Journal of Organometallic Chemistry, 86 (1975) 127—138

CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

II*. DIARYLSULFURDIIMINE COMPOUNDS OF PLATINUM

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(Received August 30th, 1974)

Summary

The preparation and properties of a series of compounds *trans*-$PtCl_2$-(diarylsulfurdiimine)L (L = Group V or VI donor ligand) are described. ^1H and ^{13}C NMR have shown that in solution in general only one isomer is formed in which the diarylsulfurdiimine is very likely in the *trans,trans* form and coordinated to the metal atom via one of the nitrogen atoms. Both intramolecular movements and intermolecular exchange reactions of the sulfurdiimine ligands have been observed. The intramolecular movements involve an N—N migration via a five-coordinate intermediate. The rate of this migration is dependent on the type of ligand L and on the aryl substituents. Some relevant data on the free ligands are also reported.

Introduction

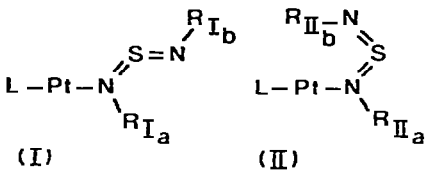
In Part I [1] it was reported that the compounds *trans*-$PtCl_2$(dialkylsulfurdiimine)L exist in two isomeric forms I and II (Fig. 1). In both isomers the sulfurdiimine ligand is in the *cis, trans* form and is bonded to the metal atom via one of the nitrogen atoms.

The isomeric form II is remarkable since the uncoordinated alkyl end of the sulfurdiimine is very close to the metal atom, probably owing to the stabilizing influence of a Pt···H—C non-bonded interaction**, also postulated by Van Baar et al. [2] for some azo and imine compounds of platinum.

The two isomers interconvert via two distinct reaction paths, which are both intramolecular. At low temperatures only movements of the sulfurdiimine occur, while the metal atom remains bonded to the same nitrogen atom. The

* For part I see ref. 1.

** A recent example of such a stabilizing interaction has been reported by Cotton and Day [3] for $[(C_2H_5)_2B(pyrazolyl)_2]C_7H_7(CO)_2Mo$..



(I) (II)

Fig. 1 Isomers of $PtCl_2$(dialkylsulfurdiimine)L.

second process, which occurs at higher temperatures, involves an N—N migration via a five-coordinate intermediate in which the sulfurdiimine is in the *trans,trans* form (see Figs. 7 and 8 of ref. 1).

It is now shown that the aryl derivatives differ in some respects quite appreciably from the alkyl compounds.

Experimental

Diarylsulfurdiimines

Diarylsulfurdiimines were prepared by a modified literature procedure [4] superior to the previously known methods of preparation [5, 6] since it has a more general applicability and gives higher yields of purer products. Certain sulfurdiimines have been prepared for the first time and are indicated in Table 1.

Gaseous SF_4 [7] (0.2 mol) is passed slowly over a vigorously stirred solution or suspension of 0.4 mol of arylamine in 2.5 mol of triethylamine at 0°. A thick precipitate is formed. After 30 minutes the reaction mixture is brought to room temperature for about 60 minutes and subsequently to 80° for about 15 minutes. It is then cooled to 0° and a cold aqueous solution of K_2CO_3 (300 ml) containing ice is added [except in the case of bis(4-nitrophenyl)sulfurdiimine]. After some minutes of vigorous shaking the organic layer is separated and dried over K_2CO_3 or Na_2SO_4. The solvent is removed in vacuo after filtration. The residue, which is oily on occasions, is recrystallized twice from cold hexane or chloroform/hexane (yields 80-90%). In the case of the nitro compound the reaction mixture is evaporated to dryness in vacuo and the solid residue dissolved in warm chloroform. After crystallization in the cold the crystals are recrystallized. Yields are about 70%.

The analytical data and colours are given in Table 1. Benzothiadiazal [8] and benzoselenodiazal [9] were prepared according to literature procedures.

Diarylsulfurdiimine compounds of platinum(II)

An example of the preparative procedure is given.

To a stirred solution of 1 mmol of $(Et_3AsPtCl_2)_2$ in chloroform is added 2 mmol of di-3,5-xylylsulfurdiimine at —20°. After concentration to about 3 ml a ten-fold excess of cold hexane at —20° containing 2 mmol of diarylsulfurdiimine is added with stirring. The solvent is decanted from the precipitate, which is washed with cold hexane to remove traces of sulfurdiimine. The precipitate is vacuum dried at room temperature.

The bis(3,5-dichlorophenyl)sulfurdiimine forms a non-isolable complex in solution, as shown by NMR, while the bis(*p*-nitrophenyl)sulfurdiimine forms

TABLE 1

ANALYTICAL DATA FOR Aryl—N=S=N—Aryl[a] AND $PtCl_2$(Aryl—N=S=N—Aryl)L[b]

Aryl group	Ligand L	M.p. (°C)	Analyses found (calcd.) (%)		
			C	H	S
4-$NO_2C_6H_4$		186-187	47.76 (47.36)	2.61 (2.65)	9.73 (10.53)
3,5-$Cl_2C_6H_3$[c]		135.7	40.94 (40.94)	1.94 (1.74)	9.22 (9.11)
3,5-$(CH_3)_2C_6H_3$[c]		34.7	71.19 (71.06)	6.74 (6.71)	11.57 (11.85)
2,4,6-$(CH_3)_3C_6H_2$[c]		47.5	72.18 (72.42)	7.28 (7.43)	10.44 (10.74)
3,5-$(CH_3)_2C_6H_3$	PEt_3	Dec.	41.05 (40.37)	5.07 (5.08)	
3,5-$(CH_3)_2C_6H_3$	PPh_3	Dec.	50.47 (51.13)	3.99 (4.16)	
3,5-$(CH_3)_2C_6H_3$	$AsEt_3$	85-87	36.78 (37.83)	4.64 (4.76)	4.45 (4.59)
3,5-$(CH_3)_2C_6H_3$	$SbEt_3$	Dec	33.57 (35.45)	4.13 (4.46)	3.74 (4.30)
4-$CH_3C_6H_4$	$AsEt_3$	Oil	35.31 (35.83)	4.35 (4.36)	4.68 (4.78)
4-$CH_3OC_6H_4$	$AsEt_3$	Oil	34.49 (33.90)	4.10 (4.13)	4.51 (4.53)
4-ClC_6H_4	$AsEt_3$	Dec.	30.25 (30.39)	3.19 (3.26)	4.00 (4.51)
4-IC_6H_4	$AsEt_3$	125-127	24.67 (24.18)	2.45 (2.59)	3.50 (3.59)
2,4,6-$(CH_3)_3C_6H_2$	$AsEt_3$	102-103	39.04 (39.67)	5.07 (5.13)	4.24 (4.41)
$C_6H_4N_2S$	$AsEt_3$	107-108	26.56 (25.54)	3.36 (3.39)	5.47 (5.68)
$(CH_3)_2C_6H_2N_2Se$	$AsEt_3$	142-143	26.82 (26.30)	3.65 (3.63)	

[a] The sulfurdiimines are red except for the orange 3,5-dichlorophenyl compound. [b] The complexes are red to dark red except for the last two yellow complexes, and the purple complexes with *p*-iodide and with $SbEt_3$. [c] Sulfurdiimines prepared for the first time.

no complex. It is generally observed that the complex becomes more stable in solution with increasing donor properties of the substituents on the aryl ring.

Analytical data and colours of relevant compounds are given in Table 1. All other compounds mentioned in this article were prepared in solution and were characterized unambigouusly by NMR.

NMR spectra were recorded on an Varian HA100 Proton spectrometer and an Varian XL-100 spectrometer with Fourier Transform (^1H and ^{13}C).

Results

Diarylsulfurdiimines

^1H and ^{13}C NMR data (Tables 2 and 3) show that at low temperatures the diarylsulfurdiimines generally occur in two isomeric forms of which the most abundant one is asymmetric (*cis,trans* isomer) and the less abundant one sym-

(continued on p. 132)

TABLE 2. ^{1}H NMR DATA (ppm RELATIVE TO TMS) FOR Aryl—N=S=N—Aryl[a]

Aryl group		Ratio (% R)	Temp (°C)	Solvent	*o*	*o'*	*m*	*m'*	*p*	*p'*	CH_3	CH_3'
3,5-$(CH_3)_2C_6H_3$	A		−70	$CDCl_3$	7.77	6.75			6.93	6.88	2.35	2.35
3,5-$(CH_3)_2C_6H_3$	B	27	−70	$CDCl_3$		6.20				6.02		2.04
3,5-$(CH_3)_2C_6H_3$			30	$CDCl_3$	6.87				6.75		2.21	
3,5-$(CH_3)_2C_6H_3$	A		−72	C_7D_8	8.15	6.45			6.52	6.48	2.07	2.00
3,5-$(CH_3)_2C_6H_3$	B	27	−72	C_7D_8		6.01				6.22		1.76
3,5-$(CH_3)_2C_6H_3$			30	C_7D_8	6.90				6.56		2.04	
												2.12[b]
2,4,6-$(CH_3)_3C_6H_2$	B	100	−70	$CDCl_3$				6.77				2.21
												2.07[b]
2,4,6-$(CH_3)_3C_6H_2$	B	100	30	$CDCl_3$				6.66				2.16
												1.96[b]
2,4,6-$(CH_3)_3C_6H_2$	B	100	−72	C_7D_8				6.33				1.90
												2.01[b]
2,4,6-$(CH_3)_3C_6H_2$	B	100	30	C_7D_8				6.47				1.99
4-$CH_3C_6H_4$	A		−70	$CDCl_3$	8.10	7.02	7.21	7.10			2.36	2.36
4-$CH_3C_6H_4$	B	<10	−70	$CDCl_3$		6.47		6.84				2.23
4-$CH_3C_6H_4$			30	$CDCl_3$	7.34		7.11				2.34	
4-$CH_3C_6H_4$	A		−76	C_7D_8	8.46	6.74	6.85	6.74			2.00	1.91
4-$CH_3C_6H_4$	B	<10	−76	C_7D_8		6.46		6.46				1.84
4-$CH_3C_6H_4$			30	C_7D_8	7.37		6.87				2.06	
4-ClC_6H_4	A		−76	C_7D_8	7.97	6.19	6.83	6.78				
4-ClC_6H_4	B	<10	−76	C_7D_8		5.78		6.37				
4-ClC_6H_4			30	C_7D_8	7.08		6.96					
4-IC_6H_4	A		−65	$CDCl_3$	7.90	6.90	7.71	7.71				
4-IC_6H_4			30	$CDCl_3$	7.15		7.63					
4-$CH_3O.C_6H_4$	A		−65	$CDCl_3$	8.24	7.13	6.93	6.93			3.86	3.82
4-$CH_3O.C_6H_4$	B	<10	−65	$CDCl_3$		6.60		6.60				3.76
4-$CH_3O.C_6H_4$			30	$CDCl_3$	7.44		6.82				3.79	
4-$(CH_3)_2NC_6H_4$	A		−65	$CDCl_3$	8.24	7.16	6.69	6.76			3.08	3.01
4-$(CH_3)_2NC_6H_4$			30	$CDCl_3$	7.49		6.65				2.96	
3,5-$Cl_2C_6H_3$	A		−65	$CDCl_3$	8.05	7.03			7.25	7.25		
3,5-$Cl_2C_6H_3$			30	$CDCl_3$	7.27				7.21			
4-$NO_2C_6H_4$			30	$CDCl_3$	7.57				8.25			
$C_6H_4N_2S$[c]			−20	$CDCl_3$	7.98(m)[d]		7.54(m)					
$C_6H_4N_2Se$[c]			−20	$CDCl_3$	7.80(m)		7.40(m)					

[a] A = *cis,trans* isomer, B = *trans,trans* isomer; *o*, *m*, *p* and CH_3 relate to *cis* aryl group. *o'*, *m'*, *p'* and CH_3' to *trans* aryl group. If present $J(o—m)$ 8.9, $J(o—p)$ 0.7-1.7, $J(CH_3—aryl)$ 0.7-0.8 Hz. [b] These values refer to the *ortho*-CH_3 protons. [c] The 3- and 6-positions are given as *ortho*, the 4- and 5-positions as *meta*. [d] m = Multiplet.

TABLE 3

^{13}C NMR DATA OF Aryl–N=S=N–Aryl (ppm FROM TMS) IN $CDCl_3$

Aryl[a,b]		Temp. (°C)	Carbon bonded to N		o	o′	m	m′	p	p′	Methyl	
3,5-$(CH_3)_2C_6H_3$		30	145.39		121.01		138.33		128.23		21.06	
3,5-$(CH_3)_2C_6H_3$	A	−65	145.51	145.19	123.59	117.88	139.81	138.29	129.81	127.75	21.31	21.31
3,5-$(CH_3)_2C_6H_3$	B	−65		143.60		120.50		136.93		127.32		21.11
4-$CH_3OC_6H_4$		30	140.00		124.78		114.09		158.30		55.47	
4-$CH_3OC_6H_4$	A	−65	140.62	139.03	128.02	121.16	114.28	113.46	157.98	157.48	55.41	55.41
4-$CH_3C_6H_4$		30	143.65		123.24		129.49		136.71		21.19	
4-$CH_3C_6H_4$	A	−65	143.95	143.16	126.27	120.03	130.16	129.45	138.39	136.20	21.66	21.14
4-ClC_6H_4		30	144.05		124.61		129.20		132.61			
4-ClC_6H_4	A	−65	144.13	143.47	127.61	121.34	129.51	128.83	132.88	131.63		
2,4,6-$(CH_3)_3C_6H_2$		30	140.23		128.27		128.17		134.28			18.91[c]
												20.68
												19.03[c]
2,4,6-$(CH_3)_3C_6H_2$	B	−65		139.6		128.10		128.10		134.44		20.81
$C_6H_4N_2Se$[d]		−20	160.15		123.23		129.34					
4,5-$(CH_3)_2C_6H_2N_2Se$[d]		30	160.15		121.26		140.58				20.46	

[a] For *o*, *m*, *p* and *o′*, *m′*, *p′* see Table 2. [b] The second isomer could be observed in one case only. [c] These values refer to the *ortho*-methyl groups. [d] See note *c* of Table 2.

metric (*trans,trans* isomer), analogous to the situation for the dialkylsulfurdiimines [1, 10, 11]. The large splitting of both the ^1H and ^{13}C signals belonging to the *ortho* atoms of the *cis,trans* isomer is remarkable. This may be due to the close proximity of the *ortho* atoms of the *cis*-aryl group to one of the double bonded nitrogen atoms [13], which situation has been found in the solid state for the ditolylsulfurdiimine [12].

The ^1H signals of the *trans,trans* isomer lie in all cases at higher field than those of the *cis,trans* isomer. From this it is concluded that the high field signals of the *cis,trans* isomer very likely belong to the *trans*-aryl group. In the case of the di-2,4,6-mesitylsulfurdiimine the symmetric isomer (*trans,trans* form) is the only isomer formed owing to steric factors.

It is relevant to mention that in the case of the aromatic *N*-sulfinylamines the most stable configuration is *cis* [13]. The proton resonances of some relevant compounds are recorded in Table 4. The resonances of the *ortho* protons of the *cis*-aryl group of Aryl—N=S=O lie about 0.3 ppm to higher field of the *ortho* signals of the *cis*-aryl group of Aryl—N=S=N—Aryl. The *meta* proton resonances lie at about the same position in the case of the first two compounds of Table 4 at 30°. The *meta* signal of the *cis*-aryl group of 2,4,6-mesityl-*N*-sulfonylamine absorbs however to lower field than the *meta* protons of the corresponding sulfurdiimine, which is understandable, since the latter compound is in the *trans,-trans* form. The same *meta* shift difference is observed with the *trans,trans* isomer of the first two compounds.

The *cis,cis* configuration, although never observed in the case of the dialkyl- and diaryl-sulfurdiimines studied by ourselves and others, may nevertheless be stabilized for obvious reasons (Fig. 2) in the case of benzothiadiazal and benzoselenodiazal.

At higher temperatures (about 0°) the ^1H and ^{13}C signals of the *cis,trans* and *trans,trans* forms coalesce.

The activation energies of the interconversion process lie in the range 11 to 12 kcal/mol while the frequency factors are about 10^{13} s^{-1}, as expected for a monomolecular reaction with a non-rigid transition state. Electron donating groups in the *para* position seem to decrease the rates of interconversion.

Comparison with the dialkylsulfurdiimines clearly shows that the interconversion rates are higher for the aryl derivatives [1].

TABLE 4

^1H NMR DATA (ppm FROM TMS) OF Aryl—N=S=O IN $CDCl_3$

Aryl group	Temp. (°C)	*ortho*	*meta*	*para*	CH_3	*J* (Hz)
4-$CH_3C_6H_4$	−20	7.81	7.21		2.39	8.5
4-$CH_3OC_6H_3$[a]	−20	7.93	6.89		3.85	8.0
3,5-$(CH_3)_2C_6H_3$	−20	7.49		7.03	2.31	∿0.8
2,4,6-$(CH_3)_3C_6H_2$[a]	−20		6.93		2.23, 2.28[b]	∿0.8
3,5-$Cl_2C_6H_3$	30	7.70		7.37		0.9

[a] These compounds have also been measured in CCl_4 by Van Woerden and Bijl-Vlieger [13]. [b] Intensity 2/1.

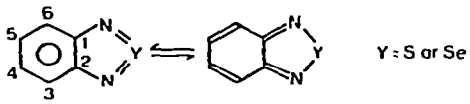


Fig. 2. Benzothiadiazal and benzoselenodiazal, and their resonance structures.

Diarylsulfurdiimine compounds of platinum(II)

The ^1H and ^{13}C NMR data of the platinum compounds are recorded in Tables 5, 6 and 7. In general only one isomer was observed in $CDCl_3$ or deuterotoluene (at −20°) for the compounds *trans*-$PtCl_2$(diarylsulfurdiimine)L.

When the chemical shifts of the proton signals of *trans,trans*-di-2,4,6-mesitylsulfurdiimine are compared with those of the coordinated ligand, which for steric reasons also must be in the *trans,trans* form, it is noted that the proton signals of both aryl groups move downfield upon coordination; however the signals of one aryl group move further than the other. The lower field signals belong to the coordinated end of the ligand, while the higher field signals have been assigned to the non-coordinated end of the sulfurdiimine.

In the case of other sulfurdiimines which are sterically less hindered the coordinated ligand may be in the *cis,trans* form (configuration I or II, Fig. 1) or in the *trans,trans* form (configuration III, Fig. 3). However, comparison of the proton signals of the metal complexes with those of the *trans,trans* form of the free ligand shows that downfield shifts of similar values to those of the di-2,4,6-mesitylsulfurdiimine occur if it is assumed that in all cases the coordinated ligand is in the *trans,trans* form (Fig. 3). If the signals of the *cis,trans* form of the free ligand were taken as a reference, the signals would move appreciably upfield upon coordination, which would be very unlikely in view of our data on the general behavior of alkylsulfurdiimine- [1], azo- and imino-platinum(II) compounds [2]. Configuration I seems therefore unlikely, but is not excluded.

Configuration II, which is in general the less abundant isomer in the case of the dialkylsulfurdiimine platinum(II) compounds, seems very unlikely since very large low field shifts would be expected [2], in particular of the *ortho* protons of the non-coordinated side of the diarylsulfurdiimine. These shifts were never observed.

A point of interest is that the ^{13}C signals of the N—C group of the coordinated end move on average to higher fields, while the *para* ^{13}C signal and the *ortho* ^{13}C signal of this group move to lower fields. This pattern indicates an overall electron donation from the ligand to the platinum atom [14].

At higher temperatures (0°) the signals of both ends of the diarylsulfurdiimine groups merge. This process is intramolecular, as the linewidth of the signals of free ligand present did not change. Furthermore, the process proved to be independent of the concentrations of complex and free ligand. At appreciably higher temperatures (30-35°) an intermolecular exchange of the sulfurdiimine groups was also observed. The rate of the intramolecular process increased with decreasing donor properties of the aryl substituents and with decreasing donor properties of the ligand (i.e. $SbEt_3 > AsEt_3 \approx AsPh_3 > PEt_3 \approx PPhMe_2 \approx PPh_3$). The activation energies are about 9-13 kcal/mol, while the

TABLE 5

^{1}H NMR DATA (ppm FROM TMS) OF $PtCl_2$(Aryl—N=S=N—Aryl)$AsEt_3$ IN $CDCl_3$[a] AT −20°

Aryl[b]	*ortho*		*meta*		*para*		CH_{3c}	CH_3	$AsEt_3$	
	o_c	o	m_c	m	p_c	p			Quartet	Triplet
3,5-$Cl_2C_6H_3$	7.21	6.65			7.16	7.14			1.99	1.28
3,5-$(CH_3)_2C_6H_3$	6.81	6.24			6.68	6.68	2.06	2.06	1.99	1.30
3,5-$(CH_3)_2C_6H_3$[c]	6.84	5.04			6.25	6.21	1.77 2.43[d]	1.71 2.01[d]	1.69	1.04
2,4,6-$(CH_3)_3C_6H_2$			6.86	6.76			2.24 2.56[d]	2.18 1.89[d]	1.93	1.24
2,4,6-$(CH_3)_3C_6H_2$[c]			6.62	6.33			2.04	1.91	1.61	1.02
4-$CH_3C_6H_4$	7.28	6.60	6.93	6.84			2.26	2.24	1.97	1.20
4-$CH_3OC_6H_4$	7.34	6.60	6.64	6.60			3.74	3.74	1.98	1.20
4-ClC_6H_4	7.38	6.70	7.15	7.10					1.98	1.20
4-IC_6H_4	7.11	6.45	7.48	7.42					1.98	1.28
$C_6H_4N_2S$[e]	8.60 (m)	7.95 (m)	7.67 (m)	7.59 (m)					2.04	1.34
$C_6H_4N_2Se$[e]	8.47 (m)	7.75 (m)	7.51 (m)	7.42 (m)					2.02	1.32

[a] In the case of the methyl-substituted aryls the CH_3 and CH_{3c} resonances appear as a doublet at −20° in deuterotoluene. [b] The *ortho*, *meta* and *para* protons of the aryl group bonded to the nitrogen atom attached to platinum are denoted as o_c, m_c and p_c. [c] In deuterotoluene at −20°. [d] See note *b* of Table 2. [e] See note *c* and *d* of Table 2.

TABLE 6

^{1}H NMR DATA (ppm FROM TMS) OF $PtCl_2$(dixylylsulfurdiimine)L IN $CDCl_3$ AT −20°[a]

Ligand L	*ortho*[b]		*para*[b]		CH_3[b]	CH_3	Ligand L[c]	
	o_c	o	p_c	p				
$AsEt_3$	6.81	6.24	6.68	6.68	2.06	2.06	1.99(q)	1.30(t)
$AsEt_3$[d]	6.84	5.94	6.25	6.21	1.77	1.71	1.67(q)	1.04(t)
PEt_3	6.79	6.25	6.68	6.68	2.07	2.07		
$SbEt_3$	6.82	6.25	6.68	6.68	2.08	2.08	1.95(q)	1.39(t)
$PPhMe_2$	6.79	6.26	6.70	6.70	2.09	2.07	1.87[e]	7.47(m)
PPh_3	6.88	6.27	6.68	6.68	2.09	2.06		
$AsPh_3$	6.90	6.26	6.69	6.69	2.09	2.05		
$SeEt_2$	6.79	6.20	6.69	6.69	2.06	2.06	2.87(m)	1.54(t)
$TeEt_2$	6.80	6.23	6.68	6.68	2.06	2.06		

[a] At higher temperatures the signals of each type merge owing to an intramolecular reaction (see text). [b] See note 2*d* of Table 5. [c] t = Triplet, q = quartet, m = multiplet. [d] In C_7D_8 at −20°. [e] *J* Pt 32, *J* P 12Hz.

frequency factors are about 10^9-10^{10} s^{-1}, which is indicative of a fairly rigid transition state. In Fig. 3 a scheme for the mechanism is given.

If the compounds possess configuration III, which is the most likely, the mechanism is given by III↔III'. The sequence I↔III↔III'↔I' would occur if the complexes had configuration I, which is less likely.

In view of the above results and earlier work [1] it was of interest to study the properties of sulfurdiimine ligands in which rotational movement and/or inversions are very unlikely. Therefore, complexes of benzothiadiazal and benzoselenodiazal were made, with the composition *trans*-$PtCl_2$(sulfurdiimine)L. It was found by NMR that in both cases the metal atom is coordinated to one of the nitrogen atoms. D NMR experiments [15] at 50° showed that probably only intermolecular exchange of the diimine ligand occurred. This is not surprising because the intramolecular movements occurring in the cases of the rotational (inversion) mechanism [1] and the N—N migration [1] are not possible for these ligands. A possible movement could be a migration of the metal atom from one N atom to the other via the sulfur atom. Although this movement is not rigorously excluded, it seems unlikely.

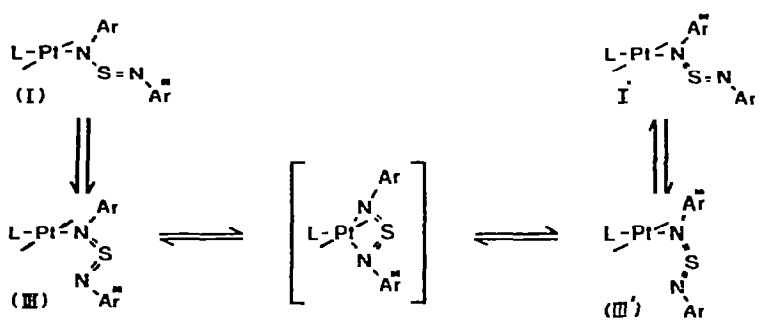


Fig. 3. Scheme for the reaction mechanism of $PtCl_2$(diarylsulfurdiimine)L.

TABLE 7

^{13}C NMR DATA (ppm FROM TMS) OF $PtCl_2$(Aryl–N=S=N–Aryl)$AsEt_3$ AT −25° IN $CDCl_3$[a]

Aryl	C–N	*ortho*[b]	*meta*[b]	*para*	CH_3	$AsEt_3$
3,5-$(CH_3)_2C_6H_3$	143.81, 142.53	121.95,[c] 119.88	137.55, 137.47	129.46, 129.36	20.95, 20.65	12.57(J_{Pt}45) 8.98(J_{Pt} 17)
4-$CH_3OC_6H_4$	137.37, 136.19	125.61, 124.70	112.70, 112.46	159.04, 158.35	55.43, 55.43	12.21(J_{Pt}44) 8.98(J_{Pt}16.5)
4-$CH_3C_6H_4$	141.38, 140.19	124.02, 121.92	128.45, 128.24	138.35, 137.91	21.29, 21.29	12.27(J_{Pt}44) 8.94(J_{Pt}16.5)
4-ClC_6H_4	142.20, 141.09	125.71, 123.00	128.62, 128.29	133.74, 133.58	19.97,[d] 19.97[d]	12.80(J_{Pt}45) 8.96(J_{Pt}16.5)
2,4,6-$(CH_3)_3C_6H_2$	137.00, 136.66	129.15, 128.12	129.00, 128.73	132.02,(129.83)	20.87, 20.87	13.12(J_{Pt}45.7) 8.92(J_{Pt}16.5)
$(CH_3)_2C_6H_2N_2Se$[e]	[f]	121.94, 120.97	143.7, 141.8		21.05, 20.49	12.80(J_{Pt}44.6) 9.00(J_{Pt}16.3)
$C_6H_4N_2Se$[e]	[f]	123.96, 123.01	131.00, 129.83			12.95(J_{Pt}44.5) 8.99(J_{Pt}16.4)

[a] Coupling constants in Hz. [b] The first value is due to the aryl group bonded to the nitrogen attached on the platinum. [c] J_{Pt} 12Hz. [d] These values refer to the *ortho* CH_3 groups. [e] See note *c* of Table 2 [f] Could not be observed.

Discussion

The first point of interest is that in the case of the free ligands the *cis,trans* form is more stable than the *trans,trans* form for both the dialkyl- and diarylsulfurdiimines* in solution, while in the solid state [12] and in the gas/phase [16] the *cis,trans* form seems to be the only isomer present. Approximate CNDO calculations [11] seem to indicate that the *cis,trans* form might be stabilized by the inclusion of *d*-orbitals on the sulfur atom in the bonding scheme. It should be pointed out, however, that in general the energy difference between both forms is fairly small.

Kinetic measurements on the rates of interconversion between both isomers indicate that the diarylsulfurdiimines interconvert much faster than the dialkylsulfurdiimines. More electron-withdrawing groups seem in general able to stabilize the transition state. From the available data no conclusions can be drawn regarding the mechanism, i.e. rotation about the N=S bond or inversion at N.

In the case of the metal complexes the close analogy between the dialkylsulfurdiimines and the diarylsulfurdiimines seems to disappear almost completely. The alkyl derivatives are in the *cis,trans* form which gives rise to configurations I and II (Fig. 1). Configuration III (Fig. 3), which holds for *trans*-$PtCl_2$(di-2,4,6-mesitylsulfurdiimine)L and which is the most likely configuration for the other compounds *trans*-$PtCl_2$(diarylsulfurdiimine)L, contains the diimine in the *trans,trans* form. In the case of the dialkylsulfurdiimine platinum compounds configuration III was only postulated as a necessary intermediate to account for the two intramolecular processes [1].

This influence of the substituent and of the metal on the configuration of the ligand is remarkable. On the basis of steric factors it is understandable that configuration II is not formed in the case of the diarylsulfurdiimines. However, configuration I seems to be quite acceptable except for the 2,4,6-trimethyl substituted derivative. It seems therefore that electronic factors play the major role. If we take into account that the energy difference between the *cis,trans* and *trans,trans* forms is generally fairly small it is possible that coordination of the platinum to the diarylsulfurdiimine might cause, by virtue of the interaction of the Pt 5*d* orbitals with the total π-bond system of the ligand, the change in the ligand configuration from the *cis,trans* form to the *trans,trans* form.

Kinetic data on the metal complexes show there is only one observable intramolecular process which involves, analogously to the di-tert-butylsulfurdiimine platinum compound, an N—N migration probably via a five-coordinate intermediate (Fig. 3). This mechanism seems to be supported by the observation that the rate of N—N migration is enhanced by less electron-donating groups on the metal and by electron-withdrawing substituents on the sulfurdiimine, so that the five-coordinate intermediate is stabilized [18, 19]. Comparison with the analogous dialkylsuldurdiimine platinum compounds shows that the rates increase in the order R = aryl > alkyl for *trans*-$PtCl_2$(RN=S=NR)L, which is also in agreement with our proposed mechanism, as the aryl group is more electron-withdrawing than the alkyl groups we used.

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* Except for the di-2,4,6-mesitylsulfurdiimine.

Subsequent papers will deal with compounds of other metals and with cationic compounds in order to study the effects of variation of the metal and variation of the formal charge on the complex.

Acknowledgement

We thank Mr. D. Prins for the analyses, Mr. A.M. Wilmans for recording the ^{13}C NMR spectra and Dr. A. Oskam for valuable help and discussions.

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