# Novel Fluxional Rearrangements in Binuclear Platinum Complexes; Intermetallic Ligand Atom Switching

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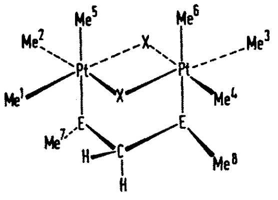
*Summary* The binuclear complexes of the type (±)-$[(Me_3PtX)_2MeE(CHR)_nEMe]$ (E = S or Se; X = Cl, Br, or I; R = H or Me; $n = 0$ or 1) have been shown to exhibit a remarkable series of fluxional phenomena over a range of temperatures; most notable of these is an intermetallic commutation by the two donor atoms of the bidentate sulphur and selenium ligands .

WE recently reported[1] the formation of novel binuclear platinum complexes of certain bidentate sulphur ligands, and now report that these and further examples of this type of complex display most interesting fluxional behaviour.

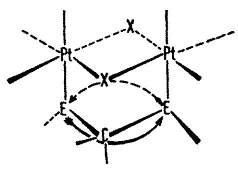
The reaction of the tetrameric trimethylplatinum (IV) halides (I) with dialkyl disulphides and diselenides, and 2,4-dithia- and -diselena-pentanes proceeds according to equation (1), where E = S or Se; X = Cl, Br, or I; R = H or Me; and $n = 0$ or 1.

$$\underset{\text{(I)}}{[(Me_3PtX)_4]} + 2MeE(CHR)_nEMe \longrightarrow 2[(Me_3PtX)_2MeE(CHR)_nEMe] \qquad (1)$$

Thus these particular ligands split the tetrameric trimethylplatinum(IV) halides (I) into binuclear species as exemplified in (II), in contrast to those ligands where $n > 1$, which produce mononuclear species.[1]



(II)



(III)

Below *ca.* −95 °C, $^1H$ spectra show that in (II) all eight methyl groups are in different environments as expected for the 'static' structure illustrated. Between −95 and −20 °C, however, reversal of the $E-CH_2-E$ part of the 6-membered $E-CH_2-E-Pt-X-Pt$ ring and sulphur (or selenium) atomic inversion become fast on the n.m.r. timescale, the two processes causing different environment averaging of E–Me and equatorial Pt–Me protons.

The energies of these processes are comparable to previously reported data for 6-membered heterocyclic ring reversals[2] and pyramidal inversions of Group 6A atoms attached to Group 8 transition metals.[3] Both processes contribute to the observed line shapes, and by detailed analysis of the $^1H$ n.m.r. spectra we can deduce separately the activation parameters for these two dynamic processes. On average the activation energies for ring inversion are 6—8 kJ mol$^{-1}$ lower than the corresponding pyramidal ligand atom inversion.

During these processes the E–Me $^1H$ resonances retain the usual 1:4:1 triplet structure [typically, $^3J$(Pt–H) = *ca.* 12 Hz], confirming the intramolecular non-dissociative nature of both the ring and ligand atom inversions.

At higher temperatures (between 0 and 70 °C), the $^1H$ resonances of the E–Me group change from a triplet (1:4:1) to a quintet (*ca.* 1:8:18:8:1) with a concomitant approximate halving of $J$(Pt–H) to *ca.* 6 Hz. The quintet structure for the E–Me signals has been reported previously in complexes where the protons are coupled equally to two platinum atoms.[4] In the present complexes an intermetallic ligand atom switching process is proposed as illustrated in (III).

Such a process averages the couplings $^3J$(Pt–H) and $^4J$(Pt–H) or $^5J$(Pt–H) for the complexes with $n = 0$ or $n = 1$, respectively. The Figure shows the observed E–Me spectra for the complex (±)-$[(Me_3PtCl)_2(MeSCHMeSMe)]$,

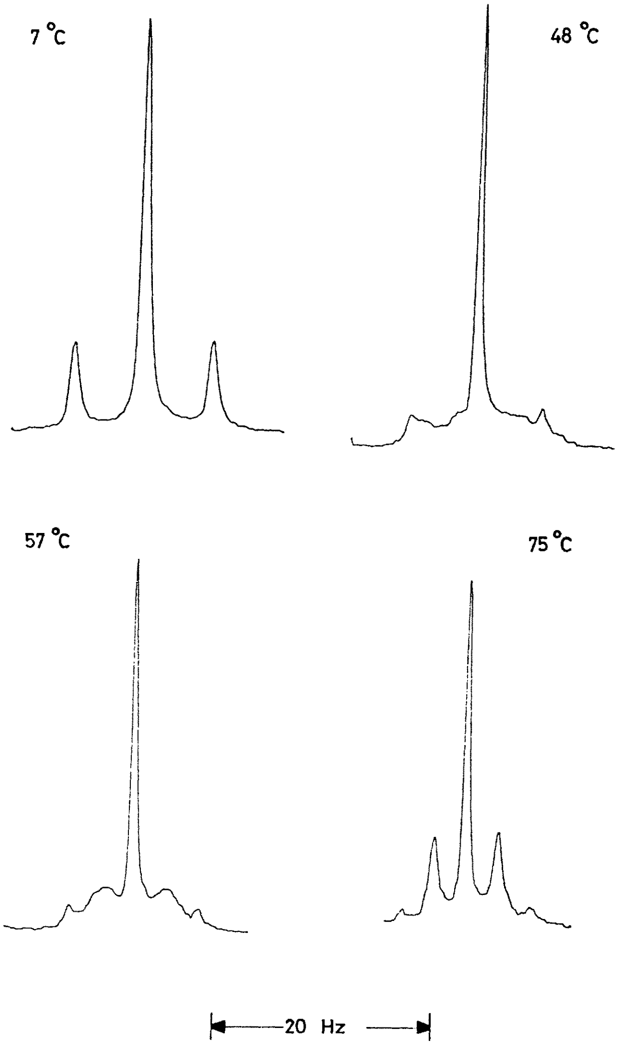


FIGURE. Variable temperature $^1H$ n.m.r. spectra of the –SMe region of (±)-$[(Me_3PtCl)_2(MeSCHMeSMe)]$ illustrating the onset of the ligand switching process.

which arise from a superposition of sub-spectra due to the species [Pt, Pt], [Pt, $^{195}$Pt], and [$^{195}$Pt, $^{195}$Pt], present in their natural abundances.

Whilst this intermetallic ligand atom switching accounts for the observed coalescence of all of the equatorial Pt–Me signals (Me$^1$, Me$^2$, Me$^3$, and Me$^4$), it does not explain a final coalescence of all six Pt–Me signals at higher temperature with retention of Pt-coupling. Here it seems likely that an intramolecular random cleavage of halogen bridges is taking place, to give a short lived 5-co-ordinate species analogous to that postulated[5] in the reductive elimination reactions of the complexes $PtXMe_3L_2$. This would allow the three platinum methyl environments to become completely averaged.

In these complexes no ligand dissociation occurs below *ca.* 100 °C or below *ca.* 40 °C in the complexes with $n = 1$ or $n = 0$, respectively. Above these temperatures, however, ligand dissociation–recombination processes are clearly evident from the loss of the averaged couplings between $^{195}$Pt and the E–Me protons.

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[1] E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Organometallic Chem.*, 1978, **145**, C18.

[2] G. Claeson, G. M. Androes, and M. Calvin, *J. Amer. Chem. Soc.*, 1960, **82**, 4428; H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org. Magnetic Resonance*, 1969, **1**, 67; A. Geens, G. Swaelens, and M. Anteunis, *Chem. Comm.*, 1969, 439.

[3] E. W. Abel, G. W. Farrow, K. G. Orrell, and V. Šik, *J.C.S. Dalton*, 1976, 42; E. W. Abel, A. K. S. Ahmed, G. W. Farrow, K. G. Orrell, and V. Šik, *J.C.S. Dalton*, 1976, 47; G. Hunter and R. C. Massey, *ibid.*, p. 2007 and references therein.

[4] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc.* (*A*), 1971, 2031; M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J.C.S. Dalton*, 1978, 516 and references therein; M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt, and K. R. Seddon, *J.C.S. Chem. Comm.*, 1978, 749.

[5] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1974, 2457.