Nuclear Magnetic Resonance Investigations of Configurational Non-rigidity in Dinuclear Platinum(IV) Complexes. Part 6.† Synchronous Pyramidal Inversion of Chalcogen Atoms in $[(PtXMe_3)_2(\overline{ECH_2CMe_2CH_2E})]$ Complexes (E = S or Se; X = Cl, Br, or I)‡

Edward W. Abel, Pramod K. Mittal, Keith G. Orrell,* and Vladimir Šik
Department of Chemistry, University of Exeter, Exeter EX4 4QD

Platinum(IV) complexes of the type $[(PtXMe_3)_2(\overline{ECH_2CMe_2CH_2E})]$ (E = S or Se; X = Cl, Br, or I) have been synthesised and shown to possess dinuclear structures with highly strained Pt_2X_2 moieties. Variable-temperature ^1H n.m.r. studies have clearly identified pyramidal inversions of the E atom pairs and scrambling of the Pt-methyl groups. Although chalcogen atom switching between the Pt atom pairs has not been unambiguously detected, this process constitutes the probable link between the other two fluxional processes. The $\Delta G^\ddagger$ data for the pyramidal inversions are in the range 66—75 kJ mol⁻¹. Such values, being in most cases *ca.* 20 kJ mol⁻¹ higher than the usual single-site inversions, are clearly associated with appreciably slower, synchronous inversions of the chalcogen atom pairs.

Dinuclear platinum(IV) complexes of type $[(PtXMe_3)_2L]$ (X = Cl, Br, or I) undergo a great variety of fluxional rearrangements which depend sensitively on the nature of the co-ordinated chalcogen ligand L.[1] For open-chain ligand complexes when L = $MeECH_2EMe$ (E = S or Se),[2] MeEEMe (E = S or Se),[3] or $MeSCH_2SeMe$,[4] the chalcogen atoms exhibit independent pyramidal inversions at the platinum centres. When this intra-atomic process becomes rapid it transforms to a more extensive intramolecular reorganisation with the chalcogen lone pairs switching between the two platinum atoms and causing 180° rotations of the ligand. For cyclic ligand complexes when L = $\overline{SCH_2SCH_2SCH_2}$,[5] and $\overline{SCH_2SCH_2SCH_2SCH_2}$,[6] sulphur pyramidal inversion was not detected although it could have occurred if both co-ordinated sulphur atoms had been part of a correlated synchronous movement. Instead, the sulphur lone pairs switch between the two platinum atoms by a pivoting process about individual S→Pt bonds. In six-membered ligand rings, this causes the ligand to undergo a series of 60° 1,3-pivots whereas in eight-membered rings 90° 1,5-pivots are the preferred movement.

In order to gain further insight into the factors that favour single-site pyramidal inversions, synchronous double inversions, ligand switchings and ligand pivots we have now synthesised complexes of type $[(PtXMe_3)_2(\overline{ECH_2CMe_2CH_2E})]$ (E = S or Se; X = Cl, Br, or I). Here the two E atoms are constrained in a ring and therefore can invert only in a synchronous manner. Furthermore, the absence of a third chalcogen atom prevents any ligand pivoting from occurring.

All the previous studies[2—6] led to fluxionality of the Pt methyl environments, generally as a result of the highly non-rigid seven-co-ordinate Pt intermediate formed by the ligand movements, and so it is of added interest to see whether such methyl scrambling also occurs in these new complexes.

A preliminary report of a portion of this work has been published.[7]

Experimental

Materials.—The ligand 4,4-dimethyl-1,2-diselenacyclopentane, $\overline{SeCH_2CMe_2CH_2Se}$, was synthesised as follows, the procedure being based on that used for preparing 2,3-diselenaspiro[4.5]decane.[8] 1,3-Dibromo-2,2-dimethylpropane (11.68 g, 0.05 mol), prepared from 2,2-dimethylpropane-1,3-diol and PBr_3, was added very slowly to a stirred solution of KSeCN (14.5 g, 0.1 mol) in diethylene glycol, $O(CH_2CH_2OH)_2$ (200 cm³). After extensive heating (140—150 °C for 2 h and *ca.* 200 °C for 20 h), a dark red-brown solution was produced. This was extracted with light petroleum (b.p. 60—100 °C; 6 × 100 cm³), washed with water and then dried over anhydrous $CaCl_2$ for 6 h. After distilling off the solvent, a viscous brown liquid resulted, to which was added a small amount of absolute alcohol. Dark brown needles (3.4 g, 30%) of the required product were obtained after recrystallisation from methanol, m.p. 34 °C (lit.,[9] 34 °C).

The other ligand 4,4-dimethyl-1,2-dithiacyclopentane, $\overline{SCH_2CMe_2CH_2S}$, was prepared by an analogous procedure to the selenium analogue using KSCN in place of KSeCN. The product was a yellow-brown liquid, b.p. 80—82 °C (15 mmHg) [lit.,[10] 84—86 °C (17 mmHg)].

All trimethylplatinum(IV) halide complexes were prepared by a similar method. The case of $[(PtIMe_3)_2(\overline{SeCH_2CMe_2CH_2Se})]$ is detailed as follows. A three-fold excess of 4,4-dimethyl-1,2-diselenacyclopentane (0.127 g, 0.55 mmol) in chloroform (3 cm³) was added to a solution of $[PtMe_3I]$ (0.269 g, 0.18 mmol) in chloroform (6 cm³). The reaction mixture was stirred under reflux for *ca.* 16 h and concentrated to *ca.* 2 cm³ volume under vacuum, followed by a slow addition of hexane. Light brown crystals of the required dinuclear complex were obtained after *ca.* 24 h at room temperature. The crystals (0.245 g, 91.5%) were washed with hexane. The analytical data for all the complexes are given in Table 1.

N.M.R. Spectra.—Hydrogen-1 spectra were recorded at 100 MHz on a JEOL PS/PFT-100 spectrometer operating in the pulsed Fourier-transform mode. A JES-VT-3 variable-temperature unit was used to control the probe temperature. Temperatures were measured immediately prior to and after recording spectra using a Comark type 5000 digital thermometer and are accurate to ±1 °C over the range studied. All the complexes were examined as solutions in $CDCl_3$. N.m.r. bandshape fittings were performed using our version of the DNMR3 program of Kleier and Binsch.[11] Matchings of experimental and computer synthesised spectra were made visually, and the errors in the

---

† Part 5 is ref. 6.

‡ *Non-S.I. unit employed:* mmHg = 133 Pa.

Table 1. Characterisation of the dinuclear complexes of the trimethylplatinum(IV) halides $[(PtXMe_3)_2L]$

Complex	X	Colour	M.p./°C (decomp.)	C (%) Calc.	C (%) Found	H (%) Calc.	H (%) Found
$[(PtXMe_3)_2(SCH_2CMe_2CH_2S)]$	Cl	Beige	209	19.25	19.55	4.10	4.15
	Br	Light brown	201	17.05	17.30	3.65	3.75
	I	Yellow	190—191	15.20	15.30	3.25	3.40
$[(PtXMe_3)_2(SeCH_2CMe_2CH_2Se)]$	Cl	Yellow	245—246	16.95	17.10	3.60	3.60
	Br	Yellow	218—220	15.20	15.25	3.25	3.25
	I	Light brown	208	13.75	13.80	2.95	2.95

Table 2. Static ${}^1H$ n.m.r. parameters[a] used for calculating the synchronous inversion energies in the complexes of the type $[(PtXMe_3)_2(ECH_2CMe_2CH_2E)]$[b]

			$-CH_2-$					Ligand $-CH_3$		
E	X	Temp. (°C)	ν_A	ν_B	${}^2J_{AB}$[c]	${}^3J(Pt-H_A)$[d]	T_2^*/s	ν_C	ν_D	T_2^*/s
S	Cl	−8.2	358.2	339.9	10.8	13.8	0.127	149.4	137.0	0.191
S	Br	−7.0	360.2	340.0	10.5	14.0	0.127	148.9	137.0	0.163
S	I	−5.2	361.7	335.9	10.7	14.6	0.127	148.7	139.0	0.114
Se	Cl	23.6	377.6	351.4	10.0	10.3	0.152	149.9	134.3	0.229
Se	Br	27.0	380.4	352.0	10.1	10.4	0.143	149.2	134.9	0.286
Se	I	25.8	382.4	351.0	10.1	10.5	0.143	148.4	136.2	0.229

[a] In Hz unless otherwise specified. [b] Recorded in $CDCl_3$ relative to $SiMe_4$. [c] ${}^2J({}^1H_A-C-{}^1H_B)$. [d] ${}^3J({}^{195}Pt-E-C-{}^1H_A)$; *n.b.* ${}^3J({}^{195}Pt-E-C-{}^1H_B) \simeq 0.0$ Hz.

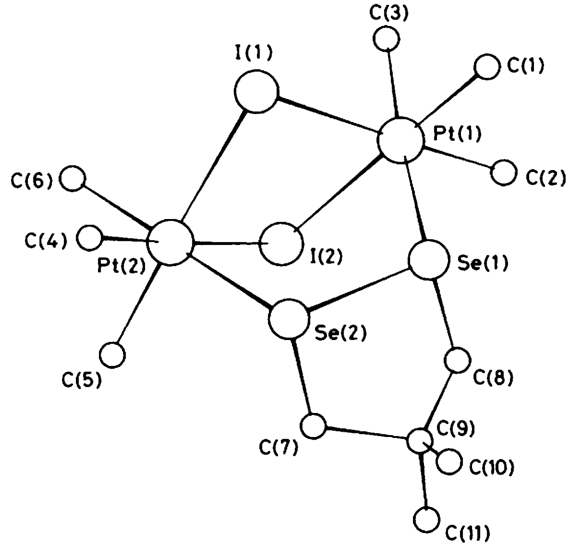


Figure 1. Solid-state structure of $[(PtIMe_3)_2(SeCH_2CMe_2CH_2Se)]$. Perspective view based on the atomic co-ordinates reported in ref. 7

$\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ parameters are expressed as previously recommended.[12]

Results

An *X*-ray crystal structure determination of $[(PtIMe_3)_2(SeCH_2CMe_2CH_2Se)]$ has already been reported[7] and confirms the dinuclear nature of the complex (Figure 1). In order to maintain approximately octahedral symmetry at the Pt atom the Pt_2I_2 moiety is forced into a severely bent geometry with an angle of 36.8° between the normals to the planes of the two PtI_2 fragments. This represents the most strained halogen-bridged dinuclear platinum(IV) complex reported to date, the previous case of $[(PtBrMe_3)_2(MeSeSeMe)]$ having its Pt_2Br_2 unit bent to the extent of 29°.[2] The other complexes were assumed to possess analogous structures and the solution ${}^1H$ n.m.r. analyses reported below were based on this assumpion.

All the six complexes $[(PtXMe_3)_2(ECH_2CMe_2CH_2E)]$ (E = S or Se; X = Cl, Br, or I) showed similar spectral features, in the temperature range −10 to 90 °C for the sulphur complexes and in the range 20 to 115 °C for the selenium complexes. The case of $[(PtClMe_3)_2(SeCH_2CMe_2CH_2Se)]$ is illustrated (Figure 2). Its room-temperature spectrum shows two groups of signals, the numbers in each region being consistent with a dinuclear structure, in which the five-membered ligand ring is pseudo-planar, with a reflection plane containing the two bridging iodine atoms and the ligand carbons 9, 10, and 11. The difference between this structure and that of the crystal arises from the pseudorotation of the five-membered ligand ring which is rapid on the n.m.r. time-scale.[13]

The ligand methylene region consists of an AB quartet with the high-frequency portion (due to H_A) showing clear ${}^3J(PtH)$ satellites. The two ligand methyls C and D are clearly identified by their lack of ${}^{195}Pt$ satellite signals. All Pt-methyl signals possessed ${}^{195}Pt$ satellites and distinction between axial and equatorial environments was made on the basis of the magnitudes of ${}^2J(PtH)$ couplings. Axial (*i.e. trans* S or Se) Pt methyl signals in such dinuclear complexes invariably have ${}^2J(PtH)$ couplings which are 1—5 Hz smaller than equatorial (*trans* X) Pt methyl signals, due to the differing *trans* influences of halogens and chalcogens.[14] Full assignments of the methylene and methyl signals are given in Tables 2 and 3.

On raising the temperature of the complex, the methylene signals broaden and coalesce at *ca.* 80 °C. Further increase in temperature produced a sharpening of the averaged signal but the final width of the signal was too great to reveal ${}^{195}Pt$ satellites. The only explanation of these changes is pyramidal inversion at the Se atoms, and since these atoms are constrained in a ring they must necessarily invert in a synchronous manner. Such a process causes a very considerable 'flapping' of the five-membered ring with respect to the dinuclear $PtXMe_3$ moiety.

In order to investigate the kinetics of this novel double-

Table 3. Static ^{1}H n.m.r. parameters[a] used for calculating the Pt-methyl scrambling energies in the complexes of the type $[(PtXMe_3)_2(ECH_2CMe_2CH_2E)]$[b]

E	X	Temp. (°C)	ν_G	ν_E	ν_F	$^2J(Pt\text{-}H_G)$[c]	$^2J(Pt\text{-}H_E)$[d]	$^2J(Pt\text{-}H_F)$[e]	T_2*/s
S	Cl	15.0	158.7	118.9	92.0	70.8	77.2	77.2	0.318
S	Br	6.5	173.3	129.9	102.8	71.3	76.4	76.4	0.286
S	I	5.6	198.8	148.7	121.0	72.5	74.5	74.6	0.305
Se	Cl	23.6	164.1	118.7	90.6	70.8	77.4	77.4	0.381
Se	Br	27.0	178.5	128.9	100.8	71.3	76.4	76.8	0.358
Se	I	25.8	204.1	146.2	118.2	72.5	74.2	74.7	0.286

[a] In Hz unless otherwise specified. [b] Recorded in $CDCl_3$ relative to $SiMe_4$. [c] $^2J(^{195}Pt\text{-}C\text{-}^1H_G)$. [d] $^2J(^{195}Pt\text{-}C\text{-}^1H_E)$. [e] $^2J(^{195}Pt\text{-}C\text{-}^1H_F)$.

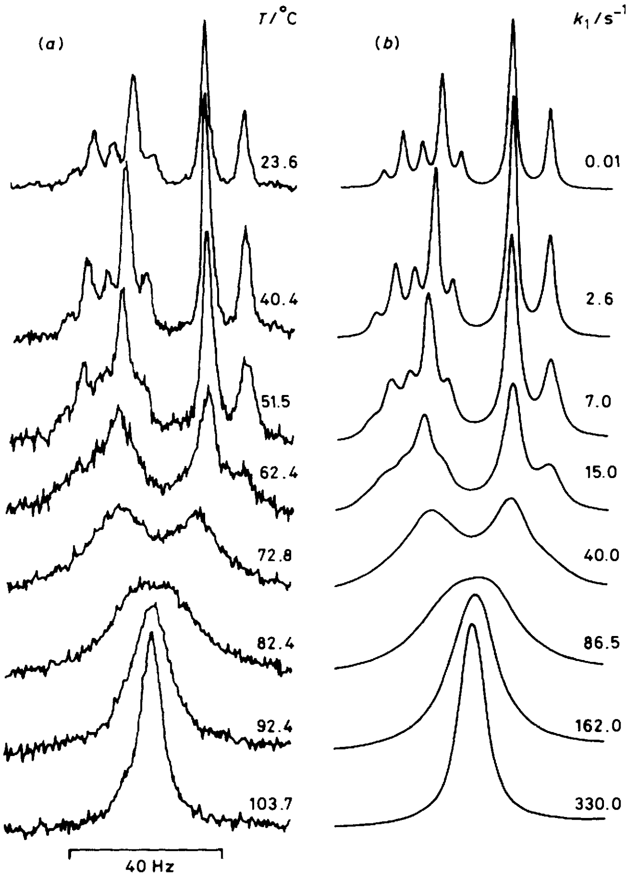
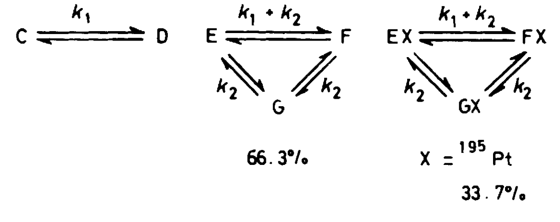


Figure 2. (*a*) Experimental and (*b*) computer synthesised spectra of the ligand methylene region of $[(PtClMe_3)_2(SeCH_2CMe_2CH_2Se)]$ showing the effects of synchronous selenium inversion

inversion process, total bandshape fittings of the ligand methylene region in the temperature range 24 to 104 °C were performed using the static parameters in Table 2. The 'best-fit' computer synthesised spectra are shown alongside the experimental spectra in Figure 2. Similarly good fittings were achieved for the other halide complexes.



Scheme 1.

This ligand 'flapping' process, illustrated in Figure 3, also averages the diastereotopic ring methyls C and D and the equatorial Pt methyls E and F. The axial Pt methyls G will, however, be unaffected and their signal should remain sharp throughout this high temperature range. The experimental spectra of the methyl signals of $[(PtClMe_3)_2(SeCH_2CMe_2CH_2Se)]$ are illustrated in Figure 4. These show the coalescence of the ligand methyl signals C and D around 70 °C, but clearly also reveal exchange between the axial and equatorial Pt-methyl environments at somewhat higher temperatures. Such a process cannot arise directly from chalcogen inversion and can only be attributed to fluxional movements between the Pt-methyl environments. In previous studies,[1–4] such Pt-methyl averagings have been associated with highly fluxional seven-co-ordinate Pt^{IV} intermediates produced by the ligand switching between the two Pt^{IV} centres. We propose an analogous mechanism in the present case although here there is no *direct* evidence for such a fluxion. Partial evidence may be adduced from the absence of any measurable ^3J(PtH) coupling in the methylene signal in the fast inversion limit (*viz.* the spectrum at 103.7 °C in Figure 2). In the absence of any ligand switching the averaged ^3J(PtH) value would be the average of $^3J(PtH_A)$ (10.3 Hz) and $^3J(PtH_B)$ ($\sim$0 Hz), namely *ca.* 5.2 Hz. If ligand switching was occurring at this temperature then the averaged value would be 5.2/2 Hz or 2.6 Hz. Since a fast-exchange linewidth of *ca.* 4 Hz was achieved at the highest temperature (103.7 °C) some evidence of a ^{195}Pt satellite coupling of 5.2 Hz might have been expected. The fact that this was *not* the case suggests that the ligand was rapidly switching between the two Pt co-ordination sites.

The computer simulated spectra of the methyl region (Figure 4) were based on two different rate constants. The rate constant values for the inversion process, k_1, were the same as those used for the ligand methylene region. These values represent the rates of exchange of the two equatorial Pt-methyl signals E and F and the exchange between the ligand methyls C and D. The mechanism of the Pt-methyl scrambling process is still somewhat unclear and in previous studies it has variously been thought to proceed *via* a random exchange process[2–5] or a rotation process.[6] Either of these movements will cause exchange between all three Pt-methyl environments at an equal rate, k_2. Thus, the dynamic processes for the methyl region of the spectrum are formulated as in Scheme 1. However, it was found that such a Scheme did not produce satisfactory fits between experimental and computed spectra. Excellent fits were obtained, however, when equatorial–equatorial exchange was considered solely as a result of double chalcogen inversion (Figure 4). In other words, the dynamic processes which accounted for the spectral changes were as in Scheme 2. This has an important implication regarding the mechanism of the Pt-methyl fluxion (see later).

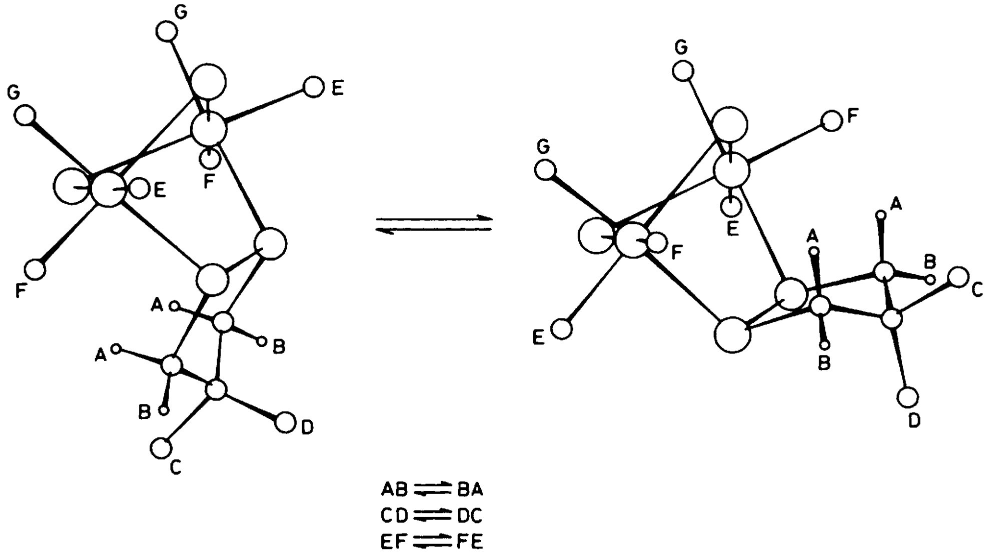
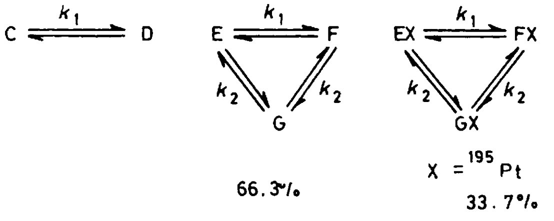


Figure 3. The effects of synchronous double inversion on the diastereotopic ligand methylene, methyl, and equatorial Pt-methyl environments. Note that the labelling refers to the chemical environments, not the atoms. The structures are based on the solid-state *X*-ray data.[7] It should therefore be noted that the ligand five-membered ring will be effectively planar in solution as a result of rapid pseudorotation

Table 4. Arrhenius and Eyring activation parameters for the synchronous inversion in the complexes of the type $[(PtXMe_3)_2(\overline{ECH_2CMe_2CH_2E})]$

E	X	E_a/kJ mol^{-1}	$\log_{10}$ (A/s^{-1})	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$*/kJ mol^{-1}
S	Cl	71.25 ± 1.70	13.67 ± 0.29	68.75 ± 1.71	8.43 ± 5.66	66.23 ± 0.02
S	Br	69.81 ± 0.96	13.46 ± 0.16	67.27 ± 0.97	4.24 ± 3.17	66.01 ± 0.02
S	I	71.23 ± 1.59	13.76 ± 0.28	68.79 ± 1.62	10.37 ± 5.49	65.69 ± 0.02
Se	Cl	76.09 ± 1.33	13.08 ± 0.20	73.24 ± 1.33	−4.03 ± 3.87	74.44 ± 0.18
Se	Br	76.89 ± 0.74	13.20 ± 0.11	74.00 ± 0.73	−1.80 ± 2.11	74.54 ± 0.10
Se	I	76.65 ± 1.13	13.25 ± 0.17	73.78 ± 1.15	−0.76 ± 3.31	74.01 ± 0.16

* At 298.15 K.



Scheme 2.

The experimental spectra were fitted according to Scheme 2 and the 'best-fit' results, based on the static parameters in Table 3, are shown in Figure 4. The similar order of magnitude of the rate constants k_1 and k_2 in the selenium complexes led to very similar activation energies for double selenium inversion and Pt-methyl scrambling. In contrast, for the sulphur complexes the energies of the two processes were significantly different.

Discussion

The Arrhenius and Eyring parameters for the synchronous double-inversion process are collected in Table 4. It should be noted that all the values of the Arrhenius pre-exponential factor A are close to 10^{13} s^{-1}, while values of the entropy changes $\Delta S^\ddagger$ are close to zero, strongly suggesting that the inversion mechanism is intramolecular and proceeds *via* a trigonal-planar intermediate. The energy data show no obvious halide dependence, which is usual in such dinuclear Pt^{IV} complexes,[2,3] but they do exhibit the usual dependence on the type of chalcogen. The $\Delta G^\ddagger$ data in Table 4 show that the energies of double selenium inversion are *ca.* 8 kJ mol^{-1} higher than those of double sulphur inversion. Such a difference in energy is comparable to that observed for single site inversion in the analogous open-chain ligand complexes $[(PtXMe_3)_2(MeEEMe)]$.[3]

In all previous studies of dinuclear Pt^{IV} complexes with bridging chalcogen ligands, the pyramidal inversion process involved independent inversion of individual chalcogen atoms. In the present complexes, the chalcogens are constrained by the five-membered ring to invert in synchronism *via* a double trigonal-planar transition state. This state is clearly of relatively high energy since the $\Delta G^\ddagger$ data for this process are *ca.* 20 kJ mol^{-1} higher than for the corresponding single-site process in related complexes. Selected single- and double-inversion energies have been collected in Table 5 for comparison purposes.

This appears to be the first clearly authenticated case of synchronous double inversion of pyramidal atom pairs. Previously[15,16] such a process has been considered as a possible mechanism for nitrogen atom pairs, but has been discounted in favour of consecutive single-site processes. In a recent study of double inversion of secondary nitrogens in *cis*-di(aziridino)-cyclopentane (3,7-diazatricyclo[4.1.0.0^{2,4}]heptane),[17] there is no way of distinguishing between consecutive single-site and synchronous double-site processes purely from the n.m.r.

spectra since only the *exo–endo* conformers of this compound exist. However, the quoted inversion energy suggests a single-site process, and indeed, it is our experience that whenever there is a choice between inversion mechanisms, the process involving uncorrelated inversion of individual pyramidal atoms will predominate.[18]

The Pt-methyl scrambling energies are listed in Table 6. These values are 3—5 kJ mol^{-1} higher than those for sulphur inversion and of comparable magnitude to those for selenium inversion. Energies for the proposed ligand switching process could not be separately computed but, following previous work,[2–4] it is assumed that this process has a very similar energy to the Pt-methyl scrambling fluxion. This is likely to be so because ligand switching appears to initiate and control the rate of Pt-methyl scrambling. Indeed, the two processes may be considered as different aspects of a more extensive fluxional rearrangement.

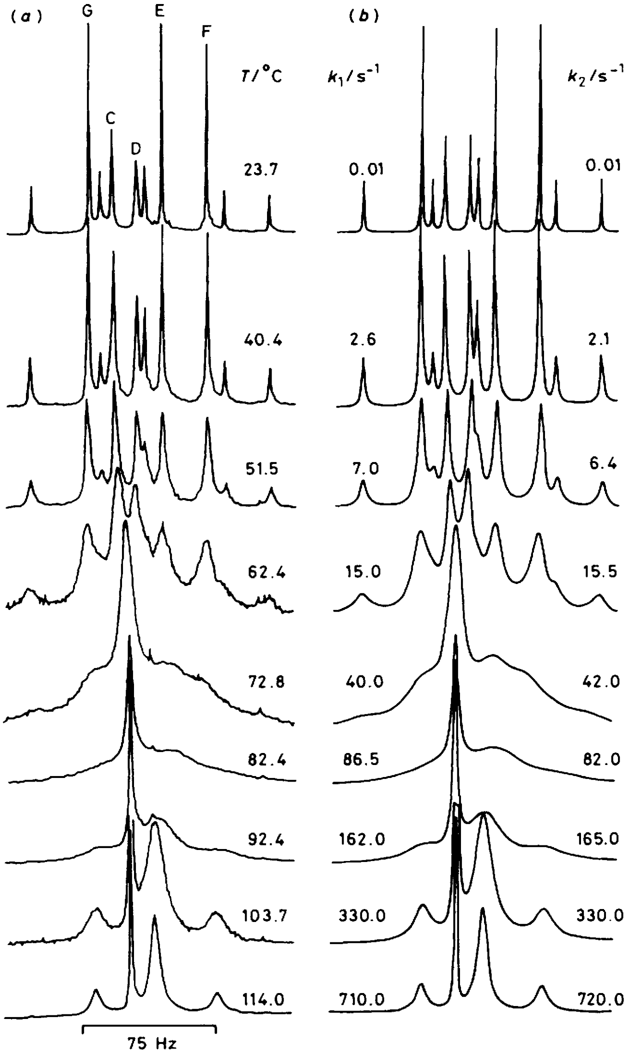


Figure 4. (*a*) Experimental and (*b*) computer synthesised spectra of the ligand-methyl and Pt-methyl regions of $[(PtClMe_3)_2(\overline{SeCH_2CMe_2CH_2Se})]$ showing the effects of synchronous selenium inversion and Pt-methyl scrambling

The $\Delta G^‡$ values in Table 6 are 3—5 kJ mol^{-1} higher for the selenium complexes than for the sulphur-ligand analogues. The data also show a small halide dependence such that Cl > Br > I. Such trends have been observed previously for complexes with open-chain ligands, namely $[(PtXMe_3)_2(MeECHMeEMe)]$ and $[(PtXMe_3)_2(MeEEMe)]$ (X = Cl, Br, or I; E = S or Se), and interpreted[4] in terms of the highly fluxional nature of the seven-co-ordinate Pt^{IV} intermediate arising from the ligand switching process, rather than involving a random cleavage of the Pt–X bridge bonds.

It is noteworthy that the $\Delta G^‡$ values for the Pt-methyl scrambling are 9—10 kJ mol^{-1} higher than for the open-chain ligand complexes $[(PtXMe_3)_2(MeEEMe)]$.[3] The main difference between these and the present complexes is the degree of distortion of the Pt_2X_2 moiety arising from the mismatching of the ligand bite and the Pt···Pt contact distance. This mismatching is very considerable in the present cyclic-ligand complexes and is likely to contribute to a higher transition-state energy.

However, the higher energies of the Pt-methyl fluxions in these complexes could also be a consequence of the different mechanism which appears to be operating here. It has been stated earlier that the spectral changes of the Pt-methyl region can only be explained on the basis of Scheme 2 which implies

Table 5. Single- and double-chalcogen inversion energies in related transition metal complexes

Complex	Process[a]	$\Delta G^‡$/ kJ mol^{-1}	Ref.
$[(PtClMe_3)_2(\overline{SCH_2CMe_2CH_2S})]$	DI	66.2	*b*
$[(PtClMe_3)_2(MeSSMe)]$	SI	41.4	3
$[(PtClMe_3)_2(\overline{SeCH_2CMe_2CH_2Se})]$	DI	74.4	*b*
$[(PtClMe_3)_2(MeSeSeMe)]$	SI	65.2	3
$[(PtBrMe_3)_2(\overline{SeCH_2CMe_2CH_2Se})]$	DI	74.5	*b*
$[(PtBrMe_3)_2(MeSeSeMe)]$	SI	64.6	3
$[Cr(CO)_5(\overline{SCH_2CMe_2CH_2S})]$	SI	47.6	*c*
$[Cr(CO)_5(\overline{SeCH_2CMe_2CH_2Se})]$	SI	67.6	*c*
$[Cr(CO)_5(Me_3SiCH_2SeSeCH_2SiMe_3)]$	SI	53.0	*d*
$[W(CO)_5(Me_3SiCH_2SSCH_2SiMe_3)]$	SI	37.3	*d*

[a] DI = Double inversion; SI = single inversion. [b] This work. [c] E. W. Abel, P. K. Mittal, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1985, 1569. [d] E. W. Abel, S. K. Bhargava, P. K. Mittal, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1985, 1561.

Table 6. Arrhenius and Eyring activation parameters for the Pt-methyl scrambling processes in the complexes of the type $[(PtXMe_3)_2(\overline{ECH_2CMe_2CH_2E})]$

E	X	E_a/kJ mol^{-1}	$\log_{10}$ (A/s^{-1})	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^{‡}$*/kJ mol^{-1}
S	Cl	76.15 ± 0.63	13.63 ± 0.10	73.42 ± 0.62	6.85 ± 1.91	71.38 ± 0.05
S	Br	76.61 ± 1.90	13.74 ± 0.31	73.98 ± 1.88	9.20 ± 5.94	71.23 ± 0.11
S	I	75.76 ± 0.48	14.04 ± 0.08	73.09 ± 0.48	14.98 ± 1.51	68.62 ± 0.04
Se	Cl	79.09 ± 0.97	13.52 ± 0.14	76.20 ± 0.98	4.31 ± 2.89	74.92 ± 0.14
Se	Br	75.98 ± 1.18	13.06 ± 0.18	73.17 ± 1.19	−4.17 ± 3.52	74.42 ± 0.14
Se	I	76.94 ± 1.22	13.41 ± 0.19	74.15 ± 1.19	2.50 ± 3.55	73.40 ± 0.13

* At 298.15 K.

that a pair-wise axial–equatorial exchange is occurring and does *not* involve any direct equatorial–equatorial methyl exchange. In earlier studies it has not been possible to be as definite as this concerning the scrambling mechanism since often there has either been no chemical shift distinction between the two equatorial Pt-methyl environments[2,3] or the shift difference has been small[2,4,5] causing the spectra to be insensitive to the rate of direct equatorial–equatorial exchange. In dinuclear Pt^{IV} complexes with heterocyclic sulphur ligands,[5,6] the Pt-methyl scrambling process occurs subsequent to a metal-pivot process becoming rapid on the n.m.r. time-scale. In the case of the six-membered trithiane complexes,[5] it is not clear whether the methyl-scrambling process causes any equatorial–equatorial interchange since this exchange is dominated by the effects of the metal-pivot process. In the eight-membered tetrathiocane complexes,[6] where the metal-pivoting and methyl-scrambling processes have identical energies (within experimental error), a mechanism involving incidental exchanges of equatorial methyls on the pseudostationary platinum atom and axial–equatorial methyl exchanges due to 120° rotations of the pivot commuting $PtMe_3$ group well explains the observed spectral changes. In general, therefore, the mechanism of Pt-methyl scrambling appears to depend on the type of dynamically exchanging structure resulting from the lower energy rate process, be it pyramidal chalcogen inversion, ligand switching or metal pivoting. The present observation of a pair-wise axial–equatorial methyl exchange can be considered to occur by 180° rotations of the Me_{ax}–Pt–Me_{eq} moieties, in contrast to the 120° rotations of the $PtMe_3$ groups postulated for the ligand-pivoting complexes.[6,19] The two mechanisms may therefore be considered as closely related rather than incompatible. Nevertheless, further studies are clearly required to discover the ground rules for methyl-scrambling mechanisms in trimethylplatinum(IV) complexes.

References

1 E. W. Abel, S. K. Bhargava, and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **32**, 1.
2 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 2208.
3 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 2220.
4 E. W. Abel, K. Kite, K. G. Orrell, V. Šik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 2439.
5 E. W. Abel, M. Booth, G. King, K. G. Orrell, G. M. Pring, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1981, 1846.
6 E. W. Abel, G. D. King, K. G. Orrell, V. Šik, T. S. Cameron, and K. Jochem, *J. Chem. Soc., Dalton Trans.*, 1984, 2047.
7 E. W. Abel, P. K. Mittal, K. G. Orrell, V. Šik, and T. S. Cameron, *J. Chem. Soc., Chem. Commun.*, 1984, 1312.
8 G. Bergson and A. Biezais, *Ark. Kemi*, 1964, **22**, 475.
9 H. J. Backer and H. J. Winter, *Recl. Trav. Chim. Pays-Bas*, 1937, **56**, 691.
10 H. J. Backer and A. F. Tamsma, *Recl. Trav. Chim. Pays-Bas*, 1938, **57**, 1183.
11 D. A. Kleier and G. Binsch, DNMR3 Program 165, Quantum Chemistry Program Exchange, Indiana University, 1970.
12 G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 411.
13 F. G. Riddell, 'The Conformational Analysis of Heterocyclic Compounds,' Academic Press, 1980.
14 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 1169.
15 J. E. Anderson and J. M. Lehn, *J. Am. Chem. Soc.*, 1967, **89**, 81.
16 S. F. Nelsen and G. R. Weisman, *J. Am. Chem. Soc.*, 1976, **98**, 1842.
17 M. W. Majchrzak, A. Kotelko, and J. B. Lambert, *Org. Magn. Reson.*, 1983, **21**, 706.
18 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 1175.
19 T. E. MacKenzie, Ph.D. Thesis, University of Exeter, 1983.

Received 24th July 1985; *Paper* 5/1268