

## Synthesis and spectroscopic characterization of molybdenum(0) and molybdenum(II) carbonyl benzophenoneazine complexes

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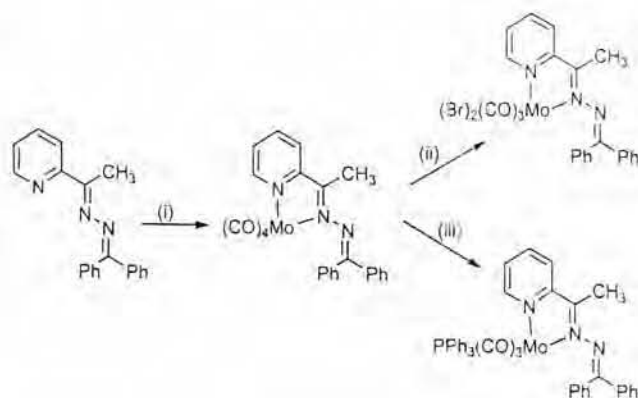
A chelating 2-methylpyridylbenzophenoneazine ligand has been prepared by the condensation of 2-acetylpyridine with benzophenone hydrazone. Reaction of the ligand with  $\text{Mo}(\text{CO})_6$  gives 12-methylpyridylbenzophenoneazine)tetracarbonylmolybdenum(0) complex where the ligand is bidentate N, N. Oxidative-addition of the tetracarbonyl complex with 1 mol equivalent of bromine, yields the neutral seven-coordinated dibromotricarbonylmolybdenum(II) azine complex. Treatment of the tetracarbonyl complex with 1 mol equivalent of  $\text{PPh}_3$  gives the expected tri-carbonylmolybdenum(0)-azine triphenylphosphine substituted complex.

Although the chemistry of molybdenum carbonyls is well established, the interest in the synthesis, chemical and physical properties of these compounds especially with new ligands of different nature and bonding behaviour are still being actively investigated by many workers<sup>1-4</sup>. In a previous paper<sup>5</sup>, we have reported the synthesis and X-ray crystal structural analysis of (2-methylpyridylbenzophenoneazine tetracarbonyl) molybdenum(0) complex **II**. The present note reports the synthesis and characterization of 2-methylpyridylbenzophenoneazine ligand, **I** and its complexes with molybdenum(0) or molybdenum(II) carbonyls (Scheme 1).

### Experimental

All chemicals were purchased from Fluka or Aldrich and were used without further purification.

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Scheme 1

Complexes of 2-methylpyridylbenzophenoneazine **I** with molybdenum. (i)  $\text{Mo}(\text{CO})_6$ , (ii)  $\text{Br}_2$  and (iii)  $\text{PPh}_3$

All solvents were dried and purified by standard methods. All reactions were carried out under nitrogen or argon atmosphere. Infrared spectra were recorded as KBr disc using a Perkin-Elmer 1600 Fourier-Transform Spectrometer. Micro-analyses were carried out using CHONS-Fisons Model EA 1108 elemental analyser.  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra were recorded on a Varian YH 400 Spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are relative to tetramethylsilane.

### Preparation of ligand **I**

2-Methylpyridylbenzophenoneazine ligand **I** was prepared by refluxing an equimolar (0.001 mol) of 2-acetyl pyridine and benzophenonehydrazone in dry ethanol (25 mL) for 6 h. The yellow reaction mixture obtained was concentrated and cooled to  $5^\circ\text{C}$  overnight. The yellow solid formed was filtered off, washed with pet-ether ( $40-60^\circ\text{C}$ ), recrystallized from hot ethanol and dried *in vacuo* over  $\text{P}_2\text{O}_5$ , yield: 2.20 g, 73%.

### Preparation of complexes

The synthesis of  $[\text{Mo}(\text{CO})_4\{\text{C}_5\text{H}_4\text{N}(\text{Me})\text{C}=\text{NN}=\text{C}(\text{Ph})_2\}]$  **II** has been reported in Ref. 5.

### $[\text{Mo}(\text{CO})_3(\text{Br}_2)\{\text{C}_5\text{H}_4\text{N}(\text{Me})\text{C}=\text{NN}=\text{C}(\text{Ph})_2\}]$ **III**

A solution of bromine in carbon tetrachloride (1.1 mL, 0.46 M,  $5 \times 10^{-4}$  mmol) was added dropwise to a solution of tetracarbonyl complex **II** (0.2537g,

$5 \times 10^{-4}$  mmol) in dry dichloromethane (15 mL) at 0 °C. The reaction mixture was put aside for 2 h after which the solvent was reduced. The light brown microcrystals obtained after addition of cold methanol, were filtered, washed with cold methanol and dried *in vacuo* over  $P_2O_5$ , yield 0.17 g, 53%.

$[Mo(CO)_3(PPh_3)\{C_5H_4N(Me)C=NN=C(Ph)_2\}]$  **IV**

The tetracarbonyl complex **II** (0.537 g,  $5 \times 10^{-4}$  mmol) was dissolved in xylene (20 mL) with constant stirring. Triphenylphosphine (0.133 g,  $5 \times 10^{-4}$  mmol) was then added and the solution refluxed for 2 h. The resulting dark purple solution obtained was allowed to cool to room temperature after which the required product **IV** precipitated out. This was filtered, washed with hexane and dried *in vacuo* over  $P_2O_5$ . Yield: 0.30 g, 80%.

### Results and discussion

2-Acetylpyridine condensed rapidly and completely with benzophenonehydrazone in ethanol to give the required azine ligand **I** in good yield. The physical and analytical data of **I** and its molybdenum complexes are presented in Table 1. The infrared spectra of the ligand and the complexes were recorded.

The infrared spectrum of **I** showed a medium intensity band at  $1565\text{ cm}^{-1}$  which is assigned as the  $\nu_{C=N}$  stretching frequency. Absorption band at  $657\text{ cm}^{-1}$  is attributable to the pyridine ring in-plane band<sup>6</sup>. The  $^1H$  NMR spectrum of **I** showed a singlet signal at 2.45 ppm which is assigned to  $CH_3C=N$  methyl hydrogen resonances. The pyridyl ring hydrogen resonances were located at 7.57 (triplet), 7.76 (triplet), 7.83 (doublet) and 8.60 (doublet) ppm due to pyridine- $H_5$ , pyridine- $H_4$ , pyridine- $H_3$  and pyridine- $H_6$  respectively. The  $^{13}C\{-^1H\}$  NMR spectrum of **I** showed two singlets at 159.06 and 159.57 ppm which are due to two azomethine  $C=N$  carbon resonances. The methyl carbon of the  $CH_3C=N$  moiety resonated as a singlet at 14.43 ppm.

We had investigated the behaviour of **I** as a ligand towards molybdenum carbonyls. Treatment of **I** with one mol of  $Mo(CO)_6$  in refluxing dry toluene displaced two carbonyls to give the required tetracarbonylmolybdenum(0) complex **II** which was isolated as red-brown micro crystals. The complex **II** showed a molar conductance of  $0.50\ \Omega^{-1}\text{ mol}^{-1}\text{ cm}^2$  in acetone ( $10^{-3}\text{ M}$ ) at 25°C which is typical for a non-electrolytes<sup>7</sup>. The electronic spectrum of the complex **II** in ethanol showed one maximum absorption band

Table I—Characterization data of **I** and its molybdenum complexes

Compound/ Stoichiometry	Colour	Found (Caled.) %		
		C	H	N
<b>I</b> $C_{20}H_{17}N_3$	Yellow	80.23 (80.20)	5.72 (5.70)	14.05 (14.04)
<b>II</b> $C_{24}H_{17}N_3O_4Mo$	Red- Brown	56.80 (56.81)	3.37 (3.37)	8.38 (8.36)
<b>III</b> $C_{23}H_{17}N_3Br_2O_3Mo$	Light Brown	43.22 (43.22)	2.68 (2.67)	6.57 (6.57)
<b>IV</b> $C_{41}H_{32}N_3O_3PMo$	Red- Brown	66.38 (66.40)	4.34 (4.34)	5.65 (5.66)

centered at 478 nm, which was clearly absent from the spectrum of the free ligand **I**. This absorption is assigned to metal-ligand charge transfer on the basis of its extinction coefficient value of  $\epsilon = 6820\text{ M}^{-1}\text{ cm}^{-1}$  (ref.8). The IR spectrum of this complex showed four sharp bands at 2012, 1906, 1872 and 1826 which are characteristic of a *cis* tetracarbonyl complex<sup>9</sup>. The  $\nu_{C=N}$  band is shifted to a lower frequency at  $1560\text{ cm}^{-1}$ , suggesting coordination of azomethine  $CH_3C=N$  nitrogen. The pyridine ring in-plane vibration band is found at a higher frequency and this suggests the coordination of the pyridine ring through its nitrogen<sup>10</sup>.

The presence of four carbonyls is further supported by  $^{13}C\{-^1H\}$  NMR data. The two axial carbonyl carbon resonances appeared equivalent and resonated as a singlet at 204.38 ppm, while the two singlet resonances at 224.14 and 222.83 ppm are due to the two equatorial carbonyl carbons<sup>11</sup>. The coordination of  $CH_3C=N$  nitrogen is supported by the observation of the downfield chemical shift of  $CH_3C=N$  imino carbon resonance.

In the  $^1H$  NMR spectrum of **II**, the methyl hydrogens of the  $CH_3C=N$  nitrogen moiety resonated as a singlet at a slightly downfield chemical shift of 2.60 ppm which further supported the coordination of  $CH_3C=N$  nitrogen to molybdenum. Additionally, all the pyridine ring hydrogen resonances were also observed at downfield chemical shifts, and this further supports the coordination of the pyridine ring nitrogen.

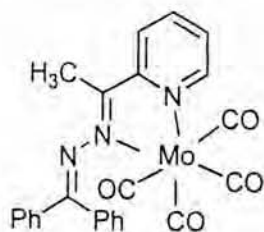
On the basis of the IR and  $^1H$  and  $^{13}C\{-^1H\}$  NMR data, the molecular structure of **II** is depicted as shown in structure **I** where the azine ligand **I** acted as a bidentate N, N chelating ligand, coordinating

Table 2— $^1\text{H}^a$  and  $^{13}\text{C}\{-^1\text{H}\}^b$  NMR data of **I** and its molybdenum complexes

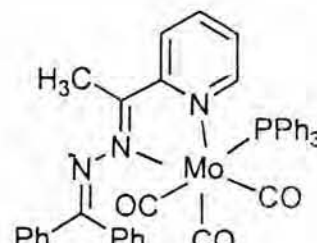
Proton/carbon atom	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>
$\text{CH}_3$	2.45 s	2.60 s	2.48 s	2.29 s
Py- $\text{H}_3$	7.83 d	7.88 t	7.91 t	*
Py- $\text{H}_4$	7.76 t	7.80 t	7.79 t	*
Py- $\text{H}_5$	7.57 td	7.70 t	7.7 t	*
Py- $\text{H}_6$	8.60 d	9.00 d	8.62 d	8.73 d
Phenyl-Hs	7.21-7.74 m	7.20-7.53 m	7.00-7.60 m	7.16-7.53 m
C=N	159.06 s	162.87 s		
	159.57 s	158.06 s	*	*
$\text{CH}_2$	14.43 s	16.32 s	*	*
$\text{C}\equiv\text{O}$	#	204.38 s	*	*
		222.83 s		
		224.14 s		
Py- $\text{C}_2$	155.80	154.08	*	*
Py- $\text{C}_3$	121.24	124.23	*	*
Py- $\text{C}_4$	135.36	136.67	*	*
Py- $\text{C}_5$	123.95	124.81	*	*
Py- $\text{C}_6$	148.56	152.94	*	*

All  $\delta$  values are in ppm relative to TMS. <sup>a</sup>Measured at 399.90 MHz in  $\text{CDCl}_3$ ;

<sup>b</sup>Measured at 100.57 MHz, # not observed; \*not obtained due to instability.



(I)

Molecular Structure of **II**

(II)

Proposed Molecular Structure of **IV**

through  $\text{CH}_3\text{C}=\text{N}$  and pyridyl nitrogens to give a five-membered chelate ring. This structure has been confirmed by a separate X-ray single crystal structure analysis which showed a distorted octahedral arrangement around the molybdenum atom, bonded to four carbonyl groups and both the imino and pyridyl nitrogens<sup>5</sup>.

We have also studied the oxidative-addition reaction of **II** by halogens. Treatment of **II** in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  with one mol equivalent of bromine in  $\text{CCl}_4$  gave the expected neutral seven-coordinated tricarbonylmolybdenum(II) complex **III** as air and moisture sensitive light brown solid. The IR spectrum of **III** showed three strong bands for  $\nu\text{C}=\text{O}$  at 2046, 1976 and  $1904\text{ cm}^{-1}$  which were in good agreement with the literature values reported for other neutral seven-coordinated tricarbonylmolybdenum(II) species containing a bidentate nitrogen donor ligand<sup>12</sup>.

The  $^1\text{H}$  NMR spectrum of **III** gave a singlet at 2.48 ppm for the imino  $\text{CH}_3\text{C}=\text{N}$  methyl hydrogens. The resonance at 7.72, 7.79, 7.91 and 8.62 ppm are due to the pyridine- $\text{H}_5$ , pyridine- $\text{H}_4$ , pyridine- $\text{H}_3$  and pyridine- $\text{H}_6$  respectively. We were unable to obtain any acceptable  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum of **III**, probably due to its instability in solution.

We have also investigated the ligand substitution reaction on the tetracarbonyl complex **II**. Treatment of **II** with one mol equivalent of  $\text{PPh}_3$  led to the displacement of one carbonyl group to give the expected monophosphine tricarbonylmolybdenum(0) complex **IV** which was isolated as a red-brown solid. Three strong absorption bands at 1911, 1815 and  $1788\text{ cm}^{-1}$  in the IR spectrum of **IV** are consistent with the values observed for zerovalent molybdenum-tricarbonyls<sup>13</sup>. The  $^1\text{H}$  NMR spectrum of **IV** showed the resonance of pyridine- $\text{H}_6$  at 8.73 ppm, while other

pyridine ring hydrogens resonances could not be observed probably obscured by the phenyl hydrogen resonances. Many attempts to obtain satisfactory  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectrum of **IV** failed, probably due to the instability of this complex in solution when kept for prolonged period. We suggest that the tricarbonyl complex **IV** probably has a facial geometry as depicted in structure **II** where one of the carbonyl is trans to triphenylphosphine.

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