Nuclear Magnetic Resonance Study of Inversion at Sulphur and Selenium Atoms in Complexes of Palladium(II) and Platinum(II). Part 1. Complexes of Bis(trimethylsilylmethyl) Sulphide and Selenide

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Total n.m.r. band-shape fitting methods have yielded some precise data for the energy barriers of inversion at S and Se when these atoms are bonded to Pd^{II} and Pt^{II} in the complexes $[MCl_2\{X(CH_2SiMe_3)_2\}_2]$ ($M = Pd^{II}$ or Pt^{II}, X = S or Se). The S barrier energies are in the range 51—56 kJ mol^{-1} and the corresponding barriers at Se are in the range 60—66 kJ mol^{-1}. The somewhat higher energies in complexes of Pt^{II} compared to Pd^{II} reflect the relative strengths of the Pd–S and Pt–S bonds.

THE use of the n.m.r. technique for the investigation of pyramidal atomic inversions is well established and has yielded much information[1] on the barrier energies and mechanisms of the inversion process which is not easily accessible by chemical or other physical methods. The n.m.r. technique, however, is limited to the measurement of barrier energies in the approximate range 20—80 kJ mol^{-1} as a result of the time scale (or interaction time) of the technique being of the order of 10^{-3} s. The majority of inversion studies to date have been devoted to nitrogen inversion where the nitrogen atom is in a bonding situation whereby its inversion rate is made relatively slow (*e.g.* incorporated in a ring). In contrast, inversion rates at sulphur and selenium are often too slow for n.m.r. detection, as for example with sulphoxides[2] and sulphonium ions.[3] However, in 1966 Abel *et al.*[4] detected sulphur inversion by variable-temperature n.m.r. in a sulphur chelate complex of Pt^{II}. Subsequently, Haake and Turley[5,6] examined a series of platinum(II) complexes with organic sulphide ligands and established that the bonding of sulphur to this

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[1] J. B. Lambert, *Topics Stereochem.*, 1971, **6**, 19.

[2] D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854.

[3] D. Darwish and R. L. Tomilson, *J. Amer. Chem. Soc.*, 1968, **90**, 5938.

[4] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58.

[5] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1967, **89**, 4611.

[6] P. C. Turley and P. Haake, *J. Amer. Chem. Soc.*, 1967, **89**, 4617.

transition metal appears to appreciably lower the barrier energies. More recently, Cross *et al.*[7-9] examined inversions at S, Se, and Te in palladium(II) and platinum(II) complexes, but only qualitative estimates of barrier heights were made. Hunter and his co-workers[10,11] studied some complexes of Pd^{II} and Pt^{II} with a variety of selenium chelate ligands, but with such ligands there is the additional problem of differentiating between inversion of the chelate rings themselves and site inversion at the selenium atoms.

There is, therefore, considerable observational evidence for inversion at S and Se atoms but a distinct lack of accurate quantitative data for the barrier energies. This absence of data is undoubtedly due to the complexities of the n.m.r. spectra studied to date which have precluded any accurate dynamic n.m.r. band-shape methods from being applied. With the aim of obtaining reliable energy data, we have prepared, and performed an n.m.r. examination of, two series of organic sulphide and selenide complexes of Pd^{II} and Pt^{II}. These complexes were carefully chosen for the tractability of their n.m.r. spectra from the point of view of performing total band-shape fittings. We report here our studies on the complexes *trans*-$[MCl_2\{X(CH_2SiMe_3)_2\}_2]$ ($X = S$ or Se, $M = Pd^{II}$ or Pt^{II}) and in the following paper we report on the complexes *trans*-$[MY_2\{XR(CH_2SiMe_3)\}_2]$ ($X = S$ or Se, $M = Pd^{II}$ or Pt^{II}, $R = Ph$ or Me, $Y = Cl$ or Br).

EXPERIMENTAL

The syntheses and characterization of the $[MCl_2\{X(CH_2SiMe_3)_2\}_2]$ complexes reported below form part of a larger study on the ligand properties of trimethylsilylmethyl bases to be reported fully elsewhere.

Interaction of Potassium Tetrachloropalladate(II) *and Bis(trimethylsilylmethyl) Sulphide and Selenide*.—The compound $K_2[PdCl_4]$ (0.5 mmol) and the ligand (1.0 mmol) were stirred together under reflux in ethanol for 3 h. On cooling the solution was filtered through Kieselguhr, solvent was removed *in vacuo*, and the residual solid was dissolved in hot hexane. Cooling this solution slowly to −20 °C yielded very pure yellow or orange crystals of respectively *trans*-bis[bis(trimethylsilylmethyl) sulphide]dichloropalladium(II) and *trans*-bis[bis(trimethylsilylmethyl) selenide]dichloropalladium(II) as characterized below.

Interaction of Potassium Tetrachloroplatinate(II) *and Bis(trimethylsilylmethyl) Sulphide and Selenide*.—The compound $K_2[PtCl_4]$ (0.5 mmol) and the ligand (1.0 mmol) were stirred in a mixture of ethanol (7 cm^3) and water (5 cm^3) under reflux for 3 h. Solvent was removed (30 °C, 0.01 mmHg),* and replaced by water (30 cm^3). The resulting solution was warmed to 60 °C and filtered. The yellow solid obtained from the filtration was washed copiously with cold water and recrystallized from ethanol–water to give pure yellow or orange crystals of respectively *trans*-bis[bis(trimethylsilylmethyl) sulphide]dichloroplatinum(II) and *trans*-bis[bis(trimethylsilylmethyl) selenide]dichloroplatinum(II) as characterized below.

N.m.r. spectra were recorded for solutions of the complexes in either deuteriochloroform or tetrachloroethylene depending on the solubility (see Table 2). All the ^1H n.m.r. spectra were obtained on a JEOL MH-100 spectrometer operating at 100 MHz under internal field frequency lock conditions, the intense $SiMe_3$ absorption of the complex being used as the lock signal. A JES-VT-3 variable-temperature unit was used to control the probe temperature. Temperatures were measured with either a thermocouple or a calibrated alcohol thermometer which could be inserted directly into the probe. Measurements were made immediately before and after recording spectra and were reliable to *ca.* ±1 °C over the range covered.

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

Complex	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis (%) Found C	Found H	Calc. C	Calc. H
trans-$[PdCl_2\{S(CH_2SiMe_3)_2\}_2]$	47	Yellow	102	32.0	7.45	32.6	7.45
trans-$[PtCl_2\{S(CH_2SiMe_3)_2\}_2]$	71	Yellow	98	28.1	6.50	28.3	6.50
trans-$[PdCl_2\{Se(CH_2SiMe_3)_2\}_2]$	72	Orange	104	28.0	6.45	28.1	6.45
trans-$[PtCl_2\{Se(CH_2SiMe_3)_2\}_2]$	69	Orange	95	24.3	5.70	24.8	5.70

Computations.—For the palladium(II) complexes a modified version of the ABSHAPE program from the NMR Program Library, Harwell, was used. For the platinum(II) complexes the presence of ^{195}Pt satellite bands necessitated the use of a modified version (see following paper) of the DNMR program of Binsch.[12]

RESULTS AND DISCUSSION

Palladium(II) *Complexes*.—The two complexes studied gave similar spectra, the main difference being that line-shape changes occurred in the range 35—120 °C for the selenide ligand complexes and in the range −50 to +50 °C for the sulphide complexes. Spectra of the methylene hydrogens of $[PdCl_2\{Se(CH_2SiMe_3)_2\}_2]$ in the range 35—100 °C are shown in Figure 1.

In the complexes $[PdCl_2\{X(CH_2SiMe_3)_2\}_2]$, each X (= S or Se) atom represents a prochiral centre.[13] Attached to these centres are prochiral trimethylsilylmethyl groups in which the pairs of methylene hydrogens are diastereotopic and hence anisochronous in the absence of any interconversion process. The pairs of CH_2SiMe_3 groups attached to different S atoms are enantiomerically related and thus the corresponding pairs of methylene hydrogens are enantiotopic. The

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[7] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, **992**.

[8] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Chem. Comm.*, 1974, 207.

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

[10] R. Donaldson, G. Hunter, and R. C. Massey, *J.C.S. Dalton*, 1974, 288.

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

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

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

methylene hydrogen spin system is thus of the type $[AB]_4$, but as no measurable spin–spin interactions between different CH_2 groups were detected the spin system could be treated as a simple AB type. The low-temperature spectra are clearly compatible with this description. On increasing the temperature the spectra clearly indicated the onset of a rate process which causes a mutual exchange of methylene hydrogen environments. The only type of process which would cause such an exchange is inversion at the X atoms. Rotations about the M–X or X–C bonds would not produce any such interchange. It has been assumed, for the sake of discussion, that these rotations are fast on the n.m.r. time scale throughout the temperature range studied. This is fully justified in the case of X–C bond rotation since the spectra can be interpreted only on the basis of this rotation being rapid. However, there is no direct information from the spectra concerning the rate of M–X bond rotation. If such rotation was slow on the n.m.r. time scale and assuming inversion occurs only at single X atoms (see below), then there would be the possibility of the existence of two chemically distinct structures, namely one with the sulphur lone pairs in a mutual *cis* relation and another with the two lone pairs

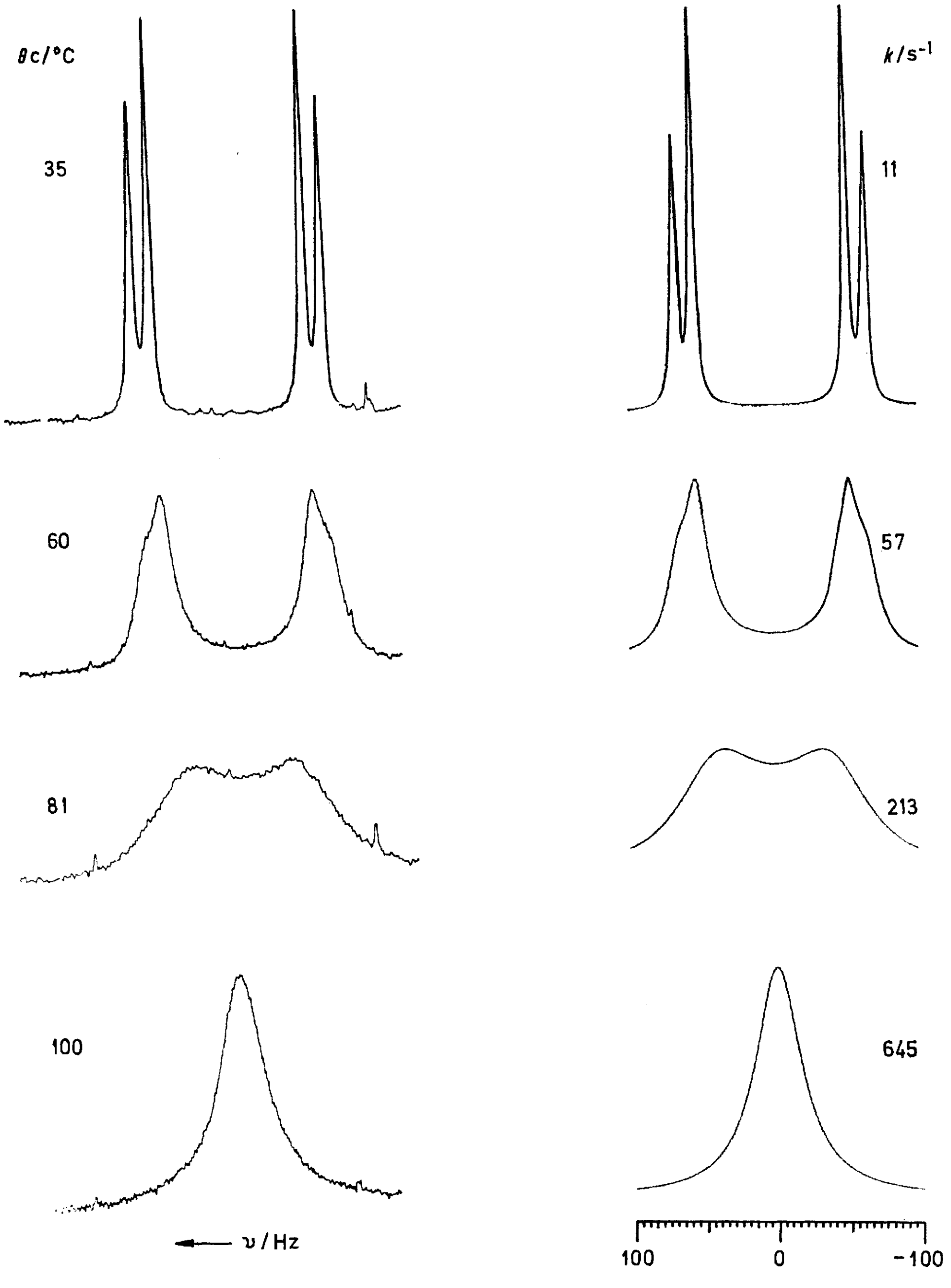

FIGURE 1 Variable-temperature spectra of the methylene absorption region of $[PdCl_2\{Se(CH_2SiMe_3)_2\}_2]$

mutually *trans*. As there is no spectral evidence for two such structures, it would then be necessary to postulate chemical-shift equivalence of all the corresponding hydrogen nuclei in the two structures. This seems somewhat unlikely and we prefer to adopt the assumption of rapid M–X bond rotation as did Haake and Turley.[5]

The effect of the inversion process is shown in Figure 2. The CH_2 hydrogens are labelled H_A, H_B and $H_{A'}$, $H_{B'}$ according to whether they are attached to X or X′ respectively. Inversion at X′ together with 180° rotation about the M–X bond and 120° rotation about the X–C bond produces the corresponding conformer of the original structure. A comparison of the new structure with the original one shows them to be chemically indistinguishable and the net effect of the inversion process is to interchange the $H_{A'}$ and $H_{B'}$ environments. The n.m.r. spin system thus changes according to AB $\rightleftharpoons$ BA. Since the four pairs of methylene hydrogens in the complexes are enantiomerically related, we are unable to distinguish between inversions at single X sites and synchronous inversions at both X sites. However, by slightly modifying the symmetry of the ligands further insight into this problem can be obtained (see following paper).

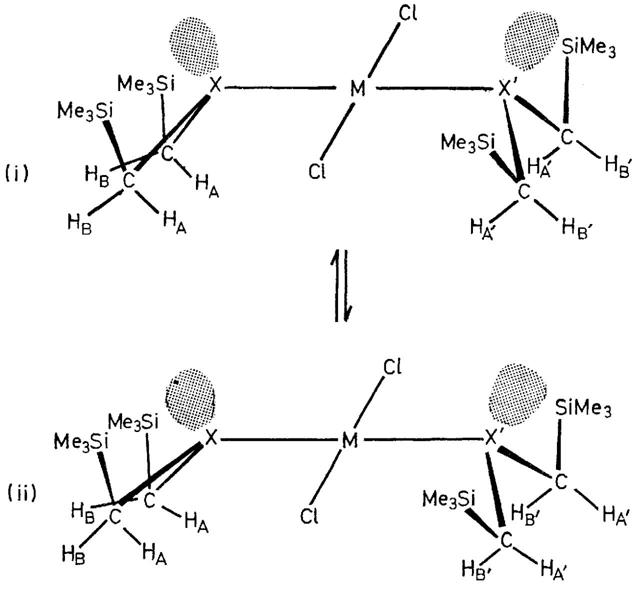

FIGURE 2 Preferred conformations of the complexes before and after single site inversion. Conformer (ii) is obtained from (i) as a result of inversion at X′ followed by 180° rotation about the M–X′ bond and 120° rotation about both X–C bonds

Platinum(II) *Complexes*.—The presence of ^{195}Pt ($I = \frac{1}{2}$) in such complexes produces the total CH_2 spin system AB $\rightleftharpoons$ BA (66.3%) and ABX $\rightleftharpoons$ BAX (33.7%). These systems were computed independently (but using the same rate-constant values for a particular temperature) and the sum of both line shapes was plotted and compared with the experimental spectra.

Total band-shape fitting methods were applied to all the spectra. Chemical-shift differences, spin-coupling constants, and natural linewidths were measured as precisely as possible and their temperature dependences determined over as wide a slow inversion temperature range as possible. The data used in the line-shape fittings are given in Table 1. In each case the coupling constants were essentially temperature independent. For each complex between seven and thirteen experimental spectra were accurately simulated using the ABSHAPE or DNMR computer programs. A typical Arrhenius plot is shown in Figure 3 and the results are collected in Table 2. The Arrhenius and activation parameters were obtained by the usual procedures, the errors being based on a regression analysis of the Arrhenius plot.

TABLE 1

Spectral parameters (Hz) of the complexes of Pd^{II} and Pt^{II}

Complex	$\nu_A - \nu_B$	J_{AB}	J_{AX}	J_{BX}	$\Delta\nu_{\frac{1}{2}}$ [a]
$[PdCl_2\{S(CH_2SiMe_3)_2\}_2]$	98.8 $\pm$ 0.150θ_c [b]	13.6			1.0
$[PtCl_2\{S(CH_2SiMe_3)_2\}_2]$	92.0 $\pm$ 0.099θ_c [b]	13.8	32.1	60.4	1.0 [c] 1.5 [d]
$[PdCl_2\{Se(CH_2SiMe_3)_2\}_2]$	117.2 [e]	12.9			1.0 [c]
$[PtCl_2\{Se(CH_2SiMe_3)_2\}_2]$	121.0 [e]	13.0	37.3	50.3	1.0 1.5 [d]

[a] Natural linewidth at half-height, $\Delta\nu_{\frac{1}{2}} = (\pi T_2^*)^{-1}$. [b] θ_c = temperature in °C. [c] Main bands. [d] Platinum-195 satellite bands. [e] No temperature dependence was detected.

Before discussing the implications of these results, it should be noted that in Table 1 it was not possible to unambiguously assign the individual hydrogens H_A, H_B (and $H_{A'}$, $H_{B'}$). However, assuming that the preferred conformation of the complex is that shown in Figure 2, and that, in the case of the platinum(II) complexes J(Pt–X–C–H)(*trans*) > J(Pt–X–C–H)(*gauche*), the lower-field hydrogens H_A or $H_{A'}$ will be those *gauche* to the transition metal.

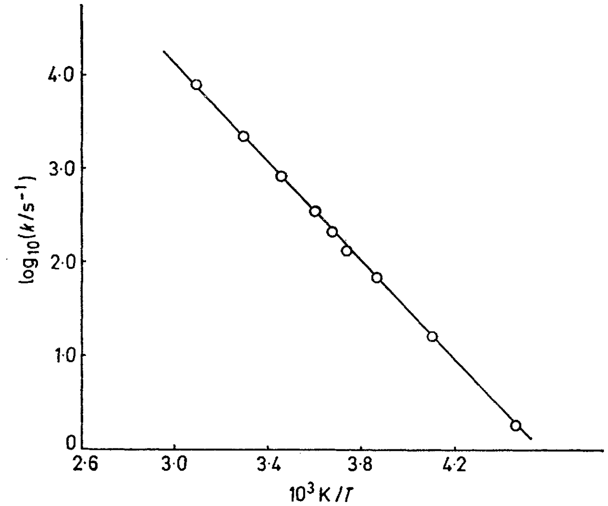

FIGURE 3 Arrhenius plot for $[PdCl_2\{S(CH_2SiMe_3)_2\}_2]$

The barrier parameters in Table 2 clearly indicate that the inversion rates in these transition-metal complexes are extremely fast when compared with those

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[14] E. W. Abel, G. W. Farrow, and K. G. Orrell, *J.C.S. Dalton*, 1976, 1160.

found in sulphoxides[2] and sulphonium ions.[3] The barriers for selenium inversion are *ca.* 10 kJ mol^{-1} higher than for the corresponding sulphur inversion. A comparison of the corresponding complexes of Pd^{II} and Pt^{II} shows that when S or Se is bonded to Pt^{II} the barrier is *ca.* 5 kJ mol^{-1} higher than when these atoms are bonded to Pd^{II}. Similar trends based simply on a comparison of coalescence temperatures were observed by Cross *et al.*[7-9] for related complexes. We are now able to provide quantitative data for such observations. The S inversion barriers reported here are significantly lower than those recently reported[14] for sulphur bonded to Rh^{III} ($E^{\ddagger}$ *ca.* 72 kJ mol^{-1}) or to Ir^{III} ($E^{\ddagger}$ *ca.* 64 kJ mol^{-1}). The differences, which are as large as 20 kJ mol^{-1} for S–Rh compared with S–Pd, probably reflect the different degrees of stabilization of the transition state arising from interaction of the p_{π} lone pairs with the d_{π} orbitals on the metal.

TABLE 2

Arrhenius and activation parameters *

Complex	Solvent	$E^{\ddagger}$ kJ mol^{-1}	$\log_{10}A$	$\Delta G^{\ddagger}$ kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}
$[PdCl_2\{S(CH_2SiMe_3)_2\}_2]$	$CDCl_3$	51.2 ± 0.3	12.2 ± 0.06	54.6 ± 0.06	48.7 ± 0.3	−19.9 ± 3.7
$[PtCl_2\{S(CH_2SiMe_3)_2\}_2]$	$CDCl_3$	56.3 ± 1.3	11.9 ± 0.2	61.3 ± 2.5	53.8 ± 1.3	−25.0 ± 12.5
$[PdCl_2\{Se(CH_2SiMe_3)_2\}_2]$	C_2Cl_4	60.7 ± 0.6	11.3 ± 0.1	69.3 ± 1.1	58.2 ± 0.6	−37.1 ± 5.8
$[PtCl_2\{Se(CH_2SiMe_3)_2\}_2]$	C_2Cl_4	65.8 ± 0.8	10.7 ± 0.1	77.9 ± 1.4	63.4 ± 0.8	−48.9 ± 7.6

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

The two most likely mechanisms for the inversion process are an intramolecular one involving a planar intermediate structure (*viz.* nitrogen inversion) and a dissociation–recombination mechanism. The latter can be definitely ruled out for the platinum(II) complexes by the observation of averaged ^{195}Pt–H spin couplings above the coalescence temperature. This clearly indicates that the X–Pt bonds remain intact throughout the inversion process. Ligand-exchange processes involving dissociation–recombination mechanisms may occur at higher temperatures as was evidenced by Cross *et al.*[9] but the present spectra up to *ca.* 130 °C showed no evidence of this and could be exactly interpreted on the basis of a purely intramolecular process.

The large rate-factor difference (*ca.* 10^{20}) between inversion in sulphoxides and in palladium(II) and platinum(II) sulphide complexes caused Haake and Turley[5] to suggest that a different inversion mechanism from the usual one involving a trigonal-planar transition state was operating in these complexes. They postulated a process involving a planar intermediate having both S lone pairs bonded to M^{II} with the configuration at sulphur being tetrahedral rather than trigonal, as in nitrogen inversion, and with M^{II} possessing a distorted five-co-ordinate configuration. In other words they considered the rate process as an internal displacement at M^{II} rather than proper inversion at the X atom. However, providing that rapid rotation about the M–X bonds is assumed the mechanism they describe is no different from the conventional one. Haake and Turley suggest that their postulated planar intermediate differs from the conventional intermediate in that both lone pairs are involved in bonding to the M^{II} atom. However, this distinction between the M–X bond being represented by a σ bond with the remaining lone pair at X in a pure p orbital, and both X lone pairs sharing in the bonding, is a purely formal one and has no physical significance. We would argue, therefore, that there is no evidence to support a new inversion mechanism and, indeed, that if rapid M–X bond rotation is assumed no new intramolecular mechanism can easily be postulated. Instead, the much lower barriers in the complexes described here and those studied by Haake and Turley can be fully attributed to effective p_{π}–d_{π} orbital overlap between X and M which stabilizes the transition structures.

Support for a purely intramolecular mechanism without any bond breaking may be obtained from the appreciably negative values of $\Delta S^{\ddagger}$. Any precise physical explanations of the magnitudes of these entropy parameters are notoriously unreliable, but we consider that the negative signs of these values are indicative of an intermediate structure with considerable steric interactions.

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