

SYNTHESIS AND PROPERTIES OF CYCLOMETALLATED CARBORANES CONTAINING BORON-TRANSITION METAL BOND

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A general method is suggested for preparing metallocyclic carborane derivatives with a boron-transition metal bond. The method involves cyclometallation of carboranes containing substituents with donor N, P or As atoms, under the action of VII and VIII group transition metal complex.

Two kinds of cyclometallation reactions are considered: 1) reactions involving no change in the formal oxidation degree of the transition metal, and 2) oxidative addition reactions. These reactions can be used for synthesizing a wide range of carborane complexes of transition metals with a boron-transition metal σ -bond (B-Mn, B-Re, B-Ru, B-Os, B-Rh, B-Ir, B-Pd and B-Pt).

Novel methods for cyclometallation of carborane-containing phosphines, arsines and amines are described, including the exchange of byclopalladated ligands, phase transfer reactions, reductive carbonylation, etc. The conditions of regioselective cyclometallation of *o*- and *m*-carborane derivatives are discussed. The main distinctive features of the resulting complexes, as determined by the presence of σ -carboranyl group, are revealed.

Key Words: Cyclometallation; Carboranes; Boron-Transition Metal Bond; Organoelement Chemistry; Metallocycles

THE discovery of a new type of polyhedral organoboron compounds, the carboranes, was a novel stage in the development of organoelement chemistry. The variety of structural types, unusual structures, increased coordination numbers of carbon and boron, electron-deficient nature of carborane systems as well as other properties gave rise to great interest for these compounds. Now the carboranes occupy one of the cardinal positions in organoelement chemistry and serve as a specific bridge connecting together organic, borane inorganic, organometal, cluster, and metallocene chemistry. The unique properties of carboranes stimulate and enhance their remarkable synthetic possibilities which predominate even over those of ferrocene compounds. The clustering nature of carboranes served as the ground of up-to-date bonding theory in the clusters of different types and the establishing of principal regularities of their electron structure, which revealed in so-called "magic numbers". The most accessible and typical representatives of these compounds are the isomeric carboranes-12 which exist as three isomers: *ortho*-, *meta*-, and *para*-carboranes depending on the interposition of the two carbon atoms in the icosahedron.¹

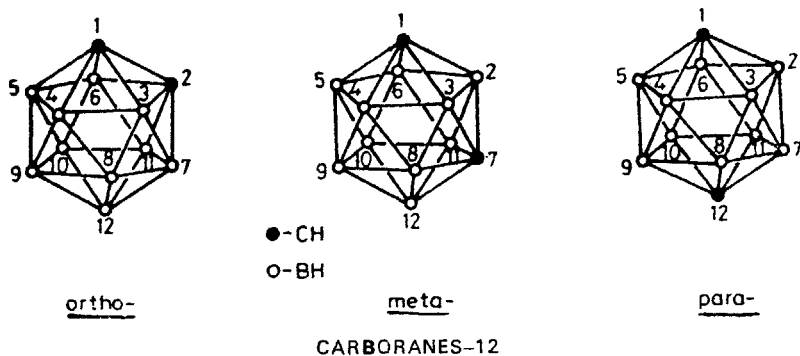


FIG 1

The chemistry of carboranes-12 has been investigated minutely enough, synthetic methods have been developed, and the properties of a great number of compounds with various functional groups on both carbon and boron atoms of the carborane cage have been studied. However, up to the latest period, both the synthesis and properties of carboranes having boron-transition metal bonds remained one of the insufficiently studied fields of the boron-substituted carborane chemistry. The progress in this area of the carborane chemistry has been hindered for a long time by the absence of convenient general methods for the preparation of compounds having the boron-transition metal bond.^{1,2}

The present work concerns the development of general methods for the synthesis of carboranes with boron-transition metal bond on the basis of the cyclometallation reaction.

The term "cyclometallation" implies such a reaction in which the ligand undergoes an intramolecular metallation to form a chelated cyclic system containing the coordination bond between the transition metal "M" and the donor atom "E" as well as the metal-carbon σ -bond, i.e. metal-boron bond in our case.

Two types of cyclometallation reactions may be distinguished: reactions occurring without a change in the formal oxidation degree of the transition metal and those attended by an increase in the coordination number and oxidation degree of the metal by two units, i.e. reactions of oxidative addition.

In the course of the present work, the authors have investigated the application of both cyclometallation types in the carborane series as the example of interaction of carborane derivatives containing substituents with donor atoms of nitrogen, phosphorus, and arsenic with complexes including transition metals of VII and VIII groups of Periodic chart.

Now we shall consider obtaining carboranes with the boron-transition metal bond in sub-groups of transition metals.

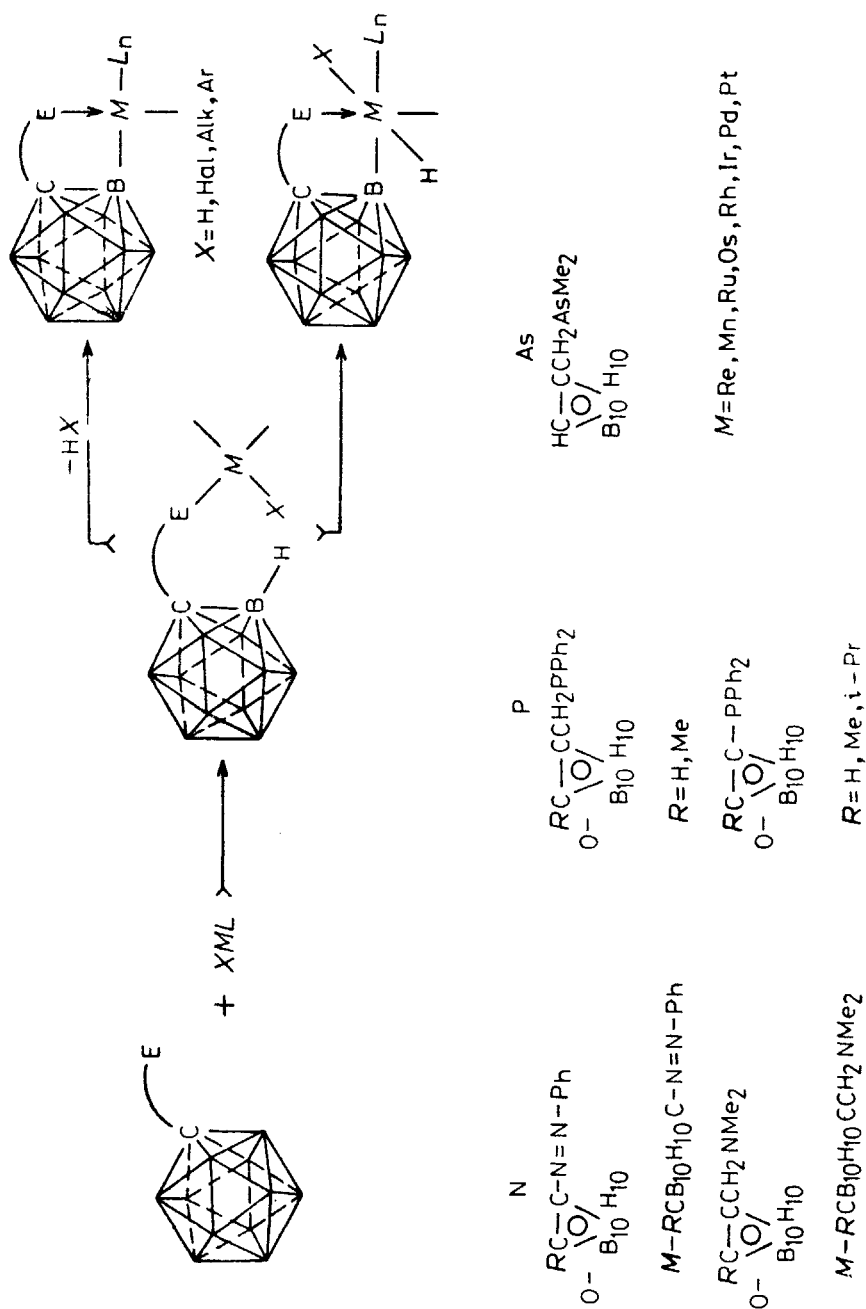


FIG 2

MANGANESE AND RHENIUM DERIVATIVES

It is known that the C-carboranyl fragments are strong electron-acceptor groups, and the basicity of amino- and phosphinocarboranes is extremely low. It was of interest to study the possibility of nitrogen atom of the carborane molecule to take part in the formation of coordination bonds in the course of cyclometallation of aromatic systems. However, it has been found that the reaction of carborane azo-derivatives with carbonyl compounds of manganese and rhenium does not give rise to the expected metallation of the benzene nucleus to form a benzochelate but, instead, involves metallation of the carborane nucleus with the formation of exo-cyclic derivatives containing the B-M bond stabilized on the score of intramolecular interaction between the nitrogen electron pair and the transition metal atom. This was the first instance for the incorporation of a transition metal into the carborane molecule without altering the formal oxidation degree of the metal.

Both phenylazoderivatives of *o*- and *m*-carboranes and N, N-dialkylamino-methylcarboranes can enter the cyclometallation reaction with manganese and rhenium carbonyl complexes.^{3,4}

All of the compounds obtained contain the five-membered cycle with the $\overline{\text{N-X-C-B-M}}$ system ($X = \text{C, N}$). Unlike nitrogen derivatives, carborane phosphines do not form cyclometallation products in the reaction with manganese or rhenium carbonyls but replace one of carbonyl groups to afford usual *n*-donor complexes. This is accounted for by a higher strength of the M-Me bond due to the coordination of the metal with phosphorus atom which prevents from the elimination of methane. This conclusion is supported by the fact that cyclometallation of nitrogen containing carboranes does not proceed in case of using $\text{MeM}(\text{CO})_4(\text{PPh})_3$ where the metal is also coordinated with phosphine atom.

Because of steric factors, the metallation of carboranes can only take place at the "ortho" positions with respect to the carbon atom containing a substituent with the electron-donor atom, *o*-carborane having two such non-equivalent positions, 3(6) and 4(5) while *m*-carborane—three ones, 2(3), 4(6), and 8. In general, with the carbon atom having a substituent, the introduction of some group to the boron atom causes the arising of chirality in the carborane molecule. So the cyclometallation leads to a mixture of two enantiomers, one of which is given on the figure.

X-Ray analysis of two cyclometallated samples performed by A I Yanovsky and Yu T Struchkov has shown that, in case of *o*-carborane, the rhenium atom is bonded to boron atom in the 4(5) position whereas, in case of *m*-carborane, in the 4(6) position. The rhenium atom in both structures has the configuration of a distorted octahedron. The metallocycles N-X-C-B-Re are of plane configuration, however due to the difference in the nitrogen atom hybridization (sp^2 and sp^3) the deflection of aminoderivatives from the ideal plane is greater than that of azoderivatives.^{5,6}

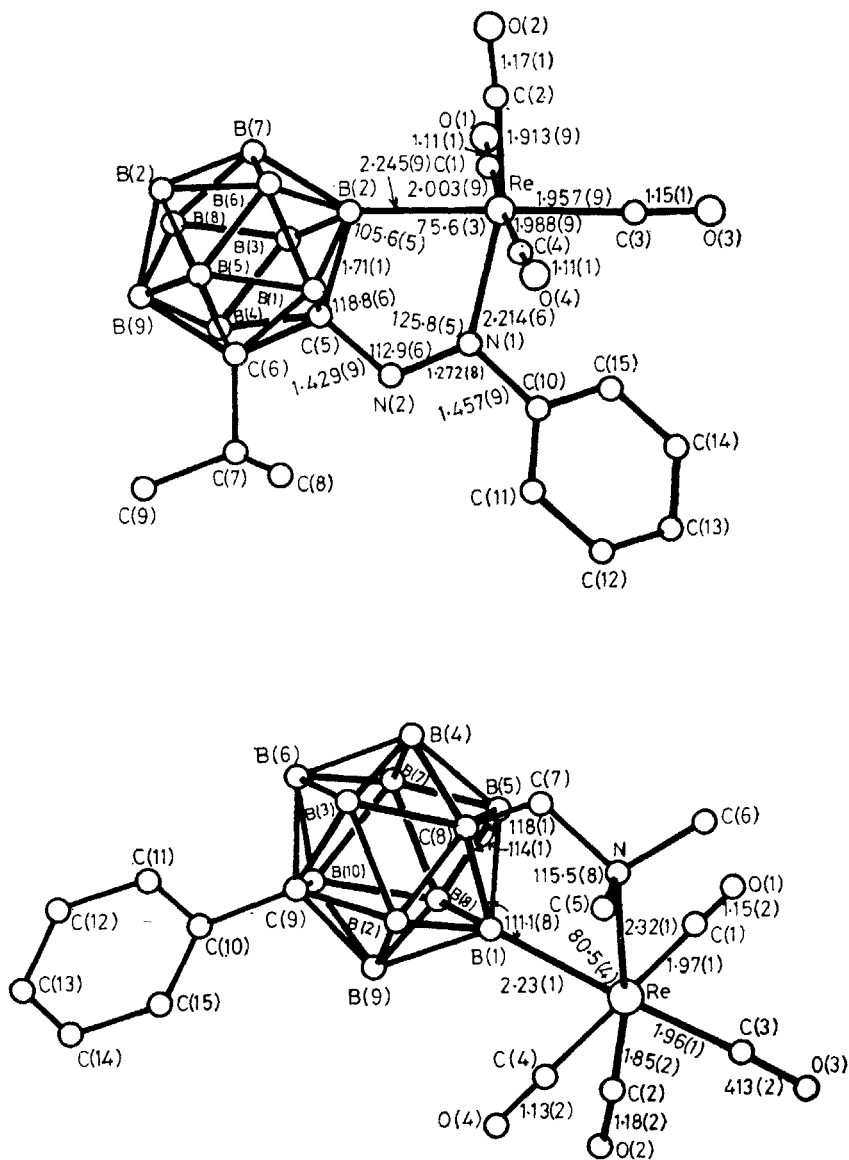


FIG 4

RUTHENIUM AND OSMIUM DERIVATIVES

The carborane derivatives with B-Ru and B-Os σ -bonds have not been known so far. We have applied the cyclometallation reaction to the synthesis of *exo*-cyclic compounds of the *o*-carborane series containing the most sterically favourable five-membered metallocycles with the $\overline{\text{M-B-C-C-P}}$ system.

The carborane phosphines react with ruthenium or osmium salts under the conditions of reductive carbonylation to form hexa-coordinated complexes in which one of coordinated sites is occupied by the bridged B-H-M bond.⁷

Specifically, only one isomer with the *cis*-disposition of C-H bond and chlorine atom is formed in case of the carborane phosphine containing the C-H bond. The methyl-substituted phosphine forms to stereoisomers.

It has been assumed that the formation of cyclometallated complexes including bulky carborane phosphines proceeds via the intermediate formation of the pentacoordinated hydridocarbonyl complex $MHCl(CO)(P \sim BH)_2$. The high lability of the hydride hydrogen atom linked to the metal facilitates an intramolecular attack on the transition metal atom at the most electrophilic B-H bond with the formation of an intermediate having the coordination vacancy which is blocked for account of the formation of intramolecular bridged B-H-M bond.

The carbonylation of the above complexes occurs with the cleavage of the bridged B-H-M bond to form a *cis*-dicarbonyl complex which undergoes a slow isomerisation in a benzene solution. When reacted with both mono- and bidental donor ligands, the complete replacement of the non-metallated carborane phosphine takes place along with a cleavage of the bridged bond, however the cyclometallation structure in coordination sphere of the metal retained.

The X-ray analysis of one of ruthenium complexes confirmed the nucleophilic nature of the cyclometallation reaction which proceeds at the most electrophilic boron atoms. The distance between boron and ruthenium is equal to 2.15Å which is 0.15Å less than the sum of covalent radii of boron and ruthenium. The B-C-C-P metalocycle has the envelope conformation with the P atom deflecting by 0.67Å from plane. A short intramolecular distance Cl...HC (5) which is equal to 2.67Å and corresponds to one of the shortest contacts Cl...H should be especially noted. This distance is less than the sum of van der Waals radii (3.0Å). This interaction is apparently a reason for the formation of only one isomer in the above cyclometallation reaction of the carborane phosphine with CH bond.⁸

RHODIUM AND IRIIDIUM DERIVATIVES

Reactions of carborane phosphines and arsines with rhodium and iridium complexes of the d^8 electron configuration, in which the metal has a higher ability for oxidative addition reaction, are of significant interest. These reactions present a principally novel, as compared with those considered above, type of cyclometallation reactions as a result of which an increase of the coordination number and oxidation degree of the metal take place owing to oxidation addition of the carborane nucleus B-H bond to the transition metal atom.

We have found a number of such reactions and demonstrated the possibility of cyclometallation of carborane phosphines with the d^6 rhodium complexes without a change in the formal oxidation degree of the metal.^{9,10}

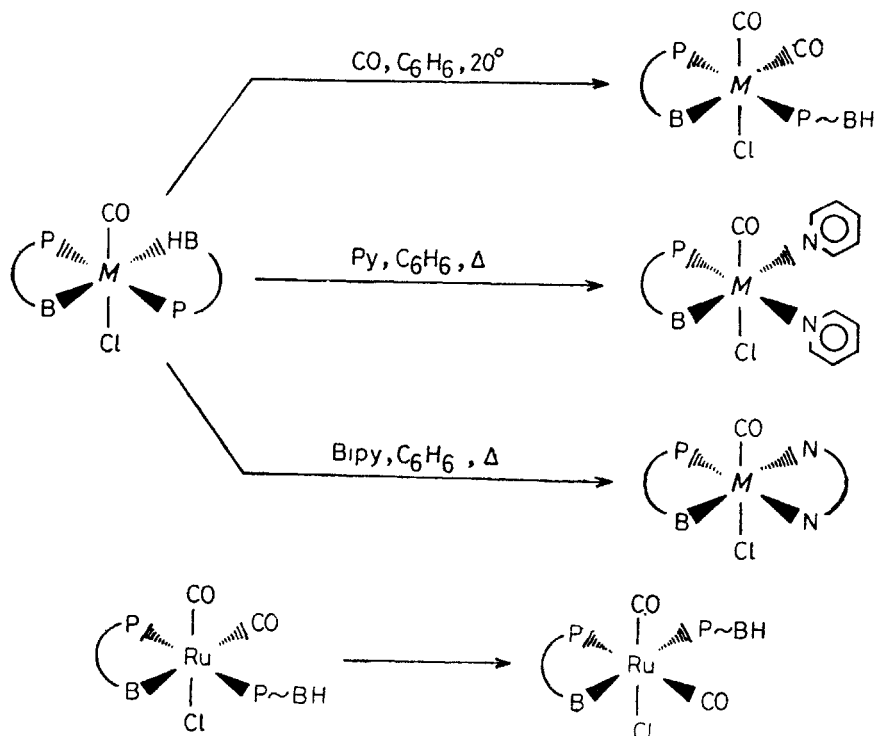


FIG 6

Prior to our study, no carboranes with the B-Rh σ -bond were known. Attempted syntheses of these compounds by the intermolecular addition of the carborane nucleus B-H bond to Rh(I) complexes proved to be unsuccessful.

It was found that cyclometallation of carborane phosphines and arsines occurs smoothly under the action of Rh(I) complexes in the presence of diverse pyridine bases as co-ligands to lead to stable chelated B- σ -carboranyl compounds. The reaction is very sensitive to steric effects of substituents while the use of 2-substituted pyridines as co-ligands does not cause the formation of cyclometallated products.

Besides usual hexa-coordinated cyclometallated rhodium complexes, carborane phosphines are able to form rhodium and iridium complexes with the bridged B-H-M bond like ruthenium and osmium complexes do.

The interaction between a carborane phosphine and olefinic complexes of rhodium produces smoothly a cyclometallation product with the B-H-Rh bond. The formation of these complexes proceeds via the oxidation addition of the carborane B-H bond to the rhodium atom. At the same time, reaction of rhodium trichloride with an excess of the phosphine in boiling ethanol occurs formally as an electrophilic attack of trivalent rhodium on the B-H bond to yield the cyclometallated product with the bridged bond.

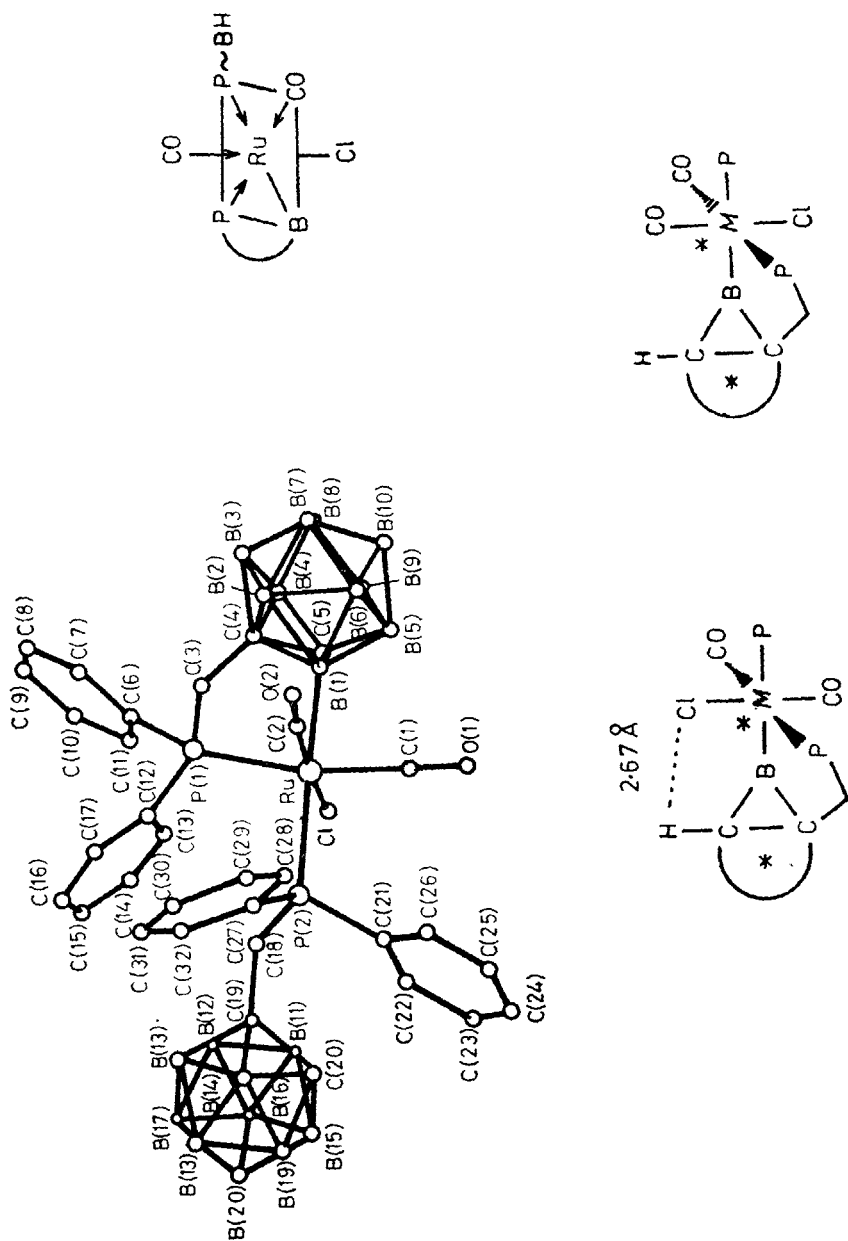


FIG. 7

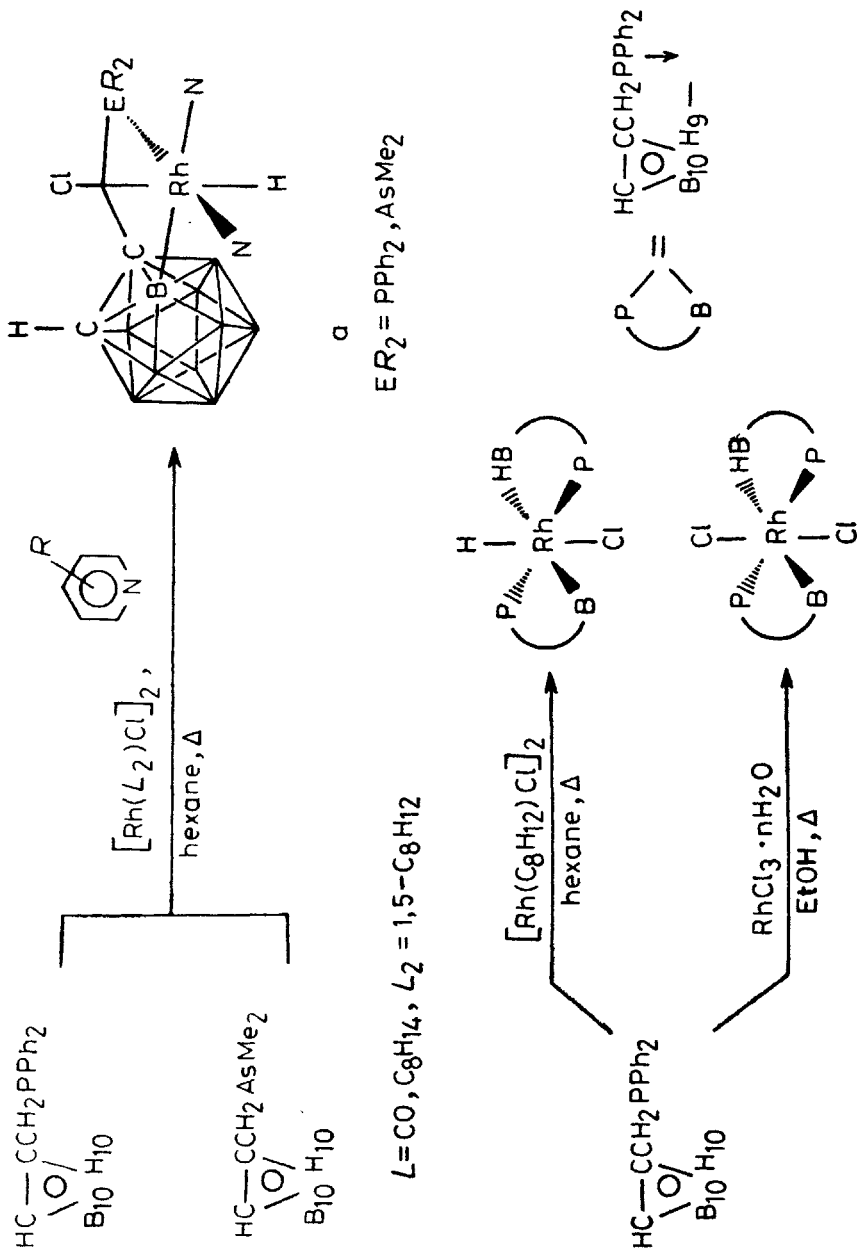


FIG 8

The presence of the bridged B-H-Rh bond has been established by a number of physico-chemical methods and supported by reactions with various ligands. Under the action of π -acceptor ligands, such as carbon monoxide and triphenylphosphite, the reductive cleavage of carborane B-H bond from the rhodium atom takes place along with the formation of monovalent rhodium complexes and the splitting of the bridged bond. The metallocycle opening is due to the fact that strong π -acceptor ligands stabilize rhodium complexes with the d^8 electron configuration to a higher extent as compared with the d^6 complexes.

The reaction with 4-methylpyridine, which is a σ -donor, involves a cleavage of the bridged B-H-Rh bond and elimination of the non-metallated carborane phosphine from the rhodium coordination sphere even without the metallocycle opening.

Carborane phosphines and arsines are readily metallated under the action of iridium cyclooctadiene complexes in ethanol at room temperature to afford five-membered exo-cyclic derivatives containing the cyclooctadiene ligand in coordination sphere of the iridium.^{9,10}

The direction of carborane phosphine reactions with monovalent iridium complexes is very sensitive to fine steric factors. For instance, even the introduction of the methyl group to the carborane carbon atom under the similar reaction conditions affects greatly the structure of products formed, so in the latter case we obtain the cyclometallated complex with the intramolecular B-H-Ir bond.

The cleavage of this bridged bond has been studied for the example of interaction with pyridine, CO, and triethylphosphine. The opening of the bridged B-H-Ir bond and addition of a ligand to the metal atom readily proceeds under the action of pyridine or CO, whereas the reaction with triethylphosphine leads to the elimination of carborane phosphine from the metal coordination sphere along with a cleavage of the bridged bond. It should be noted that the complex with pyridine can be prepared by direct cyclometallation of phosphine on action of iridium cyclooctadiene complex in the presence of pyridine.

Since the cyclometallation by monovalent rhodium and iridium complexes occurs as the oxidative addition, we have in this case the transfer of electrons from the transition metal atom to the B-H bond. Such a process must take place at sites with the least electron densities on boron atoms, that is to say at the position 3 of the carborane nucleus. This was supported by data on the intermolecular oxidative addition of the *o*-carborane B-H bond to Ir(I) complexes.¹¹

The behaviour of 1-methyl-2-diphenylphosphino-*o*-carborane in the cyclometallation reaction is interesting because, in this case, the following metallation processes are possible to proceed:—

1. At the C-H bond of methyl group to form the five-membered cycle.
2. At the aromatic C-H bond to form the four-membered cycle.
3. At the carborane nucleus B-H bond to form the four-membered cycle.

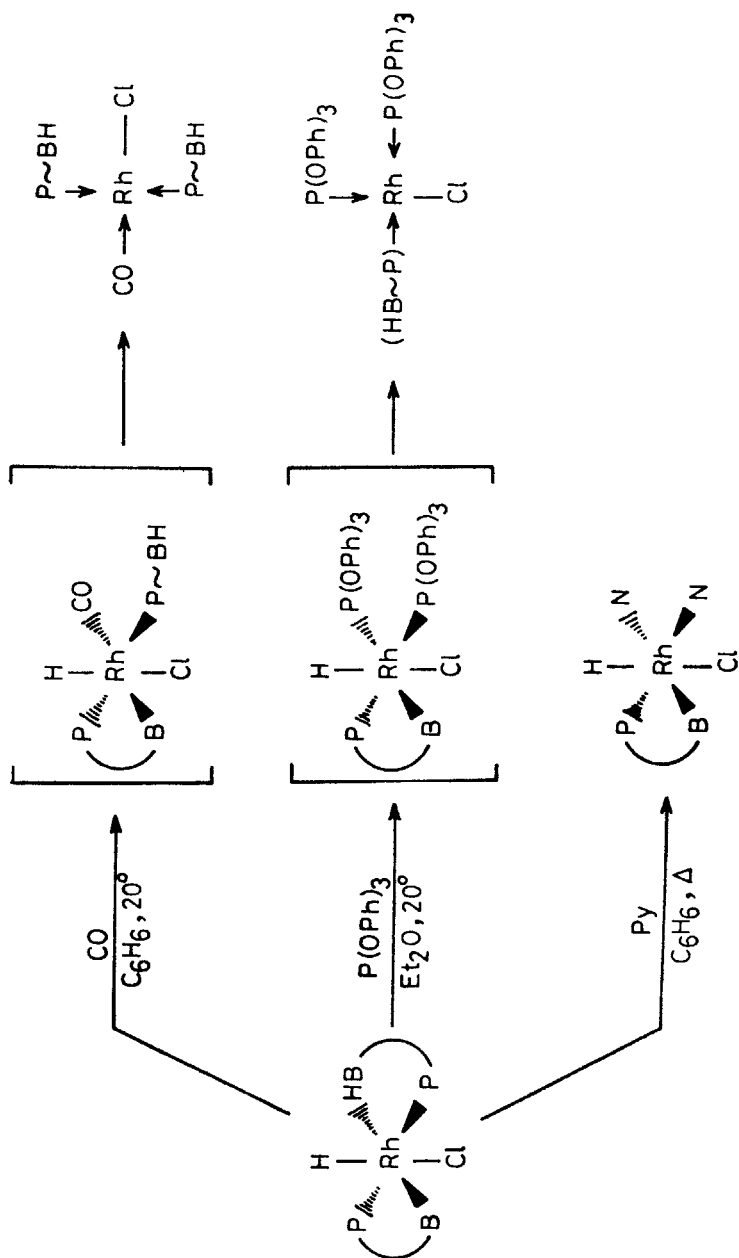


FIG 9

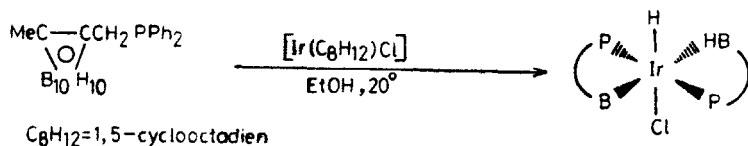
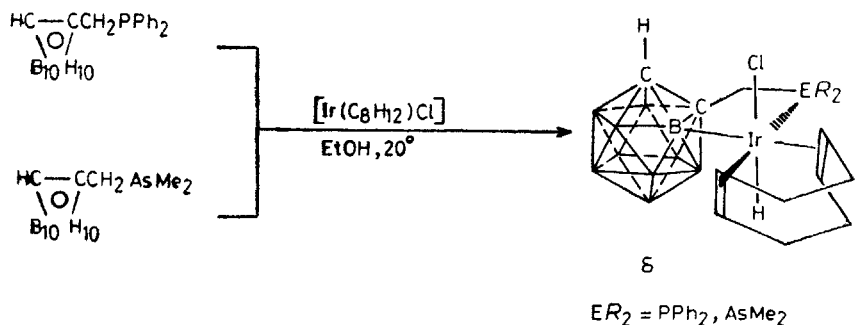


FIG 10

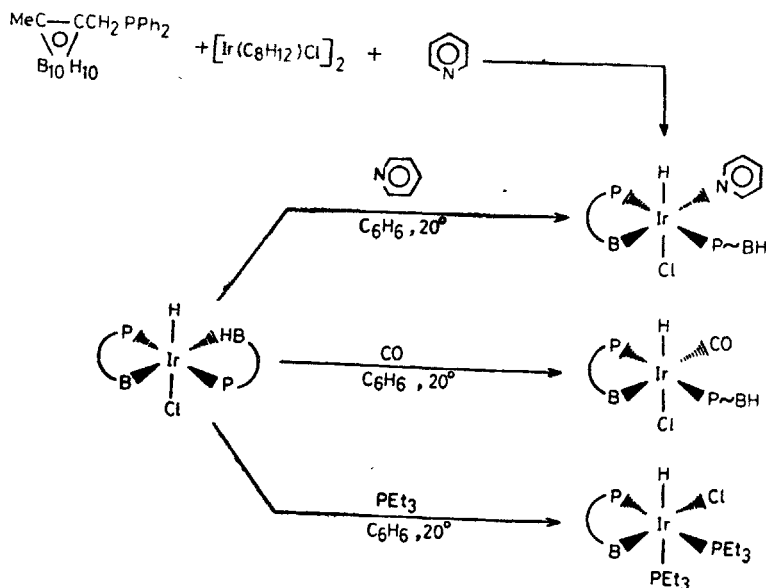


FIG 11

The only reaction product is the five-membered chelate. This is apparently conditioned, on the one hand, by the strong electron-acceptor effect of *o*-carbonyl group causing a decrease of electron density on the methyl group C-H bond, which facilitates the oxidative addition of the C-H bond to iridium atom. On the other hand, the chelate formation can be explained by the possible formation of the most sterically favourable five-membered metallocycle.¹⁰

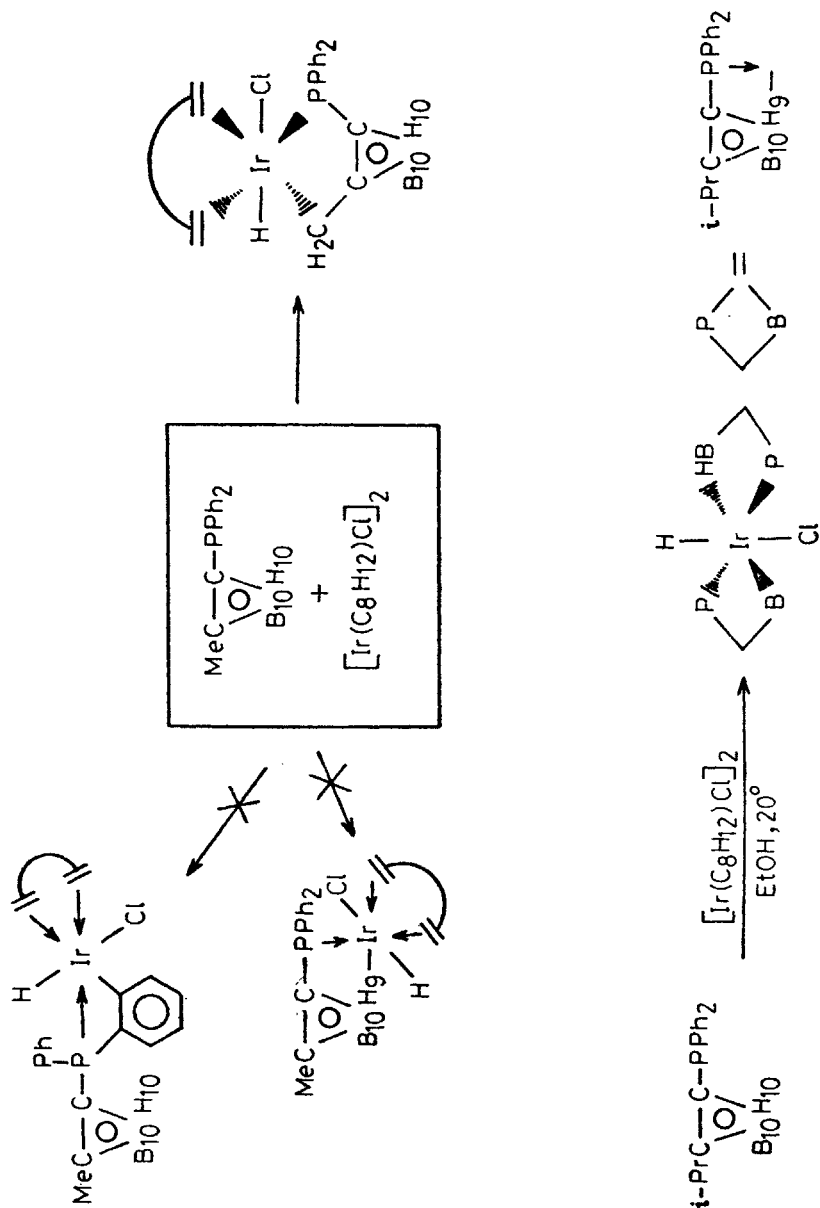


FIG 12

However, in case of isopropylcarborane phosphine, the four-membered exocyclic derivative with intramolecular B-H-M bond is formed. Such a difference in the metallation direction of carborane phosphines under the action of monovalent iridium complexes is apparently due to both electron and steric factors. The presence of two methyl groups prevents from the attack of the metal on the C-H bond of isopropyl substituent. At the same time, the electron-donor effect of these methyl groups increases electron density on the C-H bond, which also hinders the oxidative addition.

Unlike reactions of the phosphine with the cyclooctadiene complex at room temperature, boiling in ethanol leads to the formation of the *bis*-chelated cyclometallated complex of pentavalent iridium which is the first representative of cyclometallated octacoordinated complexes, with the eighth coordination site being blocked by bridged B-H-Ir bond. The isostructural iodine-substituted complex was obtained in a similar manner using an excess of sodium iodide.

Unlike all of cyclometallated complexes considered above, the B-H-Ir bridged bond in these compounds is formed at the expense of the B-H bond of metallated carborane phosphine. Interaction of the octacoordinated complexes with pyridine results in the cleavage of the bridged bond and reductive elimination of the B-H bond of one of carborane nuclei from iridium atom to form trivalent hydride iridium complexes. Carbonylation also proceeds with the opening of one of the metallocycles with the formation of a mixture of two isomers of different stereochemical structures.

The data considered show that cyclometallated compounds of pentavalent iridium are unstable towards donor ligands and undergo reductive elimination of the carborane nucleus B-H bonds to form hexacoordinated trivalent iridium complexes.

PALLADIUM AND PLATINUM DERIVATIVES

Dialkylaminomethyl-*o*- and *m*-carboranes readily undergo cyclopalladation under the action of benzonitrile complex of bivalent palladium in benzene to give dimeric complexes which were characterized as the corresponding monomeric derivatives. The latter compounds were prepared by splitting chlorous bridged bonds with pyridine. Since palladium atom has the plane-square configuration, the "envelope" conformation is the most sterically favourable for the five-membered cycle.¹²

Interaction of monomeric and dimeric palladium complexes with diphenylacetylene leads to the incorporation of two acetylene molecules at the B-H bond to form the derivative including the nine-membered metallocycle with palladium atom coordinated intramolecularly to the butadiene fragment double bond.

The cyclopalladation of amines is an electrophilic process, therefore the metallation of *tert*-amines of the carborane series will proceed at the sites with the most electron density in the carborane nucleus. Such sites accessible for the

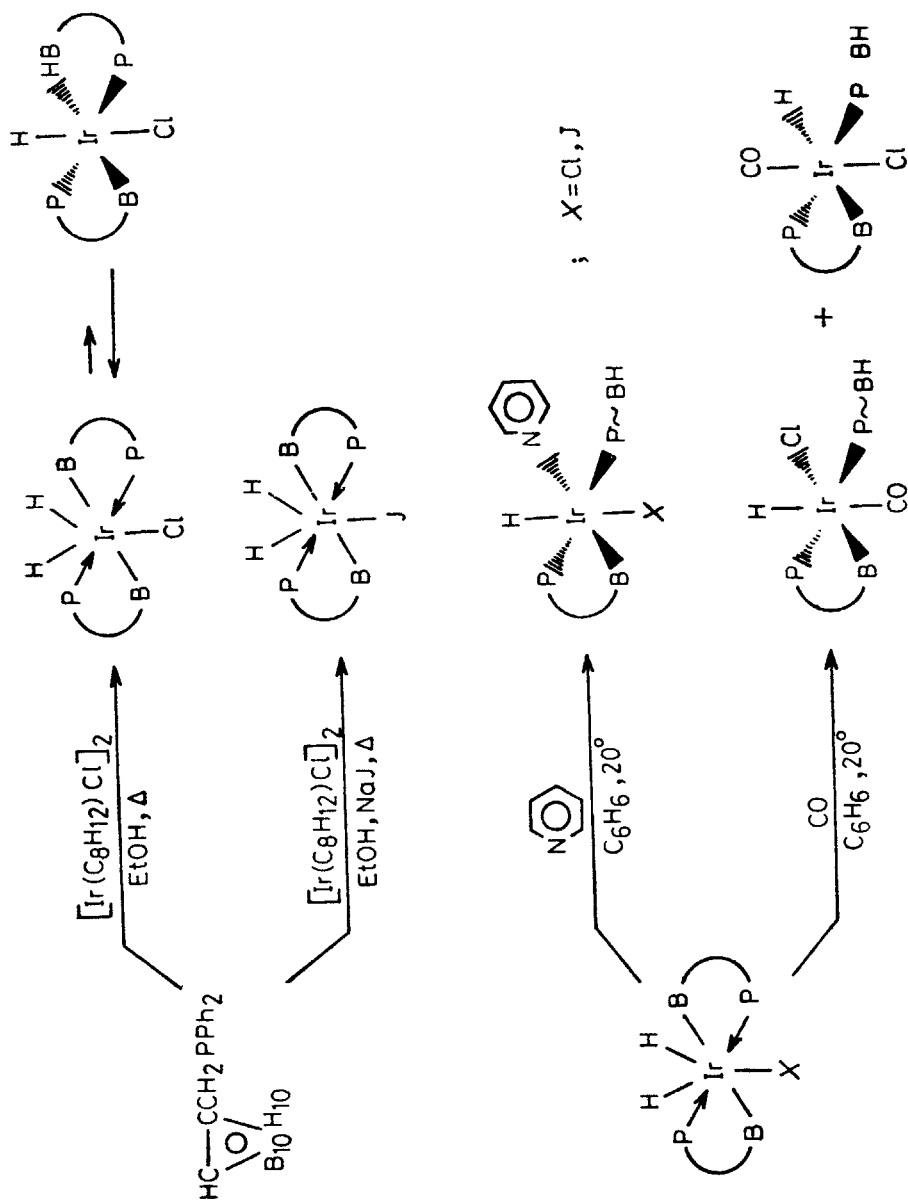


FIG 13

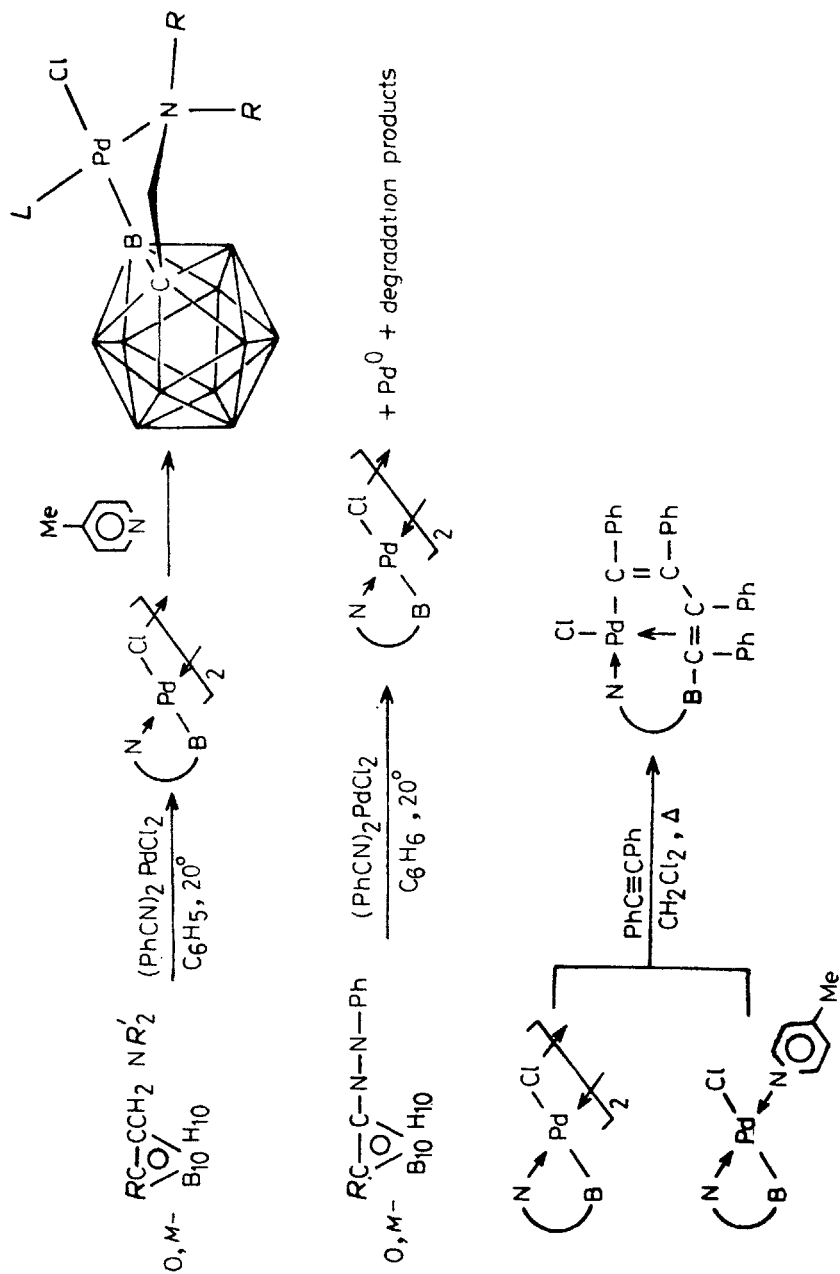


Fig 14

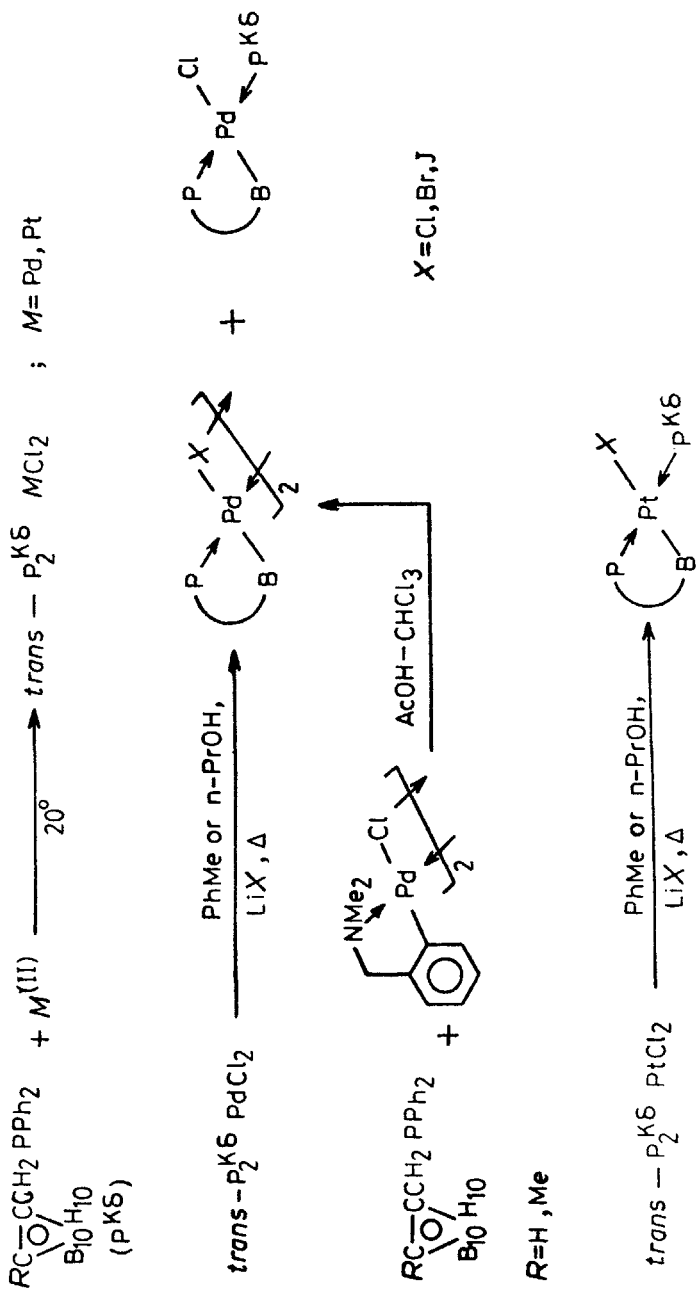


FIG 15

attack by a transition metal are in 4(5) equivalent positions in *o*-carborane and in the position 5 in *m*-carborane.

The carborane phosphines react with bivalent palladium and platinum compounds to form donor complexes of *trans*-structure. Heating these complexes in toluene gives a mixture of monomeric and dimeric cyclometallated products. When treated with pyridine, the sparingly soluble dimers readily convert to easily soluble monomeric adducts.¹³

An interesting method for the preparation of dimeric metallated products comprises the exchange reaction of cyclometallated ligands resulted from interaction of the *ortho*-palladated dimethylbenzylamine complex with phosphines in a mixture of acetic acid and chloroform.¹⁴

The halogenous bridged bond in the dimeric complex is easily cleaved under the action of phosphines: for example, triethylphosphine forms a monomeric complex of *trans*-configuration while the use of bidental 1,2-bis(diphenylphosphino)ethane leads to the elimination of chlorine atom from the coordination sphere of palladium and the formation of a cationic complex.

The carborane arsine reacts with bis(benzonitrile)palladium dichloride similarly to the corresponding phosphine reaction to form the donor complex of *trans*-structure and further the cyclometallated dimer and monomer. The dimeric complex is readily converted into respective monomer under the action of *N*-donor ligands: pyridine, triphenylphosphite.

The metallation of the arsine under the same conditions as in case of the exchange reaction of cyclopalladated ligands leads only to the dimeric product.

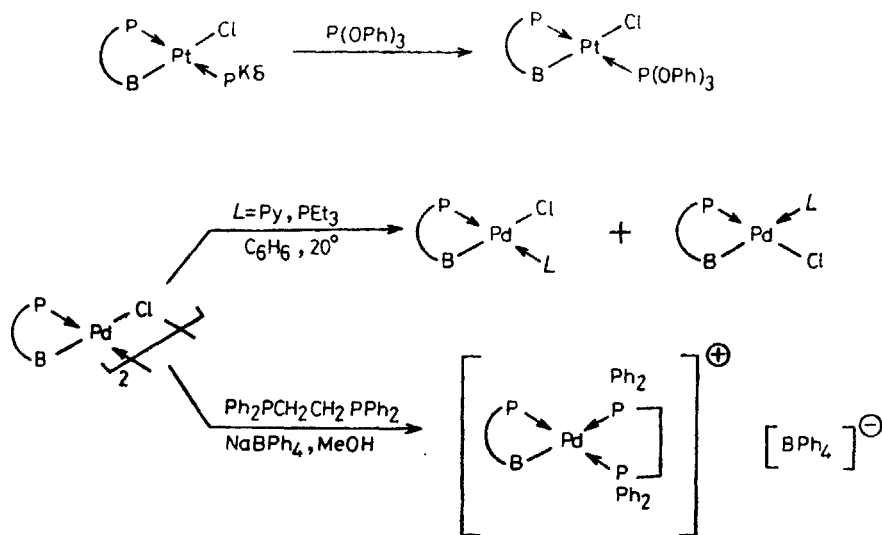


FIG 16

The preponderating formation of the 3-substituted isomer takes place in cyclopalladation reactions of carborane phosphines and arsine. The isomer contents in the mixture of cyclopalladated complexes is equal 80 to 85 per cent. Such a direction of the metallation, along with the order of alteration of the reactivity observed ($\text{Cl} < \text{Br} < \text{I}$), is consistent with the nucleophilic nature of cyclopalladation reaction.

The carborane phosphines in which palladium atom is bonded to the carborane carbon atom are promising objects for the investigation of cyclometallation reactions due to the possible metallation of both the B-H bond of carborane nucleus and C-H bonds of benzene ring to obtain four-membered metallocycles as well as C-H bonds of the substituent on the other carbon atom to yield five- or six-membered metallocycles, which was observed in case of iridium.

It turned out that cyclometallation of carborane phosphines under the action of bivalent palladium compounds proceeds even at room temperature exclusively at B-H bonds of the carborane nucleus with the formation of the four-membered palladocycle.

Under conditions of the cyclopalladated ligands exchange, the dimeric palladated complex is easily formed which is converted to monomer on treatment with an excess of the starting phosphine.

Cyclometallation of C-substituted carborane phosphines readily occurs with the formation of two boron-metallated isomers in a ratio depending on the bulkness of substituents on the carborane carbon atom. The B⁴-metallated isomer is mainly formed in case of C-isopropylcarboranylphosphine whereas amounts of B³- and B⁴-metallated isomers are equal with C-methylcarboranylphosphine.¹⁴

The cycloplatination of phosphines with sodium tetrachloroplatinate proceeds less easily in comparison with palladation. In this case, heating in benzene or toluene is necessary. Nonmetallated carborane phosphine can be readily replaced by triphenylphosphite without the opening of metallocycle.

We have found the first reaction involving the exchange of cyclopalladated ligands with the participation of only P-donor molecules for the example of reaction of a four-membered metallocyclic derivative with a carborane phosphine in a mixture of acetic acid with chloroform. In this case a more thermodynamically stable cyclometallated product is formed.¹⁵

The results presented here demonstrate that the cyclometallation reaction is a convenient and efficient method for the incorporation of a transition metal into the carborane molecule and it makes it possible to obtain a great variety of carborane metallocyclic derivatives containing a boron-transition metal σ -bond (Manganese, Rhenium, Palladium, Platinum, Ruthenium, Osmium, Rhodium Iridium).

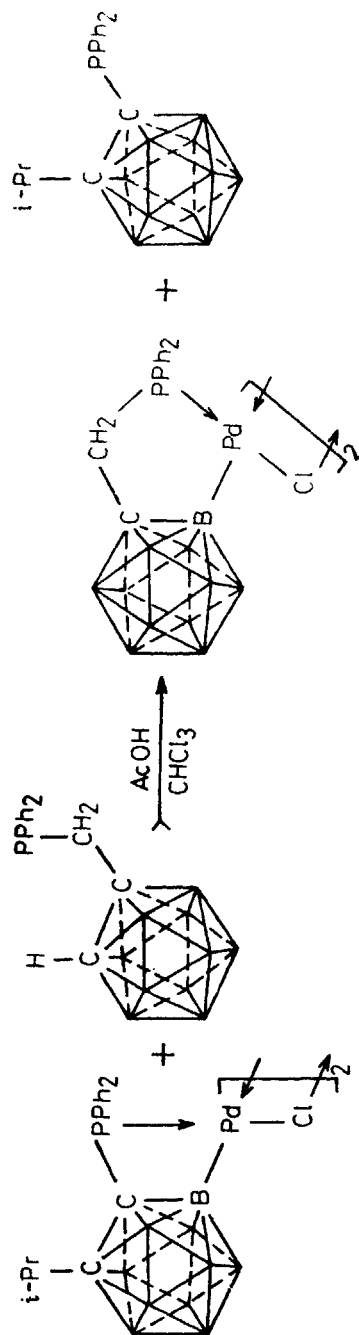


FIG 19

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