

# PHOTOCHEMICAL SYNTHESIS AND SPECTROSCOPIC STUDIES OF Cr, Mo, W METAL CARBONYL COMPLEXES WITH BIDENTATE 'N'- DONOR SCHIFF'S BASES

Amit Singhal<sup>1</sup>, Manoj Agarwal<sup>2</sup>, Manish Kaushik<sup>3</sup>

<sup>1</sup> Department of Chemistry, Monad University, Pilakhwa, Hapur, Uttar Pradesh

<sup>2,3</sup> Department of Applied Sciences, Accurate Institute of Management & Technology, Gr. NOIDA

## ABSTRACT

We have synthesized six complexes  $\{M(CO)_4[L]\}$  1a-1c and 2a-2c (1a, M = Cr, L=SB<sup>1</sup>, R = H; 1b, M = Mo, L=SB<sup>1</sup>, R = H; 1c, M = W, L=SB<sup>1</sup>, R = H; 2a, M = Cr, L=SB<sup>2</sup>, R = Ph; 2b, M = Mo, L=SB<sup>2</sup>, R = Ph; 2c, M = W, L=SB<sup>2</sup>, R = Ph) by photochemical displacement of two CO group from  $M(CO)_6$  by phenyl-N-((pyridin-2-yl)methylene)methanamine [SB<sup>1</sup>], and (Z)-phenyl-N-(phenyl(pyridin-2-yl)methylene)methanamine [SB<sup>2</sup>]. The synthesized complexes exhibit variable degree of antibacterial activity. The complexes have been characterized by elemental analysis, IR, [<sup>1</sup>H]-NMR spectroscopy and magnetic studies. The spectroscopic studies suggest a bidentate behavior of the ligand via pyrimidine-N and amine-N donor atoms with the metal (0).

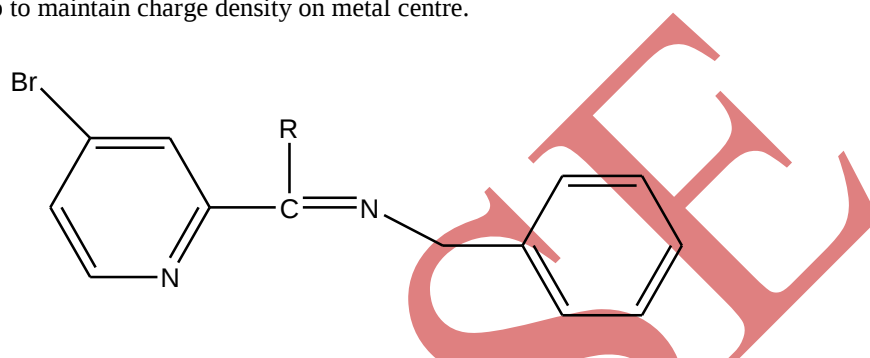
**Keywords-** Schiff Bases, Coordination Chemistry, N-Donor Schiff Bases, Antibacterial Activity.

## I INTRODUCTION

A Schiff base is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen. Schiff bases are of the general formula  $R_1R_2C=N-R_3$ , where R<sub>3</sub> is an aryl or alkyl group that makes the Schiff base a stable imine. Monodentate Schiff's bases are less known to form stable complexes, probably due to the insufficient basic strength of the imino nitrogen of the C=N group. Polydentate Schiff bases with phenolic OH or nitrogen or sulphur of the ring, suitably near to the imino nitrogen, may stabilize the metal-nitrogen bond through the formation of chelate rings. Schiff bases which are unaided by those donors but contain two azomethine nitrogen atoms, in spite of their facile ligating capabilities due to easy chances of chelation, have also been used in the CO displacement reactions of group VI metal carbonyls [1].

Metal-organic complexes containing bridged ligands are of current interest because of their continued interest due to their interesting molecular structure and their different functionalities [2-8]. Due to the versatile coordination modes of the ambidentate thiocyanate and azide ligands, these pseudohalide ligands have become the most extensively studied building blocks in the multi-dimensional complexes [9-10]. We have synthesized

polynuclear complexes of the type 1a-1c and 2a-2c (1a,  $M = Cr$ ,  $L = SB^1$ ,  $R = H$ ; 1b,  $M = Mo$ ,  $L = SB^1$ ,  $R = H$ ; 1c,  $M = W$ ,  $L = SB^1$ ,  $R = H$ ; 2a,  $M = Cr$ ,  $L = SB^2$ ,  $R = Ph$ ; 2b,  $M = Mo$ ,  $L = SB^2$ ,  $R = Ph$ ; 2c,  $M = W$ ,  $L = SB^2$ ,  $R = Ph$ ) has been synthesized by photochemical displacement of two CO groups in group-6 metal carbonyls with by phenyl-N-((pyridin-2-yl)methylene)methanamine [ $SB^1$ ] and (Z)-phenyl-N-(phenyl(pyridin-2-yl)methylene)methanamine [ $SB^2$ ]. Both the ligands & their complexes were characterized on the basis of physical properties, elemental analysis data, magnetic studies, infrared and nuclear magnetic resonance spectroscopy. It was found that the ligands have bidentate nature coordinating through two N donor atom. Thus replacing two CO group to maintain charge density on metal centre.



**Ligand  $SB^{1-2}$  (Z)-N-(1-(4-bromopyridin-2-yl)alkylidene)(phenyl)methanamine**

## II EXPERIMENTAL

Reactions were carried out under dry argon or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs and  $CH_2Cl_2$ . All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at  $120^\circ C$ , molecular weight of the complexes were determined cryoscopically in benzene, cyclooctadiene (COD), n-hexane, n-pentane, benzene were purchased from E. Merck, and  $M(CO)_6$  ( $M = Cr, Mo, W$ ), dichloromethane were purchased from Aldrich and were used as supplied.

Magnetic susceptibility measurements of the complexes were carried out by Gouy method. UV irradiation were performed with a medium pressure 400W mercury lamp through a quartz bulb.

### 2.1 SYNTHESIS OF THE LIGANDS-

#### SYNTHESIS OF LIGAND PHENYL-N-((PYRIDIN-2-YL)METHYLENE)METHANAMINE [ $SB^1$ ]

The ligand phenyl-N-((pyridin-2-yl)methylene)methanamine [ $SB^1$ ] was prepared by literature method [11] as followed. 0.107 g, (1.0 mmol) of picolinaldehyde was refluxed with 0.107 g (1.0 mmol) benzylamine (phenylmethanamine) in 20ml dehydrated alcohol. After 10h, the reaction mixture was evaporated under reduced pressure to yield gummy mass, which was dried and stored in vacuo. Yield 78.7%. Analysis Calc. for  $C_{13}H_{12}N_2$  Mol. Wt. 196.25, C, 79.56; H, 6.16; N, 14.27 found Mol. Wt. 195.62, C, 78.97; H, 5.90; N, 14.19.

The other ligands were prepared similarly.

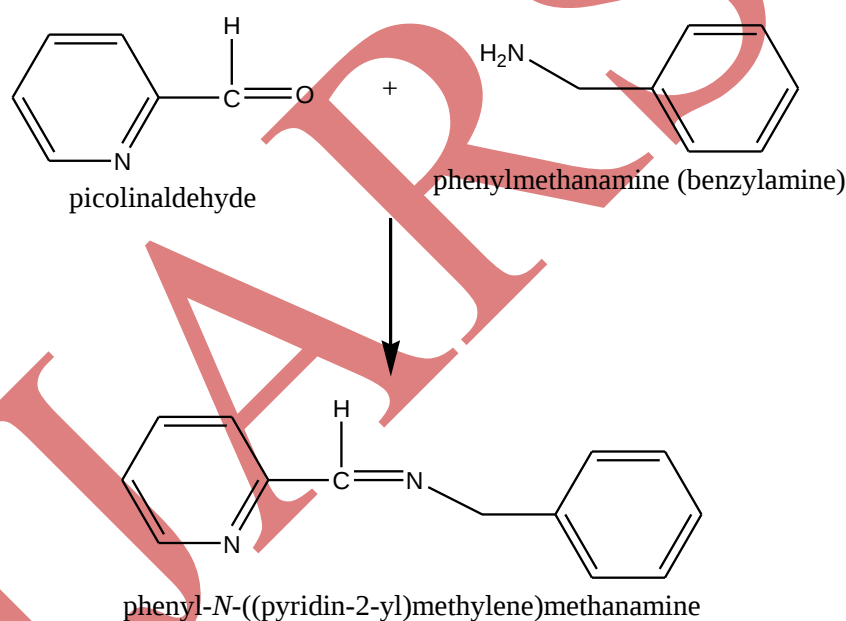
## 2.2 PREPARATION OF COMPLEXES

Complexes  $\{M(CO)_4[SB^{1-2}]\}$  were prepared by the photochemical reactions of  $M(CO)_5THF$  ( $M=Cr, Mo, W$ ) with phenyl-N-((pyridin-2-yl)methylene)methanamine [ $SB^1$ ] and (Z)-phenyl-N-(phenyl(pyridin-2-yl)methylene)methanamine [ $SB^2$ ] and obtained in 75-80% yield by similar methods of which the following is typical.

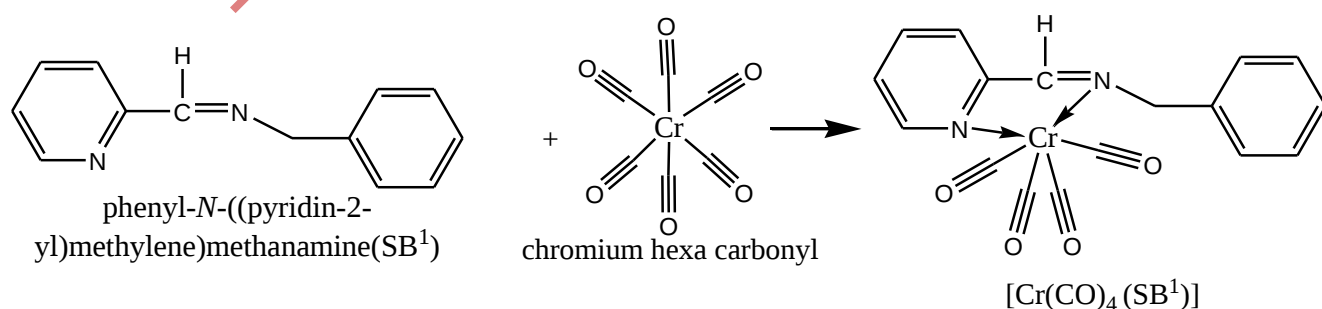
### 2.3 PREPARATION OF COMPLEX $\{Cr(CO)_4[SB^1]\}$

A solution of  $Cr(CO)_6$  (0.22g; 1.0 mmole) in 70ml of THF was irradiated to obtain  $Cr(CO)_5THF$  with UV light in a quartz vessel under a stream of argon for 2½Hr. at room temperature. A solution of  $SB^1$  (0.196 g; 1.0mmole) in 25ml of THF was added to the resulting solution of  $Cr(CO)_5THF$  intermediate. The reaction mixture was irradiated again at room temperature for 2½Hr. at same conditions. During this irradiation the solution changed from yellow to brown. The solvent was removed under vacuum afford a brown, airstable (75% yield). Unreacted  $Cr(CO)_6$  removed by washing the residue several times with light petroleum (40-60°C). The product was recrystallised in benzene.

#### Scheme 1 – Preparation of Ligand $SB^1$ : Reaction of picolinaldehyde with phenylmethanamine (benzyl amine)



#### Scheme 2 – Preparation of Complexes: Reaction of phenyl-N-((pyridin-2-yl)methylene)methanamine ( $SB^1$ ) with $Cr(CO)_6$



**Table 1a : Physical and analytical data of Ligands (SB<sup>1-2</sup>)**

| Ligands              | Molecular Formula                              | Yield (%) | M.p. (°C) | Colour | Found (Calcd.) (%) |              |                | Mol. Wt.         |
|----------------------|------------------------------------------------|-----------|-----------|--------|--------------------|--------------|----------------|------------------|
|                      |                                                |           |           |        | C                  | H            | N              |                  |
| a (SB <sup>1</sup> ) | C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> | 78.7      | 129       | Cream  | 78.9<br>(79.6)     | 5.9<br>(6.2) | 14.2<br>(14.3) | 195.6<br>(196.3) |
| b (SB <sup>5</sup> ) | C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> | 76.7      | 141       | Yellow | 82.9<br>(83.8)     | 5.4<br>(5.9) | 10.2<br>(10.3) | 271.1<br>(272.3) |

**Table 1b : Physical and analytical data of Complexes**

| Complexes | Molecular Formula                                               | Yield (%) | M.p. (°C) | Colour       | Found (Calcd.) (%) |              |              | Mol. Wt.         |
|-----------|-----------------------------------------------------------------|-----------|-----------|--------------|--------------------|--------------|--------------|------------------|
|           |                                                                 |           |           |              | C                  | H            | N            |                  |
| 1a        | C <sub>17</sub> H <sub>12</sub> CrN <sub>2</sub> O <sub>4</sub> | 78        | 146       | Light Yellow | 55.4<br>(56.1)     | 4.2<br>(4.4) | 7.5<br>(7.7) | 364.0<br>(364.3) |
| 2a        | C <sub>17</sub> H <sub>12</sub> MoN <sub>2</sub> O <sub>4</sub> | 74        | 154       | Yellow       | 49.1<br>(50.0)     | 3.5<br>(3.9) | 6.7<br>(6.9) | 408.3<br>(410.0) |
| 3a        | C <sub>17</sub> H <sub>12</sub> WN <sub>2</sub> O <sub>4</sub>  | 79        | 165       | Yellow       | 40.5<br>(41.2)     | 3.1<br>(3.3) | 5.1<br>(5.6) | 496.0<br>(496.2) |
| 1b        | C <sub>23</sub> H <sub>16</sub> CrN <sub>2</sub> O <sub>4</sub> | 76        | 167       | Light Yellow | 62.2<br>(62.7)     | 4.3<br>(4.6) | 6.1<br>(6.4) | 440.1<br>(440.4) |
| 2b        | C <sub>23</sub> H <sub>16</sub> MoN <sub>2</sub> O <sub>4</sub> | 78        | 170       | Yellow       | 56.4<br>(57.0)     | 4.0<br>(4.2) | 5.2<br>(5.8) | 484.4<br>(486.0) |
| 3b        | C <sub>23</sub> H <sub>16</sub> WN <sub>2</sub> O <sub>4</sub>  | 76        | 172       | Cream        | 48.1<br>(48.3)     | 3.3<br>(3.5) | 4.6<br>(4.9) | 572.1<br>(572.3) |

**Table 2a. Selected IR bands ( $\text{cm}^{-1}$ ) and ( $^1\text{H}$ )-NMR (ppm) data of  $\text{SB}^{1-5}$  ligands**

| Ligand | Selected IR bands ( $\text{cm}^{-1}$ ) |              | $^1\text{H}$ -NMR (in $\text{CDCl}_3$ ) $\delta$ ppm                                                          |
|--------|----------------------------------------|--------------|---------------------------------------------------------------------------------------------------------------|
|        | Imine $\nu$ ( $\text{C}=\text{N}$ )    | Pyrimidine N |                                                                                                               |
| a      | 1590                                   | 1340         | 8.45 (d, 1H, $-\text{CH}$ ), 3.74 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ )           |
| b      | 1597                                   | 1368         | 7.27 (s, 5H, $\text{C}_6\text{H}_5$ ), 4.84 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ ) |

**Table 2b. Selected IR bands ( $\text{cm}^{-1}$ ) and ( $^1\text{H}$ )-NMR (ppm) data of complexes**

| Complex | Selected IR bands ( $\text{cm}^{-1}$ ) |                                     |              | $^1\text{H}$ -NMR (in $\text{CDCl}_3$ ) $\delta$ ppm                                                          |
|---------|----------------------------------------|-------------------------------------|--------------|---------------------------------------------------------------------------------------------------------------|
|         | $\nu$ (CO)                             | Imine $\nu$ ( $\text{C}=\text{N}$ ) | Pyrimidine N |                                                                                                               |
| 1a      | 2068, 2017, 1958, 1934                 | 1574                                | 1306         | 8.10 (d, 1H, $-\text{CH}$ ), 2.60 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ )           |
| 2a      | 2067, 2015, 1957, 1932                 | 1575                                | 1308         | 8.11 (d, 1H, $-\text{CH}$ ), 2.64 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ )           |
| 3a      | 2068, 2017, 1958, 1934                 | 1577                                | 1305         | 8.13 (d, 1H, $-\text{CH}$ ), 2.61 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ )           |
| 1b      | 2069, 2013, 1949, 1930                 | 1574                                | 1314         | 7.48 (s, 5H, $\text{C}_6\text{H}_5$ ), 4.81 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ ) |
| 2b      | 2072, 2018, 1959, 1935                 | 1577                                | 1307         | 7.49 (s, 5H, $\text{C}_6\text{H}_5$ ), 4.82 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ ) |
| 3b      | 2072, 2018, 1958, 1935                 | 1570                                | 1312         | 7.47 (s, 5H, $\text{C}_6\text{H}_5$ ), 4.80 (s, 2H, $-\text{CH}_2-$ ), 7.36 (s, 5H, $-\text{C}_6\text{H}_5$ ) |

### III RESULTS AND DISCUSSION

The ligands were prepared by condensation reaction of benzylamine (phenylmethanamine) of was refluxed with corresponding 1-(pyridin-2-yl)alkyl-1-one according to Scheme-1. Complexes (1a-3c) were prepared by photochemical reaction as shown in Scheme-2. Analytical data for  $\{\text{M}(\text{CO})_4[\text{SB}^1]\}$  (1a-3a) and  $\{\text{M}(\text{CO})_4[\text{SB}^2]\}$  (1b-3b); where (M= Cr, Mo & W) complexes are given in Table-1b.

In this study, photochemical reactions of  $\text{M}(\text{CO})_6$  (M=Cr, Mo & W) with phenyl-N-((pyridin-2-yl)methylene)methanamine  $[\text{SB}^1]$  and (Z)-phenyl-N-(phenyl(pyridin-2-yl)methylene)methanamine  $[\text{SB}^2]$  ligands occurs in expected manner, and gave hither to a series of complexes (1a)-(1b); (2a)-(2b) and (3a)-(3b)

occur via the displacement of two CO from  $M(CO)_6$  ( $M=Cr, Mo \text{ \& } W$ ) and co-ordination of metal atom via imine-N and pyridine-N donor atoms yielding  $M(CO)_4L$  complexes.

The i.r. spectra of ligands and the corresponding complexes provide information about the metal-ligand bonding. Important IR spectral bands  $M(CO)_4L$  ( $L = \text{phenyl-N-((pyridin-2-yl)methylene)ethanamine [SB}^1]$  and (Z)-phenyl-N-(phenyl(pyridin-2-yl)methylene)ethanamine [SB<sup>2</sup>] and  $M=Cr, Mo \text{ \& } W$ ) are presented in Table-2b. The evidence about metal-imine nitrogen (M–N) bond formation is the shifting of C=N vibration found at  $1590\text{ cm}^{-1}$  in free ligand, shifts to lower wavelength in complexes 1a-3c, showing that the ligand coordinate to metal via the imine donor atom.[12]. The stretching vibrations found at  $3020\text{ cm}^{-1}$  in free ligand, shifts to lower wavelength in complexes showing that the ligand is coordinating via amine donor atom.

Four bands in the range ( $2068\text{--}2072\text{ cm}^{-1}$ ), ( $2013\text{--}2018\text{ cm}^{-1}$ ), ( $1949\text{--}1958\text{ cm}^{-1}$ ) and ( $1932\text{--}1936\text{ cm}^{-1}$ ) arising from  $\nu(CO)$  vibrations are seen which presumably have local  $c_{2v}$  symmetry of  $M(CO)_4$  unit in  $\{M(CO)_4SB^1\}$  (1a-3a) and  $\{M(CO)_4SB^2\}$  (1b-3b); where ( $M=Cr, Mo \text{ \& } W$ ); complexes (Scheme-2). These values are in close resemblance to the values of  $\nu(CO)$  vibration for other nitrogen containing disubstituted group-6 metal carbonyls [13-16]. The presence of normal ligand bands indicated that these bands were intact in the complexes. The nature and number of CO bands resemble closely to the bands of other known trisubstituted metal carbonyls [17-20].

In addition, magnetic susceptibility measurement shows that (1a-3e) complexes were diamagnetic. Since these complexes have  $M(0)$  [ $M=Cr, Mo, W$ ] with a low spin  $d^6$  configuration. Such diamagnetism might arise from further splitting of the d-orbital in the low symmetry complexes i.e.  $d_{xy}^2, d_{xz}^2, d_{yz}^2, d(x^2-y^2)^0, dz^2^0$  [21, 22].

#### IV CONCLUSION

SB<sup>1-2</sup> ligands behave as a bidentate ligand via imine and pyridine N donor atom in 1a-3b. In view of above, we have now investigated the fifteen new complexes 1a-3b, which have been prepared for the first time, by the photochemical reaction of metal carbonyls  $M(CO)_6$  ( $M=Cr, Mo \text{ \& } W$ ), with (Z)-N-(1-(4-bromopyridin-2-yl)alkylidene)(phenyl)ethanamine (SB<sup>1-2</sup>).

The results show that (Z)-N-(1-(4-bromopyridin-2-yl)alkylidene)(phenyl)ethanamine and its metalcarbonyl derivatives exert a moderate inhibitory effect on different bacterial activity, thus confirming our previous data about the cytotoxic activity of these compounds.

#### V ACKNOWLEDGEMENTS

Sincere thanks are due to Head, Dept. of Chemistry, A.I.M.T., Greater Noida and Head, Dept. of Chemical Sciences, Monad University, Pilakhwa, Hapur for providing research facilities. Authors are also thankful to Dr. Vivek Kumar, Professor, IIT Roorkee, (Saharanpur Campus) for his constant encouragement to carry out such research work. Special thanks are also due to CDRI, Lucknow, Intertek, Mumbai, I.I.T., Roorkee, Research Lab, Delhi University and TIFR, Mumbai for allocation of time for various analyses.

## REFERENCES

- [1]. A. Srivastava *et. al.*, *Indian Journal of Chemistry*, **41A**, 785 (2002), A. Singh, M. Kumar, M. Kaushik, *Int. J. Applied Chem.*, **6(1)**, 49-58 (2010)
- [2]. H. Abourahma, B. Moulton, V. Kravtsov, M.J. Zaworotko, *J. Am. Chem. Soc.*, **124**, 9990 (2002), A. Singh, M. Kumar, M. Kaushik, *Int. J. Applied Chem.*, **6(1)**, 49-58 (2010)
- [3]. S. R. Batten, R. Robson, *Angew. Chem.*, **110**, 1558 (1998).
- [4]. S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.*, **41**, 1561 (2002).
- [5]. S. Konar, P.S. Mukherjee, E. Zangrando, F. Lloret, N.R. Chaudhuri, *Angew. Chem.*, **114**, 1631 (2002).
- [6]. S. Konar, P.S. Mukherjee, E. Zangrando, F. Lloret, N.R. Chaudhuri, *Angew. Chem. Int. Ed.*, **41**, 1561 (2002).
- [7]. S.K. Dey, N. Mondal, M.S. El. Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardia, T. Matsushita, V. Gramlich, S. Mitra, *Inorg. Chem.*, **43**, 2427 (2004).
- [8]. You Z-L & Zhu H-L, *Z. Anorg. Allg. Chem.*, **632**, 140 (2006).
- [9]. S. K. Dey, N. Mondal, M.S. El Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardia, T. Matsushita, V. Gramlich, S. Mitra, *Inorg. Chem.*, **43**, 2427 (2004).
- [10]. S. Sailaja, K. R. Reddy, M. V. Rajasekharan, C. Hureau, E. Riviere, J. Cano, J-J. Girerd, *Inorg. Chem.*, **42**, 180 (2003).
- [11]. H. Chowdhury, R. Ghosh, B.N. Sarkar, S.P Banerjee & B. K. Ghosh, *Ind. J. of Chem.*, **46A**, 1397-1400 (2007).
- [12]. J. E. Kovacic, *Spectrochim. Acta* **23A**, 182 (1967).
- [13]. S. W. Kirtley, in G. Eilkinson, F. G. A. Stone, E. W. Abel, (eds): "Comprehensive Organometallic Chemistry", Pergamon Press, Oxford, Vol. 3, p 1079, 1255 (1982).
- [14]. A. S. Cavallo, G. Solladie, E. Tsano, *Journal of Organometallic Chemistry*, **144**, 181 (1978).
- [15]. R. Lal Sc. K. Samanta (nee Bera), I. Banerjee, *Indian Journal of Chemistry*, **40A**, 144 (2001).
- [16]. W. Kaim, S. Kohlmann, *Inorganic Chemistry*, **26**, 68 (1987).
- [17]. Cotton F.A., Kraihanzel, C.S., *J.Am. Chem. Soc.*, **84**, 4432 (1962).
- [18]. Zahida OZER, Saim. OZKAR, *Turk. J. Chem.*, **23**, 9-14, (1999).
- [19]. Timmers, F.J., Wacholtz, W.F., *J.Chem. Ed.*, **71**, 987 (1994), King, R.B., *Organometallic Syntheses*, **Vol. 1**, Academic Press, New York, 125(1965).
- [20]. Abel E., Bennett, W.M.A., Burton, R. Wilkinson G., *J. Chem. Soc.*, 4559 (1958).
- [21]. Senem Karahan, Ploinkose, and Elif Subasi Hamdi Temel; *Synthesis and reactivity in Inorganic, Metal-organic, and Nano-Metal Chemistry*, **38**, 422-427 (2008).
- [22]. Ayodhya Singh, Munesh Kumar, Manish Kaushik, Seema Singh and Anjali Singh; *Oriental Journal of Chemistry*, **26(2)**, 601-606 (2010).