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## Synthesis and Spectroscopic Studies of 2-Bromo *N, N*-Dimethylbenzylamine and Its Complexes with Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub>

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**Abstract:** The new ligand, 2-bromo-*N, N*-Dimethylbenzylamine has been prepared according to scheme 1. The synthesized ligand was further reacted with Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub> to yield 2-bromo *N, N*-Dimethylbenzylamine-Mo(CO)<sub>5</sub> and 2-bromo *N, N*-Dimethylbenzylamine-W(CO)<sub>5</sub> complexes, respectively. Both the ligand and its complexes were characterized on the basis of physical properties, elemental analysis data, infrared and nuclear magnetic resonance spectroscopy. It was found that the ligand has monodentate nature and coordinates with metal through its nitrogen atom thus replacing one CO molecule to maintain the charge density on metal centre.

**Key words:** *N, N*-Dimethylbenzylamine, spectroscopy, Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>

### INTRODUCTION

The synthesis of amine ligands and their metal complexes is a growing area of research in applied inorganic chemistry. The synthesis and study of different amine ligands have undergone tremendous growth in recent years and there complexation chemistry with a wide variety of transition metals has been extensively studied (Gao *et al.*, 1999; Liang *et al.*, 2003). The early work on cyclopalladation of benzylamine (Albert *et al.*, 2003; Beatrice *et al.*, 2004) derivatives has served notice to other authors to assume three requirements that the amine must meet. The first that the amine must be tertiary. Thus the orthopalladation using lithium tetrachloropalladate (II) was observed with *N, N*-Dimethylbenzylamine or some of its aryl substituted derivatives containing electron releasing groups. The second requirement is that the aryl group must not be deactivated as in the case of 4-nitro *N, N*-Dimethylbenzylamine.

Aromatic substitution reactions are not limited to azobenzene and benzyldeneaniline but are even more facile with *N, N*-Dimethylbenzylamine (Farooq *et al.*, 1999; Samina *et al.*, 2006). Complexes of *N, N*-Dimethylbenzylamine with transition metals in low oxidation state have been synthesized. Various analytical techniques have been used for the characterization of group 6 metal carbonyl complexes and are reported elsewhere in the literature (Yaman *et al.*, 2002; Tang *et al.*, 2004; Sert *et al.*, 2004).

The accessible approach through literature reveals that no work has been done on the synthesis and characterization of the title complexes. Keeping in view

the literature and in continuation of previous research (Tariq *et al.*, 2005), an attempt has been made to carry out this research.

### MATERIALS AND METHODS

All the chemicals were purchased from Fine Chemicals and the solvents used were dried and distilled before use. Metal carbonyls were obtained from Aldrich. I.R. Spectra were recorded on a Perkin Elmer FTIR spectrophotometer Model-621. Boiling points were determined by Gallenkamp apparatus. Elemental analyses were carried out by Perkin Elmer Elemental Analyzer 2400 CHN. NMR spectra were recorded on Bruker DPX-400 spectrometer. All the spectroscopic studies of the investigated compounds were carried out at the department of chemistry, Loughborough University United Kingdom during 2004-2005.

#### Synthesis of 2-bromo-*N, N*-dimethylbenzylamine

**Amination of 2-bromo-benzylbromide:** 2-bromo-benzylbromide (0.2499 g, 1.0 mmole) was dissolved in dichloromethane (25 cm<sup>3</sup>). The solution was added dropwise to the 33% dimethylamine solution in Ethanol (0.20 cm<sup>3</sup>, 1.5 mmole). The mixture was stirred for about 6 h in a quick-fit flask. It was then neutralized with 10% NaHCO<sub>3</sub> solution. The mixture was stirred and organic layer was separated from the aqueous layer, dried over anhydrous MgSO<sub>4</sub>, filtered and the solvent was reduced by rotary evaporator to get the pure product (yield 53%).

**Synthesis of [2-bromo-DMBA-Mo (CO)<sub>5</sub>] complex:** Mo(CO)<sub>6</sub> (0.264g, 1.0 mmol) and 2-bromo-*N, N*-

dimethylbenzylamine (0.30 cm<sup>3</sup>, 2.0 mmol) were placed in a flask containing sodium dried THF (10.0 cm<sup>3</sup>). The mixture was stirred for 4 h under UV light and in the nitrogen atmosphere to yield the yellow solution. The progress of the reaction was monitored by FT-IR spectroscopy. The solvent was reduced by Schlinck vacuum line followed by the addition of n-hexane to induce the crystallization (Yield 32%).

**Synthesis of [2-bromo-DMBA-W(CO)<sub>5</sub>] complex:** 2-bromo-DMBA-W(CO)<sub>5</sub> complex was synthesized according to same procedure as described for the synthesis of above complex by using W(CO)<sub>6</sub> as a metal carbonyl (Yield 27%).

### RESULTS AND DISCUSSION

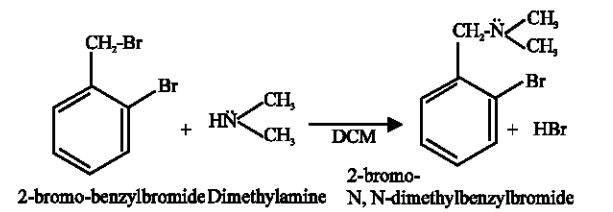
The ligand was synthesized according to scheme 1. The synthesized ligand was further reacted with group 6 metal carbonyls (Molybdenum and Tungsten) to yield respective metal complexes (Fig. 1). Both the complexes are white in color and are more soluble in organic solvents. The elemental analysis data (Table 1) confirms the composition of investigated complexes to be [ML(CO)<sub>5</sub>].

The structure of the ligand (2-bromo-*N,N*-dimethylbenzylamine) was elucidated by IR spectroscopy. The peaks of major functional groups in the IR spectrum of the ligand were assigned and are given in Table 2. The

peak at 3044 cm<sup>-1</sup> (s) is assigned to C-H stretching of benzene ring. The peak at 2981 cm<sup>-1</sup> (m) corresponds to C-H of the -CH<sub>2</sub> of the benzyl group. The presence of a band at 1593 cm<sup>-1</sup> (m) can attribute to C-C stretching. The characteristic frequency of a C-N bond of the type CH<sub>2</sub>-N(CH<sub>3</sub>)<sub>2</sub> was observed at 1272 cm<sup>-1</sup> (s).

The proton NMR spectrum of 2-bromo-DMBA was recorded and the chemical shift values against TMS are shown in Table 3. A multiplet at δ7.16 can be attributed to the H-5 proton (ortho) in the aromatic ring. Another multiplet at δ6.98 can be assigned to the proton at position four. A singlet observed at δ3.31 is due to two methylene protons adjacent to electro-negative nitrogen and phenyl ring while singlet observed at δ2.15 corresponds to six N-methyl protons. <sup>13</sup>C NMR also agrees with its proposed structure. A peak at δ138.13 corresponds to the quaternary carbon. The peaks at δ138.7 and δ132.7 are due to C-2 and C-6 of the aromatic ring, respectively while the peaks at δ133.0 and at δ127.0 correspond to C-3 and C-5, respectively. A peak at δ128.0 is due to C-4. A peak at δ63.33 is due to methylene carbon and peak at δ45.53 is probably due to methyl carbon attached to the nitrogen.

The IR spectrum of the complex (Table 4) 2-bromo-*N,N*-dimethylbenzylamine-Mo(CO)<sub>5</sub> complex exhibits the stretching frequencies of various bonds in the region expected, except for the C-N stretching frequency, where



Scheme 1: Synthesis of 2-bromo-*N,N*-dimethylbenzylamine

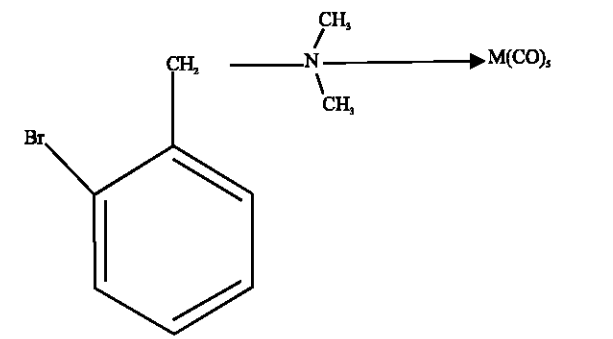


Fig. 1: Proposed structure of metal complexes, Where M = Mo and W

Table 1: Physico-analytical data of ligand and its complexes

Compound	Yield (%)	BP/DP (°C)	Colour	Percentage of elements found (calculated)		
				C	H	N
2-Br-N,N-DMBA	53	223	Pale Yellow	49.64 (50.46)	5.42 (5.60)	5.85 (6.50)
2-Br-N,N-DMBA	32	231	White	36.12 (37.33)	2.23 (2.67)	2.97 (3.11)
Mo(CO) <sub>5</sub> -2-Br-N,N-DMBA	27	227	White	30.76 (31.28)	2.15 (2.23)	2.43 (2.61)

Where DMBA = *N,N*-Dimethylbenzylamine

Table 2: I.R. Data of 2-bromo-*N,N*-dimethylbenzylamine

Compound	Aromatic C-H cm <sup>-1</sup>	C-H (-CH <sub>2</sub> ) cm <sup>-1</sup>	C-N cm <sup>-1</sup>	C-C (Aromatic) cm <sup>-1</sup>	C-Br
2-bromo-DMBA	3044 (s)	2981 (m)	1272 (s)	1593 (m)	611 (m)

Where DMBA = *N,N*-dimethylbenzylamine

Table 3: NMR of spectra of 2-bromo-*N,N*-dimethylbenzylamine

<sup>1</sup> H-NMR	δ (ppm)	<sup>13</sup> C-NMR	δ (ppm)
N-CH <sub>3</sub>	2.15 (s)	N-CH <sub>3</sub>	45.33
CH <sub>2</sub>	3.31 (s)	CH <sub>2</sub> -	63.33
H-3	7.43 (m)	C-1	138.13
H-4	6.98 (m)	C-2	138.70
H-5	7.16 (m)	C-3	133.00
H-6	7.30 (d)	C-4	128.00
		C-5	127.00
		C-6	132.70

Table 4: I.R data of 2-bromo-*N, N*-dimethylbenzylamine-Mo(CO)<sub>5</sub> complex

Compound	Aromatic V(C-H) cm <sup>-1</sup>	V(C-H) (-CH <sub>3</sub> ) cm <sup>-1</sup>	V(C-N) cm <sup>-1</sup>	V(C-Br) cm <sup>-1</sup>	V(C-C) (Aromatic) cm <sup>-1</sup>	V(M-N)	V(C=O)
2-bromo DMBA-Mo(CO) <sub>5</sub>	2970 (m)	2876 (w)	1301 (s)	671 (s)	1593 (s)	383 (s)	1888 (w)
2-bromo DMBA-Mo(CO) <sub>5</sub>	2972 (m)	2865 (m)	1218 (m)	675 (s)	1595 (s)	370 (s)	1845 (w)

DMBA = *N, N*-dimethylbenzylamine

a shift is observed towards the lower region which confirms the coordination of the ligand with the metal through nitrogen. This fact is supported by the appearance of a new low frequency band at 383 cm<sup>-1</sup> (s) assigned to metal-nitrogen bond formation. Further evidence about this interaction can be correlated with the decrease in IR frequency of CO from 2003 to 1888 cm<sup>-1</sup> (w) in the metal complex. The decrease in frequency of CO absorption is due to accumulation of charge density on molybdenum atom which stabilizes itself by transferring it back to the nearby CO (a  $\pi$ -acceptor Ligand).

In W(CO)<sub>6</sub>, the central metal atom is in zero valent oxidation state (electron rich) and shows IR stretching frequency at 2003 cm<sup>-1</sup>. The lowering of V(CO) stretching frequency from 2003 cm<sup>-1</sup> to 1845 (w) cm<sup>-1</sup> again indicates back donation of electron density from M to CO. Such sort of back donation supports the acceptance of charge density by tungsten from 2-bromo-DMBA through its Nitrogen donor atom. This metal nitrogen coordination is also confirmed by the appearance of new band at 370 cm<sup>-1</sup> (s) attributed to  $\nu$ (M-N).

The <sup>1</sup>H NMR spectra of 2-bromo-*N, N*-Dimethylbenzylamine-Mo(CO)<sub>5</sub> complex (Table 5) show a multiplet at  $\delta$ 7.35 integrating to proton H-6. A second multiplet at  $\delta$ 7.16 corresponding to H-3, a multiplet at  $\delta$ 7.12 corresponding to H-5 and a singlet at  $\delta$ 7.28 integrating to one proton due to H-4. Methylene proton shows a singlet at  $\delta$ 3.49 and six N-methyl protons show a singlet at  $\delta$ 2.24. The comparison of the NMR spectra of the ligand and complex shows an up-field shift of half the methyl protons and methylene protons the protons at ortho position on the aromatic ring. However a very small shift observed for meta protons and para protons. We can observe the up-field shift of 0.09 and 0.18 ppm for methyl and methylene protons due to electron-withdrawing effect of metal. A downfield shift of about 0.27 ppm is also observed for meta proton and an up field shift of about 0.30 ppm for para protons. The up field shift for methyl carbon in the complex about 0.08 ppm and for methylene carbon 4.0 ppm. Interestingly 1, 2, 3 and C-5 give downward shift, while 4 and C-6 give up field shifts. A peak at about  $\delta$ 190, 191, 202 show five carbonyl carbons in the complex.

The <sup>1</sup>H NMR spectra of 2-bromo-*N, N*-DMBA-W(CO)<sub>5</sub> complex (Table 6) show a multiplet at  $\delta$ 7.53 integrating to proton H-6. A second multiplet at  $\delta$ 7.36

Table 5: NMR data of 2-bromo- *N, N*-Dimethylbenzylamine - Mo (CO)<sub>5</sub> complex

<sup>1</sup> H-NMR	$\delta$ (ppm)	<sup>13</sup> C-NMR	$\delta$ (ppm)
N-CH <sub>3</sub>	2.24 (s)	N-CH <sub>3</sub>	44.41
CH <sub>2</sub>	3.49 (s)	CH <sub>2</sub> -	59.65
H-3	7.16 (m)	C-1	130.10
H-4	7.28 (m)	C-2	133.40
H-5	7.12 (m)	C-3	127.30
H-6	7.35 (m)	C-4	128.50
		C-5	125.60
		C-6	135.10
		C=O	202(1), 190.1(2), 191 (2)

Table-6: NMR spectral data of 2-bromo- *N, N*-Dimethylbenzylamine-W(CO)<sub>5</sub> complex

<sup>1</sup> H-NMR	$\delta$ (ppm)
N-CH <sub>3</sub>	2.64 (s)
-CH <sub>2</sub>	3.08 (s)
H-3	7.36 (m)
H-4	7.48 (s)
H-5	7.25 (m)
H-6	7.53 (m)

corresponding to H-3, a multiplet at  $\delta$ 7.25 corresponding to H-5 and a singlet at  $\delta$ 7.48 integrating to one proton due to H-4. Methylene proton shows a singlet at  $\delta$ 3.08 and six methyl protons show a singlet at  $\delta$ 2.64. The comparison of the NMR spectra of the ligand and complex show an up-field shift for the methyl protons and methylene protons the protons at ortho-position on the aromatic ring. However a very small shift is observed for meta-protons and para-protons. We can observe the up-field shift of 0.49 and 0.29 ppm for N-methyl and methylene protons due to electron-withdrawing effect of metal. A downfield shift of about 0.07 ppm is also observed for meta-proton and an up-field shift of about 0.50 ppm for para-protons. Similarly an up field shift was observed for 5 and H-6 proton in the spectra of the complex. These down and up field shifts in respective protons, particularly for the methyl proton directly attached to the donor nitrogen atom indicates its interaction with tungsten through coordinate bonding (Fig. 1).

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