Synthesis and reactivity of homo-bimetallic Rh and Ir complexes containing a N,O-donor Schiff base

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ABSTRACT

Binuclear complexes [{(η^5-C$_5$Me$_5$)RhCl}$_2$(μ-bsh)] (**1**) and [{(η^5-C$_5$Me$_5$)IrCl}$_2$(μ-bsh)] (**2**) containing *N,N'*-bis(salicylidine)hydrazine (H$_2$bsh) are reported. The complexes **1** and **2** reacted with EPh$_3$ (E = P, As) to afford cationic complexes [(η^5-C$_5$Me$_5$)Rh(PPh$_3$)(κ^2-Hbsh)]PF$_6$ (**3**), [(η^5-C$_5$Me$_5$)Rh(AsPh$_3$)(κ^2-Hbsh)]PF$_6$ (**4**), [(η^5-C$_5$Me$_5$)Ir(PPh$_3$)(κ^2-Hbsh)]PF$_6$ (**5**), and [(η^5-C$_5$Me$_5$)Ir(AsPh$_3$)(κ^2-Hbsh)]PF$_6$ (**6**) which were isolated as their hexafluorophosphate salts. Representative complexes **3** and **5** have been used as a metallo-ligand in the synthesis of binuclear complexes [(η^5-C$_5$Me$_5$)RhCl(μ-bsh)Ru(η^6-C$_{10}$H$_{14}$)Cl]PF$_6$ (**7**) and [(η^5-C$_5$Me$_5$)IrCl(μ-bsh)Ru(η^6-C$_{10}$H$_{14}$)Cl]PF$_6$ (**8**). The complexes under study have been fully characterized by analytical and spectral (FAB/ESI-MS, IR, NMR, electronic and emission) studies. Molecular structures of **1**, **2**, **3** and **5** have been determined crystallographically. Structural studies on **1** and **2** revealed the presence of extensive inter- and intra-molecular C–H⋯O and C–H⋯π weak bonding interactions. The complexes **1**, **2**, **3** and **5** moderately emit upon excitation at their respective MLCT bands.

1. Introduction

The chloro-bridged dimeric complexes [{(η^5-C$_5$Me$_5$)M(μ-Cl)Cl}$_2$] (M = Rh or Ir) have attracted attention of many research groups as these are indispensable organometallic precursors [1,2]. These undergo chloro-bridge cleavage reactions leading to the formation of a series of interesting neutral and cationic mononuclear half sandwich complexes of the type (C$_5$Me$_5$)ML$_n$X [3]. The half sandwich complexes based on Rh and Ir have proved to be very important because of their involvement in a number of stoichiometric and catalytic reactions including activation of carbon-hydrogen bonds and alkene oligomerisation and polymerisation [4–9]. Reactions of the chloro-bridged rhodium and iridium complexes [{(η^5-C$_5$Me$_5$)MCl(μ-Cl)}$_2$] [M = Rh, Ir] have been studied extensively with a variety of Lewis bases, *N,N'* and N,O-donor Schiff bases and *N*-heterocyclic ligands [10–17]. Despite extensive studies on reactivity of the complexes [{(η^5-C$_5$Me$_5$)MCl(μ-Cl)}$_2$] [M = Rh, Ir] with a variety of ligands, their reactions with N$_2$O$_2$ donor Schiff base ligands like, *N,N'*-bis(salicylidine)hydrazine (H$_2$bsh), *N,N'*-bis(salicylidine)-*p*-phenylenediamine (H$_2$bsp) and *N,N'*-bis(salicylidine)-*p*-biphenylenediamine (H$_2$bsb) have seldom been investigated [18].

N,N'-bis(salicylidine)hydrazine (H$_2$bsh) derived from the reaction of salicylaldehyde with hydrazine possesses four donor sites in the form of phenalato oxygen and imine nitrogen and can act as a mono-, bi-, tri- or tetradentate ligand. Generally, it interacts with metal ions as a tetradentate ligand through both the bis-chelating N,O-donor sites in κ^2:κ^2-mode after dissociation of the phenolic protons. In some cases, H$_2$bsh interacts with metal ions through only one of the bis-chelating donor sites in a κ^2-mode and acts as a bidentate ligand (Scheme 1) [19,20]. It also interacts with the metal ions in an unusual κ^2:κ^1-coordination mode and acts as a tridentate ligand. Recently we have reported arene ruthenium(II) complexes in which two ruthenium centres are bridged by two bsh^{2-} groups in an unusual κ^2:κ^1-mode [18].

Because of our interests in this area we devoted our efforts towards reactivity of the chloro-bridged dimeric rhodium and iridium complexes [{(η^5-C$_5$Me$_5$)MCl(μ-Cl)}$_2$] [M = Rh, Ir] with H$_2$bsh. In this paper, we report reproducible syntheses, spectral properties and reactivity of the homo-nuclear bimetallic complexes [{(η^5-C$_5$Me$_5$)MCl}$_2$(κ^2-bsh)] (M = Rh **1**, Ir **2**) with EPh$_3$ and crystal structures of [{(η^5-C$_5$Me$_5$)RhCl}$_2$(μ-bsh)] **1**, [{(η^5-C$_5$Me$_5$)IrCl}$_2$(μ-bsh)] **2**, [(η^5-C$_5$Me$_5$)Rh(PPh$_3$)(κ^2-Hbsh)]PF$_6$ **3** and [(η^5-C$_5$Me$_5$)Ir(PPh$_3$)(κ^2-Hbsh)]PF$_6$ **5**. Also we describe herein the results of our preliminary studies on application of representative complexes **3** and **5** as metallo-ligand in the synthesis of hetero-bimetallic complexes **7** and **8**.

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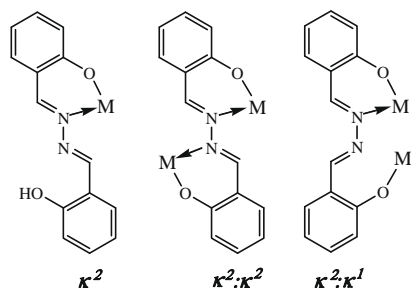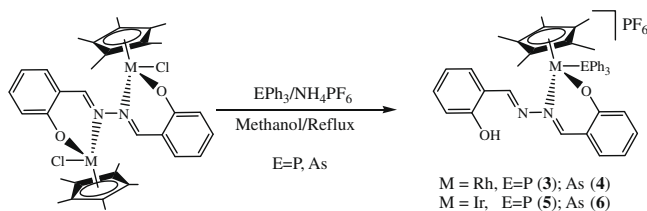
Scheme 1.

2. Results and discussion

Reactions of the chloro-bridged dimeric complexes [{(η^5-C$_5$Me$_5$)MCl(μ-Cl}$_2$] (M = Rh, Ir) with potassium derivative of H$_2$bsh (obtained from the reaction of H$_2$bsh with KOH in MeOH) under stirring conditions at room temperature afforded neutral binuclear complexes **1** and **2**, respectively (Scheme 2). Synthesis and spectral characterization of the complex **1** have already been reported by us [18]. Attempts were made to prepare hetero-bimetallic complexes containing both the Ru and Rh centres from the reactions of [{(η^6-arene)RuCl(μ-Cl}$_2$] (arene = *p*-cymene or benzene) and [{(η^5-C$_5$Me$_5$)RhCl(μ-Cl}$_2$] with potassium derivative of H$_2$bsh in methanol under analogous conditions. Surprisingly such a reaction yielded complex **1** as the major product with some unidentified side products. The formation of **1** as major product over the homo-bimetallic ruthenium complex [{(η^6-arene)-Ru}$_2$(κ^2-bsh)] or hetero-bimetallic complex containing both the Ru and Rh [{(η^6-arene)Ru}(κ^2-bsh){(η^5-C$_5$Me$_5$)RhCl}] may be attributed to higher stability of the homo-bimetallic rhodium complex **1**.

Complexes **1** and **2** upon treatment with EPh$_3$ (E = P, As) in methanol in presence of NH$_4$PF$_6$ under refluxing conditions afforded monometallic complexes **3–6** in reasonably good yields (Scheme 3). Further, reactions of one equivalent of **1** or **2** with two equivalents of EPh$_3$ could not give bsh^{2-} bridged bimetallic complexes [{(η^5-C$_5$Me$_5$)M(EPh$_3$)}$_2$(μ-bsh)](PF$_6$)$_2$. Rather, it led in the cleavage of bsh^{2-} bridged binuclear complexes to afford cationic monometallic complexes. The formation of monometallic complexes may be attributed to the steric hindrance resulting from the presence of two bulky EPh$_3$ groups.
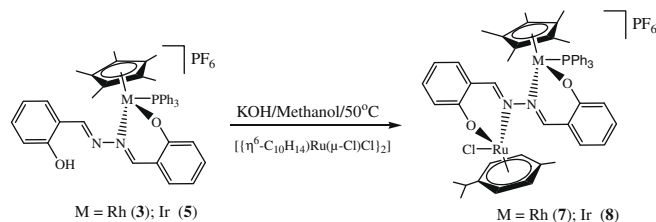
The presence of uncoordinated bis-chelating N,O-donor sites in **3–6** offers an unique opportunity for these molecules to behave as
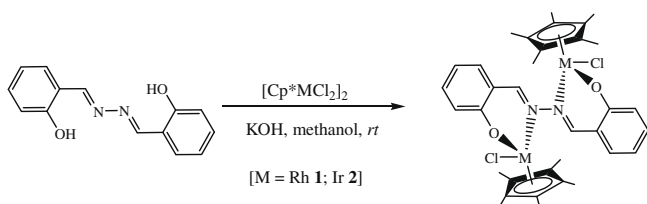
Scheme 2.

Scheme 3.

Scheme 4.

synthon in the development of hetero-bimetallic systems. To explore the possibility of their use as synthon for the construction of homo/hetero-bimetallic complexes, **3** and **5** were treated with chloro-bridged dimeric arene ruthenium complex [{(η^6-C$_{10}$H$_{14}$)Ru(μ-Cl)Cl}$_2$] in methanol. It led in the formation of binuclear complexes **7** and **8**, respectively (Scheme 4).

The complexes **1–8** gave satisfactory analyses for C, H and N. The formations of **1**, **2**, **7** and **8** have also been supported by mass spectral studies. FAB mass spectra of **1** and **2** exhibited peaks at *m/z* 749 (750) and 928 (928), respectively, corresponding to [{(η^5-C$_5$Me$_5$)MCl}(μ-bsh)(η^5-C$_5$Me$_5$)M}] (M = Rh; Ir) moieties, resulting from the loss of one chloro group from the molecular units. The presence of peaks at *m/z* 477 (476) and 565 (566), respectively in the FAB mass spectra of **1** and **2**, corresponding to the monometallic moieties [{(η^5-C$_5$Me$_5$)MCl}(κ^2-bsh)] (M = Rh; Ir) further supported formation of the complexes. The presence of various peaks in the ESI-MS spectra of **7** and **8** corroborated well to the formulation of these complexes (Figs. S1 and S2).

IR spectra of **1** and **2** displayed shift in the position of bands corresponding to $\nu_{C=N}$ and phenolic C–O by ~17 and ~67 cm^{-1}, respectively as compared to that in the uncoordinated H$_2$bsh (1621 and 1273 cm^{-1}) [18,19]. It suggested coordination of the ligand H$_2$bsh through imine nitrogen and phenolic oxygen after deprotonation. The band associated with N–N stretching vibration appeared at 1020 cm^{-1}. Coordination of H$_2$bsh to the metal centre in κ^2-mode and formation of monometallic complexes were also supported by IR spectra of the respective complexes. IR spectra of the monometallic complexes exhibited two distinct bands associated with $\nu_{C=N}$ at ~1596 and ~1465 cm^{-1}, respectively as compared to that in the respective precursor complexes **1** and **2**. The band at ~1596 cm^{-1} may be attributed to the pendent C=N group, while the one at ~1465 cm^{-1} to the coordinated C=N. Similarly, the bands at ~1190 and ~1150 cm^{-1} may be assigned to the pendent and coordinated phenolic C–O groups, respectively. The presence of characteristic vibrations associated with ν_{P-F} (at ~842 cm^{-1}) suggested cationic nature of the complexes **3–8** [21].

^{1}H NMR spectral data of the complex **1** has already been reported [18] and data for **2–8** is recorded in Section 3. In the ^{1}H NMR spectrum of **2** protons of the ligand (bsh^{2-}) resonated at δ 9.69, 7.39 (d, *J* = 7.8 Hz), 7.31–7.24 (m), 7.03 (d, *J* = 8.4 Hz) and 6.61 (t, *J* = 7.2 Hz) ppm. The singlet at δ 9.69 ppm has been assigned to the protons associated with [–C(H)=N–], while the resonances at δ 7.39 (d, *J* = 7.8 Hz), 7.31–7.24 (m), 7.03 (d, *J* = 8.4 Hz) and 6.61 (t, *J* = 7.2 Hz) ppm to aromatic protons of the ligand. The η^5-C$_5$Me$_5$ protons resonated as a singlet at δ 1.43 ppm. The position and integrated intensity of various signals corroborated well to the proposed formulation of the complex **2**. The presence of a singlet at δ 9.69 corresponding to aldehydic protons in ^{1}H NMR spectra of **1** and **2** supported proposed formulations and suggested an equivalent electronic environment about both the metal centres. Reactions of **1** and **2** with EPh$_3$ (E = P, As) disrupts symmetric coordination of H$_2$bsh with the metal centres and results in monometallic complexes **3–6**. The asymmetric mode of coordination is evidenced by presence of two singlet corresponding to –C(H)=N– proton in the ^{1}H NMR spectra of complexes **3–6**. The metal coordi-

nated imine proton resonated at $\delta \sim 10.0$ ppm, while the pendent imine proton displayed an up-fielded shift ($\delta \sim 7.7$ ppm). Aromatic protons of EPh$_3$ resonated as broad multiplet in the region $\delta \sim 7.3$–7.2 ppm. Methyl protons of η^5-C$_5$Me$_5$ in **3–6** resonated at almost same position as in the respective precursor complexes **1** and **2**.

^{1}H NMR spectrum of **7** exhibited distinct resonances corresponding to [–C(H)=N–] and aromatic phenyl protons of bsh^{2-}. These were displayed as a singlet at δ 9.32 (s, 2H), and as broad multiplet at δ 6.51 (d, $J = 7.8$ Hz), 6.93 (d, $J = 8.4$ Hz), 7.02 (t, $J = 6.3$ Hz), 7.14 (t, $J = 6.9$ Hz) ppm. The η^5-C$_5$Me$_5$ protons in this complex exhibited a downfield shift and resonated as a singlet at δ 1.47 ppm as compared to that in the complex **3** (δ 1.37 ppm). The downfield shift in the position of η^5-C$_5$Me$_5$ protons may be attributed to the coordination of {Ru(η^6-C$_{10}$H$_{14}$)Cl} moiety through pendant bis-chelating site of Hbsh$^-$ in complex **3**. The *p*-cymene protons resonated at δ 0.91 (d, $J = 6.6$ Hz, 6H), 2.61 (m, 1H), 5.12 (m, 2H), 5.34 (m, 2H) ppm. The position and integrated intensity of various signals corroborated well to the proposed formulation of **7**. The ^{1}H NMR spectrum of **8** followed the trends observed in that of **7**.

^{13}C NMR spectral data of the complexes **3–6** provided valuable information about bonding in these complexes. In the ^{13}C NMR spectra of these complexes resonances corresponding to methyl carbons of C$_5$Me$_5$ appeared at ~ 8.8 ppm, while the ring carbons resonated at ~ 97–100 ppm. Resonances corresponding to the aromatic carbons of triphenylphosphines/arsine and Hbsh$^-$ appeared at $\delta \sim 125$–135 ppm. An interesting feature of the ^{13}C NMR spectra of these complexes is the presence of two peaks associated with the imine carbons at ~ 161–172 ppm. The peak at ~ 161–165 ppm has been attributed to the signal associated with free imine carbon, while the one at ~ 168–172 ppm to the imine carbon coordinated to the metal centre. The coordination of PPh$_3$ to metal centre in **3** and **5** is further supported by the presence of signals associated with ^{31}P nuclei at δ 30.70 and δ 16.09 ppm, respectively. The ^{31}P nuclei of the counter anion PF$_6^-$ resonated in its characteristic septet pattern at ~ -130.0 ppm and supported the cationic nature of complexes **3** and **5**.

The metal centre rhodium/iridium provides filled orbitals of proper symmetry to interact with relatively low lying π^* orbitals of the ligand bsh^{2-}. It is expected to give a band associated with metal to ligand charge transfer (MLCT) transition (t$_2$g $\rightarrow \pi^*$) whose position varies with the nature of metal ion and ligand acting as a π acceptor. Absorption spectra of **1** and **2** in dichloromethane are shown in Fig. S3 and resulting data is recorded in Section 3. Low energy transitions in the UV–Vis spectra of **1** and **2** at 552 and 528 nm, respectively have been assigned to M$_{d\pi} \rightarrow$ L$_{\pi^*}$ metal to ligand charge transfer transitions, while the higher energy transitions at *ca.* 311 nm to the intra-ligand π–π^* transitions. It further suggested that the low energy transitions are localized at metal centre with the differences in absorptions attributed to electronic interaction between two metal centres [22]. The electronic spectra of monometallic complex **3** displayed absorptions at 463, 338, 262 nm and **5** at 415, 345 and 268 nm (Fig. S4). On the basis of its position and intensity the low energy bands at 463 and 415 nm, respectively have been assigned to the MLCT transitions [M(III) $\rightarrow \pi^*$ bsh]. The high intensity absorption bands in the region 335–345 nm (338 nm in **3** and 345 nm in **5**) and 260–270 nm (262 nm in **3** and 268 nm in **5**) nm have been assigned to the intra-ligand transitions. One can see that upon reaction with EPh$_3$ the bsh^{2-} bridged complexes **1** and **2** afforded cationic complexes **3–6**. The formation of monometallic species from bimetallic one, leads to a blue shift (~ 100 nm) in the position of MLCT transitions while intra-ligand transitions exhibited a red shift (~ 25 nm). The shifts in the position of various transitions may result from disruption of the bsh^{2-} bridged structure [23].

Complexes **1–3** and **5** upon excitation at their respective MLCT transitions exhibited moderate emissions centred at 538 (**1**), 548 (**2**), 560 (**3**) and 565 nm (**5**). The observed red shift in the position of emission bands for iridium complexes compared to the analogous rhodium complex is consistent with the fact that dπ orbitals of Rh(III) are more stable than those of Ir(III). The observed red shift in **3** and **5** may be attributed to destabilisation of the ground state by coordination of triphenylphosphine in place of chlorine (Supplementary material Fig. S5).

Molecular structures of **1**, **2**, **3** and **5** have been determined crystallographically. Details about data collection, solution and refinement is summarized in Table 1, selected geometrical parameters are listed in Table 2 and CCDC Mercury ellipsoid plots (at 30% probability) are depicted in Figs. 1–4. Relative configuration of these pseudo-tetrahedral metal complexes is *R*, if viewed along the M–C$_{ct}$ axis (Fig. S6). In the complexes **1** and **2**, two [(η^5-C$_5$Me$_5$)MCl] moieties are bridged by bsh^{2-} in κ^2:κ^2 mode, where both the metal centres adopt a typical *piano-stool* geometry. Coordination geometry about the metal centres is completed by imine nitrogen and

Table 1
Selected crystallographic data for **1**, **2**, **3** and **5**.

	1	2	3	5
Chemical formula	C$_{17}$H$_{20}$ClNORh	C$_{17}$H$_{20}$ClNOIr	C$_{42}$H$_{41}$F$_6$N$_2$O$_2$P$_2$Rh	C$_{42}$H$_{41}$F$_6$N$_2$O$_2$P$_2$Ir
Formula weight	392.70	481.99	884.62	973.91
Color, habit	Red, blocks	Red, blocks	Orange, blocks	Orange red, blocks
Space group	$P2_1/n$	$P2_1/n$	$Pna21$	$Pca21$
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
a (Å)	7.6593(15)	7.7523(16)	21.119(4)	21.109(4)
b (Å)	13.543(3)	13.564(3)	13.141(3)	10.827(2)
c (Å)	15.543(3)	15.328(3)	14.589(3)	17.507(4)
α (°)	90	90	90.00	90.00
β (°)	97.30(3)	97.48(3)	90.00	90.00
γ (°)	90	90	90.00	90.00
V (Å^3)	1599.3(5)	1598.1(6)	4048.8(14)	4001.4(14)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.631	2.003	1.451	1.617
T (K)	293 (2)	293 (2)	293(2)	293(2)
Number of reflections	10 913	12 155	31 087	33 630
Number of parameters	195	196	502	502
R factor all	0.1050	0.0337	0.0546	0.0481
R factor [$I > 2\sigma(I)$]	0.0862	0.0310	0.0428	0.0390
WR_2	0.1462	0.0950	0.1304	0.0954
WR_2 [$I > 2\sigma(I)$]	0.1388	0.0902	0.1158	0.0871
Goodness-of-fit (GOF)	1.296	0.620	1.082	0.973

Table 2
Important bond parameters for **1**, **2**, **3** and **5**.

|	1	2	3	5
M–C$_{av}$	2.153	2.155	2.187	2.207
M–C$_{ct}$	1.774	1.774	1.821	1.838
C–C	1.436	1.438	1.427	1.430
C–CH$_3$	1.497	1.495	1.472	1.507(12)
M–O	2.092(6)	2.102(4)	2.100(4)	2.092(5)
M–Cl/P	2.420(2)	2.4022(15)	2.3665(11)	2.3482(15)
M–N	2.156(6)	2.147(4)	2.091(4)	2.096(5)
C1–O	1.307(10)	1.312(7)	1.294(6)	1.316(8)
N–N#1	1.436(12)	1.417(8)	1.416(6)	1.405(7)
O–M–Cl	88.09(18)	84.45(13)		
O–M–N	84.0(2)	83.33(15)	85.45(15)	85.45(19)
N–M–Cl/P	91.40(18)	89.57(12)	91.78(12)	90.59(14)
O–M–P			87.71(11)	85.12(16)
C7–N–N–C8	180.0(5)	180.00(44)	−58.0(6)	−52.0(7)
O–C1–C6–C7	178.6(9)	178.6(6)	177.2(5)	−2.0(10)
O2–C–C–C			−2.4(8)	7.8(11)
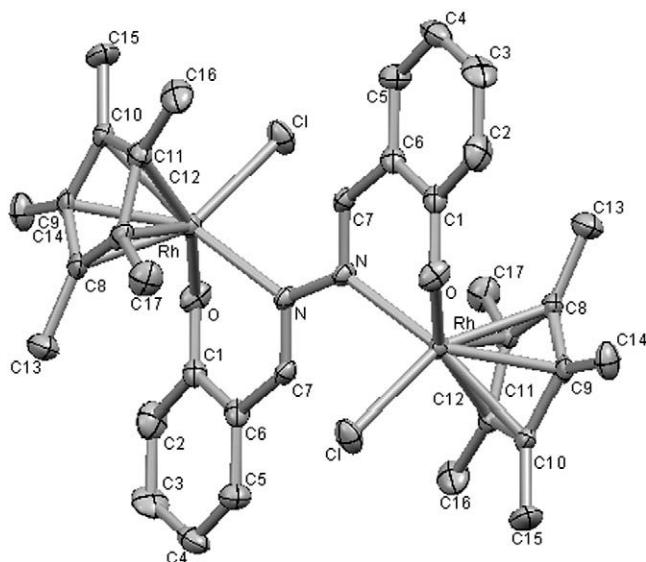
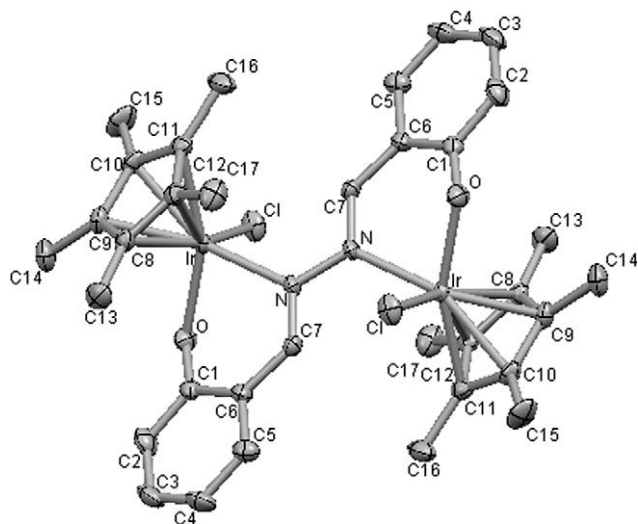**Fig. 1.** Molecular structure of complex **1**.

Fig. 2. Molecular structure of complex **2**.

phenolate oxygen from bsh^{2-}, the chloro group and C$_5$Me$_5$ ring coordinated in η^5-manner. Both the metal centres are equivalent in terms of overall geometry and arrangement of various groups. The metal centres occupy special position and only half of the molecule is labelled. Intermetallic distances in **1** and **2** are 5.264 and 5.233 Å, respectively. The salicylidimine moieties of bsh^{2-} in both the complexes are planar. The N–N bond lengths in **1** and **2** are 1.436 and 1.417 Å, respectively, which are slightly longer than that in the free ligand (1.386 Å). This distance falls in the normal range for N–N bond [24–29]. Metal to phenalato oxygen bond distances in **1** and **2** are 2.092 and 2.102 Å. These are comparable to the values reported in literature [30]. The Rh–N and Ir–N and bond distances of 2.156 and 2.147 Å are in the normal range [31,32] as the M–Cl bond distances [Rh–Cl 2.378(5) Å in **1** and Ir–Cl 2.395(3) Å in **2**] [33–36]. The metal chelate bite angles [84.0 (**1**) and 83.33° (**2**)] are almost same in both the complexes. The η^5-C$_5$Me$_5$ ring is essentially planar and coordinated to rhodium and iridium centres almost symmetrically. The M–C bond distances are almost equal with an average bond distance of 2.153 Å [range 2.14(4)–2.20(4) Å] in **1** and 2.155 Å [range 2.14(4)–2.20(4) Å] in **2**. The M-(η^5-C$_5$Me$_5$)$_{ct}$ distances (1.774 Å) are similar for the metal centres rhodium and iridium in **1** and **2** [32,35–37].

Coordination geometry about the metal centre Rh in **3** is completed by imine nitrogen and phenolate oxygen from the bsh^{2-}, phosphorus from triphenylphosphine and C$_5$Me$_5$ ring coordinated in η^5-manner. An analogous arrangement of various groups has been observed about the metal centre Ir in **5**. The Rh–C average bond distance is 2.186(5) Å [range 2.169(5)–2.208(5) Å] in **3** while, Ir–C average bond distance in **5** is 2.205(4) Å [range, 2.217(4)–2.201(4) Å]. Metal to centroid of the C$_5$Me$_5$ distances in **3** and **5** are 1.821 and 1.838 Å, respectively. These are longer than those in **1** and **2** (1.77 Å). Metal to phenalato oxygen distances are 2.100(4) and 2.091 Å, respectively in **3** and **5**, while metal to imine nitrogen bond distances are almost equal and are 2.090(4) and 2.095 Å. These values are comparable to those in the precursor complexes **1** and **2** and are consistent with the values reported in literature [32–37]. The metal to phosphorus distance is 2.366(11) Å in complex **3** and 2.348 Å in **5**. These distances are consistent with the earlier reports [38].

Weak interaction studies in **1** and **2** revealed that two C–H⋯O intermolecular contacts between methyl substituents of η^5-C$_5$Me$_5$ and phenalato oxygen results in a ladder like motif along the *b*-axis (Fig. S7). Significant interaction parameters along with the symmetry are listed in Table 3. Furthermore, methyl protons of C$_5$Me$_5$ ring are intramolecularly involved in long range C–H⋯π interactions with the phenalato ring. In complex **1**, the methyl carbon C13 approaches to C1–C2 bond of the phenalato ring with a contact distance of 2.776 Å (H⋯π 2.776 Å, C⋯π 3.523 Å, C–H⋯π 135.23°), whereas in complex **2** the methyl carbon located at the same position as in complex **1** is involved in a long range interaction with C1–C6 bond of the phenalato ring (H⋯π 3.030 Å, C⋯π 3.503 Å, C–H⋯π 111.86°) [22,23]. Further, crystal structures of **3** and **5** revealed the presence of extensive inter-molecular C–H⋯X (X = F and π) interactions. It is well established that these types of interactions plays an important role in the construction of huge supramolecular architectures [22,23]. In complex **3**, C–H⋯F (C33–H33⋯F5; 2.599 Å and C4–H4⋯F3; 2.538 Å), one C–H⋯C–H (C21–H21⋯C6–H6, 2.397 Å) and F⋯C (C4⋯F3, 3.140 Å) types of interactions are present. In this molecule hydrogen atom of coordinated phenyl ring of one molecule is attached to the F3 from the counter anion PF$_6^-$ and hydrogen of phenyl ring of another molecule is attached with F3 of the same anion leading to zig-zag chains (Fig. S8). In complex **5**, five cationic units are locked by five C–H⋯F type interactions involving PF$_6^-$ anion to form a spiral type of architecture by weak interactions along '*c*'-axis (Fig. S9). Hexafluorophosphate anions are embedded in this motif. The pendant
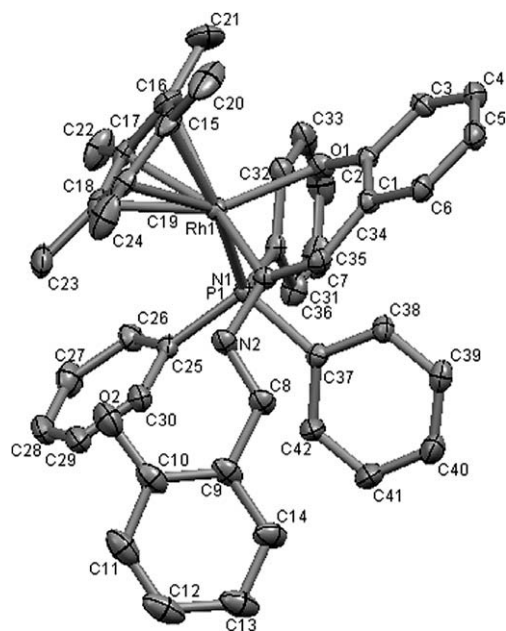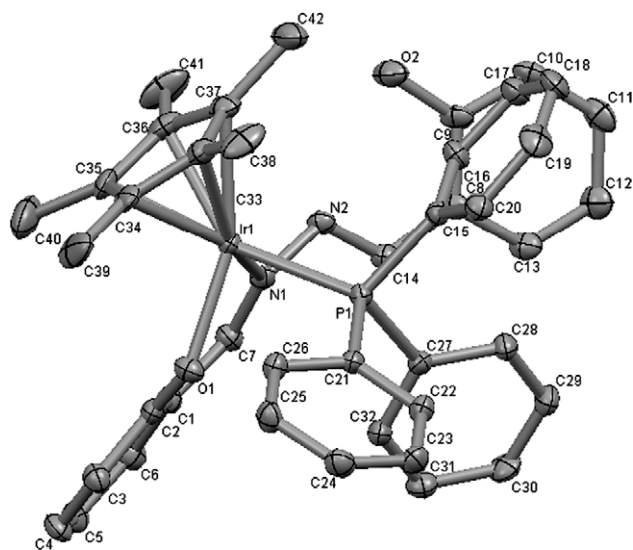
Fig. 3. Molecular structure of complex **3**.

Fig. 4. Molecular structure of complex **5**.

Table 3
Matrices for weak-interactions in **1**, **2**, **3** and **5**.

D–H···A	d(D–H) Å	d(H···A) Å	d(D···A) Å	∠(DHA)°
1				
C(7)–H(7)···Cl[a]	0.93	2.64	3.381(8)	137
C(17)–H(17c)···O[b]	0.96	2.60	3.462(11)	150
2				
C(7)–H(7)···Cl[a]	0.93	2.64	3.3481(5)	134
C(17)–H(17c)···O[b]	0.96	2.56	3.469(8)	158
3				
C(4)–H(4)···F(3)	0.93	2.55	3.1349	122
C(32)–H(32)···O(1)	0.93	2.56	3.1916	125
C(38)–H(38)···O(1)	0.93	2.47	3.2673	144
5				
O(2)–H(2)···N(2)	0.82	1.92	2.6391	147
C(6)–H(6)···F(1)[A]	0.93	2.49	3.2075	134
C(7)–H(7)···F(2)[A]	0.93	2.41	3.3325	172
C(17)–H(17)···F(6)[C]	0.93	2.41	3.2253	147
C(26)–H(26)···O(1)	0.93	2.60	3.0783	113
C(32)–H(32)···O(1)	0.93	2.59	3.3551	140
C(41)–H(41A)···F(1)[B]	0.96	2.53	3.3587	145
C(41)–H(41C)···N(2)	0.96	2.60	3.2926	129

[a] $-x, -y, -z.$
[b] $1 + x, y, z.$
[A] $-1/2 + x, 1 - y, z.$
[B] $1/2 - x, y, -1/2 + z.$
[C] $1/2 - x, -1 + y, -1/2 + z.$

coordinated C_5Me_5 and PPh_3. These molecules also have chiral centre about each metal ion. Since priority order of the ligands for the Rh/Ir centre falls in the order $Cp^* > O > N > Cl/PPh_3$ [39]. Therefore, the complexes **7** and **8** exhibits *R* configuration about the Rh/Ir centres. Same configuration is also, observed about the Ru centre.

3. Experimental

3.1. Materials and physical measurements

All chemicals were obtained from commercial sources and used directly without further purifications. Pentamethylcyclopentadiene, hydrated rhodium(III) chloride, iridium(III) chloride, triphenylphosphine, triphenylarsine, ammonium hexafluorophosphate (all Aldrich) salicylaldehyde and hydrazine (s.d. fine chem.) were used as received. The ligand *N*,*N*′-bis(salicylidine)hydrazine (H₂bsh) and the precursor complexes $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ [M = Rh, Ir] were prepared following literature procedures [40,41].

Elemental analyses on the complexes were performed by Microanalytical Laboratory, Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow. Electronic and emission spectra in dichloromethane were obtained on a Shimadzu UV-1700 and Perkin Elmer-LS 45 Luminescence spectrometer, respectively. Infrared spectra were recorded on a Perkin Elmer-3100 FT-IR spectrometer in KBr pellets. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL AL300 FT-NMR spectrometer in *d*-chloroform at 298 K. FAB mass spectra was obtained on a JEOL SX 102/DA-6000 mass spectrometer system using Xenon as the FAB gas (6 kV, 10 mA).

3.2. Syntheses

3.2.1. Preparation of $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\kappa^2\text{-}bsh)]$ **1**

$[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ (155 mg, 0.25 mmol) was added to a deprotonated solution of H₂bsh [(obtained by stirring H₂bsh (60 mg, 0.25 mmol) and KOH (0.50 mmol, 30 mg) in 25 mL of methanol] and stirred for 4 h at room temperature. Slowly, it dissolved and a dark red product separated which was filtered, washed with methanol (2 × 10 mL), distilled water (10 mL), meth-

hydroxy group of the uncoordinated N,O-donor site is involved in the intra-molecular H bonding with azine nitrogen [19].

Reactions of the complexes $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ (M = Rh, Ir) with potassium derivative of H₂bsh (obtained from the reaction of H₂bsh with KOH in MeOH) in methanol under stirring conditions at room temperature afforded neutral binuclear complexes with the formulations $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}bsh)]$. The complexes can exist as diastereomers but all efforts to separate the diastereomers were unsuccessful at our hands. Throughout this work we have taken into account only the major isomer. Further, the complexes **3**–**6** were obtained by interaction of **1** and **2**, respectively with EPh₃. From the crystal structures, it is clear that the complexes **1**, **2**, 3 and **5** adopted *R* configuration about the metal centre (*Fig.* S6). Due to the presence of uncoordinated bis-chelating N,O-donor sites **3** and **5** were used as synthon to produce chiral rhodium/ruthenium (**7**) and iridium/ruthenium (**8**). In these complexes the Rh/Ir is bonded to N,O-donor bis-chelating ligand as the Ru centre, along with

anol (2 × 10 mL), diethyl ether (2 × 10 mL) and dried under vacuum. Yield: 157 mg, 80%. Anal. Calc. for $C_{34}H_{40}N_2O_2Cl_2Rh_2$: C, 51.99; H, 5.13; N, 3.57. Found: C, 51.82; H, 5.15; N, 3.66%. UV–Vis. {CH_2Cl_2, λ nm (ε)}: 511 (5.01 × 10³), 424 (1.29 × 10⁴), 313 (1.25 × 10⁴). FAB-MS: m/z 749 (750), [M]−Cl, 40%; 477 (476), [M]−[(η^5-C_5Me_5)RhCl]−Cl, 35%.

3.2.2. Preparation of [{(η^5-C_5Me_5)IrCl}₂(κ^2-bsh)] 2

It was prepared following the above procedure adopted for 1 except that [{(η^5-C_5Me_5)IrCl(μ-Cl)}₂] (200 mg, 0.25 mmol) was used in place of [{(η^5-C_5Me_5)RhCl(μ-Cl)}₂]. Yield: 195 mg, 81%. Anal. Calc. for $C_{34}H_{40}N_2O_2Cl_2Ir_2$: C, 42.36; H, 4.18; N, 2.91. Found: C, 42.30; H, 4.15; N, 3.06%. ¹H NMR (CDCl₃, δ ppm): 9.69 (s), 7.39 (d, J = 7.8 Hz), 7.31–7.24 (m), 7.03 (d, J = 8.4 Hz), 6.61 (t, J = 7.2 Hz), 1.43 (s). UV–Vis. {CH_2Cl_2, λ nm (ε)}: 511 (6.02 × 10³), 480 (4.87 × 10³), 346 (7.91 × 10³), 311 (1.24 × 10⁴), 262 (1.62 × 10⁴). FAB-MS: m/z 928 (928), [M]−Cl, 50%; 565 (566), [M]−[(η^5-C_5Me_5)IrCl]−Cl, 75%.

3.2.3. Preparation of complex [(η^5-C_5Me_5)Rh(PPh₃)(κ^2-Hbsh)]PF₆ 3

To a suspension of 1 (195 mg, 0.25 mmol) in methanol (25 mL), PPh₃ (65 mg, 0.25 mmol) and NH₄PF₆ (40 mg, 0.25 mmol) were added and the contents of the flask were refluxed for 5 h. It was cooled to room temperature and the reaction mixture was evaporated to dryness under vacuum and the residue was extracted with CH_2Cl_2. After filtration, the filtrate was saturated with petroleum ether (60–80) and the solution left undisturbed in a refrigerator. A microcrystalline product separated within a few hours. It was filtered washed with diethyl ether, dried under vacuum and recrystallized using dichloromethane/diethyl ether. Yeild: 188 mg, 85% Anal. Calc. for $C_{42}H_{41}N_2O_2P_2RhF_6$: C, 57.01; H, 4.63; N, 3.16. Found: C, 57.06; H, 4.65; N, 3.18%. ¹H NMR (CDCl₃, δ ppm): 10.48 (s, 1H), 7.73 (s, 2H), 7.49 (d, 1H, J = 6.6 Hz), 7.45 (s, 1H) 7.31–7.24 (m, 15H, PPh₃), 7.16 (d, 1H, J = 7.8 Hz), 7.07 (d, 1H, J = 8.4 Hz), 6.97 (t, 2H, J = 7.8 Hz), 6.86 (d, 1H, J = 6.6 Hz), 6.6 (t, 1H, J = 8.4 Hz), 1.37 (s, 15H, C_5Me_5). ¹³C{¹H} NMR (CDCl₃, δ ppm): 162.9 (free C–H), 169.9 (coordinated C–H), 157.8, 134.6 (C, PPh₃), 132.2, 130.4, 127.9, 127.8, 121.2, 115.8 (C, aromatic) 98.9 (C, C_5Me_5), 8.75 (CH₃, C_5Me_5).³¹P NMR (CDCl₃, δ ppm): 30.7, −130.32 (sep.). UV–Vis. {CH_2Cl_2, λ nm (ε)}: 486 (2.22 × 10³), 415 (6.14 × 10³), 345 (1.61 × 10⁴), 268 (2.36 × 10⁴), 246 (2.36 × 10⁴). IR (cm⁻¹, KBr pellet), 1597 $v_{C=N}$, 1527 ($v_{C=C}$), 1465 ($v_{C=N}$), 1436 (v_{P-Ph}), 1308 (δ_{O-H}), 1269 (v_{N-N}), 1193 (v_{C-O}), 1151 (v_{C-O}), 842 (PF₆), 757 (δ_{C-Har}) and 696 (δ_{C-H}).

3.2.4. Preparation of complex [(η^5-C_5Me_5)Rh(AsPh₃)(κ^2-Hbsh)]PF₆ 4

It was prepared by following the above procedure adopted for 3 except that AsPh₃ was used in place of PPh₃. Yield: 197 mg, 83%. Anal. Calc. for $C_{42}H_{41}N_2O_2PAsRhF_6$: C, 54.21; H, 4.41; N, 3.02. Found: C, 54.26; H, 4.45; N, 3.06%. ¹H NMR (CDCl₃, δ ppm): 10.23 (s, 1H), 7.65 (s, 2H), 7.38 (d, 1H, J = 6.3 Hz), 7.32 (s, 1H), 7.28–7.12 (m, 15H AsPh₃), 7.02 (d, 1H, J = 7.5 Hz), 6.95 (d, 1H, J = 7.8 Hz), 6.82 (t, 2H, J = 8.1 Hz), 6.72 (d, 1H, J = 6.0 Hz), 6.55 (t, 2H, J = 8.1 Hz), 1.42 (s, 15H, C_5Me_5). ¹³C NMR (CDCl₃, δ ppm): 164.2 (free C–H), 169.8 (coordinated C–H), 154.6, 140.2 (C, PPh₃), 135.2, 132.3, 130.3, 127.9, 127.4, 118.2 (C, aromatic), 99.3 (C, C_5Me_5), 8.8 (CH₃, C_5Me_5).

3.2.5. Preparation of complex [(η^5-C_5Me_5)Ir(PPh₃)(κ^2-Hbsh)]PF₆ 5

This complex was prepared following the procedure used for 3 using complex 2 in place of 1. 204 mg, 84%. Anal. Calc. for $C_{42}H_{41}N_2O_2P_2IrF_6$: C, 46.00; H, 4.16; N, 1.66. Found: C, 45.96; H, 4.15; N, 1.68%. ¹H NMR (CDCl₃, δ ppm): 10.37 (s, 1H), 7.71 (s, 1H), 7.5 (s, 1H), 7.4 (s, 1H), 7.31–7.24 (m, 15H, PPh₃), 7.06 (d, 1H, J = 8.1 Hz), 6.69 (t, 2H, J = 7.2 Hz), 6.61 (t, 2H, J = 7.5 Hz), 6.47 (s, 1H), 1.36 (s, 15H, C_5Me_5). ¹³C NMR (CDCl₃, δ ppm): 162.1(free

C–H), 171.2 (coordinated C–H), 156.7, 142.4 (C, PPh₃), 138.4, 131.3, 130.1, 125.7, 125.5, 121.2 (C, aromatic), 96.8 (C, C_5Me_5), 8.9 (CH₃, C_5Me_5). ³¹P NMR (CDCl₃, δ ppm): 16.09, −137 (sep.). UV–Vis. {CH_2Cl_2, λ nm (ε)}: 463 (1.66 × 10⁴), 338 (1.51 × 10⁴), 262 (2.37 × 10⁴). IR (cm⁻¹, KBr pellet): 1597 ($v_{C=N}$), 1530 ($v_{C=C}$), 1465 ($v_{C=N}$), 1437 (v_{P-Ph}), 1305 (δ_{O-H}), 1269 (v_{N-N}), 1196 (v_{C-O}), 1152 (v_{C-O}), 842 (v_{P-F}), 755 (δ_{C-Hph}), 679 (δ_{C-H}).

3.2.6. Preparation of complex [(η^5-C_5Me_5)Ir(AsPh₃)(κ^2-Hbsh)]PF₆ 6

It was prepared following the procedure adopted for 5, using AsPh₃ in place of PPh₃. Yield: 221 mg, 87%. Anal. Calc. for $C_{42}H_{41}N_2O_2PAsIrF_6$: C, 49.60; H, 4.04; N, 2.76. Found: C, 49.68; H, 3.98; N, 2.73%. ¹H NMR (CDCl₃, δ ppm): 9.99 (s, 1H), 7.68 (s, 1H), 7.42 (s, 1H), 7.35 (s, 1H), 7.31–7.24 (m, 15H, AsPh₃), 7.03 (d, 1H, J = 8.1 Hz), 6.72 (t, 2H, J = 7.2 Hz), 6.56 (t, 2H, J = 7.5 Hz), 6.39 (s, 1H), 1.46 (s, 15H, C_5Me_5). ¹³C NMR (CDCl₃, δ ppm): 161.7 (free C–H), 172.6 (coordinated C–H), 155.4, 141.2 (C, PPh₃), 133.9, 132.7, 130.2, 130.1, 127.2, 121.4 (C, aromatic), 95.8 (C, C_5Me_5), 9.0 (CH₃ C_5Me_5).

3.2.7. Preparation of complex [(η^5-C_5Me_5)RhCl(μ-bsh) Ru(η^6-$C_{10}H_{14}$) Cl]PF₆ 7

To a solution of 3 [(obtained by stirring 3 (221 mg, 0.25 mmol) and KOH (15 mg, 0.25 mmol,) in 25 mL of methanol)], [{(η^6-$C_{10}H_{14}$)Ru(μ-Cl)Cl}₂] (77 mg, 0.125 mmol) was added and stirred for 4 h at 50 °C. Slowly, it dissolved and a dark brown product separated which was filtered, washed with methanol (2 × 10 mL), distilled water (10 mL), methanol (2 × 10 mL), diethyl ether (2 × 10 mL) and dried under vacuum. The crude product was purified by column chromatography Yield: 216 mg, 75%. Anal. Calc. for $C_{52}H_{54}N_2O_2ClRhRuP_2F_6$: C, 54.10; H, 4.71; N, 2.43. Found: C, 53.92; H, 4.77; N, 2.38%. (CDCl₃, δ ppm): 9.32 (br, s, 2H), 7.32–7.78 (m, 15H, PPh₃), 7.14 (t, J = 6.9 Hz, 2H), 7.02 (t, J = 6.3 Hz, 2H), 6.93 (d, J = 8.4 Hz, H), 6.51 (d, J = 7.8 Hz, 2H), 5.34 (m, 2H), 5.12 (m, 2H), 2.61 (m, 1H), 2.10 (s, 3H), 1.47 (s, 15H), 0.91 (d, J = 6.6 Hz, 6H). ESI-MS: m/z 710.9 (711.6), [M]−Cl−PF₆−PPh₃, 8%; 477 (476), [M]−[(η^6-C_6H_{14})RuCl]−Cl−PF₆−PPh₃, 100%.

3.2.8. Preparation of complex [(η^5-C_5Me_5)IrCl(μ-bsh) Ru(η^6-$C_{10}H_{14}$) Cl]PF₆ 8

It was prepared following the above procedure adopted for 7, except that 5 (243 mg, 0.25 mmol) was used in place of 3. Yield: 227 mg, 73%. Anal. Calc. for $C_{52}H_{54}N_2O_2ClIrRuP_2F_6$: C, 50.22; H, 4.38; N, 2.25. Found: C, 50.00; H, 4.15; N, 2.13%. ¹H NMR (CDCl₃, δ ppm): 9.66 (br, s, 2H), 7.36–7.82 (m, 15H, PPh₃), 7.23 (t, J = 8.1 Hz, 2H), 7.14 (t, J = 7.5 Hz, 2H), 7.03 (d, J = 7.5 Hz, H), 6.63 (d, J = 8.1 Hz, 2H), 5.77 (m, 2H), 5.42 (m, 2H), 2.78 (m, 1H), 2.23 (s, 3H), 1.39 (s, 15H), 1.01 (d, J = 6.9 Hz, 6H). ESI-MS: m/z 1208.2 (1209.0), [M]−Cl, 8%; 1063.2 (1066.9), [M]−Cl−PF₆, 15%; 801(802), [M]−Cl−PF₆−PPh₃, 40%.

3.3. X-ray crystallography

Crystals suitable for single crystal X-ray data collection for 1 and 2 were obtained by slow diffusion of a deprotonated solution of H₂bsh in methanol into the dichloromethane solution of [{(η^5-C_5Me_5)MCl(μ-Cl)}₂] [M = Rh, Ir] and for 3 and 5 crystals were obtained by slow diffusion using dichloromethane/diethyl ether. X-ray data on 1, 2, 3 and 5 were collected on a R-AXIS RAPID II diffractometer at room temperature with Mo Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXS 97) and refined by full-matrix least squares calculations on F^2 (SHELX 97) [42]. All the non-H atoms were treated anisotropically. H-atoms attached to the carbon were included as fixed contribution and were geometrically calculated and refined using the SHELX riding model.

4. Conclusions

In this work, we have described the synthesis, spectral and structural characterization of bsh^{2-} bridged complexes [{(η^5-C$_5$Me$_5$)RhCl}$_2$(κ^2-bsh)] and [{(η^5-C$_5$Me$_5$)IrCl}$_2$(κ^2-bsh)]. Structural studies supported our earlier viewpoint that reaction of [{(η^5-C$_5$Me$_5$)MCl(μ-Cl}$_2$] [M = Rh, Ir] with potassium derivative of bsh^{2-} (obtained from H$_2$bsh and KOH in MeOH) in methanol leads to homo-bimetallic complexes where the ligand interacts through both the chelating sites. Further, it has been shown that reaction of the bsh^{2-} bridged complexes with EPh$_3$ leads to stable monometallic complexes containing one vacant bis-chelating site which can be employed in the synthesis of homo/hetero-binuclear complexes.

Acknowledgements

Appendix A. Supplementary material

CCDC 656456, 656457, 692962 and 692963 contain the supplementary crystallographic data for **1**, **2**, **3** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.026.

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