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

M A Aflan*
Faculty of Resource Science and Technology, Universiti Malaysia
Sarawak
94300 Kota Samarahan, Sarawak, Malaysia

and

Ramli bin Hitam and Mustaffa bin Shamsuddin
Dept. of Chemistry, Faculty of Science, Universiti Teknologi
Malaysia, 81310 UTM, Skudai, Johor, Malaysia

Received 17 April 2002; revised 5 July 2002

A chelating 2-methylpyridylbenzophenoneazine ligand has been prepared by the condensation of 2-acetylpyridine with benzophenone hydrazine. Reaction of the ligand with Mo(CO)₆ gives 12-methylpyridylbenzophenoneazine)tetracarbonyl(molybdenum(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 dibromotetra-carbonylmolybdenum(II) azine complex. Treatment of the tetracarbonyl complex with 1 mol equivalent of PPh₃ 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 workers¹. In a previous paper³, 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 I).

Experimental

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

*Corresponding author, e-mail: aflan62@hotmail.com

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. ¹H and ¹³C{¹H} NMR spectra were recorded on a Varian YH 400 Spectrometer. ¹H and ¹³C 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 benzophenonohydrazone in dry ethanol (25 mL) for 6 h. The yellow reaction mixture obtained was concentrated and cooled to 50°C overnight. The yellow solid formed was filtered off, washed with pet-ether (40-60°C), recrystallized from hot ethanol and dried in vacuo over P₂O₅, yield: 2.20 g, 73%.

Preparation of complexes

The synthesis of [Mo(CO)₃(C₅H₇N(Me)C=NN=C(Ph)₂)] II has been reported in Ref. 5.

[Mo(CO)₃(Br)₂][C₅H₇N(Me)C=NN=C(Ph)₂] III

A solution of bromine in carbontetrachloride (1.1 mL, 0.46 M, 5 × 10⁻³ mmol) was added dropwise to a solution of tetracarbonyl complex II (0.2537 g,
$5 \times 10^{-3}$ 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$_2$O$_5$, yield 0.17 g, 53%.

\[ \text{Mo(CO)$_3$[PPh$_3$]C$_6$H$_4$N(Me)C=NN=C(Ph)$_2$]} \quad \text{IV} \]

The tetracarbonyl complex II (0.537 g, $5 \times 10^{-3}$ mmol) was dissolved in xylene (20 mL) with constant stirring. Triphenylphosphine (0.133 g, $5 \times 10^{-3}$ 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$_2$O$_5$. Yield: 0.30 g, 80%.

Results and discussion

2-Acetylpyridine condensed rapidly and completely with benzophenonehydrazine 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 I. The infrared spectra of the ligand and the complexes were recorded.

The infrared spectrum of I showed a medium intensity band at 1565 cm$^{-1}$ which is assigned as the vC=N stretching frequency. Absorption band at 657 cm$^{-1}$ is attributable to the pyridine ring in-plane band. The $^1$H NMR spectrum of I showed a singlet signal at 2.45 ppm which is assigned to CH$_3$C=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$_6$, pyridine-H$_7$ and pyridine-H$_8$, respectively. The $^{13}$C-$^1$H 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$_3$C=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 tetracarbonyl(molybdenum(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 ($10^{-3}$ M) at 25°C which is typical for a non-electrolytes. The electronic spectrum of the complex II in ethanol showed one maximum absorption band 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 $e = 6820 \text{M}^{-1}\text{cm}^{-1}$ (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. The vC=N band is shifted to a lower frequency at 1560 cm$^{-1}$, suggesting coordination of azomethine CH$_3$C=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.

The presence of four carbonyls is further supported by $^{13}$C-$^1$H 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. The coordination of CH$_3$C=N nitrogen is supported by the observation of the downfield chemical shift of CH$_3$C=N imino carbon resonance.

In the $^1$H NMR spectrum of II, the methyl hydrogens of the CH$_3$C=N nitrogen moiety resonated as a singlet at a slightly downfield chemical shift of 2.60 ppm which further supported the coordination of CH$_3$C=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 $^1$H and $^{13}$C-$^1$H 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...
through CH$_3$C=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.

We have also studied the oxidative-addition reaction of II by halogens. Treatment of II in CH$_2$Cl$_2$ at 0 °C with one mol equivalent of bromine in 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 vC=O at 2046, 1976 and 1904 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.

The $^1$H NMR spectrum of III gave a singlet at 2.48 ppm for the imino CH$_3$C=N methyl hydrogens. The resonance at 7.72, 7.79, 7.91 and 8.62 ppm are due to the pyridine-H$_5$, pyridine-H$_6$, pyridine-H$_3$ and pyridine-H$_6$ respectively. We were unable to obtain any acceptable $^{13}$C-{$^1$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 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 cm$^{-1}$ in the IR spectrum of IV are consistent with the values observed for zerovalent molybdenum-tricarbonyls. The $^1$H NMR spectrum of IV showed the resonance of pyridine-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 $^{13}$C-[$^1$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.

Acknowledgement

The authors are grateful to Universiti Teknologi Malaysia for the financial support. We would like to thank the Department of Chemistry, UKM, Bangi, Malaysia, for the CHN analyses.

References