

Short review

Semi-sandwich platinum metals metallacarboranes derived from $nido-C_2B_9H_{12}^-$: chemistry and structural studies

Igor T. Chizhevsky^{*}, Alexandr I. Yanovsky, Yuri T. Struchkov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, 117813 Moscow, Russia

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Abstract

A variety of metallacarboranes, synthesized and structurally characterized by the authors are reviewed. These complexes are derived from platinum metals (Rh, Ru, Os) and isomeric *nido*-carborane anions [$nido-C_2B_9H_{12}$]⁻ and involve non-hydrocarbon (i.e. hydride, chloride, phosphine) as well as π -diene/dienyl ligands at the metal vertex. © 1997 Elsevier Science S.A.

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1. Introduction

The diverse and fascinating polyhedral structures of boron derivatives have always been a challenge for any specialist in structural organometallic chemistry. Not surprisingly, they were the subject of deep interest and significant attention of Professor Yuri Struchkov. Suffice it to mention that Professor Struchkov was one of those few crystallographers who began structural studies of icosahedral carboranes immediately after their discovery. Since then he had reported more than a hundred structures of carboranes and metallacarboranes.

This review is based on the lecture delivered by Professor Struchkov at the INEOS Workshop-94 ‘‘The Modern Problems of Organometallics’’, May 1994. It was his idea to publish the extended lecture as a review in the *Journal of Organometallic Chemistry*. It did not occur to us at that time that he would never see this review in print.

Since Hawthorne’s pioneering studies (1965–1968) of what today we call the isolobal analogy between the π -cyclopentadienyl and π -dicarbollyl ligands, the chemistry of transition metals metallacarboranes has become an extensively studied area attracting the attention of chemists from many specialities. Significant advances have been achieved, in particular in the construction of novel semi-sandwich metallacarboranes and in the stud-

ies of their reactivity and stereochemistry, which in many aspects differed markedly from those of the closely related π -cyclopentadienyl complexes of transition metals. The reason for the present increased interest in these systems is the appreciation of their importance as a bridge between different fields of chemistry, medicine, theoretical investigations and catalysis.

A number of known metallacarborane clusters have already found wide application as catalyst precursors. Thus, some of the metallacarboranes derived from platinum metals and isomeric *nido*-carborane anions [$C_2B_9H_{12}$]⁻ are found to display high catalytic activity in various organic reactions. To date, the reactions in which catalysis by *closo*- or *exo-nido*-bis(phosphine)hydridometallacarboranes (Rh, Ir, Ru) have been observed include hydrogenation, hydroformylation, isomerization, hydrosilylation, cyclopropanation of alkenes, as well as H–D exchange (for reviews, see for example Refs. [1,2]). Recently, novel catalytically active rhodacarborane systems based upon hydrocarbon-containing *closo*-rhodacarboranes were found [3,4]. These proved to be exceptionally effective for the stereoselective hydrogenation of methacycline into doxycycline (a potent antibiotic) [5,6], as well as for the coupling reactions of aromatic aldehydes [7]. All of these findings open up new opportunities for further development of homogeneous catalysis, involving stereoselective catalytic reactions, which is considered to be one of the major subdisciplines for organometallic and metallacarborane chemistry.

^{*} Corresponding author.

One could hardly imagine the successful development of the metallocarborane chemistry without the adequate support from X-ray crystallography. This provides the detailed structural information on the geometry and ligand arrangement at the metal atoms in the clusters of complicated composition and structure. Since the successful single-crystal X-ray diffraction studies of large organometallic molecules have become possible, hundreds of new structures of transition metal metallocarboranes of various types have been reported [1,8,9]. Structural information on an increasing number of carboranes, as well as metallocarboranes, especially that obtained by high precision studies of electron density distributions, provides the unique experimental basis for wide theoretical investigations in the field. These include semiempirical molecular orbital and molecular mechanic calculations of polyhedral metallocarboranes, both existing and hypothetical, as well as correlations between the structures of clusters and the number of electrons involved in skeletal bonding.

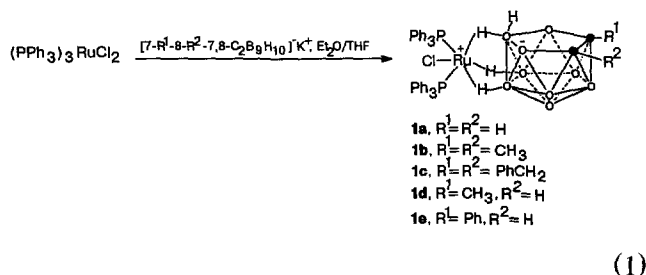
This review covers the results of the authors' research work on semi-sandwich dicarbon metallocarborane clusters of platinum group metals (Rh, Ru, Os) with non-hydrocarbon ligands (i.e. hydride, chloride, phosphine) as well as π -diene/dienyl ligands at the metal center of the metallocarborane clusters. This review has focused on those metallocarboranes whose structures were determined by X-ray diffraction studies. With this in mind, the discussion of purely chemical aspects was considerably reduced, and the reader is referred to the cited papers for more complete chemical or stereochemical information on these clusters. The results of some of the chemical and X-ray diffraction studies discussed below were performed in the frame of scientific collaboration between our group and the group of Professor Hawthorne (UCLA, USA); the acknowledgments will be given in the text where appropriate.

2. Metallocarboranes of *closo* and *exo-nido* types containing non-hydrocarbon ligands

Unlike the related $[C_5H_n(Alk)_{5-n}]^-$ ($n = 0-5$) ligands, dicarbon *nido*-carborane anions derived from $[C_2B_9H_{12}]^-$ frequently adopt an unusual coordination mode with transition metals, for instance forming an exopolyhedral two-electron, three center (2e,3c) B-H...M (metal) bonds. At the beginning, such *exo-nido*-metallocarborane species attracted considerable interest owing to their structural and bonding features [10–13], and later they played an important role in the development of metallocarborane chemistry [14,15] and homogeneous catalyses [16].

In 1991 we succeeded in preparation of the first representatives of *exo-nido*-ruthenacarborane clusters, *exo-nido*-5,6,10-[Cl(Ph₃P)₂Ru]-5,6,10- μ -(H)₃-10-H-7-

R¹-8-R²-7,8-C₂B₉H₆ (**1a–e**) (for syntheses of **1a,b** see Ref. [12]) wherein the *nido*-carborane cage functions in a tridentate manner forming in the solid state rather rare system with three (2e,3c) B-H...Ru bonds (Eq. (1)).



According to the X-ray diffraction study of **1a** (Fig. 1), the coordination geometry of the ruthenium atom in this molecule represents an octahedron whose vertices are occupied by two phosphine ligands, a Cl atom, and three boron hydrogens of the *nido*-carborane cage. An 'extra-hydrogen' atom is located exclusively at the B(10) atom of the open face; on the basis of its position and observed bond length B(10)–H(102) of 1.02(5) Å, it can be regarded as a terminal rather than a bridging boron hydride. Since the Ru atom is bonded to a Cl ligand, and taking into account that the carborane cage retains *nido*-geometry with the 'extra-hydrogen' atom over the pentagonal open face, this complex should be rationalized as zwitterionic with the Ru^{II} atom having an 18-electron configuration. The molecule of **1a** has a mirror plane bisecting the P–Ru–P angle, passing through the Cl atom and the mid-point of the C–C bond of the *nido*-carborane cage, thus adopting a symmetrical-type structure. However, all compounds of this series, independently of the nature of the cage substituents, were shown to exist in solution as a mixture of symmetrical and unsymmetrical isomers, all having *exo-nido* structures as evidenced by ¹H and ¹¹B NMR

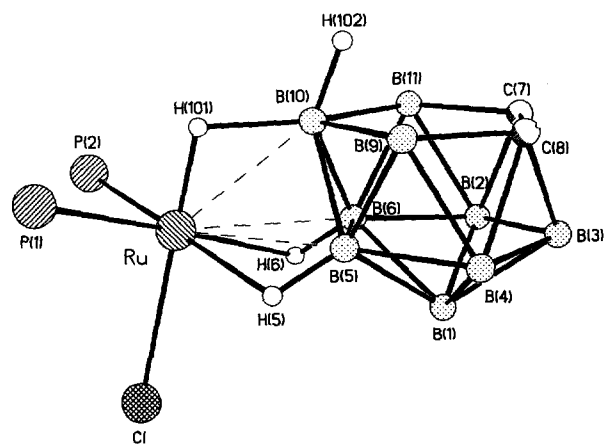


Fig. 1. Molecular structure of complex **1a**.

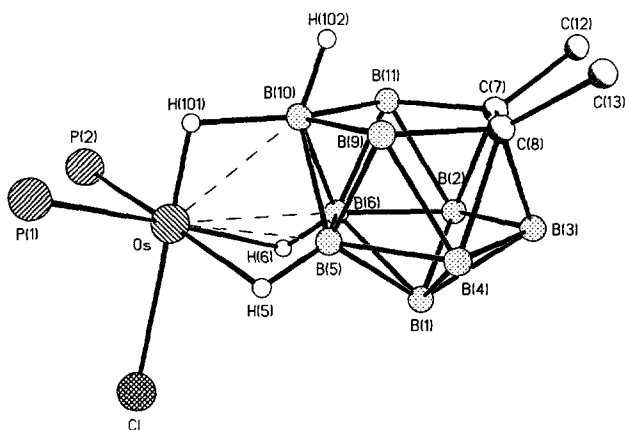
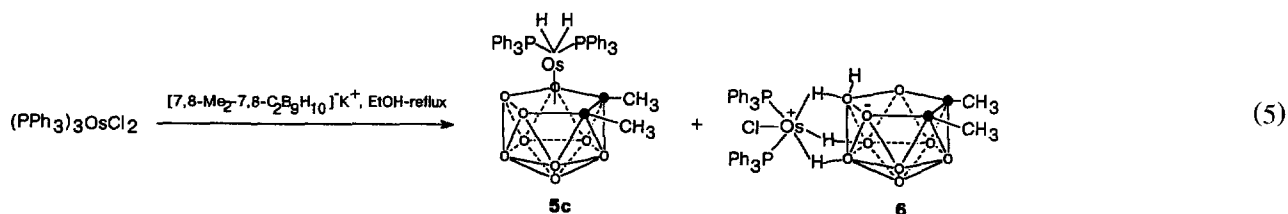
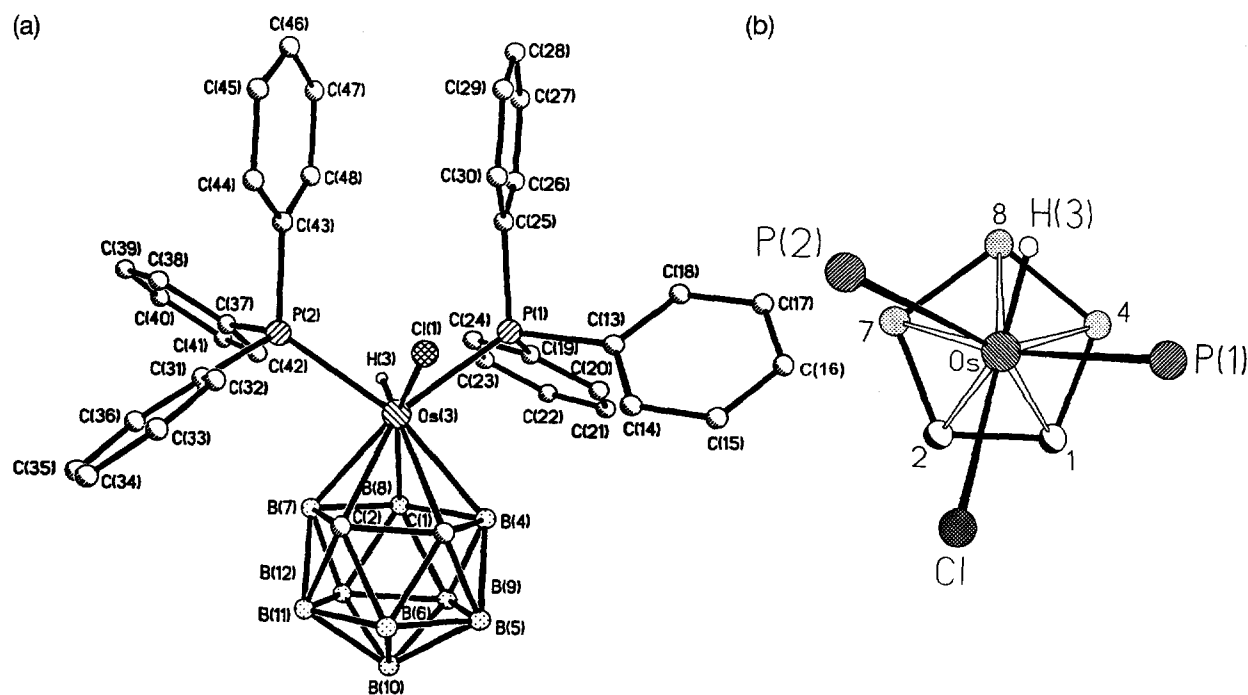


Fig. 4. Molecular structure of complex 6.

The structural studies of *closo*-osmacarboranes **5a,c** (Figs. 5 and 6 respectively), which are actually the first representatives of the structurally characterized *closo*-hydrodoosmacarborane complexes with π -dicarbollyl

ligands, revealed interesting structural peculiarities of the molecules: different orientations of the $(\text{PPh}_3)_2\text{OsHCl}$ and $(\text{PPh}_3)_2\text{OsH}_2$ moieties relative to the open face of the carborane cages were found. In particular, one of the two PPh_3 groups in **5c** turned out to be located in the considerably overcrowded environment arising from their close disposition to the cage substituents. By contrast, in molecule **5a**, as well as the closely related *closo*-ruthenacarborane **2** (see Fig. 2), all ligands at the metal vertices occupy sterically more reasonable positions. The reason of the difference in the conformations of metal-containing moieties in **5a** and **5c** is not clearly understood. This may reflect possible differences in the geometry of the HOMO–LUMO interaction between the corresponding orbitals of the π -dicarbollyl ligand and the P_2OsHCl and P_2OsH_2 moieties.

One may suggest that some of the above three-bridged *exo-nido*-metallacarborane complexes of ruthenium and osmium, owing to their availability and stability in

Fig. 5. Molecular structure of complex **5a**: an overview (a); a view of the P_2OsH_2 moiety and the C_2B_3 face coordinated to osmium (b).

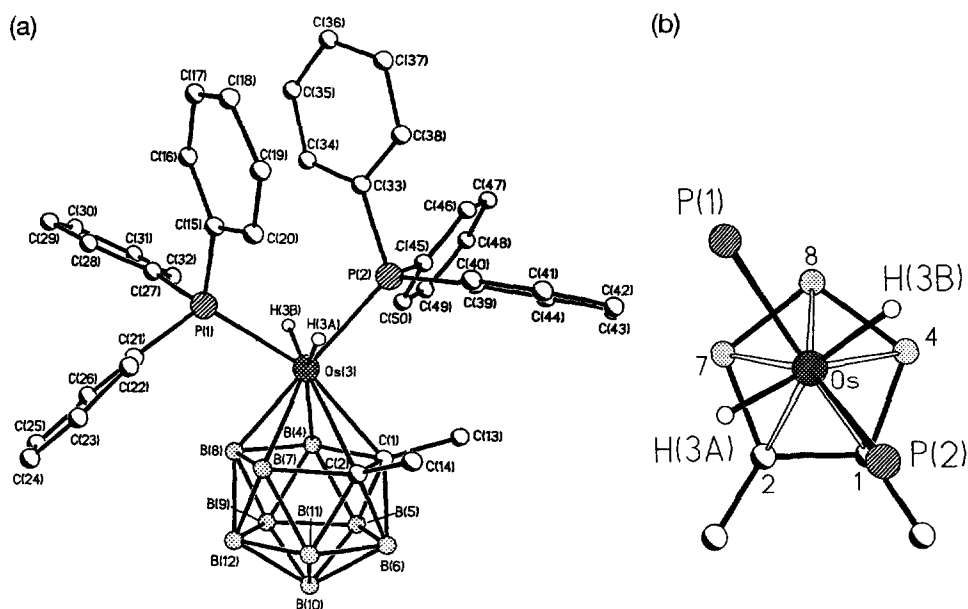
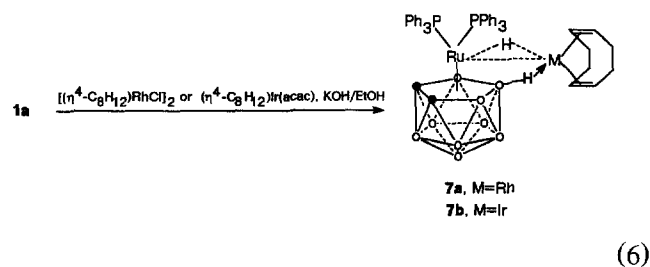


Fig. 6. Molecular structure of complex **5c**: an overview (a); a view of the P_2OsHCl moiety and the C_2B_3 face coordinated to osmium (b).

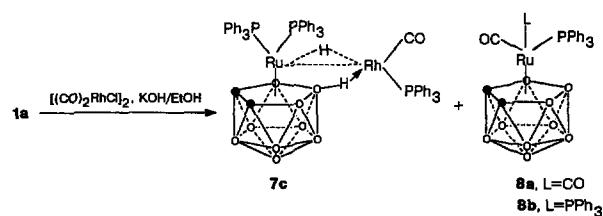
respect of the *exo-nido* \rightarrow *closo* rearrangement, could serve as potential syntons for the design of novel bimetallic carborane clusters. Provided that their open C_2B_3 face could be retained unchanged after the base-promoted removal of the 'extra-hydrogen' atom, such new 'exo-metalladicalborollide' ligands could be used for the selective coordination of other metal-containing groups by their open face, thus producing binuclear carborane-containing clusters.

In the development of this strategy we have treated *exo-nido*-ruthenacarborane **1a** with 16-electron dimeric μ -halide rhodium [17,18] and iridium [21] complexes, $[(\eta^4-COD)RhCl]_2$ or $[(CO)_2RhCl]_2$ and $(\eta^4-COD)Ir(acac)$ respectively, under basic conditions (Eqs. (6) and (7)). Indeed, this led to the construction of new mixed-metal carborane complexes (**7a–c**); however, these proved to exhibit rather different structures from those expected. It was evident from the structurally studied molecules of **7a**² and **7c** (see, for example, Fig. 7 for **7c**) that the complexes obtained can be regarded as a typical *closo*-ruthenacarboranes wherein the icosahedral fragments are attached to the metal-containing moieties by $Ru-H-M$ and $B-H \dots M$ linkages. In the reaction of **1a** with $[(CO)_2RhCl]_2$ (Eq. (7)), along with **7c**, two side-products have been isolated and identified as *closo*-3-L-3-CO-3- PPh_3 -3,2,1-Ru-7,8- $C_2B_9H_{11}$ (**8a,b**) indicating this reaction to be non-stoichiometric. All the results obtained are consistent with the facile *exo-nido* \rightarrow *closo* rearrangement of starting *exo-nido*-ruthenacarborane **1a** which occurs in the course of the above reactions. They also suggest the crucial role of the

presence of a base in the reaction mixture; this may serve not only as a 'sponge' for the 'extra-hydrogen' and chlorine atoms of **1a**, but it can probably also facilitate *exo-nido* \rightarrow *closo* rearrangement of the intermediate 'exo-ruthenadicalborollide' species formed.



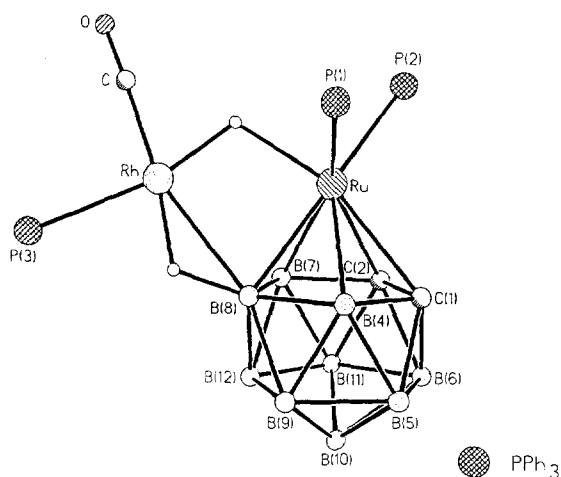
(6)



(7)

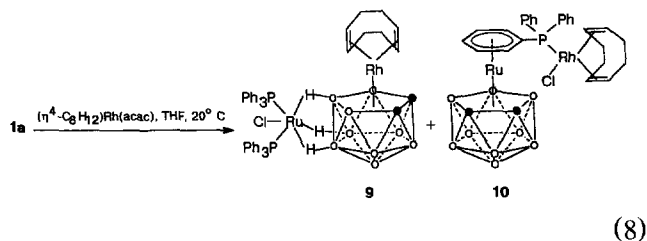
The complexes **7a–c** are actually unsaturated species having 32 valence electrons, wherein the Rh^I atom has only a 16e shell. The separations between the two metals determined from the single crystal analyses of **7a** and **7b**, 2.845(1) Å and 2.889(1) Å respectively, are within the range typical of a direct metal–metal interaction, and so it seemed that a single metal–metal bond should exist in the clusters. At the same time, the

² See footnote 1.

Fig. 7. Molecular structure of complex **7c**.

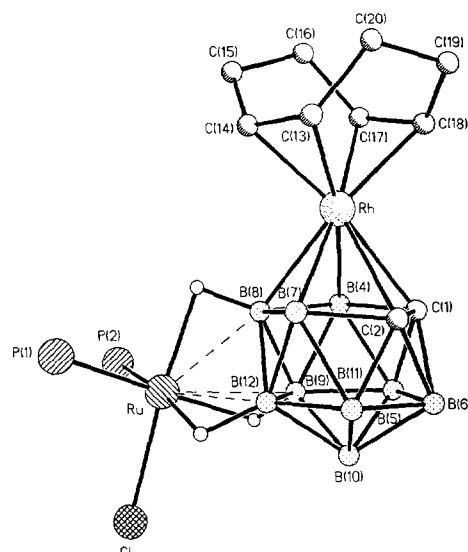
Mulliken Rh–Ru bond order in the model complex $(\text{CO})(\text{PH}_3)\text{Rh}(\mu\text{-H})\text{Ru}(\text{PH}_3)_2(\pi\text{-C}_2\text{B}_9\text{H}_{11})$, which we calculated by using an extended Hückel molecular orbital method, proved to be very small (0.025) but positive.³ Consequently, this suggests that the bonding between two metal-containing moieties in the bimetalacarboranes obtained should probably be represented as a two three-center two-electron bond system by analogy with two four-center two-electron bonds in coordinatively unsaturated dimeric complex $\{\text{HRh}[\text{P}(\text{O}^i\text{Pr})_3]_2\}_2$, as has been assumed by Muetterties and coworkers [22].

Very recently, an original alternative approach to the construction of the desired bimetallic *closo*-metallacarboranes which have a metal center at the *exo* position of the carborane cage has been developed. This includes the reaction of **1a** with $(\eta^4\text{-COD})\text{Rh}(\text{acac})$ which was carried out under mild and absolutely neutral conditions [23] as shown in Eq. (8).

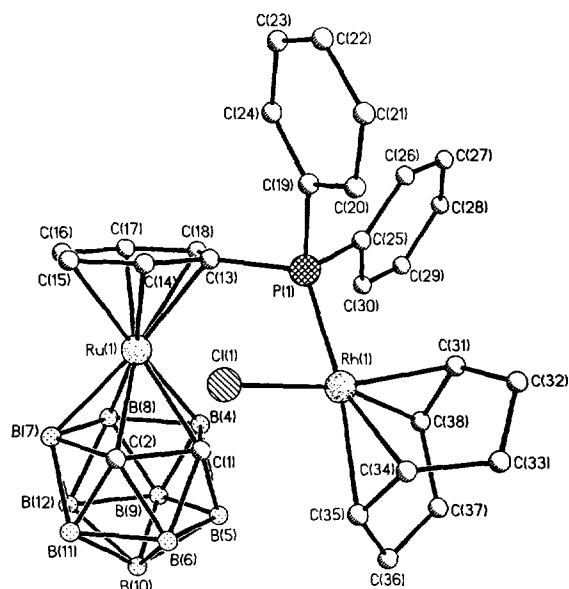


One of the major products which was successfully isolated from the reaction mixture by column chromatography in moderate yield turned out to be the complex with the expected structure, *closo*-3,3- $(\eta^4\text{-COD})$ -8,9,12-[*exo*-($\text{Cl}(\text{PPh}_3)_2\text{Ru}$)]-8,9,12- $\mu\text{-}(\text{H})_3$ -3,1,2- $\text{RhC}_2\text{B}_9\text{H}_8$ (**9**). Indeed, it involves the *closo*-($\eta^4\text{-COD}$)rhodacarborane framework with bis(phos-

³ The calculations were performed by Dr. I.A. Stankevich and Dr. A.L. Chistiakov of the Institute of Organoelement Compounds of the RAS.

Fig. 8. Molecular structure of complex **9**.

phine)chlororuthenium moiety attached at the *exo*-position and linked with the carborane cage via three (2*c*,3*c*) B–H...Ru bonds (Fig. 8). This result showed clearly that *exo-nido*-metallacarboranes of this type under appropriate conditions can be converted to open-faced *nido* species, and followed by introduction of a second metal-containing moiety can be easily transformed to bimetalacarborane complexes of various types. According to the X-ray diffraction study of the second reaction product, it represents *closo*-3- $\{(\eta^6\text{-}[(\eta^4\text{-COD})\text{RhClPPh}_2\text{C}_6\text{H}_5])\}$ -3,1,2- $\text{RuC}_2\text{B}_9\text{H}_{11}$ (**10**) wherein one of the phenyl groups of the triphenylphosphine ligand at the rhodium center acts as a π -arene ligand for the ruthenium atom (Fig. 9). Its formation is, presumably, due to the irreversible transformation of the start-

Fig. 9. Molecular structure of complex **10**.

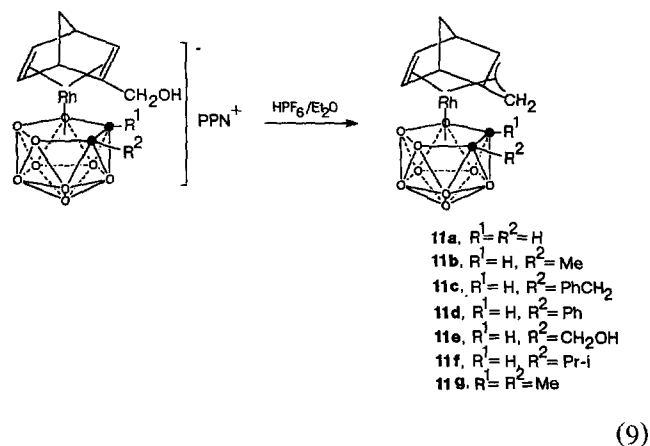
ing **1a** into the intermediate *closo* species which occurs, obviously, along with partial decomposition of **1a** leading to release of a PPh_3 and a Cl ligand.

3. *closo*-Rhodacarboranes which incorporates π -hydrocarbon ligands at the metal center

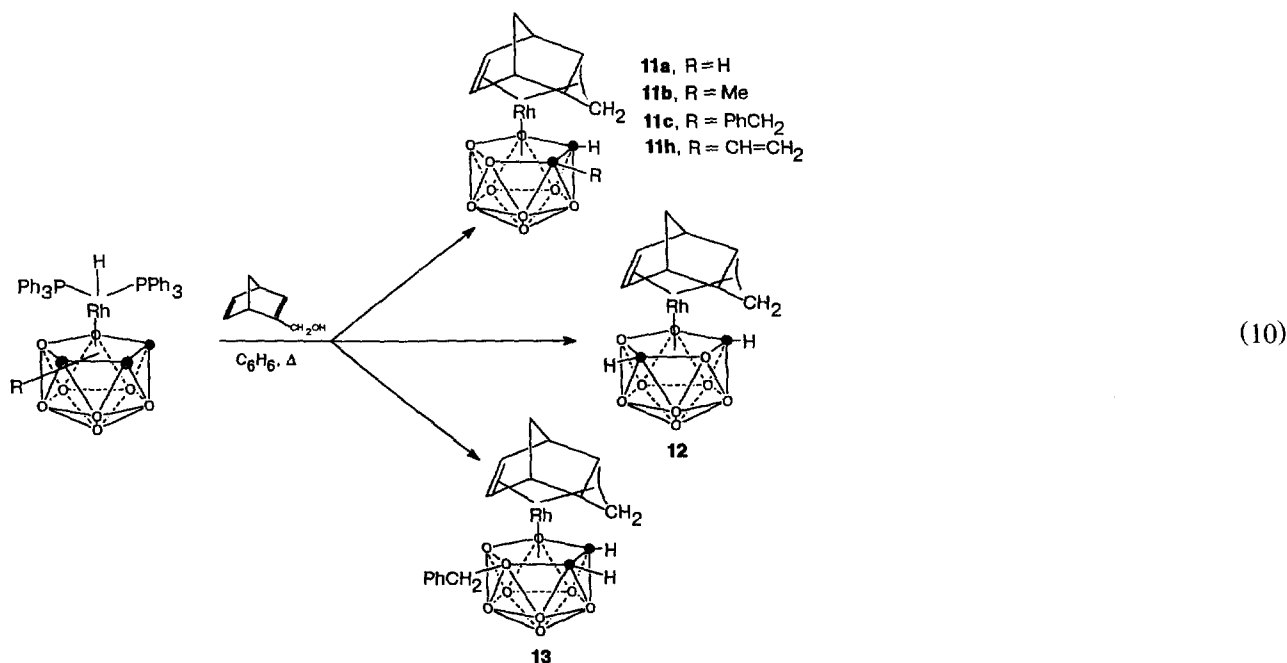
In spite of the vast diversity of *closo*-metallacarboranes containing π -hydrocarbon ligands, data on the clusters with π -dicarbollyl and π -diene/dienyl ligands in the coordination sphere of a transition metal are limited [1,9]. However, in recent years, several rational approaches to the synthesis of a series of anionic and neutral platinum metal *closo*-cyclooctadiene(y)metallacarboranes have been developed [3,4,24–27]. These include mainly the ligand-exchange methods based on the reactions of either $\{(\eta^4\text{-diene})\text{RhCl}\}_2$ or $(\eta^4\text{-diene})\text{Rh}(\text{acac})$ with various di-K or di-Tl salts of $[\text{nido-7,8-R}^1\text{R}^2\text{-C}_2\text{B}_9\text{H}_9]^{2-}$ ($\text{R}^1, \text{R}^2 = \text{H, Alk, Ar}$).

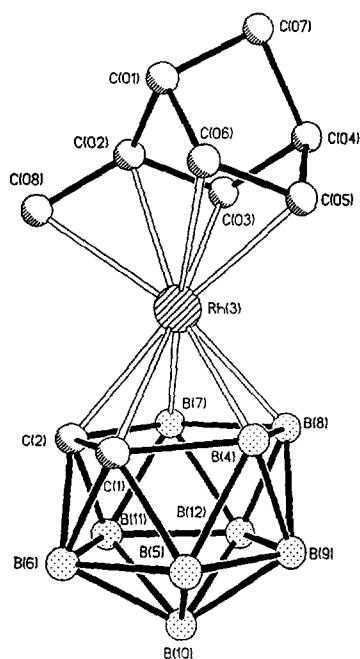
Extensive studies of the protonation of anionic *closo*-3,3-(η^4 -diene)-1-R¹-2-R²-3,1,2-dicarbollylrhodium clusters containing functional groups either at the cage carbon atom or at the hydrocarbon ligands (1,5-cyclooctadiene and 2,5-norbornadiene) have been performed [3,25–27]. As a result, in the latter case a series of neutral *closo*-3,3-($\eta^{2,3}$ -methylenenorbornadienyl)-1-R¹-2-R²-3,1,2-RhC₂B₉H₉ (**11a–g**) have been prepared

(Eq. (9)) [3,4], some of which were found to be efficient catalyst precursors for organic reactions [5–7].



We have also developed an alternative one-step synthetic method for the synthesis of these *closo*-($\eta^{2,3}$ -methylenenorbornadienyl)rhodacarboranes (for **11a,b** and **12** see Ref. [3]) which involved the gentle heating in benzene of available *closo*-bis(phosphine)hydridorhodacarborane derivatives with 2-(hydroxymethyl)norbornadiene. This approach was extended to some other complexes of this type, i.e. **11c,h** and **13** [4] (Eq. (10)).

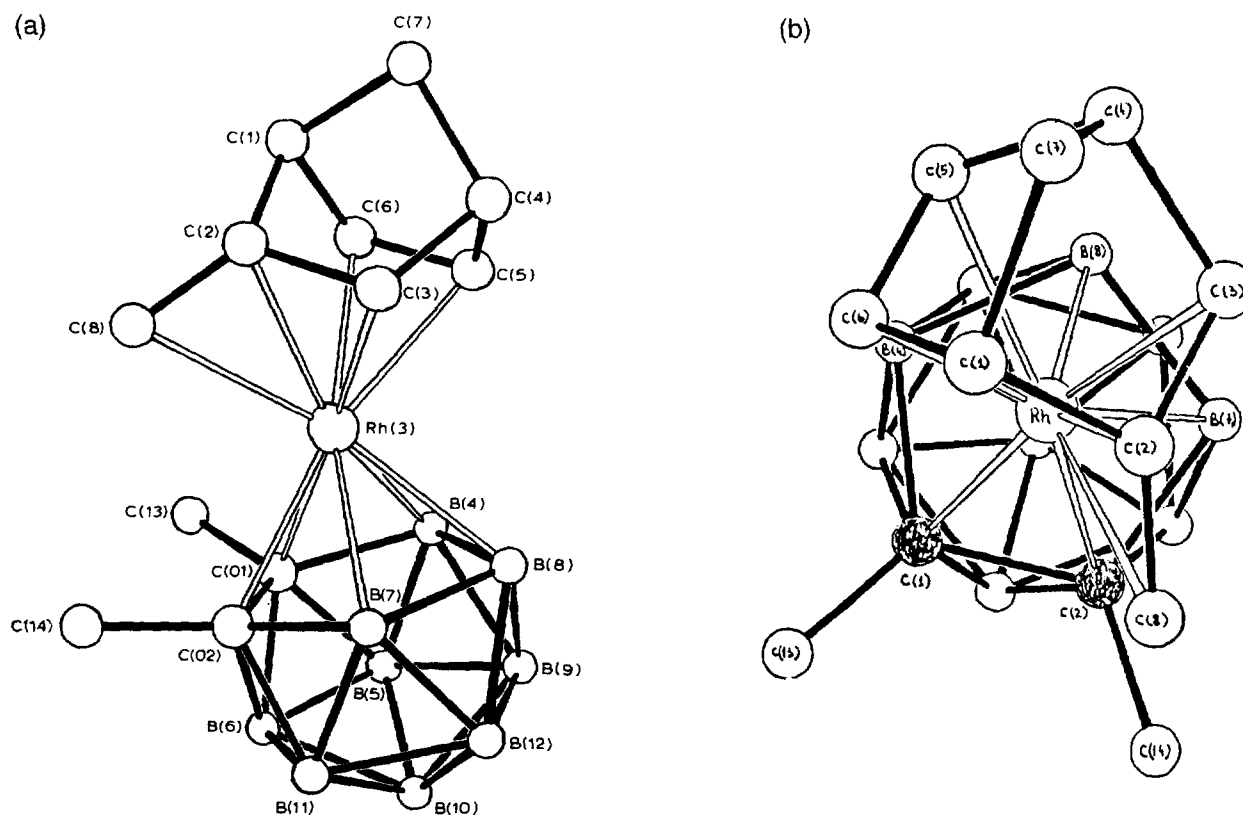


Fig. 10. Molecular structure of complex **11a**.

The structures of two of the above complexes, **11a** [3] and **11g** [6], were determined by X-ray diffraction studies as shown in Figs. 10 and 11 respectively. These

revealed an unusual coordination mode of the diene ligand by the Rh atom, namely by exocyclic η^3 -allylic and endocyclic η^2 -olefinic moieties of the hydrocarbon ligands. It is noteworthy that in molecule **11g**, as well as in the three crystallographically independent molecules in the structure of **11a**, the orientation of the $\eta^{2,3}$ -norbornadienyl ligand relative to the open carborane face was found to be quite similar; however, in the dimethyl-substituted complex **11g** one would expect considerable steric hindrances due to the relatively short contact (3.07 Å) between the exo-cyclic C(8) atom of the diene ligand and one of the methyl substituents at the carborane cage. This suggests that such orientation of the diene ligand is primarily determined by electronic factors or, more probably, by specific electrostatic interaction between π -diene and π -dicarbolly ligands in these complexes.

Clusters **11b–f** with unsymmetrical carborane ligands, originally prepared as a diastereomeric mixture, were further successfully separated into pure diastereomers by TLC, fractional crystallization or HPLC methods. Their stereochemistry has been studied by means of a correlation between the structural results for diastereomers of **11c,g** in the solid state yielded by the single-crystal X-ray diffraction and those results obtained by 2D-NMR spectroscopy in solution (^1H – ^1H and ^{11}B – ^{11}B correlations) [28].

Fig. 11. Molecular structure of complex **11g**: an overview (a); a view of the $(\pi\text{-C}_7\text{H}_7\text{CH}_2)\text{Rh}$ moiety and the C_2B_3 face coordinated to rhodium (b).

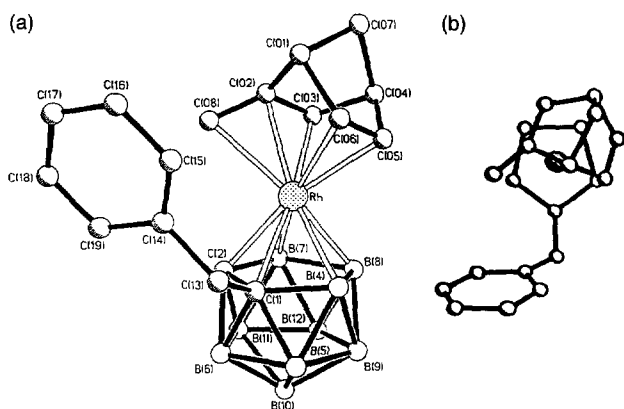


Fig. 12. Molecular structure of diastereomer **11c** of type A: an overview (a); schematic projection of the $(\pi\text{-C}_7\text{H}_7\text{CH}_2)\text{Rh}$ moiety on the pentagonal face of the carborane cage (b).

It was established by the X-ray diffraction study, performed for two pairs of diastereomers **11c** and **11g**,⁴ that the diastereomers of type A, as shown for **11c** (Fig. 12), have more sterically crowded conformation of the bicyclic ligand with respect to the substituent at the carborane open face, while for the alternative diastereomers of type B (Fig. 13) the conformation of the same ligand does not cause significant steric hindrance in the molecules. The preliminary results of molecular mechanics calculations for both types of diastereomer (A and B) of **11c** showed that the minimum energies are adopted at least for two conformations of each diastereomer of **11c**, and one of them is in a good agreement with those observed in structures of diastereomers of **11c** in the solid state [29]. Thus, the orientation of the dienyl ligand relative to the open face of the π -dicarbollyl ligand in this series of complexes can be controlled by both electronic and steric factors, depending markedly on the nature of the substituents at the carborane cage.

We have also studied the protonation reactions of anionic salts of *closo*-(η^4 -dicyclopentadiene)rhoda-

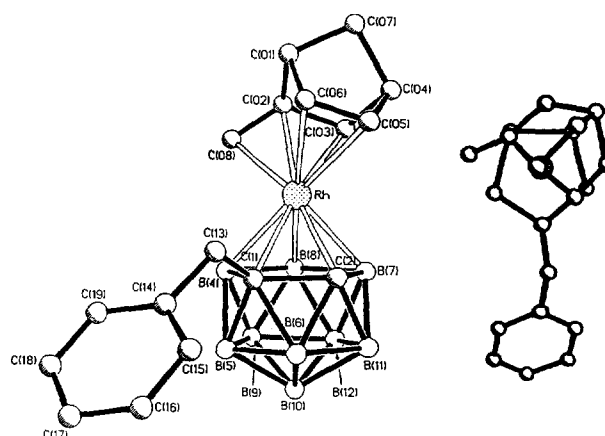
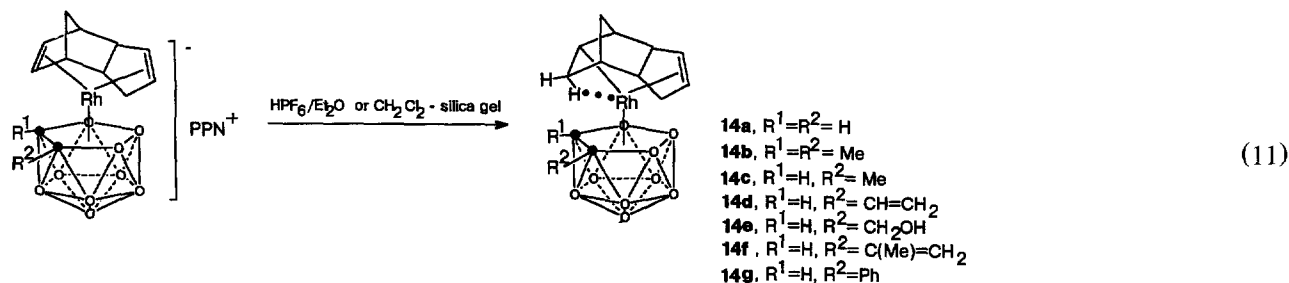
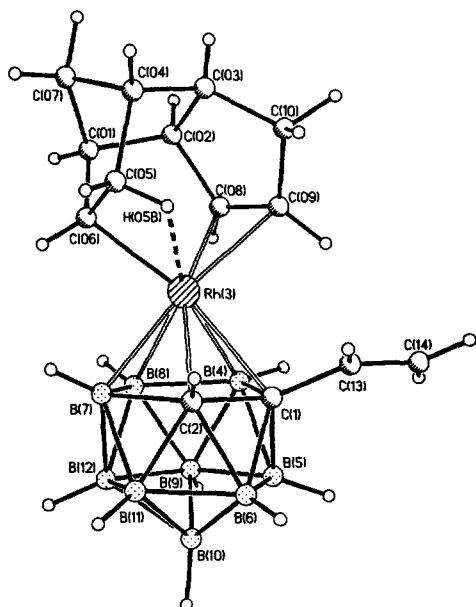


Fig. 13. Molecular structure of diastereomer **11c** of type B: an overview (a); schematic projection of the $(\pi\text{-C}_7\text{H}_7\text{CH}_2)\text{Rh}$ moiety on the pentagonal face of the carborane cage (b).

carboranes with HPF_6 in ether [27] according to Eq. (11). In all cases the protonation proceeds at the ethylene double bond of the diene ligand and affords quite stable *closo*-3,3,3-(η -dicyclopentadienyl)-1- R^1 -2- R^2 -3,1,2- $\text{RhC}_2\text{B}_9\text{H}_9$ (**14a–g**) which involve the agostic C–H...Rh bond. It was found that the same protonation reaction proceeded even on treatment of starting anionic complexes on column chromatography on silica gel using methylene chloride as an eluent (see for example Ref. [30]). Several *closo*-dicyclopentadienylrhodacarboranes of this series with symmetrical π -dicarbollyl ligands were prepared in optically active forms [31]. In the case of complexes with unsymmetrical π -dicarbollyl ligands, **14c,d**, the successful separation of initial mixtures into diastereomeric forms via fractional crystallization or by column chromatography on silica gel was achieved [32]. The structure of diastereomeric complex **14d** was determined by a single-crystal X-ray diffraction study; this confirmed clearly the existence of agostic C–H...Rh interaction in this complex (C(05)–H(A), 0.86(8); C(05)–H(B), 0.99(8); RhH(05B), 2.04(5) Å) and established its relative configuration (Fig. 14).

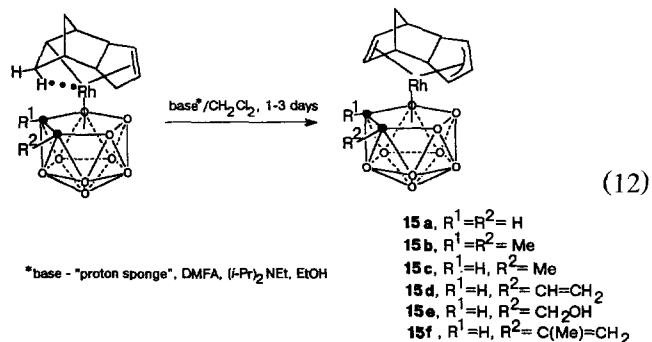
⁴ See footnote 1.



Fig. 14. Molecular structure of complex **14d**.

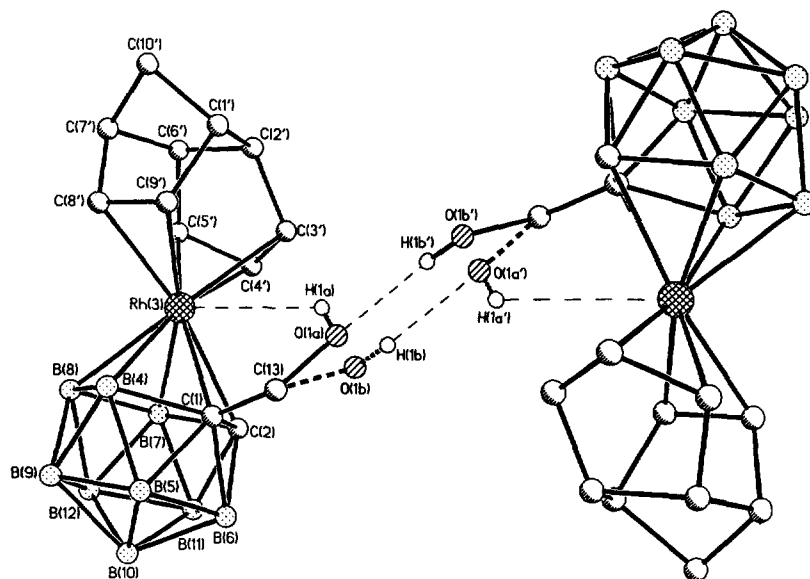
The hydrocarbon ligands in **14a–f** can be easily transformed in the coordination sphere of the rhodium atom under the base-promoted conditions into $\eta^{2,3}$ -allylolefinic-type ligands to form new *closo*-3,3-($\eta^{2,3}$ -dicyclopentadienyl)-1- R^1 -2- R^2 -3,1,2RhC₂B₉H₉ (**15a–f**) (Eq. (12)) [17,30]. In the course of this dehydrogenation reaction, complexes **14d,e** were shown to undergo kinetic resolution, and one of the diastereomers of each of

the complexes **14d,e** could be separated in pure form [32].



The structure of **15e** has been determined by a single-crystal X-ray diffraction study (Fig. 15). This complex in the solid state was proved to have a dimeric structure wherein two molecules, related by a crystallographic inversion center, are linked via O–H...O hydrogen bonds (O(1a)...O(1b'), 2.947(3) Å).

The structure of **15e** represents an interesting case of disorder caused by the non-matching numbers of donors and acceptors of H-bonds. Considering the existence of intramolecular O–H...Rh interactions, which are well documented in literature (see for instance Ref. [33]), and which in this case are confirmed by rather short O...Rh distance (Rh(3)...O(1a), 3.315(2); Rh(3)–H(1a),

Fig. 15. Molecular structure of dimeric complex **15e**.

2.98(5) Å), we will have to deal with the problem of how to distribute two 'active' hydrogens over three possible H-bonding sites. It is just this situation which is definitely resolved by means of disorder, which reflects the concerting switching of two H-bonds between two possible arrangements, thus satisfying the requirements of three H-bond acceptors.

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