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Review

Forced *exo-nido* rhoda and ruthenacarboranes as catalyst precursors: a review

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Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday. F.T. and C.V. feel indebted to Professor Shore for his guidance when Professor R. Rudolph died. His great personal and scientific qualities motivated us to pursue our research at the University of Michigan at that time.

Abstract

Forced *exo-nido* rhoda and ruthenacarboranes containing monothio and monophosphinocarboranes have been tested as catalyst precursors in different catalytic reactions. The catalyst precursors employed were [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (R = Ph, Et; R' = Ph, Me), [Rh(7-PR_2-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (R = Ph, Et, ^{i}Pr; R′ = H, Me), [Rh(7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$)(cod)], [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)], [RuX(7-PR_2-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (X = Cl, H; R = Ph; R′ = H, Me, Ph) and [RuCl(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (R = Ph, Et; R′ = Me, Ph). These complexes are obtained by the reaction of the tetramethylammonium or cesium salt of the *nido* ligand with Rh(I) or Ru(II) complexes incorporating ancillary ligands. Although two molecular structures are possible, the *closo* and the *exo-nido*, only the *exo-nido* tautomer is generally formed. The cluster is coordinated to the metal through the S or P atom and one or two B–H–M interactions, depending on the metal. These *exo-nido* rhoda and ruthenacarboranes have been shown to catalyze in very good yield the hydrogenation of terminal alkenes but they are not active in the hydrogenation of internal alkenes. Both rhoda-monothio and monophosphinocarboranes present comparable activity at $P = 45$ bar and $T = 66$°C, in the hydrogenation and isomerization of 1-hexene. However, while the monothioether precursors are active at $P = 1$ atm and $T = 25$°C, the monophosphino exhibited a very low activity. Ruthenamonophosphinocarboranes are also active in the hydrogenation of 1-hexene, with a higher selectivity that the respective rhodacarboranes. On the other hand, [Rh(7-PPh_2-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (R′ = H, Me) catalyze the hydrogenation of methacycline to doxycycline with high yield (ca. 100%) and very high diastereoselectivity, ruthenacarboranes are not active. All these complexes are recoverable after completion of the catalytic reaction. These *exo-nido* rhoda and ruthenacarboranes displayed a very low activity in the hydrogenation of internal alkenes, however, the *closo* species [*closo*-3-(C_8H_{13})-1-SR-2-R′-3,2,1-$RhC_2B_9H_9$] (R = Ph; R′ = Me, Ph) obtained from [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)] were very efficient catalysts in the hydrogenation of cyclohexene exhibiting higher activity than the parent *exo-nido* isomers. In addition to hydrogenation, *exo-nido* rhoda and ruthenamonothio and monophosphinocarboranes have also been tested as catalyst precursors in the insertion of carbenes to C=C and O–H bonds. The rhodamonophosphinocarboranes exhibited a high activity and similar stereoselectivity for the cyclopropanation of olefines (80–90%) and represent the first example of Rh(I) cyclopropanation catalysts. Furthermore, ruthenacarboranes are excellent cyclopropanation catalysts for activated olefins such as styrene and their derivatives while the cyclopropane yields were lower for cyclic olefins and terminal linear monoolefines

Keywords: Metallacarboranes; Carboranes; Catalysis; Cyclopropanation; Hydrogenation; Isomerization

1. Introduction

The discovery that metallic complexes could be used as catalyst precursors in homogeneous hydrogenation, isomerization, hydrosilylation and hydroformylation re-

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actions permitted a great development of organometallic and coordination chemistry [1]. Many metallic compounds, especially transition metal complexes, have been used in catalytic reactions to synthesize organic compounds. Catalysis is very relevant to obtain optically active compounds of interest to industrial chemistry [2]. As a consequence certain types of industries such as pharmaceutical, alimentary, essences, and others have motivated the search for catalysts to produce chiral products [3].

Nevertheless, in spite of the high number of known catalytic systems, the use of metallacarboranes as catalyst precursors has been very limited until now [4]. The use of rhodacarboranes as homogeneous catalysts for the hydrogenation and isomerization of alkenes in mild conditions of pressure and temperature was first reported by Hawthorne and co-workers [5]. Of great relevance was the observation that the 18-electron Rh(III) *closo* complexes [*closo*-3,3-$(PPh_3)_2$-3-H-3,2,1-Rh–$C_2B_9H_{10}$] were in equilibrium with the *exo-nido* 16-electron Rh(I) tautomer which was the active species in the catalytic reaction [6,7]. In the *exo-nido* species the $[Rh(PPh_3)_2]^+$ moiety is bonded to the carborane cluster cage through a pair of B–H–Rh three center, two electron bonds. The tautomeric equilibrium is based in the oxidative addition of $[Rh(PPh_3)_3]^+$ to the B–H–B of the *nido* cluster open face and in its reductive elimination. Stabilization of the *exo-nido* tautomer was feasible when the cluster carbons contained bulky alkyl or aryl substituents [8].

The formation of non-active *closo*-rhodacarborane tautomers and the involvement in the catalytic cycle of B–H–Rh^I species bonded to the less active 'lower belt' of the carborane framework have been two of the more common explanations to account for the low activity of some of the catalysts tested [7c]. As an example of possible practical use, metallacarboranes based on cyclodienyl-containing *closo*-rhodacarboranes were found to be exceptionally effective for the stereoselective hydrogenation of methacycline to doxycycline [9]. However, Rh and Ru metallacarboranes have been applied also to other uses besides hydrogenation, e.g. for the control of carbene and the coupling of aldehydes [10]. Other catalytic applications with rhodacarboranes include hydrosilylation of alkenes [11], alkynes and cyclohexanone [12]. The *closo*-rhodacarborane [*closo*-3,3-$(PPh_3)_2$-3-H-3,2,1-Rh–$C_2B_9H_{10}$] has also been used as catalyst precursors in the hydrogenolysis and hydrosilanolysis of alkenyl acetates [7c,13]. In these examples the existence of the *closo*/*exo-nido* tautomerism to form the *exo-nido* active species appears to be essential. However, in the hydrosilanolysis reaction, when the forced *exo-nido* complex [*exo-nido*-$(PPh_3)_2$Rh-7,8-μ-$(CH_2)_3$-7,8-$C_2B_9H_{10}$] was used as catalyst precursor, a lower catalytic activity was observed.

Thus, it is not always obvious whether a *closo* or a *exo-nido* species is better, for instance *closo* and *exo-nido* ruthenacarboranes have been studied as catalyst precursors in the cyclopropanation of olefins with ethyl diazoacetate, and no great differences in their activities have been observed [14]. This may be accounted for by the coexistence of both tautomers in the mechanism.

In this introduction only rhoda and ruthenacarboranes as catalyst precursors have been included, since these are the only transition metals discussed later, but this does not imply that other metallacarboranes exist that also have adequate catalytic activity.

2. The way to forced and fixed *exo-nido* metallacarboranes

As a result of the work by Hawthorne's group, three factors have been claimed to be relevant for the catalytic hydrogenation by metallacarboranes: B–H coordination to metal, *exo-nido* metal disposition and the nature of the metal. In the course of our investigations on the potential of metallacarboranes as catalytic precursors, efforts have been made to propitiate the *exo-nido* tautomer versus the *closo* form. In some cases this has been successfully achieved by adequate bulky substituents on the cluster carbon atoms [8]. On the other hand, *exo-nido* bonding to the cluster was far from producing a single isomer since several possible alternatives to produce B–H–M bonds were possible [15]. Some of the possible isomers were close in energy and the 'real image' could be better described as the metal fluctuating from one B–H to another. Besides, it seems proven that open face B–H are more prone to participate in catalysis than second belt B–H [7a]. This prompted us to assemble all the good properties *exo-nido* metallacarboranes have while diminishing the less desirable aspects, such as metal fluctuation and *exo-nido* to *closo* tautomerization.

We had observed that 7,8-dithioether derivatives of 7,8-dicarba-*nido*-undecaborate had shown an unexpected tendency to metal coordination that could not be derived from their dithioether chelating nature [16]. This was the first indication of the indirect participation of the cluster in bonding. The phenomenon can be interpreted as the consequence of dissipation of electron density from the cage to the sulfurs bonded to the cluster carbon atoms. The two thioethers in these ligands were bonded to the metal in a chelating fashion. If the metal presented square-planar stereochemistry such as Rh(I) or Pd(II), this did not leave any site for B–H interaction [17]. First observation of B–H–M bonds in this set of ligands took place when octahedral Ru(II) complexes were formed, one of the first examples being [RuCl(7,8-μ-$S(CH_2CH_2)$)S-7,8-$C_2B_9H_{10}$)$(PPh_3)_2$] and [RuCl(7,8-μ-SCH_2S-7,8-$C_2B_9H_{10}$)$(PPh_3)_2$] where a B(3)–H–Ru had been generated [18].

With the aim of forcing B–H–Rh and B–H–Ru interactions, while avoiding the *exo-nido* to *closo* tautomerism, the monothioether [7-SR-8-R′-7,8-$C_2B_9H_{10}$]$^-$ anionic ligands were generated. It was hypothesized that a strong –S–Rh bond would be formed. Additionally, and considering the bulky nature of the cluster, the metal would force the participation of a neighbor B–H in coordination. This was not unrealistic since the number of B–H–M examples with icosahedral clusters and anionic borates is very high [19]. Thus, the participation of B(11)–H and/or B(2)–H in the anionic cluster to form B(11)–H–M and/or B(2)–H–M had a sound basis.

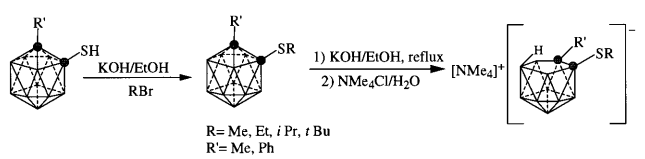
By forming the –S–M bond and considering that the B–H–M could be sufficiently stable, it was expected that the *exo-nido* to *closo* tautomerism would not take place or would be quenched. Moreover, if the similarity of cyclopentadienide anion to the C_2B_3 open face of the [$C_2B_9H_{10}$]$^-$ moiety is considered, which implies that the cluster negative charge is mostly located in the open face, it was expected that the B–H–Rh bond would take place preferentially with B–H on the C_2B_3 face, instead of B–H on the second belt of the [$C_2B_9H_{10}$]$^-$ cluster.

Considering these points, a set of monosubstituted thioether and phosphine derivatives of the [7,8-$C_2B_9H_{12}$]$^-$ fragment were synthesized.

2.1. From hypothesis to reality

2.1.1. Ligands

The reaction leading to monothioether anionic ligands is not complicated and is illustrated in Eq. (1) [20]. The S-aryl carborane ligands require the reaction of the lithiated salt with the appropriate disulfide to form the *closo*-monothiocarborane [21]. The deboronation reaction following the usual procedure works well and the *nido* species is obtained without alteration of the C–SR bond [22]. The first steps in the synthesis of monophosphines are similar to the monothioether, however precautions have to be taken to preserve the cluster C–P bond during the deboronation process to produce the anionic species. Details have been reported elsewhere [23]. More laborious is the preparation of [7-SR-7,8-$C_2B_9H_{11}$]$^-$ anionic ligands [24].



(1)

2.1.2. Complexes

These have usually been obtained in ethanol by reaction of the tetramethylammonium or cesium salts of the appropriate ligands with halocomplexes of Rh(I) and Ru(II) incorporating bulky or labile ancillary ligands. The existence of ionizable protons in the solvent (R–OH) avoided the formation of the tautomeric *closo* species. More specific details can be found in the literature for *exo*-monothiocarboranes and *exo*-monophosphinocarboranes [25–28]. The structural characterization has demonstrated that they are obtained only in the *exo-nido* form and that the cluster contributes to coordination to metal via the S or P atoms and by B(11)–H for square-planar Rh(I). When an extra coordinating group is required, as is the case for octahedral Ru(II), the cluster facilitates a second B–H bond which for geometrical reasons corresponds to B(2)–H.

The geometrical resemblance between the *exo-nido* rhodacarboranes with no external coordinating elements and those containing electron-rich substituents (S or P), was a good indication that they would be adequate for application as catalyst precursors in homogeneous catalysis. The first tests were concentrated on the well known hydrogenation reaction.

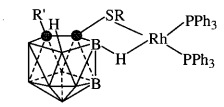
3. Catalytic reactions

3.1. Catalytic hydrogenation of alkenes

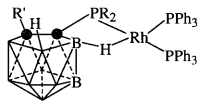
As mentioned, studies on metallacarboranes in catalysis had been done mostly on the hydrogenation reaction. As a consequence this appeared to be the best alternative to check the consistency of our opinion on the feasibility of these complexes as catalyst precursors.

As a matter of comparison families of rhoda- and ruthenacarborane complexes containing *nido*-monothio and *nido*-monophosphino clusters were studied. Eventually, complexes with *nido*-diphosphinocarborane clusters were also compared. Complexes of formulae [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (**1**–**3**), [Rh(7-PR_2-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (**4**–**7**), [Rh(7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$)(cod)] (**8**) [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)] (**9**, **10**), [*closo*-3-(C_8H_{13})-1-SR-2-R-3,2,1-Rh$C_2B_9H_9$] (**11**, **12**), [RuX(7-PR_2-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (**13**–**17**) and [RuCl(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (**18**–**20**) have been tested as hydrogenation catalyst precursors. These compounds are represented in Figs. 1 and 2.

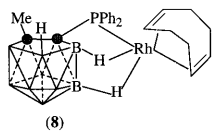
With the purpose of comparing the role of P versus S on the catalytic hydrogenation reaction, geometrically and coordinatively similar [7,8-$C_2B_9H_{12}$]$^-$ ligand derivatives were utilized. Thus, the two families of rhodacarboranes [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] and [Rh(7-PR_2-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (Fig. 1) were used. These have shown noticeable differences in the catalytic hydrogenation of 1-hexene. While the monothiorhodacarborane complexes are active catalysts at $T = 25$°C, leading to a high *n*-hexane yield, the



Compound	R'	R
(1)	Me	Ph
(2)	Me	Et
(3)	Ph	Ph



Compound	R'	R
(4)	H	Ph
(5)	Me	Ph
(6)	Me	Et
(7)	Me	^{i}Pr



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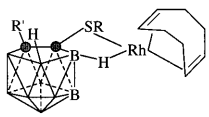
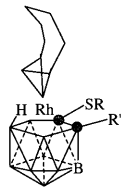
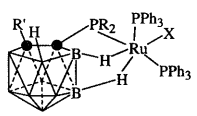


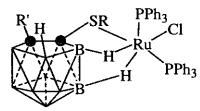


Compound	R	R'	Compound	R	R'
(9)	Ph	Me	(11)	Ph	Ph
(10)	Et	Me	(12)	Ph	Me

Fig. 1. Rhodacarboranes used as catalyst precursors.



Compound	R'	R	X
(13)	H	Ph	Cl
(14)	Me	Ph	Cl
(15)	H	Ph	H
(16)	Me	Ph	H
(17)	Ph	Ph	H



Compound	R'	R
(18)	Me	Ph
(19)	Ph	Ph
(20)	Me	Et

Fig. 2. Ruthenacarboranes used as catalyst precursors.

Table 1
Percentage conversion of 1-hexene to hexane and 2-hexenes after 1 h of reaction [a]

Complex	T (°C)	Hexane (%)	2-Hexenes (%)
1	25	98	2.0
4	25	12	0.7
5	25	6	0.3
1	66	85	11
4	66	90	9.3
5	66	61	20

[a] Experimental conditions: [1-hexene] = 3.9 M, [catalyst] = 5.21×10^{-4} M, $P = 45$ bar, THF.

monophosphino derivatives require higher pressures and temperatures. However, no great differences were found in activity and selectivity of both rhodacarboranes families at high temperature ($T = 66$°C). At this temperature, the ratio of alkene isomerization to hydrogenation has increased for both of them. Table 1 shows a few selected examples [25b].

Taking into account the high activity of monothiorhodacarboranes at low temperature, other experiments were realized under mild conditions ($P = 1$ atm) using the [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] family and the results were compared with Wilkinson's catalyst [RhCl(PPh_3)$_3$]. Complex [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (**1**) exhibited a much higher conversion to hexane than the rest, being ca. 8 times higher than Wilkinson's catalyst [25a]. It was also demonstrated that the catalytic activity was inhibited by addition of PPh_3. This fact suggests that reversible dissociation of PPh_3 is an important step preceding the activation of hydrogen in the catalytic cycle.

The need for B–H–Rh bonds was evidenced by studying rhodacarboranes containing bisdiphenylphosphine ligands [7,8-(PR_2)$_2$-7,8-$C_2B_9H_{10}$]$^-$. Compounds such as [Rh(7,8-(PR_2)$_2$-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$], [Rh(7,8-(PR_2)$_2$-7,8-$C_2B_9H_{10}$)(PMe_2Ph)$_2$] and [Rh(7,8-(PR_2)$_2$-7,8-$C_2B_9H_{10}$)(cod)], were not active catalysts with the same ratio substrate/catalyst (ca. 8000) used with monothio and monophosphinocarborane derivatives. At the same temperature ($T = 66$°C) and pressure ($P = 45$ bar), it was necessary to use a lower ratio substrate/catalyst (ca. 700) to obtain a relative catalytic activity in the hydrogenation of 1-hexene [29]. Under these conditions, only Rh(I) complexes containing cyclooctadiene (cod) as ancillary ligand exhibited a high activity (99% of hydrogenation to 1-hexane), while the same precursor with more basic ancillary ligands such as PMe_2Ph displayed a very low activity.

Ruthenacarboranes containing monothio and monophosphinocarboranes (Fig. 2) have also been tested in the hydrogenation of 1-hexene. All [RuX(7-PR_2-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] have been found to be active in the hydrogenation of 1-hexene with a similar selectivity (Table 2). The precursor [RuH(7-PPh_2-7,8-$C_2B_9H_{11}$)(PPh_3)$_2$] (**15**) is the most active ruthenium catalyst, with low alkene isomerization (5%), showing a percentage of conversion at 66°C and $P = 45$ bar similar to [Rh(7-PPh_2-7,8-$C_2B_9H_{11}$)(PPh_3)$_2$] (**4**). Both contain the same *nido*-carboranyl moiety with no substituents in the second carbon cluster atom. [RuCl(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (**18**) was the only ruthenamonothiocarborane studied and exhibited much lower activity at 1 bar than the corresponding rhodacarborane [26b].

Both rhoda and ruthenacarboranes have been shown to be recoverable upon completion of the catalytic reactions, as shown by $^1H\{^{11}B\}$, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$-

Table 2
Percentage conversion of 1-hexene to hexane and 2-hexenes using ruthenacarboranes [a]

Compound	Hexane (%)	2-Hexenes (%)
13	73	14
14	30	3
15	82	5
16	70	5
17	28	4

[a] Experimental conditions: $T = 66$ °C, $P = 45$ bar, [1-hexene] = 3.9 M, [catalyst] = 5.21×10^{-4} M, $t = 1$ h, toluene.

NMR spectroscopy. They did not exhibit any sign of deactivation and eventually converted all the 1-hexene into hexane and 2-hexenes.

Taking into account the exceptional activity (close to 95%) of some metallacarboranes [9] in the stereoselective hydrogenation reaction of methacycline into doxycycline, a potent tetracycline antibiotic extensively used in chemotherapy, several rhoda and ruthenacarborane derivatives of monophosphinocarboranes were used as catalytic precursors for this reaction [30]. The hydrogenation of methacycline may lead to the formation of two diastereomers: doxycycline and *epi*-doxycycline. Under different conditions to those described in the literature ([methacycline] = 2.2×10^{-2} M, [catalyst] = 8.7×10^{-4} M, $T = 75$°C and $P = 45$ atm, t = 7 h), precursors **4** and **5** were very active in the hydrogenation of methacycline. They exhibited conversions of 85 and 99.7% yields respectively with very high diastereoselectivity, obtaining the doxycycline as a unique product. No *epi*-doxycycline was observed in any case [25b]. On the contrary, the Ru(II) systems **13**, **14**, **15** and **16** presented a very low activity, and only 2% conversion was obtained.

3.1.1. The surprise of the closo-rhodacarboranes

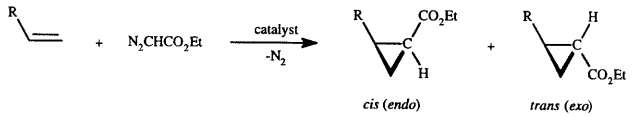
The *exo-nido* rhodacarborane complexes described above and others reported earlier exhibit relatively low activities in the hydrogenation of internal alkenes (e.g. cyclohexene) [5–7]. Although this feature can be an advantage in selective reduction of terminal versus internal olefins, efforts were made to expand the scope of these catalysts. A useful strategy to obtain enhanced hydrogenation rates consists of replacing the ancillary phosphine ligands by alkene ligands [31]. To this end, complexes of formula [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)] (Fig. 1) were developed via acid promoted removal of the acetylacetonate ligand of [Rh(acac)(cod)] followed by reaction with the appropriate *nido*-monothiocarborane ligand [32]. Structural characterization of [Rh(7-SPh-8-Ph-7,8-$C_2B_9H_{10}$)(cod)] revealed that the $[Rh(cod)]^+$ fragment is bonded to the carborane cage through S–Rh and B(11)–H–Rh bonds. Moreover, although these complexes are fluxional, dynamic NMR studies suggest that this stereochemistry is essentially retained in solution. Therefore, replacement of two PPh_3 ligands in [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] by a cod ligand does not significantly alter the structure of the resulting complexes. This observation supports our initial hypothesis on the ability of a sole thioether group to fix the interaction between the carborane cluster and the metal fragment.

A remarkable characteristic of the new cyclooctadienerhodacarborane complexes described above is the coexistence of B–H–Rh and Rh–alkene bonds within the same molecule. This unique feature imparts a new reactivity to the system. For instance, unlike their diphosphine counterparts, the *exo-nido*-cyclooctadiene complexes rearrange in solution to give the corresponding *closo* complexes of formula [*closo*-3-(C_8H_{13})-1-SR-2-R-3,2,1-$RhC_2B_9H_9$] (Fig. 1). Although this isomerization process can be formally viewed as the oxidative addition of the open face bridging B–H–B hydrogen to Rh followed by hydride transfer to olefin, deuterium labeling studies have provided evidence that the rearrangement does not proceed through this mechanism. Rather, the process appears to involve rhodium mediated transfer of terminal B(11)–H hydrogen to olefin. Since this is the proposed key step in the hydrogenation reaction catalyzed by rhodacarboranes, these complexes arise as excellent models to study different mechanistic aspects of rhodacarborane catalyzed reaction.

Both *exo-nido* and *closo* types of complexes were tested in catalytic hydrogenation of the internal olefin cyclohexene. It was previously observed that addition of one equivalent of PPh_3 inhibits *exo-nido* to *closo* isomerization during the hydrogenation reaction [32]. This feature was advantageously used to study the catalytic activity of *exo-nido* complexes without interference of *closo* isomers. Contrary to what was expected, only small differences in activity were observed between diphosphine complexes [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$)] and the monophosphine complex generated in situ from [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)] and one equivalent of PPh_3. Therefore, elimination of a phosphine ligand from the coordination sphere of the metal in monothiocarborane complexes does not result in an enhancement of activity in the hydrogenation of internal alkenes. Unexpectedly, the corresponding *closo*-cyclooctenyl complexes (**11**, **12**) showed remarkable activities compared to their *exo-nido* isomers. Contrary to the observation with *exo-nido* species, the addition of one equivalent of PPh_3 resulted in an additional activity increase. These results strongly suggest that the two systems (*exo-nido* and *closo*) operate by different mechanisms and open up new possibilities which can expand the scope of this new class of catalysts.

3.2. Carbene reactions

As mentioned, in our effort to learn about the possibilities of metallacarboranes, these have been tested in catalytic reactions other than hydrogenation. Cyclopropanation is currently an area of significant research activity [33]. To date, direct transition-metal-catalyzed carbene transfer from a diazo compound to an olefin remains the most straightforward route to cyclopropanes (Eq. (2)). Up to now, all efficient rhodium-based cyclopropanation catalysts possess the rigid dirhodium(II) lantern framework, e.g. as in dirhodium(II) tetracarboxylates and the related dirhodium(II) carboxamidates. Other rhodium complexes (e.g. $Rh_6(CO)_{16}$, $Rh_2(BF_4)_4$, and rhodium(III) porphyrins) have also been introduced as cyclopropanation catalysts but none of them has been demonstrated to be superior to rhodium carboxylates and carboxamidates. To the best of our knowledge, attempts with rhodium(I) complexes have never been successful. Owing to the exceptional activity of rhodacarboranes in hydrogenation reactions, and their ability to liberate a phosphine ligand, it was expected they could be potential Rh(I) catalysts for olefin cyclopropanation. First experiments were concluded with complexes **4**, **5** and **8** containing monophosphinocarboranes (Table 3) [34].



(2)

In the presence of styrene, which is generally the model alkene for comparative evaluations of catalyst activity, complexes **4**, **5** and **8** proved to be very efficient (90% yield). This set of complexes was investigated for cyclopropanation of other olefins. Only a few are reported in Table 3. The yields usually ranged between 85 and 95%. As seen from Table 3, complexes **4**, **5** and **8** gave virtually identical yields and stereoselectivities for the cyclopropanation of four representative olefins, regardless of the ligand pattern of the complex. Activated olefins were more reactive than non-activated ones and, in competitive cyclopropanation reactions between olefins performed in the presence of complex **4**, styrene was shown to be 10 times more reactive than cyclooctene and 1-octene. *n*-Butyl vinyl ether is also an activated olefin and it was cyclopropanated by ethyl diazoacetate with yields ranging from 80 to 90%, but in a competitive experiment in the presence of complex **4**, *n*-butyl vinyl ether was six times less reactive than styrene. With less reactive olefins, diethyl maleate and diethyl fumarate were the predominant by-products. In addition, with styrene, homologation products resulting formally from the insertion on the carbene into a vinylic C–H bond have been detected in low amounts (1–5%).

Ruthenium complexes have recently been introduced as cyclopropanation catalysts and, again, none of them has been demonstrated to be really superior to rhodium-based catalysts: most of the ruthenium catalysts often lack stereoselectivity [14,35,36]. This justifies the search for alternative catalytic systems. With this in mind, ruthenacarboranes **15** and **16** have been tested as catalysts for cyclopropanation (Table 4). It appeared that complexes **15** and **16** were excellent cyclopropanation catalysts for activated olefins such as styrene and styrene derivatives. Cyclopropane yields were however lower with cyclic olefins and with terminal linear monoolefins than with activated double bonds.

Carbene addition occurred with *trans* (*exo*) diastereoselectivity, consistently favoring the most thermodynamically stable isomer. With α-methylstyrene and cyclooctene, however, the *cis*/*trans* and *endo*/*exo* ratios were close to unity. The effects of the size of the alkene substituents were studied using various 4-X-styrene derivatives. Increasing the steric bulkiness of X led to a significant decrease in the *cis*/*trans* ratio, as is

Table 3
Cyclopropanation of olefins with ethyl diazoacetate [a]

Compound	Cyclopropanation (%) [b] (*cis*/*trans* or *endo*/*exo* ratio)			
	Styrene	4-Methyl-styrene	4-Chloro-styrene	Cyclooctene
4	91 (0.88)	90 (0.68)	89 (0.51)	86 (0.69)
5	92 (0.91)	93 (0.71)	92 (0.60)	85 (0.67)
8	91 (0.86)	94 (0.70)	87 (0.52)	88 (0.72)

[a] Experimental conditions: $T = 100$°C, olefin = 20 mmol, catalyst = 0.0075 mmol, ethyl diazoacetate = 1 mmol diluted by the olefin to 1 ml, $t = 4$ h.

[b] Based on ethyl diazoacetate and determined by GLC analysis.

Table 4
Cyclopropanation of olefins with ethyl diazoacetate [a]

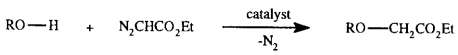
Olefin	Cyclopropanation (%) [b] (*cis*/*trans* or *endo*/*exo* ratio)	
	15	**16**
Styrene (60°C)	74 (0.65)	78 (0.62)
Styrene	97 (0.63)	96 (0.64)
4-Methylstyrene	96 (0.52)	96 (0.54)
4-*t*-Butylstyrene	93 (0.50)	91 (0.48)
4-Methoxystyrene	90 (0.61)	89 (0.56)
4-Chlorostyrene	94 (0.50)	93 (0.48)
α-Methylstyrene	98 (0.95)	97 (1.02)
Cyclooctene	51 (0.86)	65 (1.08)
1-Octene	61 (0.71)	58 (0.62)
1-Dodecene	59 (0.73)	61 (0.73)

[a] Experimental conditions: $T = 100$°C, olefin = 20 mmol, catalyst = 0.0075 mmol, ethyl diazoacetate = 1 mmol diluted by the olefin to 1 ml, $t = 4$ h.

[b] Based on ethyl diazoacetate and determined by GLC analysis.

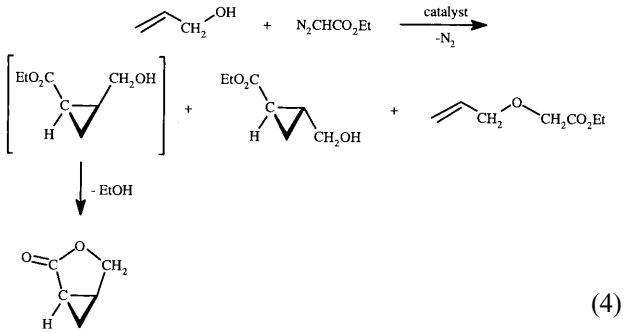
evident from Table 4 comparing the *cis*/*trans* ratio for cyclopropanation of styrene, 4-methylstyrene, and 4-*t*-butylstyrene. This could be improved further by using bulkier diazo compounds, such as *t*-butyl diazoacetate and 2,6-di-*t*-butyl-4-methylphenyl diazoacetate instead of methyl or ethyl diazoacetate [37].

It is generally agreed that olefin cyclopropanation occurs via electrophilic metal-carbene intermediates. This was confirmed by competitive cyclopropanation reactions between olefins (electron-rich olefins reacted faster) as well as by insertion of carbethoxycarbene into the O–H bond of alcohols (Eq. (3)).



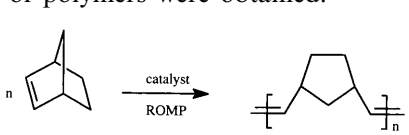
(3)

Ruthenacarboranes **15** and **16** were shown to catalyze the insertion of carbethoxycarbene into the O–H bond of isopropanol, 1-butanol, and 2-butanol with yields reaching 85% [33]. Allyl alcohol was also chosen as a starting substrate because it provides an interesting model for chemocontrol: upon addition of ethyl diazoacetate both O–H insertion and olefin cyclopropanation may occur (Eq. (4)).



(4)

Two cyclopropanes result from the reaction: the expected *trans* isomer and the γ-lactone resulting from the intramolecular transesterification of the *cis* isomer. With all rhoda and ruthenacarboranes tested so far, insertion predominated over cycloaddition. Also noteworthy was the very low cyclopropane yield obtained with norbornene (a highly strained cycloolefin) in the presence of rhodacarboranes. With this substrate, 1,3-dipolar addition of ethyl diazoacetate was the preferred pathway. In the presence of ruthenacarboranes, no cyclopropanation of norbornene took place [33]. Instead, ethyl diazoacetate and trimethylsilyldiazomethane initiated the ring-opening metathesis polymerization (ROMP) of the substrate with moderate yields (up to 42%) (Eq. (5)) [38]. With a low-strain cyclic olefin such as cyclooctene (Table 4), only minute amounts of polymers were obtained.



(5)

According to the mechanism of olefin metathesis, this outcome reveals the presence of two *cis* vacancies on the metal center for coordinating both the carbene and the olefin, giving rise to the key intermediate of the process: a ruthenacyclobutane. This implies therefore the disengagement of two ligands from the coordination sphere of the ruthenium complex. In these complexes, the B–H–Ru agostic bonds are believed to be quite stable. On the other hand, in [RuCl(7-PPh_2-8-CH_3-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (**14**), the phosphine ligands have been shown to be labile and, depending on the incoming ligand, either PPh_3 *trans* to the *exo*-cluster PPh_2, or PPh_3 *trans* to a BH participating in a B–H–Ru bond is substituted. Which of the triphenylphosphine ligands is more labile upon addition of a diazo compound, and what should be the influence of the carbene moiety on the relative lability of the remaining ligands are questions to which answers are far from being straightforward. A confirmation of this is provided by both the GPC trace and the polydispersity index (M_w/M_n) of the polynorbornenes, which indicate that at least two active catalytic species are operative during the ring-opening metathesis polymerization of norbornene. A further indication for the formation of a metallacyclobutane intermediate and, hence, for the presence of two *cis* vacancies on the metal center is provided by the observation of homologation products, which were formed in low amount (1–5%) upon addition of ethyl diazoacetate to 4-X-styrenes [39].

We cannot exclude either that, at temperatures used in carbene chemistry (60–100°C), some of the B–H–Ru agostic bonds would become more fragile, so that they could be split in the presence of diazo compounds.

4. Conclusion

To conclude, we have proven that forced *exo-nido* rhoda and ruthenacarboranes are active catalysts in hydrogenation and that the enhanced activity can be attributed to quenched *exo-nido* to *closo* tautomerism. These *exo-nido* species are good for hydrogenating terminal alkenes but poor for internal alkenes. Derived *closo* species having an η^3-allyl capped group have been shown to be efficient for internal alkenes. In addition to hydrogenation, forced *exo-nido* rhoda and ruthenacarboranes have been efficient in carbene participating catalysis and are the first representative examples of Rh(I) cyclopropanation catalysts. Carbenes have been added to C=C and O–H bonds with good yields. As a further effort to explore the possibilities of these forced *exo-nido* rhoda and ruthenacarboranes, they are being applied to the Kharasch reaction. Preliminary results indicate the feasibility of these complexes.

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