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Study of complexes of platinum group metals containing nitrogen bases derived from pyridine aldehydes: Interesting molecular structures with unpredicted bonding modes of the ligands

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ABSTRACT

A series of mono-cationic dinuclear half sandwich ruthenium, rhodium and iridium metal complexes have been synthesized using ((pyridin-2-yl)methylimino)nicotinamide (**L1**) and ((picolinamido)phenyl) picolinamide (**L2**) ligands: $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-}\mathbf{L1})Cl_3]^+$ (arene = C_6H_6, **1**; $p\text{-}^iPrC_6H_4Me$, **2**; C_6Me_6, **3**), $[(\eta^5\text{-}C_5Me_5)_2M_2(\mu\text{-}\mathbf{L1})Cl_3]^+$ (M = Rh, **4**; Ir, **5**), and $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-}\mathbf{L2})(\mu\text{-Cl})]^+$ (arene = C_6H_6, **6**; $p\text{-}^iPrC_6H_4Me$, **7**; C_6Me_6, **8**), $[(\eta^5\text{-}C_5Me_5)_2M_2(\mu\text{-}\mathbf{L2})Cl_2]^+$ (M = Rh, **9**; Ir, **10**). All the complexes have been isolated as their hexafluorophosphate salts and fully characterized by use of a combination of NMR and IR spectroscopy. The solid state structure of three representatives **4**, **6** and **9** has been determined by X-ray crystallographic studies. Interestingly, in the molecular structure of **4**, the first metal is bonded to two nitrogen atoms whereas the second metal center is coordinated to only one nitrogen atom with two terminal chloride ligands. Fascinatingly in the case of the complexes with the symmetrical ligand **L2**, both ruthenium centers having η^6-arene groups are bonded to nitrogen atoms with a bridging chloride atom between the two metal centers, whereas the metals with η^5-Cp* groups are bonded to the ligand *N,O* and *N,N* fashion.

Keywords
Arene ligands, Pyridine aldehydes, Schiff bases, Ruthenium, Rhodium and iridium

1. Introduction

The synthesis of metal complexes with multiple coordination domains is an area of significant current interest in organometallic chemistry. Such complexes have been prepared as part of studies in diverse areas such as inter-metallic communication [1], bioinorganic enzyme active site modeling [2], supramolecular approaches to chiral materials [3] and functional devices [4]. The organometallic chemistry of half sandwich complexes have been broadly developed in the past few decades, due to their wide range of potential applications as catalyst precursors for hydrogen transfer [5,6], ring opening metathesis polymerization [7,8] and olefin oxidation [9]. Arene ruthenium compounds have also been extensively investigated for their persuasive antibacterial and anticancer activity [10,11]. The arene confers great stability to ruthenium in the +2 oxidation state and the characteristic "piano-stool" structure offers the possibility to vary the additional donors *via* substitution of halide(s) with a variety of σ-donors ranging from tertiary phosphines [12] to β-diketones [13] to aliphatic as well as aromatic amines [14–16]. In recent years, we have been carrying out reactions of arene ruthenium, rhodium and iridium dimers with a variety of nitrogen-based ligands [17–25] including pyridyl-pyridazine and pyrazolyl-pyridazine ligands. Arene metal complexes of these types of nitrogen-based ligands have the capacity to function as catalysts for the oxidation of water to dioxygen [26,27].

Herein, we describe the syntheses of interesting mono-cationic dinuclear complexes of arene metals having *N,O* and *N,N* type donor ligands. Although extensive studies have been carried out in the preparation of ruthenium, silver, nickel and copper metal complexes [28–30], mono-cationic dinuclear complexes of arene ruthenium, rhodium and iridium complexes with this type of bases have not been investigated. The mode of binding of these ligands especially **L2** with these dimers (arene ruthenium and Cp* rhodium and iridium) is found to be very interesting. The dinuclear ruthenium complexes are found to be *N,N* coordinated with a terminal chloride bridged between both the metal centers whereas for rhodium and iridium, the first metal is coordinated through *N,O* while the second metal is *N,N* coordinated. The two ligands used in this study are shown below (Chart 1):

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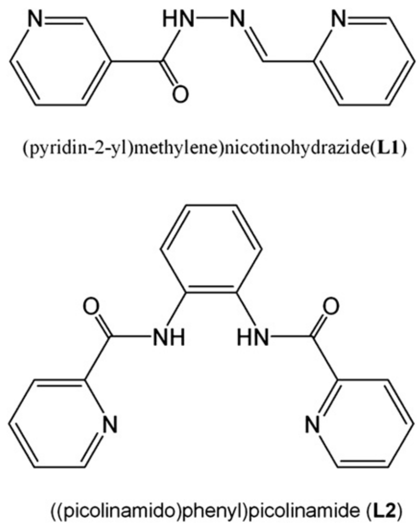
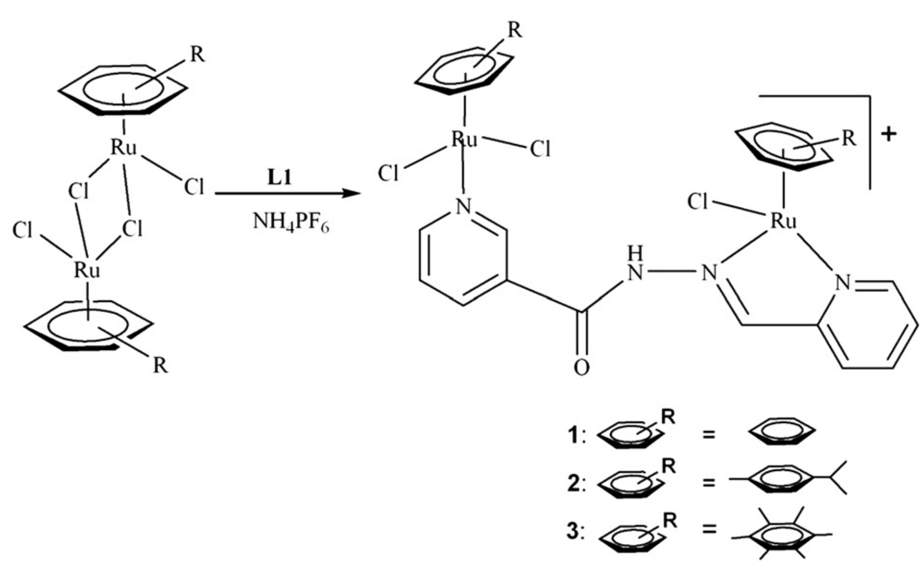


Chart 1. Ligands used in this study.

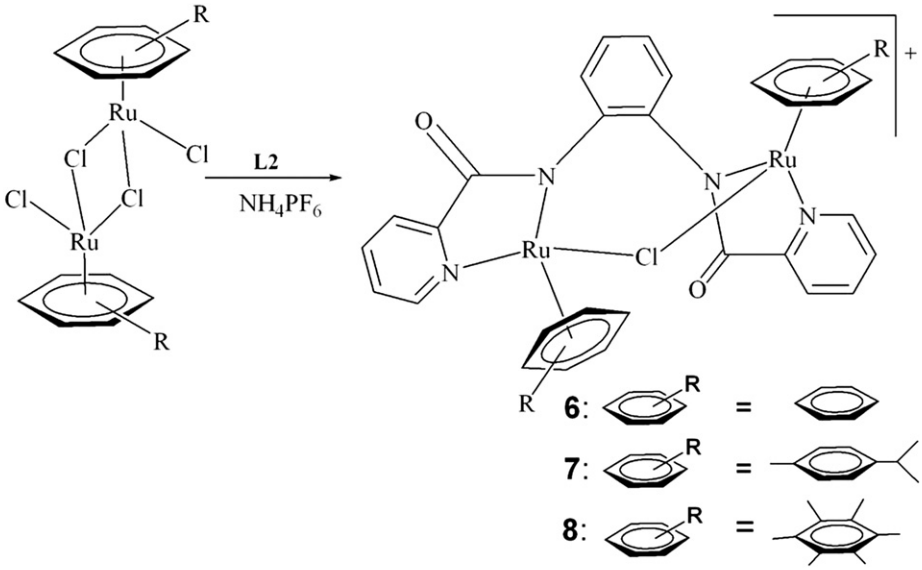
2. Results and discussion

The dinuclear arene ruthenium complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ react with the multidentate N∩O and N∩N type nitrogen bases **L1** and **L2** in methanol to afford the mono-cationic dinuclear complexes [(η^6-arene)$_2$Ru$_2$(μ-**L1**)Cl$_3$]$^+$ (arene = C_6H_6, **1**; *p*-^{i}PrC$_6$H$_4$Me, **2**; C$_6$Me$_6$, **3**), and [(η^6-arene)$_2$Ru$_2$(μ-**L2**)(μ-Cl)]$^+$ (arene = C_6H_6, **6**; *p*-^{i}PrC$_6$H$_4$Me, **7**; C$_6$Me$_6$, **8**), isolated as their hexafluorophosphate salts (Scheme 1 and 2). Cations **2**, **3, 7** and **8** are yellow in color, while **1** and **6** are brown. These salts are non-hygroscopic and stable in air as well as in solution. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone and acetonitrile but are insoluble in non-polar solvents like hexane, diethyl ether and petroleum ether. The analytical data of these compounds are consistent with the formulations. All compounds are characterized by ^{1}H NMR and IR spectroscopy. The IR spectra of these complexes exhibit sharp bands due to chelated multidentate ligands between 1637 and 1437 cm^{-1} corresponding to the different stretching frequencies of C=O, C=C and C=N bond after coordination to the metal centers (see experimental section). In addition, the infrared spectra contain a strong band between 843 and 849 cm^{-1} due to the stretching frequency of the P–F bonds of PF_6^- counter ions for these complexes. Comparing the IR spectra of the free ligands to that of the metal complexes, we find that the IR spectra of the free ligands show a sharp band at around 1672 cm^{-1} assigned to the stretching frequencies of C=O group of the ligands, but in the case of the metal complexes the stretching frequencies of C=O group appears in the lower frequency around 1637 and 1615 cm^{-1}. The decrease in the stretching frequencies and the presence of only one band shows that the metal has coordinated in only one fashion *i.e.,* either N∩N coordination or N∩O coordination which has been finally confirmed by the single crystal X-ray structure analysis of **6** and found that the mode of coordination is through N∩N and not N∩O coordination.

The proton NMR spectra of all these complexes show the ligand resonances downfield shifted as compared to that of the free ligands. For the complexes with ligand **L1**, only eight signals are apparently observed due to overlapping on two occasions, whereas with that of ligand **L2** it shows set of six signals, corresponding to the different protons of these ligands as mentioned in the experimental section. Beside these signals, complexes **1** and **6** shows two singlets each between 5.72 and 5.33 ppm respectively which arises due to the six protons of the benzene rings, complex **2** and **7** shows four doublets at *ca.* 5.73–5.49 ppm corresponding to the aromatic protons of the p-cymene ligand, two septets at around 2.67 and 2.59 ppm which is assigned to the isopropyl protons, two singlets between 2.38 and 2.15 ppm for the methyl protons and another two doublets at *ca.* 1.13–0.87 ppm due to the methyl protons of the isopropyl groups of this complex. In addition to the ligand peaks, complexes **3** and **8** show a pair of singlets each between 2.18 and 2.02 ppm respectively corresponding to the eighteen protons of the hexamethlybenzene group of these complexes. It is difficult to assign the exact structure of these complexes on the basis of spectral data, so we have carried out single crystal X-ray study of few representative compounds. We are unable to isolate single crystals of complexes **1** to **3**, so we extended the proposed structure on the basis of complex **4**. In the case of complexes **6**, **7** and **8**, the molecular structure of complex **6** was solved and presented in Fig. 1. The molecular structure of complex **6** uncovered the two metal centers are bonded by a bridging chloride. In the case of complexes



Scheme 1. Preparation of complexes 1(PF$_6$)-3(PF$_6$).



Scheme 2. Reaction scheme for the formation of complexes 6(PF_6)-8(PF_6).

6, 7 and **8**, the ligand L**2** is coordinated to both the metals in a bidentate fashion through nitrogen atoms.

In 2003, George Suss-Fink and his group reported the synthesis of tris–thiolato-bridged complexes of the type $[(\eta^6\text{-arene})_2Ru_2(l\text{-}SR^1)_3]^+$ (arene = C_6H_6, $p\text{-}^iPrC_6H_4Me$, C_6Me_6; R^1 = $p\text{-}C_6H_4Me$, CH_2CH_2OH, $p\text{-}C_6H_4OH$), accessible from the reaction of $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-}Cl)_2Cl_2]$ with the corresponding thiol [31]. In contrast, the mono and dithiolato-bridged complexes $[(\eta^6\text{-arene})_2Ru_2(l\text{-}H)_2(l\text{-}SR^1)]^+$ and $[(\eta^6\text{-arene})_2Ru_2(l\text{-}H)(l\text{-}SR^1)_2]^+$ (arene = p-$C_6H_2Me_4$, C_6Me_6; R^1 = $p\text{-}C_6H_4Me$, p-C_6H_4Br) were obtained from $[(\eta^6\text{-arene})_2Ru_2(l\text{-}H)_3]^+$ by reaction with the corresponding thiophenol [32]. Using a similar approach, complexes **6**, **7** and **8** were reacted with thiol precursors like SR^1 where R^1 = $p\text{-}C_6H_4Me$, CH_2CH_2OH, $p\text{-}C_6H_4OH$, in order to synthesize thiolato-bridged complexes [32]. Surprisingly, the reaction did not take place and only decomposition occurs giving a black color solution. We also tried a series of reactions with arene precursor containing triphenylphosphine groups with the ligand **L2** and here also the compound decomposed leaving only a black color solution. We decided to explore the exact reason of its decomposition and the study is in progress.

The reaction of the pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) with one equivalent of the ligands **L1** and **L2** in methanol results the formation of yellow colored, air stable mono-cationic dinuclear complexes $[(\eta^5\text{-}C_5Me_5)_2M_2(\mu\text{-}\mathbf{L1})Cl_3]^+$ (M = Rh, **4**; Ir, **5**) (Scheme 3) and $[(\eta^5\text{-}C_5Me_5)_2M_2(\mu\text{-}\mathbf{L2})Cl_2]^+$ (M = Rh, **9**; Ir, **10**) (Scheme 4) which are also isolated as their hexafluorophosphate salts. These complexes are characterized by ^1H NMR spectroscopy and IR spectroscopy. The

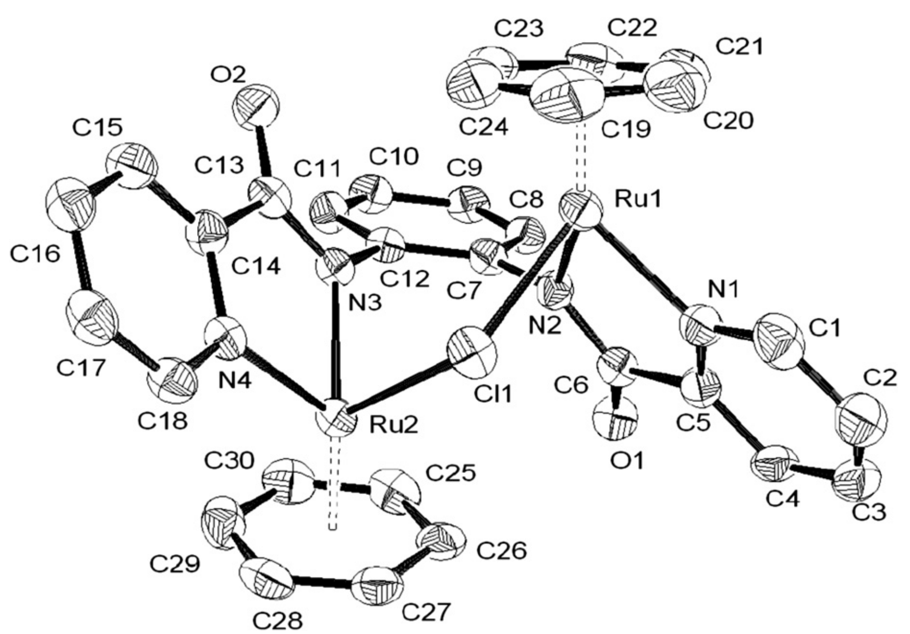
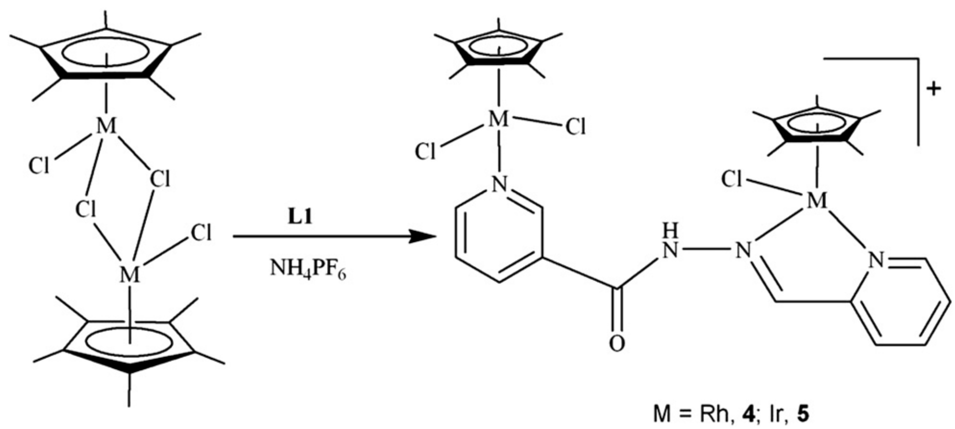


Fig. 1. Molecular structure of $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mathbf{L2})(\mu\text{-}Cl)]^+$ (**6**) at 50% probability level. Hydrogen atoms and hexafluorophosphate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 4.0679(6), Ru(1)–Cl(1) 2.4545(13), Ru(1)–N(1) 2.088(4), Ru(1)–N(2) 2.068(4), Ru(2)–N(3) 2.093(4), Ru(2)–N(4) 2.083(4), Ru(2)–Cl(1) 2.4489(12); N(1)–Ru(1)–N(2) 77.59(16), N(1)–Ru(1)–Cl(1) 83.14(11), N(2)–Ru(1)–Cl(1) 86.69(11), N(3)–Ru(2)–N(4) 77.69(15), N(3)–Ru(2)–Cl(1) 87.49(11), N(4)–Ru(2)–Cl(1) 83.17(11), Ru(1)–Cl(1)–Ru(2) 112.12(4).



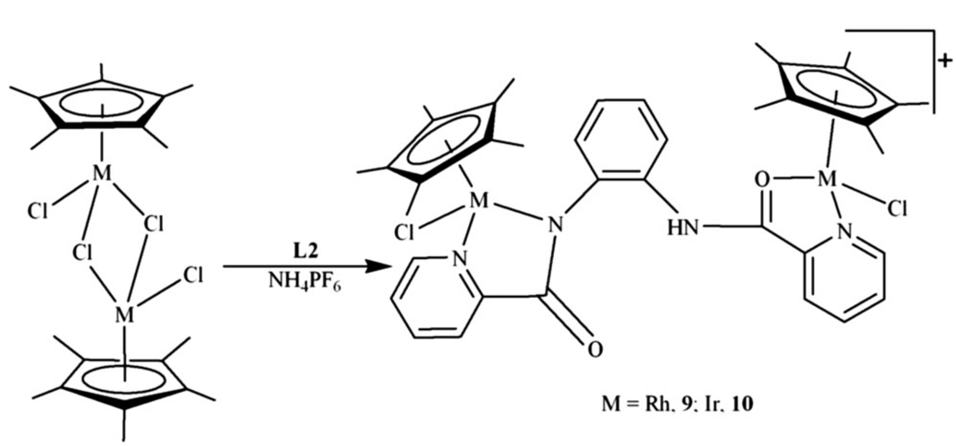
Scheme 3. Reaction scheme for the formation of complexes 4(PF_6) and 5(PF_6).

analytical data of these compounds are consistent with the formulations. The infrared spectra of all these complexes exhibit a sharp bands due to bis-chelating **L1** and **L2** ligands in between 3447 and 1435 cm^{-1} corresponding to the stretching frequencies of N—H, C═O, C═C and C═N bond of these complexes. Beside these, the infrared spectra of these complexes also display a sharp band between 845 and 839 due to the ν_{P-F} stretching frequency of the counter ion of these complexes. The ^{1}H NMR spectra of these complexes show ligand peaks a downfield shift in the position of signals associated with protons of ligands **L1** and **L2** compared to that of the uncoordinated ligands suggesting coordination of the nitrogen and oxygen atoms to the metal center in a monodentate and bidentate fashion. In complexes **4** and **5**, the ligand is coordinated in a bidentate fashion to the first metal atom while in a monodentate fashion to second metal atom with the nitrogen atoms of the ligand molecule. Whereas in case of complexes **9** and **10**, both the metals are coordinated by the ligand L**2** in a bidentate fashion but the mode of binding to the metal is interestingly different. The first metal is *N,N* coordinated while the second metal is *N,O* coordinated giving a mono-cationic dinuclear complexes. In addition to the ligands peaks as mentioned in the experimental section, the proton NMR spectra of these complexes also exhibits a pair of singlets each between 2.31 and 1.53 ppm for complexes **4**, **5**, **9** and **10**, respectively, corresponding to the protons of the pentamethylcyclopentadienyl group, which is in the downfield region as compared to that of the starting precursors. The molecular structures of complexes **4** and **9** were solved by single crystal X-ray crystallography and the structures are depicted in Figs. 2 and 3.

It is interesting to see that the ligand **L1** is bonded to the same fashion in the case of arene ruthenium dimers as well as pentamethylcyclopentadienyl rhodium and iridium dimers but in the case of ligand **L2** the bonding modes are quite different. In the case of arene ruthenium dimers, the ligand binds *N,N* fashion by bridging two metals with additional chloride bridge. Where as in the case of rhodium and iridium dimers, the ligand binds to the metal centers as a *N,N* and *N,O* fashion without chloride bridge but with terminal chloride groups. This mode of binding could be due to the bulky pentamethylcyclopentadienyl groups which do not allow the two metal centers to come closer to form chloride bridge as in the case of ruthenium dimers. We don't know the exact reason why the rhodium prefers the *N, O* fashion at second metal center unlike NN bonding mode as in the case of ruthenium.

3. Molecular structures of [4]$PF_6 \cdot H_2O$, [6]PF_6 and [9]$PF_6 \cdot H_2O$

The molecular structure of [**4**]$PF_6 \cdot H_2O$ shows **L1** to act as a tridentate ligand in which the two metal centers are non-equivalent. The dinuclear complex shows typical piano-stool geometry for both metal centers with the first rhodium atom being coordinated by the aromatic ligand, a terminal chloride and two nitrogen atoms, while the second rhodium is coordinated to the aromatic ligand, two terminal chlorides and the nitrogen atom of the 3-pyridyl group (see Fig. 2). Similarly, the molecular structure of [**9**]$PF_6 \cdot H_2O$ shows two non-equivalent metal centers, despite the potential symmetry of ligand **L2**. Indeed, the first rhodium atom is coordinated by the



Scheme 4. Reaction scheme for the formation of complexes 9(PF_6) and 10(PF_6).

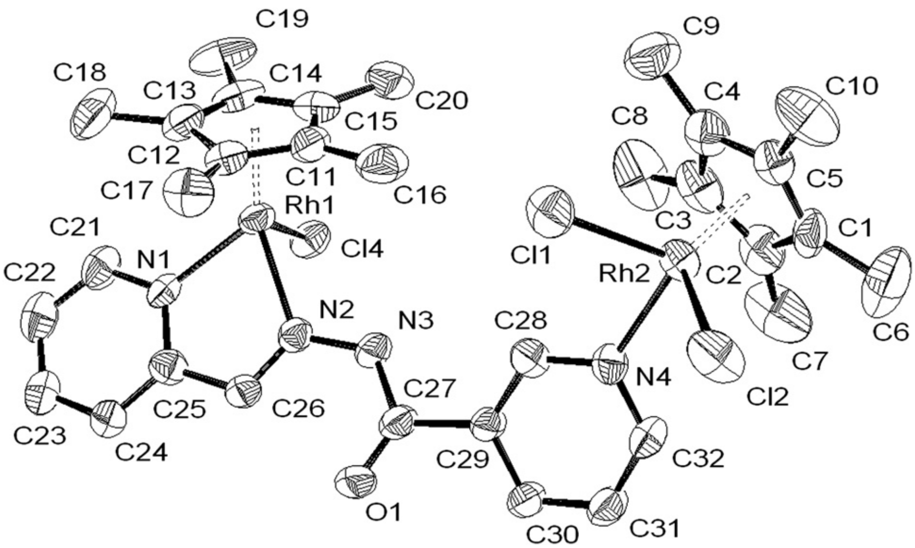


Fig. 2. Molecular structure of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mathbf{L1})Cl_3]^+$ (**4**) at 50% probability level. Hydrogen atoms and hexafluorophosphate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 7.823(3), Rh(1)–Cl(4) 2.389(2), Rh(1)–N(1) 2.089(6), Rh(1)–N(2) 2.139(6), Rh(2)–N(4) 2.152(6), Rh(2)–Cl(1) 2.393(2), Rh(2)–Cl(2) 2.428(2), N(2)–N(3) 1.406(8); N(1)–Rh(1)–N(2) 75.8(2), N(1)–Rh(1)–Cl(4) 88.60(18), N(2)–Rh(1)–Cl(4) 88.57(16), N(4)–Rh(2)–Cl(1) 88.34(18), N(4)–Rh(2)–Cl(2) 85.88(17), Cl(1)–Rh(2)–Cl(2) 91.45(9).

pentamethylcyclopentadienyl ligand, a terminal chloride and two nitrogen atoms, while the other rhodium is coordinated by the aromatic ligand, a terminal chloride, nitrogen and an oxygen atom (see Fig. 3). In both structures, the distance between the two metal centers approaches 8 Å, the Rh–Rh distance is 7.823(3) in **4** and 7.9926(7) in **9**. In both structures, the Rh-Cl, Rh-N and Rh-O bond lengths are similar to those reported for related Cp*Rh complexes [33].

Interestingly, the X-ray structure analysis of [**6**]PF_6 shows a chloro-bridged dinuclear complex (see Fig. 1). In this dinuclear complex, at 2.4545(13) and 2.4489(12) Å, the Ru-Cl distances are comparable to those found in other chloro-bridged complexes involving ruthenium centers [34,35]. Similarly, the metal–metal distance [4.0679(6) Å] lies in the typical range for single chloro-bridged dinuclear arene ruthenium complexes [36,37].

In the crystal packing of [**4**]$PF_6 \cdot H_2O$ and [**9**]$PF_6 \cdot H_2O$, the water molecule plays an important role. It forms hydrogen bonds with neighboring complexes, thus generating one-dimensional hydrogen-bonded networks in the crystal, see Figs. 4 and 5.

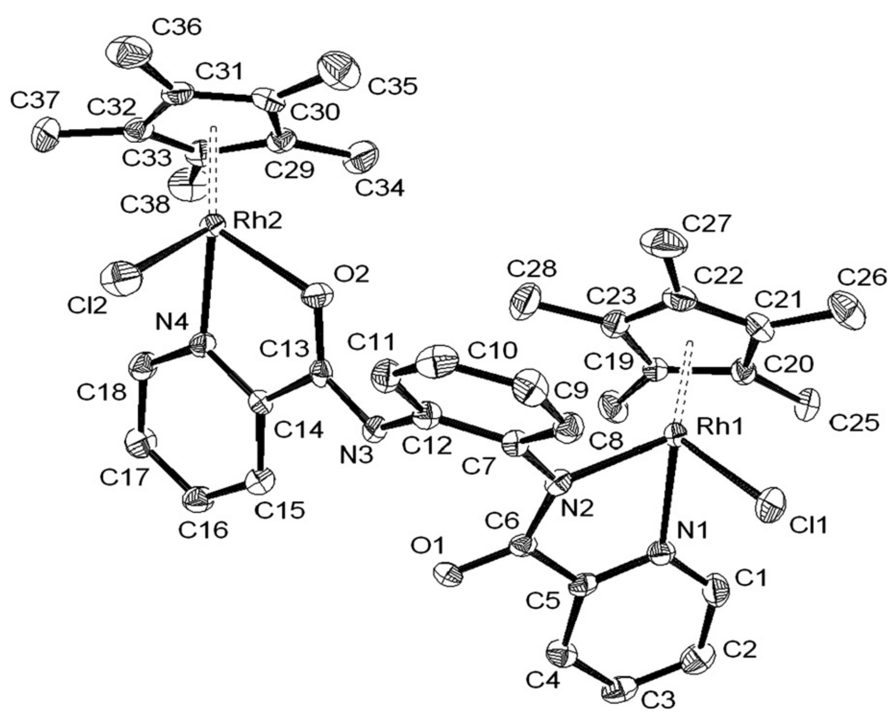


Fig. 3. Molecular structure of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mathbf{L2})Cl_2]^+$ (**9**) at 50% probability level. Hydrogen atoms, water molecule and hexafluorophosphate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 7.9926(7), Rh(1)–Cl(1) 2.4194(11), Rh(1)–N(1) 2.091(4), Rh(1)–N(2) 2.127(3), Rh(2)–N(4) 2.117(4), Rh(2)–Cl(2) 2.4060(12), Rh(2)–O(2) 2.139(3); N(1)–Rh(1)–N(2) 76.98(14), N(1)–Rh(1)–Cl(1) 87.67(10), N(2)–Rh(1)–Cl(1) 93.81(9), N(4)–Rh(2)–Cl(2) 87.54(10), N(4)–Rh(2)–O(2) 76.43(13), Cl(2)–Rh(2)–O(2) 87.20(8).

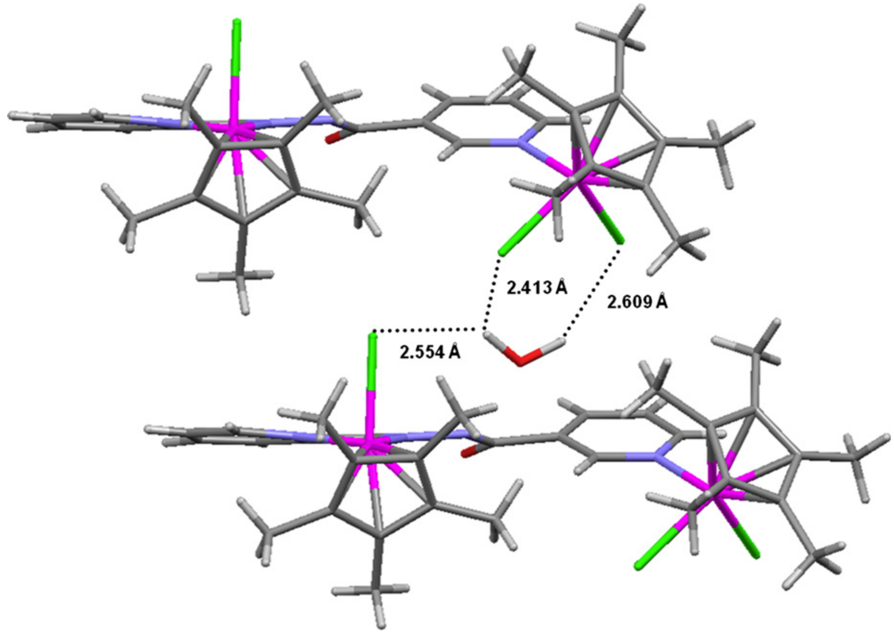


Fig. 4. Hydrogen-bonded network observed in [**4**]$PF_6 \cdot H_2O$.

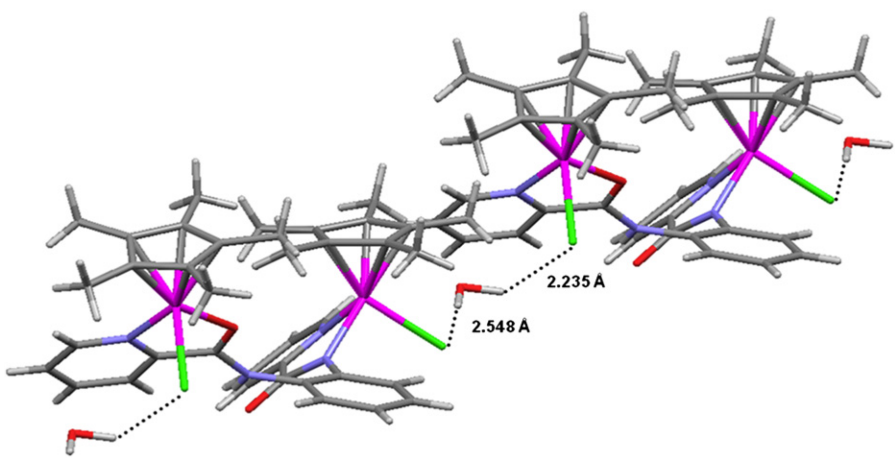


Fig. 5. Hydrogen-bonded network observed in [**9**]$PF_6 \cdot H_2O$.

In [**4**]$PF_6 \cdot H_2O$, each water molecules interact with three chlorides. The O···Cl distances are 3.160(6), 3.378(6) and 3.526(7) Å, with O–H···Cl angles of 127.03, 134.74 and 147.08° respectively. Accordingly, in [**9**]$PF_6 \cdot H_2O$, the water molecule connects along the *b* axis dinuclear complexes, thus generating one-dimensional chains of **9** in the crystal. The O···Cl distances are 3.316(5) and 3.335 (5) Å with O–H···Cl angles of 172.47 and 134.03°, respectively.

4. Conclusions

In summary, a series of novel dinuclear η^5-and η^6-cyclic π-perimeter hydrocarbon metal complexes bearing ligand **L1** and **L2**, which are remarkably stable in the solid state and in solution have been successfully synthesized in good yield. The ligand **L2** bonded the metal centers interestingly. To confirm the mode of binding, the molecular structures of three representative complexes have been determined by X-ray crystallography. In the molecular structure of **4**, interestingly, the first metal is bonded to two nitrogen atoms whereas the second metal center is coordinated to only one nitrogen atom with two terminal chloride ligands. But, in the case of the complexes with the ligand **L2**, both ruthenium centers having η^6-arene groups are bonded to nitrogen atoms with a bridging chlorine atom between the two metal centers, whereas the metals with η^5-arene groups are observed in two different coordination mode: the first metal being *N,O* coordinated while the second metal is *N,N* coordinated.

5. Experimental

5.1. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer Model 983 spectrophotometer with the sample prepared as KBr pellets. The NMR spectra were obtained using Bruker Advance II 400 spectrometer in $CDCl_3$, DMSO-d_6 and Acetone-d_6 respectively for complexes using TMS as an internal standard. All chemicals used were of reagent grade.

Table 1
Crystallographic and structure refinement parameters for complexes [**4**](PF_6)·H_2O, [**6**](PF_6) and [**9**](PF_6)·H_2O.

	[**4**](PF_6)·H_2O	[**6**](PF_6)	[**9**](PF_6)·H_2O
Chemical formula	$C_{32}H_{41}Cl_3F_6N_4O_2P\ Rh_2$	$C_{30}H_{24}ClF_6N_4O_2PRu_2$	$C_{38}H_{45}Cl_2F_6N_4O_3PRh_2$
Formula weight	970.83	855.09	1027.47
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P* −1 (no. 2)	*P* −1 (no. 2)	*P* −1 (no. 2)
Crystal color & shape	Red block	Orange block	Red block
Crystal size	0.27 × 0.24 × 0.22	0.23 × 0.19 × 0.16	0.25 × 0.20 × 0.17
a (Å)	7.928(3)	11.6270(6)	7.5847(5)
b (Å)	15.177(6)	15.5328(7)	15.6515(10)
c (Å)	17.309(7)	17.3974(9)	17.7089(13)
α (°)	68.072(12)	85.783(4)	96.534(5)
β (°)	79.373(10)	86.751(4)	98.317(5)
γ (°)	89.358(9)	72.021(4)	100.065(5)
V (Å^3)	1895.1(13)	2978.5(3)	2027.2(2)
Z	2	4	2
T (K)	203(2)	173(2)	173(2)
D_c (g cm^{-3})	1.701	1.907	1.683
μ (mm^{-1})	1.189	1.233	1.055
Scan range (°)	1.29< θ <28.44	1.76< θ <29.20	1.65< θ <29.18
Unique reflections	9318	14818	10945
Reflections used [I > 2σ(I)]	5426	10284	6691
R_{int}	0.0944	0.0775	0.1053
Final R indices [I > 2σ(I)][a]	0.0737, wR_2 0.1672	0.0520, wR_2 0.1173	0.0553, $wR_2$0.0726
R indices (all data)	0.1306, wR_2 0.2112	0.0796, wR_2 0.1261	0.1150, $wR_2$0.0831
Goodness-of-fit	0.999	0.949	0.955
Max, Min Δρ/e (Å^{-3})	1.337, −0.836	1.171, −0.954	0.669, −0.903

[a] Structures were refined on F_0^2: $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

Elemental analyses of the complexes were performed on a Perkin–Elmer 2400 CHN/S analyzer. All reactions were carried out in distilled and dried solvents. The ligand **L1** and **L2** were prepared by following literature procedures [38,29]. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, $p\text{-}^iPrC_6H_4Me$ and C_6Me_6) and $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$ (M = Rh, Ir) [39–43] were synthesized by literature procedure.

5.2. Single crystal X-ray structure analyses

Crystals of complexes [**4**](PF_6)·H_2O, [**6**](PF_6) and [**9**](PF_6)·H_2O were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS–97 [44]. Refinement and all further calculations were carried out using SHELXL–97 [45]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 1. Figs. 1–3 were drawn with ORTEP–32 [45].

5.3. Preparation of $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-}\mathbf{L1})Cl_3](PF_6)$ {arene = C_6H_6 [*1*] PF_6, $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ [*2*] PF_6, C_6Me_6 [*3*] PF_6}

A mixture of $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (0.10 mmol), L1 (50 mg, 0.10 mmol) and two equivalents 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.

5.3.1. Compound [*1*] PF_6

Yield: 110 mg, 65.8%. Elemental Anal (%) Calc. for $C_{24}H_{22}Cl_3F_6N_4OPRu_2$: C 34.49; H 2.67; N 6.68; found: C 34.80; H 2.88; N 6.34; IR (KBr pellets, cm^{-1}): 3430 (ν_{N-H}); 1615 ($\nu_{C=O}$); 1457 ($\nu_{C=N}$); 846 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.85 (s, 1H, NH), 9.66 (s, 1H), 9.06 (d, J = 6 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.2 Hz, 2H), 7.54 (dd, J = 7.6 Hz, 2H), 7.42 (dd, J = 7.6 Hz, 1H), 5.41 (s, 6H, C_6H_6), 5.33 (s, 6H, C_6H_6), 3.11 (s, 1H, CH).

5.3.2. Compound [*2*]PF_6

Yield: 121 mg, 71.6%. Elemental Anal (%) Calc. for $C_{40}H_{30}Cl_3F_6N_4OPRu_2$: C 46.38; H 2.94; N 5.38; found: C 46.72; H 3.21; N 5.06; IR (KBr pellets, cm^{-1}): 3434 (ν_{N-H}); 1637 ($\nu_{C=O}$); 1437 ($\nu_{C=N}$); 843 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.95 (s, 1H, NH), 9.65 (s, 1H), 9.20 (d, J = 5.2 Hz, 1H), 8.29 (d, J = 8 Hz, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.84 (t, J = 7.6 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H), 5.73 (d, J = 6.8 Hz, 2H, Ar_{p-cy}), 5.70 (d, J = 6.8 Hz, 2H, Ar_{p-cy}), 5.54 (d, J = 5.6 Hz, 2H, Ar_{p-cy}), 5.49 (d, J = 6 Hz, 2H, Ar_{p-cy}), 3.05 (s, 1H, CH), 2.76 (sept, 1H), 2.59 (sept, 1H), 2.32 (s, 3H), 2.15 (s, 3H), 1.07 (d, J = 7.6 Hz, 3H), 0.99 (d, J = 7.2 Hz, 3H), 0.87 (d, J = 4 Hz, 3H), 0.84 (d, J = 4 Hz, 3H).

5.3.3. Compound [*3*]PF_6

Yield: 107 mg, 71.4%. Elemental Anal (%) Calc. for $C_{36}H_{46}Cl_3F_6N_4OPRu_2$: C 43.04; H 4.64; N 5.55; found: C 43.31; H 4.79; N 5.31; IR (KBr pellets, cm^{-1}): 3433 (ν_{N-H}); 1618 ($\nu_{C=O}$); 1474 ($\nu_{C=N}$); 846 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.88 (s, 1H, NH), 9.71 (s, 1H), 9.30 (d, J = 6.2 Hz, 1H), 8.31 (d, J = 7.2 Hz, 1H), 7.88 (d, J = 7.2 Hz, 2H), 7.66 (t, J = 7.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 2.91 (s, 1H, CH), 2.18 (s, 18H, C_6Me_6), 2.09 (s, 18H, C_6Me_6).

5.4. Preparation of $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}\mathbf{L1})Cl_3]PF_6$ {M = Rh [*4*]PF_6, Ir [*5*]PF_6}

A mixture of $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-Cl})Cl]_2$ (0.10 mmol), L1 (50 mg, 0.10 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4–5 h at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

5.4.1. Compound [*4*]PF_6

Yield: 112 mg, 72.7%. Elemental Anal (%) Calc. for $C_{32}H_{40}Cl_3F_6N_4OPRh_2$: C 40.33; H 4.24; N 5.85; found: C 40.49; H 4.35; N 5.68; IR (KBr pellets, cm^{-1}): 3435 (ν_{N-H}); 1616 ($\nu_{C=O}$); 1466

($\nu_{C{=}N}$); 845 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): $\delta = 9.66$ (s, 1H, NH), 8.86 (s, 1H), 8.73 (d, $J = 4.8$ Hz, 1H), 8.47 (d, $J = 6.4$ Hz, 1H), 8.41 (d, $J = 7.6$ Hz, 1H), 8.07 (dd, $J = 7.2$ Hz, 2H), 7.83 (dd, $J = 6$ Hz, 1H), 7.49 (d, $J = 6.4$ Hz, 1H), 2.67 (s, 1H, CH), 1.63 (s, 15H, C_5Me_5), 1.53 (s, 15H, C_5Me_5).

5.4.2. Compound [**5**]PF$_6$

Yield: 105 mg, 74.0%. Elemental Anal (%) Calc. for $C_{32}H_{40}Cl_3F_6Ir_2N_4OP$: C 33.95; H 3.58; N 4.93; found: C 34.19; H 3.82; N 4.71; IR (KBr pellets, cm^{-1}): 3440 (ν_{N-H}); 1608 ($\nu_{C{=}O}$); 1475 ($\nu_{C{=}N}$); 843 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6): $\delta = 9.71$ (s, 1H, NH), 8.96 (s, 1H), 8.82 (d, $J = 4$ Hz, 1H), 8.51 (d, $J = 6.2$ Hz, 1H), 8.44 (d, $J = 7.6$ Hz, 1H), 8.18 (dd, $J = 7.6$ Hz, 2H), 7.94 (dd, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 6$ Hz, 1H), 2.85 (s, 1H, CH), 1.71 (s, 15H, C_5Me_5), 1.59 (s, 15H, C_5Me_5).

5.5. Preparation of [(η^6-arene)$_2$Ru$_2$(μ-**L2**)Cl](PF$_6$) { arene = C_6H_6 [**6**]PF$_6$, η^6-p-^{i}PrC$_6$H$_4$Me [**7**]PF$_6$, C$_6$Me$_6$ [**8**]PF$_6$}

A mixture of [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (0.10 mmol), L2 (50 mg, 0.10 mmol) and two equivalents 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.

5.5.1. Compound [**6**]PF$_6$

Yield: 113 mg, 66.1%. Elemental Anal (%) Calc. for $C_{30}H_{26}ClF_6N_4O_2PRu_2$: C 42.05; H 3.08; N 6.52; found: C 42.36; H 3.38; N 6.35; IR (KBr pellets, cm^{-1}): 1624 ($\nu_{C{=}O}$); 1565 ($\nu_{C{=}C}$); 1437 ($\nu_{C{=}N}$); 847 (ν_{P-F}); ^{1}H NMR (400 MHz, Acetone-d_6): $\delta = 9.39$ (d, $J = 5.6$ Hz, 2H), 8.19 (t, $J = 7.6$ Hz, 2H), 8.05 (d, $J = 8$ Hz, 2H), 7.70 (t, $J = 6$ Hz, 2H), 7.53 (t, $J = 3.2$ Hz, 2H), 7.17 (t, $J = 3.2$ Hz, 2H), 5.72 (s, 6H, C_6H_6), 5.57 (s, 6H, C_6H_6).

5.5.2. Compound [**7**]PF$_6$

Yield: 128 mg, 74.5%. Elemental Anal (%) Calc. for $C_{46}H_{34}ClF_6N_4O_2PRu_2$: C 52.25; H 3.27; N 5.28; found: C 52.38; H 3.51; N 5.13; IR (KBr pellets, cm^{-1}): 1617 ($\nu_{C{=}O}$); 1597 ($\nu_{C{=}C}$); 1466 ($\nu_{C{=}N}$); 844 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.26$ (d, $J = 5.2$ Hz, 2H), 8.21 (d, $J = 7.6$ Hz, 2H), 8.09 (dd, $J = 7.6$ Hz, 2H), 7.76 (dd, $J = 6.8$ Hz, 2H), 7.67 (dd, $J = 3.2$ Hz, 2H), 7.35 (t, $J = 3.6$ Hz, 2H), 5.51 (d, $J = 6.0$ Hz, 2H, Ar_{p-cy}), 5.33 (d, $J = 6.0$ Hz, 4H, Ar_{p-cy}), 5.01 (d, $J = 6$ Hz, 2H, Ar_{p-cy}), 2.81 (sept, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 1.06 (d, $J = 6.8$ Hz, 6H), 0.91 (d, $J = 7.2$ Hz, 6H).

5.5.3. Compound [**8**]PF$_6$

Yield: 113 mg, 73.9%. Elemental Anal (%) Calc. for $C_{42}H_{50}ClF_6N_4O_2PRu_2$: C 49.20; H 4.91; N 5.44; found: C 49.39; H 5.25; N 5.21; IR (KBr pellets, cm^{-1}): 1624 ($\nu_{C{=}O}$); 1457 ($\nu_{C{=}N}$); 843 (ν_{P-F}); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.29$ (d, $J = 6.2$ Hz, 2H), 8.01 (d, $J = 7.2$ Hz, 2H), 7.88 (t, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.6$ Hz, 2H), 7.42 (t, $J = 6$ Hz, 2H), 7.20 (t, $J = 3.6$ Hz, 2H), 2.14 (s, 18H, C_6Me_6), 2.02 (s, 18H, C_6Me_6).

5.6. Preparation of [(η^5-C$_5$Me$_5$)M(μ-**L2**)Cl$_3$]PF$_6$ {M = Rh [**9**]PF$_6$, Ir [**10**]PF$_6$}

A mixture of [(η^5-C$_5$Me$_5$)M(μ-Cl)Cl]$_2$ (0.10 mmol), **L2** (50 mg, 0.10 mmol) and two equivalents of NH_4PF_6 was stirred in dry methanol (30 ml) for 4–5 h at room temperature. The yellow compound which formed was filtered, washed with ethanol, diethyl ether and dried under vacuum.

5.6.1. Compound [**9**]PF$_6$

Yield: 117 mg, 71.8%. Elemental Anal (%) Calc. for $C_{38}H_{44}Cl_2F_6N_4O_2PRh_2$: C 45.17; H 4.40; N 5.54; found: C 45.49; H 4.79; N 5.43; IR (KBr pellets, cm^{-1}): 3447 (ν_{N-H}); 1618 ($\nu_{C{=}O}$); 1584 ($\nu_{C{=}C}$); 1449 ($\nu_{C{=}N}$); 839 (ν_{P-F}); ^{1}H NMR (400 MHz, Acetone-d_6): $\delta = 9.53$ (d, $J = 4.8$ Hz, 2H), 8.33 (t, $J = 7.6$ Hz, 2H), 8.18 (d, $J = 7.6$ Hz, 2H), 7.82 (dd, $J = 6.4$ Hz, 2H), 7.66 (dd, $J = 7.6$ Hz, 2H), 7.30 (dd, $J = 7.2$ Hz, 2H), 2.31 (s, 15H, C_5Me_5), 2.06 (s, 15H, C_5Me_5).

5.6.2. Compound [**10**]PF$_6$

Yield: 109 mg, 73.2%. Elemental Anal (%) Calc. for $C_{38}H_{44}Cl_2F_6Ir_2N_4O_2P$: C 38.39; H 3.74; N 4.69; found: C 38.57; H 3.99; N 4.48; IR (KBr pellets, cm^{-1}): 3446 (ν_{N-H}); 1632 ($\nu_{C{=}O}$); 1588 ($\nu_{C{=}C}$); 1457 ($\nu_{C{=}N}$); 844 (ν_{P-F}); ^{1}H NMR (400 MHz, Acetone-d_6): $\delta = 9.62$ (d, $J = 5$ Hz, 2H), 8.28 (dd, $J = 7.2$ Hz, 2H), 7.97 (d, $J = 7.2$ Hz, 2H), 7.63 (dd, $J = 6.4$ Hz, 2H), 7.42 (dd, $J = 7.2$ Hz, 2H), 7.11 (dd, $J = 7.6$ Hz, 2H), 2.09 (s, 15H, C_5Me_5), 1.88 (s, 15H, C_6Me_5).

Appendix A. Supplementary material

CCDC-788636 ([**4**]PF$_6$·H$_2$O), 788637 ([**6**]PF$_6$) and 788638 ([**9**](PF$_6$)·H$_2$O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

References

[1] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, Chem. Rev. 96 (1996) 759–834.
[2] R.H. Holm, P. Kennepohl, E.I. Solomon, Chem. Rev. 96 (1996) 2239–2314.
[3] M. Albrecht, Chem. Rev 101 (2001) 3457–3498;
C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. 97 (1997) 2005–2062.
[4] J.-C.G. Bünzli, C. Piguet, Chem. Rev. 102 (2002) 1897–1928.
[5] J. Canivet, L. Karmazin-Brelot, G. Süss-Fink, J. Organomet. Chem 690 (2005) 3202–3211.
[6] S. Ogo, T. Abura, Y. Watanabe, Organometallics 21 (2002) 2964–2969.
[7] S. Ogo, K. Uehara, T. Abura, Y. Watanabe, S. Fukuzumi, Organometallics 23 (2004) 3047–3052.
[8] A.W. Stumpf, E. Saive, A. Demonceau, F.A. Noels, J. Chem. Soc. Chem. Commun. (1995) 1127–1128.
[9] M.K. Tse, C. Döbler, S. Bhor, M. Klawonn, W. Mägerlein, H. Hugl, et al., Angew. Chem. Int. Ed 43 (2004) 5255–5260.
[10] Y.K. Yan, M. Melchart, A. Habtemariam, P.J. Sadler, J. Chem. Commun. (2005) 4764–4776 [and references therein].
[11] W.H. Ang, P.J. Dyson, Eur. J. Inorg. Chem. (2006) 4003–4018 [and references therein].
[12] B. Therrien, Coord Chem. Rev. 253 (2009) 493–519.
[13] F. Marchetti, C. Pettinari, R. Pettinari, A. Cerquetella, A. Cingolani, E.J. Chan, et al., Inorg. Chem. 46 (2007) 8245–8257 [and references therein].
[14] R.J. Restivo, G. Ferguson, J. Chem. Soc. Chem. Commun. (1973) 847–848.
[15] C.J. Jones, J.A. McCleverty, A.S. Rothin, J. Chem. Soc. Dalton Trans. (1986) 109–111.
[16] S. Bhambri, A. Bishop, N. Kaltsoyannis, D.A. Tocher, J. Chem. Soc. Dalton Trans. (1998) 3379–3390.
[17] G. Gupta, K.T. Prasad, B. Das, G.P.A. Yap, K.M. Rao, J. Organomet Chem. 694 (2009) 2618–2627.
[18] K.T. Prasad, G. Gupta, A.K. Chandra, M.P. Pavan, K.M. Rao, J. Organomet. Chem 695 (2010) 707–716.
[19] G. Gupta, B. Therrien, K.M. Rao, J. Organomet. Chem 695 (2010) 753–759.
[20] G. Gupta, G.P.A. Yap, B. Therrien, K.M. Rao, Polyhedron 28 (2009) 844–850.
[21] G. Gupta, K.T. Prasad, B. Das, K.M. Rao, Polyhedron 29 (2010) 904–910.
[22] G. Gupta, C. Zheng, P. Wang, K.M. Rao, Z. Anorg. Allg Chem 636 (2010) 758–764.
[23] K.T. Prasad, G. Gupta, A.V. Rao, B. Das, K.M. Rao, Polyhedron 28 (2009) 2649–2654.
[24] G. Gupta, K.T. Prasad, A.V. Rao, S.J. Geib, B. Das, K.M. Rao, Inorg. Chim. Acta. 363 (2010) 2287–2295.
[25] G. Gupta, S. Gloria, B. Das, K.M. Rao, J. Mol. Struct. 979 (2010) 205–213.
[26] J.K. Hurst, Coord. Chem. Rev. 249 (2005) 313–328.
[27] C. Sens, I. Romero, M. Rodriguez, A. Llobet, T. Parella, J.B. Buchholz, J. Am. Chem. Soc. 126 (2004) 7798–7799.
[28] G.M. Halpenny, P.K. Mascharak, Inorg. Chem. 48 (2009) 1490–1497.
[29] M.A. Palacios, A.R. Dieguez, A. Sironi, J.M. Herrera, A.J. Mota, J. Cano, et al., Dalton Trans. (2009) 8538–8547.
[30] A.K. Patra, M.J. Rose, K.A. Murphy, M.M. Olmstead, P.K. Mascharak, Inorg. Chem. 43 (2004) 4487–4496.
[31] F. Chérioux, C.M. Thomas, T. Monnier, G. Süss-Fink, Polyhedron 22 (2003) 543–548.
[32] M.J.-L. Tschan, F. Chérioux, B. Therrien, G. Süss-Fink, Eur. J. Inorg. Chem. 12 (2004) 2405–2411.
[33] P. Govindaswamy, B. Therrien, G. Süss-Fink, P. . Štěpnička, J. Ludvík, J. Organomet. Chem. 692 (2007) 1661–1671.

[34] J. Mattsson, B. Therrien, Acta. Cryst. E63 (2007) m2757.
[35] P. Govindaswamy, G. Süss-Fink, B. Therrien, Organometallics 26 (2007) 915–924.
[36] M. Poyatos, W. McNamara, C. Incarvito, E. Clot, E. Peris, R.H. Crabtree, Organometallics 27 (2008) 2128–2136.
[37] Y. Boutadla, O. Al-Duaij, D.L. Davies, G.A. Griffith, K. Singh, Organometallics 28 (2009) 433–440.
[38] M. Joseph, M. Kuriakose, M.R.P. Kurup, E. Suresh, A. Kishore, S.G. Bhat, Polyhedron 25 (2006) 61–70.
[39] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74–78.
[40] M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith, P.A. Tucker, Inorg. Chem. 19 (1980) 1014–1021.
[41] M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233–241.
[42] J.W. Kang, K. Moseley, P.M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5970–5977.
[43] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228–230.
[44] G.M. Sheldrick, Acta. Cryst. A64 (2008) 112–122.
[45] L.J. Farrugia, J. Appl. Cryst 30 (1997) 565–566.