The Mechanism of the Platinacyclobutane Rearrangement to give a Platinum–Alkene Complex

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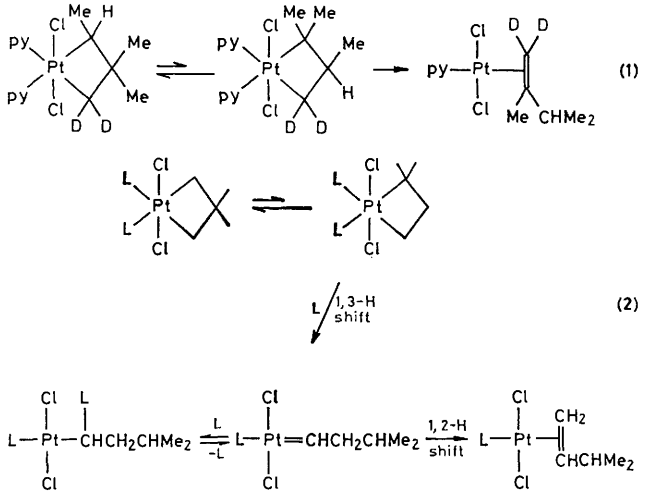
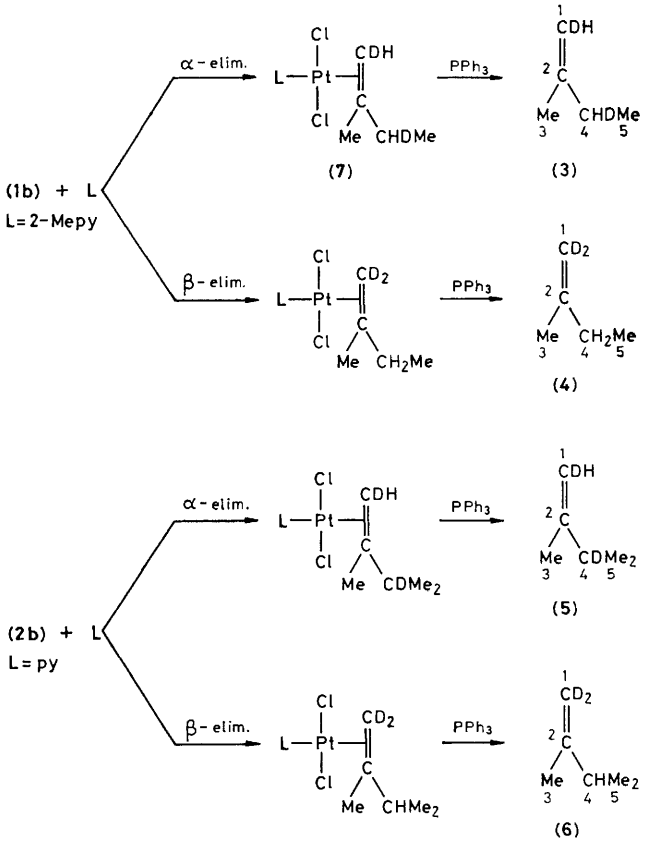
It is shown that the rearrangement of platinacyclobutanes to platinum–alkene complexes occurs by a mechanism involving an initial 1,3-H shift (α-elimination) rather than a 1,2-H shift (β-elimination) as reported previously.

Metallacyclobutanes have been proposed as intermediates in several catalytic reactions, and their rearrangement to carbene or alkene complexes is of particular significance.[1] It has been assumed that the metallacyclobutane to metal–alkene rearrangement involves a β-elimination. There is evidence for this mechanism from several studies,[2–4] but the only direct evidence using an isolated labelled metallacyclobutane was obtained from the reaction of equation (1) (py = pyridine).[5] In contrast, it has been reported that, in a closely related case, rearrangement occurred initially by α-elimination to give an ylide complex which could then rearrange to an alkene complex. The alkene complex was then formed by a sequence involving an initial 1,3-H shift followed by a 1,2-H shift [equation (2), L = 2,6-dimethylpyridine].[6] In the most recent report it was argued, based largely on the earlier labelling study,[5] that both alkene and ylide complexes are formed after an initial β-elimination.[7] Thus a very confused situation has arisen in which there are competing claims that the rearrangements of platinacyclobutanes to either alkene or ylide complexes involve initial α- or β-elimination reactions.[5–7] This is particularly unfortunate since the much studied platinacyclobutanes are often used as models for the labile metallacyclobutanes involved in catalysis.[1] We are therefore prompted to communicate new results which show that the α-elimination mechanism is dominant in all cases studied.



(1)

(2)



Scheme 1

The platinacyclobutanes (**1a, b**) and (**2a, b**) were prepared by standard methods.[8] The rearrangements of (**1a**) and (**2a**) to the corresponding alkene complexes *trans*-[$PtCl_2$(2-Mepy)-(CH_2=CMeEt)] or *trans*-[$PtCl_2$(py)(CH_2=CMePr^i)] were achieved by reaction with 2-methylpyridine or pyridine respectively, and the free alkenes were then liberated by reaction with PPh_3 followed by distillation *in vacuo*. The rearrangements are intramolecular [a mixture of (**1a**) and (**1b**) treated as above gave C_5H_{10} and $C_5H_8D_2$ with no C_5H_9D as determined by mass spectrometry] and the alkenes are those reported previously.[5–9] The key question concerns the position of the deuterium labels in the products from (**1b**) and (**2b**), for which the two opposing mechanisms predict quite different results as shown in Scheme 1.

$$[\{PtCl_2(trans\text{-}CHMeCHMeCX_2\}_4]$$

(**1**)

$$[\{PtCl_2(CHMeCMe_2CX_2)\}_4]$$

(**2**)

a; X = H
b; X = D

The major products were shown to be (**3**) and (**5**) by analysis of the ^1H, ^2H, and ^{13}C n.m.r. spectra.† For example, complex (**1b**) gave an alkene whose $^{13}C\{^1H\}$ n.m.r. spectrum contained 1:1:1 triplets for carbon atoms C-1 and C-4 due to ^1J(CD) coupling, whose ^1H n.m.r. spectrum included a doublet for the Me-5 signal due to vicinal H–H coupling, and whose ^2H n.m.r. spectrum (Figure 1) gave resonances of approximately equal intensity for the 1-DH and 4-HD groups. The data are clearly inconsistent with the alternative structure (**4**), predicted by the β-elimination mechanism,[7] which contains no deuterium at C-4. In a similar way, the major product from (**2b**) is shown to be (**5**). Again the ^2H n.m.r. spectrum (Figure 1), showing approximately equal incorporation of deuterium at C-1 and C-4, offers a particularly simple proof since the alternative structure (**6**) has no deuterium at C-4. Detailed analysis of the ^1H and $^{13}C\{^1H\}$ n.m.r. spectra fully support this conclusion,† although the formation of a minor product with ^2H-incorporation at C-5 is a complicating factor. Our spectra are quite unlike those reported earlier, when it was claimed that the major product was (**6**).[5] We have also characterised the complexes (**7**), L=CD_3CN or 2-Mepy, proving that no isomerisation of the alkene occurs on displacement from platinum.‡

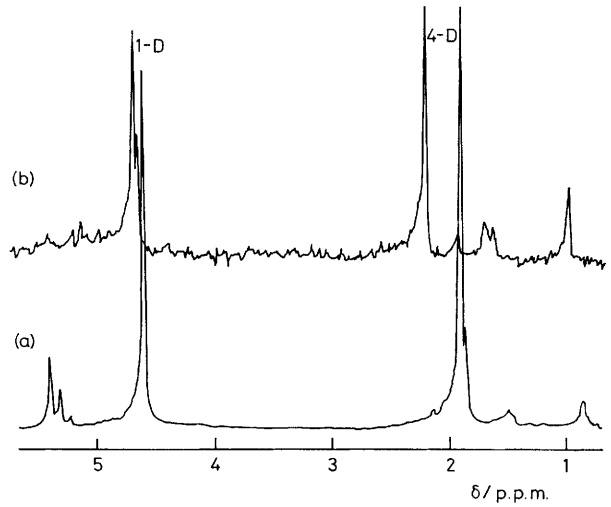


Figure 1. $^2H\{^1H\}$ n.m.r. spectra (15.4 MHz): (a) of alkenes formed from (**1b**); major product is (**3**), minor peaks are tentatively assigned to a side product *trans*-2-[$^2H_2$]pentene. (b) of alkenes formed from (**2b**); major product is (**5**), the peak at δ 0.99 p.p.m. is probably due to CH_2=CMeCHMe(CHD_2).

† N.m.r. spectra: (**3**), δ(^{13}C) 107.8[t, ^1J(CD) 23 Hz, C-1], 147.7 (s, C-2), 22.1 (s, C-3), 30.1 [t, ^1J(CD) 19 Hz, C-4], and 12.0 p.p.m. (s, C-5); δ(^1H) 4.61 (m, 1-H), 2.41 [d, ^4J(3-H, 1-H) 1.1 Hz, 3-H], 1.93[q, ^3J(4-H, 5-H) 7.4 Hz, 4-H], and 0.92 [dt, ^3J(5-H, 4-D) 1.1 Hz, 5-H]; δ(^2H) 4.61 (1-D) and 1.92 p.p.m. (4-D). (**5**), δ (^{13}C) 107.6[t, ^1J(CD) 22 Hz, C-1], 151.9 (s, C-2), 20.2 (s, C-3), 35.2(C-4), and 21.5 p.p.m. (s, C-5); δ(^1H), 4.61 and 4.66 (dm, 1-H), 1.68 [d, ^4J(3-H, 1-H) 1.0 Hz, 3-H], and 0.99 [t, ^3J(5-H, 4-D) 1.0 Hz, 5-H]; δ(^2H) 4.67 and 4.70 (1-D) and 2.23 p.p.m. (4-D). For C-4 ^1J(CD) was not resolved; the presence of ^2H at C-4 was confirmed by the low intensity compared with the unlabelled alkene.

‡ The possibility that slight changes in procedure from that used in ref. 5 could lead to different products cannot be excluded.

There are still unresolved questions. For example, it is not clear if hydridoplatinum intermediates are involved in the hydrogen shift reactions, the high selectivity of the reactions could result from several sources, and the applicability of this mechanism to rearrangements of metallacyclobutanes other than those of platinum(IV) cannot be assumed.[3,4] Nevertheless, this unexpected α-elimination mechanism will need to be given careful consideration in future studies of metallacyclobutane rearrangements.

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