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Syntheses, spectral and structural characterization of η^5- and η^6-cyclic π-perimeter hydrocarbon platinum group metal complexes containing pyridazine–NHC analogues

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ABSTRACT

A family of platinum group metal complexes containing bidentate pyridazine–NHC ligands (**L1** = 3,6-bis(*N*-*n*-methylimidazolyl)pyridazine dichloride, **L2** = 3,6-bis(*N*-*n*-butylimidazolyl)pyridazine dichloride) have been synthesized. The typical mechanism of the reactions for these syntheses involved an *in situ* carbene transfer reactions. Reaction of **L1**/**L2** with silver oxide in absence of light yielded silver–NHC complexes (**1**) and (**2**). When, the respective metal precursors were added to the silver–NHC complexes, transmetallation occurred with the possible isolation of the following cationic complexes: $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L})Cl]^{2+}$ {L = **L1** (**3**), **L2** (**5**)}, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mathbf{L})Cl]^{2+}$ {L = **L1** (**4**), **L2** (**6**)}, $[Cp^*Rh(\mathbf{L})Cl]^{2+}$ {L = **L1** (**7**), **L2** (**9**)} and $[Cp^*Ir(\mathbf{L})Cl]^{2+}$ {L = **L1** (**8**), **L2** (**10**)}. All these complexes were stable in ambient atmosphere, and could be obtained in good yield. All these complexes were characterized by spectroscopic analyses. The molecular structure of the complex **9** was determined by single crystal X-ray diffraction studies.

1. Introduction

N-Heterocyclic carbenes (NHCs) are versatile ligands, as used in a variety of organometallic and coordination complexes of almost all members of the platinum group metals [1]. Ever since the first convenient preparation method of NHC precursors was reported by Arduengo et al. [2], extensive studies have been carried out on N-heterocyclic carbenes and the corresponding organometallic derivatives. The research in the area of N-heterocyclic carbene (NHC) complexes of platinum group metals originated because of the requirement to develop high activity phosphine free catalysts [3]. Most of the NHC ligands were shown to be efficient in forming platinum group metal complexes; these platinum group complexes have been widely used as highly active and, rather selective, pre-catalysts in a variety of fundamental chemical transformations, such as hydrogenation, hydrogen transfer, hydroformylation, hydrosilylation, oxidation, isomerisation, tautomerisation and various C–C coupling reactions [4]. Ag–Ag interactions are characteristic features in many of the silver–carbene complexes, which exhibited interesting luminescent properties [5,6]. During the recent years, ruthenium complexes have shown a great potential in the design of new metal-based drugs [7]. For example, {Cp^*Ir(NHC)} complexes have been reported to be useful as water oxidation catalysts [8,9]. Some of the Ru–NHC complexes exhibit remarkable C–H and C–C bond activation chemistry [10]. It has been reported that two unusual dinuclear palladacyclic complexes formed when reacted with pyridazine-functionalized bisimidazolium salts [11]. In this communication we report the synthesis and characterization of Ru, Rh and Ir complexes containing pyridazine-functionalized bisimidazolium salts. The ligands used in the study are shown in Chart 1.

2. Results and discussion

The ligands L1/L2 are prepared by heating a neat reaction mixture of 3,6-dichloro pyridazine (1 equiv) and 1-substituted imidazole (2 equiv) for 3 h [13]. Silver–NHC complexes are generated by the deprotonation of ligand L1/L2 with silver oxide in dichloromethane, in the absence of light at room temperature. Subsequent addition of 0.5 equiv of metal precursors (Ru, Rh and Ir dimers) to the filtrate, immediately resulted in transmetallation, and AgCl precipitated out as a white solid. The reaction was set to proceed further for 12 h. The products were isolated as orange, yellowish-orange and yellow solids.

The molecular formula of all the complexes was determined by elemental analyses, and these compounds were further characterized by NMR studies.

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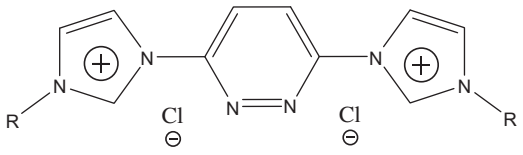


R=Me (L1)
R=Bu (L2)

L1=3,6-(N-n-methylimidazolium) pyridazine dichloride

L2=3,6-(N-n-butylimidazolium) pyridazine dichloride

Chart 1. Ligands used in the study.

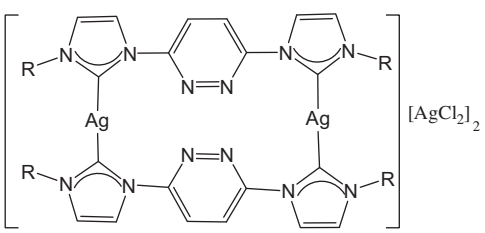
2.1. Synthesis of Ag–NHC compounds (*1*–*2*)

Several bases have been found appropriate for the deprotonation of imidazolium salts. We choose to investigate the reactions of pro-ligands **L1** and **L2** with Ag_2O [14–16]. The deprotonation of the pyridazine bis(alkyl-imidazolium) salts (L1 and L2) with 1 equiv of Ag_2O in dichloromethane yielded $[Ag_2L][AgCl_2]_2$ {L = L1 (**1**), L2 (**2**)} [11,12] (Chart 2), which is light sensitive. The deprotonation usually takes at C2–H bond of the imidazolium salt. The ^1H NMR of **1** and **2** clearly show that the carbenic protons of L1 and L2 were absent, indicated by the absence of peaks in the region of δ 10.2–10.3, from which the successful deprotonation and formation of silver–NHC complexes can be inferred.

2.2. Syntheses of mononuclear Ru, Rh and Ir complexes (*3*–*10*)$(PF_6)_2$

The arene-ruthenium complexes, $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, *p*-^{i}PrC$_6$H$_4$Me), react with Ag–NHC, which is generated *in situ*, at room temperature in the presence of NH_4PF_6. This reaction yield mononuclear cationic arene-ruthenium complexes $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L1})Cl]^{2+}$ (**3**), $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mathbf{L1})Cl]^{2+}$ (**4**), $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{L2})Cl]^{2+}$ (**5**) and $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mathbf{L2})Cl]^{2+}$ (**6**) (Scheme 1). These were isolated as their hexafluorophosphate salts. Similarly, the complexes $[Cp^*M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) react with Ag–NHC, that is generated *in situ*, and leads to the formation of the mononuclear cationic complexes $[Cp^*Rh(\mathbf{L1})Cl]^{2+}$ (**7**), $[Cp^*Ir(\mathbf{L1})Cl]^{2+}$ (**8**), $[Cp^*Rh(\mathbf{L2})Cl]^{2+}$ (**9**), and $[Cp^*Ir(\mathbf{L2})Cl]^{2+}$ (**10**) (Scheme 1).

Metal–carbene complexes have been prepared by several standard procedures [17,18]. After deprotonating the 2-carbene hydrogen, all the complexes formed in a bidentate chelating fashion through imidazolyl carbon and pyridazine nitrogen. Our trials were not successful in the syntheses of multi metallic complexes with these ligands. In the ^1H NMR spectra of all the complexes exhibited signals to the coordinated substituted-imidazole and dangling



R=Me (1)
R=Bu (2)

Chart 2. Silver–NHC complex.

substituted-imidazole in different region and peak assignments were given in Section 3.

2.3. Characterization of arene ruthenium–pyridazine NHC complexes (*3*–*6*)$(PF_6)_2$

The proton NMR spectra of complexes (**3**–**6**)$(PF_6)_2$ contain a singlet ca. δ 10.20–10.30 ppm, which indicates that one of the imidazolyl group is coordinated to the metal atom; the other imidazolyl group is free. The pyridazine protons of these complexes (**3**–**6**)$(PF_6)_2$, appear as two doublets at ca. δ 8.39–8.46 and δ 7.75–7.85. The ligand contains two imidazolyl moieties, and one of the imidazolyl moiety has undergone metallation, which shows two doublets ascribed for the two back bone protons are ca. δ 8.19–8.26 and 7.42–7.51 for the complexes (**3**–**6**)$(PF_6)_2$. The free imidazolyl moiety also shows two doublets in the region of δ 7.21–7.42 for the back bone protons. In addition, complexes **3**$(PF_6)_2$ and **5**$(PF_6)_2$ the proton NMR spectra contain one singlet for the phenyl (ring) protons, at δ 6.35 and 6.15, respectively. In the complexes **4**$(PF_6)_2$ and **6**$(PF_6)_2$ the *p*-cymene ring show two doublets which are in the aromatic region δ 5.8, 5.21 and 5.75, 5.20, respectively. In the complexes **3**$(PF_6)_2$ and **4**$(PF_6)_2$ the methyl protons of ligand shows two singlets which occur in the range δ 4.14, 4.02 and 4.10, 3.99, respectively. For the complexes **5**$(PF_6)_2$ and **6**$(PF_6)_2$, in the proton NMR spectra, the butyl groups of the ligand containing three methylene groups show multiplets and the terminal methyl group shows triplet.

2.4. Synthesis and characterization of Cp*Rh, Cp*Ir pyridazine NHC complexes (*7*–*10*)$(PF_6)_2$

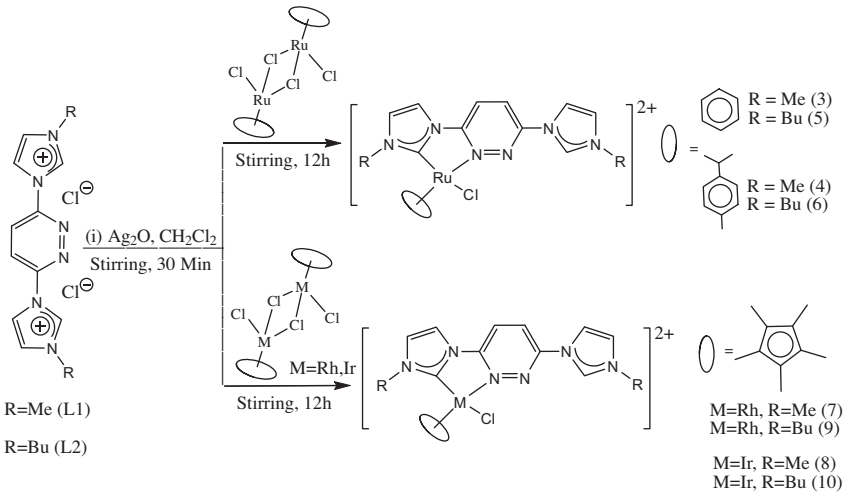
The complexes (**7**–**10**)$(PF_6)_2$ exhibits a singlet ca. δ 10.27–10.28, which indicates that one of the imidazolyl group is coordinated to the metal atom; the other imidazolyl group is free. For the complexes (**7**–**10**)$(PF_6)_2$, the pyridazine protons appear as two doublets at ca. δ 8.26–8.57 and δ 7.62–7.91. The ligand contains two imidazolyl moieties, one of the imidazolyl moiety undergone for metallation, which shows two doublets ascribed for the two back bone protons are ca. δ 8.17–8.34, 7.42–7.51 for the complexes (**7**–**10**)$(PF_6)_2$. The free imidazolyl moiety also shown two doublets for the back bone protons are in the region of δ 7.18–7.49. In the complexes **7**$(PF_6)_2$ and **8**$(PF_6)_2$, the terminal methyl protons show two singlets are δ 4.14, 4.02 and 4.12, 4.01, respectively. For the complexes **9**$(PF_6)_2$ and **10**$(PF_6)_2$, the butyl groups of the ligand containing three methylene groups show multiplets and the terminal methyl group shows triplet. The complexes (**7**–**10**)$(PF_6)_2$ contains pentamethylcyclopentadienyl ligand showing a singlet, in the region of δ 1.98–1.86 of the proton NMR spectrum.

The ionic nature of the complexes (**7**–**10**)$(PF_6)_2$ are predicted from their IR spectra which show a strong band at 840–844 cm^{-1} and a medium band at 550–558 cm^{-1} assignable to $\nu_{(P\text{-}F)}$ of the counter ion PF_6.

The *m*/*z* values of all the compounds and their stable ion peaks obtained from the mass spectra. The list of these *m*/*z* values is in Section 3, and these values are in good agreement with the theoretically expected values.

2.5. Molecular structure presentation

Single crystals of complex **9**$(PF_6)_2$ was obtained by slow diffusion of hexane into dichloromethane solution of the complex. The Rh complex (**9**)$(PF_6)_2$ has been structurally characterized by use of X-ray diffraction. The complex crystallizes in the triclinic space group $P\bar{1}$ with two units residing in the unit cell. The Rh–$C_{carbene}$ distance is 2.031 (3) Å, lying in the expected range [19–21]. The centroid distance from metal to Cp* ring is 1.811 Å. The five



Scheme 1. Syntheses of mononuclear Ru, Rh and Ir complexes (**3**–**10**)$(PF_6)_2$.

membered metal chelate-ligand C–Rh–N angle is 76.2 (1)°. The coordinated Rh–N distance is 2.109 (3) Å, which lies in the expected range [22]. A number of inter ionic short C–H...F contacts are detected in the crystal structure (**9**)$(PF_6)_2$, but these are most probably caused by crystal packing effects and should not affect distances and angles in the molecules. Details about data collection, refinement and structure solution are recorded in Table 1. The ORTEP diagram was shown in Fig. 1.

3. Experimental

All solvents were dried and distilled prior to use. Ruthenium trichloride hydrate (Arora Matthey Ltd.), 3,6-dichloro pyridazine, N-methyl imidazole and N-butyl imidazole (Aldrich) were purchased and were used as received. $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4\text{-}Me)Ru(\mu\text{-}Cl)Cl]_2$ and $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) were prepared according to the prescribed methods in the literature. The ligands L1/L2 were prepared by 3,6-dichloro pyridazine with N-methyl imidazole (L1) and N-butyl imidazole (L2) prepared by similarly prescribed methods [13]. 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 Waters (ZQ-4000) mass spectrometer, principle of operation of which is the ESI method.

Table 1
Crystallographic and structure refinement parameters for the complex **9**$(PF_6)_2$.

	9$(PF_6)_2$
Chemical formula	$C_{28}H_{40}ClF_{12}N_6P_2Rh$
λ (Å)	0.71073
Formula weight	888.96
Crystal system	triclinic
Space group	$P\bar{1}$
Crystal size (mm)	0.30 × 0.25 × 0.25
Crystal colour and habit	brown, needle
a (Å)	7.818 (2)
b (Å)	15.863 (5)
c (Å)	17.402 (5)
α (°)	63.161(4)
β (°)	89.746 (4)
γ (°)	77.203 (4)
V (Å^3)	1866.5(9)
Z	2
T (K)	173 (2)
D_x (g cm^{-3})	1.582
μ (mm^{-1})	0.704
$F(000)$	900
θ range (°)	1.48–25.99
Unique reflections	7057
Reflections used [$I > 2\sigma(I)$]	5830
R_{int}	0.0321
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0466, wR_2 = 0.1200
R indices (all data)	R_1 = 0.0567, wR_2 = 0.1286
Goodness-of-fit	0.902
Maximum, Minimum $\Delta\rho$ (e Å^{-3})	0.611, −0.386

3.1. Single-crystal X-ray structure analyses

The single crystal of the complex **9**$(PF_6)_2$ was mounted on thin glass fibre clamped on a brass pin and the data were collected at 293 K. Data for the complex **9**$(PF_6)_2$ were collected Bruker Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature. The data were integrated with SAINT [23] and semi empirical absorption correction was performed with SADABS [24]. The structure was solved and refined with X-SEED [25], a graphical interface to SHELXL [26]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Structural illustrations have been drawn with ORTEP-3 [27].

3.2. Reactions of 3,6-bis(N-n-methylimidazolyl)pyridazine dichloride with Ag_2O in CH_2Cl_2 [1]

A suspension of 3,6-bis(*N*-*n*-methylimidazolyl)pyridazine dichloride (95 mg, 0.3 mmol) in 5 ml of CH_2Cl_2 was treated with Ag_2O (80 mg, 0.35 mmol), and the mixture was stirred for 30 min. The filtrate was concentrated to ca. 2 ml, and subsequent addition of 10 ml of diethyl ether yielded **1** as a white solid. Yield: 101 mg, 82.0%. *Anal.* Calc. for $C_{30}H_{36}Ag_4Cl_4N_{12}$: C, 37.50; H, 4.20; N, 16.40. Found: C, 37.68; H, 4.03; N, 16.02%. ^{1}H NMR (DMSO-d_6): 8.53, 8.06 (both s, $imid_{backbone}$, each 4H), 7.65 (s, $H_{pyridazine}$, 4H), 4.02 (s, CH_3, 12H). ^{13}C NMR (DMSO-d_6): 179.2, 154.8, 128.2, 126.3, 121.8, 39.8.

3.3. Reactions of 3,6-bis(N-n-butylimidazolyl)pyridazine dichloride with Ag_2O in CH_2Cl_2 [2]

A suspension of 3,6-bis(*N*-*n*-butylimidazolyl)pyridazine dichloride (119.20 mg, 0.3 mmol) in 5 ml of CH_2Cl_2 was treated with Ag_2O (80 mg, 0.35 mmol), and the mixture was stirred for 30 min. The filtrate was concentrated to ca. 2 ml. and further addi-

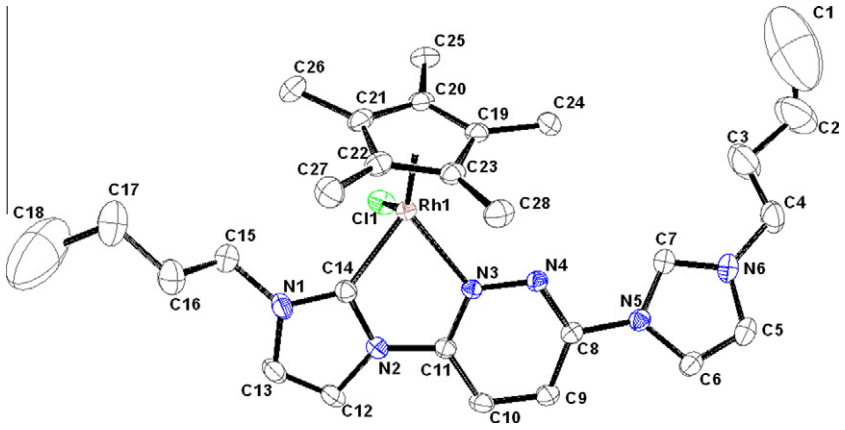


Fig. 1. ORTEP drawing of the cationic section of complex **9**$(PF_6)_2$. Thermal ellipsoids are shown at 20% probability level with hydrogen atoms and counter ions are omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)–cent. 1.811, Rh(1)–C(14) 2.031(3), Rh(1)–N(3) 2.109(3), Rh(1)–Cl(1) 2.3916(11), N(3)–N(4) 1.337(4), C(11)–N(2) 1.389(4), C(14)–Rh(1)–N(3) 76.2(1), C(14)–Rh(1)–Cl(1) 83.0 (1), Rh(1)–N(3)–C(11) 117.0, Rh(1)–C(14)–N(2) 114.92, N(3)–Rh(1)–Cl(1) 90.75(8), N(3)–C(11)–N(2) 112.3(3).

tion of 10 ml of diethyl ether yielded **2** as a white solid. Yield: 128 mg, 81.5%. *Anal.* Calc. for $C_{36}H_{48}Ag_4Cl_4N_{12}$: C, 35.38; H, 3.96; N, 13.75. Found: C, 35.62; H, 3.72; N, 13.18%. ^{1}H NMR (DMSO-d_6): 8.62, 8.15 (both s, $imid_{backbone}$, each 4H), 7.83 (s, $H_{pyridazine}$, 4H), 4.27 (t, J = 7.2, $CH_2CH_2CH_2CH_3$, 8H), 1.85 (m, $CH_2CH_2CH_2CH_3$, 2H), 1.33 (m, $CH_2CH_2CH_2CH_3$, 2H), 0.91 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 12H). ^{13}C NMR (DMSO-d_6): 180.2, 150.6, 124.2, 123.9, 120.8, 52.4, 33.1, 19.6, 13.8.

3.4. Generalized procedure for synthesis of metal complexes [*3*–*10*]$(PF_6)_2$

A suspension of the appropriate imidazolium chloride (L1/L2) (1 equiv) and silver oxide (0.5 equiv) in CH_2Cl_2 was stirred at room temperature in the dark for 30 min. The mixture was filtered through a pad of celite into the appropriate metal precursor (0.5 equiv), NH_4PF_6 (2.1 equiv) and stirred at room temperature for 12 h. The suspension was filtered through celite to remove silver salts, and the solvent was removed under reduced pressure. The resulting solid was washed with ether, dried under vacuum.

3.4.1. Complex [*3*]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L1 (40 mg, 0.128 mmol), Ag_2O (15 mg, 0.064mmol), $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ (32 mg, 0.064 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as brown solid. Yield: 67 mg, 70.5%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (s, NC<u>H</u>N, 1H), 8.42, 7.80 (d, J = 9.4 Hz, $H_{pyridazine}$, 2H), 8.23, 7.47 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 7.35, 7.25 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 6.35 (s, CH_{arom}, 6H), 4.14 (s, N–CH_3, 3H), 4.02 (s, N–CH_3, 3H). *Anal.* Calc. for $C_{18}H_{16}ClF_{12}N_6P_2Ru$: C, 29.10; H, 2.17; N, 11.31. Found: C, 28.90; H, 2.03; N, 11.13%, ESI-MS (m/z): 597.98 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P\text{-}F)}$ 844 (s), 556 (m).

3.4.2. Complex [*4*]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L1 (40 mg, 0.128 mmol), Ag_2O (15 mg, 0.064 mmol), $[(\eta^6\text{-}p\text{-}^iPrC_6H_4\text{-}Me)Ru(\mu\text{-}Cl)Cl]_2$ (40 mg, 0.064 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as orange solid. Yield: 85 mg, 83.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, NC<u>H</u>N, 1H), 8.39, 7.75 (d, J = 9.2 Hz, $H_{pyridazine}$, 2H), 8.19, 7.42 (d, J = 2.1 Hz, $imid_{backbone}$, 2H), 7.32, 7.21 (d, J = 2.1 Hz, $imid_{backbone}$, 2H), 5.8 (d, J = 6 Hz, $Ar_{p\text{-}cym}$, 2H), 5.21 (d, J = 6 Hz, $Ar_{p\text{-}cym}$, 2H), 4.10 (s, N–CH_3, 3H), 3.99 (s, N–CH_3, 3H), 2.65 (m, C<u>H</u>$(CH_3)_2$, 1H), 1.959 (s, $Ar_{p\text{-}cym}$–Me, 3H), 1.03 (d, J = 7.2 Hz, CH(C<u>H</u>$_3)_2$, 6H). *Anal.* Calc. for $C_{22}H_{27}ClF_{12}N_6P_2Ru$: C, 32.95; H, 3.39; N, 10.48. Found: C, 32.34; H, 3.05; N, 10.05%, ESI-MS (m/z): 656.98 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P\text{-}F)}$ 842 (s), 552 (m).

3.4.3. Complex [*5*]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L2 (50 mg, 0.126 mmol), Ag_2O (15 mg, 0.063mmol), $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ (32 mg, 0.063 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as brown solid. Yield: 77 mg, 73.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (s, NC<u>H</u>N, 1H), 8.46, 7.85 (d, J = 9.2 Hz, $H_{pyridazine}$, 2H), 8.26, 7.49 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 7.38, 7.23 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 6.15 (s, CH_{arom}, 6H), 4.32 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 2H), 4.23, 4.00, 3.85 (m, $CH_2CH_2CH_2CH_3$, each 2H), 1.88 (m, $CH_2CH_2CH_2CH_3$, 2H), 1.36 (m, $CH_2CH_2CH_2CH_3$, 2H), 0.99 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H), 0.75 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H). *Anal.* Calc. for $C_{24}H_{31}ClF_{12}N_6P_2Ru$: C, 34.73; H, 3.76; N, 10.13. Found: C, 34.52; H, 3.52; N, 9.89%, ESI-MS (m/z): 685.03 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P\text{-}F)}$ 843 (s), 554 (m).

3.4.4. Complex [*6*]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L2 (50 mg, 0.126 mmol), Ag_2O (15 mg, 0.063 mmol), $[(\eta^6\text{-}p\text{-}^iPrC_6H_4\text{-}Me)Ru(\mu\text{-}Cl)Cl]_2$ (38.6 mg, 0.063 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as orange solid. Yield: 94 mg, 84.15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, NC<u>H</u>N, 1H), 8.42, 7.82 (d, J = 9.2 Hz, $H_{pyridazine}$, 2H), 8.23, 7.51 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 7.42, 7.25 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 5.75 (d, J = 6 Hz, $Ar_{p\text{-}cym}$, 2H), 5.2 (d, J = 6 Hz, $Ar_{p\text{-}cym}$, 2H), 4.35 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 2H), 4.21, 3.96, 3.80 (m, $CH_2CH_2CH_2CH_3$, each 2H), 2.78 (m, C<u>H</u>$(CH_3)_2$, 1H), 1.99 (s, $Ar_{p\text{-}cym}$-Me, 3H), 1.84 (m, $CH_2CH_2CH_2CH_3$, 2H), 1.37 (m, $CH_2CH_2CH_2CH_3$, 2H), 1.12 (d, J = 7.2 Hz, CH(C<u>H</u>$_3)_2$, 6H), 0.98 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H), 0.78 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H). *Anal.* Calc. for $C_{28}H_{39}ClF_{12}N_6P_2Ru$: C, 37.95; H, 4.44; N, 9.48. Found: C, 37.49; H, 4.18; N, 9.16%, ESI-MS (m/z): 741.14 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P\text{-}F)}$ 844 (s), 553 (m).

3.4.5. Complex [*7*]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L1 (40 mg, 0.128 mmol), Ag_2O (15 mg, 0.064 mmol), $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ (39.6 mg, 0.064 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as yellowish-orange solid. Yield: 78 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, NC<u>H</u>N, 1H), 8.32, 7.69 (d, J = 9.2 Hz, $H_{pyridazine}$, 2H), 8.17, 7.39 (d,

J = 2.2 Hz, $imid_{backbone}$, 2H), 7.31, 7.23 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 4.14 (s, N–CH_3, 3H), 4.02 (s, N–CH_3, 3H), 1.89 (s, 15H, C_5Me_5). *Anal.* Calc. for $C_{22}H_{25}ClF_{12}N_6P_2Rh$: C, 32.96; H, 3.14; N, 10.48. Found: C, 32.57; H, 3.01; N, 10.16%, ESI-MS (m/z): 656.80 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P-F)}$ 845 (s), 552 (m).

3.4.6. Complex [**8**]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L1 (40 mg, 0.128 mmol), Ag_2O (15 mg, 0.064 mmol), $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ (51 mg, 0.064 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as yellow solid. Yield: 86 mg, 75.5%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, NCHN, 1H), 8.26, 7.62 (d, J = 9.2 Hz, $H_{pyridazine}$, 2H), 8.12, 7.34 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 7.36, 7.18 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 4.12 (s, N–CH_3, 3H), 4.01 (s, N–CH_3, 3H), 1.86 (s, 15H, C_5Me_5). *Anal.* Calc. for $C_{22}H_{25}ClF_{12}IrN_6P_2$: C, 29.65; H, 2.83; N, 9.43. Found: C, 29.16; H, 2.57; N, 9.16%, ESI-MS (m/z): 746.11 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P-F)}$ 845 (s), 554 (m).

3.4.7. Complex [**9**]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L2 (50 mg, 0.126 mmol), Ag_2O (15 mg, 0.063 mmol), $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl]_2$ (39 mg, 0.063 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as yellowish-orange solid. Yield: 84 mg, 75%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.27 (s, NCHN, 1H), 8.57, 7.91 (d, J = 9.2 Hz, $H_{pyridazine}$, 2H), 8.34, 7.60 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 7.49, 7.32 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 4.38 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 2H), 4.28, 4.01, 3.86 (m, $CH_2CH_2CH_2CH_3$, each 2H), 1.98 (s, 15H, C_5Me_5), 1.79 (m, $CH_2CH_2CH_2CH_3$, 2H), 1.42 (m, $CH_2CH_2CH_2CH_3$, 2H), 0.99 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H), 0.79 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H). *Anal.* Calc. for $C_{28}H_{40}ClF_{12}N_6P_2Rh$: C, 37.83; H, 4.54; N, 9.45. Found: C, 37.49; H, 4.22; N, 9.19%, ESI-MS (m/z): 743.98 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P-F)}$ 843 (s), 555 (m).

3.4.8. Complex [**10**]$(PF_6)_2$

Transmetallation was carried out in CH_2Cl_2 (10 ml) with L2 (50 mg, 0.126 mmol), Ag_2O (15 mg, 0.063 mmol), $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ (50.2 mg, 0.063 mmol), and NH_4PF_6 (22 mg, 0.135 mmol). The product was isolated as yellow solid. Yield: 88 mg, 71.4%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.27 (s, NCHN, 1H), 8.53, 7.89 (d, J = 9.2 Hz, $H_{pyridazine}$, 2H), 8.32, 7.56 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 7.42, 7.26 (d, J = 2.2 Hz, $imid_{backbone}$, 2H), 4.32 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 2H), 4.24, 3.97, 3.80 (m, $CH_2CH_2CH_2CH_3$, each 2H), 1.95 (s, 15H, C_5Me_5), 1.76 (m, $CH_2CH_2CH_2CH_3$, 2H), 1.40 (m, $CH_2CH_2CH_2CH_3$, 2H), 0.96 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H), 0.75 (t, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$, 3H). *Anal.* Calc. for $C_{28}H_{40}ClF_{12}IrN_6P_2$: C, 34.38; H, 4.12; N, 8.59. Found: C, 33.92; H, 3.97; N, 8.16%, ESI-MS (m/z): 833.29 $[M^{2+}+PF_6^-]^+$, IR (KBr, cm^{-1}): $\nu_{(P-F)}$ 842 (s), 552 (m).

4. Conclusion

A series of mononuclear ruthenium, rhodium and iridium complexes incorporating a pyridazine–NHC ligand were designed, successfully synthesized by using synthetic protocols and investigated by analytical and spectral techniques.

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Appendix A. Supplementary data

CCDC 846164 contains the supplementary crystallographic data for complex **9**$(PF_6)_2$. 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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