

STEREOSELECTIVITY IN THE INSERTION OF Pt(II) INTO THE  
CARBON-CARBON BONDS OF SUBSTITUTED CYCLOPROPANES

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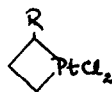
A number of strained cycloalkanes have been found to undergo insertion of transition metals, notably Pt(II) and Rh(I), into a carbon-carbon bond (1), and to be sensitive also to cycloalkane  $\longrightarrow$  diene isomerisation catalysed by  $Ag^+$ , and by a range of transition metal complexes (2). These isomerisations exhibit very marked selectivity in the reaction pathway, depending on the metal ion or complex used, and also, in a number of examples the rate of isomerisation is found to be reduced by electron withdrawing substituents (3). The implication that the available electron density in the cycloalkane is an important factor in these reactions prompts us to report that for a series of substituted cyclopropanes [1] the ease of complex formation with  $PtCl_2$  falls:  $R = \text{alkyl} > \text{aryl} \gg CO_2Me, COMe$  or  $CN$ , and that the insertion reaction:  $[1] \longrightarrow [2a]$  or  $[2b]$  occurs with marked selectivity, and most frequently with the least substituted 2,3-bond, leading to a  $PtCl_2$  derivative of structure [2a].



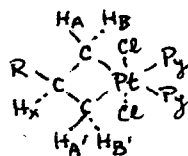
[1]



[2a]



[2b]



[3]

Reaction of the cyclopropanes with  $PtCl_2$  was conveniently effected (4) by the displacement:



Using pairs of cyclopropanes in competition established the relative order of reactivity:

$R = n-C_6H_{13} > PhCH_2 > Ph$ , and for  $R = CO_2Me, COMe$ , or  $CN$  no complex formation was observed.

The structures of the substituted dichloroplatinum trimethylene derivatives were established as [2a] rather than [2b] for the cases  $R = n-C_6H_{13}, PhCH_2, Ph$  and  $o-NO_2Ph$ , by

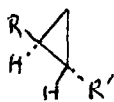
examination of the n.m.r. spectra of the bis-pyridine derivatives [3]. These bis-pyridine derivatives [3] are characterised by (i) a single  $\nu_{\text{PtCl}}$  infrared band which is consistent with trans-related chloro ligands as in [3], and (ii) by n.m.r. spectra in which four protons ( $A, A', B, B'$ ) exhibit  $^{195}\text{Pt}$  satellite signals, with, in the instances:  $R = \text{Ph}$  or  $o\text{-NO}_2\text{Ph}$  also a low field 1H signal ( $H_X$ ) for which  $^{195}\text{Pt-H}$  coupling is very small. In the case of [3],  $R = n\text{-C}_6\text{H}_{13}$ , the protons of the  $\alpha\text{-CH}_2$  group of the n-hexyl residue show no  $^{195}\text{Pt}$  satellite which would be expected of a structure derived from [2b].

The n.m.r. data (in  $\text{CDCl}_3$  with values for  $\text{C}_6\text{D}_6$  solution in parenthesis) are summarised:

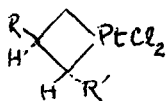
[3]	Protons,			$J_{\text{H,H}}$		$J_{\text{PtH}}$
R	A, A'	B, B'	X	AB,	AX, BX	A, B, A', B'
H		7.34 $\tau$			7.5	84 Hz
Ph	7.03 (6.59, 6.69)		5.9 (5.44)	4.4	9	79, 85
$o\text{-NO}_2\text{Ph}$	7.02		5.44	4.4	9	80, 85
$\text{PhCH}_2$	7.03 (7.0)		6.79 (6.42)	-	-	81
$n\text{-C}_6\text{H}_{13}$	7.25 and 7.58		7.25	-	-	-

Formation of products [2a] and [3], which were obtained in high yield (80-90%), established the marked stereoselectivity of the reaction; only in the case  $R = \text{Ph}$  were minor n.m.r. signals observed which may be due to a small amount of the pyridine derivative of the isomer [2b].

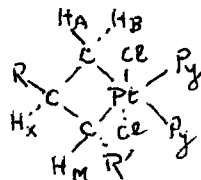
This pattern of reaction was confirmed by the behaviour of trans-1,2-diphenylcyclopropane [4,  $R=R'=\text{Ph}$ ] and trans-1-n-butyl-2-methylcyclopropane [4,  $R = n\text{-Bu}$ ,  $R'=\text{Me}$ ] which, from examination of the n.m.r. spectra of the bis-pyridine derivatives [6] were shown to form  $\text{PtCl}_2$  derivatives of structure [5].



[4]



[5]



[6]

For [6,  $R = R' = \text{Ph}$ ] the n.m.r. spectrum ( $\text{ODCl}_3$ ) showed  $H_A, H_B$  at 6.8  $\tau$ (d),  $J^{195}\text{Pt-H}_A, H_B$

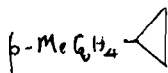
77 and 84.5 Hz,  $H_M$  at 4.88  $\tau$ (d),  $J^{195}\text{Pt}H_M$  98 Hz, and  $H_X$  at 5.25  $\tau$ , with proton proton coupling:  $J_{AB}$  4,4,  $J_{(AB)X}$  9, and  $J_{MX}$  10 Hz. For [6, R = n-Bu, R' = Me] the structure follows from the appearance of the signal for the Me-group at 9.4  $\tau$ (d,  $J$  7 Hz) with platinum satellites ( $J^{195}\text{Pt}$  24 Hz), and the absence of a corresponding satellite signal for the  $\alpha\text{-CH}_2$  protons of the n-butyl group; protons A, B, M and X appeared as two 2H signals at 7.07, and 7.6  $\tau$ , one set, cis to the n-butyl group, being relatively more shielded, cf. [3, R = n-C<sub>6</sub>H<sub>13</sub>].

Two further significant observations relate to the influence of the steric relation of the R and R' substituents in [4], and to the effect of an electron donor group in the case of [1, R = p-MeC<sub>6</sub>H<sub>4</sub>].

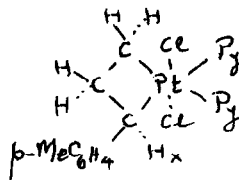
Cis-1-n-butyl-2-methylcyclopropane was found not to yield a PtCl<sub>2</sub> trimethylene derivative, but to react with isomerisation. Both the derived complex, decomposed by KCN, and the recovered unreacted hydrocarbon yielded only olefinic material, which, on hydrogenation, afforded n-octane (80%) with ca. 20% of isomeric octanes. Bicyclo[4.1.0]heptane, similarly, gave no trimethylene derivative, but a Pt-complex yielding on decomposition 1-methyl cyclohexene, methylene cyclohexane, with a little cycloheptene, and the same substances were identified in the recovered unreacted hydrocarbon. The cyclopropanes which, on the other hand, formed trimethylene derivatives gave no evidence of isomerisation in the recovered material, and the PtCl<sub>2</sub>-derivatives were decomposed (KCN, Ph<sub>3</sub>P, or CO) to reform the parent cyclopropane quantitatively.

The differing reaction pathways followed by trans- and cis-1-n-butyl-2-methylcyclopropane indicates that reaction is not solely determined by differential co-ordination of the cyclopropane via alternative cyclopropane carbon-carbon bonds, but by the energetics of the subsequent pathways of ring opening.

This conclusion is emphasised by the behaviour of p-tolylcyclopropane [7] which gave a PtCl<sub>2</sub>-complex yielding a bis-pyridine derivative for which the n.m.r. data indicate structure [8].



[7]



[8]

The n.m.r. spectrum showed  $H_X$  as a triplet ( $J$  9 Hz) at  $5.07\tau$  ( $CDCl_3$ ), or  $4.66\tau$  ( $C_6D_6$ ) with  $^{195}Pt$  coupling,  $J$  102 Hz, of the same magnitude as was observed for  $H_M$  in [6]. The remaining trimethylene protons formed a group of triplet shape at  $7.05\tau$  ( $CDCl_3$ ), or  $6.75\tau$  ( $C_6D_6$ ), and the signal for the p-Me group appeared at  $7.8\tau$  ( $CDCl_3$ ), or  $7.93\tau$  ( $C_6D_6$ ).

In terms of organic chemical precedents it might have been anticipated that phenyl cyclopropane would react with fission of the 1,2-(or 1,3)-bond. However, the energy of bond fission will be compensated by the energy of formation of the carbon-Pt bonds. In the case of p-tolylcyclopropane the balance between these terms is altered in favour of [8] by the electron donor p-Me group. The results overall indicate that in the formation of these trimethylene derivatives the donor capacity of the carbon centre forming a carbon-Pt bond is critical.

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