Conformational Studies of Chelated Sulphur- and Selenium-containing Ligands by Nuclear Magnetic Resonance. Part III.[1] Band-shape Fitting Studies for Complexes of 1,2-Bis(isopropylseleno)ethane with Palladium-(II) Halides and with Chromium, Molybdenum, and Tungsten Carbonyl Complexes

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Band-shape fitting studies have been made for the ^{1}H n.m.r. spectra of complexes of the deuteriated analogue of the chelating ligand 1,2-bis(isopropylseleno)ethane with palladium(II) halides and with chromium, molybdenum, and tungsten carbonyl complexes. These studies show conclusively that the coalescence phenomenon observed in the temperature-dependent n.m.r. spectra results from inversion of configuration about the ligand atoms and not from reversal of the chelate ring. Detailed analysis of the spectra of the chelate-ring methylene protons and thermodynamic parameters for the inversion process are reported.

RECENT calculations [2,3] on the five-membered chelate ring complexes of 1,2-diaminoethane (en) have shown that the ring can exist in two enantiomeric skew conformations, λ and δ. The size of the barrier separating these conformations is *ca.* 20 kJ mol^{-1} and corresponds to the envelope conformation in which the adjacent methylene groups are eclipsed. These workers also predicted the existence of a wide range of symmetric-and asymmetric-skew conformations whose energies are within 0.8 kJ mol^{-1} of the ground state.

A barrier to ring reversal of only 20 kJ mol^{-1} implies that the n.m.r. spectra of these chelates at room temperature will be time-averaged. Confirmation of this comes from work on tris chelates of en whose n.m.r. spectra show the results of rapid ring reversal.[4-6] Indeed because of the small size of this reversal barrier,

[1] Part II, G. Hunter and R. C. Massey, *J.C.S. Dalton*, 1975, 209.

[2] J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, 1971, **10**, 317.

[3] L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1505.

[4] J. M. Beattie and H. Elsbernd, *J. Amer. Chem. Soc.*, 1970, **92**, 1946.

[5] S. T. Spees, L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, 1966, **5**, 2103.

[6] T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, 1970, **9**, 1299.

attempts to resolve the ' frozen-out ' spectra ($k < 1$ s^{-1}) for these complexes at low temperatures proved unsuccessful.[7] Caulton[8] succeeded in obtaining the ' frozen-out ' spectra of certain chelates of $NNN'N'$-tetramethyl-1,2-diaminoethane and from the temperature of coalescence phenomena in the spectra estimated the free energy of activation, $\Delta G_{183}^{\ddagger}$, to be 37 kJ mol^{-1}. In general, however, the complexes of en, and its derivatives, are so flexible that the ' frozen-out ' spectra are beyond the present range of n.m.r. spectroscopy.

Abel *et al.*[9] reported that the ^{1}H n.m.r. spectra of the five-membered chelate rings of 1,2-bis(methylthio)ethane in [MCl$_2$(MeSC$_2$H$_4$SMe)] (M = Pd^{II} or Pt^{II}) exhibit a coalescence phenomenon above room temperature which was attributed to configurational inversion at the chiral sulphur atoms. A similar coalescence has been observed in the spectra of metal complexes of RSC$_2$H$_4$SR (R = Me, Et, Pr^n, Pr^i, or Bu^n),[10] EtSeC$_2$H$_4$SeEt,[11] and PrSeC$_2$H$_4$SePr [12,13] at temperatures between 290 and 420 K, which implies approximate values for the free energies of activation of 60—90 kJ mol^{-1}. In general, however, the configurational stabilities of sulphur and selenium are sufficient to support optical activity [14] and racemisation measurements have given inversion barriers of 105—120 kJ mol^{-1} for sulphonium [15] and 145—180 kJ mol^{-1} for sulphoxide.[16] Although it is possible that $(p-d)\pi$ overlap between the chalcogen and metal atoms would lead to a lowering of the chalcogen inversion barrier, it is also possible that the hindered rotation associated with such overlap would cause the ring reversal barrier to be more substantial than in the en complexes. We have therefore suggested that the coalescence phenomenon in the spectra of the chalcogen-containing complexes may be attributed to ring reversal.[12,13] So far, however, there has been a lack of conclusive evidence as to which of the two processes is in fact responsible for the temperature dependence observed in the spectra of these complexes.

With the advent of computer programs which allow the simulation of complex spin spectra under exchange conditions,[17] in principle it is possible to elucidate which process is responsible for the temperature dependence of an n.m.r. spectrum. This may be achieved by detailed analysis of possible exchange mechanisms and comparison, over a range of exchange rates, of the simulated spectra based on these mechanisms with the experimental spectrum at various temperatures. For complexes of 1,2-bis(alkylchalcogeno)ethanes, depending on the individual circumstances, such spectral analysis may be made for either the chelate-ring methylene protons

or for the protons of suitable alkyl groups. This paper reports the results of spectral analysis for the chelating-ring methylene protons of complexes of 1,2-bis(isopropylseleno)ethane (bise) and the following paper reports analogous results for the benzylic methylene protons of complexes of 1,2-bis(benzylthio)ethane. Both studies show conclusively that the coalescence phenomenon observed in the spectra of these complexes results from configurational inversion at the ligand atoms and not from reversal of the five-membered chelate ring.

RESULTS AND DISCUSSION

The symmetry properties of the various chelate ring conformations are the same in the octahedral complexes of 1,2-bis(isopropylseleno)ethane with chromium, molybdenum, and tungsten carbonyls as in the square-planar complexes of this ligand with palladium(II) halides. The temperature-dependent 90-MHz ^{1}H n.m.r. spectra of these two groups of complexes have already been described [12,13] and were very similar in appearance to each other in the regions of fast and slow exchange, although there were considerable differences in the temperatures at which coalescence occurs. As the results of the spectral analysis are the same for both groups of complexes, for brevity, discussion will be confined to the palladium(II) halide complexes.

At 320 K, the 90-MHz isopropyl-methyl proton spectrum of nitrobenzene solutions of the palladium(II) halide complexes consisted of three partially overlapping doublets; the intensity of the central doublet was noticeably larger than the other two doublets. The methine protons showed one septuplet, centred at τ 5.96. The magnitude of the coupling constant between the methine and the methyl protons was 6.9 Hz. At 220 MHz the isopropyl signals consisted of two, partially overlapping, methine septuplets, and four methyl doublets of similar intensity. This strongly suggests the presence of four distinct methyl absorptions for the complexes, which, because of the small chemical-shift differences involved, only showed three doublets at 90 MHz. As the temperature of the sample was increased, the 90-MHz methyl spectrum of each complex began to coalesce, such that eventually only one doublet was observed.

We have already attempted to obtain the spectral parameters for the ' frozen-out ' spectrum of the chelate-ring methylene protons of [PdCl$_2$(bise)].[13] These parameters did not, however, successfully simulate the appearance of the subsequently observed 220-MHz ^{1}H spectrum and this spectrum has therefore been reanalysed. At 320 K the methylene spectrum of this

[7] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1972, **11**, 124.
[8] K. G. Caulton, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 533.
[9] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58.
[10] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.
[11] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Chem. Comm.*, 1974, 207.
[12] R. Donaldson, G. Hunter, and R. C. Massey, *J.C.S. Dalton*, 1974, 288.

[13] G. Hunter and R. C. Massey, *J.C.S. Chem. Comm.*, 1973, 797.
[14] P. W. B. Harrison, J. Kenyan, and H. Phillips, *J. Chem. Soc.*, 1926, 2079.
[15] D. Darwish and R. L. Tomilson, *J. Amer. Chem. Soc.*, 1968, **90**, 5938.
[16] D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854.
[17] G. Binsch, *J. Amer. Chem. Soc.*, 1969, **91**, 1304.

complex showed an apparent singlet at τ 6.37, and an AA'BB' multiplet centred at τ 6.43. Analysis of this multiplet using the LAOCN 3 program [18] gave the following spectral parameters: $\Delta\nu_{AB} = \Delta\nu_{A'B'} = 0.428$ p.p.m.; $J_{AB} = J_{A'B'} = -12.7$, $J_{AB'} = J_{A'B'} = 4.7$, $J_{AA'} = 11.7$, $J_{BB'} = 7.6$ Hz. At 220 MHz the methylene spectrum of this complex was essentially unchanged, and consisted of a singlet and a widely spaced AA'BB' multiplet. Simulation of this multiplet was achieved using the parameters obtained from the revised analysis of the 90-MHz spectrum. This implies that these spectral parameters are correct, as it is most unlikely that a set of chemical shifts and coupling constants which fortuitously simulate the spectrum at 90 MHz should also simulate the spectrum at 220 MHz. The experimental and calculated spectra for this AA'BB' multiplet are shown in Figure 1. As the temperature of the sample

FIGURE 1 N.m.r. spectrum of the methylene protons of [PdCl$_2$(bise)] in nitrobenzene at 320 K: (i) at 220 MHz; (ii) at 90 MHz (absorptions marked by an arrow are due to the isopropyl methine proton)

was increased, the 90-MHz methylene spectra of the complexes began to coalesce, such that eventually a broad singlet was observed.

An X-ray crystallographic study [19] of [PdCl$_2$(bise)] has shown that in the solid state the five-membered chelate ring exists in a symmetric skew conformation. The bond angles about the selenium atoms were found to approach the expected tetrahedral angle, the fourth position about these atoms presumably being occupied

by a lone pair of electrons. Both isopropyl groups project on the same side of the chelate ring.

In principle, [PdCl$_2$(bise)] can exist in two isomeric forms, with the isopropyl groups either projected on the same (syn) or opposite (anti) sides of the chelate ring. Moreover, for symmetric-skew conformations of each isomer, the isopropyl groups may be either axially or equatorially inclined to the Se–Pd–Se plane. The effect of ring reversal is therefore to interchange the environments of these isopropyl constituents. Similarly, the ring methylene protons will also be exchanged between their axial and equatorial sites. The full conformational ring inversion paths for the syn and anti isomers are shown in Figures 2 and 3 respectively.

The temperature dependence shown by the n.m.r. spectra of these complexes may be due to either conformational or configurational exchange. Conformational exchange implies the presence of only one isomer, and that the signals below coalescence are those due to each half of the ring-reversal cycle. As the symmetric- and asymmetric-skew conformers probably have similar energies, the two sets of signals below coalescence will be the time-averaged signals of these conformers in each half of the ring-reversal cycle. Above conformational coalescence, where the interconversion of each half of the ring-reversal cycle via the envelope conformation is rapid, the resulting spectral parameters will assume the weighted-average values of the two sets of parameters found below coalescence.

Slow ring reversal of the syn isomer will give only one multiplet from the methylene protons as the conformations in each half of the ring-reversal cycle are enantiomeric and therefore give identical spectra. Each methylene proton of the symmetric-skew conformation is in a chemically distinct environment, thus giving an asymmetric ABCD multiplet. Similarly, for each asymmetric-skew conformation an ABCD signal is expected. Therefore, in the case of slow ring reversal of the syn isomer, the time-averaged signal of the symmetric-skew and its associated asymmetric-skew conformers will be an ABCD multiplet. For fast ring inversion of this isomer a symmetric AA'BB' multiplet is expected whose chemical shifts are given by equations (1) and (2) where

$$\nu_A = 0.5(\nu_{a,e} + \nu_{e,a}) \qquad (1)$$

$$\nu_B = 0.5(\nu_{a,e'} + \nu_{e,a'}) \qquad (2)$$

$\nu_{a,e}$ refers to the averaged chemical shift of a methylene proton which, when in a symmetric-skew conformation, is axially oriented and adjacent to an equatorially inclined isopropyl group projecting on the same side of the chelate rings; $\nu_{a,e'}$ refers to the averaged shift of a methylene proton which, when axially oriented, is adjacent to an equatorial isopropyl group which projects on the other side of the chelate ring (similarly for $\nu_{e,a}$ and $\nu_{e,a'}$). It is likely that the chemical-shift differences
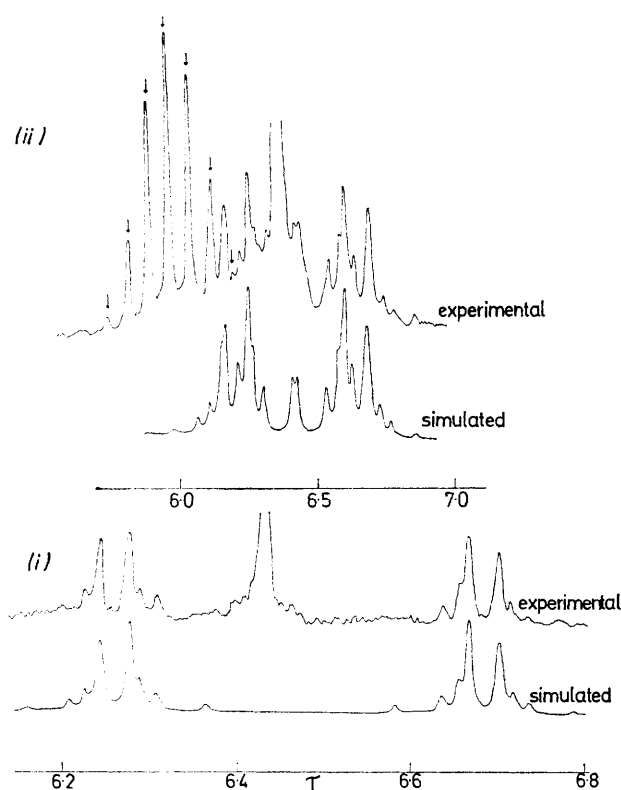
[18] A. A. Bothnerby and S. Castellano, Program 111, Quantum Chemistry Program Exchange, Indiana University.
[19] H. J. Whitfield, J. Chem. Soc. (A), 1970, 113.

between $\nu_{a,e}$ and $\nu_{a,e'}$ and between $\nu_{e,a}$ and $\nu_{e,a'}$ will be very small and the spectrum resulting from rapid ring reversal of the *syn* isomer would be a closely spaced AA'BB' multiplet which may not be properly resolved and thus appear as an A_4 singlet.

signals. Because of the C_2 axis of symmetry, each symmetric-skew conformer will give an AA'BB' multiplet. For the symmetric-skew conformer with both isopropyl groups axial, the associated asymmetric-skew conformers in this half of the ring-inversion cycle are
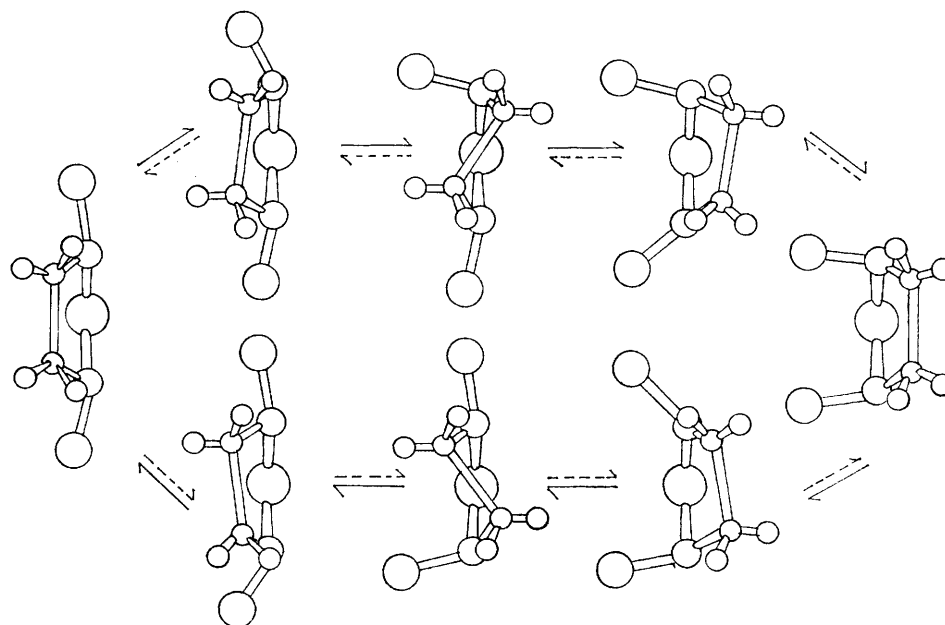

FIGURE 2   Ring-inversion cycle for the *syn* isomer of the complexes
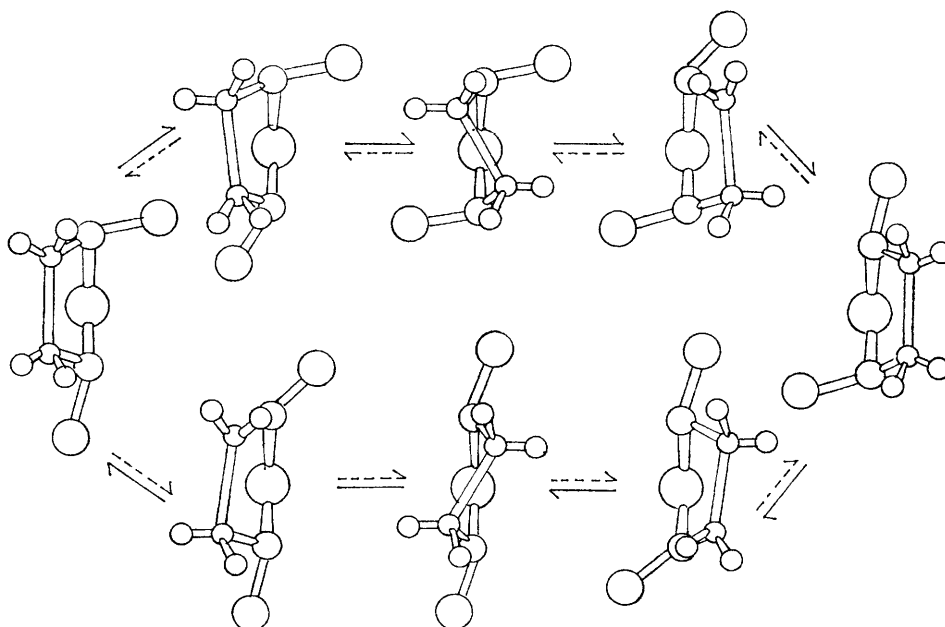

FIGURE 3   Ring-inversion cycle for the *anti* isomer of the complexes

The two symmetric-skew conformations of the *anti* isomer are not enantiomeric, as both isopropyl groups are axial in one conformer, but equatorial in the other. For slow ring reversal there will therefore be two distinct identical, which means that, although individually they constitute ABCD systems, the time-averaged methylene signal for this half of the ring-reversal cycle will be AA'BB' in appearance. Similar arguments apply to the

other half of the ring-reversal cycle. Thus two distinct AA'BB' multiplets are expected for slow conformational ring reversal of the *anti* isomer.

Fast ring reversal of the chelate ring of this isomer will give only one AA'BB' multiplet, the chemical shifts of which are given by equations (3) and (4) where P_I and

$$\nu_A = P_I \nu_a^I + P_{II} \nu_e^{II} \qquad (3)$$

$$\nu_B = P_I \nu_e^I + P_{II} \nu_a^{II} \qquad (4)$$

P_{II} refer to the relative populations of each half of the ring-reversal cycle, ν_a^I to the averaged chemical shift of a methylene proton which is axially oriented when in symmetric-skew conformer (I), and ν_e^{II} to the averaged shift of a methylene proton which is equatorially oriented when in symmetric-skew conformer (II).

If there is a large population imbalance, such as predicted by DeHayes and Busch[3] for the five-membered chelate rings of *NN'*-dimethyl-1,2-diaminoethane, in favour of one of the symmetric-skew conformations of the *anti* isomer, then the chemical-shift difference of the AA'BB' multiplet resulting from fast ring reversal will be correspondingly large. The spin–spin coupling constants obtained by the analysis of the AA'BB' multiplet of [PdCl$_2$(bise)] are consistent with a conformationally time-averaged *anti* isomer in which the λ and δ conformers are unequally populated. The magnitudes of the vicinal coupling constants are given by equations (5)—(8) where J_{aa}^I refers to the coupling constant

$$J_{AB'} = P_I J_{ea}^I + P_{II} J_{ae}^{II} = 4.7 \text{ Hz} \qquad (5)$$

$$J_{A'B} = P_I J_{ae}^I + P_{II} J_{ea}^{II} = 4.7 \text{ Hz} \qquad (6)$$

$$J_{AA'} = P_I J_{aa}^I + P_{II} J_{ee}^{II} = 11.7 \text{ Hz} \qquad (7)$$

$$J_{BB'} = P_I J_{ee}^I + P_{II} J_{aa}^{II} = 7.6 \text{ Hz} \qquad (8)$$

between the two axial methylene protons in the more populated half of the ring-reversal cycle and J_{ee}^{II} to the coupling constant between the equatorial protons in the less populated half of the ring-reversal cycle.

It therefore appears that the methylene-proton spectrum, consisting of a relatively widely spaced AA'BB' multiplet plus an apparent singlet, is more consistent with a situation where both isomers are present and undergoing rapid ring reversal than where only one isomer is present and undergoing slow ring reversal. The observed coalescence phenomenon would thus be attributable to configurational inversion at the ligand atoms causing interconversion of the *syn* and *anti* isomers. Above coalescence, where isomeric inter-conversion is rapid, the spectral parameters will assume the weighted-average values of the corresponding parameters for the *syn* and *anti* isomers. The net effect of configurational inversion is to scramble the environments of the geminal methylene protons. As is shown by observing the proton labelled with an asterisk in Figure 4, for every skew conformation in the configurational inversion cycle there exists an enantiomeric conformer in which the geminal methylene protons are

interchanged. When the rate of exchange is rapid, these protons will become magnetically equivalent, resulting in an A$_4$ singlet.

That the coalescence phenomenon is attributable to isomeric interconversion was confirmed by band-shape fitting studies. Because it was not possible to obtain spectral parameters for the methylene spectrum of the *syn* isomer, these studies were undertaken using the deuteriated analogue of bise, Me$_2$CDSeCD$_2$CH$_2$SeCDMe$_2$ (dbise). Below coalescence, the 90-MHz n.m.r. methylene-proton spectra of the palladium(II) complexes of dbise dissolved in nitrobenzene consisted of an
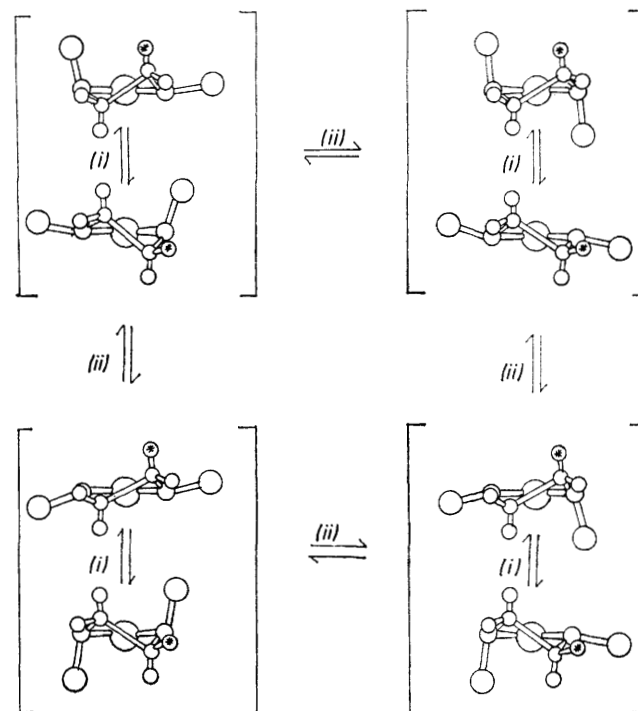

FIGURE 4 Inversion cycle for the complexes: (*i*) ring inversion; (*ii*) site inversion

AB quartet (a) and a singlet (s), while those of the metal carbonyl complexes with this ligand dissolved in CDCl$_3$ consisted of two distinct AB quartets, the less intense quartet (s) being situated between the components of the widely spaced, more intense, quartet (a).

An interesting feature of the 'frozen-out' spectra was that the downfield components of AB quartet (a) were invariably narrower than the upfield components, suggesting that, although not resolvable, the magnitude of the vicinal coupling between the methylene deuterium atoms and the methylene protons was larger for the upfield protons. If this coupling obeys a Karplus-type relation, then it would be expected that the largest vicinal coupling constant for the CH$_2$CD$_2$ fragment would be between an axial deuterium and the corresponding *trans*-axial proton. This infers that, for the predominant skew conformer of the *anti* isomer, the axial methylene proton can be attributed to the upfield

components and the equatorial protons to the downfield components.

In the 'frozen-out' spectra, for all the complexes the chemical-shift differences of AB quartet (a) were found to be linearly dependent on the temperature. No such temperature dependence was noticed for the chemical-shift differences of AB quartet (s). As the half-height linewidths of the components of the methylene signals remained constant and thus were not apparently exchange-broadened in this region of very slow exchange ($k < 1$ s^{-1}), it may well be that this chemical-shift temperature dependence results from changes in the relative populations of the skew conformers in the *anti* isomer.

Spectral Simulation.—The program DNMR2 [20] was used to simulate the methylene-proton spectra and for

perature in the region of very slow exchange. This 'off-set' decreased by *ca.* 0.1 Hz for each 5 K rise in the temperature, and it was necessary to use extrapolated values for this 'off-set' when evaluating the relative chemical shifts of the methylene protons in the intermediate- and fast-exchange regions. The values of the input parameters P_a, P_s, T_2, J_{AB}, $\Delta\nu_{AB}$, and $0.5[(\nu_A + \nu_B)_s - (\nu_A + \nu_B)_a]$ are recorded in Table 1.

Attempted band-shape simulation by simple exchange of quartet AB (a) with either A$_2$ singlet (s) or AB quartet (s) did not give the correct fast-exchange spectrum observed above coalescence, thus confirming that ring reversal was not the process causing the coalescence phenomenon. Simulation of the methylene-proton spectra for various rates of configurational exchange

TABLE 1

Input parameters for the simulation of the methylene-proton spectra

Complex	$\dfrac{T}{K}$	Solvent	P_s	$\Delta\nu_{AB,s}$	$J_{AB,s}$	P_A	$\Delta\nu_{AB,a}$	$J_{AB,a}$	$0.5[(\nu_A + \nu_B)_s - (\nu_A + \nu_B)_a]$	$\dfrac{T_2}{s}$
				Hz			Hz			
[PdCl$_2$(dbise)]	310	C$_6$H$_5$NO$_2$	0.42	0	−12.3	0.58	39.5	−12.3	−5.2	0.11
[PdBr$_2$(dbise)]	310	C$_6$H$_5$NO$_2$	0.44	0	−12.5	0.56	3.54	−12.5	−2.8	0.10
[Cr(CO)$_4$(dbise)]	240	CDCl$_3$	0.38	16.4	−12.1	0.62	110.2	−13.0	+1.5	0.13
[Mo(CO)$_4$(dbise)]	245	CDCl$_3$	0.39	18.1	−12.5	0.61	80.9	−13.0	−1.2	0.11
[W(CO)$_4$(dbise)]	225	CDCl$_3$	0.36	17.5	−12.5	0.64	104.2	−13.0	−1.5	0.11

various rates of exchange it was necessary to evaluate the input parameters.

The relative populations of the species giving rise to the signals (a) and (s) were obtained by simulating the 'frozen-out' spectra and modifying this parameter until the simulated and experimental spectra matched. As the relative populations of (a) and (s) did not measurably alter in the slow-exchange region, it was assumed that they remained constant throughout the intermediate- and fast-exchange regions. The values for the natural linewidth, and hence T_2, used in the simulations corresponded to the mean of the half-height linewidths of AB quartet (a) observed in the 'frozen-out' spectra. The geminal coupling constants of the AB quartets were temperature invariant in the region of very slow exchange and were assumed to remain constant throughout the intermediate- and fast-exchange regions. This value was also assumed for the coupling between the protons giving rise to the A$_2$ singlet observed in the methylene-proton spectra of the palladium(II) complexes. As the chemical shifts of AB quartet (a) were temperature dependent in the slow-exchange region, in order to obtain these chemical shifts at temperatures corresponding to intermediate and fast exchange it was necessary to extrapolate the values found in the slow-exchange region where the effects of exchange are negligible. Similar extrapolations have been justified by Holm and his co-workers [21] in his band-shape fitting studies for the spectra of tris chelates of α-isopropyltropolone.

The chemical-shift difference between the midpoint of AB quartet (a) and either the midpoint of quartet (s) or A$_2$ singlet (s) was linearly dependent on the tem-

required the exchange of each methylene proton between four environments, characterised by the following chemical shifts:
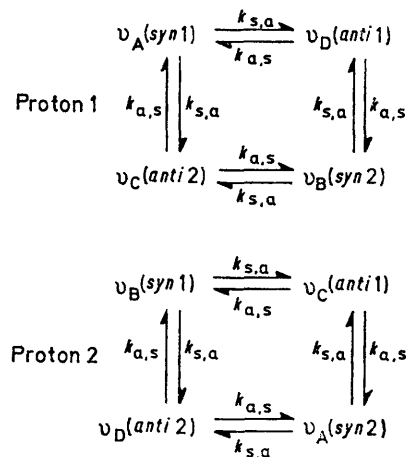
Here ν_A and ν_B are the chemical shifts of the protons in AB quartet (s) or A$_2$ singlet (s) and ν_C and ν_D are the chemical shifts of AB quartet (a); the configurational inversion rate constants, $k_{s,a}$ and $k_{a,s}$, are related by equation (9). The simulated spectra, together with the

$$k_{s,a}P_s = k_{a,s}P_A \qquad (9)$$

appropriate values of $k_{a,s}$ which give the best agreement with the experimental methylene spectra, are shown in Figure 5 for [PdCl$_2$(dbise)] and in Figure 6 for [Cr(CO)$_4$-(dbise)]. We consider that the good fit of simulated with experimental spectra in the regions of intermediate

[20] G. Binsch and D. A. Kleier, Program 140, Quantum Chemistry Program Exchange, Indiana University.

[21] S. S. Eaton, J. R. Hutchinson, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 6411.

and fast exchange confirms that configurational inversion about the ligand atoms causes the observed coalescence phenomenon. Acceptable Arrhenius plots of $\log_{10}k$ against $1/T$ were obtained and thermodynamic activation parameters calculated from these plots are recorded in

small chemical-shift differences involved, the doublets of chemically distinct methyl groups may overlap; secondly, it is well known that methyl groups of an isopropyl moiety bonded to a chiral atom are intrinsically non-equivalent, so that for such groups there may well
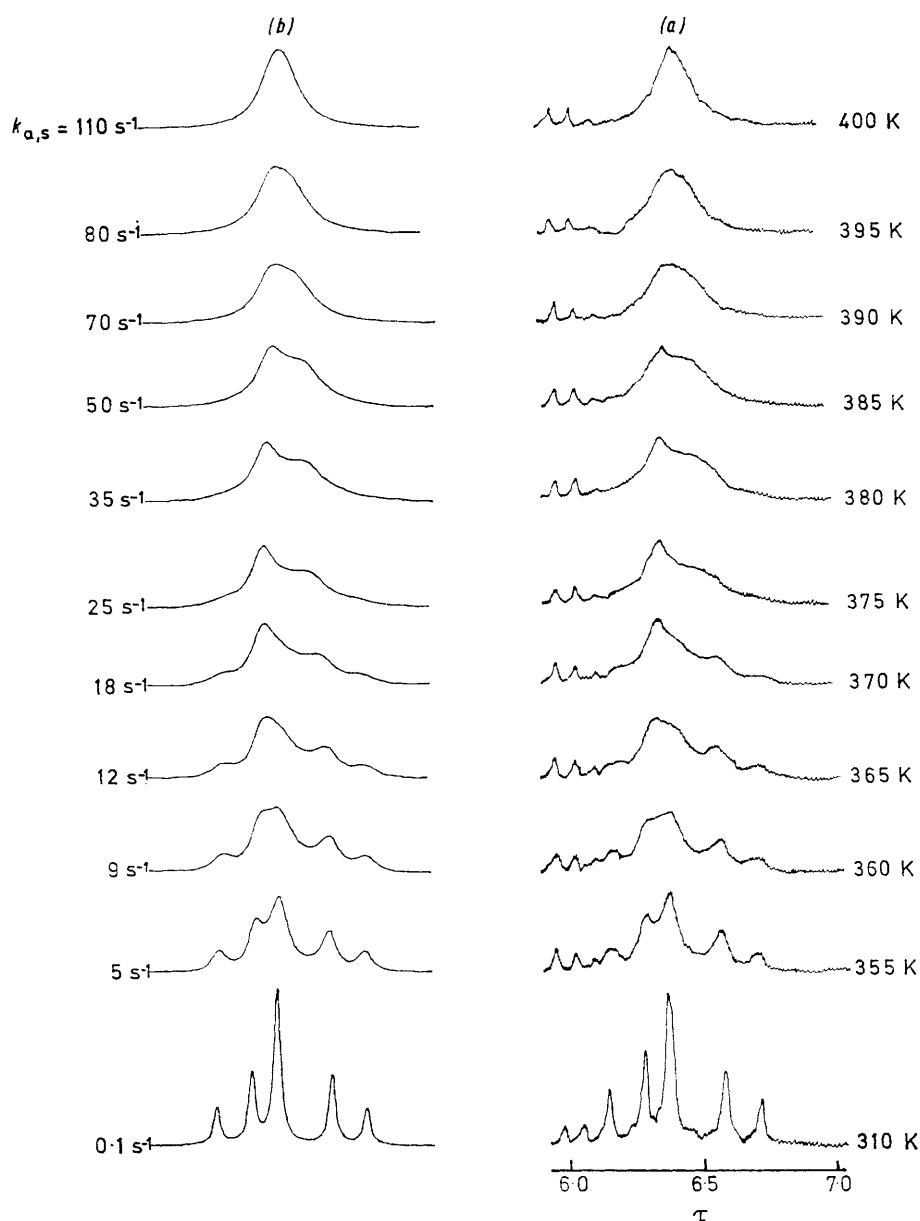

FIGURE 5   90-MHz N.m.r. methylene-proton spectra of [PdCl₂(dbise)] in PhNO₂: (a) observed; (b) simulated

Table 2.   The free-energy difference, $\Delta G_{a,s}$, between the two isomers was evaluated from expression (10).

$$(P_s/P_a) = \exp(-\Delta G_{a,s}/RT) \qquad (10)$$

For completeness it is necessary to consider the temperature dependence of the isopropyl-methyl spectra of the bise complexes.   An interpretation of the number of methyl doublets above and below coalescence may be misleading for two reasons: first, due to the relatively

be two methyl doublets for each chemically distinct isopropyl group.   From the evidence of the 90- and 220-MHz methyl spectra of all the complexes it seems likely that there are in fact four chemically distinct methyl groups which suggests that, since the selenium atoms are centres of asymmetry, there are only two chemically distinct isopropyl groups.   The presence of two distinct isopropyl groups is expected on the basis of slow configurational inversion where, because of

conformational time-averaging, there will be only one chemically distinct isopropyl group for each isomer.

The net effect of ligand-atom inversion is to interchange the methyl groups of each isopropyl moiety. Thus for every conformation in the configurational inversion cycle there is an enantiomeric conformer in which the geminal methyl groups are interchanged. For rapid ligand-atom inversion, the intrinsic non-equivalence will no longer effect the appearance of the methyl spectrum, so that, in agreement with experiment, only one doublet will be observed above coalescence.

to 1,2-bis(isopropylseleno)ethane from 1-deuterioisopropyl selenide and 1,2-dichloro-1,1'-dideuterioethane.

1-*Deuterioisopropyl Selenide*.—To 1-deuterioisopropyl alcohol (Isocommerz, 86% isotopically pure) (10 g, 0.164 mol), cooled to −10 °C, was slowly added phosphorus tribromide (16.5 g, 0.061 mol). After being stirred for 4 h, the mixture was allowed to attain room temperature and then fractionated at atmospheric pressure. The fraction distilling between 60 and 65 °C was collected as 1-*deuterioisopropyl bromide* (yield 15.3 g, 75%). 1-Deuterioisopropyl bromide (15.3 g, 0.123 mol) was treated with selenium (11.1 g, 0.14 g-atom), sodium hydroxide (5.6 g, 0.14 mol), and
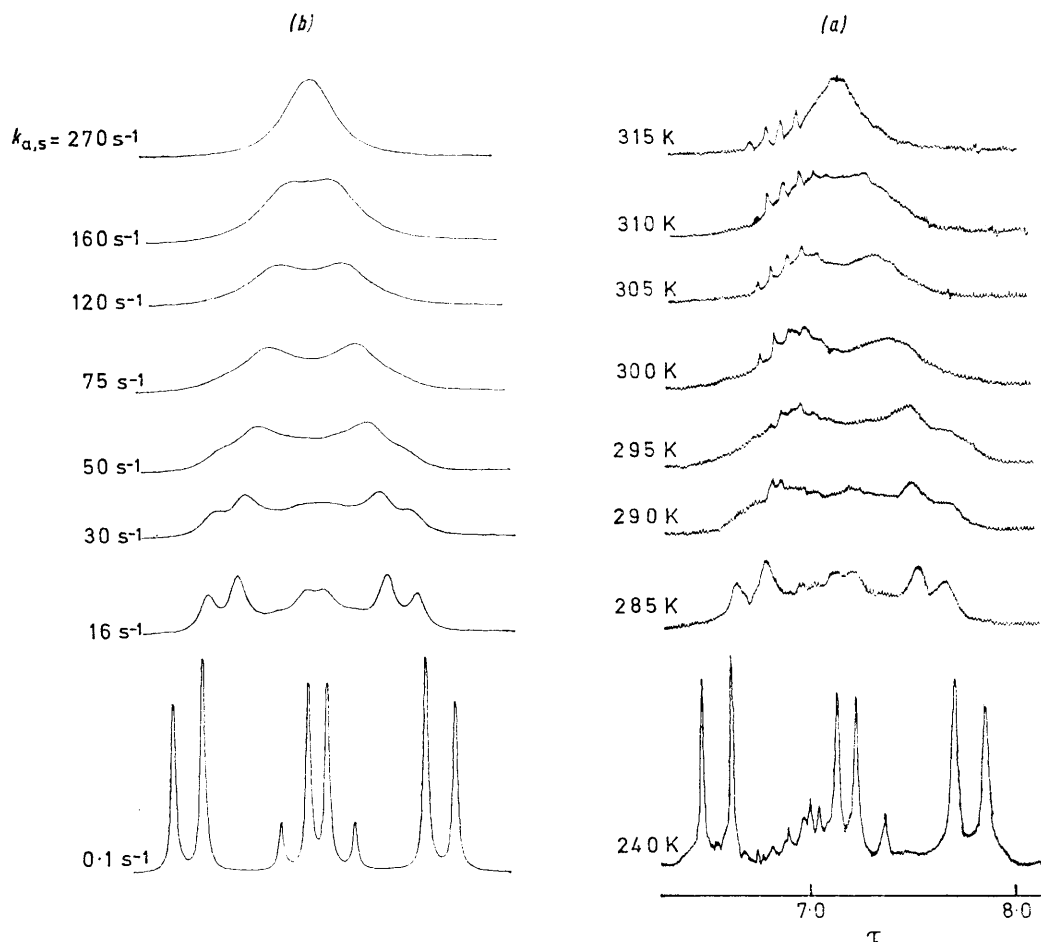

FIGURE 6   90-MHz N.m.r. methylene-proton spectra of $[Cr(CO)_4(dbise)]$ in $CDCl_3$: (a) observed; (b) simulated

TABLE 2

Thermodynamic parameters (in kJ mol⁻¹) for the configurational inversion process of the complexes

Complex	Solvent	$\Delta G_{300}(a,s)$	$E^{\ddagger}(s)$	$\Delta H^{\ddagger}_{300}(s)$	$\Delta G^{\ddagger}_{300}(s)$	$E^{\ddagger}(a)$	$\Delta H^{\ddagger}_{300}(a)$	$\Delta G^{\ddagger}_{300}(a)$
$[PdCl_2(dbise)]$	$C_6H_5NO_2$	0.81 ± 0.10	76.6 ± 9.2	74.1 ± 9.2	78.7 ± 1.7	77.8 ± 9.2	75.3 ± 9.2	79.5 ± 1.7
$[PdBr_2(dbise)]$	$C_6H_5NO_2$	0.59 ± 0.08	81.2 ± 4.2	78.7 ± 4.2	80.6 ± 2.5	80.8 ± 4.2	78.2 ± 4.2	82.0 ± 2.5
$[Cr(CO)_4(dbise)]$	$CDCl_3$	1.22 ± 0.10	66.1 ± 6.7	63.6 ± 6.7	62.8 ± 0.4	66.1 ± 6.7	63.6 ± 6.7	63.9 ± 0.4
$[Mo(CO)_4(dbise)]$	$CDCl_3$	1.11 ± 0.10	57.4 ± 13.0	54.9 ± 13.0	59.3 ± 0.8	58.2 ± 13.0	55.6 ± 13.0	60.2 ± 0.8
$[W(CO)_4(dbise)]$	$CDCl_3$	1.44 ± 0.10	70.2 ± 5.9	67.7 ± 5.9	65.2 ± 0.4	70.3 ± 5.9	67.8 ± 5.9	66.5 ± 0.4

EXPERIMENTAL

1,2-Bis(isopropylseleno)ethane and its complexes were prepared as described previously.[12,22]

1,1'-*Dideuterio-1,2-bis(1''-deuterioisopropylseleno)ethane* (*dbise*).—This compound was prepared in a similar manner

sodium hydroxymethanesulphinate (9.5 g, 0.08 mol) in water (500 cm³). The mixture was heated under reflux for 2 h and the aqueous and non-aqueous layers were separated.

²² N. N. Greenwood and G. Hunter, *J. Chem. Soc. (A)*, 1967, 1520.

The non-aqueous fraction was distilled under reduced pressure to give 1-deuterioisopropyl selenide as a vile smelling, yellow, oil (yield 11.3 g, 75%).

1,2-Dichloro-1,1'-dideuterioethane.—Chloroacetyl chloride (35.5 g, 0.314 mol) dissolved in diethyl ether (100 cm³) was added to freshly pulverised lithium tetradeuterioaluminate (7.9 g, 0.188 mol) suspended in diethyl ether (400 cm³) at such a rate as to maintain a gentle reflux. The addition was complete in 2 h, and stirring was continued for a further 2 h when 10% sulphuric acid (50 cm³) was carefully added to the mixture. The aqueous and ether layers were transferred to a liquid–liquid extractor, and the ether layer continuously extracted for 8 h. The ether extract was dried over magnesium sulphate and distilled at atmospheric pressure to remove the ether. The residue was cooled to 0 °C, pyridine (24 cm³, 0.3 mol) was added followed by thionyl chloride (22 cm³, 0.3 mol), and the mixture was then warmed to 80 °C for 1 h. On cooling, water and diethyl ether were added to the mixture and the aqueous and ether layers were separated. The ether fraction was washed with 10% sulphuric acid followed by 10% sodium carbonate solution, dried over magnesium sulphate, and distilled at atmospheric pressure. The fraction distilling at 80—86 °C was collected as 1,2-dichloro-1,1'-dideuterioethane (yield 7.5 g, 24%).

N.m.r. Spectra.—220-MHz Hydrogen-1 n.m.r. spectra were obtained by the Physico Chemical Measurement Unit, Harwell; 90-MHz spectra were obtained using a Bruker HX 90 spectrometer fitted with a variable-temperature probe. Temperatures were measured with a thermocouple mounted in the probe which was found to be accurate to $\pm 1°$ by calibration with methanol and ethylene glycol using the formulae of Van Geet.[23] Spectra were simulated using the DNMR 2 program which was modified to handle the exchange of two protons between four sets of chemical environments.

[23] A. L. Van Geet, *Analyt. Chem.,* 1968, **40**, 2227.