Journal of Organometallic Chemistry, 108 (1976) 271—280

CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

IV *. ^{1}H AND ^{13}C NMR STUDIES OF THE INTRA- AND INTER-MOLECULAR EXCHANGE PROCESSES OF CATIONIC DIALKYLSULFURDIIMINE COMPOUNDS OF Rh^{I}, Ir^{I} AND Pt^{II}

J. KUYPER, L.G. HUBERT-PFALZGRAF **, P.C. KEIJZER and K. VRIEZE*

Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam (The Netherlands)

(Received October 21st, 1975)

Summary

The preparation and properties are described of *trans*-$[(Ph_3P)_2(CO)M(R{-}N{=}S{=}N{-}R)][ClO_4]$ (M = Rh^{I}, Ir^{I}; R = Me, Et, i-Pr, t-Bu) and of *cis*- or *trans*-$[L_2Pt(R{-}N{=}S{=}N{-}R)X][ClO_4]$ (X = Cl^{-}, L = Et_2S, $PhMe_2As$, $PhMe_2P$, R = Me, t-Bu; X = CH_3, L = $PhMe_2P$, R = Me).

^{1}H and ^{13}C NMR data show the existence of various isomers in solution which may interconvert via intra- and inter-molecular exchange processes. A general reaction scheme for the intramolecular exchange processes is discussed.

Introduction

The chemistry of compounds containing S—N bonds has recently become an area of increasing interest. On the one hand, for example, it has been found that $(SN)_x$ has metallic properties [1] and on the other hand it has been observed that sulfurdiimines R—N=S=N—R (R = alkyl or aryl) have interesting properties when coordinated to metal atoms in complexes [2—7].

In previous publications [2—4] it has been shown that for Pd^{II} and Pt^{II} isostructural series can be prepared of the general formula *trans*-$[MX_2(R{-}N{=}S{=}N{-}R)L]$ where X is a halide and L is a Group V or Group VI donor ligand. Two isomers I and II were found for R = Me, Et, i-Pr and neo-Pe [2,4] (Fig. 1), while isomer I was observed for R = t-Bu [2,4] for both Pd^{II} and

---

* For parts I, II and III see refs. 2, 3 and 4 respectively.

** Present address: Laboratoire de Chimie Minérale et Structurale, Faculté des Sciences, Parc Valrose, Nice (France).

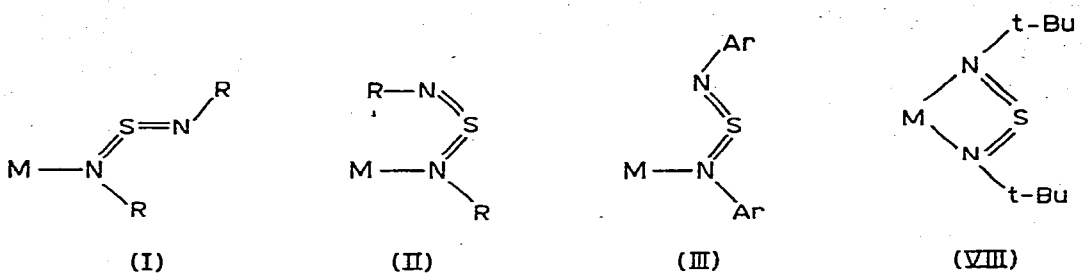

Fig. 1. Established coordination modes for dialkyl- and diaryl-sulfurdiimines bonded to a metal atom.

Pt^{II}. If R = aryl, configuration III is the preferred isomeric structure [3,4]. Finally, it was shown for $[M(CO)_4(R—N=S=N—R)]$ with M = Cr, Mo, W [5—7] that the sulfurdiimine may also act as a bidentate (Fig. 1).

Exchange processes involving the sulfurdiimine group were observed for both Pd^{II} and Pt^{II}. Intramolecular processes dominated in the case of the Pt^{II} compounds [2], intermolecular ones in the case of the Pd^{II} compounds [4].

We describe below studies of the preparation and kinetic properties of a new series of cationic complexes of Rh^I, Ir^I and Pt^{II}, directed at investigating the influence of the charge on the complex, the oxidation state of the metal atom and the steric influence of the other ligands.

Experimental

All compounds were prepared under dry air except for the iridium complexes which were prepared under dry anhydrous nitrogen. All solvents were dried before use.

Preparation of $[(Ph_3P)_2(CO)M(R—N=S=N—R)]\,[ClO_4]$ ($M = Rh^I, Ir^I$; R = Me, Et, i-Pr, t-Bu)

Dialkylsulfurdiimine (3 mmol, if R = Me, Et or i-Pr and 6 mmol if R = t-Bu) was added to a stirred solution of $[(Ph_3P)_2(CO)M(ClO_4)]$ [8] (2 mmol) in benzene (20 ml). An oily (R = Me) or solid (R = Et, i-Pr, t-Bu) precipitate was formed. Hexane (20 ml) was added and the mixture was cooled to —10°C. After a few hours the precipitate was isolated by decantation or by filtration. Recrystallization from a dichloromethane/hexane mixture containing some sulfurdiimine gave the pure crystalline compounds in 60—80% yield.

Preparation of cis-$[L_2Pt(R—N=S=N—R)Cl]\,[ClO_4]$ (R = Me, t-Bu; L = Et_2S, $PhMe_2P$, $PhMe_2As$)

$AgClO_4$ (2 mmol) in benzene (8 ml) was added dropwise to a solution of L_2PtCl_2 (2 mmol) in dichloromethane (20 ml). After 30 min stirring the AgCl was filtered off and dimethyl sulferdiimine (DMSD) (3 mmol) or di-t-butylsulfurdiimine (DBSD) (6 mmol) was added to the stirred solution. After concentration under vacuum to a small volume (~10 ml), hexane (10 ml) was added. The oily precipitate, isolated by decanting the liquid layer, was washed with hexane and subsequently vacuum dried for two hours. The DBSD compounds were obtained as solids, the DMSD compounds as oils in yields of 60—85%.

TABLE 1

ANALYTICAL DATA FOR THE CATIONIC Rh^{I}, Ir^{I} AND Pt^{II} COMPOUNDS

Compound	Colour	M.p. [a] (°C)	Analysis found (calcd.) (%)			
			C	H	S	P
$[(Ph_3P)_2(CO)Rh(DMSD)][ClO_4] \cdot CH_2Cl_2$	yellow	86—87	50.58 (51.65)	4.30 (4.12)	3.39 (3.45)	
$[(Ph_3P)_2(CO)Rh(DESD)][ClO_4] \cdot \frac{1}{2}CH_2Cl_2$	yellow	>150	54.45 (54.44)	4.58 (4.52)	3.51 (3.50)	6.9 (6.77)
$[(Ph_3P)_2(CO)Rh(DiPrSD)][ClO_4] \cdot CH_2Cl_2$	yellow	>130	53.42 (53,59)	4.74 (4.70)	3.06 (3.25)	6.2 (6.28)
$[(Ph_3P)_2(CO)Rh(DBSD)][ClO_4] \cdot CH_2Cl_2$	orange-brown	>165	52.46 (54.47)	4.77 (4.97)	2.94 (3.16)	
$[(Ph_3P)_2(CO)Ir(DMSD)][ClO_4] \cdot \frac{1}{2}C_6H_6$ [b]	yellow	>130	52.10 (51.82)	4.24 (4.04)	3.31 (3.29)	6.4 (6.36)
$[(Ph_3P)_2(CO)Ir(DESD)][ClO_4] \cdot \frac{1}{2}CH_2Cl_2$	yellow	>150	49.65 (49.60)	4.07 (4.11)	3.35 (3.19)	6.2 (6.17)
$[(Ph_3P)_2(CO)Ir(DiPrSD)][ClO_4] \cdot CH_2Cl_2$	yellow	>140	49.96 (49.14)	4.57 (4.31)	3.01 (2.99)	5.8 (5.76)
$[(Ph_3P)_2(CO)Ir(DBSD)][ClO_4] \cdot CH_2Cl_2$	orange-brown	>160	50.12 (50.06)	4.61 (4.57)	2.85 (2.90)	5.7 (5.61)
$[(PhMe_2P)_2Pt(DMSD)Cl][ClO_4] \cdot \frac{1}{2}C_6H_6$	light-yellow	oil	34.94 (34.30)	4.37 (4.25)	4.20 (4.36)	
$[(PhMe_2P)_2Pt(DMSD)Me][ClO_4]$	white	oil	32.17 (33.75)	4.33 (4.62)	4.71 (4.74)	
$[(PhMe_2As)_2Pt(DMSD)Cl][ClO_4] \cdot \frac{1}{2}C_6H_6$	light-yellow	oil	30.62 (30.63)	3.71 (3.79)	3.92 (3.89)	
$[(Et_2S)_2Pt(DBSD)Cl][ClO_4]$	yellow	96—98	26.90 (28.06)	5.34 (5.59)	13.09 (14.04)	

[a] Or decomposition points (> ... °C). [b] Not recrystallized from CH_2Cl_2/hexane.

The compound *trans*-$[(PhMe_2P)_2PtMe(Me—N=S=N—Me)][ClO_4]$ (oil) was prepared analogously at −10°C in 70% yield.

The C,H,P and S analyses (Table 1) were carried out in this laboratory. ^1H NMR and ^{13}C NMR spectra were recorded on a HA 100 and CFT 20 Varian spectrometer.

Results

Structural characterization of trans$[(Ph_3P)_2(CO)M(R—N=S=N—R)][ClO_4]$ *($M = Rh^I, Ir^I$; R = Me, Et, i-Pr, t-Bu)*

Reactions of $[(Ph_3P)_2(CO)M(ClO_4)]$ ($M = Rh^I, Ir^I$) with DMSD, diethyl sulfurdiimine (DESD), di-iso-propyl sulfurdiimine (DiPrSD) and DBSD afforded compounds of the general formula *trans*-$[(Ph_3P)_2(CO)M(R—N=S=N—R)][ClO_4]$

1. R = Me and R = Et. The ^1H NMR (Table 2), ^{13}C NMR (Table 3) and IR data (Table 4) are in accord with the above formulation.

The NMR data for DMSD show the existence of two isomers with configurations I and II (Fig. 1 and 2) analogous to the complexes $[MCl_2(DMSD)L]$ [2,4]. Moderately large upfield shifts in comparison to the complexes $[MCl_2(DMSD)L]$ were observed, which is probably due to the shielding by the two Ph_3P ligands.

In the case of DESD only isomer I was observed. Isomer II does not exist

TABLE 2

^{1}H NMR DATA FOR $[(Ph_3P)_2(CO)M(R—N=S=N—R)][ClO_4]$ (M = Rh, Ir)

(ppm relative to TMS in $CDCl_3$)

M	R	Isomer [a]	T (°C)	N—CH_{3-n} resonances [b] of R			$(CH_3)_n$ resonances [b] of R		
				Ia, IIa		Ib, IIb, VIII	Ia', IIa'		Ib', IIb', VIII'
Rh	CH_3	I	−60	3.17		2.55			
			35		2.92(br)				
Rh	CH_3	II	−60	4.16		2.86			
			35		3.32				
Ir	CH_3	I	−60	3.17		2.58			
			35	3.24		2.56			
Ir	CH_3	II	−60	4.16		2.89			
			35		3.40				
Rh	CH_2CH_3	I	−60	3.31		2.73	0.95		1.29
			35		3.23(br)			1.09(br)	
Ir	CH_2CH_3	I	30	3.46		2.97	0.98		1.18
Rh	$CH(CH_3)_2$	I	−60	3.91		3.55	1.02		0.92
			35		3.99			0.96	
Rh	$CH(CH_3)_2$	VIII	−60			~3.55			1.02
			35			3.62 [c]			1.00 [c]
Ir	$CH(CH_3)_2$	I	−60	4.22		3.56	1.05		0.89
Ir	$CH(CH_3)_2$	VIII	−60			~3.60			0.89
Rh	$C(CH_3)_3$	VIII [d]	−60 [e]						1.02
Ir	$C(CH_3)_3$	VIII [d]	−60 [e]						1.16

[a] The isomer ratio I/II = 3 and I/VIII = ~2. [b] For the assignment see Fig. 2. All resonances shift appreciably with the temperature except for R = CH_3. [c] Data obtained by the addition of free DiPrSD. [d] Also no splitting of the resonance at −80°C in CH_2Cl_2. [e] At 30°C about 50% dissociation with the formation of free DBSD.

for the Rh^I and Ir^I compounds probably because of the steric influence of the two triphenylphosphine ligands, which are both *cis* to the sulfurdiimine. Isomer II has been found in the case of *trans*-$[MCl_2(DESD)L]$ [2,4], since only one large ligand L is present *trans* to the sulfurdiimine group.

R = i-Pr and t-Bu. In the case of R = t-Bu both ^{1}H and ^{13}C NMR (Tables 2 and 3) show even at −70° to −80°C the presence of only one isomer, which

TABLE 3

^{13}C NMR DATA [a] FOR $[(Ph_3P)_2(CO)Ir(R—N=S=N—R)][ClO_4]$

(ppm relative to TMS in $CDCl_3$ at −65°C)

R	Isomer	N—$^{13}CH_{3-n}$ resonances [b] of R	$(^{13}CH_3)_n$ resonances [b] of R	P—^{13}C [a] (J(P—^{13}C) in Hz)
CH_3	I	41.92; 40.11		128.59(55)
CH_3	II	45.52; 39.97		—
CH_2CH_3	I [c]	50.35; 48.46	17.98; 16.07	128.75(55)
$CH(CH_3)_2$	I	56.71; 56.31	25.15; 22.75	128.72(53)
$CH(CH_3)_2$	VIII	57.63	—	—
$C(CH_3)_3$	VIII	64.13	32.40	130.35(46)

[a] The ^{13}C resonances of Ph_3P are observed as triplets except for the *para*-^{13}C resonance, which is observed as a singulet. [b] See also Fig. 2. [c] In $CH_2Cl_2/CDCl_3$ at −75°C.

TABLE 4

THE CARBONYL STRETCHING FREQUENCIES OF $[(Ph_3P)_2(CO)M(R{-}N{=}S{=}N{-}R)][ClO_4]$ (Nujoll)

M	R	ν(CO) cm^{-1}
Rh	CH_3	1997 (br)
Rh	CH_2CH_3	1989
Rh	$CH(CH_3)_2$	2000
Rh	$C(CH_3)_3$	1989
Ir	CH_3	1988(br)
Ir	CH_2CH_3	1994, 1983
Ir	$CH(CH_3)_2$	1990
Ir	$C(CH_3)_3$	1980

has just one proton signal for the CH_3 groups, one signal for the $^{13}C(CH_3)_3$ and one for the $^{13}CH_3$ carbons. There is no exchange with free sulfurdiimine even at elevated temperatures in the NMR time scale. The NMR data might be explained if the DBSD complex has configuration III with both sides of the sulfurdiimine interchanging their positions very rapidly and intramolecularly. Such a rapid exchange, however, at such low temperatures has never been observed for configuration III [3]. A much more likely structure is configuration VIII; i.e. the compound is five-coordinate with the sulfurdiimine acting as a bidentate (Fig. 1), a situation which has been observed for $[M(CO)_4(DBSD)]$ [5—7].

This view seems to be supported by the observation that in the case of the i-Pr group, for which two isomers were found, one isomer shows the presence of two equivalent i-Pr groups. This isomer also probably has configuration VIII, R being a bulky group once again. The second isomer contains two inequivalent i-Pr groups and it is concluded (Tables 2 and 3) that this second isomer has the configuration I.

Kinetic behaviour of $[(Ph_3P)_2(CO)M(R{-}N{=}S{=}N{-}R)][ClO_4]$

1. R = Me and R = Et. In the case of the DMSD compounds the two methyl signals of the DMSD ligand of isomer II start to broaden at about —45°C for both M = Rh^I and Ir^I. This is also the same temperature at which the free DMSD molecule starts to become fluxional [2]. At +25°C the interconversion of both ends of the sulfurdiimine ligand of II is in the fast exchange. This process is intramolecular, as the rate is independent of the concentration of the complex and of the concentration of free DMSD.

Intermolecular exchange was observed for isomer I. The rate of this ex-

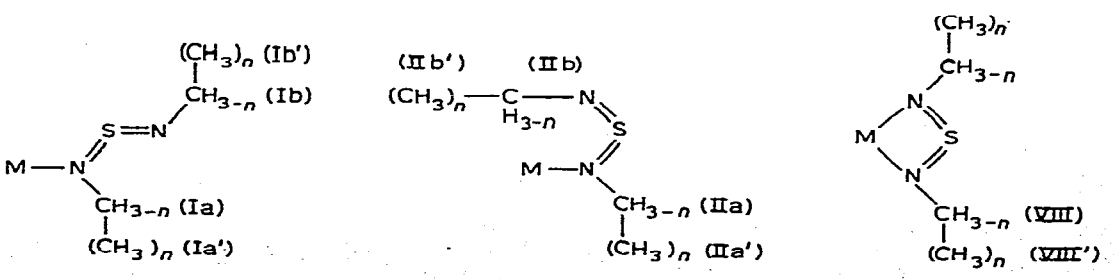

Fig. 2. The assignment of configurations I, II and VIII used for Tables 2, 3 and 5.

TABLE 5

^1H AND ^{13}C NMR DATA FOR THE CATIONIC PLATINUM COMPOUNDS

(ppm relative to TMS in $CDCl_3$)

Compound	NMR ^1H or ^{13}C	T (°C)	Isomer [a]	N—CH_{3-n} resonances [b]	$(CH_3)_n$ resonances [b]	Resonances [b] of L
$[(Et_2S)_2Pt(DBSD)Cl][ClO_4]$	^1H	−40	III		1.76; 1.55	3.06q, 2.99q; 1.46t, 1.43t
	^1H	30	III		1.65	~3.09, 3.00q; 1.50t, 1.42t
	^{13}C	−60	III	66.91, 65.48	33.53; 32.45	unresolved
	^{13}C	30	III	66.46	32.94	31.64(~65), 31.31(~65); 13.01(35), 12.56(35)
$[(PhMe_2P)_2Pt(DMSD)Cl][ClO_4]$	^1H	−60	I	3.94; 3.71(22)		1.88(36), 1.72(36) (J(P) 12 Hz)
	^1H	−60	II	4.50 [d]; 3.80(?)		unresolved
	^1H	30	I	3.87; 3.63(22)		1.85(36), 1.72(36) (J(P) 12 Hz)
	^1H	30	II	4.03 [c]		1.89(36), 1.70(36) (J(P) 12 Hz)
$[(PhMe_2P)_2PtMe(DMSD)][ClO_4]$ [e]	^1H	30	I	3.45; 3.13(20)		1.77t(32) (J(P) 7)
$[(PhMe_2As)_2Pt(DMSD)Cl][ClO_4]$	^1H	−40	I	3.90; 3.69(~26)		1.86(25), 1.70
	^1H	−40	II	4.51 [d]; 3.72(?)		unresolved
	^1H	30	I	3.86; 3.66(26)		1.76(25), 1.65(25)
	^1H	30	II	4.35 [c]; ...		1.81(25), 1.66(25)

[a] See also text. [b] See Fig. 2. J(Pt) in Hz is put in brackets, q = quartet, t = triplet. [c] Broad. [d] Probably broadened by J(Pt). [e] The Pt—Me resonance (triplet) is at 0.54 ppm, (J(P) 15 Hz, J(Pt) 77 Hz).

change, which in the presence of free sulfurdiimine started at about —50°C for Rh^I and about +35°C for Ir^I increased with increasing concentration of free sulfurdiimine.

In the absence of added sulfurdiimine this intermolecular exchange process commenced at about +10°C and +45°C for M = Rh^I and Ir^I respectively. Qualitative measurements of the concentration dependence of the rates showed that the exchange rate decreased with increasing concentration of the complex. It was impossible, however, to determine the kinetics properly, so that no reaction scheme will be proposed for this particular, and undoubtedly complicated situation.

In the case of the DESD complex the single isomer present (configuration I) participates in intermolecular exchange of diethylsulfurdiimine, which proceeds again much slower for Ir^I than for Rh^I.

2. R = i-Pr and R = t-Bu. In the case of R = i-Pr the isomer with configuration I is involved in an intermolecular exchange of sulfurdiimine similar to that for R = Et and R = Me, although the rate is slower.

Both the DBSD complex and the analogous DiPrSD compound show equivalent R groups, which are not involved in intermolecular exchange processes on the NMR time scale. No intramolecular transfer has to be proposed if the preferred structure VIII is accepted. If one assumes configuration III a very rapid intramolecular N—N jump has to occur, by analogy with $[PtCl_2(Ar—N=S=N—Ar)L]$ [3].

Finally, it should be noted that in the case of the DBSD compounds of Rh^I and Ir^I there is an appreciable but slow dissociation of the complexes, so that a relatively large amount of free DBSD is formed at higher temperatures. There is however, no observable ligand exchange on the NMR time scale between this configuration (VIII) and free DBSD.

Structural characterization and kinetic behaviour of $[L_2Pt(R—N=S=N—R)X][ClO_4]$

In the case of R = Me the compounds $[L_2Pt(DMSD)Cl][ClO_4]$ (L = $PhMe_2P$, $PhMe_2As$) are in the *cis*-configuration, since the two L groups are non-equivalent (Table 5). As with the neutral compounds $[PtCl_2(DMSD)L]$ [2], two configurations I and II were found (Table 5). The configuration II became fluxional at ~—25°C for L = $PhMe_2P$ and at ~0°C for L = $PhMe_2As$. Isomer I, however, remained rigid even at 30°C. The exchange observed for II, which interchange both ends of the sulfurdiimine, is intramolecular, as no exchange with DMSD occurred.

In the case of $[(PhMe_2P)_2Pt(DMSD)Me][ClO_4]$ the phosphine ligands are *trans* to each other, while in solution only configuration I, which is rigid even up to 30°C, seems to be present.

The compound *cis*-$[(Et_2S)_2Pt(DBSD)Cl][ClO_4]$ has, at —40°C, two inequivalent t-butyl groups (Table 5). At higher temperatures (—30°C) the resonances start to broaden and coalesce to one sharp signal above 10°C. The process is probably intramolecular, since the line shape changes are independent of the concentrations of the complex and of added free ligand. The compound probably has configuration III, as configuration II is not possible for steric reasons, and configuration I is an unlikely possibility since then fluxional behaviour would not be expected below 30°C.

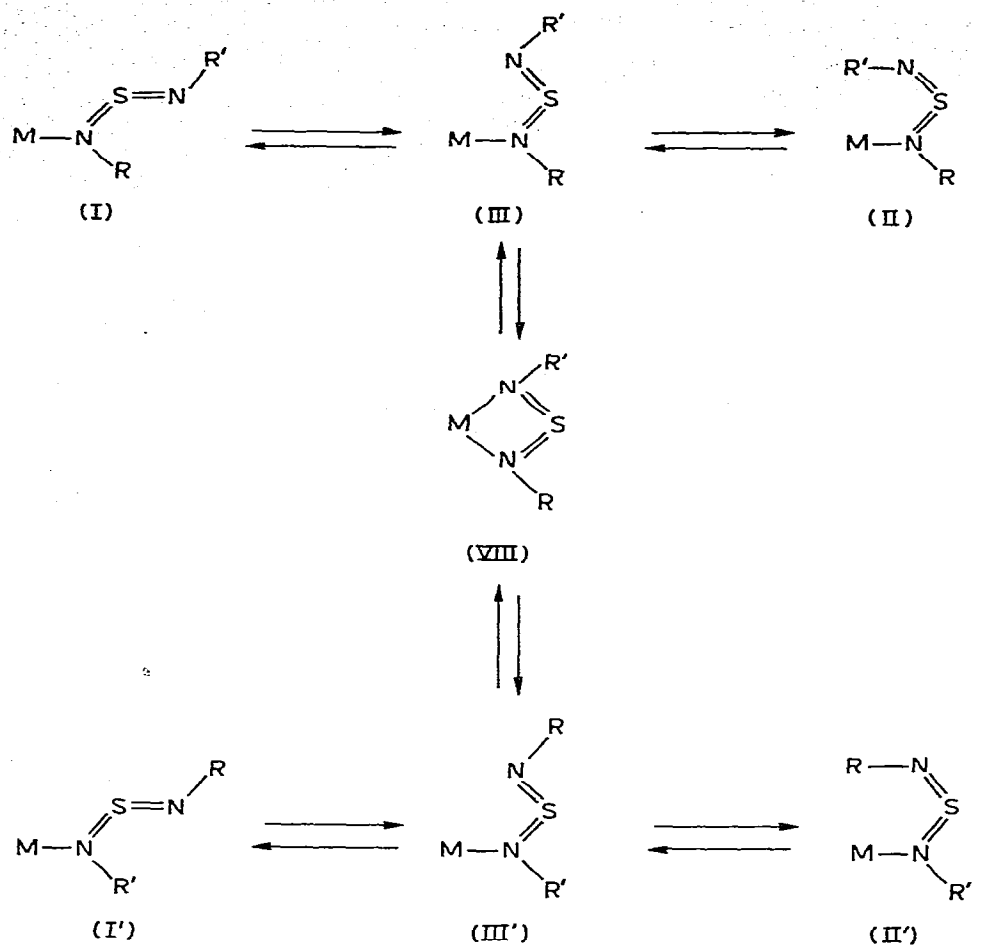

Fig. 3. The general reaction scheme for the intramolecular exchange processes observed for d^8-metal complexes.

Discussion

The work on cationic sulfurdiimine compounds of Rh^I, Ir^I and Pt^{II} presented here, and on the neutral compounds of Pd^{II} and Pt^{II} [2—4], has shown that the configurations I, II, III and VIII occur in the case of d^8-metal complexes.

In the case of the DMSD compounds configuration I and II always occur simultaneously except for $[(PhMe_2P)_2Pt(DMSD)Me][ClO_4]$ for which only I was observed, due, no doubt, to the influence of the *trans* methyl group. The formally nonbonding metal ··· H—C interactions, which were proposed previously [2,4], seem to stabilize the otherwise sterically unfavourable configuration II. The short metal ··· proton distance may be estimated from the geometry of *cis*, *trans*-DMSD in the gasphase (as determined by electron diffraction [9]) and

from the structure of *trans*-[$PtCl_2$(DBSD)(C_2H_4)] [10]. A value between 1.80 and 2.15 Å has been estimated from these data, which is very short indeed. In the case of the DESD and DiPrSD compounds configurations I and II have been observed for the neutral Pd^{II} and Pt^{II} compounds [2,4]. Steric factors, however, seem to hinder the formation of II for the Rh^I and Ir^I compounds, since they have two Ph_3P ligands *cis* to the sulfurdiimine. In the case of the DiPrSD compounds, however, another isomer, probably with configuration VIII is present for the Rh^I and Ir^I compounds. In the case of the neutral Pd^{II}- and Pt^{II}-(DBSD) complexes configuration I is only observed, as II does not exist for steric reasons [2,4]. In the case of [$(Et_2S)_2$Pt(DBSD)Cl] [ClO_4] structure III seems the preferred configuration, as proposed for [$PtCl_2$(Ar—N=S=N—Ar)L] [3] (Ar = aryl). For the Rh^I and Ir^I compounds of DBSD only one isomer exists, and this probably has configuration VIII. Models show that in this form the metal atom and the phosphine ligands are further away from the t-butyl groups. This isomer is formed preferentially if R is a bulky group (i-Pr, t-Bu) since there are two bulky ligands L.

The intramolecular exchange processes may be most fruitfully discussed with the aid of the general reaction scheme shown in Fig. 3.

In this scheme three reaction steps can be distinguished i.e.: I ↔ III, II ↔ III and III ↔ VIII, which can explain all observed processes. The step II ↔ III probably involves an inversion (or less likely a rotation) of the N=S bond at the non-coordinated side of the sulfurdiimine group. It is expected that this step will commence at about the same temperature as the fluxional movement of the free sulfurdiimine. The step I ↔ III involves a rotation (inversion is not possible) about the N=S bond of the coordinated side of the sulfurdiimine. The third step III ↔ VIII involves the formation of a five-coordinate species VIII, where the sulfurdiimine acts as a bidentate. It is expected that the steps II ↔ III and I ↔ III, while different, will each of them change relatively little in rate with a change of metal atom and of the other ligands present. The step III ↔ VIII, however, is expected to be very sensitive to factors, such as the oxidation state, the charge on the complex and the other ligands.

In the case of the neutral compounds [$PtCl_2$(R—N=S=N—R)L] (R ≠ t-Bu) the process I ↔ III ↔ II, which is relatively insensitive to L, occurs above 30°C, while the process III ↔ VIII ↔ III′, which is much more dependent on L, commences above 60°C [2]. This shows, that the step III ↔ VIII is more difficult than the other two steps. The situation is different, however, for other compounds, since the process II ↔ III ↔ VIII ↔ III′ ↔ II′ is observed for [$(Ph_3P)_2$(CO)M(DMSD)][ClO_4] (M = Rh^I, Ir^I) at 45°C, for [$(PhMe_2P)_2$-Pt(DMSD)Cl] [ClO_4] at about −25°C, for [$PdCl_2$(R—N=S=N—R)$PhMe_2As$] (R ≠ t-Bu) at about −20°C [4] and for [$(PhMe_2As)_2$Pt(DMSD)Cl][ClO_4] at about 0°C. The ease of this process is caused by the facile formation of the five-coordinate intermediate VIII for the charged complexes of Rh^I, Ir^I and Pt^{II} [12]. Indeed in the case of the compounds of Rh^I and Ir^I the temperature at which the whole process starts is similar to the temperature at which the free DMSD molecule becomes fluxional [2]. This clearly indicates that the step III ↔ VIII may start at about the same temperature as the step II ↔ III or even at a lower temperature.

As a consequence of the above one may further deduce that the step

I ↔ III, observed for $[PtCl_2(R—N=S=N—R)L]$ with R ≠ t-Bu [2], starts at about 30°C and is rate determining in the process I ↔ III ↔ II.

The step III ↔ VIII can be studied separately for $[PtCl_2(Ar—N=S=N—Ar)L]$ [3] and for $[(Et_2S)_2Pt(DBSD)Cl][ClO_4]$, since they probably occur only as isomer III. The process III ↔ VIII ↔ III′ (N—N jump) starts at about 0 and —30°C respectively, which accordingly lie in the range of temperatures discussed above for the process II ↔ III ↔ VIII ↔ III′ ↔ II′, where III ↔ VIII ↔ III′ is rate determining.

In conclusion it can be said that the N—N jump via the five-coordinate complex, which, in contrast to the two other steps, is very sensitive to the metal atom and its surroundings, may therefore start at temperatures varying from at least —45°C to 60°C. The rate of the exchange decreases in the order: Rh^I, Ir^I > neutral Pd^{II}, cationic Pt^{II} > neutral Pt^{II}.

A final point is the observation of intermolecular reactions for the isomer I of the cationic compounds of Rh^I, Ir^I and Pt^{II}, which is analogous to the situation for isomer I of neutral $[PdCl_2(DMSD)L]$ [4], while they are only rarely observed, and then only at high temperatures, for isomer II, as in the case of $[PdCl_2(DMSD)L]$ [4]. This difference in behaviour between isomers I and II is undoubtedly due to the effective five-coordination of II, since generally intermolecular exchange for d^8-compounds proceeds less easily for five- than for four-coordinated compounds.

References

1 R.L. Greene, G.B. Street and L.J. Suter, Phys. Rev. Lett., 34 (1975) 577.
2 J. Kuyper and K. Vrieze, J. Organometal. Chem., 74 (1974) 289.
3 J. Kuyper and K. Vrieze, J. Organometal. Chem., 86 (1975) 127.
4 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 108 (1976) 257.
5 R. Meij, J. Kuyper, D.J. Stufkens and K. Vrieze, to be published.
6 R. Meij and K. Olie, Cryst. Struct. Commun., 4 (1975) 575.
7 W.E. Lindsell and G.R. Faulds, J. Chem. Soc. Dalton, Trans., (1975) 40.
8 J. Peone Jr. and L. Vaska, Angew. Chem., 83 (1971) 497.
9 J. Kuyper, P.H. Isselman, F.C. Mijlhoff, A. Spelbos and G. Renes, J. Mol. Struct., in press.
10 R.T. Kops, E. van Aken and H. Schenk, Acta Crystallogr. B, 29 (1973) 913.
11 J. Kuyper, K. Vrieze and A. Oskam, J. Organometal. Chem., 46 (1972) C25.
12 A.D. Westland, J. Chem. Soc., (1965) 3060.