Dewar Hexamethylbenzenepalladium(II) Chloride

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During the course of some related studies, we became interested in the possibility of forming transition-metal complexes of Dewar benzene (bicyclo[2,2,0]hexa-2,5-diene). Here we report the first preparation of such a complex, and its role in the isomerisation of the ligand.

Dewar hexamethylbenzene (hexamethylbicyclo [2,2,O]hexa-2,5-diene), (I)[1] reacted with a deficiency of dichlorobis(benzonitrile)palladium(II) in chloroform, or more conveniently in benzene, at 25° to give yellow platelets of Dewar hexamethylbenzenepalladium chloride {dichloro(hexamethylbicyclo[2,2,0]hexa-2,5-diene)palladium} (III). The pure complex was actually isolated in 67% yield but the only other product formed was a small amount of hexamethylbenzene (IV), (approx. 0·3 moles per mole of complex formed). Since the complex decomposed slowly on standing even in the solid, a complete elemental analysis was not possible. We formulate the structure of the complex as shown, by analogy with other palladium(II) complexes of unconjugated chelating dienes,[2] on the following evidence:

(a) Analysis by combustion gave Pd, 31·0%, complex (III) requires Pd, 31·4%.

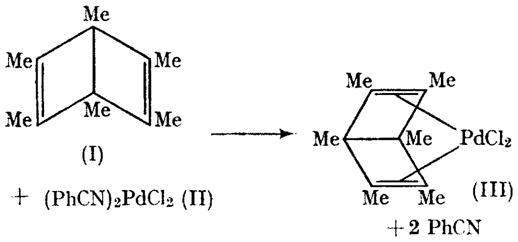
(b) Reaction with triphenylphosphine in chloroform gave Dewar hexamethylbenzene (I) and dichlorobis(triphenylphosphine)palladium quantitatively.

(c) The molecular weight was found to be 360 (osmometric in chloroform); the monomeric complex (III) requires 340.

(d) The complex (III) decomposed sharply and vigorously at 79° in a melting-point tube to palladium chloride and gave a sublimate of hexamethylbenzene.

(e) The ^{1}H n.m.r. spectrum in $CDCl_3$ showed two singlets at τ 8·04 and 8·69, with intensity ratio 2 : 1, due to the two different types of methyl groups. This is a *downfield* shift from their positions in uncomplexed Dewar hexamethylbenzene (at τ 8·45 and 8·97 in $CDCl_3$).

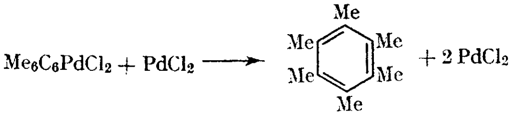
(f) The i.r. spectrum of the complex (III) no longer showed the weak ν(C=C) band at 1680 cm.$^{-1}$ which is present in Dewar hexamethylbenzene. Instead a new, strong band, which we assign to ν(C=C) when complexed to Pd^{II}, at 1532 cm.$^{-1}$ was observed.



$$\text{(III)} + 2Ph_3P \rightarrow \text{(I)} + (Ph_3P)_2PdCl_2$$

A freshly prepared solution of Dewar hexamethylbenzenepalladium chloride in $CDCl_3$ was stable for *ca.* 20 min. at 33°. After this induction period, decomposition set in very rapidly with the quantitative formation of hexamethylbenzene (IV) and palladium chloride. In the presence of small amounts of free Dewar hexamethylbenzene however, the solution was stable for longer periods of time. Addition of small amounts of palladium chloride [as (II)], to the solution of (III) catalyzed the decomposition to hexamethylbenzene (IV) and $PdCl_2$, no induction period then being observed. The decomposition of (III) in $CDCl_3$ therefore appears to be autocatalytic and the induction period which is observed is due to a slow dissociation of the complex (III) to give $PdCl_2$ which, when it is present in high enough concentration reacts with the complex (III) to give hexamethylbenzene and more palladium chloride.

These results are consistent with a novel type of reaction, *viz*:



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[1] Kindly supplied by Dr. W. Schäfer of Chemische Werke Hüls, Germany; see W. Schäfer, *Angew. Chem. Internat. Edn.*, 1966, **5**, 669.

[2] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 3413; N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Acta. Cryst.*, 1965, **18**, 924.