Complexes of Platinum(II) with Carborane [1,2- or 1,7-dicarba-*closo*-dodecaborane(12)] and Tertiary Phosphines: Loss of Hydrogen from the Ligands

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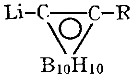
LITHIUM derivatives of alkyl- and aryl-monosubstituted 1,2-dicarba-*closo*-dodecaborane(12) (1,2-carborane) (I), or of its 1,7-isomer (II) react with the dihalides Cl_2MR_2 (M = Si, Ge, Sn, or Pb; R = aryl or alkyl) to give $(R\text{-carb})_2MR_2$ (R-carb = $-CB_{10}H_{10}C\text{-}R$ or its 1,2-isomer).[1,2]

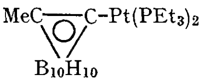


$LiCB_{10}H_{10}C\text{-}R$

(I) R = Me or Ph; (II) R = Me

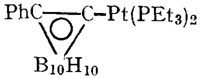
Reaction of (I) or (II) with *trans*-$PtCl_2(PEt_3)_2$

in tetrahydrofuran (THF), benzene, or diethyl ether at 30° for 2 hr. gave the following platinum(II) complexes with the unusual composition (R-carb)Pt$(PEt_3)_2$.



(m.p. 146—147°)

Me-$CB_{10}H_{10}$C-Pt$(PEt_3)_2$ (m.p. 100—101°)

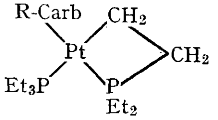


(m.p. 196—197°)

Good analytical data have been obtained for all compounds, which are monomeric in THF or CH_2Cl_2 at 25° (isopiestic osmometer), they are also nonconductors at 25° in CH_2Cl_2, THF, and ethanol, and are diamagnetic (Gouy method). No ν_{M-H} bands are evident in the i.r. spectra of the complexes with methylcarboranes (no absorption in the range 1500—2450 cm.$^{-1}$). The ^1H n.m.r. spectra (10% solution in $CDCl_3$, 37°) at 60 Mc. show no τ values between 33 and 20, showing that platinum-bonded hydrogens are absent. The CH stretching band at 3060 cm.$^{-1}$ of free carborane is absent due to the existence of platinum–carbon bonds. Moreover, the strong absorption bands of the BH stretching in the region 2540—2620 cm.$^{-1}$, typical of the $C_2B_{10}H_{10}$ nucleus of dicarba-*closo*-dodecaborane(12), show that no structural change of this group has occurred on co-ordination.

The diamagnetic properties suggest either a d^8 or a d^{10} configuration for the metal atom, spin coupling *via* metal–metal bonding of a d^9 configuration being ruled out by the fact that the compound is monomeric. On titration with iodine in benzene–water 1 mol. of the compound reacted with 2 mol. of iodine, a reaction typical of platinum(II) complexes. Thus a formal oxidation state of zero, unlikely for a carbon σ-bonded metal, was ruled out. Since three-co-ordination, involving one platinum–carbon bond and two platinum–phosphorus bonds, is excluded by the conductivity measurements, which would demand the existence of the positively-charged species $[(R\text{-}carb)Pt(PEt_3)_2]^+$, the compounds are four-co-ordinate complexes of platinum(II).

Two possible ways of attaining four-co-ordination have been considered. The first is the loss of hydrogen from the methyl (or phenyl) substituent on the carborane nucleus with the concomitant formation of a second metal–carbon σ-bond. This possibility can be ruled out as the complexes are formed by both 1,2-carborane and its 1,7-isomer. The distance between the carbon atom of the carborane nucleus and that of the R substituent in the 1,7-isomer is too large[3] to allow the formation of an exocycle C–Pt–C. We therefore suggest the metal–carbon σ-bonded structure (III) [or a possible isomer of (III)] for the compounds, which are formed by loss of hydrogen from one ethyl group of the phosphines.



(III)

Hydrogen transfer from trisubstituted phosphines to metal atoms with formation of carbon–metal bonds has been observed in complexes of of iron,[4] iridium(I),[5] ruthenium(0),[6] and cobalt(I).[7] Loss of hydrogen from the aromatic ring of azobenzene has been observed in the formation of complexes of platinum(II) and palladium(II).[8]

It seems likely that (III) is formed by elimination of HCl immediately following the replacement of the first chlorine by carborane

$$Cl_2Pt(PEt_3)_2 + \text{Li-carb-R} \rightarrow LiCl + HCl +$$
$$+ (Et_2PCH_2CH_2)Pt(\text{carb-R})(PEt_3)$$

Hydrogen chloride reacts with the excess of carborane, giving free carborane which is found in the reaction mixture.

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