

Palladiacyclopentadiene and Platiniacyclopentadiene Complexes as Intermediates in Pd⁰ and Pt⁰ Catalysed Acetylene Cyclotrimerization Reactions

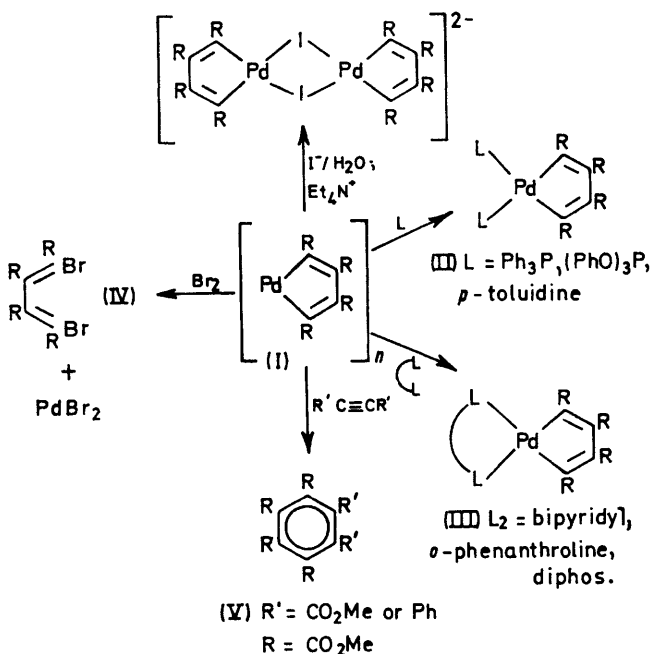
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Summary Dibenzylideneacetone-palladium(0) and -platinum(0) complexes react with dimethylacetylene dicarboxylate to give palladia- and platiniacyclopentadiene complexes, which are intermediates in the formation of hexamethyl mellitate.

In the absence of phosphines, bis(dibenzylideneacetone)-palladium(0) [Pd(dba)₂]^{1,2} trimerises dimethylacetylene dicarboxylate to give palladia- and platiniacyclopentadiene complexes, which we have isolated and characterised. Similar reactions occur with Pt(dba)₂.² The palladium reaction differs from the previously reported Pd^{II} catalysed reactions,³ both in the mode of reaction and also in an increased specificity. These results imply that an important and hitherto unrecognized factor in the metal-catalysed reactions of acetylenes is the formal oxidation state of the metal.

Pd(dba)₂ reacts with dma in a variety of solvents (acetone, benzene, benzonitrile, at 25°) to give a virtually quantitative yield of a brown microcrystalline complex [Pd(CCOOMe)₄]_n, (I) (decomp. 170°). This has been shown to be a palladiacyclopentadiene by analysis, n.m.r. (two equally intense resonances at τ 6.23 and 6.34, in benzonitrile) and by the reactions outlined in the Scheme.†



SCHEME

The palladiacyclopentadiene (I) is very soluble in complexing solvents, in which it is depolymerized, and only

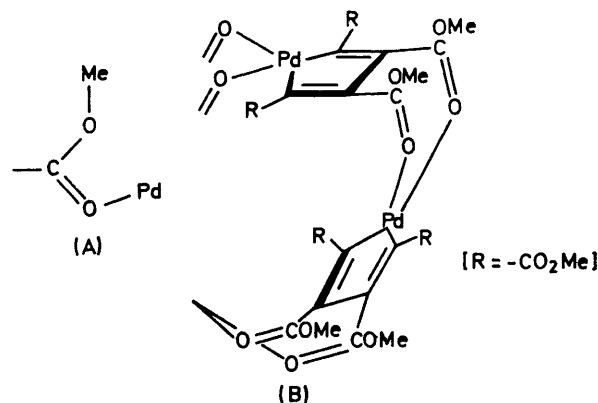
† Satisfactory analyses were obtained for all new compounds described.

sparingly soluble in non-complexing solvents. In the presence of various ligands, L, complexes of type (II) or (III) are formed; their n.m.r. spectra (CDCl₃) show two equally intense singlet resonances arising from the methoxy-carbonyl groups and integration gives results agreeing with the proposed structures.

Further evidence in favour of structure (I) came from the reaction with bromine to give (IV), and palladium bromide. In addition (I) rapidly reacted with excess dma, on warming, to give hexamethyl mellitate (V; R' = CO₂Me); certain other acetylenes (e.g., PhC:CPh) behaved analogously. The former reaction was catalytic with respect to (I).

The palladiacyclopentadiene (I) is very unusual in that it contains two Pd-C σ -bonds and is of good thermal and hydrolytic stability despite the absence of any stabilising ligands. Comparison of the i.r. spectra of (I), (II), and (III) reveals that the association of individual molecules of (I) does not arise by π -bonding but that the carbonyl functions of some of the esters are involved. Thus (II) and (III) show one (or two) very intense $\nu_{C=O}$ bands at 1705 ± 20 cm⁻¹, whereas (I) in Nujol shows an additional very intense band at 1620 cm⁻¹ which is absent in (II) and (III) and is only of medium intensity in a KBr disc where (I) presumably exists largely as K₂[Br₂Pd(CCOOMe)₄] or a similar species. A similar shift, but in the opposite direction, is seen in ν_{C-O} in the 1200–1300 cm⁻¹ region and both these changes are consistent with bonding through the carbonyl function (as in A), as has been shown by Lappert⁴ for ester complexes of a number of metal halides.

In all the complexes (I), (II), and (III), $\nu_{C=C}$ remains constant as a medium to strong band at 1560 ± 10 cm⁻¹ and we suggest that the bonding occurs as shown in (B); models suggest that a trimeric unit of this type would have considerable stability.



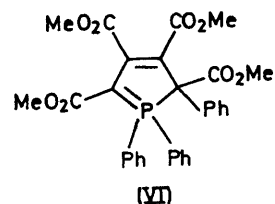
Pt(dba)₂ or Pt(dba)₃² reacted more slowly with dma in benzonitrile-benzene (1:10; 25°) to give first, a platiniacyclopentadiene analogous to (I) [detected by n.m.r., τ 6.42

and 6-47, and which was isolated and characterised as the bis(triphenylphosphine) adduct, $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CCO}_2\text{Me})_2$ and then, hexamethyl mellitate.

Both the palladium- and platinum-dba complexes only react under these conditions with acetylenes bearing at least one strongly electron-withdrawing substituent. Reactions of this type for electrophilic acetylenes have been found by a number of other workers; for example, Collman *et al.* prepared rhodia- and iridia-cyclopentadienes, $[\text{M}(\text{PPh}_3)_2\text{Cl}(\text{CCO}_2\text{Me})_2]$, somewhat analogous to (II).⁵ However, such reactions are by no means restricted to transition metals; in fact electrophilic acetylenes such as dma react with a wide variety of nucleophiles to give products in which oligomerisation of dma has occurred. In some cases products closely related to (I) are obtained; for example, triphenylphosphine gives (VI) with dma, and the mechanism of this reaction has been discussed.⁶

These reactions therefore provide evidence for the strongly nucleophilic nature of the dba-palladium and -platinum complexes. They are also in sharp contrast to the reactions of palladium(II) with acetylenes, where the reactions proceed in an entirely different manner and where the electronic nature of the substituents on the acetylene plays at most a minor role in determining the course of the reaction.⁷

Triphenylphosphine-palladium(0) or -platinum(0) complexes do not undergo such reactions. However, Bryce-Smith⁸ has reported that palladium on charcoal catalytically trimerises dma to hexamethyl mellitate in a heterogeneous reaction; there is an obvious parallel to the reaction reported here.



That the metallacyclopentadiene is indeed an intermediate in the formation of the benzene is shown by the formation of (V, $\text{R}' = \text{Ph}$) from (I). This and the cyclotrimerization reaction presumably proceed *via* a "bent-benzene" complex, evidence for which has been obtained in related reactions on other metals,^{5,9} but not as yet here.

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