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Synthesis and characterization of some metal carbonyls with 2-hydroxyacetophenone ethanesulfonylhydrazone

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Abstract

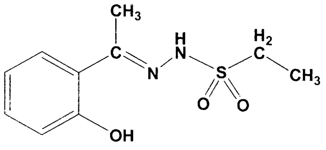
Five new complexes, [M(CO)$_5$(apesh)] [M = Cr; (**1**), Mo; (**2**), W; (**3**)], [Re(CO)$_4$ Br(apesh)] (**4**) and [Mn(CO)$_3$(apesh)] (**5**) have been synthesized by the photochemical reaction of metal carbonyls [M(CO)$_6$] (M = Cr, Mo, W), [Re(CO)$_5$ Br], and [Mn(CO)$_3$ Cp] with 2-hydroxyacetophenone ethanesulfonylhydrazone (apesh). The complexes have been characterized by elemental analysis, mass spectrometry, FT-IR, ^{1}H NMR spectroscopy. The spectroscopic studies show that apesh behaves as a monodentate ligand coordinating via imine N donor atom in (**1**)–(**4**) and as tridentate ligand in (**5**).

Keywords: Photosubstituton; 2-Hydroxyacetophenone ethanesulfonylhydrazone; Metal carbonyls

1. Introduction

There is growing pharmaceutical and chemical interst in compounds containing the sulfonylhydrazine moiety [1–9]. The numerous compounds containing a sulfonamide group or a hydrazine residue, or their combination in one molecule, show cytostatic and antibacterial activity [10,11].

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 [12–14]. Their low energy metal-to-ligand charge transfer (MLCT) transitions make these molecules attractive for luminescence and electron transfer reactions [15]. Besides this, several of these complexes have been shown to be effective catalysts in allylic alkylation reactions [16,17] and in the activation of aromatic carbon–hydrogen bonds (orthometallation) via intramolucular η^2-bonding of arenes [18]. For streoselective organic transformations, chiral metal complexes, which may have a chiral metalcenter or a chiral coordinated ligand or both, have been employed [19,20]. In view of the above, we have investigated a series five new complexes (**1**–**5**) have been prepared for the first time, by the photochemical reaction of metal carbonyls [M(CO)$_6$] (M = Cr, Mo, W), [Re(CO)$_5$ Br], [Mn(CO)$_3$ Cp] with 2-hydroxyacetophenone ethanesulfonylhydrazone (apesh).



apesh

2. Experimental

2.1. General

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 Scien-

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tific Research Council of Turkey, TUBİTAK. FT-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 $CDC1_3$ on DMSO on 400 MHz High Performance Digital FT-NMR at TUBİTAK. Electron impact mass Spectroscopy; Micromass VG Platform-II LC-MS were recorded at TUBİTAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor.

Pentane, benzene, hexane, dichloromethane, acetone, ethyl alcohol, diethylether, 2-hydroxyacetophenone, ethanesulfonyl chloride, hydrazine hydrate, silica gel were purchased from Merck and $M(CO)_6$ (M = Cr, Mo, W), $Re(CO)_5Br$ and $Mn(CO)_3Cp$ were purchased from Aldrich. These reagents were used as supplied. 2-hydroxyacetophenone ethanesulfonylhydrazone (apesh) were prepared by the literature method [9].

2.2. Synthesis

The complexes, $[M(CO)_5(apesh)]$ [M = Cr; (**1**), Mo; (**2**), W; (**3**)], $[Re(CO)_4Br(apesh)]$ (**4**), and $[Mn(CO)_3$ (apesh)] (**5**) were prepared by the photochemical reactions of metal carbonyls $M(CO)_6$ (M = Cr, Mo,W), $Re(CO)_5Br$ and $Mn(CO)_3Cp$ with 2-hydroxyacetophenone ethanesulfonylhydrazone (apesh) and were obtained in 70–80% yields by similar methods of which the following is typical.

The complex $Cr(CO)_6$ (0.44 g, 2 mmol) and apesh (0.48 g, 2 mmol) were dissolved in tetrahydrofuran (80–100 ml). The solution was irradiated for 2 h. 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 $[Cr(CO)_5(apesh)]$:76%. The composition of the compounds are confirmed by elemental analysis and EI MS.

Cr(apesh)(CO)$_5$, (1): Yield (76%). Anal. Calc. C, 41.47, H, 3.22, N, 6.45, S, 7.37. Found C, 40.22, H, 3.05, N, 6.67, S, 7.26. IR (ν, KBr): 3211 (s, NH), 2071 (m, CO), 1971 (m, CO), 1948 (s, CO), 1937 (s, CO), 1873 (m, CO), 1606 (m, C=N), 1237 (s, CO). ^{1}H NMR (δ, DMSO) = 2.21 (CH_3 C=N, s,), 3.12 (CH_2–S, s), 1.26 (CH_3–CH_2, s), 6.78–6.76, (C_6H_4, m), 10.40 (NH, s), OH (11.70, s). MS (EI, 70 eV): m/z (%) = 391(15), [M^+ – (Me + CO)]; 363(20), [M^+ – (Me + 2CO)]; 335(20), [M^+ – (Me + 3CO)]; 307(10), [M^+ – (Me + 4CO)]; 279(10), [M^+ – (Me + 5CO)].

Mo(apesh)(CO)$_5$, (2): Yield (79%). Anal. Calc. C, 37.65, H, 2.92, N, 5.85, S, 6.35. Found C, 37.81, H, 2.67, N, 5.59, S, 6.35. IR (ν, KBr): 3210 (s, NH), 2069 (m, CO), 1970 (m, CO), 1947 (s, CO), 1925 (s, CO), 1873 (m, CO), 1605 (m, C=N), 1238 (s, CO). ^{1}H NMR (δ, DMSO) = 2.21 (CH_3C=N, s,), 3.13 (CH_2–S, s), 1.17 (CH_3–CH_2, s), 6.81–6.73, (C_6H_4, m), 10.42 (NH, s), OH (11.63, s). MS (EI, 70 eV): m/z (%) = 435(10), [M^+ – (Me + CO)]; 407(15), [M^+ – (Me + 2CO)]; 379(20), [M^+ – (Me + 3CO)]; 351(22), [M^+ – (Me + 4CO)]; 323(28), [M^+ – (Me + 5CO)].

W(apesh)(CO)$_5$, (3): Yield (80%). Anal. Calc. C, 31.80, H, 2.47, N, 4.64, S, 5.65. Found C, 31.45, H, 2.59, N, 4.61, S, 5.25. IR (ν, KBr) = 3210 (s, NH), 2069 (m, CO), 1970 (m, CO), 1947 (s, CO), 1925 (s, CO), 1873 (m, CO), 1605 (m, C=N), 1238 (s, CO). ^{1}H NMR (δ, DMSO) = 2.19 (CH_3C=N, s,), 3.14 (CH_2–S, s), 1.24 (CH_3–CH_2, s), 6.77–6.74, (C_6H_4, m), 10.41 (NH, s), OH (11.57, s). MS (EI, 70 eV): m/z (%) = 508(15), [M^+ – (2Me + CO)]; 480(25), [M^+ – (2Me + 2CO)]; 452(20),[M^+ – (2Me + 3CO)]; 396(20), [M^+ – (2Me + 5CO)].

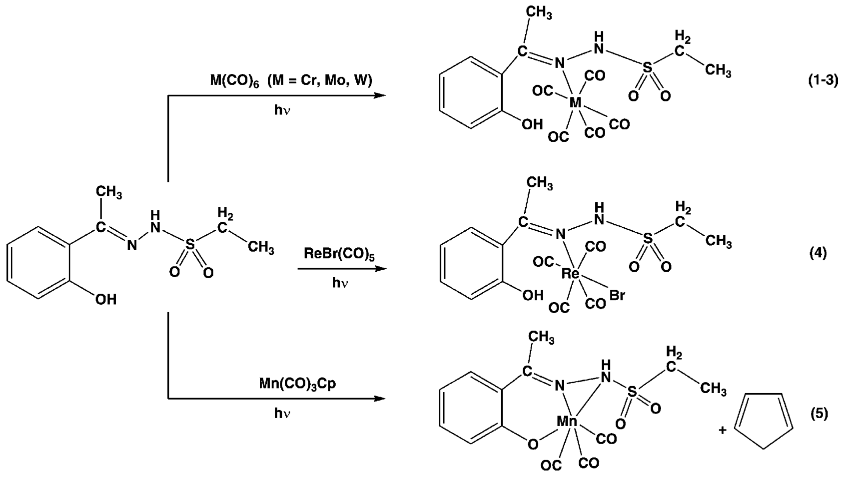
Re(apesh)(CO)$_4$Br, (4): Yield (77%). Anal. Calc. C, 27.10, H, 2.27, N, 4.52, S, 5.17. Found C, 26.95, H, 2.06, N, 4.75, S, 5.58. IR (ν, KBr) = 3211 (s, NH), 2112 (w, CO), 2023 (m, CO), 1918 (m, CO), 1909 (m, CO), 1605 (m, C=N), 1237 (s, CO). ^{1}H NMR (δ, DMSO) = 2.21 (CH_3C=N, s), 3.14 (CH_2–S, s), 1.24 (CH_3–CH_2, s), 6.88–6.55, (C_6H_4, m), 10.41 (NH, s), OH (11.58, s). MS (EI, 70 eV): m/z (%) = 534(20), [M^+ – (2Me + 2CO)]; 506(25), [M^+ – (2Me + 3CO)]; 478(25), [M^+ – (2Me + 4CO)].

Mn(apesh)(CO)$_3$, (5): Yield (74%). Anal. Calc. C, 40.94, H, 3.67, N, 7.34, S, 8.39. Found C, 40.55, H, 3.88, N, 7.56, S, 8.12 IR (ν, KBr) = 2020 (s, CO), 1975 (s, CO), 1928 (m, CO), 1602 (m, C=N), 1246 (s, CO). ^{1}H NMR (δ, DMSO): 2.09 (CH_3C=N, s,), 3.16 (CH_2–S, s), 1.24 (CH_3–CH_2, s), 6.75–7.48, (C_6H_4, m), 12.55 (NH, s). MS (EI, 70 eV): m/z (%) = 381 (100) 366(10), [M^+ – (Me)]; 338(15), [M^+ – (Me + CO)]; 310(15), [M^+ – (Me + 2CO)]; 282(25), [M^+ – (Me + 3CO)].

apesh: IR (ν, KBr) = 3213 (s, NH), 1622 (m, C=N), 1238 (s, CO), 1339 (s, *as*SO_2), 1167 (s, *s*SO_2). ^{1}H NMR(δ, DMSO) = 2.32 (CH_3C=N, s), 3.22 (CH_2–S, s), 1.27 (CH_3–CH_2, s), 6.87–7.52, (C_6H_4, m), 10.61 (NH, s), OH (11.69, s) taken from [9]

3. Results and discussion

Complexes (**1**–**5**) 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 extensively studied. These 16-electron $M(CO)_5$ fragments react quickly with any available donor atom 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 [21–23]. In this study, photochemical reactions of $M(CO)_6$(M = Cr, Mo, W), $Re(CO)_5Br$ with apesh ligand



Scheme 1. The photochemical reactions of M(CO)$_6$ (M = Cr, Mo, W), Re(CO)$_5$Br and [Mn(CO)$_3$Cp] with apesh ligand.

proceed in this expected manner, and gave a series of complexes (**1**–**4**) and however, the formation of [Mn(CO)3(apesh)], (**5**), occurs via displacement of the anionic cyclopentadienide ligand $(C_5H_5)^-$.

The rather strong C=N stretching vibration, found at 1621 cm^{-1} in the free ligand, shifts to lower wavenumber in (**1**–**5**), showing that apesh ligand coordinates to the metal via the imine donor atom [24]. This shift has been explained as weakening of the CN bond resulting from the loss of electron density from the nitrogen to the metal atom [24]. No shifting upon complex formation was observed at $\nu_{as}(SO_2)$, $\nu_{sym}(SO_2)$, ν(NH) and ν(CO) stretching vibrations indicating that SO_2, NH and CO group were not coordinated to metal atoms in (**1**–**4**). OH stretching vibration was not observed both free ligand and in (**1**–**4**) because of hydrogen bonding with the imine nitrogen atom [9].

According to number of carbonyl bands, provides important clues to the environment of the metalcenters [25]. Five carbonyl stretching bands in (**1**–**3**) are attributed to local C_{4v} symmetry of $M(CO)_5$ [21,22]. Similarly, four CO stretching absorptions in (**4**) and three in (**5**) indicate to *local* C_{2v} [26], C_{3v} [27] symmetry, respectively (shown in Scheme 1). The ν(CO) modes in (**1**–**5**) move also to lower wave numbers when compared with the starting carbonyl complexes [21,22].

In the ^{1}H NMR spectra of (**1**–**4**), a downfield shift of about 0.11 ppm for CH_3C=N proton and 0.2 ppm for NH proton relative to the free ligand were observed. The small shifting is related to a decrease in π-electron density in the C=N bond with complex formation in (**1**–**4**). According to the these data, the apesh ligand behaves as monodentate in (**1**–**4**). However, in the NMR spectrum of Mn(apesh)$(CO)_3$, (**5**), the phenolic OH^- signal disappeared which is in agreement with the formation of Mn–O bond [28,29]. NH signal was found 1.94 ppm downfield compared to the free ligand in (**5**). Because, the coordination of NH to Mn atom, like electron withdrawing groups, tends to resonate at higher frequencies. In addition, the shift of the C–O stretching vibration in the IR spectrum shows that both imine N and phenolic O donor atoms coordinate to Mn atom. Kinematic coupling of the CO group with the bonded metal ion would increase the frequencies [30]. According to the these data, the salesh ligand behaves as tridentate and ionic ligand in (**5**). The apesh ligand must act as a 6-electron donor in order to satisfy the 18-electron rule.

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

In summary, salesh behaves as monodentate ligand via N imine donor atom in (**1**–**4**), but behaves as tridentate ligand via anionic O, imine N and amine N donor atoms in (**5**).

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