



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

Ashish Kumar Singh<sup>a</sup>, Sudhakar Dhar Dwivedi<sup>a</sup>, Santosh Kumar Dubey<sup>a</sup>, Sanjay Kumar Singh<sup>a</sup>, Sanjeev Sharma<sup>a</sup>, Daya Shankar Pandey<sup>a,\*</sup>, Ru-Qiang Zou<sup>b</sup>, Qiang Xu<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, UP, India

<sup>b</sup> National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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### ABSTRACT

Binuclear complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\mu\text{-bsh})$  (**1**) and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}]_2(\mu\text{-bsh})$  (**2**) containing *N,N*-bis(salicylidine)hydrazine ( $\text{H}_2\text{bsh}$ ) are reported. The complexes **1** and **2** reacted with  $\text{EPh}_3$  ( $\text{E} = \text{P, As}$ ) to afford cationic complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{PPh}_3)(\kappa^2\text{-Hbsh})]\text{PF}_6$  (**3**),  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{AsPh}_3)(\kappa^2\text{-Hbsh})]\text{PF}_6$  (**4**),  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{PPh}_3)(\kappa^2\text{-Hbsh})]\text{PF}_6$  (**5**), and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{AsPh}_3)(\kappa^2\text{-Hbsh})]\text{PF}_6$  (**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  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-bsh})\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})\text{Cl}]\text{PF}_6$  (**7**) and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}(\mu\text{-bsh})\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})\text{Cl}]\text{PF}_6$  (**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  $\text{C}\cdots\text{H}\cdots\text{O}$  and  $\text{C}\cdots\text{H}\cdots\pi$  weak bonding interactions. The complexes **1**, **2**, **3** and **5** moderately emit upon excitation at their respective MLCT bands.

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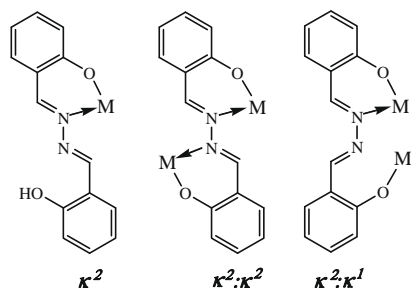
## 1. Introduction

The chloro-bridged dimeric complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\mu\text{-Cl})\text{Cl}]_2$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ) 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  $(\text{C}_5\text{Me}_5)\text{ML}_n\text{X}$  [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  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\mu\text{-Cl})]_2$  [ $\text{M} = \text{Rh, Ir}$ ] 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  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\mu\text{-Cl})]_2$  [ $\text{M} = \text{Rh, Ir}$ ] with a variety of ligands, their reactions with  $\text{N}_2\text{O}_2$  donor Schiff base ligands like, *N,N'*-bis(salicylidine)hydrazine ( $\text{H}_2\text{bsh}$ ), *N,N'*-bis(salicylidine)-*p*-phenylenediamine ( $\text{H}_2\text{bsp}$ ) and *N,N'*-bis(salicylidine)-*p*-biphenylenediamine ( $\text{H}_2\text{bsb}$ ) have seldom been investigated [18].

*N,N'*-bis(salicylidine)hydrazine ( $\text{H}_2\text{bsh}$ ) derived from the reaction of salicylaldehyde with hydrazine possesses four donor sites in the form of phenolato 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  $\kappa^2:\kappa^2$ -mode after dissociation of the phenolic protons. In some cases,  $\text{H}_2\text{bsh}$  interacts with metal ions through only one of the bis-chelating donor sites in a  $\kappa^2$ -mode and acts as a bidentate ligand (Scheme 1) [19,20]. It also interacts with the metal ions in an unusual  $\kappa^2:\kappa^1$ -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  $\text{bsh}^{2-}$  groups in an unusual  $\kappa^2:\kappa^1$ -mode [18].

Because of our interests in this area we devoted our efforts towards reactivity of the chloro-bridged dimeric rhodium and iridium complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\mu\text{-Cl})]_2$  [ $\text{M} = \text{Rh, Ir}$ ] with  $\text{H}_2\text{bsh}$ . In this paper, we report reproducible syntheses, spectral properties and reactivity of the homo-nuclear bimetallic complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}]_2(\kappa^2\text{-bsh})$  ( $\text{M} = \text{Rh}$  **1**,  $\text{Ir}$  **2**) with  $\text{EPh}_3$  and crystal structures of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}]_2(\mu\text{-bsh})$  **1**,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}]_2(\mu\text{-bsh})$  **2**,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{PPh}_3)(\kappa^2\text{-Hbsh})]\text{PF}_6$  **3** and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{PPh}_3)(\kappa^2\text{-Hbsh})]\text{PF}_6$  **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**.

\* Corresponding authors. Tel.: +91 542 2307321x105 (D.S. Pandey).  
E-mail address: dspbhu@bhu.ac.in (D.S. Pandey).



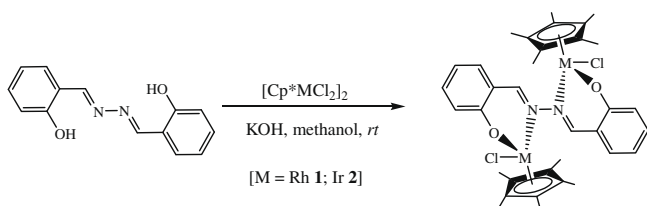
Scheme 1.

## 2. Results and discussion

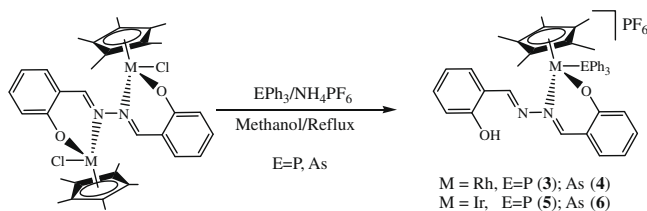
Reactions of the chloro-bridged dimeric complexes  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\mu\text{-Cl})_2\}]$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) with potassium derivative of  $\text{H}_2\text{bsh}$  (obtained from the reaction of  $\text{H}_2\text{bsh}$  with  $\text{KOH}$  in  $\text{MeOH}$ ) under stirring conditions at room temperature afforded neutral binuclear complexes **1** and **2**, respectively (Scheme 2). Synthesis and spectral characterization of 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  $[\{(\eta^6\text{-arene})\text{RuCl}(\mu\text{-Cl})_2\}]$  (arene = *p*-cymene or benzene) and  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})_2\}]$  with potassium derivative of  $\text{H}_2\text{bsh}$  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  $[\{(\eta^6\text{-arene})\text{Ru}\}_2(\kappa^2\text{-bsh})]$  or hetero-bimetallic complex containing both the Ru and Rh  $[\{(\eta^6\text{-arene})\text{Ru}\}(\kappa^2\text{-bsh})\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\}]$  may be attributed to higher stability of the homo-bimetallic rhodium complex **1**.

Complexes **1** and **2** upon treatment with  $\text{EPh}_3$  ( $\text{E} = \text{P}, \text{As}$ ) in methanol in presence of  $\text{NH}_4\text{PF}_6$  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  $\text{EPh}_3$  could not give  $\text{bsh}^{2-}$  bridged bimetallic complexes  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{EPh}_3)_2(\mu\text{-bsh})\}(\text{PF}_6)_2]$ . Rather, it led in the cleavage of  $\text{bsh}^{2-}$  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  $\text{EPh}_3$  groups.

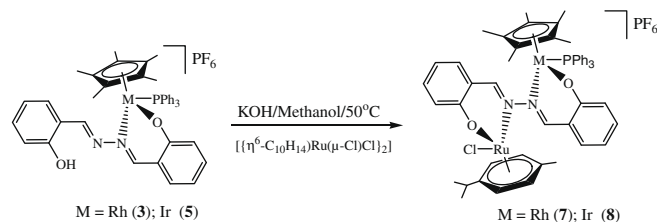
The presence of uncoordinated bis-chelating N,O-donor sites in **3–6** offers an unique opportunity for these molecules to behave as



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  $[\{(\eta^6\text{-C}_{10}\text{H}_{14})\text{Ru}(\mu\text{-Cl})\text{Cl}_2\}]$  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  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\mu\text{-bsh})(\eta^5\text{-C}_5\text{Me}_5)\text{M}\}]$  ( $\text{M} = \text{Rh}; \text{Ir}$ ) 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  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}(\kappa^2\text{-bsh})\}]$  ( $\text{M} = \text{Rh}; \text{Ir}$ ) 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  $\nu_{\text{C=N}}$  and phenolic C–O by  $\sim 17$  and  $\sim 67\text{ cm}^{-1}$ , respectively as compared to that in the uncoordinated  $\text{H}_2\text{bsh}$  ( $1621$  and  $1273\text{ cm}^{-1}$ ) [18,19]. It suggested coordination of the ligand  $\text{H}_2\text{bsh}$  through imine nitrogen and phenolic oxygen after deprotonation. The band associated with N–N stretching vibration appeared at  $1020\text{ cm}^{-1}$ . Coordination of  $\text{H}_2\text{bsh}$  to the metal centre in  $\kappa^2$ -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  $\nu_{\text{C=N}}$  at  $\sim 1596$  and  $\sim 1465\text{ cm}^{-1}$ , respectively as compared to that in the respective precursor complexes **1** and **2**. The band at  $\sim 1596\text{ cm}^{-1}$  may be attributed to the pendent C=N group, while the one at  $\sim 1465\text{ cm}^{-1}$  to the coordinated C=N. Similarly, the bands at  $\sim 1190$  and  $\sim 1150\text{ cm}^{-1}$  may be assigned to the pendent and coordinated phenolic C–O groups, respectively. The presence of characteristic vibrations associated with  $\nu_{\text{P-F}}$  (at  $\sim 842\text{ cm}^{-1}$ ) suggested cationic nature of the complexes **3–8** [21].

$^1\text{H}$  NMR spectral data of the complex **1** has already been reported [18] and data for **2–8** is recorded in Section 3. In the  $^1\text{H}$  NMR spectrum of **2** protons of the ligand ( $\text{bsh}^{2-}$ ) resonated at  $\delta$  9.69, 7.39 (d,  $J = 7.8\text{ Hz}$ ), 7.31–7.24 (m), 7.03 (d,  $J = 8.4\text{ Hz}$ ) and 6.61 (t,  $J = 7.2\text{ Hz}$ ) ppm. The singlet at  $\delta$  9.69 ppm has been assigned to the protons associated with  $[-\text{C}(\text{H})=\text{N}-]$ , while the resonances at  $\delta$  7.39 (d,  $J = 7.8\text{ Hz}$ ), 7.31–7.24 (m), 7.03 (d,  $J = 8.4\text{ Hz}$ ) and 6.61 (t,  $J = 7.2\text{ Hz}$ ) ppm to aromatic protons of the ligand. The  $\eta^5\text{-C}_5\text{Me}_5$  protons resonated as a singlet at  $\delta$  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  $\delta$  9.69 corresponding to aldehydic protons in  $^1\text{H}$  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  $\text{EPh}_3$  ( $\text{E} = \text{P}, \text{As}$ ) disrupts symmetric coordination of  $\text{H}_2\text{bsh}$  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  $-\text{C}(\text{H})=\text{N}-$  proton in the  $^1\text{H}$  NMR spectra of complexes **3–6**. The metal coordi-

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