The Reactions of Dewar Hexamethylbenzene with Platinum Chlorides

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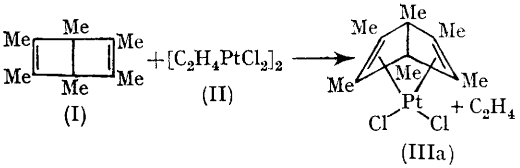
DEWAR hexamethylbenzene {hexamethylbicyclo-[2,2,0]hexadiene (I)}[1] undergoes two types of reaction with rhodium compounds, one to give Dewar hexamethylbenzenerhodium(I) chloride dimer,[2] and the other, involving a ring-contraction, to give pentamethylcyclopentadienylrhodium(III) chloride.[3]

We have now examined the reactions of Dewar hexamethylbenzene with platinum chlorides and find that again two types of product are obtainable. Ethyleneplatinum chloride (II) reacted rapidly with (I) in dry benzene to give Dewar hexamethylbenzeneplatinum chloride (IIIa) (85%); a gas (presumably ethylene) was also liberated and in addition *ca.* ½ mole of hexamethylbenzene per mole of (IIIa) was formed by isomerisation of (I).

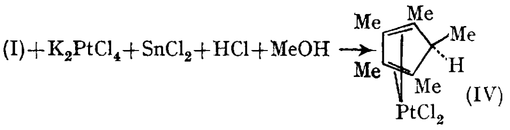
The complex (IIIa)† was characterised by analysis and spectroscopically. The ^{1}H n.m.r. spectrum showed singlets at τ 8·13 (diene methyls) and 8·86 (bridgehead methyls). Each resonance showed coupling to ^{195}Pt (abundance 34%), $J_{\text{Pt-H}}$ 35 and 5 c./sec. respectively; the observation that even the bridgehead methyl protons couple to the platinum is noteworthy. The i.r. spectrum was very similar to that of the palladium analogue (IIIb).[4] On treatment with triphenylphosphine, (IIIa) gave Dewar hexamethylbenzene and dichlorobis(triphenylphosphine)platinum quantitatively. When heated *in vacuo*, it decomposed sharply at 75° to give hexamethylbenzene, but in solution it was markedly more stable than the palladium complex (IIIb) and only decomposed slowly to hexamethylbenzene after several days at 25°.

In contrast, (I) reacted with potassium chloroplatinate and hydrochloric acid in methanol at 65° in the presence of a catalytic amount of stannous chloride to give pentamethylcyclopentadieneplatinum chloride (IV) (78%). This complex was identified by analysis, molecular weight measurement, and its ^{1}H n.m.r. spectrum, which showed signals at τ 6·65 (1H, q, $J_{\text{H-Me}}$ 6·5), 7·78 (6H, t, $J_{\text{Pt-H}}$ 20), and 8·54 (t, $J_{\text{Pt-H}}$ 10) due to two pairs of equivalent diene methyls, and 9·04 (3H, d, J 6·5 c./sec.). The ^{1}H n.m.r. spectrum and the absence of a low-frequency ν_{CH} in the i.r. (which is characteristic of complexes with an *exo*-hydrogen on the ring)[5] lead us to formulate (IV) as shown with the ring hydrogen *endo* to the metal. On treatment with triphenylphosphine, (IV) gave pentamethylcyclopentadiene and dichlorobis(triphenylphosphine)platinum. The former was identified by its ^{1}H n.m.r. and mass spectra.[6]

To our knowledge, complex (IV) represents the first example of a 1,3-diene co-ordinating to Pt$^{\text{I}}$.



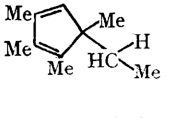
(III) Pd in place of Pt



Analysis of the methanol mother liquors from (IV) showed the presence of hexamethylbenzene and 1,1-dimethoxyethane. The overall reaction leading to (IV) can therefore be represented by:

$$\mathrm{C_6Me_6 + K_2PtCl_4 + 2MeOH \xrightarrow{H^+} (C_5Me_5H)PtCl_2 + MeCH(OMe)_2 + 2KCl}$$

Our observation that this reaction does not proceed in the absence of acid led us to consider that the true starting material for this reaction was not the Dewar benzene (I) but (Va) or (Vb). These have been shown to be formed from (I) with ease in the presence of acid.[7]



(Va) X=Cl
(Vb) X=OMe

The correctness of this assumption was shown by the fact that (Va) reacted with potassium chloroplatinate and stannous chloride in methanol

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† This has also been obtained by B. L. Shaw *et al.*; personal communication by Professor R. Mason.

to give (IV) (78%) and also by the reactions described in the following Communication.

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