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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

III *. ^{1}H NMR STUDIES OF THE INTRA- AND INTER-MOLECULAR EXCHANGE PROCESSES OF DIALKYLSULFURDIIMINE COMPOUNDS OF PALLADIUM(II)

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Summary

The preparation, properties and kinetic behaviour of *trans*-[$PdCl_2$(RN=S=NR)L] (L = $PhMe_2As$ and Et_3As; R = Me, Et, i-Pr and t-Bu) are reported.

In the case of R = t-Bu only one isomer, which participates in various intermolecular exchange reactions, is found. For R = Me, Et and i-Pr two isomers occur in solution. The most abundant isomer, which has a structure analogous to the t-butyl compound, is similarly involved in intermolecular exchange reactions of the sulfurdiimine. However, the second isomer, in which non-bonded Pd···H—C interactions between the metal atom and the uncoordinated end of the sulfurdiimine group are probably present, does not participate in intermolecular exchange reactions if free sulfurdiimine is present. For this isomer fluxional behaviour is observed.

Introduction

Previous work on cumulated double bond systems as ligands has shown that in the case of the allenes the metal atom is bonded to one of the olefinic double bonds [1—4], while the sulfurdiimines coordinate via one or both of the N atoms [5—9]. It has been found that sulfurdiimines can coordinate to the metal atom in four different ways, as shown in Fig. 1, i.e. with the sulfurdiimine in the *cis*, *trans* configuration (isomers I and II) [5], in the *trans,trans* configuration [6]

* For Parts I and II see refs. 5 and 6.

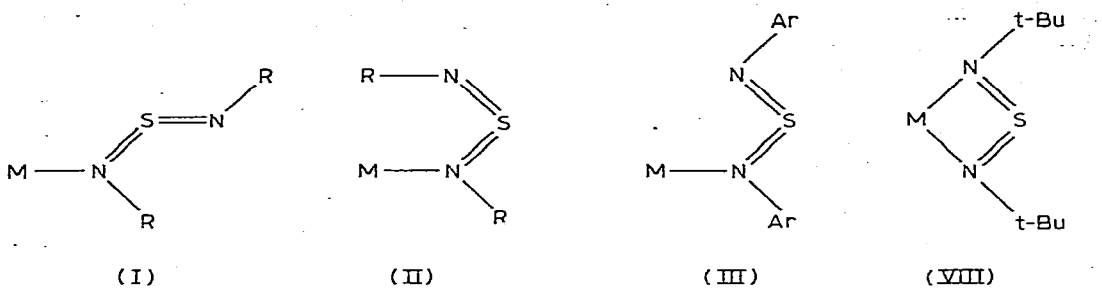

Fig. 1. Known coordination modes of dialkyl- or diaryl-sulfurdiimines to metal atoms.

(isomer III) and in the *trans,trans* configuration as a bidentate ligand, which was observed for $(CO)_4Mo$(t-BuN=S=N-t-Bu) [7—9].

^1H NMR studies have shown that with $[PtCl_2(RN{=}S{=}NR)L]$ (R = Me, Et, i-Pr and n-Pe) [5] isomers I and II interconvert via two distinct intramolecular reaction paths. The first one occurs at ambient temperatures and involves only rotations about the N=S bonds and/or inversions at N. At higher temperatures the platinum may also jump from one N atom to the other and vice versa (N—N jump) (see Fig. 3 and 7 of ref. 5). In the case of R = t-Bu isomer I was the only one observed. For this isomer a combination of N=S rotations and intramolecular N—N jumps have been found. For R = aryl (isomer III, Fig. 1) the intramolecular N—N jump is the only process observed [6].

In this report the analogous palladium compounds are discussed. It will be shown that, although the structural characteristics are very similar, the kinetic behaviour is completely different from the platinum systems since intermolecular reactions are dominant due to the ready dissociation of the Pd—N bond.

Experimental

Preparation of $[PdCl_2(RNSNR)(PhMe_2As)]$ (R = Me, Et and i-Pr).

Dialkylsulfurdiimine (1.1 mmol) was added to a stirred suspension of $[PdCl_2(PhMe_2As)]_2$ (0.5 mmol) in dichloromethane (5 ml)/hexane (5 ml). After filtration of the resultant solution, the orange filtrate was concentrated to half of its volume and some dialkylsulfurdiimine (~1 mmol) was added. Addition of hexane (10 ml) afforded precipitates of red-brown oils (R = Me, Et) or a yellow-orange crystalline solid (R = i-Pr) precipitate. The yields were increased to a total of 50—80% by further precipitation at −30°C. With Et_3As and $PhMe_2P$ (when large excesses of sulfurdiimine were necessary) analogous products were obtained. The compounds decompose slowly in air at room temperature when R = Me and Et, but with R = i-Pr the complex is fairly stable.

Preparation of $[PdCl_2(t\text{-}BuNSN\text{-}t\text{-}Bu)(PhMe_2As)]$

Di-t-butylsulfurdiimine (DBSD) (3 mmol) was added to a suspension of $[PdCl_2(PhMe_2As)]_2$ (1 mmol) in 5 ml dichloromethane. After filtration the solvent was removed under vacuum and then compressed air was blown over the oily residue until crystallization was nearly completed, after which some crystals were collected. Thereafter DBSD (7 mmol) was added to the residue and the

TABLE 1

ANALYTICAL DATA FOR $[PdCl_2(RNSNR)L]$

Compound [a]	M.p. (°C)	Analysis found (calcd.) (%)	
		C	H
$PdCl_2(DMSD)(PhMe_2As)$	oil	26.45 (26.72)	3.64 (3.81)
$PdCl_2(DESD)(PhMe_2As)$	oil	30.24 (30.18)	4.24 (4.43)
$PdCl_2(DiPrSD)(PhMe_2As)$	80.8—81.1	32.85 (33.25)	4.82 (4.98)
$PdCl_2(DiPrSD)(Et_3As)$	38.5—40	28.62 (29.68)	5.65 (6.02)
$PdCl_2(DBSD)(PhMe_2As)$	88.5—89	35.86 (36.00)	5.33 (5.48)

[a] The complexes are structurally completely analogous to the compounds $[PtCl_2(RNSNR)L]$ [5] so that only C and H analyses were carried out.

mixture was dissolved in a minimum of warm CH_2Cl_2 (30%)/hexane (70%). The solution was quickly cooled to −30°C and the collected crystals were added to avoid the precipitation of the dimer. Orange air-stable crystals were obtained at −30°C in 70% yield. Et_3As gave similar results but with $PhMe_2P$ dimer was always obtained.

Reactions of $[PdCl_2L]_2$ with diarylsulfurdiimines

Attempted preparations of the analogous diarylsulfurdiimine compounds failed. However, ^1H NMR spectra at −10°C of solutions of $[PdCl_2L]_2$ with excess diarylsulfurdiimine showed clearly the existence of complexes $[PdCl_2(RNSNR)L]$, which are isostructural with $[PtCl_2(RNSNR)L]$ [6].

The C and H analyses were carried out in this laboratory (see Table 1). ^1H NMR spectra were recorded on a HA 100 Varian spectrometer. Methanol was used in the temperature calibrations. The exchange rates were calculated in the slow exchange limit [10].

Results

Dimethyl- (DMSD), diethyl- (DESD), diisopropyl- (DiPrSD) and di-t-butylsulfurdiimine (DBSD) react with the dimer $[PdCl_2L]_2$ (L = $PhMe_2P$, $PhMe_2As$ and Et_3As) according to:

$$[PdCl_2L]_2 + 2\ RN{=}S{=}NR \rightleftharpoons 2\ PdCl_2(RN{=}S{=}NR)L$$

Except for DBSD the equilibrium lies far enough to the right to allow the isolation of $[PdCl_2(RN{=}S{=}NR)L]$ if a slight excess of sulfurdiimine is present. If a large excess of DBSD is used, the isolation of $[PdCl_2(DBSD)L]$ is possible for L = $PhMe_2As$ and Et_3As. However for L = $PhMe_2P$ the dimer is always obtained. For this reason the complexes of $PhMe_2P$ were not investigated.

Structural characterization of $[PdCl_2(RN{=}S{=}NR)L]$

From the ^1H NMR data (Table 2) it is concluded that the isomeric forms in solution are analogous to those of $[PtCl_2(RN{=}S{=}NR)L]$ [5]. In the case of DBSD only one isomer has been formed (isomer I, Fig. 1), while two isomers have been observed in the case of DMSD, DESD and DiPrSD (isomers I and II,

TABLE 2

^{1}H NMR DATA FOR [$PdCl_2$(RNSNR)($PhMe_2As$)]

ppm relative to TMS in C_7D_8 or relative to CH_2Cl_2 in CH_2Cl_2/C_6H_6

R	Solvent [a]	T, (°C)	Isomer	Ratio I/II	N—CH_{3-n} resonances [b] of R		$(CH_3)_n$ resonances of R		Resonances of $PhMe_2As$	
					I_a or II_a	I_b or II_b	I_a' or II_a'	I_b' or II_b'	CH_3	*ortho*-H
CH_3	C_7D_8	−40	I	4.4	3.46	2.75			1.37	7.63
			II		3.15	4.41			1.30	7.54
	$C_7D_8/CDCl_3$	−50	I	4.6	3.43	2.88			1.35	....
			II		3.19	4.34			1.28	....
C_2H_5	C_7D_8	−40	I	1.7	4.18	3.13	1.49	0.75	1.37	7.63
			II		3.49	5.20	1.50	....	1.30	7.54
	CH_2Cl_2/C_6H_6	−30	I	1.9	−0.52	−1.23	−3.21	−3.73	−3.20	....
			II		−1.03	0.49	−3.12	−3.42	−3.23	....
i-C_3H_7	C_7D_8	−40	I	2	4.84	3.46	1.68	0.78	1.34	7.65
			II		3.54	7.50 [c]	1.50	1.21	1.27	7.48
	CH_2Cl_2/C_6H_6	−30	I	3	....	....	−3.13	−3.70	−3.31	....
			II		....	....	−3.23	−3.55	−3.33	....
t-C_4H_9	C_7D_8	−40	I				1.92	0.85	1.32	7.64
	CH_2Cl_2/C_6H_6	−20	I				−2.76	−3.53	−3.20	....

[a] The composition of the solvent mixtures are in weight %: 40% $CDCl_3$/60% C_7D_8 and 50% CH_2Cl_2/50% C_6H_6. [b] The II_b resonances are underlined. [c] Data obtained by NMDR.

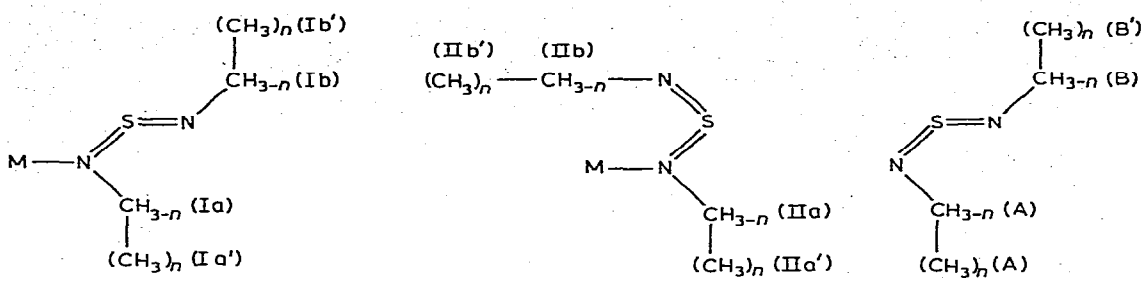

Fig. 2. *Observed isomers of* $[PdCl_2(R—N{=}S{=}N—R)(PhMe_2As)]$ (R = Me, Et, i-Pr and t-Bu) and the assignment for Table 2.

Fig. 1). The less abundant isomer II very likely has the alkyl group of the non-coordinated side of the sulfurdiimine above the coordination plane and close to the metal atom. This has been deduced, as in the case of the Pt compounds, from the observation that the underlined protons (IIb of Table 2, see also Fig. 2) of the $C\underline{H}_3$, $C\underline{H}_2CH_3$ and of the $C\underline{H}(CH_3)_2$ groups show unusually large downfield chemical shifts owing to the paramagnetic anisotropy [11] of the palladium atom.

In Table 3 it is shown that multiplication of the difference in chemical shifts between protons A of the free ligand and of IIb of the coordinated ligand (Fig. 2) by 3, 2 and 1 resp. for R = CH_3, CH_2CH_3 and $CH(CH_3)_2$ resp. gives an almost constant number, which may be compared with similar numbers of about 2.8—3.0 ppm, which have been obtained for isomer II of the analogous platinum complexes (Table 8 of ref. 5). This indicates clearly that the protons IIb are in surroundings similar to those in the analogous platinum complexes.

Kinetic behaviour of $[PdCl_2(DBSD)(PhMe_2As)]$

Mixtures of $[PdCl_2(DBSD)(PhMe_2As)]$ *and DBSD*

Line width measurements on the t-butyl signals of $[PdCl_2(DBSD)(PhMe_2As)]$ (= MD) in the concentration range of 0.05 to 0.22 mol l^{-1} and of DBSD (= D) in the concentration range of 0 to 0.60 mol l^{-1} at temperatures from 0 to +35°C in CH_2Cl_2/C_6H_6 solution (50/50 weight ratio) showed that the reciprocal of the lifetime τ of MD is proportional to [MD] (Fig. 3) and inversely proportional to [D] (Fig. 4).

TABLE 3

^1H NMR CHEMICAL SHIFT DIFFERENCE Δ BETWEEN THE II_b RESONANCE OF $[PdCl_2(RNSNR)(PhMe_2As)]$ AND THE A RESONANCE OF RNSNR

(*m* = number of protons of the $N—CH_{3-n}$ group

R	*m*	Δ (ppm)	Δ X *m*
CH_3	3	0.94	2.82
C_2H_5	2	1.37	2.74
$i\text{-}C_3H_7$	1	2.64	2.64

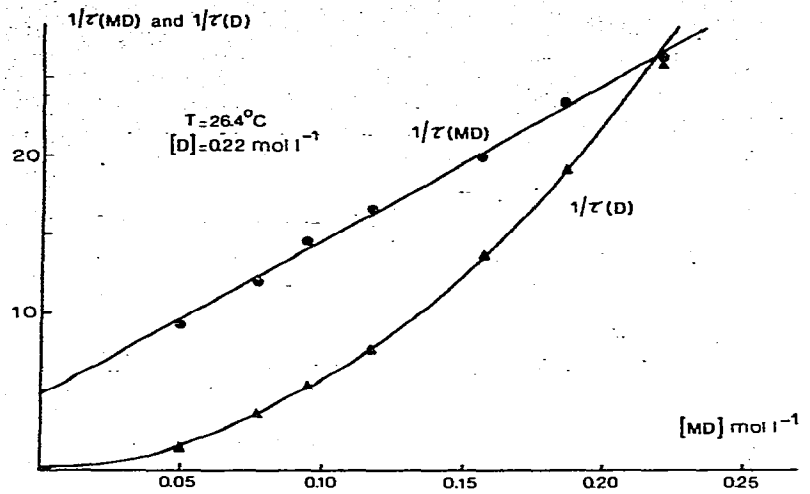

Fig. 3. Exchange rate for $[PdCl_2(DBSD)(PhMe_2As)]$ (= MD) and DBSD (= D) as a function of [MD] in mol l^{-1}.

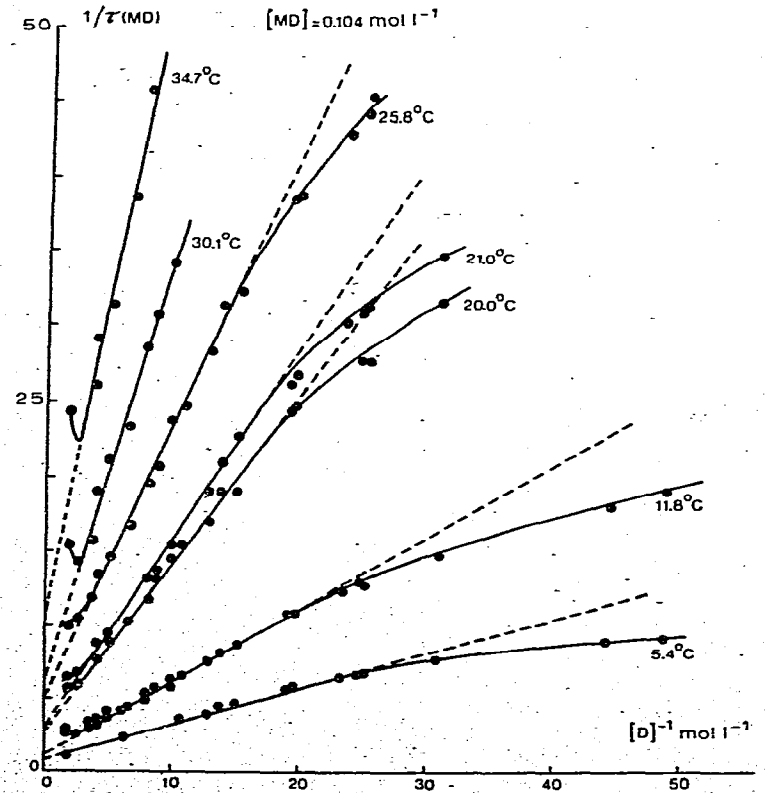

Fig. 4. Exchange rate for $[PdCl_2(DBSD)(PhMe_2As)]$ (= MD) as a function of the reciprocal of the weighed-in concentration of DBSD (= D) at different temperatures.

From Fig. 3 it is clear however that this is not the only term since the $1/\tau$ (MD) curve does not go through zero. It has been found that two terms have to be added, namely an ill defined term also showing a possible proportionality to [MD], but which is so small that it can be neglected, and a constant term. The rate formula (*a*) is:

$$1/\tau\,(\mathrm{MD}) = 10^{13.4\,\pm\,0.3}\exp(-16.8 \pm 0.3/RT)\,[\mathrm{MD}]/[\mathrm{D}]$$
$$+\,10^{12.9\,\pm\,1.0}\exp(-16.7 \pm 1.0/RT) + \text{negligible term} \qquad (a)$$

For the free DBSD ligand the following rate formula (*b*) applies (see Fig. 3 and 5).

$$1/\tau\,(\mathrm{D}) = 10^{13.4\,\pm\,0.8}\exp(-16.5 \pm 0.8/RT)\,[\mathrm{MD}]^2/[\mathrm{D}]^2 + \text{small term} \qquad (b)$$

At very low concentrations of added DBSD one finds that MD dissociates to a certain extent so that the actual concentration of DBSD is higher than the weighed-in concentration. This leads, particularly for the $1/\tau$ (MD) curve, to an apparent lowering of the $1/\tau$ (MD) values (Fig. 4). A linear relation is again obtained if it is assumed that the pure complex MD (0.104 *N*) is about 16 and 19% dissociated at temperatures of 5.4 and 11.8° C resp. These values can be calculated from the linewidths of the pure complex (0.104 *N*) at these temperatures (5.2 and 8.5 Hz resp.), if it is assumed that rate formula (*a*) is valid. The relatively high degree of dissociation is also reflected in the remarkable broadening of the methyl resonances of $PhMe_2As$ above —10° C if the concentration of added DBSD is low or zero. Above +10° C the signal is again sharp, as the intermolecular exchange processes become much more rapid.

At very high concentration of DBSD it was found that a term proportional to [D] has to be added. This term is, however, relatively small, as is clear from Fig. 4.

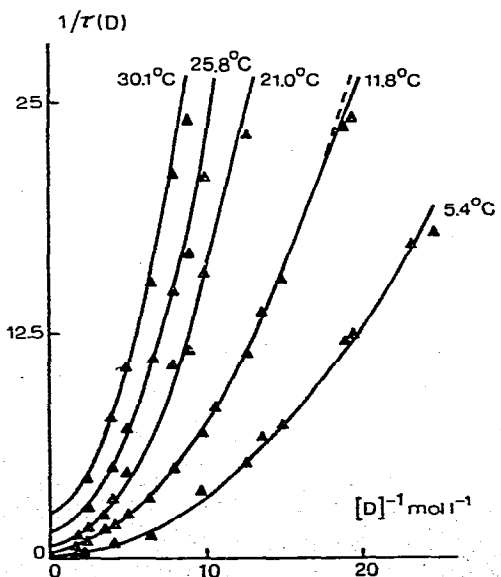

Fig. 5. Exchange rate for DBSD (= D) as a function of the reciprocal of the weighed-in concentration of DBSD with [MD] = 0.104 mol l^{-1}.

A similar behaviour for $1/\tau$ (MD) was observed if pure CH_2Cl_2 was used as solvent. Because of overlapping of signals it was, however, impossible to measure the linewidths of D accurately.

Mixtures of $[PdCl_2(DBSD)L]$ and $[PdCl_2L]_2$

In the presence of dimer $[PdCl_2L]_2$ (= M_2) there is no observable free DBSD so that only $1/\tau$ (MD) was measured. The measurements were carried out in CH_2Cl_2 owing to the low solubility of the dimer in CH_2Cl_2/C_6H_6. Although the rates are somewhat susceptible to this change of solvent, the mechanism of the intermolecular exchange is not affected.

The rate measurements show that $1/\tau$ (MD) is independent of [MD] and proportional to $[M_2]^{1/2}$ at higher $[M_2]$ values.

In Fig. 6 the solid curves show the dependence of $1/\tau$ (MD) on the weighed-in concentrations of $[M_2]$. The dotted lines, which go through zero as they should, are the curves corrected for the dissociation of the complex into dimer and ligand.

The amount of dissociation of the complex into dimer and free ligand can be estimated from the $1/\tau$ (MD) values for the pure complex MD. These are for example 8 sec^{-1} and 12 sec^{-1} at 7.9°C and 11.8°C resp. and correspond to a dissociation of about 16% and 20% resp. of the total amount of MD. If the concentrations are corrected for these dissociation equilibria the dotted curves are obtained which fit the expressions:

$1/\tau$ (MD) = $(115 \pm 5)[M_2]^{1/2}$ (at 7.9°C in CH_2Cl_2) and

$1/\tau$ (MD) = $(140 \pm 5)[M_2]^{1/2}$ (at 11.8°C in CH_2Cl_2).

Kinetic behaviour of $[PdCl_2(RN{=}S{=}NR)(Ph_2MeAs)]$ (R = Me, Et and i-Pr)

These systems were studied more qualitatively, but sufficiently thoroughly to be able to make the following conclusions. The methyl derivate is discussed first as this compound has been studied fairly extensively.

Mixtures of $[PdCl_2(DMSD)L]$ and DMSD

At −50°C ^1H NMR shows (Fig. 7) the existence of two isomers I and II (Fig. 1) in $C_7D_8/CDCl_3$ solution.

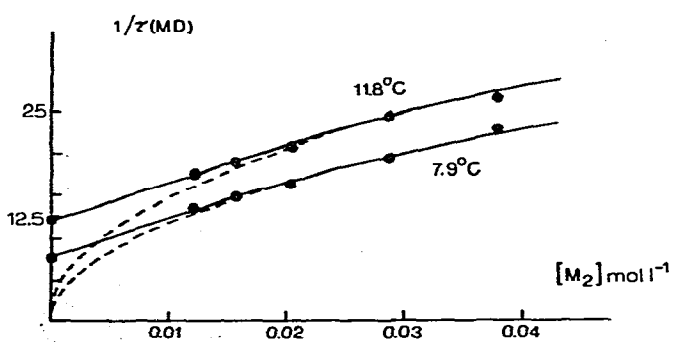

Fig. 6. Exchange rate for $[PdCl_2(DBSD)(PhMe_2As)]$ (= MD) as a function of the weighed-in concentration of $[PdCl_2(PhMe_2As)]_2$ (= M_2) with [MD] = 0.065 mol l^{-1}.

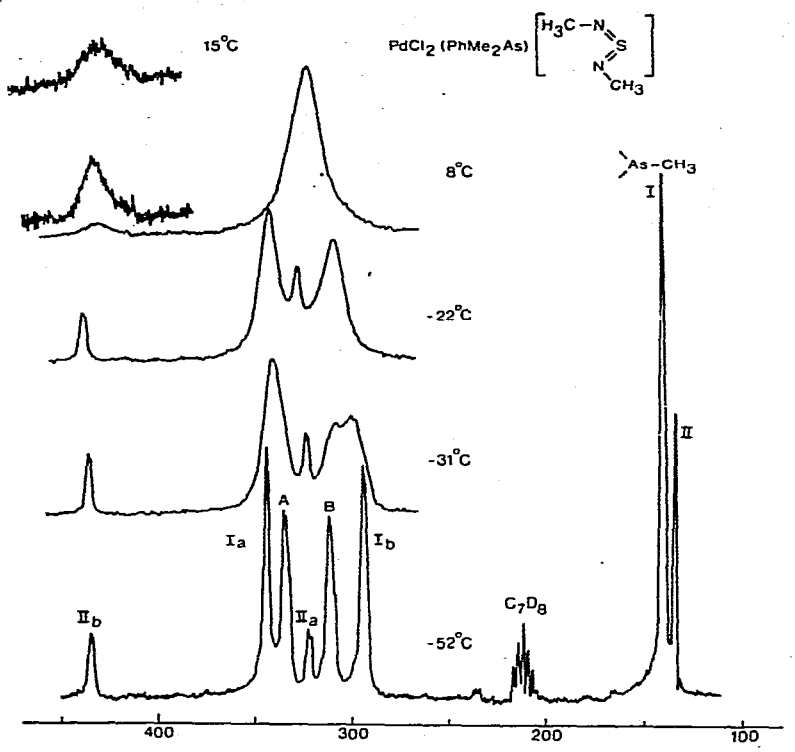

Fig. 7. ^{1}H NMR data for the system [$PdCl_2$(DMSD)($PhMe_2As$)] with DMSD at different temperatures (concentrations 0.3 mol l^{-1}).

From —50 to —22°C the signals of isomer II remain sharp. With isomer I, however, an intermolecular exchange occurs with free DMSD in the concentration range 0.1 to 0.3 mmol l^{-1} of MD and of 0 to 0.6 mol l^{-1} for D. This exchange is approximately proportional to the concentration of free DMSD if one measures $1/\tau$ (MD) and to the concentration of the ligand D if one measures $1/\tau$ (D). Of interest is the observation (Fig. 7) that exchange occurs between signals Ia and A and between Ib and B.

This implies, as is shown in Fig. 8, that the exchange is selective in the sense that the DMSD ligand attaches itself to the Pd atom via only the N atom of the *cis* side of the *cis,trans* isomer. It should be realised that in the temperature range —50 to —22°C DMSD is itself fluxional [5], but not in the rapid exchange limit.

Between —22 and +20°C one observes (Fig. 7) that signals Ia, Ib, A and B all exchange intermolecularly. This process becomes possible, as the exchange of A and B of the free DMSD is now more rapid.

In the same temperature range signals IIa and IIb also start to broaden. The broadening however, is due to an intramolecular process, as it is independent of the concentrations of D and MD, and the methyl resonances of the coordinated $PhMe_2As$ ligands of isomers I and II are still sharp. This means that there is only an intramolecular interchange of both sides of the coordinated sulfurdiimine

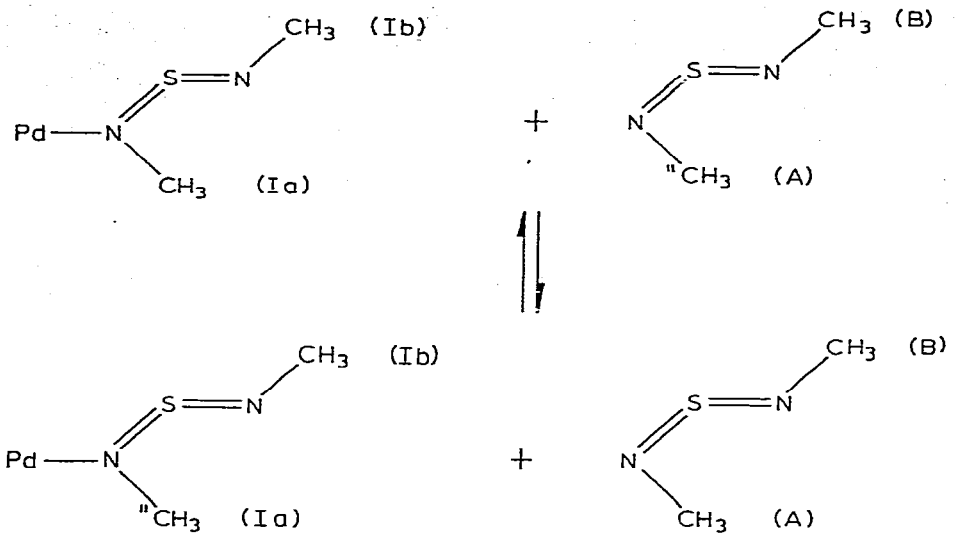

Fig. 8. Retention of the dimethylsulfurdiimine (DMSD) configuration in the exchange of DMSD with $[PdCl_2(DMSD)(PhMe_2As)]$ (reaction 6).

group in isomer II, and that there is no exchange with isomer I or with free DMSD.

At temperatures above +20°C isomers I and II start to exchange intermolecularly, as may be concluded from the broadening of the two methyl resonances of the coordinated arsine ligands.

Solutions of $[PdCl_2(DMSD)L]$

When no free ligand DMSD is present it was observed that above —30°C the signals Ia, Ib IIa and IIb broaden simultaneously. This is due to an intermolecular exchange of DMSD, as it is concentration dependent. The exchange probably proceeds via dimeric or monomeric species, which are formed from $[PdCl_2$-(DMSD)L] if no free DMSD is present.

Behaviour of $[PdCl_2(RN{=}S{=}NR)PhMe_2As]$ (R = Et and i-Pr)

The rate of the sulfurdiimine exchange of isomer I with free ligand increases with the concentration of sulfurdiimine. Comparison of the temperatures at which this direct ligand exchange becomes observable (D ~0.4 *N*) shows the following order of decreasing rate, as was measured on signals Ia, Ib, Ia′ and Ib′: DMSD (~—50°C) > DESD (~—35°C) > DiPrSD (~—10°C) > DBSD (~+10°C).

At lower concentrations of D it was found that DESD behaves similarly to DMSD, the rate increasing with increasing [D], although doing so less rapidly. However the DiPrSD system is similar to the DBSD system because the rates decrease with increasing [D].

The fluxional behaviour of isomer II, which was noted for R = Me has also been found for R = Et and i-Pr. The rates of this intramolecular interchange differ little for R = Me, Et and i-Pr, as in all cases signals IIa′ and IIb′ started to broaden at about the same temperatures (—25 to —18°C).

With DESD and the DiPrSD complex one can observe the fast exchange situ-

ation above +20°C i.e. a triplet and a doublet respectively for the collapsed resonances IIa′ and IIb′.

Discussion

From a structural point of view the compounds $[PdCl_2(RN{=}S{=}NR)L]$ are very similar to $[PtCl_2(RN{=}S{=}NR)L]$, since in the case of R = t-Bu only one isomer, I, is formed, while for R = Me, Et and i-Pr two isomers occur [5]. In view of the anomalously low-field chemical shift of protons IIb of isomer II it is concluded that for $[PdCl_2(RN{=}S{=}NR)L]$, also, the sterically rather unfavourable situation, which is shown in Fig. 1 is stabilized by formally non-bonding Pd···H—C interactions, causing isomer II to be effectively a five-coordinate compound. This has a great influence on its reactions when compared with those of the four-coordinate isomer I [5].

From a kinetic point of view the situation is, however, quite different, as the monomeric complexes $[PdCl_2(RN{=}S{=}NR)L]$ dissociate to form dimeric and monomeric species and free sulfurdiimine much more easily than the analogous platinum complexes. Therefore, while intramolecular processes dominated in the platinum systems [5], intermolecular exchanges are much more important for the palladium analogues.

With tertiary butyl derivatives, where the solutions initially contains dimer M_2, monomer MD, dissociated dimer M and ligand D, the following reactions may take place in principle (exchange reactions of $PhMe_2As$ are much slower under our reaction conditions):

The first reactions is the dissociation of MD:

$$MD \rightleftharpoons M + D \qquad (1)$$

The coordinatively unsaturated species $PdCl_2L$ may react with MD:

$$MD + M \rightleftharpoons M_2 + D \qquad (2)$$

and it may combine with another M:

$$2M \rightleftharpoons M_2 \qquad (3)$$

The dimer M_2 may react with D in two steps:

$$M_2 + D \rightleftharpoons M_2D \qquad (4)$$

$$M_2D + D \rightleftharpoons 2MD \qquad (5)$$

The complex MD may also exchange with D:

$$MD + D^* \rightleftharpoons MD^* + D \qquad (6)$$

via a five coordinate intermediate species MD_2. Finally MD may react with dimer M_2 and with MD itself:

$$MD + MM^* \rightleftharpoons M^*D + M_2 \qquad (7)$$

$$MD + MD^* \rightleftharpoons MD^* + MD \qquad (8)$$

One may also imagine reactions involving the intermediate species M_2D and MD_2, but they are not important. From the above reactions the following rate ex-

pressions may be derived:

$1/\tau\ (MD) = k_1 + k_2[M] + (k_{-5} + k_8)[MD] + k_6[D] + k_7[M_2]$

$1/\tau\ (D) = k_{-1}[M] + (k_{-2} + k_4)[M_2] + k_5[M_2D] + k_6[MD]$

In the presence of free D we have:

$[M_2] = (K_1^2K_3)[MD]^2/[D]^2$ and

$[M] = K_1[MD]/[D]$

Substitution yields:

$1/\tau\ (MD) = k_1 + k_2K_1[MD]/[D] + (k_{-5} + k_8)[MD] + k_6[D] + k_7K_1^2K_3[MD]^2/[D]^2$

and

$1/\tau\ (D) = k_1[MD]/[D] + (k_{-2} + k_4)K_1^2K_3[MD]^2/[D]^2 + k_{-5}[MD]^2/[D] + k_6[MD]$

In the presence of free dimer M_2 we have:

$[M] = K_3^{-1/2}[M_2]^{1/2}$ and

$[D] = K_1K_3^{1/2}[MD]/[M_2]^{1/2}$ so that

$1/\tau\ (MD) = k_1 + k_2K_3^{-1/2}[M_2]^{1/2} + (k_{-5} + k_8)[MD] + k_6K_1K_3^{1/2}[MD]/[M_2]^{1/2}$

$+ k_7[M_2]$

It was found, for mixtures of MD and D, that $1/\tau$ (MD) is proportional to [MD]/[D], while $1/\tau$ (D) is proportional to $[MD]^2/[D]^2$ in suitable concentration ranges, and that the activation parameters of $1/\tau$ (MD) and $1/\tau$ (D) are equal within the range of error. These results strongly indicate that in principle reaction +2 dominates for MD and reactions —2 and +4 dominate for D.

It should be realised, however, that —2 and +4 are similar, as they probably both proceed via a common intermediate M_2D. Reaction +1 is also measurable at high concentrations of D, while there are some indications that reactions —5 or +8 are significant.

It is understandable that the reaction of M_2 with D is observable although the reaction of D with M is not observable, since the concentration of M is much lower than that of M_2. It is remarkable however, that even with free D in solution one observes, for MD, a reaction with M rather than with D, although the latter reaction becomes observable at high concentrations of D (>0.4 *N*). The reason is probably that the di-t-butylsylfurdiimine ligand is so bulky that five-coordination i.e. the intermediate species MD_2 in reaction 6 is not easily achieved. On the other hand M is a coordinatively unsaturated very reactive species, which can easily combine with e.g. MD. Analogous situations have been found for the η^3-allylpalladium systems [12,13]. The proposed mechanism for the reaction of MD with M leading to M_2 + D (reactions +2 and —2) is shown in Fig. 9.

These results seem to be corroborated by the measurements of $1/\tau$ (MD) for mixtures of MD and M_2, as here $1/\tau$ (MD) is independent of [MD] and proportional to $[M_2]^{1/2}$, which therefore indicates that reaction 2 is dominant.

In the other dialkylsulfurdiimine systems it is noteworthy that for isomer I

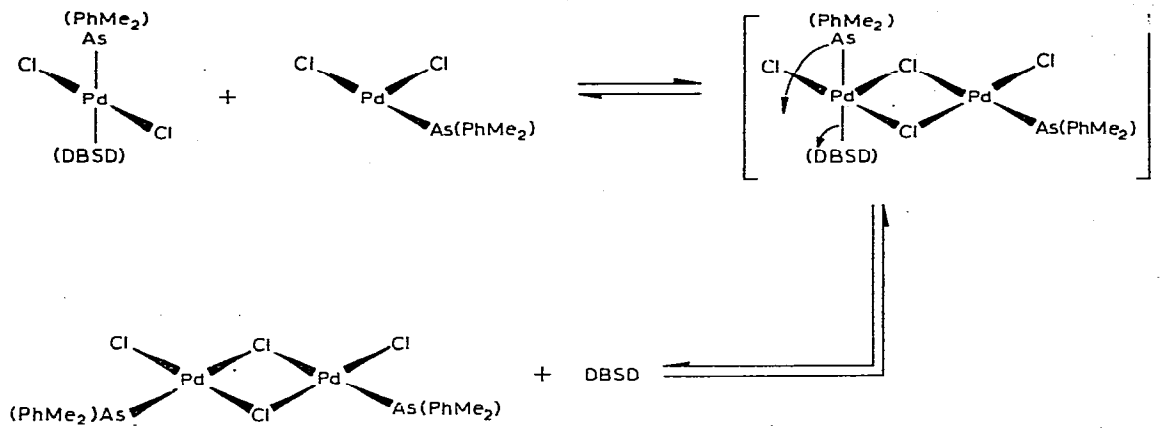

Fig. 9. Mechanism of the dominant reaction in the system of $[PdCl_2(DBSD)(PhMe_2As)]$, DBSD and $[PdCl_2(PhMe_2As)]_2$.

the bulky di-isopropylsulfurdiimine ligand behaves similarly to di-t-butylsulfurdiimine, while both behave differently from the less bulky systems (R = Me and Et) in the presence of free ligand. The direct ligand exchange (reaction 6) dominates for R = Me and Et, since the MD_2 species is more easily formed, while reaction 2 dominates for R = i-Pr in analogy to R = t-Bu. Only when a large amount of sulfurdiimine is present ($>0.4\ N$) is reaction 6 observable for all systems.

In this respect it is noteworthy that isomer II (R = Me, Et and i-Pr), because of its effective five-coordination, does not participate below +20°C in intermolecular exchange processes if free ligand is also present.

Isomer II is however involved in a fluxional intramolecular process in which the R sites of the coordinated sulfurdiimine exchange. The mechanism is probably analogous to the path II → III → III′ → II′ shown in Fig. 7 of ref. 5.

Finally is should be remarked that, as with the η^3-allylpalladium systems [12, 13], one must assume that in principle all reactions occur. The concentration dependencies of the rates tell us only which are the dominant reactions.

In our next paper we report the intra- and intermolecular reactions of cationic sulfurdiimine compounds of Rh(I), Ir(I), Pd(II) and Pt(II) [14].

References

1 K. Vrieze, H.C. Volger and A.P. Praat, J. Organometal. Chem., 21 (1970) 467.
2 H.E. Wilson and K. Vrieze, J. Organometal. Chem., 54 (1973) 403.
3 T.G. Hewitt and J.J. de Boer, J. Chem. Soc. A, (1971) 817.
4 R. Ben-Shoshan and R. Pettit, J. Amer. Chem. Soc., 89 (1967) 2231.
5 J. Kuyper and K. Vrieze, J. Organometal. Chem., 74 (1974) 289.
6 J. Kuyper and K. Vrieze, J. Organometal. Chem., 86 (1975) 127.
7 R. Meij and K. Olie, Cryst. Struct. Commun., 4 (1975) 515.
8 R. Meij, J. Kuyper, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 108 (1976) 165.
9 W.E. Lindsell and G.R. Faulds, J. Chem. Soc., Dalton Trans., (1975) 40.
10 A. Allerhand, H.S. Gutowsky, J. Jonas and R.A. Meinzer, J. Amer. Chem. Soc., 88 (1966) 3185.
11 R.G. Miller, R.D. Stauffer, D.R. Fahey and D.R. Parnell, J. Amer. Chem. Soc., 92 (1970) 1511.
12 K. Vrieze and P.W.N.M. van Leeuwen, in Progress in Inorganic Chemistry, Vol. 14, S.J. Lippard (Ed.), Wiley-Interscience, New York, 1971, p. 1.
13 K. Vrieze in Dynamic Nuclear Magnetic Resonance Spectroscopy, L.M. Jackman and F.A. Cotton (Ed.), Academic Press Inc., New York, p. 441.
14 J. Kuyper, L.G. Hubert-Pfalzgraf, P.C. Keijzer and K. Vrieze, J. Organometal. Chem., 108 (1976) 271.