

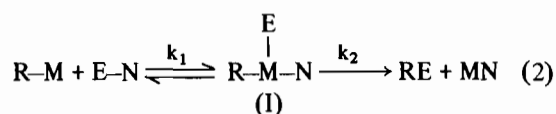
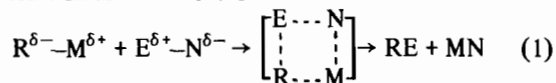
Mechanisms of Methyl Transfer Reactions from Methylplatinum(II) Complexes

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There has been considerable interest in the mechanisms of electrophilic cleavage of alkyl- or aryl-platinum(II) bonds [1, 2]. Either the S_E2 mechanisms [Mechanism (A), equation (1) for S_E2 (cyclic) mechanism] or the oxidative addition–reductive elimination mechanism [Mechanism (B), equation (2)] may operate in different cases.



Mechanism B can be further subdivided into Mechanism (Bi) in which $k_2 \gg k_1$ and Mechanism (Bii) in which $k_1 \gg k_2$. For Mechanism (Bii) the intermediate adduct (I) will be isolable or at least detectable in solution whereas for Mechanism (Bi) this will not be possible. In either (Bi) or (Bii) the intermediate (I) may require the groups R and E to be mutually *cis* so that concerted reductive elimination may occur [3].

It has previously been proposed that Mechanism (A) operates in the reactions of $[PtR_2(COD)]$, R = alkyl or aryl, with electrophiles such as HCl or $HgCl_2$, whereas Mechanism (Bi) operates in reactions of $[PtR_2(PMe_2Ph)_2]$ with these electrophiles. The change in mechanism was ascribed to the greater reactivity towards oxidative addition of the phosphine complex [2]. However, it is difficult to prove conclusively the Mechanism (Bi) since the intermediate cannot be detected, and mechanisms intermediate between (A) and (Bi) are also possible [1, 2].

It would be easier to prove the oxidative addition–reductive elimination mechanism for the extreme case (Bii), in which the intermediate (I) can be isolated. This mechanism operates with complexes $[PtR_2(PMe_2Ph)_2]$ only with atypical electrophiles

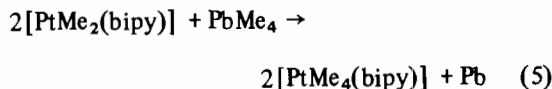
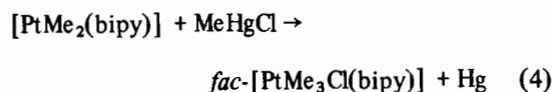
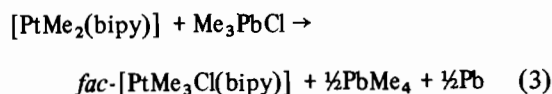
such as methyl iodide [2, 3]. Since complexes $[PtR_2(bipy)]$, *bipy* = 2,2'-bipyridine, are considerably more reactive to oxidative addition than the tertiary phosphine complexes, we have investigated reactions of $[PtMe_2(bipy)]$ with electrophiles in the expectation that Mechanism (Bii) would be favoured. Other reactions of $[PtMe_2(bipy)]$ with metal halides have been reported recently [4] and prompt this preliminary report.

The most clearcut example of Mechanism (Bii) arises in reaction of $HgCl_2$ with $[PtMe_2(bipy)]$, which initially gave a pale yellow platinum (IV) adduct of probable stereochemistry (II), $N-N=bipy$.



On heating a suspension of this complex in acetone, a slow reductive elimination occurred to give $[PtClMe(bipy)]$ and $MeHgCl$.

In other cases the reactions were less simple. For example, Me_3SnCl reacted with $[PtMe_2(bipy)]$ to give the platinum (IV) species $[PtMe_2Cl(SnMe_3)(bipy)]$ [4], but this underwent reductive elimination of Me_3SnCl to regenerate the starting materials. With Me_3PbCl , $MeHgCl$ or Me_4Pb , different forms of oxidative addition occurred (equations 3–5).



These reactions are not simple and intermediate species could be detected by n.m.r. and u.v. spectroscopy, but have not yet been fully characterised. Reaction of $[PtMe_2(bipy)]$ with *cis*- $[Pt(NO_3)_2(PMe_2Ph)_2]$ gave $[PtMe(NO_3)(bipy)]$ and $[PtMe(NO_3)(PMe_2Ph)_2]$, but no long-lived intermediate was formed and mechanism (Bi) is probable in this case.

The major conclusions from this work may be summarised as follows.

1. The mechanism of reaction of a complex $[PtR_2L_2]$ with an electrophile $E-N$ depends on the nature of L and $E-N$ (the dependence on R has yet

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to be investigated). Ligands L which strongly favour oxidative addition reactions (small, powerful donor ligands, *e.g.* bipy) will prefer the extreme mechanism (Bii), while ligands which disfavour oxidative addition reactions (bulky, weak donor ligands, *e.g.* COD) prefer the mechanism A.

2. The rate of electrophilic cleavage is generally expected to be greater for small, powerful donors L but, in the extreme case where mechanism (Bii) operates, further increasing the donor power of L reduces the overall reactivity since the rate determining step is the reductive elimination.

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