

A versatile rigid binucleating ligand for $\text{Rh}_2(\mu\text{-Cl})_2$ moieties: its application as a catalyst in hydrogenation and cyclopropanation

Crystal structure of $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}\{7,8\text{-}\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_9\text{H}_{10}\}][7,8\text{-}\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_9\text{H}_{10}]\cdot\text{THF}$

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In the occasion of the 75th anniversary of a master in Boron Chemistry for his outstanding research capacity and to pioneer Boron in application areas

Abstract

A rigid non-deforming “ MCl_2M ” binucleating ligand $[7,8\text{-}\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_9\text{H}_{10}]^-$ able to held the two rhodium atoms in a cooperative distance has been synthesized. The original two bridging chlorides are retained in $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2\{7,8\text{-}\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_9\text{H}_{10}\}]^+$. Hydrogenation of 1-hexene is 10 times faster with $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2\{7,8\text{-}\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_9\text{H}_{10}\}]^+$ than with $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$. A hydrogenation mechanism has been proposed which assumes that $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{Cl})(\text{H})\{7,8\text{-}\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_9\text{H}_{10}\}]^+$ is the first generated species in the process.

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1. Introduction

The discovery that metallic complexes could be used as catalyst precursors in homogeneous hydrogenation, isomerization, hydrosilylation, and hydroformylation reactions permitted a great development of organometallic and coordination chemistry [1]. Catalysis is very relevant to obtain optically active compounds of interest to industrial chemistry such as pharmaceutical, alimentary, essences, and other [2]. On the other hand, polyolefins are the fastest growing segment of the polymer industry [3]. Although it has been almost half

a century since polyethylene's commercialization, polyolefins remain highly technology-driven [4].

Nevertheless, in spite of the high number of known catalytic systems, the use of metallocarboranes as catalyst precursors is very limited until now [5]. 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 coworkers [6–10]. Rhoda- and ruthenacarborane complexes containing *nido*-monothio and *nido*-monophosphino were found to be exceptionally effective for the hydrogenation of alkenes [11]. Metallocarboranes were also found to be stereoselective in the hydrogenation of methacycline to doxycycline [11c,12]. Additionally, *closo*- and *exo-nido* ruthena and rhodacarboranes have been studied as catalyst precursors in the cyclopropanation of olefins

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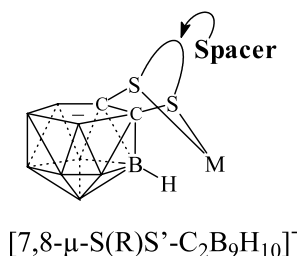


Fig. 1. 7,8-Dithioether-7,8-dicarba-*nido*-undecaborate(-1) ligands $[7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$.

with ethyl diazoacetate (EtDA) and no great differences in their activities have been observed [13].

Ligand derivatives of 7,8-dithio-7,8-dicarba-*nido*-undecaborate(-1) $[7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$, where R is a flexible alkyl spacer joining the two sulfur atoms, have been thoroughly studied in our group [14]. Variations in the length of the 7,8- $\mu\text{-S(R)S}'$ moiety, see Fig. 1, have led to distinct properties on the resulting complexes. A relevant characteristic of these $[7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ ligands is the enhanced bonding capacity of the thioether groups as compared to organic thioether. This enhancement is interpreted as if the negative charge of the cluster partly resides on the thioether [11e,15]. An example is the ready substitution of Cl^- by these ligands from a metal's coordination sphere [16], contrary to organic dithioether ligands that require the previous removal of the chloride ligand by precipitating agents like AgPF_6 [17].

On the other hand, ligand substitution reactions on pentamethylcyclopentadienyl-rhodium complexes are of considerable importance [18], especially in view of the utility of these complexes for many reaction types [19]. Examples of mixed thioether–cyclopentadienyl Rh(III) complexes are, however, scarce and up to now no structural details have been reported in the literature.

Binuclear complexes with a close metal to metal contact can be traced back to 1975 when Muetterties [20] proposed analogies between metal clusters and metal surfaces and speculated that molecular metal clusters could be found to be catalysts with novel properties. However, the anticipated evidence of catalysis by metal clusters has not emerged, which brought about the search for binuclear metal complexes with a possible metal to metal cooperation [21]. Two model types may be considered: (1) the direct contact with a bond between the two metals and (2) the bridge contact with two monoatomic bridging elements between the two metals. The $[\text{Rh}_2(\text{OAc})_4]$ complex which is very active in the catalytic cyclopropanation process [22] is one relevant example of the first type. The complex $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ [23,27] which has been proven to be a good hydrogenation catalyst [24] is one example of the second type. The dinuclear nature influence of these compounds in catalysis has been proven by comparison with similar Rh(III) mononuclear complexes. These

have shown much less catalytic activity which was interpreted as if the dinuclear complexes generate vacancies more easily than the mononuclear complexes [25].

Up to now, no hints were found indicative of the formation of binuclear complexes containing $[7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ ligands with ligand to metal ratio of 1:2. However, a geometry study of a series of $[7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ ligands pointed out that the average $\text{S}\cdots\text{S}$ distance was 3.18 Å [26]. This value is relatively close to the $\text{M}\cdots\text{M}$ distance in “ MCl_2M ” binuclear fragments where Cl are bridging elements, e.g. in $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$, the $\text{Rh}\cdots\text{Rh}$ distance is 3.7191(6) Å [27]. This brought about the possibility of producing binuclear bihalogen-bridged complexes with a third bridging moiety. In this work we report on the synthesis and bridging capacity of the first rigid and non-deforming “ MCl_2M ” binucleating anionic ligand. Interestingly, minimum distortions are created with regard to the ancient complex $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ both with “ MX_2M ” surroundings.

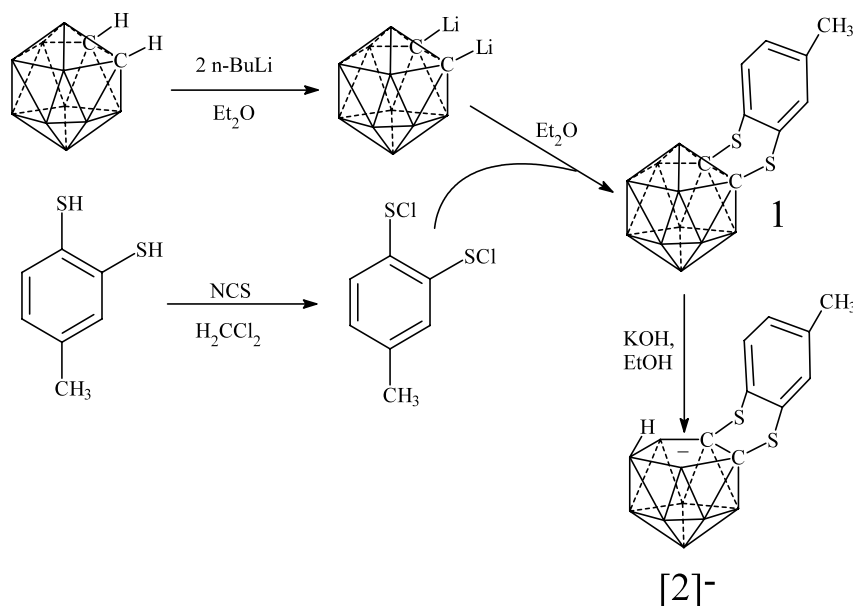
2. Results and discussion

Ligands $[7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ with flexible -S(R)S'- spacers have always shown a tendency to chelate to metal as is represented in Fig. 1; consequently, L:M = 1:1 ratios were always obtained mostly producing mononuclear complexes. Thus, although the $\text{S}\cdots\text{S}$ distance and the -S(R)S'- anionic character were adequate for binucleation, the flexible -S(R)S'- did not help for it. We have previously described the reaction of this type of ligands $[7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ with $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ and only monomeric species of the type $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}(7,8-\mu\text{-S(R)S}'\text{-C}_2\text{B}_9\text{H}_{10})]$ were obtained [28].

2.1. Designing the new disubstituted ligand

The alternative way to force binucleation was to produce a ligand with a rigid -S(R)S'- spacer. A tolyl spacer connected to the two sulfur atoms of the *o*-carborane fragment, as it is shown in Fig. 2, was designed. Although we have not considered optical resolution in this work, the methyl group on the aromatic ring was included to provide chirality.

Neither 1,2- $\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S}'\text{-C}_2\text{B}_{10}\text{H}_{10}$ (**1**) nor its *nido* derivative $[7,8-\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S}'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ (**2**)[−] had previously been synthesized. Due to the aromatic nature of the organic group in the -S(R)S'- spacer, the methods previously utilized for alkyl -S(R)S'- spacers were not valid anymore and a new synthetic method was required. Reaction of the bis(chlorosulfonyl) derivative of 3,4-dimercaptotoluene with dilithiated *o*-carborane in diethyl ether led to compound **1** in a 70% yield.

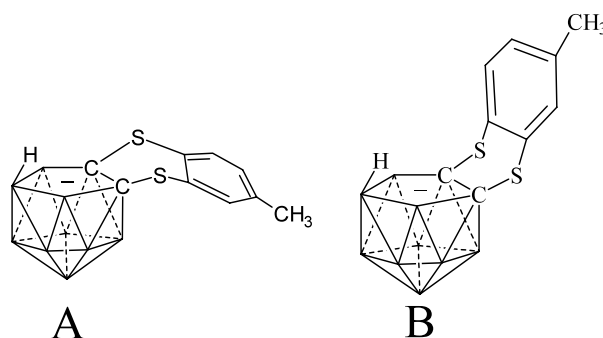
Fig. 2. Synthesis of $[7,8-\mu-S(4'-C_6H_3(Me))S-7,8-C_2B_9H_{10}]^-$ ($[2]^-$).

Partial degradation, formal removal of B^+ , of compound **1** was readily accomplished by reaction with KOH in boiling ethanol [29]. The desired dithioether *nido* derivative $[7,8-\mu-S(4'-C_6H_3(CH_3))S-C_2B_9H_{10}]^-$, $[2]^-$, was isolated as $[N(CH_3)_4][2]$ in 95% yield after the addition of $[NMe_4]Cl$. The synthetic procedure leading to this $[2]^-$ is schematically indicated in Fig. 2. A racemic mixture was obtained. Indeed, $[2]^-$ is a racemate but no attempts were made for the isolation of the two enantiomers.

2.2. Characterization of *closo* 1,2- $\mu-S(4'-C_6H_3(CH_3))S-C_2B_{10}H_{10}$ and *nido* $[7,8-\mu-S(4'-C_6H_3(CH_3))S-C_2B_9H_{10}]^-$ species

A $\nu(B-H)$ stretching frequency at 2610 cm^{-1} , typical for a *closo* compound, was observed for **1**. The resonances of the $^{11}B\{^1H\}$ -NMR integrating 2:4:4 in the range $-3/-10$ ppm also support the *closo* nature of the cluster. The 1H -, $^1H\{^{11}B\}$ -, $^{13}C\{^1H\}$ -NMR spectra, and elemental analysis were in agreement with the proposed formula.

The *nido* ligand $[2]^-$ was characterized by elemental analysis, 1H -, $^1H\{^{11}B\}$ -, $^{13}C\{^1H\}$ -, ^{11}B -, and $^{11}B\{^1H\}$ -NMR. Partial degradation was clearly proven by the appearance of a $^1H\{^{11}B\}$ resonance at -2.4 ppm attributed to the endohedral open-face hydrogen. Additionally, a $\nu(B-H)$ stretching frequency at 2530 cm^{-1} is a clear indication of the *nido* structure. The 2:1:4:1:1 pattern in the $^{11}B\{^1H\}$ -NMR in the range $-8/-44$ ppm is consistent with the cluster partial degradation. The $^1H\{^{11}B\}$ -NMR spectrum of $[N(CH_3)_4][2]$ displayed, in addition to the tetramethylammonium protons, a singlet signal at 2.2 ppm and a multiplet at 7.3 ppm in a ratio of 1:1 attributed to the methyl and aromatic hydrogens, respectively. The number and positions of the carbon signals are in agreement with the proposed formula.

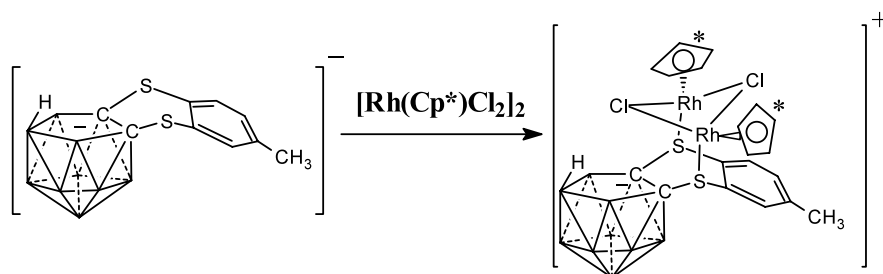
Fig. 3. The more stable conformers for $[2]^-$.

2.3. Reactivity of the new dithioether ligand to $Rh(III)$ complexes

A conformational analysis on $[2]^-$ by semiempirical methods was performed [30], indicating that the molecule presented two minima corresponding to two conformers. These two were equally possible since their energies were almost identical. They are represented in Fig. 3. Conformer B is very similar to the coordination motif for mononuclear chelation but conformer A had never been observed before.

The binuclear compound $[Rh_2(C_5Me_5)_2Cl_4]$ was utilized as the source of an “ $RhCl_2Rh$ ” moiety with the hope that the structural characteristics of this core would be preserved at the final product.

The reaction of $[NMe_4][2]$ with $[Rh_2(C_5Me_5)_2Cl_4]$ in ethanol at reflux for 4 h yielded **3** as an orange solid. Reactions of $[Rh_2(C_5Me_5)_2Cl_4]$ with chelating organic dithioethers (e.g. 1,4-dithiacyclohexane, 2,5-dithiahexane) have been described before [17], but the direct synthesis was not possible. It required the preparation of tris-solvent complexes $[Rh(C_5Me_5)(sol)_3]^{2+}$ by the reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with $AgPF_6$ in the presence of

Fig. 4. Synthesis of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})]^+$.

weakly binding ligands like MeCN, py or THF. For ligand $[\mathbf{2}]^-$ reported here there is an easy replacement of the chloride ligands from the Rh(III) coordination sphere.

Reaction of $[\text{NMe}_4][\mathbf{2}]$ with $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ in ethanol in the ratio 2:1 or 1:1 invariably produced the same compound (see Fig. 4). The spectroscopic data and elemental analysis shed some light onto the structure of the compound **3**. The IR spectra display a $\nu(\text{B}-\text{H})$ stretching frequency at 2530 cm^{-1} that corroborates the *nido* cluster structure of the complex. The $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra displayed a 2:2:1:4:5:1:1:1:1 pattern, which indicated the presence of two non-equivalent $[\mathbf{2}]^-$ units in the molecule. The $^1\text{H}\{^{11}\text{B}\}$ -NMR, in agreement with the $^{11}\text{B}\{^1\text{H}\}$ -NMR, also displayed two BHB resonances at -1.21 and -2.43 ppm, which also proved the non-equivalency of the two cages. Some resonances of the $^{11}\text{B}\{^1\text{H}\}$ -NMR of the complex matched well with those of $[\mathbf{2}]^-$. Furthermore, the $^1\text{H}\{^{11}\text{B}\}$ -NMR BHB resonance at -2.40 ppm in $[\mathbf{2}]^-$ corresponded well with this at -2.43 ppm in **3**. The tolyl methyl resonance also supported this conclusion since two distinct methyl resonances were found in **3** at 2.28 and 2.42 ppm. The methyl resonance in $[\mathbf{2}]^-$ appears at 2.26 ppm. The elemental analysis supported the stoichiometry $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}(\mathbf{2})][\mathbf{2}]$ for compound **3** which would imply the presence of two $[\mathbf{2}]^-$ ligands. All this indicated that one of the ligands was coordinated to metal while, most probably, the second one was free. To unambiguously ascertain the structure of **3**, good quality X-ray crystals were grown in ethanol and THF. The molecular structure is indicated in Fig. 5. It consists of a binuclear cation $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})]^+$ incorporating only one $[\mathbf{2}]^-$ ligand compensated by a second anion $[\mathbf{2}]^-$.

2.4. Description of the structure of $\mathbf{3} \cdot \text{THF}$

The structure of $\mathbf{3} \cdot \text{THF}$ is made of the cationic complex $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})]^+$ that consists of the di- μ -dichlorobridged dirhodium moiety connected to the dithioethercarborane anion and two C_5Me_5^- anions, a free dithioethercarborane monoanion, and THF solvent (see Fig. 5). In the cation, the dithioethercarborane anion bridges the metals via two Rh–S bonds, and two C_5Me_5^- and two chloride anions fulfill the coordination demands of the rhodium cations. The structure is similar to the

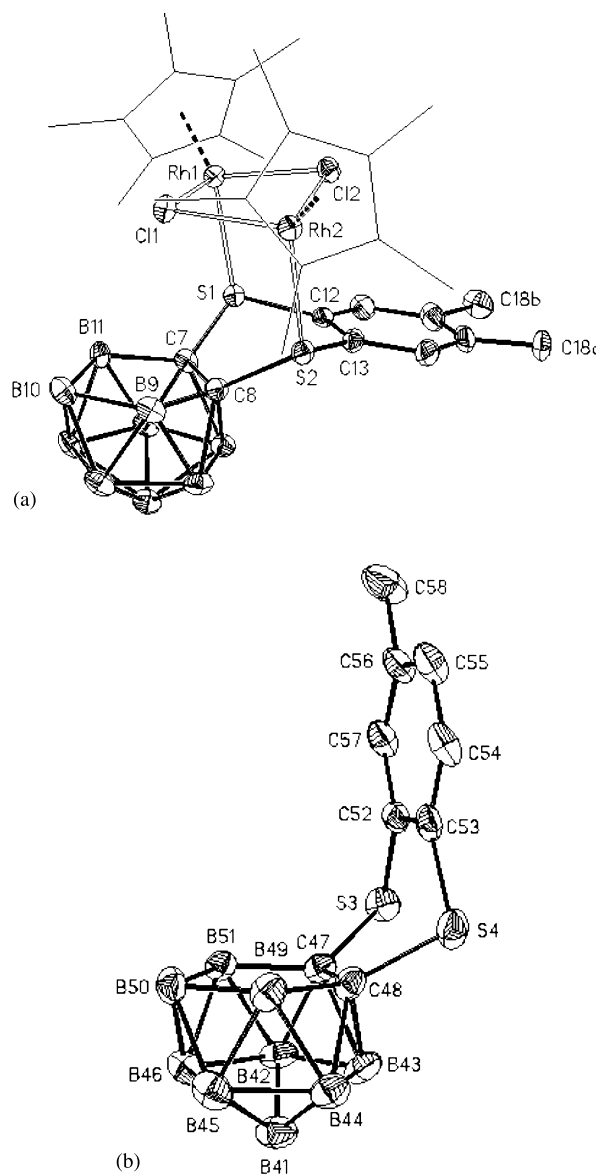


Fig. 5. (a) Simplified perspective drawing (only the important atoms are labeled) of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})]^+$. Disordered C_5Me_5 with minor occupancy, coordinated to Rh(2), has been omitted for clarity. Skeletons of C_5Me_5 have been drawn with thin lines (thermal ellipsoids are at 20% level). (b) Perspective drawing of $[\mathbf{2}]^-$ with the labeling scheme (thermal ellipsoids are at 20% level).

Table 1
Cyclopropanation of alkenes with EtDA^a

Olefin	Cyclopropanation yield (%) (<i>cis/trans</i> or <i>endo/exo</i> ratio)		
	[Rh ₂ (C ₅ Me ₅) ₂ Cl ₂ (2)]	[Rh ₂ (C ₅ Me ₅) ₂ Cl ₄]	[Rh ₂ (C ₅ H ₅) ₂ Cl ₄] [2]
Styrene	49 (0.67)	6 (1.1)	55 (0.69)
Styrene (100 °C)	66 (0.65)	11 (0.97)	60 (0.66)
4-Methyl- styrene	56 (0.45)	4 (0.75)	53 (0.54)
4-Chloro- styrene	51 (0.50)	5 (0.61)	57 (0.51)
α-Methyl- styrene	28 (0.66)	3 (0.90)	33 (1.0)
1-Octene	21 (0.52)	2	4 (0.52)
Cyclooctene	12 (0.75)	1	3 (0.70)
Cyclooctene (100 °C)	18 (0.72)	13 (0.79)	10 (0.68)

Reaction conditions: catalyst, 0.0075 mmol; olefin, 20 mmol; EtDA, 1 mmol diluted by the olefin up to 1 ml; addition time, 4 h; temperature, 60 °C.

simple dithioether complex of the dinuclear Rh(III) [31]. In both compounds the main bonding parameters around Rh(III) are very similar (Table 1 for **3**).

Important structural features in the cation are the Rh··Rh distance of 3.6142(10) Å and the dihedral angle of 14.90(12)° defined by Rh(1)Cl(1)Cl(2) and Rh(2)Cl(1)Cl(2), and the *cis* orientation of the two (C₅Me₅)[−] ligands. In [Rh₂(C₅Me₅)₂Cl₄] [27] the orientation of the (C₅Me₅)[−] ligands is *trans* and the Rh(1)Cl(1)Rh(2)Cl(2) ring is planar. In [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺ the observed deviation of the Rh₂Cl₂Rh core from planarity and movement of the Cl atoms apart from the dithiocarborane ligand, probably arises from steric crowding between the Rh centers and the dithiocarborane ligand. The two “RhClRh” fragments in the cation are highly different, one Cl is on the C₂B₃ open face while the second is on the benzene ring; therefore, a different reactivity is expected for both bridging chlorides.

The conformers of [**2**][−] in the complex and the anion are different and correspond to the two minima found in the conformational analysis of [**2**][−]. Conformer A in Fig. 3 coordinates the “RhCl₂Rh” core, while conformer B is the anion. The S··S distance (3.326(3) Å) in the coordinated anion is longer than the one in the uncoordinated species (3.174(4) Å).

Binuclear complexes have been claimed to be of particular interest due to the metal atoms' cooperative effect as a consequence of the short M··M distance [32]. The molecular structure of [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺ has proven little distortion of the “RhCl₂Rh” core with regard to the starting [Rh₂(C₅Me₅)₂Cl₄] complex. This last had been proven to be active in the hydrogenation of alkenes [33], so it was interesting to know if [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺ had preserved or, even

better, had enhanced the catalytic capacity of [Rh₂(C₅Me₅)₂Cl₄].

3. Catalytic reactions

3.1. Hydrogenation of alkenes

Catalytic hydrogenation tests on 1-hexene were performed with [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺ and were compared with data from [Rh₂(C₅Me₅)₂Cl₄] obtained under the same conditions and setup. Precursor [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺ hydrogenated 1-hexene 10 times faster than its core equivalent [Rh₂(C₅Me₅)₂Cl₄].

We interpret this data considering that in [Rh₂(C₅Me₅)₂Cl₄] a process leading to a mononuclear species is invoked in the hydrogenation mechanism [34]. This is not required for [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺ due to the extra [**2**][−] bridging fragment.

As an illustration of the possibilities of this and related compounds, we have tentatively produced the mechanism indicated in Fig. 6 which makes use of the geometrical characteristics of [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺. To simplify the drawing, the carborane cage has been indicated only once. Through the cycle the “Rh₂” moiety never splits, which would happen if the bridging dithioether carborane was not present. This is why for [Rh₂(C₅Me₅)₂Cl₄] and similar binuclear complexes the proposed mechanism always flows through mononuclear complexes. The migration of the hydrogen from one metal to the olefin on the second metal provides an easy route to the alkyl formation. The Rh··Rh proximity allows the “bridging” chlorides or hydrides to jump from one metal to another to compensate the charge. The created vacancies would be fulfilled by solvent molecules or additional alkene substrates. Through the whole mechanism the oxidation state of Rh(III) remains unaltered.

In this mechanism, the first step consists the uptake of H₂ to produce a mixed hydride chloride bridge. Thus, it was convenient to synthesize [Rh₂(C₅Me₅)₂(H)(Cl)(**2**)]⁺, the first step in the cycle, and to check its catalytic capacity to support the proposed mechanism.

The direct reaction of [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺ with a hydride source was not performed due to the existence of the acidic BHB group in [**2**][−]. Instead, the reaction of [(Rh₂(C₅Me₅)₂Cl₃(H))] with [**2**][−] was done in ethanol. The result was [Rh₂(C₅Me₅)₂Cl(H)(**2**)]⁺. The ¹¹B{¹H}-NMR displayed a 2:2:1:4:5:1:1:1:1 pattern, very similar to that of [Rh₂(C₅Me₅)₂Cl₂(**2**)]⁺. The ¹H{¹¹B}-NMR at the negative zone displayed three resonances at −0.99, −1.24, and −2.43 ppm with integration 0.3:0.7:1 and one triplet at −12.16 ppm (¹J(Rh,H) = 25 Hz) integrating 1. The resonances at −2.43 correspond to the anion's BHB, while signals at −0.99 and −1.24 ppm correspond to the BHB resonances of the coordinated [**2**][−] considering the two possible isomers shown in Fig. 7. Based on the BHB resonances, the most abundant isomer is thought to be the

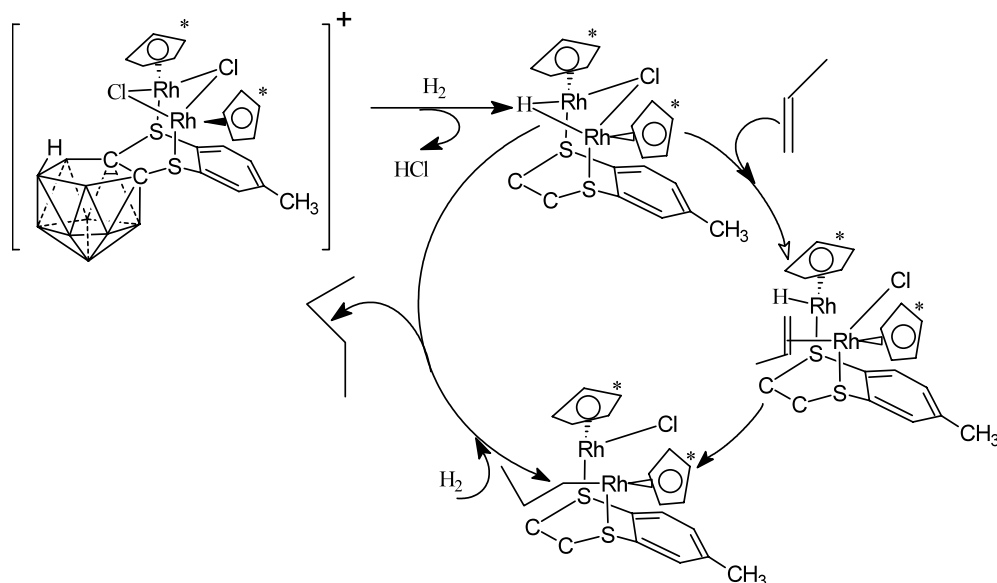


Fig. 6. Proposed catalytic system for the hydrogenation of terminal alkenes with $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\text{2})][\text{2}]$.

one with Cl closer to the C_2B_3 open face (ii) in Fig. 7. The RhHRh resonances of both isomers appear at the same position, which means that the C_2B_3 interaction with RhHRh is negligible. The Me tolyl resonance also supported the stoichiometry $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{H})(\text{2})][\text{2}]$ since two distinct Me resonances were found in the complex at 2.2 ppm for the free ligand and at 2.4 ppm for the coordinated one. Thus, ligand **2**[−] is able to hold both Rh atoms in different surroundings.

Thus, under the same experimental conditions, conversions of 6.2, 63.5, and 100% from 1-hexene to hexane have been found for $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$, $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\text{2})][\text{2}]$, and $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{H})(\text{2})][\text{2}]$, respectively. In all situations the $^{11}\text{B}\{^1\text{H}\}$ -NMR of the resulting complex after performing catalysis was comparable to the original starting material. The 100% conversion found for $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{H})(\text{2})][\text{2}]$ supports the participation of this species in the catalytic cycle.

All three catalyst precursors basically contain the same core “RhClXRh”. The last two incorporate a third bridging element, the “**2**[−]”, which possibly prevents the metal centers to move apart, facilitating an M···M cooperative effect. This is claimed to be the reason for

the enhanced efficiency in the hydrogenation of 1-hexene, which has been taken as a probe for these studies.

As mentioned, one of the main characteristics of **2**[−] is its capacity to bind the “RhCl₂Rh” cores altering very little the initial structural parameters. The “RhCl₂Rh” cores for $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ [27] and $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\text{2})][\text{2}]$ are very similar, e.g. Rh···Rh distances of 3.6142(10) and 3.614 Å, respectively. The dihedral angle defined by Rh(1)Cl(1)Cl(2) and Rh(2)Cl(1)Cl(2) are 0.00° and 14.90(12)°, respectively. The rigid bridging nature of **2**[−] and the strong coordinating capacity of these thioether groups make **2**[−] a suitable anionic ligand to test M···M cooperative effect. Work is now underway to study reactivity of **2**[−] in front other “M₂X₂” binuclear complexes.

3.2. Carbene reactions

The catalytic activity of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\text{2})][\text{2}]$ in cyclopropanation of alkenes with EtDA was also investigated Eq. (1).

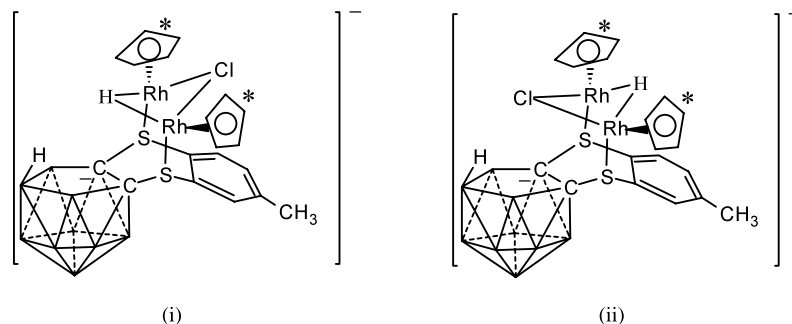
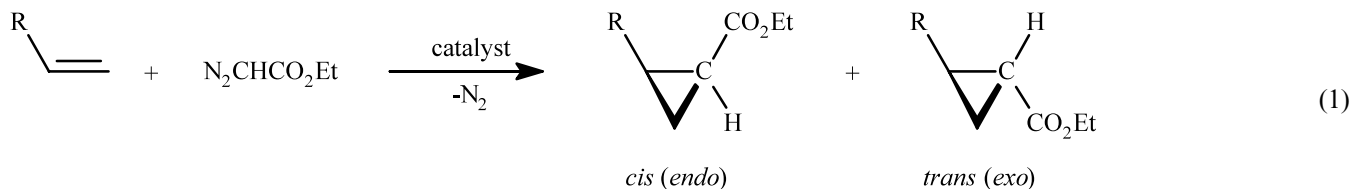


Fig. 7. Isomers of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{H})(\text{2})][\text{2}]$.



Under typical reaction conditions, EtDA was used in excess of alkene. To enhance selectivity (i.e. cyclopropanes versus coupling products (diethyl maleate and diethyl fumarate)), EtDA was added slowly via a pump syringe to a solution of alkene and catalyst. The results from several runs with different olefins are summarized in Table 1. The yields are based on EtDA and the remaining balance of EtDA is always converted to coupling products. For sake of comparison, $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ and $[\text{Rh}_2(\text{C}_5\text{H}_5)_2\text{Cl}_4]$ were also investigated under the same experimental conditions.

From Table 1 it is clear that $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})][\mathbf{2}]$ is much more active than $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$. With styrenics, the former afforded cyclopropyl esters in moderate yields (ca. 50%), whereas the latter gave very poor yields ($\approx 5\%$). The substrate selectivity indicates that activated olefins such as styrene are more reactive than non-activated substrates such as 1-octene and cyclooctene. In addition, substituting the *para* position of styrene by either electron-donating (CH_3) or electron-withdrawing groups (Cl) did not affect the yields. Disubstituted arylalkenes (α -methylstyrene) resulted in poorer yields in comparison to styrene, a monosubstituted olefin. Likewise, cyclooctene gave lower yields than 1-octene. Interestingly, $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})][\mathbf{2}]$ also tolerates O–H functionality. For example, allyl alcohol was reacted with EtDA and, in addition to the expected cyclopropanation, O–H insertion took place (Eq. (2), Table 2).

The catalytic reactions exhibited no significant stereoselectivity in the cyclopropyl ester product, which is expected for most catalysts that lack bulky ligands [35], rhodium and iron porphyrin catalysts being the exceptions [36,37]. In all cases, the thermodynamically more stable *trans (exo)* cyclopropane was the major isomer.

Table 2
Reaction of EtDA with allyl alcohol

Complex	Yields (%)	
	Cyclopropanation	O–H insertion
$[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})][\mathbf{2}]$	16	27
$[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$	15	43

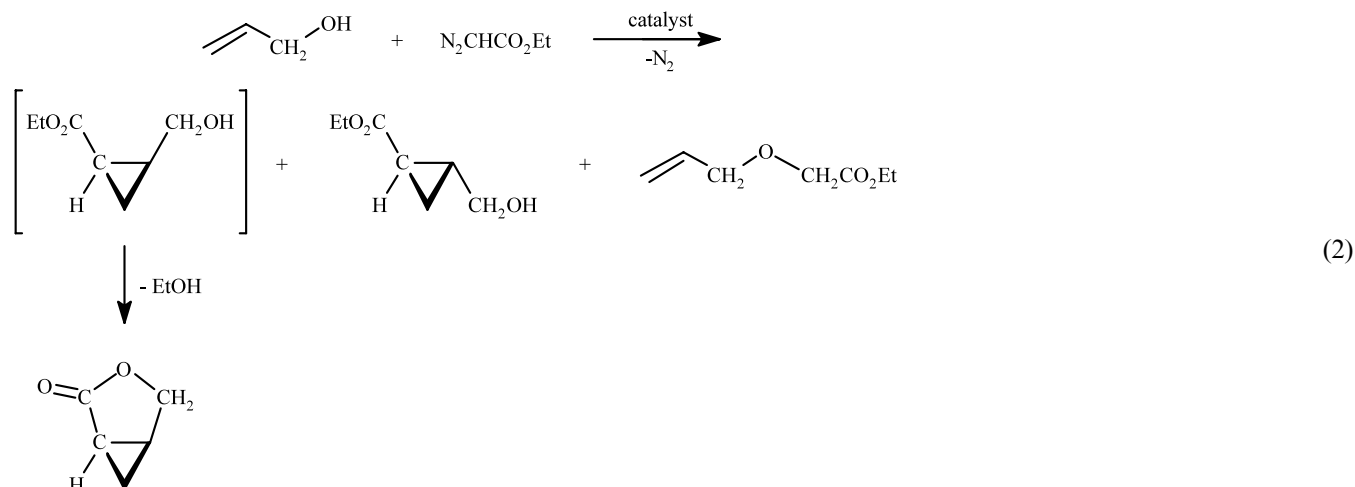
Reaction conditions are the same as in Table 1.

Due to our interest in the mechanistic chemistry of metal-mediated carbenoid transfer [38], we followed the reaction of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\mathbf{2})][\mathbf{2}]$ and $[\text{Rh}_2(\text{C}_5\text{H}_5)_2\text{Cl}_4]$ with EtDA by NMR at low temperatures. 10 equivalent of EtDA was added to a solution of the rhodium complex (10^{-2} mmol) in toluene- d_8 at 253 K. ^1H -NMR spectra were acquired at 10°C intervals from 253 to 343 K. No intermediates, viz. a rhodium–carbene complex, were detected. The spectra until room temperature (303 K) were that of EtDA and the rhodium complex. At 333 K after 2 h, the reaction was complete with maleate and fumarate as the only products. Throughout the reaction, no appreciable amounts of an intermediate were accumulated to allow its detection.

4. Experimental

4.1. Instrumentation

Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets on a Nicolet 710 FT spectrophotometer. The ^1H -NMR (300.13 MHz), ^{11}B -NMR (96.29 MHz), and $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.47 MHz) spectra were performed on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR measurements were performed at 22°C . The ^{11}B -NMR chemical shifts are referenced to external $\text{BF}_3\cdot\text{OEt}_2$, while the ^1H and ^{13}C are referenced to SiMe_4 . Chemical shifts are reported in units of parts per million (ppm). According to the IUPAC convention, positive values of the chemical shifts are to high frequency. All coupling constant values are reported in Hertz. Catalytic hydrogenations were conducted in a 35-ml autoclave built at the workshop facility of the Universitat Autònoma de Barcelona. The autoclave was equipped with a water jacket, a rupture disk, a manometer, and sample and gas inlets. GC analyses were performed with a Shimadzu GC-15A instrument using an SPB-1 capillary column (Supelco; 30 m in length, 0.25 mm inner diameter, and 1 μm thickness stationary phase).



4.2. Materials

Unless otherwise noted, all manipulations were carried out under dinitrogen atmosphere using standard vacuum line techniques. Ethyl ether and THF were distilled from sodium benzophenone prior to use and the rest of the solvents were of reagent grade quality and were used without further purification. Methylene chloride and carbon tetrachloride were distilled from CaCl_2 prior to use. 1-Hexene (Aldrich) was freshly distilled from CaH_2 prior to use. The rest of the solvents were of reagent grade quality and were used without further purification. *o*-Carborane (Dexsil Chemical Corp.), a 1.6 M solution of *n*-BuLi in hexane, and 3,4-dimercaptotoluene (Aldrich) were used as received. All organic and inorganic salts were of analytical reagent grade and were used as received. All reagents for olefin cyclopropanation were obtained from Acros and Aldrich. The starting rhodium compounds $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ and $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_3\text{H}]$ were synthesized according to the literature procedure [39].

4.3. Synthesis of 1,2- μ - $S(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_{10}\text{H}_{10}$ (**1**)

To a three-necked round-bottomed flask (50 ml) fitted with a dinitrogen inlet/outlet containing deoxygenated dry methylene chloride (10 ml) and *N*-chlorosuccinimide (0.93 g, 3.47 mmol) was added a solution of 3,4-dimercaptotoluene (0.54 g, 3.47 mmol) in methylene chloride (10 ml). After stirring for 30 min at room temperature the solid was filtered. The solvent was evaporated and 20 ml of dry CCl_4 was added. Insolubles were separated by filtering through celite. The solvent was evaporated and 30 ml of dry ethyl ether was added. To a round identical flask containing deoxygenated dry ethyl ether (100 ml) was added *o*-carborane (0.50 g, 3.47 mmol). The solution was cooled (ice water) and *n*-BuLi

(4.5 ml, 6.9 mmol, 1.4 M) was added. After stirring for 30 min at the ice water temperature, the mixture was allowed to stir at room temperature for 30 min and then cooled again (ice water). The contents of the first flask were syringed into the carborane solution. After stirring for 1 h at the ice water temperature and 1 h at room temperature the solid was filtered and the solvent evaporated. Purification by column chromatography (silica gel, 66% hexane/ H_2CCl_2) yielded analytically pure **1** after solvent evaporation as a white solid. Yield: 0.72 g (70%). $^1\text{H-NMR}$ (CDCl_3): δ = 0.00–2.80 (br, 10H, B–H), 2.38 (s, 3H, –CH₃), 7.20 (d, 1H, $^2J(\text{H,H})$ = 8, $\text{C}_{\text{aryl}}\text{--H}$), 7.26 (s, $\text{C}_{\text{aryl}}\text{--H}$), 7.55 (d, 1H, $^2J(\text{H,H})$ = 8, $\text{C}_{\text{aryl}}\text{--H}$); $^1\text{H}\{^{11}\text{B}\}\text{-NMR}$ (CDCl_3): δ = 2.19 (br s, B–H), 2.33 (br s, B–H), 2.38 (s, 3H, –CH₃), 2.54 (br s, B–H), 7.20 (d, 1H, $^2J(\text{H,H})$ = 8, $\text{C}_{\text{aryl}}\text{--H}$), 7.26 (s, 1H, $\text{C}_{\text{aryl}}\text{--H}$), 7.55 (d, 1H, $^2J(\text{H,H})$ = 8, $\text{C}_{\text{aryl}}\text{--H}$); $^{11}\text{B-NMR}$ (CDCl_3): δ = –3.7 (d, $^1J(\text{B,H})$ = 154, 2B), –8.4 (d, $^1J(\text{B,H})$ = 154, 4B), –10.0 (d, $^1J(\text{B,H})$ = 144, 4B); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CDCl_3): δ = 20.7 (s, –CH₃), 130.2, 130.6, 131.0, 141.8 (s, – C_{aryl}); IR (KBr), $\nu(\text{cm}^{-1})$: 2610 (B–H); $\text{C}_9\text{H}_{16}\text{B}_{10}\text{S}_2$ (296.46)—Calc.: C, 36.46; H, 5.44; S, 21.63; Found: C, 36.79; H, 5.33; S, 21.35%.

4.4. Synthesis of $[\text{N}(\text{CH}_3)_4][7,8\text{-}\mu\text{-S}(4'\text{-C}_6\text{H}_3(\text{CH}_3))\text{S-C}_2\text{B}_9\text{H}_{10}]$ ($[\text{N}(\text{CH}_3)_4][\textbf{2}]$)

Partial degradation of **1** was achieved following the general procedure described in the literature [29]. Yield: 0.6 g (95%); $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): δ = –2.40 (br, 1H, B–H–B), 0.00–2.80 (br, 9H, B–H), 2.26 (s, 3H, –CH₃), 3.40 (s, 12H, $\text{N}(\text{CH}_3)_4$), 6.98 (d, 1H, $^2J(\text{H,H})$ = 8, $\text{C}_{\text{aryl}}\text{--H}$), 7.10 (s, 1H, $\text{C}_{\text{aryl}}\text{--H}$), 7.13 (d, 1H, $^2J(\text{H,H})$ = 8, $\text{C}_{\text{aryl}}\text{--H}$); $^1\text{H}\{^{11}\text{B}\}\text{-NMR}$ ($(\text{CD}_3)_2\text{CO}$): δ = –2.40 (s, 1H, B–H–B), 0.21 (br s, B–H), 0.73 (br s, B–H), 1.30 (br s, B–H), 1.47 (br s, B–H), 2.14 (br s, B–H), 2.26 (s, 3H, –CH₃), 3.40 (s, 12H, $\text{N}(\text{CH}_3)_4$), 6.98 (d, 1H, $^2J(\text{H,H})$ = 8, $\text{C}_{\text{aryl}}\text{--H}$), 7.10 (s, 1H, $\text{C}_{\text{aryl}}\text{--H}$), 7.13 (d,

^1H , $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$); ^{11}B -NMR ($(\text{CD}_3)_2\text{CO}$): $\delta = -8.6$ (d, $^1J(\text{B,H}) = 139$, 2B), -12.4 (d, $^1J(\text{B,H}) = 165$, 1B), -17.3 (d, $^1J(\text{B,H}) = 143$, 4B), -32.4 (d, $^1J(\text{B,H}) = 193$, 1B), -34.8 (d, $^1J(\text{B,H}) = 145$, 1B); $^{13}\text{C}\{^1\text{H}\}$ -NMR ($(\text{CD}_3)_2\text{CO}$): $\delta = 20.1$ (s, $-\text{CH}_3$), 55.2 (s, $\text{N}(\text{CH}_3)_4$), 127.6 , 129.1 , 129.8 , 136.2 , 136.8 , 143.9 (s, $-\text{C}_{\text{aryl}}$); IR (KBr), $\nu(\text{cm}^{-1})$: 2530 (B–H); $\text{C}_{13}\text{H}_{28}\text{NB}_6\text{S}_2$ (359.79)—Calc.: C, 43.40; H, 7.84; N, 3.89; S, 17.82; Found: C, 43.47; H, 7.84; N, 3.79; S, 17.70%.

4.5. Synthesis of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(2)][2]$ (**3**)

Deoxygenated boiling ethanol (9 ml) containing $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_4]$ (50 mg, 0.08 mmol) and $[\text{N}(\text{CH}_3)_4][2]$ (58 mg, 0.16 mmol) was boiled for 4 h. By filtering the warm mixture an orange solid was isolated. The solid was washed with water, warm ethanol, and ethyl ether to yield an analytically pure solid. Yield: 75 mg (84%). ^1H -NMR ($(\text{CD}_3)_2\text{CO}$): $\delta = -2.43$ (br, 1H, B–H–B), -1.21 (br, 1H, B–H–B), 0.00 – 2.50 (br, 18H, B–H), 1.81 (s, 15H, $\text{C}^*\text{--CH}_3$), 2.28 (s, 3H, $-\text{CH}_3$), 2.42 (s, 3H, $-\text{CH}_3$), 6.98 (d, 1H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$), 7.10 (s, 1H, $\text{C}_{\text{aryl}}\text{--H}$), 7.13 (d, 1H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$), 7.43 (d, 1H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$), 7.53 (s, 1H, $\text{C}_{\text{aryl}}\text{--H}$), 7.56 (d, 1H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$); ^{11}B -NMR ($(\text{CD}_3)_2\text{CO}$): $\delta = -7.3$, -8.6 (d, $^1J(\text{B,H}) = 137$), -12.6 , -14.1 (d, $^1J(\text{B,H}) = 138$), -17.3 (d, $^1J(\text{B,H}) = 145$, 5B), -31.5 , -32.4 , -34.8 , -35.6 ; IR (KBr), $\nu(\text{cm}^{-1})$: 2530 (B–H); $\text{C}_{38}\text{H}_{62}\text{B}_{18}\text{Cl}_2\text{Rh}_2\text{S}_4$ (1118.46)—Calc.: C, 40.81; H, 5.59; S, 11.46; Found: C, 40.60; H, 5.27; S, 11.37%. A red crystal suitable for X-ray analysis was grown from THF and ethanol.

4.6. Synthesis of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{H})(2)][2]$ (**4**)

Deoxygenated boiling ethanol (10 ml) containing $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_3(\text{H})]$ (48 mg, 0.08 mmol) and $[\text{N}(\text{CH}_3)_4][2]$ (58 mg, 0.16 mmol) was refluxed for 4 h. By filtering the warm mixture a red solid was separated. This was washed with warm ethanol and ethyl ether to yield an analytically pure solid. Yield: 48 mg (55%). ^1H -NMR ($(\text{CD}_3)_2\text{CO}$): $\delta = -12.16$ (t, $^1J(\text{Rh,H}) = 25$, 1H, Rh–H–Rh), -2.43 (br, 1H, B–H–B), -1.24 (br, 0.7H, B–H–B), -0.99 (br, 0.3H, B–H–B), 1.81 (s, 15H, $\text{C}^*\text{--CH}_3$), 2.21 (s, 3H, $-\text{CH}_3$), 2.45 and 2.50 (s, 3H, $-\text{CH}_3$), 6.98 (d, 1H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$), 7.10 (s, 1H, $\text{C}_{\text{aryl}}\text{--H}$), 7.13 (d, 1H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$), 7.43 (d, 0.7H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$), 7.53 (s, 0.7H, $\text{C}_{\text{aryl}}\text{--H}$), 7.56 (d, 0.7H, $^2J(\text{H,H}) = 8$, $\text{C}_{\text{aryl}}\text{--H}$), 7.66 (s, 0.6H, $\text{C}_{\text{aryl}}\text{--H}$), 7.70 (s, 0.3H, $\text{C}_{\text{aryl}}\text{--H}$); ^{11}B -NMR ($(\text{CD}_3)_2\text{CO}$): $\delta = -7.5$, -8.6 , -12.3 , -14.0 , -17.3 , -31.5 , -32.5 , -34.8 , -37.1 ; IR (KBr), $\nu(\text{cm}^{-1})$: 2530 (B–H), 1155 (Rh–H–Rh); $\text{C}_{38}\text{H}_{63}\text{B}_{18}\text{ClRh}_2\text{S}_4$ (1084.02)—Calc.: C, 42.10; H, 5.86; S, 11.83; Found: C, 41.82; H, 5.55; S, 11.56%.

Table 3

Selected bond lengths (Å) and angles (°) for **3**·THF

Bond lengths (Å)	
Rh(1)–Cl(1)	2.4425(18)
Rh(1)–Cl(2)	2.4273(19)
Rh(2)–Cl(1)	2.4415(19)
Rh(2)–Cl(2)	2.420(2)
Rh(1)–S(1)	2.424(2)
Rh(2)–S(2)	2.428(2)
S(1)–C(7)	1.812(7)
S(1)–C(12)	1.781(7)
S(2)–C(8)	1.799(7)
S(2)–C(13)	1.767(8)
S(3)–C(47)	1.796(8)
S(3)–C(52)	1.759(9)
S(4)–C(48)	1.803(9)
S(4)–C(53)	1.751(10)
C(7)–C(8)	1.529(9)
C(47)–C(48)	1.565(11)
Bond angles (°)	
Cl(1)–Rh(1)–Cl(2)	82.89(6)
Cl(1)–Rh(1)–S(1)	93.86(7)
Cl(2)–Rh(1)–S(1)	92.42(7)
Cl(1)–Rh(2)–Cl(2)	83.05(6)
Cl(2)–Rh(2)–S(2)	92.42(7)
Rh(1)–Cl(1)–Rh(2)	95.46(6)
Rh(1)–Cl(2)–Rh(2)	96.42(7)
C(12)–S(1)–Rh(1)	108.8(2)
C(7)–S(1)–Rh(1)	112.5(2)
C(8)–S(2)–Rh(2)	113.4(2)
C(13)–S(2)–Rh(2)	108.7(3)
C(12)–S(1)–C(7)	103.8(3)
C(13)–S(2)–C(8)	104.2(3)
C(52)–S(3)–C(47)	99.2(4)
C(53)–S(4)–C(48)	100.7(4)

4.7. X-ray diffraction study

Single-crystal data collection for **3**·THF was performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo- $\text{K}\alpha$ radiation and $\omega/2\theta$ scan mode ($2\theta_{\text{max}} = 50^\circ$). An empirical absorption correction was performed (ψ scans). The structure was solved by direct methods and refined on F^2 by the SHELX-97 program package [40]. The Cp^* ion coordinated to Rh(2) is disordered assuming two orientations. The disordered Cp^* ion was refined as idealized rigid group. The partially occupied C atoms of the disordered Cp^* group were refined with isotropic but rest of the non-hydrogen atoms with anisotropic thermal displacement parameters. Hydrogen atoms were treated as riding atoms using the SHELX-97 default parameters. Oxygen atom of the THF solvent could not be very reliably identified. Selected bond lengths and angles are listed in Table 3 and crystallographic data are presented in Table 4.

4.8. General procedure for the hydrogenation of 1-hexene

To a Schlenk flask containing 10 ml of THF was added 1×10^{-5} mmol of rhodium complex, after the

Table 4
Crystallographic data for 3·THF

Empirical formula	C ₄₂ H ₇₀ B ₁₈ Cl ₂ ORh ₂ S ₄
Formula weight	1190.52
Temperature (°C)	21
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)
Unit cell dimensions	
<i>a</i> (Å)	11.985(3)
<i>b</i> (Å)	20.361(3)
<i>c</i> (Å)	11.881(3)
α (°)	91.887(17)
β (°)	101.90(2)
γ (°)	89.032(15)
<i>V</i> (Å ³)	2835.3(11)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ^{−3})	1.395
μ (cm ^{−1})	8.57
Number of reflections collected	10479
Number of unique reflections	9960
<i>R</i> _{int}	0.0324
<i>F</i> (0 0 0)	1216
Goodness-of-fit on <i>F</i> ²	1.039
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0564
<i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.1380

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$$

$$^b wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)|^2] / [\Sigma w|F_o|^2]^{1/2}.$$

dissolution of the solid 3×10^{-2} mmol of 1-hexene were added (when Et₃N was used, 1.8×10^{-2} mmol was added to the same Schlenk). Meanwhile, the autoclave had been evacuated and fitted with hoses supplying water maintained at the desired temperature (*T* = 25 °C) from the constant-temperature bath and the gas inlet had been connected to the H₂ line. Then, the mixture of the Schlenk was rapidly transferred to the autoclave through the sample inlet via syringe, the gas inlet was opened, and the system was pressurized to 12 bar of H₂. The magnetic stirring was started and the timing counter reset. From the addition of the alkene to the reset of the timing counter no more than 3 min passed. After 1.5 h, the autoclave was vented and dismantled, and the composition of the solution was analyzed by capillary GC.

4.9. General procedure for the cyclopropanation experiments

A round-bottomed flask was charged with the rhodium complex (0.0075 mmol) and appropriate olefin (20 mmol) and heated at 60 or 100 °C. EtDA (1 mmol) in 1 ml of the olefin was added via a pump syringe over 4 h and the reaction mixture was allowed to stir for 24 h prior to GC analysis.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited

with the Cambridge Crystallographic Data Centre, CCDC No. 100559 for 3·THF. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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