

## Mononuclear hydridocarbonyl ruthenium complexes incorporating N<sub>2</sub>O<sub>2</sub> bis-chelating ligands

Manoj Trivedi <sup>a</sup>, Manish Chandra <sup>a</sup>, Daya Shankar Pandey <sup>a,\*</sup>, M. Carmen Puerta <sup>b</sup>, Pedro Valerga <sup>b</sup>

<sup>a</sup> Department of Chemistry Awadhesh Pratap Singh University, Rewa 486 003, MP, India

<sup>b</sup> Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

Received 18 October 2003; accepted 9 December 2003

### Abstract

The reactions of [RuH(CO)Cl(PPh<sub>3</sub>)<sub>3</sub>] with *N,N'*-bis(salicylidine)-hydrazine (H<sub>2</sub>bsh) and *N,N'*-bis(salicylidine)-*p*-phenylene diammine (H<sub>2</sub>bsp) in presence of KOH in methanol led in the formation of neutral mononuclear complexes with the formulations [RuH(CO)(PPh<sub>3</sub>)<sub>2</sub>(L)] (L=Hbsh or Hbsp). These present the first examples where the ligands H<sub>2</sub>bsh or H<sub>2</sub>bsp provide only two of its available donor sites for interaction with the metal centre. The complexes have been characterized by elemental analyses, FAB-MS, IR, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR and electronic spectral studies. Molecular structure of the representative complex [RuH(CO)(PPh<sub>3</sub>)<sub>2</sub>(Hbsh)] have been determined by single crystal X-ray analysis.

© 2003 Published by Elsevier B.V.

**Keywords:** Ruthenium; *N,N'*-bis(salicylidine)-hydrazine(H<sub>2</sub>bsh); *N,N'*-bis(salicylidine)-*p*-phenylene diammine (H<sub>2</sub>bsp); Mononuclear

### 1. Introduction

During past couple of decades much attention has been paid towards synthesis and characterization of ruthenium (II) poly-pyridyl complexes because of their interesting photo-physical and photochemical properties and their potential use in various fields [1]. In this regard, ligands that can serve as molecular bridges between metal centers and that also contain delocalized  $\pi$  electron system have drawn special attention [2]. Because of our interests in this area we have examined reactivity of pyridyl azine ligands with metal complexes under varying conditions and have shown that the N<sub>2</sub> diazine linkage in pyridine-2-carbaldehyde azine offers several possible mononucleating and binucleating modes due to flexibility of the N–N single bond [3]. Literature survey further revealed that there are only a few reports dealing with the closely related N<sub>2</sub>O<sub>2</sub> donor

Schiff's base ligand *N,N'*-bis(salicylidine)-hydrazine wherein, the flexibility of N–N may offer several modes for interaction with the metal ions and their complexes. At the same time structurally characterized complexes of H<sub>2</sub>bsh are rare, and in the known complexes it adopted *trans* configuration [4]. As the ligand possesses four donor sites in the form of two oxygen and nitrogen donor atoms, it can act as mono, bi, tri and tetradentate ligand. In general, it interacts with the metal center through both of its bis-chelating O, N donor sites leading to the formation of binuclear complexes. There are no reports dealing with the complexes of H<sub>2</sub>bsh in which, it interacts through only one of its O, N donor sites to form mononuclear complexes. We have successfully isolated and structurally characterized mononuclear complex of the second category from the interaction of the hydrido carbonyl complex [RuH(CO)Cl(PPh<sub>3</sub>)<sub>3</sub>] with H<sub>2</sub>bsh. Also, we have isolated mononuclear complex resulting from interaction of [RuH(CO)Cl(PPh<sub>3</sub>)<sub>3</sub>] with closely related ligand H<sub>2</sub>bsp under analogous reaction conditions.

\* Corresponding author. Tel./fax: +91-7662-230684.

E-mail address: [dsprewa@yahoo.com](mailto:dsprewa@yahoo.com) (D.S. Pandey).

## 2. Results and discussion

We report herein, formation of new mononuclear complexes  $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{L})]$  (Complex **1**:  $\text{L} = \text{Hbsh}$ ; Complex **2**:  $\text{L} = \text{Hbsp}$ ) which were obtained in quantitative yield by reaction of the  $[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3]$  with respective ligand in methanol in presence of KOH as shown in Scheme 1.

The complexes **1**  $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{Hbsh})]$  and **2**  $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{Hbsp})]$  were synthesized in excellent yields and characterized by satisfactory elemental analyses and spectral data [5]. The FAB MS, analytical and NMR ( $^1\text{H}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY and  $^{31}\text{P}$ ) of the complexes corresponded to their respective formulations. In the electronic absorption spectrum of the complex **1** and **2** the MLCT transitions appeared in the visible region at 478 (15950), 450 (12300) nm while ligand-centered transitions were observed at 338 (27550) and 355 (46220) nm, respectively.

Analytical and spectral data of the complexes **1** and **2** corresponded to mononuclear complexes in which the ligand  $\text{H}_2\text{bsh}$  or  $\text{H}_2\text{bsp}$  interacted with the metal centre through only one of the O, N donor sites of the respective ligand. Further, its authentication was achieved by single crystal X-ray diffraction analysis of the representative complex  $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{Hbsh})]$  [6]. The molecular structure of the complex **1** (Fig. 1) shows that the coordination geometry about the metal centre ruthenium is distorted octahedral and is completed by N(1) and O(1) from Hbsh, P(1) and P(2) from the triphenyl phosphine, C(15) from carbonyl group and H(1). The N(1)–Ru(1)–O(1) angle is  $83.89(11)^\circ$  which suggested inward bending of the salicylidine moiety and smaller value of this angle as compared to that of ideal value of  $90^\circ$  is probably the source of observed distortion. The triphenylphosphine ligands are *trans* disposed as indicated by the P(1)–Ru(1)–P(2) angle of  $167.47(4)^\circ$ . The Ru(1)–P(1) and Ru(1)–P(2) distances are 2.3697(11) and 2.3499(11) Å, respectively. These are essentially equivalent and comparable to those in the other related complexes [7]. The Ru(1)–C(15) bond length is 1.815(4) Å, which is normal for Ru(II) carbonyls [8]. The Ru(1)–H(1) distance in the complex cation is 1.27(4) Å and is shorter than those found in the complex  $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]^+$  (1.7 Å) or  $[\text{RuHCl}(\text{PPh}_3)_3]$  (1.7 Å), and in other related complexes [9].

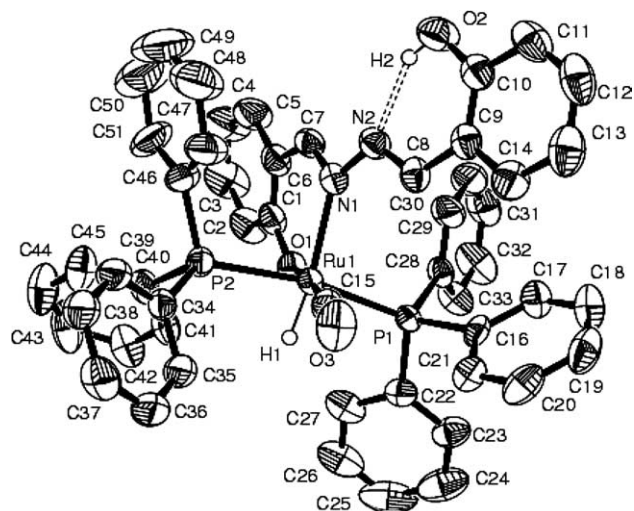
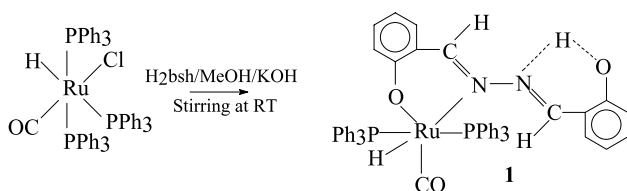


Fig. 1. Molecular structure of the complex **1**.

The ligand Hbsh is essentially planar and the C(7)–N(1)–N(2)–C(8) torsion angle is  $-166.1(4)^\circ$ . The Ru(1) to N(1) bond length is 2.219(4) Å. It is comparable to other Ru(II) ammine complexes and closely related polypyridyl complex  $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-tptz})]\text{BF}_4$  [8a]. The Ru(1)–O(1) bond is 2.102(3) Å and is comparable to those in other Ru(II) complexes [10]. The N(1)–N(2) bond distance is 1.409(5) Å, it can be defined as single bond and it is comparable with N–N bond length in ligand  $\text{H}_2\text{bsh}$  1.386(9) Å [11]. The C=N bond lengths C(7)–N(1) and C(8)–N(2) are essentially equal and are 1.287(5) and 1.282(6) Å, respectively and can be considered to have double bond character. The distance between O(2) and N(2) which are intramolecularly hydrogen bonded, is 1.641(5) Å and is comparable to those observed in analogous ligands which are thermochromic and photochromic in nature [12].

## 3. Conclusion

The results reported herein are very promising with regard to the synthesis of complexes having different coordination modes of the ligand  $\text{H}_2\text{bsh}$ . Further, it is well documented that the phenolato oxygen atom can be easily displaced by anionic species and coordinating solvents. Solvolysis of the latter kind is crucial in alkyne insertion. Due to presence of available reactive sites (Ru–O bonds) the complexes have the potential of displaying rich insertion chemistry. As N-salicylidine aniline and its derivatives are known to show photochromism and thermochromism, the complexes based on these ligands could also find applications in this area. So far, we have not looked into such possibilities. Follow up is in progress to synthesize new complexes, to optimize conditions and to look into reactivity and application of the resulting



Scheme 1.

complexes from interaction of *N, N'*-bis(salicylidine)-hydrazine and closely related ligands *N, N'*-bis(salicylidine)-*p*-phenylene diammine and *N, N'*-bis(salicylidine)-*p*-biphenylene diammine with metal complexes under varying conditions.

#### 4. Supporting information available

Crystallographic data for the complex **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 207465 in CIF format. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www://ccdc.cam.ac.uk](http://www://ccdc.cam.ac.uk)).

#### Acknowledgements

We acknowledge CSIR, New Delhi for financial assistance [HRDG 01(1784)/EMR-II/2002], the Head Department of Chemistry, A.P.S. University, Rewa for providing laboratory facilities and Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow for providing analytical and spectral facilities.

#### References

- [1] (a) R.D. Willet, D. Gatteschi, O. Kahn (Eds.), *Magneto-Structure Co-relations in Exchanged Coupled Systems*, Reidel, Dordrecht, Holland, 1985;
  - (b) R.A. Marcus, N. Sutin, *Biochem. Biophys – Acta* 265 (1985) 811;
  - (c) T.J. Meyer, *Pure & Appl. Chem.* 58 (1986) 1193;
  - (d) E. Amouyal, *Sol. Energy Matter. Sol. Cells* 38 (1995) 249;
  - (e) F. Bargiletti, L. Flamigni, *Chem. Soc. Rev.* 29 (2000) 1;
  - (f) J.M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, Germany, 1995;
  - (g) N.H. Dam-Rauer, G. Cerullo, A. Yeh, T.R. Bousie, C.V. Shank, J.K. McCusker, *Science* 275 (1997) 54;
  - (h) F.L. Carter, R.E. Siatkowski, J.N. Wohl (Eds.), *Molecular Electronics Devices*, North Holland, Amsterdam, The Netherlands, 1998;
  - (i) A. Beyeler, P. Belsler, *Coord. Chem. Rev.* 230 (2002) 29.
- [2] (a) N. Gupta, N. Grover, G.A. Neyhart, P. Singh, H.H. Thorp, *Inorg. Chem.* 32 (1993) 310;
  - (b) J. Granifo, M.E. Vargas, E.S. Dodsworth, D.H. Farrar, S. Fielder, A.B.P. Lever, *J. Chem. Soc. Dalton Trans.* (1996) 4369;
  - (c) E. Brauns, W. Sumner, J.A. Clark, S.M. Molnar, Y. Kawanishi, K.J. Brewer, *Inorg. Chem.* 36 (1997) 2861;
  - (d) C. Ceroni, F. Paolucci, S. Roffia, S. Serroni, S. Campagna, A.J. Bard, *Inorg. Chem.* 37 (1998) 2829;
  - (e) A. Klein, V. Kasack, R. Reinhardt, S. Torsten, T. Scheiring, S. Zalis, J. Fiedler, W. Kaim, *J. Chem. Soc. Dalton trans.* (1999) 575;
  - (f) P. Paul, B. Tyagi, A.K. Bilakhia, D. Partharthi, E. Suresh, *Inorg. Chem.* 39 (2000) 14;
  - (g) G. Albano, P. Belsler, C. Dual, *Inorg. Chem.* 40 (2001) 1408.
- [3] M. Chandra, A.N. Sahay, S.M. Mobin, D.S. Pandey, *J. Organomet. Chem.* 658 (2002) 43.
- [4] (a) J. Saroja, V. Manivannan, P. Chakraborty, S. Pal, *Inorg. Chem.* 34 (1995) 3099;
  - (b) S. Gopinathan, S.A. Pardhy, C. Gopinathan, V.G. Puranik, S.S. Tavale, T.N.G. Row, *Inorg. Chim. Acta* 111 (1986) 133;
  - (c) M. Mikuriya, M. Fukuya, *Chem. Lett.* (1998) 421;
  - (d) S. Pal, S. Pal, *Inorg. Chem.* 40 (2001) 4807.
- [5] (a) Preparation of [RuH(CO)(PPh<sub>3</sub>)<sub>2</sub>(Hbsh)] **1**. *N, N'*-bis(salicylidine)-hydrazine, (H<sub>2</sub>bsh) (0.240 g, 1 mmol) in methanol (30 ml) was treated with KOH (0.056 g, 1.0 mmol) and the resulting suspension was stirred at room temperature for 1.0 h. Slowly the suspension dissolved and bright orange yellow solution was obtained. It was filtered through celite to remove any solid impurities and to the filtrate [RuH(CO)Cl(PPh<sub>3</sub>)<sub>3</sub>] (0.953 g, 1.0 mmol) was added and stirred at room temperature for about 20 h. Orange red compound separated. It was filtered and extracted with diethyl ether. Upon slow evaporation it gave orange red flakes in a couple of days quantitatively. The crystals were separated by filtration dried in vacuo (0.607 g, 68%). (Found: C, 68.50; H, 4.72; N, 3.27%, C<sub>51</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Ru requires C, 68.45; H, 4.70; N, 3.13%;  $\nu$  (cm<sup>-1</sup>)(Ru–H) 2005,  $\nu$ (CO) 1954, (bands due to Hbsh, PPh<sub>3</sub>, and counter anion BF<sub>4</sub><sup>-</sup>) 1625, 1593, 1475, 1434, 1394, 1087, 1055, 950.8, 848, 746, 696;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 8.127 (s), 7.61 (m), 7.256(m), 6.91 (d, 8.4 Hz), 6.74 (t, 7.2 Hz), 6.56 (d, 7.5 Hz), 6.23 (d, 9 Hz), 6.09 (d, 8.7 Hz), 6.91 (t, 7.2 Hz), (Ru–H) –10.6 (t);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 18.90 (s); UV–VIS. (CHCl<sub>3</sub>,  $\lambda_{\text{max}}$  nm): 478 (15950), 338 (27550), 292 (38400);
  - (b) Preparation of [RuH(CO)(PPh<sub>3</sub>)<sub>2</sub>(Hbsp)] **2**. Complex **2** was prepared by the same method as described for complex **1** except that *N, N'*-bis(salicylidine)-*p*-phenylene diammine (H<sub>2</sub>bsp) was used in place of *N, N'*-bis(salicylidine)-hydrazine (H<sub>2</sub>bsh). The complex separated as mustard yellow blocks. (0.590 g, 61%). Found: C, 70.48; H, 4.72; N, 2.92%, M<sup>+</sup> 969. C<sub>57</sub>H<sub>46</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Ru requires C, 70.51; H, 4.74; N, 2.88%, M (969); cm<sup>-1</sup>  $\nu$  (Ru–H) 2001,  $\nu$ (CO) 1953.8, (bands due to Hbsp, PPh<sub>3</sub> and counter anion PF<sub>6</sub><sup>-</sup>) 1625, 1591, 1477, 1434, 1305, 1091, 997, 840, 775, 746, 696, 516;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 9.338 (d, 4.9 Hz), 8.96 (t, 2.3 Hz), 8.791(s), 8.586 (d, 6.7 Hz), 7.983 (d, 3.5 Hz), 7.45 (m, 1H), (Ru–H) –10.9 (t);  $\delta_{\text{P}}$ (CDCl<sub>3</sub>) 21.6 (s); UV–VIS. (CHCl<sub>3</sub>,  $\lambda_{\text{max}}$  nm): 450(12300), 355 (46220), 273(48900).
- [6] Crystal and structure solution data for **1**: C<sub>51</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Ru, FW = 893.88, Orthorhombic, space group = P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19), D<sub>c</sub> = 1.349 g cm<sup>-3</sup>, Z = 4, a = 11.7604(11), b = 14.5961(13), c = 25.633(2) Å, V = 4400.1(7) Å<sup>3</sup>, T = 293 K, Bruker SMART APEX 3-circle diffractometer with CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz,  $\lambda$  (Mo K $\alpha$ ) = 0.71073 Å,  $\mu$  (Mo K $\alpha$ ) = 0.474 mm<sup>-1</sup>. Of 3898 reflections measured 7759 were unique ( $R_{\text{int}}$  = 0.045). Structure was solved by direct methods. Refinement on F<sup>2</sup> concluded with the values  $R(\text{all}) = 0.0448$ ,  $R(\text{gt}) = 0.0426$ ,  $wR(\text{all}) = 0.0950$ ,  $wR(\text{gt}) = 0.0940$  and GOF = 1.040 (all = 7759 reflections and gt = 7507 reflections with  $I > 2\sigma_I$ ,  $w = [\sigma^2(F_o^2) + (0.0431P)^2 + 3.6920P]^{-1}$  where  $P = (F_o^2 + 2F_c^2)/3$ ). All non-hydrogen atoms were anisotropically refined. The hydrogen atom H(1) was localized in a regular difference Fourier map and was allowed to refine isotropically. The remaining hydrogen were geometrically calculated and refined using the SHELX riding model. The absolute structure Flack parameter was 0.01(3) for the selected enantiomorph. Minimum and maximum residual electron density peaks were –0.859 and +0.061 e Å<sup>-3</sup>, respectively.
- [7] (a) J.C. Mc Conway, A.C. Skapski, L. Phillips, R.J. Young, G. Wilkinson, *J. Chem. Soc. Chem. Commun.* (1974) 327;
  - (b) I. de Los Rios, M.J. Tenorio, M.A.J. Tenorio, M.C. Puerta, P. Valerga, *J. Organomet. Chem.* 525 (1996) 57;
  - (c) P. Ghosh, A. Chakravorty, *Inorg. Chem.* 36 (1997) 64;

- (d) O.S. Sisodia, A.N. Sahay, D.S. Pandey, U.C. Agrawala, N.K. Jha, P. Sharma, A. Toscano, A. Cabrera, *J. Organomet. Chem.* 560 (1998) 35.
- [8] (a) M. Chandra, A.N. Sahay, D.S. Pandey, M.C. Puerta, P. Valerga, *J. Organometal. Chem.* 648 (2002) 39;  
(b) M.F. McGuiggan, L.H. Pignolet, *Inorg. Chem.* 21 (1982) 2523;  
(c) A. Sahajpal, S.D. Robinson, M.A. Mazid, M. Motevalli, M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.* (1990) 2119.
- [9] (a) K. Osakada, T. Yamamoto, A. Yamamoto, A. Takenaka, Y. Sasada, *Inorg. Chim. Acta L* 9 (1979) 105;  
(b) A.C. Skapski, P.G.H. Throughton, *J. Chem. Soc. Chem. Commun.* (1968) 1230;
- (c) G.J. Philip, J.R. Steven, C.-L. Lee, B.R. James, *Inorg. Chem.* 30 (1991) 4617;  
(d) R. Atencio, B. Christina, M.A. Esteruelas, J.L. Fernando, L.A. Oro, *J. Chem. Soc. Dalton Trans.* (1995) 2171;  
(e) M.R. Churchill, K.M. Keil, F.V. Bright, S. Pandey, G.A. Baker, J.B. Keister, *Inorg. Chem.* 39 (2000) 5807.
- [10] B.K. Panda, S. Chattopadhyaya, K. Ghosh, A. Chakravorty, *Organometallics* 21 (2002) 2773.
- [11] X.-X. Xu, X.-Z. You, Z.-F. Sun, X. Wang, H.-X. Liu, *Acta Crystallogr. C* 50 (1994) 1169.
- [12] N. Hoshini, T. Inabe, Y. Maruyama, *Bull. Chem. Soc. Jpn.* 61 (1988) 4207.