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Synthesis and Characterization of Metal Carbonyls $[M(CO)_6(M = Cr, Mo, W)]$ with Indole -3-carboxyaldehydemethanesulfonylhydrazone

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Abstract
Four new complexes, $[M(CO)_5(msh4)](Cr(1), Mo(2), W(3))$,and $Re(CO)_4Br(inmsh)(4)$,were synthesized by the photochemical reaction of metal carbonyls with indole-3-carboxyaldehydemethanesulfonyl hydrazone(inmsh) and characterized by using elemental analysis, ^{1}H NMR, EI-MS and IR spectra. The spectroscopic studies show that inmsh behaves as a monodantate ligand coordinating via imine N donor atom in $[M(CO)_5(inmsh)](M = Cr, Mo, W)$ and $Re(CO)_4Br(inmsh)$.

Keywords
Sulfonylhydrazones, Metal Carbonyls, Photochemical Reactions.

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1. INTRODUCTION

The sulfonamides $(-SO_2NH-)$ are used widely as antibacterial agents because of their lower cost, lower activity and most activity against bacterial diseases[1]. Sulfo drugs are used as chemotherapeutic agents with large spectrum of activity and they are used today for various bacterial, protozoal and fungal infections[2a,b]. Methane sulfonamide derivatives possess DNA-binding ability and show cytostatic effects which have usage in cancer chemotherapy. Sulfonylhydrazones derived from sulfonamides have pharmacological properties as antibacterial, antitumor, divretic, antiviral, antinociceptive activity and enzym inhibition especially to carbonic anhydrase species[3,4]. Many of the physiologically active hydrazones have applications in the treatment of illness like tuberculosis, leprosy and mental damage.

The Schiff base metal carbonyl complexes have continued to attract attention in part because of the different possible coordination geometries which the ligand may adopt[5-7]. Their low energy metal-to-ligand charge transfer transitions make these molecules attractive for luminescence and electron transfer reactions[8]. Several of these complexes have been shown to be effective catalysts in allylic alkylation reactions[9,10]. Chiral metal complexes have been employed for stereoselective organic transformations.

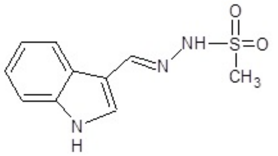

Figure 1. inmsh (indole-3-carboxaldehydemethanesulfonylhydrazone)

In this article, four new complexes $[M(CO)_5(inmsh)]$ (1-3) and $[Re(CO)_4Br(inmsh)]$ (4) have been synthesized by the photochemical reaction of metal carbonyls $M(CO)_6(M = Cr, Mo, W)$ with indole-3-carboxaldehydemethanesulfonylhydrazone(inmsh).

2. EXPERIMENTAL SECTION

All preparation were carried out under dry nitrogen using Schlenk techniques. All solvents used in the synthesis were deoxygenated. Microanalyses of C, H, N and S were performed with a Leco-CHNS-0-9320 elemental analyzer by the Technical and Scientific Research Council of Turkey, TUBITAK. FTIR spectra were recorded on samples in hexane at Ege University on a Mattson 1000 FT spectrophotometer. ^{1}H NMR spectra were recorded in DMSO on a 400 MHz FT-NMR at TUBITAK. Electron impact mass spectrocopy were recorded on a Micromass VG Platform-II LC-MS at TUBITAK. UV irradiations were performed with a medium-pressure 400W mercury lamp through a quartz-walled immersion well reactor.

Hexane, pentane, benzene, dichloromethane, acetone, ethyl alcohol, diethyl ether, silica gel and hydrazine hydrate were purchased from Merck. $M(CO)_6(M = Cr, Mo, W)$ and $Re(CO)_5Br$ were purchased from Aldrich. These reagents were used as supplied. Inmsh was prepared the literature method[11].

The complexes (1-4) were prepared by the photochemical reactions of metal carbonyls $M(CO)_6(M = Cr, Mo, W)$ and $Re(CO)_5Br$ with inmsh were obtained in 70-80% yields by similar methods of which the following is typical.

$Cr(CO)_6$ (0.44 g, 2 mmol) and inmsh (0.48 g, 2 mmol) were dissolved in tetrahydrofuran (80-100 mL). The solution was irradiated for 2 hr at room temperature. During the irradiation, the color of the reaction mixture changed from colorless to dark yellow. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a dark yellow solid. After dissolving in dichloromethane (10 mL), 50 mL of petroleum ether was added, resulting in the precipitation of a dark yellow solid, which was washed with petroleum ether and dried under vacuum. Yield of $Cr(CO)_5(inmsh)$: 80%

3. RESULTS AND DISCUSSION

Complexes 1-4 were prepared by a photochemical reaction as shown in Scheme 1. The photogeneration of $M(CO)_5$ from $M(CO)_6(M = Cr, Mo, W)$ has been studied extensively. The 16-electron $M(CO)_5$ fragments react quickly with any available donor atom to form a $M(CO)_5L$ species [12,13].In this study, photochemical reactions of $M(CO)_6(M = Cr, Mo, W)$ and $Re(CO)_5Br$ with inmsh gave a series of complexes 1-4 via CO displacement.

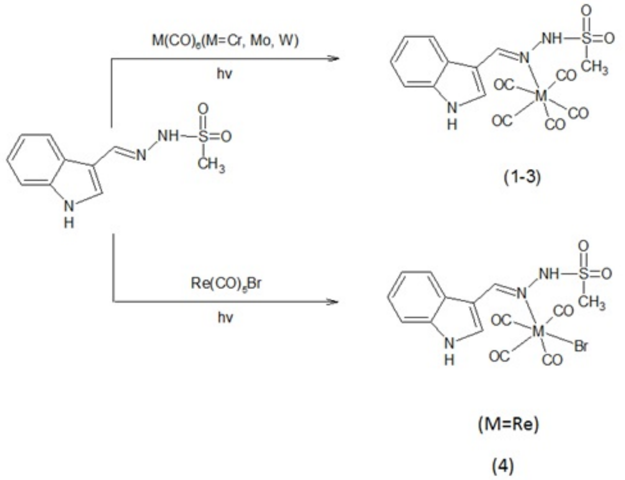

Figure 2. Photochemical reaction of metal carbonyls with the inmsh ligand.

The rather strong C=N stretching vibration, found at 1628 cm^{-1} in free inmsh shift to lower wave numbers in 1-4, showing that inmsh coordinates to the metal via the imine donor atom [14]. This shift has been explained as aweakening of the CN bond resulting from loss of electron density from thenitrogen to the metal atom. No shift was observed for the $\upsilon_{as}(SO)_2$, $\upsilon_{sym}(SO)_2$, and $\upsilon(NH)$ stretching vibrations on complex formation, showing that SO_2 and NH were not coordinated to metal atom in 1-4.

The number of carbonyl bands in the complexes provides important clues to the environment around the metal centers[15]. Five carbonyl strtching bands in 1-3 are attributed to local C_s symmetry of $M(CO)_5$. Similarly, four CO stretching absorptions in 4 indicates local C_{2v} symmetry(shown in Scheme 1).

In the ^{1}H NMR spectra of 1-4, NH proton of the free ligand at 10.01 ppm remains approximatelly unchanged in the complexes and shows that the NH group does not participate in coordination. Small shift to upfield fort he imine peak may be related to a decrease in π-electron density in the C=N bond with complex formation in 1-4. According to these data, inmsh behaves as monodentate ligand with imine nitrogen atom in 1-4.

The mass spectral data of 1-4 show fragmentation via successive loss of CO groups and organic ligands.

In summary, indole-3-carboxaldehydemethanesulfonylhydrazone behaves as monodentate ligand via the N imine donor atom in 1-4. IR and NMR spectra of the compounds show that the inmsh ligand coordinates to the metal atom for compounds

1-4 only via an imine N donor atom behaving as a monodentate neutral ligand. Also CN stretching vibrations in the IR spectra of the compounds shift to lower wave numbers, showing that the imine N donor atom coordinates to the central metal atom in compounds 1-4.

Cr(CO)$_5$(inmsh) (1): Yield: 80%. IR(KBr): 3190(s, υNH), 1610(m, υC=N), 1318(s, $\upsilon_{as}(SO)_2$), 1157(s, $\upsilon_{sym}(SO)_2$), 2070(m, $\upsilon(CO)$), 1970(m, $\upsilon(CO)$), 1947(s, $\upsilon(CO)$), 1935(s,$\upsilon(CO)$), 1872(m,$\upsilon(CO)$); ^{1}H NMR (400 MHz, DMSO-d_6): δ=12.96(s, 1H, NH_{ring}), 9.92(s, 1H, NH), 8.06(s, 1H, HC=N), 3.06(s, 3H, CH_3); EIMS m/z 444(10)[M^+], 416(20)[M^+-CO], 388(25)[M^+-2CO], 360(30)[M^+-3CO], 332(15)[M^+-4CO], 304(20)[M^+-5CO]; Anal.Calcd. for $C_{16}H_{14}CrO_7N_3S$ (444.14 g/mol): calcd. C, 43.26; H, 3.15; N, 9.45; S, 7.21; found C, 43.52; H, 3.22; N, 9.56; S, 7.12.

Mo(CO)$_5$(inmsh) (2): Yield: 77%. IR(KBr): 3190(s,υNH), 1610(m, υC=N), 1317(s, $\upsilon_{as}(SO)_2$), 1158(s, $\upsilon_{sym}(SO)_2$), 2068(m, $\upsilon(CO)$), 1971(m, $\upsilon(CO)$), 1946(s, $\upsilon(CO)$), 1926(s,$\upsilon(CO)$), 1873(m,$\upsilon(CO)$); ^{1}H NMR(400 MHz, DMSO-d_6): δ=12.98(s, 1H, NH_{ring}), 9.92(s, 1H, NH), 8.06(s, 1H, HC=N), 3.00(s, 3H, CH_3); EIMS m/z 460(10)[M^+-CO], 432(15)[M^+-2CO], 404(20)[M^+-3CO], 361(30)[M^+-4CO-Me], 252(25)[inmsh]; Anal.Calcd.for $C_{16}H_{14}MoO_7N_3S$ (489.09 g/mol): calcd. C, 39.37; H, 2.87; N, 8.60; S, 6.56; found C, 39.20; H, 2.98; N, 8.48; S, 6.46.

W(CO)$_5$(inmsh) (3): Yield: 74%. IR(KBr): 3190(s,υNH), 1609(m, υC=N), 1318(s, $\upsilon_{as}(SO)_2$), 1156(s, $\upsilon_{sym}(SO)_2$), 2069(m, $\upsilon(CO)$), 1970(m, $\upsilon(CO)$), 1930(s, $\upsilon(CO)$), 1920(s, $\upsilon(CO)$), 1878(m,$\upsilon(CO)$); ^{1}H NMR(400 MHz, DMSO-d_6): δ=12.96(s, 1H, NH_{ring}), 9.96(s, 1H, NH), 8.04(s, 1H, HC=N), 3.01(s, 3H, CH_3); EIMS m/z 561(25) [M^+-Me], 533(20)[M^+-Me-CO], 505(20)[M^+-Me-2CO], 477(20)[M^+-Me-3CO], 449(20)[M^+-Me-4CO]; Anal.Calcd.for $C_{16}H_{14}WO_7N_3S$ (576 g/mol): calcd. C, 33.33; H, 2.43; N, 7.29; S, 5.55; found C, 33.86; H, 2.48; N, 7.76; S, 5.40.

Re(CO)$_4$Br(inmsh) (4): Yield:76%. IR(KBr): 3190(s, υNH), 1608(m, υC=N),1318(s, $\upsilon_{as}(SO)_2$), 1159(s, $\upsilon_{sym}(SO)_2$), 2110(w, $\upsilon(CO)$), 2022(m, $\upsilon(CO)$), 1950(m, $\upsilon(CO)$), 1942(m, $\upsilon(CO)$); ^{1}H NMR(400 MHz, DMSO- d_6): δ=12.94(s, 1H, NH_{ring}), 9.94(s, 1H, NH), 8.04(s, 1H, HC=N),3.07(s, 3H, CH_3); EIMS m/z 602(15)[M^+-CO], 574(30)[M^+-2CO], 546(35)[M^+-3CO], 518(10) [M^+-4CO]; Anal.Calcd.for $C_{15}H_{14}O_6N_3ReSBr$ (630.25 g/mol): calcd. C, 28.58; H, 2.22; N, 6.66; S, 5.08; found C, 28.38; H, 2.18; N, 6.80; S, 5.28.

Spectroscopic data of free ligand "inmsh"(take from lit.[11]): IR(KBr): 3190(s,υNH), 1628(m, υC=N), 1317(s, $\upsilon_{as}(SO)_2$), 1157(s, $\upsilon_{sym}(SO)_2$) ; ^{1}H NMR(400 MHz, DMSO): δ=12.99(s, 1H, NH_{ring}), 10.01(s, 1H, NH), 8.36(s, 1H, HC=N), 3.08(s, 3H, CH_3).

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