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Study of half-sandwich platinum group metal complexes bearing dpt-NH_2 ligand

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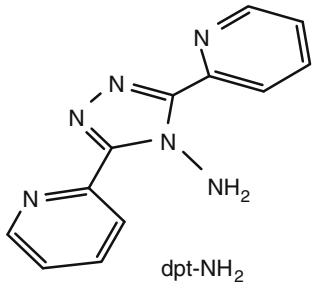
ABSTRACT

A quite general approach for the preparation of η^5-and η^6-cyclichydrocarbon platinum group metal complexes is reported. The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$ and C_6Me_6) and η^5-pentamethylcyclopentadienyl rhodium and iridium complexes $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) react with 2 equiv. of 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) in presence of NH_4PF_6 to afford the corresponding mononuclear complexes of the type $[(\eta^6\text{-arene})Ru(\text{dpt-}NH_2)Cl]PF_6$ {arene = $C_{10}H_{14}$ (**1**), C_6H_6 (**2**) and C_6Me_6 (**3**)} and $[(\eta^6\text{-}C_5Me_5)M(\text{dpt-}NH_2)Cl]PF_6$ {M = Rh (**4**), Ir (**5**)}. However, the mononuclear η^5-cyclopentadienyl analogues such as $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ complexes react in presence of 1 equiv. of dpt-NH_2 and 1 equiv. of NH_4PF_6 in methanol yielded mononuclear complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**6**), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**7**), $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**8**) and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(\text{dpt-}NH_2)]PF_6$ (**9**), respectively. These compounds have been totally characterized by IR, NMR and mass spectrometry. The molecular structures of **4** and **6** have been established by single crystal X-ray diffraction and some of the representative complexes have also been studied by UV–Vis spectroscopy.

1. Introduction

Within the large family of η^5- and η^6-cyclichydrocarbon metal complexes, piano-stool complexes of ruthenium are undeniably the most studied class of complexes. Arene metal complexes have been extensively investigated by organometallic and organic chemists for over 50 years. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized [1,2]. They have found applications in catalysis, supramolecular assemblies, molecular devices, and have shown antiviral, antibiotic, and anticancer activities. Half-sandwich complexes have proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses and therefore attracted more attention [3–6]. In addition, the four coordinated, pseudo-tetrahedral geometry makes them particularly suitable for investigation of the stereochemistry of reactions at the metal center [7]. In recent years we have been carrying out reactions of η^5- and η^6-cyclichydrocarbon metal complexes with a variety of nitrogen-based ligands [8–15] including various poly-pyridyl ligands. Ruthenium complexes of these types of nitrogen-based ligands have a capacity to function as catalysts for the oxidation of water to dioxygen [16,17]. Although comprehensive studies have been made on η^5- and η^6-transition metal complexes, complexes containing NH_2 substituted poly-pyridyl ligand of this type shown below have not yet been reported.



Ligand used in this study

Herein we describe the syntheses of nine mononuclear η^5- and η^6-cyclichydrocarbon platinum group metal complexes bearing dpt-NH_2 ligand. Attempts to prepare dimetallic derivatives by addition of a second organometallic anion were unsuccessful. All these complexes have been fully characterized by IR, NMR, mass spectrometry and UV–Vis spectroscopy. Molecular structures of the two representative complexes are also presented in this paper.

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2. Experimental

All solvents were dried and distilled prior to use. 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) was prepared using literature method [18]. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$ and C_6Me_6), $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) [19–22], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared by following the literature methods [23,22b,24–27]. NMR spectra were recorded on a Bruker 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 a ZQ mass spectrometer by the 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 results.

2.1. Single-crystal X-ray structures analyses

Crystals of **4** were grown from acetone/petroleum ether as small red plates. Crystals of **6** were grown by slow diffusion of petroleum ether into a mixture of acetonitrile and dichloromethane solution of the respective complex as deep red blocks. The crystallizations were done at room temperature. The intensity data of **4** and **6** were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART [28] software was used for data acquisition. Data integration and reduction were undertaken with the SAINT [28] and XPREP [29] softwares. Structures were solved by direct methods using SHELXS-97 [30] and refined with full-matrix least squares on F^2 using SHELXL-97 [31]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [32] for Windows. The ORTEP presentations of the representative complexes are shown in Figs. 1 and 2, respectively. The data collection

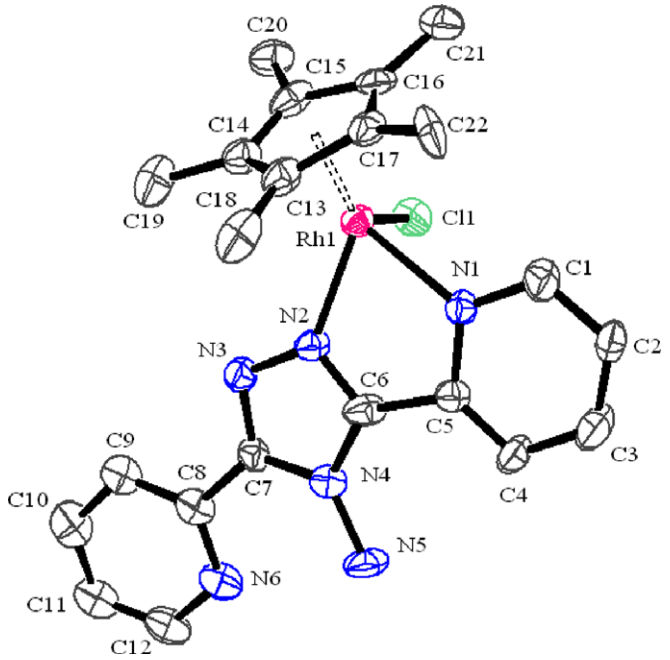


Fig. 1. Molecular structure of a complex **4** with 35% probability thermal ellipsoids. Hydrogen atoms and PF_6^- are omitted for clarity.

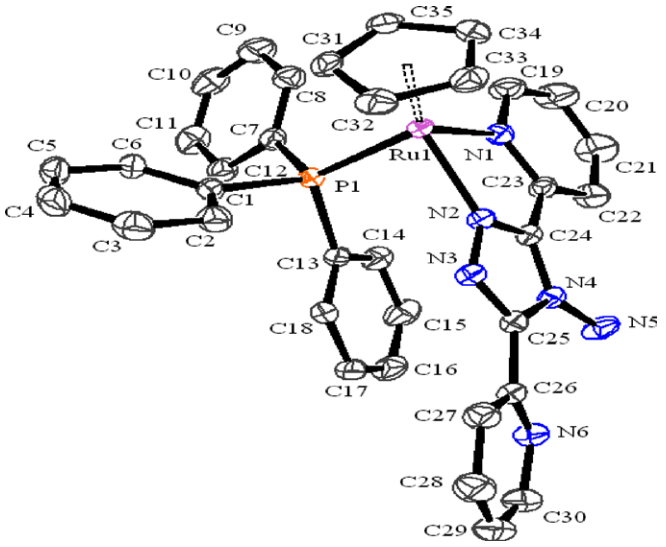


Fig. 2. Molecular structure of complex **6** with 35% probability thermal ellipsoids. Hydrogen atoms and PF_6^- are omitted for clarity.

parameters and bond lengths and angles are presented in Tables 2 and 3.

2.2. Preparation of $[(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)Ru(dpt\text{-}NH_2)Cl]PF_6$ (**1**)

A mixture of $[(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-Cl})Cl]_2$ (100 mg, 0.16 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (78 mg, 0.33 mmol) and 2 equiv. of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 h at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

Yield: 193 mg, 90%. Elemental *Anal.* Calc. for $C_{22}H_{24}ClN_6PF_6Ru$: C, 40.43; H, 3.71; N, 12.81. Found: C, 40.51; H, 3.80; N, 12.73%. IR (KBr pellets, cm^{-1}): 3430 (ν_{N-H}); 1615 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 846 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.39 (d, J = 8 Hz, 1H), 8.81 (d, J = 7.2 Hz, 1H), 8.76 (d, J = 4.4 Hz, 1H), 8.41 (d, J = 8 Hz, 1H), 8.21 (t, J = 7.6 Hz, 1H), 8.06 (t, J = 7.6 Hz, 1H), 7.74 (t, J = 7.2 Hz, 1H), 7.61 (t, J = 5.2 Hz, 1H), 7.42 (s, 2H, $-NH_2$), 5.98 (d, J = 4 Hz, 1H, $Ar_{p\text{-}cy}$), 5.90 (d, J = 6 Hz, 1H, $Ar_{p\text{-}cy}$), 5.79 (d, J = 6 Hz, 1H, $Ar_{p\text{-}cy}$), 5.67 (d, J = 6 Hz, 1H, $Ar_{p\text{-}cy}$), 2.90 (sep, 1H), 2.24 (s, 3H), 1.24 (d, J = 6.8 Hz, 3H), 1.19 (d, J = 6.8 Hz, 3H); ESI-MS (m/z): 496.7 [M−PF_6], 461.7 [M−PF_6−Cl].

2.3. Preparation of $[(\eta^6\text{-}C_6H_6)Ru(dpt\text{-}NH_2)Cl]PF_6$ (**2**)

A mixture of $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-Cl})Cl]_2$ (100 mg, 0.2 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (96 mg, 0.4 mmol) and 2 equiv. of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 h at room temperature. The brown compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

Yield: 180 mg, 75%. Elemental *Anal.* Calc. for $C_{18}H_{16}ClN_6PF_6Ru$: C, 36.19; H, 2.71; N, 14.03. Found: C, 36.28; H, 2.82; N, 13.95%. IR (KBr pellets, cm^{-1}): 3432 (ν_{N-H}); 1627 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 838 (ν_{P-F}); ^1H NMR (400 MHz, CD_3CN): δ = 9.33 (d, J = 8 Hz, 1H), 8.92 (d, J = 7.2 Hz, 1H), 8.62 (d, J = 7.6 Hz, 1H), 8.31 (d, J = 8 Hz, 1H), 8.22 (t, J = 5.2 Hz, 1H), 8.09 (t, J = 7.2 Hz, 1H), 7.69 (t, J = 6.4 Hz, 1H), 7.54 (t, J = 5.6 Hz, 1H), 7.43 (s, 2H, $-NH_2$), 6.29 (s, 6H, C_6H_6); ESI-MS (m/z): 452.8 [M−PF_6].

2.4. Preparation of $[(\eta^6\text{-}C_6Me_6)Ru(dpt\text{-}NH_2)Cl]PF_6$ (**3**)

A mixture of $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-Cl})Cl]_2$ (100 mg, 0.14 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (72 mg, 0.29 mmol) and

2 equiv. of NH_4PF_6 was stirred in dry methanol (30 ml) for 4 h at room temperature. The solvent was removed by using rotary evaporator. The solid was dissolved in dichloromethane and then filtered to remove ammonium chloride. The solution was concentrated to 2 ml and excess of diethylether was added for precipitation. The light brown color product was separated out, washed with diethylether and dried in vacuum.

Yield: 132 mg, 64.7%. Elemental *Anal.* Calc. for $C_{24}H_{28}ClN_6PF_6Ru$: C, 42.31; H, 4.11; N, 12.29. Found: C, 42.43; H, 4.19; N, 12.16%. IR (KBr pellets, cm^{-1}): 3433 (ν_{N-H}); 1618 ($\nu_{C=C}$); 1474 ($\nu_{C=N}$); 846 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.41 (d, J = 7.2 Hz, 1H), 8.96 (d, J = 8 Hz, 1H), 8.73 (d, J = 8 Hz, 1H), 8.42 (d, J = 7.6 Hz, 1H), 8.33 (t, J = 6.4 Hz, 1H), 8.16 (t, J = 7.6 Hz, 1H), 7.72 (t, J = 6.4 Hz, 1H), 7.63 (t, J = 5.6 Hz, 1H), 7.51 (s, 2H, $-NH_2$), 2.10 (s, 18H, C_6Me_6); ESI-MS (m/z): 537.2 [$M-PF_6$], 502.1 [$M-PF_6-Cl$].

2.5. Preparation of $[(\eta^5\text{-}C_5Me_5)M(dpt\text{-}NH_2)Cl]PF_6$ {M = Rh (**4**), Ir (**5**)}

A mixture of $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) (0.16 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (77 mg, 0.32 mmol) and 2 equiv. of NH_4PF_6 in dry methanol (30 ml) were stirred at room temperature for 6 h until the color of the solution changed to dark yellow. The solvent was removed using rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (5 ml), and the solution was filtered to remove ammonium chloride. The light red solution was concentrated to 2 ml, when addition of excess hexane gave the orange–yellow complex, which was separated and dried under vacuum.

*Complex [**4**]*: Yield: 150 mg, 75%. Elemental *Anal.* Calc. for $C_{22}H_{25}ClN_6PF_6Rh$: C, 40.21; H, 3.81; N, 12.81. Found: C, 40.29; H, 3.90; N, 12.73%. IR (KBr pellets, cm^{-1}): 3446 (ν_{N-H}); 1632 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 844 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.95 (d, J = 8 Hz, 1H), 8.77 (d, J = 5.6 Hz, 1H), 8.70 (d, J = 4.8 Hz, 1H), 8.35 (d, J = 4 Hz, 1H), 8.14 (t, J = 8 Hz, 1H), 7.97 (t, J = 6.4 Hz, 1H), 7.67 (t, J = 6.4 Hz, 1H), 7.51 (t, J = 5.6 Hz, 1H), 7.26 (s, 2H, $-NH_2$), 1.59 (s, 15H, C_5Me_5); ESI-MS (m/z): 511.3 [$M-PF_6$], 476.6 [$M-PF_6-Cl$].

*Complex [**5**]*: Yield: 130 mg, 68%. Elemental *Anal.* Calc. for $C_{22}H_{25}ClN_6PF_6Ir$: C, 35.44; H, 3.39; N, 11.24. Found: C, 35.53; H, 3.47; N, 11.18%. IR (KBr pellets, cm^{-1}): 3434 (ν_{N-H}); 1630 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 843 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.65 (d, J = 7.6 Hz, 1H), 9.31 (d, J = 8 Hz, 1H), 9.00 (d, J = 5.6 Hz, 1H), 8.93 (d, J = 8 Hz, 1H), 8.41 (t, J = 7.6 Hz, 1H), 8.27 (t, J = 8 Hz, 1H), 7.89 (t, J = 9.2 Hz, 1H), 7.83 (t, J = 6.4 Hz, 1H), 7.47 (s, 2H, $-NH_2$), 2.29 (s, 15H, C_5Me_5); ESI-MS (m/z): 600.8 [$M-PF_6$], 565.8 [$M-PF_6-Cl$].

2.6. Preparation of $[(\eta^5\text{-}C_5H_5)M(dpt\text{-}NH_2)(PPh_3)]PF_6$ {M = Ru (**6**), Os (**7**)}

A mixture of $[(\eta^5\text{-}C_5H_5)M(PPh_3)_2X]$ {M = Ru, X = Cl and M = Os, X = Br} (0.137 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (0.137 mmol) and 1 equiv. of NH_4PF_6 in dry methanol (30 ml) were refluxed under dry nitrogen for 12 h until the color of the solution changed from pale yellow to orange. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium halide. The orange solution was concentrated to 5 ml, upon addition of diethylether the orange–yellow complex was precipitated, which was separated and dried under vacuum.

*Complex [**6**]*: Yield: 76 mg, 68%. Elemental *Anal.* Calc. for $C_{35}H_{30}N_6P_2F_6Ru$: C, 51.78; H, 3.72; N, 10.37. Found: C, 51.89; H, 3.79; N, 10.28%. IR (KBr pellets, cm^{-1}): 3436 (ν_{N-H}); 1615 ($\nu_{C=C}$); 1440 ($\nu_{C=N}$); 844 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.37 (d, J = 8 Hz, 1H), 8.73 (d, J = 7.6 Hz, 1H), 8.69 (d, J = 7.2 Hz, 1H), 8.43 (d, J = 8 Hz, 1H), 8.20 (t, J = 6.4 Hz, 1H), 8.12 (t, J = 7.2 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.70 (t, J = 6.4 Hz, 1H), 7.50 (s, 2H, $-NH_2$), 7.38–7.21 (m, 15H, PPh_3), 4.91 (s, 5H, C_5H_5); ^{31}P {^1H} NMR ($CDCl_3$, δ): 50.82 (s, PPh_3); ESI-MS (m/z): 696 [$M-PF_6$].

*Complex [**7**]*: Yield: 71 mg, 67.6%. *Anal.* Calc. for $C_{35}H_{30}N_6P_2F_6Os$: C, 46.69; H, 3.32; N, 9.36. Found: C, 46.78; H, 3.39; N, 9.28%. IR (KBr pellets, cm^{-1}): 3431 (ν_{N-H}); 1616 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 843 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.32 (d, J = 8 Hz, 1H), 8.88 (d, J = 7.6 Hz, 1H), 8.71 (d, J = 6.4 Hz, 1H), 8.49 (d, J = 8 Hz, 1H), 8.21 (t, J = 5.6 Hz, 1H), 8.14 (t, J = 7.2 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 8 Hz, 1H), 7.48 (s, 2H, $-NH_2$), 7.38–6.80 (m, 15H, PPh_3), 4.59 (s, 5H, C_5H_5); ^{31}P {^1H} NMR ($CDCl_3$, δ): −0.26 (s, PPh_3); ESI-MS (m/z): 758.5 [$M-PF_6$].

2.7. Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(dpt\text{-}NH_2)(PPh_3)]PF_6$ (**8**)

A mixture of $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.125 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (30 mg, 0.125 mmol) and 1 equiv. of NH_4PF_6 in dry methanol (30 ml) were refluxed under dry nitrogen for 12 h until the color of the solution changed from pale yellow to orange. The solvent was removed using rotary evaporator under reduced pressure, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The orange solution was concentrated to 5 ml, when addition of excess hexane gave the orange–yellow complex, which was separated and dried under vacuum.

Yield: 73 mg, 65.7%. *Anal.* Calc. for $C_{40}H_{40}N_6P_2F_6Ru$: C, 54.47; H, 4.56; N, 9.55. Found: C, 54.51; H, 4.61; N, 9.45%. IR (KBr pellets, cm^{-1}): 3435 (ν_{N-H}); 1599 ($\nu_{C=C}$); 1437 ($\nu_{C=N}$); 844 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 7.6 Hz, 1H), 8.34 (d, J = 8 Hz, 1H), 8.27 (d, J = 7.2 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 7.84 (t, J = 6.4 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 8 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.25 (s, 2H, $-NH_2$), 7.21–7.09 (m, 15H, PPh_3), 2.03 (s, 15H, C_5Me_5); ^{31}P {^1H} NMR ($CDCl_3$, δ): 49.6 (s, PPh_3); ESI-MS (m/z): 739.8 [$M-PF_6$].

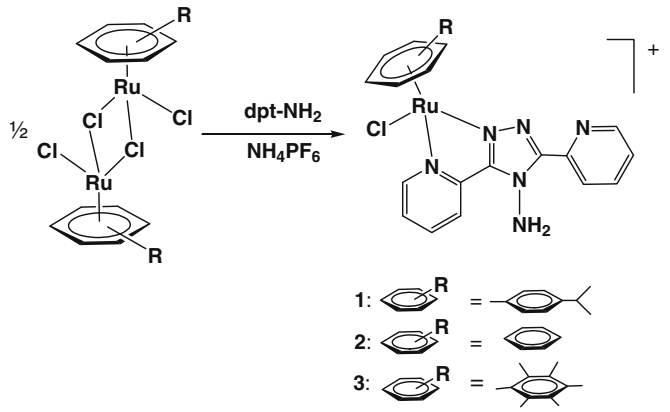
2.8. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(dpt\text{-}NH_2)(PPh_3)]PF_6$ (**9**)

A mixture of $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ (100 mg, 0.128 mmol), 4-amino-3,5-di-pyridyltriazole (dpt-NH_2) (31 mg, 0.128 mmol) and 1 equiv. of NH_4PF_6 in dry methanol (30 ml) were refluxed under dry nitrogen for 8 h until the color of the solution changed from pale yellow to dark red. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 ml), and the solution filtered to remove ammonium chloride. The red solution was concentrated to 5 ml, upon addition of diethylether the orange–red complex precipitate, which was separated and dried under vacuum. Yield: 69 mg, 61.9%. *Anal.* Calc. for $C_{39}H_{32}N_6P_2F_6Ru$: C, 54.34; H, 3.72; N, 9.78. Found: C, 54.40; H, 3.81; N, 9.66%. IR (KBr pellets, cm^{-1}): 3446 (ν_{N-H}); 1630 ($\nu_{C=C}$); 1439 ($\nu_{C=N}$); 843 (ν_{P-F}); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.22 (d, J = 5.6 Hz, 1H), 8.75 (d, J = 8 Hz, 1H), 8.67 (d, J = 4.4 Hz, 1H), 8.41 (d, J = 8 Hz, 1H), 8.25 (s, 2H, $-NH_2$), 8.23 (t, J = 7.6 Hz, 1H), 8.01 (t, J = 6.4 Hz, 1H), 7.96 (t, J = 8 Hz, 1H), 7.94 (t, J = 9.2 Hz, 1H), 7.55–7.10 (m, 22H), 4.97 (d, J = 8 Hz, 1H), 4.85 (d, J = 7.6 Hz, 1H), 4.43 (t, J = 2.4 Hz, 1H); ^{31}P {^1H} NMR ($CDCl_3$, δ): 57.10 (s, PPh_3); ESI-MS (m/z): 719.1 [$M-PF_6$].

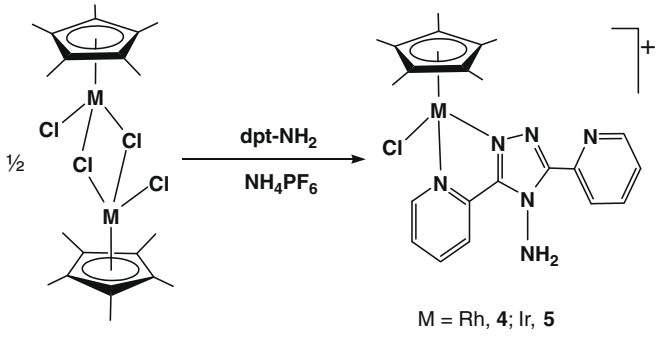
3. Results and discussion

3.1. Arene ruthenium complexes **1**, **2** and **3**

The dinuclear arene ruthenium complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$ and C_6Me_6) reacts with the *N,N′*-based ligand (dpt-NH_2) in methanol to afford the mononuclear cationic complexes **1**, **2** and **3** (Scheme 1). The complexes **1** and **3** are yellow in color while complex **2** is brown in color. These complexes are non-hygroscopic and stable in air as well as in solution. They are



Scheme 1.



Scheme 2.

sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile but are insoluble in non-polar solvents like hexane, diethylether and petroleum ether.

The analytical data of these compounds are consistent with the formulations. These complexes give only mononuclear complexes irrespective of the metal–ligand ratio. The complexes are isolated as their hexafluorophosphate salts. The infrared spectra of all these complexes exhibit a chelated *N*,*N*′-bidentate ligand as broad bands around 3430 cm^{-1}, 3432 cm^{-1}, 3433 cm^{-1}, 1615 cm^{-1}, 1627 cm^{-1}, 1618 cm^{-1}, 1457 cm^{-1}, 1451 cm^{-1} and 1474 cm^{-1} corresponding to the stretching frequencies of N–H bond of NH_2 group of triazole ring, C=C and C=N bond of the pyridine ring of the ligand, respectively. In addition, the infrared spectra contained a strong band at 846 cm^{-1} due to the stretching frequency of P–F bond of PF_6 for these complexes.

The proton NMR spectra of all these complexes show downfield shift as compared to that of the free ligand. In the free ligand, five sets of signals *viz.* two doublets, singlet and two doublet of triplets in the aromatic region at around 7.34–8.66 ppm corresponding to the pyridyl and triazole protons are observed. Whereas in the complexes, it displays a total of nine sets of signals, namely four doublets, four triplets and a singlet as mentioned in Section 2. Beside these signals complex **2** shows a singlet at 6.20 ppm corresponding to the benzene protons of the complex and complex **3** displays a singlet at 2.1 ppm which corresponds to the hexamethylbenzene protons. Complex **1** exhibits an unusual pattern of resonances for the *p*-cymene ligand. For instance, the methyl protons of the isopropyl group display two doublets at *ca.* 1.24–1.19 ppm, instead of one doublet as in the starting precursor. The aromatic protons of the *p*-cymene ligand for these complexes also display four doublets at *ca.* 5.98–5.67 ppm, instead of two doublets as in the starting precursor. This pattern is due to the diastereotopic nature of the methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand. It may also be attributed to the behaviour of the ruthenium atom which is stereogenic when coordinated with four different ligand atoms [33]. In other words we can say that the different signals are entirely due to the chiral nature of the metal [34,35].

3.2. Pentamethylcyclopentadienyl rhodium and iridium complexes *4* and *5*

The dinuclear complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) undergo a bridge cleavage reaction with *N*,*N*′-bidentate nitrogen base (dpt-NH_2) ligand in methanol at room temperature leading to the formation of chloride displaced complexes **4** and **5**, respectively (Scheme 2).

These complexes were also isolated as their hexafluorophosphate salts. Here also we are able to isolate only the mononuclear complexes. Change in concentration and longer reaction time do not change the reaction pathways. The orange–yellow complexes are air stable, soluble in polar solvents but insoluble in hexane, petroleum ether and diethylether. The infrared spectra of both the complexes exhibit a chelated *N*,*N*′-bidentate ligand as broad bands at 3446 cm^{-1}, 3434 cm^{-1}, 1632 cm^{-1}, 1630 cm^{-1} and 1457 cm^{-1} corresponding to the stretching frequencies of N–H bond of NH_2 group of triazole ring, C=C and C=N bond of the pyridine ring of the ligand, respectively. The infrared spectra of these complexes also exhibit a strong band at around 844 cm^{-1} due to the ν_{P-F} stretching frequency of the counter ion of these complexes. In proton NMR spectra of these complexes, the ligand peaks spread over a quite wide range as compared to that of the free ligand. The free ligand exhibits two doublets at around 8.37–8.66 ppm in proton NMR. However, after metallation, these doublets shifted to down field in the range of 9.31–9.65 ppm. Besides the ligand peaks as mentioned in Section 2, the proton NMR spectra of these compounds also exhibit a singlet at 1.59 ppm for complex **4** and 2.29 ppm for complex **5**, respectively, corresponding to the protons of the pentamethylcyclopentadienyl group. The molecular structure of complex **4** was solved by single crystal X-ray crystallography and the structure is presented in Fig. 1.

3.3. Cyclopentadienyl ruthenium and osmium complexes *6–9*

The mononuclear cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ and pentamethylcyclopentadienyl complex $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ react with dpt-NH_2 in refluxing methanol to give the corresponding mononuclear complexes **6–9** (Chart 1). Compounds **6–9** are soluble in halogenated solvents and polar organic solvents such as tetrahydrofuran, methanol or dimethylsulfoxide but are insoluble in non-polar solvents. All these complexes are stable in solid state as well as in solution. All complexes were characterized by IR, ^1H NMR and mass spectrometry as well as by elemental analysis (see Section 2).

The infra red spectra of these complexes exhibit a broad band between 3431 and 3446 cm^{-1} due to the stretching frequency of N–H bond NH_2 group of triazole ring and band between 1599 cm^{-1} and 1630 cm^{-1} and between 1437 and 1451 cm^{-1} corresponding to the stretching frequency of the C=C and C–N bond of the pyridine ring of the ligand. In addition to these all the complexes display a sharp peak at around 843 cm^{-1} due to the stretching frequency of the P–F bond of PF_6 for all the complexes. The protons of complexes **6–9** also show downfield shift with respect to the protons of the free ligand. Beside the aromatic protons of the ligand as mentioned in Section 2, complexes **6** and **7** show a singlet at 4.91 and 4.59 ppm which correspond to the protons of

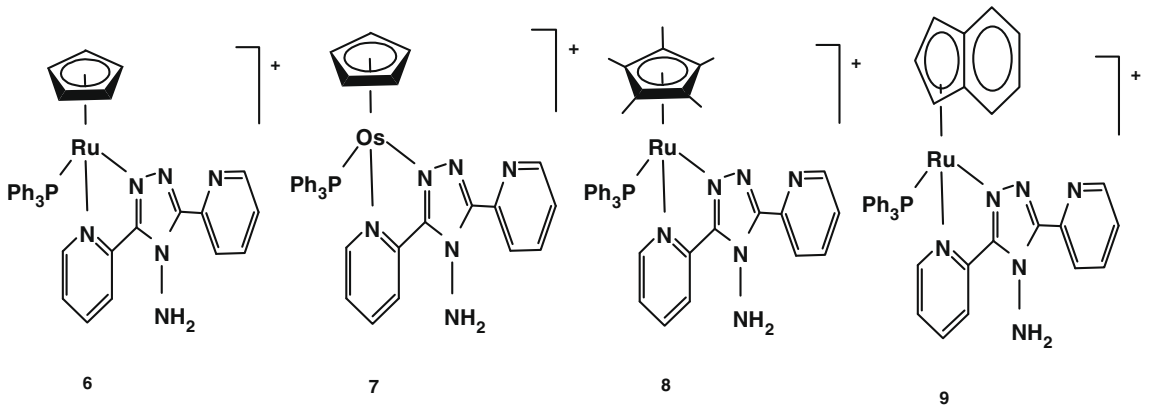


Chart 1.

the cyclopentadienyl ligand, while in the case of complex **8** it displays a singlet at 2.03 ppm corresponding to the methyl protons of the pentamethylcyclopentadienyl ligand. These complexes also show a multiplet in the range of 6.80–7.38 ppm due to the protons of the triphenylphosphine group of these complexes. Complex **9** exhibits a characteristic three sets of signals such as multiplet, triplet and doublet, for the protons of the indenyl group. The protons of the triphenylphosphine ligand exhibit a multiplet at 7.10–7.55 ppm. The $^{31}P\{^{1}H\}$ NMR spectra of the complexes **6**, **7** and **9** exhibit a single sharp resonance for triphenylphosphine around 57.10–49.6 ppm, respectively, whereas in the starting precursors the signal appear in the upfield region. In the case of complex **8** the $^{31}P\{^{1}H\}$ NMR spectra displays a sharp singlet at −0.26 ppm as compared to the starting complex which shows at −6.29 ppm. The structure of a representative complex **6** was solved by single crystal X-ray diffraction study and is presented in Fig. 2.

The *m/z* values of all these complexes and their stable ion peaks obtained from the ZQ mass spectra, as listed in Section 2, are in good agreement with the theoretically expected values. ESI mass spectra of the complexes also displayed prominent peaks corresponding to the molecular ion fragment. All the halogenated complexes displayed the prominent peak corresponding to the loss of chloride ion from the molecular ion peak, but the loss of arene or Cp or Cp* group is not observed indicating the stronger bond of metal to these groups and remains intact.

4. UV–Vis spectroscopy

UV–Vis spectra of some representative complexes were acquired in acetonitrile and spectral data are summarized in Table 1. Electronic spectra of these complexes are depicted in Fig. 3. 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) $d\pi(M) \rightarrow \pi^*$ (dpt-NH_2 ligand) bands in the visible region. Since the low spin d^6 configuration of the mononuclear complexes

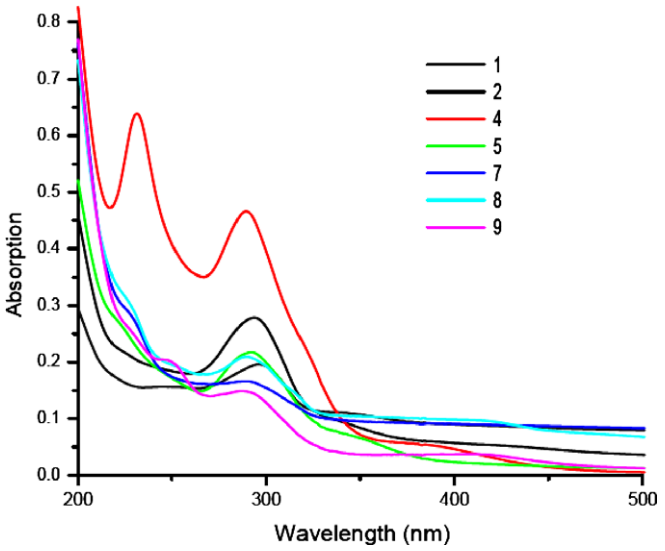


Fig. 3. UV–Vis absorption spectra of mononuclear complexes **1**, **2**, **4**, **5**, **7**, **8** and **9** in acetonitrile at 298 K.

provides filled orbitals of proper symmetry at the Ru, Rh, Ir and Os centers, these can interact with low lying π^* orbitals of the ligands. The lowest energy absorption bands in the electronic spectra of these complexes in the visible region ~429–422 and ~387–341 nm have been tentatively assigned on the basis of their intensity and position to $\pi \rightarrow \pi^*$ MLCT transitions. The bands on the higher energy side at ~302–220 nm have been assigned to ligand-centered $\pi \rightarrow \pi^*$/ $n \rightarrow \pi^*$ transitions [36,37]. In general, these complexes follow the normal trends observed in the electronic spectra of the nitrogen-bonded metal complexes, which display a ligand-based $\pi \rightarrow \pi^*$ transition for pyrazolylpyridazine ligands in the UV region and metal-to-ligand charge transfer transitions in the visible region.

Table 1
UV–Vis absorption data of the representative complexes in acetonitrile at 298 K.

Complex	λ_{max}/nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})		
1	235 (0.60)	288 (0.46)	387 (0.05)
2	220 (0.27)	291 (0.21)	352 (0.06)
4	250 (0.20)	302 (0.12)	420 (0.03)
5		294 (0.27)	429 (0.05)
7	244 (0.15)	298 (0.19)	341 (0.11)
8	229 (0.27)	294 (0.16)	
9	228 (0.30)	290 (0.20)	422 (0.09)

5. Molecular structures

Molecular structures of **4** and **6** have been determined crystallographically. The complexes crystallize in $P\bar{1}$ and $P2_1/n$ space groups. Details about data collection, refinement and structure solution are recorded in Table 2, and selected bond lengths and angles are presented in Table 3. Crystal structures of **4** and **6** with atom-numbering schemes are shown in Figs. 1 and 2. In complex **4** the metal is bonded with the major coordinated sites N1 and

Table 2
Crystallographic and structure refinement parameters for complexes **4** and **6**.

Compound	**4**	**6**
Empirical formula	$C_{22}H_{25}ClF_6N_6PRh$	$C_{35}H_{30}F_6N_6P_2Ru$
Formula weight	656.81	811.66
T (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/n$
Unit cell dimensions		
a (Å)	8.0012(15)	13.7582(5)
b (Å)	11.487(2)	14.2396(5)
c (Å)	14.975(3)	17.6420(6)
α (°)	73.695(12)	90
β (°)	88.467(14)	102.522(2)
γ (°)	87.830(14)	90
V (A^3)	1319.9(4)	3374.1(2)
Z, calculated density (Mg/m^3)	2, 1.653	4, 1.598
Absorption coefficient (mm^{-1})	0.875	0.629
F(0 0 0)	660	1640
Crystal size (mm)	0.35 × 0.24 × 0.14	0.40 × 0.25 × 0.15
Θ Range for data collection (°)	1.42–28.17	1.71–28.33
Index ranges	$-8 \le h \le 9$, $-12 \le k \le 15$, $11 \le l \le 19$	$-18 \le h \le 18$, $-18 \le k \le 19$, $-23 \le l \le 23$
Reflections collected/ unique	7835/4827	35 680/8395
$[R_{(int)}]$	0.1570	0.0261
Final R indices [$I > 2\sigma(I)$]	0.0616, wR_2 = 0.1797	0.0418, wR_2 = 0.1373
R indices (all data)	0.0965, wR_2 = 0.2483	0.0546, wR_2 = 0.1486
Largest difference in peak and hole (e $Å^{-3}$)	0.913 and −0.721	0.875 and −0.626
Goodness-of-fit (GOF) on F^2	0.994	1.088

Table 3
Selected bond lengths and angles for complexes **4** and **6**.

	4	**6**
Bond distances (Å)		
N(1)–M(1)	2.139(9)	2.125(3)
N(2)–M(1)	2.090(9)	2.069(2)
N(2)–N(3)	1.378(14)	1.373(3)
N(4)–N(5)	1.416(13)	1.402(3)
Cl(1)–M(1)	2.401(4)	
M(1)–CNT(1)	1.769	1.833
Bond angles (°)		
N(1)–M(1)–N(2)	75.8(4)	75.49(9)
N(3)–N(2)–M(1)	134.0(7)	133.52(17)
N(1)–M(1)–Cl(1)	85.5(3)	
N(2)–M(1)–Cl(1)	88.7(3)	
N(1)–M(1)–P(1)		90.84(7)
N(2)–M(1)–P(1)		88.41(6)

N2 in a k^2 manner, one chloro group, and the pentamethylcyclopentadienyl (Cp^*) ring in a η^5 manner. While in complex **6** the metal is also bonded to N1 and N2 in a k^2 manner, one phosphorus P1 of PPh_3, and the cyclopentadienyl (Cp) ring in a η^5 manner. Typical piano-stool geometry about the metal in complex **4** is maintained. The Cp^* ring is planar with an average Rh–C distance of 2.149 Å and the Rh center is displaced by 1.769 Å from the centroid of the Cp^* ring, which is comparable to the distances in other rhodium pentamethylcyclopentadienyl complexes. The Rh–N and Rh–Cl bond lengths are consistent with the values reported in the literature. The C–C bond lengths within the Cp^* ring and C–Me distances are normal [38–40]. The bond lengths and bond angles observed in the structure **6** are typical of those found in other ruthenium polypyridyl complexes containing triazoles [41]. The Ru–N bond lengths are in the range of 2.069(2)–2.125(3) Å. The N–Ru–N angle in these complexes are in the range of 75.49(9)° and 133.52(17)°, which are comparatively less than other ruthenium polypyridyltriazole complexes [42]. The distance between the ruthenium atom and the centroid of the Cp ring is 1.833 Å and is comparable to those in other reported complexes. The Ru–P distance is around 2.318 Å and N–M–P angle are normal and are in the range of 90.84(7)–88.41(6)°. The P–F lengths are consistant with the values reported previously [10].

6. Conclusion

In summary, a series of new η^5- and η^6-cyclichydrocarbon platinum metal complexes bearing dpt-NH_2 ligand, which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. Our attempts to synthesize a dimetallic derivative by addition of a second organometallic anion were unsuccessful. As a continuation of our studies, we have been able to condense the ligand dpt-NH_2 with an aldehyde to form a corresponding hexadentate ligand and this work is still in progress.

7. Supplementary data

CCDC 742500 and 742501 contain the supplementary crystallographic data for **4** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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