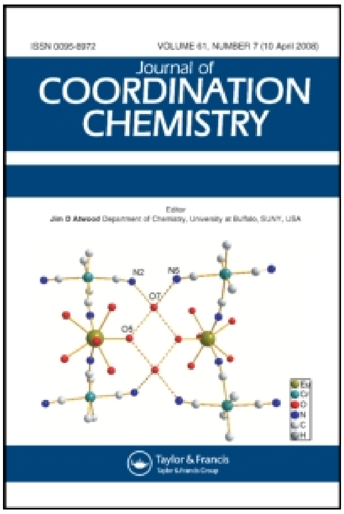

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Synthesis and Characterization of the products from reaction of Metal Carbonyls $[M(CO)_6$ (M Cr, Mo, W), $Re(CO)_5Br$, $Mn(CO)_3Cp]$ with Salicylaldehyde Methanesulfonylhydrazone

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SYNTHESIS AND CHARACTERIZATION OF THE PRODUCTS FROM REACTION OF METAL CARBONYLS [$M(CO)_6$ ($M = Cr, Mo, W$), $Re(CO)_5Br$, $Mn(CO)_3Cp$] WITH SALICYLALDEHYDE METHANESULFONYLHYDRAZONE

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Five new complexes, [$M(CO)_5$(salmsh)] ($M = Cr$; **1**, Mo; **2**, W; **3**), [$Re(CO)_4Br$(salmsh)], **4**, and [$Mn(CO)_3$(salmsh)], **5**, have been synthesized by the photochemical reaction of metal carbonyls with salicylaldehyde methanesulfonylhydrazone (salmsh). The complexes have been characterized by elemental analyses, EI mass spectrometry, FT-IR and ^1H NMR spectroscopy. The spectroscopic studies show that salmsh behaves as a monodentate ligand coordinating via the imine N donor atom in **1**–**4** and as a tridentate ligand in **5**.

Keywords: Sulfonylhydrazone; Salicylaldehyde; Methanesulfonylhydrazone; Metal carbonyls

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, 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]. Several of these complexes have also been shown to be effective catalysts in allylic alkylation reactions [16,17] and in the activation of aromatic carbon–hydrogen bonds

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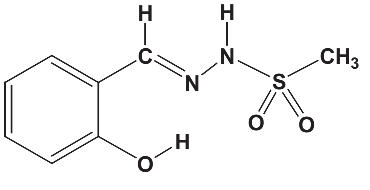
(orthometallation) via intramolecular η^2-bonding of arenes [18]. For stereoselective organic transformations, chiral metal complexes which have a chiral metal center or a chiral coordinated ligand or both, have been employed [19,20]. In view of the above, we have investigated a series of five new complexes **1–5** that have been prepared for the first time, by photochemical reaction of metal carbonyls [$M(CO)_6$] (M = Cr, Mo, W), [$Re(CO)_5Br$], [$Mn(CO)_3Cp$] with salicylaldehyde methanesulfonylhydrazone (salmsh).



salmsh

EXPERIMENTAL

Materials

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

Apparatus

Elemental analyses were performed on a LECO-CHNS-O-9320 apparatus (Technical and Scientific 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 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 TUBİTAK.

UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled, immersion-well reactor.

Preparation of Complexes

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 salmsh, and were obtained in 70–80% yields [21].

RESULTS AND DISCUSSION

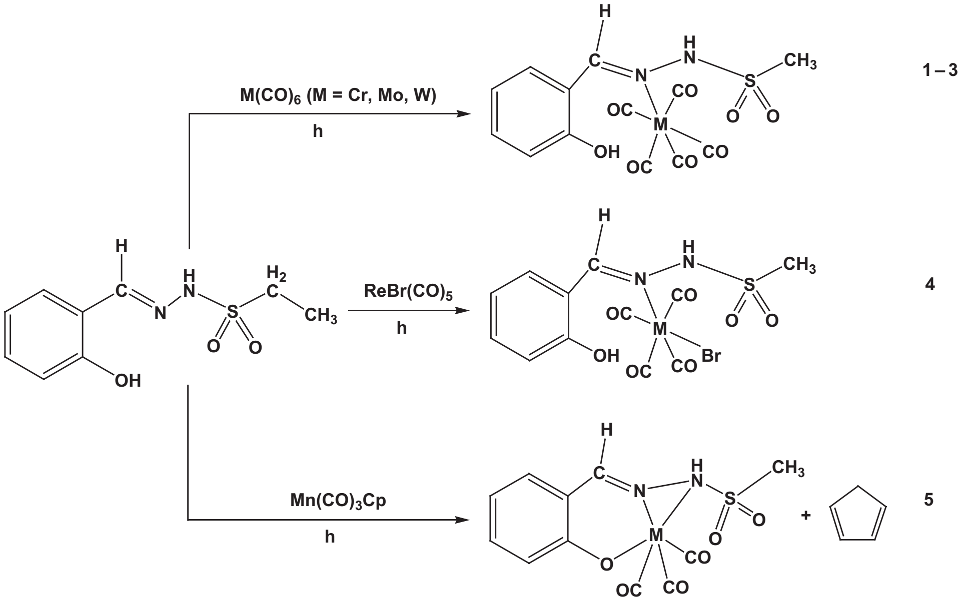
The analytical results, yields and the colors of the novel complexes **1**–**5** are given in Table I. Complexes **1**–**5** were prepared by a photochemical reaction as shown in Scheme 1. The photogeneration of $M(CO)_5$ from $M(CO)_6$ ($M = Cr, Mo, W$) has been extensively studied. These 16-electron $M(CO)_5$ 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 $M(CO)_6$ ($M = Cr, Mo, W$), and $Re(CO)_5Br$ with salmsh ligand gave a series of complexes **1**–**4** via CO displacement. However, the formation of $[Mn(CO)_3(salmsh)]$, **5**, occurs via displacement of the cyclopentadienyl ligand.

Selected infrared spectral data of **1**–**5** are presented in Table II. The rather strong C=N stretching vibration, found at $1622\,cm^{-1}$ in the free ligand, shifts to a lower wavenumber in **1**–**5**, showing that the salmsh ligand coordinates to the metal via the imine donor atom [24]. This shift has been explained as a weakening of the CN bond resulting

TABLE I Elemental analysis results and yields of hydrazones

Complexes[a]	*Yield* (%)	*Found* (*calcd.*) (%)			
		C	*H*	*N*	*S*
1	78	38.79 (38.43)	2.22 (2.48)	6.63 (6.89)	7.55 (7.89)
2	79	34.80 (34.68)	2.47 (2.24)	6.47 (6.22)	7.48 (7.12)
3	83	29.35 (29.01)	1.67 (1.87)	5.39 (5.21)	5.65 (5.96)
4	79	25.67 (24.33)	1.91 (1.70)	4.46 (4.73)	5.63 (5.41)
5	79	37.22 (37.41)	2.46 (2.85)	7.64 (7.93)	8.97 (9.08)

[a] Light yellow.



SCHEME 1 Photochemical reactions of metal carbonyls with the salmsh ligand.

TABLE II Selected IR spectral bands (cm^{-1}) of **1**–**5** and salmsh

Complex	$\nu(CO)$	$\nu(N\text{–}H)$	$\nu(C{=}N)$	$\nu(C\text{–}O)$	$\nu_{as}(SO_2)$	$\nu_{sym}(SO_2)$
salmsh[a]	–	3210s	1622m	1268s	1320s	1154s
1	2066m, 1980m, 1950s, 1930s, 1875m	3211s	1605m	1268s	1321s	1156s
2	2065m, 1991m, 1955s, 1925s, 1871m	3210s	1605m	1268s	1321s	1156s
3	2065m, 1992m, 1960s, 1924s, 1875s	3211s	1605m	1267s	1321s	1156s
4	2113w, 2018m, 1967m, 1936m	3211s	1605m	1267s	1321s	1156s
5	2018s, 1934s, 1915s	–	1601m	1280s	1318s	1156s

[a]Taken from ref. [9].

TABLE III ^{1}H NMR spectroscopic data for compounds **1**–**5** in DMSO-d_6 (ppm)

Complex	*HC=N–*	CH_3–	$(CH)_{Ar}$	*NH*	*OH*
salmsh[a]	8.27, s, 1H	3.06, s, 3H	6.88, d; 6.90,t, 2H 7.26, ddd, 1H 7.60, dd, 2H	10.21, s, br, 1H	11.00, s, br, 1H
1	8.08, s, 1H	3.00, s, 3H	6.88, d; 6.91,t, 2H 7.19, ddd, 1H 7.48, dd, 2H	10.09, s, br, 1H	11.04, s, br, 1H
2	8.07, s, 1H	2.90, s, 3H	6.87, d; 6.81,t, 2H 7.18, ddd, 1H 7.44, dd, 2H	10.08, s, br, 1H	11.06, s, br, 1H
3	8.06,s, 1H	3.01, s, 3H	6.87, d; 6.90,t, 2H 7.21, ddd, 1H 7.47, dd, 2H	10.11, s, br, 1H	11.02, s, br, 1H
4	7.99, s, 1H	3.06, s, 3H	6.87, d; 6.95,t, 2H 7.19, ddd, 1H 7.47, dd, 2H	10.01, s, br, 1H	11.06, s, br, 1H
5	7.68, s, 1H	2.90, s, 3H	6.87, d; 6.94,t, 2H 7.20, ddd, 1H 7.45, dd, 2H	11.96, s, br, 1H	–

[a]Taken from ref. [9].
s: singlet; t: triplet; br: broad; d: doublet; dd: doublet of doublets; ddd: three-fold doublet.

from loss of electron density from the nitrogen to the metal atom. No shifts were observed in SO_2 and NH stretching vibrations with complex formation, indicating that the SO_2 and NH groups of salmsh do not coordinate to metal atoms in **1**–**4**. The O–H stretching vibration of salmsh was not observed in the free ligand or **1**–**4** because of hydrogen bonding with the imine nitrogen atom.

The number of carbonyl bands in the complexes provides important clues to the environment around the metal centers [25]. Five carbonyl stretching bands in **1**–**3** are attributed to local C_s symmetry of $M(CO)_5$ [21,22]. Similarly, four CO stretching absorptions in **4** and three in **5** indicate a *local* C_{2v} [26], and C_{3v} [27] symmetry, respectively (shown in Scheme 1).

^{1}H NMR spectral data in DMSO-d_6 solutions of compounds **1**–**5** are collected in Table III. In the ^{1}H NMR spectra of **1**–**4**, the signal for the NH hydrogen of free ligand at 10.21 ppm remains unchanged. The signal of OH hydrogens of salmsh and

TABLE IV Mass spectral data for **1**–**5**

Complex	*MW*	*Relative intensities of the ions m/e and assignment*[a]
1	406	391(25), $[M^+-(Me)]$; 363(15), $[M^+-(Me+CO)]$; 335(30), $[M^+-(Me+2CO)]$; 307(25), $[M^+-(Me+3CO)]$; 279(15), $[M^+-(Me+4CO)]$; 251(10), $[M^+-(Me+5CO)]$.
2	450	4422(15), $[M^+-(CO)]$; 394(25), $[M^+-(2CO)]$; 366(25), $[M^+-(3CO)]$; 338(15), $[M^+-(4CO)]$; 310(10), $[M^+-(5CO)]$.
3	538	480(15), $[M^+-(2Me-CO)]$; 452(20), $[M^+-(2Me+2CO)]$; 424(15),$[M^+-(2Me+3CO)]$; 396(20), $[M^+-(2Me+4CO)]$; 368(15), $[M^+-(2Me+5CO)]$.
4	592	564(15), $[M^+-(CO)]$; 536(15), $[M^+-(2CO)]$; 480(20), $[M^+-(4CO)]$.
5	353	338(15), $[M^+-(Me)]$; 310(25), $[M^+-(Me+CO)]$; 282(20), $[M^+-(Me+2CO)]$; 254(15), $[M^+-(Me+3CO)]$.

[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% abundance).

in **1**–**4** complexes was observed at about 11.10 ppm, that is, there is no shift on complex formation. These data show that NH and OH groups do not participate in coordination. The signal at 8.27 ppm for salmsh due to the hydrogen from the HC=N shows a small upfield shift, which may be related to changing π-electron density in the C=N bond upon complex formation in **1**–**4**. According to these data, salmsh is a monodentate ligand in **1**–**4**.

In Mn(salmsh)$(CO)_3$ (**5**), however, the NH resonance of salmsh shifts 1.75 ppm downfield. Because electron density around the NH protons is diminished with coordination to Mn(I), the NH peak is shifted downfield.

The phenolic OH signal disappears in the NMR spectrum as expected for complex **5**. In the IR spectrum of complex **5**, shifting to higher wavenumber (12 cm^{-1}) of the CO stretching vibration shows that phenolic O donor atoms coordinate to Mn [28,29]. Kinematic coupling of the CO stretching vibration with the Mn–O stretching vibration would increase the wavenumbers. According to these data, the salmsh ligand loses OH protons, behaves as an ionic tridentate ligand in **5**, and acts as a six-electron donor. The δ_{NH} band was obscured by other ligand bands, and not observed in the IR spectra of ligand and complex **5**.

The mass spectral data of **1**–**5** are given in Table IV. The mass spectra show fragmentation via successive loss of CO groups and organic ligands.

CONCLUSION

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

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