Determination of the Separate Barrier Energies for Six-membered Ligand Ring Reversal and Pyramidal Sulphur Inversion in Complexes of Palladium(II) and Platinum(II). A Dynamic Hydrogen-1 and Carbon-13 Nuclear Magnetic Resonance Study

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The series of complexes *trans*-$[MX_2\{\overline{S(CH_2)_5}\}_2]$ (M = Pd; X = Cl, Br, or I; M = Pt; X = Cl) have been synthesised and, by accurate analysis of their variable-temperature ^1H and ^{13}C n.m.r. spectra using total band-shape fitting methods, energy barriers for ligand ring reversal and for sulphur inversion have been separated and calculated for the first time. The barriers to ring reversal in the complexes are similar to those already known for the uncoordinated ligand, whereas those for sulphur inversion are also similar to values known for analogous non-cyclic ligand complexes. The power of ^{13}C dynamic n.m.r. spectral analysis was demonstrated by the fact that no simplifications in the conformational analyses were needed in order to account for the ^{13}C spectral line changes. This was in marked contrast to the ^1H spectra, which, in order for their analyses to be possible, had to be attributed to the conformations of either six-membered heterocyclic ring rather than to total conformational structures of the complexes.

DYNAMIC n.m.r. (d.n.m.r.) studies of pyramidal nitrogen inversion have, in a number of cases, led to ambiguities in the interpretation of the observed line-shape changes.[1] Examples of such ambiguities include N atomic inversion *versus* N–P bond rotation in aminophosphines [2,3] and N atomic inversion *versus* ring reversal in six-membered-ring heterocycles.[4,5]

Nitrogen-containing six-membered rings have been studied extensively in attempts to separate the ring reversal and atomic inversion phenomena. However, where d.n.m.r. spectra are observed, the deduction as to precisely which process is being studied has proved difficult,[1] and surprisingly in only three cases (to our knowledge) have separate coalescence phenomena been noted and attributed to each of the two processes.[6-8]

Analogous Group 6B systems (Figure 1) are less common, but present similar difficulties. A number of five-membered ring complexes have been synthesised consisting of a bis-chalcogen chelate co-ordinated to a metal atom [9,10] [Figure 1, compounds (1) and (2)]. In these systems, only one coalescence was observed and attributed to atomic sulphur inversion by one group of workers [9] and to chelate ring reversal by another group.[10] A related study on six-membered chelate ring compounds (3) was also attributed to chelate ring reversal.[11] This problem was unambiguously resolved in favour of sulphur inversion by application of total band-shape fitting techniques on compounds (4) [12] and (5).[13]

1,4-Oxathiane and 1,4-oxaselenane complexes of platinum(II) and palladium(II) halides [14] [compounds (6)] represented further examples where both reversal of the co-ordinated ligand ring and/or pyramidal inversion at the co-ordinated S/Se atoms were possible. In these ring systems only one coalescence was observed and assigned, by analogy with linear systems, to sulphur inversion. A second coalescence at lower temperatures was suggested but not experimentally verified. Similar results were also obtained in a more recent study [15] of dihalogen complexes of 1,4-dithiane, compounds (7).

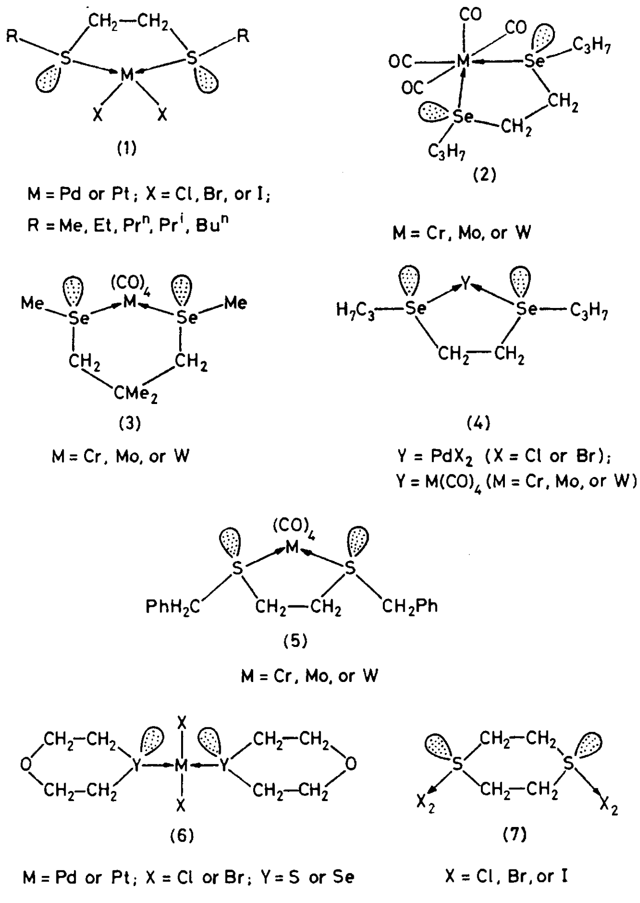


FIGURE 1 Transition-metal complexes of rings incorporating Group 6B ligand atoms

Thus no compound has yet been studied, by d.n.m.r. spectroscopy, in which a six-membered ring has been shown to separately undergo both ring reversal and inversion at a co-ordinated chalcogen atom. However, it is noteworthy that the free energy of activation for ring reversal in pentamethylene sulphide $[S(CH_2)_5]$[16] is *ca.* 40 kJ mol^{-1}, whereas values of this parameter for S inversion in dialkyl sulphide complexes of platinum(II) and palladium(II) derivatives[17] are *ca.* 55 and *ca.* 61 kJ mol^{-1} respectively. Such different magnitudes of $\Delta G^{\ddagger}$ values suggest that in complexes of the type *trans*-$[MX_2\{S(CH_2)_5\}_2]$ (M = Pd^{II} or Pt^{II}, X = Cl, Br, or I) it should be possible to separate the two rate processes by d.n.m.r. spectroscopy.

We have accordingly synthesised such complexes and herein report their ^1H and ^{13}C n.m.r. spectra measured over a wide range of temperatures.

EXPERIMENTAL

The ligand pentamethylene sulphide $[S(CH_2)_5]$ was redistilled before use and the complexes prepared by established procedures.[18] The analytical data for the complexes are given in Table 1.

Preparation of Palladium(II) *Complexes*.—The compound $K_2[PdX_4]$ (X = Cl, Br, or I) (0.5 mmol) was dissolved in water (20 cm^3) and pentamethylene sulphide (1.1 mmol) added with stirring. The mixture was stirred overnight; then the solid formed was filtered off, washed copiously with water followed by a small volume of cold ethanol, and dried. The residue was then dissolved in the minimum of hot acetone. Cooling the acetone solution slowly to -20 °C yielded crystals of the desired product *trans*-$[PdX_2\{S(CH_2)_5\}_2]$.

TABLE 1

Pentamethylene sulphide complexes of palladium(II) and platinum(II)

Complex	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis (%)* C	Analysis (%)* H
trans-$[PdCl_2\{S(CH_2)_5\}_2]$	75	Orange	139—143	30.9 (31.5)	5.25 (5.30)
trans-$[PdBr_2\{S(CH_2)_5\}_2]$	80	Orange-red	130	25.3 (25.5)	4.40 (4.30)
trans-$[PdI_2\{S(CH_2)_5\}_2]$	57	Brown	154—155	21.1 (21.3)	3.75 (3.55)
trans-$[PtCl_2\{S(CH_2)_5\}_2]$	80	Yellow	140—142	25.4 (25.5)	4.25 (4.30)

* Calculated values are given in parentheses.

Preparation of Platinum(II) *Complex*.—The compound $K_2[PtCl_4]$ (0.5 mmol) and the ligand (2 mmol) were stirred together in water (20 cm^3) overnight at room temperature. The yellow precipitate formed was filtered off and washed copiously with water followed by a small volume of cold ethanol. The residue was then dissolved in methylene dichloride and the solution filtered and dried over anhydrous magnesium sulphate overnight. Filtering off the drying agent and removal of the solvent *in vacuo* yielded a mixture of *cis*- and *trans*-$[PtCl_2\{S(CH_2)_5\}_2]$. These were separated by recrystallisation from the minimum of hot tetrachloroethylene, the *cis* isomer being largely insoluble.

Spectra.—A JEOL MH-100 or a PS/PFT-100 spectrometer was used to record the 100 MHz ^1H n.m.r. spectra. Complexes were dissolved in a CD_2Cl_2–CS_2 solvent mixture with the exception of *trans*-$[PtCl_2\{S(CH_2)_5\}_2]$, which was dissolved in $CDCl_3$ for studies at temperatures >40 °C. A standard JES-VT-3 unit was used to control the probe temperature in all cases. The 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.

The 220 MHz ^1H n.m.r. spectra were recorded on either a Varian HR 220 or a Perkin-Elmer R34 spectrometer at the P.C.M.U. Harwell.

Computations.—The computer program DNMR by Binsch[19,20] was used as the basis of the line-shape calculations. Various versions of the basic program were used, namely DNMR48, DNMR36, and DNMR8 where the numbers refer to the maximum size of submatrix involved. The LAOCNR computer program was used in the analysis of some of the 'static' spectra.

RESULTS

Hydrogen-1 *N.M.R. Spectra*.—Preliminary variable-temperature 100 MHz ^1H studies on the complex *trans*-$[PdCl_2\{S(CH_2)_5\}_2]$ indicated two separable coalescence phenomena. A more detailed study between -97 and 37 °C produced spectra of the type shown in Figures 2 and 3.

Assuming for the moment that the structure of the complex be analogous to that of *trans*-$[PtBr_2\{S(CH_2)_2O(CH_2)_2\}_2]$ where both Pt–S bonds are equatorial with respect to the ring chair conformation,[21] then the ligand conformation and nuclear spin system are as shown in Figure 4. Different coalescence phenomena of the ring methylene signals can arise from (i) chair to chair reversal of the ligand ring and (ii) pyramidal inversion at the co-ordinated sulphur atom. Since two coalescence phenomena (*ca.* -70 °C and *ca.* 0 °C) are observed between -97 °C and 37 °C the lowest-temperature spectrum must correspond to the situation where *both* processes (i) and (ii) are slow on the n.m.r. time scale. It should be noted that at -97 °C the spectral lines are still somewhat broader than usual, implying that at least one rate process is still making its presence felt. However, cooling the solution further led to greater broadening of the spectral lines. Initially we attributed this broadness to effects of solvent viscosity on the relaxation times of the protons. To achieve a greater spectral dispersion a 220 MHz spectrum was recorded in the same mixed solvent at -100 °C (Figure 5). The improvement in spectral line definition was striking, indicating that the broadness in the 100 MHz spectrum was due primarily to the similarity of certain chemical shifts at this lower magnetic field strength.

Accurate analysis of the 'static' spectrum requires consideration of all possible 'static' conformations of the complex. These are well known for nitrogen systems,[1,8] and the sulphur analogues are illustrated in Figure 6. Hydrogen-1 n.m.r. is unable to distinguish between conformers (i) and (iii) where the Pd–S bond is equatorial to the ligand ring, or between (ii) and (iv) where it is axial. The ' static ' ^{1}H spectra would thus arise from two overlapping $[\mathrm{ABCD}]_2\mathrm{EF}$ spin systems. However our attempts to fit the α-methylene region (labelled PQRS in Figure 5) as the AB parts of two overlapping ABCD type systems, using the approximations described previously,[22] were unsuccessful.

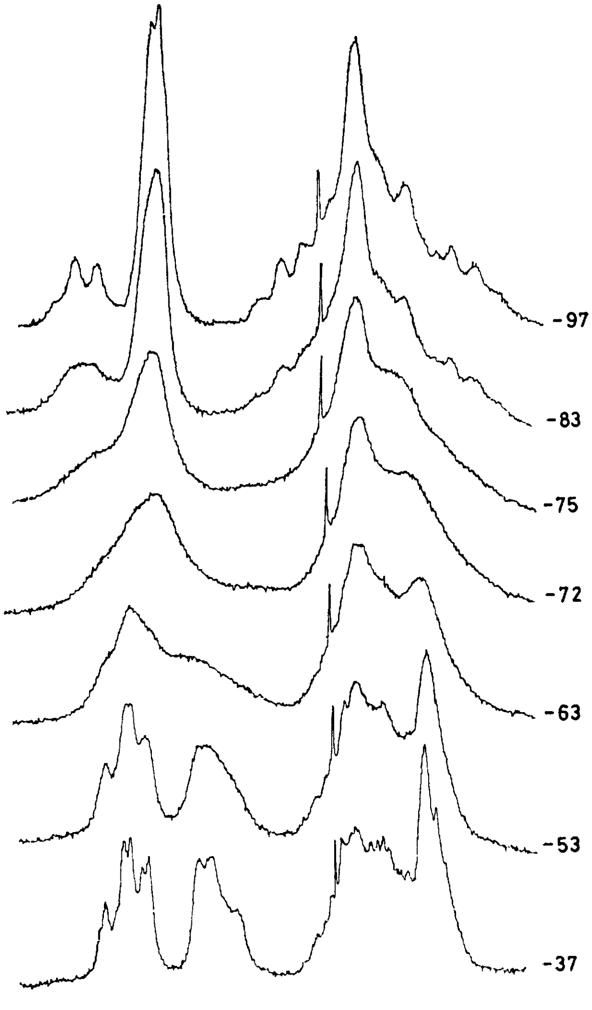


FIGURE 2 Variable-temperature 100 MHz ^{1}H n.m.r. spectra of *trans*-$[\mathrm{PdCl_2\{S(CH_2)_5\}_2}]$ (−97 to −37 °C)

Clearly the above region is more complex than this, possibly the result of more than two overlapping spectra.

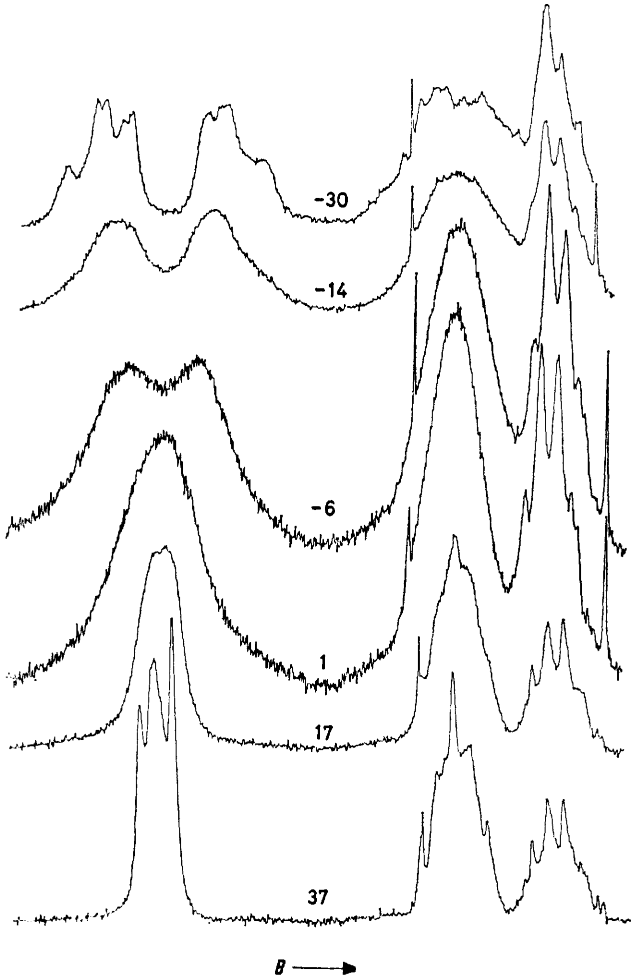


FIGURE 3 Variable-temperature 100 MHz ^{1}H n.m.r. spectra of *trans*-$[\mathrm{PdCl_2\{S(CH_2)_5\}_2}]$ (−30 to 37 °C)

Assuming that the ligand ring adopts a chair conformation, then by analogy with cyclohexane one large and three small vicinal coupling constants between the AB α-methylene and the CD β-methylene protons would be expected. Thus, with the proviso that $|\nu_A - \nu_B| \gg J_{AB}$, and with the likelihood that the small vicinal couplings are not resolved, the AB α-methylene region for either conformer will approximate to a doublet for one proton and a triplet for the other.[8]

Such a pattern is observed in regions Q and S respectively of the spectrum (Figure 5). Adjacent to the doublet Q is a similar doublet P of approximately half relative intensity. Accurate integration procedures show that the total intensity of the doublets P and Q equals that of the triplet S suggesting that the latter is comprised of two overlapping triplets of intensity ratio *ca.* 2 : 1. The central region of the spectrum R does not fit into such a simple approximation since in this case $|\nu_A - \nu_B| \approx J_{AB}$, which produces a complex second-order spectrum.

The above analysis implies more than two ' static ' conformers for *trans*-$[\mathrm{PdCl_2\{S(CH_2)_5\}_2}]$. The total number

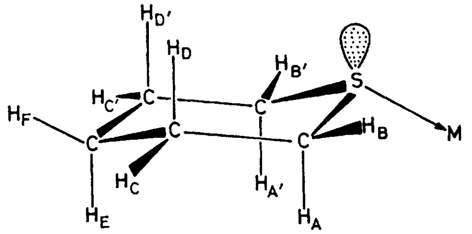


FIGURE 4 Typical spin system for co-ordinated pentamethylene sulphide $[\mathrm{S(CH_2)_5}]$

of conformers may be deduced by considering the *total* rather than the partial structure of the complex. There are four such conformers, namely, eq-eq (I), ax-ax (III), and a degenerate pair of conformers ax-eq (IV) and eq-ax (II) (Figure 7). Eight different α-methylene environments arise from these four conformers, two from each non-degenerate conformer (eq-eq and ax-ax) and four from the doubly degenerate conformers (ax-eq,eq-ax). Of these eight α-methylene chemical shifts, four must appear in region R of Figure 5.

The computer simulations in Figure 5 were produced as follows. Regions P, Q, and S were analysed as the AB portions of two overlapping ABCD spectra arising from one of the two possible orientations of the Pd–S bond (*i.e.* axial, see later). The chemical shifts C and D were chosen to accurately reproduce the region T which in turn causes the distortion of region S, a result which is only possible when the dihedral angle between the protons responsible for regions S and T is *ca.* 180°. The values for the geminal and vicinal couplings obtained from above were then used in the fittings of region R, which contains the AB portions of the two overlapping ABCD spectra arising from the other possible orientation of the Pd–S bond (*i.e.* equatorial, see later). This is possible since the nature of the Pd–S bond orientation with respect to the ring will only influence the ring methylene chemical shifts, especially the magnitudes of the AB α-methylene chemical-shift differences (Figure 5).

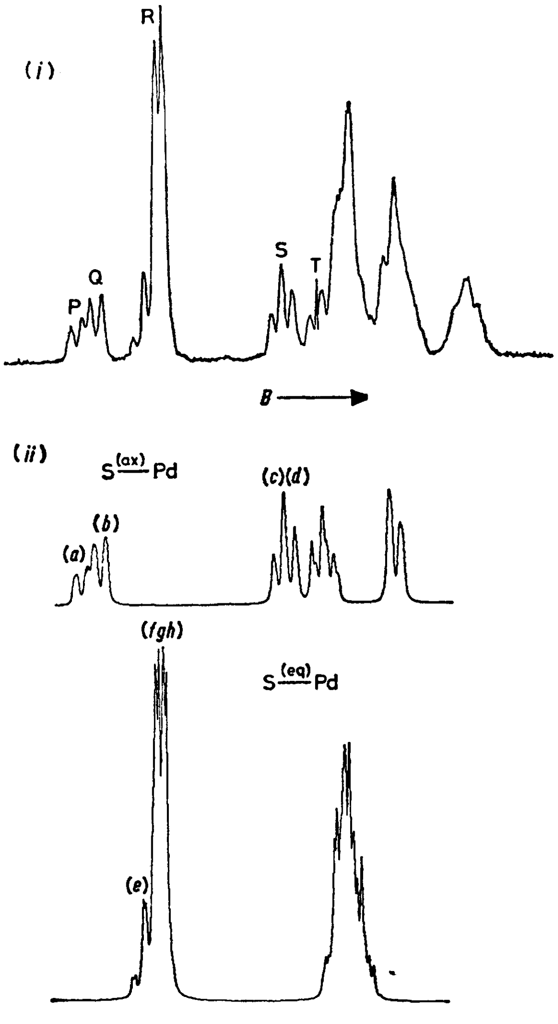


FIGURE 5 220 MHz ^1H n.m.r. spectrum (*i*) of *trans*-[$PdCl_2\{S(CH_2)_5\}_2$] at −100 °C together with its computer simulation (*ii*): (*a*) III eq; (*b*) II/IV eq; (*c*) II/IV ax; (*d*) III ax; (*e*) II/IV ax; (*f*) II/IV eq; (*g*) I ax; (*h*) I eq

To produce the final simulation the DNMR48 program was used to superimpose the four ABCD sub-spectra due to the eight α- and eight β-methylene chemical shifts using a variety of conformer populations until the best fit was obtained. It should be noted that assignment of the individual conformers is not required to produce the simulation shown in Figure 5, however in order to distinguish between the likely dynamic processes of ring reversal and sulphur inversion it is essential to make such an assignment. This task firstly requires a consideration of the likely conformer populations. The literature [23] on related pentamethylene sulphide systems produces no clear pattern as to whether axial or equatorial conformers will predominate. We therefore chose to base our assignment of conformers on the change in their relative population with halogen in the series *trans*-[$PdX_2\{S(CH_2)_5\}_2$] (X = Cl, Br, or I). This influence is pronounced as indicated by the spectra in Figure 8. Indeed, when X = I only a single conformer is evident. This may be explained by considering the PdX_2 moiety and its relationship with α-methylene protons of the ligand rings. Inspection of suitable models clearly indicates the greatest steric interaction between the PdX_2 moiety and the rings occurring when the Pd–S bond is axial. Thus as the size of X increases, the population of the axial conformer is expected to fall with concomitant increase in the equatorial conformer population. The above argument leaves no doubt as to the assignment of the single conformer of *trans*-$PdI_2\{S(CH_2)_5\}_2$] as eq-eq (Figure 7). The conformer assignments for the complexes (X = Cl and Br) follow readily with populations shown in Figure 7 and Table 2. These assignments are further supported by a crystal-structure determination of *trans*-[$PtBr_2\{S(CH_2)_2O(CH_2)_2\}_2$] [21] which indicates the eq-eq conformer to be favoured in the solid state. However, it should be noted that these conformer assignments conflict with those predicted using the criteria of Lambert and Featherman [23] (see below).

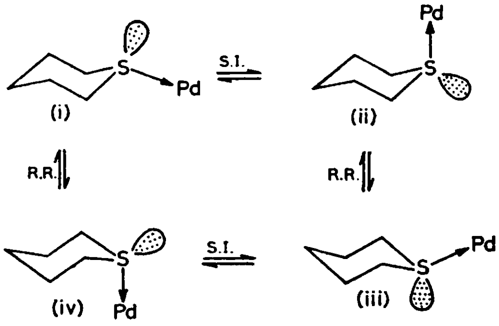


FIGURE 6 Low-temperature conformations of *trans*-[$PdCl_2\{S(CH_2)_5\}_2$] derived by analogy with piperidine. R.R. = Ring reversal, S.I. = sulphur inversion

Having assigned the individual sub-spectra to particular conformers, assignment of individual axial and equatorial α-methylene protons must be made. Considering firstly the single eq-eq conformer of *trans*-[$PdI_2\{S(CH_2)_5\}_2$], it is clear from the observed vicinal couplings of the α-methylene protons that it is the α-protons *axial* to the ligand rings which resonate at a lower field compared to the equatorial α-protons. This is true for all rings possessing an equatorial Pd–S bond. When the Pd–S bond is axial to the ring the opposite relationship holds, *i.e.* the α-methylene protons equatorial to the ligand rings produce the lower-field signals. Thus in rings possessing axial Pd–S bonds it is the α-protons *gauche* to this bond which resonate downfield from the *trans* protons. This result is in accordance with assumptions made in our earlier papers [17, 22, 24] based on the magnitudes of J_{PtH} between ^{195}Pt and the α-protons. The values for all spectral parameters are given in Table 2.

TABLE 2

220 MHz ^1H spectral parameters [a] (Hz) for *trans*-[$PdX_2\{S(CH_2)_5\}_2$] at −100 °C

X	Conformer [b]	Population (%)	ν_1	ν_2	ν_3	ν_4	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}
Cl	*eq*—eq	37.5	657.0	651.0	450.0	430.0	−13.0	2.1	12.0	3.7	2.1	−13.0
Cl	*eq*—ax	25.0	672.3	656.6	460.0	440.0	−13.0	2.1	12.0	3.7	2.1	−13.0
Cl	*ax*—eq	25.0	728.6	519.6	471.6	396.4	−13.0	2.1	3.7	12.0	2.1	−13.0
Cl	*ax*—ax	12.5	750.1	516.6	471.6	394.4	−13.0	2.1	3.7	12.0	2.1	−13.0
Br	*eq*—eq	67.0	688.0	652.5	444.0	382.0	−13.0	2.1	12.0	3.7	2.1	−13.0
Br	*eq*—ax	15.0	705.5	652.5	444.0	382.0	−13.0	2.1	12.0	3.7	2.1	−13.0
Br	*ax*—eq	15.0	779.0	574.0	444.0	400.0	−13.0	2.1	3.7	12.0	2.1	−13.0
Br	*ax*—ax	3.0	802.0	579.0	440.0	400.0	−13.0	2.1	3.7	12.0	2.1	−13.0
I	*eq*—eq	*ca.* 100	738.0	648.0	433.0	378.0	−13.0	2.1	12.0	3.7	2.1	−13.0

[a] Chemical-shift values related to the $SiMe_4$ signal. [b] The italicised portion of the total structure is the part to which the parameters refer.

The parameters computed from the 220 MHz spectrum of *trans*-[$PdCl_2\{S(CH_2)_5\}_2$] at −100 °C can be successfully reduced to fit closely the 100 MHz spectrum at −97 °C, with minor modifications in chemical shifts arising from differences in temperature and concentration between the two recordings.

It is clear from the variable-temperature spectra (Figures 2 and 3) that the dynamic processes involved at higher temperatures cause major changes in the absorption signals of the α-methylene protons. In order to analyse such changes it is strictly necessary to compute the results of four exchanging four-spin systems resulting from all α- and β-methylene environments. This computational problem is too great, and the spin system was modified in the following manner.

The 220 MHz chemical shifts for certain conformers are very similar, and will be even more similar at 100 MHz. It is therefore a reasonable approximation to return to the situation illustrated in Figure 6 where the conformation of one ligand ring is considered independent of the conformation of the other. Such a treatment involves averaging the chemical shifts of the α- and β-methylene protons in rings possessing the same orientations of the Pd–S bonds (*i.e.* either axial or equatorial). The averaged shifts calculated must take into account the different populations of the conformers involved. Namely, equation (1) where

$$\nu_{av.} = \left(\frac{p_A}{p_A + p_B}\right)\nu_A + \left(\frac{p_B}{p_A + p_B}\right)\nu_B \qquad (1)$$

for example ν_A is the chemical shift of the axial α-methylene proton (H^2) of the ax-ax conformer (III), ν_B the chemical shift of the axial α-methylene proton (H^2) for the axial portion of the ax-eq conformer (II/IV); p_A, p_B are the

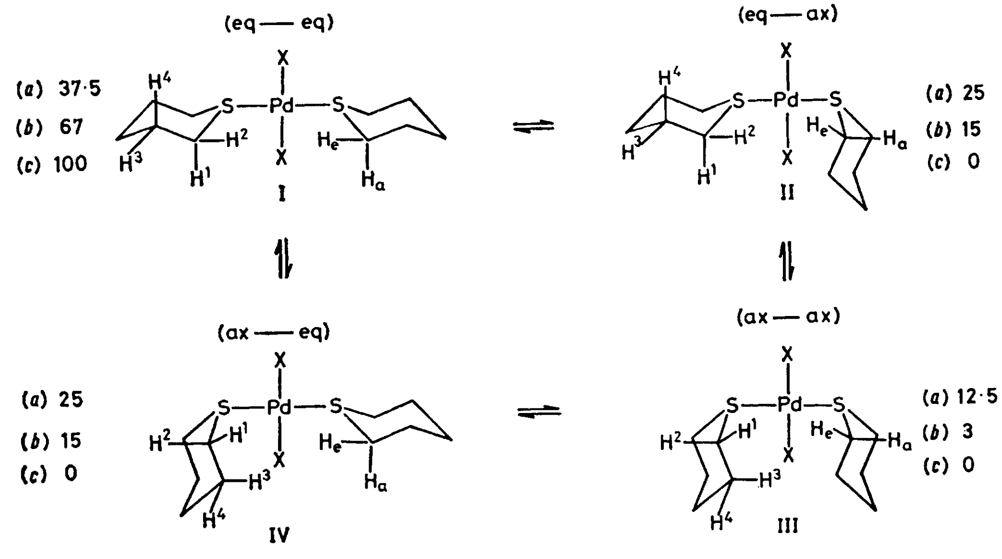


FIGURE 7 Low-temperature conformer populations (%) of *trans*-[$PdX_2\{S(CH_2)_5\}_2$], (*a*) X = Cl, (*b*) X = Br, and (*c*) X = I

populations of the above conformers, and $\nu_{av.}$ in this case is the chemical shift of the α-axial proton (H_F) in the averaged conformer ax′, Figure 9. The resulting chemical shifts of conformers ax′ and eq′ are given in Table 3.

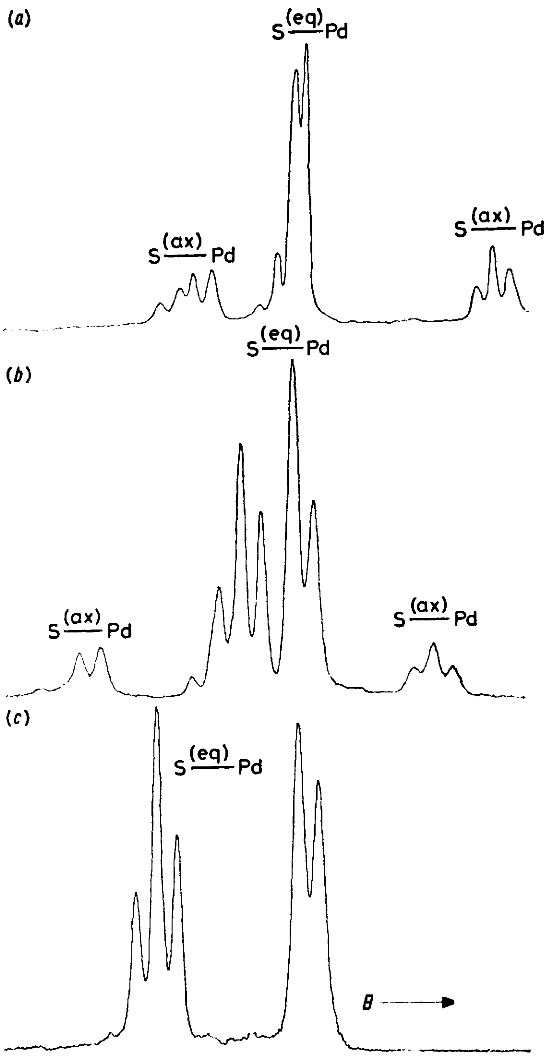


FIGURE 8 220 MHz ^{1}H n.m.r. spectra of the complexes *trans*-[$PdX_2\{S(CH_2)_5\}_2$] at −100 °C, (*a*) X = Cl, (*b*) X = Br, and (*c*) X = I

The two averaged conformers and the labelling of the α- and β-methylene protons are shown in Figure 9. The spin problem is thus reduced to one involving interconversion of two four-spin systems, the nature of interconversion depending on whether the process involved is ring reversal or sulphur inversion. If on warming the sample from *ca.* −100 °C the first dynamic rate process to occur were ring reversal, then the axial protons of one conformer would average with the equatorial protons of the other resulting in the spin system (2).

$$\text{ABCD} \rightleftharpoons \text{EFGH (ring reversal)} \qquad (2)$$

However, if sulphur inversion occurred first then the axial protons of one conformer would be averaged with the axial protons of the other conformer resulting in the spin system (3).

$$\text{ABCD} \rightleftharpoons \text{FEHG (sulphur inversion)} \qquad (3)$$

Clearly the averaged chemical shifts and coupling constants resulting from the two possible processes will differ greatly. Theoretical simulation of the 'fast-exchange' spectra using a large value for the rate constant, *k*, *clearly* showed the two resulting averaged spectra to be very different and only that generated by the onset of rapid ring reversal was compatible with the experimental spectra at −37 °C, a temperature where one rate process is rapid and the other slow.

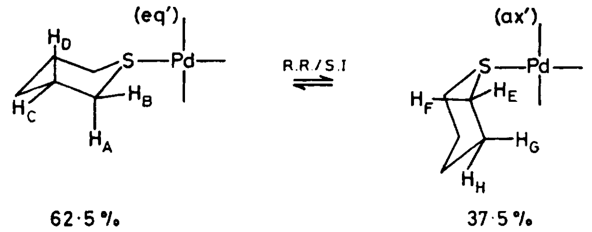


FIGURE 9 The modified low-temperature conformers of *trans*-[$PdCl_2\{S(CH_2)_5\}_2$]

Having thus conclusively assigned the lower-temperature dynamic process to reversal of the six-membered ligand ring, an accurate analysis of the α-methylene region between −77 °C and −45 °C was performed using the DNMR48

$$\langle AE\rangle\langle BF\rangle\langle CG\rangle\langle DH\rangle \qquad (4)$$

computer program, Figure 10. The values of the exchange rate constants were then treated in the usual way to obtain the activation parameters for ring reversal in *trans*-[$PdCl_2\{S(CH_2)_5\}_2$], Table 4.

The spectrum at −37 °C can be considered as the spin system (4) where ⟨AE⟩, *etc.*, signify the average chemical shift of protons A and E, *etc.*, produced by rapid ring reversal. As the rate of sulphur inversion increases there is mutual exchange of geminal α- and β-methylene environments according to (5).

TABLE 3

100 MHz spectral parameters * (Hz) for fitting dynamic ^{1}H n.m.r. spectra of *trans*-[$PdCl_2\{S(CH_2)_5\}_2$]

Conformer	Population (%)	θ_c/°C	ν_A	ν_B	ν_C	ν_D	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
eq′	62.5	−97	301.4	298.5	206.3	197.3	−13.0	2.1	12.0	3.7	2.1	−13.0
			ν_E	ν_F	ν_G	ν_H	J_{EF}	J_{EG}	J_{EH}	J_{FG}	J_{FH}	J_{GH}
ax′	37.5	−97	334.5	235.7	215.9	179.3	−13.0	2.1	3.7	12.0	2.1	−13.0
			ν_{AE}	ν_{BF}	ν_{CG}	ν_{DH}	$J_{AE,BF}$	$J_{AE,CG}$	$J_{AE,DH}$	$J_{BF,CG}$	$J_{BF,DH}$	$J_{CG,DH}$
⟨ax′eq′⟩	100	−37	315.9	271.6	209.9	190.6	−13.0	2.1	8.9	6.8	2.1	−13.0

* Chemical-shift values related to the $SiMe_4$ signal. A slight temperature dependence of certain chemical shifts was observed and allowed for.

The fully averaged spectrum is obtained at *ca.* 40 °C. Calculations using the DNMR36 program produced good fits of the experimental spectra between −30 and 20 °C

$$\langle AE\rangle\langle BF\rangle\langle CG\rangle\langle DH\rangle \rightleftharpoons \langle BF\rangle\langle AE\rangle\langle DH\rangle\langle CG\rangle \quad (5)$$

(Figure 11) and by treating the rate constants obtained in the usual way, activation parameters for sulphur inversion of this complex were calculated (Table 4).

In order to check the accuracy of the assumptions made in the analysis of these ^1H spectra and the resulting accuracy of the calculated activation parameters, a ^{13}C dynamic study on *trans*-$[PdCl_2\{S(CH_2)_5\}_2]$ was also performed.

Carbon-13 *N.M.R. Spectra*.—The proton noise decoupled ^{13}C spectrum at ambient temperatures consists of three absorptions due to the α, β, and γ carbon atoms of the ligand ring. On cooling to −100 °C the low-field α-methylene

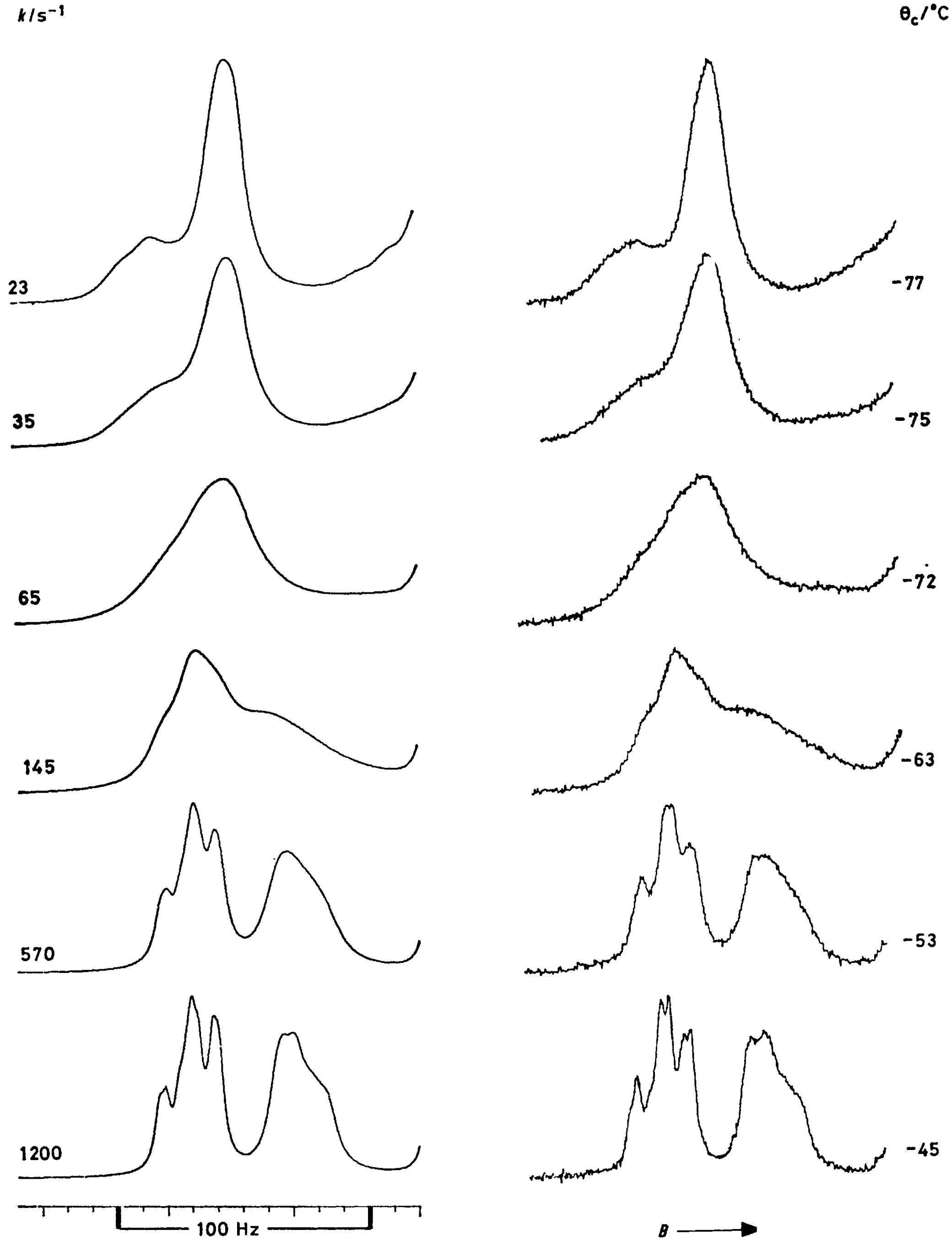


FIGURE 10 Variable-temperature ^1H n.m.r. spectra and their computed simulations as dynamic ring reversal for *trans*-$[PdCl_2\{S(CH_2)_5\}_2]$

carbon signal splits into three resolvable signals, namely an intense line considerably downfield from a less intense pair of lines (Table 5). The assignment of these signals is easily made by a consideration of the previously calculated conformer populations at −100 °C. Providing the NOE effects are similar for each α-carbon signal, the relative areas of the ^{13}C signals should match the conformer populations. On this basis the downfield signal was found to result from an overlap of the equatorial α carbons of conformers I and II/IV (Figure 7). Accordingly, the upfield pair of lines results from the axial α carbons of conformers III and II/IV, the downfield line of this pair being the α-carbon atoms of conformer III.

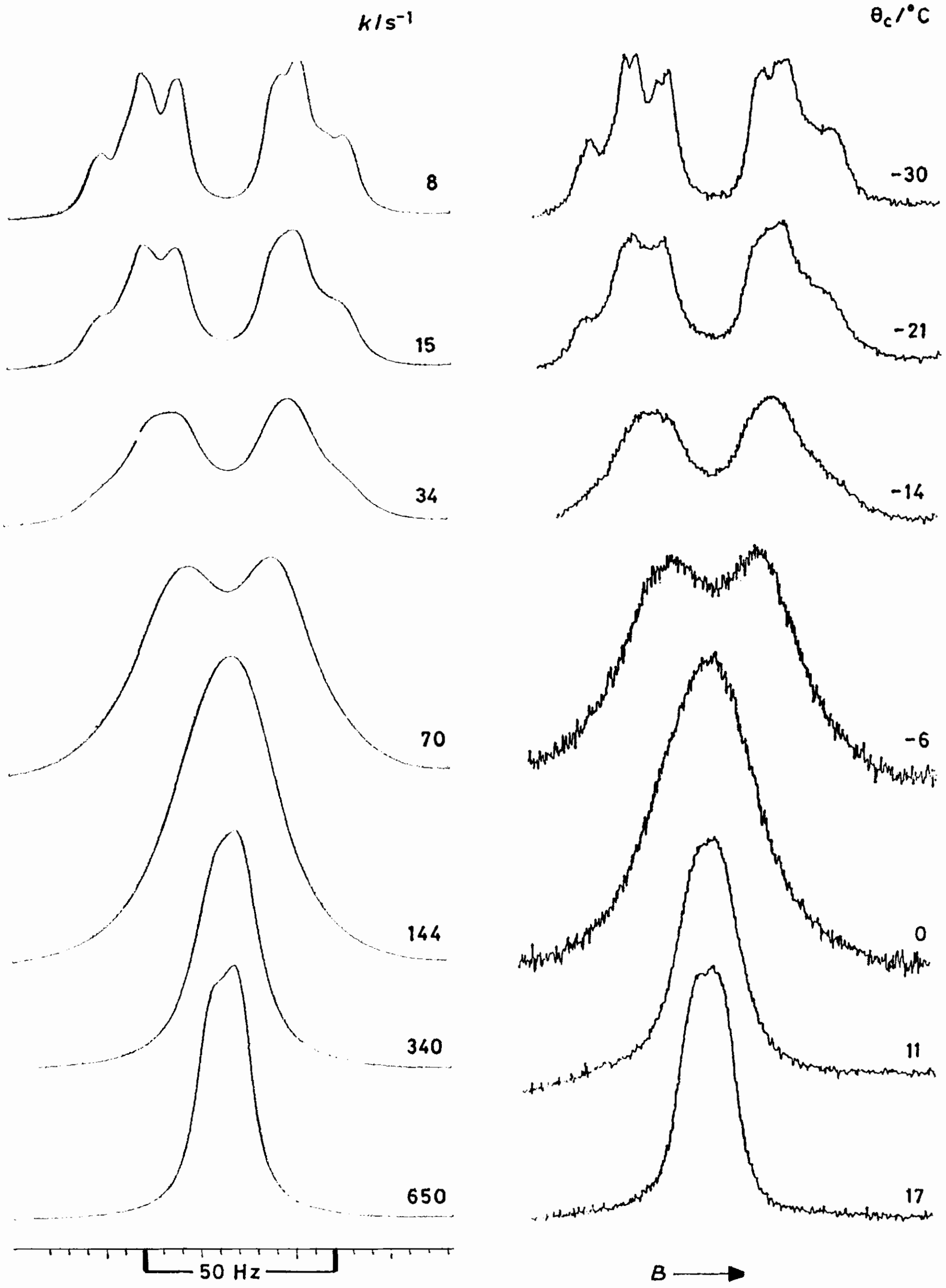
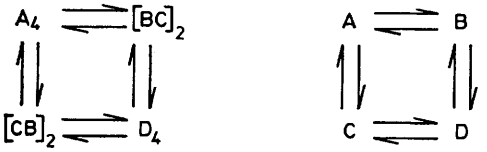


FIGURE 11 Variable-temperature ^{1}H n.m.r. spectra and their computed simulations as dynamic sulphur inversion for *trans*-[$PdCl_2\{S(CH_2)_5\}_2$]

The dynamic ^{13}C spin problem for the α-carbon atom environments in the absence of any ^{13}C–^{13}C couplings is shown in Scheme 1.

The labels A, BC, and D refer to the α carbons in conformers I, II/IV, and III respectively. Since no spin couplings are being considered these four-spin systems may be reduced to single-spin systems. It should be noted that this ^{13}C spin problem is based on the *total* conformations of the whole complex structure, and is a modest computational problem solvable by the DNMR8 program. In contrast, the ^{1}H spin problem had to be based on partial conformations (*i.e.* conformations of single ligand rings) in order for it to be tractable. The chemical shifts and other ^{13}C spectral parameters are given in Table 5.



SCHEME 1

It should be noted that the observed line-shape changes must result from a slowing down of the process with the lower energy barrier. In contrast to ^{1}H studies, dynamic ^{13}C n.m.r. cannot be used to distinguish between ring reversal and sulphur inversion processes, since the averaging of the four α-carbon chemical shifts A, B, C, and D to a single value ensues from *either* of the two processes, and when one of these processes is fast on the n.m.r. time scale the spectra are then totally insensitive to the other process. By analogy with the ^{1}H n.m.r. spectra the ^{13}C spectra will be sensitive only to the ring-reversal process. The ^{13}C spectra between −100 °C and −40 °C were analysed in the usual manner to obtain the exchange rate constants which led to the activation parameters for ring reversal as in Table 4.

TABLE 4

Arrhenius and activation parameters [a]

Complex	^{1}H/^{13}C	T_c[b]/K	R.R.[c]/S.I.[d]	E_a[e] kJ mol^{-1}	$\log_{10}A$[e]	$\Delta H^{\ddagger}$[f] kJ mol^{-1}	$\Delta S^{\ddagger}$[f] J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$ kJ mol^{-1}
trans-[PdCl$_2${S(CH$_2$)$_5$}$_2$]	^{1}H	201	R.R.	43.2 ± 1.1	13.0 ± 0.3	41.5 ± 1.0	−2.0 ± 5.1	42.1 ± 2.6
trans-[PdCl$_2${S(CH$_2$)$_5$}$_2$]	^{13}C	206	R.R.	43.8 ± 1.1	13.4 ± 0.3	42.1 ± 1.1	7.1 ± 5.2	40.0 ± 2.6
trans-[PtCl$_2${S(CH$_2$)$_5$}$_2$]	^{13}C	208	R.R.	43.9 ± 0.9	13.4 ± 0.2	42.1 ± 0.9	7.0 ± 4..3	40.0 ± 2.2
trans-[PtCl$_2${S(CH$_2$)$_5$}$_2$]	^{1}H	213	R.R.					
trans-[PdCl$_2${S(CH$_2$)$_5$}$_2$]	^{1}H	273	S.I.	55.8 ± 1.2	12.8 ± 0.2	55.6 ± 1.2	−7.3 ± 4.5	55.7 ± 2.6
trans-[PtCl$_2${S(CH$_2$)$_5$}$_2$]	^{1}H	313	S.I.					

[a] $\Delta G^{\ddagger}$ calculated for $T = 298.15$ K, and all the above error limits are based on linear-regression analysis. [b] Coalescence temperature. [c] Ring reversal. [d] Sulphur inversion. [e] E_a and $\log_{10} A$ were calculated from the Arrhenius plot. [f] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the Eyring equation.

In view of the computational time involved only one of the complexes *trans*-[PdX$_2${S(CH$_2$)$_5$}$_2$] (X = Cl, Br, or I) was subjected to a complete ^{1}H and ^{13}C study. The complex chosen was that with X = Cl since in this case the ratio of conformer populations eq′ : ax′ was closest to unity, and the change in line shape was the greatest displayed by the three complexes.

Turning now to the platinum(II) complexes, the static ^{1}H spectrum of *trans*-[PtCl$_2${S(CH$_2$)$_5$}$_2$] presents an additional problem due to the presence of the ^{195}Pt nucleus. The simplified ^{1}H spin system now becomes (6).

$$\text{ABCD} \rightleftharpoons \text{EFGH } (66.3\%) \text{ plus ABCDX} \rightleftharpoons \text{EFGHX } (33.7\%) \quad (6)$$

This problem cannot be handled by the present DNMR programs, and only values of the two coalescence temperatures can be determined from the ^{1}H spectra (Table 4).

The analysis of the ^{13}C spectra for *trans*-[PtCl$_2${S(CH$_2$)$_5$}$_2$] is again considerably easier than the ^{1}H system since it is described by Scheme 2.

This scheme can be readily handled by the DNMR8 program. However, as discussed above, it is only possible to observe the inversion process with the lower barrier energy. This leads to the determination of only one set of activation parameters, corresponding to the process associated with the lower of the two ^{1}H coalescence temper-

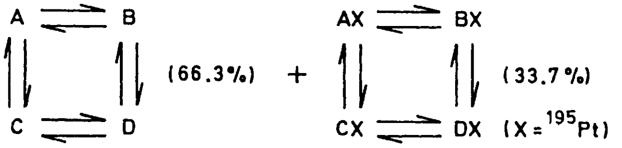
TABLE 5

25 MHz ^{13}C chemical shifts [a] (Hz) for *trans*-[MCl$_2${S(CH$_2$)$_5$}$_2$]

M	Conformer [b]	θ_c/°C	Population (%)	T_2*[c]/s	ν_α[d]	ν_β	ν_γ
Pd	*eq*—eq	−98	37.5	0.106	871.6		
Pd	*eq*—ax	−98	25	0.106	871.6		
Pd	*ax*—eq	−98	25	0.106	788.6		
Pd	*ax*—ex	−98	12.5	0.106	796.4		
Pd	Average	−45	100	0.106	843.8	661.6	636.7
Pt	*eq*—eq	−103.5	60	0.095	856.9		
Pt	*eq*—ax	−103.5	15	0.095	853.4		
Pt	*ax*—eq	−103.5	15	0.095	766.0		
Pt	*ax*—ax	−103.5	10	0.095	769.0		
Pt	Average	+30	100	0.095	837.9	652.3	643.6

[a] Values related to the SiMe$_4$ signal. [b] The italicised portion of the total structure is the part to which the parameters refer. [c] Natural line width at half height $\Delta\nu_{\frac{1}{2}} = (\pi T_2^*)^{-1}$. [d] Slightly temperature dependent.

atures. Relevant ^{13}C spectral parameters are given in Table 5. The thermodynamic parameters obtained from spectra between −100 °C and −38 °C are given in Table 4.



SCHEME 2

DISCUSSION

Nuclear Magnetic Resonance Parameters.—The spectral parameters of Tables 2, 3, and 5 reveal a number of interesting features. Perhaps the most surprising is the dependence of the α-^1H and α-^{13}C chemical shifts of a particular ligand ring, upon the conformation of the other ligand ring *trans* to it. With one or two exceptions the α-methylene chemical shifts of any ring experience a greater shielding when the other ring possesses an equatorial Pd–S bond than when this bond is axial. For example, in the case of ^1H shifts, the α-methylene protons (labelled ν_1, Table 2) where the Pd–S bond is axial are at an appreciably higher field for the ax-eq conformer (II/IV) than those for the ax-ax conformer (III). Related cases to the above in the literature are rare, the only examples we have discovered being the two cyclohexane rings in 3,3,6,6-bis(pentamethylene)-*s*-tetrathian[$CH_2(CD_2)_3CH_2CS_2CS_2CH_2(CD_2)_3CH_2$].[25] Here the two cyclohexane rings can exist in various diastereoisomeric forms depending upon their relative orientations. However, only one set of n.m.r. parameters is observed, implying that either one diastereoisomer is 100% abundant or the influence of any anisotropic shielding is minimised over the three intervening bonds C–S–S–C. Conformational studies on the related compound 1,1-dicyclohexylmethane $(C_6H_{11})_2CH_2$ do not appear to have been performed and an n.m.r. study of 4-cyclohexylpiperidines indicates that only the eq-eq conformer is present in solution.[26]

For all of our complexes the downfield α protons (ν_1, Table 2) resonate at progressively lower fields as the halogen size increases; such an effect is not uncommon and has been discussed previously.[22] The above relationship is also true for the α protons (ν_2, Table 2) in the ligand rings involving an axial Pd–S bond. However, where such a bond is equatorial little change in chemical shift is apparent. It should be noted that in such cases the spatial relationship between the Pd–X bond and the C–H_2 bond is somewhat different than in the other cases, and may well explain the negligible deshielding effects observed with changing halogen in this case.

The variation in relative conformer populations with respect to the influence of halogen size in the PdX_2 moiety has already been discussed. A similar trend is noted for the conformer populations determined by ^{13}C studies for *trans*-[$MCl_2\{S(CH_2)_5\}_2$] (M = Pd or Pt), Table 5. Here the change in going from Pd^{II} to Pt^{II} favours the equatorial conformer types at the expense of the axial ones on steric grounds due to the increasing size of the MCl_2 moiety. Literature examples of such steric effects are well documented, notably in methylcyclohexane[27] where the methyl group predominantly adopts the equatorial position to the extent of *ca.* 95%. In methyl substituted silacyclohexanes there is a preference for axial substitution, mainly as a result of attractive interaction, which changes to preferential equatorial substitution, as a result of increasing steric interaction, when the substitution is t-butyl.[28]

Lambert and Featherman[23] have formulated a set of criteria relating the observed ^1H n.m.r. α-methylene AB quartet patterns in monosubstituted thianes [$X\overset{+}{S}(CH_2)_5$] (X = $\overset{+}{N}$R, O) to a particular axial or equatorial conformer. The axial conformer was found[23] to exhibit an AB quartet pattern at a higher-field position and possessing a smaller chemical-shift difference and larger geminal coupling constant compared to the AB quartet pattern of the equatorial conformer. Our own conformational assignments obey only the first criterion. However, we see no reason to doubt our assignments which are based on the variation of conformer populations with respect to change in the MX_2 moiety. The anomaly arises presumably from the special shielding effects of the substituent, MX_2.

Further work by Lambert and co-workers[23,29,30] on the sign of the chemical-shift differences between the α-axial and α-equatorial protons δae(α), in thiane and its derivatives, results in an unusual negative value of δae(α) for thiane. The negative sign indicates that the equatorial proton absorbs at a higher field than the axial proton. In all the monosubstituted thianes δae(α) is positive.[29] Our results give the value of δae(α) as being negative for the eq′ conformers and positive for the ax′ conformers, Table 3. The negative value for the eq′ conformers is further indication of the particular magnetic anisotropy of the MX_2 moiety compared to that of oxides and imides.

Finally it is of interest to note the magnitudes of the ^{195}Pt–^{13}C couplings where $^3J(^{195}Pt-^{13}C)$ (= 31.3 Hz) > $^2J(^{195}Pt-^{13}C)$ (=10.7 Hz) a result recently observed for analogous nitrogen systems.[31]

Activation Energies.—The free energies of activation illustrated in Table 4 exhibit a number of interesting features. We have already shown, by careful spectral analysis, that the inversion process resulting in the lower-temperature coalescence of the ^1H n.m.r. spectra is due to reversal of the six-membered ligand ring. The magnitudes of the computed energy barriers further support this assignment. The barriers of *ca.* 42 and 56 kJ mol^{-1} for *trans*-[$PdCl_2\{S(CH_2)_5\}_2$] computed from the ^1H spectra compare favourably with the value of *ca.* 40 kJ mol^{-1} for thiane [$S(CH_2)_5$] ring reversal[16] and the value of *ca.* 55 kJ mol^{-1} for sulphur inversion in the complex *trans*-[$PdCl_2\{S(CH_2SiMe_3)_2\}_2$],[17] indicating that the lower-energy process is almost certainly due to ring reversal and the higher one to pyramidal sulphur inversion.

The barriers computed from the ^{13}C data for the complexes *trans*-$\mathrm{[MCl_2\{\overline{S(C}H_2)_5\}_2]}$ (M = Pd or Pt) are both *ca.* 40 kJ mol^{-1}. Thus the nature of the transition metal has little effect upon the value of the lower of the two inversion energies. Earlier work has shown that generally the barrier to sulphur inversion depends upon the nature of the transition metal; for example the barrier for platinum(II) complexes is some 7—9 kJ mol^{-1} higher than for palladium(II) complexes.[17,22] No inversion energy data could be calculated for the higher-energy process in the complex *trans*-$\mathrm{[PtCl_2\{\overline{S(C}H_2)_5\}_2]}$ for reasons given previously. However an inspection of the higher coalescence temperatures for the complexes *trans*-$\mathrm{[MCl_2\{\overline{S(C}H_2)_5\}_2]}$ shows a rise of *ca.* 40 °C in going from the palladium(II) to the platinum(II) complex. Such an increase is consistent with a higher inversion energy for Pt$^{\mathrm{II}}$ than Pd$^{\mathrm{II}}$. We have therefore no hesitation in assigning the higher of the two barriers to pyramidal inversion of the co-ordinated sulphur atom, and hence the lower barrier to reversal of the ligand ring. Such a comparison of observed energy barriers with those known for related species has been used recently by Riddell *et al.*[4,32] in assigning the inversion process observed in *NN'*-dimethyltetrahydro-1,2,5-oxadiazine and related species to one of two possible mechanisms.

The barriers for ring reversal in *trans*-$\mathrm{[MCl_2\{\overline{S(C}H_2)_5\}_2]}$ (M = Pt or Pd) calculated from the ^{13}C data are considered somewhat more reliable than those from the ^{1}H studies. These barriers are *ca.* 40 kJ mol^{-1} in both cases and are remarkably close to that of *ca.* 39.5 kJ mol^{-1} for the unco-ordinated ligand ring $\mathrm{[\overline{S(C}H_2)_5]}$.[16] The influence of a transition metal on the ring reversal transition state must therefore be very small, a fact which is not surprising in view of the minor influence on ligand ring geometry brought about by complexation to a transition metal.[21] In view of the above conclusions we note a recent paper by Graham and co-workers [33] which appears to report an increase in the barrier to ring reversal from ^{1}H studies of *ca.* 18 kJ mol^{-1} for 1,3-dithiane $\mathrm{[\overline{S(CH_2)S(C}H_2)_3]}$ upon complexation with an Fe(CO)$_4$ moiety. However, a careful examination of their results,[33] notably the variable-temperature ^{13}C n.m.r. spectra, indicates that the authors have in fact computed the value for pyramidal inversion, of the sulphur atom attached to the Fe(CO)$_4$ moiety, and not the barrier to ring reversal which would be rapid in the temperature range in which the ^{1}H n.m.r. spectra were recorded.

In contrast, the barriers to sulphur inversion in our complexes *trans*-$\mathrm{[MCl_2\{\overline{S(C}H_2)_5\}_2]}$ (M = Pd or Pt) show a marked dependence upon the nature of the transition metal, supporting the involvement of the metal atom in the stability of the sulphur inversion transition state ***via* $p\pi$–$d\pi$** overlap.[17]

The very low degree of strain in the six-membered rings explains why the value of the sulphur inversion barrier in the complex *trans*-$\mathrm{[PdCl_2\{\overline{S(C}H_2)_5\}_2]}$ of *ca.* 56 kJ mol^{-1} is very similar to that of *ca.* 55 kJ mol^{-1} for the linear dialkyl sulphide complex *trans*-$\mathrm{[PdCl_2\{S(CH_2SiMe_3)_2\}_2]}$. This is in considerable contrast to the dependence of the sulphur inversion barrier upon the smaller and more highly strained ligand rings observed in our earlier paper.[22]

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