endo-Attack on Co-ordinated Norbornadiene; Crystal Structure of Di-μ-chloro-bis(*endo*-3-phenylnorbornen-2-yl-*endo*-palladium)

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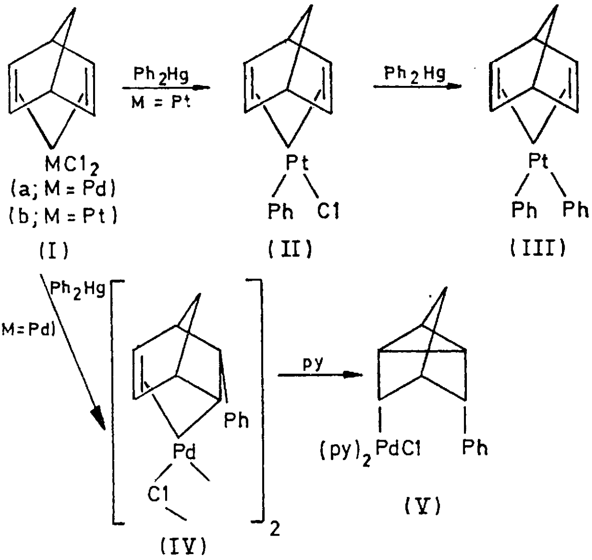
Summary Reaction of diphenylmercury with dichloronorbornadiene)palladium gave di-μ-chloro-bis(*endo*-3-phenylnorbornen-2-yl-*endo*-palladium) which was characterised by a crystal structure determination; a mechanism for its formation is suggested by analogy with the reactions of dichloro(norbornadiene)platinum and Ph_2Hg.

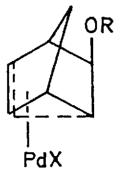
EVIDENCE has been put forward that attack on mono-olefins and chelating di-olefins co-ordinated to Pd^{II} and Pt^{II} usually occurs *exo-* with respect to the metal and does not involve an intermediate where the metal complexes the attacking group.[1] A number of cases have also been reported where mono-olefins react with Pd^{II}–X to give products which can best be understood if they arise by a mechanism involving "cis-insertion" of the olefin into the Pd-X bond.[2] A direct demonstration that this latter path does indeed occur with a di-olefin is given here.



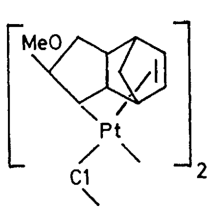
Dihalo(diene)platinum complexes are known to react with arylating and alkylating agents to give $[Pt(diene)R_2]$[3] but the reactions of analogous palladium complexes have remained obscure. We have therefore compared the reactions of dichloro(norbornadiene)-palladium and -platinum (Ia and Ib) with diphenylmercury under similar conditions.

The dichloro-platinum complex (Ib) reacted with diphenylmercury (0·5 equiv.) to give (II)† (58%) and with two equivalents to give (III) (44%); (II) was also obtained (quantitatively) by mixing equimolar amounts of (Ib) and (III).

In contrast, dichloro(norbornadiene)palladium (Ia) reacted with diphenylmercury (1 equiv.) to give (IV) (50%). The n.m.r. spectrum of (IV) showed that the phenyl was attached to the organic ligand rather than to the metal [as in (II)] but it was not possible to determine its orientation. An *X*-ray structure determination of (IV) was therefore undertaken which showed that it was a chlorine bridged dimer and that the phenyl was attached to the norbornenyl group, *endo-* to the metal.



(VI)



(VII)

Crystal data: $C_{28}H_{26}Cl_2Pd_2$, $M = 622{\cdot}16$, orthorhombic, $a = 28{\cdot}06(2)$, $b = 9{\cdot}46(1)$, $c = 8{\cdot}76(1)$ Å, $Z = 4$, space group $P2_12_12_1$. The structure analysis was based on 1955 independent reflections [$I_{obs} \geqslant 3\sigma$ (I_{obs}); Mo-K_α (graphite monochromator)] measured on a Stoe STADI 2 diffractometer, and R is currently 0·061. The stereochemistry of one norbornenyl unit and some bond lengths are shown in the Figure.‡

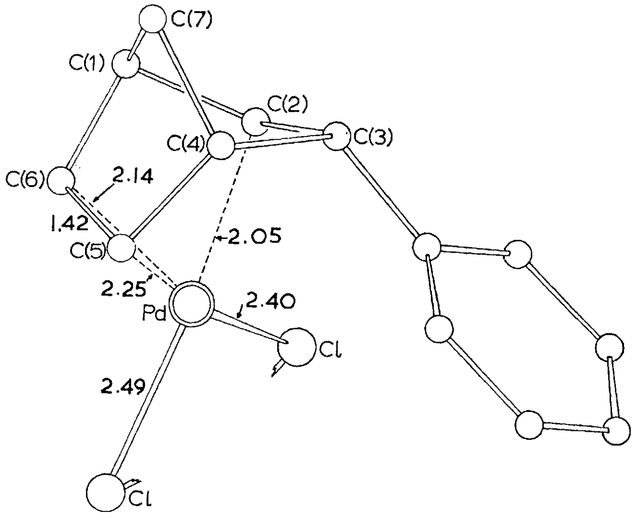


FIGURE. The structure of one half of the dimer, di-μ-chloro-bis-(*endo*-3-phenylnorbornen-2-yl-*endo*-palladium). E.s.d.'s average 0·006 (Pd–Cl), 0·02 (Pd–C), and 0·03 Å (C–C).

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† All new complexes were fully characterised by analysis, molecular weight, and spectroscopy.

‡ The electron-density distribution indicates disorder in the other half of the molecule. The other norbornenyl can have two different orientations in each of which, however, this moiety has the same stereochemistry as the undisordered norbornenyl.

A plausible route for the formation of (IV) therefore involves the formation of a σ-bonded phenylpalladium intermediate [analogous to (II)] which then undergoes "cis-insertion" to give (IV).

In common with other norbornenylpalladium complexes (IV) also undergoes rearrangement to the nortricyclenyl form (V) in pyridine. This type of reaction has led to the suggestion that the *exo*-alkoxynorbornenyl complexes, for example, are homoallylic (VI).[4]

The evidence from the crystal structure shows that this is not a correct representation of (IV) since C(2) and C(6) are too far apart (2·35 Å). Furthermore, the distances Pd–C(2), Pd–C(5), and Pd–C(6) are quite similar to those reported for the analogous Pt–C distances in (VII)[5] where homoallylic bonding is impossible. We conclude that the homoallylic form is a transition state or metastable intermediate on the the reaction path from (IV) to (V).

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