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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

V *. DIALKYLSULFURDIIMINE COMPOUNDS $M(CO)_4(RN{=}S{=}NR)$ (M = Cr, Mo, W) AND $M(CO)_5(RN{=}S{=}NR)$ (M = Cr, W); STRUCTURAL, SPECTROSCOPIC AND FLUXIONAL PROPERTIES

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Summary

The preparation and properties are reported of $M(CO)_4(RN{=}S{=}NR)$ (M = Cr, Mo, W; R = i-Pr, t-Bu), in which the ligand is bidentate and in the *trans,trans* configuration, and of $M(CO)_5(RN{=}S{=}NR)$ (M = Cr, W; R = Et, i-Pr) in which the sulfurdiimine is monodentate and in the *cis,trans* configuration. In both cases the ligand is linked to the metal atom via the N-atom(s). With $M(CO)_5$(MeN=S=NMe) a second isomer is found in which the sulfurdiimine is probably bonded via the S-atom to the metal. All the pentacarbonyl compounds are fluxional; this is attributed to a gliding movement of the metal atom along the N=S=N system.

Both $W(CO)_4$(t-BuN=S=N-tBu) and $W(CO)_5$(MeN=S=NMe) show vibronic coupling of metal to ligand charge transfer transitions with sulfurdiimine vibrations, as shown with Resonance Raman, but only for $W(CO)_5$(MeN=S=NMe) also with the symmetric mode of the equatorial carbonyl groups. The metal—sulfurdiimine bond appears to be weak for $M(CO)_5(RN{=}S{=}NR)$, but strong for $M(CO)_4(RN{=}S{=}NR)$.

Introduction

Previous work on sulfurdiimine compounds of Pt(II) [1,2,4], Pd(II) [3], Rh(I) and Ir(I) [4] has shown that sulfurdiimine in the *trans,trans* configuration may be bonded as a monodentate or bidentate ligand [4]. In the *cis,trans* configuration the ligand can only behave as a monodentate ligand. Two isomers, however,

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* For Parts I—IV see refs. 1—4.

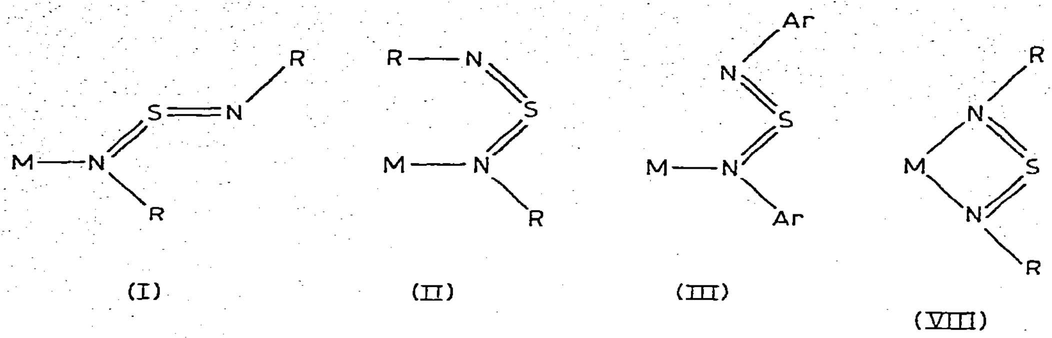

Fig. 1. Known modes of coordination of sulfurdiimines to a metal atom. The Roman numerals have been assigned in ref. 1.

are generally found depending on which N-atom is bonded to the metal atom [1—4]. (Fig. 1).

Extensive ^{1}H and ^{13}C NMR studies have shown that the isomers in which the sulfurdiimine is monodentate may interconvert intermolecularly, or intramolecularly by means of various different movements of sulfurdiimine [1—4].

In order to investigate other possible bonding modes (e.g. via S or via the N=S double bond), complexes of zerovalent metals are also being investigated. In the course of this work the compounds $M(CO)_4$(t-BuN=S=N-t-Bu) (M = Cr, Mo, W) were reported by Lindsell and Faulds [5], who made tentative proposals for the structures on the basis of ^{1}H NMR and IR. These and other compounds of formula $M(CO)_4(RN{=}S{=}NR)$ were prepared independently by us by different methods, as well as a new series of compounds of formula $M(CO)_5(RN{=}S{=}NR)$. Crystal structure determinations on $W(CO)_4$(t-BuN=S=N-t-Bu) [6] and $W(CO)_5(MeN{=}S{=}NMe)$ [7] and extensive spectroscopic studies (^{1}H and ^{13}C NMR, IR, UV, Raman and Resonance Raman) give insight into the bonding of both series and on the fluxional movements of the pentacarbonyl compounds.

Experimental

All reactions were carried out under an atmosphere of dry oxygen free nitrogen. Solvents were dried and deoxygenated with the utmost care.

Preparation of $M(CO)_5(THF)$ (M = Cr, W)

The compounds $M(CO)_5(THF)$ were prepared according to the literature [8] by the UV irradiation of $M(CO)_6$ (10 mmol) in tetrahydrofuran (300 ml), while N_2 was bubbled through the mixture. After 24 h 80—90% conversion to $M(CO)_5(THF)$ was achieved.

Preparation of $M(CO)_5(RN{=}S{=}NR)$ (M = Cr, W; R = Me, Et, i-Pr)

Sulfurdiimine (3 mmol) was added to a cooled (—20°C) THF solution (100 ml) of $M(CO)_5(THF)$ (3 mmol). The reaction mixture was allowed to stand for 1 h at room temperature after which the solvent was removed under vacuum. The red oily residue was dissolved in pentane (175 ml) and filtered. $W(CO)_5$(DMSD) (DMSD = dimethylsulfurdiimine) crystallized out at —20°C as large red crystals (yield 65%). The other products were isolated as red oils in similar yields. $Cr(CO)_5(DiPrSD)$ (DiPrSD = di-isopropylsulfurdiimine) must be kept in the cold, as otherwise the compound is slowly converted into $Cr(CO)_4(DiPrSD)$. The oils could not be further purified owing to their instability. Analyses, however, were generally satisfactory. Some impurities are probably present in $Cr(CO)_5$-(DESD) (DESD = diethylsulfurdiimine) and $Cr(CO)_5(DiPrSD)$ (Table 1). With Mo, pure compounds could not be obtained, although spectroscopic data show their existence in solution.

Preparation of $M(CO)_4(RN{=}S{=}NR)$ (M = Cr, R = t-Bu, i-Pr; M = Mo, W; R = t-Bu)

Method A. The preparation is analogous to that of the pentacarbonyl derivatives. When R = i-Pr the THF solution was allowed to stand for several hours at room temperature. Greenish looking crystals were obtained from pentane solutions. Metal hexacarbonyl was removed under vacuum. (Yields of about 40%.) $W(CO)_4(DiPrSD)$ could not be isolated, but was identified using NMR and IR.

Method B. Sulfurdiimine (2 mmol) was added to a stirred suspension of $[M(CO)_5Cl]NEt_4$ [9] (2 mmol). Reaction times of 4 h at 80°C, and 40 h at 20°C were used for W and Mo respectively. With Cr reaction only occurred on addition of $NaBPh_4$, after which the solution was allowed to stand for 40 h at 20°C. After filtration and evaporation of the solvent the products were recrystallized from pentane. The yields of 10 to 20% could be raised to 20 to 40% by the addition of $NaBPh_4$ (2 mmol) to the reaction mixture.

A different preparative method was described by Lindsell and Faulds [5].

The compounds $M(CO)_5(RN{=}S{=}NR)$ are photosensitive and very sensitive to moisture. They are soluble in common organic solvents. The tetracarbonyl metal derivatives may be sublimed, while the pentacarbonyl compounds decompose in vacuum.

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

^1H NMR spectra were recorded with Varian HA 100, XL-100 and T 60 spectrometers; ^{13}C NMR spectra with a Varian CFT-20 spectrometer. IR spectra were recorded with Beckmann IR 7 and IR 12 spectrophotometers and

TABLE 1

ANALYTICAL DATA FOR $M(CO)_x(RNSNR)$ (x = 4, 5)

Compound	Dec. temp. (°C)	Analysis found (calcd.) (%)	
		C	H
$W(CO)_4(DBSD)$	125	30.45 (30.65)	3.82 (3.86)
$W(CO)_5(DiPrSD)$	oil	28.16 (28.10)	3.33 (3.00)
$W(CO)_5(DESD)$	oil	24.76 (24.45)	2.22 (2.28)
$W(CO)_5(DMSD)$	50	20.61 (20.31)	1.55 (1.46)
$Cr(CO)_4(DBSD)$	95	41.97 (42.60)	5.46 (5.36)
$Cr(CO)_4(DiPrSD)$	76	38.60 (38.71)	4.93 (4.55)
$Cr(CO)_5(DiPrSD)$	oil	37.54 (39.05)	3.97 (4.17)
$Cr(CO)_5(DESD)$	oil	33.31 (34.85)	3.66 (3.25)
$Cr(CO)_5(DMSD)$	oil	29.30 (29.79)	2.32 (2.14)
$Mo(CO)_4(DBSD)$	85	38.02 (37.70)	4.68 (4.75)

Raman spectra with a Coderg PH 1 spectrophotometer with d.c. detection and an Ar^+/Kr^+ CRL 53 MG laser with exciting lines ranging from 647 to 458 nm. The Resonance Raman spectra of $W(CO)_4$(DBSD) (DBSD = di-t-butyl-sulfurdiimine) and of $W(CO)_5$(DMSD) were recorded for 2×10^{-3} *M* solutions in benzene, using benzene as an internal standard.

The electronic absorption spectra were recorded on a Cary 14 spectrophotometer.

Results

^1H and ^{13}C NMR spectra

M(CO)₄(RN=S=NR) (M = Cr, Mo, W; R = i-Pr, t-Bu). The complexes $M(CO)_4$-(RN=S=NR) are formed for R = t-Bu, and in the case of Cr also for R = i-Pr, but not for R = Me and Et. The R groups are equivalent as is shown by ^1H and ^{13}C NMR (Tables 2 and 3 and Fig. 2).

The chemical shifts are solvent dependent (Table 2). From the NMR data and other data (vide infra) it was concluded that the sulfurdiimine is bonded as a bidentate ligand and this was confirmed by a single crystal X-ray determination [6] (Fig. 3).

M(CO)₅(RN=S=NR) (M = Cr, W; R = Me, Et, i-Pr). The ^{13}C and ^1H NMR data (Tables 3 and 4) show the existence of one isomer if R = Et or i-Pr for both Cr and W. This isomer has two non-equivalent R groups at −25°C.

Two isomers in unequal ratio were observed for $M(CO)_5$(DMSD). The most abundant isomer has two nonequivalent R groups while the less abundant isomer, as is particularly clear from the ^{13}C NMR spectra (Table 4), has equivalent R groups even at −60°C. Both NMR and IR data showed that for R = Me and Et no tetracarbonyl species are present.

The compounds with the two non-equivalent R groups probably all have the structure shown in Fig. 4, which was determined for $W(CO)_5$(DMSD) by a single crystal X-ray investigation [7]. The sulfurdiimine is monodentate and in the *cis,trans*-configuration. The structure is similar to that of $[PtCl_2(DBSD)(C_2H_4)]$ [10].

The structure of the second less abundant isomer of $W(CO)_5$(DMSD) with

TABLE 2

^1H NMR DATA FOR $M(CO)_4$(RNSNR) (ppm rel. to TMS)

Compound	Solvent	N—CH_{3-n} resonances of R	$(CH_3)_n$ resonances of R	J (Hz)
		VIII	VIII'	
$W(CO)_4$(DBSD)	C_7D_8		1.18s	
	$CDCl_3$		1.58s	
$Cr(CO)_4$(DBSD)	C_7D_8		1.25s	
	$CDCl_3$		1.55s	
$Mo(CO)_4$(DBSD)	C_7D_8		1.17s	
	$CDCl_3$		1.57s	
$W(CO)_4$(DiPrSD)	C_7D_8	3.04h	0.87d	6
$Cr(CO)_4$(DiPrSD)	C_7D_8	3.74h	1.18d	6

s, singlet; d, doublet; h, heptet.

TABLE 3

^{13}C NMR DATA FOR $M(CO)_4(RNSNR)$ AND $M(CO)_5(RNSNR)$ (ppm, rel. to TMS in C_7D_8)

Compound	Isomer	t (°C)	$N-CH_{3-n}$ resonances [a] of R		$(CH_3)_n$ resonances [a] of R		CO resonances	
			Ia or VI	Ib or VIII	Ia′	Ib′ or VIII′	I and VIII *trans*	I, VI and VIII *cis*
$W(CO)_4(DBSD)$	VIII	36		62.12		31.61		211.83
$W(CO)_5(DMSD)$	I	36	47.91(br) [c]	38.62(br) [c]				198.32
	I	−60	47.83	38.82			201.71	197.93
	VI	−60	47.41					198.60
$W(CO)_5(DESD)$	I	−60 [b]	55.39	47.85	17.60	13.45	201.68	198.06
$Cr(CO)_5(DMSD)$	I	−60 [b]	45.86	38.96			220.89	214.08
	VI	−60 [b]	38.10					215.16
$Cr(CO)_5(DESD)$	I	20	53.93	48.00	17.67	13.64	220.77	214.46
	I	−60	53.83	48.00	17.77	13.18	220.91	214.28

[a] Assignment by analogy with $[PtCl_2(RN{=}S{=}NR)L]$ [1]. [b] At room temperature too much decomposition. [c] br, broad.

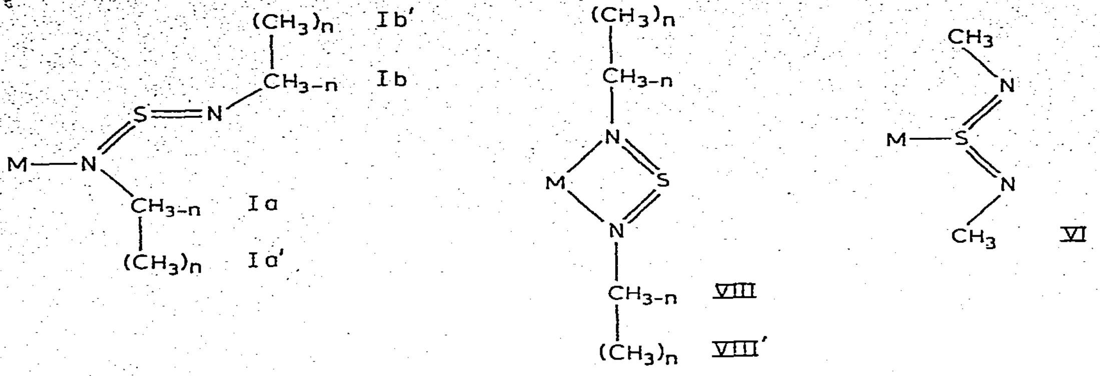

Fig. 2. The assignment of the R groups for configurations I, VI and VIII of Tables 2, 3 and 4.

the two magnetically equivalent R groups is less certain. On the basis of the NMR spectra the most likely structure involves a sulfur-coordinated ligand with the R groups in the *trans,trans*-configuration (configuration VI of [1], Fig. 5), or much less likely, with the R groups in the *cis,cis* configuration. In principle the ligand may also be in the *cis,trans* configuration, but then one has to assume a very rapid inversion at both N-atoms or, less likely, rotations about both N=S bonds. These movements, however, have never been observed below —45°C for N-coordinated monodentate sulfurdiimines [1,3,4]. Nevertheless they are not rigorously excluded, as e.g. inversions might be more rapid for S-coordinated sulfurdiimines.

The complexes $W(CO)_5(RN{=}S{=}NR)$ become fluxional at temperatures of about —6, 8 and —5°C for R = Me, Et and i-Pr respectively. The second isomer participates in the process, as is clear from Fig. 5.

With $Cr(CO)_5(RN{=}S{=}NR)$ the fluxional movements commence at about 25 and 0°C for R = Et and i-Pr respectively. The situation for R = Me could not be studied very well as the ^{1}H NMR signals are broad. It seems, however, that the complex is not fluxional below 30°C. All fluxional processes are intramolecular, as the changes of the line shapes with the temperature are independent of the concentrations of the complex and of added free ligand, while for R = i-Pr,

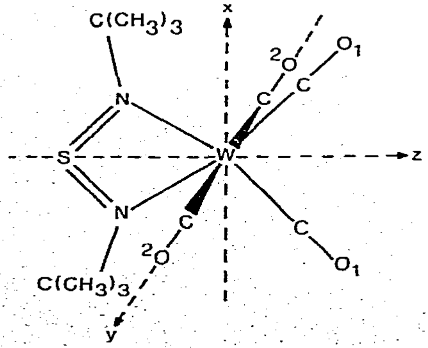

Fig. 3. The structure of $W(CO)_4(DBSD)$ [6].

TABLE 4

^{1}H NMR DATA FOR $M(CO)_5(RNSNR)$ (ppm. rel. to TMS in C_7D_8)
v, very; br, broad; q, quartet; h, heptet; t, triplet; d, doublet.

Compound	t (°C)	N—CH_{3-n} resonances of R [a]		$(CH_3)_n$ resonances of R [c]		J (Hz)
		Ia	Ib	Ia′	Ib′	
$W(CO)_5(DMSD)$ [c]	30	3.15(br)	2.83(br)			
	—25	2.97q	2.58q			1.4
$W(CO)_5(DESD)$	30	3.85(br)	3.55(br)	0.98t [b]		7
	—25	3.76q	3.12q	0.91t	0.82t	7
$W(CO)_5(DiPrSD)$	30	≈4.70(vbr)	≈3.70(vbr)	1.11d [b]		6
	—25	4.77h	3.44h	0.94d	0.83d	6
$Cr(CO)_5(DMSD)$	30	3.00(br)	2.91(br)			
	—25	2.83(br)	2.77(br)			
$Cr(CO)_5(DESD)$	30	3.64(br)	3.21(br)	0.96t	0.84t	7
	—25	3.50q	3.00q	0.98t	0.72t	[illegible]
$Cr(CO)_5(DiPrSD)$	—25	4.84h	2.98h	0.99d	0.74d	6

[a] Assignment by analogy with $[PtCl_2(RNSNR)L]$ [1]. [b] Collapsed signals. [c] The signal of the symmetric isomer VI lies at 2.86s ppm at —25°C.

where $Cr(CO)_4(DiPrSD)$ and $Cr(CO)_5(DiPrSD)$ exist together, no exchange between the two complexes was observed on the NMR time scale from —60 to 50°C.

Electronic absorption spectra

Apart from ligand-field and metal to carbonyl charge transfer bands the spectra (Table 5) of all compounds possess an extra CT band at lower energy. These CT bands are far more intense for $M(CO)_4(RN{=}S{=}NR)$ than for $M(CO)_5$-$(RN{=}S{=}NR)$.

$M(CO)_4(RN{=}S{=}NR)$. The intensities of these CT bands are high and not solvent dependent. While the CT bands of the Cr and Mo compounds are shifted to higher frequency in polar solvents, $W(CO)_4(DBSD)$ does not show any solvent shift.

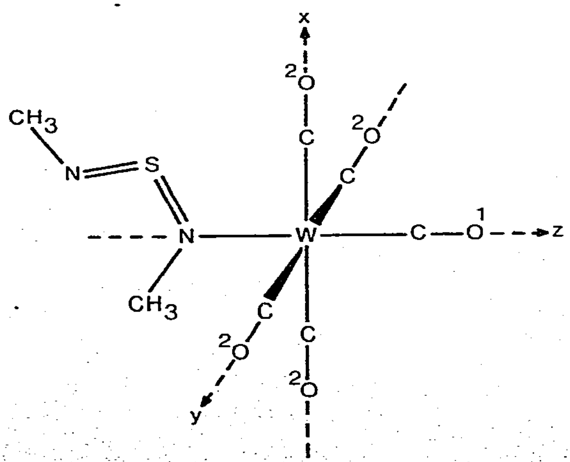

Fig. 4. The structure of $W(CO)_5(DMSD)$.

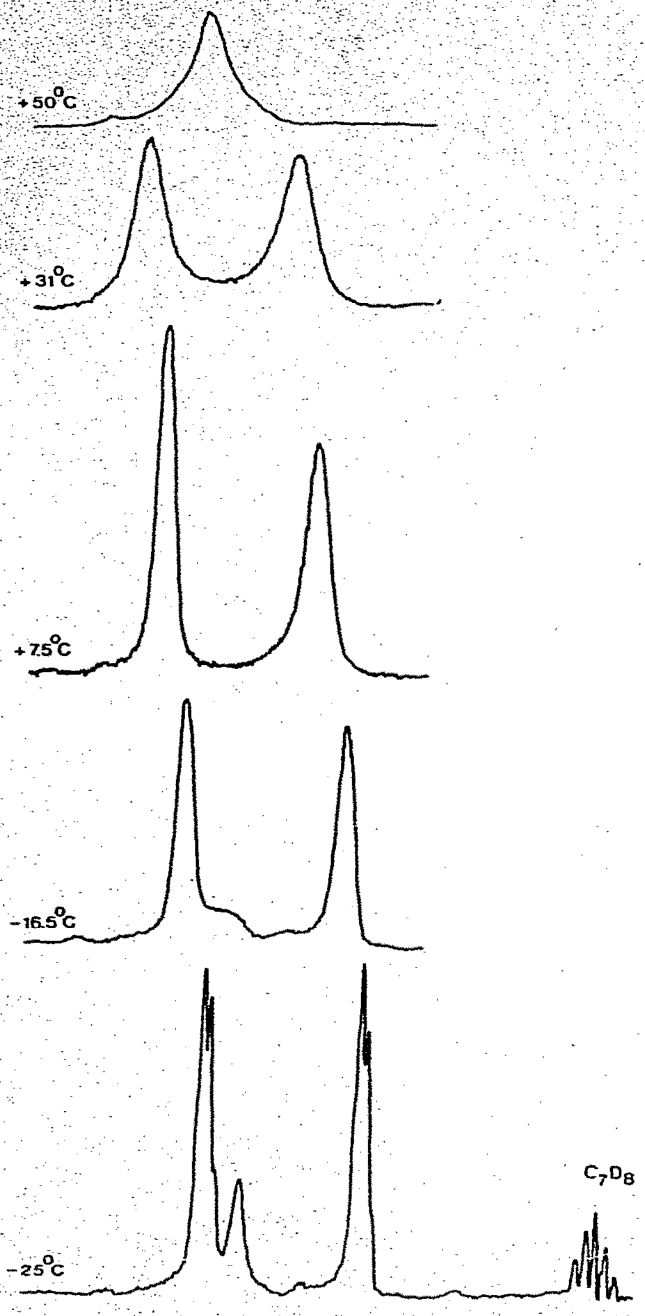

Fig. 5. The temperature dependence of the NMR spectra for the two isomers of $W(CO)_5(DMSD)$ in C_7D_8.

$M(CO)_5(RN{=}S{=}NR)$. The CT transitions of these compounds at about 500 nm are weak and broad and their positions are shifted toward higher frequencies in polar solvents. The intensities of these bands decrease in polar solvents and are strongly dependent on the nature of the ligand and the metal; e.g. on going

TABLE 5

ELECTRONIC ABSORPTION SPECTRA OF $M(CO)_4(RNSNR)$ AND $M(CO)_5(RNSNR)$

Compound	$d \rightarrow d$	$M \rightarrow L$
$Cr(CO)_5(DMSD)$	23 900 (2 000)	19 500 (1 600)
$Cr(CO)_5(DESD)$	24 000 (2 400)	19 600 (1 800)
$Cr(CO)_5(DiPrSD)$	25 300	20 000
$W(CO)_5(DMSD)$	24 800 (3 500)	19 700 (3 600)
$W(CO)_5(DESD)$	26 400 (2 000)	20 000 (700)
$W(CO)_5(DiPrSD)$	25 800 (2 500)	20 100 (1 500)
$Cr(CO)_4(DiPrSD)$	22 700 (2 000)	17 400 (15 000)
$Cr(CO)_4(DBSD)$	23 100 (2 100)	17 200 (15 000)
$Mo(CO)_4(DBSD)$	25 400 (3 000)	18 200 (20 000)
$W(CO)_4(DBSD)$	24 700 (3 700)	19 300 (19 000)

Values in cm^{-1}. The molar extinctions, in parentheses, are not very accurate because of some decomposition.

from $W(CO)_5(DMSD)$ to the less stable $W(CO)_5(DESD)$ the intensity of the band decreases appreciably. Furthermore, the much less stable Mo compounds, which have only been observed in solution, hardly show this CT band, as can be seen from Fig. 6.

Infrared and Raman spectra

Since many of the compounds decompose in the laser beam, even with the use of a spinning cell [11], the vibrational results are mainly derived from IR spectra. (Tables 6 and 7).

The C—O stretching vibrations could readily be assigned by comparison with literature values and by the solvent dependence of the *trans*-CO stretching models [12—14]. The assignment of ν(M—C) for $M(CO)_5(RN{=}S{=}NR)$ is tentative and based on recent results of Dobson et al. [15]. The δ(MCO) frequencies

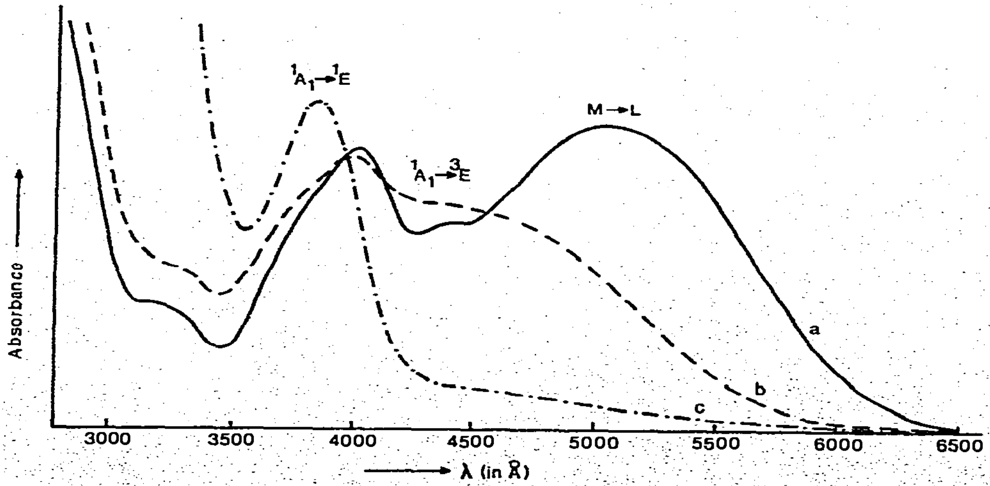

Fig. 6. The electronic absorption spectra of: $W(CO)_5(DMSD)$ in $n\text{-}C_7H_{16}$ (a), $W(CO)_5(DMSD)$ in CH_2Cl_2 (b) and of $Mo(CO)_5(DESD)$ in CH_2Cl_2 (c).

TABLE 6

VIBRATIONAL FREQUENCIES OF THE $M(CO)_5$ MOIETY IN $M(CO)_5(RNSNR)$ (in cm^{-1})

Compound	ν(CO)			δ(MCO)			ν(MC)			
	A_1^2	E	A_1^1				A_1^1	A_1^2	B	E
$Cr(CO)_5(DMSD)$	2074	1920	1920	668	653		480 [a]	384 [a]	416	440
$Cr(CO)_5(DESD)$	2071	1925	1925	670	654		482 [a]	384 [a]	406	440
$W(CO)_5(DMSD)$	2071	1933	1917	600	590	550	474 [a]	430 [a]	413 [a]	375
$W(CO)_5(DESD)$	2075	1935	1920	600	590	550				370
$W(CO)_5(DIPrSD)$	2078	1935	1917	603	591	553				370

[a] Raman results from C_6H_6 solution, other bands from the oily liquids in IR.

TABLE 7

VIBRATIONAL FREQUENCIES OF THE $M(CO)_4$ MOIETY IN $M(CO)_4(RNSNR)$ [a] (in cm^{-1})

Compound	ν(CO)				δ(MCO)			ν(MC)			
	A_1^2	A_1^1	B_1	B_2							
$Cr(CO)_4(DIPSD)$	2020	1947	1947	1898	674	632	618	455	438	409	
$Cr(CO)_4(DBSD)$	2014	1930	1913	1846	675	633	613	455	423	391	
$Mo(CO)_4(DBSD)$	2018	1925	1903	1845	636	584	568	463	425	401	379
$W(CO)_4(DBSD)$	2016	1927	1905	1884	612	570	563	467	431	419	383

[a] Results from nujol mulls in IR.

TABLE 8

VIBRATIONAL FREQUENCIES[a] OF ν_s(NSN) AND δ(NSN) FOR THE FREE AND COORDINATED SULFURDIIMINES (in cm^{-1})

	DMSD		DESD		DiPrSD		DBSD	
	ν	δ	ν	δ	ν	δ	ν	δ
L	1075	807	1071	773	1056	756	1066	678
$Cr(CO)_5L$	1062	805	1055	772				
$W(CO)_5L$	1060	809	1056	770	1023			
$Cr(CO)_4L$					1095	852	1090	755
$Mo(CO)_4L$							1089	776
$W(CO)_4L$							1070	776

[a] Raman results from C_6H_6 solution. [b] See also [1]. [c] In the light of the above results the assignments of Lindsell and Faulds [5]. obtained from IR spectra on $M(CO)_4$(DBSD) appear to be doubtful.

of both types of compound and the ν(M—C) values of $M(CO)_4$(RN=S=NR) are in close agreement with literature results [12,16,17]. The results in Table 8 show that large frequency shifts for ligand vibrations are only found for δ(NSN) in the tetracarbonyl compounds, when a shift of about 100 cm^{-1} to higher frequencies is observed.

Resonance Raman spectra

The resonance Raman spectra have been studied for $W(CO)_5$(DMSD) and $W(CO)_4$(DBSD) (see Fig. 7 and 8 and Experimental).

Although ν_s(NSN) is very weak with respect to δ(NSN) the pentacarbonyl compound shows intensity enhancements for ν_s(NSN), δ(NSN) and for the symmetric CO stretching mode of the equatorial carbonyls on approaching the maximum of the CT band at about 500 nm. Figure 7 shows that the maxima of the excitation profiles nearly coincide with the maximum of the CT band and

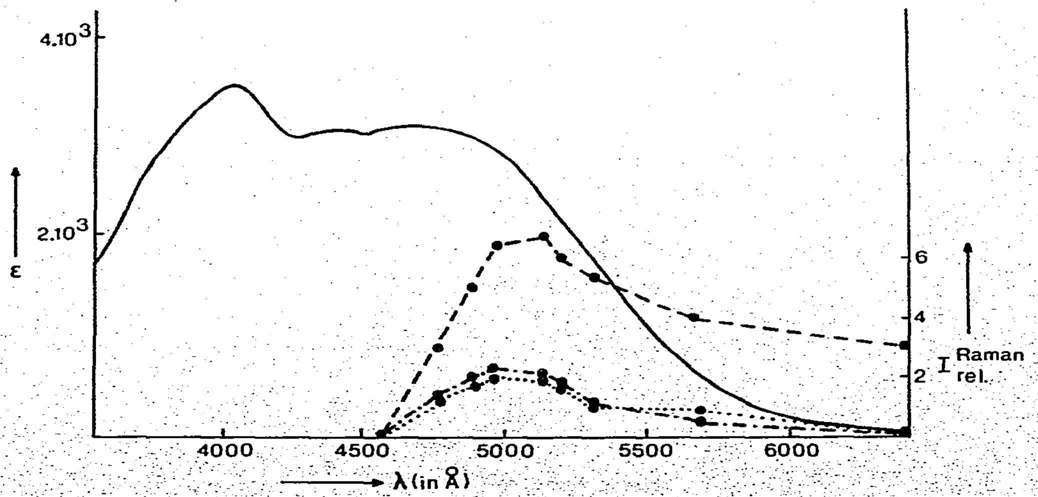

Fig. 7. Resonance Raman spectra of $W(CO)_5$(DMSD). Intensities of ν_s(NSN) (· · · · · ·), δ(NSN) (- - - - - -) and $\nu_s(CO)_{eq}$ (—·—·—) relative to the 606 cm^{-1} band of benzene.

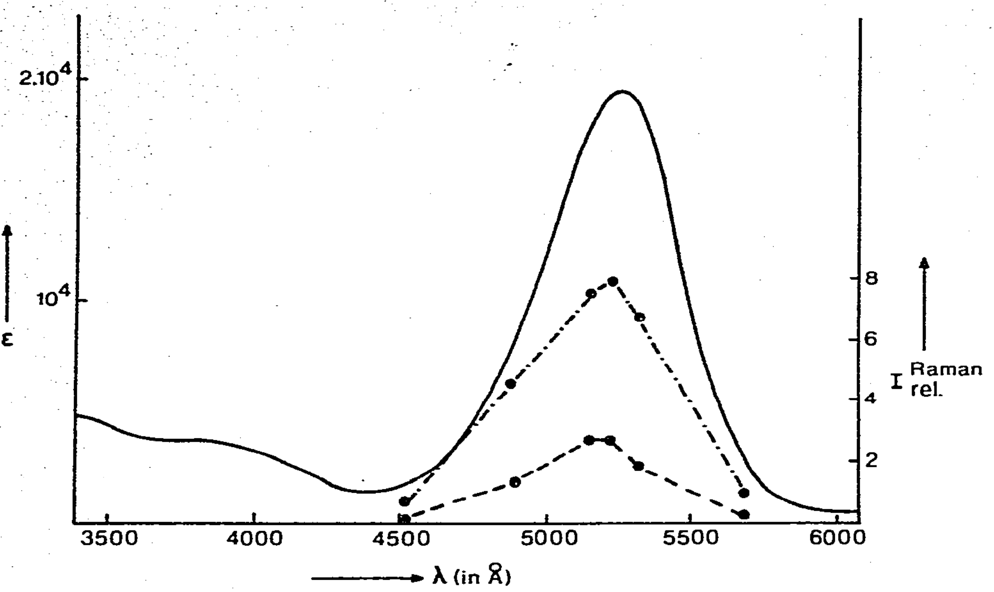

Fig. 8. Resonance Raman spectra of $W(CO)_4(DBSD)$. Intensities of ν_s(NSN) (—·—·—) and δ(NSN) (- - - - -) relative to the 992 cm^{-1} band of benzene.

that the resonance enhancement is proportional to the molar extinction coefficient ϵ.

Resonance Raman effects for $W(CO)_4(DBSD)$ are found for a number of vibrations, but are especially large for ν_s(NSN) and δ(NSN). Just as for $W(CO)_5(DMSD)$ the intensity enhancements are proportional to ϵ and the maxima of the excitation profiles nearly coincide with the maximum of the CT transition (Fig. 8). Contrary to the results for the pentacarbonyl compound, hardly any CO vibration could be observed for $W(CO)_4(DBSD)$, while both ν_s(NSN) and δ(NSN) are strong.

Discussion

The first point of interest is that the sulfurdiimine acts preferentially as a bidentate ligand if R is a bulky group (i-Pr and t-Bu), while the monodentate situation is observed for R = Me and Et and also for R = i-Pr. Therefore great similarities exist with the previously reported compounds of Rh(I) and Ir(I) [4], in which for R = t-Bu the sulfurdiimine also prefers the bidentate linkage, owing no doubt to less steric hindrance with the other ligands.

The fluxional behaviour of $M(CO)_5(RN{=}S{=}NR)$, which involves the interconversion of the R groups between different sites, cannot be explained by the N—N jump process observed for $[PtCl_2(RN{=}S{=}NR)L]$ [1]. The latter process proceeds via an intermediate in which the sulfurdiimine is bidentate and in the *trans,trans*-configuration, and which therefore is unlikely to occur for $M(CO)_5$-$(RN{=}S{=}NR)$ since the intermediate would have a 20-electron configuration. A much more likely mechanism is shown in Fig. 9, which involves a gliding movement of the metal along the sulfurdiimine from one N-atom to the other via

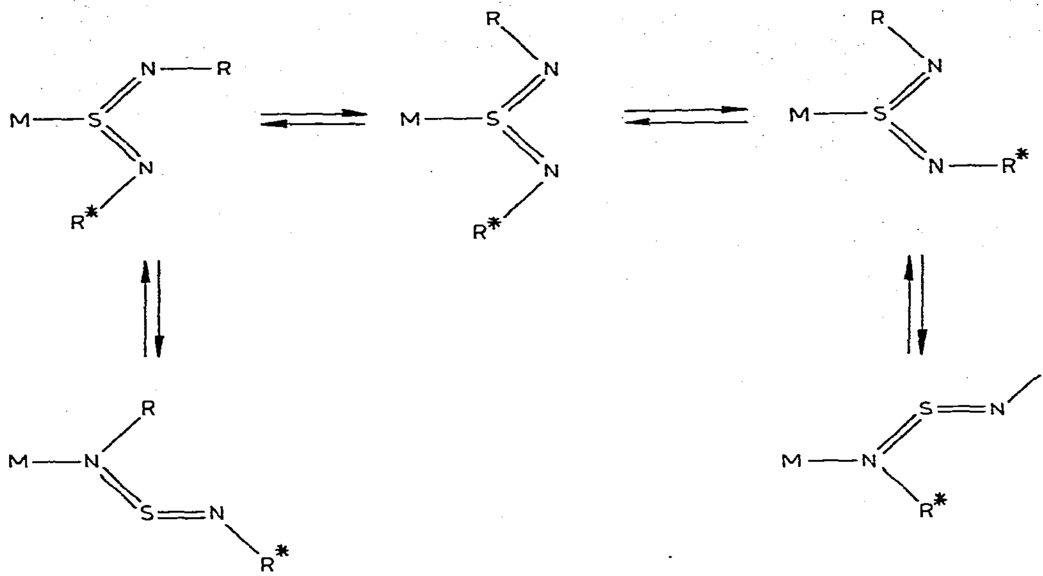

Fig. 9. The proposed mechanism for the intramolecular interconversion of the R groups of $M(CO)_5(RNSNR)$.

the sulfur atom. This can also explain the involvement of the second isomer of $W(CO)_5(DMSD)$, for which an S-bonded structure was proposed.

It is noteworthy that this process is very similar to the movements of the allene group in [$Fe(CO)_4$(TMA)] (TMA = tetramethylallene) [17] and in [$PtCl_2$(TMA)L] [19,20]. The influence of R on the process is irregular, and will not be discussed, as too little is known about the relative importance of the various steps.

The bonding properties will be discussed on the basis of the spectroscopic and structural data (Fig. 3 and 4).

In $W(CO)_5(DMSD)$ the $W(CO)_5$ moiety is influenced by the sulfurdiimine in much the same way as by amine ligands [12], as is demonstrated by the frequencies of the CO vibrations (Table 9).

The weak and broad CT transitions of the pentacarbonyl derivatives have also been found for other pentacarbonyl compounds [22]. With sulfurdiimine compounds the broadness might be caused by the instability.

As already pointed out by Lindsell and Faulds [5] the $M(CO)_4$ moiety of

TABLE 9

VIBRATIONAL STRETCHING FREQUENCIES OF THE CO GROUPS OF $W(CO)_5L$ AND $W(CO)_4L$

Compound	A_1^2	E	A_1^1	A_1^2	A_1^1	B_1	B_2
$W(CO)_5(Et_2NH)$ [a, b]	2073	1930	1919				
$W(CO)_5(C_5H_5N)$ [a, b]	2073	1934	1921				
$W(CO)_5(DMSD)$ [a]	2073	1940	1924				
$W(CO)_4$(tmen) [c, d]				2005	1872	1864	1838
$W(CO)_4$(phen) [c, d]				2003	1886	1892	1840
$W(CO)_4(DBSD)$ [c]				2019	1917	1917	1877

[a] IR results from 2,2,4-trimethylpentane or heptane solutions. [b] From ref. 12. [c] IR results from CS_2 solutions; tmen = *N,N,N',N'*-tetramethylethylene diamine; phen = phenanthroline. [d] From ref. 13.

$M(CO)_4(DBSD)$ is much more influenced by the sulfurdiimine than by other N-bonded ligands, which is clearly demonstrated by the frequencies of the CO stretching modes in these complexes (Table 9) [13]. The high frequency shifts are caused by strong π-bonding between the metal and the sulfurdiimine. This π-bonding is also reflected in the thermal stability of these compounds and is mainly responsible for the high intensity of the CT bands, which will now be discussed in some detail.

The sharp and intense CT bands of the Cr and Mo tetracarbonyl compounds shift to higher frequencies in polar solvents, which means that the electronic transitions are antiparallel to the ground state dipole moment. This moment lies along the z axis (Fig. 3) in the direction of the carbonyl groups, as shown by the solvent dependence of the stretching frequencies of the *trans*-CO's. Therefore the CT transitions are metal to sulfurdiimine in character, just as for the corresponding phenanthroline, bipyridine [21] and 1,4-heterobutadiene compounds [23]. The z-axis is totally symmetric in C_{2v} symmetry and therefore the ground- and excited states of the CT transitions must have the same symmetry. The occupied metal d orbitals belong to symmetry species A_1, A_2 and B_2, while the lowest empty orbital of the sulfurdiimine belongs to symmetry B_2. It is evident from the strong π-bonding and very intense CT bands observed that the metal and sulfurdiimine B_2 orbitals overlap strongly.

The CT band of $W(CO)_4(DBSD)$ does not show solvent dependence, which means that the mixing of the metal and sulfurdiimine B_2 orbitals is the same in ground- and excited states (see also [23]). In this case the π-bonding stabilization of the metal—sulfurdiimine bond can be calculated from half the CT transition energy to be 27.6 kcal mol^{-1}, which is similar to the value of 23 kcal mol^{-1} found for a 1,4-heterobutadiene tetracarbonyl compound [24].

The strong enhancement of Raman intensity for $\nu_s(NSN)$ and $\delta(NSN)$ in the Resonance Raman spectra of both the tetra- and penta-carbonyl compounds is in accordance with the assignment of the CT bands to metal to sulfurdiimine transitions. There is, however, an important difference between $W(CO)_5(DMSD)$ and $W(CO)_4(DBSD)$ in that the carbonyl stretching vibrations of the tetracarbonyl compound do not show enhancement of Raman intensity and could hardly even be detected. Thus the CT transition of the tetracarbonyl compound is fully localized in the metal—sulfurdiimine bonding region, without any detectable contribution of CO orbitals. On the other hand, $W(CO)_5(DMSD)$ shows Resonance enhancement for $\nu_s(CO)$ of the equatorial carbonyls. Therefore, a strong mixing with equatorial CO orbitals is present here in the excited state, as might be expected from the much weaker metal—sulfurdiimine π-bond in the pentacarbonyl compounds. The axial CO orbitals, however, do not contribute to the CT transition.

The fact that only one $\nu(CO)$ shows Resonance enhancement demonstrates that hardly any mixing of axial and equatorial CO stretching modes occurs for $W(CO)_5(DMSD)$.

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