The Interaction of Platinum$^{\text{II}}$ Chloride with a Carbon–Carbon σ-Bond

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Summary In ^{1}H–^{2}H exchange catalysed by Pt$^{\text{II}}$, cyclobutane shows a remarkably large multiple exchange factor, attributed to interaction between Pt$^{\text{II}}$ and the C–C bond; tetraphenylcyclobutane is cleaved by Pt$^{\text{II}}$ to give *trans*-stilbene while norbornane shows preferential *exo* exchange.

X-Ray data indicate a bonding interaction between the metal and a spatially proximate CH bond in PdBr(PPh$_3$)$_2$-(CR:CR·CR:CHR), R = CO$_2$Me,[1] and in molybdenum complexes[2] of the type [Et$_2$B(pz)$_2$]Mo(CO)$_2$(η^3-allyl). Related chemical evidence has also been summarised.[2] Particularly significant[3] is the observed ^{1}H-^{2}H exchange in alkanes catalysed by PtCl$_2$ in AcOD–D$_2$O–DClO$_4$. A survey of the rates of ^{1}H–^{2}H exchange of cycloalkanes CH$_2$[CH$_2$]$_n$ n = 3—7, under these conditions has now yielded data pointing to a bonding interaction between Pt$^{\text{II}}$ and the carbon–carbon bond.

The Table gives values of $k_{\varnothing}$, the initial total rate of ^{2}H incorporation, k_{b}, the rate of removal of ^{2}H$_0$-cycloalkane, and the multiple exchange factor, M = $k_{\varnothing}/k_{\text{b}}$, after reaction of the cycloalkanes at 100 °C for 4 h.

We note satisfactory numerical agreement with previously recorded[3] data for cyclopentane and cyclohexane, but also that cyclobutane shows a remarkably large $k_{\varnothing}$ value and a correspondingly large value of M.

Table

Rate of ^{1}H–^{2}H exchange[a] for CH$_2$[CH$_2$]$_n$

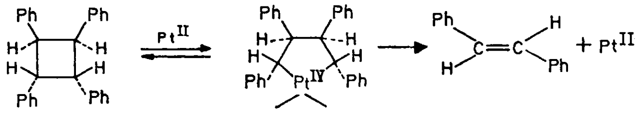
n	3	4	5	6	7
%^{2}H ..	32·2	10·8	10·3	5·0	3·7
k_{b} h^{-1} ..	22·3	17·9	22·8	12·9	10·8
$k_{\varnothing}$ h^{-1} ..	79·6	28·7	32·8	17·9	15·2
M	3·6	1·6	1·4	1·4	1·4
I.P.[b] ..	10·7	10·5	9·9	10·3	10·0

[a] Cycloalkane, 3 mM, K$_2$PtCl$_4$, 0·2 mM, DClO$_4$, 2 mM, pyrene 0·5 mM in AcOD and D$_2$O (1:1), 10 ml, at 100 °C for 4 h.
[b] Ionisation potential (eV), *cf.* ref. 4.

This behaviour of cyclobutane proved reproducible in duplicate experiments, and in absence of Pt$^{\text{II}}$ salt, cyclobutane in the ^{2}H-medium at 100° showed no ^{1}H–^{2}H exchange.

The multiple exchange factor, M, is reasonably attributed[3] to a Pt$^{\text{II}}$-alkane or -cycloalkane association with formation of a complex within which repeated activation and exchange of CH bonds may occur. In comparison with the higher cycloalkanes, cyclobutane is characterised by CH bonds of higher *s*-, and C–C bonds of higher *p*-character. Comparison of cyclobutane with cyclohexane shows no correlation between k_{b} and the CH bond *s*-character, but we suggest a correlation between the cyclobutane M value and the *p*-character of the C–C bonds which in energy terms will be raised nearer to the available levels of Pt$^{\text{II}}$. We note indeed that cyclopropanes with Pt$^{\text{II}}$ undergo insertion into a C–C bond.[5]

The conditions of the exchange reaction did not allow us to observe whether a similar insertion of Pt$^{\text{II}}$ may occur with cyclobutane, but we reasoned that under these conditions *cis,anti,cis*-tetraphenylcyclobutane[6] might exhibit catalysed fragmentation:



Tetraphenylcyclobutane (0·6 mM) with K$_2$PtCl$_4$ (0·2 mM), DClO$_4$ (2 mM), and benzene (stabiliser) (0·5 mM) in AcOH–H$_2$O (1:1, 10 ml) at 160° for 260 h yielded a product from which *trans*-stilbene (0·1 mM), m.p. 123—124°, λ_{max} 294, 307 nm, *m/e* 180, could be isolated by t.l.c. From similar treatment in absence of K$_2$PtCl$_4$ tetraphenylcyclobutane was recovered unchanged.

These results offer physical and chemical evidence of interaction of Pt$^{\text{II}}$ with the cyclobutane C–C bond. We were, however, interested to obtain some independent assessment of the importance of angle strain in the exchange reaction. Norbornane, which has ring angles[7] of 96° at position 7 and 104° at position 2 was therefore subjected to the exchange reaction at 100° for 65 h. This gave a ^{2}H-norbornane (18·9% ^{2}H) showing n.m.r. signals at τ 7·80, 8·87 and 8·57 of intensity 1:3:~1. This indicates considerable preferential exchange of *exo*-hydrogens, and lack of exchange at the more angularly strained 7-position.[8] Angle strain *per se* does not therefore appear to account for the behaviour of cyclobutane.

For the cycloalkanes there is no evident correlation between rate of ^1H–^2H exchange and ionisation potential (*cf.* Table), as has been claimed[3] for n-alkanes.[9] For the cycloalkanes the angular relation of adjacent CH bonds does not appear to be an important factor (*cf.* cyclo-butane, –pentane and -hexane), but the relatively cisoid carbon skeleton may correlate with their relatively higher rate of exchange in comparison with corresponding n-alkanes.[3] The difference is found in k_b and is presumably steric in origin.

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