

Metallacarboranes containing *exo*-thio and *exo*-phosphinocarborane ligands. Their application in catalysis

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Abstract

Metallacarboranes containing *exo*-thioether or *exo*-phosphinocarboranes were synthesized and characterized. These complexes were obtained from the reaction of tetramethylammonium or cesium salt of the *nido* ligand with Rh(I), Pd(II) or Ru(II) complexes incorporating ancillary ligands. Although two molecular structures were possible, the *closo* and the *exo-nido*, generally only the *exo-nido* tautomer was formed. The cluster was coordinated with 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 catalyzed the hydrogenation of terminal alkenes in very good yield but were not active in the hydrogenation of internal alkenes. Ruthenamonophosphinocarboranes were also active in the hydrogenation of the 1-hexene, with a higher selectivity than the respective rhodacarboranes. On the other hand, while [Rh(7-PPh₂-8-R'-7,8-C₂B₉H₁₀)(PPh₃)₂] (R' = H, Me) catalyzed the hydrogenation of methacycline to doxycycline with high yield (ca. 100%) and very high diastereoselectivity (> 99%), ruthenacarboranes were not active. The *closo* species [*closo*-3-(C₈H₁₃)-1-SR-2-R'-3,2,1-RhC₂B₉H₉] (R = Ph; R' = Me, Ph) obtained from *exo-nido*-[Rh(7-SR-8-R'-7,8-C₂B₉H₁₀)(cod)] were very efficient catalysts in the hydrogenation of cyclohexene exhibiting higher activity than the parent *exo-nido* isomers. All these complexes were recoverable after completion of the catalytic reaction. In addition to hydrogenation, *exo-nido* rhoda and ruthenamonothio and monophosphinocarboranes were also tested as catalyst precursors in the insertion of carbenes into C=C and O-H bonds.

Key words: Metallacarboranes, carboranes, catalysis, cyclopropanation, hydrogenation, isomerization.

Resum

S'han sintetitzat i caracteritzat nous metal·locarborans que contenen *exo*-tioèter o *exo*-fosfinocarborans com a lligand. Els complexos s'han obtingut fent reaccionar la sal de tetrametilamoni o de cesi del lligand *nido* corresponent amb complexos de Rh(I), Pd(II) ó Ru(II) amb altres lligands. Tot i que els nous complexos poden tenir dues estructures, la *closo* i la *exo-nido*, generalment només s'ha format el tautòmer *exo-nido*. El clúster es coordina amb el metall mitjançant l'àtom de sofre o de fòsfor i, depenent del metall, amb un o dos enllaços B-H→M. Aquests *exo-nido* rodi i rutenicarborans han catalitzat, amb molt bon rendiment, la reacció d'hidrogenació d'alquens terminals, però han estat poc actius en la d'alquens interns. Els rutenicarborans també han mostrat activitat catalítica en la hidrogenació de l'1-hexè, i una millor selectivitat que els corresponents complexos de rodi. Cal destacar que els complexos [Rh(7-PPh₂-8-R'-7,8-C₂B₉H₁₀)(PPh₃)₂] (R' = H, Me) catalitzen la reacció d'hidrogenació de la metaciclina a la doxiciclina amb un rendiment pràcticament del 100 % i una diastereoselectivitat > 99 %. Els complexos *closo* [*closo*-3-(C₈H₁₃)-1-SR-2-R'-3,2,1-RhC₂B₉H₉] (R = Ph; R' = Me, Ph) que s'han obtingut a partir dels *exo-nido* [Rh(7-SR-8-R'-7,8-C₂B₉H₁₀)(cod)] han estat uns catalitzadors molt actius en la hidrogenació del ciclohexè i, fins i tot, més que els seus precursors *exo-nido*. Tots els complexos han estat recuperats després del procés catalític. A més a més de la hidrogenació, els complexos *exo-nido* de rodi i de ruteni s'han provat com a catalitzadors en la inserció de carbens a enllaços C = C i O-H.

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The discovery that metallic complexes could be used as catalyst precursors in homogeneous hydrogenation, isomerization, hydrosilylation and hydroformylation reactions made possible important developments in organometallic and coordination chemistry [1]. Many metallic compounds, espe-

cially transition metal complexes, have been used in catalytic reactions to synthesize organic compounds. Catalysis is relevant to the development of optically active compounds of interest to the industrial chemistry [2]. As a consequence certain types of industry such as the pharmaceutical, food and essences have motivated the search for catalysts to produce chiral products [3]. On the other hand, polyolefins are the fastest growing sector of the polymer industry [4]. Although it has been almost half a century since polyethylene's commercialization, polyolefins remain highly technology-driven [5]. Nevertheless, in spite of the high number of known catalytic systems, the use of metallocarboranes as catalyst precursors has been very limited until now [6]. 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 [7]. Of great relevance was the observation that the 18-electron Rh(III) *closo* complexes [*closo*-3,3-(PPh₃)₂-3-H-3,2,1-Rh-C₂B₉H₁₀] were in equilibrium with the *exo-nido* 16-electron Rh(I) tautomer which was the active species in the catalytic reaction [8,9]. In the *exo-nido* species the [Rh(PPh₃)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 on the oxidative addition of [Rh(PPh₃)₃]⁺ to the B-H-B of the *nido* cluster open face and on its reductive elimination. Stabilization of the *exo-nido* tautomer was feasible when the cluster carbon atoms contained bulky alkyl or aryl substituents [10]. 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 [9c]. As an example of possible practical use, metallocarboranes based on cyclodienyl-containing *closo*-rhodacarboranes were found to be exceptionally effective for the stereoselective hydrogenation of methacycline to doxycycline [11]. However, Rh and Ru metallocarboranes have also been applied to other uses besides hydrogenation, e.g. for the control of carbene and the coupling of aldehydes [12]. Other catalytic applications with rhodacarboranes include hydrosilylation

of alkenes [13], alkynes and cyclohexanone [14]. The *closo*-rhodacarborane [*closo*-3,3-(PPh₃)₂-3-H-3,2,1-Rh-C₂B₉H₁₀] has also been used as a catalyst precursor in the hydrogenolysis and hydrosilylation of alkenyl acetates [9c, 15]. 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 hydrosilylation reaction, when the forced *exo-nido* complex [*exo-nido*-(PPh₃)₂Rh-7,8-(μ-(CH₂)₃-7,8-C₂B₉H₁₀)] was used as catalyst precursor, a lower rate of catalytic activity was observed.

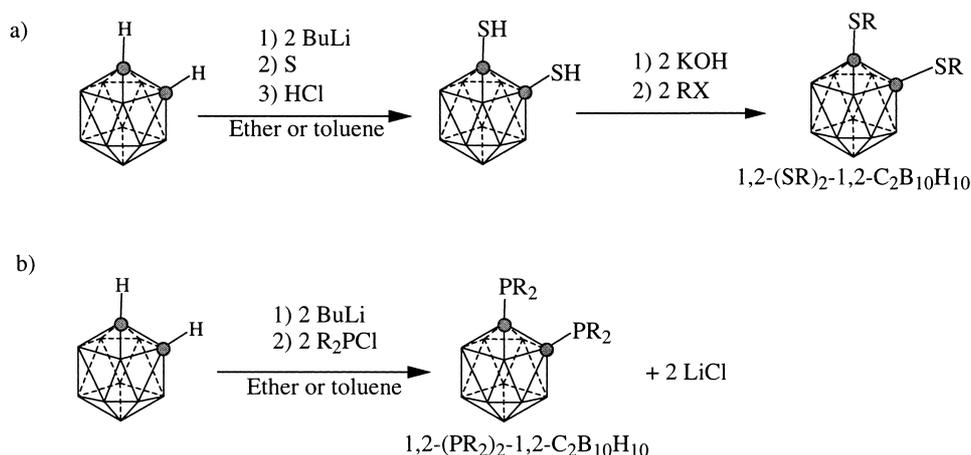
Thus, it is not always obvious whether a *closo* or a *exo-nido* species is better. For instance *closo* and *exo-nido* ruthenacarboranes have been studied as catalyst precursors in the cyclopropanation of olefins with ethyl diazoacetate, and no great differences in their activities have been observed [16]. This may be accounted for by the coexistence of both tautomers in the mechanism.

As a result of the work by Hawthorne's group, three factors have been claimed to be relevant to the catalytic hydrogenation by metallocarboranes: B-H coordination to metal, *exo-nido* metal disposition and the nature of the metal. 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 [17]. Some of the possible isomers were close in energy and the «real image» could be best 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 [9a]. In the course of our investigations on the potential of metallocarboranes as catalytic precursors, efforts have been made to propitiate the *exo-nido* tautomer vs the *closo* form and to diminish undesirable B-H fluctuations. Our goal was to find a way to forced and fixed *exo-nido*-metallocarboranes.

a) Designing the new disubstituted ligands

The starting compound used to prepare the ligands was the 1,2-dicarbaborane cluster, known as *o*-carborane. In this, carbon atom adjacency produces a positive charge on the carbons. This causes a mildly acidic hydrogen atom activity which makes it possible to prepare the *o*-carborane derivatives through reaction with *n*-butyllithium (Equation 1). Reac-

Equation 1



tion of the lithiocarborane with elemental sulfur leads mercapto-carborane lithium salt, and dithiol-*o*-carborane is obtained after protonation with HCl (Equation 1a) [18]. On the other hand, chlorophosphines react with lithiocarborane to form *exo*-diphosphinocarborane derivatives (Equation 1b).

The reaction of $[C_2B_9H_{10}S_2]^{2-}$ with XRX in ethanol under high dilution conditions yielded small macrocycles incorporating the carborane cage in the cycle (Equation 2). Crystal structures of $[1,2-(\mu-SCH_2(CH_2OCH_2)_2CH_2S)-1,2-C_2B_{10}H_{10}]$ [18d] and $[1,2-(P(iPr)_2)_2-1,2-C_2B_{10}H_{10}]$ have been reported [19].

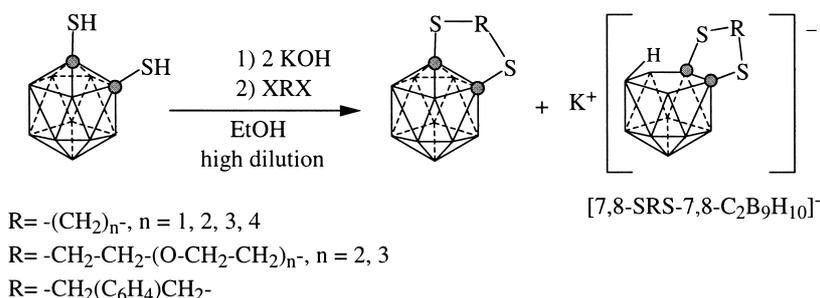
The reaction with certain dihalo organic compounds yielded two types of macrocycles, one having the carborane cage intact and the other having an icosahedron fragment from which one boron vertex had been removed (Equation 2). Reaction of *closo* dithioether-*o*-carborane derivatives with an ethoxide ion yielded a compound in which the base had attacked and removed one of the most positive boron atoms in the cage to give the 7,8-dithioether-7,8-dicarbano-*nido*-undecaborate anion (Equation 3). The boron-carbon framework of each « C_2B_9 » unit is proposed understood to be simply an icosahedron with one vertex removed. The extra hydrogen atom is considered to be located at the open face occupying the former boron atom position. The removal

of one B vertex from the neutral *closo* species to produce a *nido* system with a negative charge is known as partial degradation. The direct degradation of the *closo* dithioether and diphosphinocarborane derivatives, using the well established procedure[20] with KOH in ethanol, was successful for the dithioether derivatives but not for the diphosphine compounds. The $C_{cluster}-P$ bond in the *closo* species was very susceptible to degradation reaction conditions, producing $C_{cluster}-P$ cleavage and yielding the $[7,8-C_2B_9H_{10}]^-$ anion. Appropriate synthetic procedures to yield partial cluster degradation with $C_{cluster}-P$ bond retention by using toluene and a carborane-to-piperidine ratio of 1:50 or ethanol with a carborane-to-piperidine ratio of 1:10 have been described (Equation 4) [21]. The crystal structures of $[7,8-(\mu-SCH_2(CH_2OCH_2)_3CH_2)7,8-C_2B_9H_{10}]$ [18d] and $[7,8-(PPh_2)_2-7,8-C_2B_9H_{10}]$ have been reported [21].

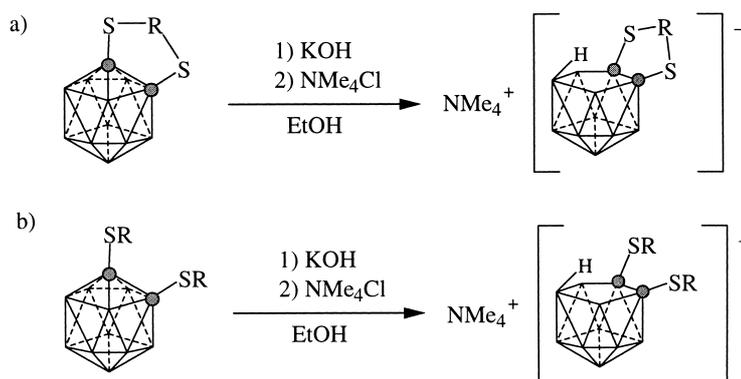
b) Reactivity of the new *exo* disubstituted ligands to transition metals

It had been observed that 7,8-dithioether-7,8-dicarbano-*nido*-undecaborate derivatives presented an unexpected tendency to coordination to metal that could not be attributed to their dithioether chelating nature [18d,e]. The exaltation of the ligand capacity has been attributed to the carborane

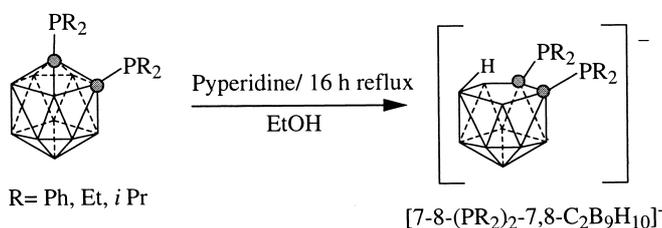
Equation 2



Equation 3



Equation 4



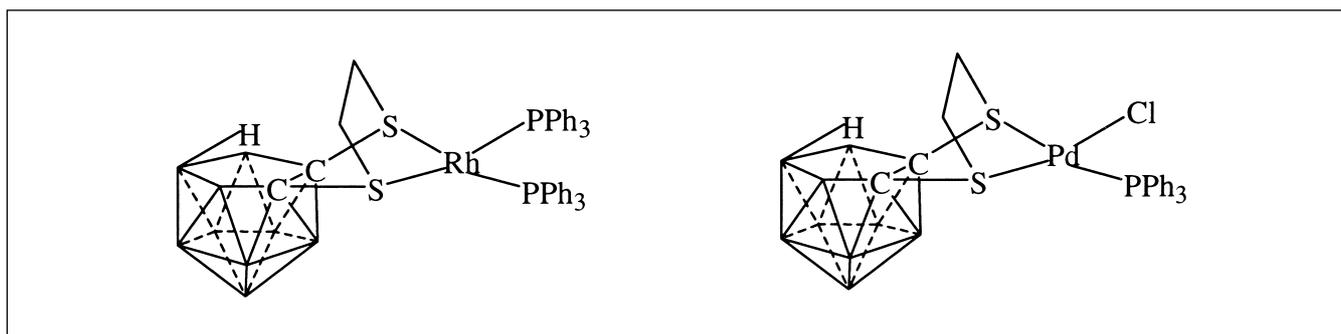


Figure 1. Structures of Pd and Rh complexes incorporating *nido*-dithioethercarborane ligands.

cage near the sulfur coordinating atoms. The phenomenon can be interpreted as the consequence of dissipation of electron density from the cage to the sulfur atom bonded to the cluster carbon atoms. The two thioether groups in these ligands bond the metal in a chelating fashion. The reaction of 7,8-dithioether-7,8-dicarba-*nido*-undecaborate(-1) derivatives with $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{PdCl}_2(\text{PPh}_3)_2]$ and $[\text{IrClCO}(\text{PPh}_3)_2]$ was carried out in ethanol [22,23,24], to yield complexes in which a partial or total substitution of the chloride atoms by the carborane ligands had taken place. Figure 1 schematically shows the structures of rhoda and pallada complexes containing *nido*-dithioethercarborane clusters. When the *nido*-diphosphinocarboranes react with $[\text{RhCl}(\text{cod})]_2$ and $[\text{PdCl}_2(\text{PPh}_3)_2]$ very similar compounds are obtained [25].

The *exo* disubstituted carborane clusters react with square-planar oriented metals such as Rh(I) or Pd(II), as bidentated ligands via the two sulfur or the two phosphorous atoms. As a consequence no site for B-H \rightarrow M interaction is left.

First observation of B-H \rightarrow M bonds in this set of ligands took place when octahedral Ru(II) complexes were formed. In this case, the ligand behaves as a tricoordinating ligand, and the three bonds are formed by the two sulfur atoms and one B-H vertex through the B-H \rightarrow Ru agostic interaction [26]. Its presence was first demonstrated by a resonance near -18 ppm observed in the ^1H NMR spectra, and was later corroborated by the crystallographic structures. The ^1H NMR spectra of a series of ruthenacarborane complexes evidence the existence of a modulation in the B(3)-H-Ru interaction depending on the external chain length. During our investigations on the coordination chemistry of small macrocyclic derivatives of *exo-nido*-dithiocarborane compounds we defined the ω angle as the dihedral angle between the S-

$\text{C}_{\text{cluster}}\text{-C}_{\text{cluster}}\text{-S}$ and S-M-S planes. There, a dependence was observed between the ω angle (Figure 2) and the exocluster chain length [27]. Shorter exocluster chain fragments (more strained) produce a smaller ω angle, and shorter B(3)-Ru distances, thus favoring the B(3)-H \rightarrow M interaction. Thus, it seemed possible that the use of short cluster chains could lead to the sought B(3)-H \rightarrow M interaction. Two of the first examples where such interactions were observed are in $[\text{RuCl}(\eta^7\text{-}7,8\text{-}\mu\text{-S}(\text{CH}_2\text{CH}_2)\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ [26] and $[\text{RuCl}(\eta^7\text{-}7,8\text{-}\mu\text{-SCH}_2\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ [27a] (Figure 3). It should be noticed that B(3) is the only boron atom in the *nido* cluster connected to both cluster carbon atoms.

Once the enhanced coordinative capacity of the *nido*-dithioethercarborane derivatives as compared to common organic thioethers was uncovered, steps began to be taken to explore the effect of incorporating S-aryl thioether groups in the « $[\eta^7\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ » fragment. Thus, the reaction of $[\eta^7\text{-}7,8\text{-}(\text{SPh})_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ with $[\text{RuCl}_2(\text{PPh}_3)_3]$ afforded two isomers of $[\text{RuCl}(\eta^7\text{-}7,8\text{-}(\text{SPh})_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ [28]. In both the metal presents an octahedral geometry, three of the positions being occupied by the carborane ligand through one S-Ru bond, and two B-H \rightarrow Ru agostic bonds. The boron atoms participating in these interactions are the B(11) at the open face and the B(2) at the lower belt. The unprecedented preference for two agostic B-H \rightarrow Ru bonds rather than a second S-Ru bond appears to be due to steric factors. However, a very recent study, provides new examples of the reaction of *nido*-diphosphinocarborane with $[\text{RuCl}_2(\text{PPh}_3)_3]$ in which the Ru(II) coordination sphere is fulfilled with the cluster behaving as a tricoordinating ligand, through a single P atom and two B-H \rightarrow Ru agostic bonds, as in the case of the *nido*-dithiophenylcarborane compounds [29].

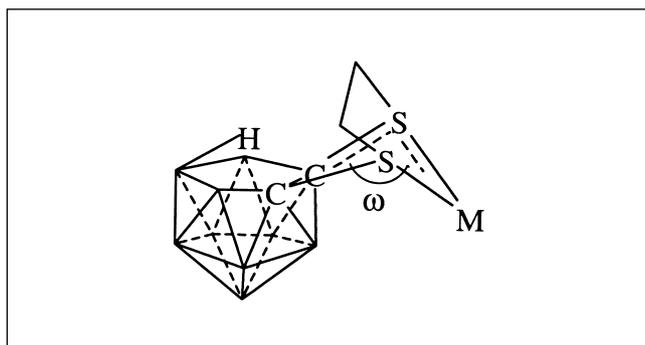


Figure 2. Graphical representation of the ω angle.

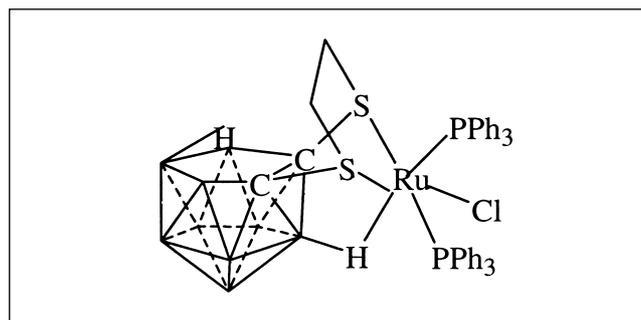


Figure 3. The B(3)-H \rightarrow Ru agostic bond in $[\text{RuCl}(\eta^7\text{-}7,8\text{-}\mu\text{-S}(\text{CH}_2\text{CH}_2)\text{S-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$.

c) Testing the new *exo*-dithioether and *exo*-diphosphinometallacarboranes as catalysts in the hydrogenation of alkenes

Studies on metallacarboranes in catalysis have been done mostly on hydrogenation reactions, so this appeared to be the best way to check the consistency of our opinions on the feasibility of these complexes as catalyst precursors.

With the purpose of comparing the role of P vs S in the catalytic hydrogenation reaction, geometrically and coordinatively similar $[7,8-C_2B_9H_{10}]^-$ ligand derivatives were utilized. 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 $[Rh(7,8-(PR_2)_2-7,8-C_2B_9H_{10})(cod)]$ (R = Ph), were not active catalysts in the hydrogenation of 1-hexene, with the substrate/catalyst ratio of 8000 at T = 66°C and P = 45 bar. However, when a lower ratio substrate/catalyst (ca. 700) was used, catalytic activity was observed only for the Rh(I) complex incorporating cyclooctadiene (cod). In this case, high activity (99% of 1-hexene hydrogenation to hexane) was observed, while the same precursor with PMe_2Ph ancillary ligands displayed very low activity [30]. The rhoda and ruthenadithioethercarboranes with phosphines as ancillary ligands were inactive. It is our opinion, that the chelating capacity of the dithioether or diphosphinocarboranes is too strong to be involved in catalysis. So, the only accessible site would be for the ancillary ligands. These ligands do not permit hydrogenation activity. However, when cod is present it is itself hydrogenated, liberating two metal *cis* positions ready for catalysis.

In these compounds the *exo-nido* to *closo* tautomerism would not take place or would be quenched. Moreover, taking into consideration the geometrical and electronic similarity of the cyclopentadienide anion to the C_2B_3 open face of the $[C_2B_9H_{10}]^-$ moiety, it was expected that the B-H→M bond would be different depending on whether the participating B-H was on the C_2B_3 face, or on a B-H on the second belt of the $[C_2B_9H_{10}]^-$ cluster, as is the B(3). The importance of the participating B-H vertex was demonstrated earlier when we discussed the catalytic ability of the dithioether and diphosphinocarborane Rh(I) and Ru(II) complexes. The Rh(I) com-

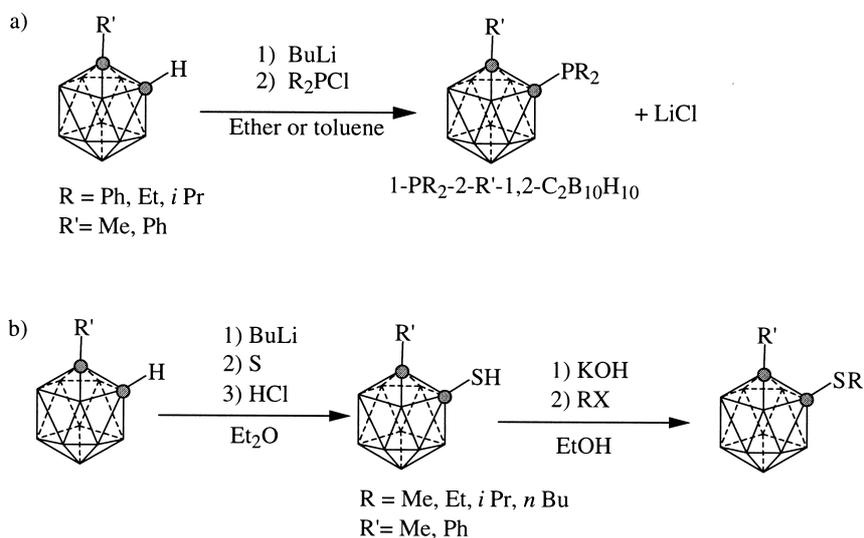
plexes do not present any B-H→Rh and are hydrogenation inactive. The Ru(II) complexes have only a second belt B(3)-H→Ru and are also inactive. Producing hydrogenation activity seems to require the existence of a B-H→M, and that this be sited and fixed in the upper belt.

d) Designing the new monosubstituted ligands

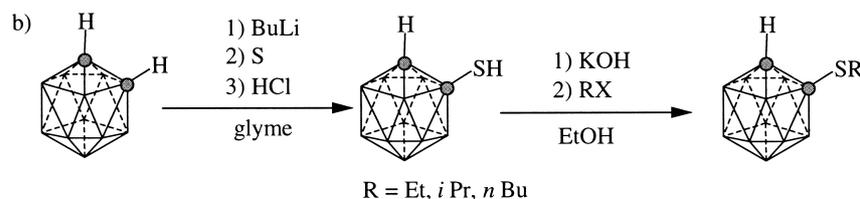
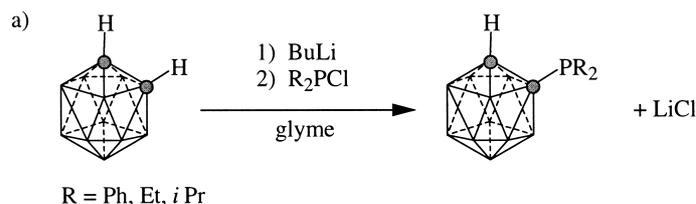
In the aim of forcing «upper belt» B-H→M interactions, while avoiding *exo-nido* to *closo* tautomerism, the monothioether $[7-SR-8-R'-7,8-C_2B_9H_{10}]^-$ and monophosphine $[7-PR_2-8-R'-7,8-C_2B_9H_{10}]^-$ anionic ligands were synthesized. Considering the bulky nature of the cluster, it was to be expected that once a first coordination had taken place, the metal would induce the participation of an adjacent B-H in coordination. This was not unrealistic considering the existing number of B-H→M examples reported [31]. Thus, the participation of B(11)-H and/or B(2)-H in the anionic cluster to form a B(11)-H→M and/or B(2)-H→M had a sound basis.

In order to study the monothioether/carborane and monophosphine/carborane synergy, derivatives of the $[7,8-C_2B_9H_{10}]^-$ fragment were synthesized. 1-phosphino-2-*R*-*o*-carborane, 1-mercapto-2-*R*-*o*-carborane and its S-alkylated derivatives were produced. [18f,19,21,32] Equation 5 illustrates the synthesis of these compounds. Preparation of monolithium derivatives of *o*-carborane is complicated by the existing equilibrium between the monolithiated species, and the dilithiated and unsubstituted compound in certain solvents [33]. The synthesis of 1-SH-*o*-carborane in almost a 100% high yield was of utmost importance to our development of new asymmetric catalysts. With the aim of getting a high-yield, reliable, one pot, and comparatively inexpensive route to monosubstituted *o*-carborane derivatives a new synthetic route was investigated [34]. The reaction yielded the monothioether 1-SR-1,2- $C_2B_{10}H_{11}$ and monophosphine 1- PR_2 -1,2- $C_2B_{10}H_{11}$ ligands as is illustrated in Equation 6. The S-aryl carborane ligands required the reaction of the lithiated salt with the appropriate disulfide to form *closo*-monothiocarborane [35]. The crystal structures of 1-thiomethyl-2-phenyl-1,2-dicarba-*closo*-dodecaborane [36]

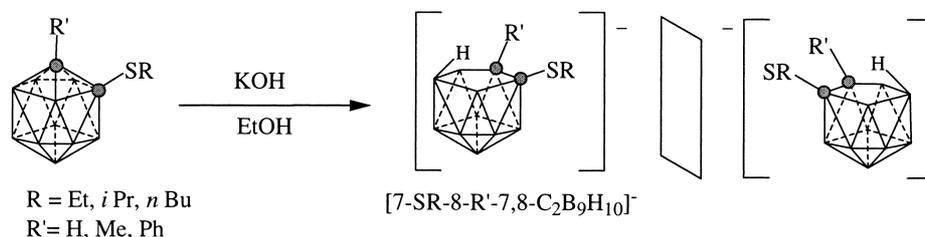
Equation 5



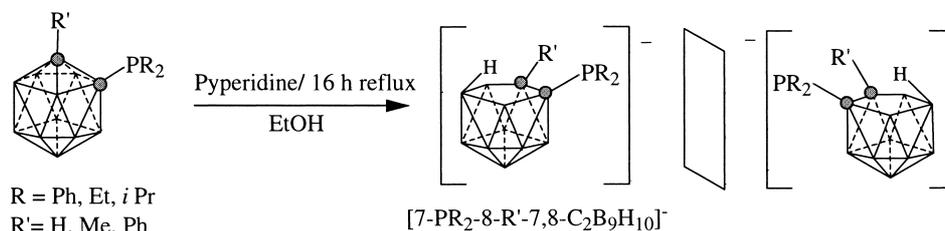
Equation 6



Equation 7



Equation 8



and 1-diphenylphosphino-1,2-dicarbano-*closo*-dodecaborane were reported [37]. The partial degradation reaction of monothioether-*o*-carborane derivatives, following the usual procedure [20], worked well, and the corresponding *nido* species were obtained without alteration of the C_{cluster}-SR bond (Equation 7) [18f,32e]. As the *exo* C_{cluster}-P bond did not resist the partial degradation conditions a new method for the preparation of [7-(PR₂)-8-R'-7,8-C₂B₉H₁₀]⁻ anionic ligands had to be investigated (Equation 8). Good degradation conditions which retained the C_{cluster}-P bond were found by using toluene as a solvent with a carborane-to-piperidine ratio of 1:50 or ethanol with a carborane-to-piperidine ratio of 1:10 [21]. The crystal structures of [7-SEt-8-Ph-7,8-C₂B₉H₁₀]⁻ [38] and the zwitterion 7-PH(*i*Pr)₂-8-Me-7,8-C₂B₉H₁₀ were reported [39].

e) Synthesis of metallocarboranes containing *exo-nido*-monothiocarborane and *exo-nido*-monophosphinocarborane ligands

No attempt to resolve the *nido*-carborane ligands into their enantiomers was made and the ligand racemic mixture was

used in the synthesis of its metallocarborane complexes. These have usually been obtained in ethanol from a reaction of the tetramethylammonium or cesium salts of the appropriate *exo*-monothiocarborane ligand with halocomplexes of Pd(II), Ru(II), and Rh(I) incorporating bulky or labile ancillary ligands [40,28,32e,41]. The existence of ionizable protons in the solvent (EtOH) prevented the formation of the tautomeric *closo* species. Structural methods have demonstrated that they are obtained only in the *exo-nido* form. The cluster contributes to coordination via the S atom and the B(11)-H for square-planar Pd(II) and Rh(I) [40,41]. 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 high activity of the upper belt B(11)-H→M interaction yielded an unexpected complex in the reaction of [NMe]₄[7-SMe-8-Me-7,8-C₂B₉H₁₀] with [PdCl₂(PPh₃)₂] in ethanol [40]. The spectroscopic data and the X-ray analysis established the formation of a novel B-PPh₂ bond at the B(11) position. The Pd had a square-planar geometry, surrounded by PPh₃, PPh₂-B, S and Cl to give the structure of [PdCl(7-SMe-8-Me-

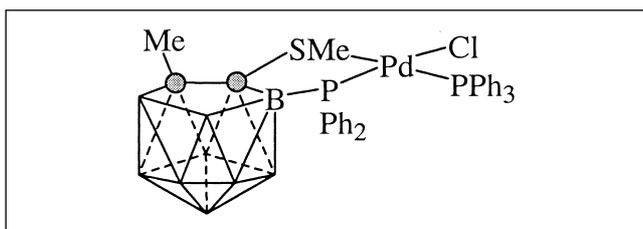


Figure 4. Representation of the structure of $[\text{PdCl}(7\text{-SMe-}8\text{-Me-}11\text{-PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)(\text{PPh}_3)]$ showing the new B-P bond formed.

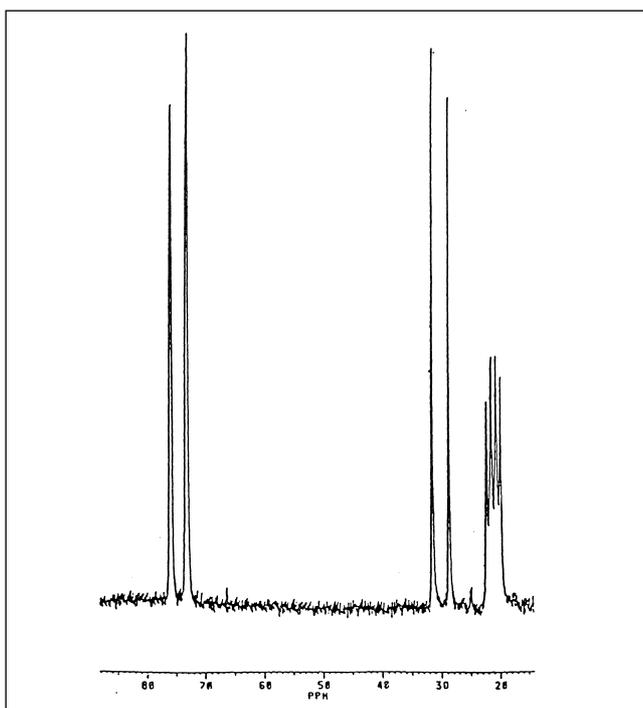


Figure 5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{PdCl}(7\text{-PPh}_2\text{-}8\text{-Me-}11\text{-PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)(\text{PPh}_3)]$.

11- $\text{PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)(\text{PPh}_3)]$ shown in Figure 4. By the formation of the B- PPh_2 bond, the initial ligand had been modified to a chelating one via a $\text{MeS-C}_{\text{cluster}}\text{-B-PPh}_2$ moiety, generated from the $\text{RS-C}_{\text{cluster}}\text{-B-H}$ fragment. Similar results were obtained for $[7\text{-PR}_2\text{-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$. The reaction of these ligands with $[\text{PdCl}_2(\text{PPh}_3)_2]$ afforded yellow complexes which showed very characteristic spectroscopic data. The $^{31}\text{P}\{^1\text{H}\}$ NMR (Figure 5) displayed three sets of resonances indicating three different phosphorus atoms in the molecule. The highest field resonance was a 1:1:1:1 quartet with a $J=129$ Hz, which indicated the presence of a B-P bond in the molecule. This information was corroborated by the $^{11}\text{B}\{^1\text{H}\}$ and ^{11}B NMR spectra that displayed a doublet resonance, at -2.9 ppm, with the same coupling constant ($J=129$ Hz), indicating the substitution of a terminal H by a P atom (Figure 6). Finally, the X-ray diffraction analysis of $[\text{PdCl}(7\text{-PPh}_2\text{-}8\text{-Me-}11\text{-PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)(\text{PPh}_3)]$ and $[\text{PdCl}(7\text{-SMe-}8\text{-Me-}11\text{-PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)(\text{PPh}_3)]$ confirmed the exocenter B-P bond formation [40,42].

On the other hand, the reaction of $\text{Cs}[7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$ ($\text{R}, \text{R}' = \text{alkyl, aryl}$) with $[\text{RhCl}(\text{PPh}_3)_3]$ afforded complexes with the stoichiometry $[\text{Rh}(7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})$

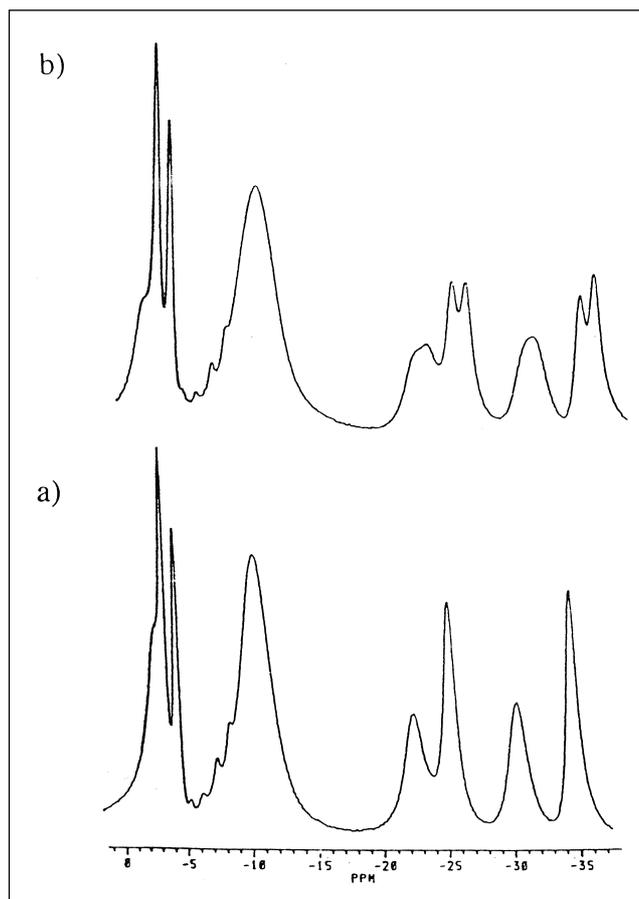


Figure 6. a) $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $[\text{PdCl}(7\text{-PPh}_2\text{-}8\text{-Me-}11\text{-PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)(\text{PPh}_3)]$. b) ^{11}B NMR spectrum of $[\text{PdCl}(7\text{-PPh}_2\text{-}8\text{-Me-}11\text{-PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_9)(\text{PPh}_3)]$.

$(\text{PPh}_3)_2]$. [41] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the complexes revealed the existence of a dynamic process. Broad resonances were displayed around 42 ppm, which were resolved at low temperature to give two doublets with the doublet characteristics of two PPh_3 bonded to a Rh atom. $^1\text{H}\{^1\text{B}\}$ NMR spectra showed resonances at high field indicating the formation of a B-H \rightarrow Rh agostic bond. An X-ray diffraction study of $[\text{Rh}(7\text{-SPh-}8\text{-Me-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ corroborated the expected *exo-nido* structure, in which the carborane cage chelates the metal by means of an S-Rh and B(11)-H-Rh interaction. A second example is the reaction with metal complexes containing alkene ligands. The reaction with $[\text{Rh}(\text{acac})(\text{cod})]$ afforded *exo-nido* complexes in which the $[\text{Rd}(\text{cod})]^+$ fragment was bonded to the carborane cage through S-Rh and B(11)-H-Rh. The only difference with the previous one was that the two PPh_3 had been replaced by a cod ligand [41c].

Metallic complexes containing *nido*-monophosphinocarborane ligands were obtained, in a similar way to the *nido*-monothiocarborane derivatives, from the reaction in ethanol of the tetramethylammonium salts of the ligands with Rh(I) [41b,43], and Pd(II) [42]. Thus, the reaction of $[\text{NMe}_4][7\text{-PR}_2\text{-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$ with Wilkinson's catalyst in a 1:1 ratio afforded *exo-nido* complexes with the formulae $[\text{Rh}(7\text{-PR}_2\text{-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$. A very illustrative $^{31}\text{P}\{^1\text{H}\}$ NMR

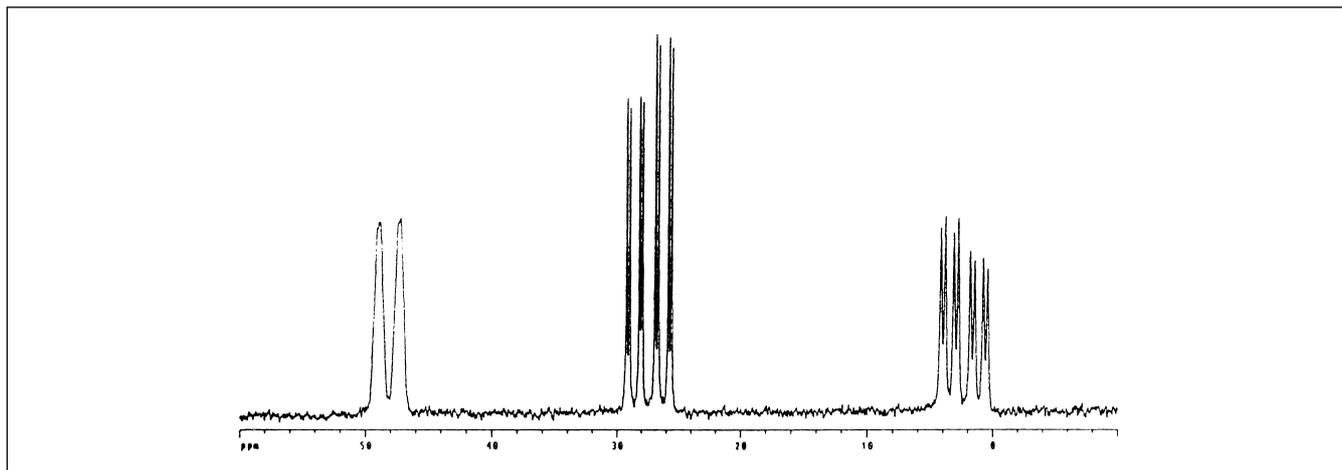
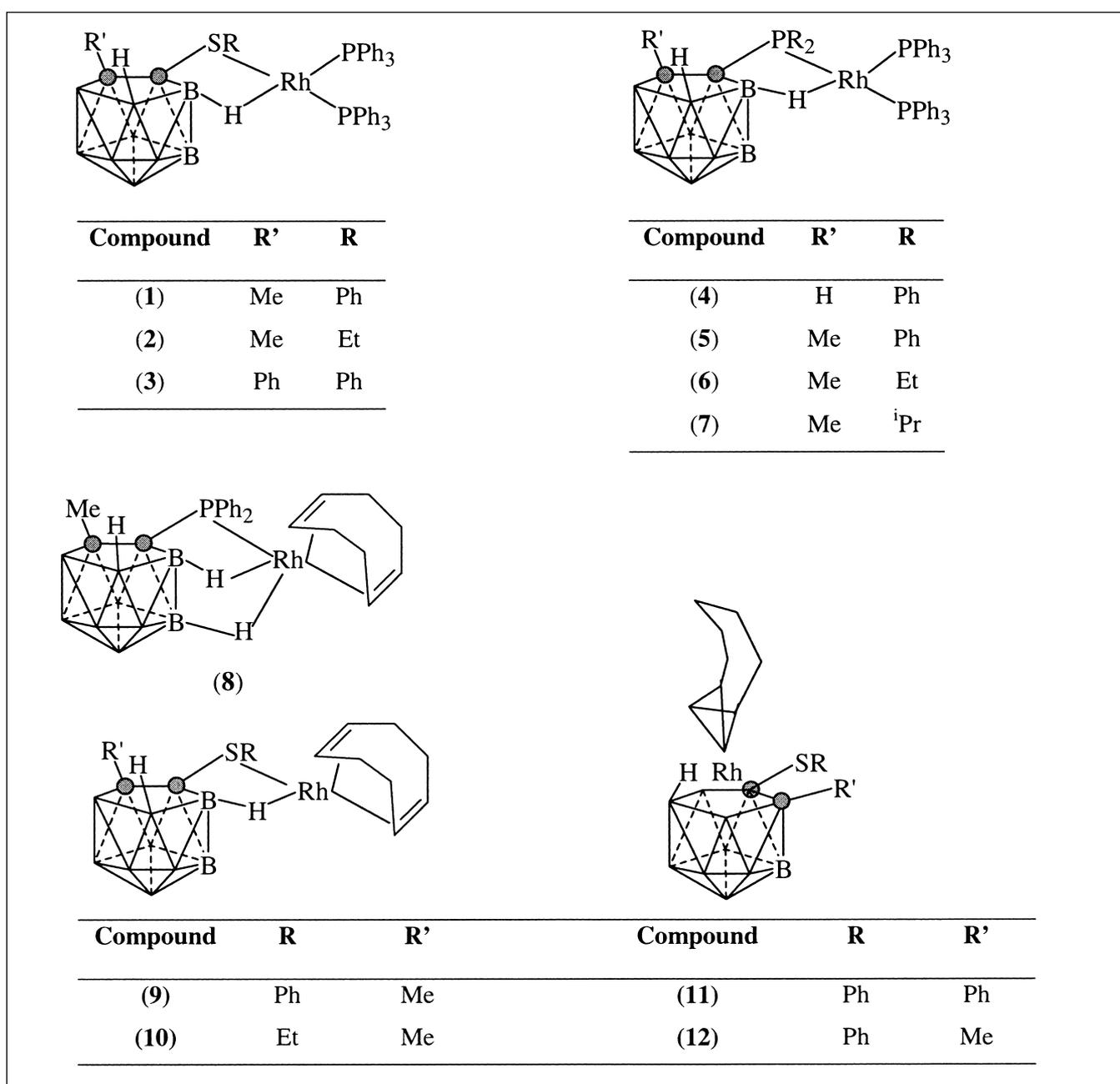
Figure 7. Illustrative $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Rh}(7\text{-PPh}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11})(\text{PPh}_3)_2]$.

Figure 8. Rhodacarboranes used as catalyst precursors.

spectrum is observed for this sort of complexes, which displayed three set of resonances indicating three different phosphorus atoms in the molecule (Figure 7). In these complexes, the ^1H NMR spectra displayed unresolved quartets in the region between -3.68 and -5.60 ppm, indicating the formation of B-H \rightarrow Rh agostic bonds. This was corroborated by the X-ray crystallographic study of $[\text{Rh}(7\text{-PPH}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{11})(\text{PPh}_3)_2]$. The Rh(I) center had a four coordinated square-planar geometry. The two bonds to Rh(I) emerging from the cage were formed by the phosphorus atom of the phosphino group and the hydrogen H(11) bonded to the B(11) at the C_2B_3 open face (Figure 8).

In contrast to the *nido*-monothioethercarboranes, the *nido*-monophosphinocarboranes reacted readily with $[\text{RuCl}_2(\text{PPh}_3)_3]$ or $[\text{RuH}(\text{AcO})(\text{PPh}_3)_3]$ in a 1:1 ratio in ethanol to give *exo-nido* complexes with the stoichiometry $[\text{RuX}(7\text{-PR}_2\text{-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{H}$) [44]. In these compounds the *nido*-monophosphinocarborane had been proven to be tridentate when bonded to Ru(II) which is an octahedrally demanding transition metal. This stoichiometry suggested that the ligand binds the metal in a tricoordinating fashion, via the *exo*-cluster PPh_2 unit and two B-H \rightarrow Ru agostic bonds. These were observed at very different chemical shifts in the ^1H -NMR spectrum, depending on their trans ancillary ligands. These B-H \rightarrow Ru resonances appeared at the negative region between -2.40 and -15.20 ppm. Finally, the crystal structure of $[\text{RuCl}(7\text{-PPH}_2\text{-}8\text{-Me-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ confirmed the *exo-nido* cluster coordination. The Ru(II) was bonded octahedrally to the *nido*-carborane cage, the chloride anion and two PPh_3 (Figure 9). The three bonds emerging from the cage were formed by the phosphorus atom and two hydrogen atoms bonded to B(2) and B(11), from the lower and upper belts respectively.

f) Testing the metallacarborane complexes containing *exo*-monothioether and *exo*-monophosphinocarboranes as catalyst in the hydrogenation of alkenes

For purposes of comparison, series of rhoda- and ruthenacarborane complexes containing *nido*-monothioether and *nido*-monophosphino clusters were studied. Complexes of formulae $[\text{Rh}(7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ (1-3), $[\text{Rh}(7\text{-PR}_2\text{-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ (4-7), $[\text{Rh}(7\text{-PPH}_2\text{-}8\text{-Me-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{cod})]$ (8), $[\text{Rh}(7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{cod})]$ (9, 10), [*closo*-3-(C_8H_{13})-1-SR-2-R-3,2,1-Rh $\text{C}_2\text{B}_9\text{H}_9]$ (11, 12), $[\text{RuX}(7\text{-PR}_2\text{-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ (13-17) and $[\text{RuCl}(7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ (18-20) were tested as hydrogenation catalyst precursors. These compounds are represented in Figures 8 and 9, where the different R's are indicated.

The two series of rhodacarboranes $[\text{Rh}(7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ and $[\text{Rh}(7\text{-PR}_2\text{-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ (Fig. 8) showed noticeable differences in the catalytic hydrogenation of 1-hexene. While the *exo-nido* monothioetherorhodacarborane complexes are active catalysts at $T = 25\text{ }^\circ\text{C}$, leading to a high *n*-hexane yield, the *exo-nido* monophosphino derivatives require higher pressures and temperatures. However, no great differences were found in activity and selectivity of both rhodacarborane series at high temperature ($T = 66\text{ }^\circ\text{C}$). At this temperature, the ratio of alkene isomerization to hydrogenation increased for both of them. Table 1 shows a few selected examples [41b].

Taking into account the high activity of *exo-nido*-monothioetherorhodacarboranes at low temperatures, other experiments were performed under mild conditions ($P = 1\text{ atm}$ and $T = 25\text{ }^\circ\text{C}$) using the $[\text{Rh}(7\text{-SR-}8\text{-R}'\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ series, and the results were compared with Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$. Complex $[\text{Rh}(7\text{-SPh-}8\text{-Me-}7,8\text{-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ (1) exhibited a much higher conversion to hexane

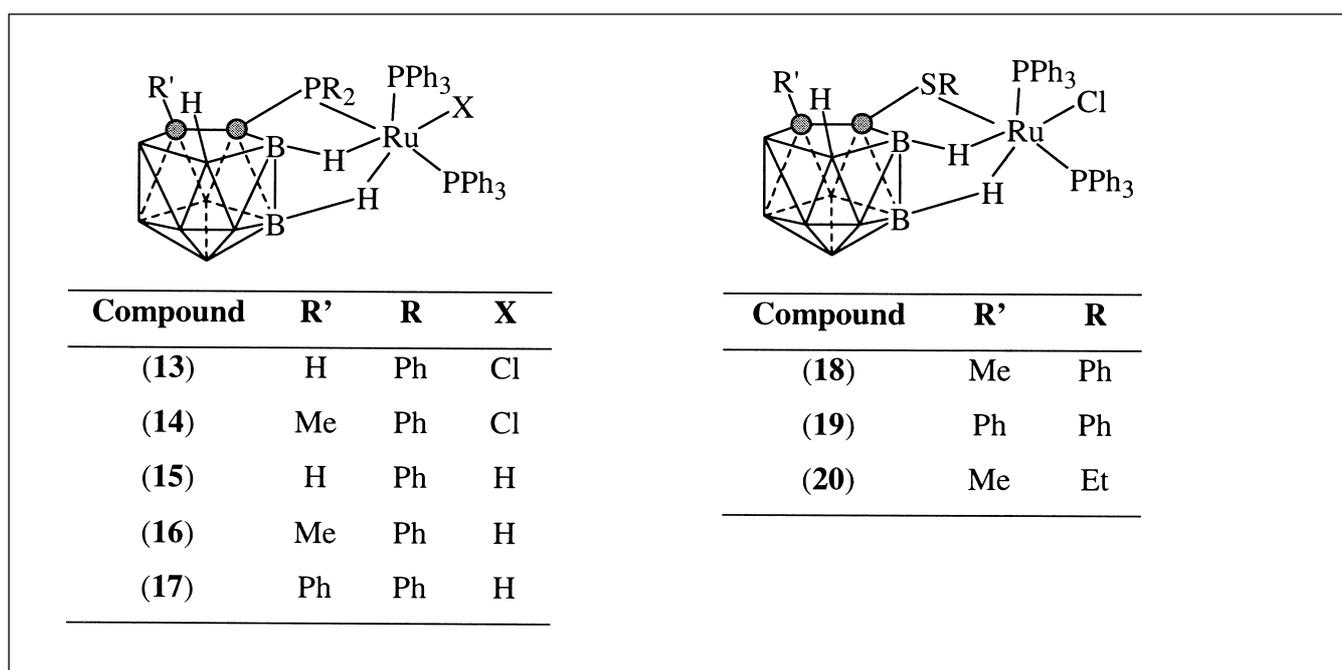


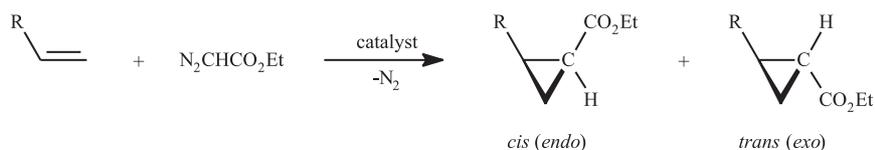
Figure 9. Ruthenacarboranes used as catalyst precursors.

Table 1. Percent 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

^aExperimental conditions: [1-hexene] = 3.9 M, [catalyst] = 5.21×10⁻⁴ M, P = 45 bar, THF.

Equation 9



than the rest, being ca. 8 times higher than Wilkinson's catalyst [41a,b]. It was also demonstrated that catalytic activity was inhibited by the addition of PPh₃. This suggests that reversible dissociation of PPh₃ is an important step preceding the activation of hydrogen in the catalytic cycle.

Ruthenacarboranes containing *exo-nido*-monothioether and *exo-nido*-monophosphinocarboranes (Figure 9) were also tested in the hydrogenation of 1-hexene. All [RuX(7-PR₂-8-R'-7,8-C₂B₉H₁₀)(PPh₃)₂] complexes were found to be active in the hydrogenation of 1-hexene with a similar selectivity (see Table 2). The precursor [RuCl(7-PPh₂-7,8-C₂B₉H₁₁)(PPh₃)₂] (13) is the more active ruthenium catalyst, with low alkene isomerization (5%), showing a percentage of conversion at 66 °C and P = 45 bar similar to [Rh(7-PPh₂-7,8-C₂B₉H₁₁)(PPh₃)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-C₂B₉H₁₀)(PPh₃)₂] (18) was the only ruthenamonothioethercarborane studied and exhibited much lower activity at 1 bar than the corresponding rhodacarborane [40b].

All *exo-nido*-rhoda and *exo-nido*-ruthenacarboranes were recoverable upon completion of the catalytic reactions, as shown by ¹H{¹¹B}, ¹¹B{¹H} and ³¹P{¹H} NMR spectroscopy. They did not exhibit any sign of deactivation and eventually converted all the 1-hexene into hexane and 2-hexenes.

Several rhoda and ruthenacarborane derivatives of monophosphinocarboranes were used as catalytic precursors in the stereoselective hydrogenation reaction of methacycline. The hydrogenation of methacycline may lead to the formation of two diastereomers: doxycycline, a potent tetracycline antibiotic extensively used in chemotherapy [45], and *epi*-doxycycline. Under different conditions [11] from 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 seen to be very active in the hydrogenation of methacycline.[41b] They exhibited conversions of 85 and 99.7% yields, respectively with very high di-

Table 2. Percent 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
(18)	–	–

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

astereoselectivity, obtaining the doxycycline as the only product. No *epi*-doxycycline was observed in any case. On the contrary, the Ru(II) systems (13), (14), (15) and (16) presented very low activity, and only 2% conversion was obtained.

The *exo-nido* rhodacarborane complexes described above and others reported earlier exhibit relatively low activity in the hydrogenation of internal alkenes (e.g. cyclohexene) [7-9]. To obtain enhanced hydrogenation rates, complexes of formula [Rh(7-SR-8-R'-7,8-C₂B₉H₁₀)(cod)] [41c] were used as catalysts (Figure 8). The *exo-nido*-cyclooctadiene complexes rearranged in solution to give the corresponding *closo* complexes of formula [*closo*-3-(C₈H₁₃)-1-SR-2-R-3,2,1-RhC₂B₉H₉] (Figure 8). Both *exo-nido* and *closo* types of complexes were tested in the catalytic hydrogenation of the internal olefin cyclohexene. It had been previously observed that addition of 1 eq. of PPh₃ inhibits *exo-nido* to *closo* isomerization during the hydrogenation reaction. This feature was advantageously used to study the catalytic activity of *exo-nido* complexes without interference from *closo* isomers. Contrary to what was expected, only small differences in activity were observed between diphosphine complexes [Rh(7-SR-8-R'-7,8-C₂B₉H₁₀)(PPh₃)₂] and the monophosphine complex generated in situ from [Rh(7-SR-8-R'-7,8-C₂B₉H₁₀)(cod)] and 1 eq. of PPh₃. Therefore, elimination of a phosphine ligand from the coordination sphere of the metal in monothio-carborane 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 activity compared to their *exo-nido* isomers. Contrary to observation of *exo-nido* species, the addition of 1 eq. of PPh₃ 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.

Table 3. Cyclopropanation of olefins with ethyl diazoacetate^a

Compound	Styrene	Cyclopropanation		
		4-Methylstyrene	4-Chlorostyrene	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 1ml, t = 4h.

^b Based on ethyl diazoacetate and determined by GLC analysis.

g) Testing metallacarboranes containing *exo*-monothio and *exo*-monophosphinocarboranes in carbene reactions

As mentioned above, in our efforts to learn about the possible applications of metallacarboranes, we tested them in catalytic reactions other than hydrogenation. 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 (Equation 9). First experiments were concluded with complexes (4), (5) and (8) containing monophosphinocarboranes (Table 3) [46].

In the presence of styrene, 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 with 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 6 times less reactive than styrene. With less reactive olefins, diethyl maleate and diethyl fumarate were the predominant by-products. In addition, with styrene, homologa-

tion products resulting from the insertion of the carbene into a vinylic C-H bond were detected in small amounts (1-5%).

Ruthenacarboranes (15) and (16) were tested as catalysts for cyclopropanation (Table 4). It appeared that complexes (15) and (16) were actually 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 1. 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 evident from the Table 4 comparison of the *cis/trans* ratio for cyclopropanation of styrene, 4-methylstyrene, and 4-*t*-butylstyrene. This could be further improved 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 [47].

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 in alcohols (Equation 10). 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% [48]. 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 (Equation 11). 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, a 1,3-dipolar addition of ethyl diazoacetate was the course of action chosen. In the presence of ruthenacarboranes, no cyclopropanation of norbornene took place [48]. Instead, ethyl diazoacetate and trimethylsi-

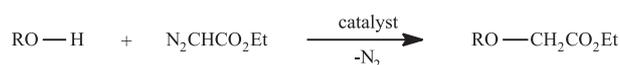
Table 4. Cyclopropanation of olefins with ethyl diazoacetate^a

Olefin	Cyclopropanation	
	(15)	% ^b (<i>cis/trans</i> or <i>endo/exo</i> ratio) (16)
Styrene	97 (0.63)	96 (0.64)
4-Methylstyrene	96 (0.52)	96 (0.54)
4- <i>t</i> -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)

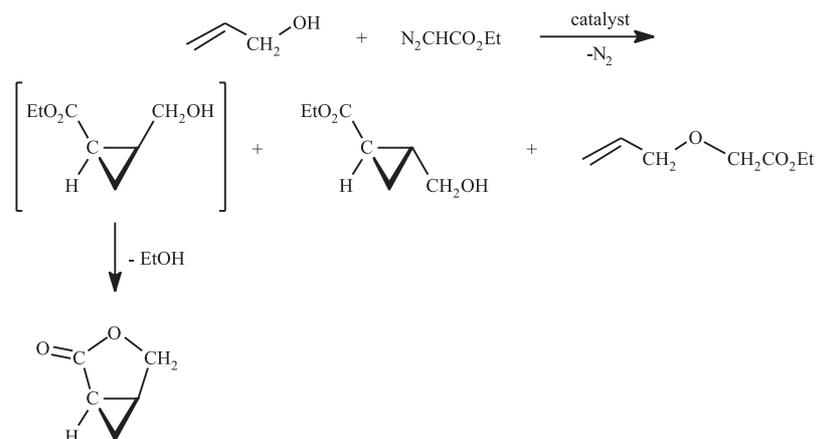
^a Experimental conditions: T = 100 °C, olefin = 20 mmol, catalyst = 0.0075 mmol, ethyl diazoacetate = 1 mmol diluted by the olefin to 1ml, t = 4h.

^b Based on ethyl diazoacetate and determined by GLC analysis.

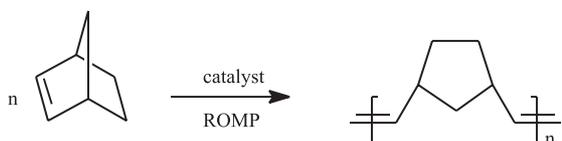
Equation 10



Equation 11



Equation 12



lyldiazomethane initiated the ring-opening metathesis polymerization (ROMP) of the substrate, with moderate yields (up to 42%) (Equation 12) [49]. With a low-strain cyclic olefin such as cyclooctene (Table 5), only minute amounts of polymers were obtained.

Consistent with the mechanism of olefin metathesis, this outcome revealed 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 $[\text{RuCl}(\text{7-PPH}_2\text{-8-CH}_3\text{-7,8-C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)_2]$ (14), the phosphine ligands were 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 was substituted. Which of the triphenylphosphine ligands is more labile upon addition of a diazo compound, and what the influence of the carbene moiety on the relative lability of the remaining ligands could be questions the answers to which are far from straightforward. This was confirmed 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 were homology products observed, which were formed in small amounts (1-5%) upon addition of ethyl diazoacetate to 4-X-styrenes [50].

Nor can we exclude the possibility that, at temperatures used in carbene chemistry (60-100°C), some of the B-H-Ru agostic bonds might become more fragile, so that they

could be split in the case of the presence of diazo compounds.

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. In 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. The series of thioether and phosphinocarboranes are enlarged by the incorporation of newly synthesized aminocarboranes. Current research in this field is extended to Ziegler-Natta polymerization catalysis.

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The group focuses its activity on the study of the molecule/ion-molecule interaction, which they have applied to catalysis, to transport phenomena and to selective recognition of ions. The group generally designs, synthesizes and characterizes its own ligands. For this reason they have won international recognition in boron chemistry, although they are the only group in Spain dedicated mainly to this field. The group has also attained a high level prestige in macrocyclic chemistry and has contributed significantly to the understanding of Ag⁺ detection. The group's new areas of interest are the development of new conducting polymers that incorporate low coordinating, low nucleophilic anion derivatives of boron clusters, and the synthesis of new metallacarboranes derived from the transition metals which when equipped with a radiometal can be used in radioimaging and radiotherapy of tumors. Finally, the group is interested in using scCO₂ (CO₂ supercritical conditions) as a solvent substitute in catalytic reactions to obtain significant benefit for the economy and the environment.