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Ruthenium Complexes Containing Pyridine-2-carbaldehyde Azine as a Synthon in the Synthesis of Bi-/Trimetallic Complexes

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Ruthenium complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\kappa^2\text{-paa})]PF_6$ (paa = pyridine-2-carbaldehyde azine) and $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-dppm})(\kappa^2\text{-paa})]BF_4$ [dppm = bis(diphenylphosphanyl)methane] have been employed as a synthon in the synthesis of homo/hetero bi-/trimetallic complexes. It is the uncoordinated *N*,*N*-donor site on paa in complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\kappa^2\text{-paa})]PF_6$, and *N*,*N*-donor site on paa and pendant phosphorus in $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-dppm})(\kappa^2\text{-paa})]BF_4$ that allows for their incorporation into bi-/trimetallic systems. The resulting complexes have been characterized by analytical, spectral and electrochemical studies. Molecular structures of homobimetallic complex $[(PPh_3)(\eta^5\text{-}C_5H_5)Ru(\mu\text{-paa})Ru(\eta^6\text{-}C_{10}H_{14})Cl](PF_6)_2$ and hetero-bimetallic complex $[(PPh_3)(\eta^5\text{-}C_5H_5)Ru(\mu\text{-paa})Rh(\eta^5\text{-}C_5Me_5)Cl](PF_6)_2$ have been authenticated crystallographically. Complexes exhibit absorptions throughout the visible region and complicated electrochemical behaviour. Metal-based Ru^{II}/Ru^{III} oxidations in the bimetallic complexes do not vary as in the trimetallic complexes.

Introduction

Synthesis and characterization of homo/hetero bi- or polymetallic complexes bridged by polypyridyl and azo aromatic ligands have attracted wide interest due to their interesting properties and potential use in various fields.[1] Although polypyridyl ligands have extensively been used in this regard,[2] the closely related pyridyl azine ligands viz., pyridine-2-carbaldehyde azine (paa), *p*-phenylene-bis(picolino)-aldimine (pbp), *p*-biphenylene-bis(picoline)-aldimine (bbp) have scarcely been studied.[3] Among pyridyl azine ligands, pyridine-2-carbaldehyde azine (paa) forms some unusual and rather interesting coordination compounds with the first series transition metal ions. Because of the flexibility of the pyridine-2-carbaldehyde azine around the N–N single bond, the N_2 diazine linkage offers several possible mono- and bi-nucleating modes and gives rise to complexes having different geometries.[4]

Further, hetero bimetallic complexes based on κ^1 dppm have been developed and extensively studied as a catalyst for methanol oxidation.[5] It has been shown that the cooperative effect of different metal centres in homo/hetero bi-/polymetallic complexes can enhance interesting properties, bwhich are usually not observed in the monometallic systems. Hetero bimetallic complexes are of particular interest, since differing reactivity of the metals may be exploited in chemical transformations.[6,7] However, it is often difficult to determine whether the observed reactivity is due to the bimetallic complex itself or monometallic complexes formed upon dissociation of starting complexes under reaction conditions.[7a] The nature of the bridging ligand has a significant influence upon communication between metal centres in these multimetallic complexes. In the case of a weak interaction, the properties of polymetallic complexes are simply the addition of their molecular components. However, in the case of strong interactions properties are different when compared with those of the monometallic components.

Recently we have reported ruthenium complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\kappa^2\text{-paa})]PF_6$ and $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-dppm})(\kappa^2\text{-paa})]BF_4$ containing paa and κ^1-bonded dppm.[8] To examine the applicability of these complexes as metallo-ligands in the synthesis of homo/hetero bi-/trimetallic systems we carried out their reactions with various precursors like $[Pt(DMSO)_2Cl_2]$, $[\{(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)\}_2]$ (arene = benzene, *p*-cymene), $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ and $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$. We found that such reactions afforded homo/hetero bi- and trimetallic complexes. In this article we describe reproducible synthesis, spectral and electrochemical characterization of some bi- and trimetallic complexes. We also present herein the molecular structure of the bimetallic complexes $[(PPh_3)(\eta^5\text{-}C_5H_5)Ru(\mu\text{-paa})Ru(\eta^6\text{-}C_{10}H_{14})Cl](PF_6)_2$ and $[(PPh_3)(\eta^5\text{-}C_5H_5)Ru(\mu\text{-paa})Rh(\eta^5\text{-}C_5Me_5)Cl](PF_6)_2$.

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Results and Discussion

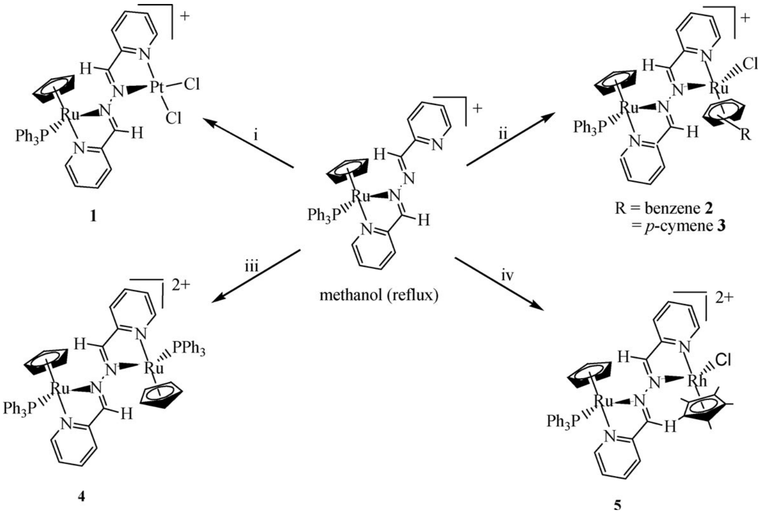
Complexes [(η^5-C_5H_5)Ru(PPh_3)(κ^2-paa)]PF_6 and [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4 were prepared following our previously published procedure.[8] Reaction of complex [(η^5-C_5H_5)Ru(PPh_3)(κ^2-paa)]PF_6 with [Pt($DMSO)_2Cl_2$], [{(η^6-arene)RuCl(μ-Cl)}$_2$], (η^6-arene = benzene, *p*-cymene), [(η^5-C_5H_5)RuCl($PPh_3)_2$] and [({(η^5-C_5Me_5)RhCl(μ-Cl)}$_2)_2$] in methanol under refluxing conditions afforded bimetallic complexes [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)$PtCl_2$]BF_4 (**1**), [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Ru(η^6-C_6H_6)Cl]($PF_6)_2$ (**2**), [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Ru(η^6-$C_{10}H_{14}$)Cl]($PF_6)_2$ (**3**), [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Ru(η^5-C_5H_5)(PPh_3)]($PF_6)_2$ (**4**) and [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Rh(η^5-C_5Me_5)Cl]($PF_6)_2$ (**5**). On the other hand, reactions of [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4 with the aforesaid precursors under analogous conditions afforded bimetallic complex [(η^5-C_5H_5)Ru(μ-paa)(κ^1-dppm)$PtCl_2$]BF_4 (**6**) and trimetallic complexes [Cl_2(η^6-C_6H_6)Ru(μ-dppm)(η^5-C_5H_5)Ru(μ-paa)Ru(η^6-C_6H_6)Cl]($BF_4)_2$ (**7**), [Cl_2(η^6-$C_{10}H_{14}$)Ru(μ-dppm)(η^5-C_5H_5)Ru(μ-paa)Ru(η^6-$C_{10}H_{14}$)Cl]($BF_4)_2$ (**8**), [(PPh_3)(η^5-C_5H_5)ClRu(μ-dppm)Ru(η^5-C_5H_5)(μ-paa)(η^5-C_5H_5)RuCl]($BF_4)_2$ (**9**) and [Cl_2(η^5-C_5Me_5)Rh(μ-dppm)(η^5-C_5Me_5)Ru(μ-paa)Rh(η^5-C_5Me_5)Cl]($PF_6)_2$ (**10**) in appreciably good yield. A simple Scheme showing the synthesis of the bi- and trimetallic complexes is depicted in Schemes 1 and 2, respectively.

Complexes **1**–**10** are air-stable solids and their solutions did not show any signs of decomposition after exposure to air for several days. The complexes may exist as diastereomers, though all efforts to separate the diastereomers were unsuccessful, however, it was supported by ill-resolved NMR spectroscopic data. In the respective spectra, signals representing minor diastereomers are hidden or not well resolved therefore, we are unable to make a precise interpretation of the different signals. Herein, we have taken into account only the major isomers.

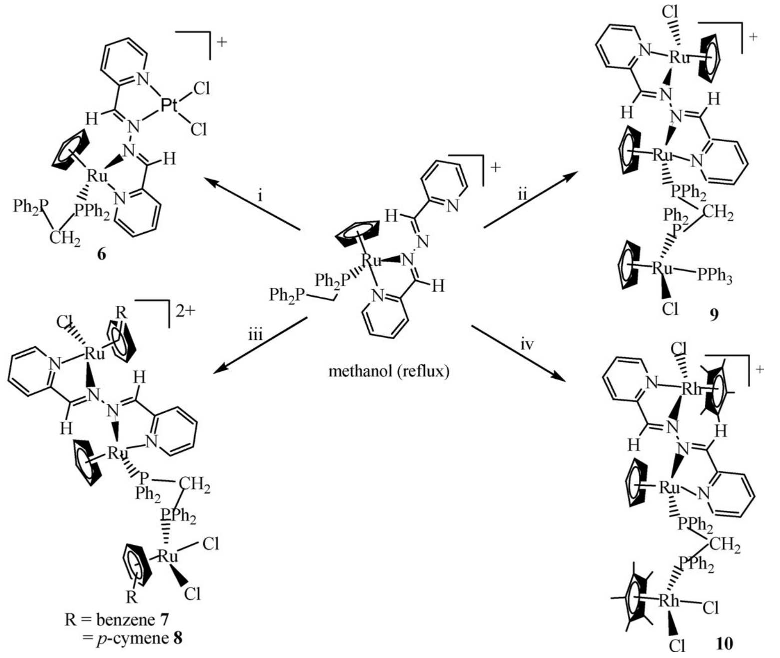
Complexes **1**–**10** have been fully characterized by elemental analyses, FAB-MS, IR, NMR (^1H and ^{31}P), electronic spectral and electrochemical studies. Analytical data of complexes are in good agreement with the proposed formulations. Information about composition of complexes was also obtained by FAB mass spectral studies. The resulting data along with their assignments are recorded in the Experimental Section. Representative FAB-MS spectra of bimetallic complex **6** and trimetallic complexes **7**, **8** and **10** are shown in Figures S1–S4. The position of various peaks and overall fragmentation patterns in the FAB mass spectra of complexes conformed well to their formulations.

IR spectra of the respective complexes exhibit characteristic bands associated with paa, η^5-C_5H_5, η^5-C_5Me_5, η^6-C_6H_6, η^6-$C_{10}H_{14}$ rings and counter anions. The $\nu_{C=N}$ band in the complexes is shifted towards lower wave numbers and appears at about 1610 cm^{-1} compared to that in the free ligand (1638 cm^{-1}). The band associated with the pyridyl ring vibrations appears at about 1032 cm^{-1}. A shift in the position of the bands corresponding to ν_{C-N}, the pyridyl ring and diazine moiety suggests coordination of paa to the metal ion through pyridyl and diazine nitrogen. Bands associated with counter anion BF_4^- and PF_6^- appear in the respective complexes at about 1118 and 842 cm^{-1}, respectively.

^1H NMR spectra of the complexes display resonances associated with paa, η^5-C_5H_5 and η^6-C_6H_6, η^6-$C_{10}H_{14}$ and η^5-C_5Me_5 ring protons as expected; data are summarized in the Experimental Section.[8,9a] The positions and integrated intensities of various resonances in the complexes agree well with their respective formulations. $^{31}P\{^1H\}$ NMR spectroscopic data of the complexes provide valuable information about bond relationships in these complexes. In the $^{31}P\{^1H\}$ NMR spectra of homo/hetero-bimetallic Ru/Ru and Ru/Rh complexes **1**–**5**, ^{31}P nuclei of coordinated PPh_3 resonate in the range δ = 47.85–49.54 ppm. The $^{31}P\{^1H\}$ NMR spectrum of complex **6** displays two distinct signals at δ = –6.35 and 43.09 ppm. The signal at δ = –6.35 ppm has been assigned to ^{31}P nuclei of pendant phosphorus, while the one at δ = 43.09 ppm corresponds to Ru-bound phosphorus



Scheme 1. Synthesis of homo/hetero bimetallic complexes **1**–**5**. (i) [Pt($DMSO)_2Cl_2$], (ii) [{(η^6-arene)$RuCl_2$}$_2$], (iii) [(η^5-C_5H_5)RuCl($PPh_3)_2$], (iv) [{(η^5-C_5Me_5)$RhCl_2$}$_2$].



Scheme 2. Synthesis of homo/hetero trimetallic complexes **6**–**10**. (i) $[Pt(DMSO)_2Cl_2]$, (ii) $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$, (iii) $[\{(\eta^6\text{-arene})RuCl_2\}_2]$, (iv) $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$.

($Ru–PPh_2–CH_2–PPh_2$). The presence of a resonance at δ = –6.35 ppm in the $^{31}P\{^1H\}$ NMR spectrum of complex **6** suggests bonding of dppm to the metal centre ruthenium through only one phosphorus in monodentate coordination mode (κ^1). This finding indicates linkage of paa in a bridging mode anchoring metal centres platinum and ruthenium and formation of a bimetallic instead of a trimetallic complex.[5,9]

$^{31}P\{^1H\}$ NMR spectra of **7**, **8** and **9** display different trends compared to Ru/Pt complex **6**. For example, complex **9** displays signals at δ = 48.01 and 24.96 ppm, in addition to the resonance at δ = 36.47 ppm associated with Ru-bound ^{31}P nuclei of PPh_3. These resonances can be assigned to ^{31}P nuclei of dppm. The absence of a signal associated with pendant ^{31}P nuclei of dppm in the high field side suggests that dppm is coordinated to the metal centre ruthenium through both the phosphorus atoms in κ^2 manner. This further supports the formation of a trimetallic complex. An analogous trend was observed for trimetallic Ru/Ru/Ru complexes **7** and **8**, wherein ^{31}P nuclei of the bridged dppm resonate at δ = 53.40, 24.11 and 50.32, 24.75 ppm, respectively. $^{31}P\{^1H\}$ NMR spectroscopic data strongly support the formation of trimetallic complexes involving interaction of both the phosphorus donor centres of dppm and uncoordinated bis-chelating site of paa with metal centres.

The electronic absorption spectra of complexes **1**–**10** (Table S1, Figure S5, S6) were recorded for acetonitrile solutions at room temperature. Low-spin d^6 ruthenium provides filled orbitals of proper symmetry to interact with the relatively low-lying π^* orbital of the ligand paa. This is expected to give rise to a band associated with a metal-to-ligand charge transfer (MLCT) transition ($t_2g \rightarrow \pi^*$) whose position varies with the nature of the metal ion and the ligand acting as the π acceptor.[10] All the compounds display intense bands in the UV/Vis range. The spectrum of the precursor complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\kappa^2\text{-paa})]PF_6$ and $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-dppm})(\kappa^2\text{-paa})]BF_4$ shows two high energy bands (292, 314 and 289, 317 nm, respectively[8]) and one low energy band (461 and 470 nm, respectively). The high energy bands correspond to intra-ligand $\pi \rightarrow \pi^*$ transitions. On the basis of its position and intensity the band in the low energy region has been assigned to MLCT transitions [$Ru^{II}d\pi \rightarrow \pi^*$ paa]. Introduction of one more metal centre Pt/Ru/Rh (**1**–**6**) or two Ru/Rh metal centres (**7**–**10**) in precursor complexes produces a significant red shift in the position of the low-energy MLCT band (Table S1). The red shift in the position of $Ru^{II}d\pi \rightarrow \pi^*$ paa charge transition may be attributed to stabilization of π^* orbitals of paa. In general, coordination of another metal centre at the remote coordination site stabilizes π^* orbitals of the bridging ligands leading to enhanced $\pi \rightarrow \pi^*$ overlap which, in turn leads to a decrease in the HOMO–LUMO gap. This results in a lower energy shift of the MLCT bands in the binuclear complexes.[11] Stabilization of the π^* orbitals of the ligand also leads to a red shift in the position of intra-ligand $\pi \rightarrow \pi^*$ transitions. The electronic spectroscopic data strongly support formation of bi-/trinuclear complexes and are consistent with other reports.[12]

Electrochemistry

Mixed-metal complexes of pyridyl azine ligands display a rich electrochemistry with reversible metal-based oxidations and ligand-based reductions. Cyclic voltammetry for homo/

hetero bimetallic complexes **3** and **5** and homo/hetero trimetallic complexes **8** and **10** was performed in acetonitrile solution at room temp. (scan rate 100 mV/s) and the resulting data is summarized in Table 1. The cyclic voltammogram of complexes **3** and **8** is depicted in the Supporting Information (Figure S7). In the anodic potential window (0 to +2 vs. SCE) the homo bi-/trimetallic complexes **3** (Ru/Ru) and **8** (Ru/Ru/Ru) exhibited irreversible peaks at 1.23 V and 1.18 V, respectively. This may be attributed to metal-based $Ru^{II/III}$ oxidations.[13] On the other hand, in the cathodic potential window (0 to –2 vs. SCE) **3** and **8** exhibited three ligand (paa) based reduction peaks (Figure S7 and S9). The presence of only one oxidation peak in the homo nuclear bi-/trimetallic complexes **3** and **8** may be due to oxidation of the metal centre ruthenium at almost the same potential. Although the arrangement of various groups about the metal centre in these complexes is different, the coordination geometry and overall electronic environment is very close therefore, these oxidize at the same potential. The mononuclear precursor complex $[(\eta^5\text{-}C_5H_5)\text{-}Ru(PPh_3)(\kappa^2\text{-paa})]BF_4$, displays only two ligand-based reversible reduction peaks[8] in its cyclic voltammogram. The presence of a third peak at –1.39 V and –1.25 V, respectively in **3** and **8** suggested coordination of the ligand paa to another metal centre. The hetero bi-/trimetallic complexes Ru/Rh **5** and Rh/Ru/Rh **10** exhibited two irreversible peaks at 1.24 V, 1.04 V and 1.18 V, 0.91 V, respectively, attributable to metal-based oxidations $Ru^{II/III}$ and $Rh^{III/IV}$. The presence of a second oxidation peak in **5** and **10** suggested the formation of hetero bi-/trimetallic systems. The splitting of the metal-centred oxidations at slightly less positive potential at 1.04 V and 0.91 V may be attributed to the presence of a second hetero metal atom, i.e. Rh.

Table 1. Electrochemical data for homo/hetero bi-/trimetallic complexes in acetonitrile solution.

Complexes	Oxidation		Reduction			
	$E_{1/2}$ I	$E_{1/2}$ II	$E_{1/2}$ I	$E_{1/2}$ II	$E_{1/2}$ III	$E_{1/2}$
Precursor 1[8]	0.987		–1.05	–1.66		
Precursor 2[8]	1.12		–1.09	–1.71		
3	1.23*		–0.48	–0.85	–1.39	
5	1.24*	1.04*	–0.49	–0.78	–0.99*	–1.35
8	1.18*		–0.52	–0.84	–1.25*	8
10	1.18*	0.91*	–0.75	–0.84	–1.21	10

Asterisks * indicate irreversible peaks

The molecular structure of complexes **3** and **5**, which crystallize in the *Pbcn* and $P\bar{1}$ space groups respectively, has been established crystallographically (Figure 1 and Figure 2, Table 2). Provided with four nitrogen donor atoms, paa generally acts as a bi- or tetradentate ligand. In general, it interacts with metal centres through both the bis-chelating N,N donor sites leading to formation of binuclear complexes. In homo binuclear complex **3** (Figure 1) and hetero binuclear complex **5** (Figure 2), metal centres Ru1, Ru2 and Ru1, Rh1, respectively are bridged by the ligand paa. The coordination geometry about metal centre Ru1 in complex **3** is completed by N1 (pyridyl ring) and N2 (azine moiety) from paa in κ^2 manner, phosphorus from triphenylphosphane and the Cp ring [C(1)–C(5)] in η^5-manner while, the geometry about Ru2 is completed by N4 (pyridyl ring) and N3 (azine moiety) from paa in κ^2 manner, the chloro group and *p*-cymene ring [C(39)–C(45)] coordinated in η^6-manner. The coordination geometry about Ru1 in complex **5** is analogous to that observed in complex **3** while, the geometry about Rh1 is completed by N4 (pyridyl ring) and N3 (azine moiety) from paa in κ^2 manner, the chloro group and Cp* ring [C19,C20,C22,C24,C26] coordinated in η^5-manner. In complex **3** Ru1–C average bond lengths are 2.197(4) Å [range 2.183(4)–2.215(4) Å] while, Ru2–C average bond lengths are 2.205(4) Å [range, 2.174(4)–2.252(4) Å]. In complex **5** average Ru1–C bond lengths are almost the same as in complex **3** [average 2.199(5) Å; range, 2.179(5)–2.221(5) Å] and the average Rh1–C distance is 2.162(5) Å [range, 2.152(5)–2.181(5) Å]. The M–C and M–N (M = Ru, Rh) bond lengths are consistent with the values reported in the literature.[14,15]

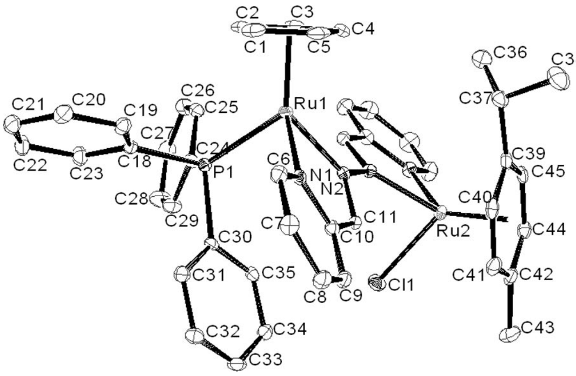


Figure 1. Molecular structure of the complex $[PPh_3(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}paa)Ru(\eta^6\text{-}C_{10}H_{14})Cl]^{2+}$.

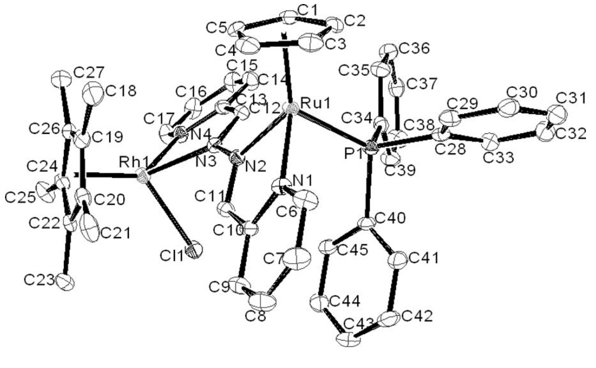


Figure 2. Molecular structure of the complex $[PPh_3(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}paa)Rh(\eta^5\text{-}C_{10}H_{15})Cl]^{2+}$.

The crystal structure of complexes **3** and **5** revealed the presence of extensive intermolecular C–H···X (X = F and π) interactions. Matrices of the intermolecular interactions in **3** and **5** are recorded in Table S3 (Supporting Information). It is well established that these types of interactions play an important role in construction of huge supra-

Table 2. Crystallographic data for the complexes **3** and **5**.

	3	**5**
Chemical formula	$C_{45}H_{44}ClF_{12}N_4P_3Ru_2$	$C_{45}H_{45}ClF_{12}N4O_{0.50}P_3RhRu$
Formula weight	1199.34	1210.19
Colour, habit	dark brown, block	dark brown, block
Crystal size [mm]	0.33 × 0.27 × 0.21	0.38 × 0.34 × 0.31
Space group	*Pbcn*	$P\bar{1}$
Crystal system	orthorhombic	triclinic
a [Å]	29.381(11)	13.126(5)
b [Å]	14.8956(10)	13.175(5)
c [Å]	21.4257(8)	15.898(5)
α [°]	90	72.337(5)
β [°]	90	89.568(5)
γ [°]	90	72.936(5)
V [Å^3]	9377(3)	2494.3(16)
Z	8	2
$D_{calcd.}$ [g cm^{-3}]	1.699	1.611
μ [mm^{-1}]	0.890	0.866
T [K]	150(2)	150(2)
Reflections	8241	8777
Parameters	607	618
R factor (for all)	0.0673	0.0605
R factor [$I > 2\sigma(I)$]	0.0351	0.0431
$wR2$	$wR2$ = 0.0750	0.1454
$wR2$ [$I > 2\sigma(I)$]	0.0646	0.1355
GOF	1.006	0.895

molecular architectures.[16] In complex **5**, two types of C–H···F (C8–H8···F3 2.466 Å and C16–H16···F3 2.597 Å) interactions are present, wherein the hydrogen atom of the coordinated pyridyl ring of one molecule is attached to F3 of the anion PF_6^- and the hydrogen of the pyridyl ring of another molecule is also attached to F3 of the same anion leading to a single layer. This layer is interlinked with another single layer generated in the same fashion through π···O111···F4 interactions. The oxygen atom O111 interacts with the C12–C13 π cloud (ca. 3.119 Å) of the chelate ring generated by N4–C12–C13–N3–Rh1. The O111 to centroid distance of the chelate ring is 3.57 Å. Further, O111 is interlinked with another chain by O111···F4 interactions (2.848 Å). The water molecule O111 in the crystal lattice is acting as a linker between two layers leading to a double-layered chain-like network (see part a of Figure 3). Weak interaction studies in complex **3** shows three types of C–H···π interactions leading to a single helical motif (Figure 3, b).

Through this work we have shown that complexes [(η^5-C_5H_5)Ru(PPh_3)(κ^2-paa)]PF_6 and [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4, containing bis-chelating ligand paa coordinated in κ^2 manner and κ^1-bonded dppm act as a potential synthon in the construction of homo/hetero, bi-/trimetallic complexes. Details of their spectroscopic and electrochemical properties have been investigated and molecular structures of **3** and **5** have been determined crystallographically. At this stage it has not been possible for us to verify the structure of the trimetallic complexes however, FAB mass and other spectroscopic data strongly support the formation of trimetallic complexes.

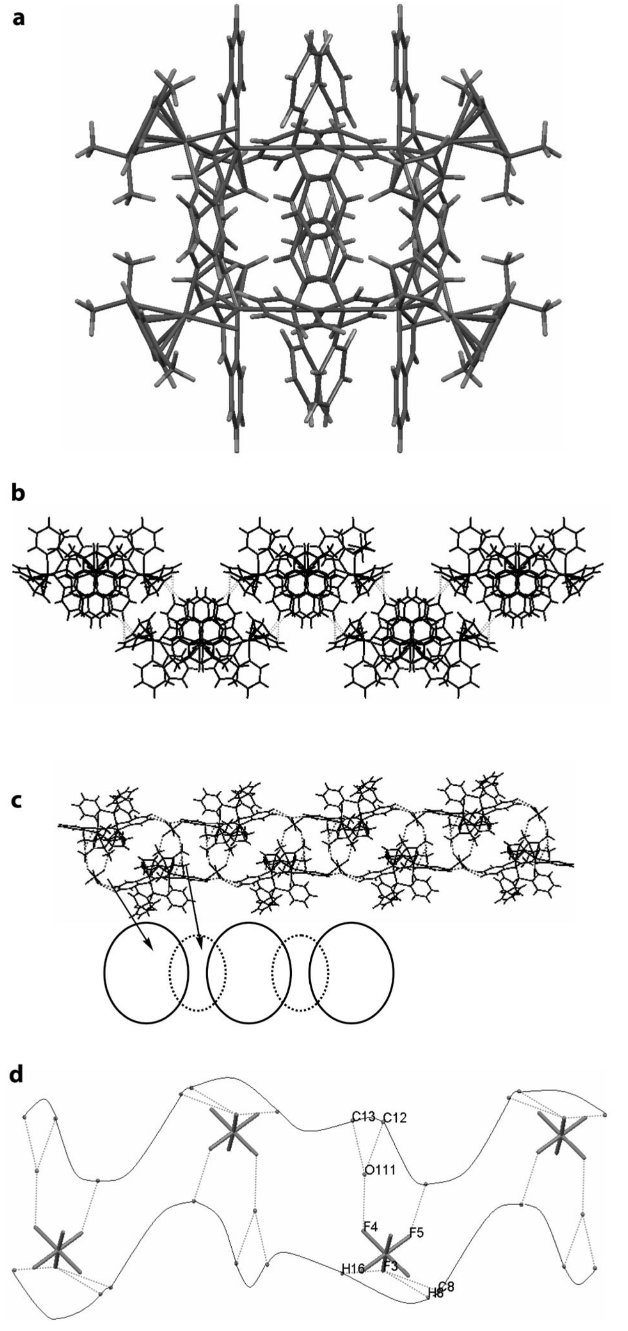


Figure 3. (a) Top view of layer structure formed through three types of C–H···π interactions in **3**; (b) C–H···π weak interaction leading to a helical motif in **3**; (c) straight chain arising from different types of C–H···F and C–H···O···F interactions in **5**; (d) view of the C12–C13···O111···F4 interaction acting as a linker between the two layers in **5**.

Experimental Section

General Procedures: Analytical or chemically pure grade reagents were used throughout. All the synthetic manipulations were performed under nitrogen atmosphere. Solvents were dried and distilled by standard procedures before use.[17] Hydrated ruthenium(III) chloride, 1,2-bis(diphenylphosphanyl)methane, ammonium hexafluorophosphate and ammonium tetrafluoroborate (all Aldrich) were used as received. The ligand pyridine-2-carbaldehyde azine (paa), precursor complexes [(η^5-C_5H_5)RuCl(PPh_3)$_2$],[18] [(η^5-C_5H_5)RuCl(dppm)],[18] [{(η^6-C_6H_6)RuCl(μ-Cl)}$_2$],[19] [(η^5-C_5H_5)Ru(PPh_3)$_2$(κ^2-paa)]PF_6 and [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4[8] were prepared and purified following literature procedures. Microanalyses on the complexes were performed by the micro-analytical division of SAIF, Central Drug Research Institute, Lucknow. Infrared and electronic spectra were recorded with a Perkin–Elmer 577 and Shimadzu UV-1601 spectrophotometer, respectively. Electrochemical experiments were carried out in an airtight single-compartment cell using platinum as the counter electrode, a glassy carbon electrode as the working electrode and a Ag/Ag$^+$ reference electrode on a CHI 620c electrochemical analyzer. ^{1}H and ^{31}P NMR spectra were recorded with a JEOL AL 300 FT-NMR machine at an operating frequency of 300 MHz and 121.5 MHz, respectively. Tetramethylsilane and phosphorus trichloride were used as the internal reference for ^{1}H and ^{31}P NMR spectroscopic studies, respectively. FAB mass spectra were acquired with a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and spectra were recorded at room temperature with *m*-nitrobenzyl alcohol as the matrix.

Synthesis of [(η^5-C_5H_5)Ru(μ-paa)(PPh_3)$PtCl_2$]PF_6 (1): To a suspension of [(η^5-C_5H_5)Ru(PPh_3)(κ^2-paa)]PF_6 (0.783 g, 1.0 mmol) in methanol (25 mL), Pt(DMSO)$_2$Cl$_2$ (0.422 g, 1.0 mmol) was added. The contents of the flask were heated at reflux for 8 h, whereupon most of the solid dissolved and gave a black brown solution. After cooling to room temperature the mixture was filtered to remove any solid residue and the filtrate was concentrated under reduced pressure to one fourth of its volume. A black microcrystalline product appeared which was separated by filtration, washed with methanol, diethyl ether and dried under vacuum resulting in 70% (0.735 g) yield. $C_{35}H_{30}Cl_2F_6N_4PPtRu$ (1018.67): calcd. C 40.04, H 2.86, N 5.34; found C 40.31, H 2.74, N 5.21. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.10 (s, 2 H, Py-CHN$_2$CH-Py), 8.82 (m, 2 H, Py-H), 7.60 (m, 6 H, Py-H), 6.90–7.32 (br. m, 20 H of dppm), 4.94 (s, 5 H, Cp-H) ppm. ^{31}P NMR ($CDCl_3$): δ = 49.54 (s) ppm. MS (FAB): *m/z* calcd. (found), 904 (904) [M – PF_6]$^+$, 642 (643) [M – PF_6 – PPh_3]$^+$, 607 (607) [M – PF_6 – PPh_3 – Cl]$^+$.

Synthesis of [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Ru(η^6-C_6H_6)Cl](PF_6)$_2$ (2): To a suspension of [(η^5-C_5H_5)Ru(PPh_3)(κ^2-paa)]PF_6 (0.783 g, 1.0 mmol) in methanol (25 mL), [{(η^6-C_6H_6)Ru(μ-Cl)Cl}$_2$] (0.250 g, 0.5 mmol) was added and refluxed for 8 h. The reaction mixture was cooled to room temperature and filtered. A saturated methanolic solution of NH_4PF_6 was added to the filtrate and left for slow crystallization. A blue-black crystalline product was obtained. This was separated by filtration, washed with diethyl ether and dried under vacuum resulting in 72% (0.823 g) yield. $C_{41}H_{36}ClF_{12}N_4P_3Ru_2$ (1143.26): calcd. C 43.05, H 3.15, N 4.89; found C 43.26, H 3.28, N 4.63. ^{1}H NMR (DMSO, 300 MHz): δ = 9.66 (s, 2 H, Py-CHN$_2$CH-Py), 9.54 (m, 2 H, Py-H), 8.29 (d, $J_{H,H}$ = 6.6 Hz, 1 H), 8.10 (d, $J_{H,H}$ = 6.6 Hz,1 H), 7.94 (d, $J_{H,H}$ = 6.3 Hz, 1 H), 7.82 (t, $J_{H,H}$ = 8.1 Hz, 2 H), 7.59 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 6.94–7.46 (br. m, 15 H of PPh_3), 6.30 (s, 6 H, Ph-H), 5.43 (s, 5 H, Cp-H) ppm. ^{31}P NMR (DMSO): δ = 48.72 (s) ppm. MS (FAB): *m/z* calcd. (found), 998 (999) [M – PF_6]$^+$, 853 (853) [M – 2PF_6]$^+$, 638 (639) [M – 2PF_6 – RuC_6H_6Cl]$^+$, 376 (377) [M – 2PF_6 – RuC_6H_6Cl – PPh_3]$^+$.

Synthesis of [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Ru(η^6-$C_{10}H_{14}$)Cl](PF_6)$_2$ (3): Complex **3** was prepared by the reaction of [(η^5-C_5H_5)Ru(PPh_3)(κ^2-paa)]PF_6 with [{(η^6-$C_{10}H_{14}$)Ru(μ-Cl)Cl}$_2$] (0.306 g, 0.5 mmol) in methanol following the procedure adopted for **2**. It separated as a brown solid in 75% (0.900 g) yield. $C_{45}H_{46}ClF_{12}N_4P_3Ru_2$ (1201.38): calcd. C 45.04, H 3.67, N 4.67; found C 45.04, H 3.53, N 4.79. ^{1}H NMR (DMSO, 300 MHz): δ = 9.71 (d, $J_{H,H}$ = 4.8 Hz, 1 H), 9.56 (s, 2 H, Py-CHN$_2$CH-Py), 9.32 (d, $J_{H,H}$ = 4.7 Hz, 1 H), 8.32 (t, $J_{H,H}$ = 4.8 Hz, 1 H), 7.95 (m, 3 H, Py-H), 7.66 (d, $J_{H,H}$ = 7.8 Hz, 1 H), 7.45 (d, $J_{H,H}$ = 7.2 Hz, 1 H), 7.38–6.93 (br. m, 15 H of PPh_3), 6.41 (d, $J_{H,H}$ = 6.0 Hz, 1 H), 6.34 (d, $J_{H,H}$ = 6.6 Hz, 1 H), 6.11 (m, 2 H, Ph-H), 5.35 (s, 5 H, Cp-H), 2.74 (m, 1 H, *i*Pr), 2.24 (s, 3 H, CH_3), 1.11 (dd, 6 H, *i*Pr) ppm. ^{31}P NMR (DMSO): δ = 47.85 (s) ppm.

Synthesis of [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Ru(η^5-C_5H_5)PPh_3](PF_6)$_2$ (4): Complex **4** was prepared by the reaction of [(η^5-C_5H_5)Ru(PPh_3)(κ^2-paa)]PF_6 with [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$] (0.726 g, 1.0 mmol) in methanol following the procedure for **2**. It separated as a black-brown solid in 70% (0.869 g) yield. $C_{58}H_{50}F_{12}N_4P_4Ru_2$ (1357.08): calcd. C 51.33, H 3.69, N 4.13; found C 51.45, H 3.85, N 4.35. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.51 (m, 2 H, Py-H), 9.04 (s, 2 H, Py-CHN$_2$CH-Py), 8.83 (m, 2 H), 8.48 (m, 2 H, Py-H), 7.98 (t, $J_{H,H}$ = 8.1 Hz, 1 H), 7.83 (t, $J_{H,H}$ = 7.8 Hz, 1 H), 7.08–7.36 (br. m, 20 H of PPh_3), 5.29 (s, 10 H, Cp-H) ppm.

Synthesis of [(PPh_3)(η^5-C_5H_5)Ru(μ-paa)Rh(η^5-C_5Me_5)Cl](PF_6)$_2$ (5): Complex **5** was prepared by the reaction of [(η^5-C_5H_5) Ru(PPh_3)(κ^2-paa)]PF_6 with [{(η^6-C_5Me_5)Rh(μ-Cl)Cl}$_2$] (0.309 g, 0.5 mmol) in methanol following the procedure employed for **2** and isolated in 75% (0.901 g) yield. $C_{45}H_{45}ClF_{12}N_4P_3RhRu$ (1202.21): calcd. C 44.93, H 3.74, N 4.67; found C 44.74, H 3.66, N 4.79. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.87 (d, $J_{H,H}$ = 6.0 Hz, 1 H), 9.73 (s, 1 H, NCH-Py), 9.49 (s, 1 H, NCH-Py), 9.25 (d, $J_{H,H}$ = 5.7 Hz, 1 H), 8.39 (t, $J_{H,H}$ = 7.8 Hz, 1 H), 8.10 (t, $J_{H,H}$ = 6.6 Hz, 1 H), 7.91 (m, 2 H, Py-H), 7.62 (d, $J_{H,H}$ = 8.1 Hz, 1 H), 7.51 (d, $J_{H,H}$ = 5.7 Hz, 1 H), 7.13–7.46 (br. m, 15 H of PPh_3), 5.50 (s, 5 H, Cp), 1.79 (s, 15 H, CH_3-Cp*) ppm. ^{31}P NMR ($CDCl_3$): δ = 48.15 (s) ppm.

Synthesis of [(κ^1-dppm)(η^5-C_5H_5)Ru(μ-paa)$PtCl_2$]BF_4 (6): This complex was prepared by the reaction of [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4 with Pt(DMSO)$_2$Cl$_2$ (0.422 g, 1.0 mmol) in methanol following the procedure adopted for **1** and was obtained in 75% (0.835 g) yield. $C_{42}H_{37}BCl_2F_4N_4P_2PtRu$ (1113.59): calcd. C 45.68, H 3.52, N 5.03; found C 45.79, H 3.64, N 5.15. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.28 (d, $J_{H,H}$ = 4.8 Hz, 1 H), 8.97 (s, 2 H, Py-CHN$_2$CH-Py), 8.56 (d, $J_{H,H}$ = 6.0 Hz, 2 H), 8.32 (t, $J_{H,H}$ = 3.0 Hz, 2 H), 7.90 (t, $J_{H,H}$ = 6.0 Hz, 1 H), 7.68 (t, $J_{H,H}$ = 6.0 Hz, 2 H), 6.75–7.52 (m, 20 H of d), 4.94 (s, 5 H, Cp-H), 3.35 (m, 2 H, P-CH_2-P) ppm. ^{31}P NMR ($CDCl_3$): δ = 43.09 (d), –6.43 (d) ppm. MS (FAB): *m/z* calcd. (found), 1027 (1026) [M]$^+$, 990 (990) [M – Cl]$^+$, 570 (569) [M – Cl, dppm]$^+$.

Synthesis of [(η^6-C_6H_6)$RuCl_2$(μ-dppm)(η^5-C_5H_5)Ru(μ-paa)(η^6-C_6H_6)RuCl](BF_4)$_2$ (7): This complex was prepared by the reaction of [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4 with [{(η^6-C_6H_6)Ru(μ-Cl)Cl}$_2$] (0.500 g, 1.0 mmol) in methanol according to the procedure adopted for **1**. It separated in 75% (1.119 g) yield. $B_2C_{54}Cl_3F_8H_{49}N_4P_2Ru_3$ (1399.13): calcd. C 45.82, H 3.79, N 3.90; found C 45.87, H 3.81, N 3.93. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.34 (d, $J_{H,H}$ = 4.5 Hz, 1 H), 9.14 (s, 2 H, Py-CHN$_2$CH-Py), 8.45 (d, $J_{H,H}$ = 3.0 Hz, 2 H), 8.25 (t, $J_{H,H}$ = 3.0 Hz, 2 H), 7.89 (t, $J_{H,H}$ = 5.4 Hz, 2 H), 7.70 (t, $J_{H,H}$ = 5.4 Hz, 1 H), 7.31–7.55 (m, 20 H of PPh_3), 6.85 [s, 12 H, (C_6H_6-Ru)$_2$], 4.95 (s, 5 H, Cp-Ru), 3.56 (m, 2 H, P-CH_2-P) ppm. ^{31}P NMR ($CDCl_3$): δ = 53.40 (d), 24.11 (d) ppm. MS (FAB): *m/z* calcd. (found), 1312 (1310) [M]$^+$, 1225 (1226) [M – BF_4]$^+$, 1011 (1013), [M – (η^6-C_6H_6)RuCl]$^+$, 550 (551) [M – (η^6-C_6H_6)$RuCl_2$, paa]$^+$.

Synthesis of [(η^6-$C_{10}H_{14}$)$RuCl_2$(μ-dppm)(η^5-C_5H_5)Ru(μ-paa)(η^6-$C_{10}H_{14}$)RuCl](BF_4)$_2$ (8): Complex **8** was prepared by the reaction of [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4 with [{(η^6-$C_{10}H_{14}$)Ru(μ-Cl)Cl}$_2$] (0.612 g, 1.0 mmol) in methanol according to the procedure employed for **1**. The yield of the complex was 65% (0.982 g). $C_{62}H_{65}B_2Cl_3F_8N_4P_2Ru_3$ (1511.35): calcd. C 49.02, H 4.30, N 3.70; found C 49.31, H 4.23, N 3.93. ^{1}H NMR (DMSO, 300 MHz): δ = 9.55 (d, $J_{H,H}$ = 5.78 Hz, 1 H), 9.49 (s, 2 H, Py-CHN_2CH-Py), 9.18 (d, $J_{H,H}$ = 6.0 Hz, 1 H), 8.86 (d, $J_{H,H}$ = 2.7 Hz, 1 H), 8.53 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 8.34 (t, $J_{H,H}$ = 7.5 Hz, 1 H), 8.03 (d, $J_{H,H}$ = 5.6 Hz, 1 H), 7.97 (t, $J_{H,H}$ = 6.3 Hz, 1 H), 7.86 (t, $J_{H,H}$ = 7.2 Hz, 1 H), 7.20–7.57 (br. m, 20 H of PPh_2), 7.01 (d, $J_{H,H}$ = 8.1 Hz, 2 H), 6.80 (d, $J_{H,H}$ = 8.1 Hz, 2 H), 6.59 (d, $J_{H,H}$ = 10.8 Hz, 2 H), 6.31 (d, $J_{H,H}$ = 6.3 Hz, 2 H), 5.26 (s, 5 H, Cp-H), 2.26 (m, 2 H, $2CH_3CHCH_3$), 1.68 (s, 6 H, $2CH_3$), 1.25 (m, 2 H), 1.12 (d, $J_{H,H}$ = 6.6 Hz, 3 H), 1.06 (d, $J_{H,H}$ = 6.6 Hz, 3 H), 0.85 (d, $J_{H,H}$ = 6.9 Hz, 3 H), 0.62 (d, $J_{H,H}$ = 6.9 Hz, 3 H) ppm. ^{31}P NMR (DMSO): δ = 50.32 (d), 24.75 (d) ppm. MS (FAB): *m/z* calcd. (found), 1424 (1426) $[M - BF_4]^+$, 1337 (1337) $[M - 2BF_4]^+$, 1031 (1032) [M – $2BF_4$ – {Ru(*p*-cymene)Cl_2}]$^+$.

Synthesis of [PPh_3(η^5-C_5H_5)ClRu(μ-dppm)Ru(η^5-C_5H_5)(μ-paa)(η^5-C_5H_5)RuCl](BF_4) (9): Complex **9** was prepared by the reaction of [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4 with [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$] (1.838 g, 2.0 mmol) in methanol following the procedure employed for **1** and it separated in 73% (1.103 g) yield. $C_{70}H_{62}BCl_2F_4N_4P_3Ru_3$ (1513.13): calcd. C 56.28, H 4.10, N 3.98; found C 56.30, H 4.07, N 4.02. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.64 (d, $J_{H,H}$ = 5.4 Hz, 1 H), 9.16 (s, 2 H, Py-CHN_2CH-Py), 8.77 (d, $J_{H,H}$ = 4.8 Hz, 2 H), 8.05 (t, $J_{H,H}$ = 6.0 Hz, 2 H), 7.86 (t, $J_{H,H}$ = 6.9 Hz, 1 H), 7.65 (t, $J_{H,H}$ = 6.9 Hz, 2 H), 7.19–7.55 (m, 35 H), 4.96 (s, 10 H), 4.75 (s, 5 H) 3.50 (m, 2 H) ppm. ^{31}P NMR ($CDCl_3$): δ = 48.01 (d), 36.47, 24.96 ppm. MS (FAB): *m/z* calcd. (found), 1425 (1425) $[M]^+$, 1389 (1388), 10 $[M - Cl]^+$, 1353 (1353), 5 $[M - 2Cl]^+$, 1090 (1089), 10 $[M - 2Cl - PPh_3]^+$, 925 (924), 20 [M – 2Cl – PPh_3 – (η^5-C_5H_5)]$^+$, 760 (761), 10 [M – 2Cl – PPh_3 – (η^5-C_5H_5)-(Ru–η^5-C_5H_5)]$^+$.

Synthesis of [(η^5-C_5Me_5)RhCl_2(μ-dppm)(η^5-C_5H_5)Ru(μ-paa)(η^5-C_5Me_5)RhCl_2](PF_6)$_2$ (10): Complex **10** was prepared by the reaction of [(η^5-C_5H_5)Ru(κ^1-dppm)(κ^2-paa)]BF_4 with [{(η^5-C_5Me_5)-Rh(μ-Cl)Cl}$_2$] (0.618 g, 1.0 mmol) in methanol following the procedure adopted for **1**. The yield of this complex was 71% (1.056 g). $C_{62}H_{67}Cl_3F_{12}N_4P_4Rh_2Ru$ (1633.36): calcd. C 45.56, H 3.49, N 3.43; found C 45.71, H 3.57, N 3.69. ^{1}H NMR (DMSO, 300 MHz): δ = 9.02 (s, 2 H, Py-CHN_2CH-Py), 8.84 (m, 2 H, Py-H), 8.73 (d, $J_{H,H}$ = 6.0 Hz, 1 H), 8.20 (d, $J_{H,H}$ = 7.8 Hz, 1 H), 8.07 (t, $J_{H,H}$ = 6.9 Hz, 1 H), 7.98 (d, $J_{H,H}$ = 7.5 Hz, 1 H), 7.89 (t, $J_{H,H}$ = 7.8 Hz, 1 H), 7.67 (t, $J_{H,H}$ = 6.8 Hz, 1 H), 7.10–7.39 (m, 20 H of d), 4.97 (s, 5 H, Cp-H), 1.70 (s, 30 H, Cp*-H) ppm. ^{31}P NMR (DMSO): δ = 51.16 (d), 29.20 (d) ppm. MS (FAB): *m/z* calcd. (found), 1488 (1489) $[M - PF_6]^+$, 1343 (1342) $[M - 2PF_6]^+$, 1034 (1035) [M – $2PF_6$ – RhCp*Cl_2]$^+$.

Crystallographic Data: Crystals suitable for single-crystal X-ray analyses for the complexes **3** and **5** were grown from a mixture of acetone and ethanol at room temperature. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected with an Enraf–Nonius MACH3 diffractometer using graphite-monochromated Mo-K_α radiation. The crystal orientation, cell refinement and intensity measurements were made using the programme CAD-4 PC. The structure was solved by direct methods and refined using SHELX-97.[20a] The non-hydrogen atoms were refined with anisotropic thermal parameters.[20b] All the hydrogen atoms were geometrically fixed and refined using a riding model.

CCDC-668678 (for **3**) and -668679 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see also the footnote on the first page of this article): FAB-mass spectra of **6**, **7**, **8** and **10**, UV/Vis spectroscopic data for **1**–**10** and selected bond length and bond angles and matrices of intermolecular interactions for **3** and **5**.

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