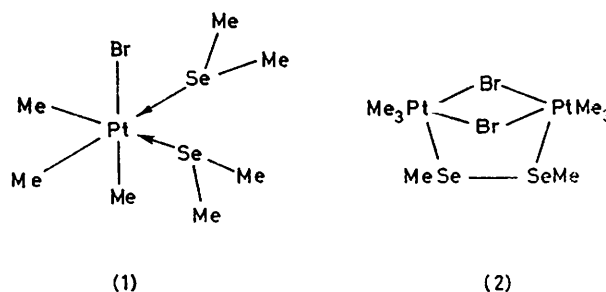


Synthesis and X-Ray Crystal Structure of the Bridging Diselenide Complex $[(\text{PtMe}_3\text{Br})_2\text{MeSeSeMe}]$, and Unusual Prochirality at a Selenium Centre in the Complex $[\text{PtMe}_3\text{Br}(\text{Me}_2\text{Se})_2]$

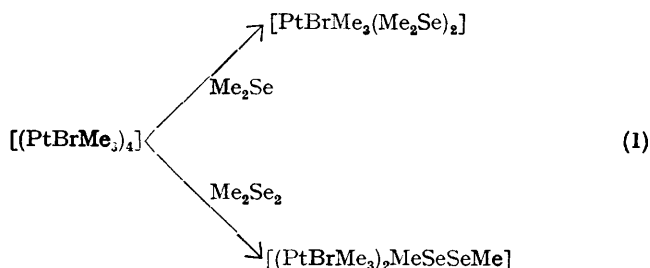
By EDWARD W. ABEL, A. RAUF KHAN, KENNETH KITE, KEITH G. ORRELL, and VLADIMIR ŠIK
(Department of Chemistry, The University, Exeter EX4 4QD)

and T. STANLEY CAMERON and RUTH CORDES
(Department of Chemistry, Dalhousie University, Halifax B3H 4J3, Canada)

Summary The tetrameric bromotrimethylplatinum $[(\text{Me}_3\text{PtBr})_4]$ reacts with dimethyl diselenide and dimethyl selenide to form respectively the dinuclear complex $[(\text{Me}_3\text{PtBr})_2\text{MeSeSeMe}]$ and the mononuclear complex $[\text{Me}_3\text{PtBr}(\text{Me}_2\text{Se})_2]$; the crystal structure of the dimer shows a novel diselenide bridge, and the atomic inversion about selenium has been studied in both complexes exploiting the presence of anisochronous methyl groups.



RECENT reports that MeSSMe^1 and $\text{Ph}_2\text{PPPPh}_2^2$ can bridge the metal atoms in $[\{\text{ReBr}(\text{CO})_3\}_2(\text{L-L})]$ prompt us to report the structure of the first example of a diselenide in such a bridging role. Bromotrimethylplatinum undergoes reaction with dimethyl selenide and dimethyl diselenide according to equation (1). The mononuclear $[\text{Me}_3\text{PtBr}(\text{Me}_2\text{Se})_2]$ has the octahedral structure (1), and the dinuclear $[(\text{PtBrMe}_3)_2\text{MeSeSeMe}]$ structure (2) (see later).



Below -30°C the selenium methyl groups show two separate ^1H n.m.r. resonances of equal intensity, with $J_{\text{Pt-Se-C-H}}$ ca. 10.7 and 9.5 Hz for the high and low field signals. On warming, the resonances collapse to a sharp singlet, but with retention of the Pt-H coupling. This phenomenon is observable because although the two selenium atoms are themselves equivalent, in the absence of a Me_2PtSe_2 mirror plane the two methyl groups on each tetrahedral selenium atom are not symmetry related, and are hence anisochronous. As Pt-H coupling is retained in the high temperature spectrum, only atomic inversion about selenium can explain the observed coalescence. We have determined a value of $57.0 \pm 5.1 \text{ kJ mol}^{-1}$ for the activation energy (ΔG^\ddagger), from computer simulation of line shapes over a range of temperatures.

The structure of the diselenide bridged dinuclear complex (2) has been obtained. *Crystal data:* $\text{C}_8\text{H}_{24}\text{Br}_2\text{Pt}_2\text{Se}_2$,

orthorhombic, $a = 9.358(1)$, $b = 12.425(2)$, $c = 14.977(3)$ Å, space group $P2_12_12_1$, $Z = 4$, $D_c = 3.158$ g cm $^{-3}$, Mo- K_α radiation ($\lambda = 0.71069$ Å), four circle diffractometry, 1581 independent observable reflections, of which 713 had $I > 3\sigma(I)$. The structure was solved by tangent and Fourier methods and refined by least squares. The conventional R is 0.04 with isotropic temperature factors on the carbon and hydrogen and anisotropic temperature factors on the heavier atoms. The structure was also refined in the opposite enantiomer to that given in the Figure. This structure converged with $R = 0.05$, so the molecule as shown is probably in the correct absolute configuration.† The two platinum atoms in the molecule are held together by three bridging groups. Two of these are conventional halogen bridges; the third is a very unusual biselenium bridge. The Pt...Pt distance is 3.740(3) Å which compares³ with 3.23 Å for the weak Pt...Pt interaction in Pt(dimethylglyoxime)₂. The Pt-Br bond lengths are all equivalent within 1 e.s.d. (± 0.007 Å), and have a mean value of 2.629 Å. The Pt-Br-Pt angles are both 90.7(2)°. The bond lengths are somewhat longer than those reported⁴ for Pt₂Br₆²⁻ (2.43 Å), where the Pt-Br-Pt angles are 94°, and the Pt...Pt contact is 3.55 Å. The Se-Se bond length is 2.36(1) Å, which is within, but near the higher limit of, the range of acceptable values.⁵ The Pt-Se-Pt angles [mean 105.3(2)°], as well as the C-Se-X angles [mean 99(2)°], are equivalent. The configuration about each platinum atom is approximately octahedral, with interbond angles in the range of 173–178° and 82–96°. Since the Se-Se bond length is 1.19 Å shorter than the Pt...Pt contact distance, it is not possible for the four atoms of the Pt₂Br₂ ring to be coplanar while the platinum atoms retain even an approximately octahedral environment. The Pt₂Br₂ unit therefore forms a bent system, with an angle of 29° between the normals to the planes of the two Br-Pt-Br fragments, as shown in the Figure.

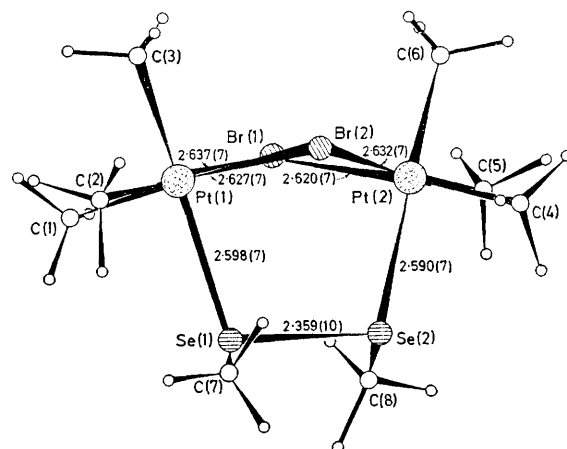


FIGURE. Crystal structure of [(PtMe₂Br)₂MeSeSeMe].

Below -50 °C the ^1H n.m.r. spectrum of this dinuclear complex is precisely as expected for the structure indicated. On warming to -26 °C selenium atom inversion causes equivalence of the equatorial methyl groups [C(1), C(2), C(4), and C(5)] (with retention of Pt-Se-C-H coupling). The activation energy of this process (ΔG^\ddagger) is 53.2 ± 3.7 kJ mol $^{-1}$, and the spectral line shape changes are compatible with a synchronous double-site atomic inversion of the two selenium atoms in the complex.⁶ At 20 °C a further change in the ^1H n.m.r. spectrum takes place which is due to the intermetallic ligand atom switching of MeSeSeMe, with a resultant averaging of $^3J(\text{Pt-H})$ and $^4J(\text{Pt-H})$. This remarkable process⁷ of two selenium centres exchanging platinum atoms has an activation energy (ΔG^\ddagger) of 64.5 ± 6.2 kJ mol $^{-1}$.

(Received, 9th April 1979; Com. 372.)

† 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.

¹ I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *Israel J. Chem.*, 1976/77, **15**, 153.

² J. L. Atwood, J. K. Newell, W. E. Hunter, I. Bernal, F. Calderazzo, I. P. Mavini, and D. Vitali, *J.C.S. Dalton*, 1978, 1189.

³ E. Frasson, C. Panattoni, and R. Zannetti, *Acta Cryst.*, 1959, **12**, 1027.

⁴ N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 587.

⁵ A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, 1975, p. 593.

⁶ E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Organometallic Chem.*, 1978, **145**, C18.

⁷ E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J.C.S. Chem. Comm.*, 1979, 126.