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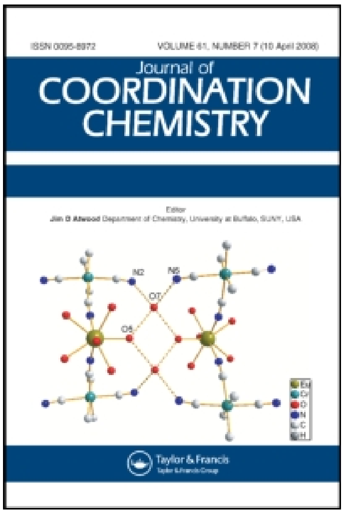

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Photochemical reactions of metal carbonyls [M(CO)$_6$ (M = Cr, Mo, W)] with *N*,*N*′-bis(salicylidene)-1,2-bis-(*o*-aminophenoxy)ethane

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The complexes [M(CO)$_4$(η^2-H$_2$L)] [M = Cr; **1**, Mo; **2**, W; **3**] have been synthesized by photochemical reactions of VIB metal carbonyls [M(CO)$_6$] [M = Cr, Mo, W] with *N*,*N*′-bis(salicylidene)-1,2-bis-(*o*-aminophenoxy)ethane (H$_2$L) in THF and characterized by elemental analyses, FTIR, ^{1}H NMR and mass spectra. The H$_2$L ligand is coordinated to the central metal as a bidentate ligand via the central azomethine nitrogen atoms in **1**–**3**.

Keywords: *N*,*N*′-bis(salicylidene)-1,2-bis-(o-aminophenoxy)ethane; Metal carbonyls
Schiff base

1. Introduction

Schiff bases play an important role as chelating ligands in main group and transition metal coordination chemistry [1–5]. Recently, interest in the chemistry of transition metal compounds that contain Schiff bases has increased greatly. Transition metal complexes of Schiff base ligands find applications as models of certain metal enzymes and in catalysis and materials chemistry [6]. Schiff base complexes are known to show antifungal activity, which is increased by the presence of a hydroxy group in the ligand [7]. 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 [8–10]. Their low energy metal-to-ligand charge transfer (MLCT) transitions make these molecules attractive for luminescence and electron transfer reactions [11]. In addition, several of these complexes have been shown to be effective

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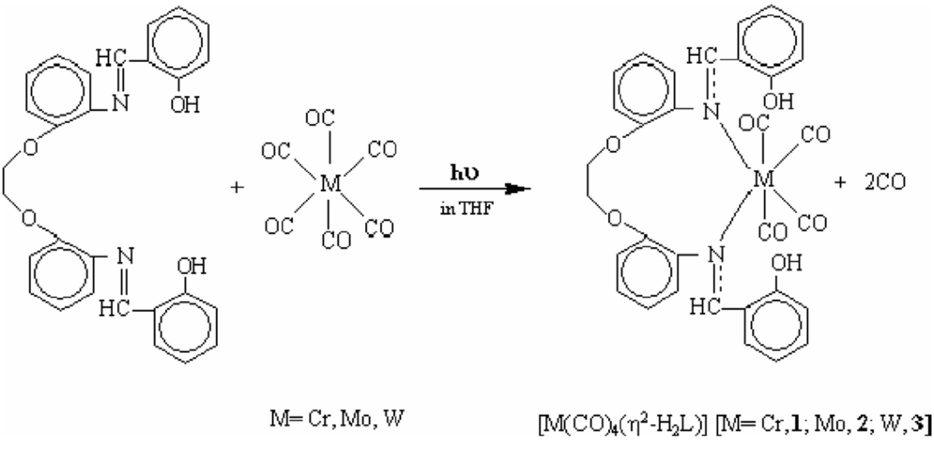
catalysts in allylic alkylation reactions [12, 13] and in the activation of aromatic carbon-hydrogen bonds (orthometallation) via intramolecular η^2-bonding of arenes [14]. Polydentate Schiff bases containing nitrogen and oxygen donor atoms are useful for the synthesis of transition metal complexes which play important roles in biological systems [15, 16]. Such ligands were also found to provide catalytic characteristics especially for epoxidation reactions [17–20]. The versatile chemistry of these reactions has prompted us to investigate the reactions of VIB metal carbonyls [M(CO)$_6$] [M = Cr, Mo, W] with *N*,*N*′-bis(salicylidene)-1,2-bis-(*o*-aminophenoxy)ethane (H$_2$L), scheme 1, under UV photolysis. Three new complexes [M(CO)$_4$(η^2-H$_2$L)] [M = Cr; **1**, Mo; **2**, W; **3**] have been synthesized and characterized.

2. Experimental

2.1. *Materials and methods*

Reactions were carried out under an oxygen-free nitrogen atmosphere using Schlenk techniques. All glassware was oven-dried at 120°C. All solvents were dried and degassed using standard techniques [21] and stored under nitrogen until used. THF, petroleum ether, dichloromethane and silica gel were purchased from Merck and M(CO)$_6$ (M = Cr, Mo, W) from Aldrich. H$_2$L was prepared by a literature method [22].

Elemental analyses were performed on a Leco 932 instrument by the Technical and Scientific Research Council of Turkey, TUBITAK. FTIR spectra were recorded (KBr pellets) on a Mattson 1000 FT spectrophotometer. ^{1}H NMR spectra were recorded in CDCl$_3$ or DMSO-d$_6$ on a 500 MHz High Performance Digital FT-NMR and chemical shifts are referenced to tetramethylsilane (TMS). Mass spectra were recorded on a Jeol AX505 FAB spectrometer. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor, which was cooled by circulating water.



Scheme 1. Photogeneration of [M(CO)$_4$(η^2-H$_2$L)] [M = Cr; **1**, Mo; **2**, W; **3**].

2.2. *Preparation of complexes*

The complexes [$M(CO)_4(\eta^2\text{-}H_2L)$] [M = Cr; **1**, Mo; **2**, W; **3**] were prepared by the photochemical reactions of [$M(CO)_6$] (M = Cr, Mo, W) with *N*,*N*′-bis(salicylidene)-1,2-bis-(*o*-aminophenoxy)ethane (H_2L) and obtained in 60–70% yield by similar methods; the following is typical. $Cr(CO)_6$ (0.44 g, 1 mmol) and H_2L (0.54 g, 1 mmol) were dissolved in THF (80–100 cm^3) and the solution irradiated for 2 h. During the irradiation, the solution changed colour from colourless to dark brown. After irradiation the solvent was removed under vacuum to yield a dark brown solid, which was extracted with CH_2Cl_2 (10 cm^3). Addition of petroleum ether (50 cm^3) resulted in the precipitation of an orange solid which was washed with petroleum ether and dried under vacuum, and shown to be [$Cr(CO)_4(\eta^2\text{-}H_2L)$], (**1**) (68% yield). Traces of unreacted hexacarbonylchromate(0) was sublimed onto a cold finger at −20°C while keeping the complex at 0°C in an ice bath.

3. Results and discussion

Photogeneration of $M(CO)_5$ from $M(CO)_6$ (M = Cr, Mo, W) has been extensively studied [23–30]. These 16-electron $M(CO)_5$ fragments react avidly with any available donor to form $M(CO)_5L$ species, where L is a chelating bidentate ligand, and rapid conversion to the chelating $M(CO)_4L$ or bridging $M_2(CO)_{10}(\mu - L)$ products may occur [31]. Moreover, photogeneration of $M(CO)_4$ (M = Re), $M(CO)_3$ and $M(CO)_2$ (M = Mn) from [$Re(CO)_5Br$] and [$Mn(CO)_3Cp$] has been reported [32–36]. The photochemical reactions of $M(CO)_6$ (M = Cr, Mo, W) with H_2L proceed in the expected manner to yield the hitherto unknown complexes **1**–**3**. The synthetic route shown in scheme 1 is suggested. Analytical data for complexes **1**–**3** are summarized in table 1. The complexes are air-stable and soluble in chlorinated solvents.

Characteristic IR data are listed in table 2. The IR spectrum of **1**, for example, exhibits four prominent bands at 2021, 1974, 1942 and 1917 cm^{-1}in the CO

Table 1. Elemental analyses results for the complexes.

			Found (Calcd) (%)		
Complex	Yield (%)	Colour	C	H	N
1	68	Orange	62.26 (62.33)	3.52 (3.90)	4.24 (4.55)
2	62	Orange	58.04 (58.18)	3.50 (3.64)	4.09 (4.24)
3	70	Orange	51.12 (51.35)	3.02 (3.21)	3.51 (3.74)

Table 2. Characteristic FTIR bands (cm^{-1}) of H_2L and the complexes.

Complex	ν(CO)	ν(C=N)	ν(O–H)[b]	ν(phen C–O)
H_2L[a]		1617s	2882br	1286s
1	2021m, 1974s, 1942s, 1917s	1586s		1285s
2	2021m, 1974s, 1940s, 1917s	1584s		1286s
3	2020m, 1975s, 1942s, 1912s	1581s		1286s

[a] Taken from Ref. [22]. [b] Intramolecular hydrogen bonded –OH.

stretching region. The four band ν(CO) pattern indicates the local $C_{2\nu}$ symmetry of $M(CO)_4$ skeleton [37]. These modes are at lower wave numbers as compared to $Cr(CO)_6$. IR spectra of the other two complexes exhibit essentially the same ν(CO) absorption pattern as observed for **1**. IR spectra of **1**–**3** display characteristic bands of H_2L with appropriate shifts due to complex formation. The strong band at 1617 cm^{-1} in the IR spectrum of free H_2L corresponds to C=N stretching [22]. This band shifts towards lower frequency in **1**–**3**, showing that H_2L ligand coordinates to the metal via the imine (C=N) nitrogen donor atoms. This shift has been assessed as a weakening of the C=N bond resulting from the transfer of electron density from the nitrogen to the metal atom. A broad band in the IR spectrum of the Schiff base at 2882 cm^{-1} is assigned to the intramolecular hydrogen bonded –OH stretch [22]. This band disappears in the IR spectra of the complexes. Phenolic C–O stretching vibrations at ca 1286 cm^{-1} in the IR spectra of **1**–**3** show no shift upon complex formation.

^{1}H NMR data for DMSO-d$_6$ solutions of **1**–**3** are collected in table 3. Except for the HC=N proton, all other chemical shifts of coordinated H_2L have similar values to those of the free ligand. In ^{1}H NMR spectra of the complexes the shift of the OH proton remains virtually unchanged from that of the free ligand at 13.12 ppm, and shows that the OH group does not participate in coordination. The down-field shift of the HC=N imine proton may be related to a decrease in π-electron density in the C=N bond with complex formation. Data for mass spectra of **1**–**3** are given in table 4, and show fragmentation via successive loss of CO groups and organic ligands.

In summary, FTIR and ^{1}H NMR spectra of the compounds show that H_2L coordinates to the metal atom via both azomethine nitrogen atoms, behaving as a neutral bidentate ligand. C=N stretching in IR spectra of the compounds and shift to lower wave number, and four prominent carbonyl bands in the CO stretching region are consistent with the formulation of the complexes **1**–**3**. ^{1}H NMR data exhibited expected integrals and shifts. Mass spectra fragmentation patterns are in line with the proposed structures of **1**–**3**.

Table 3. ^{1}H NMR data for the ligand H_2L and **1**–**3** in DMSO-d$_6$ solution.[a]

Complex	HC=N	–OH	Arom. CH	O–CH$_2$
H$_2$L[b]	8.80, s, 2H	13.12, s, 2H	7.04–7.90, m, 16H	4.40, s, 4H
1	8.96, s, 2H	13.10, s, 2H	7.02–7.92, m, 16H	4.40, s, 4H
2	8.94, s, 2H	13.12, s, 2H	7.03–7.89, m, 16H	4.42, s, 4H
3	8.94, s, 2H	13.11, s, 2H	7.04–7.90, m, 16H	4.41, s, 4H

[a] δ in ppm. [b] Taken from Ref. [22].

Table 4. Mass spectroscopy data for **1**–**3**.

Complex	M.W.	Relative intensities of the ions m/z[a]
1	616	588 (45), [M^+–(CO)]; 560 (17), [M^+–2(CO)]; 439 (7), [M^+–3(CO)–C_6H_4OH]; 266 (9), [M^+–Cr–4(CO)–2(C_6H_4OH)].
2	660	511 (7), [M^+–2(CO)–C_6H_4OH]; 239 (15), [M^+–Mo–4(CO)–2(C_6H_4OH)–(HC=N)].
3	748	720 (45), [M^+–(CO)]; 692 (17), [M^+–2(CO)]; 266 (7), [M^+–W–4(CO)–2(C_6H_4OH)].

[a] Relative intensities are given in parentheses and assignments in square brackets.

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