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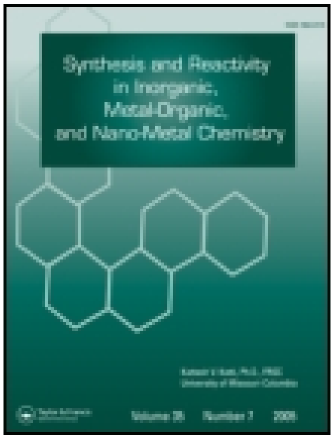

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Photochemical Complexation Reactions of $M(CO)_6$ (M=Cr, Mo, W) and $Re(CO)_5Br$ with Rhodanine (4-Thiazolidinone-2-thioxo) and 5-Substituted Rhodanines

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Photochemical Complexation Reactions of $M(CO)_6$ (M = Cr, Mo, W) and $Re(CO)_5Br$ with Rhodanine (4-Thiazolidinone-2-thioxo) and 5-Substituted Rhodanines

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The new complexes [$M(CO)_5$-DABRd] [M = Cr; 1, Mo; 2, W; 3], [*cis*-$Re(CO)_4Br$-DABRd] (4), [$M(CO)_5$-BRd] [M = Cr; 5, Mo; 6, W; 7] and [$Mo(CO)_5$-L] [L = Rd, 8; 2CBRd, 9; 2HNARd, 10; IBRd, 11] have been synthesized by the photochemical reactions of VIB and VIIB group metal carbonyls [$M(CO)_6$] [M = Cr, Mo, W] and [$Re(CO)_5Br$] with 5-(4-dimethylaminobenzylidene)rhodanine (DABRd), 5-benzylidenerhodanine (BRd), rhodanine (Rd), 5-(2-chlorobenzylidene)rhodanine (2CBRd), 5-(2-hydroxynaphtylidene)rhodanine (2HNARd), 5-(4-isopropylbenzylidene)rhodanine (IBRd) and characterized by elemental analysis, FT-IR, ^1H and ^{13}C-{^1H}-NMR spectroscopy and by Mass spectrometry. The spectroscopic studies show that all rhodanine ligands act as monodentate ligands coordinating via the sulfur (C=S) donor atom in (1–11).

Keywords rhodanine (4-thiazolidinone-2-thioxo), 5-benzylidenerhodanines, metal carbonyl complexes, organometallic compounds

INTRODUCTION

The heterocyclic ligands that contain the C(=S)-NH-fragment have continued to attract attention in part because of their capability of thione-thiol tautomerism, usually involves the evolution of the ligand towards its thiol form and the formation of a strong M-S bond and a secondary M··N bond.[1–3] The nucleophilic activity of the methylene carbon atom at position 5 of the rhodanine ring allows reaction with electrophilic centers and the ready formation of 5-substituted derivatives.[4] Rhodanine derivatives have been extensively investigated due to their use in analytical chemistry and their biological activity. These compounds exhibit various biological activities, particularly: antibacterial and bacteriostatic, fungucidal and fungustatic, antiparasitic, antituberculous and tuberculostatic, antiviral, antitumoral.[5–8]

Some derivatives of rhodanine were found to have higher sensitivity and selectivity for the spectrophotometric analyses of some noble metal ions and heavy metal ions.[9–12]

Rhodanine is coordinated through the thiocarbonylic sulfur in the neutral form or through the thiocarbonylic sulfur and the endocyclic nitrogen atoms in neutral or deprotonated form.[13,14] Although many papers are available on the metal complexes of 5-arylidenerhodanines, there is no previous work on the carbonyl compounds.[15,16] 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.[17]

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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.[18]

As ligands, rhodanines have more than one potential donor atoms. Therefore, we tried to observe the sites of substitution of these ligands to the metal center. Along with our continued interest in the photochemical synthesis and structural aspects of group VIB and VIIB metal carbonyls led us to launch us an exploratory investigation into the photolytic behaviour of the VIB and VIIB metal carbonyls, $[M(CO)_6]$ [M = Cr, Mo, W] and $[Re(CO)_5Br]$ with the title ligands DABRd, BRd, Rd, 2CBRd, 2HNARd and IBRd which contain the pentagonal heterocycle rhodanine. In this paper, the hitherto unknown new complexes $[M(CO)_5\text{-DABRd}]$ [M = Cr; **1**, Mo; **2**, W; **3**], [*cis*-$Re(CO)_4Br$-DABRd] (**4**), $[M(CO)_5\text{-BRd}]$ [M = Cr; **5**, Mo; **6**, W; **7**] and $[Mo(CO)_5\text{-L}]$ [L = Rd, **8**; 2CBRd, **9**; 2HNARd, **10**; IBRd, **11**] have been prepared by the photochemical reactions of $[M(CO)_6]$ [M = Cr, Mo, W] and $[Re(CO)_5Br]$ with 5-(4-dimethylaminobenzylidene)rhodanine (DABRd), 5-benzylidenerhodanine (BRd), rhodanine (Rd), 5-(2-chlorobenzylidene)rhodanine (2CBRd), 5-(2-hidroxynaphthylidene)rhodanine (2HNARd), 5-(4-isopropylbenzylidene)rhodanine (IBRd) and characterized by elemental analyses, FT-IR, ^{1}H and ^{13}C-{^{1}H}-NMR spectroscopy and Mass spectrometry. The spectroscopic studies show that the rhodanine ligands act as monodentate ligands coordinating via the sulfur (C=S) donor atom in (**1**–**11**).

EXPERIMENTAL

Reactions were carried out under a dry N_2 atmosphere using Schlenk techniques. All solvents were dried and degassed using standard techniques.[19] Elemental analyses were performed on a LECOCHNS-O-9320 instrument at Technical and Scientific Research Council of Turkey, TUBITAK. FT-IR spectra of samples were recorded in KBr at Dokuz Eylul University on a Varian 1000 FT spectrophotometer. ^{1}H- and ^{13}C-{^{1}H}-NMR spectra were recorded in $CDCl_3$ on DMSO on 500 MHz High Performance Digital FT-NMR instrument at Ege University and chemical shifts were referenced to tetramethylsilane (TMS). Electron impact mass spectroscopy; Micromass VG Platform-II LC-MS were recorded at TUBITAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor.

Organic solvents and silica gel were purchased from Merck and $M(CO)_6$ (M = Cr, Mo, W), $[Re(CO)_5Br]$, Rd and aldehydes were from Aldrich. DABRd, BRd, 2CBRd, 2HNARd and IBRd were prepared by literature method.[20]

The complexes, $[M(CO)_5\text{-DABRd}]$ [M = Cr; **1**, Mo; **2**, W; **3**], [*cis*-$Re(CO)_4Br$-DABRd] (**4**), $[M(CO)_5\text{-BRd}]$ [M = Cr; **5**, Mo; **6**, W; **7**] and $[Mo(CO)_5\text{-L}]$ [L = Rd, **8**; 2CBRd, **9**; 2HNARd, **10**; IBRd, **11**] were prepared by the photochemical reactions of $[M(CO)_6]$ (M = Cr, Mo, W) and $[Re(CO)_5Br]$ with DABRd, BRd, Rd, 2CBRd, 2HNARd and IBRd and obtained in 55–82% yield by similar methods of which the following is typical.

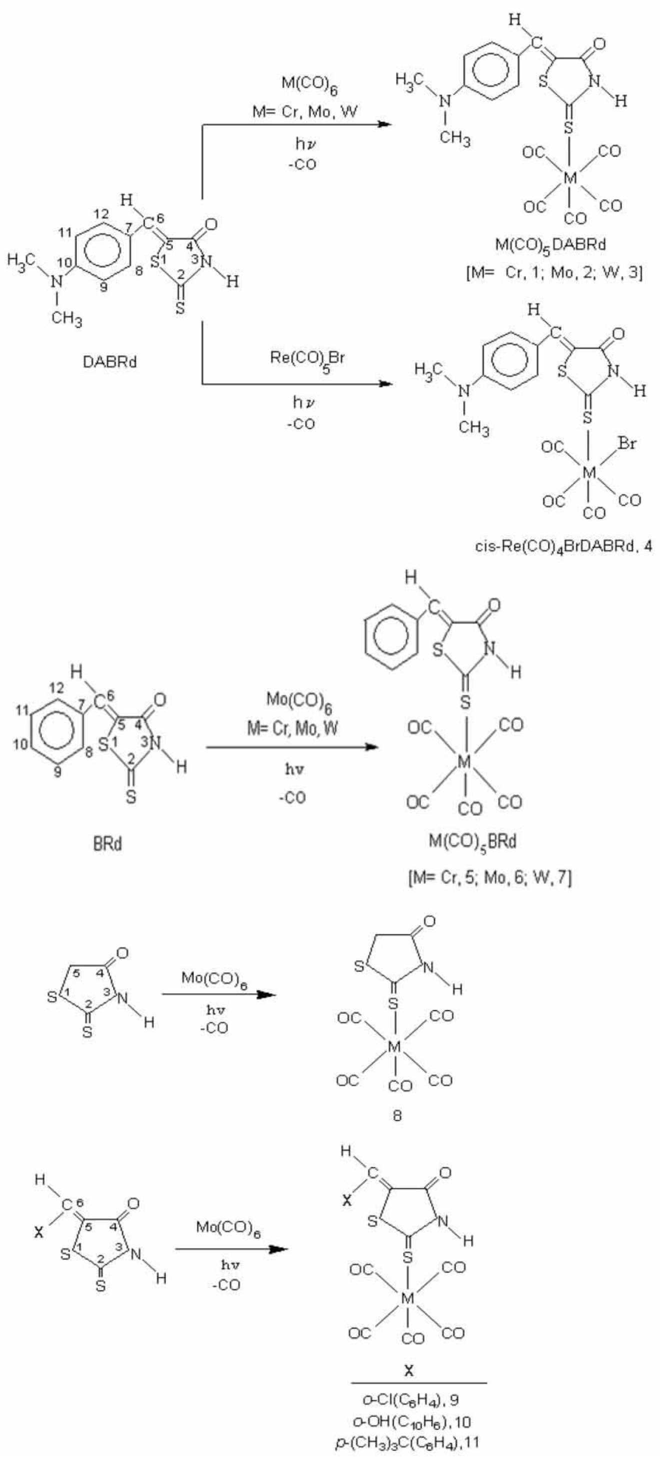

FIG. 1. The photogenerations of (**1**–**11**).

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TABLE 1
Elemental analysis results and physical properties of the complexes (**1–11**)

			Elementel analyses found (Calcd.) (%)			
Complex[a]	Empirical formula (formula weight)	Yield (%)	C	H	N	S
1	$C_{17}H_{12}CrN_2O_6S_2$ (456.0)	73	46.22 (44.73)	2.54 (2.63)	6.24 (6.14)	14.40 (14.03)
2	$C_{17}H_{12}MoN_2O_6S_2$ (499.9)	82	42.04 (40.80)	2.49 (2.40)	5.69 (5.60)	13.16 (12.80)
3	$C_{17}H_{12}WN_2O_6S_2$ (587.8)	70	35.59 (34.71)	2.02 (2.04)	4.81 (4.76)	11.12 (10.88)
4	$C_{16}H_{12}ReN_2O_5S_2Br$ (642.2)	68	30.51 (29.89)	1.88 (1.87)	4.50 (4.36)	10.18 (9.97)
5	$C_{15}H_7CrNO_6S_2$ (413.0)	66	43.51 (43.58)	1.26 (1.69)	3.23 (3.39)	15.33 (15.49)
6	$C_{15}H_7MoNO_6S_2$ (456.9)	65	39.11 (39.39)	1.22 (1.53)	3.03 (3.06)	13.88 (14.00)
7	$C_{15}H_7WNO_6S_2$ (544.8)	72	33.00 (33.03)	1.19 (1.28)	2.23 (2.57)	11.52 (11.74)
8	$C_8H_3MoNO_6S_2$ (368.9)	66	25.95 (26.00)	0.75 (0.81)	3.60 (3.79)	17.05 (17.34)
9	$C_{15}H_6MoNO_6S_2Cl$ (491.4)	74	36.36 (36.62)	1.10 (1.22)	12.54 (12.85)	12.98 (13.02)
10	$C_{19}H_9MoNO_7S_2$ (522.9)	62	43.00 (43.60)	1.70 (1.72)	2.44 (2.68)	12.02 (12.23)
11	$C_{19}H_{15}MoNO_6S_2$ (512.9)	55	32.25 (44.45)	2.78 (2.92)	2.69 (2.73)	12.34 (12.48)

[a] Reddish brown.

The complexes $Cr(CO)_6$ (0.44 g, 2 mmol) and DABRd (0.54 g, 2 mmol) were dissolved in THF (80–100 mL) and the solution was irradiated for 2 hr using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the solution changed from colourless to redish-brown. After irradiation the solvent was evaporated under the vacuum yielding a redish-brown solid which was extracted with CH_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a dark brown solid which was washed with petroleum ether and dried under vacuum, and shown to be [$Cr(CO)_5$-DABRd] (0.12 g, 73% yield). Traces of unreacted hexacarbonylchromate(0) was sublimed out in vacuum on a cold finger at $-20^\circ C$ while keeping the complex at $0^\circ C$ in an ice bath.

TABLE 2
Important infrared spectral bands (cm^{-1}) of the ligands and their complexes

Complex	ν(CO)	ν(C=S)	ν(NH)	ν(C=O)	ν(C-S$_{ring}$)
HDABRd[a]	—	685 s, 610 s	3150 m, 3060 m	1690 s	810 s
BR	—	677 s, 602 s	3165 m, 3072 m	1695 s	816 s
Rd	—	681 s, 606 s	3166 m, 3083 m	1710 s	822 s
2CBRd	—	674 s, 633 s	3149 m, 3067 m	1693 s	814 s
2HNARd	—	685 s, 610 s	3170 m, 3067 m	1690 s	810 s
IBRd	—	675 s, 602 s	3146 m, 3051 m	1690 s	820 s
1	2060 s, 1972 s, 1940 s, 1917 s, 1886 m	730 s, 578 s	3150 m, 3060 m	1689 s	810 s
2	2069 s, 1963 s, 1931 s, 1906 s, 1898 m	716 s, 556 s	3150 m, 3060 m	1690 s	805 s
3	2068 s, 1969 s, 1942 s, 1910 s, 1880 m	703 s, 586 s	3150 m, 3060 m	1688 s	816 s
4	2106 m, 2024 m, 1920 m, 1892 m	697 s, 594 s	3150 m, 3060 m	1690 s	812 s
5	2070 s, 1970 s, 1940 s, 1916 s, 1880 m	694 s, 520 s	3160 m, 3070 m	1695 s	817 s
6	2069 s, 1969 s, 1942 s, 1910 s, 1886 m	722 s, 581 s	3165 m, 3070 m	1690 s	815 s
7	2070 s, 1974 s, 1940 s, 1910 s, 1886 m	724 s, 585 s	3165 m, 3072 m	1690 s	810 s
8	2070 m, 1972 s, 1946 s, 1935 s, 1870 m	735 s, 593 s	3165 m, 3085 m	1709 s	816 s
9	2072 s, 1971 m, 1948 m, 1937 s, 1873 s	695 s, 603 s	3150 m, 3065 m	1690 s	810 s
10	2075 s, 1970 s, 1946 s, 1937 s, 1872 s	691 s, 587 s	3168 m, 3063 m	1690 s	805 s
11	2070 s, 1972 m, 1945 s, 1936 s, 1870 s	690 s, 584 s	3142 m, 3050 m	1690 s	816 s

[a] Taken from Ref. [3].

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TABLE 3

^{1}H- and ^{13}C-{^{1}H}-NMR data for the ligands and their complexes in DMSO-d_6 solution[a]

	DABRd	BRd	Rd	2CBRd	2HNARd	IBRd	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
^{1}H-n.m.r.																	
δ(N(3)-H)	13.56 s[b]	13.55 s	13.56 s	13.50 s	13.60 s	13.56 s	13.56 s	13.56 s	13.55 s	13.50 s	13.55 s	13.48 s	13.50 s	13.55 s	13.50 s	13.60 s	13.54 s
δ(C(6)-H)	7.49 s[b]	7.50 s	—	7.84 s	7.80 s	7.49 s	7.52 s	7.52 s	7.50 s	7.50 s	7.50 s	7.52 s	7.50 s	7.48 s	7.84 s	7.79 s	7.47 s
^{13}C-n.m.r.																	
δ[C(2)]	195.1 s[b]	204.5 s	195.1	212.7	220.1	193.9	207.4 s	206.2 s	209.1 s	210.5 s	212.2 s	213.1 s	210.4 s	176.8	198.6	195.9	174.3
δ[C(4)]	169.5 s[b]	172.4 s	169.5	176.2	182.1	171.8	171.9 s	170.0 s	170.4 s	169.6 s	171.2 s	172.5 s	172.4 s	171.8	174.5	183.0	170.5
δ[C(5)]	117.4 s[b]	122.3 s	117.4	127.5	134.4	123.2	118.7 s	119.1 s	119.5 s	117.7 s	121.2 s	122.4 s	122.3 s	114.4	127.8	132.0	122.1
δ[C(6)]	133.5 s[b]	142.4 s	133.5	140.5	152.6	138.5	135.2 s	133.7 s	134.5 s	134.2 s	142.5 s	143.5 s	142.1 s	133.0	143.5	153.7	136.5
δ[ax.(CO)]	—	—	—	—	—	—	220.4 s	216.8 s	207.2 s	—	217.3 s	222.4 s	218.9 s	224.2	218.3	226.9	222.8
δ[eq.(4CO)]	—	—	—	—	—	—	214.2 s	205.0 s	194.3 s	—	209.2 s	198.0 s	186.5 s	205.4	201.2	203.5	200.6
δ[eq.(2CO)]	—	—	—	—	—	—	—	—	—	215.6 s	—	—	—	—	—	—	—
δ[eq.&ax(CO)]	—	—	—	—	—	—	—	—	—	218.2 s, 186.4 s	—	—	—	—	—	—	—

[a] δ in ppm, J in Hz.

[b] Taken from Ref. [3].

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RESULTS AND DISCUSSION

Recently, photogeneration of $M(CO)_5$ from $M(CO)_6$ (M = Cr, Mo, W) has been extensively studied.[21–27] These 16-electron containing $M(CO)_5$ fragments react avidly with any available donor to form $M(CO)_5L$ species, where L is a chelating bidentate ligand, and rapid continuation to the chelating $M(CO)_4L$ or bridging $M_2(CO)_{10}$-L products may occur. Moreover, photogeneration of $M(CO)_4$ (M = Re), $M(CO)_3$ and $M(CO)_2$ (M = Mn) from $[Re(CO)_5Br]$ and $[Mn(CO)_3Cp]$ have been synthesized by our working group.[17,28–32] The photochemical reactions of $M(CO)_6$ (M = Cr, Mo, W) and $[Re(CO)_5Br]$ with DABRd and of $M(CO)_6$ (M = Cr, Mo, W) with BRd, Rd, 2CBRd, 2HNARd and IBRd proceed in this expected manner to yield the previously unknown series of complexes (**1–11**) in Figure 1. The analytical results and some physical properties of the novel complexes (**1–11**) are summarized in Table 1.

The changes observed in the FT-IR spectrum of the free ligands upon coordination may be compared with the spectral changes in rhodanine in its metal carbonyl complex. The ν(N-H) ligand bands at 3150 and 3060 cm^{-1} appear, as expected for N(3)-H of DABRd, BRd, Rd, 2CBRd, 2HNARd and IBRd in the complexes (**1–11**). All of the complexes exhibit no changes in the intensity or position of the bands in the range 1700–1660 cm^{-1} that are indicative of coordination via ν(C═O), this is in keeping with there are no metal = oxygen interactions in these complexes. The stretching vibrations of C-S_{ring} observed at 810–816 cm^{-1} in the free ligands shift to just slightly lower wave numbers in the spectra of the (**1–11**). The divisions between strong symmetric and asymmetric stretching vibrations of C═S in DABRd, BRd, Rd, 2CBRd, 2HNARd and IBRd are increased in the spectra of the (**1–11**), showing that the rhodanine ligands coordinate to the metal via their sulfur (C═S) atoms in (**1–11**). Important FT-IR spectral data of (**1–11**) are presented in Table 2. As expected, five bands arising from ν(CO) vibrations are seen for complexes (**1–3** and **5–11**) which presumably have the local C_{4v} $(2A_1 + E)$ symmetry of the $M(CO)_5$ unit (M = Cr, Mo, W). Similarly, there are four CO stretching mode in the IR spectra of (**4**). According to IR spectra, the $Re(CO)_4$ unit in compound (**4**) has local $C_{2v}(2A_1 + B_1 + B_2)$ symmetry.[17,33] The ν(CO) modes of (**1–11**) move to lower wave numbers when compared with the starting $M(CO)_6$ (M = Cr, Mo, W) and $[Re(CO)_5Br]$ molecules.[17,28–32]

^{1}H- and ^{13}C-{^{1}H}-NMR spectra data in DMSO-d_6 solutions of compounds (**1–11**) are listed in Table 3 together with the assignments of the signals. The presence of the low field N(3)-H signal in the ^{1}H-NMR spectra of the complexes (**1–11**) indicate that deprotonation of the ligands from their N(3)-H on coordination to the organometallic moiety is not possible. It was clearly seen from the ^{13}C-{^{1}H}-NMR spectra that the coordination of the ligand to the metal from (C═S) sulfur atom, deshields the thiazolidine ring carbons. The relatively slight deshielding of C(2) is compatible with the

TABLE 4
The mass spectral data of (**1–11**)

Complex	M.W.	Relative intensities of the ions m/e
1	456	456 (5), [M^+]; 428 (15), [M^+-(CO)]; 400 (27), [M^+-2(CO)]; 372 (20), [M^+-3(CO)]; 316 (25), [M^+-5(CO)].
2	499.9	500 (7), [M^+]; 444 (15), [M^+-2(CO)]; 416 (22), [M^+-3(CO)]; 388 (15), [M^+-4(CO)]; 360 (12), [M^+-5(CO)].
3	587.8	588 (10), [M^+]; 560 (14), [M^+-(CO)]; 532 (20), [M^+-2(CO)]; 504 (20) [M^+-3(CO)]; 476 (15), [M^+-4(CO)]; 448 (20) [M^+-5(CO)].
4	642.2	642 (5), [M^+]; 534 (10), [M^+-(CO)-Br]; 506 (20), [M^+-2(CO)-Br]; 478 (15) [M^+-3(CO)-Br]; 450 (12), [M^+-4(CO)-Br].
5	413	413 (10), [M^+]; 385 (15), [M^+-(CO)]; 357 (24), [M^+-2(CO)]; 329 (18) [M^+-3(CO)]; 301 (26), [M^+-4(CO)]; 273 (15), [M^+-5(CO)].
6	456.9	457 (12), [M^+]; 429 (20), [M^+-(CO)]; 401 (14), [M^+-2(CO)]; 373 (15) [M^+-3(CO)]; 345 (10), [M^+-4(CO)]; 317 (12), [M^+-5(CO)].
7	544.8	545 (8), [M^+]; 517 (15), [M^+-(CO)]; 489 (22), [M^+-2(CO)]; 461 (18) [M^+-3(CO)]; 433 (14), [M^+-4(CO)]; 405 (10), [M^+-5(CO)].
8	368.9	369 (102), [M^+]; 313 (15) [M^+-2(CO)]; 257 (30), [M^+-4(CO)]; 229 (10), [M^+-5(CO)].
9	491.4	491.4 (20), [M^+]; 436 (15), M^+-2(CO)]; 379 (20), [M^+-4(CO)]; 352 (25), [M^+-5(CO)].
10	522.9	523 (10), [M^+]; 495 (10) [M^+-CO]; 411 (15), [M^+-4(CO)].
11	512.9	513 (15), [M^+]; 457 (15), [M^+-2(CO)]; 429 (15), [M^+-3(CO)]; 373 (20), [M^+-5(CO)].

For the mass spectral data relative intensities are given in parentheses; probable assignments in square bracket.

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maintenance of the thione form of the ligand in solution, because conversion to the thiol form would result in stronger shielding as in the S-coordinated methyl- and phenylmercury(II) complexes of rhodanine [HgR(Rd)].[17,34]

The mass spectral data of (**1–11**) are given in Table 4, and show fragmentation via successive loss of CO groups and organic ligands. For the mass spectral data relative intensities are given in parantheses; probable assignments in square brackets. For all assignments the most abundant isotopes of Cr, Mo, W and Re have been selected (^{52}Cr, 83.76%; ^{98}Mo, 24%; ^{184}W, 30.7%; ^{187}Re, 62.9% abundant).

We have presented the novel photochemical reactions between $M(CO)_6$ (M = Cr, Mo, W); $[Re(CO)_5Br]$ with DABRd and $M(CO)_6$ (M = Cr, Mo, W) with BRd, Rd, 2CBRd, 2HNARd and IBRd. The spectroscopic studies show that the rhodanine ligands act as monodentate ligands coordinating via their (C=S) atom in (**1–11**) and behave as a two-electron donor in order to satisfy the 18-electron rule in metal carbonyl complexes (**1–11**). Furthermore, the ν(CO) modes move to low wave number when compared with the starting $M(CO)_6$ (M = Cr, Mo, W) and $[Re(CO)_5Br]$ molecules. Apparently, the metallation cause the deshielding of all the carbons of the pentagonal ring in ^{1}H- and ^{13}C-{^{1}H}-NMR spectra. The mass spectra of the complexes (**1-11**) show fragmentation via successive loss of CO groups and fragmentation of the DABRd, BRd, Rd, 2CBRd, 2HNARd and IBRd ligands.

REFERENCES

1. Casas, J. S.; Castellano, E. E.; Macías, A.; Playá, N.; Sánchez, A.; Sordo, J.; Varela, J. M.; Vázquez-López, E. M. Methyl- and phenylmercury(II) complexes of 5-(4′-dimethylaminobenzylidene) rhodanine (HDABRd) and 5-(2′-thiophenomethylene)rhodanine (HTRd). The crystal and molecular structure of [HgPh(DABRd)] and [HgMe(TRd)]. *Polyhedron* **2001**, *20*, 1845.
2. Bravo, J.; Casas, J. S.; Mascarenhas, Y. P.; Sánchez, A.; Santos, C. O. P.; Sordo, J. Methyl(2-mercapto-4-methypymidinato) mercury (Ii): A methylmercury(Ii) derivate with and unusual metal-metal interaction. *J. Chem. Soc., Chem. Commun.* **1986**, 1100.
3. Casas, J. S.; Playá, N.; Sánchez, A.; Sordo, J.; Varela, J. M.; Vázquez-López, E. M. Synthesis and characterization of phenyl [5-(2-thiohydantoinato]mercury (II), and the crystal and molecular structures of its dmso solvate. *Polyhedron* **1999**, *18*, 187.
4. (a) Brown, F. C. *Chem. Rev.* **1961**, *61*, 463; (b) Casas, J. S.; Macías, A.; Playá, N.; Sánchez, A.; Sordo, J.; Varela, J. M. Synthesis spectroscopic properties and X-ray structure of dimethyl(*p*-dimethylaminobenzylidenerhodaninato)thallium(III). *Polyhedron* **1992**, *11*, 2231.
5. Singh, S. P.; Parmar, S. S.; Raman, K.; Stenberg, V. I. Chemistry and biological activity of thiazolidinones. *Chem. Rev.* **1981**, *81*, 175.
6. Hanefeld, W.; Schtitzer, M. Nitrosations with hydrazine derivatives. 6. Novel reaction of oral antidiabetics of the sulfonylsemicarbazide type under nitrosating conditions. *Arch. Pharm.* **1993**, *326*, 887.
7. Suzen, S.; Buyukbingol, M. Recent studies of aldose reductase enzyme inhibition for diabetic complications. *Curr. Med. Chem.* **2003**, *10* (15), 1329.
8. Vajpai, R.; Tiwari, B. M. L.; Tiwari, K. S. A comparative study of synthesis, characterisation and applications of 5-(salicylidene) rhodanine and 5-(2-hydroxy naphthalidene) rhodanine. *Asian J. Chem.* **1999**, *11* (2), 414.
9. Tang, E.; Yang, G.; Yin, J. Studies on the synthesis of 5-(p-aminobenzylidene)-rhodanine and its properties. *Spectrochim. Acta A, Mol. Biomol. Spectrosc.* **2003**, *A 59*, 651.
10. Tarek, M.; Zaki, M.; Abdel-Rahman, R. M.; El-Sayed, A. Y. Use of arylidenerhodanines for the determination of Cu(II), Hg(II) and CN^-. *Anal. Chim. Acta* **1995**, *307*, 127.
11. Turak, F.; Özgür, M.; Erçağ, A. Simultaneous determination of rhodium and gold by derivative spectrophotometric method. *Rev. Anal. Chem.* **2003**, *22* (3), 157.
12. Kocsis, L.; Horvath, E.; Kristof, J.; Frost, R. L.; Redey, A.; Mink, J. Effect of the preparation conditions on the surface-enhanced Raman-spectrometric identification of thin-layer-chromatographic spots. *J. Chrom. A* **1999**, *845*, 197.
13. Fabretti, C. A.; Peyronel, G. Silver(I) and gold(I) complexes of rhodanine. *Trans. Met. Chem.* **1977**, *2* (1), 207.
14. Cauletti, C.; Sestili, L.; Zanoni, R. An XPS investigation of pentatomic heterocyclic ligands containing N, O and S and their Cu complexes. *Inorg. Chim. Acta* **1988**, *147* (2), 237.
15. Borissova, R. Spectrophotometric determination of gold(III) with *p*-dimethylaminobenzilidenerhodanine in hydrochloric acid-ethanol medium. *Talanta* **1975**, *22*, 797.
16. Pourezza, N.; Rastegarzadeh, S. Simultaneous determination of gold and palladium with 5(p-dimethylaminobenzylidene)rhodanine by using the H-point standard addition method in micellar media. *Anal. Chim. Acta* **2001**, *437*, 273.
17. (a) Sert, S.; Ercag, A.; Senturk, O. S.; Sterenberg, B. T.; Udachin, K. A.; Ozdemir, U.; Ugur, F. Photochemical reactions of $Re(CO)_5Br$ with tetraalkyldiphosphine disulfides (R = Me, Et, Pr-n, Bu-n, Ph) and the crystal structure of $[ReBr(CO)_3\ (Et_2P(S)P(S)Et_2)]$. *Polyhedron* **2003**, *22*, 1689; (b) Vahrenkamp, Muller, A., Krebs, B., Eds., *Sulfur: its significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology*; Elsevier: Amsterdam, 1984; (c) Adams, R. D.; Wang, S. Facile activation of hydrogen by an unsaturated metal carbonyl cluster. The Addition of H_2 to $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HCCCO_2Me)$. *Organometallics* **1986**, *5*, 1272.
18. (a) Hogarth, G.; Taylor, N. J.; Meyer, A. A one step synthesis of phosphine substituted sulphur capped clusters from phosphine sulphides: X-ray crystal structures of $[Fe_3(CO)_8(\mu_2\text{-}CO)(\mu_3\text{-}S)(Ph_2PC_2Pr^i))$ and $(Ru_3(CO)_8(\mu_3\text{-}S)_2(PhPC_2But)]$. *J. Chem. Soc., Chem. Commun.* **1988**, 834; (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; Wiley Interscience: New York, 1988, p. 1047.
19. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd Ed.; Pergamon: Oxford, 1980.
20. Hussain, M. I.; Shukla, S. Synthesis & biodynamic activities of 5-(substituted benzylidene)-3-[p-(*N,N*-disubstituted carbamoyl)-phenylaminomethyl]4-oxothiazolidine-2-thiones. *Ind. J. Chem.* **1985**, *24B*, 761.
21. Senturk, O. S.; Adil, H.; Sert, S.; Ugur, F.; Ozdemir, U. Photochemical reactions of $Re(CO)_5Br$ with tetraalkyldiphosphine

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disulfides (R = Me, Et, Pr-n, Bu-n, Ph) and the crystal structure of [ReBr(CO)$_3$(Et$_2$P(S)P(S)Et$_2$)]. *Polyhedron* **2003**, *22*, 1659.

22. Subası, E.; Senturk, O. S.; Ugur, F. Photochemical reactions of Re(CO)$_5$Br with Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1, dppm; 2, dppe; 3, dppp). *Trans. Met. Chem.* **2004**, *29*, 16.
23. Subası, E.; Senturk, O. S.; Ugur, F. Photochemical reactions of Re(CO)$_5$Br with Ph$_2$P(S)(CH$_2$)$_n$P(S)Ph$_2$ (n = 1, 2, 3). *Z. Naturforsch.* **2004**, *59b*, 836.
24. Almond, M. J.; Sarıkahya, F.; Senturk, O. S. Photochemical and thermal synthesis of metal carbonyl complexes of tetraalkyl diphosphine disulfides [M(CO)$_4$(R$_2$P(S)P(S)R$_2$] M = Mo, W; R = Me, Et, Pr-n, Bu-n). *Polyhedron* **1997**, *16*, 1101.
25. Sert, S.; Senturk, O. S.; Sarıkahya, F. Photochemical reactions of chromium hexacarbonyl with tetraalkyldiphosphine disulfides. *Trans. Met. Chem.* **2002**, *27*, 700.
26. Sert, S.; Senturk, O. S.; Sarıkahya, F. Photochemical reactions of M(CO)$_6$ (M = Cr, Mo, W) with Ph$_2$P(S)P(S)Ph$_2$. *Trans. Met. Chem.* **2002**, *28*, 133.
27. Sarıkahya, F.; Senturk, O. S. Photochemical synthesis of metal carbonyl complexes of tetraalkyldiphosphine disulfides, [M$_2$(CO)$_{10}$(μ-R$_2$P(S)P(S)R$_2$)] (M = Mo, W; R = Me, Et, n-Pr, n-Bu). *Synth. React. Inorg. Met.-Org. Chem.* **2001**, *31*, 1843.
28. Sert, S.; Sentürk, O. S.; Ozdemir, U.; Karacan, N.; Ugur, F. Photochemical reactions of metal carbonyls [M(CO)$_6$ (M = Cr, Mo and W), Re(CO)$_5$Br, Mn(CO)$_3$Cp] with 2-hydroxyacetophenone methanesulfonylhydrazone (apmsh). *Trans. Met. Chem.* **2003**, *28*, 443.
29. Senturk, O. S.; Ozdemir, U.; Sert, S.; Karacan, N.; Ugur, F. Synthesis and characterization of some metal carbonyls with 2-hydroxyacetophenone ethanesulfonylhydrazone. *Inorg. Chem. Commun.* **2003**, *6*, 926.
30. Senturk, O. S.; Ercag, A.; Sert, S.; Ugur, F.; Ozdemir, U. Photochemical reactions of metal carbonyls [M(CO)$_6$ (M = Cr, Mo, W), Re(CO)$_5$Br, Mn(CO)$_3$Cp] with 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (DTTT) and the crystal structure of [W(CO)$_5$(DTTT)]. *Polyhedron* **2003**, *22*, 1689.
31. Ozdemir, U.; Sentürk, O. S.; Sert, S.; Karacan, N.; Ugur, F. Synthesis and characterization of metal carbonyl complexes of M(CO)$_6$ (M = Cr, Mo, and W), Re(CO)$_5$Br, and Mn(CO)$_3$Cp with—acetonemethanesulfonylhydrazone (amsh) and methanesulfonylhydrazone (msh). *Synth. Reac. Inorg. Metal-Org. Chem.* **2004**, *34*, 1057.
32. Ozdemir, U.; Sentürk, O. S.; Sert, S.; Karacan, N.; Ugur, F. Synthesis and characterization of the products from reaction of metal carbonyls [M(CO)$_6$ (M = Cr, Mo, W), Re(CO)$_5$Br, Mn(CO)$_3$Cp] with salicylaldehyde methanesulfonylhydrazone. *J. Coord. Chem.* **2004**, *57*, 183.
33. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 4th Ed.; Wiley: New York, 1986, p. 236.
34. Playá, N.; Macías, A.; Varela, J. M.; Sánchez, A.; Casas, J. S.; Sordo, J. Mono-organomercury and diorganothallium derivatives of rhodanine: Crystal structure of dimethyl(rhodaninato)-thallium(III). *Polyhedron* **1991**, *10*, 1465.