Nuclear Magnetic Resonance Study of Inversion at Sulphur and Selenium Atoms in Complexes of Palladium(II) and Platinum(II). Part 2.[1] Complexes of Methyl and Phenyl Trimethylsilylmethyl Sulphide and Selenide

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Inversion barriers at sulphur and selenium atoms in organic sulphide and selenide complexes of Pd^{II} and Pt^{II}, $[MY_2\{XR(CH_2SiMe_3)\}_2]$ (M = Pd^{II} or Pt^{II}, Y = Cl or Br, X = S or Se, R = Me or Ph), have been measured by accurate n.m.r. band-shape methods. The energies vary within the range 51—84 kJ mol^{-1} and depend to various extents on the nature of the pyramidal atom, the attached transition metal, and the organic ligand. Selenium barrier energies are 15—20 kJ mol^{-1} higher than corresponding sulphur barrier energies. Detailed line-shape studies indicate that the inversion mechanism is intramolecular and occurs predominantly at single S or Se atoms. Any synchronous double inversion is of low probability and does not contribute significantly to the observed changes in n.m.r. line shape.

THE preceding paper[1] described the measurement of inversion-barrier energies at sulphur and selenium when these atoms were attached to Pd^{II} and Pt^{II} in complexes of general type *trans*-$[MCl_2\{X(CH_2SiMe_3)_2\}_2]$ (X = S or Se). The inversion process was studied by observing the change of line shape of the diastereotopic[2] methylene hydrogens. As a result of the high symmetry of these complexes, the four pairs of methylene hydrogens were enantiomerically related and the resulting spectra were relatively simple and very amenable to total line-shape analysis. However, with such complexes important insight into the kinetics of the inversion process is lost since it is not possible to distinguish between inversion at single X centres and simultaneous inversion at both X centres. With a view to further investigating this problem, we have prepared and studied a series of slightly different complexes of type *trans*-$[MY_2\{XR(CH_2SiMe_3)\}_2]$ (M = Pd^{II} or Pt^{II}, X = S or Se, R = Me or Ph, and Y = Cl or Br).

Sulphide and selenide complexes of palladium(II) and platinum(II)

Complex	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis (%) Found C	Found H	Calc. C	Calc. H
trans-$[PdCl_2\{SMe(CH_2SiMe_3)\}_2]$	58	Yellow	91	26.4	6.25	26.9	6.30
trans-$[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$	59	Orange	132	41.8	5.60	42.2	5.60
trans-$[PtCl_2\{SMe(CH_2SiMe_3)\}_2]$	72	Yellow	110	22.3	5.25	22.5	5.30
trans-$[PtCl_2\{SPh(CH_2SiMe_3)\}_2]$	76	Yellow	117	36.3	4.90	36.5	4.90
trans-$[PtBr_2\{SMe(CH_2SiMe_3)\}_2]$	75	Orange	133	18.9	4.45	19.3	4.55
trans-$[PtBr_2\{SPh(CH_2SiMe_3)\}_2]$	70	Orange	141	31.9	4.25	31.8	4.30
trans-$[PdCl_2\{SePh(CH_2SiMe_3)\}_2]$	35	Orange	106	35.2	4.75	36.2	4.85
trans-$[PtBr_2\{SePh(CH_2SiMe_3)\}_2]$	63	Orange	118	28.2	3.70	28.6	3.85

EXPERIMENTAL

The new palladium and platinum complexes utilized in these studies were prepared, purified, and characterized as outlined below.

Interaction of Potassium Tetrachloropalladate(II) *and Methyl Trimethylsilylmethyl Sulphide*.—The compound $K_2[PdCl_4]$ (0.5 mmol) and the ligand (1.0 mmol) were stirred together under reflux in ethanol for 3 h. On cooling the solution was filtered through Kieselguhr. Solvent was removed *in vacuo* and the residue dissolved in hot hexane and filtered. Slow cooling to −20 °C yielded yellow crystals of *trans*-dichlorobis(methyl trimethylsilylmethyl sulphide)palladium(II). In an exactly analogous manner were prepared *trans*-dichlorobis(phenyl trimethylsilylmethyl sulphide)palladium(II) and *trans*-dichlorobis(phenyl trimethylsilylmethyl selenide)palladium(II).

Interaction of Potassium Tetrachloroplatinate(II) *and Methyl Trimethylsilylmethyl Sulphide*.—The compound $K_2[PtCl_4]$ (0.5 mmol) and the ligand (2 mmol) were stirred together in water (10 cm^3) for 20 h at room temperature. The yellow precipitate formed was filtered off and washed copiously with water. The complex was dissolved in methylene chloride and the solution dried with anhydrous $Mg[SO_4]$. The drying agent was filtered off and solvent was removed from the filtrate. The residue was dispersed in a small volume of hot hexane, and dissolved completely by adding the minimum amount of methylene chloride. Cooling the solution slowly to −20 °C yielded yellow crystals of *trans*-dichlorobis(methyl trimethylsilylmethyl sulphide)platinum(II). In an exactly analogous manner was prepared *trans*-dichlorobis(phenyl trimethylsilylmethyl sulphide)platinum(II).

Interaction of Platinum(II) *Bromide and Methyl Trimethylsilylmethyl Sulphide*.—Platinum(II) bromide (0.5 mmol) and the ligand (2.0 mmol) were stirred in acetone (10 cm^3) for 20 h at room temperature. The resulting solution was filtered through Kieselguhr and then the solvent was removed *in vacuo*. The orange residue was dissolved in hot hexane and after filtration the solution was slowly cooled to −20 °C to produce crystals of *trans*-dibromobis(methyl trimethylsilylmethyl sulphide)platinum(II) which were washed with a little cold hexane and dried *in vacuo*. In an analogous manner were prepared *trans*-dibromobis(phenyl

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[1] Part 1, E. W. Abel, G. W. Farrow, K. G. Orrell, and V. Šik, preceding paper.

[2] W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.

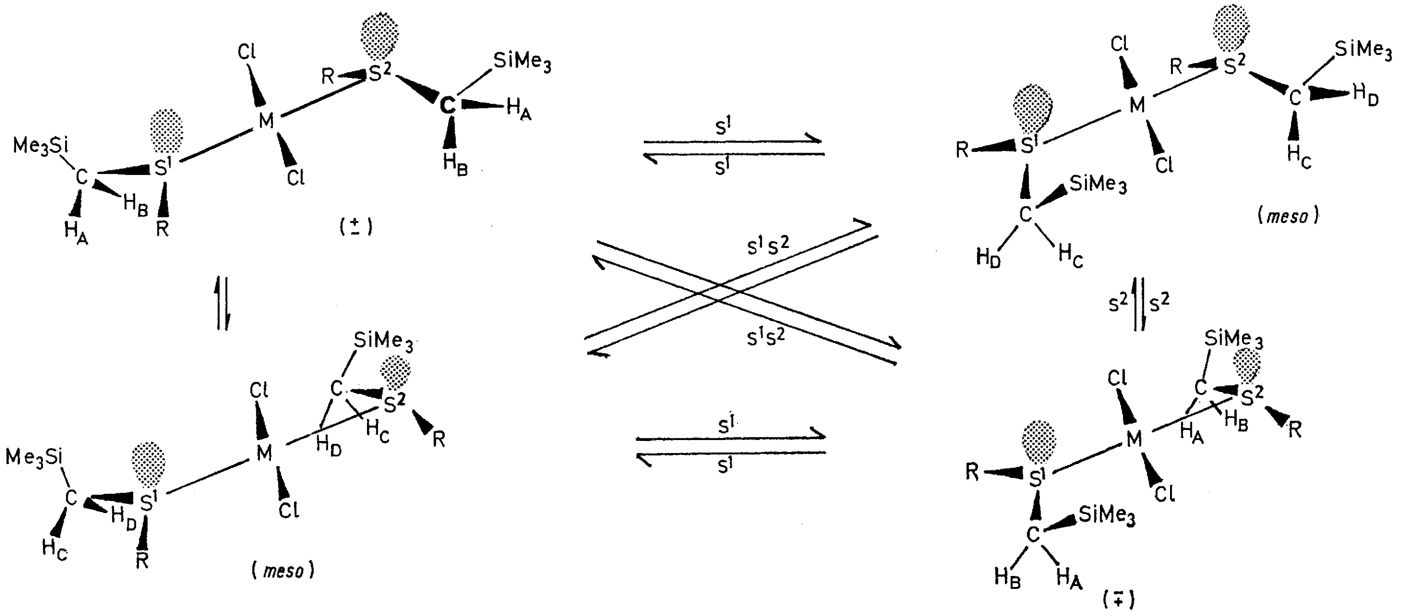

FIGURE 1 Effects of sulphur inversion on the magnetic environments of the diastereotopic CH_2 hydrogens of the SCH_2SiMe_3 groups. Rotation about the M–S and S–C bonds is assumed and only the preferred conformers are shown (see preceding paper)

trimethylsilylmethyl sulphide)platinum(II) and *trans*-dibromobis(phenyl trimethylsilylmethyl selenide)platinum(II)

N.m.r. spectra were recorded for solutions of the complexes in a variety of solvents (see Table 2 for details). A JEOL MH-100 spectrometer was used under internal field–frequency lock conditions for all the spectra recorded. A standard JES-VT-3 unit was used to control the probe temperature. Temperature measurements using a precisely calibrated thermocouple were made immediately before and after recording the spectra. Temperatures are considered accurate to at least ±1 °C.

Computations.—The computer program DNMR by Binsch [3] was used as the basis of the line-shape calculations. The program, however, required generalizing in order to handle spin systems interconverting between four nuclear configurations [4] (see below), and in the case of the platinum(II) complexes required extending in order to compute both the main band and the satellite spectra separately followed by plotting of the total spectra.

TABLE 1

Chemical shifts of methylene hydrogens

The temperature dependences of the shifts * are given by the expression ν_i/Hz = $a + b(T/\mathrm{K})$ where a and b have the values shown

Complex		ν_A/Hz		ν_B/Hz		ν_C/Hz		ν_D/Hz	
		a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$[PdCl_2\{SMe(CH_2SiMe_3)\}_2]$	(1)	197.99	0.1060	149.50	−0.0393	190.95	0.1792	149.26	−0.0384
$[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$	(2)	231.17	0.1733	264.01	−0.2476	165.62	0.3961	317.46	−0.4333
$[PtCl_2\{SMe(CH_2SiMe_3)\}_2]$	(3)	209.37	0.1026	92.36	0.1485	209.37	0.1026	92.36	0.1485
$[PtCl_2\{SPh(CH_2SiMe_3)\}_2]$	(4)	245.32	0.1836	198.97	−0.1171	217.73	0.2677	208.89	−0.1313
$[PtBr_2\{SMe(CH_2SiMe_3)\}_2]$	(5)	226.98	0.0722	157.62	−0.002 26	193.31	0.179	176.47	−0.0625
$[PtBr_2\{SPh(CH_2SiMe_3)\}_2]$	(6)	242.67	0.215	273.82	−0.208	203.48	0.342	303.89	−0.302
$[PdCl_2\{SePh(CH_2SiMe_3)\}_2]$	(7)	261.20	0.0973	195.76	−0.0953	257.78	0.1016	193.09	−0.1068
$[PtBr_2\{SePh(CH_2SiMe_3)\}_2]$	(8)	306.25	0.0136	181.63	−0.0206	288.50	0.0584	187.59	−0.305

* Values are relative to the $SiMe_3$ signal.

RESULTS AND DISCUSSION

Palladium(II) *Complexes*.—In the complexes $[PdCl_2\{XR(CH_2SiMe_3)\}_2]$ each X (= S or Se) atom is a centre of chirality. Diastereoisomerism thus exists leading to n.m.r. distinguishable (±) and *meso* forms. Attached to each X atom is a prochiral trimethylsilylmethyl group in which the methylene hydrogens are diastereotopic and thus anisochronous if no interconversion process is operating. The CH_2SiMe_3 groups attached to different X atoms are enantiomerically related and thus the corresponding hydrogens are enantiotopic and indistinguishable by n.m.r. The methylene hydrogen spin system for a particular diastereoisomer [*e.g.* the (±) isomer, Figure 1] is of the type $[AB]_2$. For a *racemic* mixture of isomers, as is apparently the case for these complexes, the total methylene spin system is of the type $[AB]_2 + [CD]_2$. However, as there was no

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[3] G. Binsch, *J. Amer. Chem. Soc.*, **1969**, **91**, 1304.

[4] G. Binsch, *J. Magnetic Resonance*, **1970**, **3**, 146.

measurable spin coupling between the CH_2 hydrogens on different X atoms, the spin systems may be considered simply as AB + CD. Thus, in the absence of any rate process which leads to an interconversion of methylene environments, the spectra should consist of two AB-type patterns. This is illustrated by the low-temperature spectrum of $[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$ (Figure 2).

Let us now consider how inversion at the S atoms affects the environments of the methylene hydrogens.

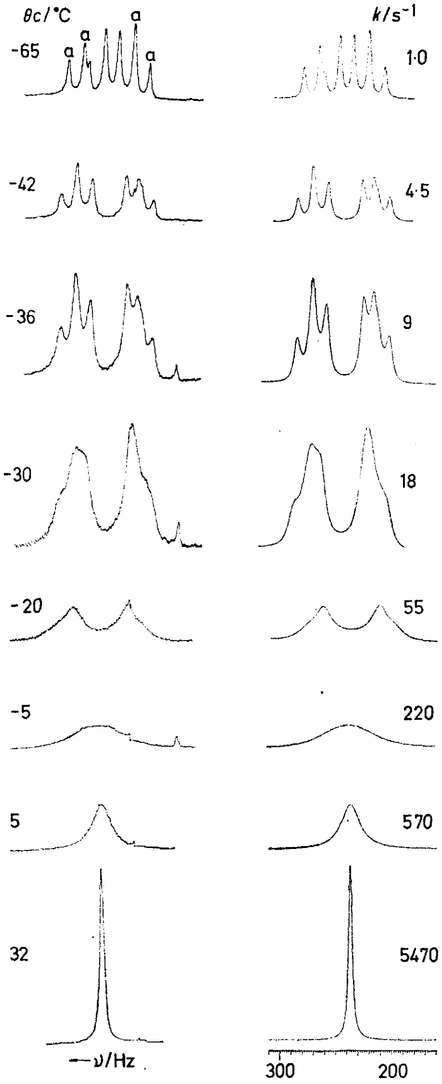
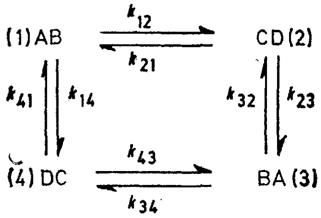


FIGURE 2 Variable temperature spectra of the methylene absorption region of $[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$

The problem is summarized in Figure 1. Commencing with the (±) isomer, inversion at S^1 converts the structure to the *meso* form and alters the magnetic environments of the diastereotopic methylenes to produce the spin system CD. Inversion at S^2 produces the (±) isomer again but with the methylene environments reversed with respect to the original (±) isomer. Thus we have the system BA. Inversion at S^1 and then at S^2 completes the cycle. It should be noted that in illustrating these inversions we are assuming, as previously,[1] rapid rotation about the M–S and S–C bonds and each diastereoisomer is represented by its energetically favoured conformer. It can be seen that inversion at single sulphur centres leads to interconversion between four distinct nuclear configurations in the n.m.r. sense.[4] We thus have the system in Scheme 1.

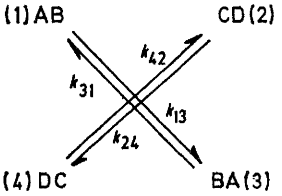
If synchronous inversion at both S atoms occurs this will lead to a mutual exchange between the two (±) configurations and between the two *meso* configurations



SCHEME 1

but not between (±) and *meso* forms. Thus we have Scheme 2. If both types of inversion are occurring then a combination of Schemes 1 and 2 must be considered. In both these schemes the forward and reverse rate constants, k_{ij} and k_{ji}, are exactly equal since the system is always at equilibrium. In Scheme 1, since configurations AB and BA (and likewise CD and DC) are chemically identical, all the rate constants are equal. In Scheme 2, $k_{13} = k_{31}$ and $k_{24} = k_{42}$ but the rate constants for mutual (±) and mutual *meso* interconversion are not necessarily equal, *e.g.* $k_{13} \neq k_{24}$, but in fact are unlikely to be greatly different.

It was decided to try to interpret the n.m.r. line-shape changes first on the basis of exclusive single-site inversion (Scheme 1). The results for $[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$ are shown in Figure 2. Before performing the computer simulations of the line shapes, it was necessary to determine as precisely as possible the static parameters, namely chemical shifts, spin–spin coupling constants, and linewidths, in the absence of site inversion. These parameters were measured over a wide temperature range (usually *ca.* 30 °C) in the slow inversion range. The temperature dependences of the chemical shifts were appreciable and their precise measurement was a critical factor in determining the quality of the fitting of experimental and simulated spectra. The data used for all the complexes are given in Tables 1 and 2.



SCHEME 2

The assignment of the two AB-type quartets in the lowest-temperature spectra could not be made visually because of the near equality of the geminal coupling constants. However, a conclusive assignment of the lines was achieved by the INDOR technique.[5a] The lines labelled ' a ' in Figure 2 comprised one quartet which was designated AB and assigned to the (±) isomer. The unlabelled lines in Figure 2 accordingly comprised the CD quartet of the *meso* isomer. These assignments are uncertain since it was not possible to unambiguously distinguish between the two diastereoisomers. However, if the main factor influencing the magnitude of the internal chemical shifts in the quartets is the anisotropic shielding of the aromatic rings, then models suggest that there may be larger internal shifts for the (±) isomer where the aromatic ring is *cis* to the CH_2 hydrogens. This assumption is the basis of the above assignments. For exchange between two (or more) AB-type systems it is usually essential to know the assignments of all the lines in order to decide between the two possible modes of exchange.[5b] However, in the present instance such knowledge is not essential because of the closed nature of the exchanging spin system. In Scheme 1 each nucleus interconverts between all the four anisochronous environments, A, B, C, and D, during the inversion process and thus the labelling is arbitrary. It was also not possible to unambiguously assign the individual methylene hydrogens in any of the complexes. It is, however, significant that the chemical shifts of the lower-field members of the quartets, A and C, moved downfield on increasing the temperature, in contrast to the nuclei B and D which moved upfield. Furthermore, the latter pair of nuclei exhibited strikingly larger couplings with ^{195}Pt than did A and C. If it is assumed that $J(Pt-X-C-H)$(*trans*) > $J(Pt-X-C-H)$(*gauche*) as much previous data suggest,[6-8] then the correct labelling of the two low-temperature non-interconverting structures is that shown in the (±) and *meso* structures on the right-hand side of Figure 1.

TABLE 2

Spin–spin coupling constants, J_{ij}/Hz, and transverse relaxation times, T_2^*/s

Complex	J_{AB}	J_{CD}	J_{AX}	J_{BX}	J_{CX}	J_{DX}	T_2^*
(1)	13.4	13.4					0.318
(2)	13.3	13.2					0.318
(3)	12.9	12.9	32.7	73.0	32.7	73.0	0.159 [a] 0.127 [b]
(4)	12.9	12.7	35.4	75.5	35.0	73.4	0.159 [a] 0.080 [b]
(5)	12.9	12.9	24.6	70.9	23.4	69.2	0.159
(6)	13.1	13.1	32.0	71.0	32.0	71.0	0.212
(7)	13.3	13.3					0.159
(8)	12.5	12.5	36.7	59.5	36.0	58.7	0.212 [a] 0.159 [b]

[a] Main bands. [b] Satellite bands.

The above assumption regarding the relative magnitudes of vicinal Pt–H couplings is justified since it is well established[6,7] that Pt–N–C–H couplings obey a Karplus-type[8] relation involving the dihedral angle between the Pt–N–C and N–C–H planes. Replacement of nitrogen by sulphur or selenium is not thought likely to seriously change this relation. The dihedral angles for the *trans*- and *gauche*-CH_2 hydrogens in the present complexes are *ca.* 120 and 0° respectively. Previous data[6] suggest that the vicinal coupling approaches a maximum for $\phi = 180°$ and a minimum for $\phi = 0°$. This therefore implies that $^3J(Pt-S-C-H)$(*trans*) > $^3J(Pt-S-C-H)$(*gauche*).

Figure 2 illustrates the changes in line shape of the methylene absorption of $[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$ between −65 and 32 °C. At ambient temperatures the inversion process was rapid on the n.m.r. time scale and a single averaged line was observed. The simulated spectra for the rate constants shown in Figure 2 are in excellent agreement with the experimental curves. It therefore appears that the n.m.r. results can be explained on the basis of uncorrelated inversion at individual sulphur atoms. However, we wished to explore the possibility of obtaining definitive evidence for the existence or otherwise of synchronous double inversion (Scheme 2) or a combination of both single and double inversions. We first assumed only synchronous double inversion (with $k_{13} = k_{24}$, *etc.*) and attempted to fit our experimental spectra. This was possible near the slow-inversion limit and, somewhat surprisingly, near the fast-inversion limit. In this latter case there is a theoretical difference between the time-averaged spectra for single and double inversion. For single inversion, a single averaged line is predicted whereas for exclusive double inversion, two lines are expected with a separation $\frac{1}{2}(\nu_A + \nu_B - \nu_C - \nu_D)$. Unfortunately, the close similarities of ν_A and ν_B compared with ν_C and ν_D did not allow such a distinction to be made. However, the intermediate temperature range (*ca.* −10 to −40 °C) was very sensitive to the assumed inversion process. Figure 3 shows the experimental spectra at −30 and −20 °C and the closest simulated spectra assuming solely double inversion. The matching is unacceptably

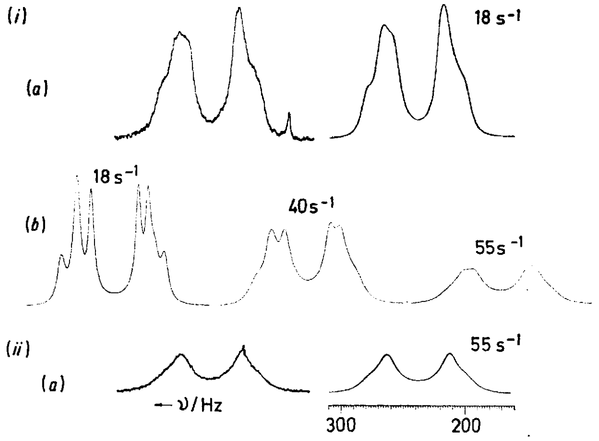


FIGURE 3 Methylene region spectra of $[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$ at −30 (*i*) and −20 °C (*ii*) with simulated (*a*) single-inversion and (*b*) synchronous double-inversion spectra

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[5] (*a*) E. B. Baker, *J. Chem. Phys.*, 1962, **37**, 911; (*b*) B. Nilson, P. Martinson, K. Olsson, and R. E. Carter, *J. Amer. Chem. Soc.*, 1973, **95**, 5615.

[6] L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *J. Amer. Chem. Soc.*, 1968, **90**, 6371.

[7] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1971, **10**, 1717.

[8] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

poor confirming that synchronous double inversion is not the sole process. We then examined the case of equal probabilities of single and double inversion and again found that the intermediate-range spectra could not be as satisfactorily fitted as when only single-site inversion is assumed. We therefore feel able to conclude that single-site inversion is the dominant process in this temperature range (and probably throughout the whole range although we have no direct evidence to support this) but we cannot completely exclude the possibility of double inversion. It does not, however, appear to contribute significantly to the observed n.m.r. line-shape changes, suggesting that the frequency of this rate process is below the limit of n.m.r. detection.

It might have been expected that further evidence for the type of inversion process occurring would have been obtained by observing the changes in line shapes of the $SiMe_3$ and, in the case of the complexes of $SMe(CH_2SiMe_3)$, the CH_3 signals. However, in none of the complexes did inversion lead to changes of the CH_3 absorption and only in the case of $[PtBr_2\{SePh(CH_2SiMe_3)\}_2]$ was a small splitting observed in the $SiMe_3$ signal at low temperatures. This splitting disappeared at higher temperatures indicating that single and not solely double inversion was occurring, but the line-shape changes were too slight for any quantitative measurements. The general absence of such splittings must be attributed to the distance of the $SiMe_3$ groups from the prochiral centres rendering the hydrogens insufficiently anisochronous for separate detection.[2]

The other palladium(II) complexes produced similar methylene absorption spectra to $[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$ but the precise line shapes and the temperature range over which the changes occurred depended on the solvent used, the X atom, and the nature of the co-ordinating ligand (*i.e.* whether R = Ph or Me). In CS_2 and C_2Cl_4 solvents the diastereotopic methylenes experience much larger internal chemical shifts than in $CDCl_3$ (see Table 1). In the complexes with R = Ph (*e.g.* Figure 2) there is appreciable distinction at low temperatures between the diastereoisomers, whereas when R = Me this distinction is only just apparent and the spectra resemble a pair of almost exactly overlapping AB-type quartets. This difference in the spectra of the two series of complexes is almost certainly due to the appreciable anisotropic shielding of the aromatic ring. In view of the outcome of the detailed studies on $[PdCl_2\{SPh(CH_2SiMe_3)\}_2]$, the line-shape fittings for the other complexes of Pd^{II} were made assuming only single site inversions. The results are collected in Table 3. The activation energies are based on Arrhenius plots involving at least 12 points and the errors are based on least-squares analyses.

Platinum(II) *Complexes*.—The presence of hydrogen spin–spin coupling to ^{195}Pt in the spectra of these complexes produces a satellite spectrum in addition to the main band (Pt, $I = 0$) spectrum. In other words, in addition to the two-spin four-configuration problem there is a three-spin problem of the type in Scheme 3. Using the extended DNMR program, total band-shape analyses were performed. The results for $[PtCl_2\{SPh(CH_2SiMe_3)\}_2]$ are shown in Figure 4. As with the palladium(II) complexes, the experimental line shapes could be accurately simulated for the case of single-site inversion. The fast inversion spectra exhibited averaged ^{195}Pt–H couplings indicating that the inversion process is purely intramolecular with the Pt and X atoms remaining in close proximity throughout the inversion process. This excludes any possibility of a dissociation–recombination mechanism for these complexes. It is reasonable to assume that the same mechanism is operating in the palladium(II) complexes, although no evidence from spin–spin interactions is possible. Intermolecular ligand exchange might possibly be occurring at higher temperatures, as was observed by Cross *et al.*[9] in related complexes, but in the temperature range of interest here there is no evidence of such a process. This was further confirmed by introducing a small amount of free ligand to one of the complexes and observing separate signals due to the free and complexed ligands at temperatures where the latter were undergoing rapid X inversion.

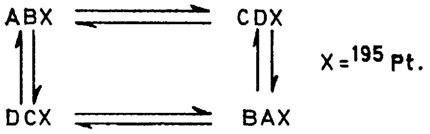
In the preceding paper[1] we discussed at some length

TABLE 3

Arrhenius and activation parameters *

Complex	Solvent	$E^‡$ kJ mol^{-1}	$\log_{10}A$	$\Delta G^‡$ kJ mol^{-1}	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}
(1)	$CDCl_3$	51.0 ± 0.5	12.2 ± 0.1	54.5 ± 1.1	48.6 ± 0.5	−19.9 ± 5.3
(2)	$CDCl_3$	56.2 ± 0.4	13.3 ± 0.07	53.2 ± 0.8	53.7 ± 0.4	1.7 ± 3.9
(3)	CS_2	55.9 ± 0.5	11.8 ± 0.08	61.3 ± 0.9	55.5 ± 0.5	−19.6 ± 4.8
(4)	CS_2	62.5 ± 0.4	13.4 ± 0.07	59.3 ± 0.8	60.0 ± 0.4	2.4 ± 4.2
(5)	$CDCl_3$	59.2 ± 1.2	12.5 ± 0.2	60.9 ± 2.4	56.7 ± 1.2	−14.1 ± 11.9
(6)	$CDCl_3$	54.5 ± 0.6	12.0 ± 0.1	59.0 ± 1.1	52.0 ± 0.6	−23.3 ± 5.8
(7)	C_2Cl_4	71.1 ± 0.7	13.2 ± 0.1	68.7 ± 1.4	68.6 ± 0.7	−0.3 ± 7.0
(8)	C_2Cl_4	83.8 ± 1.0	13.4 ± 0.1	80.3 ± 1.8	81.3 ± 1.0	3.4 ± 9.4

* $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ were calculated for T = 298.15 K.



SCHEME 3

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[9] R. J. Cross, T. H. Green, R. Keat, and J. F. Paterson, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 145.

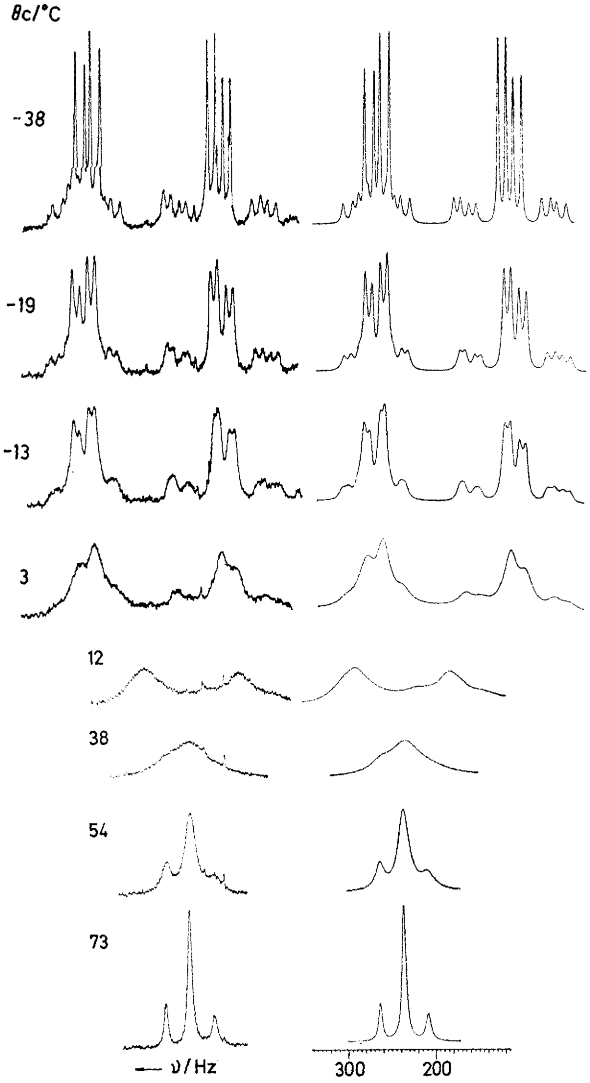

FIGURE 4 Variable-temperature spectra of the methylene absorption region of $[PtCl_2\{SPh(CH_2SiMe_3)\}_2]$

the nature of the inversion mechanism in *trans*-$[MCl_2\{X(CH_2SiMe_3)_2\}_2]$ complexes. The same mechanism is undoubtedly operative in the present complexes and, as we have shown, it is essentially a matter of personal preference as to whether the process is visualized in the usual way involving a trigonal-planar intermediate with a lone pair on the X atom or whether the description of Haake and Turley[10,11] is adopted of a planar intermediate with both X lone pairs involved in the M^{II}–X bonding.

A number of interesting trends in the Arrhenius energy and activation parameters are apparent (Table **3**). The activation energies depend on the nature of X and M such that Pd–S < Pt–S < Pd–Se < Pt–Se with values varying from 51 to 84 kJ mol^{-1}. In addition, there is a small but significant dependence of the inversion barrier on the group R attached to X. Changing from R = Me to Ph appears to lead to a slight increase (*ca.* 5—6 kJ mol^{-1}) in the activation energy in most cases. This trend, however, is not reflected in the dibromide complexes but here the results are somewhat less certain due to the lower quality of the experimental spectra from the point of view of line-shape fittings. The results do not reflect any obvious dependence on the nature of the halogen attached to M^{II}. In complexes of types $[MY_2(XR_2)_2]$ and $[MY_2(RXC_2H_4XR)]$ (Y = halide), Cross *et al.*[12,13] suggested that the inversion barriers at X depend primarily on the *trans* influence of the halogen. In the present complexes with the halogens being mutually *trans* no such correlation is possible and any dependence on the halogen (any '*cis* influence') is expected to be small and possibly non-existent. Similarly equivocal results for the effects of different *cis*-halogens on sulphur and selenium inversion barriers have recently been reported by Barnes *et al.*[14] on chelate complexes of Pd^{II} and Pt^{II}.

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