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The Mechanism of Isomerisation of Platinacyclobutanes

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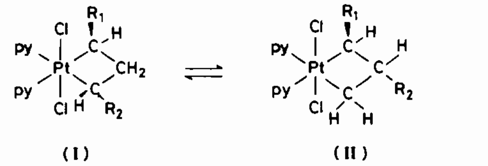
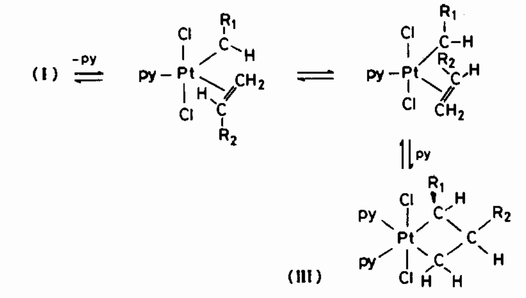
The recently discovered molecular rearrangement [1] (equation 1, R_2 = Ph, R_1 = H) has relevance to several transition metal catalysed reactions [2] and we have therefore investigated the mechanism of reaction

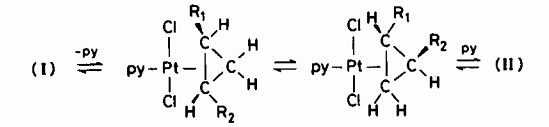


(1)

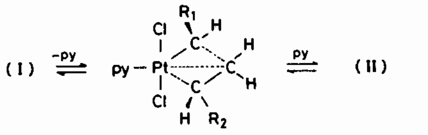
We have considered the three mechanisms shown in equations (2)–(4).



(2)



(3)



(4)

It can be seen that the carbene–olefin mechanism (equation 2) leads to *cis–trans* isomerism about the platinacyclobutane ring, while the 'edge complex' (equation 3) [3] or concerted mechanism (equation 4) [1] gives retention of stereochemistry. Previous work has shown that if R_1, R_2 = Me, Ph or 4-tolyl the substituents R_1 and R_2 remain *trans* during the skeletal isomerisation of equation (1), but since steric hindrance is more severe in complexes with mutually *cis* substituents this could be due to thermodynamic rather than kinetic control [1, 4]. We now report experiments which prove that the stereochemistry is retained as a result of kinetic control.

Extended reaction of $[Pt_2Cl_4(C_2H_4)_2]$ with *cis*-1,2-diphenylcyclopropane and then with pyridine gave an impure platinacyclobutane $[PtCl_2py_2(C_3H_4Ph_2)]$. This complex was heated in $CDCl_3$ under conditions where the analogous complex derived from *trans*-1,2-diphenylcyclopropane undergoes skeletal rearrangement (2 days, 45 °C), and treatment with PPh_3 [5] then gave back *cis*-1,2-diphenylcyclopropane. Thus no *cis–trans* rearrangement occurred. Reaction of $[Pt_2Cl_4(C_2H_4)_2]$ with 1-phenyl-2-deuteriocyclopropane (80% *trans*, 20% *cis*, prepared from largely *trans*-β-deuteriostyrene [6] by methylene addition) gave complex (I), R_1 = D, R_2 = Ph (together with a complex having the grouping $\overline{\mathrm{PtCHPhCHDCH}}_2$), and this was subsequently isomerised to an equilibrium mixture of (I) and (II) [1]. Treatment of either (I) or the equilibrium mixture of (I) and (II) with PPh_3 then gave back the same (80% *trans*, 20% *cis*) 1-phenyl-2-deuteriocyclopropane [7]. This again proves that no *cis–trans* isomerisation of the substituents R_1 and R_2 took place during skeletal isomerisation (I) $\rightleftharpoons$ (II) and hence the carbene–olefin mechanism (equation 2) can be eliminated.

The reaction (1) is intramolecular as shown by experiments in which the isomerisation (I) $\rightleftharpoons$ (II), R_1 = H, R_2 = Ph was carried out in the presence of 4-fluorostyrene or 4-tolylcyclopropane. No exchange products (*e.g.* (I) or (II), R_1 = H, R_2 = 4-FC_6H_4 or 4-tolyl) were formed. Either mechanism of equation (3) or (4) is consistent with all the above results. The recent observation of a strong platinum–carbon transannular interaction in the ground state of a platinacyclobutane [8] lends credence to the concerted mechanism (4), which can be considered to have features in common with both mechanisms (2) and (3).

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