1626 m, 1593 m, 1482 m, 1369 m, 1026 m, 844 s, 783 m, 559 m. ^{1}H NMR (acetone-d_6, δ): 1.16 (s, 15H, C_5Me_5), 6.51 (d, 1H, $J_{H\text{-}H}$ = 6.28 Hz), 6.86–7.13 (m, 2H), 7.43 (t, 1H, $J_{H\text{-}H}$ = 5.24 Hz), 7.62 (d, 1H, $J_{H\text{-}H}$ = 7.12 Hz) 7.94 (t, 1H, $J_{H\text{-}H}$ = 6.44 Hz), 8.12–8.46 (m, 2H), 8.76 (d, 1H, $J_{H\text{-}H}$ = 4.22 Hz), 9.15 (d, 1H, $J_{H\text{-}H}$ = 5.28 Hz). Anal. Calc. for $C_{24}H_{25}RhN_4ClPF_6$ (%): C, 44.15; H, 3.85; N, 8.58. Found: C, 44.36, H; 3.24; N, 8.37. UV-Visible (CH_2Cl_2): λ_{max} = 389 nm.

[(η^5-C_5Me_5)IrCl(bpp)]PF_6, **6**: yield 96 mg (76%). IR: 1600 m, 1537 m, 1473 m, 1410 m, 1096 m, 850 s, 783 m, 568 m. ^{1}H NMR (acetone-d_6): 1.21 (s, 15H, C_5Me_5), 6.48 (d, 1H, $J_{H\text{-}H}$ = 5.86 Hz), 6.74–7.44 (m, 4H), 7.76 (d, 1H, $J_{H\text{-}H}$ = 6.32 Hz), 7.89 (dd, 1H, 7.82 Hz), 8.04–8.36 (m, 2H), 8.94 (d, 1H, $J_{H\text{-}H}$ = 4.82 Hz). Anal. Calc. for $C_{24}H_{25}IrN_4ClPF_6$ (%): C, 38.84; H, 3.39; N, 7.54. Found: C, 38.92; H, 3.43; N, 7.51. UV-Visible (CH_2Cl_2): λ_{max} = 372 nm.

[(η^5-C_5Me_5)RhCl(bpq)]PF_6, **7**: yield 105 mg (74%). IR: 1593 m, 1480 m, 1361 m, 1222 m, 1082 m, 844 s, 791 m, 565 m. ^{1}H NMR (acetone-d_6): 1.66 (s, 15H, C_5Me_5), 7.32 (d, 1H, $J_{H\text{-}H}$ = 6.36 Hz), 7.46 (t, 1H, $J_{H\text{-}H}$ = 6.02 Hz), 7.87 (t, 1H, $J_{H\text{-}H}$ = 6.44 Hz), 8.33–8.65 (m, 4H), 8.72–8.83 (m, 3H), 8.89 (d, 1H, $J_{H\text{-}H}$ = 5.62 Hz), 9.24 (d, 1H, $J_{H\text{-}H}$ = 6.26 Hz). ^{13}C NMR (acetone-d_6): 8.20 (CH_3, C_5Me_5), 79.61 (C, C_5Me_5), 124.69–149.62 (ligand signals). Anal. Calc. for $C_{28}H_{27}RhN_4ClPF_6$ (%): C, 47.85; H, 3.87; N, 7.97. Found: C, 47.61; H, 3.83; N, 8.02. UV-Visible (CH_2Cl_2): λ_{max} = 366 nm.

[(η^5-C_5Me_5)IrCl(bpq)]PF_6, **8**: yield 115 mg (84%). IR: 1639 m, 1474 m, 1401 m, 1367 m, 1036 m, 844 s, 784 m, 559 m. ^{1}H NMR (acetone-d_6): 1.70 (s, 15H, C_5Me_5), 7.45 (d, 2H, $J_{H\text{-}H}$ = 8.28 Hz), 7.76 (t, 1H, $J_{H\text{-}H}$ = 5.52 Hz), 7.91 (t, 1H, $J_{H\text{-}H}$ = 6.1 Hz), 8.05 (t, 1H, $J_{H\text{-}H}$ = 7.75 Hz), 8.20–8.45 (m, 3H), 8.61–8.64 (m, 2H), 8.72 (d, 1H, $J_{H\text{-}H}$ = 4.73 Hz), 9.16 (d, 1H, $J_{H\text{-}H}$ = 5.54 Hz). ^{13}C NMR (acetone-d_6): 13.10 (CH_3, C_5Me_5), 95.73 (C, C_5Me_5), 130.09–155.85 (ligand signals). Anal. Calc. for $C_{28}H_{275}IrN_4ClPF_6$ (%): C, 42.45; H, 3.43; N, 7.07. Found: C, 42.73; H, 3.44; N, 7.15. UV-Visible (CH_2Cl_2): λ_{max} = 371 nm.

[(η^5-C_5Me_5)RhCl(tptz)]PF_6, **9**: yield 107 mg (72%). IR: 1633 m, 1546 m, 1480 m, 1414 m, 1341 m, 1261 m, 1023 m, 850 s, 771 m, 565 m. ^{1}H NMR (acetone-d_6 + $CDCl_3$, δ): 1.34 (s, 15H, C_5Me_5), 7.45–7.55 (dd, 2H, $J_{H\text{-}H}$ = 3.17 Hz, 2.77 Hz), 7.73 (t, 1H), 7.88 (m, 2H), 8.01 (t, 1H, $J_{H\text{-}H}$ = 6.49 Hz), 8.11–8.13 (m, 2H), 8.34 (t, 1H, $J_{H\text{-}H}$ = 7.91 Hz), 8.96–9.09 (m, 2H), 9.25 (d, 1H, $J_{H\text{-}H}$ = 7.97 Hz). Anal. Calc. for $C_{28}H_{27}RhN_6ClPF_6$ (%): C, 46.01; H, 3.72; N, 11.49. Found: C, 46.13; H, 3.74; N, 11.26. UV-Visible (CH_2Cl_2): λ_{max} = 412 nm, 366 nm.

[(η^5-C_5Me_5)IrCl(tptz)]PF_6, **10**: yield 123 mg (87%). IR: 1639 m, 1553 s, 1500 s, 1401 m, 1261 m, 1036 m, 850 s, 784 m, 565 m. ^{1}H NMR ($CDCl_3$): 1.27 (s, 15H, C_5Me_5), 7.62–7.65 (qd, 2H, $J_{H\text{-}H}$ = 4.64 Hz, 1.84 Hz), 7.98–8.02 (td, 1H, $J_{H\text{-}H}$ =6.4 Hz, 9.12 Hz), 8.04–8.07 (td, 2H, $J_{H\text{-}H}$ = 1.72 Hz, 6.04 Hz), 8.85–9.00 (m, 6H), 9.12 (d, 1H, $J_{H\text{-}H}$ = 7.88 Hz). Anal. Calc. for $C_{28}H_{27}IrN_6ClPF_6$ (%): C, 41.00; H, 3.31; N, 10.24. Found: C, 41.46; H, 3.41; N, 10.33. UV-Visible (CH_2Cl_2): λ_{max} = 364 nm.

[(η^5-C_5Me_5)RhCl(tppz)]PF_6, **11**: yield 210 mg (80%). IR: 1593 m, 1487 m, 1394 s, 1295 m, 1248 m, 1135 m, 1029 m, 844 m, 784 m, 559 m. ^{1}H NMR ($CDCl_3$): 1.27 (s, C_5Me_5), 6.56–7.82 (m, 12H), 8.01 (t, 1H, $J_{H\text{-}H}$ = 5.36 Hz), 8.21 (m, 1H), 8.68 (d, 1H, $J_{H\text{-}H}$ = 6.24 Hz), 9.03 (d, 1H, $J_{H\text{-}H}$ = 4.68 Hz). Anal. Calc. for $C_{34}H_{31}RhN_6ClPF_6$: C, 50.60; H, 3.87; N, 10.41. Found: C, 49.50; H, 3.82; N, 10.52. UV-Visible (CH_2Cl_2): λ_{max} = 371 nm, 344 nm.

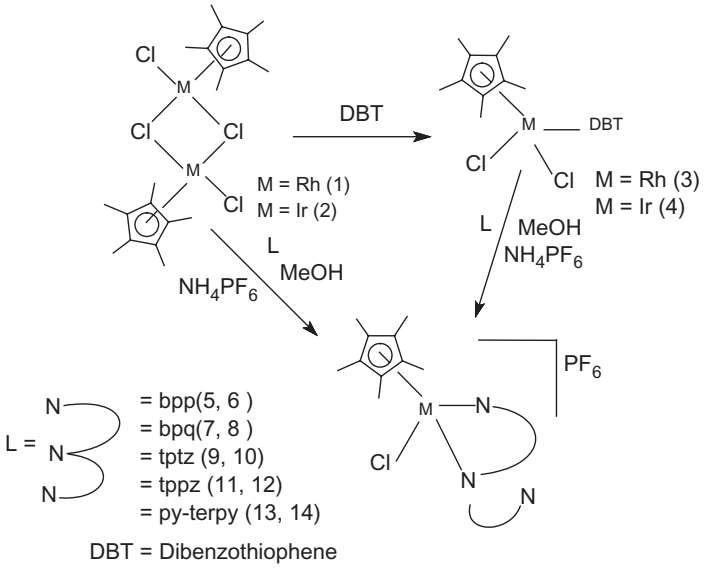
[(η^5-C_5Me_5)IrCl(tppz)]PF_6, **12**: yield 193 mg (86%). IR: 1593 m, 1487 m, 1460 m, 1394 s, 1241 m, 1135 m, 1036 m, 844 s, 764 s, 559 s. ^{1}H NMR ($CDCl_3$, δ): 1.31 (s, 15H, C_5Me_5), 6.62–7.74 (m, 12H), 7.96 (t, 1H, $J_{H\text{-}H}$ = 4.48 Hz), 8.32 (d, 1H, $J_{H\text{-}H}$ = 5.42 Hz), 8.53 (d, 1H, $J_{H\text{-}H}$ = 6.64 Hz), 8.95 (d, 1H, $J_{H\text{-}H}$ = 4.44 Hz). Anal. Calc. for $C_{34}H_{31}IrN_6ClPF_6$ (%): C, 45.56; H, 3.48; N, 9.37. Found: C, 45.49; H, 3.52; N, 9.41. UV-Visible (CH_2Cl_2): λ_{max} = 372 nm, 348 nm.

[(η^5-C_5Me_5)RhCl(py-terpy)]PF_6, **13**: yield 198 mg (84%). IR: 1600 s, 1533 m, 1487 m, 1401 m, 1235 m, 1162 m, 844 s, 797 m, 565 m. ^{1}H NMR ($CDCl_3$): 1.13 (s, 15H, C_5Me_5), 7.67 (t, 2H, $J_{H\text{-}H}$ = 6.68 Hz), 7.77–7.92 (m, 3H), 8.12 (t, 2H, $J_{H\text{-}H}$ = 6.76 Hz), 8.66–8.90 (m, 6H), 9.01 (d, 1H). Anal. Calc. for $C_{30}H_{29}RhN_4ClPF_6$ (%): C, 49.43; H, 4.01; N, 7.68. Found: C, 49.85; H, 4.07; N, 7.77. UV-Visible (CH_2Cl_2): λ_{max} = 338 nm, 326 nm.

[(η^5-C_5Me_5)IrCl(py-terpy)]PF_6, **14**: yield 172 mg (84%). IR: 1600 m, 1540 m, 1480 m, 1401 m, 1235 m, 1162 m, 1082 m, 1036 m, 850 s, 797 m, 751 m. ^{1}H NMR ($CDCl_3$): 1.14 (s, 15H, C_5Me_5), 7.38–7.77 (m, 2H), 7.90 (dd, 2H, $J_{H\text{-}H}$ = 1.64 Hz, 4.56 Hz), 7.95–8.21 (m, 2H), 8.52–8.75 (m, 3H), 8.78 (t, 1H, $J_{H\text{-}H}$ = 22.04 Hz), 8.83–8.96 (m, 3H), 9.10 (d, 1H, $J_{H\text{-}H}$ = 54.36 Hz). Anal. Calc. for $C_{30}H_{29}IrN_4ClPF_6$ (%): C, 44.03; H, 3.57; N, 6.84. Found: C, 44.09; H, 3.50; N, 6.81. UV-Visible (CH_2Cl_2): λ_{max} = 374 nm, 362 nm, 343 nm.

3. Results and discussion

Dinuclear complexes [{(η^5-C_5Me_5)M(μ-Cl)Cl}$_2$] {M = Rh (**1**), Ir (**2**)} and mononuclear complexes [(η^5-C_5Me_5)M(DBT)Cl_2] {M = Rh (**3**), Ir (**4**)} undergo bridge cleavage and substitution with polypyridyl (scheme 1) in methanol to yield the mononuclear cationic compounds **5–14** (scheme 2). The orange-yellow complexes are air-stable microcrystalline solids, partially soluble in chloroform, methanol and benzene, soluble in dichloromethane and acetone, and insoluble in hexane, petroleum ether and diethylether.

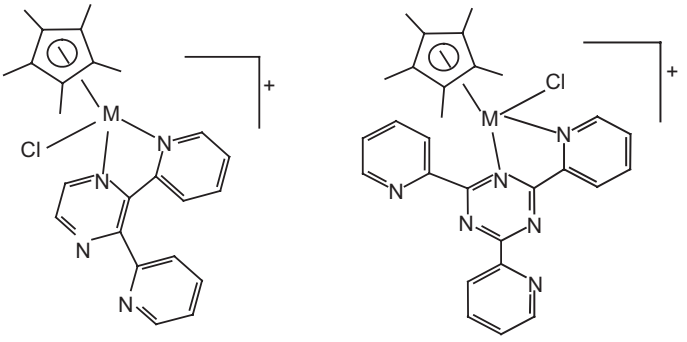


Scheme 2. Synthetic pathways.

The presence of Cp* and polypyridyl ligands as well as uncoordinated hexafluorophosphate is confirmed via infrared spectroscopy, and elemental analyses are consistent with the reported stoichiometries. IR spectra exhibit sharp bands with medium intensities in the range 1553–1639 cm^{-1} originating from the polypyridyl $\nu_{(C=N)}$ stretch. In addition, the complexes give a sharp band at $\sim$850 cm^{-1} due to the PF_6 anion.

All complexes showed a sharp singlet in the region of 1.13–1.70 ppm in ^1H NMR spectra, which can be assigned unambiguously to the resonance of pentamethylcyclopentadienyl ligand. The α proton of the pyridyl group appears as a doublet at around 9 ppm, closely related to reported complexes. The complexes also exhibit doublets and multiplets in the range of 6.51–9.09 ppm, which can be assigned to β and γ protons of the pyridine ring, and the arene protons of compounds **5**–**8** of the ligand overlap with pyridine protons of the ligand. ^{13}C $\{^1H\}$ NMR spectra exhibit appropriate signals for the complexes **7**[PF_6] and **8**[PF_6]. Resonances for the methyl carbons and the ring carbons of the pentamethylcyclopentadienyl group at 8.20 ppm and 79.61 ppm for complex **7**[PF_6] and 13.10 ppm and 95.73 ppm for complex **8**[PF_6], respectively, are consistent with reported values. Resonances observed in the range 124–156 ppm are assigned to the aromatic carbons of the phenyl and pyridyl groups.

The low spin d^6 configuration of the mononuclear complexes provides filled orbital of proper symmetry, which can interact with low lying π^* orbitals of the polypyridyl ligands. One should therefore expect a band attributable to the MLCT ($t_{2g} \rightarrow \pi^*$) transition in electronic spectra. Further, the energies of these transitions should vary with the nature of the chelating ligand acting as an π acceptor. The electronic spectra of rhodium(III) and iridium(III) complexes are dominated by charge transfer transitions as typically observed in polypyridyl complexes [16, 23]. Two charge transfer bands are also seen in the electronic spectra of the complexes at 338–412 nm, but they also



Scheme 3. Proposed structures.

display a lower intensity long wavelength transition, assigned to a d-d transition. Again this is consistent with observations on rhodium(III) and iridium(III) polypyridyl complexes [16, 23].

On the basis of the spectroscopic data and previous reports [16, 17a,b] the structures of scheme 3 are proposed. An interesting aspect of these complexes concerns the polypyridyl ligand acting as a bidentate like bipyridine or *o*-phenanthroline, replacing solvent molecule [16, 17].

4. Concluding remarks

We have isolated complexes of the type $[(\eta^5\text{-}C_5Me_5)MCl(\text{poly-py})]^+$ (M = Rh and Ir; poly-py = polypyridyl ligands) by reaction of dimers with polypyridyl ligands. Here we observe an interesting difference between pentamethylcyclopentadienyl complexes of ruthenium and pentamethylcyclopentadienyl complexes of rhodium and iridium even though these are all isoelectronic. The cyclopentadienyl ruthenium(II) complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ with polypyridyl ligands in methanol yielded mononuclear $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)]^+$ complexes [17a], and in the case of pentamethylcyclopentadienyl ruthenium with polypyridyl ligands yielded complexes without any organic group [17b,c]. The pentamethylcyclopentadienyl rhodium and iridium chloro dimers $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) with polypyridyl ligands yielded mononuclear cationic complexes, indicating that pentamethylcyclopentadienyl rhodium and iridium complexes are more stable than pentamethylcyclopentadienyl ruthenium complexes towards polypyridyl ligands. Whereas bpp and bpq ligands gave complexes with arene ruthenium dimer smoothly, rhodium and iridium dimers did not react with bpp and bpq. To synthesize these complexes in the case of rhodium and iridium we have had to use the dibenzothiophene complex as starting material [22a].

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