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Mono and dinuclear complexes of half-sandwich platinum group metals (Ru, Rh and Ir) bearing a flexible pyridyl-thiazole multidentate donor ligand

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ABSTRACT

The mononuclear cationic complexes $[(\eta^6\text{-}C_6H_6)RuCl(L)]^+$ (**1**), $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl(L)]^+$ (**2**), $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)]^+$ (**3**), $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(L)]^+$ (**4**), $[(\eta^5\text{-}C_5Me_5)RhCl(L)]^+$ (**5**), $[(\eta^5\text{-}C_5Me_5)IrCl(L)]^+$ (**6**) as well as the dinuclear dicationic complexes $[\{(\eta^6\text{-}C_6H_6)RuCl\}_2(L)]^{2+}$ (**7**), $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl\}_2(L)]^{2+}$ (**8**), $[\{(\eta^5\text{-}C_5H_5)Ru(PPh_3)\}2(L)]^{2+}$ (**9**), $[\{(\eta^5\text{-}C_5Me_5)Ru(PPh_3)\}_2(L)]^{2+}$ (**10**), $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(L)]^{2+}$ (**11**) and $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(L)]^{2+}$ (**12**) have been synthesized from 4,4′-bis(2-pyridyl-4-thiazole) (**L**) and the corresponding complexes $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ and $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$, respectively. All complexes were isolated as hexafluorophosphate salts and characterized by IR, NMR, mass spectrometry and UV–vis spectroscopy. The X-ray crystal structure analyses of $[\mathbf{3}]PF_6$, $[\mathbf{5}]PF_6$, $[\mathbf{8}](PF_6)_2$ and $[\mathbf{12}](PF_6)_2$ reveal a typical piano-stool geometry around the metal centers with a five-membered metallo-cycle in which 4,4′-bis(2-pyridyl-4-thiazole) acts as a *N,N′*-chelating ligand.

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1. Introduction

Metal complexes based on polypyridyl ligands constitute versatile components for the construction of multifunctional supramolecular systems in molecular photonics and molecular electronics, sensors, photo-catalysis, solar energy conversion, artificial photosynthesis, non-linear optics, and electrochemo-luminescence amongst others [1–15]. Despite the diversity of these potential applications, relatively little is known about how the properties of electron transfer between a single donor and acceptor is influenced by their inclusion into larger supramolecular assemblies. In this regard, ruthenium complexes bridged by multiple nitrogen donor polypyridyl ligands have received considerable recent attention because of their possible applications in homogeneous catalysis [16–21], as multi electron storage system [22–24], in the designing of new materials [25–28] and in photophysical and photochemical molecular devices [29–33]. One of the simplest linker used in assembling metals in such arrays is 4,4′-bis(2-pyridyl-4-thiazole) (**L**). This molecule has been principally explored with Co, Cu and Zn transition metal atoms and has been shown to generate helical structures [34–36]. Besides these helical structures, this molecule acts as a bis-chelating ligand to bridge two metal centers for the formation of dinuclear complexes. Inclusion of the five-membered thiazolyl rings in the backbone results in a more pronounced partitioning of the ligand into distinct bidentate domains than is the case with linear polypyridines. This facilitates the formation of mononuclear and dinuclear systems. The former one has the potential to behave as metallo-ligands in the development of homo/hetero bimetallic systems [37–40].

Arene ruthenium complexes play an important role in organometallic chemistry. Reactions of the chloro bridged arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ with Lewis bases and a variety of different ligands have been extensively studied. Recently, we have reported a series of mononuclear arene ruthenium complexes of the type $[(\eta^6\text{-arene})RuCl(H\text{-}bpp)]^+$ and the dinuclear complexes $[\{(\eta^6\text{-arene})RuCl\}_2(bpp)]^{2+}$ (arene = C_6H_6, $p\text{-}^iPrC_6H_4Me$; bpp = 3,3-bis(2-pyridyl)pyrazole) [41]. However, there are no reports dealing with half-sandwich ruthenium/rhodium/iridium complexes with ligands consisting of pyridyl units connected to thiazolyl ring backbone.

In the present contribution, we have synthesized new mononuclear and dinuclear complexes with arene ruthenium, rhodium and iridium complexes with polypyridyl ligand as thiazolyl rings backbone. All these new complexes were characterized by elemental analyses, ^{1}H NMR, UV–vis and mass spectrometry as well as X-ray crystallographic analyses for some representatives.

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[4,4'-bis(2-pyridyl-4-thiazole)] (**L**)
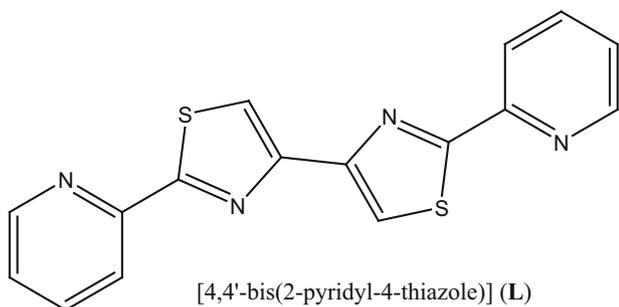
2. Experimental

All reagents were purchased either from Aldrich or Fluka and used as received. All the experiments were performed under normal conditions. The dinuclear complexes $[(\eta^6-C_6H_6)Ru(\mu-Cl)Cl]_2$, $[(\eta^6-p-^iPrC_6H_4Me)Ru(\mu-Cl)Cl]_2$ [42–44], and $[(\eta^5-C_5Me_5)M(\mu-Cl)Cl]_2$ (M = Rh and Ir) [45–47], the mononuclear complexes $[(\eta^5-C_5H_5)Ru(PPh_3)_2Cl]$ [48] and $[(\eta^5-C_5Me_5)Ru(PPh_3)_2Cl]$ [49] as well as 4,4'-bis(2-pyridyl-4-thiazole) [34] were prepared according to literature methods. NMR spectra were recorded on an AMX-400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer-2400 CHN/S analyzer. Mass spectra were obtained from ZQ mass spectrometer by ESI method. Absorption spectra were obtained at room temperature using a Perkin–Elmer Lambda 25 UV/visible spectrophotometer.

2.1. Syntheses of the mononuclear complexes [1]PF₆–[6]PF₆

2.1.1. $[(\eta^6-C_6H_6)Ru(L)Cl]PF_6$ ([**1**]PF₆)
A mixture of $[(\eta^6-C_6H_6)Ru(\mu-Cl)Cl]_2$ (50 mg, 0.1 mmol) and **L** [4,4'-bis(2-pyridyl-4-thiazole)] (66 mg, 0.21 mmol) was suspended in methanol (20 ml) and stirred at room temperature for 2 h. Then, the insoluble materials were filtered through celite and potassium hexafluorophosphate (48 mg, 0.25 mmol) was added to the filtrate. After stirring for 4 h at room temperature a precipitate was observed. The precipitate was filtered, washed with methanol and diethylether (3 × 10 ml) and dried *in vacuo*.

Yield 85 mg (62%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.46 (d, 1H, ^3J = 4.76 Hz), 9.15 (s, 1H, tz-H), 8.67 (d, 1H, ^3J = 3.20 Hz), 8.66 (s, 1H, tz-H), 8.36–8.08 (dd, 3H), 8.13 (t, 1H, ^3J = 3.32 Hz), 7.63 (t, 2H, ^3J = 2.54 Hz), 5.95 (s, 6H, C₆H₆); IR (cm⁻¹): 1614 (m), 1454 (s), 1437 (s), 844 (s), 788 (s), 558 (s); ESI-MS: 537.1 [M⁺], 492.2 [M−Cl]; UV–vis {acetonitrile, λ_{max} nm (ε 10⁻⁵ M⁻¹ cm⁻¹)}: 338 (0.19); Anal. Calc. for C₂₂H₁₆N₄S₂RuClPF₆ (682.01): C, 38.74; H, 2.36; N 8.21. Found: C, 38.53; H, 2.47; N, 8.18%.

2.1.2. $[(\eta^6-p-^iPrC_6H_4Me)Ru(L)Cl]PF_6$ ([**2**]PF₆)
Compound [**2**]PF6 was prepared by the same procedure as described above for [**1**]PF₆ using $[(\eta^6-p-^iPrC_6H_4Me)Ru(\mu-Cl)Cl]_2$ (60 mg, 0.09 mmol), **L** [4,4'-bis(2-pyridyl-4-thiazole)] (65 mg, 0.20 mmol) and potassium hexafluorophosphate (36 mg, 0.23 mmol).

Yield 113 mg (78%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.30 (d, 1H, ^3J = 5.66 Hz), 9.15 (s, 1H), 9.06 (s, 1H), 8.67 (d, 1H, ^3J = 3.72 Hz), 8.13 (t, 2H, ^3J = 7.6 Hz), 8.01 (d, 2H, ^3J = 2.72 Hz), 7.79 (t, 2H, ^3J = 6.40 Hz), 5.59 (d, 1H, ^3J = 6.00 Hz, Ar_p-cy), 5.52 (d, 1H, ^3J = 6.00 Hz, Ar_p-cy), 5.46 (d, 1H, ^3J = 6.00 Hz, Ar_p-cy), 5.39 (d, 1H, ^3J = 5.60 Hz, Ar_p-cy) 2.70 (sept, 1H, CH(CH₃)₂), 2.33 (s, 3H, Ar_p-cy-Me), 1.71 (d, 3H, ^3J = 6.20 Hz, CH(CH₃)₂), 1.69 (d, 3H, ^3J = 6.80 Hz,

CH(CH₃)₂); IR (cm⁻¹): 1604(m), 1449(s), 1437(s), 843(s), 783(s), 558(s); ESI-MS: 593.1 [M⁺], 458.1 [M−Cl]; UV–vis {acetonitrile, λ_{max} nm (ε 10⁻⁵ M⁻¹ cm⁻¹)}: 336 (0.20); Anal. Calc. for C₂₆H₂₄ClF₆N₄PRuS₂ (738.1): C, 42.31; H, 3.28; N, 7.59. Found: C, 42.27; H, 3.31; N, 7.57%.

2.1.3. $[(\eta^5-C_5H_5)Ru(L)(PPh_3)]PF_6$ ([**3**]PF₆)
A mixture of $[(\eta^5-C_5H_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.13 mmol), **L** [4,4'-bis(2-pyridyl-4-thiazole)] (48 mg, 0.15 mmol) and potassium hexafluorophosphate (26 mg, 0.15 mmol) was suspended in methanol (35 ml) and refluxed for 12 h. Then, the insoluble materials were filtered through celite and the filtrate was evaporated to dryness. The residue dissolved in dichloromethane and filtered through celite to remove excess potassium hexafluorophosphate and ammonium chloride. The filtrate was reduced to 2 ml on rotary evaporator and excess hexane was added to induce dark red color precipitate. The precipitate was separated by centrifugation, washed with diethylether (3 × 10 ml) and then dried *in vacuo*.

Yield 70 mg (56%). ^{1}H NMR (400 MHz, CD₃CN δ = 9.07 (d, 1H, ^3J = 4.40 Hz), 9.01 (s, 1H), 8.66 (d, 1H, ^3J = 7.60 Hz), 8.16 (s, 1H), 7.82 (t, 1H, ^3J = 8.00 Hz), 7.60 (t, 1H, ^3J = 6.40 Hz), 7.51 (t, 2H, ^3J = 7.20 Hz), 7.46 (d, 1H, ^3J = 6.42 Hz), 7.28 (d, 1H, ^3J = 4.28 Hz), 7.19–7.10 (m, 15H), 4.58 (s, 5H, C₅H₅); ^{31}P {^{1}H} (CD₃CN) δ = 49.34 ppm; IR (cm⁻¹): 1604(m), 1454(s), 1438(s), 844(s), 785(s), 559(s); ESI-MS: 750.8 [M⁺]; UV–vis {acetonitrile, λ_{max} nm (ε 10⁻⁵ M⁻¹ cm⁻¹)}: 341 (0.15); Anal. Calc. for C₃₉H₃₀F₆N₄P₂RuS₂ (895.82): C, 52.29; H, 3.38; N 6.25. Found: C, 52.11; H, 3.29; N, 6.17%.

2.1.4. $[(\eta^5-C_5Me_5)Ru(L)(PPh_3)]PF_6$ ([**4**]PF₆)
Compound [**4**]PF₆ was prepared by the same procedure as described above for [**5**]PF₆ using $[(\eta^5-C_5Me_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.12 mmol), **L** [4,4'-bis(2-pyridyl-4-thiazole)] (44 mg, 0.13 mmol) and potassium hexafluorophosphate (26 mg, 0.15 mmol).

Yield 82 mg (79%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.17 (d, 1H, ^3J = 5.60 Hz), 9.01 (s, 1H), 8.76 (d, 1H, ^3J = 4.48 Hz), 8.30 (s, 1H), 7.86 (t, 1H, ^3J = 7.60 Hz), 7.72 (t, 1H, ^3J = 6.40 Hz), 7.61 (t, 2H, ^3J = 6.00 Hz), 7.49 (d, 1H, ^3J = 4.20 Hz), 7.22 (d, 1H, ^3J = 3.28 Hz), 7.29–7.10 (m, 15H), 2.01 (s, 15H, C₅Me₅); ^{31}P {^{1}H} (CD₃CN) δ = 51.54 ppm; IR (cm⁻¹): 1624(m), 1458(s), 1437(s), 843(s), 778(s), 557(s); ESI-MS: 820.1 [M⁺]; UV–vis {acetonitrile, λ_{max} nm (ε 10⁻⁵ M⁻¹ cm⁻¹)}: 334 (0.55); Anal. Calc. for C₄₄H₄₀F₆N₄P₂RuS₂ (965.95): C, 54.71; H, 4.17; N, 5.80. Found: C, 54.59; H, 4.08; N, 5.68%.

2.1.5. $[(\eta^5-C_5Me_5)Rh(L)Cl]PF_6$ ([**5**]PF₆)
A mixture of $[(\eta^5-C_5Me_5)Rh(\mu-Cl)Cl]_2$ (50 mg, 0.08 mmol) and **L** [4,4'-bis(2-pyridyl-4-thiazole)] (55 mg, 0.17 mmol) was suspended in methanol (20 ml) and refluxed for 4 h. Then, the insoluble materials were passed through celite and potassium hexafluorophosphate (36 mg, 0.22 mmol) was added to the filtrate. After refluxing for an hour a precipitate was observed. The precipitate was filtered, washed with methanol and diethylether (3 × 10 ml) and dried *in vacuo*.

Yield 90 mg (78%). ^{1}H NMR (400 MHz, CD₃CN) δ = 8.95 (d, 1H, ^3J = 5.28 Hz), 8.71 (s, 1H), 8.66 (d, 1H, ^3J = 4.40 Hz), 8.30 (s, 1H), 7.86 (t, 1H, ^3J = 7.40 Hz), 7.62 (t, 1H, ^3J = 6.80 Hz), 7.52 (t, 2H, ^3J = 6.40 Hz), 7.32 (d, 1H, ^3J = 6.44 Hz), 7.22 (d, 1H, ^3J = 6.00 Hz), 2.11 (s, 15H, C₅Me₅); IR (cm⁻¹): 1603(m), 1458(s), 1437(s), 845(s), 785(s), 558(s); ESI-MS: 560.3 [M⁺], 525.1 [M−Cl]; UV–vis {acetonitrile, λ_{max} nm (ε 10⁻⁵ M⁻¹ cm⁻¹)}: 333 (0.72); Anal. Calc. for C₂₆H₂₅F₆N₄PRhS₂ (705.5): C, 44.26; H, 3.57; N 7.94. Found: C, 44.13; H, 3.43; N, 7.86%.

2.1.6. [(η⁵-C₅Me₅)Ir(L)Cl]PF₆ ([6]PF₆)

Compound [6]PF₆ was prepared by the same procedure as described above for [5]PF₆ using [(η⁵-C₅Me₅)Ir(μ-Cl)Cl]₂ (66 mg, 0.08 mmol), **L** [4,4′-bis(2-pyridyl-4-thiazole)] (57 mg, 0.18 mmol) and potassium hexafluorophosphate (46 mg, 0.25 mmol).

Yield 79 mg (60%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.01 (d, 1H, ^3J = 5.60 Hz), 8.91 (s, 1H), 8.76 (d, 1H, ^3J = 6.40 Hz), 8.35 (s, 1H), 7.89 (t, 1H, ^3J = 7.00 Hz), 7.72 (t, 1H, ^3J = 6.80 Hz), 7.52 (t, 2H, ^3J = 6.00 Hz), 7.42 (d, 1H, ^3J = 5.60 Hz), 7.28 (d, 1H, ^3J = 6.48 Hz), 1.87 (s, 15H, C₅Me₅); IR (cm^{-1}): 1606(m), 1454(s), 1437(s), 844(s), 785(s), 558(s); ESI-MS: 649.8 [M⁺], 614.6 [M−Cl]; UV–vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 336 (0.74); Anal. Calc. for C₂₆H₂₅F₆IrN₄PS₂ (794.8): C, 39.29; H, 3.17; N 7.05. Found: C, 39.13; H, 3.21; N, 6.99%.

2.2. Syntheses of the dinuclear complexes [7](PF₆)₂ to [12](PF₆)₂

2.2.1. [{(η⁶-C₆H₆)RuCl}₂(μ-L)](PF₆)₂ ([7](PF₆)₂)

A mixture of [(η⁶-C₆H₆)Ru(μ-Cl)Cl]₂ (83 mg, 0.16 mmol) and **L** [4,4′-bis(2-pyridyl-4-thiazole)] (53 mg, 0.16 mmol) was suspended in methanol (20 ml) and stirred at room temperature for 6 h. Then, potassium hexafluorophosphate (46 mg, 0.25 mmol) was added to the reaction mixture and further stirred for 3 h. The precipitate was filtered, washed with methanol and diethylether (3 × 10 ml) and dried *in vacuo*.

Yield 110 mg (60%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.38 (d, 2H, ^3J = 4.80 Hz), 8.67 (s, 2H, tz-H), 8.22 (d, 2H, ^3J = 8.40 Hz), 8.13 (t, 2H, ^3J = 7.20 Hz), 7.43–7.51 (m, 2H), 6.01 (s, 6H, C₆H₆), 5.99 (s, 6H, C₆H₆); IR (cm^{-1}): 1604(m), 1449(s), 1437(s), 843(s), 783(s), 558(s); ESI-MS: 891.8 [M²⁺+PF₆⁻]⁺; UV–vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 311 (0.35) and 356 (0.31); Anal. Calc. for C₂₈H₂₂Cl₂F₁₂N₄P₂Ru₂S₂ (1041.6): C, 32.29; H, 2.13; N 5.38. Found: C, 32.15; H, 2.05; N, 5.28%.

2.2.2. [{(η⁶-p-^{i}PrC₆H₄Me)RuCl}₂(μ-L)](PF₆)₂ ([8](PF₆)₂)

Compound [8](PF₆)₂ was prepared by the same procedure as described above for [7](PF₆)₂ using [(η⁶-p-^{i}PrC₆H₄Me)Ru(μ-Cl)Cl]₂ (63 mg, 0.1 mmol), **L** [4,4′-bis(2-pyridyl-4-thiazole)] (33 mg, 0.1 mmol) and potassium hexafluorophosphate (23 mg, 0.12 mmol).

Yield 101 mg (85%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.37 (d, 2H, ^3J = 5.20 Hz), 8.67 (s, 2H, tz-H), 8.26 (d, 2H, ^3J = 5.60 Hz), 8.06 (t, 2H, ^3J = 7.00 Hz), 7.57 (t, 2H, ^3J = 6.80 Hz), 5.86 (d, 2H, ^3J = 6.00 Hz, Ar$_{p-cy}$), 5.56 (d, 2H, ^3J = 5.60 Hz, Ar$_{p-cy}$), 5.47 (d, 2H, ^3J = 6.00 Hz, Ar$_{p-cy}$), 5.38 (d, 2H, ^3J = 6.40 Hz Ar$_{p-cy}$), 2.42 (sept, 2H, CH(CH₃)₂), 2.05 (s, 6H, Ar$_{p-cy}$-Me), 1.38 (d, 3H, CH(CH₃)₂); 1.17 (d, 3H, CH(CH₃)₂), 1.08 (d, 3H, CH(CH₃)₂), 0.98 (d, 3H, CH(CH₃)₂); IR (cm^{-1}): 1614(m), 1454(s), 1437(s), 844(s), 788(s), 558(s); ESI-MS: 1008.2 [M²⁺+PF₆⁻]⁺; UV–vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 312 (0.56) and 355 (0.35); Anal. Calc. for C₃₆H₃₈Cl₂F₁₂N₄P₂Ru₂S₂ (1153.7): C, 37.47; H, 3.32; N 4.86. Found: C, 37.33; H, 3.27; N, 4.77%.

2.2.3. [{(η⁵-C₅H₅)Ru(PPh₃)}₂(μ-L)](PF₆)₂ ([9](PF₆)₂)

A mixture of [(η⁵-C₅H₅)Ru(PPh₃)₂Cl] (100 mg, 0.13 mmol), **L** [4,4′-bis(2-pyridyl-4-thiazole)] (22 mg, 0.068 mmol) and ammonium hexafluorophosphate (46 mg, 0.28 mmol) was suspended in methanol (35 ml) and refluxed for 12 h. Then, the insoluble materials were filtered through celite and filtrate was evaporated to dryness. The residue was dissolved in dichloromethane and filtered through celite to remove ammonium chloride and excess ammonium hexafluorophosphate. The filtrate was reduced to 2 ml and excess hexane was added to induce dark red color precipitate. The precipitate was separated by centrifugation, washed with diethylether (3 × 10 ml) and dried *in vacuo*.

Yield 81 mg (80%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.29 (d, 2H, ^3J = 5.60 Hz), 8.67 (s, 2H, tz-H), 8.26 (d, 2H, ^3J = 4.40 Hz), 8.06 (t, 2H, ^3J = 7.20 Hz), 7.57 (m, 2H), 7.29–7.02 (m, 30H), 4.86 (s, 10H, C₅H₅); ^{31}P {^{1}H} (CD₃CN) δ = 49.28; IR (cm^{-1}): 1624(m), 1458(s), 1437(s), 843(s), 778(s), 557(s); ESI-MS: 1179 1 [M²⁺+PF₆⁻]²⁺; UV–vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 314 (0.72) and 356 (0.32). Anal. Calc. for C₆₂H₅₀F₁₂N₄P₄Ru₂S₂ (1469.2): C, 50.68; H, 3.43; N 3.81. Found: C, 50.56; H, 3.57; N, 3.77%.

2.2.4. [{(η⁵-C₅Me₅)Ru(PPh₃)}₂(μ-L)](PF₆)₂ ([10](PF₆)₂)

Compound [10](PF₆)₂ was prepared by the same procedure as described above for [9](PF₆)₂, using [(η⁵-C₅Me₅)Ru(PPh₃)₂Cl] (100 mg, 0.12 mmol), **L** [4,4′-bis(2-pyridyl-4-thiazole)] (20 mg, 0.06 mmol) and potassium hexafluorophosphate (23 mg, 0.12 mmol).

Yield 71 mg (69%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.32 (d, 2H, ^3J = 5.20 Hz), 8.78 (s, 2H, tz-H), 8.26 (d, 2H, ^3J = 4.40 Hz), 8.11 (t, 2H, ^3J = 7.80 Hz), 7.57 (t, 2H, ^3J = 6.40 Hz), 7.29–7.08 (m, 30H), 1.97 (s, 30H); ^{31}P {^{1}H} (CD₃CN) δ = 51.33; IR (cm^{-1}): 1604(m), 1454(s), 1438(s), 844(s), 785(s), 559(s); ESI-MS: 1319.8 [M²⁺+PF₆⁻]²⁺; UV–vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 310 (0.81) and 358 (0.33); Anal. Calc. for C₇₂H₇₀F₁₂N₄P₄Ru₂S₂ (1609.5): C, 53.73; H, 4.38; N, 3.48. Found: C, 53.61; H, 4.27; N, 3.39%.

2.2.5. [{(η⁵-C₅Me₅)RhCl}₂(μ-L)](PF₆)₂ ([11](PF₆)₂)

A mixture of [(η⁵-C₅Me₅)Rh(μ-Cl)Cl]₂ (75 mg, 0.12 mmol) and **L** [4,4′-bis(2-pyridyl-4-thiazole)] (39 mg, 0.1 mmol) was suspended in methanol (20 ml) and refluxed for 4 h. Then, potassium hexafluorophosphate (23 mg, 0.13 mmol) was added to the reaction mixture and further refluxed for an hour. During this time was precipitate was observed. The precipitate was filtered, washed with methanol and diethylether (3 × 10 ml) and dried *in vacuo*.

Yield 118 mg (89%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.11 (d, 2H, ^3J = 5.20 Hz), 8.72 (s, 2H, tz-H), 8.21 (d, 2H, ^3J = 5.60 Hz), 8.11 (t, 1H, ^3J = 7.20 Hz), 7.96 (t, 1H, ^3J = 7.24 Hz), 7.57 (t, 2H, ^3J = 6.40 Hz), 2.15 (s, 30H, C₅Me₅); IR (cm^{-1}): 1606(m), 1454(s), 1437(s), 844(s), 785(s), 558(s); ESI-MS: 943.6 [M²⁺+PF₆⁻]⁺; UV–vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 312 (0.78) and 356 (0.33); Anal. Calc. for C₃₆H₄₀F₁₂N₄P₂Rh₂S₂ (1088.6): C, 39.72; H, 3.70; N, 5.15. Found: C, 39.53; H, 3.67; N, 5.07%.

2.2.6. [{(η⁵-C₅Me₅)IrCl}₂(μ-L)](PF₆)₂ ([12](PF₆)₂)

Compound [12](PF₆)₂ was prepared by the same procedure as described above for [11](PF₆)₂ using [(η⁵-C₅Me₅)Ir(μ-Cl)Cl]₂ (72 mg, 0.09 mmol), **L** [4,4′-bis(2-pyridyl-4-thiazole)] (29 mg, 0.09 mmol) and potassium hexafluorophosphate (23 mg, 0.12 mmol).

Yield 91 mg (79%). ^{1}H NMR (400 MHz, CD₃CN) δ = 9.44 (d, 2H, ^3J = 5.60 Hz), 8.90 (s, 2H, tz-H), 8.28 (d, 2H, ^3J = 8.00 Hz), 8.15 (t, 1H, ^3J = 7.20 Hz), 7.98 (t, 1H, ^3J = 6.80 Hz), 7.57 (t, 2H, ^3J = 6.44 Hz), 1.54 (s, 30H, C₅Me₅); IR (cm^{-1}): 1603(m), 1458(s), 1437(s), 845(s), 785(s), 558(s); ESI-MS: 1122.5 [M²⁺+PF₆⁻]⁺; UV–vis {acetonitrile, λ_{max} nm (ε 10^{-5} M^{-1} cm^{-1})}: 310 (0.74) and 358 (0.32); Anal. Calc. for C₃₆H₄₀F₁₂Ir₂N₄P₂S₂ (1267.2): C, 34.12; H, 3.18; N, 4.42. Found: C, 34.02; H, 3.09; N, 4.37%.

2.3. X-ray crystallography

Crystals of complexes [3]PF₆·(CH₃)₂CO, [5]PF₆·(CH₃)₂CO, [8](PF₆)₂·CH₃CN and [12](PF₆)₂·CH₂Cl₂ were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS-97 [50]. Refinement and all further calculations were carried out using SHELXL-97 [51]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined

Table 1
Crystallographic and structure refinement parameters for complexes [**3**]PF$_6$·(CH$_3$)$_2$CO, [**5**]PF$_6$·(CH$_3$)$_2$CO, [**8**](PF$_6$)$_2$·CH$_3$CN and [**12**](PF$_6$)$_2$·CH$_2$Cl$_2$.

	[**3**]PF$_6$·(CH$_3$)$_2$CO	[**5**]PF$_6$·(CH$_3$)$_2$CO	[**8**](PF$_6$)$_2$·CH$_3$CN	[**12**](PF$_6$)$_2$·CH$_2$Cl$_2$
Chemical formula	C$_{42}$H$_{36}$F$_6$N$_4$OP$_2$RuS$_2$	C$_{29}$H$_{31}$ClF$_6$N$_4$OPRhS$_2$	C$_{38}$H$_{41}$Cl$_2$F$_{12}$N$_5$P$_2$Ru$_2$S$_2$	C$_{37}$H$_{42}$Cl$_4$F$_{12}$Ir$_2$N$_4$P$_2$S$_2$
Formula weight	953.88	799.03	1194.86	1423.01
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_12_12$ (no. 18)
Crystal color and shape	Orange block	Orange rod	Orange block	Orange rod
Crystal size	0.23 × 0.17 × 0.16	0.28 × 0.23 × 0.18	0.35 × 0.26 × 0.21	0.27 × 0.19 × 0.16
a (Å)	9.995(1)	8.588(2)	12.0713(12)	11.809(2)
b (Å)	13.505(2)	11.802(2)	13.3379(13)	25.787(5)
c (Å)	15.294(2)	16.802(3)	15.1076(16)	7.588(2)
α (°)	98.163(17)	70.68(3)	67.863(11)	90
β (°)	91.233(16)	89.32(3)	80.764(12)	90
γ (°)	96.897(15)	80.92(3)	88.372(12)	90
V (Å^3)	2027.2(5)	1585.4(5)	2222.5(4)	2310.7(9)
Z	2	2	2	2
T (K)	173(2)	173(2)	173(2)	173(2)
D_{calc} (g cm^{-3})	1.563	1.674	1.785	2.045
μ (mm^{-1})	0.636	0.872	1.053	6.227
Scan range (°)	2.18 < θ < 26.21	2.40 < θ < 26.10	2.07 < θ < 26.13	2.34 < θ < 26.03
Unique reflections	7491	5827	8164	4541
Reflections used [$I > 2\sigma(I)$]	1896	3376	5144	2982
R_{int}	0.1776	0.0484	0.0441	0.2056
Flack parameter	–	–	–	0.38(3)
Final R indices [$I > 2\sigma(I)$][a]	0.0479, wR_2 0.0895	0.0348, wR_2 0.0620	0.0335, wR_2 0.0675	0.0922, wR_2 0.2146
R indices (all data)	0.2140, wR_2 0.1243	0.0797, wR_2 0.0685	0.0669, wR_2 0.0750	0.1300, wR_2 0.2394
Goodness-of-fit	0.531	0.752	0.831	0.986
Maximum, minimum $\Delta\rho$ (e Å^{-3})	0.428, −0.829	0.654, −1.051	0.757, −0.899	4.272, −3.043

[a] Structures were refined on F_o^2: $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

anisotropically, using weighted full-matrix least-square on F^2. In [**12**](PF$_6$)$_2$···CH$_2$Cl$_2$ the max./min. residual density 4.510/ −3.120 e Å^{-3} are located at less than 1 Å from the iridium atoms. Crystallographic details are summarized in Table 1 and selected bond lengths and angles are presented in Table 2. Figs. 1–4 of complexes [**3**]PF$_6$·(CH$_3$)$_2$CO, [**5**]PF$_6$·(CH$_3$)$_2$CO, [**8**](PF$_6$)$_2$·CH$_3$CN and [**12**](PF$_6$)$_2$·CH$_2$Cl$_2$ were drawn with ORTEP-32 [52], respectively.

3. Results and discussion

3.1. Synthesis of the mononuclear complexes [**1**]PF$_6$ to [**6**]PF$_6$ as hexafluorophosphate salts

The mononuclear cationic arene ruthenium as well as cyclopentadienyl and pentamethylcyclopentadienyl ruthenium, rhodium or

Table 2
Selected bond lengths (Å) and angles (°) for complexes [**3**]PF6, [**5**]PF6, [**8**](PF6)2 and [**12**](PF6)2.

	[**3**]PF$_6$	[**5**]PF$_6$	[**8**](PF$_6$)$_2$	[**12**](PF$_6$)$_2$
Distances (Å)				
M–N1	2.067(8)	2.100(3)	2.094(3)	2.06(2)
M–N2	2.105(7)	2.146(3)	2.156(3)	2.193(15)
M–N3	–	–	2.112(3)	2.06(2)[i]
M–N4	–	–	2.111(3)	2.193(15)[i]
M–P1	2.322(2)	–	–	–
M–Cl1	–	2.4068(12)	2.3789(10)	2.402(6)
M-Cl2	–	–	2.4004(12)	2.402(6)[i]
M–centroid 1	1.820	1.785	1.689	1.818
M–centroid 1	–	–	1.690	1.818
M1–M2	–	–	6.073(1)	6.558(2)[i]
Angles (°)				
N1–M–N2	76.3(3)	76.51(13)	77.12(12)	75.5(8)
N3–M–N4	–	–	77.04(11)	75.5(8)[i]
N1–M–P1	89.1(2)			
N2–M–P1	91.69(19)			
N1–M–Cl1	–	87.36(9)	82.43(9)	84.2(6)
N2–M–Cl1	–	94.54(9)	83.90(8)	89.7(8)
N3–M–Cl2	–	–	82.54(10)	84.2(6)[i]
N4–M–Cl2	–	–	85.19(10)	89.7(8)[i]

i = 1 − x, −y, z.

iridium complexes having 4,4′-bis(2-pyridyl-4-thiazole) (**L**) ligand viz., [(η^6-C$_6$H$_6$)RuCl(L)]PF$_6$ [**1**]PF$_6$, [(η^6-p-^{i}PrC$_6$H$_4$Me)RuCl(L)]PF$_6$ [**2**]PF$_6$, [(η^5-C$_5$H$_5$)Ru(PPh$_3$)(L)]PF$_6$ [**3**]PF$_6$, [(η^5-C$_5$Me$_5$)Ru (PPh$_3$)(L)]PF$_6$ [**4**]PF$_6$, [(η^5-C$_5$Me$_5$)RhCl(L)]PF$_6$ [**5**]PF$_6$ and [(η^5-C$_5$Me$_5$)IrCl(L)]PF$_6$ [**6**]PF$_6$ (Scheme 1) have been prepared by the reaction of arene or cyclopentadienyl or pentamethylcyclopentadienyl complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C$_6$H$_6$ and p-^{i}PrC$_6$H$_4$Me), [(η^5-Cp)Ru(PPh$_3$)$_2$Cl] (Cp = C$_5$H$_5$ and C$_5$Me$_5$) and [(η^5-C$_5$Me$_5$)M(μ-Cl)Cl]$_2$ (M = Rh and Ir) with appropriate equivalents of ligand **L** [4,4′-bis(2-pyridyl-4-thiazole)] in methanol. These complexes are isolated as hexafluorophosphate salts and complexes [**1**]PF$_6$ to [**6**]PF$_6$ are orange-red, resulting as non-hygroscopic, air-stable, shiny crystalline solids. They are sparingly soluble in methanol, dichloromethane and chloroform, but well soluble in acetone and acetonitrile. All these complexes were fully characterized by IR, ^{1}H NMR and electronic spectroscopy. In addition to these complexes **3** and **4** were characterized by ^{31}P NMR also. Analytical data of the complexes conformed well to their respective formulations. Further information about composition of the complexes has also been obtained from mass spectrometry.

Infrared spectra of the ligand **L** [4,4′-bis(2-pyridyl-4-thiazole)] display an absorption bands at 1452 and 1437 cm^{-1} assignable to the stretching frequencies of C=N and C=S bands, respectively, consistent with the fact that C=N and C=S stretching frequencies of thiazole appear in the range 1452 and 1437 cm^{-1}, respectively [53]. Upon coordination with metal atoms the same bands appeared around 1449–1458 and 1437 cm^{-1}, respectively. The change only in the position of $\nu_{C=N}$ of thiazole suggested that the coordination of the metal ion is through nitrogen atom of thiazole not with the sulfur atom. In addition to these bands a strong band in the region 843 cm^{-1} has been assigned to counter ion PF$_6$.

In the mass spectra they give, as expected, rise to the corresponding [M]$^+$ molecular peaks m/z at 537, 593, 750, 820, 560 and 649, respectively. The ^{1}H NMR spectrum of free ligand **L** (4,4′-bis(2-pyridyl-4-thiazole)) exhibit a characteristic set of five resonances for the thiazole and pyridyl ring protons. Upon coordination with the metal atom, the mononuclear cationic complexes [**1**]PF$_6$ to [**6**]PF$_6$ exhibit between seven and nine distinct reso-

Fig. 1. Molecular structure of complex **3** showing ellipsoids at the 50% probability level. Hydrogen atoms, PF$_6$ anion and solvent molecule are omitted for clarity.

Fig. 2. Molecular structure of complex **5** showing ellipsoids at the 50% probability level. Hydrogen atoms, PF$_6$ anion and solvent molecule are omitted for clarity.
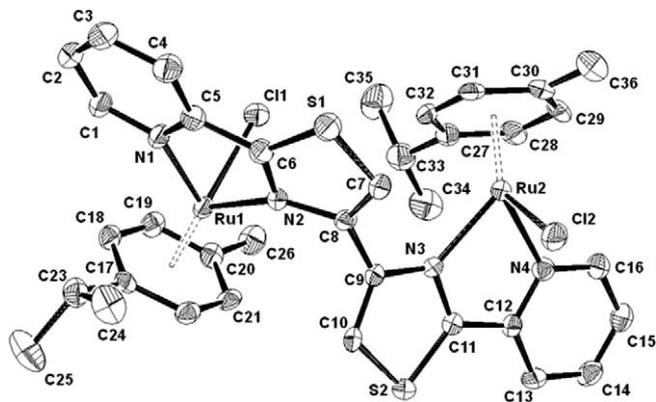
Fig. 3. Molecular structure of complex **8** showing ellipsoids at the 50% probability level. Hydrogen atoms, PF$_6$ anions and solvent molecules are omitted for clarity.

nances assignable to thiazolyl and pyridyl ring protons of the **L** [4,4′-bis(2-pyridyl-4-thiazole)] ligand indicating formation of mononuclear complexes. Besides these resonances complex [**1**]PF$_6$ exhibit a singlet at δ = 5.95 for the protons of the benzene ligand and complex [**2**]PF$_6$ exhibits two doublets at δ = 1.71 and
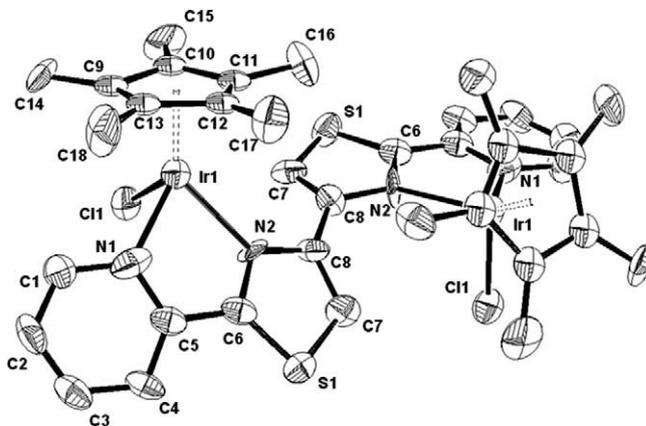
Fig. 4. Molecular structure of complex **12** showing ellipsoids at the 50% probability level Hydrogen atoms, PF$_6$ anions and solvent molecule are omitted for clarity.

1.69, as well as a septet at δ = 2.70 for the protons of the isopropyl group and a singlet at 2.33 ppm for methyl proton of *p*-cymene ligand. The two doublets observed at 5.59 and 5.39 ppm correspond to the aromatic *p*-cymene ring CH protons. This unusual pattern is due to the diastereotopic methyl protons of the isopropyl group and aromatic protons of the *p*-cymene ligand, since the ruthenium atom is stereogenic due to the coordination of four different ligand atoms and chiral nature of metal atom [53–55]. Complex [**3**]PF$_6$ exhibited a strong peak at δ = 4.58 which is assigned to cyclopentadienyl ligand and complexes [**4**]PF$_6$ to [**6**]PF$_6$ exhibit a strong peak at δ = 2.01, 2.11 and 1.84 for the pentamethylcyclopentadienyl ligand, respectively, which are slightly shifted downfield in comparison to the starting precursors.

The ^{31}P {^{1}H} NMR spectra of complexes [**3**]PF$_6$ and [**4**]PF$_6$ exhibit a strong peak at δ = 49.34 and 51.54, respectively, for the triphenylphosphine ligand which is shifted down field as compared to starting neutral precursors δ = 42.00 and 38.50 [56,57]. This down field chemical shift of phosphorus nucleus indicates the formation of cationic complexes.

3.2. Crystal structure analysis of [(η^5-C$_5$H$_5$)Ru(PPh$_3$)(L)]PF$_6$ ([**3**]PF$_6$) and [(η^5-C$_5$Me$_5$)Rh(L)(Cl)]PF$_6$ ([**5**]PF$_6$)

The molecular structure of [(η^5-C$_5$H$_5$)Ru(PPh$_3$)(L)]PF$_6$ [**3**]PF$_6$ and [(η^5-C$_5$Me$_5$)Rh(L)(Cl)]PF$_6$ [**5**]PF$_6$ have been established by single-crystal X-ray structure analysis. Both complexes show a typical piano-stool geometry with the metal center coordinated by the aromatic ligand, a terminal triphenylphosphine or chloride and a chelating *N,N*′-ligand (see Figs. 1 and 2). The metal atom is in octahedral arrangement and the L ligand is found to coordinate through the N1 atom of the pyridine moiety and the N2 atom of the thiazolyl ring to generate a five-membered ring metallo-cycle (see Figs. 1 and 2). In these complexes, the S atom points away from the metal center and show no interaction with neighboring cations. Selected bond lengths and angles for complexes [**3**]PF$_6$ and [**5**]PF$_6$ are presented in Table 2. In the mononuclear complexes [**3**]PF$_6$ and [**5**]PF$_6$ the metal to nitrogen (N1) bond distance (2.067(8) and 2.100(3) Å) of the pyridine is shorter than the corresponding metal–thiazole nitrogen distance (2.105(8) and 2.146(4) Å), which are comparable to those in [(η^6-C$_6$H$_6$)RuCl(C$_5$H$_4$N-2-CH=N=C$_6$H$_4$-*p*-NO$_2$)]PF$_6$ [58], [Ru(mes)Cl{C$_5$H$_4$N-2-C(Me)=N(CHMePh)}]BF$_4$ [59], [(η^5-C$_5$Me$_5$)RhCl(C$_5$H$_4$N-2-CH=N=C$_6$H$_4$-*p*-NO$_2$)]BF$_4$ [60], but unlike in [(η^6-C$_6$H$_6$)Ru(2-(2-thiazolyl)-1,8-naphthyridine)Cl]PF$_6$, [53], [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl(2,3-bis (2-pyridyl)pyrazine)]BF$_4$ [61] [(η^6-C$_6$H$_6$)RuCl(2-(1-imidazol-2-yl)pyridine)]PF$_6$ [62] and [(η^5-C$_5$Me$_5$)Ir(2-(2′-pyridyl)imidaz-
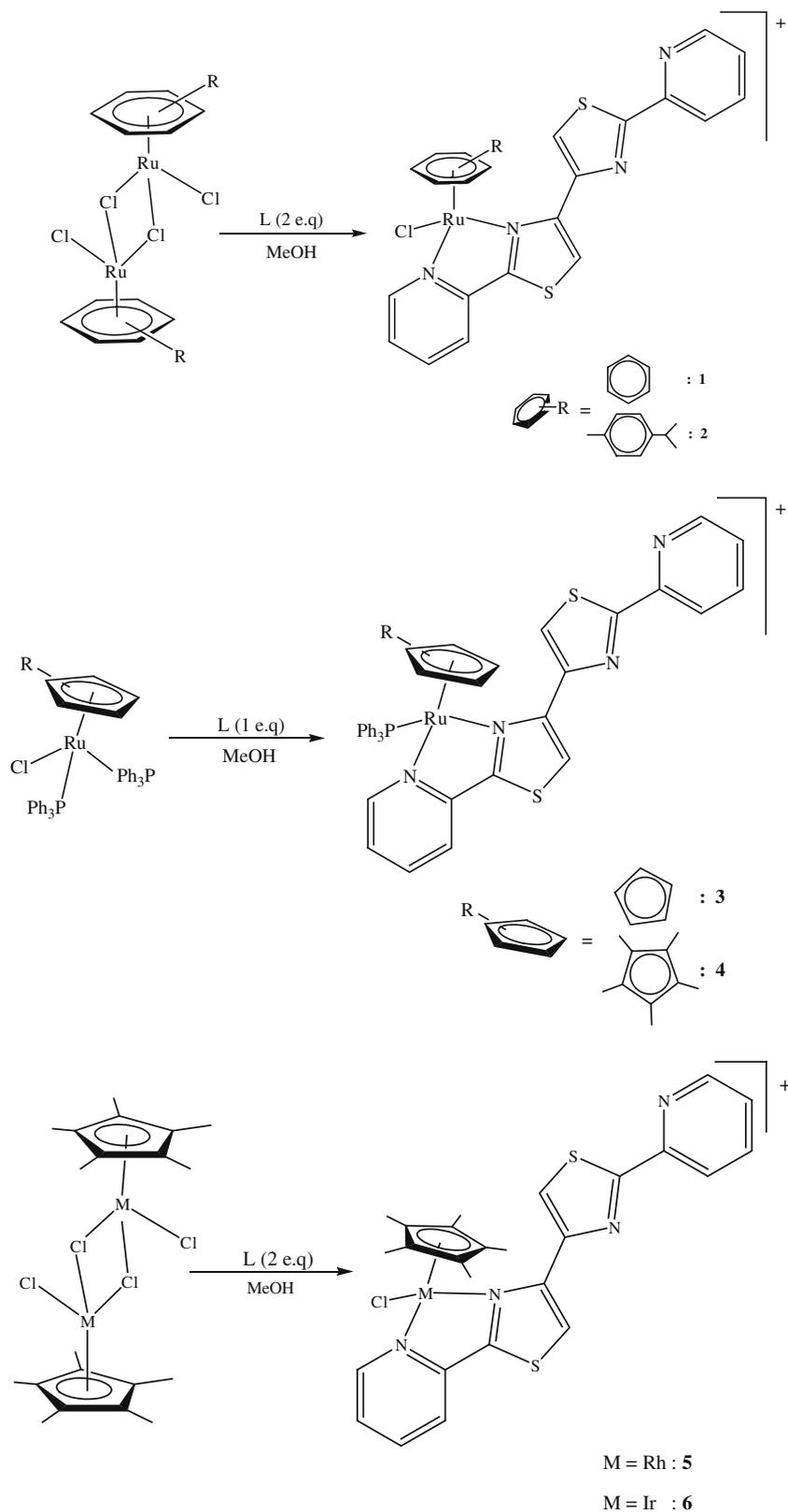
Scheme 1.

ole)Cl]PF$_6$ [63]. Accordingly, there is no significant difference in the M - Cl bond length in **5** [2.407(12) Å] and reported values [64]. The N(1)–M(1)–N(2) bond angle in complexes **3** and **5** is found to be [76.40(3)°] and [76.51(1)°], respectively, which are similar to those of complexes [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]$^+$

[N(1)–Ru(1)–N(2) = 76.5(2)°] [59] and [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl(2,3-bis(2-pyridyl)quinoxaline)]$^+$ [N(1)–Ru(1)–N(2) = 76.2(2)°] [65]. The distances between the ruthenium atom and the centroid of the η^5-C$_5$H$_5$ ring is 1.820 Å in complex [**3**]PF$_6$, whereas the distance between the rhodium atom and the centroid of the

η^5-C$_5$Me$_5$ ring is 1.785 Å in complex [**5**]PF$_6$. These bond distances are comparable to those in the related complex cations [Ru(η^5-C$_5$H$_5$)(PPh$_3$)(κ^2-paa)]$^+$, [Ru(η^5-C$_5$H$_5$)(κ^1-dppm)(κ^2-paa)]$^+$ [63] and [(η^5-C$_5$Me$_5$)Rh(3,6-bis(2-pyridyl)4-phenylpyridazine)Cl]PF$_6$ (1.789 Å) and [(η^5-C$_5$Me$_5$)Ir(pyNp)Cl]PF$_6$ (PyNp = 2-(2-pyridyl)-1,8-naphthyridine) (1.79 Å) [53].

3.3. Synthesis of the dinuclear complexes [7](PF$_6$)$_2$–[12](PF$_6$)$_2$ as hexafluorophosphate salts

The reaction of the chloro bridged dinuclear complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C$_6$H$_6$, *p*-Pr^{i}C$_6$H$_4$Me); [(η^5-C$_5$Me$_5$)M(μ-Cl)Cl]$_2$ (M = Rh, Ir) with 1 equiv. of ligand **L** [4,4′-bis(2-pyridyl-4-
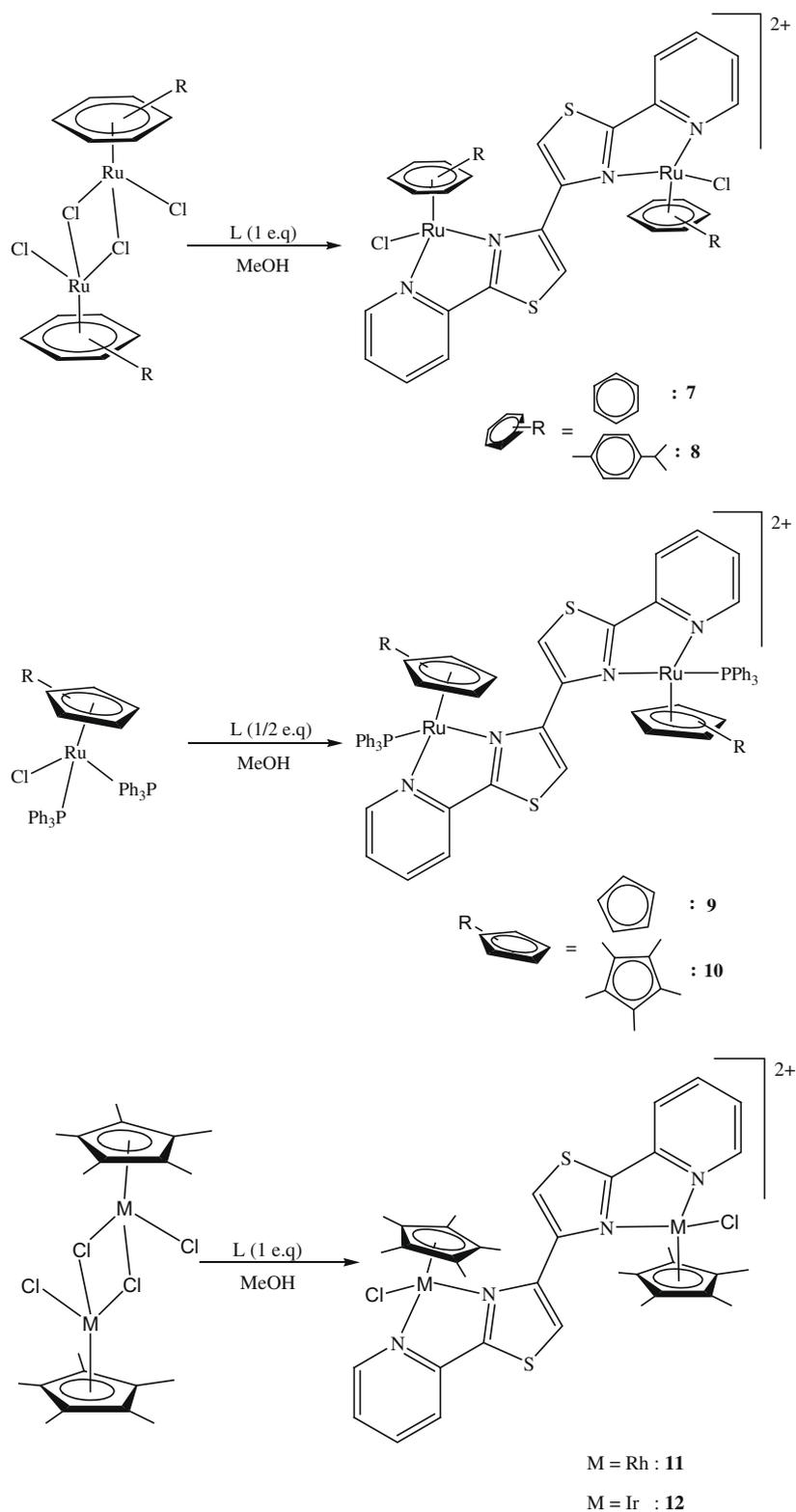
Scheme 2.

thiazole)] in methanol results in the formation of the orange color, air-stable dinuclear dicationic complexes $[\{(\eta^6\text{-}C_6Me_6)RuCl\}_2(L)]^{2+}$ (**7**), $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl\}_2(L)]^{2+}$ (**8**), $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(L)]^{2+}$ (**11**) and $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(L)]^{2+}$ (**12**). Similarly reactions of cyclopentadienyl/pentamethylcyclopentadienyl ruthenium triphenylphosphine complexes $[(\eta^5\text{-}Cp)Ru(PPh_3)_2Cl]$ (Cp = C_5H_5 and C_5Me_5) and half equivalent of ligand **L** in methanol at 55 °C leads to the formation of $[\{(\eta^5\text{-}C_5H_5)Ru(PPh_3)\}_2(L)]^{2+}$ (**9**) and $[\{(\eta^5\text{-}C_5Me_5)Ru(PPh_3)\}_2(L)]^{2+}$ (**10**). All these complexes are isolated as their hexafluorophosphate salts (Scheme 2) and they were characterized by mass, ^{1}H NMR spectrometry, and elemental analyses. In addition to these complexes **9** and **10** were also characterized by ^{31}P NMR spectrometry. On top of these mono and dinuclear complexes we were tried to synthesize hetero dinuclear, tri and tetra nuclear complexes by using varieties of transition metals, but results were not fruitful.

Infrared spectra of these dinuclear complexes $[\mathbf{7}](PF_6)_2$ to $[\mathbf{12}](PF_6)_2$, showed a similar trend as the mononuclear cationic complexes $[\mathbf{1}]PF_6$ to $[\mathbf{6}]PF_6$. In the mass spectra the complexes **7**, **8**, **11** and **12** hexafluorophosphate salts give rise to two main peaks; a minor peak with an approximately 50% intensity attributed to $[M^{2+} + PF_6^-]^+$ at m/z 891, 1008, 943 and 1122, respectively, and a major peak which corresponds to loss of $[(\text{arene})MCl]^+$ fragment to the formation of mononuclear cations **1**, **2**, **5** and **6** at m/z = 537, 593, 560 and 649, respectively.

The ^{1}H NMR spectra of the dinuclear cationic complexes $[\mathbf{7}](PF_6)_2$ to $[\mathbf{12}](PF_6)_2$ exhibited five distinct resonances assignable to thiazolyl ring and pyridyl ring protons of the L ligand indicating formation of dinuclear complexes. Besides these resonances complex $[\mathbf{7}](PF_6)_2$ exhibit two singlets at δ = 6.01 and δ = 5.99 for the protons of the benzene ligands and complex $[\mathbf{8}](PF_6)_2$ exhibits four doublets at δ = 1.38–0.98, and septets at δ = 2.42 for the protons of the isopropyl group. The four doublets observed at δ = 5.86–5.38 correspond to the aromatic *p*-cymene ring CH protons. Complexes $[\mathbf{9}](PF_6)_2$ to $[\mathbf{12}](PF_6)_2$ exhibit a strong peak at δ = 4.86 and 1.97, 2.15, 1.54 for the cyclopentadienyl and pentamethylcyclopentadienyl ligands, which are slightly shifted downfield in comparison to the starting complexes. In the dinuclear complexes each arene ligand has exhibited set of individual resonances for each set of protons due to free rotation in solution ($[\mathbf{7}](PF_6)_2$ and $[\mathbf{8}](PF_6)_2$), where as pentamethylcyclopentadienyl ligand containing complexes ($[\mathbf{11}](PF_6)_2$ and $[\mathbf{12}](PF_6)_2$) exhibits only one set of resonance for both pentamethylcyclopentadienyl ligands due to center of inversion in these molecules.

The ^{31}P NMR spectra of complexes $[\mathbf{9}](PF_6)_2$ and $[\mathbf{10}](PF_6)_2$ exhibit a strong peak at δ = 49.28 and 51.33, respectively, which are shifted downfield as compared to starting neutral precursors δ = 42.00 and 38.50 [56,57]. This down field chemical shift of phosphorus nucleus indicates the formation of cationic complexes.

3.4. Crystal structure analysis of $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl\}_2(L)]^{2+}$ ($[\mathbf{8}](PF_6)_2$) and $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(L)]^{2+}$ ($[\mathbf{12}](PF_6)_2$)

The molecular structure of $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl\}_2(L)]^{2+}$ ($[\mathbf{8}](PF_6)_2$) and $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(L)]^{2+}$ ($[\mathbf{12}](PF_6)_2$) have been established by single-crystal X-ray structure analysis. Selected bond lengths and angles for complexes $[\mathbf{8}](PF_6)_2$ and $[\mathbf{12}](PF_6)_2$ are presented in Table 2. In the dinuclear complexes $[\mathbf{8}](PF_6)_2$ and $[\mathbf{12}](PF_6)_2$, the metal centers are stereogenic. However, while $[\mathbf{8}](PF_6)_2$ crystallized as racemic crystals with the centrosymmetric space group $P\bar{1}$, $[\mathbf{12}](PF_6)_2$ crystallizes as a racemic mixture of enantiopure crystals with the non-centrosymmetric space group $P2_12_12$. As well both the complexes show a typical piano-stool geometry with the metal center coordinated by the aromatic ligand, a terminal chloride and a chelating *N,N*-ligand (see Figs. 3 and 4). The compounds $[\mathbf{8}](PF_6)_2$ and $[\mathbf{12}](PF_6)_2$ contain two metal centers (Ru(II) or

Ir(III)) bonded to an $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ or $\eta^5\text{-}C_5Me_5$ ligands, respectively, which are bridged by the L ligand through its nitrogen atoms. Interestingly, the dinuclear dication $[\mathbf{8}](PF_6)_2$ reveals a *trans* conformation of the two chloro ligands (see Fig. 3), while the *cis* isomer is observed in the case of $[\mathbf{12}](PF_6)_2$ (see Fig. 4). The average distances between the metal atom and the carbon atoms of the η^6-$p\text{-}^iPrC_6H_4Me$ ring are at 2.20 Å. This bond length is comparable to those in related $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ ruthenium complexes such as $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(2\text{-acetylthiazoleazine})Cl]PF_6$ [2.10 Å] [66] and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(2\text{-}(2\text{-thiazolyl})\text{-}1,8\text{-naphthyridine})Cl]PF_6$ [2.19 Å] [53]. The Ru–N bond distances ranging from 2.093(3) to 2.157(3) Å are longer than in the mononuclear complex $[\mathbf{3}]PF_6$ [2.067(8) and 2.105(8) Å], while the ruthenium-chlorine bond distances are comparable. In complex $[\mathbf{8}](PF_6)_2$, the isopropyl group of the *p*-cymene ligand is located opposite to the halide ligand in order to limit steric interaction. The average distances between the metal atom and the carbon atoms of the $\eta^5\text{-}C_5Me_5$ ring is at 2.18 Å, which is almost identical to those reported iridium or rhodium complexes such as $[(\eta^5\text{-}C_5Me_5)Ir((S)\text{-}1\text{-phenylethylsalicylaldiimine})]$ [2.17 Å] and $[(\eta^5\text{-}C_5Me_5)RhCl((S)\text{-}1\text{-phenylethylsalicylaldiimine})]$ [2.16 Å] [67]. The Ir–Cl bond lengths are 2.406(2) Å [in $[\mathbf{12}](PF_6)_2$], which is almost identical to the reported cationic polypyridyl iridium complex $[\{(\eta^5\text{-}C_5Me_5)IrCl\}2(2,2'\text{-bipyrimidine})]^{2+}$ [2.408(8) Å] [68], while Ir–N bond distances are similar to mononuclear rhodium complex ($[\mathbf{5}]PF_6$). The N(1)–M(1)–N(2) and N(3)–M(2)–N(4) bond angles in complex $[\mathbf{3}]PF_6$ and $[\mathbf{5}]PF_6$ are found to be [77.13(1)° and 77.03(1)°] and [75.61(9)° and 75.61(9)°], respectively. The distances between the ruthenium atom and the centroid of the $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ ring is 1.689 Å in complex $[\mathbf{8}](PF_6)_2$, whereas the distance between the iridium atom and the centroid of the $\eta^5\text{-}C_5Me_5$ ring is 1.811 Å in complex $[\mathbf{12}](PF_6)_2$. These bond distances are comparable to those in the related complex cations $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(2\text{-acetylthiazoleazine})Cl]PF_6$ [66] and $[(\eta^5\text{-}C_5Me_5)Ir(pynp)Cl]PF_6$ (PyNp=2-(2-pyridyl)-1,8-naphthyridine) (1.79 Å) [53].

3.5. UV–vis spectroscopy

Electronic absorption spectra of complexes $[\mathbf{1}]PF_6$ to $[\mathbf{12}](PF_6)_2$ were acquired in acetonitrile, at 10^{-5} M concentration in the range 250–550 nm. The spectral data of these complexes conformed well to their respective formulations. The spectra of these complexes are characterized by two main features, *viz.*, an intense ligand-localized or intra-ligand $\pi \rightarrow \pi^*$ transition in the ultraviolet region and metal-to-ligand charge transfer (MLCT) $d\pi(M) \rightarrow \pi^*$ (L – ligand) bands in the visible region [69]. Since the low spin d^6 configuration of the mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II), Rh(III) and Ir(III) centers, these can interact with low lying π^* orbitals of the ligands. All the mononuclear complexes $[\mathbf{1}]PF_6$ to $[\mathbf{6}]PF_6$ show only an intense band in the region 333–341 nm, while all dinuclear complexes $[\mathbf{7}](PF_6)_2$ to $[\mathbf{12}](PF_6)_2$ show two bands, one is at 310–312 nm with high intensity as well as a second one at 355–358 nm observed as a shoulder peak (see Fig. 5). The high intensity band in UV region for both mononuclear and dinuclear complexes is assigned to inter and intra-ligand $\pi-\pi^*$/$n-\pi^*$ transitions [68,70,71], while the low energy absorption band in the visible region for dinuclear complexes is assigned to metal-to-ligand charge transfer (MLCT) ($t_{2g}-\pi^*$). Representative spectra of these complexes are represented in Fig. 5.

4. Conclusions

In summary, in this work ligand **L** [4,4′-bis(2-pyridyl-4-thiazole)] reacted with series of arene and cyclopentadienyl ruthenium, rhodium and iridium complexes yielded novel series of
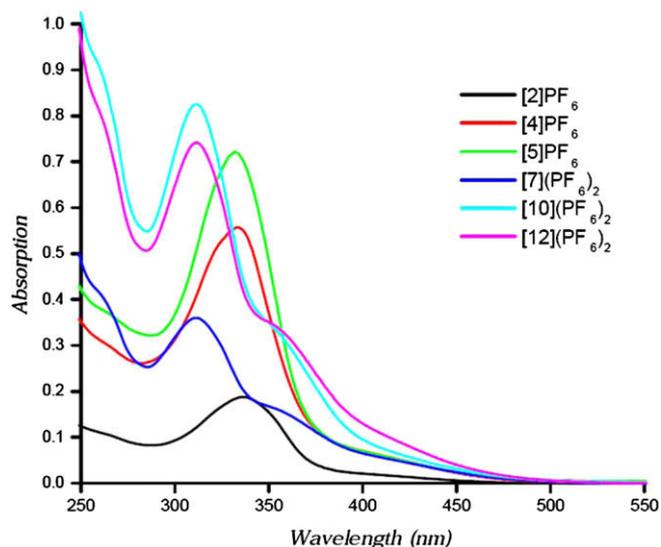
Fig. 5. UV–vis electronic spectra of representative complexes in acetonitrile at 298 K.

mononuclear complexes [**1**]PF$_6$ to [**6**]PF$_6$ as well as dinuclear complexes [**7**](PF$_6$)$_2$ to [**12**](PF$_6$)$_2$ in good yield, which are remarkably stable in air as well as in solution. In all these, both mono and dinuclear complexes, the metal atom is bonded with the major coordinated sites N1 and N2 or N3 and N4 and not with the other possible coordinated sites N1 and S1 or N3 and S2. But our effort to make hetero-nuclear complexes by using other binding site sulfur was unsuccessful.

Acknowledgement

Appendix A. Supplementary material

CCDC 745007, 745008, 745009 and 745010 contains the supplementary crystallographic data for [**3**]PF$_6$·(CH$_3$)$_2$CO, [**5**]PF$_6$·(CH$_3$)$_2$CO, [**8**](PF$_6$)$_2$·CH$_3$CN and [**12**](PF$_6$)$_2$·CH$_2$Cl$_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.007.

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