ONE POT SYNTHESIS OF GROUP 6 HOMO-BIMETALLIC CARBONYL COMPLEXES INCORPORATING A SCHIFF BASE AND BIDENTATE PHOSPHINE LIGANDS

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Abstract: A simple route to the synthesis of two homo-bimetallic molybdenum carbonyl complexes $[Mo_2(CO)_6(HL)_2(dppm)]$ (**1**) and $[Mo_2(CO)_4(HL)_2(dppb)]$ (**2**) (HL = (E)-2-((2-hydroxybenzylidene)amino)phenol; dppm = bis(diphenylphosphino)methane, dppb = 1,4-bis(diphenylphosphino)butane) have been developed. The two compounds were obtained pure by thermal decarbonylation of $Mo(CO)_6$ using a Schiff base ligand previously prepared by condensation reaction of salicylaldehyde and 2-aminophenol, in the presence of either dppm or dppb. Compounds **1** and **2** were characterized using elemental analysis, IR and NMR (^1H, ^{13}C and ^{31}P) spectroscopy. Elemental analysis and spectroscopic data revealed bimetallic complexes with three and two carbonyl remaining in the structure of complex **1** and **2** respectively with diphosphines acting as bridge between the two metals.

Keywords: Molybdenum hexacarbonyl, bimetallic complexes, diphosphines, decarbonylation, biological activity

Introduction

Bimetallic complexes with two nuclear centers continued to be an area of extensive investigation over the years due to their biological and industrial applications (Patel *et al.*, 2004; Dismukes, 1996). Some of these complexes, especially the homo-bimetallic types, have been reported as constituents of multimetallic enzymes responsible for the catalysis of diverse reactions ranging from alkaline oxidation to biopolymer degradation (Wilcox, 1996). These complexes have found extensive applications in homogeneous and heterogeneous catalysis and have also been located at the active sites of many metalloenzymes (Fenton and Okawa, 1993). There is however an expanded interest in molybdenum bimetallic complexes due to their biochemical role in metalloenzymes and their interesting but complex chemistry (Williams and Da Silva, 2002). Apart from its significant role in biology systems, molybdenum also plays important roles in a variety of chemical reactions such as hydrodesulfurization, oxygen transfer reactions and high catalytic activities (Chisholm, 1983). Their catalytic activity has been explained in terms of their coordinative unsaturation at the molybdenum centres (Mitchell and Finney, 2001; Belgacem *et al.*, 1992).

Research into syntheses of transition metal complexes containing linear polydentate phosphine ligands have also continued to attract interest from synthetic chemists over the years (Cotton and Hong, 1992). This is due to their ability to coordinate to metal centers in a variety of ways ranging from mononuclear triligate to tetranuclear tetraligate and with variety of structures such as tetraligate trigonal pyramidal, tetraligate square pyramidal, tetraligate trigonal bipyramidal and tetraligate octahedral (Balch and Fung, 1990). Linear phosphines are extremely reactive and have been reported as excellent ligands in transition metal chemistry. They are versatile homogeneous catalysts in processes such as hydrogenation of carbonyl compounds (Na *et al.*, 1996; Ito *et al.*, 2001), carbonylation of metal methyl bonds (Dekker *et al*., 1992), polystyrene immobilization (Mansour and Portnoy, 2001) and as therapeutic agents in anticancer drugs (Zou *et al.*, 2015). Many Schiff base transition metal complexes have been reported with excellent catalytic activity in various reactions at high temperatures (>100°C) in the presence of moisture. They have also found applications in medicine as antibiotics and anti-inflammatory agents as well as in

the industry as anticorrosion agents (Ahamad *et al.*, 2010; Antonijevic and Petrovic, 2008). Therefore, syntheses of transition metal complexes incorporating Schiff bases and linear phosphines as ligands is expected to be an important approach to the design of novel compounds with catalytic and highly selective biological activity. We hereby report the synthesis and structural characterization of novel homobinuclear molybdenum complexes containing Schiff base derived from 2-aminophenol and salicylaldehyde with dppm and dppb as co-ligands.

Experimental

Materials and measurements

All chemicals used were of analytical reagent (AR) grade commercially sourced from Sigma Aldrich. Solvents were purified according to the standard procedures (Armarego and Perrin, 2000). The melting point of the ligand and complexes were determined in capillary tubes using Electro thermal IA1900 Vo.29 melting point apparatus. Thin layer chromatography (TLC) of the complexes was carried out in suitable solvents at different ratio and viewed under a UV lamp to determine the purity of the compounds. Elemental analyses were carried out using Carlo Erba Model EA1108 elemental analyzer at MEDAC Laboratory, UK. The solid state Infrared Spectra of the synthesized Schiff base and metal-carbonyl complexes were determined, using SHIMADZU IRAffinity-1S FTIR Spectrophotometer with samples prepared as KBr pellets. High-resolution ^1H and $^{13}C\{^1H\}$NMR spectra were recorded on a Bruker Avance III HD 500-MHz spectrometer at 298 K. The ^1H and $^{13}C\{^1H\}$chemical shifts were calibrated to solvent peaks, which are reported relative to TMS while ^{31}P NMR chemical shifts were measured relative to 85% H_3PO_4.

Synthesis of the Schiff base ligand [**HL**]

The Schiff base was prepared by following a reported procedure (Hossain *et al.*, 2012). A solution of salicylaldehyde (2.443 g, 20 mmol) in 5 mL ethanol was added drop wise to a solution of 2-aminophenol (2.183 g, 20 mmol) in 20 mL ethanol. The mixture was heated to reflux for 1 hour under constant stirring. The red solution formed was allowed to cool to room temperature after which a red precipitate was obtained; the red precipitate was collected through filtration, washed severally with ethanol and allowed to dry in air. The product was then re-

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574

crystallized from hot methanol, red crystalline solids was obtained which was then stored in a desiccator over $CaCl_2$. Yield: 3.628 g (85%), m.p., 190°C. Anal. Calcd for $C_{13}H_{11}NO_2$ (%): C, 73.23; H, 5.20; N, 6.57. Found (%): C, 73.20; H, 5.12; N, 6.58. IR (KBr disc): 3423 br, 1629 m cm^{-1}. ^{1}HNMR (500 MHz, DMSO-d$_6$, δ ppm): 6.89 (d, 1H); 6.99 (d, 2H); 7.14 (d, 1H); 7.36 (dd, 1H); 7.53 (d, 1H); 7.62 (s, 1H); 8.98 (s, 1H); 13.80 (s, 1H). ^{13}C NMR (DMSO-d$_6$, δ ppm): 162.3 (C–OH), 161.2 (C=N), 151.6 (phenolic C–OH), 135.4-117.2 (aromatic C=C).

Synthesis of the metal complexes

[Mo$_2$(CO)$_6$(HL)$_2$(dppm)] (1)

1, 1-bis(diphenylphosphino)methane (dppm) (0.384 g , 1 mmol) dissolved in benzene (10 mL) and **HL** (0.213 g, 1 mmol) in hot benzene (10 mL) were added to a solution of molybdenum hexacarbonyl (0.264 g, 1 mmol) in benzene (10 mL). The resulting mixture was heated to reflux for 4 h under constant stirring; a deep brown clear solution was obtained. The solution was allowed to cool to room temperature after which the solvent was removed using a rotary evaporator. To the residual solid was added about 30 mL of hot methanol and allowed to stand for 15 min, a light brown solid precipitate was obtained. The solid precipitate was collected through filtration, washed severally with hot methanol and allowed to dry in a desiccator. The product was then re-crystallized from hot ethanol. The product was collected as lemon green crystals, dried in air and then stored in a desiccator over $CaCl_2$. m.pt = 165°C ,M. wt. = 1174.87 g/mol; IR (KBr, cm^{-1}): 3454 ν(O–H), 2019, 1921, 1865 ν(CO), 1581 ν(HC=N), 613 ν(Mo–P), 578 ν(Mo–O), 433 ν(Mo–N); ^{1}H NMR (δ, ppm): 1.25-1.27 (CH$_2$ protons), (4.35-4.62) (OH protons), (8.74) (H-C=N protons), (7.36-7.75) (m, aromatic protons); ^{13}C NMR (δ, ppm) (48.86-49.16) (CH$_2$ carbon), (128.51-131.84) (m, aromatic carbon), (136.05-136.48) (C=N carbon) (210.46, 210.54 and 210.60) (CO-Carbonyl carbon); ^{31}P (δ, ppm) (2.59). Anal. Calcd for $C_{68}H_{79}Mo_2N_2O_{10}$ (%): C, 61.03; H, 5.20; N, 2.09. Found (%): C, 59.90; H, 4.20; N, 1.87.

[Mo$_2$(CO)$_4$(SB)$_2$(dppb)] (2)

1, 4-bis(diphenylphosphino)butane (dppb) (0.394 g , 1 mmol) dissolved in benzene (10 mL), and Schiff base (0.213 g, 1 mmol) in hot benzene (10 mL) was added to a solution of the molybdenum hexacarbonyl (0.264 g, 1 mmol) in benzene (10 mL). The mixture was heated to reflux for 4 h under constant stirring; a deep brown clear solution was obtained. The solution was allowed to cool to room temperature, after which the solvent was removed using a rotary evaporator. To the residual solid was added a hot solution of methanol and allowed to stand for 30 min, a light brown solid was obtained. The solid was collected through filtration, washed severally with hot methanol. A sandy brown crystalline solid was obtained. The product was then re-crystallized from hot methanol. A white crystalline solid was obtained which was then stored in a desiccator over $CaCl_2$. M. wt. = 1172.94g/mol, m.pt = 185°C, IR (KBr, cm^{-1}): ν(C=N) (1680), ν(Mo-N) (416) ν(Mo-O) (584)'ν (Mo-P) (651), $_\nu$(CO) (1876, 1919, 2015); ^{1}H NMR (δ, ppm) (0.84-2.49) (CH$_2$ protons); (7.52) (H-C=N protons), (7.30-7.73) (aromatic protons) ^{13}C NMR (δ, ppm) (CH$_2$) carbon (23-30), (128.34-132.09) (m, aromatic carbon) (138.40-138.82) (C=N carbon) (210.29-214.79) (CO-Carbonyl carbon); ^{31}P (δ, ppm) (29.52). Anal. Calcd for $C_{78}H_{104}Mo_2N_2O_8$ (%): C, 64.54; H, 7.22; N, 1.93. Found (%): C, 64.67; H, 6.80; N, 1.76.

Results and Discussion

The metal carbonyl derivatives synthesized are in crystalline forms. The synthesis of [Mo$_2$(CO)$_6$(SB)$_2$(dppm)] in air produced a crystalline lemon solid with melting point of 165°C. While, [Mo$_2$(CO)$_4$(SB)$_2$(dppb)] synthesized in air is crystalline white with a melting point of 185°C. Thus, it is observed that the synthesized complexes have melting points higher than that of the molybdenum hexacarbonyl (150°C) suggesting the formation of more air stable products than the hexacarbonyl.
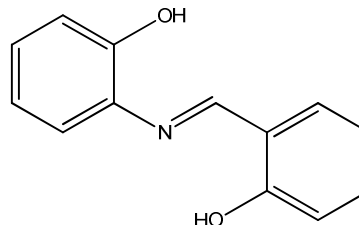

Fig. 1: The ligand

Infrared spectra

The relevant infrared bands of the ligand and complexes are presented in the experimental section. In the FT-IR spectrum of the Schiff base there was a disappearance of the N-H band of 2-aminopheol and C=O band of salicylaldehyde indicating bond formation through the carbonyl carbon of salicylaldehyde and the nitrogen atom of the 2-aminophenol. The azomethine group (C=N) is observed at 1629 cm^{-1}, a major functional group of Schiff bases (Ali *et al*., 2013). Also, the OH band in the Schiff base spectra was observed at 3423.65 cm^{-1}, a shift from the OH of 2-aminophenol (3375 cm^{-1}).

In the infrared spectra of both complexes, absorption bands for the CO moieties were observed. For complex **1** these bands appeared as strong bands at 1865 cm^{-1} and 1921cm^{-1} while for complex **2** the bands appeared as strong bands at 1875 cm^{-1} and 1919 cm^{-1} (Coates, 2000). The (C=N) band found in the free Schiff base at1629 cm^{-1} shifted to a lower band at 1581 cm^{-1} in complex **2**, suggesting coordination of the ligand to the metal through the nitrogen of the azomethine group (Prabhakaran *et al*., 2013). This is confirmed by the appearance of new bands at 433 cm^{-1} and 416 cm^{-1} attributed to M–N stretching vibrations for compounds **1** and **2,** respectively. The infrared spectrum of complex **2** showed a broad and moderate OH absorption band at 3454 cm^{-1} a shift of 31 cm^{-1} downfield from the OH of the Schiff base. Possibly, suggesting that one OH is still present in the compound with the deprotonation of one of the –OH group of the Schiff base ligand for bonding to the metal (Bhatt and Ram, 2012). In contrast, no OH absorption band was observed in the infrared spectrum of compound **2** suggesting the deprotonation of both OH groups of the Schiff base for bonding to the metal (Krishnankutty *et al*., 2007). The M–O stretching vibrations for compound **1** and **2** are observed as absorption bands at 578 and 651 cm^{-1} respectively. This is an evidence for the coordination of the Schiff base to the respective metal through N and O atoms. Coordination of the diphosphine in the complex can be observed by a P–CH$_2$ bend, medium band, at 1440-1400 cm^{-1} region for both complexes and an M–P band at 613 and 651 cm^{-1} for compounds **1** and **2,** respectively (Krishnankutty *et al*., 2007). Coordination of the diphosphines is further confirmed with the ^{31}P NMR analysis.

575

FUW Trends in Science & Technology Journal, www.ftstjournal.com
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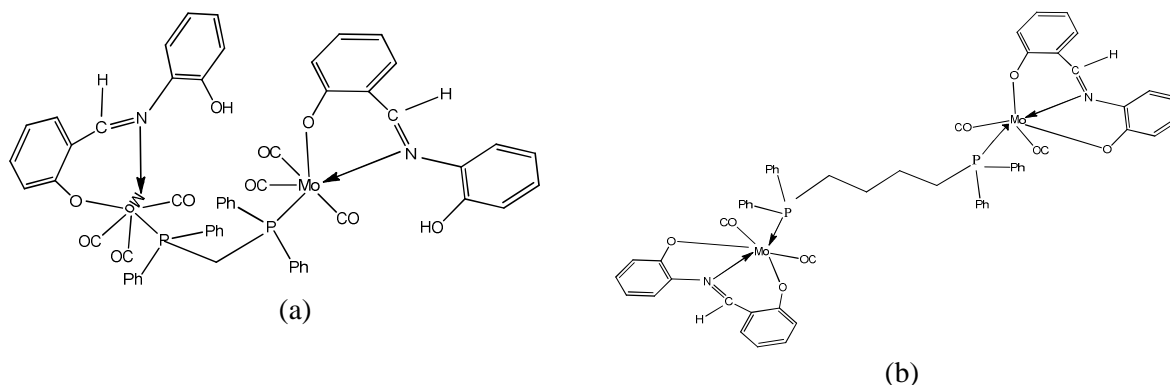
(a)

(b)

Fig. 2: The proposed structures for the Schiff base metal complexes (a) complex 1 (b) complex 2

^{31}C NMR spectra

In complex **1**, three CO peaks were observed at 210.46, 210.54, and 210.60 ppm for terminal carbonyls while methylene carbon (CH_2) peak appeared at 48.86, aromatic carbon appeared as multiple overlapping peaks within the range of 128.51-131.84 ppm while C=N appeared also in the same range of 136.48 ppm. Three terminal carbonyls peaks at 210.29, 210.36 and 210.43 were also observed in the ^{13}C NMR spectrum of complex **2**. Two peaks for the CH_2 were observed between 23 and 30 ppm (Hegelund *et al.*, 1996). Aromatic carbons were observed as multiple overlapping peaks within the range of 128 to 132 ppm while the C=N carbon peak was assigned a chemical shift of 138.82 ppm.

^{31}P NMR analysis for complex (1) and (2)

The ^{31}P NMR spectroscopy chemical shifts for uncoordinated dppm and dppb in $CDCl_3$ were observed at -21.53 and -15.36 ppm respectively (Asali *et al.*, 2006). The ^{31}P NMR signal of the corresponding dppm complex **1** was observed as a very intense single peak at 2.59 ppm. Such data indicates that the two PPh_2 groups in **1** are in the same chemically equivalent environment and were coordinated to the metal centre with a coordination shift of 24.12 ppm downfield of the free dppm. For the dppb derivative **2**, the ^{31}P NMR signal was observed as a very sharp intense signal at 29.52 ppm with a coordination shift of 44.88 ppm from the free dppb an indication that in this complex, the two phosphorus atoms of the diphosphine were in the same chemical environment.

Conclusion

The diphosphines coordinated to the metal centre as bidendate ligands. The Schiff base also coordinated to the metal using the azomethine nitrogen and one phenol oxygen atom in complex **1** and with two phenol oxygen atoms in complex **2** leaving three CO ligands in compound **1** and two in complex **2.** This led to the proposed bimetallic structures with an octahedral geometry for both complexes.

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576

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577