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Preliminary communication

REACTIONS OF METHYL IODIDE WITH SOME DIMERIC ORGANOPLATINUM(II) COMPLEXES

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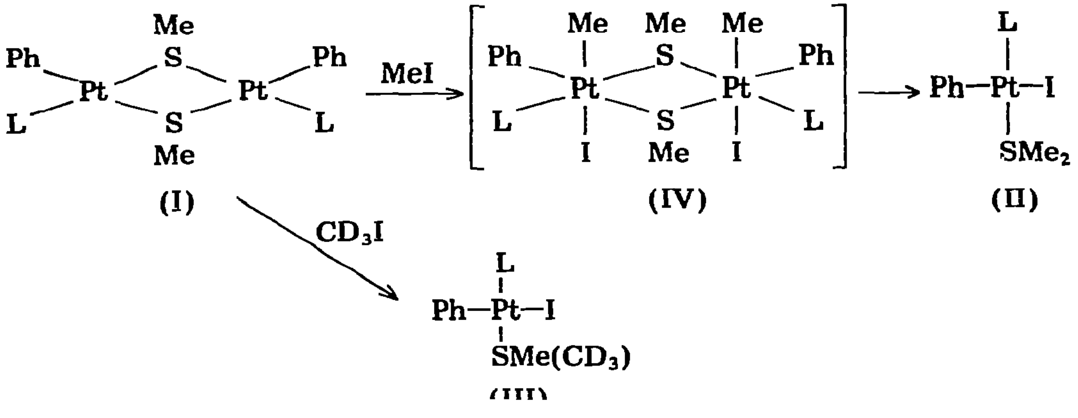
Summary

Methyl iodide reacts with $Pt_2(\mu\text{-}SMe)_2Ph_2(PMe_2Ph)_2$ to give $PtIPh(SMe_2)(PMe_2Ph)$ and with $Pt_2(\mu\text{-}SMe)_2Me_2(PMe_2Ph)_2$ to give $PtI_2Me_2(SMe_2)(PMe_2Ph)$ via an isolable intermediate $Pt_2I_2(\mu\text{-}SMe)_2Me_4(PMe_2Ph)_2$. The mechanisms of the reactions are discussed.

In view of the importance of oxidative addition reactions in many catalytic systems, and of recent interest in relating homogeneous and heterogeneous transition metal catalysis through studies of the properties of polynuclear transition metal complexes [1], we wish to report results of a study of reactions of methyl halides with the dimeric organoplatinum(II) complexes $[Pt_2(\mu\text{-}SMe)_2R_2L_2]$, where R = Me or Ph and L = PMe_2Ph.

Reaction of I with methyl iodide gave, within 12 h at room temperature, II (NMR in CH_2Cl_2; $\tau(CH_3P)$ 8.36 ppm, doublet, $^2J(PH)$ 3.6 Hz, $^3J(PtH)$ 40 Hz; $\tau(CH_3S)$ 7.88 ppm, doublet, $^4J(PH)$ 10.8 Hz, $^3J(PtH)$ 46 Hz; integration: $CH_3P/CH_3S = 1/1$) and with CD_3I it gave III (NMR as above, but integration CH_3P/CH_3S 2/1).

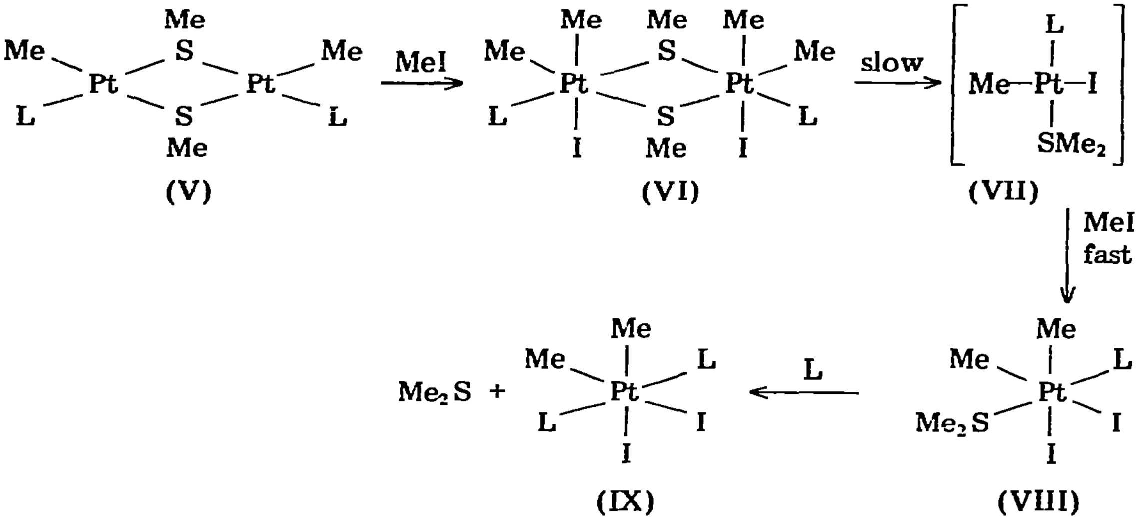


No intermediates could be detected during the reaction, and two possible mechanisms (A and B) can be envisaged.

(A) Methyl iodide gives an oxidative addition reaction [2] with I to give the short-lived intermediate IV, which then undergoes reductive elimination at both platinum centres by cleavage of the Pt—Me and Pt—SMe bonds to yield II.

(B) Direct nucleophilic attack by the bridging sulphur atom of I on methyl iodide followed by rearrangement could give II without intermediate oxidation of platinum.

We have been able to show that mechanism A operates in the reaction of V with methyl iodide which gave VIII as the final product. The structure of VIII was deduced from its NMR spectrum, and by conversion into the known complex IX by reaction with dimethylphenylphosphine [3].



In this reaction an intermediate was isolated and was identified as VI by its NMR spectrum. Thus the NMR spectrum contained resonances due to methylplatinum groups at $\tau 9.05$ and 8.77, with satellites due to coupling with ^{195}Pt with respective coupling constants $^2J(PtH)$ 61 and 72 Hz, consistent with methylplatinum groups *trans* to sulphur and iodide respectively in a platinum(IV) complex [4]. The NMR spectrum of the corresponding adduct with CD_3I contained only the former peak, indicating that stereospecific *trans*-addition of CD_3I had occurred as in oxidative additions with monomeric methylplatinum(II) complexes [2].

Thus mechanism A is proved for this reaction, and is likely for the reaction with I also. The differences in reactions of I and V apparently arise from the lower stability of oxidation state (IV) for platinum in the phenylplatinum compared with the methylplatinum complexes [5]. Thus with I the initial product of oxidative addition IV is very short-lived and the product of its reductive elimination, II, does not react further with methyl iodide. In contrast the adduct VI undergoes reductive elimination only slowly, and the product VII rapidly adds methyl iodide to give VIII.

References

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