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Preliminary communication

A CYCLOPROPYLPLATINUM TO π -ALLYLPLATINUM REARRANGEMENT

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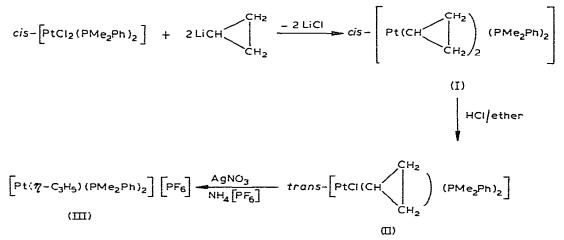
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Summary

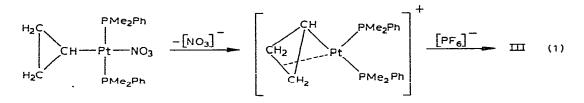
The rearrangement of a cyclopropylplatinum(II) to an η -allylplatinum(II) complex is demonstrated for the first time; a similar rearrangement is thought to occur in the reaction of *trans*-[PtH(NO₃)(PPh₃)₂] with methylenecyclopropane.

Rearrangement of a cyclopropylpalladium to η -allylpalladium complex has been suggested in order to rationalise the products of reaction of cyclopropene derivatives with palladium(II) chloride [1]. Isolable cyclopropyl derivatives of nickel, [Ni(C₃H₅)(η -C₅H₅)(PPh₃)], and of iron, [Fe(C₃H₅)(η -C₅H₅)(CO)₂], are known, but they have not been shown to rearrange to the corresponding η -allyl derivatives [2, 3]. We now present the first unequivocal proof that such rearrangements can occur readily.

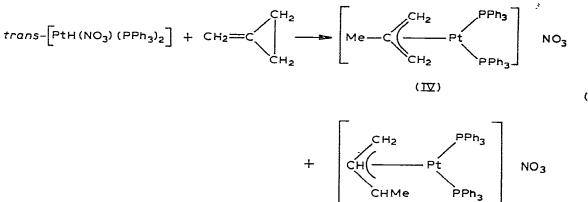
SCHEME 1



The reactions shown in Scheme 1 all occur readily at room temperature. Noteworthy is the observation that II is stable and can be crystallised without decomposition, but, on treatment with silver nitrate, ring opening to give the η -allylplatinum derivative, III [4], occurs very rapidly. We suggest that the ringopening proceeds via a three coordinate platinum(II) species formed by dissociation of the weakly bound nitrate ligand as shown in eq. 1.



Reaction of *trans*- $[PtH(NO_3)(PPh_3)_2]$ with methylenecyclopropane gives a mixture of η -allylplatinum products as shown in eq. 2.

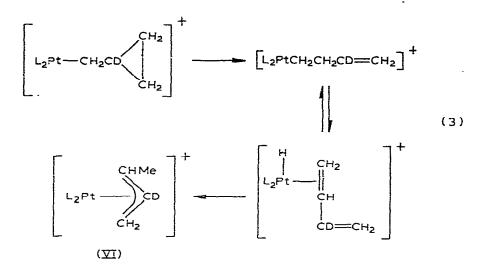


Complex V is probably formed by addition of the Pt—H bond to the C=C bond of methylenecyclopropane to give trans-[Pt(NO₃)(CH₂CH|)(PPh₃)₂]

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followed by ring opening and rearrangement [2, 5]. Consistent with this theory is the observation that reaction of trans-[PtD(NO₃)(PEt₃)₂] with methylenecyclopropane gave very largely the η -1-methyl-2-deuterioallyl derivative, VI, probably formed according to eq. 3, L = PEt₃.

The 2-methylallyl derivative, IV is probably formed by initial addition to give trans-[Pt(NO₃)(C (PPh₃)₂] followed by ring opening of the 1-methyl-Me CH₂ (2)



cyclopropylplatinum derivative. Such cyclopropyl to η -allyl conversions may prove to be quite general with co-ordinatively unsaturated transition metal complexes.

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