Journal of Organometallic Chemistry, 128 (1977) 203—211

CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

VI *. CARBONYL COMPOUNDS OF CHROMIUM(0), MOLYBDENUM(0) AND TUNGSTEN(0) CONTAINING SULFURDIIMINE LIGANDS. MECHANISM OF THE FLUXIONAL PROCESS AND RESONANCE RAMAN RESULTS

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(Received August 6th, 1976)

Summary

The preparation and properties are reported of $Mo(CO)_5(RNSNR)$ (R = = Me,Et,i-Pr) and $M(CO)_{6-x}$(5,6-dimethyl-2,1,3-benzothiadiazal)$_x$ (M = Cr, x = 1; M = Mo and W; x = 1,2). In all cases the sulfurdiimine is linked as a monodentate ligand to the metal via the N-atom. All the complexes show fluxional behaviour. This is attributed to a gliding movement of the metal atom along the N=S=N system. Resonance Raman spectra of $M(CO)_5(RNSNR)$ (M = W, R = i-Pr; M = Cr, R = Me,Et), $W(CO)_5$(5,6-dimethyl-2,1,3-benzothiadiazal) and $M(CO)_4$(t-BuNSN-t-Bu) (M = Cr, Mo) show a vibrational coupling of the metal to sulfurdiimine CT transition not only with vibrations of the sulfurdiimine but also with the symmetric stretching vibration of the *cis* carbonyls in the complex.

Introduction

Previous work on sulfurdiimine compounds of Pt(II) [1,2], Pd(II) [3], Rh(I) and Ir(I) [4], in which the sulfurdiimine is bonded as a monodentate via one of the N-atoms, show fluxional behaviour of the NSN group. One of the movements, which involved interchange of both ends of the sulfurdiimine, has been ascribed to an N—N jump. The sulfurdiimine compounds $M(CO)_5(RN{=}S{=}NR)$ of Cr(0) and W(0) [5], also show a fluxional behaviour, which has been ascribed, however, to a gliding movement of the metal along the NSN system. In order to obtain more evidence for this proposed mechanism, complexes $M(CO)_5(DMB)$ (M = Cr, Mo,W; DMB = 5,6-dimethyl-2,1,3-benzothiadiazal) have been prepared and in-

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* For parts I—V see refs. 1—5.

vestigated. Furthermore, attention has been paid to the preparation of the hitherto unobtainable $Mo(CO)_5(RNSNR)$ compounds [5]. Finally, our previous resonance Raman results [5] prompted us to have a closer look at other penta- and tetra-carbonyl compounds of sulfurdiimines.

Experimental

All reactions were carried out under dry, oxygen-free nitrogen. Solvents were dried and deoxygenated.

Preparation of $Mo(CO)_5(THF)$

$Mo(CO)_6$ (5.68 mmol) in 110 ml THF was irradiated with a medium pressure mercury lamp. After 4 h ~30—40% was converted to $Mo(CO)_5(THF)$. The same result was achieved when $Mo(CO)_6$ (5.68 mmol) in 250 ml THF was irradiated for 3 h in a Rayonet, equipped with 300 nm tubes.

Preparation of $Mo(CO)_5(RNSNR)$ (R = Me,Et,i-Pr)

The solution of $Mo(CO)_5THF)$ (2.1 mmol) in 110 ml. THF was then cooled to —30°C. Immediately after the irradiation was stopped 2 mmol sulfurdiimine was added in the dark, the mixture was set aside for a few hours at —30°C and then concentrated. $Mo(CO)_6$ crystallized out in the cold. After filtration the solvent was removed under vacuum and the red oily residue was recrystallized from pentane at —30°C in low yields. The products are not stable at room temperature. In the cold they can be kept only in pentane solutions. They are soluble in common organic solvents and very sensitive to moisture. Along with decomposition $Mo(CO)_5$(DiPrSD) (red) was converted at room temperature in THF solution in to $Mo(CO)_4$(DiPrSD) (purple), in which DiPrSD is bidentate and which is more stable than the pentacarbonyl derivative. This reaction was also observed for $Cr(CO)_5$(DiPrSD) [5].

Preparation of $M(CO)_{6-x}(DMB)_x$ ($M = W$, $x = 1,2$; $M = Cr$, $x = 1$)

DMB (7 mmol) was added to a cooled (—20°C) THF solution (100 ml) of $M(CO)_5(THF)$ (7 mmol). The mixture was allowed to stand for 1 h at room temperature after which the solvent was removed under vacuum. Recrystallization from pentane gave red crystals of $M(CO)_5(DMB)$ at —20°C, sometimes with a green gloss (yield 70%). After recrystallization of $W(CO)_5(DMB)$ a dark blue, pentane-insoluble residue remained, with the formula $W(CO)_4(DMB)_2$. Yield 6%. $Cr(CO)_5(DMB)$ is photosensitive in solution.

Preparation of $Mo(CO)_4(DMB)_2$

DMB [6] (4 mmol) was added to a THF solution (50 ml) of $Mo(CO)_4$ (bicycloheptadiene) [7] (2 mmol). After 12 h the solvent was removed under vacuum. From the purple residue, traces of the starting compound and hexacarbonyl were removed under vacuum at 50°C for 18 h. After washing with pentane, in order to remove $Mo(CO)_5DMB)$, pure $Mo(CO)_4(DMB)_2$ (purple) was obtained. Yield 53%. The compound is very sensitive to light in solution.

The C and H analyses were carried out in this laboratory (Table 1).

TABLE 1

ANALYTICAL DATA FOR $M(CO)_{6-x}(DMB)_x$

Compound	Analyses found (calcd.) (%)	
	C	H
$Cr(CO)_5(DMB)$	43.72 (43.83)	2.18 (2.26)
$W(CO)_5(DMB)$	31.93 (31.99)	1.97 (1.65)
$Mo(CO)_4(DMB)_2$	44.76 (44.78)	3.12 (3.01)

Spectra

The ^1H NMR spectra were recorded with a Varian HA 100 spectrometer. ^{13}C NMR spectra with a Varian CFT-20 spectrometer. IR spectra were recorded with Beckman IR 7, IR 11 and IR 4250 spectrophotometers. Raman spectra were recorded using a Coderg PH 1 spectrophotometer with CRL 52 Kr^+, Ar^+ lasers and a CRL model 490 tunable dye laser. The Resonance Raman spectra were recorded for 1—3 × 10^{-3} *M* solutions in C_6H_6 and $CHCl_3$, using the solvent as an internal standard. The electronic absorption spectra were recorded on a Cary 14 spectrophotometer.

Results

$Mo(CO)_5(RNSNR)$ (R = Me, Et, i-Pr)

The preparation of the molybdenum compounds was more difficult than that of the corresponding chromium and tungsten derivatives [5], mainly because the yield of the intermediate $Mo(CO)_5(THF)$ was only ~30—40%, compared with 90—100% for Cr and W. Furthermore $Mo(CO)_5(THF)$ appeared to be unstable, so that the reaction with sulfurdiimine had to be carried out immediately after the irradiation, in the dark and at —30°. In this way we obtained unstable $Mo(CO)_5$-(RNSNR). It was not possible to obtain analytically pure products and the NMR spectra indicated the presence of impurities. Strohmeier et al. [8] also reported poor yields and impure products from this indirect method. Direct irradiation in the presence of the ligands is not possible because sulfurdiimines are photochemically unstable [9].

The ^1H NMR spectra at —25°C show that the two R-groups of the sulfurdiimine are not equivalent On raising the temperature to —10°C the sulfurdiimine bebecomes fluxional (Table 2 and Fig. 1). The fluxional process is intramolecular, since variations of the line shape with temperature are independent of the concentration of the complex or of added free ligand. This process is thus analogous to that of the corresponding Cr and W compounds [5]. Just as for $W(CO)_5(DMSD)$ a second isomer is found for $Mo(CO)_5(DMSD)$ at —25°C that participates in the process (VI, Fig. 1). The vibrational and electronic absorption spectra of all Mo-compounds (Table 3) are similar to those for the Cr- and W-compounds [5]. A CT band at the low-energy side of the ligand field transitions has been observed. The intensity of this band is, however, much lower (ϵ_{max} ~ 1000) than for the Cr and W compounds, which is consistent with the instability of these compounds. Because of this instability no reliable values of ϵ_{max} could be obtained.

TABLE 2

^{1}H NMR DATA FOR $Mo(CO)_5(RNSNR)$ IN C_7D_8 (ppm, rel. to TMS)

Compound	T (°C)	$N—CH_{3-n}$ reson. of R^a Ia	Ib	$(CH_3)_n$ reson. of R Ia'	Ib'	J(Hz)
$Mo(CO)_5(DMSD)$ ^{b}	30	2.97 (br)				
	−25	2.91 (q)	2.68 (q)			1.4
$Mo(CO)_5(DESD)$	−25	3.63 (q)	3.10 (q)	0.89 (t)	0.84 (t)	7

[a] See Fig. 1. [b] The signal of the symmetric isomer VI lies at 2.76 (s) ppm at −25°C; Br = broad; q = quartet; t = triplet; s = singlet.

$M(CO)_5(DMB)$ (M = Cr, W)

From ^{1}H and ^{13}C NMR spectra (Table 4,5 and Fig. 1) one may conclude that DMB is asymmetrically bonded to the metal. At elevated temperatures (>60°C) DMB becomes fluxional. At 85°C the two aromatic protons are in the intermediate and the two methyl groups in the fast exchange. The fluxional process is intramolecular, since the variation of the line shape with temperature is independent of the concentration of the complex or added free ligand.

The absorption spectra (Table 3) of these complexes also possess a low energy CT band. Furthermore, an extra band with vibrational progression is found at about 32000 cm^{-1} which is assigned to a $\pi \rightarrow \pi^*$ transition of the coordinated ligand. Some relevant vibrational spectral data are listed in Table 3.

$M(CO)_4(DMB)_2$ (M = Mo, W)

In the preparation of $W(CO)_5(DMB)$ a second, dark blue product was isolated, for which the composition $W(CO)_4(DMB)_2$ is proposed on the basis of the reasoning below.

The ^{1}H NMR spectrum of $W(CO)_4(DMB)_2$ (at 30°C) is similar to that of $W(CO)_5(DMB)$ except that the positions differ slightly. One aromatic proton signal lies exactly under the solvent signal of C_7D_8. At lower temperature this signal shifted away from the solvent signal and could thus be assigned. From these results we conclude that the DMB ligands in $W(CO)_4(DMB)_2$ are bonded to the metal in the same way as in $W(CO)_5(DMB)$ i.e. via one of the N-atoms. At higher temperatures (60°C) the complex becomes fluxional. The rate of this intramolecular process is about the same as that for $W(CO)_5(DMB)$. There is no chemical

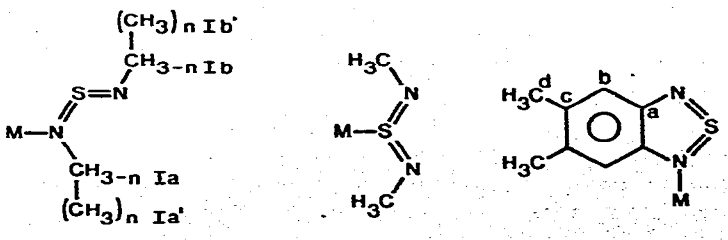

Fig. 1. The assignment used in Tables 2,4 and 5 for $Mo(CO)_5(RNSNR)$ and $M(CO)_{6-x}(DMB)_x$ (x = 1,2)

TABLE 3

ν(CO) FREQUENCIES AND ABSORPTION MAXIMA FOR $M(CO)_{6-x}(DMB)_x$[h] and $Mo(CO)_{6-x}(RNSNR)_x$ (cm^{-1})

Compound	ν(CO)[a]				Absorption maxima (cm^{-1})[b]		
	A_1^2	E	A_1^1		$M \rightarrow \pi^*(L)$	$d \rightarrow d$	$\pi(L) \rightarrow \pi^*(L)$
$Cr(CO)_5(DMB)$	2070	1947	1927		19680 (3.5)	24240 (3.5)	32000 (14)
$W(CO)_5(DMB)$	2078	1945	1925		20410 (4.5)	25000 (3.7)	32000 (12)
$Mo(CO)_5(DMB)$[c]	2078		1925[d]		20500	25000	30960
$Mo(CO)_5(DMSD)$[h]	2078	1945	1925		20600	25800	
$Mo(CO)_5(DESD)$[h]	2078	1945	1928		20700	25600	
$Mo(CO)_5(DiPrSD)$[h]	2075	1944	1925		21300	25450	
	A_1^2	B_1	A_1^1	B_2[e]			
$Mo(CO)_4(DiPrSD)$[c]	2025	1905	1943	1852	18200	25200	
$W(CO)_4(DMB)_2$	2004	1905	1880	1826	14700; 16300		
$Mo(CO)_4(DMB)_2$	2026	1926	1887	1835			
$Mo(CO)_4(C_7H_5NS)_2$[f]	2010	1898	1861	1808			
$Mo(CO)_4(DB)_2$[g]	2016	1904	1857	1824			

[a] IR results from pentane solutions. [b] Solvent is n-heptane. The molar extinctions (×10^{-3}) are given in parentheses. [c] Not isolated, but only measured in solution. [d] Very broad. [e] Ir results from nujol mulls. [f] Ref. 10; C_7H_5NS: benzothiazole. [g] Ref. 11; DB: 1,4 diazabutadiene. [h] DMB = 5,6-dimethyl-2,1,3-benzothiadiazal; DMSD = dimethylsulfurdiimine; DESD = diethylsulfurdiimine; DiPrSD = diisopropylsulfurdiimine.

exchange between $W(CO)_5(DMB)$ and $W(CO)_4(DMB)_2$ on the NMR time scale from −60°C to +85°C (Table 4).

The IR spectra of $W(CO)_4(DMB)_2$ and of $Mo(CO)_4(DMB)_2$ (the latter was prepared from $Mo(CO)_4$(bicycloheptadiene) and DMB) are very similar to those of $Mo(CO)_4$(benzothiazole)$_2$ [10] and $Mo(CO)_4$(1,4-diazabutadiene) [11] (Table 3), but different from that of the dimeric [$Mo(CO)_4$(1,4-diazabutadiene)]$_2$ [11], in which the ligand is bridging. It can therefore be concluded that the complexes are monomeric, while the DMB ligands are in a *cis* position with respect to each other.

The electronic absorption spectra of $W(CO)_4(DMB)_2$ differ greatly from those of $W(CO)_4(DBSD)$ [5], $W(CO)_5(RNSNR)$ and from $W(CO)_5(DMB)$ (Table 3). Two

TABLE 4

^{1}H NMR DATA FOR $M(CO)_{6-x}(DMB)_x$ IN C_7D_8 (ppm rel. to TMS)

Compound	T(°C)	Chemical shift of[a]			
		d		*b*	
DMB	30	1.86		7.46	
$Cr(CO)_5(DMB)$	30	1.76	1.83	7.12	7.53
	85	1.89		v.br.[b]	
$W(CO)_5(DMB)$	30	1.76	1.77	7.11	7.39
	85	1.84		v.br.	
$W(CO)_4(DMB)_2$	30	1.70	1.73	7.07	7.64
	85	1.89		v.br.	

[a] See Fig. 1. [b] v.br. = very broad.

TABLE 5

^{13}C NMR DATA FOR $M(CO)_5(DMB)$ IN C_6D_6 (ppm rel. to TMS)

Compound	Chemical shift of [a]								CO	
	d		*b*		*c*		*a*		*trans*	*cis*
DMB	20.26		120.06		140.00		154.73			
$Cr(CO)_5(DMB)$	19.94	20.73	118.11	121.25	141.06	143.98	154.67	156.60	201.10	197.51
$W(CO)_5(DMB)$	19.89	20.76	119.14	121.03	141.38	144.70	153.84	156.18		214.33

[a] See Fig. 1.

CT bands are found in the low energy region, which are shifted to the red with respect to W(CO)$_5$(DMB). Such a red shift, although smaller, is also observed in going from the mono- to the bis-substituted pyridine derivatives [12,13]. Similar low values for CT bands have been found in e.g. Mo(CO)$_2$(PPh$_3$)$_2$(2,2'-bipyridyl) (14164 cm^{-1} in C_6H_6) [14]. The blue shift of both bands on changing the solvent from n-heptane to benzene agrees with an assignment of these bands to CT transitions. The higher energy part of the spectrum could not be investigated because of the additional presence of bands due to the mono-product (formed from the bis-species in solution).

It should finally be noted that the complexes M(CO)$_4$(DMB)$_2$ are not very stable in solution, which is probably the result of steric interaction between the two DMB groups. As a consequence the compounds could not be recrystallized. Molecular weight measurements and ^{13}C NMR spectra failed for obvious reasons. Also the ^{1}H NMR spectra of Mo(CO)$_4$(DMB)$_2$ could not be obtained.

Resonance Raman spectra

The Resonance Raman spectra have shown [5] that orbitals of both sulfurdiimine and of the *cis* carbonyls are mixed into the first excited state of W(CO)$_5$-(DMSD), but that the first excited state of W(CO)$_4$(DBSD) is fully localized in the metal—sulfurdiimine bonding region. In order to get more information about the general behaviour of other penta- and tetra-carbonyl compounds, Resonance Raman measurements have been extended to include W(CO)$_5$(DiPrSD), Cr(CO)$_5$-

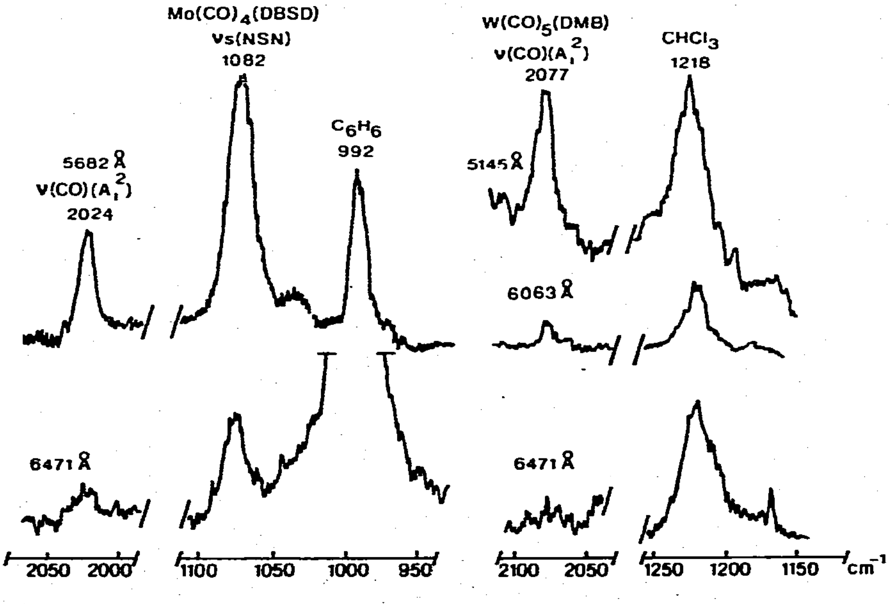

Fig. 2. Raman spectra of Mo(CO)$_4$(DBSD) in C_6H_6 (with 6471 Å and 5682 Å laser excitations) and W(CO)$_5$(DMB) in CHCl$_3$ (with 6471 Å, 6063 Å and 5145 Å laser excitations). The concentration of W(CO)$_5$(DMB) in CHCl$_3$ for the excitation with 5154 Å is 30% that for the solutions using 6063 Å and 6471 Å.

(DMSD), $Cr(CO)_5$(DESD), $W(CO)_5$(DMB), $Cr(CO)_5$(DMB), $Mo(CO)_4$(DBSD) and $Cr(CO)_4$(DBSD). All these complexes showed apart from ligand vibrations, an enhancement of the symmetric vibrations of the *cis*-carbonyls (Fig. 2).

Discussion

NMR studies of coordinated sulfurdiimine groups have shown that the sulfurdiimine group may be bonded as a monodentate (N- or sometimes S-bonded) or as a bidentate via the two N-atoms [1—5]. Fluxional and intermolecular exchange processes involving the sulfurdiimine ligand occur readily. One of these processes, involving interchange between the two R sites of neutral complexes of Pt(II) [1,2], Pd(II) [3] and of the cationic complexes of Rh(I), Ir(I) and Pt(II) [4], in which the sulfurdiimine ligands are monodentate, involves in addition to rotation about the N=S bond and/or inversions at N and N—N jump via a five coordinate intermediate in which the sulfurdiimine is bidentate.

In contrast, the penta-carbonyl sulfurdiimine complexes $M(CO)_5(RN{=}S{=}NR)$ (M = Cr, Mo,W; R = Me,Et,i-Pr) [5], in which the ligand is monodentate are the first sulfurdiimine complexes in which intramolecular interchange of the two R sites probably involves a gliding movement of the metal along the sulfurdiimine from one N-atom to the other via the sulfur atom (see ref. 5, Fig. 9). It was argued that such a process is much more likely than an N—N jump, as in the latter case a seven coordinate intermediate would have to be assumed. Furthermore this gliding movement neatly explains the involvement of the second, sulfur bonded, isomer of $M(CO)_5(RN{=}S{=}NR)$.

The use of the DMB ligand has given us now more evidence for the type of process occurring, as rotations about the N=S bond and/or inversions at N are impossible, while an intramolecular N—N jump seems very unlikely in view of the relative spatial arrangements of the free electron pairs on the two N-atoms. The most likely process seems therefore the proposed gliding movement from one N-atom via S to the other N-atom (see Fig. 3).

Whether during this process the metal atom is also linked for a short time to the double bond of the N=S groups is uncertain (N.B. see behaviour of allene in $Fe(CO)_4$TMA [15] and in platinum compounds [16,17]). As long as there is no evidence for a linkage between a metal and one of the double bonds of RN=S=NR, we prefer our present explanation.

It should be noted that in the case of $PtCl_2$(benzothiadiazal)($AsEt_3$) [2] intermolecular exchange of the ligand was observed. A contribution of an intramolecular process was not excluded. The intermolecular process probably dominates, however, as generally planar Pt-complexes are more susceptible to bimolecular ligand exchange than six-coordinate compounds.

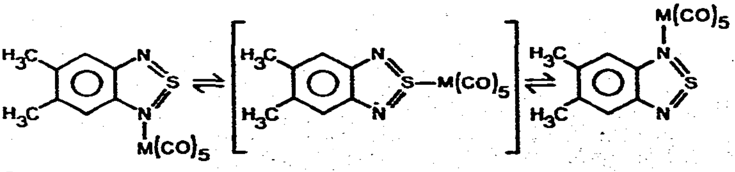

Fig. 3. The mechanism for the intramolecular interconversion of DMB in $M(CO)_5$(DMB).

All measured complexes, both tetra- and penta-carbonyls, show a Resonance Raman effect, just as $W(CO)_5(DMSD)$ [5], for both the sulfurdiimine symmetrical stretching and bending mode and the totally symmetric vibration of the *cis* carbonyls. Obviously there is in both tetra- and penta-carbonyls a mixing between *cis* π^*-CO and π^*-ligand orbitals in the lowest excited state of the complex. A strong mixing of axial π^*-CO and π^*-ligand orbitals is not possible, and thus no Resonance Raman effect for the totally symmetric vibration of the axial carbonyls is found.

In this respect, the behaviour of $W(CO)_4(DBSD)$ [5] is of interest, since in contrast with all the studied pentacarbonyl compounds and with $Mo(CO)_4(DBSD)$ and $Cr(CO)_4(DBSD)$, this compound does not show a Resonance Raman effect for any CO stretching mode. Apparently the lowest excited state of $W(CO)_4$-(DBSD) is fully localized on the metal and the sulfurdiimine. This result will be the subject of a further investigation.

Acknowledgement

Messrs Th. Snoeck and L. Winnubst are to be thanked for their experimental cooperation.

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