

Preliminary communication

CATALYSIS OF METHYL FOR HALOGEN EXCHANGE REACTIONS IN PLATINUM(II) COMPLEXES

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Summary

The symmetrisation reaction between cis -[PtMe₂(PMe₂Ph)₂] and cis -[PtCl₂(PMe₂Ph)₂] to give cis -[PtClMe(PMe₂Ph)₂] is catalysed by [Pt₂Cl₂(μ-Cl)₂(PMe₂Ph)₂].

The reaction of cis -[PtMe₂(PMe₂Ph)₂] with cis -[PtCl₂(PMe₂Ph)₂] to give initially cis -[PtClMe(PMe₂Ph)₂] is very slow in dichloromethane solution, the second order rate constant being $5.5 \times 10^{-6} \text{ l mol}^{-1} \text{ sec}^{-1}$ at 34°C [1]. However, in the presence of [Pt₂Cl₂(μ-Cl)₂(PMe₂Ph)₂] a very rapid conversion to cis -[PtClMe(PMe₂Ph)₂] occurs. The nature of the catalysis, for which there appears to be no precedent, is illustrated in Fig. 1.

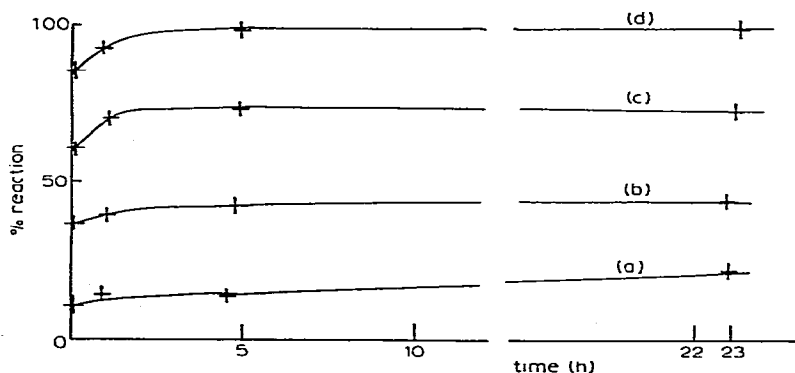


Fig. 1. Extent of reaction vs. time for the catalysed reaction. Initial concentration of both [PtMe₂(PMe₂Ph)₂] and [PtCl₂(PMe₂Ph)₂] was 0.1164 M. Concentration of catalyst: (a) $4 \times 10^{-4} \text{ M}$; (b) 10^{-3} M ; (c) $2 \times 10^{-3} \text{ M}$; (d) 10^{-2} M . In the absence of catalyst about 1% conversion took place in 5 h.

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The following features are considered important:

1. A catalyst concentration of 9% was needed to give complete conversion to *cis*-[PtClMe(PMe₂Ph)₂]. At lower catalyst concentrations a rapid catalytic conversion occurred but the reactions did not proceed to completion. After the initial catalytic effect a plateau was reached in which the reaction proceeded very slowly as in the uncatalysed reaction. Addition of more catalyst at this stage caused a further rapid conversion to occur.

2. In order for the catalytic effect to be observed it was necessary to add the catalyst to *cis*-[PtCl₂(PMe₂Ph)₂] followed by addition of *cis*-[PtMe₂(PMe₂Ph)₂]. If the catalyst was added to *cis*-[PtMe₂(PMe₂Ph)₂] followed by addition of *cis*-[PtCl₂(PMe₂Ph)₂] no catalytic effect was observed.

3. In an independent experiment *cis*-[PtMe₂(PMe₂Ph)₂] was found to react rapidly with [Pt₂Cl₂(μ-Cl)₂(PMe₂Ph)₂] to give *cis*-[Pt₂Me₂(μ-Cl)₂(PMe₂Ph)₂] (I), which did not catalyse the symmetrisation reaction.

The data can be rationalised in terms of the catalyst, [Pt₂Cl₂(μ-Cl)₂(PMe₂Ph)₂], for the symmetrisation reaction being destroyed in a competing reaction with *cis*-[PtMe₂(PMe₂Ph)₂] to give the inactive I. We tentatively suggest that the catalysis proceeds by methylation of [Pt₂Cl₂(μ-Cl)₂(PMe₂Ph)₂] by *cis*-[PtMe₂(PMe₂Ph)₂] to give *cis*-[PtClMe(PMe₂Ph)₂] and a reactive dimeric methylplatinum species, perhaps with a bridging methyl group. This can then either react with *cis*-[PtCl₂(PMe₂Ph)₂] to give *cis*-[PtClMe(PMe₂Ph)₂] with regeneration of [Pt₂Cl₂(μ-Cl)₂(PMe₂Ph)₂] or react with more *cis*-[PtMe₂(PMe₂Ph)₂] to give the inactive I. Complex I is not a powerful methylating agent and does not react with *cis*-[PtCl₂(PMe₂Ph)₂]. The suggested mechanism is fully consistent with the formation of the thermodynamically less stable *cis*-isomer [2] of [PtClMe(PMe₂Ph)₂] in the catalysed reaction.

The observation that very rapid catalysed transfer of alkyl groups between transition metal centres can take place may have relevance to the study of the decomposition of alkylic transition metal compounds by mechanisms involving intermolecular coupling of alkyl groups [3], and of catalytic processes involving alkylic transition metal compounds as intermediates [4].

References

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