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Review

# Large-cage (11–13-vertex) dicarbon metallacarboranes of platinum metals with mono- and polycyclic diolefin ligands

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## Contents



**Abstract**

Different types of 11–13-vertex metallacarboranes of platinum metals with unsaturated π-hydrocarbon ligands derived from mono- and polycyclic diolefins are reviewed. The purpose is to provide an overview of significant findings and trends in the synthetic and structural chemistry of these compounds. Some basic information on their catalytic and unique chemical properties, including the results on fluxional behavior and transformations of agostic (C–H···M) metallacarboranes in solution, are also discussed.


*Keywords:* Metallacarboranes; Platinum metals; Synthesis; Reactivity; Dynamic behavior; Catalysis by metallacarboranes

## 1. Introduction

Metallacarborane clusters with metal-coordinated hydrocarbon ligands based on cyclic polyolefins comprise a rather large group of compounds. Even though we are going to limit ourselves only to large-cage metallacarboranes, we will still cover a huge field of complexes showing great diversity of structural types (*closo*, *exo-nido*, *exo-closo*, *etc.*). The existence of a variety of geometrically distinct metallacarboranes within this particular family is primarily determined by structural differences of dicarbon carboranes, which can belong to multiple classes, such as *nido*, *closo*, *arachno*, *etc.* This diversity is undoubtedly enhanced by the versatile bonding capabilities of transition metal atoms as well as of cyclodiolefin-based lig-

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ands. Thus, in many related compounds belonging to classical 12-vertex *closo*-metallacarboranes, hydrocarbon ligands of a similar framework display different hapticity to metal atoms. For example, if L is a $C_8$-ring ligand originating from 1,5-COD, different metal-to-ligand coordination modes, such as $\eta^4$-L, $\eta^{3,2}$-L, and $\sigma,\eta^2$-L can occur. Moreover, in combination with other organic or inorganic groups, carboranes can participate in mono- and bimetallic systems, wherein one of the metal-containing moieties is exopolyhedrally attached to the cage ligand. This family of *exo*-metal carborane derivatives includes several subgroups, which differ not only in heteroborane cluster structures (*nido*, *closo*, *etc.*) but also in the binding mode of the cage to metal centers, *e.g.* either through multiple three-center two-electron $\{B–H\}_n\cdots M$ ($n = 1–3$) bonds or *via* one or two M–E bonds (E is a phosphorus- or sulfur-containing cage substituent) which may simultaneously be supported by one or two $B–H\cdots M$ linkages.

This review summarizes all presently known types of higher metallacarborane complexes with cyclodiolefin-based ligands with a number of vertices varying from 11 to 13. Preference is given to the preparative chemistry of metallacarboranes, rationalizing their cluster structures and studies of their stereochemistry and reactivity, as well as the dynamic behavior in solution, including properties responsible for their successful use in homogeneous catalysis as catalysts or catalyst precursors.

## 2. Mono- and polynuclear metallacarboranes with $\eta^4$-cyclodiolefin ligands

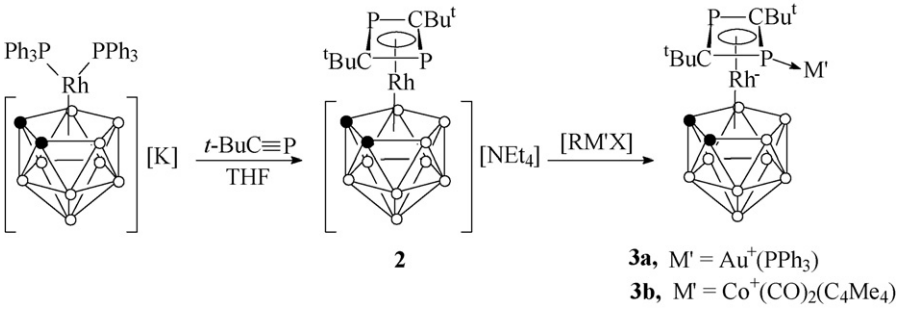
### 2.1. Neutral mononuclear closo-metallacarboranes

First neutral *closo*-metallacarboranes [3,3-($\eta^4$-$C_4Ph_4$)-1,2-$R_2$-3,1,2-*closo*-$PdC_2B_9H_9$] (**1a**, **b**: **a**, R = H; **b**, R = $CH_3$) containing the cyclic diene ligand, *viz.*, tetraphenylcyclobutadiene, were described in early studies by Hawthorne and co-workers [1]. Both complexes were prepared in low yield (at most 10%) by the reaction of [($\eta^4$-$C_4Ph_4$)$PdCl_2$]$_2$ with the corresponding dicarbollide dianions $Na_2$[7,8-$R_2$-7,8-*nido*-$C_2B_9H_9$] in THF. These compounds have sandwich structures: the metallabonded $C_2B_3$ face of the carborane ligand and the cyclobutadiene $C_4$-ring were found to be almost parallel in the solid-state structure of **1b** studied by X-ray diffraction.

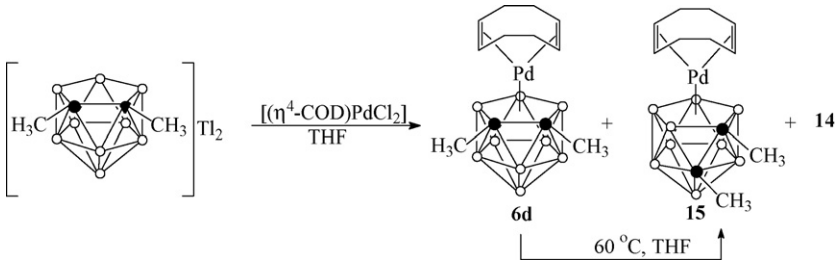
Stone et al. [2] reported the reaction of the $K^+$ salt of the [3,3-($Ph_3P$)$_2$-3,1,2-*closo*-$RhC_2B_9H_{11}$] anion with phosphaalkyne *t*-BuC≡P. The latter reagent undergoes cyclodimerization resulting finally in the stable anionic complex [$NEt_4$][3,3-{$\eta^4$-(*t*-$Bu_2C_2P_2$)}-3,1,2-*closo*-$RhC_2B_9H_{11}$] (**2**) (Scheme 1). According to X-ray diffraction data, the 1,3-diphosphacyclobutadiene ligand in **2** is nearly planar, with the average P–C distance of 1.785 Å. This fact reflects the partial double-bond character of the $C_4$-ring bonds coordinated to the metal atom. The reactions of **2** with the electrophilic reagents [$AuCl(PPh_3)$] and [$Co(CO)_2(NCCH_3)(\eta^4$-$C_4Me_4)$][$PF_6$] were studied. These reactions produced the zwitterionic complexes [3,3-{$\eta^4$-(*t*-$Bu_2C_2P_2M'$)}-3,1,2-*closo*-$RhC_2B_9H_{11}$] (**3a**, M′ = $AuPPh_3$; **b**, M′ = $Co(CO)_2(\eta^4$-$C_4Me_4)$), respectively, wherein the incoming metal groups are coordinated by the phosphorus atom of the {$\eta^4$-(*t*-$Bu_2C_2P_2$)} ring.

Neutral platinacarborane [3,3-($\eta^4$-COD)-1-R-2-$R^1$-3,1,2-*closo*-$PtC_2B_9H_9$] (**5a**, R = $R^1$ = H) was prepared in 38.5% yield by the same ligand-exchange method starting from [($\eta^4$-COD)$PtCl_2$] (**4**) and the di-$Li^+$ salt of the [7,8-*nido*-$C_2B_9H_{11}$]$^{2-}$ dianion [3]. The analogous palladacarborane [3,3-($\eta^4$-$C_8H_{12}$)-1-R-2-$R^1$-3,1,2-*closo*-$PdC_2B_9H_9$] (**6a**, R = $R^1$ = H) was synthesized in 70% yield by the diamine-COD ligand displacement reaction of [3,3-{$(CH_3)_2N(CH_2)_2N(CH_3)_2$}-3,1,2-*closo*-$PdC_2B_9H_{11}$] (**7**) with an excess of COD in the presence of gaseous HCl in $CH_2Cl_2$ (it was reported that the reaction does not proceed under neutral conditions) [4]. Complex **6a** was also generated, along with other unidentified products, in the reaction of $Tl_2$[7,8-*nido*-$C_2B_9H_{11}$] (**8**) [5] with the cationic complex [($\eta^4$-$C_8H_{12}$)Pd($\eta^5$-$C_5H_5$)][$BF_4$] [6]. The results of a comparative crystallographic study of complexes **6a** [6] and **7** [4] showed that the asymmetry in the bonding of the metal atom to the $C_2B_9$ cage ('slipping' distortion of the {$PdC_2B_9$} framework) in **7** (Pd···B(4, 7), 2.182 Å; Pd···B(8), 2.205 Å; Pd···C(1, 2), 2.623 and 2.608 Å) is substantially smaller than that observed in complex **6a** (Pd···B(4, 7, 8), 2.178–2.294 Å; Pd···C(1, 2), 2.377 and 2.432 Å). This fact has been attributed to the difference in the π-acid character of the exopolyhedral ligands in these complexes [6].

The synthesis of a short series of two COD palladium and two COD platinum metallacarboranes with C-mono- and C,C′-diphenylated carborane ligands was reported [7]. It was shown that the reactions of [($\eta^4$-COD)$PdCl_2$] (**9**) with $Tl_2$[7-Ph-7,8-*nido*-$C_2B_9H_{10}$] (**10**) or $Tl_2$[7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_9$] (**11**) in $CH_2Cl_2$ afforded complexes **6**(**b**, R = H, $R^1$ = Ph; **c**, R = $R^1$ = Ph), each being isolated as the major reaction product along with




Scheme 1. Formation of anionic rhodacarborane **2** and its transformation to mixed-metal zwitterionic complexes **3a** and **b** [2].



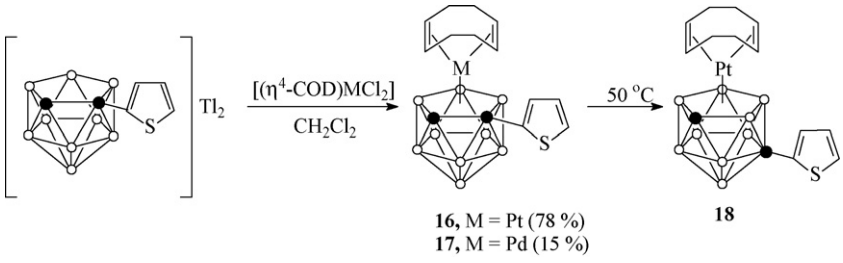

Scheme 2. Synthesis of Pd complex **6d** and its thermally induced "1,2 → 1,2" rearrangement to **15** [9].

five minor species, which were chromatographically separated but not identified. An X-ray diffraction study confirmed that complex **6b** has the {1,2-$Ph_2$-3,1,2-*closo*-$PdC_2B_9$} architecture. It is thus the first species, in which the sterically encumbered C,C′-diphenyl groups are not separated from each other by one or more boron units due to polyhedral isomerization. Nevertheless, both a heavily slipping distortion, whereby the metal atom is slipped away from the cage carbon atoms toward the three borons on the open face (Pd-B(4, 7, 8), 2.177–2.230 Å; Pd···C(1, 2), 2.669 and 2.710 Å; C(1)–C(2), 1.521 Å), and a substantial deformation in the coordination mode of the COD ligand observed in **6c** are indicative of overcrowding of this species. A similar reaction of **10** with COD platinum reagent **4** in $CH_2Cl_2$ at ambient temperature afforded *closo* complex **5**(**b**, R = H, $R^1$ = Ph), the platinum analogue of **6b**. In view of these results, it is remarkable that the only isolable product from the reaction of **4** with C,C′-diphenylated di-$Tl^+$ salt **11** under absolutely identical conditions was the isomerized species [2,2-($\eta^4$-COD)-1,8-$Ph_2$-2,1,8-*closo*-$PtC_2B_9H_9$] (**12**), in which the carbon atoms are separated by one boron unit. It was noted that complex **6c** undergoes an analogous polyhedral rearrangement (*e.g.* the so-called "1,2 → 1,7" cage carbon atom isomerization) only upon heating in toluene at 55 °C, whereas no isomerization is observed for the less sterically crowded complex **6b**.

Related to these C-phenyl- and C,C′-diphenyl substituted complexes **5b**, **6b**, **c** and **12** are two independently synthesized C,C′-dimethylated complexes of platinum **5**(**c**, R = $R^1$ = $CH_3$) [8] and palladium **6**(**d**, R = $R^1$ = $CH_3$) [9], which were isolated as the major products in the reactions of $Tl_2$[7,8-$(CH_3)_2$-7,8-*nido*-$C_2B_9H_9$] (**13**) [5] with COD-metal complexes **4** and **9**, respectively. In addition to **6d**, the latter reaction produced two minor species with "1,2 → 1,2" polytopically isomerized carborane ligands formulated as [*commo*-4,4′-Pd{1,2-$(CH_3)_2$-1,2-$C_2B_9H_9$}$_2$] (**14**, a mixture of *meso*- and *d*,*l*-isomers) and [4,4-($\eta^4$-$C_8H_{12}$)-1,2-$(CH_3)_2$-4,1,2-*closo*-$PdC_2B_9H_9$] (**15**). The structure of the latter complex was determined by X-ray diffraction, which showed that the methylated carbon atoms move from the upper to lower pentagonal belts of the cage ligand but, in contrast to **12**, these atoms still occupy the adjacent positions in this cluster (Scheme 2). It was found that the polyhedral rearrangement **6d** → **15** (*e.g.* the so-called "1,2 → 1,2" cage carbon atom isomerization) can proceed under mild heating of a solution of **6d** in THF. However, at a temperature of about 60 °C, isomerization occurs only with 40% conversion, whereas heating at higher temperature leads to decomposition.

Metallacarboranes of the type [3,3-($\eta^4$-COD)-1-($C_4H_3S$)-3,1,2-*closo*-$MC_2B_9H_{10}$] (**16**, M = Pt; **17**, M = Pd; $C_4H_3S$ is thien-2-yl) were synthesized by the reaction of $Tl_2$[7-($C_4H_3S$)-7,8-*nido*-$C_2B_9H_{10}$] with COD-metal reagents **4** and **9**, respectively (Scheme 3) [10]. It has also been found that heating of a solution of **16** in $CD_2Cl_2$ to 50 °C in a sealed NMR tube resulted in the "1,2 → 1,7" rearrangement of this compound to give the isomeric complex [2,2-($\eta^4$-COD)-8-($C_4H_3S$)-2,1,8-*closo*-$PtC_2B_9H_9$] (**18**). By contrast, complex **17** did not undergo the rearrangement even at 55 °C and even after a more prolonged heating, which agrees well with the fact that C-monophenylated palladium complex **6b** is not subjected to thermal isomerization [7].

These results are consistent with a higher tendency of metallacarborane complexes of third-row transition metals to polyhedral rearrangements compared to their second-row analogues. Stone et al. were the first to note this fact when studying the behavioral chemistry of the related molybda- and tungstacarboranes [11]. However, this conclusion, as applied to complexes **16** and **17**, is in contradiction with the facile rearrangement observed for palladium complex **6d** [9]. The difference in the reactivity toward the thermally induced skeletal rearrangement of the related palladium and platinum complexes provides experimental evidence that not only the nature of metal but also the influence of steric interactions in metallacarborane




Scheme 3. Synthesis of Pt and Pd complexes **16** and **17**, and "1,2 → 1,7" Pt isomer **18** [10].

systems should be taken into account in these reactions [7,10]. More recently, this was strongly confirmed by Welch et al. in a series of papers on low-temperature polyhedral rearrangements of sterically overcrowded *closo*-metallacarboranes [12].

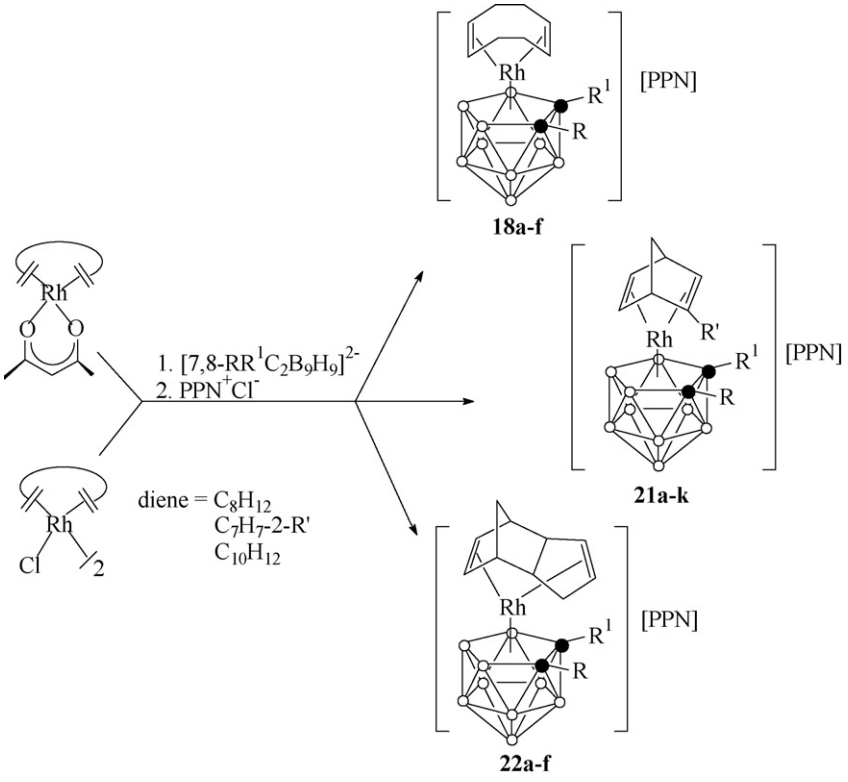
### 2.2. Anionic mononuclear closo-metallacarboranes

The synthesis of anionic *closo*-($\eta^4$-cyclodiene)metallacarboranes is generally based on the ligand-exchange method with the use of dicarbollide dianions as a source of carborane ligands. First anionic rhodacarboranes with the 1,5-cyclooctadiene (COD) ligand at the metal vertex [PPN][3,3-($\eta^4$-COD)-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**18a–c**: **a** $R = R^1 = CH_3$; **b**, R = H, $R^1$ = Ph; **c**, $R = R^1$ = H; PPN is the bis(triphenylphosphine)iminium cation) were prepared nearly 20 years ago by Hawthorne and co-workers [13]. These complexes were synthesized starting from the COD-rhodium dimeric complex $[(\eta^4\text{-COD})_2Rh_2(\mu\text{-Cl})_2]$ (**19**) and the corresponding dicarbollide dianions [7-R-8-$R^1$-7,8-*nido*-$C_2B_9H_9]^{2-}$ (**20a–c**) generated *in situ* from the parent dicarba-*nido*-undecaborate salts [K][7-R-8-$R^1$-7,8-*nido*-$C_2B_9H_{10}$] in the presence of the strong base *i*-PrONa/*i*-PrOH.

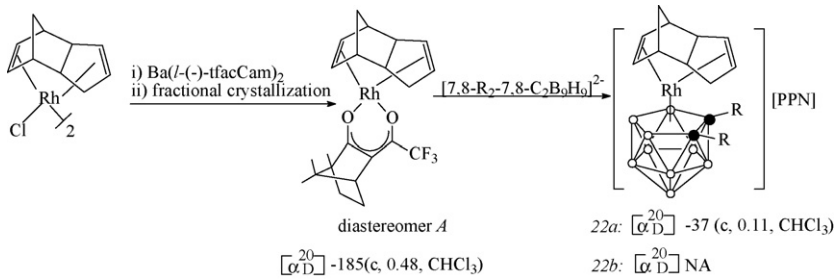
Since that time a number of new anionic *closo*-(η-cyclodiene)metallacarborane species have been synthesized according to an analogous scheme or with the use of the mononuclear complexes [($\eta^4$-cyclodiene)Rh(acac)] instead of μ-chloride rhodium dimers. Among these compounds are new representatives of *closo*-($\eta^4$-COD)rhodacarboranes **18**(**d–f**: **d**, $R = CH_2OH$, $R^1$ = H [14]; **e**, $R = CH{=}CH_2$, $R^1$ = H; **f**, $R = C(CH_3){=}CH_2$, $R^1$ = H [15]) and the related complexes with 2-R′-NBD ligands, [PPN][3,3-{$\eta^4$-(NBD-2-R′)}-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**21a–k**: **a**, R′ = H, $R = R^1 = CH_3$ [16]; **b**, $R' = CH_2OH$, $R = R^1$ = H; **c**, R′ = CHO, $R = R^1 = CH_3$; **d**, $R' = CH_2OH$, $R = R^1 = CH_3$; **e**, $R' = CH_2OH$, R = H, $R^1 = CH_3$; **f**, $R' = CH_2OH$, R = H, $R^1$ = Ph [17]; **g**, $R' = R$ = H, $R^1 = CH_2OH$ [14]; **h**, $R' = R = CH_2OH$, $R^1$ = H; **i**, $R' = CH_2OH$, R = *i*-Pr, $R^1$ = H; **j**, $R' = CH_2OH$, $R = CH_2Ph$, $R^1$ = H; **k**, $R' = C(CH_3)_2OH$, $R = R^1$ = H [18]). The research has also been extended to anionic *closo*-rhodacarboranes with the dicyclopentadiene (DCPD) ligand bound to the metal vertex [19–23]. The synthesis of the following complexes was reported: [PPN][3,3-($\eta^4$-DCPD)-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**22a–f**: **a**, $R = R^1$ = H; **b**, $R = R^1 = CH_3$ [19]; **c**, R = H, $R^1 = CH_3$; **d**, R = H, $R^1 = CH{=}CH_2$; **e**, R = H, $R^1 = C(CH_3){=}CH_2$ [20]; **f**, R = H, $R^1 = CH_2OH$) [21] (Scheme 4).

We have also synthesized first chiral anionic *closo*-($\eta^4$-DCPD)rhodacarboranes [22,23]. Optically active complexes *l*-(−)-**22a**, **b** were obtained in 95 and 64% yields, respectively, by the exchange of the *tfacCam* ligand (*tfacCam* is *l*-3-(trifluoroacetyl)camphorate) with dicarbollide dianions **20a** and **b** in the diastereomeric complex *l*-(−)-[($\eta^4$-DCPD)Rh(tfacCam)] (**A**, prepared with 93% diastereomeric purity from *l*-3-bromocamphor according to a procedure published in [24]) (Scheme 5).

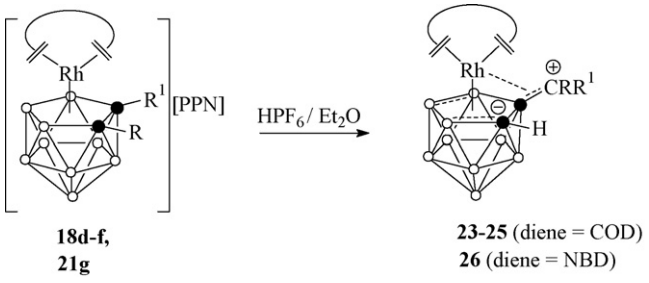
In the study of the reactivity of anionic *closo*-(π-cyclodiene)rhodacarborane complexes containing functional groups at the cage ligand, attention was given to proto-




Scheme 4. Synthesis of anionic *closo*-($\eta^4$-cyclodiene)rhodacarboranes **18-a–f** [13–15], **21a–k** [14,16–18], and **22a–f** [19–21].




Scheme 5. Synthesis of chiral anionic complexes **22a** and **b** by the ligand-exchange method [22].




Scheme 6. Formation of pseudofulvenoid-type complexes **23**–**26** from anionic precursors [14,15].

nation reactions. For example, the acidification of compounds **18d–f** and **21g** with $HPF_6$ afforded the stable zwitterionic pseudofulvenoid-type complexes [3,3-{$\eta^4$-(L-L)}-3,1,2-*closo*-Rh{$\eta^2$:$\eta^4$-(1-CRR$^1$-1,2-$C_2B_9H_{10}$)}] (**23**, L-L = COD, R = R$^1$ = H; **24**, L-L = COD, R = H, R$^1$ = $CH_3$; **25**, L-L = COD, R = R$^1$ = $CH_3$; **26**, L-L = NBD, R = R$^1$ = H), respectively [14,15]. In these complexes, the positive charge, which is initially generated at the exopolyhedral carbon atom, is substantially delocalized over the dicarbollide ligand and, partially, at the rhodium atom and the coordinated diene ligand (Scheme 6).

High stability of compounds **23**–**26** both in the solid state and in solution agrees well with the participation of the rhodium atom in stabilization of the exopolyhedrally attached carbocationic center in these complexes. Comparative $^{13}C\{^1H\}$/$^{13}C$ NMR data on complex **23** and its anionic precursor **18d** (Table 1) clearly confirmed this conclusion. Thus, in the $^{13}C\{^1H\}$ NMR spectrum of **23** the doublet resonance at $\delta$ 55.8 arising from the $C_{exo}$ carbon atom shows the $J(C_{exo},{}^{103}Rh)$ coupling of 5.8 Hz which is characteristic of the carbon-carbon double bond coordinated to the rhodium atom. In addition, the $J(C_{exo}, H)$ value of 170 Hz found from the proton-coupled $^{13}C$ NMR spectrum of **23** is indicative of $sp^2$ hybridization of this carbon atom. Both these factors, taken together, provide convincing evidence for the additional $\pi$-coordination of the rhodium atom in the complex by the $C_{carb}$–$C_{exo}$ bond having the partially double-bond character. On the contrary, these data ruled out the formation of the Rh–$C_{exo}$ $\sigma$ bond in complex **23**; otherwise, the coupling constant $J(C_{exo},{}^{103}Rh)$ would be substantially greater than the observed value of 5.8 Hz (*cf.*, for example, the $J$(σ-C, Rh) value of 16 Hz observed in the $^{13}C\{^1H\}$ NMR spectrum of the σ, $\eta^2$-type complex formed by protonation of **22a** [19]). Accordingly, all four CH unit resonances of the COD ligand are observed in the room-temperature $^{13}C\{^1H\}$ NMR spectrum as separate doublets, unlike those equivalent signals revealed for its anionic precursor **18d** (see Table 1). The latter fact can, apparently, be attributed to hindered rotation of the ($\eta^4$-COD)Rh moiety with respect to the carborane ligand in **23**.

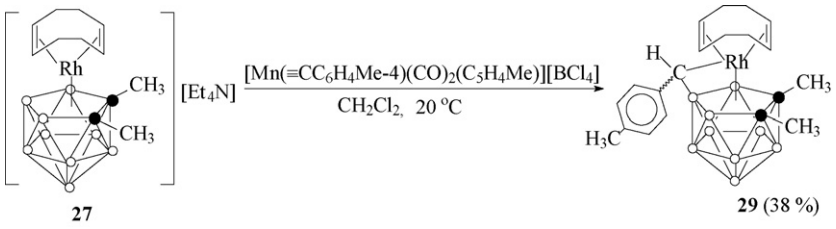
It has also been demonstrated that the treatment of anionic complexes **18e** and **f** containing alkenyl cage substituents with $HPF_6$ afforded not only zwitterionic compounds **24** and **25** but also *closo* complexes with the $\eta^3$-cyclooctenyl ligand at the metal vertex. The latter species are generated as products of the competitive protonation reaction at the COD double bond. Protonation of the anionic complexes **21b**, **d–f**, **h–k** bearing functionalized 2-R′-NBD ligands resulted in a series of *closo* complexes with the $\eta^2$:$\eta^3$-norbornadienyl ligands. Analogously, compounds **22a–f** react with acids to give stable *closo*-(σ:$\eta^2$-dicyclopentenyl)rhodacarboranes with an agostic C–H···Rh bonding interaction. These and other reactions of anionic complexes resulting, for example, in changes of the diene/dienyl ligand frameworks will be discussed in details in the following sections.

The anionic complex [$NEt_4$][3,3-($\eta^4$-COD)-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$)] (**27**) has been exploited by Stone and co-workers [25] as the starting material in the reaction with the electrophilic manganese alkylidene reagent [Mn(≡$CC_6H_4CH_3$-

Table 1
$^{13}C\{^1H\}$ NMR spectroscopic data for complexes **18d** and **23** [14]

| Complexes, $CD_2Cl_2$ | Chemical shift $^{13}C$ (ppm)/multiplicity ($J$(C, Rh) (Hz)) | | | | |
|---|---|---|---|---|---|
| | $C_{carb}$ | $CH_{carb}$ | C(1′, 2′, 5′, 6′) | C(3′, 4′, 7′, 8′) | *exo*-$C_\alpha$ |
| **18d**[a] | 67.4/m | 45.8/m | 75.1/d (5.8), 74.9/d (5.8) | 32.9/s, 33.6/s | 69.9/s |
| **23** | 107.4/m | 63.5/m | 100.9/d (7.3), 93.3/d (5.8), 90.4/d (8.7), 88.8/d (8.7) | 35.7/s, 32.0/s, 31.3/s, 30.5/s | 55.8/d (5.8)[b] |

[a] PPN resonances: +132.7/m, 130/m, 128.9/m.
[b] $J(C_{exo}, H)$ = 170 Hz.




Scheme 7. Formation of zwitterionic complex **29** from anionic precursor **27** [25].

4)$(CO)_2$(η-$C_5H_4Me$)][$BCl_4$] (**28**) for the synthesis of the zwitterionic complex [3,3-(η$^4$-COD)-3,1,2-*closo*-Rh{η$^1$:η$^5$-{8-(CH($C_6H_4CH_3$-4)-1,2-$(CH_3)_2C_2B_9H_8$)}}] (**29**) (Scheme 7). Formally, complex **29** is generated through the insertion of the alkylidene group, that comes from reagent **28**, at the B(8)–H bond of the carborane cage ligand followed by the formation of a Rh–$C_{exo}$ σ-bond as a result of the direct involvement of the metal atom in stabilization of the boron-attached carbocationic center formed at the *exo*-CH($C_6H_4CH_3$-4) fragment. Since the resonance for the exo-polyhedrally bound carbon atom was not observed in the $^{13}C\{^1H\}$ NMR spectrum of complex **29**, it was impossible to estimate the value of $J(C_{exo},^{103}Rh)$ and $J(C_{exo},H)$ coupling constants. It was however evident from the solid-state structure of one of analogues of **29**, [3-CO-3-$PPh_3$-3,1,2-*closo*-Rh{η$^1$:η$^5$-{8-(CH($C_6H_4CH_3$-4)$C_2B_9H_{10}$)}}] (**30**), studied earlier by X-ray diffraction [26], that hybridization about *exo*-CHPhMe-4 is more likely to be sp$^2$ rather than sp$^3$, and the Rh–$C_{exo}$ distance (2.374 Å) is too long to be considered as a σ bond. Taking all these into account, it seems reasonable that the complexes of both series, **23–26** and **29**, **30**, can be discussed in the same terms of rhodium-to-cage bonding interactions, *i.e.* as complexes having the "pseudofulvenoid" coordination mode.

In connection with this, it should be noted that the chemical behavior of complex **23** with respect to nucleophilic reagents is very similar to that of complex **30**. For example, complex **23** can add neutral Lewis bases ($PEt_3$ and pyridine) at the *exo*-carbon electrophilic center to form the inner-salts [3,3-{η$^4$-(COD)}-1-($CH_2$R)-3,1,2-*closo*-Rh(η$^5$-$C_2B_9H_{10}$)] (R = $PEt_3$ or $C_5H_5N$) [27]. In turn, complex **30** can add the hydride ion *via* the treatment with K[BH(CHMeEt)$_3$] in THF to give, after the addition of $NEt_4Cl$, the stable anionic complex [$NEt_4$][*closo*-3-CO-3-$PPh_3$-8-{$CH_2$($C_6H_4CH_3$-4)}-3,1,2-Rh(η$^5$-$C_2B_9H_{10}$)] [26].

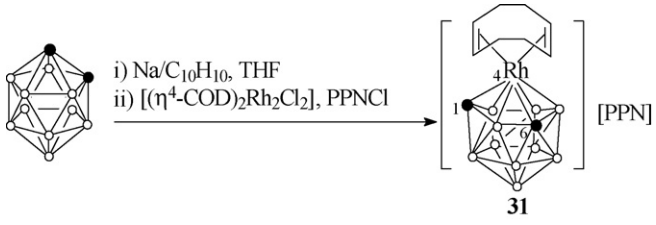
The first anionic 13-vertex *closo*-(η$^4$-cyclodiene)metallacarborane [PPN][4,4-(η$^4$-COD)-4,1,6-*closo*-$RhC_2B_{10}H_{12}$] (**31**) has recently been prepared by the reaction between COD-rhodium dimer **19** and $Na_2$[*nido*-$C_2B_{10}H_{12}$] generated *in situ* from [*closo*-1,2-$C_2B_{10}H_{12}$] and Na/naphthalene in THF (Scheme 8) [28]. The overall docosahedral structure of **31**, in which the carborane cage is η$^6$-coordinated to Rh, was confirmed by X-ray diffraction study. In the same paper [28], various reactions of complex **31** with electrophilic metal-containing reagents were investigated, and a number of neutral dinuclear Rh–Cu, Rh–Rh and Rh–Ru *exo-closo* complexes were prepared and structurally characterized (for details, see Section 2.3).

### 2.3. Zwitterionic and cationic charge-compensated *closo*-metallacarboranes

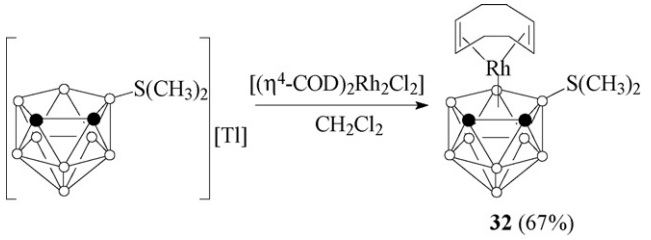
A series of zwitterionic and cationic *closo*-(π-cyclodiene)metallacarboranes with so-called 'charge-compensated' carborane ligands bearing positively charged heteroatom-containing substituents at the cage carbon or boron atoms has also been documented.

Douek and Welch have synthesized first metallacarboranes of this type with COD derivatives as ancillary ligands [29]. The complex [3,3-(η$^4$-COD)-4-S$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_{10}$] (**32**) was prepared in 67% yield by the reaction of COD-rhodium dimer **19** with a twofold excess of [Tl][9-$(CH_3)_2$S-*nido*-7,8-$C_2B_9H_{10}$] in $CH_2Cl_2$ (Scheme 9). The structure of **32** in the solid state has been studied by X-ray diffraction. The conformation of the {(η$^4$-COD)Rh} fragment with respect to the metal-bonded $C_2B_3$ face in the crystal of **32** proved to be in good agreement with that theoretically predicted by extended Hückel molecular orbital calculations (EHMO) performed for an idealized model complex.

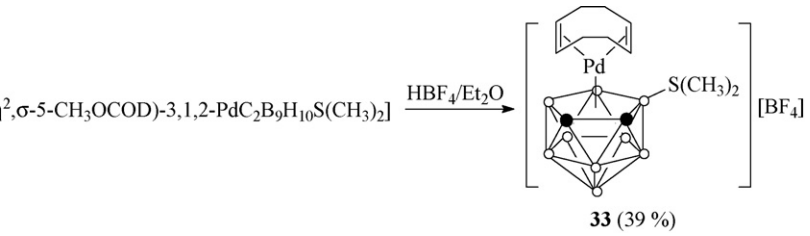
In the same report, the authors have shown that protonation of palladacarborane [3,3-{σ:η$^2$-(5-$CH_3OC_8H_{12}$)}-4-S$(CH_3)_2$-3,1,2-*closo*-$PdC_2B_9H_{10}$] (for the synthesis of this species, see Section 3.1) with $HBF_4$ resulted in the cationic complex [3,3-(η$^4$-COD)-4-S$(CH_3)_2$-3,1,2-*closo*-$PdC_2B_9H_{10}$][$BF_4$] (**33**)




Scheme 8. Synthesis of the first 13-vertex cyclodiene-containing anionic complex **31** [28].




Scheme 9. Synthesis of the first diene-containing 'charge-compensated' Rh complex **32** [29].

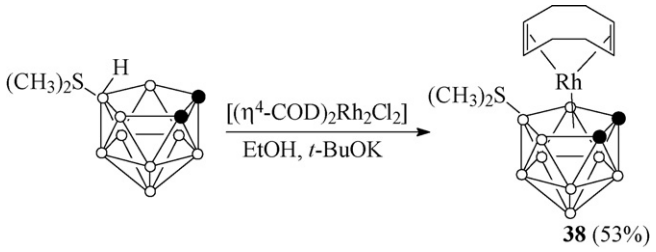



Scheme 10. Synthesis of cationic Pd complex **33** [29].

(Scheme 10), the structure of which was determined by X-ray diffraction. Fully charge-iterated EHMO calculations were also performed for models of **32** and **33** which showed that in both complexes the positive charge is accumulated at the cage carborane ligand and the metal atom to a greater extent than at the sulfur atom of the pendant substituent.

Starting from [Na][9-$S(CH_3)_2$-*nido*-7,8-$C_2B_9H_{10}$] and the dinuclear COD-iridium complex [$(\eta^4$-COD)$_2Ir_2(\mu$-Cl)$_2$] (**34**) in THF, *closo*-iridacarborane [3,3-($\eta^4$-COD)-4-$S(CH_3)_2$-3,1,2-*closo*-$IrC_2B_9H_{10}$] (**35**) was synthesized in high yield [30]. More recently, the structure of the resulting complex **35** was determined by X-ray crystallography [31]. The treatment of this complex with acids HX (X = Cl, Br, or I) in $Ac_2O$ led to elimination of the diene ligand to form dinuclear μ-halide complexes of Ir(III), for which the structure of [η-(4-$S(CH_3)_2C_2B_9H_{10}$)$IrX_2$]$_2$ were postulated; this was based on the fact that these compounds are readily soluble in strongly coordinating solvents (it was assumed that dissolution of the dimers in such solvents afforded mononuclear solvate complexes of the general formula [η-(4-$S(CH_3)_2C_2B_9H_{10}$)$IrX_2$(solv.)] [30]).

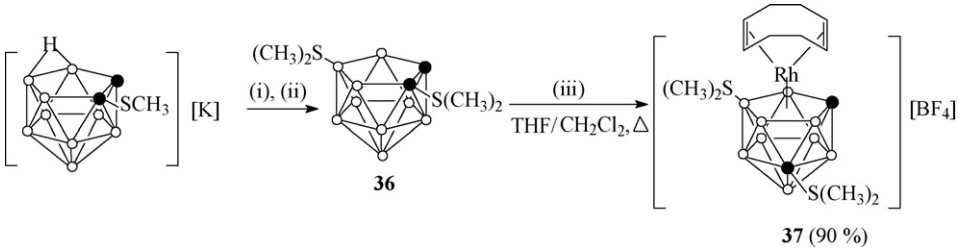
It is theoretically envisaged that the neutral *nido*-$C_2B_9$-carborane ligands could be obtained by the formal replacement of two terminal hydrogen atoms of the $\{nido\text{-}C_2B_9\}^{2-}$ dianion with two charge-compensating heteroatom-containing substituents. Until recently, only a few metallacarborane complexes with doubly charge-compensated carborane ligands have been documented [32]. Recently, Teixidor and co-workers have published a novel synthetic approach that has been first profitably employed in metallacarborane chemistry [33]. This was exemplified by the direct synthesis of neutral carborane [7,10-$\{S(CH_3)_2\}_2$-*nido*-7,8-$C_2B_9H_9$] (**36**) and its successful use for the preparation of cationic *closo*-rhodacarborane [2,2-($\eta^4$-COD)-8,11-$\{S(CH_3)_2\}_2$-2,1,8-*closo*-$RhC_2B_9H_9$][$BF_4$] (**37**), in which the cage carbon atoms proved to be separated by one boron unit (Scheme 11). The low-temperature reaction (−63 °C) between **36** and $\{(COD)Rh\}^+$, generated *in situ* from




Scheme 12. Synthesis of zwitterionic complex **38** [34].

Rh(COD)(acac) and $HBF_4$ in THF, also produced complex **37**. It was therefore suggested that a steric interaction between two crowded cage substituents is the most important factor, which promotes the observed "1,2 → 1,7" isomerization process. Since ligand **36** was considered as the polyhedral analogue of benzene, the above diene-rhodium complex **37** thus prepared could, in principle, be considered as analogue of the cationic species $[(COD)Rh(arene)]^+$ [33].

More recently, the same authors have performed the synthesis of a new series of zwitterionic *closo*-rhodacarborane complexes containing either two $PPh_3$ ligands or one $\eta^4$-coordinated COD ligand at the Rh(I) vertex [34]. This was based on the charge-compensated dicarbollide ligand of the general formula [10-L-*nido*-7-R-7,8-$C_2B_9H_9]^-$ (R = H or Me; L are different sulfur-containing substituents), which were used in metallacarborane chemistry much more rarely than other ligands. In particular, the reaction of COD-rhodium dimer **19** with *in situ* generated the $K^+$ salt of the [10-$S(CH_3)_2$-*nido*-7,8-$C_2B_9H_{10}]^-$ anion in ethanol was found to afford the complex [3,3-($\eta^4$-COD)-8-$S(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_{10}$] (**38**) (Scheme 12), whose solid-state structure was confirmed by X-ray diffraction [34]. In contrast to the related bis(phosphine)thiorhodacarborane complexes, for example, [3,3-$(PPh_3)_2$-8-$S(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_{10}$], which were shown to undergo the unexpected chloroform-induced Rh(I) → Rh(III) oxidation reaction to form




Scheme 11. Synthesis of cationic complex **37** with a doubly charge-compensated carborane ligand [33]: (i) $S(CH_3)_2$, $CH_3CHO/H^+$/toluene; (ii) NaOH, $CH_3I/CH_3OH$; (iii) ($\eta^4$-COD)Rh(acac), $HBF_4$, THF.

metal–chloride complexes of the general formula [3-$PPh_3$-3,3-$Cl_2$-8-R,R′S-3,1,2-*closo*-$RhC_2B_9H_{10}$] (R,R′ = Alk, ArAlk, *etc.*), complex **38** proved to be stable to halogenated solvents.

Novel 13-vertex zwitterionic *closo*-rhodacarborane [4,4-($\eta^4$-COD)-7-{$(CH_2)_4O$}-4,1,6-*closo*-$RhC_2B_{10}H_{12}$] (**39**) containing the THF molecule inserted at the cage boron atom has recently been prepared by the reaction of docosahedral anionic complex **31** with the hydride-abstracting reagent $[Ph_3C][BF_4]$ in THF [27]. In this complex, the THF molecule serves as the charge-compensating substituent covalently bound to the boron vertex through the oxygen atom (the B(7)–O(THF) distance found in the crystal structure of **39** is 1.5220 Å). The structurally identical product is generated in other reactions of **31** with electrophilic reagents, such as $[NO][BF_4]$ or $CF_3SO_3CH_3$, if THF-containing solvents are used.

## 3. ($\eta^4$-Cyclodiolefin)metallacarboranes with exopolyhedral B–E···M (E is a heteroatom) and/or B–H···M and σ-B–M bonds

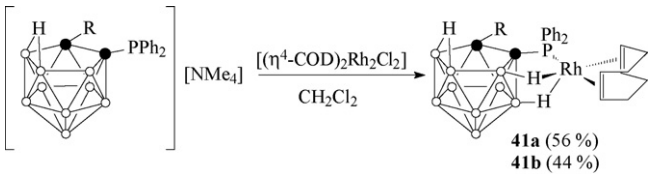
### 3.1. *exo-nido*-Metallacarboranes

In recent years, the chemistry of *exo-nido*-metallacarboranes, in which a metal-containing group bearing a cycloolefin-based ligand is bound to the *nido*-$C_2B_9$-carborane cage ligand either exclusively by one or two *exo*-polyhedral M–E bonds (E is heteroatom-containing cage substituents) or *via* M–E bonds supported by bridged B–H···M linkages, has been extensively developed primarily by the effort of Teixidor's research group.

The first such complex containing the COD ligand at the *exo*-metal center, which is linked to the cage ligand through two exocluster phosphorus atoms, [*exo-nido*-7,8-{($\eta^4$-COD)Rh}-7,8-($\mu$-$PPh_2$)$_2$-7,8-$C_2B_9H_{10}$] (**40**), was synthesized by heating COD-rhodium dimer **19** and the $[NMe_4]^+$ salt of the [7,8-($PPh_2$)$_2$-7,8-*nido*-$C_2B_9H_{10}]^-$ anion in ethanol (Scheme 13) [35]. The *nido*-carborane ligand in complex **40** acts not only as chelate four-electron diphosphine but also as a counterion with respect to the cationic 12e $\{CODRh\}^+$ unit thus forming a zwitterionic metallacarborane system.

In spite of stability of formally 16-electron complex **40** in the solid state, the diene ligand in this complex is rather labile and can easily be replaced with CO to form [*exo-nido*-7,8-{$Rh(CO)_2$}-7,8-($\mu$-$PPh_2$)$_2$-7,8-$C_2B_9H_{10}$], which, in turn, proved to be reactive toward different mono- and di-P- or N-donor ligands.

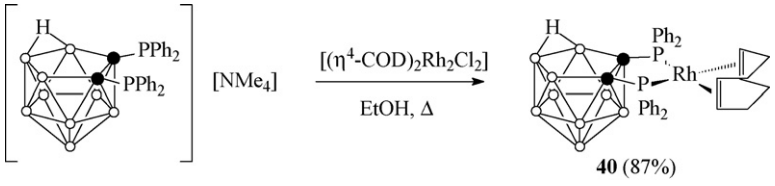
The reaction of dimer **19** with $NMe_4^+$ salts of the monophosphine-substituted anions [7-$Ph_2$P-8-R-7,8-*nido*-$C_2B_9H_{10}]^-$ (R = H or Me) in $CH_2Cl_2$ produces the first "three-bridge" *exo-nido* complexes [*exo-nido*-2,7,11-{($\eta^4$-COD)Rh}-2,11-($\mu$-H)$_2$-7-$\mu$-$PPh_2$-8-R-7,8-$C_2B_9H_8$)] (**41a**, R = H; **b**, R = Me) with cyclodiene as an ancillary ligand [36]. In contrast to **40**, the *nido*-carborane ligand in the latter complexes is attached to the metal atom *via* two 2e, 3c B–H···Rh bonds and one P–Rh bond thus acting as a tridentate six-electron ligand, and the Rh(I) atom has therefore a saturated 18-electron configuration (Scheme 14). In spite of the fact that the structure of complex **41b** in the solid state was established by X-ray diffraction, both the normal and low-temperature $^1$H NMR spectra of **41a** and **b** do not reveal high-field resonances from the B–H···Rh bonds. Due to the large *trans* influence of the diene ligand, these resonances are believed to fall in the positive spectral region from $\delta$ 1 to 3 ppm, where they overlap with other cluster B–H resonances [36]. A high-field shift and sharpening of the resonances from the boron vertices involved in the B–H···Rh bond systems observed in the $^{11}$B NMR spectra of **41a** and **b** were considered as evidence that the "three-bridge" structure of these species is retained in solution.



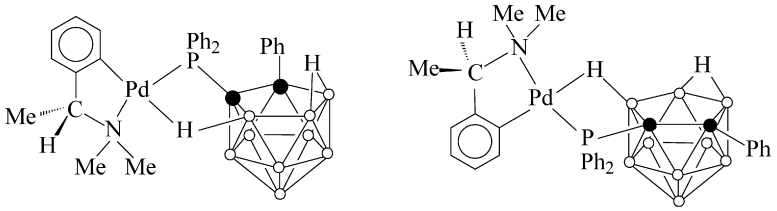

Scheme 14. Synthesis of "three-bridge" *exo-nido*-monophsphinorhodacarboranes **41a** and **b** [36].

With the aim of exploring the catalytic properties of *exo-nido*-rhodacarboranes with planar-chiral C-monophosphine-substituted carborane ligands, one of the racemic *nido*-carboranes, $[NEt_4]$[7-$PPh_2$-8-Ph-7,8-*nido*-$C_2B_9H_{10}$] (**42**), synthesized earlier by Teixidor and co-workers [37], was successfully resolved into enantiomers *via* internally diastereomeric *exo-nido*-palladacarboranes (**43a**-*R*,*R*) and (**43b**-*R*,*S*) with chiral (*R*)-PhCHMeN$Me_2$ (Fig. 1) [38]. The stereochemistry of one of the resulting diastereomers in the solid state, *viz.*, isomer **43a**-*R*,*R*, was established by X-ray diffraction.

Liberation of the chiral *nido*-carborane ligands (**42a**-*R*) and (**42b**-*S*) from diastereomeric complexes **43a**-*R*,*R* and **43b**-*R*,*S* upon successive treatment of the latter with HCl in acetone and with NaCN/$NEt_4$Cl in the two-phase $CH_2Cl_2$–$H_2O$ solvent mixture followed by the reaction with COD-rhodium complex **19** in refluxing EtOH resulted in the formation of chiral *exo-nido*-($\eta^4$-COD)rhodacarboranes (**44a**-*R*) or (**44b**-*S*) in 43% yield (Scheme 15).

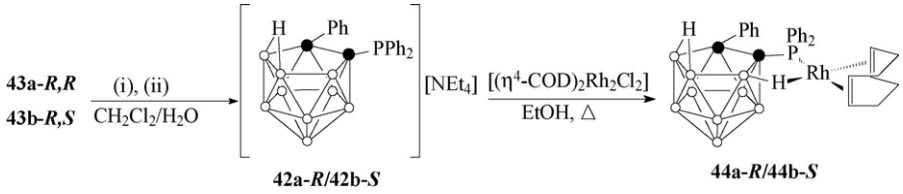



Scheme 13. Synthesis of *exo-nido*-diphosphinorhodacarborane **40** [35].




**43a-*R,R*** **43b-*R,S***

Fig. 1. Stereochemical structure of diastereomeric *exo-nido*-palladacarboranes **43a**-*R*,*R* and **43b**-*R*,*S* [37].



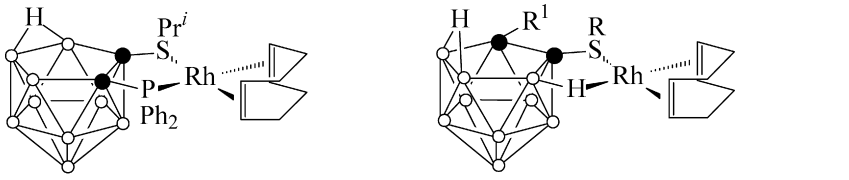

**42a-*R*/42b-*S*** **44a-*R*/44b-*S***

Scheme 15. Synthesis of chiral *exo-nido*-rhodacarboranes **44a**-*R* and **44b**-*S* [37]: (i) HCl/acetone; (ii) NaCN/$NEt_4Cl$.

It should also be noted that, although the structure of complex **44b**-*S* was established by X-ray diffraction, the possibility of the formation of the additional B(2)···Rh bond analogous to that in the structure of mono-C-methyl-substituted analog **41b** was not discussed despite the fact that the Rh···B(2) distance in the structure of **44b**-*S* (2.617 Å) is only slightly longer than that in **41b** (2.522 Å [36]). On the other hand, only one broad 1H resonance is clearly observed in the $^1$H NMR spectrum of **44b**-*S* in the range from $\delta$ 0 to −1.0 ppm being, therefore, assigned to the proton of the only cluster BH group involved in the B–H···Rh bonding interaction. All other resonances of protons from the cluster BH units with a total intensity of 8H were observed at lower field in between $\delta$ 0.5 and 2.5 ppm.

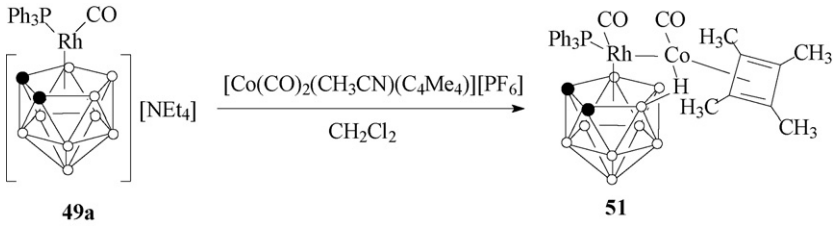
The chelate complex [*exo-nido*-7,8-{($\eta^4$-COD)Rh}-7-μ-$PPh_2$-8-μ-S(Pr-*i*)-7,8-$C_2B_9H_{10}$] (**45**) (Fig. 2, left), prepared by heating the C,C′-heterodisubstituted *nido*-carborane [$NMe_4$][7-$PPh_2$-8-S(Pr-*i*)-7,8-*nido*-$C_2B_9H_{10}$] and the dimer **19** in ethanol, was then used as a model for comparing the coordinating abilities of the two-electron SR and $PPh_2$ *nido* cage substituents [39]. Analysis of the COD-Rh bond lengths in the structure of complex **45** (*trans* to C–S(Pr-*i*), 2.17 and 2.19 Å; *trans* to C–$PPh_2$, 2.21 and 2.19 Å for two independent molecules) demonstrated that the σ-donor properties of the S(Pr-*i*) group coordinated to Rh(I) are somewhat stronger than those of the $PPh_2$ group.

A series of new *exo-nido* complexes of the type [*exo-nido*-7,11-{($\eta^4$-COD)Rh}-11-(μ-*H*)-7-(μ-SR-8-$R^1$-7,8-$C_2B_9H_9$)] (**46a–c**: **a**, R = $R^1$ = Ph; **b**, R = Ph, $R^1$ = Me; **c**, R = Et, $R^1$ = Me) (Fig. 2, right) were synthesized in [40]. It is interesting that under the conditions (toluene/EtOH (8:1), 20 °C) developed earlier for the synthesis of bis(triphenylphosphine)rhodacarboranes [41] or the structurally similar complex [*exo-nido*-7,11-{($PPh_3$)$_2$Rh}-11-(μ-*H*)-7-(μ-PhS-8-Me-7,8-$C_2B_9H_9$)] [42], the reaction of COD rhodium dimer **19** with the $NMe_4^+$ or $Cs^+$ salts of monothio-substituted *nido*-carborane [7-SR-8-$R^1$-7,8-*nido*-$C_2B_9H_{10}$]$^-$ anion (**47a**, R = Ph, $R^1$ = Me) did not produce the expected chelate complex. Only the reactions of $NMe_4^+$ or $Cs^+$ salts of **47a** and **47**(**b**, R = $R^1$ = Ph; **c**, R = Et, $R^1$ = Me) anions with the use of the chlorine-free [($\eta^4$-COD)Rh(acac)] reagent instead of **19** in the presence of 1 equiv. of mineral acids $HClO_4$ or $HBF_4$ (which were taken as promoters for removal of the *acac* ligand from this reagent) finally afforded complexes **46a–c** in yields from 37 to 89%. The structure of complex **46b** was established by X-ray diffraction. Investigation of the variable-temperature $^1H\{^{11}B\}$ NMR spectra of **46a–c** demonstrated that all these complexes in solution are fluxional at ambient temperature exhibiting rapid rotation of the COD ligand coupled with a rapid exchange process between the bridging B–H···Rh and terminal B–H hydrogens. Moreover, complexes **46b** and **c** in a $CD_2Cl_2$ solution exist in equilibrium with the "monobridge" *exo-nido* species [*exo-nido*-7-{($\eta^4$-COD)Rh(Sol)}-7-(μ-SR)-8-$R^1$-7,8-($C_2B_9H_9$)] (**48b** and **c**), which contains only one μ-SR–Rh bond and in which the free coordination site is occupied by a solvent molecule. It appeared that the dynamic behavior is responsible for the reactivity of complexes **46a–c**. In a chloroform solution, these complexes are irreversibly transformed into *closo*-




**45** (52 %) **46a-c: a** (76 %); **b** (89 %); **c** (37 %)

Fig. 2. Structure of C,C′-heterodisubstituted *exo-nido* complexes **45** [39] and **46a–c** [40].




**49a** **51**

Scheme 16. Synthesis of *exo-closo*-bimetallacarborane cluster **51** (α-isomer) [44].

and/or *pseudocloso*-($\eta^3$-cyclooctenyl)thiorhodacarboranes (see Section 3.2).

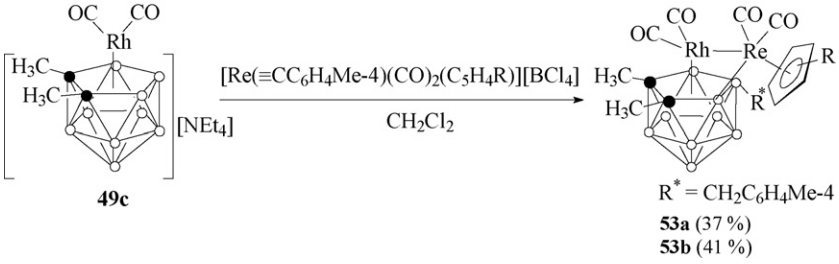
### 3.2. Homo- and heterometallic exo-closo-bimetallacarboranes

Among *exo-closo*-metallacarboranes of platinum metals, there are two groups of complexes containing cyclodiolefin ligands or their derivatives. One group discussed herein includes compounds, in which one metal atom (M) with a coordinated η-carbocyclic (usually diene) or other ligands is $\eta^5$-coordinated by the carborane cage ligand forming a *closo*-metallacarborane framework, the latter being simultaneously bound *via* bridging B–H···M′ and/or M–H–M′ bonds (with or without M–M′ and/or B–M′ σ-bonds) to a variety of other transition metal (M′) sources. Since these compounds contain at least two metals and one carborane cage ligand, they can formally be assigned to low-nuclearity homo/heterometallacarborane clusters. A number of binuclear mixed-metal dicarbon or monocarbon *exo-closo*-metallacarboranes also exist in which metal atoms either at the *exo* or *closo* position carry ligands other than carbocyclic dienes (*i.e.* phosphines, CO, CNR, terminal or bridging alkylidene or alkyne, *etc.*). It is, at present, an area of significant research interest due primarily to the seminal contributions by Stone's research group, and some review articles are available that have covered chemical aspects of this field [43]. Another group of *exo-closo* metallacarboranes that will be discussed below (Section 3.3) includes mononuclear complexes based on dicarbon and/or monocarbon *closo*-carboranes, which are bound to the metal diene fragment *via* M–E linkages (E are phosphorus-, nitrogen-, or sulfur-containing groups) and which can additionally be supported by one or two bridging B–H···M bonds.

In one of early papers by Stone et al. [44] on exploration of the anionic complexes [X][Rh(CO)L($\eta^5$-$C_2B_9H_9R_2$)] (**49a–c**: **a**, X = $NEt_4$, L = $PPh_3$, R = H; **b**, X = $N(PPh_3)_2$, L = CO, R = H; **c**, X = $NEt_4$, L = CO, R = Me; **d**, X = $NEt_4$, L = $PPh_3$, R = Me), the reaction of **49a** with [$Co(CO)_2$(MeCN)($\eta^4$-$C_4Me_4$)][$PF_6$] (**50**, where $C_4Me_4$ is tetramethylcyclobutadiene) was investigated as applied to the synthesis of low-nuclearity metallacarboranes of dissimilar transition metals. As a result, the first *exo-closo*-bimetallacarborane cluster [*exo*-3,4-{($\eta^4$-$C_4Me_4$)Co(CO)}-4-(μ-*H*)-3-CO-3-$PPh_3$-3,1,2-*closo*-$RhC_2B_9H_{10}$] (**51**) with the cyclic diene ligand at the exocluster metal atom (Co) was isolated and structurally characterized (Scheme 16). It should be noted that two isomeric forms, **51** and **51′**, of which both have a B–H···Co bond but involve different cage-boron atoms (either at the α or β site with respect to the CH units of the open face), were found in a solution of this complex, whereas single-crystal X-ray diffraction study revealed only isomer **51** with the B–H···Co bridge involving the boron atom in the α position with respect to the cluster CH group.

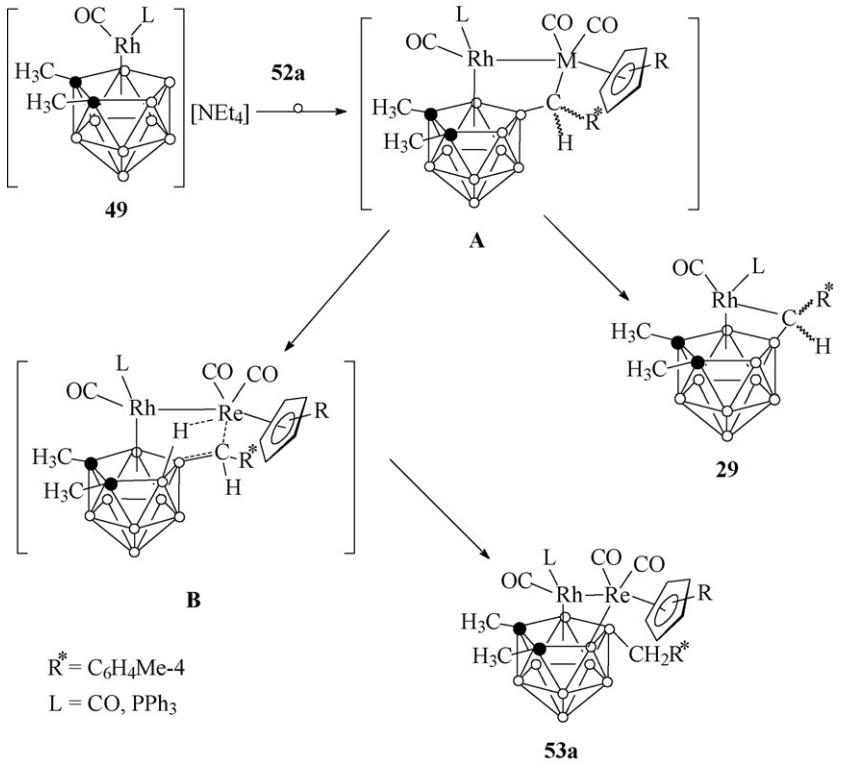
The reactions of complexes **49a–c** with the electrophilic rhenium alkylidene complexes [Re(≡$CC_6H_4$Me-4)$(CO)_2$($\eta$-$C_5H_4R$)][$BCl_4$] (**52a**, R = $CH_3$; **b**, R = H) were also studied [25]. In contrast to the reaction of **49a** with **28** (the manganese analogue of **52a**) giving rise to unusual mononuclear rhodium complex **29**, those between **49c** with **52a** and **b** follow a different pathway, resulting in the formation of two *exo-closo*-type binuclear complexes [*exo*-3,4-σ-{Re$(CO)_2$($\eta^5$-$C_5H_4R$)}-3-(CO)-3-L-1,2-$(CH_3)_2$-4-($CH_2C_6H_4$Me-4)-3,1,2-*closo*-$RhC_2B_9H_7$] (**53a**, R = $CH_3$, L = CO; **b**, R = H, L = CO), wherein the carbocyclic ligand, like that in **51**, is bound to the exocluster metal atom (Re) (Scheme 17). The third complex of this series, **53**(**c**, R = H, L = $PMe_2Ph$), was prepared by the substitution reaction of **53b** with $PMe_2Ph$ in $CH_2Cl_2$.

In all these reactions referred to above, dinuclear complex **A** (Scheme 18) is considered as the key intermediate. It was suggested that, depending on the nature of the incoming metal (Re or Mn), which forms respectively a more robust (Re–Rh) or less robust (Mn–Rh) bond in the intermediate **A**, either the exopolyhedrally bound metal-containing fragment




**49c**

Scheme 17. Synthesis of *exo-closo*-bimetallacarborane clusters **53a** and **b** [25].



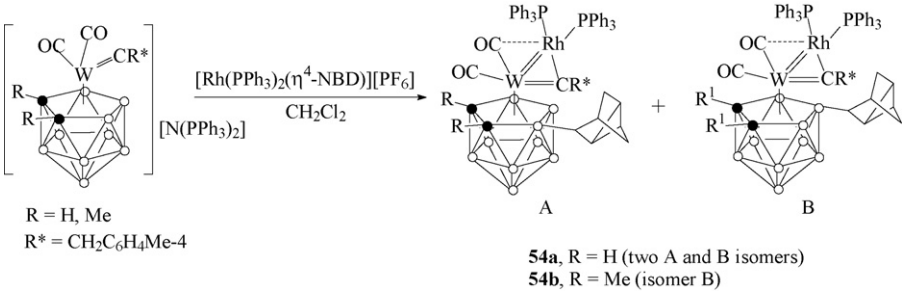

Scheme 18. Scheme of the formation of complexes **29** and **53a** from anions **49** and electrophilic alkylidene reagents exemplified here by **52a** or **28** [25].

$\{Mn(CO)_2(\eta^5\text{-}C_5H_4R)\}$ can be eliminated to form complexes **29** or this fragment $\{Re(CO)_2(\eta^5\text{-}C_5H_4R)\}$ is retained in **A**, thus being involved in stabilization of the carbocationic center at $\{CH(C_6H_4Me\text{-}4)\}^+$ and simultaneously promoting the hydrogen atom transfer from the adjacent B–H bond to the cationic center (through intermediate **B**) to afford finally complexes **53a**.

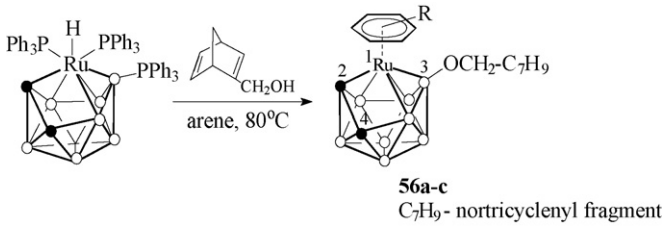
The B–H bond in *nido*-$C_2B_9$-carboranes can also be activated by the bimetallic Rh–W center. Thus, the reaction of the anionic complexes [PPN][$W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9R_2)$] (R = H or Me) with the electrophilic reagent $[Rh(PPh_3)_2(NBD)][PF_6]$ was found to produce the dinuclear complexes $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta^5\text{-}C_2B_9H_8(C_7H_9)R_2)]$ (**54a**, R = H (two isomers); **b**, R = Me), in which the NBD ligand was unexpectedly inserted into a B–H bond of the $C_2B_9$-cage ligand accompanied by the C–C bond formation to give the nortricyclene moiety (Scheme 19) [45].

In relation to these unexpected insertion reactions, an unusual behavior of the non-icosahedral $\{1,2,4\text{-}C_2B_8PPh_3\}$ ligand has also been described [46]. The reactions of the 11-vertex complex $[1,1,1\text{-}(PPh_3)_3\text{-}1\text{-}H\text{-}1,2,4\text{-}RuC_2B_8H_9]$ (**55**) [47] with [2-(hydroxymethyl)-bicyclo[2.2.1]hepta-2,5-diene], which were carried out in different arene solvents, afforded the ruthenium arene clusters $[1\text{-}(\eta^6\text{-arene})\text{-}3\text{-}(C_7H_9CH_2O)\text{-}1,2,4\text{-}isonido\text{-}RuC_2B_8H_9]$ (**56a–c**: **a**, arene = $C_6H_6$; **b**, arene = $C_6H_5Me$; **c**, arene = 1,3,5-$C_6H_3$), each being shown to consist of at least three geometric isomers [46]. Again, the norbornadiene ligand in these reactions proved to undergo partial cyclization giving rise to the nortricyclene-containing unit, $\{C_7H_9CH_2O\}$. The latter is attached, through the boron-oxygen bond, at position 3 of the $\{1,2,4\text{-}C_2B_8\}$-cage ligand formally replacing the pendant $PPh_3$ group in the initial complex **55** (Scheme 20). In the paper, the possible mechanism of these reactions was discussed.

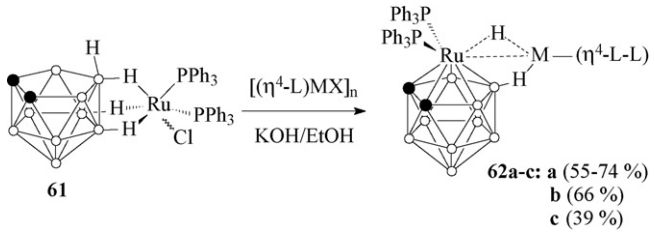
The dinuclear rhodium–copper *exo-closo* complex [*exo*-3,8-$\{Cu(PPh_3)\}$-8-($\mu$-*H*)-3,3-($\eta^4$-COD)-3,1,2-*closo*-$RhC_2B_9H_{10}$] (**57**) was synthesized by the treatment of anionic *closo*-($\eta^4$-



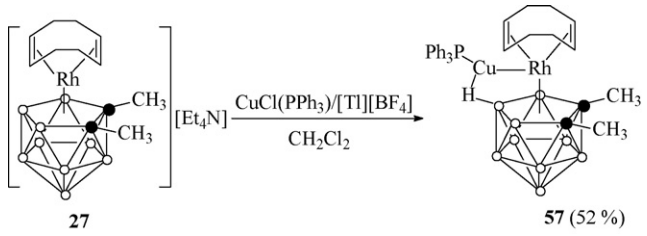

Scheme 19. The cage B–H bond activation by the bimetallic Rh–W center to form hydroboration products **54a** and **b** [45].




Scheme 20. Synthesis of $C_7H_9CH_2O$-substituted 11-vertex complexes **56a–c** [46].




Scheme 22. Formation of *exo-closo*-bimetallacarboranes **62a–c** from *exo-nido*-ruthenacarborane **61** [49,50].




Scheme 21. Synthesis of Rh–Cu *exo-nido*-bimetallacarborane **57** [48].

COD)rhodacarborane **27** with $[CuCl(PPh_3)]_4$ in the presence of $[Tl][BF_4]$ (Scheme 21). In this complex, the diene ligand is retained at the metal atom (Rh) occupying the *closo* vertex [48]. X-ray diffraction study demonstrated that the rhodium atom in **57** is involved in a metal–metal bonding interaction with the *exo*-copper center (Rh–Cu, 2.633 Å), which is supported by one B–H···Cu bond with the B(4)···Cu separation of 2.107 Å.

New anionic 13-vertex *closo*-rhodacarborane **31** was studied in reactions with electrophilic metal-containing reagents, such as $[CuCl(PPh_3)]_4$, $[Rh(COD)(PPh_3)_2][PF_6]$, and dinuclear complex **19** [28]. These reactions in the presence of $[Tl][PF_6]$ produced the "two-bridge" bimetallacarborane complexes [4-($\eta^4$-COD)-3,4,7-{*exo*-($CuPPh_3$)}-3,7-($\mu$-*H*)$_2$-4,1,6-*closo*-$RhC_2B_{10}H_{10}$] (**58**) and [4-($\eta^4$-COD)-3,8-{*exo*-Rh(L,L)}-3,8-($\mu$-*H*)$_2$-4,1,6-*closo*-$RhC_2B_{10}H_{10}$] (**59a**, L = $PPh_3$; **b**, L,L = $\eta^4$-COD), respectively (Fig. 3). Based on X-ray diffraction data, **58** was formulated as a 13-vertex bimetallic species having a single metal–metal bond (Rh–Cu, 2.7317 Å) supported by two B–H···Cu agostic-type bonding interactions, in contrast to 12-vertex bimetallacarborane **57**, which has only one such linkage. Structures of both zwitterionic complexes **59a** and **b** have also been confirmed by single-crystal X-ray diffraction. In the same work, starting from **31** and $[RuCl_2(PPh_3)_3]$, the novel "three-bridge" 13-vertex bimetallacarborane complex [4-($\eta^4$-COD)-3,7,8-{*exo*-($RuClPPh_3$)}-3,7,8-($\mu$-*H*)$_3$-4,1,6-*closo*-$RhC_2B_{10}H_{10}$] (**60**) has been prepared and crystallographically characterized as an asymmetric species (Fig. 3, on the right). In solution, **60** displays a "static" behavior on the NMR time scale, unlike complex **59a**, in which the *exo* metal fragment was found to be fluxional undergoing both rotational and translational processes with respect to the cage surface.

We have reported the synthesis and structure characterization of a series of mixed-metal *exo-closo*-metallacarboranes [49–53] starting from zwitterionic "three-bridge" *exo-nido*-ruthenacarborane [5,6,10-*exo*-{$Cl(Ph_3P)_2Ru$}-5,6,10-($\mu$-*H*)$_3$-10-*H*-7,8-*nido*-$C_2B_9H_8$] (**61**) [54]. Several dinuclear ruthenium–iridium [49] and ruthenium–rhodium [50] complexes of the type [*exo*-3,8-{($\eta^4$-L-L)M}-3,8-($\mu$-*H*)$_2$-3,3-($PPh_3$)$_2$-3,1,2-(*closo*-$RuC_2B_9H_{11}$)] (**62a–c**: **a**, L-L = COD, M = Ir; **b**, L-L = COD, M = Rh; **c**, L-L = NBD, M = Rh) have been prepared by the reaction of **61** with the corresponding iridium [($\eta^4$-COD)IrX]$_n$ (X = HCl, $n$ = 2; X = *acac*, $n$ = 1) or rhodium reagents **19** and [($\eta^4$-NBD)$_2$$Rh_2$($\mu$-Cl)$_2$] (**63**) in the presence of KOH in ethanol (Scheme 22). A combination of analytical and multinuclear NMR data ($^1$H, $^{11}$B/$^{11}$B{$^1$H}, $^{13}$C{$^1$H} and $^{31}$P{$^1$H}), including single-crystal X-ray diffraction study performed for complex **62b**, was used to assign the structures of **62a–c**. It has been unambiguously established that it was the "old" Ru atom rather than the incoming Rh or Ir atom that moved to the position of the free vertex of the starting *exo-nido*-ruthenacarborane **61** during the synthesis of **62a–c**. It should also be noted that there is a heterometallic interaction between formally 16-electron Rh(I) or Ir(I) and 18-electron Ru(II) in all these bimetallacarborane complexes, and this interaction most probably occurs by a donor-acceptor mechanism (Ru → Rh or Ru → Ir), which does not imply a significant degree of metal–metal bonding (the value of the

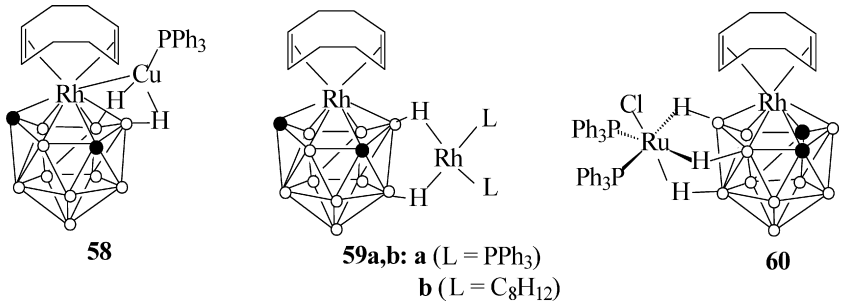
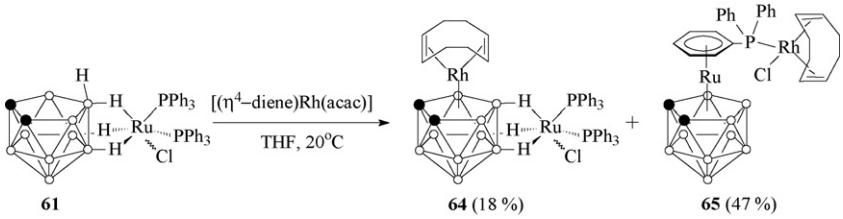



Fig. 3. Structures of Rh–Cu, Rh–Rh, and Rh–Ru "two-" and "three-bridge" *exo-closo*-bimetallacarboranes **58–60** [28].




Scheme 23. Alternative synthesis of *exo-closo*-bimetallacarborane **64** from *exo-nido*-ruthenacarborane **61** [51].

Mulliken Ru–Rh bond order calculated for a model complex proved to be positive, but very small, *ca.* 0.025). Alternatively, complex **62a** could be prepared using the reactions of [3,3-$(Ph_3P)_2$-3-Cl-3-*H*-3,1,2-*closo*-$RuC_2B_9H_{11}$] or the anionic complex $[Et_4N]$[3,3-$(Ph_3P)_2$-3-*H*-3,1,2-*closo*-$RuC_2B_9H_{11}$] with COD-rhodium dimer **19**, respectively.

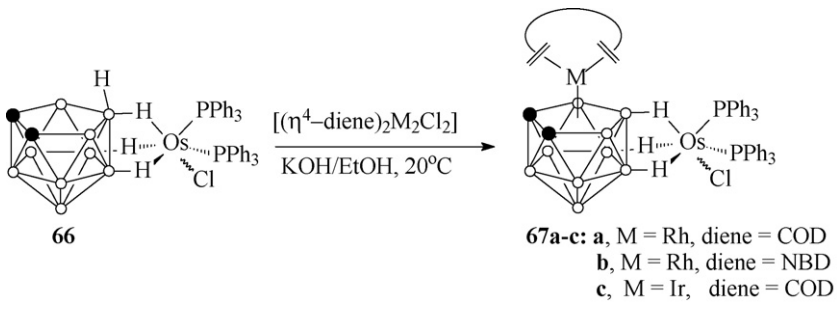
A new alternative approach to the construction of heterometallic *exo-closo*-(π-cyclodiene)bimetallacarboranes was developed using versatile *exo-nido* ruthenium reagent **61**. It was demonstrated [51] that under conditions hindering the spontaneous *exo-nido* → *closo* rearrangement of **61**, it is possible to perform selective $\eta^5$-bonding of the open $C_2B_3$ faces of this complex with other transition metals with retention of the exopolyhedral group $\{MCl(PPh_3)_2\}$ (M = Ru or Os) in the starting position. For example, the reaction of **61** with [($\eta^4$-COD)Rh(acac)] in THF or benzene in the absence of strong bases or acids (*cf.* the above studies [50] and [40]) produced [3,3-($\eta^4$-COD)-8,9,12-{*exo*-$[Cl(Ph_3P)_2Ru]$}-8,9,12-(μ-*H*)$_3$-3,1,2-*closo*-$RhC_2B_9H_8$] (**64**, a mixture of symmetrical and unsymmetrical isomers) along with the unusual by-product [3-{$\eta^6$-$(C_6H_5PPh_2)$RhCl($\eta^4$-COD)}-3,1,2-*closo*-$RuC_2B_9H_{11}$] (**65**) (Scheme 23). Both species **64** (symmetrical isomer) and **65** were characterized by X-ray diffraction [51].

Interestingly, when the osmium congener of complex **61**, [5,6,10-*exo*-$\{Cl(Ph_3P)_2Os\}$-5,6,10-(μ-*H*)$_3$-10-*H*-7,8-*nido*-$C_2B_9H_8$] (**66**) [52], was used in the reactions with diene-metal reagents **19**, **63**, or **34** in the presence of KOH in ethanol, all reactions proceed selectively to form [3,3-{$\eta^4$-(L–L)}-8,9,12-{*exo*-$[Cl(Ph_3P)_2Os]$}-8,9,12-(μ-*H*)$_3$-3,1,2-*closo*-$MC_2B_9H_8$] (**67a–c**: **a**, L-L = COD, M = Rh; **b**, L-L = NBD, M = Rh; **c**, L-L = COD, M = Ir), respectively (Scheme 24) [53]. Alternatively [51], COD-rhodium dimer **19** can be successfully substituted for [($\eta^4$-COD)Rh(acac)] in the room-temperature synthesis of complex **67a** in benzene. In this case, however, the known species [3,3-$(PPh_3)_3$-3-Cl-3-*H*-3,1,2-*closo*-$OsC_2B_9H_{12}$] [55] was formed as a by-product in small amounts due apparently to the mild *exo-nido-to-closo* conversion of the starting complex **66**.

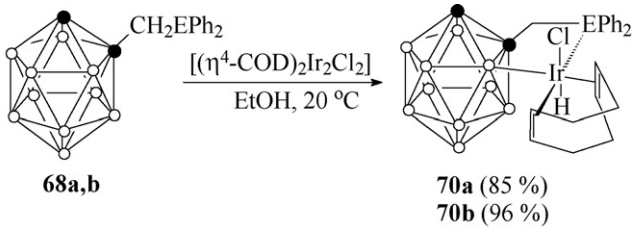
### 3.3. Mononuclear exo-closo-metallacarboranes based on mono- and dicarbon closo-carborane polyhedra

In earlier studies by Kalinin et al. [56,57], 12-vertex *closo*-carboranes [1-$(R_2ECH_2)$-1,2-*closo*-$C_2B_{10}H_{11}$] (**68a**, E = P, R = Ph; **b**, E = As, R = $CH_3$) and [1-$Ph_2$P-2-$CH_3$-1,2-*closo*-$C_2B_{10}H_{10}$] (**69**) were metallated with Rh(I) and Ir(I) complexes. Metallation of carboranes **68a** and **b** with some Rh(I) complexes, including COD-rhodium dimer **19**, in the presence of pyridine derivatives as co-ligands afforded a series of B,P-chelate octahedral rhodium complexes [*exo*-{2,3-σ-$(Py_2RhHX)$-2-(μ-$CH_2R$)}-1,2-*closo*-$C_2B_{10}H_{10}$] (X = Cl or I, R = $PPh_2$, or $AsMe_2$, Py = $C_5H_5N$, 3- or 4-$MeC_5H_4N$, *etc.*), in which the hydride or halide ligands at the metal atom are in *trans* positions with respect to each other. Unlike these reactions, metallation of **68a** and **b** with COD-iridium complex **34** by refluxing in *n*-hexane or ethanol gave rise to the cyclometallated *exo-closo* complexes [*exo*-2,3-{σ-Ir($\eta^4$-COD)HCl-2-(μ-$CH_2ER_2$)}-1,2-*closo*-$C_2B_{10}H_{10}$] (**70a**, E = P, R = Ph; **b** E = As, R = $CH_3$), in which the COD ligand is retained in the coordination sphere of the metal atom (Scheme 25).

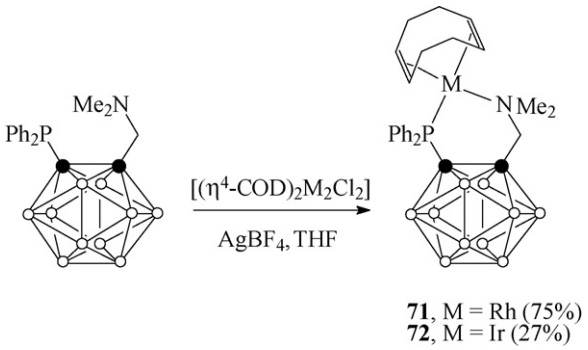
Interestingly, carborane **69** is not metallated with Rh(I) complexes under these conditions, whereas the reaction with iridium dimer **34** produces the chelate complex with the Ir–C σ-bond, [*exo*-1,2-{Ir($\eta^4$-COD)HCl}-1-{(μ-$PPh_2$)-2-(μ-$CH_2$)}-1,2-*closo*-$C_2B_{10}H_{10}$] [57]. The formation of the latter was attributed to low electron density on the C–H bond of the methyl group in the starting C-methylated carborane **69**.




Scheme 24. Synthesis of heterobimetallic *exo-closo* complexes **67a–c** [53].



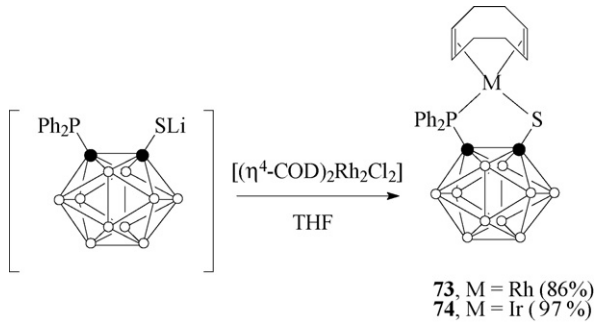

Scheme 25. Synthesis of cyclometallated *exo-closo*-iridacarboranes **70a** and **b** [56].




Scheme 26. Synthesis of N,P-chelate *exo-closo*-metallacarboranes **71** and **72** [58].

The reaction of [1-{$(CH_3)_2NCH_2$}-2-$Ph_2P$-1,2-*closo*-$C_2B_{10}H_{10}$] with COD-metal reagents **19** and **34**, which were treated, prior to use, with a slight excess of $AgBF_4$ in THF, afforded the N,P-chelate *exo-closo* Rh(I) and Ir(I) complexes, [*exo*-1,2-{($\eta^4$-COD)M}-1-($\mu$-$CH_2NMe_2$)-2-($\mu$-$PPh_2$)-1,2-*closo*-$C_2B_{10}H_{10}$] (**71**, M = Rh; **72**, M = Ir), respectively (Scheme 26), and the structures of both complexes were determined by X-ray crystallography [58]. In solution, these complexes are fluxional due to an inversion process occurring at the nitrogen atom. The compounds were shown to produce the corresponding pentacoordinate metal species [$(PPh_3)_2M(CO)_3$][$BF_4$] when treated with CO in the presence of 2 equiv. of the free $PPh_3$ ligand.

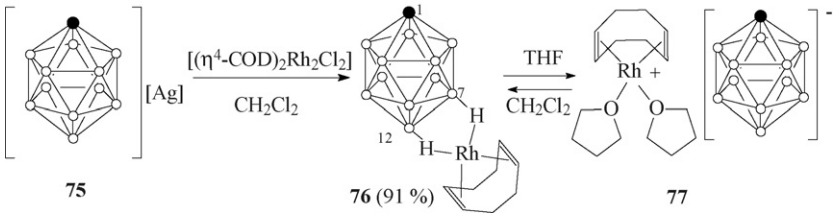
The synthesis of the structurally similar S,P-chelate complexes [*exo*-1,2-{($\eta^4$-COD)M}-1-($\mu$-$PPh_2$)-2-($\mu$-S)-1,2-*closo*-$C_2B_{10}H_{10}$] (**73**, M = Rh; **74**, M = Ir) with the phosphinethiolate *closo*-carborane ligand was reported [59]. The synthetic scheme was based on the reaction of the S-lithium derivative [*closo*-1-$PPh_2$-2-SLi-1,2-$C_2B_{10}H_{10}$] with the same COD-metal reagents **19** and **34** in THF (Scheme 27). The structures of the resulting chelates **73** and **74** in the solid state were confirmed by X-ray diffraction studies.



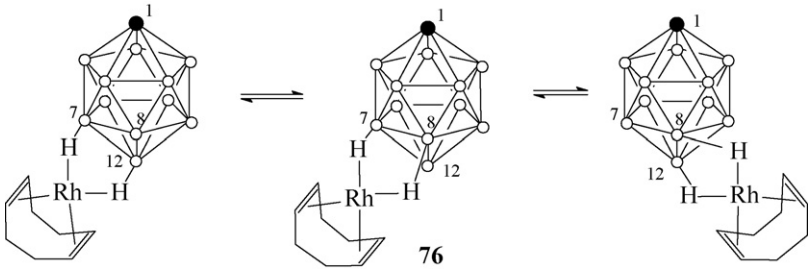

Scheme 27. Synthesis of S,P-chelate *exo-closo*-metallacarboranes **73** and **74** [59].

Weller and co-workers have developed new approaches to the design of the $\eta^4$-cyclodiene-containing *exo-closo*-metallacarboranes based on weakly coordinated monocarbon carborane anions, such as [1-*closo*-$CB_{11}H_{12}]^-$ or its functionalized derivatives [60–64]. Metallacarboranes of this type are of interest as efficient catalyst precursors for the hydrogenation of sterically demanding olefin substrates (see, Section 5). Thus, the reaction between [Ag][*closo*-1-$CB_{11}H_{12}$] (**75**) and COD-rhodium dimer **19** produced the monocarbon *exo-closo*-rhodacarborane species [*exo*-7,12-{($\eta^4$-COD)Rh}-7,12-($\mu$-*H*)$_2$-1-(*closo*-$CB_{11}H_{10}$)] (**76**) (Scheme 28) [60]. The solid-state structure of **76** revealed that the carborane ligand is bound to the Rh(I) center *via* two exopolyhedral B–H···Rh bonds, of which one involves the most negatively charged B(12) atom located antipodal with respect to the cluster CH unit, whereas another bond involves the B(7) atom from the lower $B_5$ belt. The low nucleophilicity of the [*closo*-1-$CB_{11}H_{12}]^-$ anion made it possible to use this carborane as the counterion for the synthesis of the direct analogue of the solvated cationic species $[Rh(L_2)(solvent)_2]^+$, which is known to be a widely used precursor in Lewis-acid-catalyzed olefin hydrogenation reactions and other important organic processes as well. The ionic complex [$CB_{11}H_{12}$][($\eta^4$-COD)Rh($C_4H_8O$)$_2$] (**77**) obtained on dissolution of **76** in THF was actually isolated as a stable crystalline solid, and was structurally characterized by X-ray diffraction study.

In solution, complex **76** is fluxional, showing both a symmetrical time-averaged environment of the COD ligand and the equivalence of all the lower pentagonal belt B*H* atoms of the carborane cage in the $^1H/^1H\{^{11}B\}$ NMR spectra in the temperature range from −90 to +25 °C. The plausible mechanism to account for the fluxionality of **76** was initially suggested as processing around the lower $B_5$ pentagonal




Scheme 28. Synthesis of monocarbon *exo-nido*-rhodacarborane **76** and its conversion to THF-solvated species **77** [60].




**76**

Scheme 29. Proposed mechanism for the fluxionality of complexes of type **76** (given as an example) or **78** in solution [61].

belt, whereas the rhodium center remains attached to the carborane moiety *via* the unique B(12)–H···Rh bond [60]. In more recent studies of these authors [61,62], a series of new *exo-closo*-bis(phosphine)rhodacarboranes [*exo*-{$(L_2Rh)$}-*closo*-$CB_{11}H_{12}$] (**78a–c**: **a**, L = $Cy_3P$; **b**, L = $P(OMe)_3$; **c**, L = dppe) were prepared, and all these complexes were found to display the dynamic behavior in solution analogous to **76**. Based on the results of the crystallographic study of **78a** and DFT calculations on idealized model system **78**(**d**, L = $PMe_3$), which showed that the energy difference between two 7,8-{BH···Rh} and 7,12-{BH···Rh} isomers is very small (1 kcal/mol), a modified mechanism was suggested for the observed fluxionality of these and all other fluxional complexes of this series studied earlier. This involves the metal-containing fragments $\{LRh\}^+$ (L is diene or two phosphine ligands) "walking" over the lower polyhedral surface in the 7, 12 ⇔ 7, 8 ⇔ 8, 12 processes (Scheme 29) [61].

As part of continuing studies of the reactivity of *exo-closo* complexes based on the anionic monocarbon carborane [*closo*-$CB_{11}H_{12}]^-$ anion and its derivatives, a number of new rhodium and iridium ionic complexes [{$(PPh_3)_2$M(diene)}][1-*H*-*closo*-$CB_{11}X$] (M = Rh, diene = NBD, X = $H_{11}$ [62]; M = Rh, diene = NBD, X = $Br_6H_5$ [62]; M = Ir, diene = COD, X = $Br_6H_5$ [62]; M = Ir, diene = 3 × ($\eta^2$-$C_2H_4$) or 2 × ($\eta^2$-$C_2H_4$), X = $Br_6H_5$ [63]; M = Ir, diene = COD, X = $Me_{11}$ [64]) were synthesized. These complexes were prepared by the reactions of $Ag^+$ salt **75** or salts of other highly brominated and/or methylated *closo*-carboranes [Cs][1-*H*-*closo*-$CB_{11}Br_6H_5$] or [Ag][1-*H*-*closo*-$CB_{11}Me_{11}$] and appropriate Rh(I)- or Ir(I)-containing sources, such as $(Ph_3P)_3$RhCl or NBD rhodium complex **63**, in the presence of the free NBD ligand, *etc.* Some ionic complexes of this type were used in the presence of $H_2$ as convenient precursors in the synthesis of catalytically active 16- and 18-electron monocarbon *exo-closo*-metallacarboranes of rhodium and iridium. Thus, the treatment of the above-mentioned NBD phosphine ionic complexes derived from [*closo*-$CB_{11}H_{12}]^-$ carborane with $H_2$ in $CH_2Cl_2$ resulted in reduction of the NBD ligand and coordination of *closo*-carborane *via* two B–H···M bonds to the remaining cationic metal-containing moieties to form catalytically active bis-phosphine complexes of the general formula [*exo*-{$(L_2Rh)$}-*closo*-$CB_{11}H_{12}$] [61]. Under the same conditions, the reaction of [$(PPh_3)_2$Ir(COD)][*closo*-$CB_{11}H_6Br_6$] with $H_2$ produced the dihydride complex [$(PPh_3)_2IrH_2$][*closo*-$CB_{11}H_6Br_6$], which was structurally characterized as a double solvate with $C_6H_5F$ (Ir–P(1, 2), 2.322 and 2.335 Å; Ir–Br(7, 8), 2.680 and 2.655 Å) [63].

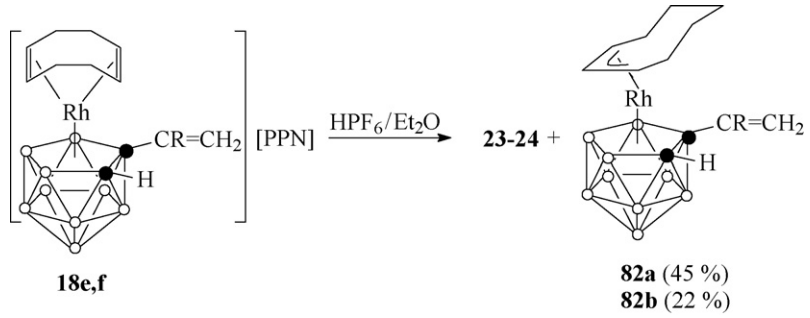
In connection with this, it should be noted that in the early study by Hawthorne and co-workers [65], the authors briefly described the synthetic procedure by which *closo* and *exo-nido*-iridacarborane complexes could be prepared starting from the ion pair [$(PR_3)_2$Ir(COD)][*nido*-7,8-$C_2B_9H_{12}$] (**79a**, R = Ph; **b**, R = $C_6H_4$-Me-4) and hydrogen. For example, when **79a** and **b** were treated with $H_2$ in *n*-pentane, a mixture of the complexes [3,3-$(PR_3)_2$-3-*H*-3,1,2-*closo*-$IrC_2B_9H_{11}$] (**80a** and **b**) and [*exo*-3,9-{$(R_3P)_2IrH_2$}-3,9-($\mu$-*H*)$_2$-7,8-*nido*-$C_2B_9H_{10}$] (**81a** and **b**), respectively, was obtained.

## 4. Mono- and polynuclear *closo*-metallacarboranes with η-cyclodiolefin-based derivatives

This section is concerned with three types of *closo*-metallacarborane complexes with $\eta^3$-cycloalkenyl, $\sigma,\eta^2$-cycloalkenyl, and $\eta^{3,2}$-cyclodienyl ligands based on cyclic diolefins COD, NBD, and DCPD, *etc.* In most cases, complexes with a $\eta^3$-allylic or $\eta^{2,3}$-allylolefinic metal-to-ligand coordination mode are stable both in the solid state and in solution. Examples of sufficiently stable *closo*-($\sigma,\eta^2$-cycloenyl)metallacarborane complexes prevail in the case of bi- and tricyclic diolefin derivatives and are scarce within the family of monocyclic diolefins. Among all the above metallacarboranes, species having an agostic C–H···M bonding system are of most interest because they often exhibit dynamic behavior in solution and, in some cases, show low energy barriers for the ligand C–C bond cleavage reactions. An exploration of both lines may generate novel discoveries in the field.

### *4.1. Metallacarboranes with $\eta^3$- and $\sigma,\eta^2$-cycloalkenyl-type ligands*

As was mentioned in Section 2.2, protonation of anionic *closo*-($\eta^4$-COD)rhodacarboranes **18e** and **f** containing alkenyl substituents at one of the cage carbon atoms with $HPF_6{\cdot}Et_2O$ [14] produced, along with zwitterionic complexes **23** and **24**, a reasonable amount of *closo* complexes with the $\eta^3$-cyclooctenyl ligand [3-($\eta^3$-$C_8H_{13}$)-1-{C(R)=$CH_2$}-3,1,2-*closo*-$RhC_2B_9H_{10}$] (**82a**, R = H; **b**, R = $CH_3$), which were generated from the competitive protonation at the coordinated double bond of the COD ligand in the starting anionic complexes (Scheme 30).




Scheme 30. Formation of $\eta^3$-cyclooctenyl complexes **82a** and **b** *via* the competitive protonation of anionic precursors [14].

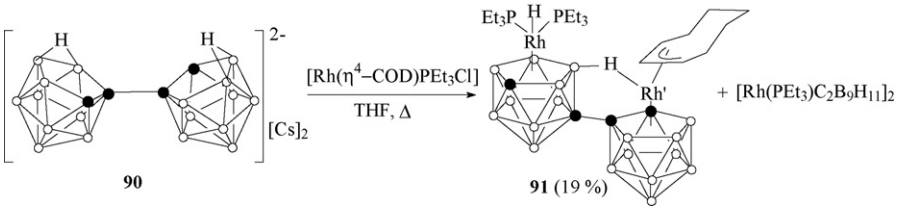
The mechanism of formation of the related complexes [3-($\eta^3$-$C_8H_{13}$)-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**83a–c**: **a**, R = $R^1$ = Me; **b**, R = Ph, $R^1$ = H; **c**, R = $R^1$ = H) in the protonation reaction of anions **18a–c** with $CF_3COOH$ ($CH_2Cl_2$, −73 °C) has been studied earlier by Hawthorne and co-workers [13]. According to this mechanism, the first step of the reaction involves protonation of anionic complexes **18a–c** at the double bond of the coordinated COD ligand to form the thermally unstable agostic (C–H···Rh) σ,$\eta^2$-complexes [3-(σ,$\eta^2$-$C_8H_{13}$)-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**84a–c**), respectively, which are highly fluxional in solution (Section 4.1.1). Mild heating of these compounds from –73 °C to + 7 °C led to their irreversible transformation into 16-electron *closo*-($\eta^3$-cyclooctenyl)rhodacarboranes **83a–c**. Interestingly, complexes **83a–c** proved to be quite different in stability in the solid state. As a result, only **83a** was obtained as a crystalline solid and characterized by single-crystal X-ray diffraction analysis.

More recently, Stone and co-workers [66] have studied the reactions of 16-electron complex **83a** with donor molecules, such as CO, P(Alk)$_3$ (Alk = Me, Et), and $PPh_3$. Thus, the reaction of **83a** with CO in a $CH_2Cl_2$ solution produced the stable 18-electron complex [3-($\eta^3$-$C_8H_{13}$)-3-CO-1,2-$Me_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**85**). Although the structure of the latter complex was not determined by X-ray diffraction, IR spectroscopic data ($\nu_{CO}$ = 2047 $cm^{-1}$) as well as the $^1H$ and $^{13}C\{^1H\}$ NMR spectra, which show all resonances expected for the $\eta^3$-$C_8H_{13}$ ligand and the cage CMe groups (except for a signal of CO in the $^{13}C\{^1H\}$ NMR spectrum which is not found), are consistent with the above formulation. The reactions of **83a** with an excess of $PMe_3$ and $PEt_3$ produce [3-Cl-3,3-($PMe_3$)$_2$-1,2-$Me_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**86**) and [3-H-3,3-($PEt_3$)$_2$-1,2-$Me_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**87**) [66], respectively; however, the reaction with $PPh_3$ affords the *exo-nido* complex [*exo-nido*-Rh($PPh_3$)$_2$($\eta^5$-$C_2B_9H_{10}Me_2$)] [67], which exists in solution in equilibrium with its *closo* isomer, [*closo*-RhH($PPh_3$)$_2$($\eta^5$-$C_2B_9H_{10}Me_2$)].

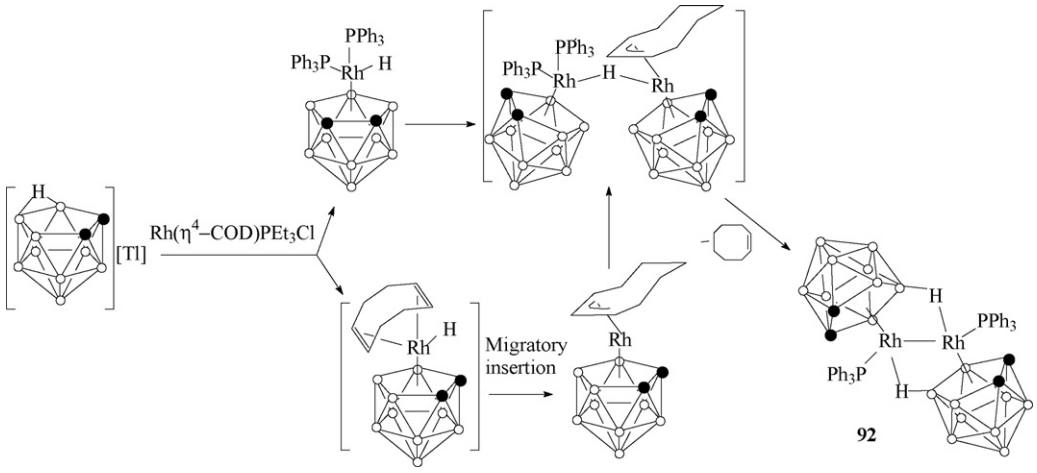
A likely reaction pathway for the formation of *closo*-bis(phosphine)hydridorhodacarborane **87** from **83a** and $PEt_3$ was discussed in the study [66]. The monophosphine-substituted complex [3-($\eta^3$-$C_8H_{13}$)-3-$PEt_3$-1,2-$Me_2$-3,1,2-*closo*-$RhC_2B_9H_9$], which retains the $\eta^3$-cyclooctenyl ligand at the metal vertex, was considered as the primary intermediate. This complex can exist in equilibrium with the isomeric *exo-nido* species, in which the hydride transfer from the $\eta^3$-$C_8H_{13}$ group to the metal center followed by a loss of the carbocyclic ligand in the form of either 1,3- or 1,5-COD could occur. The unsaturated complex formed in this step, [RhH($PEt_3$)($\eta^5$-$C_2B_9H_9Me_2$)], would add another phosphine molecule giving rise to the final product **87**. In turn, complex **86** is assumed to be formed *via* the replacement of rhodium hydride in the intermediate [RhH($PMe_3$)$_n$($\eta^5$-$C_2B_9H_9Me_2$)] ($n$ = 1 or 2) by the Cl ligand from $CH_2Cl_2$ that was used as the solvent.

Recently [28], the protonation of anionic 13-vertex *closo*-rhodacarborane **31** has been studied in order to compare its reactivity with that of related anionic 12-vertex complexes **18a–c**. Upon treatment with $CF_3SO_3H$ in THF, complex **31** gives the $\eta^3$-cyclooctenyl-type complex, [4-($\eta^3$-$C_8H_{13}$)-*closo*-4,1,6-$RhC_2B_{10}H_{12}$] (**88**), in which, according to X-ray diffraction data, there is an agostic interaction between the rhodium atom and one of *endo*-C–H bonds of the carbocyclic ligand at the position adjacent to the allylic unit (Rh···$C$H$_{ag}$, 2.6052 Å; Rh···H$_{ag}$, 2.183 Å). The $^1H$ and $^{13}C\{^1H\}$ NMR spectra at 233 K are consistent with **88** having a "static" C–H···Rh agostic structure, in which no molecular symmetry plane exists.

The preparation of [3-($\eta^3$-$C_8H_{13}$)-1-$CH_3$-7-Ph-2,1,7-*closo*-$RhC_2B_9H_9$] (**89**) was briefly described in [68]. This complex was unexpectedly formed in the reaction of [($\eta^4$-




Scheme 31. Synthesis of dinuclear $\eta^3$-cyclooctenyl complex **91** [69].



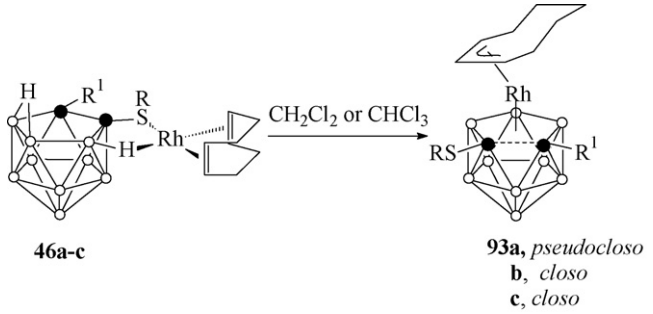

Scheme 32. Proposed synthesis of dimer **92** *via* binuclear reductive elimination mechanism [69].

COD)Rh{(P(*o*-tolyl)$_3$}$_2$][PF$_6$] with the mono-Tl$^+$ salt of the [7-CH$_3$-9-Ph-7,9-*nido*-C$_2$B$_9$H$_{10}$]$^-$ anion in toluene at room temperature. The structure of complex **89** was assigned based on the IR and $^1$H NMR spectroscopic data, by comparison with those of $\eta^3$-cyclooctenyl-type rhodium complexes, which have been prepared earlier by protonation of anions **18a–c** with CF$_3$COOH [13].

When studying the reaction of [($\eta^4$-COD)Rh(PEt$_3$)Cl] with Cs$_2$[7-(7′-*nido*-7′,8′-C$_2$B$_9$H$_{11}$)-*nido*-7,8-C$_2$B$_9$H$_{11}$] (**90**), Hawthorne and co-workers [69] have isolated the bimetallic Rh–Rh cluster [Rh(PEt$_3$)($\eta^5$-C$_2$B$_9$H$_{11}$)]$_2$, along with approximately equal amounts of an unusual dinuclear complex formulated as [RhH(PEt$_3$)$_2$($\eta^5$-C$_2$B$_9$H$_{10}$)Rh′($\eta^3$-C$_8$H$_{13}$)($\eta^5$-C$_2$B$_9$H$_{10}$)] (**91**). According to X-ray diffraction data, complex **91** consists of two cluster halves, each being substantially different in the architecture. One half contains the {2-*H*-2,2-(PEt)$_2$-2,1,8-RhC$_2$B$_9$} cluster fragment generated *via* the "1,2 → 1,7" polyhedral rearrangement, which occurred in the course of the reaction, and the other half retains the {3,1,2-Rh′C$_2$B$_9$} structural unit with the Rh atom coordinated by the $\eta^3$-cyclooctenyl ligand (Scheme 31.).

The synthesis and identification of complex **91** have played a considerable role in the development of an acceptable scheme, which accounts for the formation of the dinuclear compounds such as [Rh(PR$_3$)C$_2$B$_9$H$_{10}$R$^1$]$_2$ (R and R$^1$ = Alk or Ar). An example is the reaction of [($\eta^4$-COD)Rh(PPh$_3$)Cl] with [Tl][*nido*-7,8-C$_2$B$_9$H$_{12}$] resulting in the dinuclear complex [Rh(PPh$_3$)C$_2$B$_9$H$_{11}$]$_2$ (**92**) and cyclooctene (Scheme 32) [69].

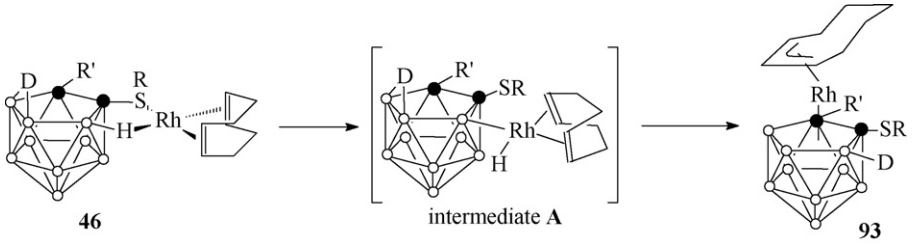
An interesting example of the *exo-nido* → *closo* rearrangement giving rise to the formation of *closo*- and/or




Scheme 33. Synthesis of $\eta^3$-(cyclooctenyl)thiorhodacarboranes of *pseudocloso* (**93a**) and *closo* (**93b** and **c**) structure [40].

*pseudocloso*-$\eta^3$-(cyclooctenyl)thiorhodacarboranes was documented [40]. The formation of the [3-($\eta^3$-C$_8$H$_{13}$)-1-SR-2-R$^1$-3,1,2-RhC$_2$B$_9$H$_9$] complexes (**93a–c**: **a**, R = R$^1$ = Ph; **b**, R = Ph, R$^1$ = CH$_3$; **c**, R = Et, R$^1$ = CH$_3$) occurs in a CHCl$_3$ or CH$_2$Cl$_2$ solution of the corresponding *exo-nido* isomers **46a–c** at ambient temperature (for **93b** and **c**) or under mild heating (for **93a**) (Scheme 33). It should be noted that complexes **46b** and **c** undergo isomerization even in the solid state to form **93b** and **c**.

The probable mechanism of the *exo-nido-to-closo* rearrangement of compounds **46a–c** was discussed [40]. Based on the chemical data, which were obtained with the use of specifically deuterium-labeled *exo-nido* complexes, as well as on the results of a kinetic study, preference was given to the reaction pathway presented in Scheme 34. According to this scheme, it is the cluster BH hydride (presumably H(11)) rather than the B–H–B bridging hydrogen that is transferred by an oxidative addition




Scheme 34. Proposed mechanism of the *exo-nido-to-closo* rearrangement of thiorhodacarboranes of the type **46** to form isomeric species **93** [40].

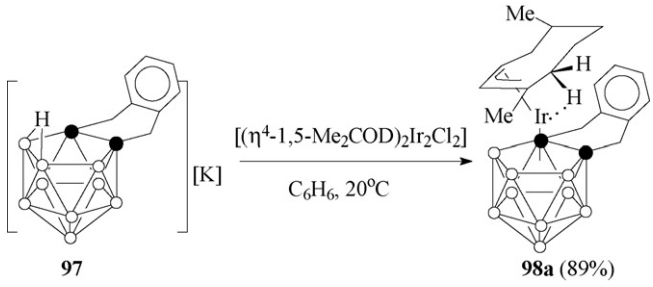
mechanism to the rhodium atom in the initial *exo-nido* species to form the diene hydride intermediate **A**.

It should be emphasized that, according to X-ray diffraction data, **93a** has the structure of a typical *pseudocloso* cluster with a broken C–C polyhedral connectivity of 2.427 Å and the shortened Rh···B(6) interatomic distance of 3.003 Å (*cf.* 1.6–1.74 and 3.5 Å, respectively, in non-deformed *closo* systems). The $^{11}$B NMR spectrum of **93a** shows that all boron resonances are shifted to higher frequencies, and the weighted average $^{11}$B NMR chemical shift, $\langle\delta\ ^{11}B\rangle$, is + 3.1 ppm, which is indicative of *pseudocloso* clusters [12]. On the contrary, the corresponding $\langle\delta(^{11}B)\rangle$ calculated from the $^{11}$B NMR spectra of complexes **93b** and **c** are −3.9 and −3.6 ppm, suggesting their *closo* structure.

We have described a convenient procedure for the synthesis of a number of hydrocarbon-containing *closo*-rhoda- and *closo*-iridacarboranes, including those with $\eta^3$- and $\sigma,\eta^2$-cyclooctenyl-type ligands [70–73]. According to this method, the $K^+$ salt of the *nido*-$C_2B_9$-carborane monoanion without prior deprotonation by a strong base reacts with an appropriate diene-containing metal reagent in a $C_6H_6$–EtOH mixture or just solely in a $C_6H_6$ solution at ambient temperature affording metallacarborane exclusively of the *closo* structure. Note that similar conditions have been primarily employed by Hawthorne et al. [41] in the synthesis of *exo-nido*-bis(phosphine)rhodacarborane starting from $RhCl(PPh_3)_3$ and $Cs^+$ or $Tl^+$ salts (but not ammonium salts) of *nido*-carborane monoanions and by others [42,74] for the preparation of *exo-nido*-metallacarboranes with heteroatom-containing substituents at the carborane ligands.

A series of new $\eta^3$-cyclooctenyl-type rhodium complexes [3-{$\eta^3$-($C_8H_{11}$-1, 5-$R'_2$)}-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**95a–c**: **a**, R′ = H, R, $R^1$ = μ-1′,2′-$(CH_2)_2C_6H_4$ [70]; **b**, R′ = R = $R^1$ = Me [70]; **c**, R′ = Me, R, $R^1$ = μ-1′,2′-$(CH_2)_2C_6H_4$ [75]), as well as previously known [13,76] *closo*-rhodacarborane **83a**, have been prepared with the use of the above methodology starting from the new rhodium reagent [{$\eta^4$-COD-1,5-$(CH_3)_2$}$_2$$Rh_2$(μ-Cl)$_2$] (**94**) [70,72] or from COD-rhodium dimer **19** and $K^+$ salts of the corresponding *nido*-$C_2B_9$-carborane monoanions in a $C_6H_6$–EtOH (4:1) mixture. It is noteworthy that under these conditions ($C_6H_6$–EtOH, room temperature) complexes **83a** and **95a–c** were formed together with the $\eta^2,\eta^3$-cyclooctadienyl rhodium complexes of the general formula [3,3-($\eta^2,\eta^3$-$C_8H_9$-1,5-$R'_2$)-1-$R^1$-2-$R^2$-3,1,2-*closo*-$RhC_2B_9H_9$] (for details, see Section 4.2). However, when these reactions were carried out in a solution of pure benzene instead of a $C_6H_6$–EtOH mixture, all the above-mentioned and, in addition, some other $\eta^3$-cyclooctenyl-type complexes of the following series: **83b** and **d** and **95**(**d**, R′ = H, R = Me, $R^1$ = Ph), were shown to be formed as the only reaction products isolated in moderate to high yields [75].

Several first *closo*-iridacarboranes with $\eta^3$-cyclooctenyl-type ligands were also synthesized according to the general procedure published in [70–73]. Thus, the reaction between [K][7,8-$(CH_3)_2$-7,8-*nido*-$C_2B_9H_{10}$] and COD-iridium reagent **34** in a $C_6H_6$–EtOH mixture produced the [3-($\eta^3$-COD)-1,2-$(CH_3)_2$-3,1,2-*closo*-$IrC_2B_9H_9$] complex (**96**), along with the corresponding *closo*-($\eta^2,\eta^3$-cyclooctadienyl)iridium complex [70] (see Section 3.2). A similar reaction of new

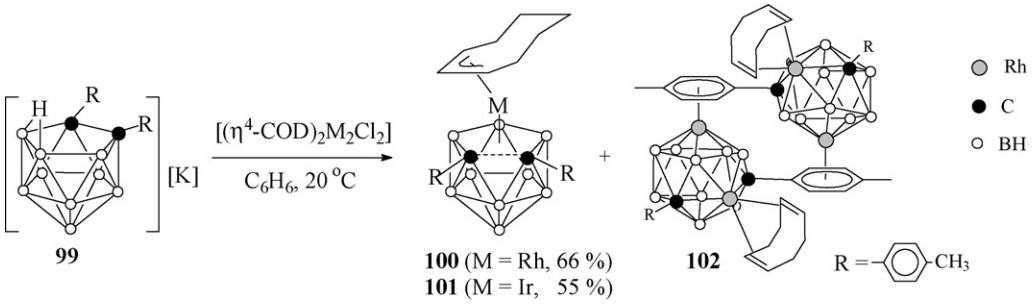



Scheme 35. Synthesis of the first agostic (C–H···Ir) *closo*-($\eta^3$-cyclooctenyl)metallacarborane **98a** [72].

iridium reagent **94** with [K][7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$)-7,8-*nido*-$C_2B_9H_9$] (**97**) in a solution of a $C_6H_6$-EtOH (4:1) mixture or solely in $C_6H_6$ afforded either the agostic (C–H···Ir) complex [3-{$\eta^3$-($C_8H_{11}$-1,5-$(CH_3)_2$)}-1,2-μ-(*ortho*-xylylene)-8-R-3,1,2-*closo*-$IrC_2B_9H_8$] (**98a**, R = H), along with **98**(**b**, R = EtO), or only **98a** in high yield (Scheme 35) [72]. The presence of an agostic interaction between the iridium atom and one of the *endo*-C–H bonds at the adjacent position with respect to the allylic unit of the $C_8$-ring in **98a** was supported by the low-temperature $^1$H and $^{13}C\{^1H\}$/$^{13}$C NMR data ($\delta H_{ag}$ = −2.8 ppm; $\delta CH_{ag}$ = 33.8 ppm, $^1J$(C,H) = 132 and 104 Hz) and its X-ray diffraction study (Ir···$H_{ag}$, 2.22 Å; Ir···$CH_{ag}$, 2.66 Å).

Metallation of the $K^+$ salt of the novel sterically demanding *nido*-carborane [7,8-(4′-$MeC_6H_4)_2$-7,8-*nido*-$C_2B_9H_{10}]^-$ anion (**99**) [77] with COD-metal reagents **19** and **34** in benzene was found to afford the 16-electron (non-agostic) *pseudocloso*-type complexes [3,3-($\eta^3$-$C_8H_{13}$)-1,2-(4′-$MeC_6H_4)_2$-3,1,2-*pseudocloso*-$MC_2B_9H_9$] (**100**, M = Rh; **101**, M = Ir), respectively (Scheme 36) [78]. Both *pseudocloso* species were characterized by a combination of multinuclear NMR spectroscopic data and, in the solid state, by a single-crystal X-ray diffraction study. The latter studies revealed an anomalous lengthening of the cage C(1)···C(2) connectivity in these structures (2.420(2) Å in **100** and 2.438(3) Å in **101**) as well as the presence of the tetragonal M(3)C(1)C(1)B(6) open face and the contracted M(3)···B(6) distances (3.007(2) and 2.998(2) Å, respectively), which are indicative of *pseudocloso* metallacarborane structures [12]. Note that the former reaction produced, along with *pseudocloso* complex **100**, a minor amount of dimeric rhodacarborane species **102** as a by-product, whose structure was established by NMR spectroscopy and X-ray diffraction. The molecule exists as two 13-vertex bimetallic {$Rh_2C_2B_9$} henicosahedral fragments joined together, each fragment having the $\eta^4$-coordinated 1,5-COD ligand at one of the metal vertices. It is remarkable that the carborane ligands in **102** underwent a polyhedral rearrangement involving the migration of the C-arylated carbon vertices away from one another to the positions separated by two cage boron atoms.

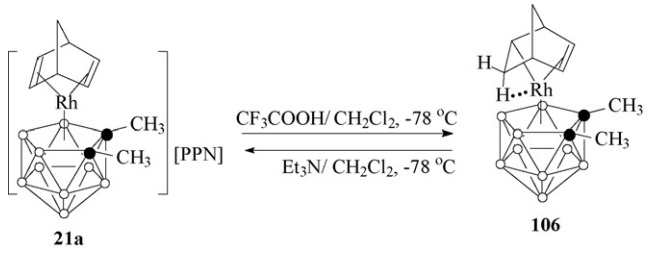
The reactions of the $K^+$ salt of *nido*-carborane **97** with the same COD-metal reagents **19** and **34** in a $C_6H_6$–EtOH mixture produced first *closo*-($\sigma,\eta^2$-cyclooctadienyl)metallacarborane complexes [3,3-($\sigma,\eta^2$-$C_8H_{13}$)-1,2-μ-(*ortho*-xylylene)-3,1,2-*closo*-$MC_2B_9H_9$] (**103**, M = Ir; **104**, M = Rh) in 89 and 49% yields, respectively, which are stable in the solid state [73].




Scheme 36. Synthesis of *pseudocloso*-($\eta^3$-cyclooctenyl)metallacarboranes **100** and **101** and the dimer **102** [78].

According to single-crystal X-ray diffraction data, the iridium atom in **103** is $\eta^2$-coordinated by the C–C double bond to the carbocyclic $C_8H_{13}$ ligand and also forms a σ-bond with one of the carbon atoms of the ring (Ir–$C_\sigma$, 2.098 Å; Ir···C=C, 2.202 and 2.190 Å). Moreover, the iridium atom is involved in a very strong agostic C–H···Ir bonding interaction with the *endo*-C–H group adjacent to the σ-bonded carbon atom in the $C_8H_{13}$-ring (Fig. 4, the crystal structure: Ir···$CH_{ag}$, 2.313 Å; Ir···$H_{ag}$, 1.77 Å). Of special note is the presence of a double intramolecular C–H···Ir/C–H···π interaction involving the agostic hydrogen atom. Actually, the latter is the C–H···π hydrogen bond between the agostic hydrogen atom and the aromatic ring (or only one of the aromatic bonds) that can be the basic center acts as the proton acceptor. Such a specific interaction occurring in **103** substantially influences the orientation of the $C_8H_{13}$ ligand observed in the crystal structure, which is, actually, far less reasonable due to close steric contacts of this ligand with other parts of the molecule than one would expect.

In solution, complex **103** is fluxional and exhibits both rapid "side-to-side" agostic hydrogen migration (Fig. 4, structure **A** and **A′**) and a reversible conversion into the isomeric complex [3-($\eta^3$-$C_8H_{13}$)-1,2-μ-(*ortho*-xylylene)-3,1,2-*closo*-$IrC_2B_9H_9$] (**105**) (for details, see Section 4.1.1). σ,$\eta^2$-Cyclooctenyl rhodium complex **104** proved to be less stable than its iridium congener and is readily converted into the corresponding $\eta^3$-cyclooctenyl isomer **95a** both in the solid state and in solution [73].




Scheme 37. Formation of agostic (C–H···Rh) complex **106** *via* the protonation of diene-rhodium complex **21a** and regeneration of the anionic species [16].

Stable zwitterionic palladacarborane [*closo*-3,3-{σ:$\eta^2$-(5-$MeOC_8H_{12}$)}-4-$SMe_2$-3,1,2-$PdC_2B_9H_{10}$] was synthesized from the dimeric palladium complex [(σ:$\eta^2$-5-$MeOC_8H_{12}$)$PdCl]_2$ and mono-$Tl^+$ salt **33** [29]. Study by $^1$H NMR spectroscopy demonstrated that this complex exists as two geometric isomers, which differ in the position of the methoxy function in the carbocyclic ligand with respect to the asymmetrically substituted carborane cage ligand. As has already been mentioned, the resulting complex was used as the starting material in the synthesis of cationic *closo*-palladacarborane **34**.

Hawthorne and co-workers have studied the protonation reaction of anionic complex **21a** containing the bicyclic NBD ligand at the metal vertex with $CF_3COOH$ [16]. It was shown that the protonation proceeds *via* the initial formation of the agostic species [3,3-(σ,$\eta^2$-$C_7H_9$)-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**106**) (Scheme 37), whose solid-state structure, in spite of thermal instability, was successfully determined by low-temperature

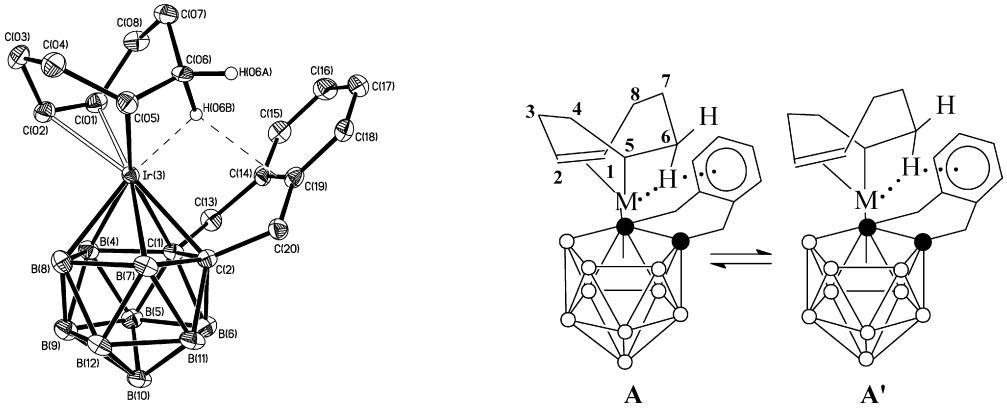
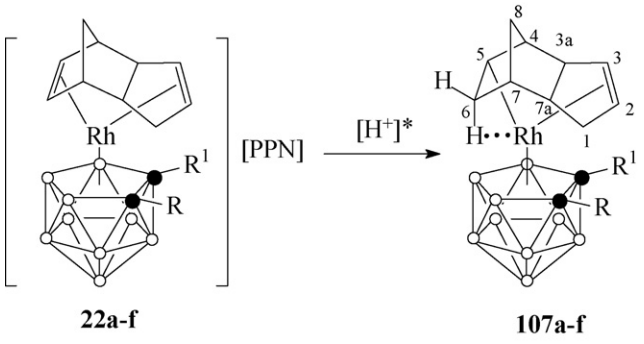



Fig. 4. Crystal (on the left) and solution (on the right) structures of complex **103** [73].




Scheme 38. Synthesis of *closo*-(σ,η$^2$-dicyclopentenyl)metallacarboranes **107a–f** [19–21].

X-ray diffraction (Rh···$C$H$_{ag}$, 2.36 Å; Rh···H$_{ag}$, 1.9 Å; Rh–C$_\sigma$, 2.08 Å). Starting diene species **21a** could be recovered by the low-temperature treatment of agostic complex **106** with $Et_3N$. In the same report, the thermal rearrangement of **106** to form complexes with the skeletally transformed hydrocarbon ligands has been studied in details (see Section 4.2).

The protonation of anionic rhodacarboranes **22a–f** containing the tricyclic η$^4$-DCPD ligand with acids (70% $HPF_6$ or $CH_3COOH$) was also documented [19–21,23]. All reactions produced monoprotonated agostic (C–H···Rh) complexes of the type [3,3-(σ,η$^2$-$C_{10}H_{13}$)-1-R-2-R$^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**107a–f**: **a**, R = R$^1$ = H; **b**, R = R$^1$ = $CH_3$ [19]; **c**, R = H, R$^1$ = $CH_3$; **d**, R = H, R$^1$ = CH=$CH_2$; **e**, R = H, R$^1$ = C($CH_3$)=$CH_2$ [20]; **f**, R = H, R$^1$ = $CH_2OH$ [20,21]) (Scheme 38). The use of $d_4$-acetic acid in the protonation of **22a** and **b** leads exclusively to the *endo*-addition of the proton at the C(5)=C(6) double bond of the DCPD ligand [19], the reaction pathways being independent of the presence or absence of basic substituents ($CH_2OH$, CH=$CH_2$, *etc.*) in the carborane ligand in the starting anionic complexes [21]. In addition, it was found that complexes **107a–f** are readily formed in good yields even upon chromatography of the corresponding anionic *closo*-(η$^4$-DCPD)rhodacarboranes on a silica gel column using $CH_2Cl_2$ as the eluent [20,21].

In the case of agostic complexes **107c–f** with unsymmetrically substituted carborane ligands, the separation of initial mixtures of diastereomers into individual isomeric compounds was achieved: complexes **107c** and **e** were separated by silica gel column chromatography; **107d**, by preparative HPLC; **107f**, by crystallization from $CHCl_3$. Diastereomers **107d** and **107f** adopting the opposite (*SR*/*RS*) and (*SS*/*RR*) relative configurations were studied by X-ray diffraction. Interestingly, two independent molecules of isomer **107f** are optical antipodes that are linked to one another *via* an intermolecular O–H···O hydrogen bond (Fig. 5). X-ray diffraction study demonstrated that in complexes (*SR*/*RS*)-**107d** and (*SS*/*RR*)-**107f** the metal-coordinated C(2)=C(3) bond and the CH–H···Rh fragment are located on the opposite sides of the plane passing through the midpoint of the C(5)=C(6) bond and the C(2) and C(8) atoms (Fig. 5). The possible factors responsible for this phenomenon, which are associated with the geometrical features of the DCPD ligand and its specific coordination to transition metals, were discussed in [20].

The protonation reaction of anionic *closo*-(η$^4$-DCPD)rhodacarboranes *l*-(−)-**22a**,**b** with $HPF_6$·$Et_2O$ has been used to prepare the first optically active *closo*-(σ,η$^2$-dicycloalkenyl)rhodacarboranes, *d*-(+)-**107a**,**b** [23].

### *4.1.1. Dynamic behavior and transformations of agostic complexes in solution*

It is well known that most of agostic (C–H···M) transition metal complexes containing carbocyclic ligands exhibit dynamic behavior in solution and undergo a rapid intramolecular exchange of agostic hydrogen with other hydrogen atoms of the coordinated ligand [79]. In two papers, Hawthorne and co-workers have studied the dynamic behavior of thermally unstable agostic complexes **84a–c** [13] and **106** [16] in solution. Both *closo*-(σ,η$^2$-cycloalkenyl)rhodacarboranes **84a** and **106** proved to be highly fluxional in solution on the NMR time scale and prone to intramolecular rearrangements. In a $CD_2Cl_2$ solution, complex **84a** exhibited exchange of the agostic hydrogen with other hydrogen atoms of the $C_8$ ring *via* extremely rapid 1,2- and 1,4-hydrogen shifts. Upon heating, complexes **84a–c** are readily isomerized to give, through a

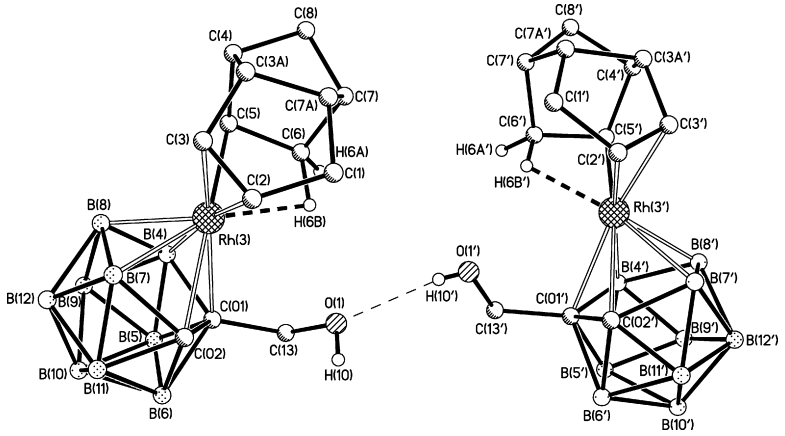
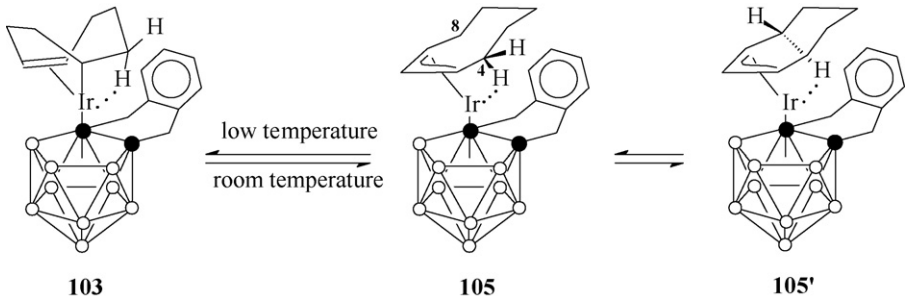



Fig. 5. Molecular structure of diastereomeric complex (*SS*,*RR*)-**107f** [20].




Scheme 39. Interconversion process observed for σ,η²-cyclooctenyl complex **103** in solution [73].

series of rapid 1,2-hydrogen shifts, the corresponding *closo*-(η³-cyclooctenyl)rhodacarboranes **83a**–**c**. In spite of the 16-electron structure of the latter, no direct evidence for the presence of a C–H···Rh agostic bonding interaction in these molecules was obtained either from NMR experimentations or from the solid-state structure of **83a** studied by X-ray crystallography.

In contrast to **83a**, complex **106** was shown to retain an agostic structure both in the solid state and in solution [16]. According to the low-temperature (−78 °C, $CD_2Cl_2$) $^1H$ NMR spectrum, complex **106** displays symmetry of the carbocyclic ligand with respect to the cage methyl substituents. The spectrum shows a broad high-field triplet ($\delta$ −0.85 ppm, $J$ = 10 Hz), which is indicative of the agostic (C–H···M) hydrogen atom undergoing rapid 1,4-hydride shifts. Such a solution behavior of **106** closely resembles the behavior reported for the known σ,η²-complex generated *via* the protonation of [(η⁴-NBD)Fe(CO)₃] [80] or [(η⁴-NBD)Co(η⁵-Cp*)] [81], where the rapid "side-to-side" migration of the agostic hydrogen was postulated to occur.

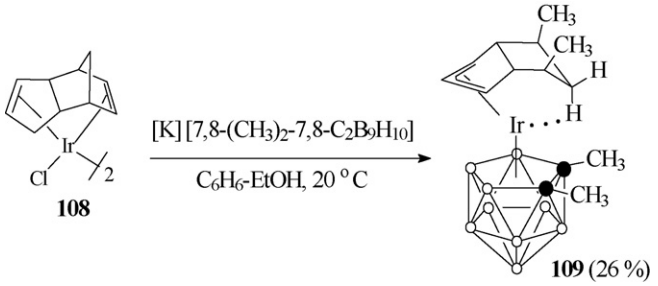
Recently [73], we have studied the fluxional behavior of σ,η²-cyclooctenyl complexes **103** and **104** in solution by variable-temperature $^1H$ and $^{13}C/^{13}C\{^1H\}$ NMR techniques. Agostic complex **103** was found to undergo rapid metal-assisted 1,4-hydride shifts (Fig. 4, right) and, in addition, it exists in solution in temperature-labile equilibrium with agostic η³-cyclooctenyl isomer **105**. In this equilibrium, σ,η²-cyclooctenyl complex **103** was shown to be favored at low temperature, whereas its η³-cyclooctenyl isomer **105** predominates at room temperature (Scheme 39). Both the room-temperature $^1H$ NMR and [$^1H$–$^1H$] EXSY spectra of **103** provide conclusive evidence for such an interconversion process between these two species in solution. This is, actually, the only known example of the reversible behavior for agostic-type σ,η²- and η³-cyclooctenyl isomeric complexes.

Complex **105** is also fluxional in solution due to a rapid exchange of the agostic interaction between the *endo* C–H bonds at positions 4 and 8 adjacent to the allyl moiety in the $C_8$-ring. At the lowest temperature limit that was achieved experimentally (−93 °C), this species is still dynamic, existing as two **105** and **105′** equilibrating forms.

In contrast to **103**, analogous σ,η²-cyclooctenyl rhodium complex **104** is relatively labile due to the fast irreversible conversion into stable η³-cyclooctenyl isomer **95a**. Hence, the solution behavior of the latter species was studied by a combination of standard homo- and heteronuclear 2D NMR techniques, including 2D [$^1H$–$^1H$] EXSY spectroscopy. It should be emphasized that the 2D [$^1H$–$^1H$] EXSY spectrum of **95a** provided evidence for the presence of an agostic C–H···Rh bonding interaction in this complex. The exchange processes both between the *endo* hydrogen atoms, on one hand, and the *exo* and allylic hydrogens of the $C_8$-ring, on the other hand, characteristic of agostic η³-cyclooctenyl metal systems, were shown to occur in **95a** in solution [73].

An unusual intramolecular skeletal transformation of the η⁴-DCPD ligand into the η³-dimethylpentalenyl ligand has been found to occur in the course of the reaction of the known dinuclear complex [(η⁴-DCPD)₂Ir₂Cl₂] (**108**) [82] with [K][7,8-$(CH_3)_2$-7,8-*nido*-$C_2B_9H_{10}$] in a $C_6H_6$–EtOH mixture [71]. This reaction unexpectedly afforded the [3-(η³-$C_{10}H_{15}$)-1,2-$(CH_3)_2$-3,1,2-*closo*-$IrC_2B_9H_9$] complex (**109**) containing a rather strong agostic C–H···Ir bond ($\delta H_{ag}$ = −5.82 ppm) (Scheme 40). The structure of complex **109** and the position of the C–H bond of the ligand involved in an agostic interaction with the metal atom were unambiguously established by X-ray diffraction (Ir···$CH_{ag}$, 2.898 Å; Ir···$H_{ag}$, 1.89; C–$H_{ag}$, 1.15 Å).

Formally, the η³-dimethylpentalenyl ligand in **109** is formed *via* the cleavage of the C–C double bond in the norbornene fragment in the DCPD ligand of the starting dimer **108** in the course of its reaction with the *nido*-$C_2B_9$-carborane anion followed by reduction of the terminal carbon atoms to give two methyl groups. Although the reaction patway remains unknown, it is reasonable to suggest that the agostic σ,π intermediate [3-(σ,η²-$C_{10}H_{13}$)-1,2-$(CH_3)_2$-3,1,2-*closo*-$IrC_2B_9H_9$] is formed in the first step of the reaction, in which the C–C bond of the former norbornene moiety of the DCPD ligand appeared to




Scheme 40. Formation of agostic (C–H···Ir) η³-dimethylpentalenyl complex **109** from dimer **108** *via* the skeletal transformation of the η⁴-DCPD ligand [71].

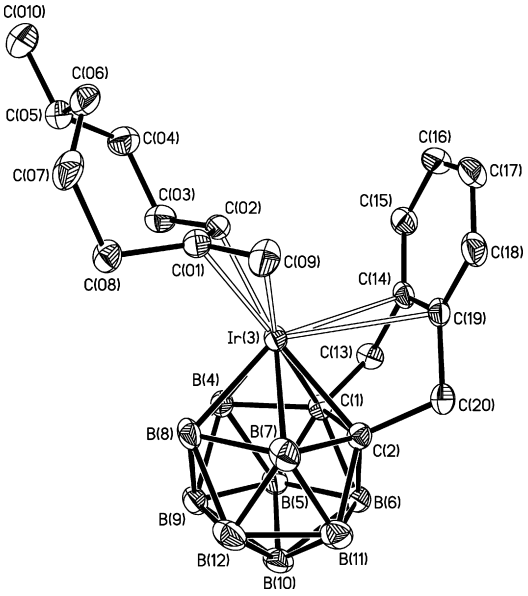



Fig. 6. Molecular structure of 18-electron complex **110** [72].

be already activated for the further metal-assisted C–C bond cleavage. In the literature, examples of such reactions are rare compared to C–H activation processes. In most cases, these processes involve strained cyclic hydrocarbons with iridium–metal complexes [83].

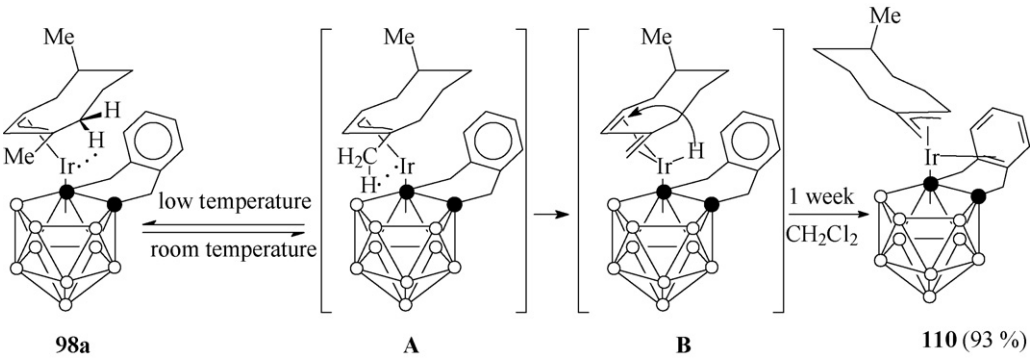
An unusual *endo-to-exo* allylic-type isomerization of agostic complex **98a** giving rise to *exo*-$\eta^3$-cyclooctenyl *closo*-iridacarborane was documented [72]. Stirring of a solution of **98a** in $CH_2Cl_2$ for 1 week leads to its quantitative rearrangement into isomeric [3-{$\eta^3$-(1-*exo*-$CH_2$-5-$MeC_8H_{12}$)}-1,2-μ-(*ortho*-xylylene)-3,1,2-*closo*-$IrC_2B_9H_9$] (**110**), which does not retain the agostic C–H···Ir bonding interaction. X-ray diffraction study of **110** revealed the existence of both a $\eta^3$-allylic system and a weak metal-to-*ortho*-xylylene $\eta^2$-coordination (Ir···C=C midpoint, 2.698 Å; C=C, 1.410 Å). This, in fact, stabilizes the iridium 16-electron center providing two additional electrons to the electronically deficient metal atom (Fig. 6).

The rearrangement **98a** → **110** occurs, presumably, through the initial formation of the diene-hydride intermediate [3,3-{$\eta^2$-*endo*-$\eta^2$-*exo*-(5-$MeC_8H_{11}CH_2$)}-1,2-μ-(*ortho*-xylylene)-3,1,2-*closo*-$IrC_2B_9H_9$] (Scheme 41, intermediate **B**), which, in turn, could be formed as a result of the competitive involvement of the methyl group bound to the allyl fragment in an agostic interaction with the Ir atom in complex **98a** (Scheme 41, intermediate **A**).

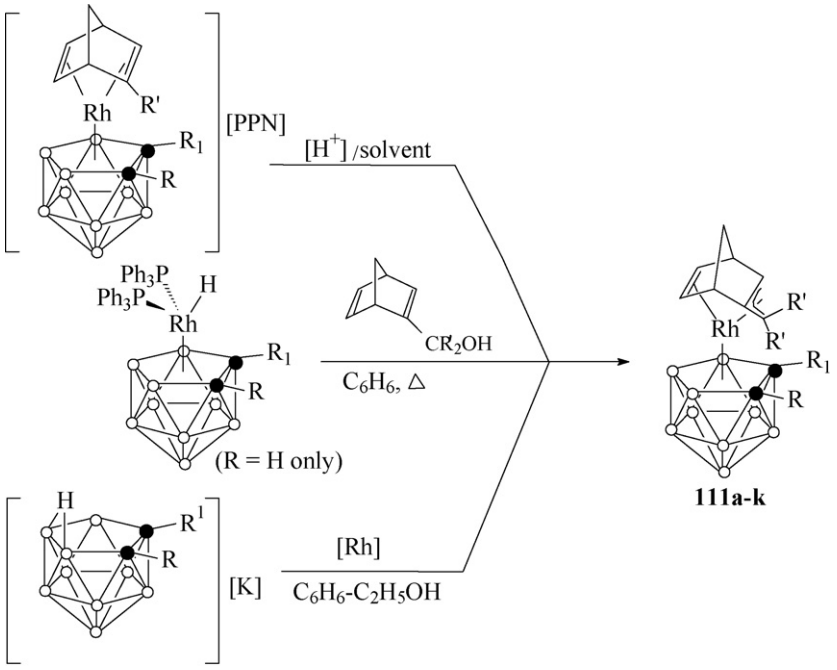
### 4.2. Metallacarboranes with $\eta^3$,$\eta^2$-cycloallylolefinic-type ligands

Most of platinum metal *closo*-metallacarboranes with formally five-electron carbocyclic ligands belong to the group of $\eta^5$-R-cyclopentadienyl- [84] and $\eta^5$-indenyl- [85] type complexes. The further development of the chemistry of ($\eta^5$-cyclohexadienyl)metallacarborane clusters incorporating platinum metals [86] may be also envisaged. Another group of *closo*-metallacarboranes involves the $\eta^3$,$\eta^2$-cycloallylolefinic-type ligands based on polycyclic diolefins. This group includes three types of complexes, of which two are characterized by either exocyclic $\eta^3$-allylic and endocyclic $\eta^2$-olefinic or, *vice versa*, exocyclic $\eta^2$-olefinic and endocyclic $\eta^3$-allylic metal-to-hydrocarbon ligand coordination modes, and the third type is with a solely endocyclic $\eta^3$,$\eta^2$-allylolefinic metal-to-ligand binding.

In a series of papers, we have reported our results on the synthesis [17,18,70,87–90], structural and stereochemical studies [87–90], and the application in catalysis [90–93] of *closo*-(π-norbonadienyl)rhodacarboranes based on [7,*n*-*nido*-$C_2B_9H_{11}]^{2-}$ derivatives ($n$ = 8 or 9). Thus, complexes of the type [3,3-{(2,3,8-$\eta^3$):(5,6-$\eta^2$)-($C_7H_7$-2-$CR'_2$)}-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**111a**–**k**: **a**, R = $R^1$ = R′ = H; **b**, R = $R^1$ = $CH_3$, R′ = H [17,70]; **c**, R = $CH_3$, $R^1$ = R′ = H; **d**, R = Ph, $R^1$ = R′ = H [17]; **e**, R = $PhCH_2$, $R^1$ = R′ = H; **f**, R = Pr-*i*, $R^1$ = R′ = H; **g**, R = $CH_2OH$, $R^1$ = R′ = H [18]; **h**, R = $R^1$ = R′ = $CH_3$ [70,89]; **i**, R = $CH_3$, $R^1$ = Ph, R′ = H [70]; **j**, R = $R^1$ = H, R′ = $CH_3$; **k**, R = CH=$CH_2$, $R^1$ = R′ = H [18]), as well as [3,3-{(2,3,8-$\eta^3$):(5,6-$\eta^2$)-($C_7H_7$-2-$CH_2$)}-4-($PhCH_2$)-3,1,2-*closo*-$RhC_2B_9H_{10}$] (**112**) [18] and [2,2-{(2,3,8-$\eta^3$):(5,6-$\eta^2$)-($C_7H_7$-2-$CH_2$)}-3,1,2-*closo*-$RhC_2B_9H_{11}$] (**113**) [17,70] were prepared by three different synthetic methods. These are as follows: (i) the protonation of the $PPN^+$ salts of the corresponding anionic *closo*-{$\eta^4$-($C_7H_7$-2-$CR_2OH$)}rhodacarborane complexes with $HPF_6$ (synthesis of **111a**–**g**), (ii) the thermal reaction in benzene between carbinols NBD-2-$CR'_2OH$ (R′ = H or Me) and the




Scheme 41. Proposed mechanism of the *endo-to-exo* allylic-type isomerization of agostic complex **98a** [72].




Scheme 42. Synthesis of *closo*-($\eta^3$,$\eta^2$-norbonadienyl)rhodacarboranes **111a–k** [17,18,70,89]: [H$^+$] = $HPF_6/Et_2O$; $CH_3COOH/Et_2O$; silica gel/$CH_2Cl_2$; [Rh] = [{$\eta^4$-$C_7H_7$-2-C(OH)R′$_2$}$_2$$Rh_2Cl_2$].

appropriate known bis(phosphine)hydridorhodacarborane complexes [3,3-$(PPh_3)_2$-3-*H*-1-R-3,1,2-*closo*-$RhC_2B_9H_{10}$] [94], [2,2-$(PPh_3)_2$-2-*H*-2,1,7-*closo*-$RhC_2B_9H_{11}$] [94] or [3,3-$(PPh_3)_2$-3-*H*-4-$(PhCH_2)$-3,1,2-*closo*-$RhC_2B_9H_{10}$] [18] (synthesis of **111a**, **c**, **k**, **112** and **113**, respectively), and (iii) the metallation reaction of the $K^+$ salts of the corresponding [*nido*-7,*n*-R,R$^1$-$C_2B_9H_{10}$] (*n* = 8 or 9) monoanions with the diene-rhodium complexes [{($\eta^4$-$C_7H_7$)-2-C(OH)R′$_2$}$_2$$Rh_2Cl_2$] (R′ = H, $CH_3$) [70] (synthesis of **111a**, **b**, **h**, **i** and **113**) (see Scheme 42 for the synthesis of **111a–k**).

Using chiral stationary phase HPLC, racemic complexes **111a**, **b**, **h** and **113** were successfully resolved into enantiomers and their chiroptical properties (rotation angles and CD spectra) were investigated [87].

*closo*-($\eta^3$,$\eta^2$-Norbonadienyl)rhodacarboranes with mono-C-substituted carborane ligands were usually formed in the reactions as mixture of diastereomers. In the case of **110c** and **e**, these mixtures were successfully separated into individual isomeric complexes, whose relative configurations were unambiguously established by X-ray diffraction studies [88,89]. An important stereochemical feature of these series of (*RS*/*SR*)- and (*SS*/*RR*)-diastereomeres is the different orientation of the norbornadienyl ligands relative to the substituents in the pentagonal $C_2B_3$ plane of the cage ligand (see, for example, Fig. 7). In this context, it should be noted that both unsubstituted **111a** [90] and C,C-′dimethylated **111b** [17] complexes adopt conformations similar to that of (*RS*/*SR*)-**111e**, although in the latter complex **111b** there is a short contact (3.074 Å) between the *exo*-C atom of the norbornadiene ligand and one of the methyl groups at the cage carborane ligand. Based on the results of conformational analysis performed for diastereomeric complexes **111c** and **e** [89], such an unusual conformation observed in their crystal structures was attributed to both the electronic effects caused by the cage substituents and specific steric interactions occurring between the carborane and norbornadienyl ligands.

Most recently [77], we have studied the metallation reaction of the $K^+$ salt of sterically demanding *nido*-carborane **99** with the reagent [{($\eta^4$-$C_7H_7$)-2-$CH_2OH$}$_2$$Rh_2Cl_2$]. Under mild conditions ($CHCl_3$ or $C_6H_6$, 22 °C), this reaction was found to proceed according to the low-temperature "1,2 → 1,7" C-atom isomerization scheme through the formation of the intermediate of the type [3,3-{(2,3,8-$\eta^3$):(5,6-$\eta^2$)-($C_7H_7$-2-$CH_2$)}-1,2-($C_6H_4CH_3$-4′)$_2$-3,1,2-*pseudocloso*-$RhC_2B_9H_9$] (**114**) to give finally two isomerized diastereomeric complexes [2,2-{(2,3,8-$\eta^3$):(5,6-$\eta^2$)-($C_7H_7$-2-$CH_2$)}-1,8-($C_6H_4CH_3$-4′)$_2$-2,1,8-*closo*-$RhC_2B_9H_9$] (**115a** and **b**) (Scheme 43). All three compounds were characterized by single-crystal X-ray diffraction studies. The fact that intermediate complex **114** is irreversibly converted into isomeric compounds **115a** and **b** was proved by *in situ* $^1$H NMR monitoring. Together with the data on metallation of [$Li_2$][*nido*-7,8-$Ph_2$-7,8-$C_2B_9H_9$] with [($\eta$-$C_7H_7$)$Mo(MeCN)_3$][$BF_4$], which were independently obtained by Welch and co-workers [95], these experimental results are among the first confirming the formation of *pseudocloso* complexes in the first step of the transformation of overcrowded (transient) *closo* compounds of the {1,2-$R_2$-3,1,2-$MC_2B_9$} architecture (such as **A** in Scheme 43) into the final isomeric {1,8-$R_2$-2,1,8-$MC_2B_9$} products.

Stone and co-workers [66] have synthesized the first metallacarborane complex with the *endo*-$\eta^3$,$\eta^2$-cyclooctadienyl ligand at the metal vertex, [3,3-{(1-3-$\eta^3$):(5,6-$\eta^2$)-$C_8H_{11}$}-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**116**). This complex was prepared in 62% yield by the reaction of the $[NEt_4]^+$ salt of anionic COD-rhodium complex **27** with the hydride-abstracting

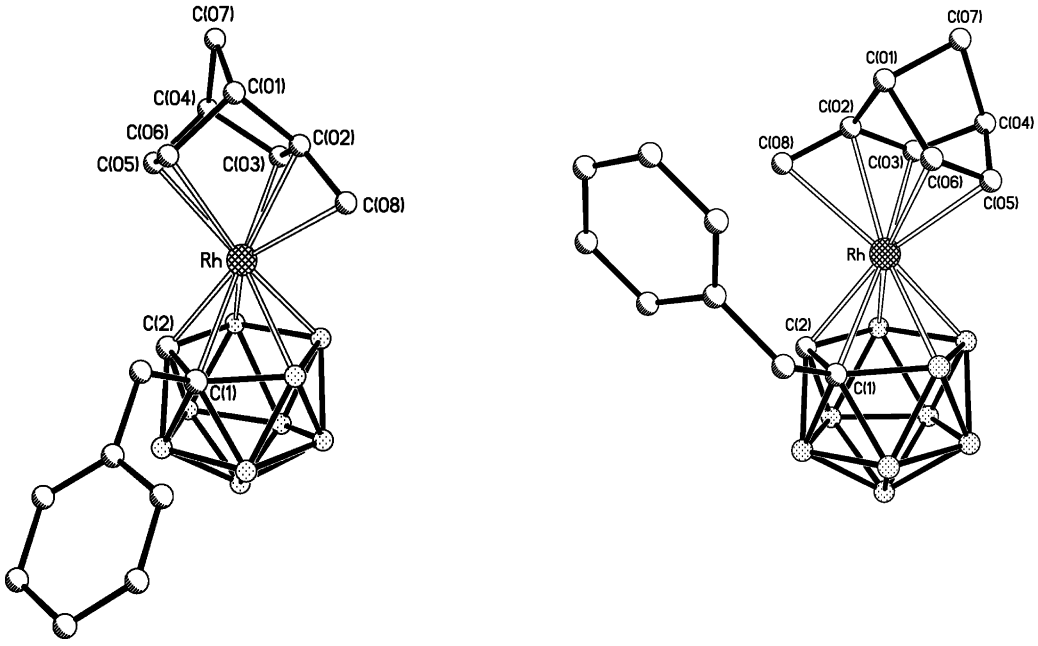
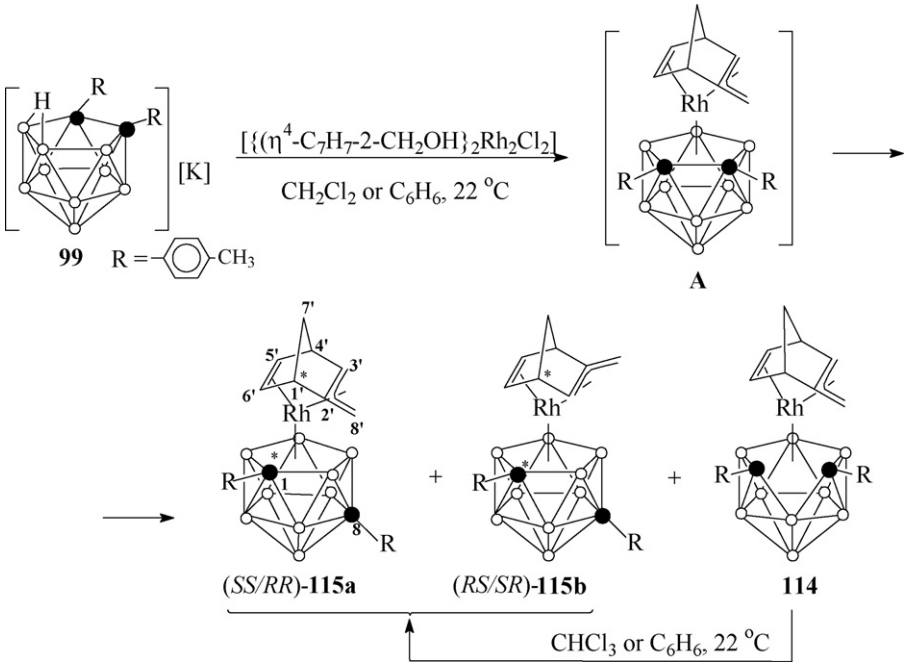



Fig. 7. Molecular structures of diastereomers (*SS*/*RR*)-**111c** (left) and (*RS*/*SR*)-**111e** (right) [88,89].

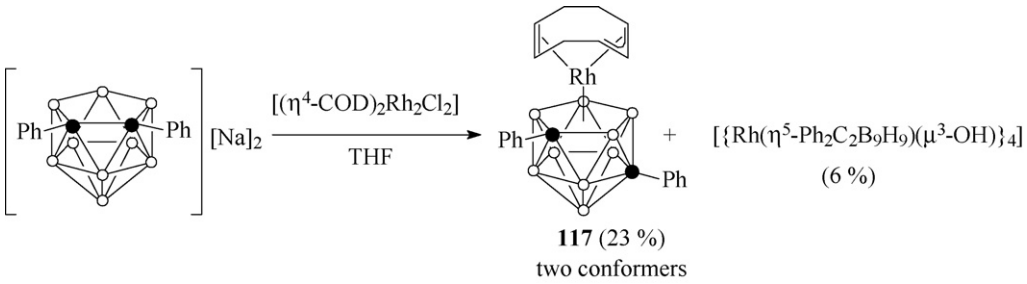
reagent $[CPh_3][BF_4]$. The structure of **116** was established by X-ray diffraction.

Related *closo*-(*endo*-$\eta^3$,$\eta^2$-cyclooctadienyl)rhodacarboranes were also synthesized by metallation of the di-$Na^+$ salt of the [*nido*-7,8-$Ph_2$-7,8-$C_2B_9H_9$]$^{2-}$ dianion with COD-rhodium reagent **19** in THF [96]. This reaction produced the "1,2 → 1,7" isomerized product [3,3-{(1-3-$\eta^3$):(5,6-$\eta^2$)-$C_8H_{11}$}-1,8-$Ph_2$-2,1,8-*closo*-$RhC_2B_9H_9$] (**117**) as the major species along with small amounts of the tetrameric cubane-like cluster [{Rh($\eta^5$-$Ph_2C_2B_9H_9$)($\mu_3$-OH)}$_4$] (Scheme 44). An examination of complex **117** by multinuclear NMR methods showed that it exists as two stable conformers, which differ in the orientation of the $\eta^3$,$\eta^2$-$C_8$ ring relative to the carborane cage ligand. In single crystals, **117** also consists of two conformers in a ratio of *ca.* 3:1 as established by X-ray crystallography.

As mentioned in Section 3.1, the reaction of COD iridium reagent **34** with the salt [K][7,8-$(CH_3)_2$-7,8-*nido*-




Scheme 43. Metallation of *nido*-carborane salt **99** with the Rh(I) reagent and the conversion of intermediate *pseudocloso* species **114** into the "1,2 → 1,7" isomerised diastereomeric complexes **115a** and **b** [77].




Scheme 44. Formation of "1,2 → 1,7" isomerised complex **117** *via* metallation of the C,C′-diphenylated *nido*-carborane dianion with the Rh(I) reagent [96].

$C_2B_9H_{10}$] produced a mixture of two $\eta^3$-cyclooctenyl and $\eta^3,\eta^2$-cyclooctadienyl complexes [70], which were successfully separated by silica gel column chromatography and in the very recent past the structure of [3,3-{(1-3-$\eta^3$):(5,6-$\eta^2$)-$C_8H_{11}$}-1,2-$(CH_3)_2$-3,1,2-*closo*-$IrC_2B_9H_9$] (**118**) in the solid state has been studied by X-ray diffraction (Ir–C(all), 2.18–2.33 Å; Ir–C(alken), 2.22, 2.24 Å) [97].

An unexpected $\sigma,\eta^2 \rightarrow \eta^3,\eta^2$ transformation of the dicyclopentenyl ligand in complex **107f** was reported [21]. Storage of a low-concentrated ($2 \times 10^{-3}$ M) ethanolic solution of **107f** at room temperature for a week afforded, after column chromatography, the complex [3,3-{(1-3-$\eta^3$):(5,6-$\eta^2$)-$C_{10}H_{11}$}-1-$(CH_2OH)$-3,1,2-*closo*-$RhC_2B_9H_{10}$] (**119**) in 34% yield. This reaction is believed to proceed *via* the intermolecular hydrogen transfer from the coordinated $\sigma,\eta^2$-$C_8H_{13}$ ligand to free COD, which is presumably formed in the course of partial decomposition of **107f** in solution. The X-ray structure showed that complex **119** (Fig. 8) consists of centrosymmetric dimeric associates and exhibits an interesting type of crystallographic disorder of the OH group over two centers of basicity in the molecule. Two OH hydrogen atoms in the dimer are simultaneously involved both in the O–H···Rh (Rh···H, 2.98 Å; Rh···O, 3.315 Å; O–H···Rh, 125°) and O–H···O (O···O, 2.74 Å, O–H···O, 170°) hydrogen bonding interaction.

An interesting type of σ,π-norbornene ligand rearrangements was observed by Hawthorne and co-workers when studying the solution structure of thermally unstable agostic complex **106** [16]. It was found that storage of complex **106** in a $CH_2Cl_2$ solution (25 °C, 20 h) led to the hydrocarbon C-C bond cleavage to form a 18-electron species with the *exo*-$\eta^2$-vinyl-*endo*-$\eta^3$-cyclopentenyl ligand at the Rh(III) vertex, [3,3-{(1,2,3-$\eta^3$):(6,7-$\eta^2$)-$CH_2$=$CHC_5H_6$}-1-R-2-$R^1$-3,1,2-*closo*-$RhC_2B_9H_9$] (**120a**, $R = R^1 = CH_3$). Thermolysis of the latter species ($C_6H_6$, 40 °C, 3 days) gave the final $\eta^5$-ethylcyclopentadienyl *closo* product, [3,3-($\eta^5$-$CH_3CH_2C_5H_6$)-1,2-$(CH_3)_2$-3,1,2-*closo*-$RhC_2B_9H_9$] (**121**) in high yield (Scheme 45). The structure of complex **120a** was unambiguously confirmed by single-crystal X-ray diffraction analysis.

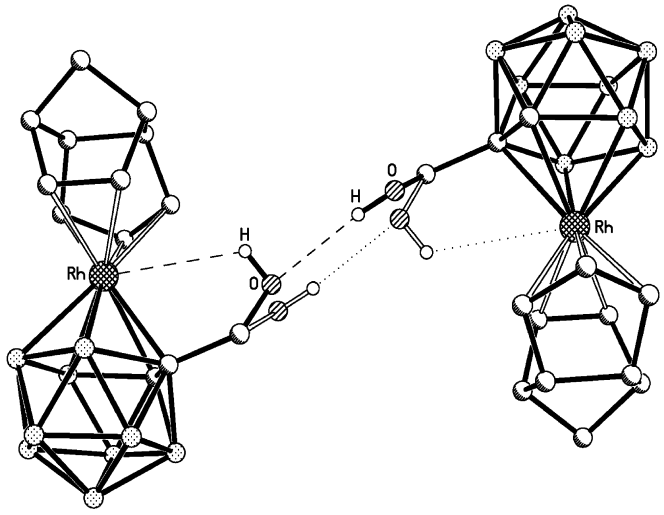
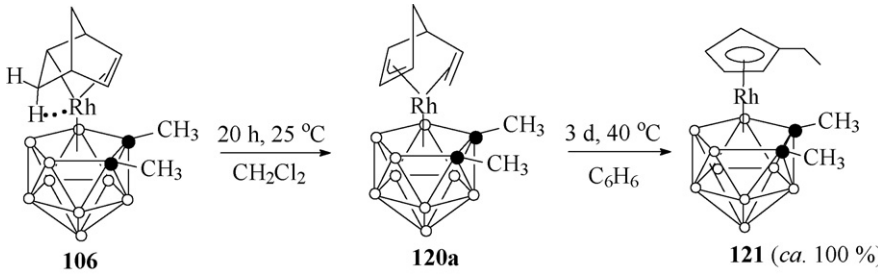



Fig. 8. Molecular structure of *closo*-($\eta^3,\eta^2$-dicyclopentadienyl)rhodacarborane **119** [21].

More recently [98], a series of related *closo*-($\eta^2,\eta^3$-vinylcyclopentenyl)rhodacarboranes **120**(**b–d**: **b**, $R = R^1 = H$; **c**, $R,R^1 = 1',2'$-$(CH_2)_2C_6H_4$; **d**, $R = CH_3$, $R^1 = Ph$) (including known **120a**) were prepared in moderate to high yields by the direct reaction of NBD-rhodium complex **63** with the $K^+$ salts of the corresponding {*nido*-$C_2B_9$}-carborane monoanions.




Scheme 45. Step-wise thermal transformation of agostic complex **106** into *closo*-($\eta^5$-cyclopentadienyl)rhodacarborane derivative **121** [16].

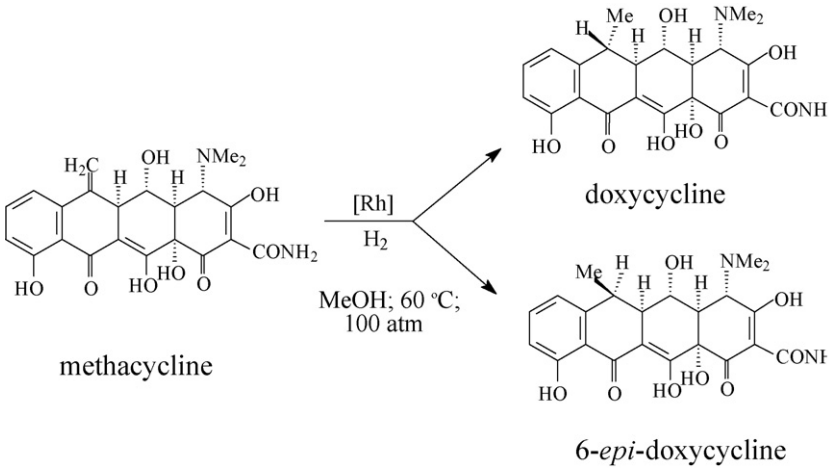
## 5. Catalytic properties of metallacarboranes with η-cyclodiolefin-based ligands

Since the mid-1980s important progress has been made in discovering efficient catalytic systems within the family of platinum metal metallacarboranes. This work proceeded through the innovative catalyst design and an in-depth mechanistic understanding of their activity [99]. In the case of *closo*-bis(phosphine)hydridorhodacarboranes, which are the most intensively studied catalyst precursors of this family, the catalytic activity has been attributed to the presence in solution of a unique equilibrium between the 16-electron Rh(I) *exo-nido*- and 18-electron Rh(III) *closo*-rhodacarborane tautomers [41], wherein the key catalytically active species involves the *exo-nido* B-Rh(III)–H array formed by the intramolecular oxidative addition of the terminal B–H bond to the *exo-nido* Rh(I) center [100]. These pioneering studies by Hawthorne and co-workers clearly indicated that metallacarborane clusters might find an extensive application in a variety of organic processes as homogeneous catalysts or catalyst precursors. This strategy is now confirmed by the appearance of numerous examples of catalytically active metallacarborane clusters that increased the efficacy and extended the range of metallacarborane-catalyzed organic reactions [101]. Among those complexes working as catalyst precursors for homogeneous organic processes, a number of *closo*- and *exo-nido*- as well as *exo-closo*-metallacarboranes of platinum metals with cyclodiene(dienyl)- or cycloalkene-type ligands are now known to display high activity and stereoselectivity.

Catalytic systems based on *closo*-($\eta^3$,$\eta^2$-norbornadienyl)rhodacarboranes have been found to be exceptionally effective for the highly diastereoselective hydrogenation of methacycline (MC) into doxycycline (DC), a potent tetracycline antibiotic extensively used in chemotherapy (Scheme 46) [90–92]. Among complexes tested, the least substituted species **111a** and **113** proved to exhibit the highest catalytic activity and selectivity in the formation of DC (conversion of MC is 95–96%; the DC:EDC (6-*epi*-doxycycline) ratio is *ca.* 95–96:2.5). Other complexes containing mono- or disubstituted carborane ligands (complexes **111c**, **e** and **111b**, respectively) as well as complex **107b** (taken as an example of catalyst precursors derived from agostic *closo*-(σ,$\eta^2$-dicyclopentenyl)rhodacarboranes) were also active, but not too efficient, in this process. A remarkable effect of the ligand arrangement on the activity and diastereoselectivity in the formation of DC have been observed when the related cationic $\eta^5$-($R_n$-cyclopentadienyl)rhodium complexes [{(2,3,8-$\eta^3$):(5,6-$\eta^2$)-($C_7H_7$-2-$CH_2$)}Rh($\eta^5$-$C_5R_n$)]$^+PF_6^-$ (**122a–c**: **a**, $R_n = H_5$; **b**, $R_n = H_2$-1,2,4-$Ph_3$; **c**, $R_n = (CH_3)_5$) were tested in this reaction in parallel with the rhodacarborane catalysts [90]. Thus, the selectivity of less active catalyst **122c** (conversion of MC is 51%) and that of more active catalysts **122a** and **b** (conversion of MC is 99–99.5%) proved to be inverted (DC:EDC ratios are 45:5.5 and *ca.* 12:71, respectively); at the same time, for the former catalyst precursor the selectivity is consistent with that observed for complexes of the *closo*-rhodacarborane family.

Furthemore, some *closo*-rhodacarboranes with the $\eta^3$,$\eta^2$-norbornadienyl ligands have been successfully applied to alcoholysis of silicon hydrides, such as $Et_3SiH$ and $PhMe_2SiH$, by carbinols (a potent method for the protection of hydroxy functions in organic chemistry) [102,103]. It was found [102] that complex **111a** more actively promotes the reaction between $PhMe_2SiH$ or $Et_3SiH$ and ROH (R = Me, *i*-Pr, Et, *t*-Bu, MeCH=$CHCH_2$, PhOH, *etc.*) to give silyl ethers $ROSiMe_2Ph$ or $ROSiEt_3$, respectively, as compared to [3,3-($Ph_3P$)$_2$-3-*H*-3,1,2-*closo*-$RhC_2B_9H_{11}$] and even to Wilkinson's catalyst. The above-mentioned and two other *closo*-rhodacarboranes (zwitterionic complex **25** and related species **82b**) were also tested as catalyst precursors in the reactions of $Me_2PhSiH$ or $Et_3SiH$ with aliphatic carbinols MeOH and *i*-PrOH, where *closo*-($\eta^3$-cyclooctenyl)rhodacarborane, **82b**, proved to exhibit the highest catalytic activity [103].

The reaction of $PhCH_2CHO$ under syngas [93] catalyzed by *closo*-rhodacarboranes **111a** and **b** and **111c** (two separated diastereomers) afforded three princi-




Scheme 46. Hydrogenation of methacycline to doxycycline catalyzed by *closo*-rhodacarboranes **111a–c**, **e** and **113** [90].

pal coupling products, *viz.*, $PhCH_2CH_2CH(Ph)CHO$ (DFBAL), $PhCH_2CH_2CH(Ph)CH_2OH$ (DFBOL), and $PhCH_2CH{=}C(Ph)CHO$ (DFBEAL). Dimerization with the use of **111a** and **b** in combination with additives ($PPh_3$, $PPh_3 + H_2O$, or $H_2O$), which proved to be the catalytic systems of choice in this reaction, gave products in moderate to good yields (up to 90%). However, the selectivity of the formation of all these homocoupling compounds remained poor as compared to that observed with Wilkinson's catalyst, which afforded DFBAL in 80% yield along with insignificant amounts (<2%) of two other coupling products, DFBOL and DFBEAL [104].

Several monophosphinorhodacarboranes and monothiorhodacarboranes of both *exo-nido* and *closo* structures bearing $\eta^4$-COD or $\eta^3$-$C_8H_{13}$ as ancillary ligands were tested as precatalysts for the hydrogenation of alkenes. In particular, it was briefly mentioned [101f] that complex **41a** and the related *exo-nido*-7-R-rhodacarboranes proved to be highly active catalyst precursors for the hydrogenation of 1-hexene (at 66 °C and a hydrogen pressure of 45 bar, the conversion into 1-hexane is 99%). However, this was achieved with the use of a rather low substrate-to-catalyst ratio of *ca.* 700. Catalytic hydrogenation reactions of cyclohexene as internal olefin were carried out with the use of isomeric *exo-nido*-, *closo*-, and *pseudocloso*-rhodathiocarborane complexes bearing $\eta^4$-cyclooctadiene and $\eta^3$-cyclooctenyl ligands [40]. An examination of *exo-nido* species **46b** and **c** in combination with 1 equiv. of $PPh_3$ showed only a moderate conversion of cyclohexene into cyclohexane. Moreover, the activity of such catalytic systems, generated *in situ*, proved to be very similar to that observed with the parent diphosphine *exo-nido* complexes $[(Ph_3P)_2Rh(7\text{-}SR\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})]$ (R = Ph and Me), which, for comparison, were independently tested as catalyst precursors in the same hydrogenation process. On the contrary, isomeric *closo* complexes bearing $\eta^3$-cyclooctenyl ligand proved to be highly active. When *pseudocloso* and *closo* complexes **93a** and **b** were tested as catalysts in this reaction (either with or without $PPh_3$ as an additive), the conversion into hexane varies from 76 to 98% and the turnover frequencies (TOF) were also substantially larger than those observed for the respective *exo-nido* species.

Chiral *exo-nido*-($\eta^4$-COD)rhodacarborane complexes **44a**-*R* and **44b**-*S*, among other metallacarboranes with chelating bis(phosphines), such as (*S*)-BINAP or (*R*,*R*)-/(*S*,*S*)-DIOP, were tested as potential enantioselective catalysts for the hydrogenation of (*Z*)-PhCH=C(NHAc)COOH (ADZA) and ketopantolactone (KPL) as well as for the hydrosilylation of $PhCOCH_3$. In all cases, only complexes containing the ancillary COD and DIOP ligands were catalytically active [38]. Thus, in the hydrogenation of ADZA and KPL, enantiomerically pure **44a**-*R* gave 60–62 and 23% ee of the corresponding reduction products (*N*-acetyl-L-phenylalanine as its methyl ester and (*R*)-pantolactone, respectively). In the case of enantiomerically less pure complex **44b**-*S*, the enantioselectivity in both reactions was somewhat lower. The hydrosilylation of acetophenone with $Ph_2SiH_2$ in the presence of **44a**-*R* resulted in only 7–9% ee of (*R*)-$PhCH(OH)CH_3$.

Silica-immobilized chiral complexes **44a**-*R* and **44b**-*S* were also used as diastereoselective heterogeneous catalysts for the hydrogenation of folic acid at the C=N double bond of the pyrazine ring to form (6*S*,*S*)-5,6,7,8-tetrahydrofolic acid in 87.3% de [105].

Two ionic rhodium complexes $[(PPh_3)_2Rh(NBD)][closo\text{-}CB_{11}H_{12}]$ and $[(PPh_3)_2Rh(NBD)][closo\text{-}CB_{11}H_6Br_6]$ were shown to operate as good to excellent precatalysts in the hydrogenation of internal alkenes (cyclohexene, 1-methylcyclohex-1-ene, and 2,3-dimethylbut-2-ene) under very mild conditions (10 psi of $H_2$ and room temperature, 1 mol% of the catalyst) [62]. Moreover, a comparison of their catalytic activity with that of the known catalysts $[(PPh_3)_2Rh(NBD)][BF_4]$ (**A**) and $[(Py)(PCy_3)Ir(COD)][PF_6]$ (**B**, Grabtree's catalyst) shows a remarkable counterion effect on both the overall yield of the products and TOF. For example, while the former rhodacarborane gives the 43% yield of hydrogenated cyclohexene after 2 h ($TOF = 22\ h^{-1}$), the hydrogenation with the latter rhodacarborane is completed within 0.5 h ($TOF > 200\ h^{-1}$), and this was far superiror to that exhibited by the known catalyst **A** (2 h, the 29% yield of the saturated product). The related ionic iridium complex $[(PPh_3)_2Ir(COD)][closo\text{-}CB_{11}H_6Br_6]$ was explored by the same research group for the generation of $[(PPh_3)_2Ir(H_2)(closo\text{-}CB_{11}H_6Br_6)]$, which exhibits catalytic activity in the hydrogenation of cyclohexene (room temperature, the catalyst-to-substrate ratio of 1:100) almost identical to that of the above-mentioned rhodium congener, giving rise to complete reduction of the substrate after 30 min at *ca.* 10 psi of $H_2$ [63]. The most remarkable fact, however, is that this catalyst, on consumption of cyclohexene, may be reused in a number of cycles without notable decomposition into inactive polymetallic hydride species.

Another type of ionic rhodium and iridium *exo-closo* complexes **71** and **72** was also reported to be active in the hydrogenation of cyclohexene [58]. However, the reaction proceeds with 100% conversion at 300 psi of $H_2$ (MeOH, 80 °C, 50 min) and only with the use of rhodium species **71** as a precatalyst. Under the same conditions complex **72** gave the hydrogenated product in lower yield (52.8%), a higher conversion of up to 90% can be achieved in 1,2-dichloroethane at 80 °C.

## 6. Summary

Metal derivatives of *nido*-$C_2B_nH_n$ ($n = 8$–10) bearing cyclodiolefin-based ligands provide a range of structurally interesting and potentially useful complexes. These complexes open new possibilities in the construction and further development of polymetallic carborane-containing clusters, which may have versatile applications in chemistry. A number of systems both of *closo*- and *exo-nido*-, as well as of *exo-closo*, structures have already been successfully used as catalysts or catalyst precursors in various organic processes. Since some of the neutral, anionic, or the cage-compensated *closo*- and *exo-nido*-($\pi$-diene)metallacarboranes of platinum metals are, at present, available in diastereo- or enantiomerically pure forms, one may also expect their potential application as stereoselective catalysts for asymmetric reactions.

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