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Substitution reactions at boron atoms in metallacarboranes

V I Bregadze, S V Timofeev, I B Sivaev, I A Lobanova

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Abstract. Data on substitution reactions at boron atoms in 10 – 12-vertex metallacarboranes, which are of fundamental and applied significance, are generalised. The possible mechanisms of substitution reactions and the influence of the metal fragment on substitution positions in the polyhedron are discussed. The bibliography includes 161 references.

I. Introduction

For many years, metallacarboranes † were of only academic interest.[2 – 7] Most studies of this period were devoted primarily to the construction of unusual chemical structures and investigation of their structural features. Metallacarboranes, whose polyhedral cage contains both transition and main-group metals of all groups of the periodic table, have already been synthesised. In recent years, practical aspects of the use of metallacarboranes have attracted increasing interest [8] because some compounds of this class were found to possess useful properties. For example, particular metallacarboranes show promise as catalysts,[9 – 12] extractants for nuclear waste processing,[13 – 18] new materials for microelectronics [19 – 23] or drugs in nuclear medicine.[24 – 28]

The synthesis of new compounds and materials possessing desired properties is associated with the necessity of changing the structural parameters responsible for the qualitative and quantitative characteristics of compounds. In the case of metallacarboranes, such changes can be achieved by varying either components of the molecule (metal atoms and organic ligands involved in the metal coordination sphere) or the structure and electronic properties of the carborane fragment. The latter can be achieved by introducing various substituents, which are responsible for the final properties of the compounds synthesised, into the carborane fragment.

Therefore, the synthesis and investigation of substituted metallacarboranes are of both fundamental and applied importance.

V I Bregadze, S V Timofeev, I B Sivaev, I A Lobanova A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation.
Fax (7-095) 135 50 85. Tel. (7-095) 135 74 05. E-mail: bre@ineos.ac.ru (V I Bregadze). Tel. (7-095) 135 92 42. E-mail: sivaev@ineos.ac.ru (I B Sivaev). Tel. (7-095) 135 92 37 (S V Timofeev, I A Lobanova)

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In this connection, studies of substitution reactions in metallacarborane systems and elucidation of the characteristic features of these processes are of particular interest.

There are two approaches to the synthesis of substituted metallacarboranes: (1) the synthesis from substituted carborane ligands and metal complexes (salts), (2) substitution in the already available metallacarborane molecule. The first approach is used primarily for the construction of metallacarboranes containing substituents at carbon atoms [5, 6, 29 – 32] and is virtually the only procedure for the synthesis of such derivatives. Examples of substitution at carbon atoms in metallacarboranes are scarce.[33, 34] Metallacarboranes containing substituents at boron atoms are synthesised primarily with the use of the second procedure.

The present review surveys data on substitution in metallacarboranes, which were published primarily in the last 15 years, some earlier investigations being also included.

The published data are classified according to the types of carborane ligands. Substitution reactions in small metallacarboranes, *viz*., *nido*-C_2B_4-carborane derivatives, are beyond the scope of our review because the chemistry of the latter has been covered in the excellent review by Grimes [35] (see also recent studies [36 – 40]).

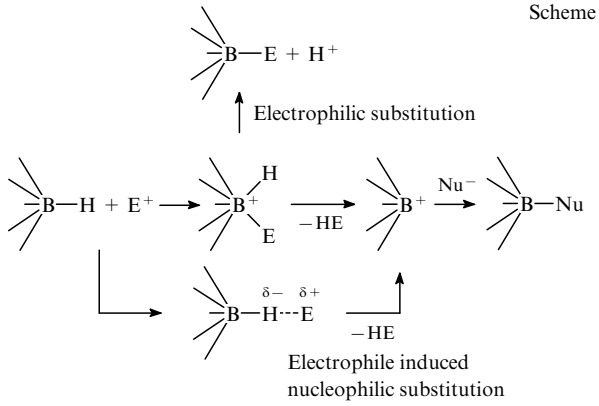
II. Mechanisms of substitution in metallacarboranes

At pesent, polyhedral boron hydrides are commonly considered as three-dimensional aromatic systems.[41] In particular, halogenation and mercuration of carboranes are adequately described within the framework of the mechanism of electrophilic aromatic substitution. Since metallacarboranes are derivatives of polyhedral boron hydrides, it is reasonable to assume that this mechanism is one of the main mechanisms of substitution in metallacarboranes. Apparently, most substitution reactions considered below proceed according to this mechanism.

At the same time, taking into account the hydride character of hydrogen atoms in polyhedral boron hydrides, another possible mechanism may involve the attack of an electrophilic agent resulting in elimination of the hydride hydrogen atom to form a pseudoelectrophilic centre on the boron atom, which is then subjected to the attack of a nucleophilic species (Scheme 1). This mechanism is called Electrophile Induced Nucleophilic Substitution (EINS).[42, 43] The nature of the intermediate generated upon the attack of the electrophilic agent remains unclear. Probably, this is the arenium ion (Wheland intermediate), from which both

† First representatives of this class were synthesised in 1965.[1]

Scheme 1



the electrophilic species and the hydride hydrogen atom are simultaneously eliminated. Another possible intermediate is an ion pair formed by the electrophilic species and the hydride hydrogen atom.

Electrophile induced nucleophilic substitution is the mechanism of numerous reactions of polyhedral boron hydrides with solvent molecules accompanied by the formation of numerous charge-compensated derivatives, in which the solvent molecule (tetrahydrofuran, 1,4-dioxane or tetrahydropyran) serves as a substituent bound to the boron atom.[44–47] Acid-catalysed nucleophilic substitution reactions, in particular, the formation of acetoxy and hydroxy derivatives, also proceed according to this mechanism.[48–50]

It should be noted that many substitution reactions can occur by two competitive mechanisms to form mixtures of products of both electrophilic and nucleophilic substitution. An example is acylation of the dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ giving rise both to the acyl derivative $[B_{12}H_{11}COR]^{2-}$ (product of electrophilic substitution) and the hydroxy derivative $[B_{12}H_{11}OH]^{2-}$ (product of electrophile induced nucleophilic substitution).[51] The ratio between the products of electrophilic and nucleophilic substitution is determined by the strength of the attacking electrophilic agent.

In addition to substitution reactions typical of all polyhedral boron hydrides, substitution reactions involving the metal atom occur in metallacarboranes containing labile ligands in the metal coordination sphere.

It is of importance to determine the substitution position in metallacarboranes. Earlier studies of electrophilic substitution of hydrogen atoms in icosahedral *o*- and *m*-carboranes $C_2B_{10}H_{12}$ have demonstrated that the reactions proceed primarily at the boron atoms, which are most spatially remote from carbon atoms, *i.e.*, at the boron atoms in position 9.[52,53] The presence of the metal fragment has a substantial effect on the direction of substitution in the metallacarborane moiety.

III. Substitution in 12-vertex metallacarboranes

1. Derivatives based on the 7,8-dicarbollyl ligand $[7,8\text{-}C_2B_9H_{11}]^{2-}$

Since the 7,8-dicarbollyl ligand $[7,8\text{-}C_2B_9H_{11}]^{2-}$ is readily accessible, substitution in icosahedral metallacarboranes based on this ligand has been well studied. This ligand is prepared by partial destruction of the icosahedral carborane cage *o*-$C_2B_{10}H_{12}$ with bases.[52] Among numerous metallacarboranes, cobalta-, ferra- and nickelacarboranes $[3\text{-L-}3,1,2\text{-}MC_2B_9H_{11}]^{n-}$ based on the 7,8-dicarbollyl ligand (Fig. 1) were studied in most detail.[5,6]

Bromination of bis(1,2-dicarbollyl)cobalt [*commo*-3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ (**1**) (the atomic numbering scheme is shown in Fig. 1 *d*)[54] was the first example of substitution in metallacarboranes. Later on, halogenation of anion **1** was studied by different research groups of chemists. Substitution was demonstrated to proceed stepwise. Initially, the hydrogen atoms at

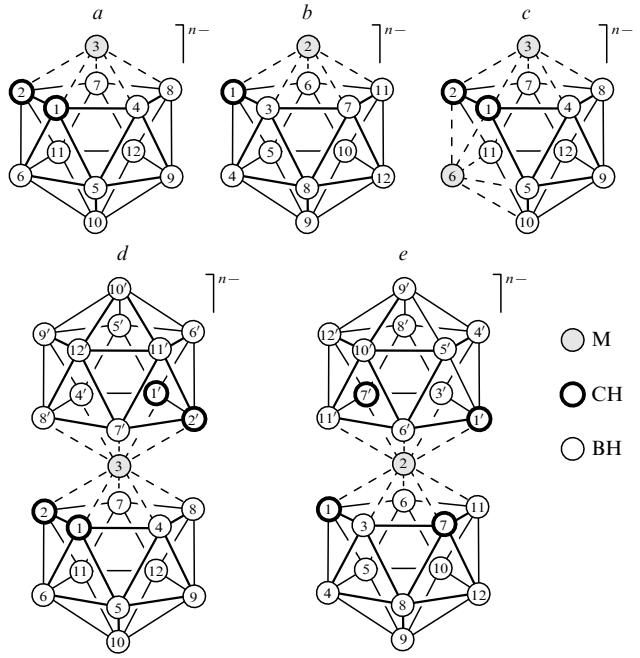


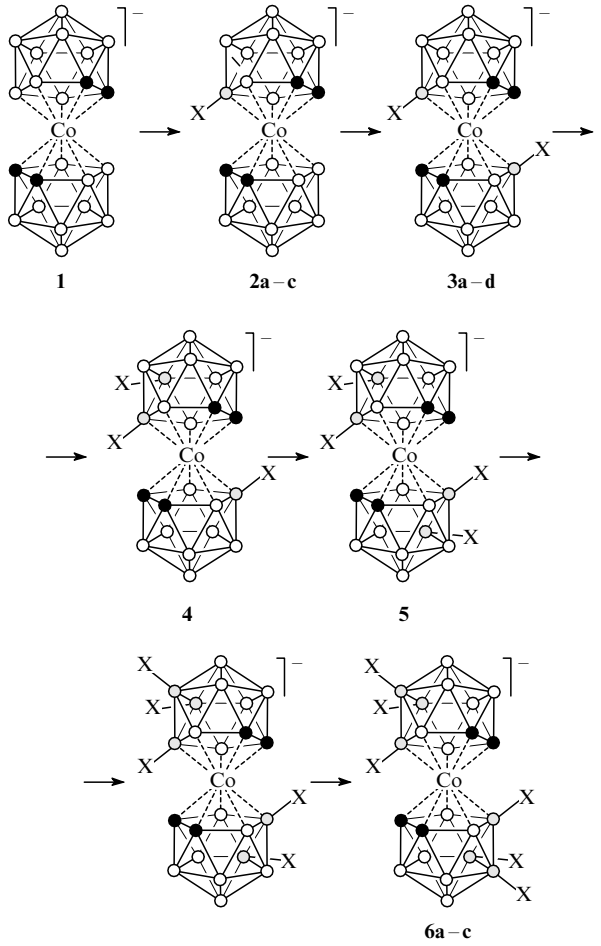
Figure 1. Atomic numbering schemes for different types of icosahedral metallacarboranes.
(*a*) 1,2-dicarba-3-metalla-*closo*-dodecaborane, (*b*) 1-carba-2-metalla-*closo*-dodecaborane, (*c*) 1,2-dicarba-3,6-dimetalla-*closo*-dodecaborane, (*d*) *commo*-3,3′-metallabis(1,2-dicarbollide), (*e*) *commo*-2,2′-metallabis(1,7-dicarbollide).

positions 8 and 8′ adjacent to the metal atom are replaced. In the next step, the hydrogen atoms at positions 9, 9′ and 12, 12′, which are most remote from the carbon atoms, are replaced. Examples are chlorination of *o*- and *m*-carboranes (Scheme 2). For instance, when passed through a solution of Cs[*commo*-3,3′-Co(1,2-$C_2B_9H_{11})_2$] (Cs[**1**]) in an EtOH – CCl_4 or $PhNO_2$ – CCl_4 mixture, chlorine successively replaces the hydrogen atoms at the B(8), B(8′), B(9), B(9′), B(12) and B(12′) atoms to form Cs[8-Cl-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (Cs[**2a**]), Cs[8,8′-Cl_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (Cs[**3a**]), Cs[8,8′,9-Cl_3-3,3′-Co(1,2-$C_2B_9H_9$)(1′,2′-$C_2B_9H_{10}$)] (Cs[**4**]), Cs[8,8′,9,9′-Cl_4-3,3′-Co(1,2-$C_2B_9H_9)_2$] (Cs[**5**]) and Cs[8,8′,9,9′,12,12′-Cl_6-3,3′-Co(1,2-$C_2B_9H_8)_2$] (Cs[**6a**]).[55]

The reaction of Cs[**1**] with bromine in methanol at room temperature affords either Cs[8-Br-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (Cs[**2b**]) or Cs[8,8′-Br_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (Cs[**3b**]) depending on the reagent ratio.[55] The reaction of [Me_3NH][**1**] with bromine in boiling tetrahydrofuran produces the dibromo derivative [Me_3NH][**3b**].[56] The reaction of Rb[**1**] with an excess of bromine in boiling acetic acid yields the hexabromo derivative Rb[8,8′,9,9′,12,12′-Br_6-3,3′-Co(1,2-$C_2B_9H_8)_2$] (Rb[**6b**]).[54]

The reaction of Cs[**1**] with iodine in methanol at room temperature produces the monoiodo derivative Cs[8-I-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (Cs[**2c**]),[55] whereas the reaction with a small excess of iodine in ethanol[55] or in acetic acid (at 100 °C)[57] gives rise to the diiodo derivative Cs[8,8′-I_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (Cs[**3c**]). The latter can also be prepared by refluxing Cs[**1**] with iodine chloride.[58] The cross-coupling reactions of the monoiodo-substituted derivative Cs[**2c**] with organomagnesium and -zinc compounds in the presence of a Pd catalyst afford the corresponding alkyl and aryl derivatives [8-R-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (R = Me, Et, Ph, CH_2CH_2Ph, C_6H_4Bu-4, C_6H_4OMe-4, C_6H_4Ph-4, 9-anthracenyl, 2-thienyl).[59,60] The reactions of Cs[**3c**] with RMgBr (R = Me or

Scheme 2



Here and below ● CH ○ BH ⊙ B;
X = Cl (**a**), Br (**b**), I (**c**), F (**d**).

Et) form Cs[8,8′-R_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$] along with [8-R-8′-OH-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$ as a by-product.[58]

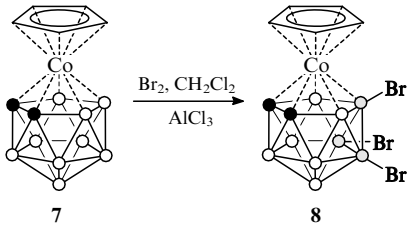
The reaction of Cs[**1**] with a high excess (more than sixfold) of iodine in the presence of $AlCl_3$ in benzene made it possible to prepare the hexaiodo derivative Cs[8,8′,9,9′,12,12′-I_6-3,3′-Co(1,2-$C_2B_9H_8)_2$] (Cs[**6c**]).[55] The compound Cs[**6c**] can also be synthesised with the use of iodine chloride.[61] The iodine atoms in Cs[**6c**] are readily replaced with methyl groups by the reaction with MeMgBr in the presence of $PdCl_2(PPh_3)_2$ and CuI in boiling THF. The corresponding hexamethyl derivative [8,8′,9,9′,12,12′-Me_6-3,3′-Co(1,2-$C_2B_9H_8)_2$]$^-$ was isolated as the triphenylmethylphosphonium salt.[61]

The difluoro derivative [Bu_4N][8,8′-F_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$] ([Bu_4N][**3d**], the yield was 80%) was prepared by the reaction of [Bu_4N][**1**] with an excess of 4-chloromethyl-1-fluorobicyclo[2.2.2]octane-1,4-diazonium bis(tetrafluoroborate) in acetone at 50 °C.[62]

The structures of the compounds Cs[**2c**],[63] K[**3a**],[64] [$(Ph_3P)_2N$][**3a**],[56] Cs[**3c**],[65] [Bu_4N][**3d**],[62] [Me_4N][**6b**][66] and Cs[**6b**][67] were established by X-ray diffraction analysis. In the di- and hexahalogen-substituted derivatives, the dicarbollyl ligands adopt a transoid conformation.

It should be noted that the replacement at other positions of bis(dicarbollyl)cobalt (**1**) does not occur even under severe conditions. Such derivatives can be synthesised by the direct assembly of the metallacarborane fragment from $CoCl_2$ and the corresponding substituted carboranes. This procedure was used for the preparation of [9,9′-Cl_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$,[55] [9,9′,12,12′-Cl_4-3,3′-Co(1,2-$C_2B_9H_9)_2$]$^-$,[55] [9,9′-Br_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$,[68] [9,9′,12,12′-Br_4-3,3′-Co(1,2-$C_2B_9H_9)_2$]$^-$,[68] [4,4′,7,7′-Cl_4-3,3′-Co(1,2-$C_2B_9H_9)_2$]$^-$,[69] [4,4′,7,7′-Br_4-3,3′-Co(1,2-$C_2B_9H_9)_2$]$^-$ (see Ref. 69) and [9,9′-I_2-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$^-$.[70]

Halogenation of unsymmetrical cobaltacarborane 3-Cp-3,1,2-$CoC_2B_9H_{11}$ (**7**) was studied in less detail. Depending on the reagent ratio, the reaction of compound **7** with bromine in dichloromethane in the presence of $AlCl_3$ affords mono-, di- and trisubstituted products. It is assumed that the first step of the reaction involves the replacement of the hydrogen atom at position 8 [like in the case of bis(dicarbollyl)cobalt] followed by the replacement of the hydrogen atoms at positions 9 and 12 of the dicarbollyl ligand. In the presence of an excess of bromine, the reaction yields the tribromo derivative 8,9,12-Br_3-3-Cp-3,1,2-$CoC_2B_9H_8$ (**8**).[71,72]



Refluxing of compound **7** in benzene with an excess of AlX_3 (X = Cl, Br, I) affords the corresponding monohalogen-substituted derivatives.[73] It is assumed that the substitution occurs at position 8. However, no evidence for this structure of the halogenation product was reported.

Due to the paramagnetic nature of Fe^{III}-based metallacarboranes, substitution in these compounds was studied in much less detail compared to substitution in Co^{III}-based metallacarboranes. Nevertheless, it can be assumed that these reactions proceed analogously. For example, chlorination of [*commo*-3,3′-Fe(1,2-$C_2B_9H_{11})_2$]$^-$ (**9**) affords the dichloro derivative [8,8′-Cl_2-3,3′-Fe(1,2-$C_2B_9H_{10})_2$]$^-$ (**10**). The structure of its potassium salt was established by X-ray diffraction analysis.[64]

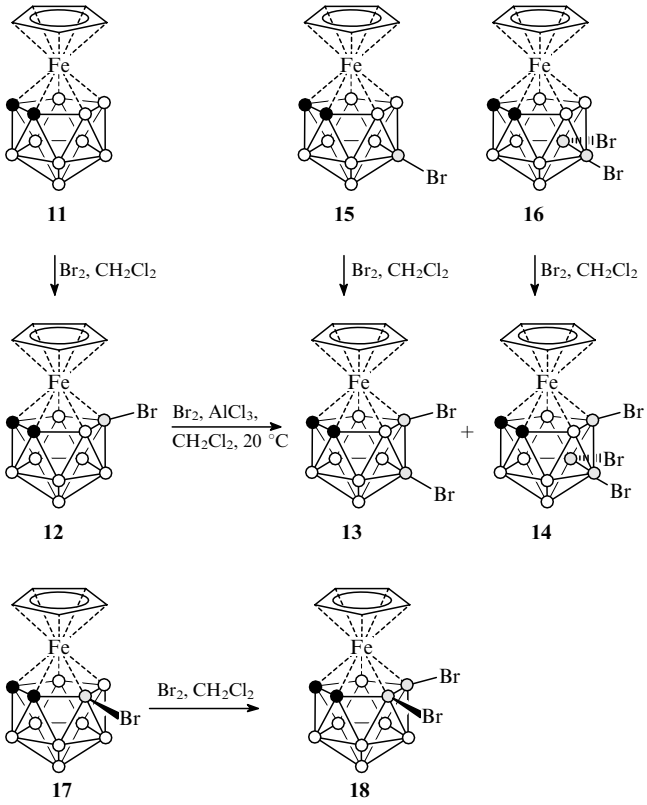
Halogenation of ferracarborane 3-Cp-3,1,2-$FeC_2B_9H_{11}$ (**11**) was studied more thoroughly. Bromination of compound **11** in dichloromethane at room temperature in the absence of a catalyst gives rise to the monobromo derivative 8-Br-3-Cp-3,1,2-$FeC_2B_9H_{10}$ (**12**) (Scheme 3). In the presence of $AlCl_3$, the substitution occurs less selectively and affords monobromide **12** along with dibromo [8,9-Br_2-3-Cp-3,1,2-$FeC_2B_9H_9$ (**13**)] and tribromo [8,9,12-Br_3-3-Cp-3,1,2-$FeC_2B_9H_8$ (**14**)] derivatives. Bromination in acetic acid and nitromethane proceeds analogously. The dibromo derivative **13** can also be prepared by bromination of 9-Br-3-Cp-3,1,2-$FeC_2B_9H_{10}$ (**15**) and the tribromo derivative can be synthesised by bromination of 9,12-Br_2-3-Cp-3,1,2-$FeC_2B_9H_9$ (**16**), which was prepared by direct synthesis from the corresponding substituted *nido*-carborane (Scheme 3).[74]

Bromination of 4-Br-3-Cp-3,1,2-$FeC_2B_9H_{10}$ (**17**) derived from the corresponding *nido*-carborane produces 4,8-Br_2-3-Cp-3,1,2-$FeC_2B_9H_9$ (**18**).[74]

The published data on mercuration of anion **1** are contradictory. The reaction of the mercury salt Hg[**1**]$_2$ with mercury acetate in boiling acetic acid forms the disubstituted product Hg[9,9′-$(AcOHg)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$]$_2$. It was hypothesised that the hydrogen atoms most remote from the carbon atoms, *viz.*, those at positions 9,9′, are replaced.[75]

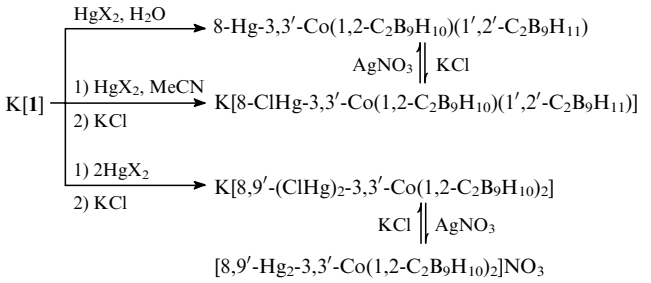
By contrast, mercuration of K[**1**] in an aqueous–organic medium leads to the replacement of one dicarbollyl ligand at position 8 followed by the replacement of another ligand at position 9′ (Scheme 4).[76] However, it should be noted that the proposed structures of the reaction products were not supported by rigorous evidence.

Scheme 3



The reaction of bis(dicarbollyl)nickel(IV), *viz*., *commo*-3,3′-Ni(1,2-$C_2B_9H_{11})_2$ (**19**), with mercury oxide in boiling trifluoroacetic acid followed by the replacement of the trifluoroacetate group with the chlorine atom gave rise to the disubstituted derivative $(ClHg)_2$-3,3′-Ni(1,2-$C_2B_9H_{10})_2$ (substitution positions were not established).[77]

Scheme 4

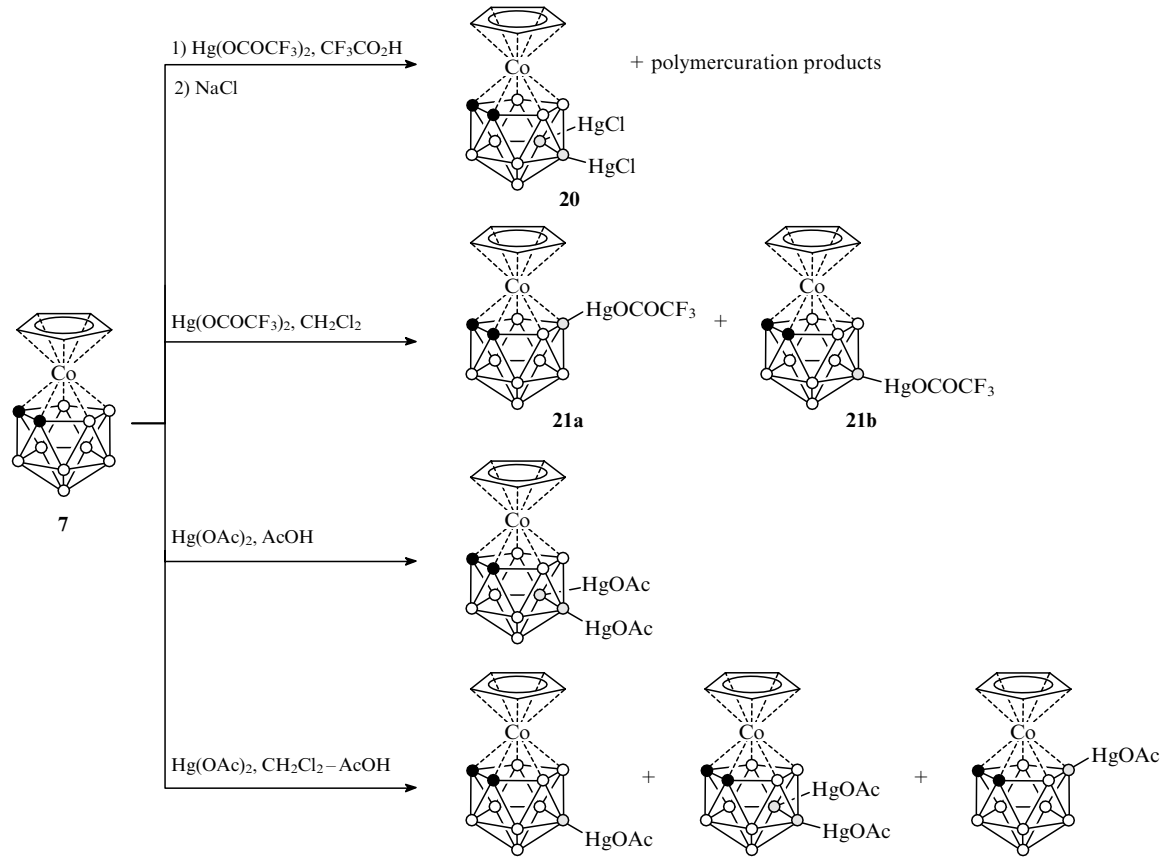


X = BF_4, AcO, CF_3CO_2.

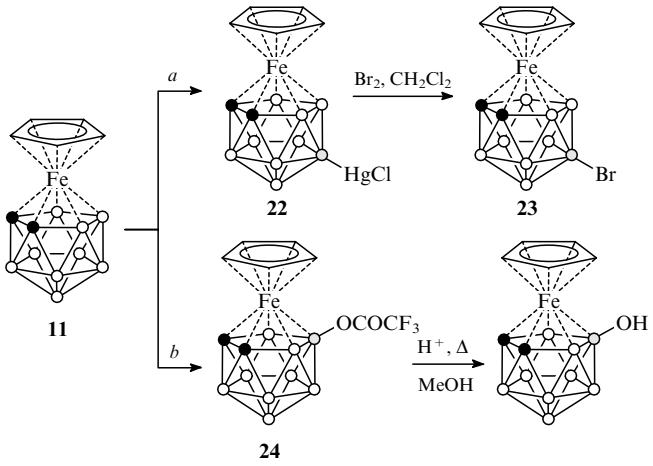
Mercuration of compound **7** was examined in the studies.[75,78] It was noted that different products can be prepared by varying the reaction conditions. For example, mercuration under severe conditions, *i.e*., the reaction of cobaltacarborane **7** with mercury trifluoroacetate in trifluoroacetic acid followed by treatment with NaCl in a water–acetone system, afforded the disubstituted derivative 9,12-$(ClHg)_2$-3-Cp-3,1,2-$CoC_2B_9H_9$ (**20**) and polymercuration products (Scheme 5). The reaction with the use of a softer system (mercury trifluoroacetate in dichloromethane) yielded a mixture of two isomeric 8- (**21a**) and 9-substituted (**21b**) monomercury derivatives in a ratio of 1 : 5. The structure of the 9-substituted monomercury derivative was confirmed by X-ray diffraction analysis.[78] A diacetomercury-substituted derivative was prepared by the reaction of compound **7** with mercury acetate in acetic acid, whereas the reaction in the CH_2Cl_2–AcOH system gave rise to a disubstituted complex along with two isomeric 8- and 9-substituted monomercury derivatives.

The 9-chloromercury derivative 9-ClHg-3-Cp-3,1,2-$FeC_2B_9H_{10}$ (**22**) was synthesised by mercuration of ferracarborane **11** with mercury trifluoroacetate in a trifluoroacetic acid–

Scheme 5



Scheme 6



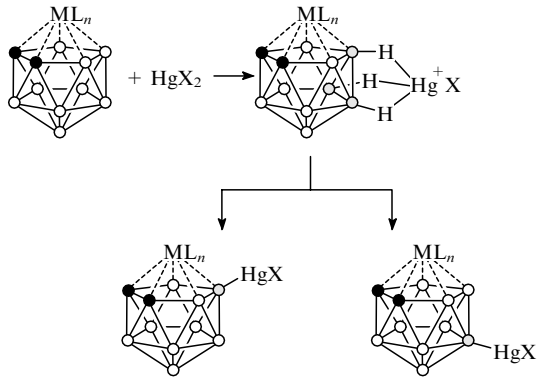
(*a*): 1) $Hg(OCOCF_3)_2$, $CF_3COOH - CH_2Cl_2$, 2) NaCl, H_2O;
(*b*): $Tl(OCOCF_3)_3$, Δ, CF_3COOH.

dichloromethane mixture followed by the replacement of the trifluoroacetoxy group with chlorine (Scheme 6). The reaction of compound **22** with bromine in dichloromethane afforded the corresponding bromide, *viz*., 9-Br-3-Cp-3,1,2-$FeC_2B_9H_{10}$ (**23**).[79]

In attempting to prepare a thallium derivative by heating ferracarborane **11** with thallium(III) trifluoroacetate in trifluoroacetic acid, the 8-trifluoroacetoxy derivative 8-CF_3COO-3-Cp-3,1,2-$FeC_2B_9H_{10}$ (**24**) was isolated instead of the expected thallation product. The structure of this reaction product was established by X-ray diffraction analysis.[80] The reaction with cobaltacarborane **7** proceeds analogously. However, this reaction afforded the 8-trifluoroacetoxy derivative 8-CF_3COO-3-Cp-3,1,2-$CoC_2B_9H_{10}$ along with a small amount of the 8-hydroxy derivative 8-OH-3-Cp-3,1,2-$CoC_2B_9H_{10}$.[80]

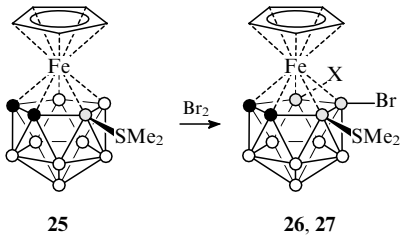
The mechanism of formation of trifluoroacetoxy derivative **24** remains unclear. Apparently, it may involve both the electrophilic substitution followed by elimination of thallium and the electrophile induced nucleophilic substitution with the initial attack of the thallium reagent followed by the attack of the trifluoroacetate anion (see below). The ricochet mechanism also cannot be ruled out.

Analysis of the above data shows that halogenation of metallacarboranes $[3\text{-L-}3,1,2\text{-}MC_2B_9H_{11}]^{n-}$ occurs first at position 8 and then at positions 9 and 12 of the metallacarborane moiety. Unlike halogenation, mercuration generally gives rise to a mixture of 8- and 9-substituted metallacarboranes with the 9-substituted isomer predominating. This anomaly is attributable to the fact that the first step of the process gives rise to an intermediate, in which the mercury atom coordinates the B(8)B(9)B(12) face of the metallacarborane moiety. The subsequent substitution can occur at both positions 8 and 9(12), and the product ratio depends on the electronic properties of the intermediate.



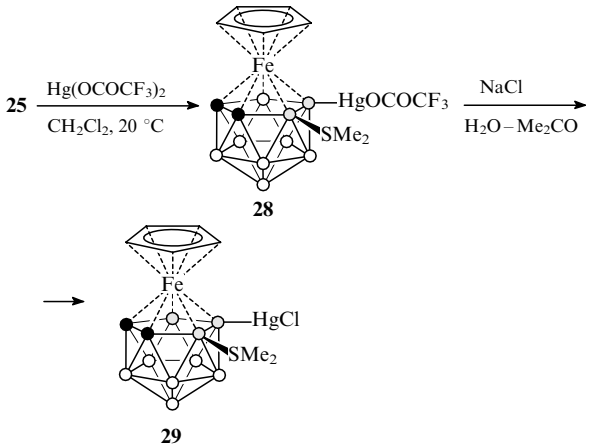
The formation of such boron hydride complexes with various transition metals is well known. The mercury complex $[Ph_4P][1,2,3\text{-}PhHg\text{-}1,2,3\text{-}(\mu\text{-}H)_3B_6H_3]$ was isolated and characterised by X-ray diffraction analysis.[81]

The influence of the *exo*-polyhedral substituents on the direction of substitution in metallacarborane systems is of interest. Let us consider the effect of the Me_2S^+ substituent in the carborane cage of diamagnetic ferracarborane 4-Me_2S-3-Cp-3,1,2-$FeC_2B_9H_{10}$ (**25**) on the mechanism of substitution. The reaction of compound **25** with 1 equiv. of bromine in dichloromethane affords the monobromo derivative 8-Br-4-Me_2S-3-Cp-3,1,2-$FeC_2B_9H_9$ (**26**), whereas the reaction with two or more equivalents of bromine gives rise to the disubstituted derivative 7,8-Br_2-4-Me_2S-3-Cp-3,1,2-$FeC_2B_9H_8$ (**27**). The use of $AlCl_3$ as the catalyst does not allow one to introduce more than two boron atoms into the ferracarborane moiety and the reaction forms dibromo derivative **27** as the final product. The structure of complex **27** was confirmed by X-ray diffraction analysis.[82]



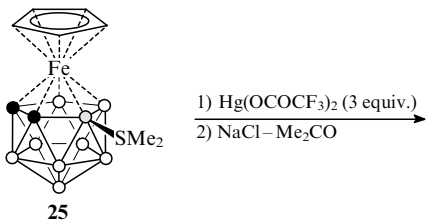
X = H (**26**), Br (**27**).

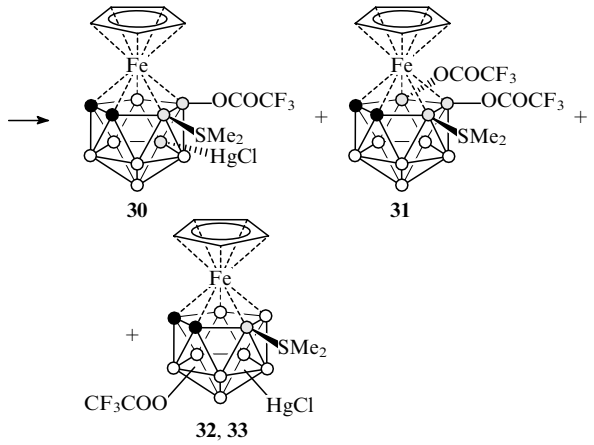
The reaction of compound **25** with mercury trifluoroacetate in a ratio of 1 : 1 in dichloromethane at room temperature yields 8-CF_3COOHg-4-Me_2S-3-Cp-3,1,2-$FeC_2B_9H_9$ (**28**) as the only product.[82]



The position of the substituent in ferracarborane **28** was determined by ^{11}B and $^{11}B-^{11}B$ COSY NMR spectroscopy and confirmed by X-ray diffraction study of its chloro derivative **29**.

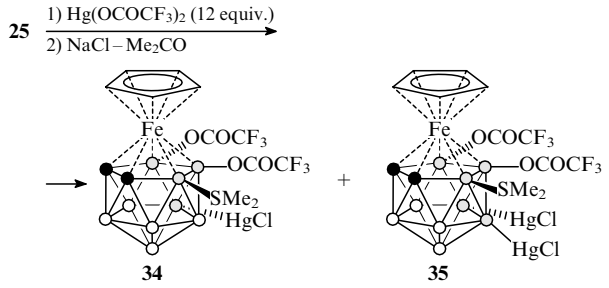
The reaction of ferracarborane **25** with a threefold excess of mercury trifluoroacetate gave a mixture of four products,[83] which were isolated as HgCl derivatives after treatment with sodium chloride in acetone.





This reaction afforded 8-CF_3COO-12-HgCl-4-Me_2S-3-Cp-3,1,2-$FeC_2B_9H_8$ (**30**) as the major product in 52% yield. In addition, the reaction produced small amounts of 7,8-$(CF_3COO)_2$-4-Me_2S-3-Cp-3,1,2-$FeC_2B_9H_8$ (**31**) containing three substituents at the open face and two isomers **32** and **33** each bearing one HgCl group and one CF_3COO fragment, the positions of which were not unambiguously determined.

The reaction with a 12-fold excess of the mercurating agent followed by treatment of the reaction mixture with NaCl gave a mixture of complexes **34** and **35**. The structures of the reaction products were determined by spectroscopic methods. The structure of ferracarborane **35** was confirmed by X-ray diffraction analysis.[83]



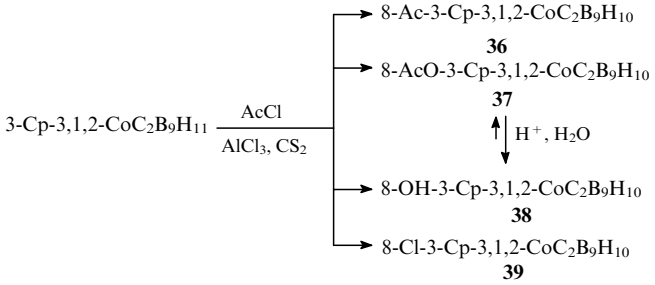
Therefore, from one to four substituents can be introduced into the carborane moiety depending on the ratio between the starting ferracarborane **25** and the mercurating agent (mercury trifluoroacetate).[82, 83]

It should be noted that further substitution in ferracarboranes depends on the nature of the substituents. For example, like in the case of unsubstituted derivative **11**, bromination of bromine-substituted ferracarboranes **15**, **16** and **17** leads to substitution at position 8. The introduction of the Me_2S^+ substituent has a much more substantial effect on the direction of substitution. Mercuration of unsubstituted ferracarborane **11** results in the replacement of the hydrogen atom at position 9(12), whereas mercuration of its 4-Me_2S^+-substituted derivative **25** leads to substitution of the hydrogen atom at position 8. Substitution at position 9 or 12 requires an excess of the mercurating agent, substitution at position 9 being attained only in the presence of a large excess of mercury trifluoroacetate due, apparently, to the deactivating effect of the Me_2S^+ group.

An analogous situation was observed earlier in the study of substitution in the *closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$. In this compound, the effect of *exo*-polyhedral substituents on the replacement of hydrogen atoms with electrophilic reagents is much less pronounced compared to carboranes and is manifested only in the presence of strong electron-withdrawing substituents (R_2O^+, R_2S^+ or R_3N^+).[84, 85] Unfortunately, data on the influence of the *exo*-polyhedral substituents on substitution in metallacarboranes are insufficient to give an unambiguous answer to this question. This problem requires additional investigation.

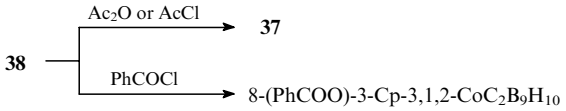
The reactions of metallacarboranes $[3\text{-L-}3,1,2\text{-}MC_2B_9H_{11}]^{n-}$ with arylsulfenyl chlorides provide yet another typical example of electrophilic substitution in this class of compounds. For instance, the reaction of 4-nitrophenylsulfenyl chloride with ferracarborane **11** in acetonitrile affords 8-(4-$NO_2C_6H_4S$)-3-Cp-3,1,2-$FeC_2B_9H_{10}$, whereas the analogous reaction with K[**1**] yields $[8,8'\text{-}(4\text{-}NO_2C_6H_4S)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$. Interestingly, the reactions of phenylsulfenyl and 2-nitrophenylsulfenyl chlorides with K[**1**] form the monosubstituted derivatives $[8\text{-ArS-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ (Ar = Ph or $C_6H_4NO_2$-2) as the final products even in the presence of an excess of ArSCl. This difference in the behaviour of sulfenyl halides was accounted for by the difference in the basicity of the sulfur atoms in the monosulfides that formed. In the case of phenylsulfenyl and 2-nitrophenylsulfenyl chlorides, protonation of sulfur with HCl that is eliminated affords the sulfonium salt, whose positive charge deactivates the molecule and hinders the replacement in the second dicarbollyl ligand.[86]

The use of other electrophilic reagents can give unexpected results. For instance, the reaction of cobaltacarborane **7** with acetyl chloride in carbon disulfide in the presence of $AlCl_3$ produced a complex mixture of acetyl (**36**), acetoxy (**37**), hydroxy (**38**) and chlorine derivatives (**39**).[73]



The substitution positions in 8-Ac-3-Cp-3,1,2-$CoC_2B_9H_{10}$ (**36**) and 8-AcO-3-Cp-3,1,2-$CoC_2B_9H_{10}$ (**37**) were determined by X-ray diffraction analysis.[73]

Acid hydrolysis of acetoxy derivative **37** gives the corresponding hydroxy derivative **38**. The reactions of the latter with acetic anhydride, acetyl chloride and benzoyl chloride afford the corresponding acyloxy derivatives.



Reduction of acetyl derivative **36** with zinc in hydrochloric acid gives the corresponding ethyl derivative 8-Et-3-Cp-3,1,2-$CoC_2B_9H_{10}$.[73]

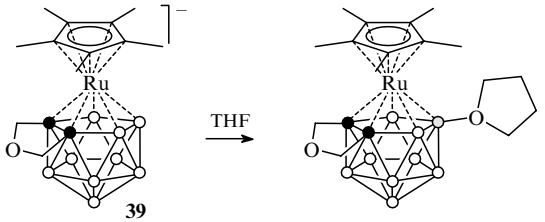
The reactions of cobaltacarborane **7** and its methyl- [1-Me-3-Cp-3,1,2-$CoC_2B_9H_{10}$ (**7a**)] and phenyl-substituted derivatives [1-Ph-3-Cp-3,1,2-$CoC_2B_9H_{10}$ (**7b**)] with acetyl chloride in dichloroethane in the presence of $AlCl_3$ form the corresponding hydroxy derivatives, *viz.*, 8-OH-3-Cp-3,1,2-$CoC_2B_9H_{10}$ (**38**), 1-Me-8-OH-3-Cp-3,1,2-$CoC_2B_9H_9$ (**38a**) and 1-Ph-8-OH-3-Cp-3,1,2-$CoC_2B_9H_9$ (**38b**).[29] Heating of compound **7** and CrO_3 in a mixture of acetic anhydride, acetic acid and sulfuric acids affords a mixture of hydroxy, acetoxy and diacetoxy derivatives.[29]

The above results provide evidence that the substitution in carbon disulfide occurs by competitive mechanisms of electrophilic and electrophile induced nucleophilic substitution, whereas substitution in dichloroethane occurs predominantly by the latter mechanism.

Analogously, the reactions of Cs[8,8′,9-Cl_3-3,3′-Co(1,2-$C_2B_9H_9$)(1′,2′-$C_2B_9H_{10}$)] (**4**) with alkyl halides in the presence of $AlCl_3$ afford complex mixtures of halogen- and alkyl-substituted derivatives.[87] In our opinion, this fact can also be attributable to competition between two substitution mechanisms.

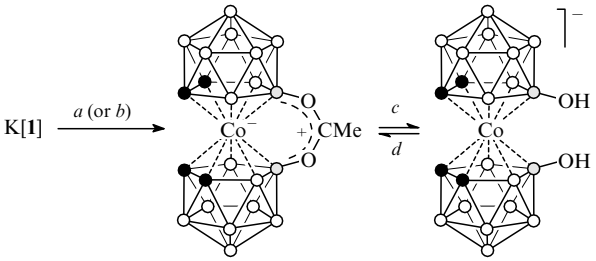
We believe that the formation of nitrates 8-NO_3-3-Cp-3,1,2-$CoC_2B_9H_{10}$, 1-Ph-8-NO_3-3-Cp-3,1,2-$CoC_2B_9H_9$ and 8-NO_3-3-(η^5-$C_5H_4C_6H_4NO_2$)-3,1,2-$CoC_2B_9H_{10}$ by nitration of the compounds **7**, **7b** and 3-(η^5-C_5H_4Ph)-3,1,2-$CoC_2B_9H_{11}$ with a mixture of nitric and sulfuric acids in dichloromethane [87] also occurs by the mechanism of electrophile induced nucleophilic substitution. Reduction of these nitrates with tin in hydrochloric acid affords the corresponding hydroxy derivatives.[87]

The reaction of the [3-C_5Me_5-3,1,2-$RuC_2B_9H_{11}$]$^-$ complex with [CpFe(C_6H_6)]$^+$ in tetrahydrofuran under UV irradiation produces 8-$(CH_2)_4O$-3-C_5Me_5-3,1,2-$RuC_2B_9H_{10}$, which is a product of electrophile induced nucleophilic substitution.[88] An analogous result was obtained in the reaction of [1,2-(μ-CH_2OCH_2)-3-C_5Me_5-3,1,2-$RuC_2B_9H_9$]$^-$ (**39**) with [(C_5Me_5)RuCl]$_4$ in tetrahydrofuran.[88]



39

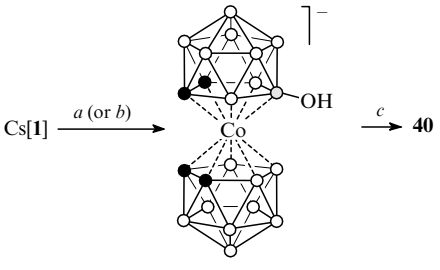
The reaction of acetic anhydride with K[**1**] in sulfuric acid or in acetic acid in the presence of $HClO_4$ proceeds in an unusual way.[89,90] Apparently, this reaction also occurs by the mechanism of electrophile induced nucleophilic substitution but gives 8,8′-(μ-AcO)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$ (**40**) in which two dicarbollyl ligands are linked by the bridging acetate group through the B(8) and B(8′) atoms.[89,90] The structure of compound **40** was established by X-ray diffraction analysis.[90] Hydrolysis of the acetate derivative in boiling aqueous ethanol affords the corresponding diol [8,8′-(HO)$_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$ (**41**).[89,90]



40 **41**

(*a*) Ac_2O, H_2SO_4, 80 °C; (*b*) Ac_2O, AcOH, $HClO_4$;
(*c*) H^+, 50% EtOH, 80 °C; (*d*) Ac_2O, H_2SO_4, 80 °C.

Dihydroxy derivative **41** can also be prepared by heating Cs[**1**] in 80% sulfuric acid to 140 °C. Heating of Cs[**1**] in 60% sulfuric acid at 120 °C affords the monohydroxy derivative [8-OH-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ (**42**). The latter was prepared also by heating Cs[**1**] with acetic anhydride in a mixture of acetic and sulfuric acids.



42

(*a*) 60% H_2SO_4, 120 °C; (*b*) Ac_2O, AcOH, $HClO_4$; (*c*) Ac_2O, H_2SO_4, 80 °C.

The reactions of both mono- and dihydroxy derivatives with acetic anhydride in sulfuric acid produce bridged acetate derivative **40**.[90]

The reaction of Cs[**41**] with $POCl_3$ in chloroform in the presence of triethylamine yields the bridged [Et_3NH][8,8′-(μ-OPO(Cl)O)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] derivative (**43**). Hydrolysis of the latter affords acid [8,8′-(μ-OPO(OH)O)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$.

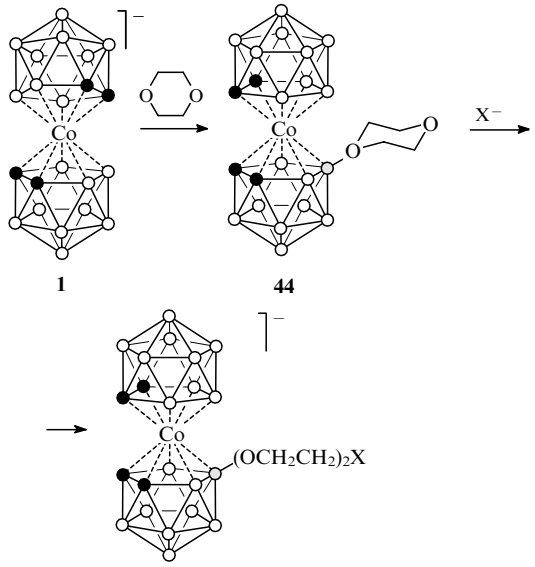
The reaction of compound **43** with diethylamine produces the corresponding amide [Et_3NH][8,8′-(μ-OPO(NEt_2)O)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] (**43a**).[91] The structures of compounds **43** and **43a** were established by X-ray diffraction analysis.[90] The reactions of monohydroxy derivative **42** with $POCl_3$ and $PhPOCl_2$ followed by hydrolysis afford [8-PO_2(OH)$_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ and [8-HO_2P(Ph)O-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$, respectively.[91]

It should be noted that the formation of bridged derivatives is typical of the chemistry of cobalt and iron bis(dicarbollyl) complexes, although the latter complex was studied to a much lesser extent.

The reaction of Cs[**1**] with dimethyl sulfate in the presence of $AlCl_3$ at 80 °C forms the sulfate-bridged derivative [8,8′-(μ-OSO_2O)-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$. The structure of its tetramethylammonium salt was determined by X-ray diffraction analysis.[92]

Heating of Cs[**1**] with dimethyl sulfate and sulfuric acid in 1,4-dioxane affords the oxonium derivative 8-O(CH_2CH_2)$_2$O-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$) (**44**).[92] This compound was also prepared by heating Cs[**1**] with $BF_3 \cdot OEt_2$ in 1,4-dioxane.[93] It should be noted that monosubstituted bis(dicarbollyl)cobalt derivatives are generated primarily by introducing onium substituents, whose involvement in the carborane ligand gives rise to neutral charge-compensated products. The presence of the positive charge on the onium substituent causes a substantial electron density redistribution in the metallacarborane moiety and deactivation of the second dicarbollyl ligand.

The reactions of compound **44** with various nucleophilic agents are accompanied by the dioxane-ring opening to form various functional derivatives with composition [8-X(CH_2CH_2O)$_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]$^-$ [X = OH, OR, CN, NH_2, $CH(NH_2)COOH$, P(O)$(OBu)_2$, P(O)(OBu)OH, NEt_3, Py].[18,27,93,94]

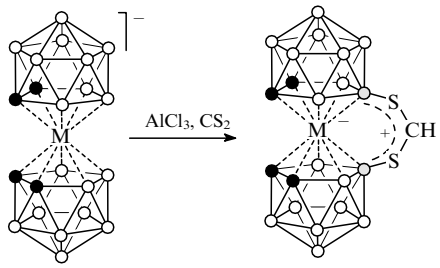


1 **44**

Analogously, the reaction of Cs[**1**] with dimethyl sulfate in the presence of sulfuric acid in tetrahydropyran yields 8-$C_5H_{10}O$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$) (**45**). The tetrahydropyran-ring opening in the reactions of derivative **45** with nucleophiles made it possible to prepare a series of derivatives of the [8-X(CH_2)$_5$O-3,3′-

$Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ type (X is 1-pyrrolyl, 1-indolyl or 9-carbazolyl).[95]

Thioformate-bridged bis(dicarbollyl) derivatives of cobalt and iron, 8,8′-(μ-HCS_2)-3,3′-M(1,2-$C_2B_9H_{10})_2$ (**46** and **47**), were prepared by the reactions of K[**1**] and K[**9**], respectively, with carbon disulfide in the presence of aluminium chloride.[89,96] The structure of compound **46** was determined by X-ray diffraction analysis.[96]



1, **9** **46**, **47**

M = Co (**1**, **46**), Fe (**9**, **47**).

Hydrolysis of compound **46** in boiling 50% ethanol affords the dimercapto derivative [8,8′-$(HS)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**48**). Oxidation of the latter with hydrogen peroxide gives [8,8′-(μ-S_2)-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**49**), in which the dicarbollyl fragments are linked by the disulfide bridge.[89,96] Derivative **49** was also prepared by heating Cs[**1**] with S_2Cl_2 in dichloromethane.[97]

Refluxing of $[(Me_2SO)_2H]^+$[**1**]$^-$ with acetic anhydride in benzene gives rise to the monosubstituted dimethylsulfonium derivative 8-Me_2S-3,3′-Co(1,2-$C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})$ (**50**),[97] which can also be prepared by assembly from $CoCl_2$ and the corresponding dicarbollyl ligands.[98] The analogous diethylsulfonium derivative 8-Et_2S-3,3′-Co(1,2-$C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})$ (**51**) was synthesised by the reaction of [Ph_3PMe][**1**] with diethyl sulfide in a strongly acidic medium.[99]

Treatment of a suspension of ferracarborane [Ph_3PMe][**9**] with gaseous HCl in diethyl sulfide yields a mixture of 8-Et_2S-3,3′-Fe^{III}(1,2-$C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})$ (**52**) and 8,8′-$(Et_2S)_2$-3,3′-Fe(1,2-$C_2B_9H_{10})_2$ (**53**).[99] The charge-compensated complex **52** can also be synthesised by oxidation of the [8-Et_2S-3,3′-Fe^{II}(1,2-$C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ anion.[99]

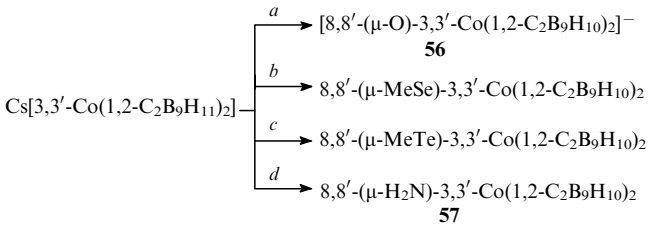
The carborane derivative [8,8′-(μ-S)-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ (**54**) containing a one-atom sulfide bridge was synthesised[100] by refluxing $[(Me_2SO)_2H]$[**1**] with S_2Cl_2 in dichloromethane followed by methanolysis and reprecipitation. Complex **54** can also be prepared by refluxing compound **1** with sulfur in benzene in the presence of $AlCl_3$.[97]

The reaction of complex **54** with dimethyl sulfate produces the neutral complex 8,8′-(μ-MeS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ (**55a**).[97,100] The latter can also be prepared by intramolecular cross-linking of compound **50** in boiling benzene in the presence of $AlCl_3$ [the reaction gives 8-Me_2S-8′-Cl-3,3′-Co(1,2-$C_2B_9H_{10})_2$ as the second product].[97]

The sulfonium derivatives 8,8′-(μ-RS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ [R = Et (**55b**), Bu (**55c**), Bn (**55d**), $CH_2CH{=}CH_2$ (**55e**), $CH_2C{\equiv}CH$ (**55f**) and CH_2COOH (**55g**)] were prepared by the reactions of compound **54** with the corresponding halides.[15,97] Protonation of derivative **54** with sulfuric acid in benzene affords very active acid 8,8′-(μ-HS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$, which readily reacts with acrylonitrile and formaldehyde to form 8,8′-(μ-RS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ [R = CH_2CH_2CN (**55h**), CH_2OMe (**55i**)].[97,101] The reaction of complex **54** with bromine in acetic acid gives unstable bromide 8,8′-(μ-BrS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$, which immediately reacts with benzene in the presence of $AlCl_3$ to form 8,8′-(μ-PhS)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ (**55j**).[97]

Oxygen, selenium, tellurium and nitrogen atoms can also serve as bridges linking the dicarbollyl ligands (Scheme 7).[42]

Scheme 7



(*a*) HCHO, H_2SO_4, Ac_2O; (*b*) 1) SeO_2, H_2SO_4, Ac_2O, C_6H_6, 2) KOH – Me_2SO_4; (*c*) 1) Te, H_2SO_4, Ac_2O, 2) KOH – Me_2SO_4; (*d*) $NaNO_2$, H_2SO_4, C_6H_6.

Heating of cobaltacarborane Cs[**1**] with formaldehyde in acetic anhydride in the presence of sulfuric acid affords the [8,8′-(μ-O)-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ complex (**56**)[42,102] [in the absence of formaldehyde, 8,8′-(μ-EtO)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ was obtained[42]]. Derivative **56** was also prepared by refluxing [8-Me-8′-HO-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ with iodine in ethanol.[58]

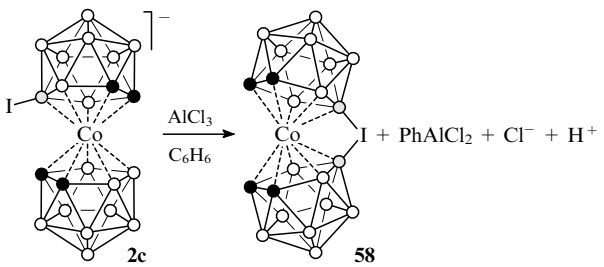
The reaction of ferracarborane **9** with formaldehyde in the presence of HCl produces 8,8′-(μ-MeO)-3,3′-Fe(1,2-$C_2B_9H_{10})_2$. Its structure was established by X-ray diffraction analysis.[103] By contrast, the reaction of nickelacarborane **19** with formaldehyde in a strongly acidic medium affords a mixture of the methoxy derivatives 8-MeO-3,3′-Ni(1,2-$C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})$ and 8,8′-$(MeO)_2$-3,3′-Ni(1,2-$C_2B_9H_{10})_2$ (the structure of the disubstituted derivative was established by X-ray diffraction analysis[104]) rather than the bridged derivative.

The reaction of Cs[**1**] with H_2SeO_3 in a mixture of benzene, acetic anhydride and sulfuric acid followed by treatment of the intermediate with dimethyl sulfate yields 8,8′-(μ-MeSe)-3,3′-Co(1,2-$C_2B_9H_{10})_2$, whereas heating of Cs[**1**] with tellurium in a mixture of acetic anhydride and sulfuric acid followed by treatment of the intermediate with dimethyl sulfate gives 8,8′-(μ-MeSe)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ (see Scheme 7).[42]

The reaction of Cs[**1**] with $NaNO_2$ in a $C_6H_6 - H_2SO_4$ mixture produces a mixture of 8,8′-(μ-H_2N)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ (**57**) (47%), 4,8′-(μ-H_2N)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ (6%) and 8,8′-(μ-NH_2O)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ (21%).[42,105,106] Methylation of compound **57** with dimethyl sulfate in a benzene – water mixture in the presence of KOH gives rise to the *N*-methyl derivative 8,8′-(μ-MeNH)-3,3′-Co(1,2-$C_2B_9H_{10})_2$, whereas methylation in an aqueous solution affords the *N*,*N*-dimethyl derivative 8,8′-(μ-Me_2N)-3,3′-Co(1,2-$C_2B_9H_{10})_2$.[87] The reaction of compound **57** with chloroacetic acid in methanol in the presence of KOH yields 8,8′-(μ-$HOOCCH_2NH$)-3,3′-Co(1,2-$C_2B_9H_{10})_2$.[107]

Refluxing of Cs[**1**] with white phosphorus in benzene in the presence of $AlCl_3$ followed by alkylation with dimethyl sulfate in alkaline ethanol affords a mixture of 8,8′-(μ-Me_2P)-3,3′-Co(1,2-$C_2B_9H_{10})_2$ and 8-Me_3P-3,3′-Co(1,2-$C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})$ in low yields.[107]

The iodonium-bridged derivative Cs[8,8′-(μ-I)-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (**58**) was synthesised by refluxing Cs[**2c**] in benzene in the presence of $AlCl_3$.[108]



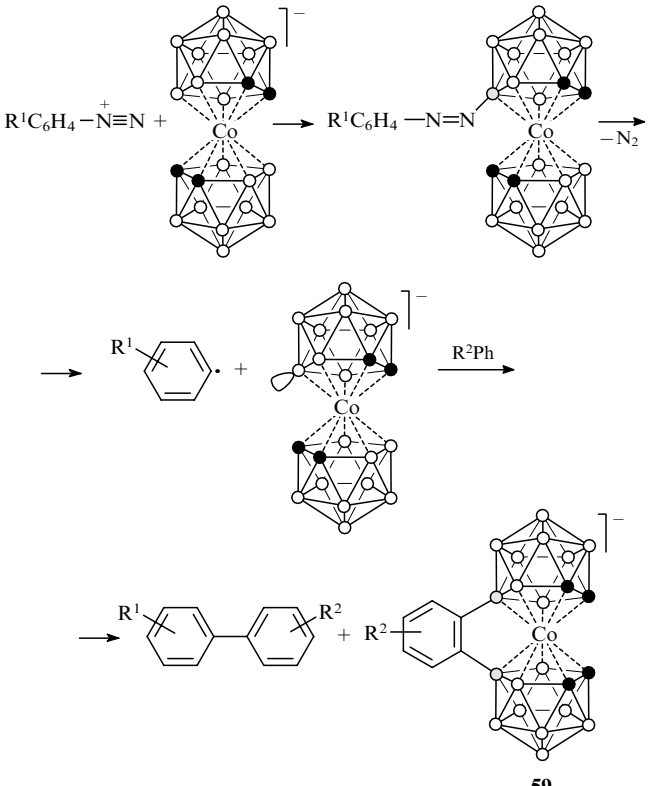
2c **58**

Compound **58** is highly reactive and is readily transformed into the corresponding bifunctional derivatives 8-I-8′-L-3,3′-$Co(1,2\text{-}C_2B_9H_{10})_2$ under the action of Lewis bases L, such as SMe_2, C_5H_5N, Me_3N and NH_3. An analogous bromonium-bridged derivative is very unstable due to which it was not isolated in the individual state. However, products of its reactions with dimethyl sulfide and dioxane with composition 8-Br-8′-L-3,3′-$Co(1,2\text{-}C_2B_9H_{10})_2$ (L = Me_2S and 1,4-$O_2C_4H_8$, respectively) were isolated.[109]

An interesting result was obtained when performing the reaction of an aqueous solution of K[**1**] with phenyldiazonium borofluoride. The reaction was accompanied by cation exchange to form the phenyldiazonium salt of bis(dicarbollyl)cobalt [PhN_2][**1**] instead of the expected arylation or coupling products.[110] At room temperature, this salt is virtually insoluble in benzene, but it completely dissolves on heating above 60 °C with elimination of N_2 to give biphenyl and the [8,8′-(μ-1,2-C_6H_4)-3,3′-$Co(1,2\text{-}C_2B_9H_{10})_2]^-$ complex (**59**).

Refluxing of the unstable phenyldiazonium salt of bis(dicarbollyl)iron [PhN_2][**9**] in benzene also affords the 1,2-phenylene-bridged [8,8′-(μ-1,2-C_6H_4)-3,3′-$Fe(1,2\text{-}C_2B_9H_{10})_2]^-$ compound.[111]

Decomposition of the phenyldiazonium salt in toluene and decomposition of the tolyldiazonium salt in benzene give rise to tolyl- and phenylene-bridged complexes, respectively, and methylbiphenyl (this is evidence that the aryl group of the diazonium cation is not involved in the reaction product).[110, 111]

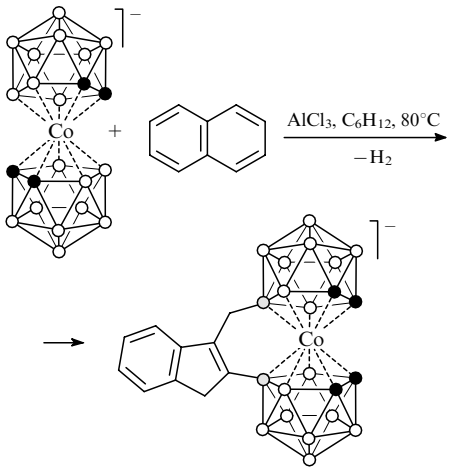


59

R^1, R^2 = H, Me.

The reaction of cobaltacarborane **1** with benzene in the presence of aluminium chloride produces bridged compound **59** (R^2 = H) and cobaltacarborane [4,8′-8,4′-(μ-1,2-C_6H_4)$_2$-3,3′-$Co(1,2\text{-}C_2B_9H_9)_2]^-$ containing two bridging 1,2-phenylene groups. The structures of these compounds were confirmed by X-ray diffraction analysis.[111, 112]

The reaction of compound **1** with naphthalene at 80 °C yields a 1-methyleneinden-2-yl-bridged derivative (which was proved by X-ray diffraction analysis).[113]

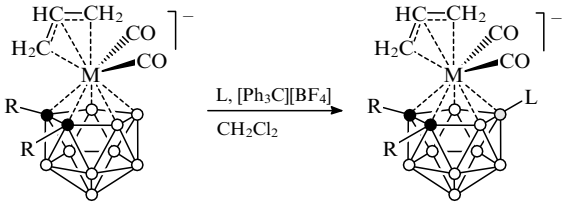


An interesting result was obtained in the reaction of $Me_3SiC{\equiv}CH$ with the complex Cs[**2c**] in the presence of a Pd catalyst (under conditions of the Sonogashira reaction). This reaction gives the ethene-bridged derivative [8,8′-(μ-CH = CH)-3,3′-$Co(1,2\text{-}C_2B_9H_{10})_2]^-$ instead of the expected addition product of acetylene with composition [8-$Me_3SiC{\equiv}$C-3,3′-$Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$. The structure of the caesium salt of the reaction product was established by X-ray diffraction analysis.[114] The synthesis of the alkyl and aryl derivatives [8-R-3,3′-$Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ by Pd-catalysed cross-coupling of the complex [**2c**] with organomagnesium and -zinc reagents was mentioned above.[59, 60]

The phenyl derivative [8-Ph-3,3′-$Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ was also prepared by the direct reaction of Cs[**1**] with dimethyl sulfate in benzene at 80 °C in the presence of concentrated sulfuric acid.[92] The diphenyl derivative [6,6′-Ph_2-3,3′-$Co(1,2\text{-}C_2B_9H_{10})_2]^-$ was synthesised by the reaction of Na_2[3-Ph-7,8-$C_2B_9H_{10}$] with $CoCl_2$ in tetrahydrofuran followed by precipitation as the tetramethylammonium salt.[115]

Metallacarborane complexes containing labile ligands in the metal coordination sphere are characterised by diverse chemistry because the presence of labile ligands increases the probability of substitution reactions involving the metal atom. In addition, such metallacarboranes can be involved in the above-mentioned electrophilic and electrophile induced nucleophilic substitution reactions.

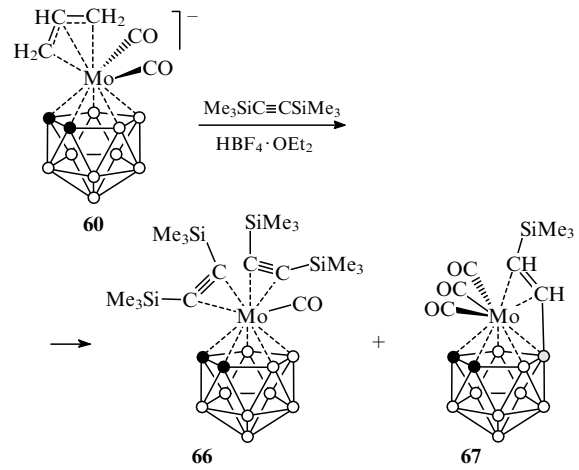
For example, the reaction of [Et_4N][3-(η^3-C_3H_5)-3,3-$(CO)_2$-3,1,2-$MoC_2B_9H_{11}$] (**60**) with [Ph_3C][BF_4] and Et_2O in dichloromethane affords 8-Et_2O-3-(η^3-C_3H_5)-3,3-$(CO)_2$-3,1,2-$MoC_2B_9H_{10}$ (**61**), which is a typical product of electrophile induced nucleophilic substitution. The reactions of [Et_4N][1,2-Me_2-3-(η^3-C_3H_5)-3,3-$(CO)_2$-3,1,2-$MoC_2B_9H_9$] (**62**) with various donor molecules L proceed analogously. This procedure was used for the synthesis of various charge-compensated complexes 8-L-1,2-Me_2-3-(η^3-C_3H_5)-3,3-$(CO)_2$-3,1,2-$MoC_2B_9H_8$ (**63a**–**f**) (L = OEt_2, THF, SMe_2, PPh_3, Py, 4,4′-bipy). The reaction of [Et_4N][1,2-Me_2-3-(η^3-C_3H_5)-3,3-$(CO)_2$-3,1,2-$WC_2B_9H_9$] (**64**) with [Ph_3C][BF_3] and Et_2O also yields the 8-substituted derivative 8-Et_2O-1,2-Me_2-3-(η^3-C_3H_5)-3,3-$(CO)_2$-3,1,2-$WC_2B_9H_8$ (**65**).[116]



60, **62**, **64** **61**, **63a**–**f**, **65**

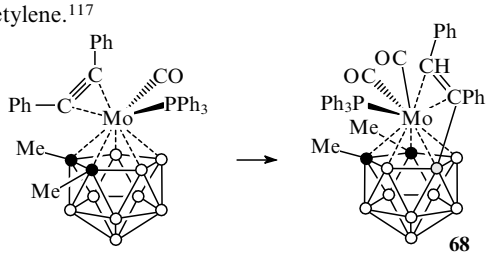
Compound	M	R	L	Compound	M	R	L
60	Mo	H	–	**63d**	Mo	Me	PPh_3
61	Mo	H	OEt_2	**63e**	Mo	Me	Py
62	Mo	Me	–	**63f**	Mo	Me	4,4′-bipy
63a	Mo	Me	OEt_2	**64**	W	Me	–
63b	Mo	Me	THF	**65**	W	Me	OEt_2
63c	Mo	Me	SMe_2				

Treatment of compounds **63a** and **65** with nucleophilic agents ($K[HBBu^s_3]$ and Et_4NX, where X = Cl or F) leads to elimination of one ethyl group to form $[Et_4N][8\text{-EtO-1,2-Me}_2\text{-3-}(\eta^3\text{-C}_3\text{H}_5)\text{-3,3-(CO)}_2\text{-3,1,2-MC}_2\text{B}_9\text{H}_8]$ (M = Mo, W), whereas treatment of the tetrahydrofuran derivative $8\text{-(CH}_2)_4\text{O-1,2-Me}_2\text{-3-}(\eta^3\text{-C}_3\text{H}_5)\text{-3,3-(CO)}_2\text{-3,1,2-MoC}_2\text{B}_9\text{H}_8$ (**63b**) with the R_4NF salt (R = Et, Bu) results in the tetrahydrofuran-ring opening to give $[R_4N][8\text{-F(CH}_2)_4\text{O-1,2-Me}_2\text{-3-}(\eta^3\text{-C}_3\text{H}_5)\text{-3,3-(CO)}_2\text{-3,1,2-MoC}_2\text{B}_9\text{H}_8]$.[116] By contrast, the reaction of complex **60** with $Me_3SiC{\equiv}CSiMe_3$ in the presence of $HBF_4\cdot Et_2O$ gives rise to a mixture of $3,3\text{-}(\eta^2\text{-Me}_3\text{SiC}{\equiv}\text{CSiMe}_3)_2\text{-3-CO-3,1,2-MoC}_2\text{B}_9\text{H}_{11}$ (**66**) and $8,3\text{-}(\sigma,\eta^2\text{-Me}_3\text{SiCH}{=}\text{CH})\text{-3,3,3-(CO)}_3\text{-3,1,2-MoC}_2\text{B}_9\text{H}_{10}$ (**67**).[117] It is assumed that the first step involves the replacement of the labile (allyl and carbonyl) ligands with the alkyne molecule $Me_3SiC{\equiv}CSiMe_3$. The second step involves, apparently, the formation of the vinylidene fragment $Mo{=}C{=}CHSiMe_3$ followed by its insertion into the B–H bond of the pentagonal face of the dicarbollyl ligand.



60 **66** **67**

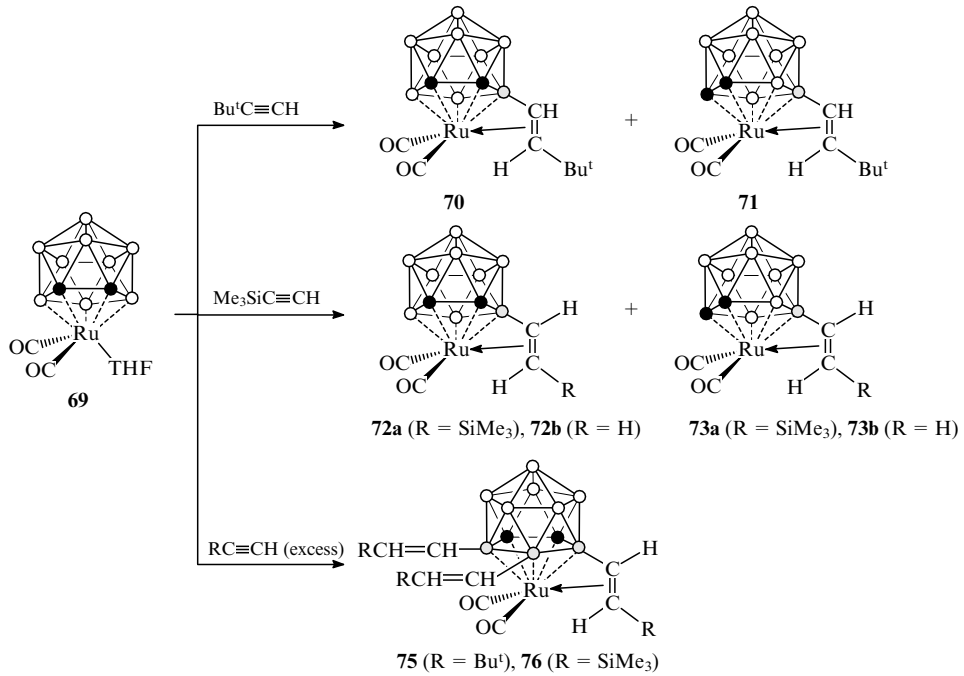
An analogous complex with composition $8,3\text{-}(\sigma,\eta^2\text{-PhCH}{=}\text{CPh})\text{-1,2-Me}_2\text{-3,3-(CO)}_2\text{-3-Ph}_3\text{P-3,1,2-MoC}_2\text{B}_8\text{H}_8$ (**68**) was prepared by the rearrangement of $1,2\text{-Me}_2\text{-3-CO-3-Ph}_3\text{P-3-}(\eta^2\text{-PhC}{\equiv}\text{CPh})\text{-3,1,2-MoC}_2\text{B}_9\text{H}_9$ in dichloromethane at room temperature, which is evidence for the formation of the acetylene complex in the first step of the reaction of metallacarborane with acetylene.[117]



68

Ruthenacarborane $3,3\text{-(CO)}_2\text{-3-THF-3,1,2-RuC}_2\text{B}_9\text{H}_{11}$ (**69**) reacts with $Bu^tC{\equiv}CH$ to give a mixture of isomeric derivatives (Scheme 8), *viz.*, $4,3\text{-}(\sigma,\eta^2\text{-Bu}^t\text{CH}{=}\text{CH})\text{-3,3-(CO)}_2\text{-3,1,2-}$

Scheme 8



69

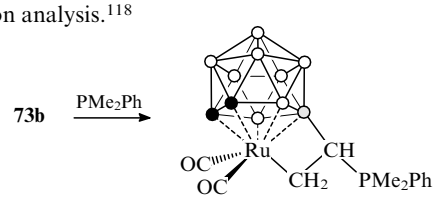
70 **71**

72a (R = $SiMe_3$), **72b** (R = H) **73a** (R = $SiMe_3$), **73b** (R = H)

75 (R = Bu^t), **76** (R = $SiMe_3$)

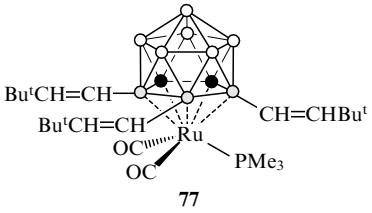
$RuC_2B_9H_{10}$ (**70**)‡ and 8,3-(σ,η^2-Bu^{t}CH = CH)-3,3-$(CO)_2$-3,1,2-$RuC_2B_9H_{10}$ (**71**).[118] The reaction of compound **69** with $Me_3SiC{\equiv}CH$ is accompanied by partial elimination of the $SiMe_3$ group to form a mixture of isomers 4,3-(σ,η^2-RCH = CH)-3,3-$(CO)_2$-3,1,2-$RuC_2B_9H_{10}$ (**72a**,**b**) and 8,3-(σ,η^2-RCH = CH)-3,3-$(CO)_2$-3,1,2-$RuC_2B_9H_{10}$ (**73a**,**b**) (R = $SiMe_3$, H), respectively, with the 4-isomer **72a** predominating.

Compound **73b** reacts with $PhMe_2P$ in heptane to give the ylide complex 8-[σ-$CH_2CH(PMe_2Ph)$]-3,3-$(CO)_2$-3,1,2-$RuC_2B_9H_{10}$ (**74**). Its structure was determined by X-ray diffraction analysis.[118]

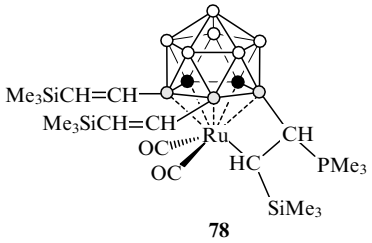


74

The reactions with an excess of alkyne RC≡CH (R = Bu^t, Me_3Si) produce the 4,3-(σ,η^2-RCH = CH)-7,8-(RCH = CH)$_2$-3,3-$(CO)_2$-3,1,2-$RuC_2B_9H_8$ complexes (**75**, R = Bu^t; **76**, R = $SiMe_3$) containing three alkene fragments in the open face of the dicarbollyl ligand. Treatment of complex **75** with trimethylphosphine leads to the replacement of the vinyl substituent from the metal coordination sphere to form 4,7,8-(Bu^{t}CH = CH)$_3$-3,3-$(CO)_2$-3-Me_3P-3,1,2-$RuC_2B_9H_8$ (**77**), whose structure was established by X-ray diffraction analysis. The reaction of PMe_3 with trimethylsilyl derivative **76** yields ylide 4-[σ-CH($SiMe_3$)CH(PMe_3)]-7,8-(Me_3SiCH = CH)$_2$-3,3-$(CO)_2$-3,1,2-$RuC_2B_9H_8$ (**78**).[118]



77



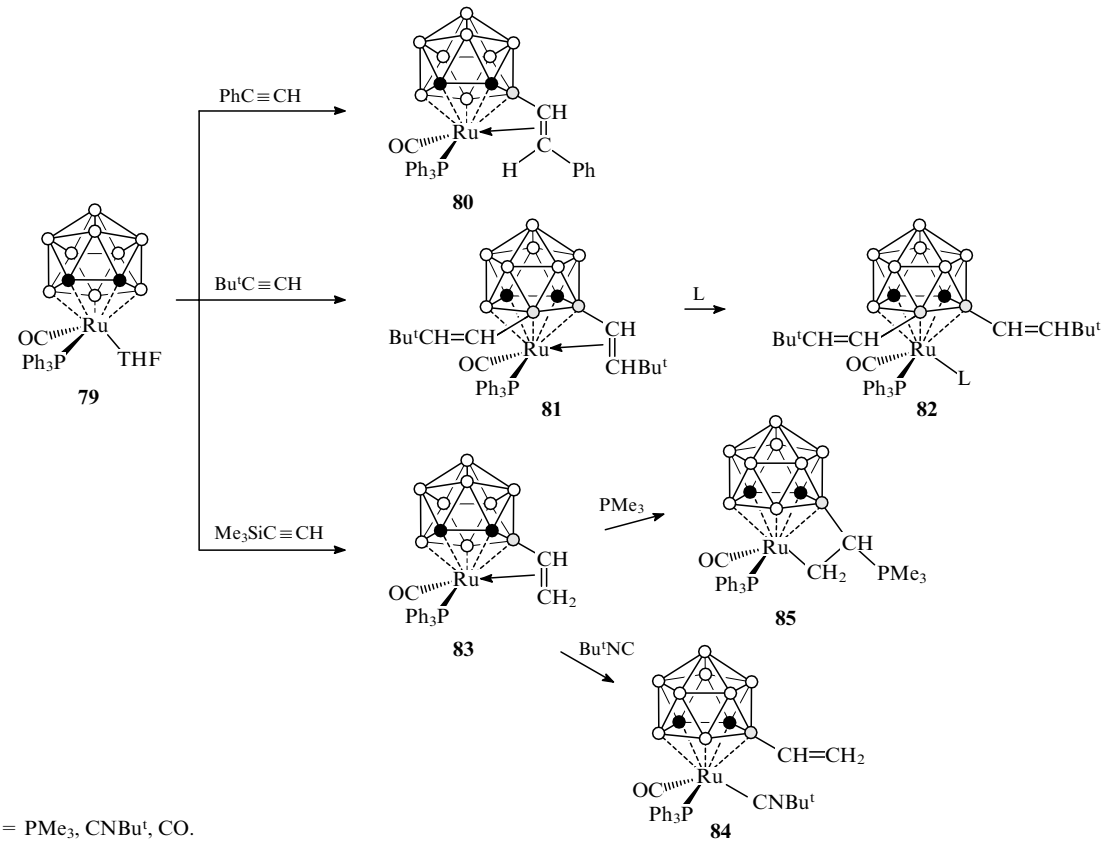
78

Interestingly, the reaction of ruthenacarborane 3-CO-3-Ph_3P-3-THF-3,1,2-$RuC_2B_9H_{11}$ (**79**) containing the triphenylphosphine ligand with a threefold excess of PhC≡CH is accompanied by the selective replacement of the hydrogen atom at position 4 nearest to the carbon atom of the dicarbollyl ligand to form the 4,3-(σ,η^2-PhCH = CH)-3-CO-3-Ph_3P-3,1,2-$RuC_2B_9H_{10}$ complex (**80**), whose structure was established by X-ray diffraction analysis.[119] By contrast, the reaction with a threefold excess of Bu^{t}C≡CH gives the disubstituted derivative 4,3-(σ,η^2-Bu^{t}CH = CH)-8-(Bu^{t}CH = CH)-3-CO-3-Ph_3P-3,1,2-$RuC_2B_9H_9$ (**81**) (Scheme 9). The reactions of the latter with PMe_3, CNBu^t and CO are accompanied by the displacement of the vinyl substituent from the metal coordination sphere to form 4,8-(Bu^{t}CH = CH)$_2$-3-CO-3-Ph_3P-3-L-3,1,2-$RuC_2B_9H_9$ (**82**) (L = PMe_3, CNBu^t and CO, respectively). The reaction of compound **79** with $Me_3SiC{\equiv}CH$ yields the 4,3-(σ,η^2-H_2C = CH)-3-CO-3-Ph_3P-3,1,2-$RuC_2B_9H_{10}$ isomer (**83**) as the only product. The latter reacts with CNBu^t and Me_3P to form 4-(H_2C = CH)-3-CO-3-Ph_3P-3-Bu^{t}NC-3,1,2-$RuC_2B_9H_{10}$ (**84**)§ and ylide 4-[σ-$CH_2CH(PMe_3)$]-3-CO-3-Ph_3P-3,1,2-$RuC_2B_9H_{10}$ (**85**), respectively.[119]

‡ The structure of complex **70** was established by X-ray diffraction.[118]

§ The structure of compound **84** was established by X-ray diffraction.

Scheme 9



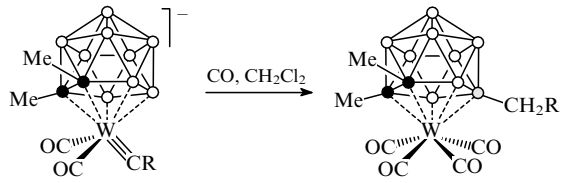
79 **80** **81** **82** **83** **85** **84**

L = PMe_3, CNBu^t, CO.

In most of the above-described examples, the reactions with the use of an excess of alkyne lead to the replacement of the H atoms in the band of the dicarbollyl ligand nearest to the metal atom; the degree of substitution may be as high as 3 (compounds **75** and **76**). The assumed mechanism of substitution involves the replacement of the labile ligand (for example, THF or CO) with the alkyne group η^2-RC≡CR, the rearrangement of the latter to form the vinylidene fragment Ru=C=CHR, its subsequent insertion into the B–H bond of the dicarbollyl ligand, and the displacement of the vinyl substituent from the metal coordination sphere with the next alkyne molecule. However, the degree of substitution in ruthenacarborane **79** containing the PPh_3 ligand in the presence of an excess of alkyne is no higher than 2, which is attributable to steric hindrance caused by the bulky triphenylphosphine substituent. However, the influence of the electronic properties of the ligands involved in the coordination environment about the metal atom on the depth of substitution cannot also be ruled out.

Recently, it has been demonstrated that metal-induced activation of the B–H bond can occur not only in metallacarboranes but also in metal complexes containing substituted *o*-carborane derivatives as a ligand. For example, the reaction of the Cp*Rh(1,2-S_2-1,2-$C_2B_{10}H_{10}$) complex with HC≡CCOOMe affords the substituted Cp*Rh(3,6-(μ-MeOOCCH=CH)$_2$-1,2-S_2-1,2-$C_2B_{10}H_8$) complex.[120, 121]

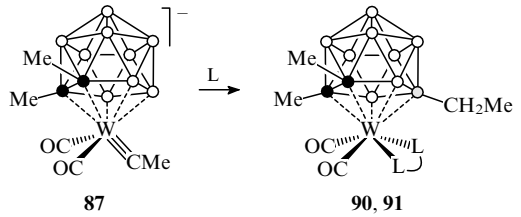
The rearrangement of the alkylidyne complexes belong to another type of reactions involving metal. The reaction of [Et_4N][1,2-Me_2-3-(≡CR)-3,3-$(CO)_2$-3,1,2-$WC_2B_9H_9$] [R = C_6H_4Me-4 (**86**), Me (**87**)] with $HBF_4 \cdot Et_2O$ in a saturated CO solution in dichloromethane is accompanied by the migration of the alkylidyne group to the carborane moiety to form the 8-RCH_2-1,2-Me_2-3,3,3,3-$(CO)_4$-3,1,2-$WC_2B_9H_8$ complexes (**88**, **89**).[122]



86, **87** **88**, **89**

R = C_6H_4Me-4 (**86**, **88**), Me (**87**, **89**).

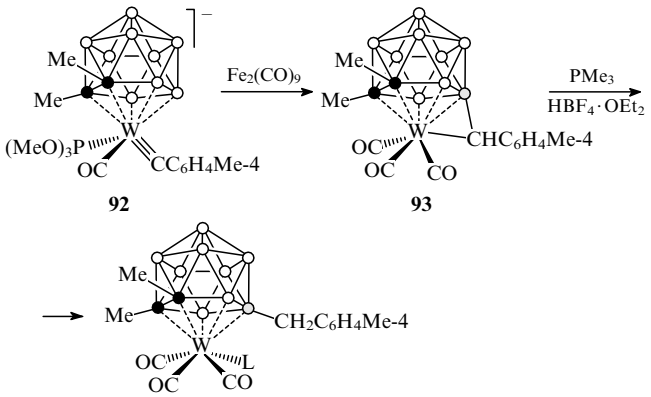
The reactions of compound **87** with $HBF_4 \cdot Et_2O$ and $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Me_2PCH_2CH_2PMe_2$ (dmpe) in dichloromethane produce 8-Et-1,2-Me_2-3,3-$(CO)_2$-3,3-(μ-L_2)-3,1,2-$WC_2B_9H_8$ [L_2 = dppe (**90**) or dmpe (**91**)].[123]



87 **90**, **91**

L–L = dppe (**90**), dmpe (**91**).

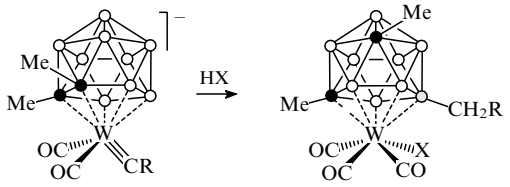
The reaction of [Et_4N][1,2-Me_2-3-(≡CC_6H_4Me-4)-3-CO-3-$P(OMe)_3$-3,1,2-$MoC_2B_9H_9$] (**92**) with $Fe_2(CO)_9$ proceeds through the intermediate formation of 8-[σ-CH(C_6H_4Me-4)]-1,2-Me_2-3,3,3-$(CO)_3$-3,1,2-$MoC_2B_9H_8$ (**93**), which was isolated in the individual state. Treatment of compound **93** with $HBF_4 \cdot Et_2O$ and PMe_3 afforded a mixture of 8-(4-$MeC_6H_4CH_2$)-1,2-Me_2-3,3,3,3-$(CO)_4$-3,1,2-$MoC_2B_9H_8$ (**94**) and 8-(4-$MeC_6H_4CH_2$)-1,2-Me_2-3,3,3-$(CO)_3$-3-Me_3P-3,1,2-$MoC_2B_9H_8$ (**95**).[124]



92 **93**

94 (L = CO), **95** (L = PMe_3)

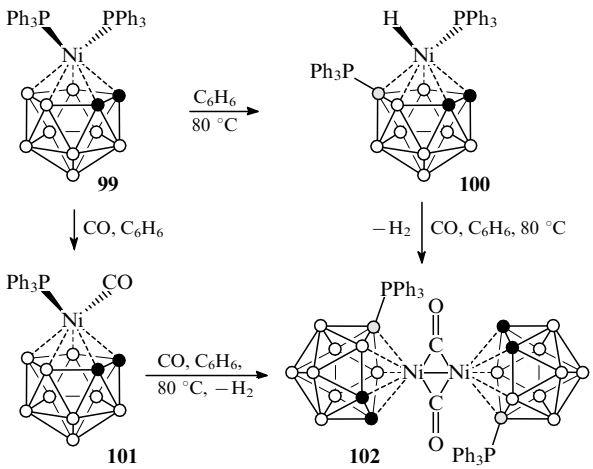
The reaction of the complex Y[**86**] (Y = $(Ph_3P)_2N$ (PPN), Ph_4P or Et_4N) with 1 equiv. of HX (X = Cl or I) proceeds in a more complex way and is accompanied not only by migration of the alkylidyne group from metal to the boron atom but also by the skeletal rearrangement of the dicarbollyl ligand to form Y[11-(4-$MeC_6H_4CH_2$)-1,8-Me_2-2-X-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8$] [X = Cl (**96**) or I (**97**)]. The reaction of the complex [Et_4N][**87**] with HI proceeds analogously to give [Et_4N][11-Et-1,8-Me_2-2-I-2,2,2-$(CO)_3$-2,1,8-$WC_2B_9H_8$] (**98**).[124, 125]



86, **87** **96**–**98**

R = C_6H_4Me-4 (**86**, **96**, **97**), Me (**87**, **98**); X = Cl (**96**), I (**97**, **98**).

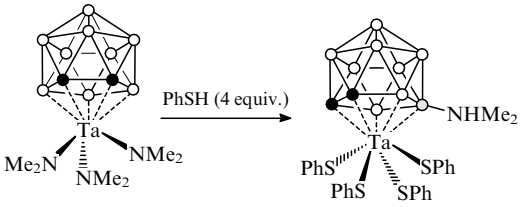
The rearrangement of 3,3-$(Ph_3P)_2$-3,1,2-$NiC_2B_9H_{11}$ (**99**) into 3,8-$(Ph_3P)_2$-3-H-3,1,2-$NiC_2B_9H_{10}$ (**100**) in boiling benzene[126] provides another example of substitution caused by migration of a ligand from the metal atom to the carborane moiety. The reaction of nickelacarborane **99** with CO is accompanied by the replacement of one Ph_3P ligand with the carbonyl group to form complex **101**. Refluxing of the latter in benzene under CO pressure results not only in migration of the triphenylphosphine ligand to the carborane moiety but also in dimerisation to give *closo*-[3-(μ-CO)-8-Ph_3P-3,1,2-$NiC_2B_9H_{10}$]$_2$ (**102**) containing the Ni–Ni bond. The structure of complex **102** was established by X-ray diffraction analysis.[127, 128] Compound **102** can also be prepared by refluxing compound **100** in benzene under CO pressure.



99 **100**

101 **102**

The reaction of tris(dimethylamino)-*closo*-tantalacarborane **103** with four equivalents of thiophenol producing the charge-compensated 8-Me_2HN-3,3,3,3-$(SPh)_4$-3,1,2-$TaC_2B_9H_{10}$ complex (**104**) is yet another example of migration of a ligand from the metal atom to the carborane cage. The structure of compound **104** was determined by X-ray diffraction analysis.[129]

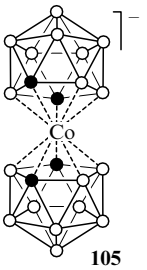


103 **104**

It should be noted that the primary substitution in all metallacarboranes containing the 7,8-dicarbollyl ligand (except for mercuration reactions) occurs at the position adjacent to the metal atom, *i.e.*, the hydrogen atoms at the boron atoms belonging to the open pentagonal face of the ligand are replaced. In the case of both electrophilic and electrophile induced nucleophilic substitution, the primary attack occurs at position 8 of metallacarborane, whereas the substitution with the direct involvement of the metal atom proceeds less selectively.

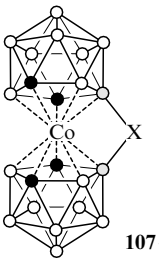
2. Derivatives based on the 7,9-dicarbollyl ligand $[7,9\text{-}C_2B_9H_{11}]^{2-}$

Substitution in metallacarboranes based on the 7,9-dicarbollyl ligand was exemplified by the only metallacarborane, *viz.*, bis(1,7-dicarbollyl)cobalt [*commo*-2,2′-$Co(1,7\text{-}C_2B_9H_{11})_2]^-$ (**105**) (the atomic numbering scheme is shown in Fig. 1 *e*). Substitution in complex **105** resembles that in analogous complex **1** (see p. 435) and is accompanied by the formation of compounds containing various bridges between two dicarbollyl ligands. For instance, the reaction of complex **105** with carbon disulfide in the presence of $AlCl_3$ and HCl affords (μ-HCS_2)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ (**106**) with the three-atom SCS bridge.[89]



105

The reaction of complex **105** with formaldehyde in an HCl(conc.)–$CHCl_3$ mixture at 60 °C gives rise to the bridged 6,6′-(μ-MeO)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ compound (**107**) in high yield. The latter is readily demethylated with Lewis bases in methanol to form [6,6′-(μ-O)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2]^-$.[130]



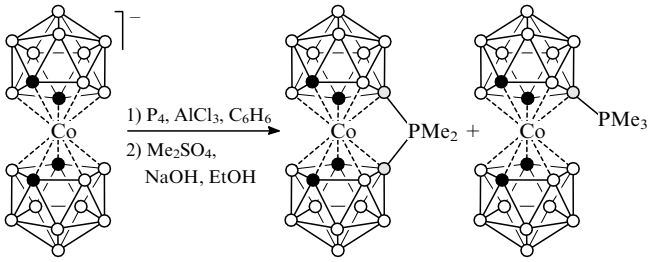
107–**119**

X = OMe (**107**), NH_2 (**108**), NMe_2 (**109**), NHMe (**110**), S (**111**), SEt (**112**), SPr^n (**113**), SPr^i (**114**), SBu^n (**115**), SC_6H_{13} (**116**), $SCH_2CH{=}CH_2$ (**117**), $SCH_2C(O)OMe$ (**118**), PMe_2 (**119**).

The reaction of compound **105** with $NaNO_2$ in benzene in the presence of sulfuric acid produces the corresponding derivative 6,6′-(μ-H_2N)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ (**108**) with a one-atom nitrogen bridge. Treatment of the latter with dimethyl sulfate in 30% NaOH affords the *N*,*N*-dimethylation product 6,6′-(μ-Me_2N)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ (**109**). The monoalkylated complex 6,6′-(μ-MeNH)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ (**110**) was prepared by treatment of a benzene suspension of [Me_4N][6,6′-(μ-HN)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$] with diiodomethane in 10% aqueous alkali.[130]

The reaction of complex **105** with sulfur in benzene in the presence of $AlCl_3$ at 80 °C yields the [6,6′-(μ-S)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2]^-$ complex (**111**),[131] whose alkylation with various alkyl halides in isopropyl alcohol affords the corresponding alkylsulfonium derivatives 6,6′-(μ-RS)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ [R = Et (**112**), Pr^n (**113**), Pr^i (**114**), Bu^n (**115**), C_6H_{13} (**116**) or $CH_2CH{=}CH_2$ (**117**)].[130, 132] The reaction of complex **105** with chloroacetic acid in an aqueous Na_2CO_3 solution gives an acid, whose esterification in methanol in the presence of $SOCl_2$ affords 6,6′-(μ-$MeOC(O)CH_2S$)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ (**118**).[130]

The reaction of compound **105** with phosphorus in benzene at 80 °C followed by reaction with dimethyl sulfate in the presence of sodium hydroxide in ethanol gives rise to a mixture of 6,6′-(μ-Me_2P)-2,2′-$Co(1,7\text{-}C_2B_9H_{10})_2$ (**119**) and 6-Me_3P-2,2′-$Co(1,7\text{-}C_2B_9H_{10})(1',7'\text{-}C_2B_9H_{11})$ (**120**).[108]



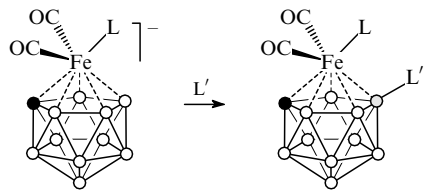
105 **119** **120**

It should be noted that in all the above-described reactions, substitution in metallacarboranes occurs at position 6 adjacent to the metal atom.

3. Derivatives based on the carbollyl ligand $[CB_{10}H_{11}]^{3-}$

There are abundant data on substitution in metallacarboranes based on the carbollyl ligand $[CB_{10}H_{11}]^{3-}$. As in the case of metallacarboranes based on the 7,8-dicarbollyl anion, substitution in metal complexes with carbollyl ligands can occur involving both the metal and boron atoms (by the mechanism of electrophilic or electrophile induced nucleophilic substitution).

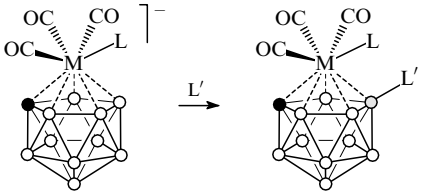
The reactions of ferracarboranes [PPN][2,2-$(CO)_2$-2-L-2,1-$FeCB_{10}H_{11}$] [L = SMe_2 (**121**) or PPh_3 (**122**)] with sulfuric acid in dimethyl sulfide or tetrahydrofuran produce charge-compensated products of electrophile induced nucleophilic substitution with composition 7-L′-2,2-$(CO)_2$-2-L-2,1-$FeCB_{10}H_{10}$ [L = SMe_2: L′ = SMe_2 (**123**), $O(CH_2)_4$ (**124**); L = PPh_3: L′ = SMe_2 (**125**), $O(CH_2)_4$ (**126**)] containing the L′ substituent in the open face at position 7, which is one of the most remote from the carbon atom.[133]



121, **122** **123**–**126**

L = SMe_2 (**121**, **123**, **124**), PPh_3 (**122**, **125**, **126**);
L′ = SMe_2 (**123**, **125**), $O(CH_2)_4$ (**124**, **126**).

The reactions with the [PPN][2,2,2-(CO)$_3$-2-L-2,1-MCB$_{10}$H$_{11}$] complexes [L = Ph$_3$P: M = Mo (**127**), W (**128**); L = Bu^{t}NC: M = Mo (**129**), W (**130**)] proceed analogously. For example, the reactions of compounds **127** – **130** with CF_3SO_3Me or sulfuric acid in the presence of the donors of L′ [L′ = SMe$_2$, OEt$_2$, O(CH$_2$)$_4$, S(CH$_2$)$_4$, cyclo-1,4,7-S$_3$(CH$_2$)$_6$, NCBu^t, CNBu^t, CNC$_6$H$_3$Me$_2$-2,6] give rise to the corresponding zwitterionic 7-L′-2,2,2-(CO)$_3$-2-L-2,1-MCB$_{10}$H$_{10}$ complexes (**131** – **134**).[134] The structure of molybdacarborane 7-CNBu^t-2,2,2-(CO)$_3$-2-Ph$_3$P-2,1-MoCB$_{10}$H$_{10}$ (**131g**) was confirmed by X-ray diffraction analysis.[134]



127 – **130** **131a** – **h**, **132a** – **h**, **133**, **134**

L = PPh$_3$: M = Mo (**127**, **131a** – **h**), W (**128**, **132a** – **h**); L′ = SMe$_2$ (**a**), OEt$_2$ (**b**), O(CH$_2$)$_4$ (**c**), S(CH$_2$)$_4$ (**d**), cyclo- 1,4,7-S$_3$(CH$_2$)$_6$ (**e**), NCBu^t (**f**), CNBu^t (**g**), CNC$_6$H$_3$Me$_2$-2,6 (**h**);
L = CNBu^t: M = Mo (**129**, **133**), W (**130**, **134**); L′ = OEt$_2$ (**133**, **134**).

Treatment of compounds **132b** and **132c** with trimethylamine oxide in the presence of Ph$_4$PBr in tetrahydrofuran affords the corresponding alkoxy derivatives [Ph$_4$P][7-RO-2,2,2-(CO)$_3$-2-Ph$_3$P-2,1-WCB$_{10}$H$_{10}$] (R = Et, (CH$_2$)$_3$CHO).[134]

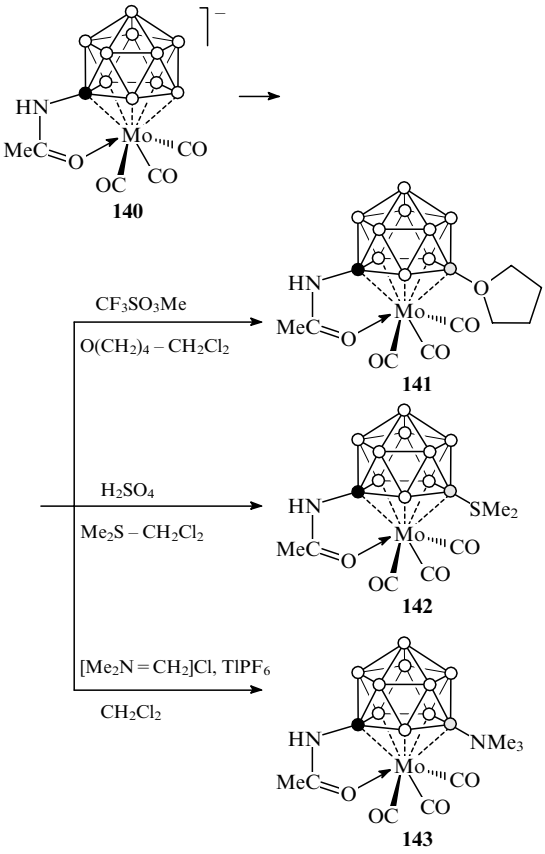
The reaction of cobaltacarborane [PPN][2-Et$_3$P-2-NO-2,1-CoCB$_{10}$H$_{11}$] with methyl triflate in a mixture of CH_2Cl_2 and THF yields the corresponding charge-compensated derivative 7-(CH$_2$)$_4$O-2-Et$_3$P-2-NO-2,1-CoCB$_{10}$H$_{10}$,[133] whereas the reaction in a mixture of CH_2Cl_2 and acetonitrile affords 7-MeCN-2-Et$_3$P-2-NO-2,1-CoCB$_{10}$H$_{10}$ with an impurity of *closo*-7-(NMe=CHMe)-2-Et$_3$P-2-NO-2,1-CoCB$_{10}$H$_{11}$.[135]

The reactions of ferracarboranes [PPN][2,2-(CO)$_2$-2-L-2,1-FeCB$_{10}$H$_{11}$] [L = PPh$_3$ (**122**), CO (**135**), Bu^{t}NC (**136**)] with methyl triflate in acetonitrile produce 7-[(*E*)-MeCH=NMe]-2,2-(CO)$_2$-2-L-2,1-FeCB$_{10}$H$_{10}$ (**137** – **139**) [L = PPh$_3$ (**137**), CO (**138**), Bu^{t}NC (**139**)] (Scheme 10).[133] It is assumed that acetonitrile is initially methylated with methyl triflate to form the *N*-methylnitrilium cation [MeC≡NMe]$^+$,[136] which is involved in electrophile induced nucleophilic substitution (Scheme 10).

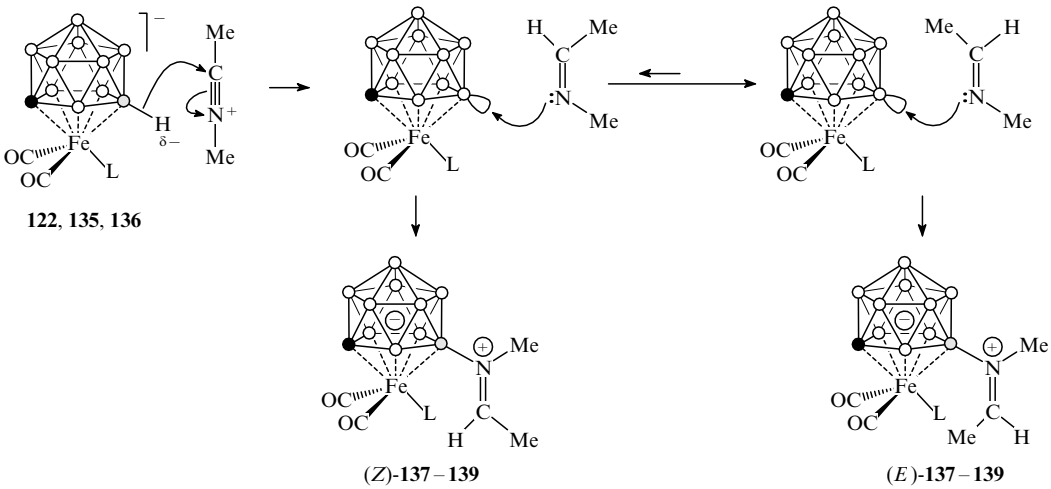
The *E* form of an imine is, apparently, more stable due to which only one isomer is formed. Complex **138** is readily hydrolysed in the presence of bases as catalysts to give 7-MeH$_2$N-2,2,2-(CO)$_3$-2,1-FeCB$_{10}$H$_{10}$ and is reduced to 7-Me(Et)HN-2,2,2-(CO)$_3$-2,1-FeCB$_{10}$H$_{10}$ in the presence of Na[BH$_3$CN].[133]

As in the case of analogous iron complexes, the reactions of compounds **127** and **128** with CF_3SO_3Me in acetonitrile produce the iminium derivatives 7-[(*E*)-MeCH=NMe]-2,2,2-(CO)$_3$-2-Ph$_3$P-2,1-MCB$_{10}$H$_{10}$ (M = Mo, W). The reaction with the use of Bu^{t}NC instead of acetonitrile gives rise to a mixture of *E* and *Z* isomers of 7-(MeCH=NBu^t)-2,2,2-(CO)$_3$-2-Ph$_3$P-2,1-MCB$_{10}$H$_{10}$.[134]

Substitution in *C*-substituted molybdacarborane [PPN][1,2-[μ-MeC(O)NH]-2,2,2-(CO)$_3$-2,1-MoCB$_{10}$H$_{10}$] (**140**) occurs analogously. The reaction of complex **140** with CF_3SO_3Me in a mixture of THF and dichloromethane yields the charge-compensated 7-(CH$_2$)$_4$O-1,2-[μ-MeC(O)NH]-2,2,2-(CO)$_3$-2,1-MoCB$_{10}$H$_9$ complex (**141**). The reaction of complex **140** with concentrated sulfuric acid in a CH_2Cl_2 – SMe$_2$ mixture affords the



Scheme 10



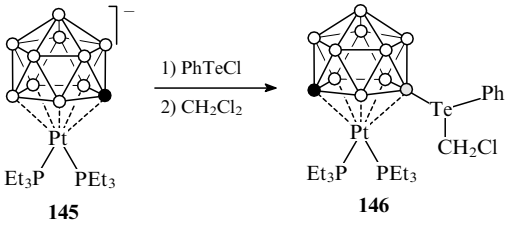
122, **135**, **136** (*Z*)-**137** – **139** (*E*)-**137** – **139**

L = PPh$_3$ (**122**, **137**), CO (**135**, **138**), Bu^{t}NC (**136**, **139**).

dimethylsulfonium derivative 7-Me_2S-1,2-[μ-MeC(O)NH]-2,2,2-$(CO)_3$-2,1-$MoCB_{10}H_9$ (**142**), whereas the reaction of this complex with $[Me_2N=CH_2]Cl$ and $TlPF_6$ in dichloromethane gives the corresponding trimethylammonium derivative 7-Me_3N-1-[μ-MeC(O)NH]-2,2,2-$(CO)_3$-2,1-$MoCB_{10}H_9$ (**143**).[137]

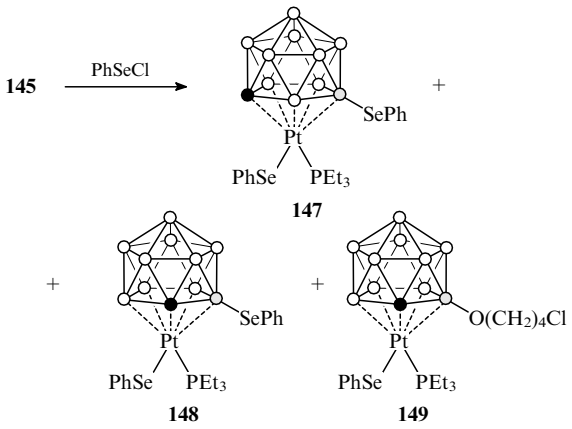
Interestingly, the reaction of [PPN][2,2-$(CO)_2$-2-(η^2-Bu^{t}C≡CH)-2,1-$MCB_{10}H_{11}$] (M = Mo, W) with CF_3SO_3Me in a $CH_2Cl_2-Et_2O$ mixture produces the corresponding charge-compensated derivatives 7-Et_2O-2,2-$(CO)_2$-2-(η^2-Bu^{t}C≡CH)-2,1-$MCB_{10}H_{10}$ rather than leads to the rearrangement of the Bu^{t}C≡CH ligand followed by the insertion of the alkene fragment at the B—H bond (which occurs in the reactions of alkyne dicarbollyl complexes).[134] By contrast, the reaction of ferracarborane **135** with *tert*-butylacetylene in THF in the presence of Me_3NO forms 3-[η^2-(*E*)-Bu^{t}CH = CH]-2,2,2-$(CO)_3$-2,1-$FeCB_{10}H_{10}$ (**144**), *i.e.*, substitution (as in the case of metallacarboranes based on the dicarbollyl ligand) occurs at the position adjacent to the carbon atom in the open face of the carborane ligand. The reaction of complex **144** with CF_3SO_3Me in acetonitrile affords 3-[η^2-(*E*)-Bu^{t}CH=CH]-7-(MeCH=NMe)-2,2,2-$(CO)_3$-2,1-$FeCB_{10}H_9$, in which the imine fragment is located in the open face of the carborane ligand occupying the position most remote from the carbon atom and the boron atom bearing the alkene substituent.[133]

Under similar conditions, the reactions of platinacarborane Na[2,2-$(Et_3P)_2$-2,1-$PtCB_{10}H_{11}$] (**145**) with PhSeCl and PhTeI in tetrahydrofuran proceed differently. The reaction with PhTeI proceeds according to the electrophilic mechanism to give (after chromatography with the use of CH_2Cl_2 as the eluent) the charge-compensated 7-$ClCH_2$(Ph)Te-2,2-$(Et_3P)_2$-2,1-$PtCB_{10}H_{10}$ complex (**146**), whose structure was established by X-ray diffraction analysis. By contrast, the reaction with PhSeCl proceeds with the participation of the metal atom to give a mixture of 7,2-$(PhSe)_2$-2-Et_3P-2,1-$PtCB_{10}H_{10}$ (**147**), 3,2-$(PhSe)_2$-2-Et_3P-2,1-$PtCB_{10}H_{10}$ (**148**) and 3-$Cl(CH_2)_4O$-2-PhSe-2-Et_3P-2,1-$PtCB_{10}H_{10}$ (**149**).¶ It is assumed that complex **149** is generated as a result of the tetrahydrofuran-ring opening in the oxonium derivative under the action of the chloride ion.[138]



145 **146**

¶ The structure of complex **149** was established by X-ray diffraction.

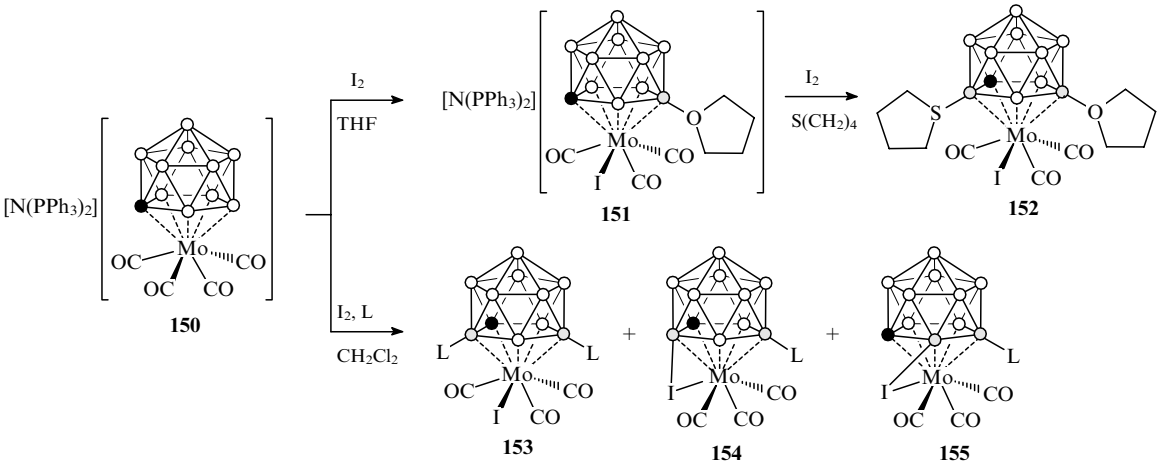


147 **148** **149**

The reactions of metallacarboranes, which contain labile ligands in the metal coordination sphere, with halides proceed in an unusual way. For example, treatment of the molybdenum complex [PPN][2,2,2,2-$(CO)_4$-2,1-$MoCB_{10}H_{11}$] (**150**) with iodine in tetrahydrofuran leads not only to the replacement of one of the carbonyl ligands with iodine but also to the replacement of the hydrogen atom at position 7 of the carborane moiety with tetrahydrofuran to form [PPN][7-$(CH_2)_4$O-2,2,2-$(CO)_3$-2-I-2,1-$MoCB_{10}H_{10}$] (**151**) (Scheme 11). The structure of complex **151** was determined by X-ray diffraction analysis. The reaction of a solution of compound **151** in tetrahydrothiophene with iodine is accompanied by the replacement of one more hydrogen atom in the open face of the carborane ligand with tetrahydrothiophene to give the neutral 3-$(CH_2)_4S$-11-$(CH_2)_4O$-2,2,2-$(CO)_3$-2-I-2,1-$MoCB_{10}H_9$ complex (**152**). The reaction of complex **150** with iodine in CH_2Cl_2 in the presence of cyclic thioesters (L) also affords two types of substituted molybdacarboranes. In both cases, the substitution involves the metal atom (one of the carbonyl groups at the Mo atom is replaced with the iodide ion). Derivatives of one type, *viz.*, 3,11-L_2-2,2,2-$(CO)_3$-2-I-2,1-$MoCB_{10}H_9$ (**153**), contain two sulfonium substituents in the open face of the monocarbollyl ligand, whereas derivatives of another type, *viz.*, 7-L-2,3-(μ-I)-2,2,2-$(CO)_3$-2,1-$MoCB_{10}H_9$ (**154**) and 11-L-2,3-(μ-I)-2,2,2-$(CO)_3$-2,1-$MoCB_{10}H_9$ (**155**), bear the sulfonium substituent along with the bridging iodine atom between Mo and the boron atom at the position nearest to the carbon atom.[139]

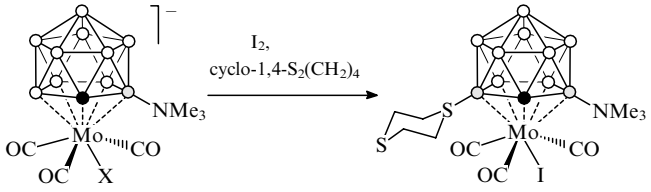
The reactions of the molybdenum complexes [PPN][3-Me_3N-2,2,2-$(CO)_3$-2-X-2,1-$MoCB_{10}H_{10}$] [X = I (**156**) or Br (**157**)] with 1,4-dithiane and iodine in dichloromethane afford the 3-Me_3N-6-$S(CH_2CH_2)_2S$-2,2,2-$(CO)_3$-2-I-2,1-$MoCB_{10}H_9$ complex containing substituents in the pentagonal face of the monocarbollyl ligand at the positions adjacent to the carbon atom. Interestingly,

Scheme 11

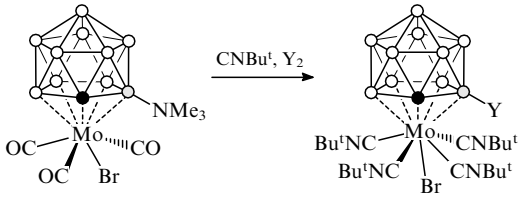


150 **151** **152** **153** **154** **155**

the reaction of [PPN][3-Me_3N-2,2,2-$(CO)_3$-2-Br-2,1-$MoCB_{10}H_{10}$] (**157**) with Bu^tNC and iodine (or bromine) in dichloromethane leads to the replacement of the trimethylamino group in the monocarbollyl ligand with the halogen atom to form 3-Y-2,2,2,2-$(Bu^tNC)_4$-2-Br-2,1-$MoCB_{10}H_{10}$ [Y = Br (**159**) or I (**160**)].[140]



156 (X = I), **157** (X = Br) **158**



157 **159** (Y = Br), **160** (Y = I)

Y = Br, I.

It should be noted that in none of the above-considered reactions does the replacement of the hydrogen atom with halogen occur through the mechanism of electrophilic substitution.

4. Dicobaltacarborane derivatives

The reaction of dicobaltacarborane 3,6-Cp_2-3,6,1,2-$Co_2C_2B_8H_{10}$ (**161**) containing two CpCo fragments with mercury acetate in boiling dichloromethane (Scheme 12) followed by the replacement of the acetate group with chlorine gives rise to a mixture of 3,6-Cp_2-8-HgCl-3,6,1,2-$Co_2C_2B_8H_9$ (**162**)† and 3,6-Cp_2-9-HgCl-3,6,1,2-$Co_2C_2B_8H_9$ (**163**) in a ratio of 1 : 1.2.[141]

† The structure of 8-monomercury derivative **162** was confirmed by X-ray diffraction.[126]

The reaction with an excess of mercury acetate in acetic acid allows one to introduce up to four substituents into the carborane moiety to form the 3,6-Cp_2-8,10,9,12-$(HgCl)_4$-3,6,1,2-$Co_2C_2B_8H_6$ complex (**164**).

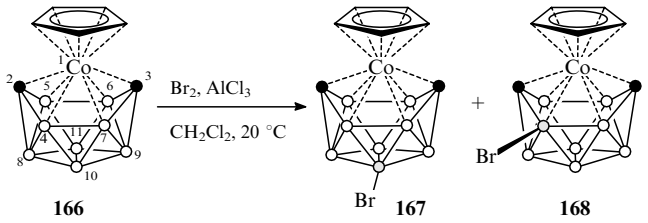
An attempt to prepare a thallium derivative by the reaction of complex **161** with thallium(III) trifluoroacetate in trifluoroacetic acid failed; instead, this reaction gave 8,9-bistrifluoroacetate derivative **165**.[141]

IV. Substitution in non-icosahedral metallacarboranes

Substitution in non-icosahedral metallacarboranes has received less study because these compounds are less readily accessible. Substitution in 10- and 11-vertex metallacarboranes was studied only for CpCo carboranes.

1. Substitution in 11-vertex cobaltacarboranes

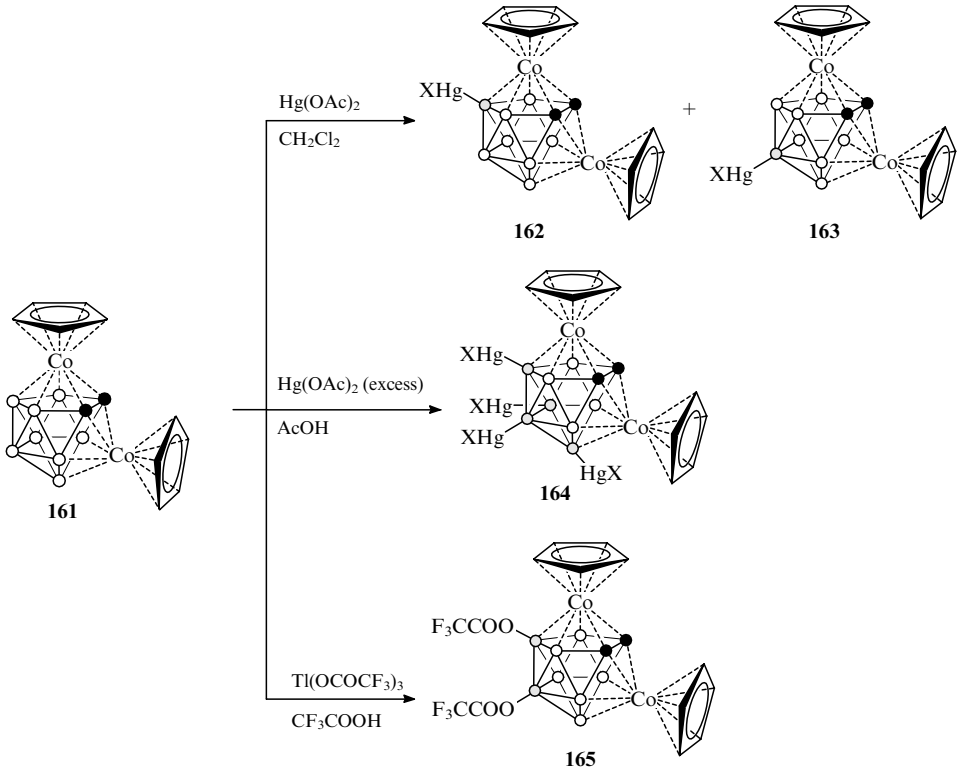
Zakharkin *et al.*[142] studied bromination of 1-Cp-1,2,3-$CoC_2B_8H_{10}$ (**166**). The reaction of complex **166** with 1 equiv. of bromine in dichloromethane in the absence of a catalyst or in the presence of $AlCl_3$ produces a mixture of the isomeric bromine derivatives 10-Br-1-Cp-1,2,3-$CoC_2B_8H_9$ (**167**) and 4-Br-1-Cp-1,2,3-$CoC_2B_8H_9$ (**168**). The reaction with the use of glacial acetic acid as the solvent gives a mixture of the same monobromides with an impurity of dibromo derivatives. The ratio between the 10- and 4-isomers is (4.5 – 6) : 1. The structure of complex **166** was established by X-ray diffraction analysis.[142]



166 **167** **168**

The reactions of complex **166** with two, three or four equivalents of bromine in the presence of $AlCl_3$ yield a mixture of di-,

Scheme 12

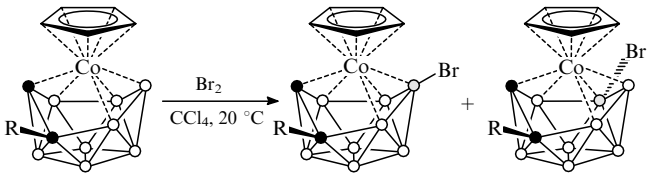


161 **162** **163** **164** **165**

tri- and tetrabromo derivatives. Attempts to separate these derivatives failed. The pentabromo derivative 4,5,6,10,11-Br_5-1-Cp-1,2,3-$CoC_2B_8H_5$ was synthesised by refluxing compound **166** with 8 equiv. of bromine in the presence of $AlCl_3$ in dichloromethane.[142]

Based on the above results, it was hypothesised that the electron density on the boron atoms of the π-carborane ligand decreases in the series B(10, 11) > B(4, 5, 6, 7) > B(8, 9).

The reaction of cobaltacarborane *isonido*-1-Cp-1,2,4-$CoC_2B_8H_{10}$ (**169**) (which is isomeric to compound **166**) with 1 equiv. of bromine in CCl_4 produces two isomeric monobromides, *viz*., 3-Br-1-Cp-1,2,4-$CoC_2B_8H_9$ (**170**) and 6-Br-1-Cp-1,2,4-$CoC_2B_8H_9$ (**171**), in a ratio of 1 : 10.[143]



169, **172** **170**, **173** **171**, **174**

R = H (**169**, **170**, **171**), Me (**172**, **173**, **174**).

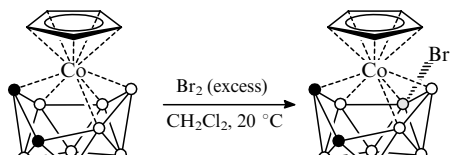
The reaction of complex **169** with *N*-bromosuccinimide also gives rise to a mixture of monobromides **170** and **171**, but in much lower yields.

At room temperature, each isomer in a benzene solution slowly (during two days) undergoes rearrangement to form an equilibrium mixture of monobromides **170** and **171** in a ratio of 1 : 1.3. This suggests that isomer **171** is a kinetic substitution product, whereas isomer **170** is a rearrangement product.

Only 6-Br-4-Me-1-Cp-1,2,4-$CoC_2B_8H_8$ (**174**) was isolated as a product of bromination of the *C*-methyl derivative *isonido*-4-Me-1-Cp-1,2,4-$CoC_2B_8H_9$ (**172**). This product underwent partial rearrangement into complex **173** (presumably) upon prolonged storage in a benzene solution. However, the percentage of **173** (according to the ^{11}B NMR spectroscopic data) was no higher than 10%.[143] Evidently, the introduction of the methyl substituent at the C(4) atom hinders the rearrangement of the substitution product.

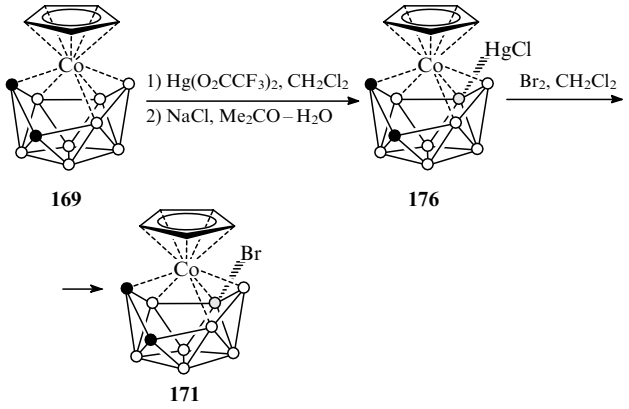
It should be noted that chloro-substituted derivatives of isostructural metallacarboranes 3-Cl-1-(η^6-Ar)-1,2,4-$RuC_2B_8H_9$ and 6-Cl-1-(η^6-Ar)-1,2,4-$RuC_2B_8H_9$ (Ar = C_6H_6, PhMe, 1,4-$Me_2C_6H_4$, 1-Me-4-$Pr^iC_6H_4$, 1,2,4-$Me_3C_6H_3$, 1,3,6-$Me_3C_6H_3$, 1,2,4,5-$Me_4C_6H_2$, C_6Me_6) were prepared by the reactions of $RuCl_2(PPh_3)_3$ with *nido*-5,6-$C_2B_8H_{12}$ in benzene and other aromatic solvents.[144] The reaction of *nido*-7-Br-5,6-$C_2B_8H_{11}$ with $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ also produces a mixture of isomers 5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$ and 7-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$.[145] The formation of such pairs of halogen derivatives indicates that the rearrangements of various metallacarboranes with the 1,2,4-MC_2B_8 skeleton occur by a similar mechanism.

The reaction of compound **169** with a tenfold excess of bromine produces exclusively the dibromo derivative 6,9-Br_2-1-Cp-1,2,4-$CoC_2B_8H_8$ (**175**). Derivatives containing the bromine atom at position 3 of the cobaltacarborane moiety were not found.[143]



169 **175**

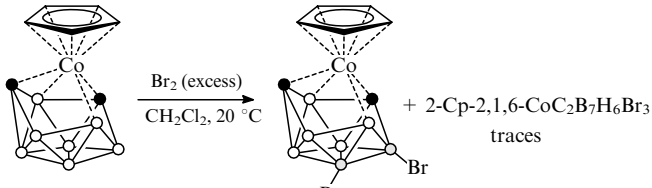
The chloromercury derivative 6-HgCl-1-Cp-1,2,4-$CoC_2B_8H_9$ (**176**) was synthesised by mercuration of complex **169** with mercury trifluoroacetate followed by treatment of the resulting complex with NaCl. The structure of compound **176** was established by X-ray diffraction analysis. The reaction of compound **176** with bromine in dichloromethane at room temperature affords monobromide **171**.[143]



169 **176** **171**

2. Substitution in 10-vertex cobaltacarboranes

Hawthorne and co-workers [146] studied bromination and acylation of 2-Cp-2,1,6-$CoC_2B_7H_9$ (**177**). The reaction of compound **177** with an excess of bromine in CCl_4 produces dibromo derivative **178**, in which the bromine atoms occupy positions 8 and 10, with a small impurity of tribromide.



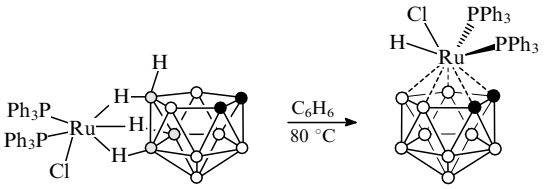
177 **178**

Acylation of complex **177** with acetyl chloride in the presence of $AlCl_3$ in dichloromethane gives the monoacetyl derivative 8-Ac-2-Cp-2,1,6-$CoC_2B_7H_8$.[146]

It should be noted that the above results agree well with the data on substitution in purely polyhedral boron hydrides devoid of the metal fragment. For example, electrophilic substitution in the ten-vertex polyhedra $[B_{10}H_{10}]^{2-}$ and $[1\text{-}CB_9H_{10}]^-$ occurs predominantly at the five-coordinate boron atoms.[147, 148] In the case of structurally flexible eleven-vertex polyhedral boron hydrides, which readily undergo rearrangement (for example, $[B_{11}H_{11}]^{2-}$), the substitution position is determined by the relative stability of intermediate and substitution products.[149–151]

V. Substitution in *exo-nido*-metallacarboranes

Interesting results were obtained in the study of substitution in ruthenacarboranes containing the hydride ligand in the metal coordination sphere. Metallacarboranes with the hydride ligand can exist as two isomers, *viz*., *closo*- and *exo-nido*-metallacarboranes. Stability of a particular form depends on the nature of the metal atom and substituents in the carborane ligand.[152] For example, ruthenacarborane *exo-nido*-5,6,10-[$Cl(Ph_3P)_2Ru$]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$ (**179**) [153] undergoes isomerisation into *closo*-3,3-$(PPh_3)_2$-3-H-3-Cl-3,1,2-$RuC_2B_9H_{11}$ (**180**) [154] on heating in benzene at 80 °C

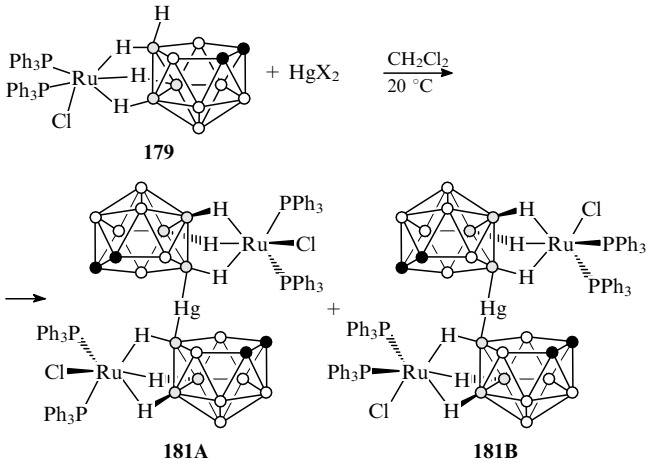


179 **180**

Isomers **179** and **180** differ in chemical behaviour. For example, isomer **180** does not react with $Hg(OAc)_2$ in CH_2Cl_2 or acetone and decomposes in acetic acid, whereas isomer **179** is involved in substitution reactions with various mercurating agents to form *exo-nido*-ruthenacarboranylmercury derivatives.[155]

It should be noted that ruthenacarborane **179** exists in solution as an equilibrium mixture of two geometric isomers (*cis* and *trans*) due to isomerism of the ligands at the six-coordinate ruthenium atom. The *cis* : *trans* isomer ratio is $\sim 1:1$.[156]

The reaction of complex **179** with mercury acetate or trifluoroacetate in dichloromethane at 20 °C affords the symmetrical mercury derivative 10,10′-Hg-[*exo-nido*-5,6,10-$(Cl(Ph_3P)_2Ru)$-5,6,10-$(\mu\text{-}H)_3$-7,8-$C_2B_9H_8]_2$ (**181**) in 46% yield. The latter was prepared as a mixture of geometric isomers, *viz*., *cis* (**A**) and *trans* (**B**). According to the ^{31}P NMR spectroscopic data, the **A** : **B** ratio was 5 : 1.[155]



179

181A **181B**

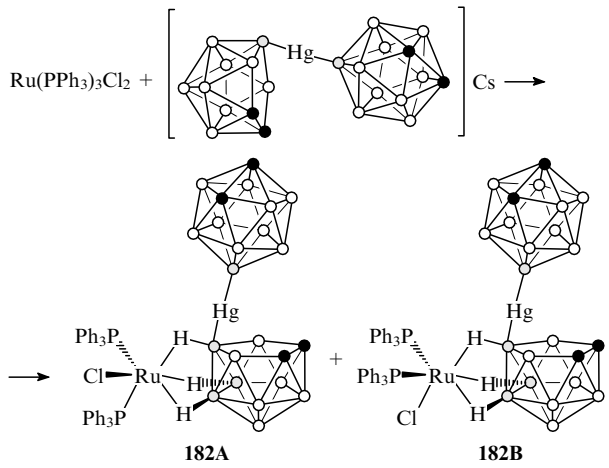
X = AcO, CF_3COO.

In the isomers **A** and **B**, the hydrogen atom at B(10) in the open face of the *exo-nido*-carborane ligand and the chlorine atom at the ruthenium atom are in the *cis* and *trans* positions, respectively.

An analogous mixture of isomers was prepared by the reaction of $Ru(Ph_3P)_3Cl_2$ with the symmetrical mercury derivative of the *nido*-7,8-dicarbaundecaborate anion $Cs_2[10,10'\text{-}Hg\text{-}(7,8\text{-}C_2B_9H_{11})_2]$.[157] Here, as in the first case, the isomer **A** prevails.[155]

In the study,[155] it was proposed to use trifluoroacetoxy-*o*-carboranylmercury 9-$CF_3COOHgC_2B_{10}H_{11}$ (see Ref. 158) along with mercury salts. The reaction of complex **179** with this reagent affords mercurated ruthenacarborane *exo-nido*-5,6,10-$[Cl(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-$(C_2B_{10}H_{11}Hg)$-7,8-$C_2B_9H_8$ (**182**) containing both the *closo*- and *nido*-carborane moieties.[155] It should be noted that, unlike complex **181**, compound **182** is generated predominantly as the *trans* isomer (**182B**). According to the ^{31}P NMR spectroscopic data, the *cis* : *trans* ratio is 1 : 2.

The independent synthesis of compound **182** by the reaction of $Ru(PPh_3)_3Cl_2$ with $Cs[10\text{-}(9\text{-}HgC_2B_{10}H_{11})(7,8\text{-}C_2B_9H_{11})]$ gave an analogous result.[159]

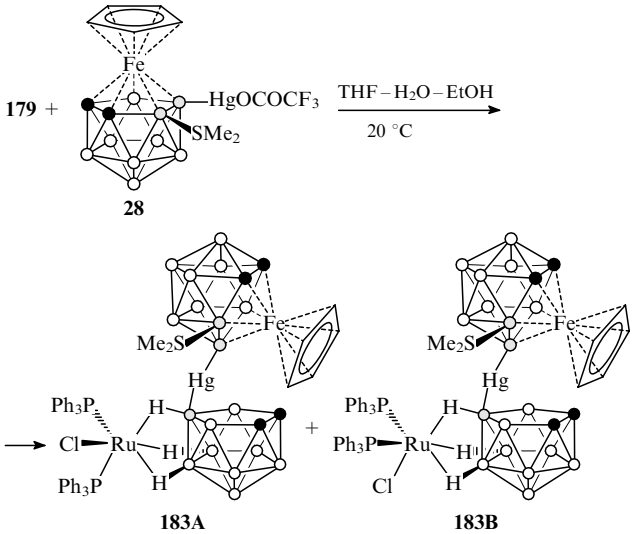


182A **182B**

Isomers **182A** and **182B** were isolated in the individual state. The structure of isomer **182B** was confirmed by X-ray diffraction analysis.

Refluxing of complexes **181** and **182** in benzene does not lead to their *exo-nido* → *closo* rearrangement. Carbon-substituted *exo-nido*-ruthenacarboranes behave analogously.[154] The B—Hg bond in compounds **181** and **182** is resistant to the action of HCl and $HgCl_2$ in acetone or THF at room temperature.

In the studies,[160, 161] mercurated ferracarborane **28** and cobaltacarborane **21** were used as mercurating agents for the first time.‡ The reaction of complex **179** with 1 equiv. of ferracarborane **28** affords the only product, *viz*., *exo-nido*-5,6,10-$[Cl(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-$(3'\text{-}Cp\text{-}4'\text{-}SMe_2\text{-}8'\text{-}Hg\text{-}3',1',2'\text{-}FeC_2B_9H_9)$-7,8-$C_2B_9H_8$ (**183**), as a mixture of geometric isomers.

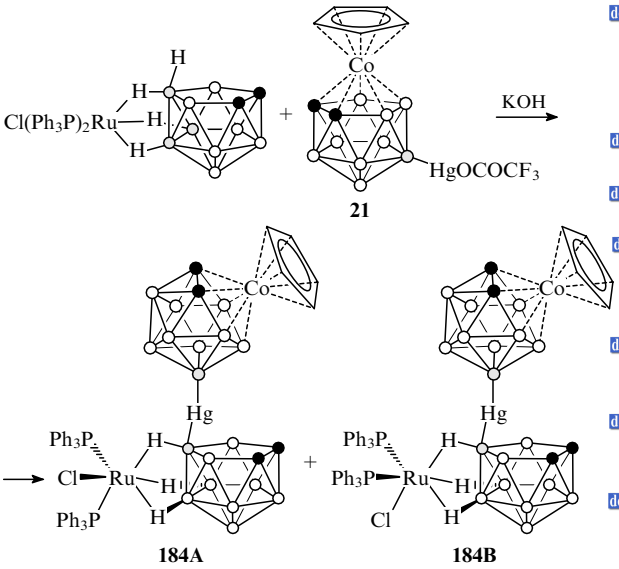


28

183A **183B**

Analogous results were obtained when performing mercuration of complex **179** with cobaltacarborane **21**. Like the above-described complexes **181**, **182** and **183**, complex **184** exists as a mixture of geometric (*cis* and *trans*) isomers (due to isomerism of the ligands with respect to the six-coordinate ruthenium atom). The structure of complex **183B** was confirmed by X-ray diffraction data.

‡ The synthesis of derivatives **21** and **28** was described in the studies.[78, 83]



Analysis of the published data on substitution in metallacarboranes makes it possible to compare these reactions with analogous reactions of other polyhedral boron hydrides and draw a conclusion about the influence of the metal atom and the coordinated ligands as well as of the substituents in the polyhedral moiety on the direction of substitution and possible mechanisms of the process.

The above-considered data provide evidence in favour of three major mechanisms of substitution: electrophilic aromatic substitution, electrophile induced nucleophilic substitution and substitution with direct involvement of the metal atom. In some cases, the reactions proceed simultaneously through several competitive mechanisms to give a mixture of substitution products.

The direction of substitution in metallacarboranes often differs from that in carboranes. For example, electrophilic substitution in *o*- and *m*-carboranes occurs at the boron atoms most remote from carbon atoms, whereas the influence of the metal fragment in metallacarboranes is manifested in that the replacement of hydrogen atoms generally occurs at positions adjacent to the metal atoms.

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