

## Synchronous Pyramidal Inversion of Chalcogen Atom Pairs in Trimethylplatinum(IV) Halide Complexes with Dithia- and Diselena-cyclopentanes. X-Ray Crystal Structure of $[(PtMe_3)_2(Me_2\overline{C}CH_2SeSeCH_2)]$

Edward W. Abel,<sup>a</sup> Pramod K. Mittal,<sup>a</sup> Keith G. Orrell,<sup>\*a</sup> Vladimir Šik,<sup>a</sup> and T. Stanley Cameron<sup>b</sup>

<sup>a</sup> Department of Chemistry, The University, Exeter EX4 4QD, U.K.

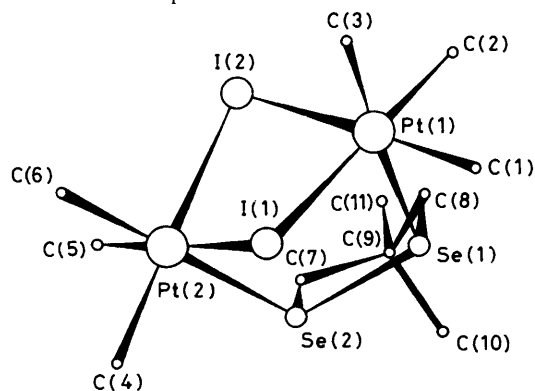
<sup>b</sup> Department of Chemistry, Dalhousie University, Halifax B3H 4J3, Canada

Dinuclear Pt<sup>IV</sup> complexes of type  $[(PtXMe_3)_2(Me_2\overline{C}CH_2EECH_2)]$  (E = S, Se, X = halogen) have been synthesised and shown by X-ray analysis to involve the cyclic ligand bridging the two Pt<sup>IV</sup> atoms, with the Pt<sub>2</sub>X<sub>2</sub> moiety adopting a highly bent geometry; <sup>1</sup>H n.m.r. studies have identified a relatively slow, *synchronous* inversion of the co-ordinated chalcogen atom pairs;  $\Delta G^\ddagger$  data for the process are in the range 66–75 kJ mol<sup>-1</sup>, these values being, in most cases, ca. 20 kJ mol<sup>-1</sup> higher than for the more normal single site inversion.

A strikingly large variety of intramolecular fluxional phenomena have been revealed in sulphur and selenium complexes of transition metals,<sup>1</sup> with trimethylplatinum(IV) complexes being particularly notable in this respect.<sup>2–5</sup> These complexes can be either mononuclear {e.g.  $[(PtXMe_3)L]$ }<sup>5</sup> or dinuclear {e.g.  $[(PtXMe_3)_2L]$ }<sup>2–4</sup> depending on the nature of the bidentate ligand L. The cyclic ligands 4,4-dimethyl-1,2-dithia- and -1,2-diselena-cyclopentane,  $Me_2\overline{C}CH_2EECH_2$ , E = S, Se, (L'), which are usually monodentate {e.g.  $[M(CO)_5L']$ , M = Cr, Mo, W},<sup>6</sup> are here shown to bridge a pair of Pt<sup>IV</sup> atoms to form dinuclear complexes of type  $[(PtXMe_3)_2L']$ . Syntheses of all the complexes were carried out by refluxing a three-fold excess of the ligand<sup>6</sup> with trimethylplatinum(IV) halide in chloroform for ca. 16 h. An X-ray analysis of  $[(PtMe_3)_2(Me_2\overline{C}CH_2SeSeCH_2)]$  was carried out.

*Crystal data:*† C<sub>11</sub>H<sub>28</sub>I<sub>2</sub>Pt<sub>2</sub>Se<sub>2</sub>, M = 962.2, monoclinic, space group P2<sub>1</sub>/n, a = 9.519(3), b = 13.317(4), c = 16.182(5) Å, β = 94.28(3)°, Z = 4, D<sub>c</sub> = 3.12 g cm<sup>-3</sup>, Mo-K<sub>α</sub> radiation, λ = 0.70926 Å, μ = 194.37 cm<sup>-1</sup>. 2738 Unique reflections [1555 with I > 3σ(I)] were collected on a CAD4 four-circle diffractometer. The structure was solved by Patterson and Fourier methods and refined by large-block least-squares to a final R of 0.077. The structure (Figure 1) is shown projected perpendicular to the c axis.

The two Pt<sup>IV</sup> atoms are held by two conventional iodine bridges and a novel diselenium bridge. The Pt ··· Pt distance is 3.90 Å which compares with 3.23 Å for the weak Pt ··· Pt



**Figure 1.** View of the solid state structure of  $[(PtMe_3)_2(Me_2\overline{C}CH_2SeSeCH_2)]$ .

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

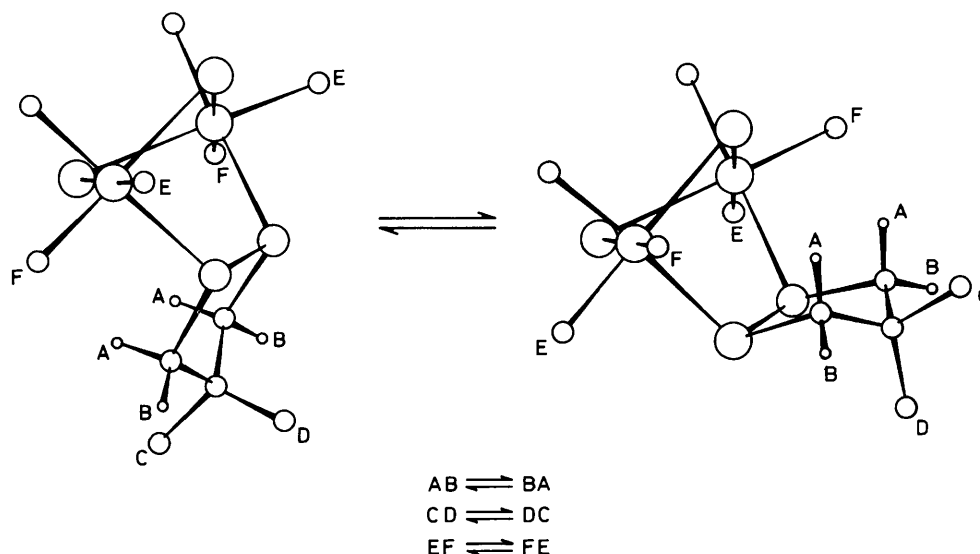
interaction in Pt(dimethylglyoxime).<sup>7</sup> The Pt–I bond lengths differ slightly [Pt–I(1) 2.77, Pt–I(2) 2.79 Å] but the Pt–I–Pt angles are both 89°. These bond lengths are slightly shorter than those reported<sup>8</sup> for  $[(PtMe_3)_4]$  (2.83 Å average). As no X-ray data appear to be available for Pt<sub>2</sub>I<sub>6</sub><sup>2-</sup> in contrast to Pt<sub>2</sub>Cl<sub>6</sub><sup>2-</sup>,<sup>9</sup> and Pt<sub>2</sub>Br<sub>6</sub><sup>2-</sup>,<sup>10</sup> no close comparisons of the dinuclear unit Pt<sub>2</sub>I<sub>2</sub> are possible. However, it is noteworthy that the Pt ··· Pt contact distances of 3.41 Å (Pt<sub>2</sub>Cl<sub>6</sub><sup>2-</sup>)<sup>9</sup> and 3.55 Å (Pt<sub>2</sub>Br<sub>6</sub><sup>2-</sup>)<sup>10</sup> suggest that the value for Pt<sub>2</sub>I<sub>6</sub><sup>2-</sup> would be significantly less than that observed in the present complex. The Se–Se bond length is 2.36 Å as in the complex  $[(PtBrMe_3)_2(MeSeSeMe)]$ .<sup>3</sup> The configuration about each Pt atom is approximately octahedral with interbond angles in the ranges 176–179° and 86–95°. However, the remarkable feature of this structure lies in the fact that the Se–Se bond length is 1.54 Å shorter than the Pt ··· Pt contact distance. Thus, in order to maintain approximate octahedral geometry at the Pt atoms the Pt<sub>2</sub>I<sub>2</sub> unit is forced into a severely bent geometry with an angle of 36.8° between the normals to the planes of the two PtI<sub>2</sub> fragments. This is the most strained halogen bridged dinuclear Pt<sup>IV</sup> complex reported to date, the previous case of  $[(PtBrMe_3)_2(MeSeSeMe)]$  having its Pt<sub>2</sub>Br<sub>2</sub> unit bent to the extent of 29°.<sup>2</sup>

Solution <sup>1</sup>H n.m.r. studies of the complexes  $[(PtXMe_3)_2(Me_2\overline{C}CH_2EECH_2)]$  (E = S, X = Cl; E = Se, X = Cl, I) revealed some very novel stereodynamics. Ambient temperature spectra could be interpreted in terms of either structure in Figure 2. However, on warming, the separate pairs of signals due to the diastereotopic methylenes (H<sub>A</sub>, H<sub>B</sub>), the diastereotopic ring methyls (C, D), and the equatorial Pt-methyls (E, F), broadened, coalesced, and then sharpened, platinum-195 coupling being maintained throughout. This implies that mutual interchange is occurring between these pairs of proton environments, as shown in Figure 2. The only explanation of these changes is pyramidal inversion of the

**Table 1.** Single and double inversion energies in related complexes.

Complex	Process <sup>a</sup>	$\Delta G^{\ddagger b/}$ kJ mol <sup>-1</sup>	Ref.
$[(PtClMe_3)_2(Me_2\overline{C}CH_2SSCH_2)]$	DI	66.23 ± 0.02	c
$[(PtClMe_3)_2(Me_2\overline{C}CH_2SeSeCH_2)]$	DI	74.44 ± 0.18	c
$[(PtMe_3)_2(Me_2\overline{C}CH_2SeSeCH_2)]$	DI	74.01 ± 0.16	c
$[(PtClMe_3)_2(MeSSMe)]$	SI	41.4 ± 1.5	3 <sup>d</sup>
$[(PtClMe_3)_2(MeSeSeMe)]$	SI	52.4 ± 0.4	3 <sup>d</sup>
$[Cr(CO)_5(Me_2\overline{C}CH_2SSCH_2)]$	SI	47.6 ± 0.6	6
$[Cr(CO)_5(Me_2\overline{C}CH_2SeSeCH_2)]$	SI	67.6 ± 0.1	6

<sup>a</sup> DI = synchronous double inversion, SI = single site inversion. <sup>b</sup> At 298.15 K. <sup>c</sup> Present work. <sup>d</sup> Errors as in ref. 4.



**Figure 2.** The effects of synchronous double inversion on the diastereotopic methylene, ring methyl, and equatorial Pt-methyl environments. Note that the labelling refers to the chemical environments, not the atoms. The structures are PLUTO (ref. 13) projections of the *X*-ray data. It should also be noted that the ligand five-membered ring will be effectively planar in solution as a result of rapid pseudorotation.

E atoms, and since these atoms are constrained in a ring they are forced to invert in a *synchronous* manner producing a considerable 'flapping' of the 5-membered ring (see Figure 2). Table 1 shows clearly that the synchronous process is far less favoured energetically compared to the usual single site process, with comparable  $\Delta G^\ddagger$  data differing by over 20 kJ mol<sup>-1</sup>. This is the first clearly authenticated case of synchronous double inversion of chalcogen atoms. Previously<sup>11,12</sup> it has been considered as a possible mechanism for nitrogen atom pairs, but has been discounted in favour of a consecutive process.

Received, 14th June 1984; Com. 835

## References

- 1 E. W. Abel, S. K. Bhargava, and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **32**, in the press.
- 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, S. K. Bhargava, K. Kite, K. G. Orrell, V. Šik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1982, 583.
- 6 E. W. Abel, P. K. Mittal, K. G. Orrell, and V. Šik, manuscript in preparation.
- 7 E. Frasson, C. Panattoni, and R. Zannetti, *Acta Crystallogr.*, 1959, **12**, 1027.
- 8 G. Donnay, L. B. Coleman, N. G. Kriehoff, and D. O. Cowan, *Acta Crystallogr., Sect. B*, 1968, **24**, 157.
- 9 C. D. Cowman, J. C. Thiebeault, R. F. Ziolo, and H. B. Gray, *J. Am. Chem. Soc.*, 1976, **98**, 3209.
- 10 N. C. Stephenson, *Acta Crystallogr.*, 1964, **17**, 587.
- 11 J. E. Anderson and J. M. Lehn, *J. Am. Chem. Soc.*, 1967, **89**, 81.
- 12 S. F. Nelsen and G. R. Weisman, *J. Am. Chem. Soc.*, 1976, **98**, 1842.
- 13 S. Motherwell, PLUTO Crystal and Molecular Structure Plotting Program, Cambridge Crystallographic Centre, 1980.