



Photochemical Reactions of Metal Carbonyls $[M(CO)_6]$ ($M = Cr, Mo, W$), $Mn(CO)_3C_p$ with 3[4-Ethyl(phenyl)imino][1*H*-indol-2-one] and 3[4-Butyl(phenyl)imino][1*H*-indol-2-one]

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Four new complexes of $M(CO)_5(ISE)$ [$M = Mo$ (1), Cr (2), W (3)] and $Mn(CO)_3(ISE)$ (4), where ISE is 3[4-ethyl(phenyl)imino][1*H*-indol-2-one] has been synthesized by the photochemical reactions of metal carbonyls $M(CO)_6$ ($M = Mo, Cr, W$) and $Mn(CO)_3C_p$ with ISE (1-4). Four new complexes of $M(CO)_5(ISB)$ [$M = Mo$ (5), Cr (6), W (7)] and $Mn(CO)_3(ISB)$ (8), where ISB is 3[4-butyl(phenyl)imino][1*H*-indol-2-one] has been synthesized by photochemical reactions of metal carbonyls $M(CO)_6$ ($M = Mo, Cr, W$) and $Mn(CO)_3C_p$ with ISB (5-8). The complexes have been characterized by elemental analysis, FT-IR, 1H and ^{13}C NMR spectroscopy. The spectroscopic studies show that, 3[4-ethyl(phenyl)imino][1*H*-indol-2-one] and 3[4-butyl(phenyl)imino][1*H*-indol-2-one] ligands, behave as a monodentate ligand and coordinate *via* C=N donor atom to the central metal atom in $M(CO)_5(ISE)$ (1-3) and $M(CO)_5(ISB)$ (5-7) where $M = Mo, Cr, W$ and as a tridentate ligand coordinating *via* imine nitrogen donor atom (C=N), oxygen donor atom (C=O) and ring NH donor atom in $Mn(CO)_3(ISE)$ (4) and $Mn(CO)_3(ISB)$ (8).

Keywords: Isatin, 1,2,4-Triazole, Schiff base, Metal carbonyl, Photochemical reaction.

INTRODUCTION

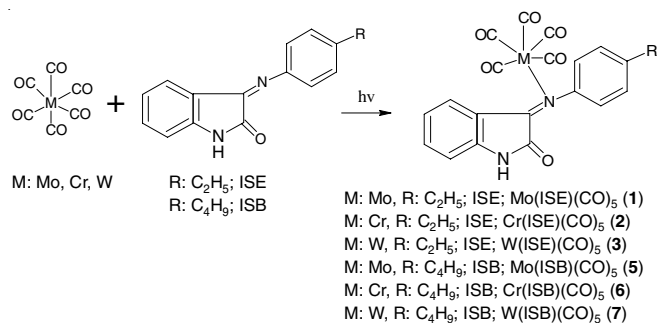
The synthetic versatility of isatin (1*H*-indol-2,3-dione) has led to extensive use in organic synthesis. It has stemmed from the interest in the biological and pharmacological properties of the derivatives [1,2]. Isatin and derivatives of isatin have been used as reagent in dye industry as well. Although, it was firstly synthesized for nearly hundred years ago, recently it was discovered in mammalian tissues and in body fluid. It was observed that monoamine oxidase was inhibited by isatin and derivatives *in vitro* studies [3]. The Schiff bases are an important class of ligands in the coordination chemistry [4-6]. Schiff bases of isatin were reported to possess antibacterial [7-9], antifungal [10-12], antiviral [13-15], anti-HIV [16-18], anti-protozoal [19,20] and antihelminthic [21,22] activities.

Our interest in this category of ligands is justified by their already proved medical and biological implications [23-25]. In the previous studies, metal complexes of 3[4-ethyl(phenyl)imino][1*H*-indol-2-one] (ISE) and 3[4-butyl(phenyl)imino][1*H*-indol-2-one] (ISB) were not synthesized by metal salts. In this paper, a novel photochemical route to form four new complexes; $M(CO)_5(ISE)$ [$M = Mo$ (1), Cr (2), W (3)] and $Mn(CO)_3(ISE)$ (4) where ISE is 3[4-ethyl(phenyl)imino][1*H*-indol-2-one] and four new complexes of $M(CO)_5(ISB)$ [$M = Mo$ (5), Cr (6), W

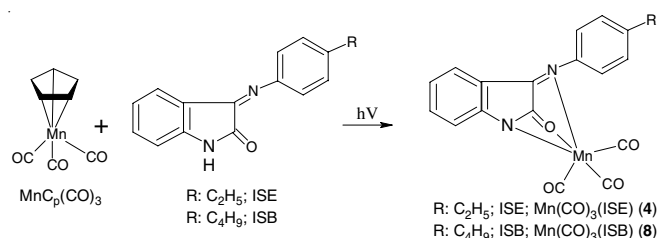
(7)] and $Mn(CO)_3(ISB)$ (8), where ISB is 3[4-butyl(phenyl)imino][1*H*-indol-2-one] have been described. The complexes are characterized by elemental analysis, FT-IR, 1H and ^{13}C NMR spectroscopy. ISE coordinates to the metal *via* imine nitrogen donor atom in $M(CO)_5(ISE)$ (1-3) (Scheme-I) and *via* imine nitrogen, ring CO oxygen donor atom and ring NH nitrogen donor atoms in $[Mn(CO)_3(ISE)]$ (4) (Scheme-II). ISB coordinates to the metal *via* imine nitrogen donor atom in $M(CO)_5(ISB)$ (5-7) (Scheme-I) and *via* imine nitrogen, ring CO oxygen donor atom and ring NH nitrogen donor atom in $[Mn(CO)_3(ISB)]$ (8) (Scheme-II).

EXPERIMENTAL

Reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried and degassed prior to use. Elemental analyses were carried out using a LECOCHNS-O-9320 by Technical and Scientific Research Council of Turkey, TUBITAK. Micromass VG Platform-II LC-MS were recorded at TUBITAK as well. IR spectra were recorded on samples with KBr at the Ege University on a Mattson 1000 FT spectrophotometer. 1H NMR spectra were recorded in DMSO on a 400 MHz High Performance Digital FT NMR at TUBITAK. UV irradiations were performed with a medium-pressure 400 W mercury

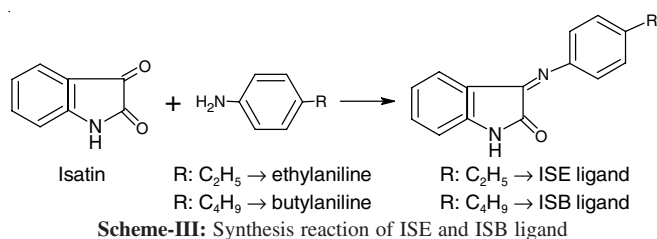


Scheme-I: Photochemical reaction of metal carbonyl and ISE and ISB

Scheme-II: Photochemical reaction of Mn(Cp)(CO)₃ with ISE and ISB

lamp through a quartz-walled immersion well reactor. Melting points were determined on Boetius heating-plate microscope.

Synthesis of 3[4-ethyl(phenyl)imino][1H-indol-2-one] (ISE): For the prepreparation of ISE, a solution of isatin (1 mmol) in ethanol (25 mL) was added to a magnetically stirred solution of ethylaniline (1 mmol) in ethanol (25 mL). The mixture was refluxed for 4 h on water bath. The orange precipitated products formed during reflux was cooled at room temperature. It was filtered, washed with ethanol and dried over P₂O₅ in vacuum. The products thus obtained was recrystallized from methanol to give ISE ligand (Scheme-III) [26].



Scheme-III: Synthesis reaction of ISE and ISB ligand

Spectral data of ISE: IR (KBr, $\nu_{\max}$, cm⁻¹): 2978, 2953, 2927, 2365 (b, NH ring), no observed (CO), 1753 (CO ring), 1650 (m, C=N-C), 1523, 1472 (T₁-ring), 1375, 1344, 1260, 1217 (T₂-ring), 1184, 1012 (T₃-ring), 930 (T₄-ring), 815 (benzene). ¹H NMR (δ , DMSO-*d*₆): 11.9 (NH), 7.0, 7.40 ((CH)benzene), 6.43, 6.65 (CH indol), 2.50 (CH, CH₂ alkyl), 1.23 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): no observed (CO), 163.58 (C=N-C), 154.65 (CO-ring), 27.63 (CH, CH₂ alkyl), 15.57 (CH, CH₃ alkyl) ppm.

Synthesis of 3[4-butyl(phenyl)imino][1H-indol-2-one] (ISB): For the prepreparation of 2, a solution of isatin (1 mmol) in ethanol (25 mL) was added to a magnetically stirred solution of butyl aniline (1 mmol) in ethanol (25 mL). The mixture was refluxed for 4 h on water bath. The orange precipitated products formed during reflux was cooled room temperature. It was filtered, washed with ethanol and dried over P₂O₅ in vacuum. The products thus obtained was recrystallized from methanol to give ISB ligand (Scheme-III) [26].

Spectral data of ISB: IR (KBr, $\nu_{\max}$, cm⁻¹): 2978, 2953, 2927, 2365 (b, NH ring), no observed (CO), 1753 (CO ring), 1650 (C=N-C), 1523, 1472 (T₁-ring), 1375, 1344, 1260, 1217 (T₂-ring), 1184, 1012 (T₃-ring), 930 (T₄-ring), 815 (benzene). ¹H NMR (δ , DMSO-*d*₆): 10.85 (NH), 7.0, 7.35 (CH)benzene), 6.65 (CH indol), 4.05 (CH, CH₂ alkyl), 1.28 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): no observed (CO), 165.2 (C=N-C), 156.8 (CO-ring), 34.31 (CH, CH₂ alkyl), 13.78 (CH, CH₃ alkyl) ppm.

Synthesis of metal carbonyl complexes: Reactions were carried out under nitrogen using Schlenk techniques. All solvents were dried and degassed prior to use. The complexes, M(CO)₅(ISE) (1-3) [M = Mo, Cr, W] and Mn(CO)₃(ISE) (4) [ISE: 3[4-ethyl(phenyl)imino][1H-indol-2-one] and M(CO)₅(ISB) (5-7) [M = Mo, Cr, W] and, Mn(CO)₃(ISB) (8) [ISB: 3[4-butyl(phenyl)imino][1H-indol-2-one] were prepared by the photochemical reactions of metal carbonyls and Mn(CO)₃Cp with ISE and ISB, respectively in 70-80 % yields.

Synthesis of Mo(ISE)(CO)₅ (1): Mo(CO)₆ (1 mmol) and ISE (1 mmol) were dissolved in tetrahydrofuran (80 mL). The solution was irradiated for 1 h using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor while stirring at -78 °C in ice-acetone mixture. During irradiation, the colour of the solution changed from colourless to yellow. After irradiation, the reaction mixture was evaporated under vacuum, yielding a light yellow solid. The solid was then filtered, washed with alcohol and hexane and dried under vacuum [27]. Yield: (72 %). m.p.: 245 °C. Found (%): C, 51.45, H, 3.14, N, 2.97. Anal. calcd. for (%): C, 53.4, H, 2.99, N, 2.87.

Spectral data of Mo(ISE)(CO)₅: IR (KBr, $\nu_{\max}$, cm⁻¹): 2969 (b, NH ring), 2076 (s, CO), 1976 (s, CO), 1876 (s, CO), 1723 (CO ring), no observed (C=N-C), 1507, 1469 (T₁-ring), 1353, 1269, 1207 (T₂-ring), 1115 T₃-ring), 976 (T₄-ring), 838, 753 (benzene). ¹H NMR (δ , DMSO-*d*₆): 12.3 (NH), 7.3, 7.9 (CH)benzene), 6.1, 6.3 (CH indol), 2.73, 2.67 (CH, CH₂ alkyl), 1.35 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): 205.23, 198.68, 185.66 (CO), 169.7 (C=N-C), 164.7 (CO-ring), 29.42 (CH, CH₂ alkyl), 17.2 (CH, CH₃ alkyl) ppm.

Synthesis of Cr(ISE)(CO)₅ (2): A similar synthetic procedure as that used for 1a was used except that Mo(CO)₆ was replaced by Cr(CO)₆, giving pale-yellow crystals. Yield: (76 %). m.p.: 252 °C. Found (%): C, 60.0, H, 3.00, N, 2.96. Anal. calcd. for (%): C, 58.9, H, 3.29, N, 3.32.

Spectral data of Cr(ISE)(CO)₅: IR (KBr, $\nu_{\max}$, cm⁻¹): 2969 (b, NH ring), 2061 (s, CO), 1930 (s, CO), 1723 (CO ring), 1576 (m, C=N-C), 1500, 1453 (T₁-ring), 1376, 1269, 1207 (T₂-ring), 1092, 1038 (T₃-ring), 930 (T₄-ring), 815 (benzene). ¹H NMR (δ , DMSO-*d*₆): 12.7 (NH), 7.0, 7.55 ((CH)benzene), 6.45, 6.53 (CH indol), 2.65, 2.4 (CH, CH₂ alkyl), 1.48 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): 222.70, 201.40, 195.80 (CO), 173.50 (C=N-C), 161.30 (CO-ring), 32.61 (CH, CH₂ alkyl), 16.50 (CH, CH₃ alkyl) ppm.

Synthesis of W(ISE)(CO)₅ (3): A similar synthetic procedure as that used for 1a was used except that Mo(CO)₆ was replaced by W(CO)₆, giving pale-yellow crystals. Yield: (81 %). m.p.: 250 °C. Found (%): C, 47.14, H, 3.20, N, 3.27. Anal. calcd. for (%): C, 45.03, H, 2.52, N, 2.37.

Spectral data of W(ISE)(CO)₅: IR (KBr, $\nu_{\max}$, cm^{-1}): 2969 (b, NH ring), 2069 (s, CO), 1976, 1923 (s, CO), 1807 (s, CO), 1715 (CO ring), no observed (C=N-C), 1515, 1469 (T₁-ring), 1330, 1261, 1200 (T₂-ring), 1100, 1030 (T₃-ring), 976 (T₄-ring), 815 (benzene). ¹H NMR (δ , DMSO-*d*₆): 12.1 (NH), 7.0, 7.45 (CH)benzene, 1H, m), 6.21, 6.8 (CH indol), 2.50, 2.40 (CH, CH₂ alkyl), 1.54 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): 203.60, 201.30, 195.80 (CO), 175.60 (C=N-C), 160.2 (CO-ring), 30.78 (CH, CH₂ alkyl), 16.3 (CH, CH₃ alkyl) ppm.

Synthesis of Mn(ISE)(CO)₃ (4): MnCp(CO)₃ (1 mmol) and ISE (1 mmol) were dissolved in tetrahydrofuran (80 mL). The solution was irradiated for 1 h using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor while stirring at -78 °C in ice-acetone mixture. During irradiation, the colour of the solution changed from colourless to yellow. After irradiation, the reaction mixture was evaporated under vacuum [27], yielding a light yellow solid. The solid was then filtered, washed with alcohol and hexane and dried under vacuum. Yield: (69 %). m.p.: 267 °C. Found (%): C, 60.90, H, 3.50, N, 3.75. Anal. calcd. for (%): C, 62.32, H, 3.47, N, 3.9.

Spectral data of Mn(ISE)(CO)₃: IR (KBr, $\nu_{\max}$, cm^{-1}): 2010 (s, CO), 1930 (s, CO), 1650 (CO ring), 1580 (m, C=N-C), 1505, 1771 (T₁-ring), 1366, 1255 (T₂-ring), 1100, 1010 (T₃-ring), 987 (T₄-ring), 810 (benzene). ¹H NMR (δ , DMSO-*d*₆): 7.20, 7.60 ((CH)benzene), 6.55 (CH indol), 2.70 (CH, CH₂ alkyl), 1.34 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): 82.45, 81.65 (CO), 171.43 (C=N-C), 160.19 (CO-ring), no observed (C_p) ppm.

Synthesis of Mo(ISB)(CO)₅ (5): Mo(CO)₆ (1 mmol) and ISB (1 mmol) were dissolved in tetrahydrofuran (80 mL). The solution was irradiated for 1 h using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor while stirring at -78 °C in ice-acetone mixture. During irradiation, the colour of the solution changed from colourless to yellow. After irradiation, the reaction mixture was evaporated under vacuum, yielding a light yellow solid. The solid was then filtered, washed with alcohol and hexane and dried under vacuum [27]. Yield: (67 %). m.p.: 243 °C. Found (%): C, 56.28, H, 3.96, N, 2.88. Anal. calcd. for (%): C, 54.34, H, 3.32, N, 2.18.

Spectral data of Mo(ISB)(CO)₅: IR (KBr, $\nu_{\max}$, cm^{-1}): 2938, 2346 (b, NH ring), 2069 (s, CO), 1892 (s, CO), 1715 (CO ring), no observed (C=N-C), 1507, 1469 (T₁-ring), 1361, 1284, 1207 (T₂-ring), 1100, 1023 (T₃-ring), 969 (T₄-ring), 846, 753 (benzene). ¹H NMR (δ , DMSO-*d*₆): 11.79 (NH), 7.50, 8.00 (CH)benzene), 5.80, 6.70 (CH indol), 4.20 (CH, CH₂ alkyl), 1.35 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): 202.13, 196.58, 181.56 (CO), 170.09 (C=N-C), 168.05 (CO-ring), 37.72 (CH, CH₂ alkyl), 14.78 (CH, CH₃ alkyl) ppm.

Synthesis of Cr(ISB)(CO)₅ (6): A similar synthetic procedure as that used for 1a was used except that Mo(CO)₆ was replaced by Cr(CO)₆, giving pale-yellow crystals. Yield: (71 %). m.p.: 258 °C. Found (%): C, 57.91, H, 4.16, N, 3.17. Anal. calcd. for (%): C, 59.73, H, 3.65, N, 3.35.

Spectral data of Cr(ISB)(CO)₅: IR (KBr, $\nu_{\max}$, cm^{-1}): 2953, 2930 (b, NH ring), 2061 (s, CO), 1984, 1930, 1884 (br,

CO), 1723 (CO ring), 1592 (C=N-C), 1523, 1461 (T₁-ring), 1376, 1323, 1284, 1207 (T₂-ring), 1100, 1061, 1023 (T₃-ring), 915 (T₄-ring), 884, 815, 746 (benzene). ¹H NMR (δ , DMSO-*d*₆): 12.1 (NH), 7.20, 7.51 (CH)benzene), 6.00, 6.53 (CH indol), 4.4 (CH, CH₂ alkyl), 1.48 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): 219.15, 198.58, 185.56 (CO), 168.76 (C=N-C), 162.12 (CO-ring), 35.40 (CH, CH₂ alkyl), 13.50 (CH, CH₃ alkyl) ppm.

Synthesis of W(ISB)(CO)₅ (7): A similar synthetic procedure as that used for 1a was used except that Mo(CO)₆ was replaced by W(CO)₆, giving pale-yellow crystals. Yield: (85 %). m.p.: 261 °C. Found (%): C, 45.47, H, 3.06, N, 2.44. Anal. calcd. for (%): C, 46.02, H, 2.81, N, 2.27.

Spectral data of W(ISB)(CO)₅: IR (KBr, $\nu_{\max}$, cm^{-1}): 2938 (b, NH ring), 1953 (s, CO), 1723 (CO ring), no observed (C=N-C), 1523, 1476 (T₁-ring), 1323, 1276 (T₂-ring), 1192, 1123, 1038 (T₃-ring), 938 (T₄-ring), 884, 815, 746 (benzene). ¹H NMR (δ , DMSO-*d*₆): 10.76 (NH), 7.0, 7.45 (CH)benzene), 6.20, 6.80 (CH indol), 4.45 (CH, CH₂ alkyl), 1.54 (CH, CH₃ alkyl) ppm. ¹³C NMR (δ , DMSO-*d*₆): 206.19, 201.78, 194.56, 190.48, 185.06 (CO), 175.03 (C=N-C), 159.46 (CO-ring), 30.59 (CH, CH₂ alkyl), 12.06 (CH, CH₃ alkyl) ppm.

Synthesis of Mn(ISB)(CO)₃ (8): MnCp(CO)₃ (1 mmol) and ISB (1 mmol) were dissolved in tetrahydrofuran (80 mL). The solution was irradiated for 1 h using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor while stirring at -78 °C in ice-acetone mixture. During irradiation, the colour of the solution changed from colourless to yellow. After irradiation, the reaction mixture was evaporated under vacuum, yielding a light yellow solid. The solid was then filtered, washed with alcohol and hexane and dried under vacuum [27]. Yield: (77 %). m.p.: 272 °C. Found (%): C, 61.85, H, 3.38, N, 3.62. Anal. calcd. for (%): C, 62.31, H, 3.40, N, 3.74.

Spectral data of Mn(ISB)(CO)₃: IR (KBr, $\nu_{\max}$, cm^{-1}): 2012 (s, CO), 1932 (br, CO), 1624 (CO ring), 1579 (C=N-C), 1532, 1777 (T₁-ring), 1315, 1260 (T₂-ring), 1112, 1002 (T₃-ring), 933 (T₄-ring), 820 (benzene). ¹H NMR (δ , DMSO-*d*₆): 6.90, 7.40 ((CH)benzene), 6.90 (CH indol, 1H, m), 3.90 (CH, CH₂ alkyl), 1.25 (CH, CH₃ alkyl), no observed (C_p) ppm. ¹³C NMR (δ , DMSO-*d*₆): 83.55, 82.95 (CO), 177.56 (C=N-C), 165.32 (CO-ring), no observed (C_p) ppm.

RESULTS AND DISCUSSION

The assignments of FTIR bands were made taking into consideration literature data for compounds containing appropriate structural fragments. There are four medium intensity bands around 2978, 2953, 2927 and 2365 cm^{-1} in the spectrum of the ligand due to the interaction between $\nu(\text{N-H})$ [28]. This fact is further supported by the appearance of a band around 1753 cm^{-1} assignable to $\nu(\text{C=O})$ [28]. A broad band around 1650 cm^{-1} can be assigned to $\nu(\text{C=N})$ vibration mode [28]. The ligand molecule contains a thioamide group, H-C=O and gives rise to four characteristic bands in the IR spectra. The thioamide band has major and minor contributions from $\nu(\text{N-H})$ and $\nu(\text{C=N})$, respectively and is observed at around 1525-1470 cm^{-1} in the IR spectra. Due to the minor contribution from $\nu(\text{C=N})$, the shift toward a higher wave number is not

significant and the overall effect is a shift toward the lower wave number. The thioamide band II has a major contribution from $\nu(\text{C}=\text{N})$ and is observed around $1375\text{--}1217\text{ cm}^{-1}$. The thioamide band III has a major contribution from $\nu(\text{C}=\text{N})$ and minor contribution from $\nu(\text{C}=\text{O})$ in the spectral region of $1184\text{--}1012\text{ cm}^{-1}$. The thioamide band IV seems to have a contribution only from $\nu(\text{C}=\text{O})$ around 930 cm^{-1} [28].

The ligand molecule also displays a band around 1650 cm^{-1} due to $\nu(\text{C}=\text{N})$ band which shifts to around 1576 cm^{-1} in the complex indicating that the nitrogen atom is involved in the coordination to the metal. Also, the four characteristic thioamide bands in the spectra of the ligand molecule change upon complexation. Due to the tautomerism of the thioamide moiety and the redistribution of the electron cloud as a result of complex formation, there is a systematic shift in these bands in the IR spectra of the complex in comparison to that of the ligand [28]. These shifts are consistent with the ability of the imine atom to coordinate to the metal [28].

As expected, the three bands arising from $\nu(\text{CO})$ vibration seen in complexes presumably have the local $\text{C}_{4v} (2\text{A}_1 + \text{E})$ symmetry of the $\text{M}(\text{CO})_5$ unit. The $\nu(\text{CO})$ modes of complexes move to lower wave numbers compared to those of $\text{M}(\text{CO})_6$ [29–33].

The ^1H NMR data of $\text{DMSO-}d_6$ solutions for the pure ligand shows five signals around 12, 7.50, 6.5, 2.5 and 1.3 ppm relative to TMS, assigned to ring NH, H-benzene, H-indol, CH_2 and CH_3 protons, respectively [34]. ^{13}C NMR data of $\text{DMSO-}d_6$ solutions of the pure ligand shows two signals at 165 and 155 ppm which are assigned to the $(\text{C}=\text{N})$ and $(\text{C}=\text{O})$ carbons, respectively. A signal due to the second $\text{C}=\text{N}$ of the coordinated ligand appears at around 175 ppm whereas the signal due to $(\text{C}=\text{O})$ the same appears in the complexes. The signal observed around 165 ppm due to the imine carbon atom $[\text{N}=\text{C}]$ of the ligand is shifted upfield in the spectra of the complexes. The small shifting for $[\text{N}=\text{C}]$ carbon may be related to the decreasing π -electron density in the $\text{C}=\text{N}$ bond by the complex formation [31]. According to this data, the ligand that coordinates through nitrogen $[\text{N}=\text{C}]$ to the metal carbonyl acts as a monodentate in complexes **1–3** and **5–7**.

In the NMR data of $\text{DMSO-}d_6$ solutions of $\text{Mn}(\text{ISE})(\text{CO})_3$ and $\text{Mn}(\text{ISB})(\text{CO})_3$, ring NH signal of the ligand disappeared in agreement with the formation of the $(\text{Mn}-\text{N})$ bond. The $\text{C}=\text{O}$ and $\text{C}=\text{N}$ signals shifted upfield in the complex compared to that of the free ligand since the coordination of $\text{N}-\text{H}$, $\text{C}=\text{N}$ and $\text{C}=\text{O}$ to Mn atom, tends to resonate at higher frequencies as seen with electron withdrawing groups. Furthermore, the shifts of the NH, $\text{C}=\text{O}$ and $\text{C}=\text{N}$ stretching vibrations in the IR spectrum show that both imine nitrogen atom, Oxygen atom ($\text{C}=\text{O}$) and NH group coordinate to Mn atom. According to this data, the ISE and ISB ligands behave as a tridentate ionic ligand in complexes **4** and **8**. The ISE and ISB ligands must act as a 6-electron donor in order to satisfy the 18-electron rule.

Conclusion

The photogeneration of $\text{M}(\text{CO})_5$ from $\text{M}(\text{CO})_6$ has been extensively studied. The 16-electron $\text{M}(\text{CO})_5$ fragments react rapidly with any available donor to form $\text{M}(\text{CO})_5\text{L}$ species where L is a chelating bidentate ligand and $\text{M}_2(\text{CO})_{10}(\mu\text{-L})$ bridged dimers. In this study, the new complexes $\text{M}(\text{CO})_5(\text{ISE})$,

$\text{M}(\text{CO})_5(\text{ISB})$ and $\text{Mn}(\text{CO})_3(\text{ISE})$, $\text{Mn}(\text{CO})_3(\text{ISB})$ were prepared by the photochemical reaction of between $\text{M}(\text{CO})_6$, $\text{Mn}(\text{CO})_3\text{C}_p$ with ISE and ISB. The spectroscopic studies show that, ISE and ISB behave as a monodentate ligands coordinating *via* nitrogen $[\text{Ar}-\text{C}=\text{N}-\text{Ar}]$ exocyclic donor atom in the complexes, $\text{M}(\text{CO})_5(\text{ISE})$ (**1–3**); $\text{M}(\text{CO})_5(\text{ISB})$ (**5–7**). ISE behaves as tridentate ligand coordinating *via* $\text{Ar}-\text{C}=\text{N}-\text{Ar}$ exocyclic, $\text{C}=\text{O}$ endocyclic and ring N donor atoms in the complex $\text{Mn}(\text{CO})_3(\text{ISE})$ (**4**) and $\text{Mn}(\text{CO})_3(\text{ISB})$ (**8**).

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