Mechanisms of Formation of Alkene or Ylide Complexes from Platinacyclobutanes

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Summary The formation of an ylide complex by decomposition of a platinacyclobutane derivative is shown to involve a 1,3-H shift, consistent with a mechanism involving α-elimination, and it is shown that an alkene complex can be formed from an ylide complex, in reactions which have relevance to homogeneous catalysis.

Metallacyclobutanes have recently been proposed to be intermediates in alkene polymerisation and other catalytic reactions,[1] but their chemistry is not understood at all well. Isolated metallacyclobutanes may decompose to give alkene complexes,[2] ylide complexes,[3] or π-allyl complexes[4] by reactions involving hydrogen atom shifts, or to yield alkenes and probably metal–carbene complexes by a reaction involving C–C bond cleavage.[5] Platinacyclobutanes undergo stereospecific skeletal isomerisation,[6] which may interconvert the groupings $\overline{\text{PtCHPhCH}_2\text{CH}_2}\rightleftharpoons\overline{\text{PtCH}_2\text{CHPhCH}_2}$. The recent discovery that platinacyclobutanes rapidly decompose to alkene complexes or ylide complexes on treatment with bulky ligands facilitates

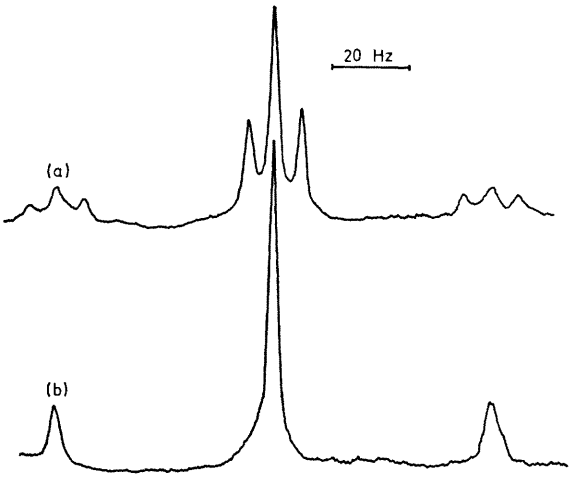
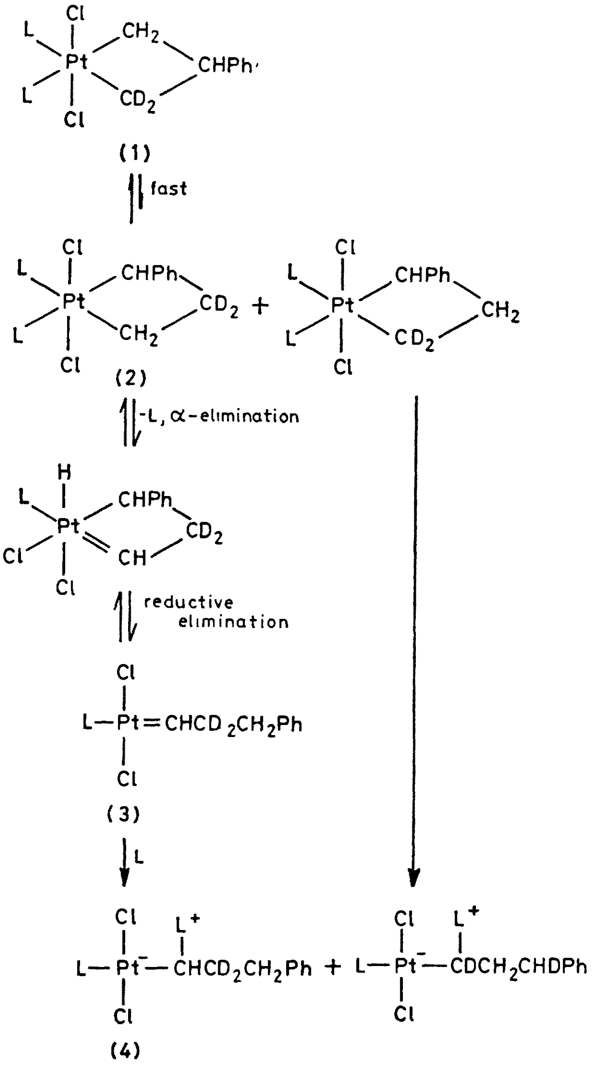


Figure. ^{1}H n.m.r. spectra in $CDCl_3$ solution of (a) *trans*-$[PtCl_2\{CH(L)CH_2CH_2Ph\}L]$ and (b) *trans*-$[PtCl_2\{CH(L)CD_2CH_2Ph\}L]$ showing only the ylide CH resonance. In each case the resonance is centred at δ 5·6 p.p.m. with ^2J(PtH) 112 Hz.

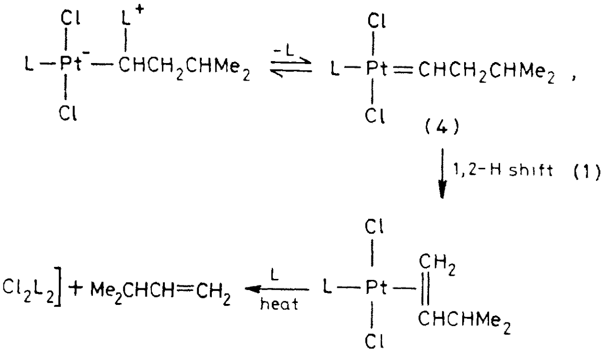
the study of mechanism,[3] and we now report on this aspect of these reactions.

Reaction of the complex $[\{\mathrm{PtCl_2(\overline{CHPhCH_2CH_2})}\}_4]$ with 2-methylpyridine, L, at room temperature gave the ylide complex *trans*-$[\mathrm{PtCl_2\{CH(L)CH_2CH_2Ph\}L}]$ which is characterised in the ^{1}H n.m.r. spectrum by a triplet signal (with satellites due to coupling with ^{195}Pt) due to the ylide hydrogen atom.[3] Similar reaction of the isomeric mixture $[\{\mathrm{\overline{PtCl_2(CHPhCH_2CD_2})}\}_4]$ and $[\{\mathrm{\overline{PtCl_2(CHPhCD_2CH_2})}\}_4]$, prepared from the labelled cyclopropane $\mathrm{Ph\overline{CHCH_2CD_2}}$, gave *trans*-$[\mathrm{PtCl_2\{CH(L)CD_2CH_2Ph\}L}]$ as the only species containing an ylide hydrogen atom. Thus the signal due to the ylide hydrogen appeared as a singlet in the ^{1}H n.m.r. spectrum (Figure). This proves that a 1,3-H shift occurs. If the product were formed by two 1,2-H shifts, as in a mechanism involving a series of β-elimination steps, the product would be *trans*-$[\mathrm{PtCl_2\{CH(L)CHDCHDPh\}L}]$ and the ylide signal would appear as a doublet in the ^{1}H n.m.r. spectrum. The results are fully consistent with a mechanism involving α-elimination from the platinacyclobutane (see the Scheme) and this provides the first evidence for α-elimination in alkyl-platinum complexes.[7]



SCHEME. The pre-equilibrium (**1**) $\rightleftharpoons$ (**2**) in the system was established by low temperature ^{1}H n.m.r. studies.

α-Elimination may also be involved in the formation of alkene complexes in some cases.† Thus the reaction of $[\{\mathrm{\overline{PtCl_2(CH_2CMe_2CH_2})}\}_4]$ in $\mathrm{CDCl_3}$ with 2,6-dimethylpyridine, L, at room temperature gives the alkene complex *trans*-$[\mathrm{PtCl_2(CH_2{=}CHCHMe_2)L}]$[3] but the ylide complex *trans*-$[\mathrm{PtCl_2\{CH(L)CH_2CHMe_2\}L}]$, (**5**) could be detected at an intermediate stage by ^{1}H n.m.r. spectroscopy at -30 °C [$\delta(\mathrm{PtC}H)$ 6·10 t, $^3J(\mathrm{HH})$ 7, $^2J(\mathrm{PtH})$ 108 Hz]. The stable ylide complex (**5**), L = pyridine, decomposes on heating to give the free alkene $\mathrm{Me_2CHCH{=}CH_2}$. We suggest that these products are formed, at least in part, by the mechanism of equation (1).



Use of space-filling molecular models indicates that (**5**), L = 2,6-dimethylpyridine, will be sterically congested owing to interactions between the *ortho* methyl substituents of the pyridine ylide group and the $\mathrm{PtCl_2}$ group, and this explains the low stability of the ylide complex in this case.

The evidence for carbene intermediates of the type (**3**) or (**4**) in these reactions is strong. If these intermediates could react with added alkene to regenerate a higher platinacyclobutane, as occurs for example in alkene metathesis,[9] this would provide a mechanism for alkene polymerisation. The mechanism is similar to that proposed recently by Ivin, Green, and their co-workers,[1] but is somewhat simpler. In the presence of excess of alkene, according to the present Scheme, if a metallacyclobutane decomposes by C–C bond cleavage this would lead to alkene metathesis, but, if it decomposes by α-elimination–reductive elimination, this would lead to polymerisation of alkene. Decomposition of metallacyclobutanes to alkene complexes provides a termination step for either of the above chain reactions.

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† We believe that alkene complexes are formed by a β-elimination process in some cases, for example in the decomposition of *trans*-1,2-dimethylpropane-1,3-diylplatinum(IV) complexes. The β-elimination mechanism has recently been probed in one case by deuterium labelling experiments.[8]

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