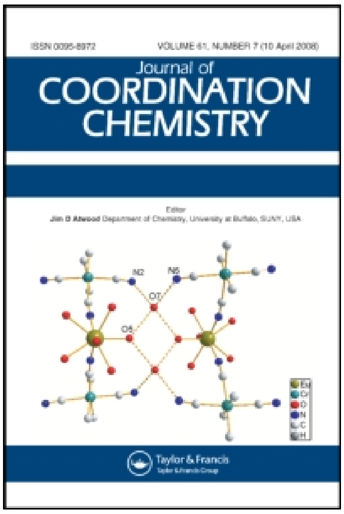

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Reaction of metal carbonyls with 2-hydroxy-1-naphthaldeyde methanesulfonylhydrazone and characterization of the substitution products

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Reaction of metal carbonyls with 2-hydroxy-1-naphthaldeyde methanesulfonylhydrazone and characterization of the substitution products

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Five new complexes, [M(CO)$_5$(nafmsh)] [M = Cr, **1**; Mo, **2**; W, **3**], [Re(CO)$_4$Br(nafmsh)], **4** and [Mn(CO)$_3$(nafmsh)], **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-hydroxy-1-naphthaldehyde methanesulfonylhydrazone (nafmsh). The complexes have been characterized by elemental analysis, EI mass spectrometry, FT-IR, and ^{1}H NMR spectroscopy. The spectroscopic studies show nafmsh is a monodentate ligand coordinating via the imine N donor atom in **1**–**4** and as a tridentate ligand in **5**.

Keywords: Photosubstitution; Methanesulfonylhydrazone; Metal carbonyls, Cyclopentadienyl

1. Introduction

There is growing pharmaceutical and chemical interest 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].

Schiff base metal carbonyl complexes attract attention in part because of the different possible coordination geometries which the ligand may adopt [12, 13]. Their low energy metal-to-ligand charge transfer (MLCT) transitions make these molecules attractive for luminescence and electron transfer reactions [14]. Several of these complexes have also been shown to be effective catalysts in allylic alkylation reactions [15, 16] and in the activation of aromatic carbon-hydrogen bonds (ortho-metallation) via intramolecular η^2-bonding of arenes [17]. For stereoselective organic transformations, chiral metal complexes, which may have a chiral metal center or a chiral coordinated ligand or both,

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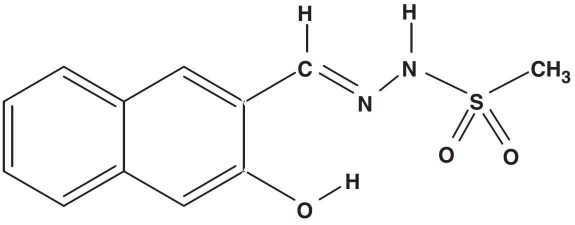
have been employed [18, 19]. We have now investigated five new complexes **1–5** which have been prepared by the photochemical reaction of metal carbonyls $M(CO)_6$ ($M = Cr$, Mo, W), $Re(CO)_5Br$, and $Mn(CO)_3Cp$ with 2-hydroxy-1-naphthaldehydemethanesulfonyl-hydrazone.



nafmsh

2. Experimental

2.1. *Materials*

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

2.2. *Apparatus*

Elemental analyses were performed on an apparatus LECO-CHNS-O-9320 by the Technical and Scientific Research Council of Turkey, TUBITAK. FT-IR spectra were recorded on samples in CH_2Cl_2 at the Ege University on a Mattson 1000 FT spectrophotometer. ^1H NMR spectra were recorded in DMSO-d_6 on a 400 MHz High Performance Digital FT-NMR at TUBİTAK. Electron impact mass spectra were recorded on a Micromass VG Platform-II LC-MS at TUBITAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor.

2.3. *Preparation of complexes*

Complexes **1–5** were prepared by photochemical reactions of metal carbonyls $M(CO)_6$ ($M = Cr$, Mo, W), $Re(CO)_5Br$ and $Mn(CO)_3Cp$ with nafmsh, and were obtained in 70–80% yields by similar methods [20] of which the following is typical.

Reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried and degassed prior to use. Hexane and THF were distilled from Na/benzophenone. Dichloromethane was distilled over calcium hydride and further purified by vacuum distilation from P_2O_5.

The complex $Cr(CO)_6$ (0.44 g, 2 mmol) and nafmsh (0.52 g, 2 mmol) were dissolved in tetrahydrofuran (80–100 mL). The solution was irradiated for 2 h. During the irradiation, the colour of the reaction mixture changed from colourless to dark yellow. After irradiation, the reaction mixture was evaporated under vacuum, yielding a dark yellow solid. After dissolving in dichloromethane (10 mL), 50 mL of hexane was added, resulting in the precipitation of a dark yellow solid. The air-stable complex was washed with hexane and dried under vacuum. Yield $[Cr(CO)_5(nafmsh)]$: 79%.

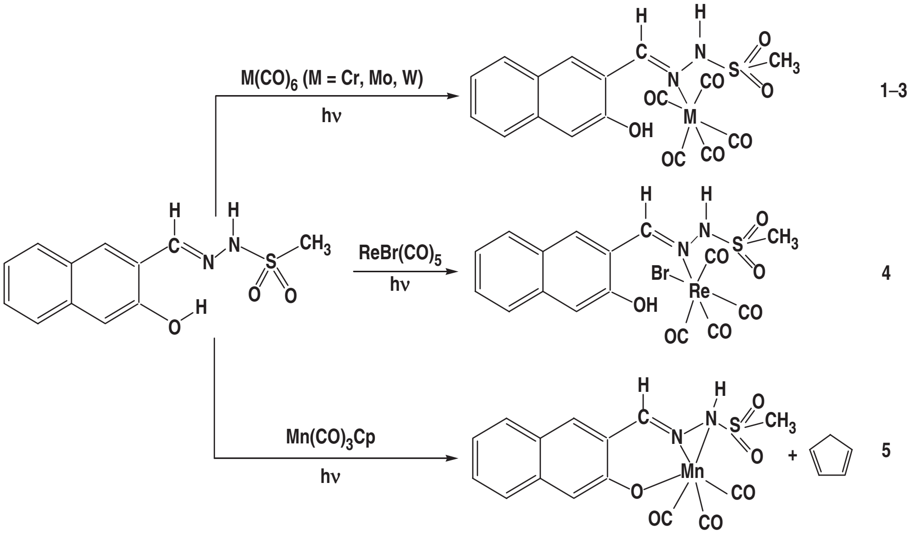
3. Results and discussion

The analytical results, yields and colours of complexes **1**–**5** are given in table 1. 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

Table 1. Elemental analysis results and yields of hydrazones.

Complexes[a]	Yield (%)	Found (Calcd) (%)			
		C	H	N	S
1	79	44.85 (44.74)	2.62 (2.65)	6.48 (6.14)	7.27 (7.03)
2	77	40.62 (40.81)	2.81 (2.42)	5.88 (5.60)	6.68 (6.41)
3	84	34.69 (34.71)	2.39 (2.06)	4.88 (4.76)	5.55 (5.45)
4	79	29.78 (29.91)	1.55 (1.88)	4.48 (4.36)	5.07 (4.99)
5	77	44.36 (44.68)	3.53 (3.00)	6.87 (6.95)	7.75 (7.95)

[a] Light yellow.



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

Table 2. Selected infrared spectral bands (cm^{-1}) of **1**–**5** and nafmsh.

Complex	ν (CO)	ν (N–H)	ν (C=N)	ν (C–O)	ν_{as} (SO_2)	ν_{sym} (SO_2)
nafmsh[a]	–	3210s	1624m	1245s	1332s	1166s
1	2065m, 1941br, 1930sh	3211s	1607m	1246s	1333s	1166s
2	2068m, 1939br, 1912sh	3212s	1607m	1246s	1332s	1167s
3	2070m, 1943br, 1931sh	3211s	1607m	1245s	1334s	1165s
4	2112w, 2019m, 1954m, 1932m	3210s	1608m	1245s	1334s	1168s
5	2017s, 1920s, 1893s	–	1601m	1264s	1318s	1156s

[a] Taken from ref. [9].

donor atom to form $M(CO)_5L$. 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 nafmsh gave a series of complexes **1**–**4** via CO displacement. However, formation of $[Mn(CO)_3(nafmsh)]$, **5**, occurs via displacement of the cyclopentadienyl ligand.

Complexes 1–4. ^1H NMR spectra data in DMSO-d_6 solutions of all compounds are collected in table 2. Free nafmsh has three donor atoms, imine nitrogen, amine nitrogen and phenolic oxygen. In the ^1H NMR spectra of free nafmsh, CH=N imine, NH amine and OH protons give three signals 8.93, 11.10 and 11.15 ppm, respectively. Similarly, proton NMR spectra of **1**–**4** have peaks at approximately 8.65, 10.95 and 11.13 ppm corresponding to imine, amine and hydroxyl protons, respectively. No shift of amine and hydroxyl protons with complex formation shows that NH and OH groups do not coordinate to metal atoms. Small shifts to upfield for the imine peak may be related to changing π-electron density in the C=N bond with complex formation in **1**–**4**. According to these data, nafmsh behaves as monodentate ligand with imine nitrogen atom in **1**–**4**.

Selected infrared spectral data are presented in table 3. The rather strong C=N stretching vibration, found at 1624 cm^{-1} in free nafmsh shifts to lower wavenumber in **1**–**4**, showing that nafmsh coordinates to the metal via the imine [24]. This shift has been explained as a weakening of the CN bond resulting from loss of electron density from the nitrogen to the metal atom [24]. No shifts were observed for SO_2 and NH stretching vibrations upon complex formation showing that SO_2 and NH were not coordinated to metal atoms in **1**–**4**. OH stretching vibration was not observed in free ligand because of hydrogen bonding with the amine nitrogen atom [9].

Furthermore, no observed OH stretching vibration in **1**–**4** may be accounted for in terms of hydrogen bonding between OH hydrogen atom and π electrons of the imine [25].

Complex 5. A 2.11 ppm NH peak in **5** shows that nafmsh coordinates to metal atoms through the amine. Because electron density around the NH protons is diminished with coordination to Mn, the NH peak shifts downfield. The disappearance of the OH proton shows that it dissociates in complex **5**.

Furthermore, shifting to higher wavenumber ca 19 cm^{-1} of the CO stretching vibration in the IR spectrum of complex **5** shows that phenolic O donor atoms coordinate to Mn atom [26–27]. Kinematic coupling with the Mn–O is not the only

Table 3. ^{1}H NMR spectroscopic data for compounds **1**–**5** in DMSO-d$_6$ (ppm).

Complex	HC=N$^-$	CH$_3^-$	(CH)$_{Ar}$	NH	OH
nafmsh[a]	8.93, s[b], 1H	3.13, s, 3H	7.22, d[e]; 7.39, t[c], 2H 7.57, ddd[g], 1H 7.87, dd[f], 2H 7.91 8.52	11.10, s, br[d], 1H	11.25, s, br, 1H
1	8.63, s, 1H	3.10, s, 3H	7.20, d[e]; 7.36, t[c], 2H 7.54, ddd[g], 1H 7.86, dd[f], 2H 7.92 8.54	10.94, s, br, 1H	11.13, s, br, 1H
2	8.63, s, 1H	3.03, s, 3H	7.21, d[e]; 7.37, t[c], 2H 7.54, ddd[g], 1H 7.85, dd[f], 2H 7.93 8.52	10.95, s, br, 1H	11.12, s, br, 1H
3	8.65, s, 1H	3.07, s, 3H	7.20, d[e]; 7.37, t[c], 2H 7.55, ddd[g], 1H 7.88, dd[f], 2H 7.92 8.51	10.96, s, br, 1H	11.12, s, br, 1H
4	8.65, s, 1H	3.08, s, 3H	7.24, d[e]; 7.37, t[c], 2H 7.57, ddd[g], 1H 7.88, dd[f], 2H 7.92 8.55	10.94, s, br, 1H	11.13, s, br, 1H
5	8.65, s, 1H	3.05, s, 3H	7.22, d[e]; 7.42, t[c], 2H 7.58, ddd[g], 1H 7.83 7.92, dd[f], 2H 8.17	13.21, s, br, 1H	–

[a] Taken from ref. [9].

reason for an increase. The rather strong N–H stretching vibration, found at 3210 cm^{-1} in free nafmsh shifts to lower wavenumber, 3188 cm^{-1} in complex **5**.

As known, carbonyl elimination takes place in the photolysis of CpMn(CO)$_3$ [28, 29]. In fact, the dissociation energy of Mn–Cp bond is reported to be 50.7 kcal mol^{-1} and the average dissociation energy of the Mn–CO bond is 34.0 kcal mol^{-1} in CpMn(CO)$_3$ [30]. However, in complex **5**, η^5-cyclopentadienyl in CpMn(CO)$_3$ is displaced with nafmsh via nucleophilic substitution along with simultaneous hydrogen atom transfer from nafmsh to the cyclopentadienyl to form cyclopentadiene. The presence of bulky ligands, can lead to dissociation of Cp instead of CO. It is known that, for many dissociation reactions the effect of ligand crowding may be more important than electronic effect [31]. Majima has reported that Mn–CO and Mn–Cp bonds dissociate in the infrared multiple-photon decomposition (IRMPD) of CpMn(CO)$_3$ [32].

The mass spectral data of **1**–**5**, given in table 4, show fragmentation via successive loss of CO groups and organic ligands.

Table 4. The mass spectral data of **1**–**5**.

Complex	MW	Relative intensities of the ions m/e and assignment[a]
1	406	428(10) $[M^+ - (CO)]$, 400(15) $[M^+ - (2CO)]$, 372(25) $[M^+ - (3CO)]$, 316(10) $[M^+ - (5CO)]$
2	450	485(10) $[M^+ - (Me)]$, 457(15) $[M^+ - (Me + CO)]$, 429(20) $[M^+ - (Me + 3CO)]$, 401(15) $[M^+ - (Me + 4CO)]$, 373(15) $[M^+ - (Me + 5CO)]$
3	538	573(10) $[M^+ - (Me)]$, 545(15) $[M^+ - (Me + CO)]$, 517(10) $[M^+ - (Me + 2CO)]$, 489(20) $[M^+ - (Me + 3CO)]$, 433(15) $[M^+ - (Me + 5CO)]$
4	592	614(10) $[M^+ - (CO)]$, 586(25) $[M^+ - (2CO)]$, 530(15) $[M^+ - (4CO)]$
5	353	375(15) $[M^+ - (CO)]$, 347(15) $[M^+ - (2CO)]$, 319(35) $[M^+ - (3CO)]$

[a] For the mass spectral data relative intensities are given in parentheses; probable assignments in square brackets. For all assignments the most abundant isotopes of Cr, Mo, W, Re and Mn have been selected (^{52}Cr, 83.76%, ^{98}Mo, 24%, ^{184}W, 30.7%, ^{187}Re, 62.9%, ^{55}Mn, 100% abundant).

4. Conclusions

nafmsh behaves as a monodentate ligand via N imine in **1**–**4**, but as a tridentate ligand via anionic O, imine N and amine N donor atoms in **5**.

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