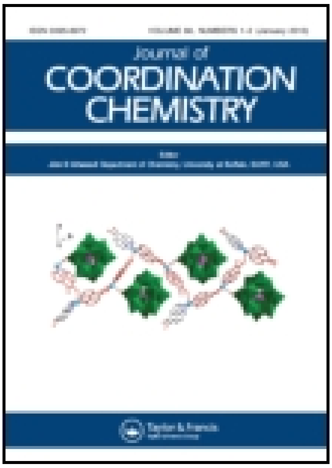

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Photochemical reactions of metal carbonyls with heteroaromatic methanesulfonylhydrazone-based ligands

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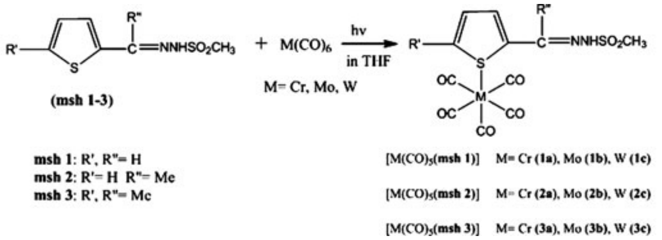

Three new heteroaromatic methanesulfonylhydrazone derivatives: thiophene-2-carboxy aldehyde-methanesulfonylhydrazone (**msh 1**), 2-acetylthiophenemethanesulfonylhdrazone (**msh 2**), and 2-acetyl-5-methylthiophenemethanesulfonylhydrazone (**msh 3**) were prepared and their metal carbonyl complexes ([M(CO)$_5$(**msh 1**)] M = Cr, **1a**; Mo, **1b**; W, **1c**); ([M(CO)$_5$(**msh 2**)] M = Cr, **2a**; Mo, **2b**; W, **2c**); and ([M(CO)$_5$(**msh 3**)] M = Cr, **3a**; Mo, **3b**; W, **3c**) were synthesized by photochemical reactions of [M(CO)$_6$ M = Cr, Mo, W] with **msh 1–3**. Heteroaromatic methanesulfonylhydrazones, **msh 1–3,** and their metal carbonyl complexes were characterized by elemental analysis, mass spectrometry, IR, and ^{1}H and ^{13}C–{^{1}H} NMR spectroscopy. According to all the spectroscopic data, **msh 1–3** are monodentate and coordinate via thiophene ring sulfur. The **msh 1–3** must act as two-electron donors to satisfy the 18-electron rule.

Keywords: Heteroaromatic methanesulfonylhydrazone; Metal carbonyls; Photochemical reactions

1. Introduction

There is growing pharmaceutical and chemical interest in compounds containing the sulfonyl hydrazine moiety [1–5]. Sulfonamide drugs are widely used chemotherapeutic agents with large spectrum of activity [2]. Methanesulfonamide residue has also appeared as a suitable pharmacophoric equivalent to replace functional groups in drug design [6]. Many compounds

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*Corresponding author. Email: ummuhan@gazi.edu.tr containing hydrazine, e.g. carboxylic acid hydrazides and their Schiff bases, have shown cytostatic activity [3]. Methane sulfonic acid hydrazide (MSH), $CH_3S(O)_2NHNH_2$, is the simplest organic representative of the compounds containing both sulfonamide and hydrazine. In our previous studies, we reported antibacterial and cytotoxic effect of MSH and its hydrazone derivatives [5]. In addition, structure and vibrational spectroscopy of MSH were reported by Lenco *et al.* [7].

Carbonyl compounds with sulfur and nitrogen donors attract attention for their fascinating structural chemistry, ability to act as electron reservoirs, and potential in catalysis [8]. Schiff base metal carbonyl complexes continue to attract attention because of the different possible coordination geometries which the ligand may adopt [9–11]. Their low-energy metal-to-ligand charge transfer transitions make these molecules attractive for luminescence and electron-transfer reactions [12]. Several of these complexes have been shown to be effective catalysts in allylic alkylation reactions [13, 14] and in the activation of aromatic carbon–hydrogen bonds (orthometallation) via intermolecular η^2-bonding of arenes [15]. For stereoselective organic transformations, chiral metal complexes, which may have a chiral metal center, or a chiral-coordinated ligand, or both, have been employed [16, 17].

$[M(CO)_5(apmsh)]$ [M = Cr, Mo, W]; $[Re(CO)_4Br(apmsh)]$ containing monodentate apmsh and $[Mn(CO)_3(apmsh)]$ containing tridentate apmsh [apmsh; 2-hydroxyacetophenonemethanesulfonylhydrazone] were prepared by the photochemical reaction of metal carbonyls $[M(CO)_6]$ (M = Cr, Mo, W), $[Re(CO)_5Br]$, and $[Mn(CO)_3Cp]$ with apmsh [18]. $[M(CO)_5(amsh)]$ [M = Cr, Mo, W], $[Re(CO)_4Br(amsh)]$ and $[Mn(CO)_2(amsh)Cp]$ (amsh = acetonemethanesulfonylhydrazone), and $[M(CO)_5(msh)]$ [M = Cr, Mo, W]; $[Re(CO)_4Br(msh)]$ (msh = Methane sulfonic acid hydrazide) were also synthesized photochemically from the corresponding metal carbonyl $[M(CO)_6]$ (M = Cr, Mo, W), $[Re(CO)_5Br]$, and $[Mn(CO)_3Cp]$ with amsh/msh [19]. $M(CO)_5(nafesh)$ (M = Cr, Mo, W), $[Re(CO)_4Br(nafesh)]$, and $[Mn(CO)_3(nafesh)]$ (nafesh = 2-hydroxy-1-napthaldehydeethane sulfonylhydrazone) were synthesized by the photochemical reaction of metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), $Re(CO)_5Br$, and $Mn(CO)_3Cp$ with nafesh [20]. $[M(CO)_5(salmsh)]$ (M = Cr, Mo, W), $[Re(CO)_4Br(salmsh)]$ and $[Mn(CO)_3(Salmsh)]$ (salmsh = salicylaldehyde methanesulfonylhydrazone) were synthesized by the photochemical reaction of metal carbonyls with salmsh [21].

The literature is rich with transition metal-thiophene complexes containing thiophene ligands bound in many ways (i.e. η^1(S), η^2, η^4, η^5, and η^6) to a variety of metal centers, but organometallic complexes of group VIB metals containing thiophene ligands are still relatively rare. The complexes $[Mo(CO)_5(\eta^1\text{-(S)-thiophene})]$ and $[Mo(CO)_5(\eta^5\text{-thiophene})]$ have been proposed to be theoretically possible on the basis of MO calculations, but neither complex has been prepared [22]. In fact, only two Mo complexes containing coordinated thiophene ligands have been reported. The first reported stable Mo–thiophene complex, $[Mo(CO)_3(2,5\text{-}(Ph_2PCH_2CH_2)_2C_4H_2S]$, exists as a pair of chelating ligands that are bound to Mo through the phosphine groups and sulfur. The second complex, $[Mo(\eta^6\text{-2MeBT})_2]$, is a sandwich complex consisting of a Mo coordinated to two 2-methylbenzothiophene (2-MeBT) ligands through the arene rings in an η^6 fashion [23].

As ligands, methanesulfonylhydrazones (**msh 1–3**) have more than one potential donor. Therefore, we tried to observe the sites of substitution of these ligands to the metal center. Our continued interest in the photochemical synthesis and structural aspects of group VIB and VIIB metal carbonyls led us to launch an exploratory investigation into the photolytic behavior of the VIB metal carbonyls $[M(CO)_6]$ [M = Cr, Mo, W] with **msh 1–3** which contain thiophene ring. First, here we report the synthesis, IR, and ^1H and $^{13}C\text{–}\{^1H\}$ NMR spectroscopic characterization of three new heteroaromatic methane sulfonylhydrazones: thiophene-2-carboxyaldehydemethanesulfonylhydrazone (**msh 1**), 2-acetyl thiophenemethanesulfonylhydrazone (**msh 2**), and 2-acetyl-5-methylthiophenemethanesulfonyl hydrazone (**msh 3**). Then, the new complexes ([M(CO)$_5$(**msh 1**)] M = Cr, **1a**; Mo, **1b**; W, **1c**); ([M(CO)$_5$(**msh 2**)] M = Cr, **2a**; Mo, **2b**; W, **2c**); ([M(CO)$_5$(**msh 3**)] M = Cr, **3a**; Mo, **3b**; W, **3c**) as shown in figure 1 were prepared by the photochemical reactions of [M(CO)$_6$] [M = Cr, Mo, W] with **msh 1–3** and characterized by elemental analysis, mass spectrometry, IR, and ^{1}H and ^{13}C–{^{1}H} NMR spectroscopy. According to all the spectroscopic data, **msh 1–3** are monodentate and coordinated via thiophene ring sulfur. The **msh 1–3** ligands must be two-electron donor in order to satisfy the 18-electron rule.

2. Experimental

2.1. *Materials and instrumentation*

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 LECO-CHNS-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 in hexane at the Ege University on a Mattson 1000 FT spectrophotometer. ^{1}H NMR spectra were recorded in CDC1$_3$ or DMSO on a 400 MHz High Performance Digital FT-NMR at TUBITAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor. Melting points (m.p.), uncorrected, were determined on a Boetius heating-plate microscope.

Pentane, benzene, hexane, dichloromethane, acetone, ethyl alcohol, diethylether, 2-hydroxyacetophenone, ethanesulfonyl chloride, hydrazine hydrate, and silica gel were purchased from Merck and M(CO)$_6$ (M = Cr, Mo, W) from Aldrich. These reagents were used as supplied. Methane sulfonyl chloride, hydrazine mono hydrate, thiophene-2-carboxyaldehyde, 2-acetylthiophene, 2-acetyl-5-methylthiophene, and 2-acetyl-5-chlorothiophene were commercial products (purum). The solvents used were purified and distilled according to routine procedures [24].

2.2. *Preparation of heteroaromatic methanesulfonylhydrazones*

The preparation of heteroaromatic methanesulfonylhydrazones **1–3** is similar to that applied by Dodoff [5]. Thus, solution of 2.20 g (0.02 M) of MSH is dissolved in 10 mL of ethanol. Then, the solution that consists of 3.00 g (0.03 M) of the corresponding carbonyl compound (thiophene-2-carboxylaldehyde, 2-acetylthiophene, 2-acetyl-5-methylthiophene, respectively) dissolved in 10 mL of ethanol is added. The mixture is stirred for 30 min. The precipitating product is kept overnight in a deep freeze and then filtered. The precipitate is recrystallized from water and filtered, followed by rinsing with ether. Finally, it is dried on P$_2$O$_5$ in a vacuum desicator.

2.2.1. Synthesis of thiophene-2-carboxylaldehydemethanesulfonylhydrazone (msh 1).

(**msh 1**): Yield (78%). Anal. Calcd C, 35.28, H, 3.95, N, 13.71, S, 31.40. Found C, 35.75, H, 3.86, N, 13.70, S, 31.30. IR (v, KBr): 3180 (s, NH), 3090 (w, CH$_{\text{ring}}$), 1607 (m, CN), 1332 (s, $(SO_2)_{asym}$), 1158 (s, $(SO_2)_{sym}$), 844 (m, $(CSC)_{ring}$), 770 (m, $(CS)_{sym}$), 664 (m, $(CS)_{asym}$). ^{1}H NMR (δ, DMSO) = 3.02 (CH_3SO_2, 3H, s), 7.08 (CH_{ring}, 1H, s), 7.30 (CH_{ring}, 1H, s), 7.50 (CH_{ring}, 1H, s), 8.18 (HCN, 1H, s), 10.97 (NH, 1H, s). ^{13}C NMR (δ, DMSO) = 38.45 (CH_3SO_2), 127.29; 128.71; 130.76; 138.27 (CH_{ring}), 142.11 (CN).

2.2.2. Synthesis of 2-acetylthiophenemethanesulfonylhydrazone (msh 2). After recrystallizing the precipitate from water, needle-type colorless crystals obtained are filtered, rinsed with ether, and finally dried on P_2O_5 in a vacuum desiccator. (**msh 2**): Yield (73%). Anal. Calcd C, 41.36, H, 5.21, N, 12.06, S, 27.60. Found C, 41.52, H, 5.46, N, 12.21, S, 27.33. IR (ν, KBr): 3226 (s, NH), 3093 (w, CH_{ring}), 1593 (w, CN), 1331 (s, $(SO_2)_{asym}$), 1166 (s, $(SO_2)_{sym}$), 845 (m, $(CSC)_{ring}$), 771 (m, $(CS)_{sym}$). ^{1}H NMR (δ, DMSO) = 2.25 (CH_3CN, 3H, s), 3.02 (CH_3SO_2, 3H, s), 7.08 (CH_{ring}, 1H, s), 7.47 (CH_{ring}, 1H, s), 7.59 (CH_{ring}, 1H, s), 10.03 (NH, 1H, s). ^{13}C NMR (δ, DMSO) = 14.56 (CH_3CN), 37.82 (CH_3SO_2), 127.55; 127.82; 128.66; 142.20 (CH_{ring}), 150.19 (CN).

2.2.3. Synthesis of 2-acetyl-5-methylthiophenemethanesulfonylhydrazone (msh 3). (**msh3**): Yield (75%). Anal. Calcd C, 35.51, H, 4.62, N, 12.83, S, 29.38. Found C, 38.45, H, 4.76, N, 12.68, S, 29.44. IR (ν, KBr): 3233 (s, NH), 3024 (w, CH_{ring}), 1598 (w, CN), 1331 (s, $(SO_2)_{asym}$), 1169 (s, $(SO_2)_{sym}$), 923 (m, $(CSC)_{ring}$), 703 (m, $(CS)_{sym}$), 583 (m, $(CS)_{asym}$). ^{1}H NMR (δ, DMSO) = 2.18 (CH_3CN, 3H, s), 2.42 ($(CH_3)_{ring}$, 3H, s), 3.01 (CH_3SO_2, 3H, s), 6.77 (CH_{ring}, 1H, s), 7.27 (CH_{ring}, 1H, s), 9.93 (NH, 1H, s).^{13}C NMR (δ, DMSO) = 14.13 (CH_3CN), 15.18 ($(CH_3)_{ring}$), 37.68 (CH_3SO_2), 125.85; 128.02; 138.96; 142.40 (CH_{ring}), 150.29 (CN).

2.3. *Synthesis of metal carbonyl complexes*

The complexes, ([M(CO)$_5$(**msh 1**)] M = Cr, **1a**; Mo, **1b**; W, **1c**), ([M(CO)$_5$(**msh 2**)] M = Cr, **2a**; Mo, **2b**; W, **2c**), and ([M(CO)$_5$(**msh 3**)] M = Cr, **3a**; Mo, **3b**; W, **3c**) were prepared by photochemical reactions of metal carbonyls $M(CO)_6$ (M = Cr, Mo, W) with (**msh 1–3**) and were obtained in 50–70% yields. The methods employed for the preparation of the complexes are very similar, so that the preparation of [Cr(CO)$_5$(**msh 1**)] (**1a**) is given in detail as a representative example.

2.3.1. Cr(msh 1)(CO)$_5$, (1a). $Cr(CO)_6$ (0.44 g, 2 mM) and **msh 1** (0.22 g, 1 mM) were dissolved in tetrahydrofuran (80–100 mL). The solution was irradiated for 2 h using a 400 W medium-pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the color of the reaction mixture changed from colorless to light brown. After irradiation, the reaction mixture was evaporated under vacuum, yielding a light brown solid. After dissolving in dichloromethane (10 mL), 50 mL of petroleum ether was added, resulting in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum. Traces of unreacted hexacarbonylchromium were sublimed out in vacuum on a cold finger at −20 °C. The composition of compounds is confirmed by elemental analysis. Yield: (55%). Found (%): C, 33.79; H, 2.22; N, 7.63; S, 16.55. Calcd for $CrC_{11}H_8N_2O_7S_2$ (%): C, 33.34; H, 2.03; N, 6.45; S, 7.07. IR (ν, KBr): 2060 (w, CO), 1921 (br, CO), 1894 (sh, CO), 858 (w, CSC_{ring}), 805 (m, CSC_{ring}), 650 (s, $(CS)_{sym}$), 603 (w, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 3.01 (CH_3SO_2, 3H, s), 7.15 ($(CH)_{ring}$, 1H, m), 7.43 (CH_{ring}, 1H, m), 7.64 (CH_{ring}, 1H, m), 8.17 (HC=N, 1H, s), 10.97 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d_6): 39.35 (CH_3SO_2), 132.74; 134.84; 137.70; 139.27 (CH_{ring}), 142.99(C=N), 192.47; 196.98; 199.85; 201.25; 207.34 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 353(18), [M^+ − (Me + CO)]; 325(22), [M^+ − (Me + 2CO)]; 297(16), [M^+ − (Me + 3CO)]; 269(10), [M^+ − (Me + 4CO)]; 241(14), [M^+ − (Me + 5CO)].

2.3.2. Mo(msh 1)(CO)$_5$, (1b). A similar synthetic procedure as that used for **1a** was used except that $Cr(CO)_6$ was replaced by $Mo(CO)_6$, giving pale-yellow crystals. Yield: (57%). Found (%): C, 30.80; H, 1.47; N, 6.47; S, 14.48. Calcd for $MoC_{11}H_8N_2O_7S_2$ (%): C, 30.01; H, 1.83; N, 6.36; S, 14.57. IR (ν, KBr): 2069 (w, CO), 1925 (br, CO), 1892 (s, CO), 853 (w, CSC_{ring}), 805 (m, CSC_{ring}), 670 (m, $(CS)_{sym}$), 592 (w, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 3.02 (CH_3SO_2, 3H, s), 7.17 ($(CH)_{ring}$, 1H, m), 7.42 (CH_{ring}, 1H, m), 7.63 (CH_{ring}, 1H, m), 8.18 (HC=N, 1H, s), 10.97 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d_6): 39.32 (CH_3SO_2), 132.66; 134.39; 137.76; 139.87 (CH_{ring}), 142.89 (C=N), 192.41; 196.36; 199.59; 201.97; 207.69 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 397(17), [M^+ − (Me + CO)]; 369(27), [M^+ − (Me + 2CO)]; 341(21), [M^+ − (Me + 3CO)]; 313(7), [M^+ − (Me + 4CO)]; 285(18), [M^+ − (Me + 5CO)].

2.3.3. W(msh 1)(CO)$_5$, (1c). A similar synthetic procedure as that used for **1a** was used except that $Cr(CO)_6$ was replaced by $W(CO)_6$, giving pale-yellow crystals. Yield: (58%). Found (%): C, 25.35; H, 1.67; N, 5.39; S, 12.85. Calcd for $WC_{11}H_8N_2O_7S_2$ (%): C, 25.01; H, 1.53; N, 5.30; S, 12.14. IR (ν, KBr): 2069 (w, CO), 1921 (br, CO), 1885 (s, CO), 852 (w, CSC_{ring}), 804 (m, CSC_{ring}), 677 (m, $(CS)_{sym}$), 581 (s, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 3.01 (CH_3SO_2, 3H, s), 7.11 ($(CH)_{ring}$, 1H, m), 7.44 (CH_{ring}, 1H, m), 7.66 (CH_{ring}, 1H, m),8.17 (HC=N, 1H, s), 10.97 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d_6): 39.34 (CH_3SO_2), 132.72; 134.84; 137.72; 139.29 (CH_{ring}), 142.93 (C=N), 192.44; 196.99; 199.89; 201.35; 207.39 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 485(15), [M^+ − (Me + CO)]; 457(20), [M^+ − (Me + 2CO)]; 429(20), [M^+ − (Me + 3CO)]; 401(10), [M^+ − (Me + 4CO)]; 373(10), [M^+ − (Me + 5CO)].

2.3.4. Cr(msh 2)(CO)$_5$, (2a). A similar synthetic procedure as that used for **1a** was used except that **msh 1** was replaced by **msh 2**, giving pale-yellow crystals. Yield: (46%). Found (%): C, 35.67; H, 2.91; N, 6.46; S, 15.63. Calcd for $CrC_{12}H_{10}N_2O_7S_2$ (%): C, 35.12; H, 2.46; N, 6.83; S, 15.41. IR (ν, KBr): 2060 (w, CO), 1935 (br, CO), 1859 (sh, CO), 852 (m, CSC_{ring}), 798 (w, CSC_{ring}), 655 (w, $(CS)_{sym}$), 591 (w, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 2.24 (CH_3C=N, 3H, s), 3.02 (CH_3SO_2, 3H, s), 7.19 ($(CH)_{ring}$, 1H, m), 7.53 (CH_{ring}, 1H, m), 7.64 (CH_{ring}, 1H, m), 10.03 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d_6):14.55 (CH_3C=N), 38.08 (CH_3SO_2), 129.35; 135.44; 143.11; 144.80 (CH_{ring}), 150.73 (C=N), 191.49; 192.22; 198.42; 201.45; 203.68 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 367(18), [M^+ − (Me + CO)]; 339(22), [M^+ − (Me + 2CO)]; 311(12), [M^+ − (Me + 3CO)]; 283(15), [M^+ − (Me + 4CO)]; 255(23), [M^+ − (Me + 5CO)].

2.3.5. Mo(msh 2)(CO)$_5$, (2b). A similar synthetic procedure as that used for **1b** was used except that **msh 1** was replaced by **msh 2**, giving pale-yellow crystals. Yield: (50%). Found

(%): C, 31.22; H, 2.42; N, 6.64; S, 14.97. Calcd for $MoC_{12}H_{10}N_2O_7S_2$ (%): C, 31.73; H, 2.22; N, 6.17; S, 14.12. IR (*v*, KBr): 2064 (w, CO), 1936 (br, CO), 1892 (sh, CO), 876 (w, CSC_{ring}), 802 (m, CSC_{ring}), 660 (w, $(CS)_{sym}$), 584 (w, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 2.24 (CH_3C=N, 3H, s), 3.02 (CH_3SO_2, 3H, s), 7.19 ($(CH)_{ring}$, 1H, m), 7.55 (CH_{ring}, 1H, m), 7.65 (CH_{ring}, 1H, m), 10.03 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d_6): 14.54 (CH_3C=N), 38.06 (CH_3SO_2), 129.34; 135.43; 143.11; 144.81 (CH_{ring}), 150.73 (C=N), 191.39; 192.23; 198.02; 201.55; 203.71 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 411 (19), [M^+ − (Me + CO)]; 383(25), [M^+ − (Me + 2CO)]; 355(29), [M^+ − (Me + 3CO)]; 327 (12), [M^+ − (Me + 4CO)]; 299(14), [M^+ − (Me + 5CO)].

2.3.6. W(msh 2)(CO)$_5$, (2c). A similar synthetic procedure as that used for **1c** was used except that **msh 1** was replaced by **msh 2**, giving pale-yellow crystals. Yield: (52%). Found (%): C, 26.22; H, 1.46; N, 5.33; S, 11.23. Calcd for $WC_{12}H_{10}N_2O_7S_2$ (%): C, 26.58; H, 1.86; N, 5.17; S, 11.83. IR (*v*, KBr): 2069 (sh, CO), 1935 (br, CO), 1864 (sh, CO), 852 (m, CSC_{ring}), 815 (w, CSC_{ring}), 680 (w, $(CS)_{sym}$), 591 (m, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 2.24 (CH_3C=N, 3H, s), 3.02 (CH_3SO_2, 3H, s), 7.18 ($(CH)_{ring}$, 1H, m), 7.52 (CH_{ring}, 1H, m), 7.65 (CH_{ring}, 1H, m), 10.03 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d_6): 14.55 (CH_3C=N), 38.06 (CH_3SO_2), 129.34; 135.46; 143.16; 144.86 (CH_{ring}), 150.73 (C=N), 191.41; 192.19; 198.02; 201.57; 203.41 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 499 (17), [M^+ − (Me + CO)]; 471(26), [M^+ − (Me + 2CO)]; 443(12), [M^+ − (Me + 3CO)]; 415 (7), [M^+ − (Me + 4CO)]; 387(32), [M^+ − (Me + 5CO)].

2.3.7. Cr(msh 3)(CO)$_5$, (3a). A similar synthetic procedure as that used for **1a** was used except that **msh 1** was replaced by **msh 3**, giving pale-yellow crystals. Yield: (41%). Found (%): C, 36.27; H, 2.22; N, 6.76; S, 15.38. Calcd for $CrC_{13}H_{12}N_2O_7S_2$ (%): C, 36.79; H, 2.85; N, 6.60; S, 15.11. IR (*v*, KBr): 2070 (w, CO), 1940 (br, CO), 1889 (sh, CO), 955 (s, CSC_{ring}), 870 (m, CSC_{ring}), 618 (m, $(CS)_{sym}$), 577 (s, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 2.18 (CH_3C=N, 3H, s), 2.42 ($(CH_3)_{ring}$, 3H, s), 3.01(CH_3SO_2, 3H, s), 6.81 ($(CH)_{ring}$, 1H, m), 7.35 (CH_{ring}, 1H, m), 9.93 (NH, 1H, s) ppm.^{13}C NMR (δ, DMSO-d_6): 14.13 (CH_3C=N), 15.28 ($(CH_3)_{ring}$), 37.72 (CH_3SO_2), 128.67; 135.02; 140.69; 143.10 (CH_{ring}), 150.99 (C=N), 191.22; 192.27; 198.15; 201.44; 203.89 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 381(15), [M^+ − (Me + CO)]; 353(24), [M^+ − (Me + 2CO)]; 325(26), [M^+ − (Me + 3CO)]; 297(12), [M^+ − (Me + 4CO)]; 269(8), [M^+ − (Me + 5CO)].

2.3.8. Mo(msh 3)(CO)$_5$, (3b). A similar synthetic procedure as that used for **2a** was used except that **msh 1** was replaced by **msh 3**, giving pale-yellow crystals. Yield: (50%). Found (%): C, 33.52; H, 2.67; N, 5.55; S, 13.88. Calcd for $MoC_{13}H_{12}N_2O_7S_2$ (%): C, 33.34; H, 2.58; N, 5.98; S, 13.69. IR (*v*, KBr): 2072 (w, CO), 1942 (br, CO), 1892 (sh, CO), 957 (s, CSC_{ring}), 870 (m, CSC_{ring}), 619 (m, $(CS)_{sym}$), 580 (s, $(CS)_{asym}$) cm^{-1}. ^1H NMR (δ, DMSO-d_6): 2.18 (CH_3C=N, 3H, s), 2.42 ($(CH_3)_{ring}$, 3H, s), 3.01(CH_3SO_2, 3H, s), 6.82 ($(CH)_{ring}$, 1H, m), 7.34 (CH_{ring}, 1H, m), 9.93 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d_6): 14.13 (CH_3C=N), 15.28 ($(CH_3)_{ring}$), 37.72 (CH_3SO_2), 128.66; 135.33; 140.71; 143.11 (CH_{ring}), 150.99 (C=N), 191.20; 192.29; 198.18; 201.49; 203.88 (CO) ppm. MS (LC, 70 eV): *m/z* (%) = 425(21), [M^+ − (Me + CO)]; 397(17), [M^+ − (Me + 2CO)]; 369(20), [M^+ − (Me + 3CO)]; 341(14), [M^+ − (Me + 4CO)]; 313(10), [M^+ − (Me + 5CO)].

2.3.9. W(msh 3)(CO)$_5$, (3c). A similar synthetic procedure as that used for **3a** was used except that **msh 1** was replaced by **msh 3**, giving pale-yellow crystals. Yield: (42%). Found (%): C, 28.31; H, 2.96; N, 5.48; S, 11.67. Calcd for $WC_{13}H_{12}N_2O_7S_2$ (%): C, 28.07; H, 2.17; N, 5.04; S, 11.53. IR (v, KBr): 2073 (w, CO), 1932 (br, CO), 1885 (sh, CO), 962 (m, CSC_{ring}), 872 (m, CSC_{ring}), 619 (w, $(CS)_{sym}$), 578 (s, $(CS)_{asym}$) cm^{-1}. ^{1}H NMR (δ, DMSO-d$_6$): 2.18 (CH_3C=N, 3H, s), 2.42 ($(CH_3)_{ring}$, 3H, s), 3.01(CH_3SO_2, 3H, s), 6.84 ($(CH)_{ring}$, 1H, m), 7.33 (CH_{ring}, 1H, m), 9.93 (NH, 1H, s) ppm. ^{13}C NMR (δ, DMSO-d$_6$): 14.13 (CH_3C=N), 15.28 ($(CH_3)_{ring}$), 37.72 (CH_3SO_2), 128.65; 135.02; 140.69; 143.11 (CH_{ring}), 150.99 (C=N), 191.26; 192.23; 198.17; 201.44; 203.87 (CO) ppm. MS (LC, 70 eV): m/z (%) = 513(14), $[M^+ - (Me + CO)]$; 485(20), $[M^+ - (Me + 2CO)]$; 457(18), $[M^+ - (Me + 3CO)]$; 429(10), $[M^+ - (Me + 4CO)]$; 401(22), $[M^+ - (Me + 5CO)]$.

3. Results and discussion

3.1. *Synthesis*

The analytical results and some physical properties of the new heteroaromatic methanesulfonylhydrazones **msh 1–3** are summarized. They are colorless crystalline solids, stable at room temperature, and soluble in methanol, ethanol, acetonitrile, THF, CH_2Cl_2, DMF, DMSO, and poorly soluble in benzene and water.

3.2. *Spectroscopic characterization*

The assignments of the FTIR bands were made taking into consideration literature data for compounds containing appropriate structural fragments: sulfonamides [25–29], sufonyl hydrazines and sulfonylhydrazones [5, 30–32], methanesulfonyl derivatives [33–36] and Schiff bases of salicyaldehyde, and related compounds [37–40]. Infrared revealed that absorption due to C=N of the free ligand is 1610–1590 cm^{-1} [5]. The N–H absorption appeared at 3230–3180 cm^{-1}. The medium C–S–C asymmetric stretch is 850–800 cm^{-1} [41].

^{1}H and ^{13}C–{^{1}H} NMR data of DMSO-d$_6$ solutions of the heteroaromatic methanesulfonylhydrazones are collected in the experimental section. The comparison of spectra of ketone derivatives facilities distinguishing the signals of the methyl protons from CH_3–C (**msh 2**), CH_3C=N (**msh 2**, **msh 3**), and CH_3SO_2 (**msh 1–3**) fragments, the assignment of the latter being in accord with the data reported [5]. The position of the signal of the HC=N protons in the spectrum of **msh 1** is in agreement with the data for the other ketone and aldheyde Schiff bases [5, 12–14]. The signals of the HC=N and CH_3C=N protons show no splitting, and the positions of the signals of the ring protons are typical. In the region of ring protons, **msh 1** and **msh 3** exhibit three signals and **msh 2** exhibits two signals. The NH signals of several methanesulfonylhydrazones of ketones and aldheydes, and substituted derivatives have been assigned at 8–10.5 ppm [5]. ^{13}C NMR spectra are useful spectroscopic probes for structure elucidation. Thus, the imine carbon resonances in **msh 1–3** are found at 140–150 ppm.

The carbonyl complexes, ([M(CO)$_5$(**msh 1**)] M = Cr, **1a**; Mo, **1b**; W, **1c**), ([M(CO)$_5$(**msh 2**)] M = Cr, **2a**; Mo, **2b**; W, **2c**), and ([M(CO)$_5$(**msh 3**)] M = Cr, **3a**; Mo, **3b**; W, **3c**) (**msh**

1 = thiophene-2-carboxyldehydemethanesulfonylhydrazone, **msh 2** = 2-acethythiophenemethane sulfonylhdrazone, and **msh 3** = 2-acetyl-5-methylthiophenemethane sulfonylhydrazone) were prepared by a photochemical reaction as shown in figure 1. The photogeneration of $M(CO)_5$ from $M(CO)_6$ (M = Cr, Mo,W) has been extensively studied. These 16-electron $M(CO)_5$ fragments react quickly with any available donor to form $M(CO)_5L$ species. If L is a bidentate ligand, $M(CO)_4L$, chelate, or bridging $M_2(CO)_{10}(\mu\text{-}L)$ compounds may occur [42–44]. Photochemical reactions of $M(CO)_6$ (M = Cr, Mo,W) with **msh 1–3** gave complexes **1 a–c**, **2 a–c**, and **3 a–c**. The spectroscopic studies show that **msh 1–3** are monodentate coordinating via the thiophene ring sulfur (C–S–C) in the complexes. Analytical data of the complexes are given in the experimental section.

Important infrared spectral data of the complexes are presented in the synthesis section. Spectral shifts observed for a number of peaks in the vibrational spectra of **msh 1–3** ligands are significant. The medium intensity band at ~840 cm^{-1} observed in free ligand ascribed to $\nu(CSC)_{ring}$ stretch is divided in two bands, to higher values with 40 cm^{-1} and to lower values with 40 cm^{-1} for all compounds, suggesting involvement of sulfur in the bonding with the metal [45, 46]. The bands assigned to symmetric ν(C–S) and asymmetric ν(C–S) shift to lower frequency after complexation in all the complexes. This also confirms that sulfur is taking part in complex formation [45]. These observations are consistent with η^1-(S)-coordinated thiophene, where electron density is increased within the C=C–C=C fragment, while being significantly reduced in the C–S bonds. No shifts were observed at $\nu_{asym}(SO_2)$, $\nu_{sym}(SO_2)$, ν(NH), and ν(C=N) with complex formation, showing that SO_2, NH, and C=N were not coordinated in the complexes. Three bands arising from ν(CO) vibrations are seen for complexes which presumably have local C_{4v} ($2A_1$ + E) symmetry of the $M(CO)_5$ unit

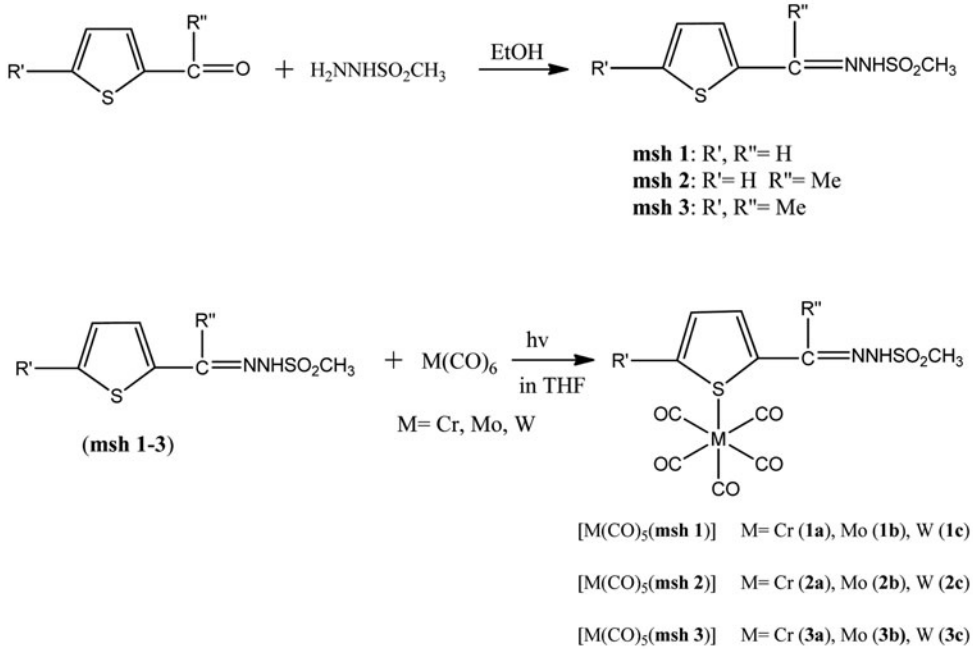

Figure 1. Synthesis of **msh 1–3** and the photochemical reaction of $M(CO)_6$ (M = Cr, Mo, W) with **msh 1–3**.

(M = Cr, Mo, W). The *v*(CO) modes of the complexes move to lower wave numbers when compared with the starting M(CO)$_6$ (M = Cr, Mo, W) molecules [47].

^{1}H and ^{13}C NMR spectra in DMSO-d$_6$ solutions of compounds are reported in the experimental section. In the ^{1}H NMR and ^{13}C NMR spectra, an upfield shift of about 0.13 ppm for the ring protons and about 2–5 ppm for the ring carbons relative to the free ligand were observed. The small shift is related to a decrease in π-electron density in the ring protons and the carbons with complex formation [48].

The mass spectra show fragmentation via successive loss of CO groups and organic ligands.

4. Conclusion

We synthesized a series of three new Schiff bases **msh 1–3** and prepared their VIB metal carbonyls derivatives by photochemical reaction of [M(CO)$_6$ M = Cr, Mo, W]. According to all the spectral data, **msh 1–3** are monodentate coordinating to the metal center via thiophene sulfur. The **msh 1–3** ligand are two-electron donors in order to satisfy the 18-electron rule.

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