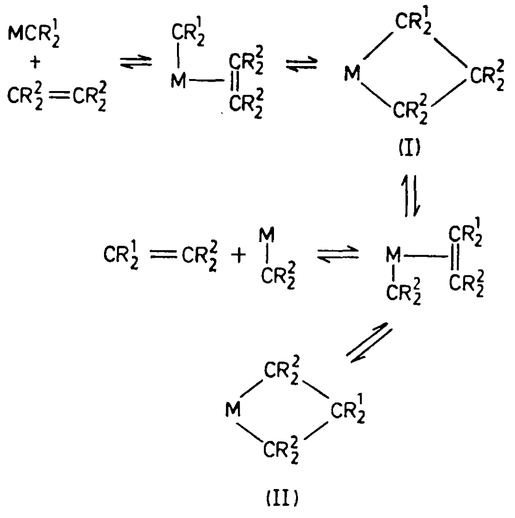
Easy Isomerisation of a Metallocyclobutane Complex, and its Relevance to the Mechanism of Olefin Metathesis

By Richard J. Puddephatt,* Mohammed A. Quyser, and Charles F. H. Tipper

(Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX)

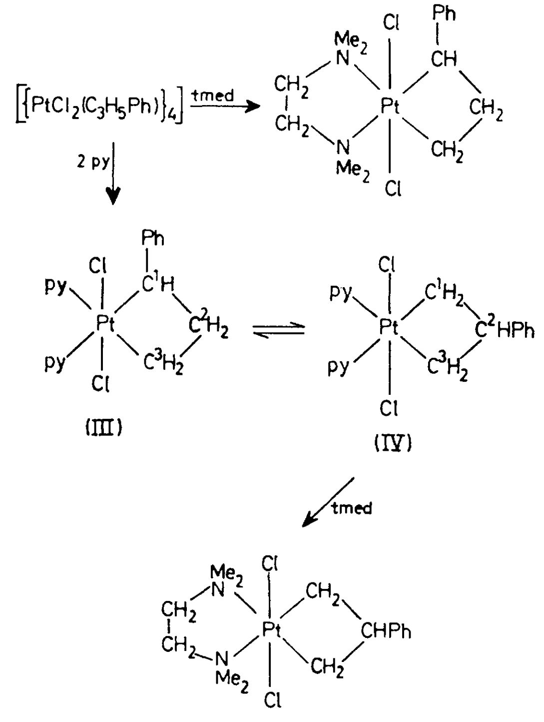
Summary The easy isomerisation of the metallocyclobutane complexes $[\overline{Pt(CHPhCH_2CH_2})Cl_2(py)_2]$ and $[\overline{Pt(CH_2CHPhCH_2})Cl_2(py)_2]$ (py = pyridine) is demonstrated and the relevance to the mechanism of olefin metathesis is discussed.

The mechanism of olefin metathesis catalysed by tungsten complexes is now thought to involve metal carbene and metallocyclobutane intermediates (Scheme 1).[1,2] In a system where the metallocyclobutane complexes are stable, it follows that isomerisation (I) ⇌ (II) might be expected to occur readily. We now report the first example of this form of isomerisation.



Scheme 1

Reaction of Zeise's dimer $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$ with phenylcyclopropane gave $[PtCl_2(C_3H_5Ph)]$, which is probably a tetramer, and this with pyridine (py) gave $[PtCl_2(py)_2(C_3H_5Ph)]$.[3,4] This, when freshly prepared, had structure (III) but isomerised readily to give an equilibrium mixture of (III) and (IV) in relative proportions 1 : 2·3 ± 0·3 (Scheme 2). The isomerisation was complete in 45 min at 50 °C in $CDCl_3$ solution.



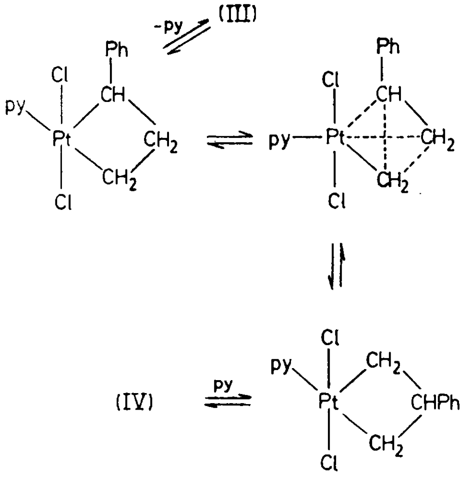
Scheme 2. py = pyridine; tmed = *NNN'N'*-tetramethylethylenediamine.

The complexes (III) and (IV) are most readily characterised by their ^1H and ^{13}C n.m.r. spectra.[4,5] Thus the ^{13}C n.m.r. spectrum of (III) shows δ 5·6 [C-1, ^1J(Pt–C) 326 Hz], 35·1 [C-2, ^2J(Pt–C) 112 Hz], and −11·3 [C-3, ^1J(Pt–C) 354 Hz] p.p.m., and that of (IV) shows δ −4·9 [C-1 and

C-3, ^1J(Pt–C) 369 Hz] and 48·1 [C-2, ^2J(Pt–C) 100·5 Hz] p.p.m.

The isomerisation (III) $\rightleftharpoons$ (IV) is strongly retarded in the presence of free pyridine and the similar complexes with the chelate ligand *NNN'N'*-tetramethylethylenediamine (tmed) did not isomerise at 50 °C. These observations indicate that the isomerisation of (III) takes place *via* an intermediate formed by reversible dissociation of a pyridine ligand.

One possible mechanism (A) involving formation of a platinum–carbene–olefin complex would require ligand dissociation since a carbene and alkene donate a total of 4 electrons to the metal whereas in the metallocyclobutane complexes the organic ligand donates only 2 electrons. Thus unless dissociation of pyridine takes place a '20-electron' intermediate would be involved; such complexes are unknown in platinum chemistry. However, if mechanism (A) did operate then a second form of isomerisation should take place with interconversion of complexes derived from *cis*- and *trans*-1,2-disubstituted cyclopropanes, whereas the limited data available suggest that such a process does not occur readily.[3,4]

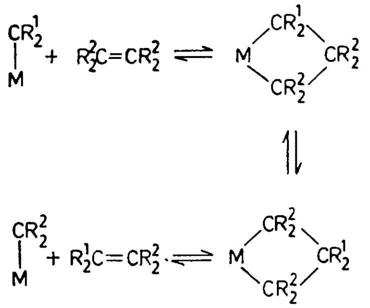


SCHEME 3. Mechanism (B). py = pyridine.

A probable alternative mechanism (B) which is fully consistent with the available data involves a concerted process in which complete C–C bond cleavage to give a carbene complex does not occur (Scheme 3).

It should be pointed out that thermolysis of (III) or (IV) gives isomers of PhC$_3$H$_5$ (propenylbenzenes and phenylcyclopropane) and some propylbenzene but no styrene or ethylene, so that formation of carbene complexes as in mechanism (A) is perhaps less favourable than in the tungsten complex catalysis of the olefin metathesis reaction. However, if the isomerisation (III) $\rightleftharpoons$ (IV) takes place without the intermediacy of a metal–carbene–olefin complex and this is a general effect in metallocyclobutane complexes, a simplified mechanism for the olefin metathesis can be proposed (Scheme 4).

The driving force for the isomerisation (III) → (IV) may well be the relief of steric interactions between the phenyl group and the proximal pyridine ligand in (III). The relative stabilities of isomeric complexes analogous to (III) and (IV) may influence the ratio of productive to non-productive olefin metathesis in catalytic systems.[1] Complexes with bulkier substituted pyridine ligands are being studied to test the hypothesis that steric effects are dominant.



SCHEME 4. M = metal.

The characterisation of the pyridine complexes has previously been used to deduce the initial position of ring opening of substituted cyclopropanes by platinum complexes.[4] The reasonable but incorrect assumption was made that isomerisation of the pyridine complexes did not occur readily and the conclusions may thus be in error. For instance, the complex derived from phenylcyclopropane was identified as (IV) by its ^{1}H n.m.r. spectrum, and the conclusion that phenylcyclopropane was cleaved at the least substituted edge was made. This is now shown to be incorrect.

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[1] M. T. Mocella, M. A. Busch, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1976, **98**, 1283.

[2] T. J. Katz and J. McGinnis, *J. Amer. Chem. Soc.*, 1975, **97**, 592; C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 1974, **96**, 7808; R. H. Grubbs, P. L. Burk, and D. D. Carr, *J. Amer. Chem. Soc.*, 1975, **97**, 3265; D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[3] W. J. Irwin and F. J. McQuillin, *Tetrahedron Letters*, 1968, 1937.

[4] F. J. McQuillin and K. G. Powell, *J.C.S. Dalton*, 1972, 2123.

[5] P. W. Hall, R. J. Puddephatt, and C. F. H. Tipper, *J. Organometallic Chem.*, 1974, **71**, 145.

[6] F. Iwanciw, M. A. Quyser, R. J. Puddephatt, and C. F. H. Tipper, *J. Organometallic Chem.*, 1976, **113**, 91.