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Photochemical Reactions of *cis*-[(η^4-NBD)M(CO)$_4$] (NBD = Norbornadiene; M = Cr, Mo) Olefin Complex with Ligand, Containing S and N Donor Atoms[1]

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Abstract—New complexes *cis*-[M(CO)$_4$-DABRd] (M = Cr(I), Mo(II) and *fac*-[M(CO)$_3$-SAT] (M = Cr(III), Mo(IV)) have been synthesized by the photochemical reactions of *cis*-[(η^4-NBD)M(CO)$_4$] (NBD is norbornadiene; M = Cr, Mo) with 5-(4-dimethylaminobenzylidene) rhodanine (DABRd) and salicylidene-3-amino-1,2,4-triazole (SAT) ligands and characterized by elemental analysis, FT-IR and ^{1}H NMR spectroscopy, and mass spectrometry. The spectroscopic studies show that the DABRd ligand acts as a bidentate ligand coordinating via both NH–(S)C=S sulfur donor atoms in **I** and **II** and SAT ligand behaves as a tridentate ligand coordinating via its all imine nitrogen –C=N– donor atoms in **III** and **IV** to the metal center.

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INTRODUCTION

Photosubstitution of group VI metal carbonyls is a highly efficient process which provides convenient access to a large variety of mono- and polysubstituted derivatives [1]. 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 [2]. 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 [3].

Photosubstitutions of CO with the formation of M(CO)$_5$L (M = Cr, Mo, W) from VIB group metal carbonyls M(CO)$_6$ were studied with a variety of σ-donor ligands L (L are Schiff base derivatives) [4]. In order to contribute to these studies, we tried to substitute these ligands to the metal center as bi- or polydentate chelates. Along with our continued interest in the photochemical synthesis and structural aspects of VIB group metal carbonyls led us to launch an exploratory investigation into the photolytic behavior of the *cis*-[(η^4-NBD)M(CO)$_4$] (NBD is norbornadiene) complexes in the presence of ligands containing sulfur and nitrogen donor atoms [5].

Initially, here we describe a particularly convenient photochemical route to the synthesis of *cis*-[(η^4-NBD)M(CO)$_4$] (M = Cr, Mo). Then we investigated the behavior of *cis*-[(η^4-NBD)M(CO)$_4$] (M = Cr, Mo) with the title ligands 5-(4-dimethylaminobenzylidene)rhodanine (**DABRd**) and salicylidene–3-amino–1,2,4-triazole (**SAT**) which contain the pentagonal heterocycle rhodanine and 1,2,4-triazole ring, respectively. New complexes *cis*-[M(CO)$_4$-DABRd] (M = Cr (I), Mo (II)) and *fac*-[M(CO)$_3$-SAT] (M = Cr (III), Mo (IV)) have been synthesized by the photochemical reactions of [(η^4-NBD)M(CO)$_4$] (M = Cr, Mo) with DABRd and SAT ligands and characterized by elemental analysis, FT-IR and ^{1}H NMR spectroscopy, and mass spectrometry. The spectroscopic studies show that DABRd ligand acts as a bidentate ligand coordinating via both sulfur NH–(S)C = S donor atoms in **I** and **II**, and SAT ligand behaves as a tridentate ligand coordinating via its all imine nitrogen –C = N– donor atoms in **III** and **IV** to the metal center.

EXPERIMENTAL

Materials and methods. All reactions and manipulations were carried out under argon and in argon-saturated solvents using Schlenk techniques. All solvents were dried and degassed using standard techniques [6]. All organic solvents and silica gel were purchased from Merck and M(CO)$_6$ (M = Cr, Mo, W) were from Aldrich. DABRd [7] and SAT [8] were prepared by litera-

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[1] The article was submitted by the authors in English.

ture methods. Elemental analyses were performed on a LECOCHNS-O–9320 instrument at the Technical and Scientific Research Council of Turkey, (TUBITAK). FT-IR spectra of samples were recorded in KBr at the Dokuz Eylul University on a Varian 1000 FT spectrophotometer. ^{1}H NMR spectra were recorded in DMSO on a 500 MHz High Performance Digital FT-NMR instrument at the Ege University and chemical shifts were referenced to tetramethylsilane (TMS). Electron impact mass spectra (Micromass VG Platform-II LC-MS) were recorded at the TUBITAK. Photochemical reactions in a preparative scale were carried out in a water-cooled quartz-walled immersion well reactor equipped with a Philips HPK 125-W high-pressure mercury lamp [9].

Synthesis of the [(η^4-NBD)M(CO)$_4$] [M = Cr, Mo, W] complexes were carried out by the photochemical reactions of [M(CO)$_6$] (M = Cr, Mo, W) with NBD. The yields were 56–72%.

$$\mathrm{M(CO)_6 + NBD} \xrightarrow[\text{Hexane}\atop -2\text{CO}]{h\nu} cis\text{-}[(\eta^4\text{-NBD})\mathrm{M(CO)_4}], \qquad (1)$$

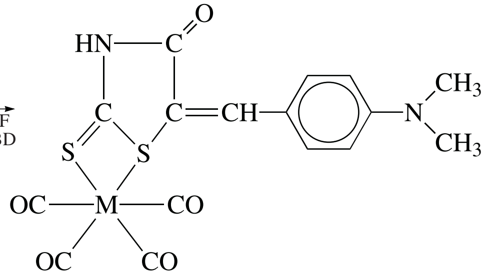
$$\mathrm{M = Cr, Mo}$$

$$\mathrm{M(CO)_6 + NBD} \xrightarrow[\text{Hexane}]{h\nu} cis\text{-}[(\eta^4\text{-NBD})\mathrm{M(CO)_4}]$$
$$+ \mathrm{[W(CO)_5]_2(\mu\text{-NBD})}. \qquad (2)$$
$$\mathrm{M = W.}$$

These complexes were prepared by similar methods, for example, a method for *cis*-[M(CO)$_4$-DABRd] is the following. Cr(CO)$_6$ (0.22 g, 1 mmol) and NBD (0.276 g, 3 mmol) were dissolved in hexane (70 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 colorless to yellow. After irradiation the solvent was evaporated under the vacuum yielding a yellow solid. After subliming out any traces of unreacted white hexa-carbonylchromate(0) at 25–50°C, the probe is cleaned and the sublimation is continued at 70–90°C to give 0.16 g (72%) yield of bright golden yellow crystalline [(η^4-NBD)Cr(CO)$_4$].

Syntheses of the *cis*-[M(CO)$_4$-DABRd] (M = Cr (I), Mo (II)) and *fac*-[M(CO)$_3$-SAT] (M = Cr (III), Mo (IV)) complexes were carried out by the photochemical reactions of *cis*-[(η^4-NBD)M(CO)$_4$] (M Cr, Mo) DABRd and SAT. The yields were 40–60%.

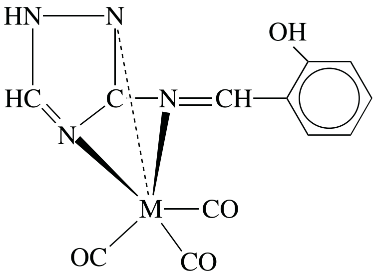
cis-[(η^4-NBD)M(CO)$_4$] + DABRd $\xrightarrow[\text{THF}\atop -\text{NBD}]{h\nu}$
M = Cr, Mo



(3)

cis-[M(CO)$_4$-DABRd],
M = Cr (I); Mo (II)

cis-[(η^4-NBD)M(CO)$_4$] + SAT $\xrightarrow[\text{THF}\atop -\text{NBD, }-\text{CO}]{h\nu}$
M = Cr, Mo



(4)

fac-[M(CO)$_3$-SAT],
M = Cr (III); Mo (IV)

These complexes were prepared by similar methods, for example, a method for [Cr(CO)$_4$-DABRd] is the following. The *cis*-[(η^4-NBD)Cr(CO)$_4$] complexe (0.256 g, 1 mmol) were dissolved in THF (80–100 ml), and the solution was irradiated for 1.5 h using a 125 W medium-pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the solution changed from yellow to lightbrown. After the irradiation and cooling system was cut off from the photochemical reactor, DABRd (0.27 g, 1 mmol) was added to the solution and mixed under argon atmosphere for 3 h. Then solvent was evaporated under vac-

Table 1. The elemental analysis data and physical properties for olefin and **I–IV** complexes

Complex	Empirical formula (M.w.)	Content (found/calcd), %				Color	Yield, %
		C	H	N	S		
$[(\eta^4\text{-NBD})Cr(CO)_4]$	$CrC_{11}H_8O_4$ (256)	50.95/51.56	3.10/3.13			Yellow	72
$[(\eta^4\text{-NBD})Mo(CO)_4]$	$MoC_{11}H_8O_4$ (300)	43.67/44.00	2.56/2.66			Yellow	66
$[(\eta^4\text{-NBD})W(CO)_4]$ + + $[W(CO)_5]_2(\mu\text{-NBD})$	$WC_{11}H_8O_4 + W_2C_{17}H_8O_{10}$ (388 + 740)	29.67/29.78	1.36/1.42			Yellow	56
I	$C_{16}H_{12}O_5CrN_2S_2$ (428)	44.77/44.86	2.75/2.80	6.60/6.54	14.05/14.95	Brown	62
II	$C_{16}H_{12}O_5MoN_2S_2$ (472)	40.37/40.68	2.35/2.54	5.60/5.93	13.05/13.56	Brown	54
III	$C_{12}H_8O_4CrN_4$ (324)	44.37/44.44	2.35/2.45	17.06/17.28		Brown	60
IV	$C_{12}H_8O_4MoN_4$ (368)	38.87/39.13	1.95/2.17	18.06/18.48		Brown	47

uum yielding a brown solid, which was extracted with CH_2Cl_2 (10 ml). Addition of petroleum ether (50 cm^3) resulted in precipitation of a dark brown solid, which was washed with petroleum ether, dried under vacuum, and shown to be $[Cr(CO)_4\text{-DABRd}]$ (**I**). The yield was 62%.

RESULTS AND DISCUSSION

Treatment of the photochemically produced $M(CO)_5$. The intermediates with the ligands in THF led to the expected monosubstituted complexes [10]. 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 continuation to the chelating $M(CO)_4L$ or bridging $M_2(CO)_{10}L$ products can occur. Moreover, photochemical occurence 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 done [11]. In this photochemical complexation study, we considered it worthwhile to irradiate *cis*-$[(\eta^4\text{-NBD})M(CO)_4]$ (M = Cr, Mo, W) in the presence of rhodanine and 1,2,4-triazole derivative ligands, because they have never been investigated and can be interesting examples for substitution reactions.

Photolysis of $M(CO)_6$ (M = Cr, Mo, W) in the presence of NBD afforded high yields of the olefin-substituted derivatives *cis*-$[(\eta^4\text{-NBD})M(CO)_4]$ (M = Cr, Mo, W). The relatively stable *cis*-$[(\eta^4\text{-NBD})M(CO)_4]$ (M = Cr, Mo) complexes could be isolated as pure solids (eq. (1)), while the *cis*-$[(\eta^4\text{-NBD})W(CO)_4]$ complex was found to be contaminated with $[W(CO)_5]_2(\mu\text{-NBD})$ (Eq. (2)). Therefore, only the *cis*-$[(\eta^4\text{-NBD})M(CO)_4]$ (M = Cr, Mo) complexes were reacted with the title ligands as shown in Eq. (1). Assignments of the FT-IR spectra were made by reference to literature data and the data is in accord with the previous publications on the related complexes [12].

New complexes *cis*-$[M(CO)_4\text{-DABRd}]$ (M = Cr (I), Mo (II)) and *fac*-$[M(CO)_3\text{-SAT}]$ (M = Cr (III), Mo (IV)) have been synthesized by the photochemical reactions of $[(\eta^4\text{-NBD})M(CO)_4]$ (M = Cr, Mo) with DABRd and SAT ligands and characterized by elemental analysis, FT-IR and ^1H NMR spectroscopy, and mass spectrometry. The photochemical reactions of $[(\eta^4\text{-NBD})M(CO)_4]$ (M = Cr, Mo) with DABRd and SAT proceed in this expected manner to yield the hitherto unknown series of complexes **I–IV** Eqs. (1), (2). The analytical results and some physical properties of the novel complexes **I–IV** are summarized in Table 1. The complexes are air-stable and soluble in chlorinated solvents.

As shown in Table 2, the FT-IR spectrum of **I**, for example, exhibits four prominent bands at 2014 m, 1939 s, 1893 v.s, and 1832 s cm^{-1} in the CO stretching vibrational region. The four ν(CO) patterns indicate the local C_{2v} $(2A_1 + B_1 + B_2 + E)$ symmetry of the $M(CO)_4$ skeleton. These modes shift to lower wave numbers when compared with that of $Cr(CO)_6$ [13]. The FT-IR spectra of **II** exhibit essentially the same ν(CO) absorption pattern as that observed for **I**. Important FT-IR spectral data of **III** and **IV** are presented in Table 2 as well. As anticipated, the chromium and molybdenum complexes exhibit a two-band pattern in the ν(CO) IR region at 1870 s and 1731 v.s cm^{-1}, which is consistent with a tricarbonyl derivative of approximately C C_{3v} $(A_1 + E)$ symmetry of the $M(CO)_3$ unit (M = Cr, Mo). The ν(CO) modes of **III** and **IV** move to lower wave numbers when compared with the starting $M(CO)_6$ (M = Cr, Mo) molecules [13]. The changes observed in the FT-IR spectra of the free ligands upon coordination can be compared with the spectral changes in 5-substituted rhodanine and 1,2,4-triazole in its metal carbonyl complex. The ν(N–H) ligand bands at 3150 and 3060 cm^{-1} appear, as expected for N–H of DABRd in the complexes **I** and **II**. Both complexes exhibit no changes in the intensity or position of the bands in the range 1695–1690 cm^{-1} that are indicative of coordination *via* ν(C=O), this is in keeping with that there are no metal–oxygen interactions in these complexes. The stretching vibrations of $C–S_{ring}$ observed at 810 cm^{-1} in the free ligands shift to lower wave numbers in the spectra of **I** and **II**. The divisions between strong symmetric and asymmetric stretching vibrations of C = S in

Table 2. Important IR absorption bands (cm^{-1}) of olefin complexes, free ligands and their complexes **I–IV**

Compound*	ν(CO)	ν(C=S) (asym, sym)	ν(NH)	ν(C=O)	$\nu(C\text{–}S_{ring})$	ν(OH)	ν(C=N)	ν(C–O)
DABRd[a]		685 s, 610 s	3150 m, 3060 m	1690 s	810 s			
SAT[b]	2033 m, 1960 s, 1944 v.s, 1915 s		2937 s			3400 s	1573 s, 1514 s, 1615 s	1290 s
$[(\eta^4\text{-NBD})Cr(CO)_4]$	2032 m, 1980 s, 1923 v.s, 1875 s							
$[(\eta^4\text{-NBD})Mo(CO)_4]$	2071 m, 2014 m, 1980 s, 1972 m, 1945 m, 1920 v.s, 1870 s							
$[\eta^4\text{-NBD})W(CO)_4]$ + $W(CO)_5](\mu\text{-NBD})$	2014 m, 1939 s, 1893 m, 1832 m							
I	2014 m, 1940 s, 1892 m, 1830 m	697 s, 594 s	3123 m, 3057 m	1690 s	804 s			
II	1870 s, 1731 v.s	703 s, 591 s	134 m, 3054 m	1690 s	805 s			
III	1874 s, 1732 v.s		2936			3990 s	1564 s, 1501 s, 1596 s	1290 s
IV			2940			3985 s	1565 s, 1508 s, 1603 s	1290 s

* Taken: [a] from [7] [b] from [8].

Table 3. ^1H NMR data for the free ligands and **I–IV** complexes in DMSO-d_6 solution

Compound	δ, ppm					
	HC=N	0H	CH_{Ar}	NH	N(3)–H	C(6)–H
DABRd*					13.56 s, 1H	7.49 s, 1H
SAT*	8.96 s, 6.30 s, 2H	12.82 s, 1H	6.80–7.90 m, 2H			
I					13.55 s, 1H	7.48 s, 1H
II					13.55 s, 1H	7.48 s, 1H
III	9.97 s, 7.23 s, 2H	12.85 s, 1H	6.80–7.90 m, 2H	6.60 s, 1H		
IV	10.03 s,7.34 s, 2H	12.85 s, 1H	6.80–7.90 m, 2H	6.60 s, 1H		

* Taken from [7] and [8].

DABRd are increased in the spectra of **I** and **II**, showing that the DABRd ligands coordinate to the metal via both sulfur NH–(S)C = S donor atoms in **I** and **II**. The FT-IR spectra of complexes **III** and **IV** displayed the characteristic bands of SAT with the appropriate shifts due to complex formation. The strong bands at 1615, 1573, and 1514 cm^{-1} in the FT-IR spectra of free SAT belong to the C=N stretching vibrations. These bands shift toward lower frequency in compounds **III** and **IV** showing that the SAT ligand behaves as a tridentate ligand coordinating via its all imine nitrogen –C=N– donor atoms to the metal center. The shifts have been assessed as weakening of the all C = N bonds resulting from the transfer of electron density from the nitrogen atoms to the metal atom. The sharp bands in the FT-IR spectrum of the SAT at 2937 and 1290 cm^{-1} are assigned to the stretching vibrations of ring NH and phenolic C–O, respectively, and show no shift upon complex formation in **III** and **IV**.

The ^1H NMR spectral data in DMSO-d_6 solutions of compounds **I** and **II** are presented together with the assignments of the signals in Table 3. The presence of the low-field N–H signal in the ^1H NMR spectra of the complexes indicates that deprotonation of the ligands from their N–H on coordination to the organometallic moiety is not possible. It was clearly seen from the ^1H NMR spectra that no signal belongs to the thiol proton confirming the 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)] [14]. The ^1H NMR data in

Table 4. The mass spectral data for **I–IV**

Complexes	M.w.	Relative intensities of ions, m/z
I	428	428.00 (10), [M^+]; 372.00 (15) [M^+ – 2(CO)]; 316.00 (23), [M^+ – 4(CO)]
II	472	472.00 (7), [M^+]; 416.00 (11) [M^+ – 2(CO)]; 360.00 (22), [M^+ – 4(CO)]
III	324	324.00 (12), [M^+]; 296.00 (08) [M^+ – CO]; 268.00 (14), [M^+ – 2(CO)]; 240.00 (22), [M^+ – 3(CO)]
IV	368	368.00 (17), [M^+]; 340.00 (06) [M^+ – CO]; 312.00 (23), [M^+ – 2(CO)]; 284.00 (12), [M^+ – 3(CO)]

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

DMSO-d_6 solutions of compounds **III** and **IV** are collected. Except for the chemical shift of –HC=N– imine protons, all of the other proton signals of the coordinated SAT ligand of compounds **III** and **IV** have almost similar values to those of the free ligand. In the ^{1}H NMR spectra of the compounds OH and NH, protons of the free ligand at 12.82 and 6.59 ppm remains approximately unchanged in the complexes and show that the OH and NH groups do not participate in coordination. As expected, the down-field shift of the HC=N imine protons can be related to a decrease in the π-electron density in the C=N bonds with complex formation in **III** and **IV**.

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

So, at first, we described a particularly convenient photochemical route to the synthesis of *cis*-[(η^4-NBD)M$(CO)_4$] (M = Cr, Mo) and presented the novel photochemical reactions between [(η^4-NBD)M$(CO)_4$] (M = Cr, Mo) with 5-(4-dimethylaminobenzylidene)rhodanine (DABRd) and salicylidene–3-amino–1,2,4-triazole (SAT) ligands. The spectroscopic studies show that the rhodanine ligand DABRd acts as a bidentate ligand coordinating via both sulfur NH–(S)C=S donor atoms in **I** and **II** and SAT ligand behaves as a tridentate ligand coordinating via its all imine nitrogen –C=N– donor atoms in **III** and **IV** to the metal center. DABRd and SAT behave as bidentate and tridentate chelates, respectively, in order to satisfy the 18-electron rule in metal carbonyl complexes. Furthermore, the ν(CO) modes move to lower wave number when compared with M$(CO)_6$ (M = Cr, Mo) molecules. The ^{1}H NMR spectra confirm that the DABRd ligand keeps its thione form while substituting to the metal center via its sulfur donor atoms in **I** and **II**. Apparently, the metallation cause the deshielding of all the imine protons of the SAT ligands in **III** and **IV** in ^{1}H NMR spectra. The mass spectra of complexes **I–IV** show fragmentation via successive loss of CO groups and fragmentation of the DABRd and SAT ligands.

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