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THE CHEMISTRY OF CYCLOPROPANE $PtCl_2$ COMPLEXES

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Recognition of the role of π-complexed olefins and other metal organic intermediates in catalytic hydrogenation (1) led us to consider the case of cyclopropanes for which π-bonded intermediates have been recognised in chemical reactions (2) and inferred in catalytic hydrogenation (3).

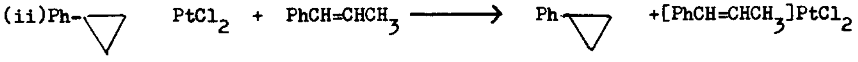
By means of the displacement reaction:

(i) $(C_2H_4\ PtCl_2)_2$ + cyclopropane $\longrightarrow$ C_2H_4 + (cyclopropane $PtCl_2)_n$

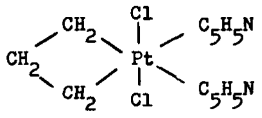
we were able to prepare $PtCl_2$ complexes of the substituted cyclopropanes [2] - [6]. These derivatives formed pale yellow to white, rather insoluble, solids which are clearly chlorine bridged polymers. The derived [cyclopropane] $PtCl_2(C_5H_5N)_2$ complexes, however, could be crystallised, and by T.L.C. on silica behaved as single substances. 1,1-Diphenylcyclopropane [7] gave a more soluble product $Ph_2C_3H_3PtCl$, i.e. the π-allyl derivative [8]. All the complexes on analysis gave C,H,Cl and Pt percentages in very good agreement with the required values. The N.M.R. spectra of the bis-pyridine derivatives show in each case a general downfield shift of the cyclopropane protons in comparison with the parent cyclopropane.

Tipper (4) described the parent cyclopropane complex $C_3H_6PtCl_2$ which on the basis of the N.M.R. spectrum (5), and X-ray data (6) for the bis-pyridine derivative was formulated as [1].

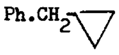
We made the following observations. (a) Excess of the cyclopropane recovered from the preparation as in (i) contained no products of ring opening, or isomerisation, or inversion, e.g. of cis- to trans- 1,2-diphenylcyclopropane. (b) From the $PtCl_2$ complex of each of [2] to [6] the parent cyclopropane was recovered pure and quantitatively by treatment with aqueous potassium cyanide solution. (c) Phenylcyclopropane was similarly displaced on treatment of the complex with propenylbenzene:



(d) Phenylcyclopropane was similarly regenerated on treatment of the $PtCl_2$ complex with


[1]


[2]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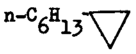
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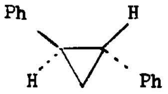
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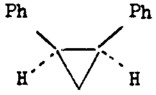
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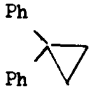
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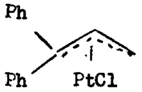
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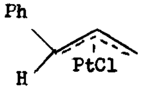
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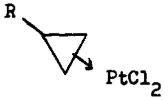
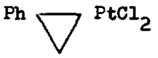
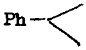
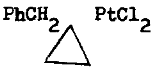
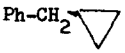
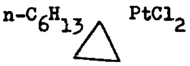
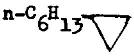
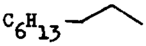
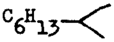
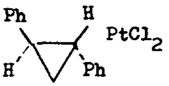
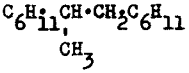
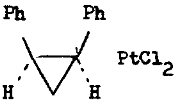
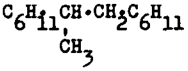
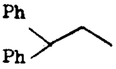
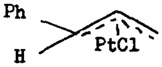

[10]

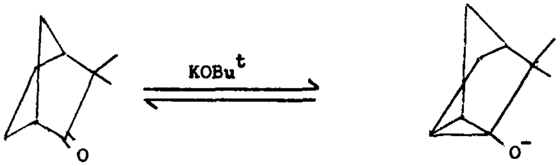
boiling water, together with only trace amounts of propiophenone and phenyl ethyl carbinol, and deposition of platinum metal. (e) In competitive reactions with $(C_2H_4\ PtCl_2)_2$ the following relative reactivity was observed: [2]/[3] = 1:4, [2]/[4] = 2:3, [3]/[4] = 5.4:4.6, i.e. an order [3] $\approx$ [4] $>$ [2]. We infer that complexing parallels the electron density in the cyclopropane ring. (f) The phenylcyclopropane $PtCl_2$ complex heated under carbon tetrachloride slowly formed the more soluble π-allyl derivative [9], with loss of hydrogen chloride. (g) All the complexes reacted immediately when shaken in alcohol with gaseous hydrogen; g.l.c. gave the product analyses shown in the Table.

We note that ring opening of the cyclopropanes to give the π-allyl complexes [8] and [9] is uni-directional. The cyclopropane $PtCl_2$ complexes, on the other hand, undergo normal- and iso- fission on hydrogenolysis, and from the complexes [3] and [4] some of the parent cyclopropane is reformed. The complexes from [2] and [3] on reduction with lithium aluminium hydride in ether also released a good deal of the parent cyclopropane.

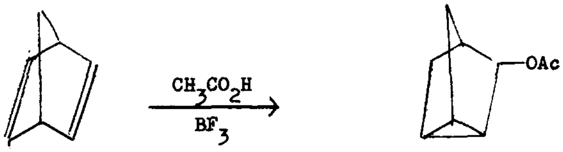
Reformation of the cyclopropane by $CN^{\ominus}$, by water, or by lithium aluminium hydride, or hydrogen reduction is difficult to reconcile with a structure of the type [1] for these complexes. Ring opening must be accompanied by some release of ring strain and there is no evident reason why this ring strain energy should be restored in face of a variety of

COMPLEX	PRODUCTS %			
	 56	 14	$C_6H_{11}Pr$ 30	
	 20	 26	 51	$C_6H_{11}CH_2Pr$ 3
	 40	 15	 45	
	$C_6H_{11}(CH_2)_3C_6H_{11}$ 36		 $C_6H_{11}CH(CH_3)CH_2C_6H_{11}$ 64	
	$C_6H_{11}(CH_2)_3C_6H_{11}$ 9.5		 $C_6H_{11}CH(CH_3)CH_2C_6H_{11}$ 90.5	
	 100			
	 100			

alternative routes of reaction. With the proviso that the carbon-carbon bonds will be lengthened by polarisation, a type of edge co-ordination complex [10] will most easily accommodate the chemical results. Moreover, we may note the examples [11] and [12] in which



[11]



[12]

C-C bonding is initiated over a distance of some 2Å (7,8), and that trimethylaluminium is a dimer. The structure [1] may therefore retain appreciable bonding between the separated $-CH_2-$ groups and the representations [1] and [10] become essentially equivalent.

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