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

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ABSTRACT

We have synthesized six complexes {$M(CO)_4[L]$} 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) by photochemical displacement of two CO group from $M(CO)_6$ by phenyl-N-((pyridin-2-yl)methylene)methanamine [SB^1], and (Z)-phenyl-N-(phenyl(pyridin-2-yl)methylene)methanamine [SB^2]. The synthesized complexes exhibit variable degree of antibacterial activity. The complexes have been characterized by elemental analysis, IR, [^{1}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).

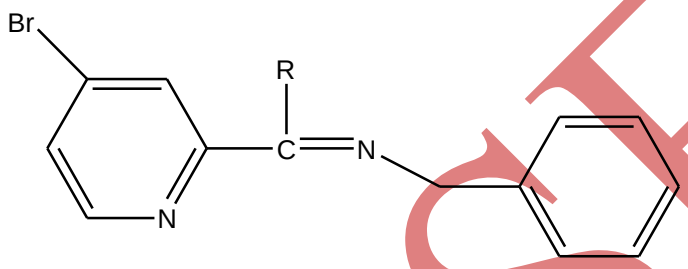
Keywords- Schiff Bases, Coordination Chemistry, N-Donor Schiff Bases, Antibacterial Activity.

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_3 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. Ploydentate 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°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 (phenylmethamine) 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.

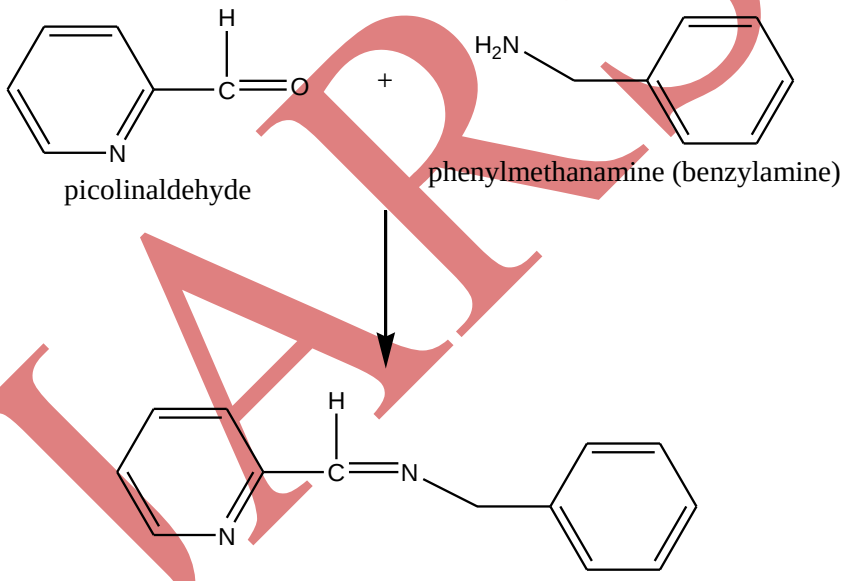
2.2 PREPARATION OF COMPLEXES

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 in typical.

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

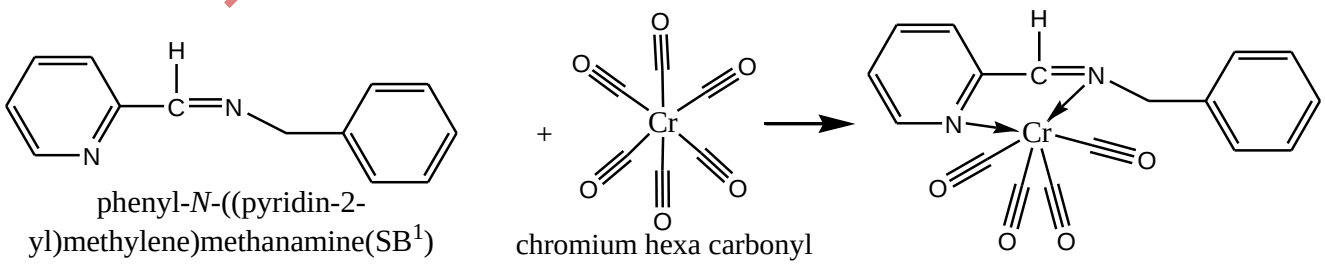
A solution of $Cr(CO)_6$ (0.22g; 1.0 mmole) in 70ml of THF was irradiated to obtain $Cr(CO)_5$ THF with UV light in a quartz vessel under a stream of argon for 2½Hr. at room temperature. A solution of SB^1 (0.196 g; 1.0mmole) in 25ml of THF was added to the resulting solution of $Cr(CO)_5THF$ intermediate. 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)



picolinaldehyde + phenylmethanamine (benzylamine) → phenyl-*N*-((pyridin-2-yl)methylene)methanamine

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



phenyl-*N*-((pyridin-2-yl)methylene)methanamine(SB^1) + chromium hexa carbonyl → $[Cr(CO)_4(SB^1)]$

Table 1a : Physical and analytical data of Ligands (SB^{1-2})

Ligands	Molecular Formula	Yield (%)	M.p. (^oC)	Colour	Found (Calcd.) (%)			Mol. Wt.
					C	H	N	
a (SB^1)	$C_{13}H_{12}N_2$	78.7	129	Cream	78.9 (79.6)	5.9 (6.2)	14.2 (14.3)	195.6 (196.3)
b (SB^5)	$C_{13}H_{12}N_2$	76.7	141	Yellow	82.9 (83.8)	5.4 (5.9)	10.2 (10.3)	271.1 (272.3)

Table 1b : Physical and analytical data of Complexes

Complexes	Molecular Formula	Yield (%)	M.p. (^oC)	Colour	Found (Calcd.) (%)			Mol. Wt.
					C	H	N	
1a	$C_{17}H_{12}CrN_2O_4$	78	146	Light Yellow	55.4 (56.1)	4.2 (4.4)	7.5 (7.7)	364.0 (364.3)
2a	$C_{17}H_{12}MoN_2O_4$	74	154	Yellow	49.1 (50.0)	3.5 (3.9)	6.7 (6.9)	408.3 (410.0)
3a	$C_{17}H_{12}WN_2O_4$	79	165	Yellow	40.5 (41.2)	3.1 (3.3)	5.1 (5.6)	496.0 (496.2)
1b	$C_{23}H_{16}CrN_2O_4$	76	167	Light Yellow	62.2 (62.7)	4.3 (4.6)	6.1 (6.4)	440.1 (440.4)
2b	$C_{23}H_{16}MoN_2O_4$	78	170	Yellow	56.4 (57.0)	4.0 (4.2)	5.2 (5.8)	484.4 (486.0)
3b	$C_{23}H_{16}WN_2O_4$	76	172	Cream	48.1 (48.3)	3.3 (3.5)	4.6 (4.9)	572.1 (572.3)

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

Ligand	Selected IR bands (cm^{-1})		^{1}H-NMR (in $CDCl_3$) δ ppm
	Imine ν (C=N)	Pyrimidine N	
a	1590	1340	8.45 (d, 1H, -CH), 3.74 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)
b	1597	1368	7.27 (s, 5H, C_6H_5), 4.84 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)

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

Complex	Selected IR bands (cm^{-1})			^{1}H-NMR (in CDCl3) δ ppm
	ν (CO)	Imine ν (C=N)	Pyrimidine N	
1a	2068, 2017, 1958, 1934	1574	1306	8.10 (d, 1H, -CH), 2.60 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)
2a	2067, 2015, 1957, 1932	1575	1308	8.11 (d, 1H, -CH), 2.64 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)
3a	2068, 2017, 1958, 1934	1577	1305	8.13 (d, 1H, -CH), 2.61 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)
1b	2069, 2013, 1949, 1930	1574	1314	7.48 (s, 5H, C_6H_5), 4.81 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)
2b	2072, 2018, 1959, 1935	1577	1307	7.49 (s, 5H, C_6H_5), 4.82 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)
3b	2072, 2018, 1958, 1935	1570	1312	7.47 (s, 5H, C_6H_5), 4.80 (s, 2H, $-CH_2-$), 7.36 (s, 5H, $-C_6H_5$)

III RESULTS AND DISCUSSION

The ligands were prepared by condensation reaction of benzylamine (phenylmethamine) 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 $\{M(CO)_4[SB^1]\}$ (1a-3a) and $\{M(CO)_4[SB^2]\}$ (1b-3b); where (M= Cr, Mo & W) complexes are given in Table-1b.

In this study, photochemical reactions of $M(CO)_6$ (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] 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 & 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 = phenyl-N-((pyridin-2-yl)methylene)methanamine [SB^1] and (Z)-phenyl-N-(phenyl(pyridin-2-yl)methylene)methanamine [SB^2] and M=Cr, Mo & 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 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 3020cm^{-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 (2068-2072 cm^{-1}), (2013-2018 cm^{-1}), (1949-1958 cm^{-1}) and (1932-1936 cm^{-1}) arising from ν (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 & W); complexes (Scheme-2). These values are in close resemblance to the values of ν (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^{1-2} ligands behave as a bidentate ligand via imine and pydidine 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 & W), with (Z)-N-(1-(4-bromopyridin-2-yl)alkylidene)(phenyl)methanamine (SB^{1-2}).

The results show that (Z)-N-(1-(4-bromopyridin-2-yl)alkylidene)(phenyl)methanamine 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.

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