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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

I. DIALKYLSULFURDIIMINE COMPOUNDS OF PLATINUM*

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Summary

The preparations and properties of a new series of compounds of the formula *trans*-[$PtCl_2$(dialkylsulfurdiimine)L] are reported. In the case of the dimethyl-, diethyl-, diisopropyl- and dineopentyl-sulfurdiimine platinum compounds two isomers are present in solution, but only one isomer was observed for the di-t-butylsulfurdiimine derivative. ^1H and ^{13}C NMR data show that the two isomers interconvert intramolecularly by two different routes. In one of the isomeric forms, unusually large low-field chemical shifts indicate the existence of non-bonded metal—alkyl interactions.

Introduction

Sulfurdiimines, RN=S=NR, have recently received increasing attention because of several interesting properties such as photoconductivity [2]. They may, in principle, coordinate via the sulfur atom (cf. SO_2), via the N-atom or through the N=S double bond, analogous to the situation in metal—allene compounds [3]. It seemed to us of interest to find out how the type of coordination of the sulfurdiimine to the metal atom can be influenced by the substituents R, the oxidation state and electronic configuration of the metal, and the nature of the ligands attached to the metal atom. We have already shown that the compound *trans*-[$PtCl_2$(t-BuN=S=N-t-Bu)C_2H_4] exists in solution as two isomers [1], while a crystal structure determination showed that only one isomer was present in the solid state, and in this the ligand was bonded to the platinum atom through the nitrogen atom [4]. This publication describes further studies of alkylsulfurdiimines and their platinum compounds, and aryl derivatives will be described in Part II.

* For a preliminary communication see ref. 1.

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Experimental

I. Dialkylsulfurdiimines

The dialkylsulfurdiimines were prepared by a modification of the published procedures [5—7] . 0.2 mole of gaseous SF_4 is passed ver a stirred solution of 2 mole alkylamine in 150 ml pentane, the temperature being kept below —40°C. (In the case of dimethylsulfurdiimine 3 mole of methylamine is necessary, and no pentane is added.) A thick precipitate of RNH_3F is formed. The temperature is then slowly raised to 0°C and kept there for 1 h.

In the case of the diethyl-, diisopropyl-, di-t-butyl- and dineopentyl-sulfurdiimine, 150 ml of an ice-cold saturated aqueous K_2CO_3 solution containing ice is added in one portion to the reaction mixture. After 2 min of vigorous shaking two layers are formed. The layers are quickly separated, and the pentane layer containing the diimine is dried with potassium carbonate or sodium sulfate. After filtration the pentane is removed under reduced pressure (0°C, 1 cm Hg). The residue is vacuum distilled through a Vigreux column. Redistillation in vacuum gives very pure products.

In the case of the dimethylsulfurdiimine, the excess amine and the diimine are vacuum distilled in a cold trap (—60°C), while the reaction mixture is slowly warmed up to 40°C. Unchanged amine is removed at 0°C and at 1 cm Hg. The residue is vacuum distilled.

II. Dialkylsulfurdiimine compounds of platinum(II)

The preparation of *trans*-$[PtCl_2PEt_3(MeN{=}S{=}NMe)]$ is given as an example.

100 mg (1.11 mmole) of dimethylsulfurdiimine in 1 ml benzene at 0°C is added to a stirred suspension of 384 mg (0.5 mmole) of $[(Et_3P)PtCl_2]_2$ [8] in 10 ml of dry benzene. Stirring is continued until the dimer has dissolved, which takes about 5 min. After filtration of the solution the solvent is removed at reduced pressure. The residue, which is sometimes oily, is dissolved in ether. After filtration, hexane is added and the solution is concentrated at 20°C until crystallization is observed. Further crystallization takes place in the cold (—30°C) (80% yield).

A different preparative route is used for the triphenylstibine compounds, for which the corresponding ethylene complex was used as a starting material. The preparation of the ethylene complex is described because it is new.

trans-$[PtCl_2(Ph_3Sb)C_2H_4]$. To a stirred suspension of 600 mg (1.02 mmole) $[(C_2H_4)PtCl_2]_2$ in fluorochloroform or chloroform (25 ml) is added dropwise a solution of 600 mg Ph_3Sb (1.70 mmole) in the same solvent (10 ml) at —30°C. After filtration of the yellow solution the solvent is evaporated off at —20°C. The remaining yellow solid, which should be kept cool, is recrystallized from chloroform/hexane (at —50°C). The yield is 80% ($\delta(C_2H_4) = 4.21$ ppm).

trans-$[PtCl_2(DBSD)(Ph_3Sb)]$. To a cold (—25°C) solution of 1.0 mmole $[PtCl_2(C_2H_4)(Ph_3Sb)]$ in 2.5 ml chloroform, a molar equivalent of dibutylsulfurdiimine in 10 ml chloroform is added. After some evolution of gas the solution is filtered. The solvent is evaporated off. The resulting residue is recrystallized from benzene/hexane in a refrigerator at —35°C.

Analytical data of the yellow-to-cream-coloured compounds are given in Table 1.

TABLE 1

ANALYTICAL DATA FOR $LPtCl_2$(DIALKYLSULFURDIIMINE).

Compound	M.p.	Analysis found (calcd.) (%)				
	(°C)	C	H	Cl	S	Pt
PEt_3PtCl_2 (DMSD)[a]	46.0—46.3	20.37 (20.25)	4.65 (4.46)	14.90 (14.95)		
$AsEt_3PtCl_2$ (DMSD)	55.0—55.2	18.45 (18.54)	4.18 (4.08)	13.90 (13.86)		
PPh_3PtCl_2 (DMSD) · $^1/_2C_6H_6$[b]	85.4—85.6	42.14 (42.02)	3.63 (3.68)	10.60 (10.78)		
$AsPh_3PtCl_2$ (DMSD) · C_6H_6[b]	83.4—83.6	42.02 (42.17)	3.71 (3.68)	9.17 (9.58)	4.15 (4.33)	
SPr_2PtCl_2 (DMSD)	46.2—46.4	20.85 (20.25)	4.44 (4.25)	15.41 (14.95)	12.91 (13.51)	
$SeEt_2PtCl_2$ (DMSD)		14.63 (14.61)	3.42 (3.27)	13.80 (14.38)	6.62 (6.50)	
PEt_3PtCl_2 (DESD)	51.9—52.1	23.86 (23.91)	5.17 (5.02)	14.09 (14.12)		
$AsEt_3PtCl_2$ (DESD)	50.5—50.7	22.16 (21.99)	4.83 (4.62)	12.96 (12.98)	5.54 (5.87)	
PPh_3PtCl_2 (DESD) · $^1/_2C_4H_{10}O$[b]		42.20 (42.17)	4.49 (4.42)	10.33 (10.37)		
PEt_3PtCl_2 (DiPrSD)	38.5—38.7	27.19 (27.16)	5.61 (5.51)	13.11 (13.37)	6.19 (6.04)	
$AsEt_3PtCl_2$ (DiPrSD)	42.1—42.3	25.03 (25.09)	5.10 (5.09)	12.47 (12.35)	5.50 (5.58)	
$AsPh_3PtCl_2$ (DiPrSD)		40.32 (40.12)	4.35 (4.07)	9.56 (9.86)	4.46 (4.43)	
PEt_3PtCl_2 (DBSD)	87.8—88.8	30.52 (30.11)	6.17 (5.96)	12.47 (12.69)	5.63 (5.74)	
$AsEt_3PtCl_2$ (DBSD)	102.1	27.94 (27.90)	5.68 (5.52)	11.61 (11.77)	5.25 (5.32)	
PPh_3PtCl_2 (DBSD)		44.03 (44.43)	4.96 (4.73)	10.32 (10.09)	4.80 (4.56)	26.90 (27.70)
$AsPh_3PtCl_2$ (DBSD)		41.41 (41.83)	4.56 (4.46)	9.48 (9.50)	4.14 (4.29)	26.76 (26.13)
$SbPh_3PtCl_2$ (DBSD)		39.14 (39.36)	4.42 (4.19)	8.99 (8.94)	4.42 (4.04)	
$(C_2H_4)PtCl_2$ (DBSD)		25.64 (25.64)	4.65 (4.70)		6.67 (6.84)	41.58 (41.68)
PEt_3PtCl_2 (DnPSD)	70.0—70.2	33.21 (32.75)	6.57 (6.36)	12.09 (12.09)	5.58 (5.47)	
$AsEt_3PtCl_2$ (DnPSD)	49.0—49.2	30.80 (30.47)	6.06 (5.91)	11.04 (11.25)	5.11 (5.09)	
PPh_3PtCl_2 (DnPSD)		45.98 (46.01)	5.22 (5.10)	9.75 (9.70)		

[a] DMSD = dimethylsulfurdiimine; DESD = diethylsulfurdiimine; DiPrSD = diisopropylsulfurdiimine; DBSD = dibutylsulfurdiimine; DnPSD = dineopentylsulfurdiimine. [b] C_6H_6 = benzene, $C_4H_{10}O$ = ether.

Results

I. Dialkylsulfurdiimines

At temperatures of −60°C the ^{1}H and ^{13}C NMR spectra (Tables 2 and 3) show the presence of two isomers in unequal ratio for R = methyl, ethyl, isopropyl and neopentyl, but of only one isomer for R = t-butyl. In all cases the most abundant isomer has the asymmetric *cis,trans* configuration, as shown by the presence of two sets of signals of equal intensity for the $N—CH_{3-n}$ (signals *A* and *B* in Table 2) and the $(CH_3)_n$ groups (signal *A'* and *B'* in Table 2). In the case of the less abundant isomer, only one signal is observed for the $N—CH_{3-n}$ and $(CH_3)_n$ groups (signals *C* and *C'* in Table 2). The assignment is shown in Fig. 1. The *trans,trans* configuration is assigned to the less abundant isomer, as the *cis,cis* configuration is sterically much less likely.

The long range coupling of 1.4 c sec^{-1} of the MeN=S=NMe compound is noteworthy. The similarity between the strong solvent dependence of the high-

TABLE 2. ^{1}H NMR DATA FOR R—N=S=N—R[a] (Chemical shifts in ppm rel. TMS, *J* in c sec^{-1})

R	Temp. (°C)	Solvent	*A*	*B*	*C*	*A'*	*B'*	*C'*	*J*(H—H)
CH_3	30	$CDCl_3$		3.57					
	30	C_7D_8		3.27					
	−60	$CDCl_3$	3.52	3.64	3.84				1.4
	−70	C_7D_8	3.47	2.96	3.05				1.4
C_2H_5	30	$CDCl_3$		3.88			1.29		7.1
	30	C_7D_8		3.66			1.11		7.1
	−60	$CDCl_3$	3.85	3.90	4.16	1.37	1.30		7.1
	−70	C_7D_8	3.83	3.29	3.46	1.21	0.93	0.97	7.1
i-C_3H_7[b]	30	$CDCl_3$		4.46			1.24		6.2
	30	C_7D_8		4.31			1.13		6.2
	−60	$CDCl_3$	4.71	4.22	4.70?	1.31	1.29	1.31?	6.2
	−70	C_7D_8	4.86	3.56	4.31	1.24	0.97	1.03?	6.2
t-C_4H_9	30	$CDCl_3$					1.42		
	30	C_7D_8					1.35		
	−60	$CDCl_3$				1.51	1.36		
	−70	C_7D_8				1.57	1.07		
neo-C_5H_{11}[c]	30	$CDCl_3$		3.59			0.95		
	30	C_7D_8		3.48			0.91		
	−60	$CDCl_3$	3.56	3.58	3.85	1.00	0.91	1.00?	
	−70	C_7D_8	3.66	3.06	3.59	1.01	0.78	0.89	

[a] The values given at 30°C are the measured signals of the collapsed *A*, *B* and *C*, and the collapsed *A'*, *B'* and *C'* resonances respectively. [b] Very little of isomer *C*. [c] In this case *A'*, *B'* and *C'* represent the resonances of the CH_3 groups.

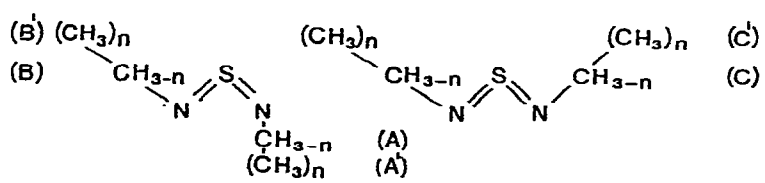

Fig. 1. Structures of the sulfurdiimines and the assignment for Table 2.

field resonance of the asymmetric isomer and that of the resonance of the symmetric isomer is a reason for assignment of the signals B and B' to the *trans*-R group protons.

At higher temperatures the ^{1}H NMR signals coalesce. The process responsible for the coalescence is probably the intramolecular conversion of the *cis,trans* isomer into the *trans,trans* isomer through rotation about the N=S bond or inversion at the N-atoms*. The activation parameters for DBSD are $A = 10^{13}$ sec^{-1} and $\Delta E = 13$ kcal mole^{-1}. The rates decrease in the order t-Bu > i-Pr ~ Et ~ Me.

The ^{13}C spectra (Table 3) show the interesting result that in almost all cases the groups A absorb at higher field than the groups B. Similarly A' absorbs at higher field than B'. The opposite is observed for the proton spectra, A and A' absorbing at lower field than B and B', respectively, in C_7D_8.

IR and Raman data are given for a number of sulfurdiimines in Table 4. The symmetric and asymmetric N=S=N stretching frequencies lie at about 1060 and 1190 cm^{-1}.

II. Dialkylsulfurdiimine compounds of Pt^{II}

A. Di-t-butylsulfurdiimine compounds of Pt^{II}

^{1}H and ^{13}C NMR spectra (Tables 5 and 9) of $[PtCl_2(DSBD)L]$ (L = PR_3, AsR_3, SbR_3, SR_2, SeR_2 and TeR_2; DSBD = di-t-butylsulfurdiimine) in solution

TABLE 3. ^{13}C NMR DATA[a] FOR R—NSN—R IN C_7D_8 (ppm relative to TMS)

R	Temp. (°C)	*A*	*B*	*C*	*A'*	*B'*	*C'*	Other resonances
CH_3	30		37.38					
	−64	37.31	37.90	37.65				
C_2H_5	30		45.77			17.16		
	−64	45.55	46.51	45.90	15.76	18.70	17.90	
i-C_3H_7	30		51.99			24.68		
	−64	50.90	53.11		22.99	26.16	25.30	
t-C_4H_9	30		60.43			30.56		
	−64	60.00	60.93		28.73	31.54		
neo-C_5H_{11}	30		62.55			32.59[b]		27.47[c]
	−64	62.27	62.68		32.24[b]	32.81[b]		27.59[c]; 27.15[c]

[a] The values given at 30°C are the measured signals of the collapsed *A*, *B* and *C* and the collapsed *A'*, *B'* and *C'* resonances respectively. [b] Resonances of the tertiary carbon atoms. [c] Resonances of the $^{13}CH_3$ groups.

TABLE 4. ν_s, ν_{as} AND δ (cm^{-1}) FOR THE SULFURDIIMINES, DERIVED FROM IR AND RAMAN DATA

Compound	ν_s(NSN)	ν_{as}(NSN)	δ(NSN)[a]
DMSD	1075	1207	807
DESD	1071	1184	773
DiPrSD	1056	1185	756
DBSD	1064	1194	677

[a] The assignment of δ is somewhat doubtful.

* During the preparation of this paper, Grunwell et al. [9] described the temperature dependence of the proton signals of R—N=S=N—R (R = Me, t-butyl). Their results agree with ours.

TABLE 5

^{1}H NMR DATA[a] OF $LPtCl_2(DBSD)$ AT 30° C (Chemical shifts in ppm rel. TMS, coupling constants in c sec^{-1} The resonances of the free ligand are at —60° C; 1.58 and 1.08 in C_7D_8 and 1.51 and 1.36 in $CDCl_3$.

L	Solv.	I_a	J(Pt)	I_b	Resonances of L
PEt_3	C_7D_8	1.93	2.7	0.98	
	$CDCl_3$	1.77	2.7	1.44	1.90m; 1.19m
$AsEt_3$	C_7D_8	1.96	3.5	0.98	1.68q; 1.09t
	$CDCl_3$	1.81	3.5	1.45	1.93q; 1.27t
$SbEt_3$	C_7D_8	1.95	2.5[b]	1.00	1.56q; 1.16t
PPh_3	C_7D_8	1.99	2.2	0.99	
$AsPh_3$	C_7D_8	2.02	3	0.99	
$SbPh_3$	C_7D_8	2.03	2.5[b]	0.99	7.80m; 7.00m
	$CDCl_3$	1.90	2.5[b]	1.48	7.68m; 7.40m
	C_6D_6	2.06	2.5[b]	0.95	7.80m; 7.00m
SPr_2	C_6D_6	1.97	2.5	0.92	
	$CDCl_3$	1.83	2.5	1.49	
$SeEt_2$	C_6D_6	1.99	2.5	0.92	2.50m; 1.13t
$TeEt_2$	C_6D_6	2.01	2.5	0.94	
PPh_2Me	C_6D_6	1.93		0.94	1.54 J(P) = 11.5; J(Pt) = 34
	$CDCl_3$	1.81		1.47	1.83 J(P) = 11.5; J(Pt) = 34
C_2H_4[c]	$CDCl_3$	1.84	1.5	1.54	4.76 J(Pt) = 68

[a] m = multiplet; q = approx. quartet; t = approx. triplet. [b] The intensity of the Pt-satellites is lower than the expected 1/4/1 ratio. [c] Measurement at —60° C. A second isomer exists for this compound with the resonances: δ(DBSD) 1.69 and $\delta(C_2H_4)$ 4.52 with J(Pt) = 68 c sec^{-1}.

($CDCl_3$, C_6D_5 and C_7D_8) show the existence of only one isomer. There is a low field methyl signal with a ^{195}Pt-coupling of about 2—4 c sec^{-1} and a high field signal, which is strongly solvent dependent, without ^{195}Pt-coupling (Table 5). This is in contrast to the ^{13}C spectra, which show Pt-coupling of about 8 c sec^{-1} with the $^{13}CH_3$ signal lying at high field, while no Pt-coupling with the low field $^{13}CH_3$ signal is observed. ^{13}C off resonance experiments show that the low field ^{1}H signal and the high field ^{13}C signal belong to the same $N—C(CH_3)_3$ group. Since both signals show ^{195}Pt-coupling and have a down-field chemical shift it is concluded that this group is coordinated to the Pt-atom via the N-atom, the structure being analogous to that in $[PtCl_2(DBSD)C_2H_4]$ in the solid state [4]. The ligand L is *trans* to the DSBD group, as in $[PtCl_2(DSBD)C_2H_4]$ which was confirmed by dipole moment studies (dipole moments of 3.2—3.9 D for $[PtCl_2$-$(RNSNR)L]$ with R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11} and L = $AsEt_3$ and PEt_3) and by the Pt—Cl stretching frequencies in the IR and Raman spectra at about 300 to 350 cm^{-1}.

The proposed structure is shown in Fig. 2. At higher temperatures (60—100°C)

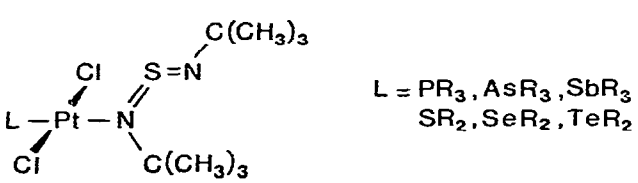

Fig. 2. Structure of $[PtCl_2(DBSD)L]$.

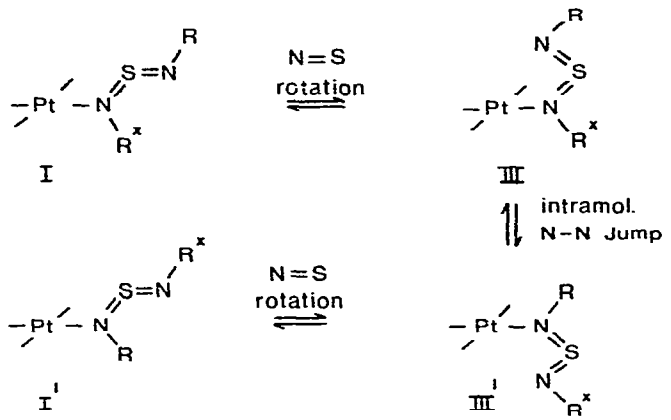

Fig. 3. Exchange mechanism of the two inequivalent chemical sites of $[PtCl_2(DBSD)L]$.

the methyl ^{1}H signals broaden. This broadening is independent of the concentration of the complex and of added free ligand. The absence of intermolecular sulfurdiimine exchange is further confirmed by double resonance experiments at +50°C, which show that there is exchange only between the t-butyl sites of the complexed ligand. It is concluded that the reaction scheme of Fig. 3 is responsible for the observed coalescence.

The exchange rates calculated from the broadening of the methyl signals fall in the following order: $AsEt_3 > AsPh_3 \sim PEt_3 > PPh_3$ (measured from 65—90°C). The activation parameters are in the range 10^{12}—10^{13} sec^{-1} (A) and 18—19 kcal $mole^{-1}$ (ΔE).

B. Dimethyl, diethyl, diisopropyl, and dineopentyl compounds of Pt^{II}

1. Structural determination. The results for the t-butylsulfurdiimine metal systems prompted us to investigate the influence of the bulkiness of the R-groups by successively replacing the protons in the methyl group of $[PtCl_2(MeN{=}S{=}NMe)L]$.

In Tables 6, 7 and 9 the ^{1}H and ^{13}C NMR resonances are recorded for compounds $[PtCl_2(RN{=}S{=}NR)L]$ with R = methyl, ethyl, isopropyl, neopentyl and t-butyl. Except in the case of R = t-butyl, two isomers were observed, in varying ratios. The concentration of the less abundant isomer decreases in the order methyl < ethyl ~ isopropyl > neopentyl ≫ t-butyl (not observed). The ^{1}H NMR pattern for the methyl derivative is shown schematically in Fig. 4 as an example. From integration of the signals and on basis of the long-range CH_3—CH_3 coupling of 1.4 c sec^{-1}, it is concluded that signals A and C belong to the less abundant isomer. For this isomer the ^{195}Pt—CH_3 coupling constants lie in the range 11—16 and 20—34 c sec^{-1}, respectively. The signals B and D belong to the more abundant isomer with ^{195}Pt—CH_3 coupling only to signal B in the range 20—34 sec^{-1}.

The ^{13}C spectra show similar patterns, but they are less informative owing to overlapping of peaks.

In principle there are seven possible isomeric forms (Fig. 5) for *trans*-$[PtCl_2$-(Me—N=S=N—Me)L], if we exclude the possibility in which the sulfurdiimine is bonded to the Pt-atom via the N=S double bond. Such bonding is unlikely,

(continued on p. 298)

TABLE 6

^{1}H NMR DATA FOR $LPtX_2$ (DMSD) (chemical shifts in ppm rel. TMS, coupling constants in c sec^{-1})

L	X	Isomer	Ratio I/II	Solvent	Resonances of Ia or IIa; J(Pt); J(P)	DMSD[a] Ib or IIb; J(Pt)	Resonances of L[b]
PEt_3	Cl	I	2.3	C_6D_6	3.62; 20.5; 2.7	2.72	
PEt_3	Cl	II	2.3	C_6D_6	3.26; 21; 2.7	4.42 ; 10.5	
PEt_3	Cl	I	2	$CDCl_3$	3.74; 19	3.73	
PEt_3	Cl	II	2	$CDCl_3$	3.74; 19	4.46; 11	
$AsEt_3$	Cl	I	2.2	C_6D_6	3.62; 26	2.69	1.70q; 1.07t
$AsEt_3$	Cl	II	2.2	C_6D_6	3.31; 26	4.51; 13.5	1.63q; 1.01t
$AsEt_3$	Br	I	1	C_6D_6	3.64; 26	2.73	1.81q; 1.06t
$AsEt_3$	Br	II	1	C_6D_6	3.32; 26	4.52; 14	1.73q; 1.00t
$AsEt_3$	I	I	0.5	C_6D_6	3.60; 27	2.69	1.97q; 1.01t
$AsEt_3$	I	II	0.5	C_6D_6	3.29; 28	4.47; 13.5	1.88q; 0.94t
$AsEt_3$	Cl	I	2	$CDCl_3$	3.77; 26	3.73	1.96q; 1.28t
$AsEt_3$	Cl	II	2	$CDCl_3$	3.77; 26	4.56; 13.5	1.93q; 1.28t
$SbEt_3$	Cl	I	3	C_6D_6	3.66; 27.5	2.71	1.60q; 1.15t
$SbEt_3$	Cl	II	3	C_6D_6	3.37; 27	4.58; 14	1.54q; 1.13t
PPh_3	Cl	I	2.5	C_6D_6	3.69; 23; 3	2.69	
PPh_3	Cl	II	2.5	C_6D_6	3.34; 22.5; 2.7	4.45; 11.5	
$AsPh_3$	Cl	I	1.9	C_6D_6	3.67; 30	2.69	
$AsPh_3$	Cl	II	1.9	C_6D_6	3.37; 29	4.55; 13	
$PPhMe_2$	Cl	I	3	C_7D_8	3.61; 21; 3	2.75	1.56; J(Pt) 11.5; J(P) 33
$PPhMe_2$	Cl	II	3	C_7D_8	3.28; 22; 3	4.34; 10.5	1.49; J(Pt) 11.5; J(P) 33
SPr_2	Cl	I	1.5	C_6D_6	3.59; 32.5	2.66	0.86t
SPr_2	Cl	II	1.5	C_6D_6	3.26; 33.5	4.51; 16	0.82t
$SeEt_2$	Cl	I	1.4	C_6D_6	3.61; 33.5	2.68	1.16t
$SeEt_2$	Cl	II	1.4	C_6D_6	3.29; 33.5	4.54; 16.5	1.08t
$TeEt_2$	Cl	I	2	C_6D_6	3.64; 30.5	2.68	1.21t
$TeEt_2$	Cl	II	2	C_6D_6	3.33; 33	4.56; 15	1.17t

[a]All DMSB resonances have a long-range methyl—methyl coupling of 1.4 sec^{-1}. [b]q and t refer respectively to approximate quartet and triplets

TABLE 7

^{1}H NMR DATA FOR $LPtCl_2$ (RNSNR)[a] (Chemical shifts rel TMS in C_6D_6 or where indicated in parentheses, $CDCl_3$; Coupling constants in c sec^{-1})

L	R	Temp. (°C)	Isomer	Ratio	N—CH_{3-n} resonances of R		$(CH_3)_n$ resonances of R	
				I/II	Ia or IIa; J(Pt); J(P)	Ib or IIb; J(Pt)	Ia′ or IIa′; J(Pt)	Ib′ or IIb′
$AsEt_3$	DMSD	30 (30)	I	2.2 (2)	3.62 (3.77); 26	2.69 (3.73)		
			II		3.31 (3.77); 26	4.51 (4.56); 13.5		
$AsEt_3$	DESD	30 (—20)	I	1.4 (1.2)	4.37 (4.32); 29	3.12 (4.00)	1.50 (1.51?)	0.73 (1.35?)
			II		3.75 (4.09); 32	5.38 (5.24); 13	1.52 (1.70?)	1.40 (1.46?)
$AsEt_3$	DiPrSD	0 (—20)	I	1.1 (1.3)	5.18 (5.12); 31	3.50 (4.35)	1.71 (1.59)	0.76 (1.31)
			II		3.99 (4.53); 34	7.92 (7.63); 12	1.55 (1.66)	1.49 (1.41)
$AsEt_3$	DESD	30 (30)	I				1.96 (1.81); 3.5	0.98 (1.45)
$AsEt_3$	DnPSD	30 (—20)	I	2.7 (3.3)	4.52 (4.28); 34	2.96 (3.63)	1.33 (1.24)	0.65 (0.93)
			II		3.75 (3.85); 37	5.18 (4.88); 12	1.22 (.....)	1.11 (1.05)
PEt_3	DESD	30 (30)	I	1.6 (1.2)	4.35 (4.31); 24; 4	3.13 (3.99)	not distinguishable	
			II		3.73 (4.13); 24; 4	5.21 (5.09); 11	not distinguishable	
$AsPh_3$	DESD	30	I	1.1	4.42; 33	3.15	1.55	0.73
			II		3.77; 36	5.45; 11	1.57	1.32
PEt_3	DiPrSD	30[b]	I	2.3	5.21; ?; 6	3.57	1.69	0.82
			II		4.15; ?; 6	7.56; ?	1.60	1.52
$AsPh_3$	DiPrSD	30[b]	I	1.2	5.21; ?	3.59	1.79	0.80
			II		4.08; ?	8.02; ?	1.61	1.42
PEt_3	DnPSD	—20[c]	I	4	4.49; 26; 4	2.85	1.27	0.62
			II		3.65; 29; 4	4.98; 10.5	1.13	1.05
PPh_3	DnPSD	0[c]	I	5	4.55; 30; 5	2.93	1.33	0.64
			II		3.72; 31; 5	5.14; 10	1.20	1.06

[a] The H—H coupling constants are those in the free ligands (Table 2). The IIb signal is underlined. [b] The observed resonances are broadened at this temperature. [c] In C_7D_8.

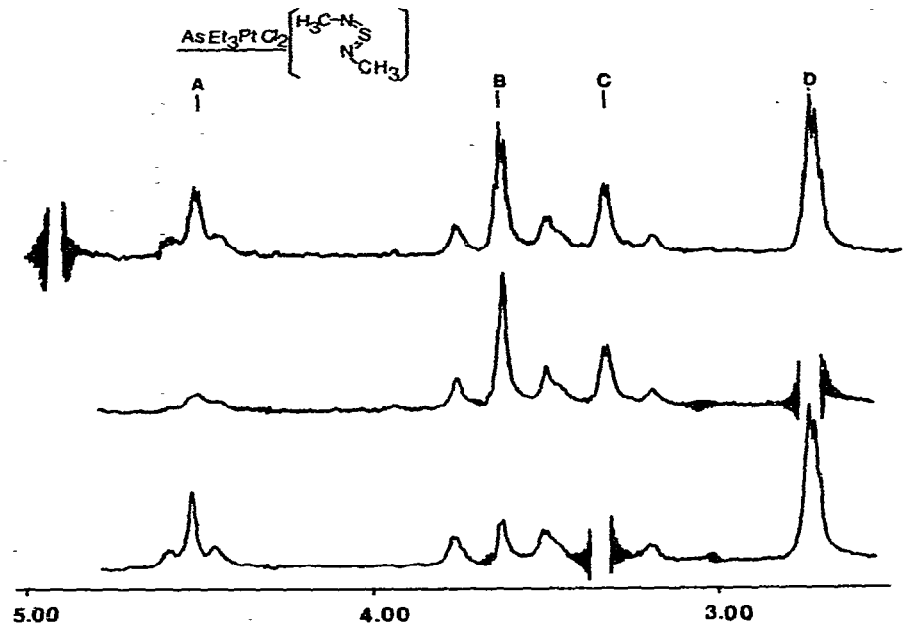

Fig. 4. General ^1H NMR pattern and NMDR results for DMSD in the complexes $[PtCl_2(DMSD)L]$ in C_7D_8 at 30°C.

since even at low temperature one Me-signal for $PMe_2Ph(=L)$ is found. Furthermore the double bond systems seem undisturbed, as the long range methyl—methyl couplings are the same as in the free ligand.

The isomeric form I has been found in the solid state for *trans*-$[PtCl_2$-(DBSD)L] with L = C_2H_4 [4]. Signals *B* and *D* are assigned to this configuration. Signal *B*, which lies at lower field than *D*, probably belongs to the N—CH_3 group directly bonded to Pt, as it has a large Pt-coupling and a small phosphorus coupling in the case of the phosphine compounds. Signal *D*, showing no Pt-coupling and strong solvent dependence thus relates to the free N—CH_3 group of isomer I.

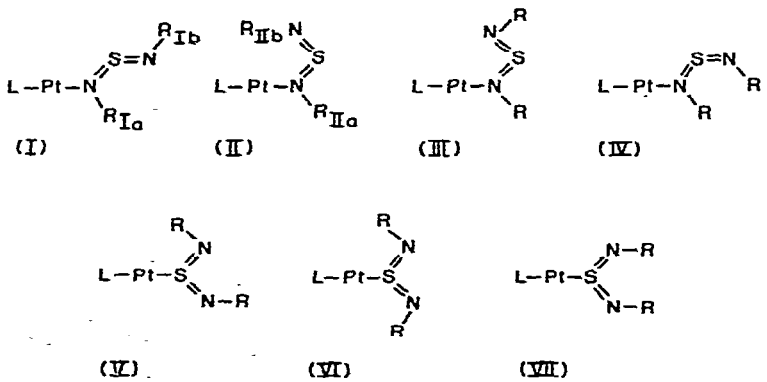

Fig. 5. Possible isomers of $[PtCl_2(DMSD)L]$.

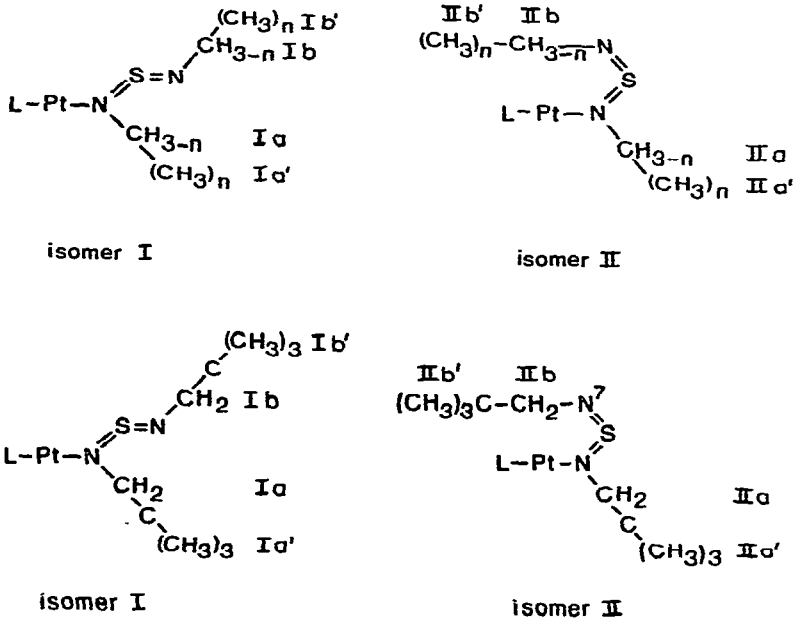

Fig. 6. Structures of $[PtCl_2(RNSNR)L]$ and the assignment for Table 7.

Isomeric form II (Fig. 5) is assigned to the less abundant isomer of $[PtCl_2$-(MeN=S=NMe)L]. Signal *C* with a chemical shift and coupling constant $J(Pt-CH_3)$ similar to signal *B* is assigned to the $N-CH_3$ bonded to Pt. In the case of the phosphine compounds, signal *C* also shows phosphorus coupling of the same order of magnitude, as is observed for signal *B* of isomer I. Signal *A*, which shows Pt-coupling of about 10—16 c sec^{-1}, but no phosphorus coupling, has a very low chemical shift. These factors strongly indicate that the protons responsible for signal *A* are situated very near to the platinum atom.

Configurations IV to VII can readily be excluded on the basis of the NMR and kinetic results. Configuration III might be an alternative for the less abundant isomer of $[PtCl_2(MeN=S=NMe)]$, but in this case much higher chemical shifts and stronger solvent dependencies would be expected for the $N-CH_3$ protons of the non-coordinated end of the sulfurdiimine, as found for the more abundant isomer (configuration I).

The $N-CH_{3-n}$ and $(CH_3)_n$ ($n = 0, 1, 2, 3$) NMR resonances of $[PtCl_2$-$((CH_3)_nCH_{3-n}N=S=N-CH_{3-n}(CH_3)_n)L]$ and the CH_2 and CH_3 signals of $[PtCl_2$(neopentyl N=S=N neopentyl)L] are shown in Table 7, the notation used being shown in Fig. 6. It is especially significant that the signals of the $N-CH_{3-n}$ groups *all* follow the same chemical shift sequence with the chemical shifts of the ^1H NMR resonances falling in the order IIb < Ia < IIa < Ib. It is clear from Table 7 that the IIb group again lies at the lowest field. The low field shift is particularly large for the N—CH-group (IIb) of the isopropyl compound (~ 3 ppm) relative to the free ligand.

The comparison of the chemical shift differences between the lowest field resonance IIb and the corresponding lowest field resonance of the free *cis,trans*

TABLE 8

^{1}H CHEMICAL SHIFT DIFFERENCE Δ BETWEEN THE IIb RESONANCE OF $LPtCl_2$ (RNSNR) AND THE *A* RESONANCE OF RNSNR (*m* = number of protons of the N—CH_{3-n} group).

R	*m* = 3—*n*	$AsEt_3$ (Δ)	Δ X *m*	PEt_3 (Δ)	Δ X *m*
CH_3	3	1.04	3.12	0.94	2.82
CH_2CH_3	2	1.55	3.10	1.38	2.76
$CH_2C(CH_3)_3$	2	1.52	3.04	1.32	2.64
$CH(CH_3)_2$	1	3.06	3.06	2.70	2.70

isomer (as shown in Table 8) is very revealing. If these figures are multiplied by 3, 2, 1 and 2 for R = Me, Et, i-Pr and neo-P, respectively i.e. by the number of protons of the N—CH_{3-n} group, almost constant values of about 3.08 for L = $AsEt_3$ and 2.73 for L = PEt_3 are obtained. The results indicate that there is still free rotation of the methyl group IIb in the isomer II of $[PtCl_2(DMSD)L]$, but that rotation of the IIb group is rather restricted for isomer II in the other compounds.

The results also indicate that the Pt—H distances between Pt and the protons of the free N—CH_{3-n} group IIb of isomer II is probably fairly constant. Models show that the Pt—H distance may vary between extremes of 1.55 and 2.4 Å, which is short by comparison with the sum of the covalent radii of Pt^{2+} and H (about 1.72—1.82 Å).

In agreement with our assignment we find that the chemical shift pattern of the $(CH_3)_n$ groups, which are *further* away from the platinum atom, are different from that of the N—CH_{3-n} groups. In particular the IIb′ signal is never found at the lowest fields (Table 7).

The ^{13}C results are given in Table 9. The chemical shift differences between IIb and the *A* absorption of the free ligand are 4 to 6 ppm, i.e. again fairly constant.

Finally it is noteworthy that platinum coupling occurs with IIb, Ia′ and IIa′, but not with the other absorptions and that this coupling is of an unusual type. Direct through space coupling with the IIb proton and carbon atoms is a possibility in view of the structure of configuration II.

2. Kinetic measurements. At temperatures above room temperature the signals of all four methyl groups of isomers I and II of $[PtCl_2(MeN{=}S{=}NMe)L]$ broaden, from which one might conclude that all four Me-groups exchange with each other. However, double resonance experiments at ambient temperature have shown conclusively that *A* exchanges only with *D*, and *B* only with *C* (Fig. 4). This interchange is intramolecular, as is shown by concentration dependence measurements in the presence of free sulfurdiimine. Furthermore there is no indication of a disappearance of the Pt-satellites when the double resonance experiments are carried out on the central resonances of the *B* and *C* absorptions. Finally, if the exchange were intermolecular, signal *A* would exchange also with *C* and *B* with *D*, which is not the case.

The kinetic results may be explained by the reaction scheme shown in Fig. 7. In this the sulfurdiimine remains bonded to the metal atom by the same

TABLE 9

^{13}C NMR DATA FOR THE DIALKYLSULFURDIIMINES AND THEIR COMPLEXES $LPtCl_2$ (RNSNR) (Chemical shifts in ppm rel. TMS, coupling constants in c sec^{-1})

L	R	Isomer	Solvent	Temp. (°C)	Ia or IIa	Ib or IIb; J(Pt)	Ia′ or IIa′; J(Pt)	Ib′ or IIb′	L; J(Pt); J(P)	L; J(Pt); J(P)
PEt_3	DMSD	I	C_7D_8	30	39.68	39.32			14.92; 35; 40	7.78; 23; 3
PEt_3	DMSD	II	C_7D_8	30	39.55	42.66; 10			14.52; 35; 40	7.66; 23; 3
$AsEt_3$	DMSD	I	C_7D_8	30	40.09	39.51			13.23; 47	8.96; 16
$AsEt_3$	DMSD	II	C_7D_8	30	40.09	42.52; 12			12.85; 47	8.96; 16
$AsEt_3$	DMSD	I	C_6D_6	30	40.27	39.35			13.26; 46	8.97; 16
$AsEt_3$	DMSD	II	C_6D_6	30	40.27	42.63; 12			12.86; 46	8.97; 16
$PPhMe_2$	DMSD	I	C_6D_6	30	40.04	39.40			12.48[a]; 3β; 4δ	
$PPhMe_2$	DMSD	II	C_6D_6	30	40.04	42.40; 10			12.08[a]; 3β; 4δ	
PEt_3	DESD	I	C_7D_8	0	47.00	48.20; 12	15.34;	17.43	14.55; 35; 40	7.75; 23; 3.5
PEt_3	DESD	II	C_7D_8	0	48.97	50.50; 12	18.72;	16.05	14.14; 35; 40	7.53; 23; 3
$AsEt_3$	DESD	I	C_6D_6	30	47.64	48.29	15.43; 7	17.32	13.19; 46	8.97; 16
$AsEt_3$	DESD	II	C_6D_6	30	49.48	50.45; 17	18.66; 7	16.04	12.82; 46	8.90; 16
PEt_3	DiPrSD	I	C_7D_8	−50	55.68	55.44	22.69; 7	25.22	13.76; 35; 40	7.71; 22; 3
PEt_3	DiPrSD	II	C_7D_8	−50	58.04	55.03; 20	26.42; 7	23.59	13.50; 35; 40	7.35; 22; 3
$AsEt_3$	DiPrSD	I	C_7D_8	−20	56.24	55.53	22.95; 10	25.27	12.48; 45	9.00; 22
$AsEt_3$	DiPrSD	II	C_7D_8	−20	58.57	54.97; 20	26.45; 10	23.63	12.23; 45	8.76; 22
$AsEt_3$	DiPrSD	I[b]	C_6D_6	30	56.47	55.63	23.07	25.27	12.97; 47	8.93; 22
$AsEt_3$	DiPrSD	II[b]	C_6D_6	30	58.83	55.03; 20	26.44	23.68	12.97; 47	8.93; 22
PEt_3	DBSD	I	C_7D_8	30	68.54	63.50	29.64; 8	31.11	14.70; 37; 40	7.73; 24; 3.5
$AsEt_3$	DBSD	I	C_6D_6	30	69.19	63.75	29.85; 8	31.18	13.06; 48	8.97; 17
PEt_3	DnPSD	I	C_7D_8	−20	63.78	60.04	34.96[c]	32.74[c]	14.41; 35; 40	7.64; 23; 3
							28.60	26.80		
PEt_3	DnPSD	II	C_7D_8	−20	64.16	68.68	33.13[c]	32.33[c]	14.21; 35; 40	7.64; 23; 3
							28.21	27.48		
$AsEt_3$	DnPSD	I	C_7D_8	−20	63.78	60.06	34.92[c]	32.74[c]	12.68; 44	8.89; 15
							28.59	26.88		
$AsEt_3$	DnPSD	II	C_7D_8	−20	64.21	68.73	33.12[c]	32.26[c]	12.39; 44	8.89; 15
							28.19	27.52		

[a] Only the $^{13}CH_3$ resonances of the L are given. [b] The signals are broad, and the resonances of L have coalesced, for both isomers. [c] For all the DnPSD compounds values are given for the β and γ ^{13}C-atom of the ligand.

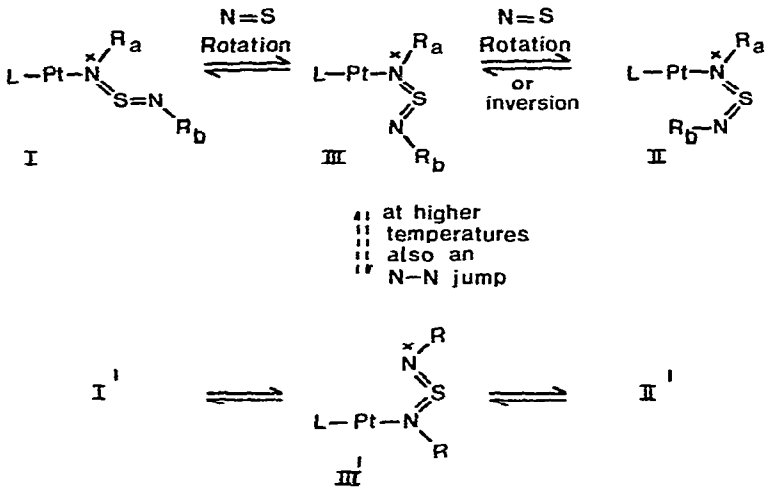

Fig. 7. The interconversion of the two isomers of $[PtCl_2(DMSD)L]$.

N-atom (I ↔ III ↔ II). If an N—N jump occurs, as in the case of the t-butylsulfurdiimine compounds, signals *B* and *D* would exchange and also signals *A* and *C*. The interconversion rates decrease in the order Cl > Br > I and $AsEt_3 \sim AsPh_3 > SPr_2 > PEt_3 \sim PPh_3$. The kinetic parameters have values of 10^{12-13} sec^{-1} (*A*) and 17—18 kcal $mole^{-1}$ (ΔE) for the more abundant isomer.

Double resonance experiments revealed that the kinetic behaviour of the ethyl (at 0° C) and isopropyl derivatives (at —20° C) is similar to that of the methyl compounds (at 30° C), i.e. isomers I and II interconvert by rotations (or inversions at N), while the platinum atom remains bonded to the same nitrogen atom. The kinetic behaviour of the neopentyl compound could not be satisfactorily established, as the amount of isomer II is too small for precise measurements, but the features appear to be similar. The interconversion rates decrease in the order i-Pr > Et > Me.

At temperatures higher than those considered above, both line width change and NMDR measurements show that in addition to the above reaction type there is also a reaction involving an intramolecular migration of the platinum atom from one N-atom to the other and vice versa; such migration was observed for the t-butylsulfurdiimine metal compounds.

C. Ligand resonances

The ligand of interest is PMe_2Ph, as the methyl resonance gives information about the trans influence of the *trans* ligand. For all compounds the methyl peak appears at about 1.80 ppm (in $CDCl_3$) and a $^{195}Pt—CH_3$ coupling of about 33—35 c sec^{-1} and a $^{31}P—CH_3$ coupling of about 12 c sec^{-1}. Very similar values are observed for *cis*-$(PMe_2Ph)_2PtCl_2$ [10]. This indicates that the RN=S=NR ligands have *trans* influences of the same order as Cl^-. As far as can be observed, for all compounds, the L resonances (^1H) of isomer II are at higher fields than those of isomer I (by 0.1 ppm).

Discussion

The sulfurdiimines themselves have received little attention. A preliminary report by Leandri et al. [11] revealed that the compound *p*-$MeC_6H_4N{=}S{=}NC_6H_4$-Me-*p'* crystallises in the *cis,trans* configuration. In agreement, we find that in solution the *cis,trans* configuration is the most stable, in contrast to the predictions of Grunwell and Danison [12] for MeN=S=NMe*. The latter authors also predicted that interconversion between the *cis,trans* isomer and the *trans,trans* isomer should proceed by inversion at the nitrogen atom for the H—N=S=N—H compound, but by rotation about the N=S bond in the case of MeN=S=NMe. We are not able to choose between these two mechanisms, although the rotational process must occur in the metal compounds (see later). Finally it is relevant to note that in the case of the imines $\rangle C{=}N\langle$ the inversion mechanism is probably always responsible for the interconversion of *syn* into *anti* isomers and vice versa [13].

The results on the alkylsulfurdiimine platinum compounds show that in all cases the sulfurdiimine is very probably coordinated via the N-atom. Coordination via the S-atom may be less favoured, because the N-atom carries the higher negative charge. It must be appreciated, however, that the sulfurdiimines are structurally similar to sulfur dioxide, which is known to coordinate almost always via the sulfur atom. Also, there is no valid reason why coordination via the N=S double bond should not occur. Further research is being directed to investigating whether the last two modes of coordination can be realised in other complexes.

If we now consider the differences between the various alkylsulfurdiimine platinum compounds, it is clear that steric factors are an important influence on the type and ratio of the isomers I and II and on the kinetic behaviour. From steric considerations structure I should in general be the more stable, as is observed. However, the structure of isomer II is fairly stable, which may be due to the stabilising influence of a Pt$\cdots$H—C interaction in a situation otherwise sterically rather unfavourable. This interaction may increase in the series $LPtX_2$-(DMSD) in the order X = Cl < Br < I (Table 6) owing to increasing mutual polarisation (soft—soft interaction), so that isomer II may become relatively more stable as long as the steric interaction of the methyl group with the halogen atom is not too large.

Especially interesting is the large low-field chemical shift of the protons IIb in the first coordination sphere, and even of the carbon atoms in the second coordination sphere. The origin of this phenomenon has been little studied [1, 16] and merits more attention. The major cause of the antishielding is probably the paramagnetic anisotropy of the platinum atom, which causes downfield shifts if the protons are situated close to the metal and above the bonding plane of the planar molecule. A similar suggestion was made by Miller et al. [15] in the case of alkenylaryl compounds of Ni^{II} and Pd^{II}.

From the kinetics of the interconversions, it is clear that in the case of the t-butylsulfurdiimine metal compounds the only observable process is an intramolecular N—N jump (Fig. 3), which probably proceeds via a five-coordinated

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* Grunwell et al. [9] recently reported that the *cis,trans* configuration for R = Me and t-Bu is the most stable, as found by ^1H NMR.

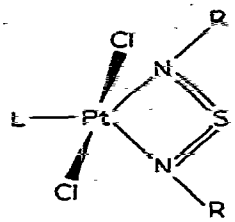

Fig. 8. A possible intermediate in the exchange of the two t-butyl groups of $[PtCl_2(DBSD)L]$.

complex with a distorted trigonal bipyramidal structure, in which the diimine acts as a bidentate ligand (Fig. 8). Inspection of such a five-coordinated compound shows that the diimine must be in the *trans* configuration (configuration III as intermediate) (Fig. 3), as the electron pairs are then in a favourable position for bonding to the platinum atom. In agreement with this is the observation that the rate of this process decreases from L = AsR_3 to L = PR_3, which is the trend generally observed for decreasing stability of five-coordinated compounds [17, 18].

This N—N migration is also observed for other alkylsulfurdiimine metal compounds at elevated temperatures, but it occurs alongside the process in which the platinum atom remains bonded to the same N-atom and which is significant at even lower temperatures The first step of this latter process must involve rotation about the N=S bond, as an inversion at the nitrogen atom cannot give the observed result (Fig. 6). The second step is a rotation about the other N=S bond (or an inversion at the noncoordinated nitrogen atom). The rate of the process decreases with increasing donor ability of L. The fall in rate may therefore be caused by an increasing N=S bond strength, although steric factors will be involved also.

Acknowledgement

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