Synthesis and Characterization of Metal Carbonyls $[M(CO)_6(M = Cr, Mo, W), Re(CO)_5Br, Mn(CO)_3Cp]$ with 2-Hydroxy-1-napthaldehyde Ethanesulfonylhydrazone (nafesh)

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Z. Naturforsch. 58b, 1124-1127 (2003); received December 18, 2002

Five new complexes, $M(CO)_5$ (nafesh) (M = Cr (1), Mo (2), W (3)), Re(CO)_4Br(nafesh) (4) and Mn(CO)_3(nafesh) (5) have been synthesized by the photochemical reaction of metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), Re(CO)_5Br, and Mn(CO)_3Cp with 2-hydroxy-1-napthaldehyde ethane-sulfonylhydrazone (nafesh). The complexes have been characterized by elemental analysis, EI mass spectrometry, FT-IR, ¹H NMR spectroscopy. The spectroscopic studies show that nafesh behaves as a monodentate ligand coordinating *via* imine N donor atom in $M(CO)_5$ (nafesh) (M = Cr, Mo, W) and Re(CO)_4Br(nafesh) and as tridentate ligand in Mn(CO)_3(nafesh).

Key words: Hydrazone, 2-Hydroxy-1-napthaldehyde Ethanesulfonylhydrazone, Metal Carbonyls

Introduction

There is growing pharmaceutical and chemical interst in compounds containing the sulfonylhydrazine moiety [1-9]. 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(*ortho*-metallation) *via* intramolecular η^2 -bonding of arenas [18]. For stereoselective organic transformations, chiral metal complexes, which may have a chiral metal center or a chiral coordinated ligand or both, have been employed [19–20].

In view of the above, we have now investigated the five new complexes 1-5 which have been pre-



pared for the first time, by the photochemical reaction of metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), Re(CO)₅Br, Mn(CO)₃Cp with 2-hydroxy-1-napthaldehyde ethanesulfonylhydrazone.

Nafesh

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 a $M(CO)_5L$ species. If L is a bidentate ligand, $M(CO)_4L$ chelate or bridging $M_2(CO)_{10}(\mu-L)$ compounds may occur [21–23]. In this study, photochemical reactions of $M(CO)_6(M = Cr, Mo, W)$, Re(CO)₅Br with nafesh ligand proceed in this expected manner, and gave a series of complexes (1–4) and however the formation of (5) occurs via displacement of the anionic cyclopentadienide ligand (C₅H₅).

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Scheme 1. Synthesis of complexes 1-5 from $M(CO)_6(M = Cr, Mo, W)$, $Re(CO)_5Br$ and $[Mn(CO)_3Cp]$ and the nafesh ligand.

The rather strong C=N stretching vibration, found at 1623 cm^{-1} in the free ligand, shifts to lower wavenumber in 1-5, showing that the nafesh ligand coordinates to the metal *via* the imine donor atom [24]. This shift has been explained as a 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 for the $v_{as}(SO_2)$, $v_{sym}(SO_2)$, v(NH) and v(CO) stretching vibrations indicating that SO₂, NH and CO groups were not coordinated to metal atoms in 1-4. OH stretching vibration was not observed for the free ligand nor for 1-4 because of hydrogen bonding with the imine nitrogen atom [9].

The 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 v(CO) modes in 1-5 move also to lower wave numbers when compared with the starting carbonyl complexes [21, 22].

In the ¹H NMR spectra of **1**–**4**, NH proton of free ligand at 11.11 ppm remains approximately unchanged, inferring involvement of the NH group in the complexes. These data also show that NH group do not participate in coordination. The small shifting for HC=N proton may be related to decreasing π -electron density in the C=N bond with complex formation in **1**–**4**). According to the these data, nafesh ligand behaves as monodentate in **1**–**4**.

However, in the NMR spectrum of Mn(nafesh)(CO)₃, 5, the phenolic OH signal disappeared which is in agreement with the formation of Mn-O bond [28, 29]. The NH signal was found 2.24 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 nafesh ligand behaves as tridentate and ionic ligand in 5. The nafesh 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, nafesh behaves as monodentate ligand *via* N imine donor atom in 1-5, but behaves as tridentate ligand via anionic O, imine N and amine N donor atoms in 5.

Experimental Section

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 Scientific Research Council of Turkey, TUBİTAK. FTIR spectra were recorded on samples in hexane at the Ege University on a Mattson 1000 FT spectrophotometer. ¹H and ¹³C{¹H} NMR spectra were recorded in CDC1₃ or DMSO on a 400 MHz Digital FT-NMR at TUBİTAK. Electron impact mass spectra were recorded on a Micromass VG Platform-II LC-MS at TUBİTAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor.

The solvents, 2-hydroxy-1-napthaldehyde, ethanesulfonyl chloride, hydrazine hydrate, and 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-Hydroxy-1-napthaldehyde ethanesulfonylhydrazone (nafesh) was prepared by the literature method [9].

Syntheses

The complexes, 1-5 were prepared by the photochemical reactions of metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), Re(CO)₅Br and Mn(CO)₃Cp with nafesh and were obtained in 70-80% yields by methods of which the following is typical.

The complex $Cr(CO)_6$ (0.44 g, 2 mmol) and nafesh (0.56 g, 2 mmol) were dissolved in THF (80 – 100 cm³). The solution was irradiated for 2 h. During the irradiation, the colour of the reaction mixture changed from colourless to dark yellow. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a dark yellow solid. After dissolving in CH₂Cl₂ (10 cm³), petroleum ether (50 cm³) 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(nafesh)]: 79%.

Cr(CO)₅(nafesh) (1): Yield: 79%. IR (KBr): v = 3220(s, NH), 2066 (m, C=O), 1980 (m, C=O), 1939 (s, C=O), 1926 (s, C=O), 1885 (m, C=O), 1606 (m, C=N), 1241 (s, C-O) cm⁻¹. – ¹H NMR (400 MHz, DMSO): $\delta = 1.16$ (s, 3H, CH₃-CH₂), 3.10 (s, 2H, CH₂-S), 7.20, 7.36, 7.54, 7.86, 7.92, 8.52 (m, 6H, C₁₂H₆), 8.62 (s, 1 H, HC=N), 10.84 (s, 1H, NH), 11.79 (s, 1H, OH). – MS (EI, 70 eV): m/z(%) = 442 (12) [M⁺–CO], 414 (15) [M⁺–2CO], 386 (28) [M⁺–3CO], 358 (10) [M⁺–4CO], 330(10) [M⁺–5CO]. – C₁₈H₁₄CrO₈N₂S (420.3): calcd. C 45.9, H 3.0, N 5.9, S 6.8; found C 45.9, H 2.9, N 5.8, S 6.6.

Mo(CO)₅(nafesh) (**2**): Yield: 77%. IR (KBr): v = 3219 (s, NH), 2069 (m, C=O), 1985 (m, C=O), 1947 (s, C=O), 1917 (s, C=O), 1873 (m, C=O), 1606 (m, C=N), 1242 (s, C-O) cm⁻¹. – ¹H NMR (400 MHz, DMSO): $\delta = 1.16$ (s, 3H, CH₃-CH₂), 3.09 (s, 2H, CH₂-S), 7.21, 7.37, 7.54, 7.85,

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7.93, 8.52 (m, 6H, $C_{12}H_6$), 8.63 (s, 1H, HC=N), 10.85 (s, 1H, NH), 11.78 (s, 1H, OH). – MS (EI, 70 eV): m/z (%) = 486 (10) [M⁺–CO], 458 (15) [M⁺–2CO], 430 (28) [M⁺–3CO], 374(10) [M⁺–5CO]. – $C_{18}H_{14}MoO_8N_2S$ (420.3): calcd. C 42.0, H 2.7, N 5.5, S 6.2; found C 42.3, H 2.8, N 5.7, S 6.3.

W(CO)₅(nafesh) (**3**): Yield: 79%. IR (KBr): v = 3222(s, NH), 2074 (m, C=O), 1989 (m, C=O), 1949 (s, C=O), 1934 (s, C=O), 1888 (m, C=O), 1606 (m, C=N), 1241 (s, C=O) cm⁻¹. – ¹H NMR (400 MHz, DMSO): $\delta = 1.17$ (s, 3H, CH₃-CH₂), 3.07 (s, 2H, CH₂-S), 7.20, 7.37, 7.55, 7.88, 7.92, 8.51 (m, 6H, C₁₂H₆), 8.65 (s, 1H, HC=N), 10.86 (s, 1H, NH), 11.79 (s, 1H, OH). – MS (EI, 70 eV): m/z (%) = 574 (12) [M⁺–CO], 546 (15) [M⁺–2CO], 518 (10) [M⁺–3CO], 490 (25) [M⁺–4CO], 462(15) [M⁺–5CO]. – C₁₈H₁₄WO₈N₂S (420.3): calcd. C 35.9, H 2.3, N 4.7, S 5.3; found C 35.8, H 2.4, N 4.8, S 5.5.

Re(CO)₄Br(nafesh) (4): Yield (79%). IR (KBr): v = 3220 (s, NH), 2115 (w, C=O), 2017 (m, C=O), 1958 (m, C=O), 1934 (s, C=O), 1606 (m, C=N), 1242 (s, C-O) cm⁻¹. – ¹H NMR (400 MHz, DMSO): $\delta = 1.16$ (s, 3H, *CH*₃-CH₂), 3.08 (s, 2H, *CH*₂-S), 7.24, 7.37, 7.57, 7.88, 7.92, 8.55 (m, 6H, C₁₂*H*₆), 8.65 (s, 1H, *H*C=N), 11.84 (s, 1H, N*H*), 11.78 (s, 1H, O*H*). – MS (EI, 70 eV): *m*/z (%) = 628 (12) [M⁺-CO], 600 (20) [M⁺-2CO], 544 (10) [M⁺-4CO]. – C₁₇H₁₄O₇N₂ReSBr (606.4): calcd. C 31.1, H 2.2, N 4.4, S 4.9; found C 31.1, H 2.5, N 4.4, S 5.0.

 $\begin{array}{l} Mn(CO)_{3}(nafesh) \ \textbf{(5)}: \ Yield \ (74\%). \ IR \ (KBr): \ \nu = 2019 \\ (s, C=O), \ 1925 \ (s, C=O), \ 1899 \ (s, C=O), \ 1603 \ (m, C=N), \\ 1262 \ (s, C-O) \ cm^{-1}. \ ^{-1}H \ NMR \ (400 \ MHz, \ DMSO): \ \delta = \\ 1.18 \ (s, \ 3H, \ CH_3-CH_2), \ 3.03 \ (s, \ 2H, \ CH_2-S), \ 7.22, \ 7.38, \\ 7.42, \ 7.58, \ 7.96, \ 8.17 \ (m, \ 6H, \ C_{12}H_6), \ 8.65 \ (s, \ 1 \ H, \ HC=N), \\ 13.35 \ (s, \ 1H, \ NH). \ - \ MS \ (EI, \ 70 \ eV): \ m/z \ \ (\%) = \ 388 \\ (15) \ [M^+-CO], \ 332 \ (18) \ [M^+-3CO]. \ - \ C_{16}H_{14}MnO_6N_2S \\ (606.4): \ calcd. \ C \ 46.2, \ H \ 3.2, \ N \ 6.7, \ S \ 7.7; \ found \ C \ 46.4, \\ H \ 3.3, \ N \ 6.8, \ S \ 7.7. \end{array}$

Spectroscopic data of free ligand "nafesh" (taken from lit. [9]): IR (KBr): v = 3220 (s, NH), 1623 (m, C=N), 1242 (s, CO). – ¹H NMR (400 MHz, DMSO): $\delta = 1.15$ (s, 3H, CH₃-CH₂), 3.15 (s, 2H, CH₂-S), 7.22, 7.39, 7.42, 7.58, 7.87, 8.54 (m, 6H, C₁₂H₆), 8.81 (s, 1H, HC=N), 11.11 (s, 1H, NH), 11.15 (s, 1H, OH).

Acknowledgements

This research was supported by Gazi University Research Found under Project No 05-98/24. We thank BP (Turkey) for the provision of photochemical apparatus and Research Foundation of Ege. We thank TUBİTAK for allocation of time at the NMR, mass spectra and elemental analyses.

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