On the Existence and Stability of a Tri-t-butyl("Dewar Benzene")palladium Chloride Complex

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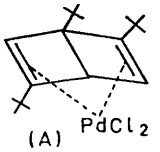
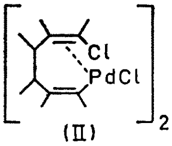
Summary The complex $(Bu^tC_2H)_3PdCl_2$ recently claimed to be a "Dewar benzene" complex has been shown to be dimeric and not to have this structure; it was not possible to isolate an authentic tri-t-butyl ("Dewar benzene") complex.

A RECENT paper by Nenitzescu and his co-workers has claimed that t-butylacetylene is trimerised by $(PhCN)_2PdCl_2$ in benzene to a complex (I), formulated as (A), the organic ligand of which was assigned a "Dewar benzene" structure largely on the basis of the analysis and n.m.r. spectrum (three non-equivalent t-butyl groups and three non-equivalent hydrogens).[1] Because of the considerable current interest in the mechanism of acetylene trimerisation on metal catalysts and since this structure appears to be inconsistent with work by one of us[2–4] on the structure of a complex, $[Cl(MeC_2Me)_3PdCl]_2$, (II), derived from dimethylacetylene and $(PhCN)_2PdCl_2$ in benzene, we have reinvestigated the problem of tri-t-butyl("Dewar benzene")-palladium chloride complexes.

$$Bu^tC{\equiv}CH + (PhCN)_2PdCl_2 \xrightarrow{C_6H_6} [(Bu^tC_2H)_3PdCl_2]_n$$



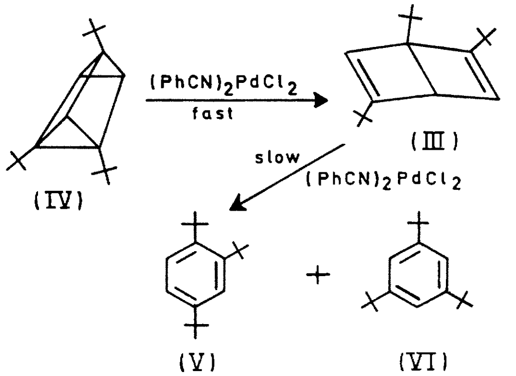
(A)



(II)

In view of the great stability of (I) it should also be readily obtainable from the known tri-t-butyl("Dewar benzene") (1,2,5-tri-t-butylbicyclo[2,2,0]hexadiene) (III);[5] both the unsubstituted ("Dewar benzene")- and the hexamethyl("Dewar benzene")-palladium chloride complexes were prepared by this route.[6,7]

A mixture containing the prismane (IV) and the "Dewar benzene" (III) was prepared by irradiating a solution of 1,2,4-tri-t-butylbenzene, (V), in hexane.[8] On addition of $(PhCN)_2PdCl_2$ in benzene or $CDCl_3$ to this mixture, a rapid conversion of the prismane into the "Dewar benzene" was observed by n.m.r. A further slow reaction was also observed in which the resonances due to (III) decreased and those due to the tri-t-butylbenzenes (V) and (VI) increased.



The tri-t-butyl("Dewar benzene") (III) was isolated by preparative g.l.c. in better than 90% purity and samples of it were treated with a deficiency of $(PhCN)_2PdCl_2$ (molar ratio 1 : 0·8, to minimise isomerisation) in both benzene and chloroform. In neither case was the formation of a complex detectable by n.m.r., and only the slow reaction to give (V) and (VI) in a 3 : 1 ratio was observed. Under identical conditions hexamethyl("Dewar benzene") gave the previously reported hexamethyl("Dewar benzene")palladium chloride complex.[7] These observations suggest that a tri-t-butyl("Dewar benzene") complex, probably (A), is formed as an intermediate but that its rate of decomposition is greater than its rate of formation.

By contrast, the complex (I) was completely stable under similar conditions; indeed, we have yet to observe a reaction in which it yields either (V) or (VI). It was stable in refluxing acetone even in the presence of an excess of t-butylacetylene and in the presence of a large excess of $(PhCN)_2PdCl_2$ in $CDCl_3$. On reaction with either *o*-phenanthroline or triphenylphosphine new complexes were obtained. Thermal decomposition, reaction with acid, or reduction with zinc amalgam all gave unidentified organic products and did not contain any of the benzenoid isomers (V) or (VI).

Further evidence that the Nenitzescu complex is not (A) comes from osmometric molecular-weight measurements in benzene which show (I) to be dimeric (837); a monomeric structure (A) requires 424. Nenitzescu and his co-workers showed that the two chlorines in (I) were inequivalent, and that one could easily be replaced by bromide to give $[(Bu^tC_2H)_3PdClBr]_n$. We have shown that this complex is also dimeric (*M*, 918; $C_{36}H_{60}Br_2Cl_2Pd_2$ requires *M*, 936). The hexamethyl("Dewar benzene")palladium chloride complex is monomeric and both chlorines are replaced on reaction with bromide.[9]

The complex (I) is therefore *not* a "Dewar benzene" complex and does not appear to be a direct intermediate in the $(PhCN)_2PdCl_2$-catalysed trimerisation of t-butylacetylene to 1,3,5-tri-t-butylbenzene which Nenitzescu and his co-workers observed to occur in acetone. Some properties of (I) are similar to those of the complex $[Cl(MeC_2Me)_3PdCl]_2$, (II), and it is tempting to suggest a similar structure for (I). However, this must await an *X*-ray structure determination. "Dewar benzene" structures have also been suggested for complexes derived from other acetylenes and palladium chloride.[10] In view of this and previous work,[3,4] these complexes also merit closer examination.

We thank the National Research Council of Canada and the Alfred P. Sloan Foundation for financial support.

(*Received, April* 30*th*, 1970; *Com.* 645.)

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