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DYNAMIC NMR STUDIES OF FERROCENYLSULPHIDE-PALLADIUM(II) AND -PLATINUM(II) COMPLEXES

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Summary

The stereodynamics of ferrocenylsulphide-palladium(II) and -platinum(II) complexes, $Fe(C_5H_4SR)_2MX_2$, ($M = Pd^{II}$, Pt^{II}; $X = Cl$, Br; R = Ph, i-Pr and i-Bu), have been examined by variable temperature NMR. At temperatures down to ca. −100°C, the pyramidal inversion of the S atoms could be slowed down sufficiently to yield accurate energy data, while the reversal of the ferrocenophane ring remained fast on the NMR time scale. $\Delta G^{\neq}$ data for the S inversion process were in the range 47 to 65 kJ mol^{-1} and were influenced to varying extents by the nature of the transition metal, the halogen, and the R substituent on the sulphur.

Introduction

The stereodynamics of metal complexes of coordinated sulphur ligands have recently been reviewed [1]. Coordination of sulphur atoms to transition metals greatly increases the rate of pyramidal S inversion as a result of $(p-d)\pi$ conjugation effects and brings it within the range of NMR detection. Previous studies on palladium(II) and platinum(II) complexes have yielded $\Delta G^{\neq}$ values for the pyramidal inversion in the range 48–79 kJ mol^{-1}, the values being very dependent on whether the complexes are *cis* or *trans* isomers and, in the case of cyclic sulphides, on the ring size [2–7].

When S atoms are incorporated as bridging atoms in [3]-ferrocenophanes, their inversion characteristics are no longer measurable but their presence endows the complexes with a bridge reversal fluxion [8–10]. Such a fluxion, which is somewhat akin to the chair-to-chair reversal of six-membered rings, is a relatively high energy process when chalcogen atoms are incorporated in the bridge [10,11]. When carbon and oxygen form the bridging atoms the ring reversal process is greatly accelerated on account of the lower torsional barriers of C–C and C–O bonds compared to S–S bonds [12]. Cooling of solutions of these complexes to ca. −100°C is required to slow the bridge reversal process sufficiently to reveal the spectra of the "static" conformers [12].

The present ferrocenylsulphide metal(II) complexes have the potentiality to undergo both S pyramidal inversion and ferrocenophane bridge reversal, and the present work was undertaken to explore these processes further by dynamic NMR methods.

Experimental

Materials. The complexes $Fe(C_5H_4SR)_2MX_2$, ($M = Pd^{II}, Pt^{II}$; $X = Cl, Br$; $R =$ Ph, i-Pr, i-Bu), were prepared by a general method described elsewhere [13]. Complexes with R = Me were also prepared [13] but proved insoluble in all common organic solvents and were not further studied here. NMR studies were performed on $CDCl_3$ solutions of the other complexes.

NMR studies

^1H NMR studies were performed on a JEOL PS/PFT-100 spectrometer operating at 100 MHz in the FT mode. Two of the platinum(II) complexes (R = i-Bu; X = Cl, Br) were also submitted to 400 MHz ^1H analysis at the University of Warwick, England. The 19.1 MHz ^{195}Pt spectrum of the platinum(II) complex (R = i-Bu; X = Cl) was obtained at the City of London Polytechnic. The ^1H spectra, which were subsequently submitted to total band shape analysis, were recorded in the approximate temperature range −60 to +60°C, temperatures being accurately measured with a Comark digital thermometer before and after each recording.

NMR band shape fittings were performed with the authors' version of the DNMR3 program of Binsch [14]. Arrhenius and Eyring activation parameters were based on least-squares fittings of the appropriate plots and errors are expressed as r.m.s. values, the errors for $\Delta G^{\neq}$ being as prescribed by Binsch [15].

Results

(i) Low temperature spectra

The low temperature ^1H spectra (ca. −30°C and below) of all the complexes reveal four equal intensity "pseudo-singlets" for the ferrocene ring protons. The remaining parts of the spectra depend on the nature of the R substituent on sulphur. For R = i-butyl, the CH_2 protons show as an *AB* part of an *ABX* system, the CH proton (*X* part) appears as an unresolved multiplet, and the non-equivalent methyls show as an overlapping pair of doublets. For R = i-propyl, the methyls are again non-equivalent and appear as a pair of doublets, while the CH signal is a binomial septet. In the case of the Pt^{II} complexes, the R substituent proton signals show evidence of 3- and 4-bond ^{195}Pt–^1H couplings. For R = phenyl and benzyl, the signals are essentially singlets. At above-ambient temperatures, the spectra in all cases simplify as a result of the four different cyclopentadiene proton environments changing to two averaged environments, the diastereotopic methyls of the i-propyl and i-butyl groups becoming isochronous, and the CH_2 protons of i-butyl also becoming equivalent.

The changes in spectral features are consistent with a single type of internal site exchange process. The two rate processes which may be occurring are pyramidal inversion of the S atoms and reversal (inversion) of the S–MX_2–S portion of the ferrocenophane ring. If both processes are slow on the NMR time scale, then four structural isomers can exist, *meso*-1, *meso*-2 and a pair of degenerate *DL* forms (Fig. 1). Independent inversion of individual S atoms will interconvert all four forms, whereas bridge reversal will mutually interconvert the pair of *meso* isomers and the degenerate *DL* pair (Fig. 1). It should be noted, however, that bridge reversal also causes an exchange of the S atom labelling (i.e. topomerisation [16]) which is not indicated in Fig. 1. This does not affect the spectral interpretation although strictly all eight topomers should be represented as the eight corners of a regular cube (Fig. 2). Sulphur inversion interconverts species on the front or rear faces of the cube, while bridge reversal interconverts adjacent species on the front and rear faces. In such a representation mirror image pairs are at diametrically opposite corners of the cube; in the case of *DL* species these are true diastereoisomers while for *meso* they are simply topomers.

Returning to Fig. 1, it can be seen that if all three distinct structural isomers exist at low temperatures, then the spectra would be far more complex than was found, (e.g. up to 16 cyclopentadienyl proton signals would be expected). The equal intensity of the four ring proton signals implies that only one static or conformationally averaged isomer is present. Two possible interpretations of the low temperature spectra need to be considered.

(a) S inversion fast, bridge reversal slow. S inversion interconverts all four isomeric species and therefore when inversion is rapid the spectra will be totally insensitive to the effects of bridge reversal. No temperature dependence of the spectra would ensue in contrast to observations. This case can therefore be excluded.

(b) Bridge reversal fast, S inversion slow. In this case, the spectra will be characteristic of conformationally averaged *meso* 1/2 forms or *DL* forms. In other words, there will be rapid interconversion of adjacent structures on the front and rear faces of the cubic graph diagram (Fig. 2). In the case of the degenerate *DL*

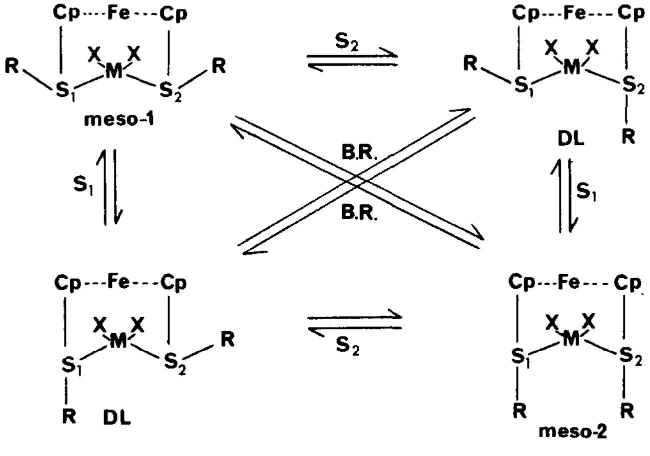


Fig. 1. Interconversion of *meso*- and *DL*-forms of $Fe(C_5H_4SR)_2MX_2$ as a result of sulphur inversion (S_1 or S_2) or bridge reversal (B.R.) (Simplified diagram).

species, the time averaged structure involves a pseudo-planar S_1–M–S_2 bridge. Of the two *meso*-forms, molecular models indicate very severe steric interactions between R substituents in *meso*-2, and thus any averaging of *meso*-forms will be very much weighted in favour of *meso*-1. Indeed, it is not unreasonable to assume that *meso*-2 is of undetectably low abundance. The low temperature ^{1}H NMR spectra consisting, in the majority of cases, of just four equal intensity ring proton signals can therefore be associated with either *meso*-1 or *DL* species. The variable temperature spectra clearly indicate that S inversion exchanges pairs of cyclopentadiene ring protons. This could result either from $\langle DL \rangle \rightleftharpoons \langle DL \rangle$ exchange or from *meso*-1 $\rightleftharpoons$ *meso*-1 exchange (Figs. 2, 3). We are inclined to the view that the signals arise from predominant *DL* species for the following reasons:

(i) Molecular models favour a *trans* arrangement of these bulky R groups.

(ii) In the case of the Pt^{II} complexes greater shielding is expected for ^{195}Pt in the *meso* compared to *DL* species. When R = i-Bu, two very unequal intensity ^{195}Pt signals separated by ca. 75 ppm are observed (see later). The very high intensity signal appears at lower applied field and is very likely attributed to the predominant *DL*-isomer.

(iii) Studies [7] of the complexes *cis*-[MX_2L], (M = Pd^{II}, Pt^{II}; L = $MeS(CH_2)_2SMe$), indicate that *DL* isomers are marginally favoured over *meso*-isomers. With more bulky alkyl groups than methyl this preference is likely to be more pronounced.

Subsequent to this conclusion being reached an X-ray crystal analysis of (C_5H_4S-i-Bu)$_2PdCl_2$ revealed that the i-Bu groups were in a mutual *trans* disposition [13], with the dihedral angle between the plane containing the iron and the two sulphur atoms and that containing the palladium and the sulphurs being 75.4°. Rapid bridge

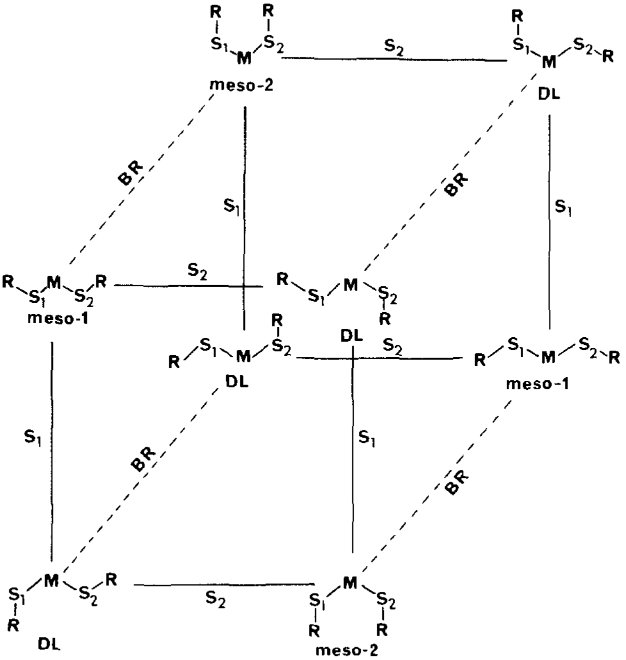
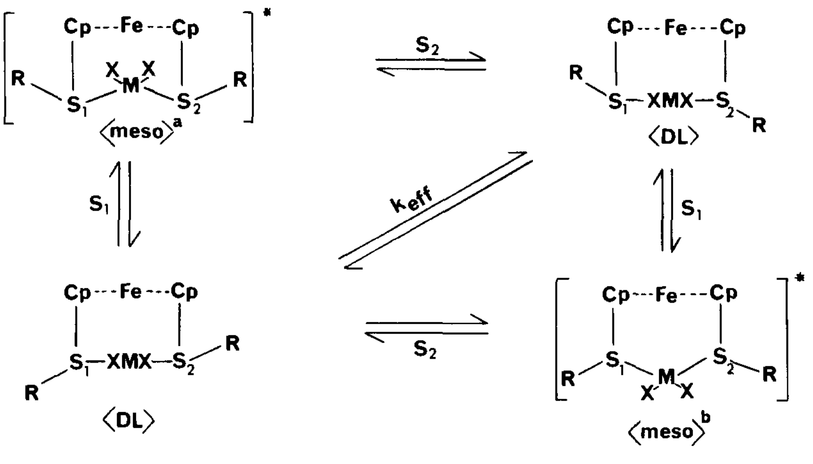


Fig. 2. Graph diagram depicting the inter-relationship of the eight diastereoisomers of Fe(C_5H_4SR)$_2MX_2$.

reversal in solution averages the dihedral angle to zero and the solid state structure of the complex becomes transformed into the conformationally averaged *DL* solution structure.

The spectra can therefore be explained on the basis of the bridge reversal process, and indeed any S–C or C–C bond rotation process being always fast on the NMR time scale, and the spectral changes with temperature arise from varying rates of inversion of the S atoms in the *DL* isomers which exchange the environments of pairs of cyclopentadienyl protons, and, in some cases, the environments of the R substituents.

The spectral parameters (chemical shifts and coupling constants) of the ring protons of these low temperature spectra are collated in Table 1. In the cases of the complexes $Fe(C_5H_4S\text{-i-Bu})_2PtCl_2$ and $Fe(C_5H_4S\text{-i-Bu})_2PtBr_2$, the ^1H spectra showed additional sets of weak signals which, following the above discussion, were ascribed to the conformationally averaged *meso*-isomer. The very different chemical shifts of this species lend further support to the assumption that they are due to the effectively static *meso*-1 isomer, *meso*-2 being of undetectably weak abundance. This would also account for the large geminal chemical shift distinction of the CH_2 protons of the i-Bu group in *meso*-1, compared to the corresponding shifts in the *DL* species, these latter shifts being already conformationally averaged. The 400 MHz spectrum of $Fe(C_5H_4S\text{-i-Bu})_2PtBr_2$ (Fig. 4) clearly indicates the distinctive features of the two diastereoisomers. This distinction was also revealed in the low temperature ^{195}Pt spectra of these two Pt^{II} complexes (see later). The four ring proton signals were assigned on the basis of a high frequency shift imposed on the ring protons by the SR group, the protons H_A and H_B, *ortho* to the substituent being more affected than protons H_C and H_D. Distinction between H_A and H_B and between H_C and H_D was less certain but is not essential for the line shape fitting procedure. The



* Not observed in most cases
a Essentially *meso*-1
b Essentially *meso*-2

Fig. 3. Interconversion of the conformationally averaged diastereoisomers by inversion of individual S atoms, Due to the non-observance of *meso*-forms, in most cases, k_{eff} represents the effective S inversion rate constant between the averaged *DL* pair.

TABLE I

CYCLOPENTADIENE RING PROTON SHIFTS [a] AND COUPLING CONSTANTS [b] IN $Fe(C_5H_4SR)_2MX_2$ COMPLEXES

Complex			T (°C)	ν_A (Hz)	ν_B (Hz)	ν_C (Hz)	ν_D (Hz)
M	X	R					
Pd	Br	Ph	−63.0	587.4	501.7	483.9	458.5
Pd	Br	CH_2Ph	−38.0	570.6	417.5 [c]	460.0	413.6 [c]
Pd	Cl	i-Pr	−31.0	575.4	484.1	465.1	433.8
Pd	Br	i-Pr	−53.5	567.6	484.6	461.7	436.5
Pd	Cl	i-Bu	−62.8	567.1	493.4	463.6	432.9
Pd	Br	i-Bu	−41.3	561.0	489.3	458.0	432.4
Pt	Br	Ph	−57.5	571.3	502.2	486.6	456.5
Pt	Cl	i-Pr	−15.2	550.3	478.3	465.1	434.3
Pt	Br	i-Pr	−42.2	549.2	480.7	463.6	436.5
Pt	Cl	i-Bu [d]	−4.1	545.2	483.9	462.4	432.1
		i-Bu [e]	−100	503.9	500.3	440.0	436.8
Pt	Br	i-Bu [d]	−24.4	542.2	485.8	460.2	433.8
		i-Bu [e]	−100	505.4	501.0	443.1	436.7

[a] Shifts measured at 100 MHz relative to Me_4Si. See text for proton labelling. [b] The following values from ref. 11 were used in all cases: $J_{AB} = J_{AD} = J_{BC} = 1.3$ Hz, $J_{AC} = J_{BD} = J_{CD} = 2.5$ Hz. [c] Assignments possibly reversed. [d] *DL*-diastereoisomer, 96% (X = Cl), 85% (X = Br). [e] *meso*-diastereoisomer, 4% (X = Cl), 15% (X = Br). Shift values measured at 400 MHz and converted to 100 MHz shifts for comparison purposes.

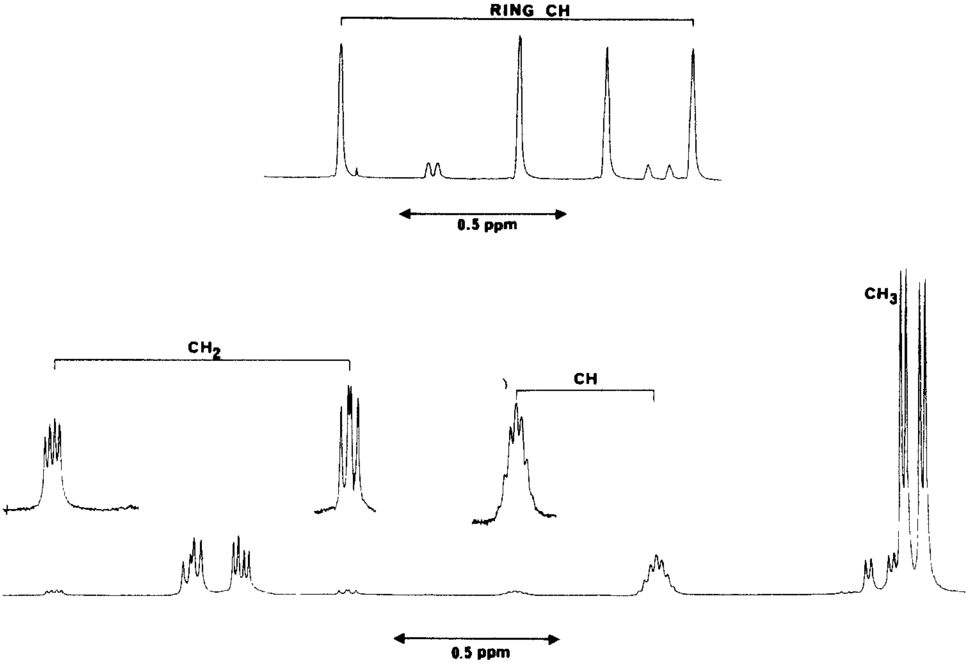
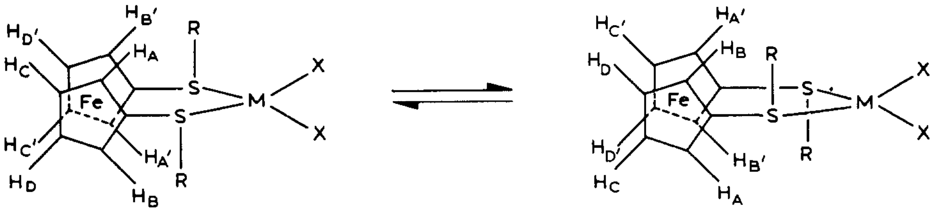


Fig. 4. 400 MHz ^1H NMR spectrum at −40°C of $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtBr_2$ showing both *DL*- and *meso*-diastereoisomers. The abundance ratio is *DL*/*meso* ≈ 85/15.

assignments given in Table 1 are based on the assumption that the SR group will exert greater shielding on the proton H_B which is *cis* to the R substituent than on H_A. A similar assumption was made in distinguishing between H_C and H_D. The shielding anisotropy of the SR groups attenuated with distance such that the internal chemical shifts (ν_A–ν_B) and (ν_C–ν_D) were in the ranges 56–91 and 25–31 Hz respectively. The single exception to this was the SCH_2Ph derivative where both internal shifts were approximately twice as large, presumably due to the ring current anisotropy of the benzene ring (see later).

(ii) Dynamic studies

Accurate band shape analyses were performed on the ring CH region of the ^1H spectra of all the complexes. In some cases, additional fittings were carried out on the methyl regions of the i-Pr or i-Bu derivatives to confirm or supplement the ring CH region fittings. The dynamic spin problem involves interconversion between a degenerate pair of *DL* conformers in which the dihedral angle between the FeS_2 plane and the MX_2 plane is now averaged to zero by the rapid bridge reversal fluxion. The interchange is represented by:



and the spin problem is of the type $[ABCD]_2 \rightleftharpoons [BADC]_2$ which can be simplified to $ABCD \rightleftharpoons BADC$ in the absence of inter-ring couplings.

Spectra were computed using the chemical shifts and coupling constants given in Table 1. The $^3J(HH)$ and $^4J(HH)$ values were difficult to measure directly from the low temperature spectra of the complexes, and the values used in the computation were taken from some earlier studies on bridged ferrocenophanes [11]. These values gave good fittings with the experimental low temperature spectra, whereas the exchange broadened spectra were not greatly influenced by the *J* values chosen. Good agreement was obtained between experimental and computer synthesised spectra over a temperature range of 50 to 60°C. The typical case of $(C_5H_4S\text{-i-}Bu)PdCl_2$ is illustrated in Fig. 5. Sets of best-fit rate constants as functions of sample temperature were submitted to the usual Arrhenius and Eyring theoretical treatment and the energy data obtained are listed in Table 2. The variation in these energies with complex type will be discussed below.

In the case of the complex $(C_5H_4S\text{-i-}Bu)_2PtCl_2$, the S inversion process was also observed via its ^{195}Pt NMR spectra. The two signals observed at $-20°C$ with an internal chemical shift of 76.7 ppm were in the intensity ratio 20/1 and were accordingly assigned to the *DL*- and *meso*-diastereoisomers respectively, the *DL* signal being at lower applied field. On raising the sample temperature the weaker line broadened considerably and virtually disappeared in the spectral base-line at 40°C, whereas the stronger line hardly changed its shape over this temperature range. Approximate band shape fittings were performed on the *meso* signal and an

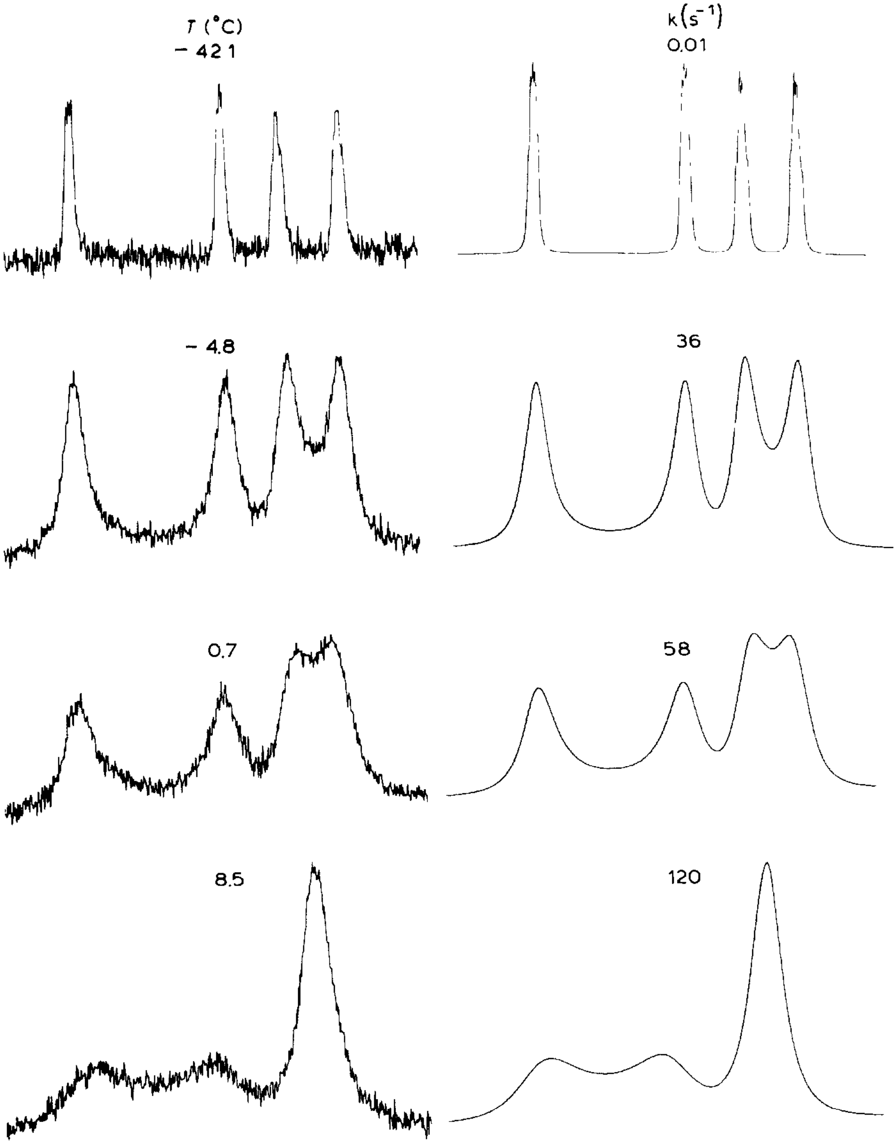
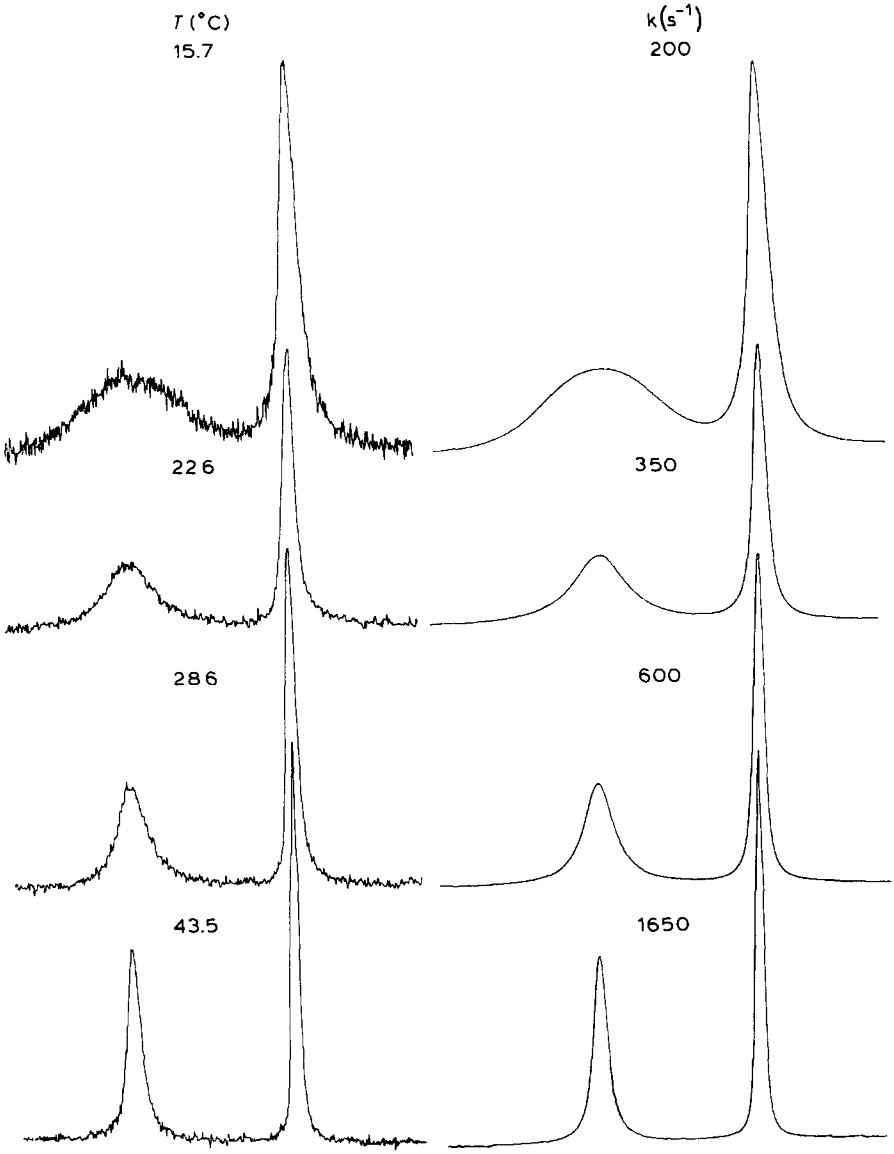


Fig. 5. Experimental and computer synthesised 100 MHz ^{1}H NMR spectra of the ring CH region of $(C_5H_4S\text{-i-Bu})_2PdCl_2$ in the temperature range −42 to +43.5°C showing the effects of S inversion. The "best fit" rate constants are indicated alongside the theoretical spectra

approximate $\Delta G^{\neq}$ value for the *meso* → ⟨*DL*⟩ interconversion was obtained (Table 2).

Discussion

Before discussing trends in sulphur inversion energies, there are a number of points of interest arising from the trends in the ring proton chemical shifts (Table 1).



The paper describing the preparations of these complexes [13], comments on the strong downfield shifts experienced by the inversion-averaged protons H(2,5) (i.e. $H_{A,B}$) on complexation. This has been attributed to the magnetic anisotropy or inductive effect of the metal dihalide moiety. Similar deshielding effects are observable in the slow inversion spectra. The relative influences of Pd^{II} and Pt^{II} are reflected in upfield shifts of 16–25 Hz for proton H_A on changing from Pd^{II} to Pt^{II} complexes. Such a trend is quite usual [1], and is probably associated with the greater electron density around the platinum nucleus which increases the local diamagnetic term in the Ramsey equation compared to palladium. The ring proton H_A also experiences a consistent but small upfield shift of 1–8 Hz on going from

TABLE 2

ARRHENIUS[a] AND EYRING ACTIVATION PARAMETERS[a] FOR SULPHUR INVERSION IN $Fe(C_5H_4SR)_2MX_2$ COMPLEXES

No.	Complex			E_a (kJ mol^{-1})	$\log_{10}$(A s^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
	M	X	R					
1	Pd	Br	Ph	45.6±4.4	12.2±1.0	47.7±0.5	50.3±2.0	8.7±8.2
2	Pd	Br	CH_2Ph	57.0±2.7	13.1±0.5	55.2±0.13	54.6±2.7	−1.9±9.5
3	Pd	Cl	i-Pr	62.9±0.7	13.4±0.1	59.4±0.02	60.5±0.7	3.6±2.3
4	Pd	Br	i-Pr	65.0±0.8	14.1±0.2	57.4±0.02	62.6±0.8	17.4±2.9
5	Pd	Cl	i-Br	55.9±0.7	12.4±0.1	58.0±0.04	53.5±0.7	−14.9±2.5
6	Pd	Br	i-Bu	54.7±0.3	12.5±0.1	56.1±0.05	52.3±0.3	−12.7±1.1
7	Pt	Br	Ph	53.5±2.3	12.4±0.5	55.8±0.35	51.4±2.2	−14.8±8.7
8	Pt	Cl	i-Pr	67.7±2.4	13.0±0.4	66.7±0.03	65.2±2.4	−4.9±7.8
9	Pt	Br	i-Pr	74.0±1.4	14.2±0.2	66.0±0.07	71.4±1.3	18.1±4.3
10	Pt	Cl	i-Bu	61.5±0.7	12.2±0.1	65.0±0.04	58.9±0.7	−20.6±2.1
				61.6[b]	13.4[b]	58.0[b]	59.1[b]	3.5[b]
11	Pt	Br	i-Bu	55.4±1.9	11.4±0.3	63.1±0.06	52.8±1.9	−34.5±6.2

[a] Data refer to ⟨*DL*⟩ ⇌ ⟨*DL*⟩. [b] Approximate values from ^{195}Pt spectra. Data refer to *meso*-1 ⇌ ⟨*DL*⟩. The difference in $\Delta G^{\neq}$ values is due to the different ground state energies of ⟨*DL*⟩ and *meso*-1 species. [c] Values refer to 298.15 K.

chloride to bromide complexes, reflecting the relative electronegativities of Cl and Br.

The dependence on the S–R substituent is also reflected in the H_A proton shifts. For example, in the case of the $PdBr_2$ complexes, a steady upfield trend in shifts is apparent on going from R = Ph to CH_2Ph to i-Pr to i-Bu, the increments being −16.8, −3.0 and −6.6 Hz. The deshielding effect of the aromatic ring in the Ph derivative is clearly seen. This is also seen in the relative shifts of H_B. More dramatic changes, however, are observed in the shifts of protons H_B and H_D in the benzyl derivative. Models show that in certain conformations of the CH_2Ph substituent, the protons *cis* to this substituent, namely $H_{B,D}$ (particularly H_B), are situated directly above the aromatic ring in a shielding zone, and thus experience large, low frequency shifts (of the order of 84 Hz for ν_B). This is in striking contrast with the Ph derivatives where the protons $H_{B,D}$ can only experience Ph ring deshielding.

As usual in this type of work [11,12] discussion of the relative magnitudes of S inversion energies will be in terms of the $\Delta G^{\neq}$ parameter. A careful study of these values in Table 2 reveal a number of very consistent trends.

(i) Transition metal dependence. A comparison of the pairs of complexes (1,7), (3,8), (4,9), (5,10) and (6,11) in Table 2 reveals that $\Delta G^{\neq}$ values increase by 8.1, 7.3, 8.6, 7.0 and 7.0 kJ mol^{-1}, respectively, on going from palladium(II) to platinum(II). This is fully in accord with the expected dependence on transition metal mass/size [1,7] and reflects the somewhat stronger Pt–S bonds compared to Pd–S bonds.

(ii) Halogen dependence. This is observed by examining the pairs of complexes (3,4), (5,6), (8,9) and (10,11). $\Delta G^{\neq}$ magnitudes for the chloride complexes are higher than for the bromide complexes by 2.0, 1.9, 0.7 and 1.9 kJ mol^{-1} respectively. This clearly reflects the greater *trans* influence of Br compared to Cl, with concomitant weakening of the M–S bond [1,17]. The effect here is small but well outside the error limits of the $\Delta G^{\neq}$ data. The consistency of the trends provides strong vindication for the accuracy of the band shape fitting procedure.

(iii) S-substituent dependence. This is most clearly observed for the $PdBr_2$ series of complexes, numbered 1, 2, 4 and 6 in Table 2. The $\Delta G^{\neq}$ (kJ mol^{-1}) values are 47.7 (Ph), 55.2 (CH_2Ph), 57.4 (i-Pr) and 56.1 (i-Bu). The value for the SPh derivative clearly results from ligand $(3p\text{–}2p)\pi$ conjugation between the Ph ring and the S atom, this being more effective in the planar transition state of the sulphur atom than in the pyramidal ground state. A similar effect has been observed previously in other palladium(II) and platinum(II) complexes [7]. There also appears to be a slight conjugation effect associated with the benzyl group in the present complexes. The $\Delta G^{\neq}$ variation with i-Pr and i-Bu is also well defined, since in other pairs of complexes (e.g. complexes (3,5), (8,10) and (9,11)), $\Delta G^{\neq}$ values invariably decrease by 1.4–2.9 kJ mol^{-1} on changing from i-Pr to i-Bu. This suggests that the inversion barrier is less affected by the mass/size of the R group than by steric considerations.

In summary, the $\Delta G^{\neq}$ variation is fully in accordance with established factors which influence pyramidal inversion energies, and lends further weight to the conclusion that the temperature dependencies of the ^1H spectra are due to varying rates of S inversion rather than reversal of the S–MX_2–S portion of the six-membered ferrocenophane ring.

Consideration must now be given as to why this bridge reversal process in these complexes is too rapid for ^1H NMR detection. The fluxionality of [3]-ferrocenophanes with carbon, oxygen or chalcogen bridging atoms manifests itself by the central bridging atom moving above and below the plane containing the iron atom and the outer bridging atoms [11,12]. The rate of this bridge reversal, however, varies greatly with the nature of the bridging atoms and has been shown to be a function of the total length of the C–X–Y–X–C bridge and/or the torsional barriers of the bridge bonds. In the case of $Fe(C_5H_4S)_2S$, the bridge reversal energy is relatively high ($\Delta G^{\neq}$ 80.4 kJ mol^{-1}) [11], and the complex requires heating to ca. 200°C before the reversal process becomes rapid in an NMR chemical shift sense [18]. However, when the central bridging sulphur is replaced by CH_2 in the compound $Fe(C_5H_4S)_2CH_2$, the bridge reversal process is greatly accelerated ($\Delta G^{\neq}$ 47.2 kJ mol^{-1}) [12] to such an extent that cooling of the sample to ca. −80°C is now required to obtain a 'static' NMR spectrum. This dramatic difference in bridge reversal rates has been explained in terms of the relative magnitudes of the torsional barriers for S–S and C–S bonds [11,12]. Literature data [19–21] suggest that C–S torsional barriers are lower than S–S barriers by ca. 20 kJ mol^{-1}, thus accounting for the much greater ease of bridge reversal in the S–CH_2–S bridged ferrocenophane.

Such a drastic lowering of the bridge reversal barrier by replacing the central bridging sulphur either by CH_2, as previously [12], or by an MX_2 moiety, as in the present work has an immediate explanation in terms of the isolobal theory pioneered by Hoffmann [22]. Any d^8 ML_4 fragment possesses a pair of frontier orbitals which are very akin to those of CH_2, and therefore $Pd^{II}X_2$ or $Pt^{II}X_2$ are isolobal with CH_2. It is therefore reasonable to expect that a d^8 MX_2 moiety in the centre of the three-atom bridge will exert a similar electronic influence on the bridge reversal process to a central CH_2 group. Its actual influence is clearly somewhat greater than that of CH_2 since the dynamic process is now too rapid to be detected by NMR (i.e. $\Delta G^{\neq}$ must now be < ca. 35 kJ mol^{-1}). This must be due presumably to the smaller torsional barriers associated with Pd–S or Pt–S bonds compared to C–S bonds, this being also reflected in the relative bond lengths. For example, in $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$, Pd–S bonds are 233 pm [13] whereas in $Fe(C_5H_4S)_2S$, the S–S bonds have been found to be 204.9 pm [23]. No data have been found for torsional barriers associated with Pd–S or Pt–S bonds but extrapolation of previous data suggest that they will be less than 8 kJ mol^{-1}, and probably considerably less.

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