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Cationic half-sandwich complexes (Rh, Ir, Ru) containing 2-substituted-1,8-naphthyridine chelating ligands: Syntheses, X-ray structure analyses and spectroscopic studies

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ABSTRACT

Reactions of the dinuclear complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, *p*-^{i}PrC$_6$H$_4$Me) and $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) with 2-substituted-1,8-naphthyridine ligands, 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp), lead to the formation of the mononuclear cationic complexes $[(\eta^6\text{-}C_6H_6)Ru(L)Cl]^+$ {L = pyNp (**1**); tzNp (**2**); fuNp (**3**)}, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(L)Cl]^+$ {L = pyNp (**4**); tzNp (**5**); fuNp (**6**)}, $[(\eta^5\text{-}C_5Me_5)Rh(L)Cl]^+$ {L = pyNp (**7**); tzNp (**8**); fuNp (**9**)} and $[(\eta^5\text{-}C_5Me_5)Ir(L)Cl]^+$ {L = pyNp (**10**); tzNp (**11**); fuNp (**12**)}. All these complexes are isolated as chloro or hexafluorophosphate salts and characterized by IR, NMR, mass spectrometry and UV/Vis spectroscopy. The molecular structures of [**1**]Cl, [**2**]PF_6, [**4**]PF_6, [**5**]PF_6 and [**10**]PF_6 have been established by single crystal X-ray structure analysis.

1. Introduction

Mononuclear complexes of platinum group metals containing heterocyclic nitrogen based ligands have received considerable attention owing to their photochemical properties [1], catalytic activities [2], electrochemical behaviour [3], as well as in the development of new biologically active agents [4]. Ruthenium, rhodium and iridium unsubstituted 1,8-naphthyridine based complexes are interesting in their own right of uses as dye – sensitized solar cells and photophysical effects [5]. The reactivity of these metals with substituted 1,8-naphthyridine based ligands have also been reported: Examples with dinuclear metal–metal bonded compounds [6], and mononuclear compounds [6c,7] being known. However no reports dealing with η^5-pentamethylcyclopentadienyl or η^6-arene platinum group metal (Rh, Ir, or Ru) in connectivity with substituted 1,8-naphthyridine ligands have been reported so far.

Herein, we describe the synthesis of twelve η^5-C_5Me_5 rhodium, iridium and η^6-C_6H_6, η^6-*p*-^{i}PrC$_6$H$_4$Me ruthenium complexes incorporating 2-substituted-1,8-naphthyridine ligands; 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp). All complexes are characterized by IR, NMR, mass spectrometry and UV/Vis spectroscopy. The molecular structures of five representative complexes are presented as well.

2. Experimental

2.1. General remarks

All solvents were dried and distilled prior to use. Ruthenium trichloride hydrate (Arora Matthey Ltd.), 2-aminonicotinaldehyde (Acros Organics), 2-acetylpyridine, 2-acetylthiazole and 2-acetylfuran (Aldrich) were purchased and used as received. $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-Cl})Cl]_2$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-Cl})Cl]_2$ [8], and $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) [9] were prepared according to literature methods. The ligands pyNp, tzNp and fuNp were prepared by the Friedlander condensation of 2-aminonicotinaldehyde with the corresponding acyl derivatives [10]. NMR spectra were recorded on AMX-400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer 983 spectrophotometer; elemental analyses of the complexes were performed on a Perkin–Elmer-2400 CHN/S analyzer. Mass spectra were obtained from ZQ mass spectrometer by ESI method. Absorption spectra were obtained at room temperature using a Perkin–Elmer Lambda 25 UV/Vis spectrophotometer. All the new complexes gave satisfactory CHN values.

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2.2. Preparation of the cationic complexes **1–6**

*Synthesis of [(η^6-C_6H_6)Ru(pyNp)Cl]Cl ([**1**]Cl)*: A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.09 mmol) and pyNp (42 mg, 0.18 mmol) in 10 ml of acetonitrile was refluxed for 90 min. A colour change from light brown to dark brown was observed. The resulting solution was concentrated under vacuum (2 ml). Then 15 ml of hexane was added to induce precipitation. The yellowish brown solid was filtered off, washed with diethyl ether and dried under vacuum.

Yield: 80 mg, (87%). Anal. Calc. for $C_{19}H_{15}Cl_2N_3Ru$ (457.31): C, 49.90; H, 3.31; N, 9.19. Found: C, 50.08; H, 3.69; N, 9.15%.

^{1}H NMR ($CDCl_3$, δ): 9.56 (d, 1H, J_{H-H} = 8 Hz), 9.38 (q, 1H), 8.76 (d, 1H), 8.58 (m, 2H), 8.48 (d, 1H), 7.91 (td, 1H), 7.90 (q, 1H), 7.78 (td, 1H), 6.15 (s, 6H, C_6H_6). ESI-MS (*m*/*z*): 419.8 (100%) [M−Cl]$^+$.

*Synthesis of [(η^6-C_6H_6)Ru(tzNp)Cl]PF_6 ([**2**]PF_6)*: A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.09 mmol), tzNp (43 mg, 0.20 mmol) and 2.5 equiv. of NH_4PF_6 in 10 ml of acetonitrile was stirred at room temperature for 12 h. A color change was observed from light brown to yellowish brown during the process. The reaction mixture was filtered off and washed with acetonitrile. The filtrate was reduced under vacuum (2 ml) and 15 ml of diethyl ether was then added to induce precipitation. After standing for 15 min, a yellow precipitate was settled down. The resulting precipitate was filtered, washed with diethyl ether and dried under vacuum.

Yield: 85 mg (76%). Anal. Calc. for $C_{17}H_{13}ClN_3F_6SPRu$ (572.85): C, 35.64; H, 2.29; N, 7.34. Found: C, 35.75; H, 2.35; N, 7.46%.

^{1}H NMR (CD_3CN, δ): 9.40 (q, 1H), 8.74 (d, 1H, J_{H-H} = 8.12 Hz, tz-H_1), 8.69 (d, 1H), 8.56 (dd, 1H), 8.24 (d, 1H, J_{H-H} = 4 Hz, tz-H_2), 8.19 (d, 1H), 7.9 (q, 1H), 6.20 (s, 6H, C_6H_6). ESI-MS (*m*/*z*): 425.2 (100%) [M−PF_6]$^+$, 389.4 (20%) [M−PF_6−Cl]$^+$.

*Synthesis of [(η^6-C_6H_6)Ru(fuNp)Cl]PF_6 ([**3**]PF_6)*: A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.09 mmol), fuNp (36 mg, 0.18 mmol) and 2.5 equivalents of NH_4PF_6 was used and treated following a procedure similar to that described in the synthesis of complex [**2**]PF_6. The resulting precipitate was filtered, washed with benzene and dried under vacuum.

Yield 70 mg, (63%). Anal. Calc. for $C_{18}H_{14}ClF_6N_2OPRu$ (555.80): C, 38.90; H, 2.54; N, 6.38. Found: C, 38.70; H, 2.45; N, 6.56%.

^{1}H NMR ($CDCl_3$, δ): 9.52 (dd, 1H), 8.49 (dd, J_{H-H} = 7.12 Hz, 1H), 8.09 (dd, 1H, J_{H-H} = 8.08 Hz), 7.84 (d, 1H), 7.71 (d, 1H), 7.67 (q, 1H), 7.57 (q, 1H), 6.81 (q, 1H), 5.93 (S, 6H, C_6H_6). ESI-MS (*m*/*z*): 408.9 (100%) [M−PF_6]$^+$, 374.1 (20%) [M−PF_6−Cl]$^+$.

*Synthesis of [(η^6-*p*-^{i}PrC_6H_4Me)Ru(pyNp)Cl]PF_6 ([**4**]PF_6)*: A mixture of [(η^6-*p*-^{i}PrC_6H_4Me)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.081 mmol), pyNp (34 mg, 0.163 mmol) and 2.5 equiv. of NH_4PF_6 in 10 ml of acetonitrile were stirred at room temperature for 5 h. A white precipitate (NH_4Cl) was removed by filtration. The filtrate was concentrated to 2 ml and diethyl ether was added to induce precipitation. After standing for 15 min, an orange-yellowish precipitate was observed. After filtration, the solid was washed with diethyl ether and dried under vacuum.

Yield: 82 mg, (81%). Anal. Calc. for $C_{23}H_{23}ClF_6N_3PRu$ (622.93): C, 44.35; H, 3.72; N, 6.75. Found: C, 44.70; H, 4.05; N, 6.76%.

^{1}H NMR (CD_3CN, δ): 9.46 (d, 1H, J_{H-H} = 12 Hz,), 9.37 (q, 1H, J_{H-H} = 4 Hz), 8.73 (d, 1H), 8.57 (m, 2H), 8.48 (d, 1H), 8.26 (td, 1H), 7.91 (q, 1H), 7.78 (td, 1H), 6.21 (d, 1H, J_{H-H} = 5.4 Hz, $Ar_{p\text{-}cy}$), 6.13 (d, 2H, J_{H-H} = 6.2 Hz, $Ar_{p\text{-}cy}$), 5.79 (d, 1H, J_{H-H} = 5.2 Hz, $Ar_{p\text{-}cy}$), 2.47 (sept, 1H, J_{H-H} = 4.4 Hz, $CH(CH_3)_2$), 2.27 (s, 3H, CH_3), 0.91 (d, 3H, $CH(CH_3)_2$), 0.83 (d, 3H, $CH(CH_3)_2$). ESI-MS (*m*/*z*): 475.9 (100%) [M−PF_6]$^+$, 440 (8%) [M−PF_6−Cl]$^+$, 306.4 (4%) [M−PF_6−Cl−*p*-cy]$^+$.

*Synthesis of [(η^6-*p*-^{i}PrC_6H_4Me)Ru(tzNp)Cl]PF_6 ([**5**]PF_6)*: A mixture of [(η^6-*p*-^{i}PrC_6H_4Me)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), tzNp (35 mg, 0.17 mmol) and 2.5 equiv. of NH_4PF_6 in 10 ml of methanol was refluxed for 3 h. A color change from brown to yellowish brown was observed. The solution was evaporated and the residue extracted with dichloromethane. The white insoluble material was filtered off. The filtrate was concentrated to 2 ml and diethyl ether was added to induce precipitation. The yellowish orange precipitate was washed with diethyl ether and dried under vacuum.

Yield: 80 mg, (78%). Anal. Calc. for $C_{21}H_{21}ClF_6N_3SPRu$ (628.96): C, 40.10; H, 3.37; N, 6.68. Found: C, 40.43; H, 3.35; N, 6.76%.

^{1}H NMR ($CDCl_3$, δ): 9.35 (q, 1H), 8.74 (d, 1H, J_{H-H} = 3.36 Hz), 8.62 (d, 1H), 8.45 (dd, 1H), 8.15 (d, 1H, J_{H-H} = 8.32 Hz), 8.06 (d, 1H), 7.86 (q, 1H), 6.31 (d, 1H, J_{H-H} = 6.2 Hz, $Ar_{p\text{-}cy}$), 6.26 (d, 1H, J_{H-H} = 6 Hz, $Ar_{p\text{-}cy}$), 6.11 (d.1H, J_{H-H} = 5.68 Hz, $Ar_{p\text{-}cy}$), 5.99 (d, 1H, J_{H-H} = 6 Hz, $Ar_{p\text{-}cy}$), 2.79 (sept, 1H, J_{H-H} = 4.14 Hz, $CH(CH_3)_2$), 2.28 (s, 3H, CH_3), 1.08 (d, 3H, $CH(CH_3)_2$), 1.02 (d, 3H, $CH(CH_3)_2$). ESI-MS (*m*/*z*): 481.9 (100%) [M−PF_6]$^+$, 445.6 (45%) [M−PF_6−Cl]$^+$.

*Synthesis of [(η^6-*p*-^{i}PrC_6H_4Me)Ru(fuNp)Cl]PF_6 ([**6**]PF_6)*: The reaction of [(η^6-*p*-^{i}PrC_6H_4Me)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), fuNp (32 mg, 0.16 mmol) and 2.5 equiv. of NH_4PF_6 was carried out following a procedure similar to that described in the synthesis of [**2**]PF_6.

Yield: 70 mg, (70%). Anal. Calc. for $C_{22}H_{22}ClF_6N_2OPRu$ (611.91): C, 43.18; H, 3.62; N, 5.79. Found: C, 43.23; H, 3.73; N, 5.46%.

^{1}H NMR (CD_3CN, δ): 9.58 (dd, 1H), 9.05 (dd, 1H), 8.32 (dd, 1H, J_{H-H} = 8.12 Hz), 8.10 (d, 1H), 7.99 (d, 1H), 7.76 (d, 1H), 7.57 (q, H), 6.81 (q, 1H), 5.81 (d, 2H, J_{H-H} = 6.24 Hz, $Ar_{p\text{-}cy}$), 5.56 (d, 2 H, J_{H-H} = 6.14 Hz, $Ar_{p\text{-}cy}$), 2.86 (sept, 1H, J_{H-H} = 4.04 Hz, $CH(CH_3)_2$), 2.16 (s, 3H, CH_3), 1.18 (d, 3H, $CH(CH_3)_2$), 1.07 (d, 3H, $CH(CH_3)_2$). ESI-MS (*m*/*z*): 464.9 (100%) [M−PF_6]$^+$, 429.2 (15%) [M−PF_6−Cl]$^+$.

2.3. Preparation of the cationic complexes **7–12**

General procedure: A mixture of [(η^5-C_5Me_5)M(μ-Cl)Cl]$_2$ (0.07 mmol), 2-substituted-1,8-naphthyridine ligand (0.14 mmol) and 2.5 equiv. of NH_4PF_6 in dry methanol (10 ml) was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. After filtration, the volume was reduced to 2 ml and excess diethyl ether was added to induce precipitation. The precipitate was washed with diethyl ether and dried under vacuum.

*[(η^5-C_5Me_5)Rh(pyNp)Cl]PF_6 ([**7**]PF_6)*: Orange-yellow solid, yield: 70 mg (79%). Anal. Calc. for $C_{23}H_{24}ClF_6N_3PRh$ (625.77): C, 44.14; H, 3.87; N, 6.71. Found: C, 44.70; H, 4.06; N, 6.76%.

^{1}H NMR (CD_3CN, δ): 9.32 (q, 1H, J_{H-H} = 4.08 Hz), 9.03 (d, 1H, J_{H-H} = 4 Hz), 8.78 (d, 1H), 8.55 (m, 2H), 8.5 (d, 1H), 8.29 (td, 1H), 7.87 (td, 2H), 1.60 (s, 15H, C_5Me_5). ESI-MS (*m*/*z*): 480.81 (100%) [M-PF_6]$^+$, 444.1 (70%) [M−PF_6−Cl]$^+$.

*[(η^5-C_5Me_5)Rh(tzNp)Cl]PF_6 ([**8**]PF_6)*: Orange solid, yield: 80 mg (89%). Anal. Calc. for $C_{21}H_{22}ClF_6N_3SPRh$ (628.96): C, 39.72; H, 3.51; N, 6.65. Found: C, 40.03; H, 3.45; N, 6.86%.

^{1}H NMR (CD_3CN, δ): 9.34 (q, 1H, J_{H-H} = 1.92 Hz), 8.76 (d, 1H, J_{H-H} = 8.4 Hz), 8.57 (dd, 1H), 8.38 (d, 3H), 8.29 (d, 1H, J_{H-H} = 8.4 Hz), 8.23 (d, 1H), 7.87 (q, 1H), 1.71 (s, 15H, C_5Me_5). ESI-MS (*m*/*z*): 485.28 (100%) [M−PF_6]$^+$, 450.1 (9%) [M−PF_6−Cl]$^+$.

*[(η^5-C_5Me_5)Rh(fuNp)Cl]PF_6 ([**9**]PF_6)*: Orange-yellow solid, yield: 68 mg (78%). Anal. Calc. for $C_{22}H_{23}ClF_6N_2OPRh$ (614.75): C, 42.98; H, 3.77; N, 4.56. Found: C, 42.23; H, 3.73; N, 4.34%.

^{1}H NMR (CD_3CN, δ): 9.42 (dd, 1H), 9.09 (dd, 1H), 8.52 (d, 1H), 8.12 (dd, 1H), 7.79 (d, 1H), 7.76 (d, 1H), 7.67 (q, 1H), 7.52 (q, 1H), 1.55 (s, 15H, C_5Me_5). ESI-MS (*m*/*z*): 468.6 [M−PF_6]$^+$, 433.1 (7%) [M−PF_6−Cl]$^+$.

*[(η^5-C_5Me_5)Ir(pyNp)Cl]PF_6 ([**10**]PF_6)*: Orange-yellow solid, yield: 80 mg (89%). Anal. Calc. for $C_{23}H_{24}ClF_6N_3PIr$ (715.09): C, 38.63; H, 3.38; N, 5.58. Found: C, 38.80; H, 3.65; N, 5.66%.

^{1}H NMR ($CDCl_3$, δ): 9.38 (d, 1H), 9.3 (q, 1H), 8.73 (d, 1H), 8.55 (m, 2H), 8.49 (d, 1H), 8.28 (td, 1H), 7.96 (q,1H), 7.87 (td, 1H), 1.71 (s, 15H, C_5Me_5). ESI-MS (*m*/*z*): 569.1 (100%) [M−PF_6]$^+$, 533.2 (23%) [M−PF_6−Cl]$^+$.