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Photosubstitution of Thiosemicarbazide to VI B and VII B Group Metal Carbonyls

E. SUBASI* and S. ÇETIN

Department of Chemistry, Faculty of Science, Dokuz Eylul University, Buca-Tinaztepe, 35160 Izmir, Turkey

*Corresponding author: Fax: +90 232 4534188; Tel: +90 232 3018692; E-mail: elif.subasi@deu.edu.tr

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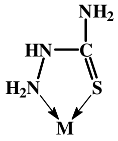
A series of new metal carbonyl complexes of **VIB** and **VIIB** groups having the general compositions *cis*-[M(CO)$_4$(η^2-N,S-TSC)], [M = Cr; **1**, Mo; **2**, W; **3**] and *fac*-[ReBr(CO)$_3$ (η^2-*N,N*-TSC)], **4** and [(η^5-Cp)Mn(CO)(η^2-*N,N*-TSC)], **5** have been prepared by photochemical reactions of thiosemicarbazide (TSC) and metal carbonyls in THF. The complexes have been characterized by elemental analysis, LC- mass spectrometry, FT-IR and ^{1}H NMR spectroscopy. The spectral data suggest the involvement of sulfur and terminal amino nitrogen of thiosemicarbazide in coordination to the central metal ion for **VIB** metal carbonyl complexes whereas the terminal amino nitrogen and thioamide nitrogen of thiosemicarbazide in coordination to the central metal ion for **VIIB** metal carbonyl complexes. On the basis of spectral studies, an octahedral geometry has been assigned for all of the complexes.

Key Words: Thiosemicarbazide, Transition metal carbonyls, Photochemical reactions.

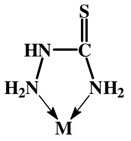
INTRODUCTION

Thiosemicarbazide-based compounds have been extensively studied over the last couple of decades[1-3]. Various Schiff bases of thiosemicarbazide (thiosemicarbazones) have attracted much attention because of the large number of potentially useful biological properties such as antibacterial, antifungal, antitumor, antimalarial, antiviral and antiinflammatory activities[4-9]. Their activities have frequently been thought to be due to their ability to chelate metals. It is well known that the compounds containing > C=S moiety have a strong ability to form metal complexes. Sulfur compounds have been the subject of interest in coordination and organometallic chemistry. Although many structures of thiosemicarbazone complexes have been reported, there are a few for complexes of the precursor thiosemicarbazide[10].

Thiosemicarbazide is an ambidentate ligand capable of forming five-membered metallocycles during coordination (**A**, **B**) or monodentate bonding through sulfur (**C**)[11]. Thiosemicarbazide usually acts as a chelating ligand for transition metal ions by bonding through the sulfur and terminal amino nitrogen atom, although in some cases they behave as monodentate ligands where bound through sulfur only[12].



(A)



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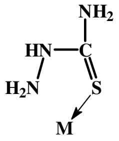


(C)

Carbonyl compounds with sulfur and nitrogen donor ligands continue to attract considerable attention not only on account of their fascinating structural chemistry, but also because of their ability to act as electron reservoirs and their potential in catalysis[13]. Features of the chemistry of these molecules, which are currently of interest include the mechanisms and sites of substitution as well as the modification of reactivity accompanying carbonyl replacement by donor ligands[14].

As a ligand, thiosemicarbazide has more than one potential donor atoms. Therefore, we tried to observe the sites of substitution of these ligands to the metal center. Our continued interest in the photochemical synthesis and structural aspects of group **VIB** and **VIIB** metal carbonyls prompted us to make an exploratory investigation into the photolytic behaviour of the **VIB** and **VIIB** metal carbonyls, [M(CO)$_6$] [M = Cr, Mo, W], [Re(CO)$_5$Br] and [(η^5-Cp)Mn(CO)$_3$] with thiosemicarbazide[15-24]. In this paper, the *hitherto* unknown new complexes, *cis*-[M(CO)$_4$(η^2-N,S-TSC)], [M = Cr; **1**, Mo; **2**, W; **3**] have been prepared by the photochemically synthesized [M(CO)$_5$THF] [M = Cr, Mo, W] and *fac*-[ReBr(CO)$_3$(η^2-*N,N*-TSC)], **4** and [(η^5-C$_p$)Mn(CO)(η^2-*N,N*-TSC)], **5** have been prepared by the photochemical reactions of [Re(CO)$_5$Br] and [(η^5-C$_p$)Mn(CO)$_3$] with thiosemicarbazide respectively and all of the complexes have been characterized by elemental analyses, FT-IR, ^{1}H NMR spectroscopy and Mass spectrometry.

The spectral data suggest the involvement of sulfur and terminal amino nitrogen of thiosemicarbazide in coordination to the central metal ion for **VI B** metal carbonyl complexes whereas both terminal hydrazine and thioamide nitrogens of thiosemicarbazide in coordination to the central metal ion for **VII B** metal carbonyl complexes. On the basis of spectral studies, an octahedral geometry has been assigned for all of the complexes.

EXPERIMENTAL

Reactions were carried out under an oxygen-free nitrogen atmosphere using Schlenk techniques. All glassware was oven-dried at 120 ºC. All solvents were dried and degassed using standard techniques and stored under nitrogen until used[25]. Thiosemicarbazide, THF, petroleum ether, dichloromethane, ethanol and silica gel were purchased from Merck and $M(CO)_6$ (M = Cr, Mo, W), $ReBr(CO)_5$ and $[(\eta^5\text{-}Cp)Mn(CO)_3]$ from Aldrich.

Elemental analyses were performed on a Leco 932 instrument at Technical and Scientific Research Council of Turkey, TUBITAK. FT-IR spectra were recorded (KBr pellets) on a Varian 1000 FT spectrophotometer. ^{1}H NMR spectra were recorded in DMSO-d_6 on a 500 MHz high performance digital FT-NMR and chemical shifts were referenced to tetramethylsilane. LC- Mass spectra analyses were performed on Agilent 1100 MSD device at TUBITAK. UV irradiations were performed with a medium-pressure 125 W mercury lamp through a quartz-walled immersion well reactor, which was cooled by circulating water.

Syntheses of *cis*-[M(CO)$_4$(η^2-N,S-TSC)], [M = Cr; 1, Mo; 2, W; 3]: The complexes, *cis*-[M(CO)$_4$(η^2-N,S-TSC)], [M = Cr; **1**, Mo; **2**, W; **3**] were prepared by the photochemical reactions of $M(CO)_5THF$ (M = Cr, Mo, W) with thiosemicarbazide and obtained in 55-75 % yield by similar methods as follows:

A solution of $Cr(CO)_6$ (0.22 g, 1 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.30 h at room temperature. A solution of thiosemicarbazide (0.045 g, 0.50 mmol) in 20 mL of warm ethanol was added to the resulting solution of the $Cr(CO)_5THF$ intermediate. The reaction mixture was stirred at room temperature for 0.75 h. During stirring process, the solution changed from yellow to light brown. The solvent was then removed under vacuum and afford a solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a light brown solid which was washed with petroleum ether and dried under vacuum and shown to be *cis*-[Cr(CO)$_4$(η^2- N,S-TSC)], **1**, (60 % yield). Trace of unreacted metal carbonyl was sublimed out in vacuum at -20 ºC.

Syntheses of *fac*-[ReBr(CO)$_3$(η^2-*N,N*-TSC)], 4; [(η^5-Cp)Mn(CO)(η^2-N,N-TSC)], 5: The complexes, *fac*-[ReBr(CO)$_3$(η^2-N,N-TSC)], **4** and [(η^5-Cp)Mn(CO)(η^2-N,N-TSC)], **5** were prepared by the photochemical reactions of $ReBr(CO)_5$ and $[(\eta^5\text{-}Cp)Mn(CO)_3]$ with thiosemicarbazide, respectively and obtained in 60-70 % yield by similar methods as follows:

The complexes $ReBr(CO)_5$ (0.203 g, 0.50 mmol) and thiosemicarbazide (0.027 g, 0.30 mmol) were dissolved in THF (80-100 mL) and the solution was irradiated for 2 h using a 125 W medium pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the solution changed from colourless to orange. After irradiation the solvent was evaporated under the vacuum yielding an orange solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a light brown solid, which was washed with petroleum ether and dried under vacuum and shown to be *fac*-[ReBr(CO)$_3$(η^2-N,N-TSC)], (0.12 g, 73 % yield). Trace of unreacted metal carbonyl was sublimed out in vacuum at -20 ºC.

RESULTS AND DISCUSSION

Photogeneration of $M(CO)_5$ from $M(CO)_6$ (M = Cr, Mo, W) has been extensively studied. These 16-electron containing $M(CO)_5$ fragments react avidly with any available donor to form $M(CO)_5L$ species and where L is a chelating bidentate ligand, rapid continuation to afford the $M(CO)_4L$ product can occur[26]. The photochemical reactions of $M(CO)_5THF$ (M = Cr, Mo, W), [Re(CO)$_5$Br] and $[(\eta^5\text{-}Cp)Mn(CO)_3]$ with thiosemicarbazide proceed in this expected manner to yield the *hitherto* unknown series of complexes **1-5** as shown in Fig. 1. The complexes were synthesized by reacting thiosemicarbazide with the metal carbonyls in 2:1 (M:L) ratio in THF. The analytical data and spectral analysis agree well with the proposed composition of the complexes **1-5**. The analytical data for novel complexes are summarized in Table-1. The stoichiometry of the ligands and their complexes were confirmed by their elemental analyses.

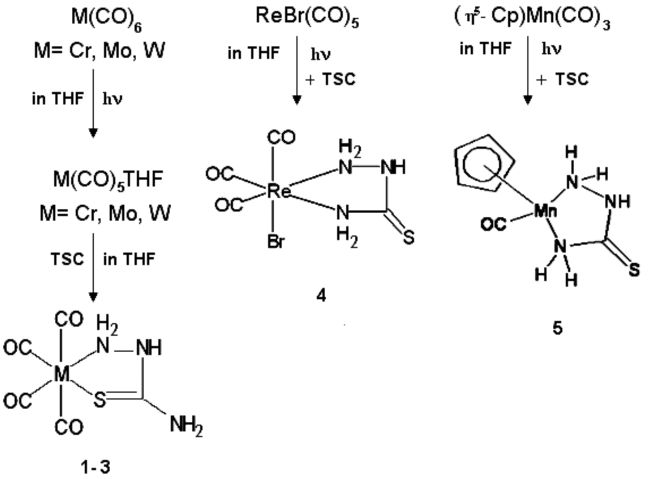


Fig. 1. Photogeneration of *cis*-[M(CO)$_4$(η^2-N,S-TSC)], [M = Cr; **1**, Mo; **2**, W; **3**]; *fac*-[ReBr(CO)$_3$(η^2-N,N-TSC)], **4** and *cis*-[(η^5-Cp)Mn(CO)(η^2-N,N-TSC)], **5**

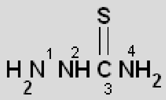
TABLE-1
ELEMENTAL ANALYSIS RESULTS AND PHYSICAL PROPERTIES FOR THE COMPLEXES

Complex	Yield (%)	Colour	Found (calcd.) (%)		
			C	H	N
1	60	Light brown	23.78 (23.53)	2.14 (1.96)	16.74 (16.47)
2	65	Light brown	20.45 (20.07)	1.88 (1.67)	14.54 (14.05)
3	70	Dark yellow	15.89 (15.5)	1.43 (1.29)	10.99 (10.85)
4	73	Light brown	11.05 (10.91)	1.32 (1.14)	9.85 (9.55)
5	67	Dark brown	35.32 (35.15)	4.37 (4.18)	17.83 (17.57)

TABLE-2
CHARACTERISTIC FT-IR BANDS (cm^{-1}) OF TSC AND THE COMPLEXES

Complex	ν(CO)	νN^{1}H)	νN^{2}H	νN^{4}H	δ(NH$_2$)	ν(N-N)	ν(C=S)
$Cr(CO)_6$	1999s	-	-	-	-	-	-
$Mo(CO)_6$	2001s	-	-	-	-	-	-
$W(CO)_6$	1996s	-	-	-	-	-	-
$ReBr(CO)_5$	1991s, 2047vs, 2158s	-	-	-	-	-	-
$CpMn(CO)_3$	1939, 2025	-	-	-	-	-	-
TSCa	-	3345	3266	3165	1640	1000	799
1	2061, 1972, 1930, 1890	3434	3264	3170	1697	1048	872, 822
2	2061, 1986, 1932, 1888	3434	3266	3170	1697	1046	872, 822
3	2067, 1990, 1922, 1890	3422	3272	3170	-	1034	875, 819
4	2032, 1972, 1921	3293	3167	3170	1654	1037	800
5	2073	3379	3292	3170	1620	1049	802

a



$$\overset{1}{H_2N}\,\overset{2}{NH}\,\overset{\overset{S}{\|}}{\underset{3}{C}}\,\overset{4}{NH_2}$$

IR Spectra: The assignments of the significant IR spectral bands of thiosemicarbazide and its metal carbonyl complexes are presented in Table-2. An insight about the mode of chelation for each ligand is gathered by comparing the FT-IR spectra of the thiosemicarbazide with its complex and by considering the previous work on similar compounds.

The IR spectra of thiosemicarbazide ligand showed characteristic bands due to the functional groups N-H, C=S and N-N bonds. The IR spectra of all complexes displayed the ligand characteristic bands with appropriate shifts due to complex formation. The bands at 3365 cm^{-1} and 3266 cm^{-1} in thiosemicarbazide due to $\nu_{asym}(NH_2)$ and $\nu_{sym}(NH_2)$ is shifted to higher frequencies in the complexes (**1-5**). Thiosemicarbazide has two bands at 1640 and 1619 cm^{-1}. The former is the deformation mode, $\delta(NH_2)$, of the amine in the hydrazine residue and the latter is the amide(II) band of primary amine. These bands shift towards higher frequencies due to the involvement of one of the (NH$_2$) group in coordination. Strong evidence is the appearance of the 459-430 cm^{-1} band due to ν(M-N). The ν(N-N) of thiosemicarbazide is found at 1000 cm^{-1}. The increase in the frequency of this band in the spectra of the complexes, due to the increase in the bond strength, again confirms the coordination *via* terminal amino nitrogen of thiosemicarbazide in each complex. Although strong band at 800 cm^{-1} assigned to C=S stretching vibration shifts to higher frequencies and splits into two peaks in the complexes, indicating the involvement of thioketo sulfur in complex formation in complexes (**1-3**), the ν(C=S) bands remain unaffected in the spectra of complexes (**4-5**). Thiosemicarbazide ligand coordinates to the central metal ion through terminal hydrazine nitrogen and sulfur donor atoms in (**1-3**), whereas thiosemicarbazide coordinates to the central metal ion through both terminal hydrazine and thioamide nitrogens in complexes (**4-5**). Thus, it is concluded that the ligand acts as a bidentate chelating agent in all of the metal complexes (**1-5**).

The number of carbonyl bands provides important clues to the environment of the centres.

The IR spectra of complexes (**1-3**) exhibit four prominent bands between 2067 cm^{-1} and 1888 cm^{-1} in the CO stretching vibrational region. These four bands belong to terminal CO groups. These modes shift to lower wave numbers when compared with $M(CO)_6$ (M: Cr, Mo and W). The presence of four CO bands in the IR spectra suggested that thiosemicarbazide bound to the metal in *cis* positions[27]. The ν(CO) pattern indicates local C_{2v} symmetry of $M(CO)_4$ unit[28] in complexes (**1-3**).

Facial geometry around the rhenium atom is suggested by the three strong ν(CO) bands in the range 2030-1900 cm^{-1} in the spectrum of *fac*-[ReBr(CO)$_3$(η^2-N,N-TSC)], **4** (the lowest-energy vibration is a shoulder). The FT-IR spectrum is consistent with a structure in which the rhenium atom is octahedrally co-ordinated to three carbonyl carbon atoms in *fac* arrangement, a bromine atom and two nitrogen atoms of thiosemicarbazide ligand, with which the metal forms a five-membered chelate ring. The FT-IR spectra of the complexes contain three strong carbonyl bands allowing an unequivocal assignment of the compound as the *fac*-isomer of CS symmetry[29,30].

As expected, only one band arising from ν(CO) vibration is seen for the complex, [(η^5-Cp)Mn(CO)(η^2-N,N-TSC)], **5** which presumably have the local C_{4v} (A_1) symmetry of the M(CO) unit[29,30]. The ν(CO) mode of the complex move to lower wave numbers compared with the starting (η^5-C_5H_5)Mn(CO)$_3$ molecule, as weakening of the CO bond on complexation would result in a shift to lower wave number[31].

^{1}H NMR spectra: ^{1}H NMR data in DMSO-*d*$_6$ solutions of the complexes are collected in Table-3. The ^{1}H NMR spectra of the chromium and manganese complexes of thiosemicarbazide could not be obtained since the former was not sufficiently soluble in DMSO-*d*$_6$ and the latter was paramagnetic. Thiosemicarbazide ligand shows three prominent signals belong to NH, (S=C-NH$_2$) and NH$_2$ (hydrazine residue) functional group protons at 11.01; 7.90 and 7.43 ppm respectively. In ^{1}H NMR spectra of the complexes **2**, **3** and **4**, primer amine NH$_2$ (hydrazine residue) proton signals have been observed in lower field than those of free ligand. Except the chemical shift of NH$_2$ (hydrazine residue) proton value, all of the other chemical shifts of the coordinated thiosemicarbazide ligand of the compounds **2** and **3** have almost similar values to those of the free ligand. However, (S=C-NH$_2$) and NH$_2$ (hydrazine

TABLE-4
MASS SPECTROSCOPY DATA FOR (**1-5**)

Complex	m.w.	Relative intensities of the ions m/z [a]
1	255	255(50), [$CrC_5H_5N_3O_4S$]; 227(36), [$CrC_4H_5N_3O_3S$-(CO)]; 199 (8.8), [$CrC_3H_5N_3O_2S$-(CO)]; 183 (30), [$CrC_3H_3N_2O_2S$ – (NH_2)] 155(16), [$CrC_2H_3N_2OS$-(CO)]; 127(21), [$CrCH_3N_2S$-(CO)]
2	299	299 (15) [$MoC_5H_5N_3O_4S$]; 283 (73), [$MoC_5H_3N_2O_4S$ -(NH_2)]; 255 (30), [$MoC_4H_3N_2O_3S$ -(CO)];227(22) [$MoC_3H_3N_2O_2S$-(CO)]; 212 (18), [$MoC_3H_2NO_2S$-(NH)]; 196 (22), [MoC_3O_2S -(NH_2)];168(42), [MoC_2OS-(CO)]; 140(17)[MoCS]
3	387	387 (10), [$WC_5H_5N_3O_4S$]; 371(17), [$WC_5H_3N_2O_4S$]-(NH_2)]; 315(15)[$WC_3H_3N_2O_2S$-(CO)-(CO)] 287 (12),[$WC_2H_3N_2OS$-(CO)]; 259 (30), [WCH_3N_2S-(CO)]
4	440	440 (30), [$ReC_4H_5N_3O_3SBr$]; 412 (19),[$ReC_3H_5N_3O_2SBr$-(CO)]; 384(20), [$ReC_2H_5N_3OSBr$] -(CO)]; 356 (11), [$ReCH_5N_3SBr$-(CO)]
5	239	239 (11), [$MnC_7H_{10}N_3OS$]; 211(14) [$MnC_6H_{10}N_3S$ -(CO)]; 195(45) [$MnC_7H_8N_2OS$-(NH_2)]

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

residue) proton signals alteration have been found for rhenium complex, **4**. This situation supports the coordination of ligand to the metal center as a bidentate ligand *via* its nitrogen and sulfur donor atoms in **2** and **3** and *via* both nitrogen donor atoms in **4**.

TABLE-3
^1H NMR DATA FOR TSC AND METAL COMPLEXES
IN DMSO-d_6 SOLUTIONA

Complex	N^2H (1H, br, s)	N^4H_2 (2H, br, s)	N^1H_2 (2H, br, s)
TSC	11.01	7.90	7.43-7.40
2	11.02	7.91	7.70-7.50
3	11.02	7.91	7.70-7.45
4	12.55	9.45	7.82-7.79

a δ in ppm

Mass spectra: Data for mass spectra of **1-5** are given in Table-4 and show fragmentation *via* successive loss of CO groups and thiosemicarbazide ligand.

Conclusion

In summary, thiosemicarbazide ligand coordinates to VI and VIIB group metal carbonyls in two different manners. The spectral data suggest the involvement of sulfur and terminal amino nitrogen of thiosemicarbazide in coordination to the central metal ion for VI B metal carbonyl complexes *cis*-[$M(CO)_4(\eta^2$-N,S-TSC)], [M= Cr; **1**, Mo; **2**, W; **3**] whereas both of the terminal amine and thioamide nitrogens of thiosemicarbazide in coordination to the central metal ion for VII B metal carbonyl complexes, *fac*-[$ReBr(CO)_3(\eta^2$-*N,N*-TSC)], **4** and *cis*-[(η^5-Cp)Mn(CO)(η^2- *N,N*-TSC)], **5**. On the basis of spectral studies, an octahedral geometry has been assigned for all of the complexes. IR spectra of the complexes and observation of carbonyl bands in the CO stretching region are consistent with the formulation of the complexes **1-5**. ^1H NMR data exhibited expected integrals and shifts. Mass spectra fragmentation patterns are in line with the proposed structures of **1-5**.

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