Annex

(Treballs pendants de publicació)
Synthesis and characterization of new phosphine $\eta^5$-Ru(II) complexes containing monoanionic charge compensated ligands

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Ruthenocarbaboranes complexes of formula [3-H-3,3-(PPh3)2-8-L-3,1,2-RuC2B9H10] (L = SMe2 (2a), SEt2 (2b), S(CH2)4 (2c), SEtPh (2d)) and [1-Me-3-H-3,3-(PPh3)2-8-L-3,1,2-RuC2B9H10] (L = SMe2 (2e), SEt2 (2f)) were prepared by reaction of the respective monoanionic charge-compensated ligands [10-L-7,8-C2B9H10] and [7-Me-10-L-7,8-C2B9H10] with [RuCl2(PPh3)3]. Similarly, complexes [3-H-3,3,8-(PPh3)2-3,1,2-RuC2B9H10] (4a) and [3-H-3,3,8-(PPh3)2-3-PPhMe-3,1,2-RuC2B9H10] (4b) were prepared for the corresponding phosphonium ligands. The reaction is done in one-pot by reacting the ligand with the Ru(II) complex in a 1.5:1 ratio. All compounds have been fully characterized by multinuclear NMR spectroscopy, and the molecular structures for 2a and 2f have been elucidated by single crystal X-ray diffraction analysis. The Ru(II) atom in this complex is on the open face of the monoanionic charge-compensated ligand adopting a pseudo-octahedral coordination. Formally, three positions are supplied by the C2B3 open face, two PPh3 occupy two other positions and a hydride fulfill the remaining one. The hydride complexes were generated with no special reagent while they result from a dehalogenation in the presence of ethanol.

Introduction

First examples of metallacarboranes were prepared about 35 years ago by Hawthorne et al., using the dicarbobollide, [C2B9H11]+ as ligand to form closo-M-C3B6 isocehedral clusters. This ligand has been compared to [C2H4]2, as both behave as formal 6-electron donors to metal atoms via $\eta^5$-face bonding. Thus, a great number of researchers from a variety of scientific backgrounds have developed this field. However, both type of ligands differ in their charges. To establish detailed comparisons between analogous cyclopentadienyl-metal and carborane-metal compounds, charge-compensated monoanionic carborane ligands of the type [LC2B3H10]+ (L = pyridine, THF, SR2, PPh3, etc) have been described. Many transition metal (Rh, Fe, Ru, Pd, Mo, etc) complexes of these monoanionic carboranes have been prepared and fully characterized. The majority of these charge-compensated complexes contain the carborane ligands with the substituent at the 9 position, [9-L-7,8-C2B9H10]+ or [9-L-7,8-R2-C2B9H10]+. Ligands with the substituent at the 10 position, [10-L-7,8-nido-C2B9H10]+ have been much less studied. The preparation of closo metallic complexes with monoanionic charge-compensated carborane ligands bearing an SR2 or PR3 group at the B(9) atom has been accomplished using two methods. The first one, generally used for [9-SMe2-nido-7,8-C2B9H9]3+ ligands, consists in the addition of the thallium salts of the ligand to a solution of the metallic complex in CH2Cl2. The second method consists in the deprotonation of the charge-compensated carborane ligand with KOH or NaH in a solvent at reflux, for several hours, followed by treatment with a convenient source of metal. The latter has also been used to prepare the few known complexes of [10-L-7-nido-7,8-C2B9H9]3+ ligands with Co, Mo and Fe.

We describe here the first systematic study of the preparation of a series of Ru(II) metallacarborane complexes incorporating the monoanionic charge-compensated ligands [10-L-7-R-7,8-nido-C2B9H9] (L = SMe2, SEt2, S(CH2)4, SEtPh, PPh3, PPhMe; R = H, Me). A new and rapid method involving a one pot reaction is described to synthesize the complexes in pure form. The aim in designing and preparing these complexes was their controlled radical polymerization, ATRP and Kharasch addition reactions. Some results about their catalytic activity have already been published by us. Crystal structures of [3-H-3,3-(PPh3)2]-SMe2-3,1,2-RuC2B9H10 and [3-H-3,3,8-(PPh3)2]-3,1,2-RuC2B9H10 are also described. Some aspects of this work have been previously reported as a communication.

Results

Synthesis and Characterization of [3-H-3,3-(PPh3)2]-SMe2-3,1,2-RuC2B9H10 and [1-Me-3-H-3,3-(PPh3)2]-SMe2-3,1,2-RuC2B9H10]

The reaction of 10-L-7,8-C2B9H10 (L = SMe2 (1a), SEt2 (1b), S(CH2)4 (1c), SEtPh (1d)) with t-BuOK and [RuCl2(PPh3)3] in 1:1:1.5:1 ratio in EtOH, at 50 °C for one hour, resulted in the formation of yellow solids of general formula [3-H-3,3-(PPh3)2]-SMe2-3,1,2-RuC2B9H10 and [1-Me-3-H-3,3-(PPh3)2]-SMe2-3,1,2-RuC2B9H10]. (L = SMe2, SEt2, S(CH2)4, SEtPh) and [RuCl2(PPh3)3]. Similar reaction for [3-H-3,3,8-(PPh3)3]-3,1,2-RuC2B9H10] (4a) and [3-H-3,3,8-(PPh3)2]-3-PPhMe-3,1,2-RuC2B9H10] (4b) were prepared for the corresponding phosphonium ligands. The reaction is done in one-pot by reacting the ligand with the Ru(II) complex in a 1:5:1 ratio. All compounds have been fully characterized by multinuclear NMR spectroscopy, and the molecular structures for 2a and 2d have been elucidated by single crystal X-ray diffraction analysis. The Ru(II) atom in this complex is on the open face of the monoanionic charge-compensated ligand adopting a pseudo-octahedral coordination. Formally, three positions are supplied by the C2B3 open face, two PPh3 occupy two other positions and a hydride fulfill the remaining one. The hydride complexes were generated with no special reagent while they result from a dehalogenation in the presence of ethanol.

Scheme 1 Formation of [1-R-3-H-3,3-(PPh3)2]-SMe2-3,1,2-RuC2B9H10].

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1. O. Tutusaus is enrolled in the UAB PhD program.
Table 1 Chemical shift of the protons corresponding to the substituent on the B(10) for complexes 2a-f.

<table>
<thead>
<tr>
<th>Complex</th>
<th>CH₃</th>
<th>S-CH₂</th>
<th>CH₂</th>
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<tr>
<td>2a</td>
<td>2.28 (6H)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2b</td>
<td>1.21 (6H)</td>
<td>2.67 (2H)</td>
<td>3.09 (2H)</td>
</tr>
<tr>
<td>2c</td>
<td>-</td>
<td>2.82 (2H)</td>
<td>1.82 (2H)</td>
</tr>
<tr>
<td>2d</td>
<td>0.84 (3H)</td>
<td>2.95 (2H)</td>
<td>-</td>
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<tr>
<td>2e</td>
<td>1.79 (3H)</td>
<td>2.93 (2H)</td>
<td>-</td>
</tr>
<tr>
<td>2f</td>
<td>2.64 (3H)</td>
<td>2.35 (2H)</td>
<td>1.50 (3H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.77 (1H)</td>
</tr>
</tbody>
</table>

* The number between brackets corresponds to the protons area.

The spectroscopic data and elemental analysis of 2a-f were consistent with the proposed formula. The IR spectra of these complexes displayed a v(B-H) absorption, between 2520 and 2551 cm⁻¹. Low intensity bands were observed in the region 1600–2100 cm⁻¹ attributable to v(Ru-H). The absorptions at 1433, 1096, 744 and 695 cm⁻¹ are typical of PPh₃ containing compounds.

The ¹H NMR spectra for compounds 2a-f showed no resonances attributable to B-H-B, near –1 ppm, indicating the formation of closo-species. Resonances assigned to Ru-H were found ca. –10.30 ppm for compounds 2a-d, and near –12.10 ppm for 2e-f. These Ru-H resonances present different coupling patterns as a function of the symmetry of the molecule (Fig. 1). In the case of symmetric compounds 2a-c, they appear as a triplet (2J(PP)= 33-34 Hz) (Fig. 1a), however for the asymmetric compounds 2d-f the signal appears as a doublet of doublets with two different ³J(PP) (Fig. 1b). In addition, resonances attributable to aromatic hydrogen atoms from the phenyl groups, Carborane-H (Cc-H), and hydrogen atoms on the sulfonium groups are found for 2a-f. The Cc-H resonances for complexes 2a-c appear as a singlet around 2.17 ppm, while the Cc-H proton of 2e-f is observed at 2.21 ppm. Compound 2d, with non-equivalent substituents on sulfur, displays two Cc-H signals at 2.56 and 1.75 ppm whose average value is comparable to the Cc-H chemical shift for 2a-c. Methyl proton resonances for 2a, 2b, 2e and 2f are given in Table 1. The S-CH₂ protons in complexes 2b-d,f are magnetically non-equivalent, one for the geminal protons (³J(HH) = 13.4 Hz) and a second one for the neighbor CH₂ or CH₃ protons (³J(HH) = 7.4 Hz).

The ¹³C{¹H} NMR spectra for 2a-f display peaks corresponding to the organic groups bonded either to the sulfur and/or phosphorus atoms. The ¹¹B{¹H} spectra for 2a-f was in agreement with the proposed symmetry; in all complexes the resonance at lower field was assigned to the sulfur-bearing atom B(8) by comparison with the ¹¹B NMR spectra. The ³¹P{¹H} NMR spectra for 2a-c display singlets in agreement with the presence of a symmetry plane in the molecule, which were split into doublets in the ³¹P NMR spectra with ³J(PP) ca. 30 Hz; a doublet of doublets is found for 2d-f due to the non-equivalence of the two phosphorus atoms, as indicated by the ³J(PP), ranging 25-30 Hz (Table 2).

### Table 2 ³¹P chemical shifts reported in ppm, ³J(PP) values and ³J(PP) values expressed in Hz for compounds 2a-f.

<table>
<thead>
<tr>
<th>Complex</th>
<th>δₚ</th>
<th>³J(PP)</th>
<th>³J(PP)</th>
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<tr>
<td>2a</td>
<td>55.88</td>
<td>33</td>
<td>-</td>
</tr>
<tr>
<td>2b</td>
<td>55.77</td>
<td>33</td>
<td>-</td>
</tr>
<tr>
<td>2c</td>
<td>55.80</td>
<td>34</td>
<td>-</td>
</tr>
<tr>
<td>2d</td>
<td>58.18 / 53.01</td>
<td>31 / 30</td>
<td>31</td>
</tr>
<tr>
<td>2e</td>
<td>52.31 / 46.72</td>
<td>40 / 30</td>
<td>26</td>
</tr>
<tr>
<td>2f</td>
<td>51.98 / 46.71</td>
<td>40 / 31</td>
<td>26</td>
</tr>
</tbody>
</table>

Following a similar procedure as for the preparation of 2a-f, the reaction of the potassium salts of [10-PPh₃-7,8-C₂B₉H₁₀](3a) and [10-PMePh₃-7,8-C₂B₉H₁₀](3b) with [RuCl₂(PPh₃)₃] led to the formation of complexes [3-H-3,3,8-(PPh₃)₃-3,1,2-RuC₂B₉H₁₀] (4a) and [3-H-3,3-(PPh₃)₂-8-PPh₂Me-3,1,2-RuC₂B₉H₁₀] (4b), respectively (see Scheme 2).

![Scheme 2 Formation of [3-H-3,3-(PPh₃)₂-8-PPh₂R'-3,1,2-RuC₂B₉H₁₀].](image)

The IR spectra indicated the presence of the Ru-H bond through low intensity bands in the region 2050-2100 cm⁻¹. The ¹H NMR spectra for 4a and 4b confirmed the Ru-H bond by the resonance observed near –10 ppm, as a doublet of triplets (³J(PP) = 33 Hz, ³J(PP) = 11-12 Hz) (Fig. 1c), the latter splitting being due to coupling to phosphorus of the phosphonium moiety, B-PPh₃. Resonances due to the two Cc-H protons are observed as a singlet around 3 ppm, and those due to the phenyl groups are found in the 6.90-7.50 ppm region.

The ³¹P{¹H} NMR spectra of 4a, at room temperature, has shown a singlet at 58.59 ppm, attributed to two equivalent PPh₃ ancillary ligands, and a tetraplet at 12.70 ppm due to the B-PPh₃ group (³J(BP) = 126 Hz). The equivalent resonances for 4b are observed at 57.98 ppm, for PPh₃, and 2.17 ppm, for the B-PPh₂Me group (³J(BP) = 140 Hz), the resonances at 58.59 ppm for 4a and 57.98 ppm for 4b become a doublet with ³J(P,H) = 33 Hz in the ³¹P NMR spectra. A doublet is observed both in the ¹¹B{¹H} and ¹¹B NMR spectra at ~5.3 ppm for 4a and ~7.6 ppm for 4b, due to the B-P coupling.

![Fig. 1 Selected ¹H NMR portion corresponding to the hydride region in (a) compound 2b, (b) compound 2d and (c) compound 4a.](image)
**X-ray Diffraction Studies of [3-H-3,3-(PPh3)2-8-SMe2-3,1,2-RuC2B9H10] (2a)**

Yellow crystals of 2a crystallized from a 1:1 CH2Cl2/hexane solution, under nitrogen, to give yellow crystals adequate for X-ray diffraction analysis. The ORTEP view of 2a·CH2Cl2 is represented in Figure 2. Crystal data and selected interatomic dimensions being listed in Table 3 and 4, respectively. The single-crystal structure analysis confirmed a Ru(II) complex in which the metal adopts a pseudo-octahedral coordination, with three formal coordination sites occupied by the C2B3 open face, two by the PPh3 ligands and the remaining site by the hydride. The present coordination is similar to that observed in [3-H-3,3-(PPh3)2-3,1,2-RhC2B9H11], with the P-M-P angle larger and P-M-H angles smaller than the expected values for typical octahedral arrangements. The large P1-Ru3-P2 angle can be due to intramolecular crowding of the phosphine ligands, as is suggested by the short C···C distances observed between the C11 to C16 and the C41 to C46 rings (distance C11···C42 = 3.166(13) Å and distance C16···C42 = 3.236(16) Å). The distance from Ru3 to the open face of C2B9, defined as the mean plane of C1, C2, B4, B7 and B8, is 1.735(5) Å, with coordination distances to these atoms ranging from 2.203(11) Å to 2.307(10) Å. These distances are larger than those observed in rhutenium metallacarboranes with pentamethylcyclopentadienyl instead of phosphine ligands. The τ parameter, which, in this case, represents the torsion angle B4-B8-S-S(lone pair), is -36.8(1.5)º. This large value and the fact that the B4-B8-S angle is larger than B7-B8-S suggest that the interaction S(lone pair)···H4 is not dominating of the sulphonium group conformation. Like in the case of [3-(Cp*)-4-SMe2-3,1,2-closo-RuC2B9H10] and similar compounds, this conformation can be explained by steric repulsion between the SMe2 hydrogen and the phosphine groups of the neighbour molecule, as there are two short H···H distances observed between the hydrogens of these groups: distance H1C···H25(1+X, Y, Z) of 2.423 Å and distance H2A···H64(1+X, Y, Z) of 2.424 Å.

**X-ray Diffraction Studies of [3-H-3,3,8-(PPh3)3-3,1,2-RuC2B9H10] (4a)**

Crystals of 4a suitable for a single-crystal X-ray study were obtained by slow evaporation of a CH2Cl2/hexane/PPh3 solution of the complex. A drawing of the compound may be seen in Figure 3, with crystal data and selected interatomic dimensions listed in Table 5.
Intramolecular crowding of the phenyl groups in the PPh$_3$ ligands is evidenced by the Ru(3)-P2 angle, 96.12(10)$^\circ$ and 95.26(4)$^\circ$ respectively, and the shorter distance to that for the phosphonium group. In both complexes, Nido to B4, B7 and B8 are found in the range of 2.285(4) Å to 2.312(4) Å, probably due to the presence of a less crowded sulfonium substituent, instead of the phosphonium one. In complex 4a, the large P1-Ru(3)-P2 angle, 96.12(10)$^\circ$ and 95.26(4)$^\circ$ respectively, and the short C1-C distances between different rings have been found (C21--C46 = 3.157(9), C22--C16 = 3.266(8), C52--C66 = 3.157(9), C46--C46 = 3.182(9) Å) which evidence again the intramolecular crowding of the phenyl groups in the PPh$_3$ ligands.

In complex 4a, the angles B4-B8-P3 and B7-B8-P3 are very close, while the angle Ru3-B8-P3 is longer than Ru3-B8-S in 2a, suggesting a larger steric repulsion between the phosphonium group and the PPh$_3$ ligands. This repulsion may be clearly observed in the crystal structure, because the orientation of the PPh$_3$ groups coordinated to the metal with respect to the substituent on the B(8) is different for both complexes; in 4a the PPh$_3$ groups are situated as far as possible from the phosphonium group.

**Discussion**

To synthesize Ru(II) complexes of [10-L-nido-7,8-C$_2$B$_9$H$_{10}$] ligands, preliminary studies of the reaction of [RuCl$_2$(PPh$_3$)$_3$] with 1a were done using a 1:1:1 ratio of 1a/t-BuOK/Ru(II). The K[t-BuO] in EtOH removes the open face proton forming the partially charge-compensated monoanionic carborane ligand [10-L-nido-7,8-C$_2$B$_9$H$_{10}$] that is made to react with [RuCl$_2$(PPh$_3$)$_3$]. In one hour, a precipitate containing a mixture of 2a (ca. 90%) and the starting [RuCl$_2$(PPh$_3$)$_3$] (ca. 10%) was obtained, as indicated by the NMR spectroscopy. Further addition of K[t-BuO] (50%) leads to the transformation of the remaining [RuCl$_2$(PPh$_3$)$_3$] to a carbonyl containing Ru complex (vide infra), as a result of the base catalyzed decarboxylation of alcohols.$^{11}$ These reaction conditions produce 2a impurified with a complex of the type [RuH(CO)(PPh$_3$)$_3$]. Pure 2a is obtained in 70% yield by extraction with ethyl acetate. An improved procedure consists in increasing the ratio ligand/K[t-BuO][RuCl$_2$(PPh$_3$)$_3$] to 1.5:1.5:1. In this way, complexes 2a-f were obtained as pure solids after 30 minutes of reaction, in very good yield. The excess of ligand might be recovered from the filtered solution in the neutral form, by protonation and extraction in organic solvents.

The room temperature $^{31}$P{H} NMR spectra for compounds 2a-c and 4a,b,c has shown the equivalency of both ancillary PPh$_3$ ligands, which is in agreement with the existence of a mirror plane in the molecule. A $^{31}$P{H} NMR dynamic study for 2a-c and 4a,b was carried out so as to investigate the rotational behavior of these complexes. Interestingly, the $^{31}$P{H} NMR spectra for compounds 2a-c were invariant from 25 °C to -95 °C. The equivalence of the two phosphine ligands was removed for compounds 4a,b in lowering temperature (see Figure 4). A transition from an A$_2$ spin system to an AB spin system was observed. If the $^{31}$P{H} NMR spectra of 4a at room temperature is considered, only a singlet at 58.59 ppm is found. Near -60 °C the decoalescence of this resonance takes place and two different phosphorus signals were clearly observed at -95 °C. These resonances consist of two doublets with a $3J$(PP) = 38 Hz and were consistent with an AB spin system. This fact reveals a dynamic process, most probably a rotation of the metal fragment upon the open face of the cage, which breaks down at low temperature. Therefore, it is important to remark that even though both 4a,b are symmetrical molecules, the AB spin system at low temperature implies the absence of a mirror plane bisecting both the carborane ligand and the metal fragment. This unusual feature can be rationalized in terms of conformational isomers (see Figure 5). The NMR data indicate that rotamers I and II, for which one phosphorus signal is observed, are the predominant conformations at higher temperatures; while rotamer III, for which two phosphorus resonances with equal intensities are observed, is the major species at low temperature.$^{12}$ The fact that in 4a,b a non-equivalence of the phosphine groups is generated at low temperature while this is not observed for the equivalent ones with sulfonium groups, 2a-c, is a clear consequence of the larger steric hindrance for the moiety PRPh$_3$ respect to SR$_2$.

The characterization of the ruthenacarborane complexes unambiguously indicated that a hydride ligand was present in the molecule. This was initially unexpected since the starting Ru(II) complex contained chloride ligands and the bridging B-H-B had been removed on purpose. However, it is known that some chloride Ru systems can be converted into hydride or deuteride in the presence of a base in alcoholic solutions.$^{13,14}$ For instance, [CpRuL$_2$Cl] and [Cp*RuL$_2$Cl] can be easily converted into...
Method I) The procedure was similar as before using a 1.5:1 ligand/Ru(II) complex ratio: 1a (100 mg, 0.514 mmol), t-BuOK (58 mg, 0.514 mmol), and [RuCl2(PPh3)3] (329 mg, 0.342 mmol). The mixture was stirred for one hour at this temperature to form a yellow solid. The solid was filtered off and washed with two 10 mL portions of water, 10 mL of cold ethanol and two 10 mL portions of warm hexane. Finally, the solid was dried in vacuo. Compound (2a) was obtained as a yellow solid (252 mg, 90 %) respect to the metal. (Found: C, 58.16; H, 5.50; S, 3.61. C42H49B9P2SRu requires C, 58.83; H, 5.77; S, 3.79 %). Method II) The process was the same as for compound 2a using 100 mg (0.484 mmol) of 1b, 50 mg (0.484 mmol) of K[BF4] and 286 mg (0.299 mmol) of [RuCl2(PPh3)3] in 10 mL of deoxygenated ethanol (Method II). The mixture was stirred for 1 h at 50 °C obtaining yellow suspension. The solid was filtered and washed as described above to give 2b (238 mg, 94 %), (Found: C, 59.02; H, 5.84; S, 3.43. C36H43B9P2SRu requires C, 59.47; H, 6.06; S, 3.78 %). Method III) The process was the same as for compound 2a using 100 mg (0.484 mmol) of 1b, 50 mg (0.484 mmol) of K[BF4] and 286 mg (0.299 mmol) of [RuCl2(PPh3)3] in 10 mL of deoxygenated ethanol (Method II). The mixture was stirred for 1 h at 50 °C obtaining yellow suspension. The solid was filtered and washed as described above to give 2b (238 mg, 94 %), (Found: C, 59.02; H, 5.84; S, 3.43. C36H43B9P2SRu requires C, 59.47; H, 6.06; S, 3.78 %).

Conclusion
These results demonstrate the preparation of ruthenacarborane complexes from 7-R-10-L-7,8-C2B9H10 charge-compensated ligands, through a very simple one-pot reaction of the ligands with [RuCl2(PPh3)3] after deprotonation with K[BF4]. The new closo-complexes have shown, after full characterization, to posses two PPh3 groups and a hydride ligand in their molecule.

Experimental
General Procedures
Unless otherwise noted, all manipulations were carried out under a dinitrogen atmosphere using standard vacuum line techniques. Solvents were purified by distillation from appropriate drying agents before use. Deuterated solvents for NMR (Flurochem) were freeze-pump-thawed three times under N2 and transferred to the NMR tube using standard vacuum line techniques. The reagents 1a-c, 1d-f, 2a, 3b, 3c, and [RuCl2(PPh3)3] were prepared according to literature methods. Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyser. IR spectra were recorded with KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The 1H NMR (300.13 MHz), 13C{1H} (75.47 MHz), 11B, 11B{1H} NMR (86.29 MHz) and 11B{1H} NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories at room temperature. All NMR measurements were performed in deuterated solvents at 22 °C. Chemical shift data for 1H and 13C{1H} NMR spectra were referenced to SiMe4, those for 11B{1H} and 11B{1H} NMR spectra were referenced to external BF3·Et2O and those for 31P{1H} NMR spectra were referenced to external external 85 % H3PO4 (minus values upfield). Chemical shifts were reported in ppm, followed by a description of the multiplet (e.g. d = doublet), its relative intensity and observed coupling constants (in Hz).

Synthesis of the complex [3-H-3,3-(PPh3)-8-SMe2-3,1,2-RuC2B9H10] (2a)

Method I) To a deoxygenated solution of ethanol (10 mL) containing 1a (100 mg, 0.514 mmol) was added K[BF4] (58 mg, 0.514 mmol). The mixture was heated at 50 °C, and [RuCl2(PPh3)3] (493 mg, 0.514 mmol) was added. The mixture was stirred for one hour at 50 °C, to observe a brown-yellow precipitated. At this point a 50% more of t-BuOK was added to obtain a yellow solid after 30 minutes stirring. The solid was filtered off and washed with two 10 mL portions of water, 10 mL of cold ethanol and two 10 mL portions of warm hexane. The resulting solid was treated with ethyl acetate to separate a white solid and a yellow solution. The solution was evaporated in vacuo to give a yellow solid (2a). Yield (337 mg, 70 %) respect to the ligand.
(C$_2$H$_5$)$_3$: 12.93 (s, CH$_3$), 38.15 (s, S-CH$_3$) and 127.70-139.90 (C$_6$H$_5$).

Synthesis of the complex [1-Me-3-H-3,3-(PPh$_3$)$_2$-8-SMe-3,1,2-RuC$_2$B$_9$H$_{10}$] (2e)

The process was the same as for compound 2a using 100 mg (0.423 mmol) of [RuCl$_2$(PPh$_3$)$_3$] in 10 mL of deoxygenated ethanol. The mixture was stirred for 1 h at 50 ºC to give orange solid. The solid was filtered and washed as described above to give 2e (227 mg, 85%) (Found: C, 59.80; H, 5.54; S, 3.60; C$_{56}$H$_{56}$B$_9$P$_3$Ru requires C, 65.92; H, 5.53% ). The process was the same as for compound 2a using 100 mg (0.100 mmol) of [RuCl$_2$(PPh$_3$)$_3$] in 10 mL of deoxygenated ethanol. The mixture was stirred for 2 days at 50 ºC to give yellow solid which was filtered and washed as described above to give 4a (214 mg, 88%) (Found: C, 63.92; H, 5.68; S, 2.27; C$_{51}$H$_{54}$B$_9$P$_3$Ru requires C, 63.92; H, 5.68% ).

Synthesis of the complex [1-Me-3-H-3,3-(PPh$_3$)$_2$-8-SEt-3,1,2-RuC$_2$B$_9$H$_{10}$] (2f)

The process was the same as for compound 2a using 100 mg (0.282 mmol) of [RuCl$_2$(PPh$_3$)$_3$] in 10 mL of deoxygenated ethanol. The mixture was stirred for 1 h at 50 ºC to give orange solid. The solid was filtered and washed as described above to give 2f (214 mg, 88%) (Found: C, 60.11; H, 5.94; S, 1.65; C$_{65}$H$_{65}$B$_9$P$_3$Ru requires C, 60.11; H, 5.94%).

Acknowledgements

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References
Formation of new $\eta^5$-Rh(III) complexes from $\eta^5$-Rh(I) rhodacarboranes containing charge-compensated ligands

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A series of new Rh(I) semi-sandwich complexes of formula $[3,3-(PPh_3)_2-8-L-3,1,2-RhC_2B_9H_10]$ have been synthesized, hence has been the most widely studied. We have also transition metal complexes such as $[\text{Cp'}Rh(PPh_3)Cl_2]$, have demonstrated to be efficient catalysts for olefin hydrogenation, among other. Nevertheless, until now, few Rh(I) and Rh(II) complexes with dicarbollide charge-compensated ligands have been described. In this paper we report on the synthesis and characterization of a new series of half-sandwich rhodium complexes analogous to $[\text{Cp'}Rh(PPh_3)_2]$ and $[\text{Cp'}Rh(PPh_3)Cl_2]$, respectively, in which the Cp' has been replaced by the dicarbollide charge-compensated ligand $[10-\text{L}-7,8-C_2B_9H_{10}]$. The donating capacity of the ligand makes it able to stabilize both Rh(I) and Rh(III) complexes, metal ions in oxidation states separated by two units.

Introduction

To date, a large number of metallacarboranes using the $[C_3B_7H_{11}]^{10^-}$ dianionic dicarbollide ligand have been developed to form closo-$M-C_2B_9$ icosahedral clusters. Also a few transition metal complexes with monoanionic charge-compensated ligands of the type $[L-C_2B_9H_{10}]^{-}$ ($L = \text{pyridine, THF, SR, PPh_3, OEt_2, NR_3, etc}$) have been reported. In general, all these complexes have been designed to establish detailed comparisons with their analogous cyclopentadienyl-metal complexes. The main difference between both type of dicarbollide ligands is the total charge. In this respect, it is generally accepted that the dianionic $[C_3B_7H_{11}]^{10^-}$ cluster stabilizes higher oxidation states than the monoanionic $[L-C_2B_9H_{10}]^{-}$ ligands. Among the latter, the ligand $[9-SMe_2-7,8-C_2B_9H_{10}]^{-}$ is the most convenient to be synthesized, hence has been the most widely studied. We have recently reported a series of charge-compensated monocarboranes and neutral charge-compensated monoanionic charge-stabilized rhodacarboranes from $[\text{RhCl(PPh_3)_3}]$ and $[\text{RhCl}2\text{cod}]$. The reaction of any of the monoanionic ligands with $[\text{RhCl}2\text{cod}]$ has also been prepared by reaction of the respective monoanionic charge-compensated ligands $[10-L-7,8-C_2B_9H_{10}]^{-}$ and $[7-Me-10-L-7,8-C_2B_9H_9]^{-}$ with $[\text{RhCl}2\text{cod}]$. Complexes $2a$ and $2c$ may be easily oxidized to the corresponding Rh(III) complexes $4a$ and $4d$ under inert conditions in some halogenated solvents such as CCl$_4$, CHCl$_3$, among others. The complexes have been fully characterized by IR and NMR spectroscopy and the crystal structure of $2a$, $3$ and $4a$ have been elucidated by single crystal X-ray diffraction analysis. An EPR spectrum analysis has revealed clear evidences of the formation of free radicals as intermediates in the evolution of $2a$ to $4a$ complexes. The capacity of the $[10-SMe_2-7,8-C_2B_9H_{10}]^{-}$ system to stabilize both Rh(I) and Rh(III) oxidation states may be attributed to its donor capacity together with the presence of labile ligands in the molecule.

Results and Discussion

Synthesis and characterization of $[3,3-(PPh_3)_2-8-L-3,1,2-RhC_2B_9H_{10}]$ and $[1-Me-3,3-(PPh_3)_2-8-L-3,1,2-RhC_2B_9H_{10}]$ ($L = \text{SMe}_2, \text{SEt}_2, \text{S(CH}_2)_4$). The neutral charge-compensated nido-carboranes of general formula $7-R-10-L-7,8-C_2B_9H_{10}$ ($R = \text{H}, \text{L} = \text{SMe}_2$; $2a$), $\text{Et}_2$, $\text{S(CH}_2)_4$ ($2c$), $\text{SEt}_2$ ($2d$), $\text{S(CH}_2)_4$ ($2e$) react quantitatively with $\text{K}[10-SMe}_2-7,8-C_2B_9H_{10}]$ in degassed ethanol to form the corresponding anionic species. The reaction of any of the anionic ligands with $[\text{RhCl}2\text{PPh}_3]_3$ in a 1:1 ratio, afforded dark-yellow solids formulated as $[1-R-3,3-(PPh_3)_2-8-L-3,1,2-RhC_2B_9H_{10}]$ ($R = \text{H}; L = \text{SMe}_2$; $2a$), $\text{Et}_2$, $\text{S(CH}_2)_4$ ($2c$), $\text{SEt}_2$ ($2d$) and $R = \text{Me}; L = \text{SMe}_2$; $2e$, $\text{SEt}_2$ ($2f$). The reaction is shown in Scheme 1.

![Scheme 1 Formation of $[1-R-3,3-(PPh_3)_2-8-R'(R'=3,1,2-RhC_2B_9H_{10})]$.](image)
Table 1 Proton chemical shift data for the alkyl substituent on B(10) sulfonium moiety.

<table>
<thead>
<tr>
<th>Complex</th>
<th>CH₃</th>
<th>S-CH₂-</th>
<th>CH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>2.33 (6H)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2b</td>
<td>1.30 (6H)</td>
<td>2.77 (2H)</td>
<td>3.05 (2H)</td>
</tr>
<tr>
<td>2c</td>
<td>—</td>
<td>2.96 (2H)</td>
<td>3.31 (2H)</td>
</tr>
<tr>
<td>2d</td>
<td>0.78 (3H)</td>
<td>3.00 (2H)</td>
<td>—</td>
</tr>
<tr>
<td>2e</td>
<td>2.36 (3H)</td>
<td>2.73 (3H)</td>
<td>—</td>
</tr>
<tr>
<td>2f</td>
<td>1.05 (3H)</td>
<td>2.45 (1H)</td>
<td>2.59 (1H)</td>
</tr>
</tbody>
</table>

*The number between brackets corresponds to the protons area.

Table 2 ¹³P chemical shifts reported in ppm, ¹J(Rh, P) values and ²J(Pₓ, Pᵧ) values expressed in Hz for compounds 2a-f.

<table>
<thead>
<tr>
<th>Complex</th>
<th>¹³P</th>
<th>¹J(Rh, P)</th>
<th>²J(Pₓ, Pᵧ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>43.91</td>
<td>192</td>
<td>—</td>
</tr>
<tr>
<td>2b</td>
<td>42.47</td>
<td>192</td>
<td>—</td>
</tr>
<tr>
<td>2c</td>
<td>43.86</td>
<td>192</td>
<td>—</td>
</tr>
<tr>
<td>2d</td>
<td>42.97</td>
<td>192</td>
<td>—</td>
</tr>
<tr>
<td>2e</td>
<td>43.14 / 33.93</td>
<td>202 / 181</td>
<td>43</td>
</tr>
<tr>
<td>2f</td>
<td>42.12 / 33.33</td>
<td>199 / 182</td>
<td>47</td>
</tr>
</tbody>
</table>

The ¹H NMR, ³¹P NMR and ¹¹B NMR spectra of complexes 2a-d are consistent with a Cₛ symmetry molecule, while complexes 2e and 2f exhibit a C₁ symmetry. In the ¹H NMR spectra, the two distinct methylene protons in complexes 2b, 2c and 2f exhibit an ABC₃ spin system with ¹J(Hₓ, Hᵧ) = 13.4 Hz and ¹J(Hₓ, Hₓ) = 7.4 Hz (Table 1). The aromatic region shows resonances centered at 7.45 ppm, fitting six phenyl rings for all complexes, except for 2d, which fits seven. The ³¹B [¹H] resonances appear between 2.0 and -23.0 ppm, in the usual region for closo complexes. All signals are split into doublets (¹J(B, H) = 129-145 Hz), except the lowest field resonance assigned to the sulfur bearing B(8) vertex. The ³¹P [¹H] NMR spectra of compounds 2a-d display one doublet with ¹J(Rh, P) = 192 Hz (Table 2). Two doublets of doublets are observed for complexes 2e and 2f with ¹J(Rh, P) being in the range 181-202 Hz and ²J(Pₓ, Pᵧ) near 45 Hz. Although two different sulfur substituents exist in complex 2d, only one doublet resonance due to Rh-P coupling, is observed in the ³¹P [¹H] NMR at room temperature. The variable temperature ³¹P [¹H] NMR spectra of 2d in CD₂Cl₂ are displayed in Figure 1. It can be interpreted as an AₓM spin system at room temperature which coalesces at ~40 °C. At ~90 °C the spectrum features two doublets of doublets corresponding to an ABM spin system. These details are in agreement with the hindered rotation of the Rh[PPh₃]₃ moiety about the metal-carbide ligand axis.⁷

The spectroscopic data and the elemental analysis are consistent with closo-rhodacarborane complexes containing one charge-compensated monoanionic ligand and two triphenylphosphane ligands coordinated to one Rh(I) atom per molecule. To confirm the molecular architecture of these complexes a single-crystal diffraction study was performed on 2a. A simplified drawing of the complex unit is depicted in Figure 2 and selected geometrical parameters are collected in Table 3. Two triphosphane ligands, C(2), and B(4) and B(7) form short bonds to Rh(I) forming a pseudo square-planar geometry around Rh(I). The midpoint of five membered ring is 1.812(2) Å from Rh(I). The C1-C2 distance is 1.559(6) Å.

Sulfonium moiety.

Synthesis and characterization of [3,3-cod-8-SMe₂-3,1,2-RhC₂B₁₀H₁₄]

In a similar way, the reaction of a degassed ethanolic solution of K[10-SMe₂-7,8-C₂B₁₀H₁₄] with 0.5 equivalents of [Rh(cod)Cl]₂ led to the formation of the yellow compound 3. All NMR spectra are consistent with a molecule of Cₛ symmetry. The ¹H NMR spectrum displays resonances at 2.25, 2.43, and 4.37 ppm attributable to the cycloocta-1,5-diene ligand,⁶ and a broad resonance at 3.12 ppm due to the Cc-H protons. The ¹¹B NMR resonances appear in the region between 3.2 to ~25.0 ppm, common for closo compounds.

Complex 3 crystallized from CHCl₃ to give good-quality yellow crystals for X-ray diffraction analysis. The drawing of 3 is shown in Figure 3 and selected bond parameters are given in Table 4. The molecule consists of a rodacarborane in a closo-icosahedral geometry. The structure is similar to that of 2a, but in 3 a cod molecule has replaced phosphanes. This results in that the midpoint of the boron cage anion moves towards Rh(I)ion and is at the distance of 1.73(2) Å from Rh(I). In 2a the relevant distance is 1.812(2). The C1-C2 distance is 1.559(7) Å identical to that of 2a.

Rh(III) from Rh(I) metallacarboranes. Dynamic behaviour in halogenated solutions

Complexes 2a-d are stable under anaerobic conditions in CH₂Cl₂ and in non-halogenated solvents such as toluene, THF and acetone. In the presence of oxygen, however, complete decomposition is observed. Nevertheless, when using halogenated solvents such as CHCl₃, CCl₄, CHBr₃ or CICH₂CH₂Cl, a change of colour from dark-yellow to red takes place under N₂ at room temperature, to form the new complexes 4a-d. Contrarily, solutions of 2e-f in the latter solvents are unstable, even under N₂, leading to total decomposition of the
Compound 3 is stable in all solvents showing no change. The spectroscopic data provided some details about the behaviour of 2a-d in some halogenated solvents. The $^{31}$P{1H} NMR spectra showed that the conversion of 2a-d to 4a-d is accompanied by the formation of non-identified phosphorous containing by-products, which are dependent on the halogenated solvent used. In addition, the rate of the reaction depends on the halogenated solvent used suggesting an active participation of the solvent in the process. Halogenated solvents can be sorted out depending on the speed of the conversion: a) in halogenated solvents such as CCl$_4$ and CHBr$_3$, the evolution was immediate, b) in CDCl$_3$ or CHCl$_3$ reaction was slower reaching completion after several hours, and c) in CH$_2$Cl$_2$ and halogen containing aromatic solvents no reaction took place.

The NMR characterization of compounds 4a-d was originally performed in situ, from the evolved solutions of 2a-d in CDCl$_3$. In all cases the $^{11}$B{1H} spectra showed a 1:3:2:1:2 pattern in the closo region and the $^{31}$P{1H} NMR spectra showed doublets at ca. 25 ppm. These resonances coexist with other minor peaks corresponding to phosphorus containing by-products. These data suggest a similar molecular architecture for compounds 4a-d.

Scheme 2 Proposed mechanism of formation of 4a-d from 2a-d in some chlorinated solvents.

| Table 3 Selected bond lengths (Å) and angles (º) for 2a-0.912CH$_2$Cl$_2$. |
|----------------------|----------------------|----------------------|
| Rh3-C1 2.422(4)     | Rh3-P1 2.246(10)     |
| Rh3-C2 2.299(4)     | Rh3-P2 2.2718(12)    |
| Rh3-B4 2.289(5)     | S-B8 1.914(5)        |
| Rh3-B7 2.291(4)     | C1-C2 1.559(6)       |
| Rh3-B8 2.321(5)     |                       |
| P1-Rh3-P2 97.13(4)  | B7-B8-S 122.8(3)     |
| S-B8-Rh3 108.0(2)   | B4-B8-S 123.8(3)     |

| Table 4 Selected bond lengths (Å) and angles (º) for 3. |
|----------------------|----------------------|----------------------|
| Rh3-C1 2.279(5)     | Rh3-C15 2.153(5)     |
| Rh3-C2 2.293(5)     | Rh3-C16 2.137(5)     |
| Rh3-B4 2.240(5)     | Rh3-C19 2.160(5)     |
| Rh3-B7 2.247(5)     | Rh3-C20 2.147(5)     |
| Rh3-B8 2.278(5)     | S-B8 1.906(5)        |
| C1-C2 1.559(7)      |                       |
| B7-B8-S 120.9(3)    | S-B8-Rh3 112.1(2)    |
| B4-B8-S 126.8(3)    |                       |

After a solution of 2a in CHCl$_3$, red crystals of 4a precipitated which were good for full characterization by NMR spectroscopy and for single crystal X-ray diffraction analysis. The $^{1}$H NMR spectrum shows a singlet in the aliphatic region (2.28 ppm).
attributed to the SM$_2$ protons. The cage-carbon hydrogen atoms for $4a$ appear at 3.87 ppm, 1.82 ppm shifted to lower field in relation to its precursor $2a$. The aromatic region shows resonances integrating 15 protons, due to a PPh$_3$ unit. The $^{11}$B{$_1$H} NMR spectrum displays a 1:3:2:1:2 pattern in the range 11 to -14 ppm, thus maintaining the initial closo structure of $2a$.

The $^{31}$P{$_1$H} NMR spectrum features a doublet at 33.50 ppm, with a coupling constant $J$(Rh, P) = 124 Hz. A drawing of the complex is shown in Figure 4 and selected geometrical parameters are displayed in Table 5. The structure reveals the formation of [3-PPh$_3$-3,3-Cl$_2$-8-SMe$_2$-3,1,2-RhC$_2$B$_9$H$_{10}$] $4a$, a closo Rh(III) complex in which the metal exhibits a pseudo-octahedral coordination, with the anionic charge-compensated ligand occupying three facial coordination sites and two chloride ions and a triphenylphosphane ligand occupying the remaining sites. The change from Rh(I) to Rh(III) result in that the boron cage come closer to Rh center: in $4a$ the midpoint of the belt is 1.618(5) Å from the Rh(III) cation. This causes that the belt must open and for ex. C1-C2 distance becomes 1.649(18) Å and is about 0.1 Å longer than in $2a$ and $3$.

**Mechanistic study**

The formation of the new Rh(III) complexes $4a$-$d$ from halogenated solutions of the corresponding Rh(I) precursors $2a$-$d$ is unprecedented. It is likely that this transformation requires the loss of a PPh$_3$ ligand in addition to the solvent assisted oxidation of Rh(I) to Rh(III), which implies coordination of two chlorine atoms.

To elucidate the mechanism of the formation of the Rh(III) complexes from their related Rh(I) species and to understand the nature of the key steps, the transformation of $2a$ to $4a$ was studied in CDCl$_3$ and CHCl$_3$ using different spectroscopic techniques. Firstly, the importance of the release of the phosphane ligand was evaluated by $^{31}$P{$_1$H} NMR by following the progress of a solution of $2a$ in CDCl$_3$, containing PPh$_3$ in excess. This slowed down the formation of $4a$. Based on reactions in which a phosphane dissociative pathway has been well established,12 we propose that the first step of the reaction involves the dissociation of PPh$_3$ producing an unsaturated 16-electron Rh complex ($5a$), as shown in step A of Scheme 2. In the light of these results, the stability of complex $3$ in halogenated solvents may be rationalized as a result of the chelating effect of the cod ligand.

Secondly, the time dependence of the conversion of $2a$ to $4a$ was monitored in CDCl$_3$ by NMR spectroscopy (Figure 5). The $^{31}$P{$_1$H} spectrum of the starting $2a$ showed a doublet at 43.91 ppm. As the reaction proceeded, two doublets at 43.91 and 26.93 ppm attributed to $2a$ and $4a$, respectively, and peaks assigned to PPh$_3$ (-4.84 ppm) and OPPh$_3$ (29.67 ppm) were observed. After
Conclusions
In view of the results, we can deduce that Rh(I) complexes containing the charge-compensated cluster [10-L-7,8-C2B9H10]- and PPh3 as ancillary ligands may be easily oxidized to Rh(III) complexes under inert conditions in some halogenated solvents. The donor capacity of the B(10)-substituted cluster, facilitated by the presence of labile ligands in the molecule may be the key to cause the process. The capacity to stabilize both Rh(I) and Rh(III) oxidation states by the same system may be attributed to the to-and-fro electron density possibilities of [10-L-7,8-C2B9H10]-. This property could be essential in some catalytic processes that leads to think that the rhodium systems will be active as catalysts. The catalytic activity of these compounds are being studied in detail.

Experimental Section

Instrumentation
Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyser. IR spectra were recorded with KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The 1H NMR (300.13 MHz), 13C(1H) NMR (75.47 MHz) and 31P{1H} NMR spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories at room temperature. All NMR measurements were performed in deuterated solvents at 22 °C. Chemical shift data for 1H and 13C (1H) NMR spectra were referenced to SiMe4, those for 11B(1H) and 11B RMN spectra were referenced to external BF3Et2O and those for 31P(1H) RMN spectra were referenced to external 85 % H3PO4 (minus values upfield). Chemical shifts were reported in ppm, followed by a description of the multiplet (e.g. d = doublet), its relative intensity and observed coupling constants (in Hz).

Materials
All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were purified by distillation from appropriate drying agents before use. Deuterated solvents for NMR (Fluorochem) were freeze-pump-thawed three times under N2 and transferred to the NMR tube using standard vacuum line techniques. 1a-c were synthesized as is described in the literature. 1d-f were also freshly prepared. [RhCl(PPh3)]3 and [Rh(cod)Cl]2 were synthesized according to the literature. All organic and inorganic salts were Fluka or Aldrich analytical reagent grade and were used as purchased. The solvents were reagent grade.

Synthesis of [3,3-(PPh3)2-8-SEt2-3,1,2-RhC2B9H10] (2a)
To a deoxygenated solution of ethanol (15 mL) containing carborane zwitterion 1a (110 mg, 0.565 mmol) and K[ter-BuO] 67 mg, 0.597 mmol) was added RhCl(PPh3)(522 mg, 0.564 mmol) and the mixture was stirred for 3 hours at room temperature. Within 1 hour the colour of the mixture changed from red-brown, characteristic of Wilkinson’s catalyst, to pale brown-yellow. After this time, the solid was filtered off and washed with two 15 ml portions of water, 15 ml of ethanol and two 15 ml portions of diethyl ether. Finally, the solid was dried in vacuo. Compound 2a was obtained as an amorphous solid. Yield (364 mg, 79 %). 1H NMR (CDCl3): δ 2.05 (br s, 2H, C2-H), 2.33 (s, 6H, S-CH3), 6.90-7.92 (m, 30H, C6H), 3.3 (s, 1B), -16.8 (d, 4B). FTIR (KBr), ν (cm-1): 2945 (s), 2845 (s), 1710 (m), 1380 (m), 1195 (m), 1035 (m), 770 (m). Anal. Calcd for C69H54P3Rh: C, 58.52; H, 5.65; P, 3.91 %. Found: C, 58.49; H, 5.77; P, 3.79.

Synthesis of [3,3-(PPh3)2-8-SEt2-3,1,2-RhC2B9H10] (2b)
The process was the same as for compound 2a using 130 mg (0.584 mmol) of 1b, 69 mg, (0.615 mmol) of K[ter-BuO] and 537

Fig. 6 Simulated and experimental EPR spectrum of PBN adducts observed in a CHCl3 solution of 2a.
mg (0.580 mmol) of RhCl(PPh3)3 in 15 mL of deoxygenated ethanol. The mixture was stirred for 3 h at room temperature, obtaining a pale brown-yellow solid. The solid was filtered and washed as described above. [3-(PPh3)-3,3-Cl2-8-SEt2-3,1,2-RhC2B9H10] (2b). 

(Yield: 376 mg, 76%). 1H NMR (CDCl3): δ 1.04 (t, 3H, J(H, H) = 7.3 Hz, CH3), 1.61 (t, 3H, J(H, H) = 7.3 Hz, CH3), 1.29 (br s, 1H, C2H). 1.69 (s, 3H, CH3), 2.45 (m, 1H, S-CH2-), 2.59 (m, 1H, S-CH2), 2.96 (m, 1H, S-CH2), 3.30 (m, 1H, S-CH2), 7.05-7.90 (m, 30H, C2H). 13P{1H} NMR (CDCl3): δ 42.12 (dd, 1J(P, Rh) = 19 Hz, 2J(P, P) = 47 Hz), 33.33 (dd, 1J(P, Rh) = 182 Hz, 2J(P, P) = 47 Hz). 1B NMR (CDCl3): δ 1.0 (s, 1B), -16.3 (d, 1J(B, H) = 134 Hz, 2B), -17.8 (1B), -19.9 (1B), -22.1 (d, 1J(B, H) = 140 Hz, 2B), -23.5 (1B), -26.3 (1B). FTIR (KBr), v (cm-1): 2521, 2551, 2573 (B-H). Anal. Calc. for C6H8B2SpRhC: C, 59.84; H, 6.07; S, 7.31 % Found: C, 59.36; H, 5.87; S, 3.22.

Synthesis of [3-(PPh3)-3,3-C12-8-SEt2-3,1,2-RhC2B9H10] (3) To a deoxygenated solution of ethanol (15 mL) containing carbobnitrile 1a (100 mg, 0.515 mmol) and K[3-BuO] (64 mg, 0.540 mmol) was added [Rh(CO)2] (124 mg, 0.256 mmol) and the mixture was stirred for 2 hours at room temperature. After this time, a bright yellow solid was formed which was washed and dried with 10 mL of ethanol. Finally, the solid was dried in vacuo. Compound 3 was obtained as a bright yellow solid. Yield (110 mg, 53 %). 1H NMR (CDCl3): δ 2.25 (m, 4H, CH2), 2.43 (m, 4H, CH2), 2.63 (s, 6H, S-CH2), 3.12 (br s, 2H, C2H, 4.37 (m, 4H, CH2). 13C NMR (CDCl3): δ 1.4 (d, 1J(B, H) = 118 Hz, 2B), -15.6 (2B), -21.9 (d, 1J(B, H) = 109 Hz, 5B). FTIR (KBr), v (cm-1): 2565, 2533, 2513 (B-H). Anal. Calc. for C6H8B2P3RhC: C, 61.66; H, 5.51; S, 3.58 %. Found: C, 61.67; H, 5.51; S, 3.65.

Synthesis of [3-(PPh3)-3,3-Cl2-8-SMe2-3,1,2-RhC2B9H10] (4a) When compound 2a was dissolved in CH2Cl2, the colour of the solution changed from the initial pale brown-yellow to red. When X=Br, I, the reaction occurred immediately but when X=Cl, it took 3 hours. Red crystals of 4a were obtained after leaving the solution for 2 days in CHCl3 (85 %). 1H NMR (acetone-d6): δ 2.28 (s, 6H, S-CH2-), 3.87 (br s, 2H, C2H, 7.35-8.02 (m, 15H, C2H). 13P{1H} NMR (acetone-d6): δ 35.30 (d, 1J(P, Rh) = 124 Hz). 1B NMR (CDCl3): δ 10.8 (d, 1J(B, H) = 141 Hz), 5.7 (3B), -3.2 (d, 1J(B, H) = 139 Hz, 2B), -10.8 (1B), -14.2 (d, 1J(B, H) = 159 Hz, 2B). 13C{1H} NMR: δ 26.5, 128.4, 130.5, 132.0, 133.6, 134.9. FTIR (KBr), v (cm-1): 2553, 2679 (B-H). Anal. Calc. for C6H8B2P3RhC: C, 38.12; H, 4.63; S, 4.13 %. Found: C, 38.23; H, 4.45; S, 4.49.

Synthesis of [3-(PPh3)-3,3-Cl2-8-SMe2-3,1,2-RhC2B9H10] (4b) Complex 4b was formed from a solution of compound 2b in 5 mL of CDCl3. The formation of this complex was only monitored by NMR in solution, but 4b was not isolated. 1H NMR (CDCl3): δ 1.04 (s, 3H, CH3), 2.36 (m, 2H, S-CH2), 2.73 (s, 3H, S-CH3), 7.10-7.53 (m, 30H, C2H). 13P{1H} NMR (CDCl3): δ 43.14 (dd, 1J(P, P) = 43 Hz), 33.93 (dd, 1J(P, H) = 181 Hz, 2J(P, P) = 43 Hz). 1B NMR (CDCl3): δ 1.7 (s, 1B), -12.2 (d, 1J(B, H) = 130 Hz, 1B), -15.0 (1B), -17.2 (d, 1J(B, H) = 143 Hz, 2B), -19.3 (1B), -21.0 (d, 1J(B, H) = 122 Hz, 2B), -24.3 (1B). FTIR (KBr), v (cm-1): 2516, 2550 (B-H). Anal. Calc. for C6H8B2P3RhC: C, 58.97; H, 5.79; S, 3.84 %. Found: C, 58.26; H, 5.53; S, 3.41.

Synthesis of [3-(PPh3)-3,3-Cl2-8-SeT2-3,1,2-RhC2B9H10] (2f) The procedure was the same as for compound 2a using 113 mg (0.477 mmol) of RhCl(PPh3)3 in 15 mL of deoxygenated ethanol. The mixture was stirred for 3 h at room temperature, obtaining a brown-yellow solid. The solid was filtered and washed as described above. [3-(PPh3)-3,3-Cl2-8-SeT2-3,1,2-RhC2B9H10] (2f). (Yield: 280 mg, 68%). 1H NMR (CDCl3): δ 1.05 (t, 3H, J(H, H) = 7.3 Hz, CH3), 1.61 (t, 3H, J(H, H) = 7.3 Hz, CH3), 1.29 (br s, 1H, C2H). 1.69 (s, 3H, CH3), 2.45 (m, 1H, S-CH2-), 2.59 (m, 1H, S-CH2), 2.96 (m, 1H, S-CH2), 3.30 (m, 1H, S-CH2), 7.05-7.90 (m, 30H, C2H). 13P{1H} NMR (CDCl3): δ 42.12 (dd, 1J(P, Rh) = 19 Hz, 2J(P, P) = 47 Hz), 33.33 (dd, 1J(P, Rh) = 182 Hz, 2J(P, P) = 47 Hz). 1B NMR (CDCl3): δ 1.0 (s, 1B), -16.3 (d, 1J(B, H) = 134 Hz, 2B), -17.8 (1B), -19.9 (1B), -22.1 (d, 1J(B, H) = 140 Hz, 2B), -23.5 (1B), -26.3 (1B). FTIR (KBr), v (cm-1): 2521, 2551, 2573 (B-H). Anal. Calc. for C6H8B2SpRhC: C, 59.84; H, 6.07; S, 7.31 % Found: C, 59.36; H, 5.87; S, 3.22.
The process was the same as for compound space group, and absolute configuration of the 1H{11B}, 31P{1H} and 11B{1H} NMR spectra at preselected C2d MAT98-0921.

Acknowledgement

We thank MCyT (project MAT01-1575) and Generalitat de Catalunya 2001/SGR/00337 for the partial support of this research. Thanks to MCyT for a FPI grant from the project MAT98-0921.

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**Table 6 Crystallographic parameters for 2a 0.912CH2Cl3, 3 and 4a CHCl3.**

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<tr>
<th>Compound</th>
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<th>Crystal habit, color</th>
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<td>γ (Å)</td>
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<tr>
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<td>γ (deg)</td>
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| Synthesis of [3-PPh3-3,3-Cl2-8-SEtPh-3,1,2-RhC2B9H10] (4d) |

The process was the same as for compound 4b using compound 2d in 5 mL of CDCl3. ¹H NMR (CDCl3); δ 1.13 (t, 3H, CH3), 2.83 (br s, 1H, C4-H3), 3.24 (m, 1H, S-C4-H3), 5.6 (1B), 0.8 (1B) –1.7 (2B), -5.9 (2B), -10.3 (d, 1B), 7.08-8.02 (m, 20H, C6-H). ¹³C{¹H} NMR: δ 103.6(7), 125.8(7), 140.5(7). 11B NMR (CDCl3): δ 24.84 (d, 1B, H) = 118 Hz). 13C{1H} NMR: δ 33.3(2), 3.22 (m, 1H, S-C4-H3), 7.08-8.02 (m, 20H, C6-H).

**References**


Highly stable neutral and positively charged dicarbollide sandwich complexes

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Introduction

Boron cluster ligands provide structural and bonding possibilities distinct from conventional organic ligands.1 The best known of the η3 boron ligands is the dicarbollide anion [7,8-C2B9H11]2−; [Dcb]2−. The synthesis and properties of first metallacarborane sandwich complexes analogous to the C2B9H112− are compared to other analogous sandwich complexes with [Dcb]2− or [Cp]− anions.

Results and Discussion

Synthesis and structures

Reaction of NiCl2·6H2O with an ethanolic solution of K[10-SMe2-7,8-C2B9H10] (prepared by deprotonation of the neutral charge-compensated ligand with BuOK)15 at room temperature yielded a yellow suspension from which the paramagnetic complex commo-[3,3′-Ni(8-(SMe2)-1,2-C2B9H10)2], 1, was isolated as an analytically pure solid in 66% yield (Scheme 1). Complex 1 is air and moisture-stable in solution and in solid state, in contrast to the air-sensitive complex commo-[3,3′-Ni(1,2-C2B9H10)2] which rapidly oxidized to a Ni(III) complex.15 Infrared data and elemental analysis are in agreement with the proposed stoichiometry. The infrared spectrum of 1 shows a broad band centred at 2518 cm−1 is due to the vibration v(B-H). Since 1 is paramagnetic the 11B [1H] NMR spectrum extended over 260 ppm in a chemical shift range of δ +140 ppm to -120 ppm, and no evidence of B-H coupling is observed in the 11B NMR. The 1H NMR spectrum shows B-H and C-H broad resonances in the range of δ +85 to -170 ppm. The ultraviolet and visible spectral data of 1 in acetonitrile are given in Table 1.

Table 1 Electronic spectral data for complexes 1-5 in acetonitrile.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λmax (nm)</th>
<th>ε (1000 M−1 cm−1)</th>
</tr>
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<tr>
<td>1</td>
<td>217 (11300) 257 (6700) 351 (12000) 495 (85) 745 (54)</td>
<td></td>
</tr>
<tr>
<td>2-C1</td>
<td>215 (5900) 250 (6100) 330 (23700) 464 (280)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>222 (17800) 265 (11400) 339 (9500) 442 (220)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>198 (54000) 223 (37000) 336 (30) 362 (610) 481 (60)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>221 (32200) 268 (8900) 383 (130) 520 (180)</td>
<td></td>
</tr>
</tbody>
</table>

Shoulder.

The structure of compound 1 was determined by X-ray diffraction analysis, and represent the first example of a nickel sandwich incorporating two charge-compensated anionic carborane ligands. The solid-state structure of 1 is presented in Figure 1 and selected geometrical parameters are gathered in Table 2. Asymmetric unit of 1 consists of half of commo-[3,3′-Ni(8-(SMe2)1,2-C2B9H10)2] complex unit, with the metal lying on a C2 axis, which coincides with the crystallographic c axis. The two C2B3 bonding faces have a staggered conformation and the Cl-C2 and C1—C2 vectors have a transoid configuration.

The mean planes defined by the atoms of the two ligating rings are almost parallel, being inclined at 3.8° to each other. The Ni

Scheme 1. Formation of commo-[3,3′-M{8-(SMe2)-1,2-C2B9H10}]2+.

O.Tutusaus is enrolled in the UAB PhD program.
atom is located 1.671 Å above the mean C\(_{2B3}\) plane, with the nickel atom shifted 0.08 Å off center. When compared to other electron-rich metal (d\(^8\) or d\(^9\)) bis-dicarbollyl complexes, such as the isoelectronic Cu(III) \([3,3’-Cu(1,2-C\(_2\)B\(_9\)H\(_{10}\))\(_2\)]\(^-\) anion for which an 0.6 Å shift was observed and the analogous Ni(II) \([3,3’-Ni(1,2-C\(_2\)B\(_9\)H\(_{10}\))\(_2\)]\(^2-\) dianion for which a 0.6 Å shift was estimated,\(^7\) the present structure seems to belong to the \(\pi\)-sandwich rather then \(\pi\)-allyl classification. This irregular behaviour was already observed for the d\(^8\) Ni(II) \([3,3’-Ni(1,2-C\(_2\)B\(_9\)H\(_{10}\))\(_2\)]\(^2-\) dianion for which a 0.15 Å shift was reported.\(^1\)

The cage C atoms are separated by 1.586 Å. The average Ni–C and Ni–B distances are 2.194 and 2.230 Å, respectively. The dicarbollide bonding faces are noticeably slanted with a B\(_{10-2}\)–Ni\(_3\)–B\(_{10}\) angle of 172.9º, moving the B\(_4\) and B\(_{4-2}\) atoms further apart than the C\(_2\) and C\(_{2-2}\) atoms. An electronic effect is believed to be the cause of this distortion as the SMe\(_2\) steric influence can be excluded as the driving force in a gauche configurated complex.

Three probable minimum energy rotamers are expected, A, B and C (Figure 2), for these zwiterionic B(8)-B(8’) substituted sandwich complexes. The rotamer A, in which a cluster is rotated 36º respect to the other, represents a cisoid configuration and would be the less energetically stable considering the high steric hindrance. In rotamer B the clusters are mutually rotated 108º, adopting a gauche configuration, and would correspond to a balanced situation between steric and electronic requirements. Finally, rotamer C, in which a transoid configuration is attained (180º of rotation), would be the most stable from a steric point of view; however, it wouldn’t be electronically favoured considering the trans effect, as the two carbon atoms of both clusters would be in a trans position. The crystal structure of complex 1 shows a gauche configuration in which each cluster is rotated approximately 107º, matching rotamer B structure. To corroborate that this rotamer is the lowest in energy, an analysis of the calculated energy profiles has been carried out, using the semi-empiric method ZINDO/1.

The energy profile for 1 (Figure 3) suggested the existence of two different relative energy minima, corresponding to three different conformations. The most stable isomer corresponds to a rotation angle of 115º, while two relative minima are observed at 49º and 180º rotation angles. Calculations yields a theoretical rotational barrier between the two most stable conformations of 1 of 4.5 Kcal·mol\(^{-1}\). Thus, the calculated energy indicates that the most stable rotamer is that with a rotation angle of 115º, only slightly different from that found in the X-ray crystal structure results for complex 1, and which would correspond to rotamer B.

The relatively easy preparation of the above Ni(II) complex, leads us to prepare the analogous Co complex. In a similar reaction, the anionic charge-compensated ligand K\([10-SMe\(_2\)-7,8-C\(_2\)B\(_9\)H\(_{10}\)]\) and anhydrous CoCl\(_2\) in MeOH or EtOH afforded a greenish precipitate, after addition of water to the mixture (Scheme 1), from which a yellow solid was obtained after treatment with HCl, a NaCl water solution and ethyl acetate. The solid was dissolved in ethyl acetate and the organic phase of the filtrate was evaporated and treated with MeOH/H\(_2\)O to yield commo-[3,3’-Co(8-(SMe\(_2\))-1,2-C\(_2\)B\(_9\)H\(_{10}\))\(_2\)]Cl, 2·Cl. As observed in the synthesis of other cobaltacarborane sandwich complexes,
The resonance at 9.61 ppm was assigned to the sulfur-bearing of two sandwiches of Cs symmetry with a 1:1:4:2:1 pattern each. The electronic spectrum data for the substituted B(8) of the cluster. The electronic spectrum of the anion, yielding the formation of the cationic Co(III) complex, was characterized in solution by 1H and 11B NMR spectroscopy. A simplified drawing of the cationic complex is depicted in Figure 4 and selected geometrical parameters are collected in Table 3. The crystallographic data corroborates the structure of 2, as the first cationic cobaltacarborane incorporating two dicarbollide ligands crystallographically characterized. The inclusion of one molecule of ethanol in the unit cell is also established, forming strong intermolecular interactions with the Cl anion. Indeed, the coordination sphere of the chlorine atom consists of three hydrogen atoms: an ethanolic hydrogen (2.232 Å) and two carbon cage hydrogen atoms from a neighbouring {3,3'-Co{8-(SMe2)-1,2-C2B9H10}}+ unit with distances of 2.390 and 2.644 Å.

The structure of 2 consists of two \([10\text{-SMMe}_2\text{-7,8-C}_2\text{B}_{10}H_{10}]^+\) charge-compensated anions sandwiched around a formal Co^3+ ion. The cisoid rotamer of the ligands is preferred in the solid state, despite the presence of substituents on both B(8) atoms, adopting a similar conformation to that found for the analogous unsubstituted \([3,3'\text{-Co(1,2-C}_2\text{B}_8\text{H}_{11}])^+\) complex, the cosane anion.4b,18. Any potential steric crowding from the SMMe2 groups is avoided by canting the dicarbollide bonding faces so that the B10'-Co3-B10 angle is 175.2º, moving the B8 and B8' atoms further apart than the carbon atoms. This feature cannot necessarily be interpreted as a steric perturbation arising from the SMMe2 substituents, because a similar distortion is apparent in the cisoid rotamer of the cosane anion.4b Thus, it appears that the SMMe2 moieties exert minimal steric influence on the overall structural details of \([3,3'\text{-Co(8-(SMMe2)-1,2-C}_2\text{B}_8\text{H}_{10}])^+\], and that the major structural features of cosane anion and 2 cation are primarily electronic in origin.

The mean planes defined by the atoms of the ligating rings of the two unique cages are almost parallel, being inclined at 1.6º to each other. The cobalt atom is located 1.482 and 1.485 Å from the least-squares planes of each face, a displacement that is comparable to the 1.475 Å found in the "parent" cosane anion.4b Compound 2 is a cationic sandwich complex, in which the calculated energy profiles shows three relative energy minima (Figure 5), corresponding to three different conformations. Two rotational barriers are detected with energies atom B(8), because it was not split into a doublet due to the B-H coupling. The only example of a cationic cobaltacarborane sandwich found in the literature is the complex \([\text{cosano-3,3'-Co(4-(4-(C}_2\text{H}_4\text{N})\text{CO}_3\text{-CH}_3)-3,1,2-C}_2\text{B}_8\text{H}_{10}]^+\) synthesized by Hawthorne et al.12f This complex was obtained from the corresponding 9-substituted charge-compensated ligand, however, no crystal structure was available due to its instability, which was attributed to the net positive charge.

The air stable diamagnetic Co(III) complex \([\text{Cl-EtOH}]^+\) crystallized from a EtOH/H2O solution as orange crystals suitable for X-ray diffraction analysis. A simplified drawing of the cationic complex is depicted in Figure 4 and selected geometrical parameters are collected in Table 3. The crystallographic data corroborates the structure of 2, as the first cationic cobaltacarborane incorporating two dicarbollide ligands crystallographically characterized. The inclusion of one molecule of ethanol in the unit cell is also established, forming strong intermolecular interactions with the Cl anion. Indeed, the coordination sphere of the chlorine atom consists of three hydrogen atoms: an ethanolic hydrogen (2.232 Å) and two carbon cage hydrogen atoms from a neighbouring \([3,3'-\text{Co}(8-(\text{SMMe}_2)-1,2-\text{C}_2\text{B}_8\text{H}_{10}])^+\) unit with distances of 2.390 and 2.644 Å.

The structure of 2 consists of two \([10\text{-SMMe}_2\text{-7,8-C}_2\text{B}_{10}H_{10}]^+\) charge-compensated anions sandwiched around a formal Co^3+ ion. The cisoid rotamer of the ligands is preferred in the solid state, despite the presence of substituents on both B(8) atoms, adopting a similar conformation to that found for the analogous unsubstituted \([3,3'\text{-Co(1,2-C}_2\text{B}_8\text{H}_{11}])^+\) complex, the cosane anion.4b,18. Any potential steric crowding from the SMMe2 groups is avoided by canting the dicarbollide bonding faces so that the B10'-Co3-B10 angle is 175.2º, moving the B8 and B8' atoms further apart than the carbon atoms. This feature cannot necessarily be interpreted as a steric perturbation arising from the SMMe2 substituents, because a similar distortion is apparent in the cisoid rotamer of the cosane anion.4b Thus, it appears that the SMMe2 moieties exert minimal steric influence on the overall structural details of \([3,3'\text{-Co}(8-(\text{SMMe}_2)-1,2-\text{C}_2\text{B}_8\text{H}_{10}])^+\], and that the major structural features of cosane anion and 2 cation are primarily electronic in origin.

The mean planes defined by the atoms of the ligating rings of the two unique cages are almost parallel, being inclined at 1.6º to each other. The cobalt atom is located 1.482 and 1.485 Å from the least-squares planes of each face, a displacement that is comparable to the 1.475 Å found in the "parent" cosane anion.4b Compound 2 is a cationic sandwich complex, in which the calculated energy profiles shows three relative energy minima (Figure 5), corresponding to three different conformations. Two rotational barriers are detected with energies

---

**Table 3** Selected bond lengths (Å), angles (º) and torsion angles (º) for complex 2·Cl·EtOH.

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</tr>
</tbody>
</table>

---

**Fig. 4** Thermal ellipsoid plot (50% probability) of complex 2·Cl·EtOH (cluster hydrogen atoms removed for clarity).

**Fig. 5** Calculated energy profile for complex 2 by ZINDO/1 method.
Table 4 Selected bond lengths (Å), angles (º) and torsion angles (º) for 3.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length (Å)</th>
<th>Angle (º)</th>
<th>Torsion (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co3-C1</td>
<td>2.170</td>
<td>C1-C2</td>
<td>1.592</td>
</tr>
<tr>
<td>Co3-C2</td>
<td>2.092</td>
<td>C1-B4</td>
<td>1.684</td>
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<tr>
<td>Co3-B7</td>
<td>2.140</td>
<td>C2-B7</td>
<td>1.717</td>
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<tr>
<td>Co3-B8</td>
<td>2.166</td>
<td>B4-B8</td>
<td>1.805</td>
</tr>
<tr>
<td>Co3-B4</td>
<td>2.132</td>
<td>B7-B8</td>
<td>1.749</td>
</tr>
<tr>
<td>B8-S</td>
<td>1.908</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B4-B8-S: 122.7, Co3-B8-S: 112.2, B7-B8-S: 123.1, B7-B8-S: 176.0

Fig. 6 Thermal ellipsoid plot (50% probability) of complex 3.
corroborated the formation of \( \text{C}_2\text{B}_{9}\text{H}_{10}\)\(_2\], which is the first sandwich of Ru(II) containing \text{C}_{10}\text{H}_{8}\text{Ru} \{8-(\text{SMe}_2)-1,2-\text{C}_2\text{B}_{9}\text{H}_{10}\}\] and FeCl\(_2\cdot4\text{H}_2\text{O}\), in this work we describe a sandwich complex, 20 for which the \text{C}_{10}\text{H}_{8}\text{Ru} \{8-(\text{SMe}_2)-1,2-\text{C}_2\text{B}_{9}\text{H}_{10}\}\] crystallizes in two different modifications, which had been previously defined and reported.\(^{16,18}\)

The \text{C}_2\text{B}_9\text{H}_{10}\] mean planes of the coordinating faces are nearly parallel, being inclined at 4.1º and 3.5º to each other for isomers A and B, respectively. The distance of the Ru atom from the mean \text{C}_2\text{B}_9\text{H}_{10}\] mean planes are virtually identical (1.641 and 1.632 Å for isomer A, 1.643 and 1.632 Å for isomer B). The dicarbollide bonding faces are noticeably inclined with an B10'-Ru3-B10 angle of 172.8º for rotamer A and B30'-Ru3-B30 of 174º for rotamer B, approaching the C2' (C21') to the C2' (C22) atoms for isomer A(B). This phenomenon has already been noted in the other complexes presented in this work so far.

The calculated energy profiles observed for complex 4 shows a different behaviour of this compound respect to other neutral complexes such as Ni(II) or Co(II) sandwiches. Four relative energy minima corresponding to the rotation angles 48º, 93º, 116º and 176º are observed, although the angle region between 93º and 116º could be considered as a very broad minimum, since the difference in energy is practically unappreciable (Figure 8). The three first minima are the lowest energy one and would correspond to rotamers A, D and B slightly distorted, respectively (Figure 2), while the minimum of higher energy at 176º corresponds to rotamer C. The rotation barrier between the two states with similar relative energy is slightly below of 2 Kcal, while the rotation barrier between the lowest and the higher relative energy minima is about 5 Kcal/mol. This is the first example in which a energy minimum at 93º has been observed for this type of sandwich complexes. The mutual configuration of the rotamer D represent a sandwich complex where the two open face of both zwitterions are practically superposed (Figure 2). The analysis X-ray of the crystal structure shows that compound 4 crystallizes in two different conformations in the crystal network, one with a rotation angle of about 89º and a second one slightly rotated (80º). Thus, we may conclude that rotamer D is the main conformational rotamer found in the crystal structure.

![Fig. 7 Thermal ellipsoid plot (50% probability) of complex 4 (cluster hydrogen atoms removed for clarity).](image)

![Fig. 8 Calculated energy profile for complex 4 by ZINDO/1 method.](image)

Table 6 Selected bond lengths (Å), angles (º) and torsion angles (º) for 4.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Angle (º)</th>
<th>Torsion Angle (º)</th>
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<tbody>
<tr>
<td>Ru3-C1</td>
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<td>Ru3-C2</td>
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<td>Ru3-B11</td>
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<td>Ru3-B8</td>
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<tr>
<td>Ru3-B4</td>
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<tr>
<td>Ru3-C1'</td>
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<td>Ru3-C2'</td>
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<tr>
<td>Ru3-B7'</td>
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<tr>
<td>Ru3-B8'</td>
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<tr>
<td>Ru3-B4'</td>
<td>2.204</td>
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</tr>
<tr>
<td>C1-C2</td>
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<tr>
<td>C1-B4</td>
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<tr>
<td>C2-B7</td>
<td>1.703</td>
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<tr>
<td>B4-B8</td>
<td>1.781</td>
<td></td>
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<td>B7-B8</td>
<td>1.791</td>
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<tr>
<td>C1'-C2'</td>
<td>1.641</td>
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<tr>
<td>C1'-B4'</td>
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<td>C2'-B7'</td>
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<td>B4'-B8'</td>
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<td>B7'-B8'</td>
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<tr>
<td>B8-S1</td>
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<tr>
<td>B8'-S2</td>
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<tr>
<td>B4-B8-S8-S1</td>
<td>121.8</td>
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<tr>
<td>B7-B8-S8-S1</td>
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<tr>
<td>Ru3-B8-S1</td>
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<td>B4'-B8'-S2</td>
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<tr>
<td>B7'-B8'-S2</td>
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<td>Ru3-B8'-S2</td>
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<tr>
<td>B7'-B8'-S2-S1</td>
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</tr>
<tr>
<td>B7'-B8'-S2-C14</td>
<td>8.9</td>
<td>-4.0</td>
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<tr>
<td>B27'-B28'-S2-C35</td>
<td>153.6</td>
<td>B7'-B8'-S2-C15 135.3</td>
</tr>
</tbody>
</table>

The crystal structure determination by X-ray diffraction corroborated the formation of \textit{commo-[3,3'-Ru\{8-(\text{SMe}_2)-1,2-\text{C}_2\text{B}_{9}\text{H}_{10}\}]_2]\] 4, which is the first sandwich of Ru(II) containing two dicarbollide ligands found in the literature. A simplified drawing of 4 is shown in Figure 7 and selected bond parameters are collected in Table 6. Interestingly, two different rotamers A and B appear in the unit cell; any attempts to increase the crystal symmetry results in discrepancy with the hkI data thus obtained. Intriguingly, the two monoanionic ligands don’t show the usual staggered conformation found for sandwiched complexes, on the contrary a mutual rotation of 81º and 89º is observed, for rotamers A and B, respectively, as measured by the dihedral angle subtended by the two planes through ruthenium and bisecting de C1-C2 (C21-C22) and C1'-C2' (C21'-C22') bonds. Such angles don’t correspond to an eclipsed conformation either, in fact the situation can be considered as a \textit{pseudo-gauche} configuration. As far as we are concerned, this intermediate configuration has never been observed on a non-bridged (thus, freely rotating) bis-dicarbollyl sandwich complex,\(^{29}\) for which cisoid, gauche and transoid configurations had been previously defined and reported.\(^{30,31}\)

Although complex \textit{commo-[3,3'-Fe\{8-(\text{SMe}_2)-1,2-\text{C}_2\text{B}_{9}\text{H}_{10}\}]_2}\] (5) had been previously prepared by Plesek et al.,\(^{19}\) using [10-\text{SMe}_2-7,8-\text{C}_2\text{B}_{9}\text{H}_{10}\] and Fe\(_2\)Cl\(_4\)\(_4\text{H}_2\text{O}\), in this work we describe a new and rapid method in which the yield of 5 has been improved. In this method, the reaction of K[10-\text{SMe}_2-7,8-\text{C}_2\text{B}_{9}\text{H}_{10}\] and Fe\(_2\)Cl\(_4\)\(_4\text{H}_2\text{O}\) in thf with Fe\(_2\)Cl\(_4\)(dppe) in a 2:1 ratio leads to the formation of 5 in a 63% yield. The UV/Vis data are recompiled in Table 1.

The energy profile data for 5 is very similar to those observed for complexes of Ni(II) (Figure 3) and Co(II), showing three relative energy minima from which the lowest energy minimum corresponds to a rotation angle of 108 (rotamer B). The X-ray crystal structure, previously reported by Plesek et al.,\(^{19}\) shows a \textit{gauche} conformation very similar to that observed in compound 1 and 3, which is in agreement with the calculated energy minimum.
Table 7  $E^*$ values\(^a\) for charged-compensated bis(dicarbollide) and others $\eta^1$ sandwich complexes redox couples and gas-phase ionization potentials (IP\(_j\), eV) of the corresponding metals.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[3,3'-Ni(8-SMe(_2)-1,2-C(_2)B(<em>9)H(</em>{10}))] (1)</td>
<td>1.29 (54.9)</td>
<td>0.38 (52.4)</td>
<td>-1.06 (18.2)</td>
<td>This work</td>
</tr>
<tr>
<td>[3,3'-Na(1,2-C(_2)B(<em>9)H(</em>{10}))]</td>
<td>0.25</td>
<td>-0.59</td>
<td>-2.10</td>
<td>3, 21</td>
</tr>
<tr>
<td>Cp:Ni</td>
<td>0.81(^a)</td>
<td>0.01(^c)</td>
<td>-1.85(^c)</td>
<td>22</td>
</tr>
<tr>
<td>[3,3'-Co(8-SMe(_2)-1,2-C(_2)B(<em>9)H(</em>{10}))] (3)</td>
<td>-0.35 (33.5)</td>
<td>-1.23 (17.1)</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>[3,3'-Co(1,2-C(_2)B(<em>9)H(</em>{10}))]</td>
<td>1.57 (51.3)</td>
<td>-1.46</td>
<td>-2.24</td>
<td>3, 21</td>
</tr>
<tr>
<td>Cp:Fe</td>
<td>3.15(^b)</td>
<td>-0.90(^c)</td>
<td>-1.91(^c)</td>
<td>22</td>
</tr>
<tr>
<td>[3,3'-Ru(8-SMe(_2)-1,2-C(_2)B(<em>9)H(</em>{10}))] (4)</td>
<td>-1.04 (28.5)</td>
<td>-</td>
<td>This work</td>
<td></td>
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<tr>
<td>Cp:Ru</td>
<td>-</td>
<td>0.88(^f)</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>[3,3'-Fe(8-SMe(_2)-1,2-C(_2)B(<em>9)H(</em>{10}))] (5)</td>
<td>-</td>
<td>0.54 (30.6)</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>[3,3'-Fe(1,2-C(_2)B(<em>9)H(</em>{11}))]</td>
<td>-</td>
<td>-0.42</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Cp:Fe</td>
<td>-</td>
<td>0.42</td>
<td>-</td>
<td>22</td>
</tr>
</tbody>
</table>

$E^*$ = ($E_p^* + E_n^*)/2$ vs. SCE. \(^b\) In THF. \(^c\) 0.1 M [NBu\(_4\)][B(C\(_6\)F\(_5\))\(_4\)] as supporting electrolyte in THF.

$E^*$ values are valid for Cp\(_4\)M and [C\(_2\)B\(_9\)H\(_{11}\)]M complexes among others, where a\(_i\) is a constant characteristic of each ligand (≈4.16 for Cp\(_4\) and ≈4.10 for [C\(_2\)B\(_9\)H\(_{11}\)]) and $j=1,2,\ldots$. The a\(_i\) constant gives an approximate idea of the electronic stabilizing effect of the ligand, making it useful for comparison purposes. As expected, the $E^*$ vs IP\(_j\) plots for 1, 3, 4, and 5 revealed that the ligand [10-SMe\(_2\)-C\(_2\)B\(_9\)H\(_{10}\)] also displays a similar linear behaviour with a slope of −3.12 (Figure 9). On the other hand, the $E^*$ value for the Cp\(_4\)Ni\(_{12}\) couple deviated from the expected value, for which we still haven’t found any suitable explanation.

The a\(_i\) constant found for [10-SMe\(_2\)-C\(_2\)B\(_9\)H\(_{10}\)] corresponds to a +1 V comparative inductive effect when compared to both the dicarbollide and cyclopentadienyl ligand. Thus, the addition of a positively charged -SMe\(_2\) group in the dicarbollide cluster resulted in a much more strongly electron-withdrawing ligand and in a shift on the scope of the metal oxidation states available.

**Experimental**

**General procedures, materials and physical methods**

All manipulations were carried out under a dinitrogen atmosphere by using standard vacuum line techniques. Solvents were purified by distillation from appropriate drying agents before use. Deuterated solvents for NMR (Fluorochem) were freeze-pump-thawed three times under N\(_2\) and transferred to the
NMR tube using standard vacuum line techniques. Elemental analyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyser. IR spectra were recorded with KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The $^1$H NMR (300.13 MHz), $^{13}$C{[1]H} NMR (75.47 MHz), $^{11}$B and $^{19}$F{[1]H} spectra were recorded using a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories at room temperature. All NMR measurements were performed in deuterated solvents at 22 °C. Chemical shift data for $^1$H and $^{13}$C spectra were referenced to SiMe$_4$, those for $^{11}$B{[1]H} and $^{19}$F{[1]H} NMR spectra were referenced to external BF$_3·$Et$_2$O and those for $^{13}$C{[1]H} NMR spectra were referenced to external 85 % H$_3$PO$_4$ (minus values upfield). Chemical shifts were reported in ppm, followed by a description of the multiplet (e.g. d = doublet), its relative intensity and observed coupling constants (in Hz).

Preparation of $[3,3'$-Co(8-[SMe$_2$]-1,2-C$_{2}B$_9H$_{10}$)]$^2$ (3)

A solution of CoCl$_2$ (418 mg, 3.22 mmol) in 8 mL of MeOH was added dropwise to a Schlenk charged with a solution of 10-SMe$_2$-7,8-C$_{2}B$_9H$_{10}$ (25.9 mg, 0.137 mmol) and BuOK (24 mg, 0.204 mmol) in 4 mL of EtOH, and the yellow suspension was stirred for 5 minutes. After concentration of the solvent in vacuo to 1 mL and cooling to 0 °C, a yellow solid was isolated by filtration, washed with cold EtOH (2 mL) and dried in vacuo to afford 66 mg of $[3,3'$-Co(1,2-C$_{2}B$_9H$_{11}$)$_2$·Cl] (65 %). $^{1}$H{[11]B} (22 °C): $\delta$ = 4.96 (br s, 4H, CH$_{cage}$), 3.95 (br s, 4H, CH$_{cage}$), 2.83 (s, 12 H, SCH$_3$), $^{13}$C{[1]H} (22 °C): $\delta$ = 9.6 (2B), 7.1 (2B), 4.3 (2B), 1.9 (2B), -5.4 (16B), -13.7 (4B), -16.7 (4B), -19.7 (2B), -22.2 (2B). $^{11}$B (22 °C): $\delta$ = 9.6 (s, 2B), 7.1 (2B, J(HB) = 141 Hz), 4.3 (d, 2B, J(HB) = 142 Hz), 1.9 (d, 2B, J(HB) = 136 Hz), -5.4 (16 B), -13.7 (d, 4B, J(HB) = 167 Hz), -16.7 (d, 4B, J(HB) = 157 Hz), -19.7 (2B), -22.2 (2B, J(HB) = 173 Hz). IR(KBr): v = 2585, 2557, 2535, 2501 (m, BH); elemental analysis calc (%) for C$_{9}$H$_{18}$B$_{10}$CoS$_2$: C 18.7, H 7.0, S 8.3; found: C 19.0, H 6.9, S 7.2.

Preparation of $[3,3'$-Co(8-[SMe$_2$]-1,2-C$_{2}B$_9H$_{10}$])$^2$·Cl in 100 mL of MeOH/H$_2$O (60:40). At that point, activated metallic Zn (211 mg, 3.23 mmol) was added and the suspension was stirred overnight giving a fading of the solution. The solid was filtered off, partially dissolved in CH$_2$Cl$_2$ and treated with an excess amount of hexane. The resulting greyish solid was collected by filtration, in oxygen absence, afford 86 mg of 3 (60 %). Crystals of 3 suitable for X-ray analysis were grown from a solution of CH$_3$Cl/hexane (1:1), under N$_2$ atmosphere.

$^{1}$H{[11]B} (22 °C): $\delta$ = 26.6, 3.43, 2.87, 2.10, 7.50, 7.80, -37.55, -44.76, -59.43. $^{13}$C{[1]H} (22 °C): $\delta$ = 6.82 (4B), 51.2 (2B), 11.8 (2B), -30.6 (4B), -14.6 (2B). $^{11}$B (22 °C): $\delta$ = 6.82 (4B), 11.8 (2B), -30.6 (4B), J(HB) = 136 Hz), -30.6 (4B, J(HB) = 143 Hz), -34.4 (d, 6B, J(HB) = 129 Hz). IR(KBr): v = 2562, 2578, 2548, 2518 (m, BH); elemental analysis calc (%) for C$_{9}$H$_{18}$B$_{10}$CoS$_2$: C 21.7, H 7.2, S 14.4; found: C 21.7, H 7.3, S 13.6.

Preparation of $[3,3'$-Co(8-[SMe$_2$]-1,2-C$_{2}B$_9H$_{10}$])$^2$·Cl (2-CI)

A solution of CoCl$_2$ (57.0 mg, 0.439 mmol) in 4 mL of MeOH was added dropwise to a Schlenk charged with a solution of 10-SMe$_2$-7,8-C$_{2}B$_9H$_{11}$ (51.4 mg, 0.265 mmol) and BuOK (54.4 mg, 0.460 mmol) in 6 mL of MeOH. Immediately, a dark yellow solution was observed, from which a yellow solid precipitated. The addition of 6.5 mL of water to the mixture darkened the colour of the precipitate to green. The mixture was filtered and washed with 15 mL of MeOH/H$_2$O (60:40). The remaining greenish solid was treated with a mixture of HCl (1mL), 5 mL of concentrated NaCl water solution and 5 mL of ethyl acetate, and then filtered to give a yellow solid. This filtrate was combined with the yellow solution resulting from dissolving the residual solid in 10 mL of ethyl acetate and transferred to a separatory funnel. The lower aqueous red layer was discarded and the organic phase was gently heated under moderately reduced pressure for 5 minutes. The resulting orange solid was collected and redissolved in 10 mL of EtOH. Orange crystals of $[3,3'$-Co(8-[SMe$_2$]-1,2-C$_{2}B$_9H$_{10}$)$_2$·Cl] suitable for an X-ray diffraction study were grown by slow evaporation of this solution at room temperature.

$^{1}$H{[11]B} (22 °C): $\delta$ = 4.9 (br s, 4 H, CH$_{cage}$), 2.84 (s, 12 H, SCH$_3$), $^{13}$C{[1]H} (22 °C): $\delta$ = 9.7 (2B), 4.3 (2B), -5.4 (8B), -13.8 (4B), -19.8 (2B). $^{11}$B (22 °C): $\delta$ = 9.7 (2B), 4.3 (d, 2B, J(HB) = 135 Hz), -5.4 (8B), -13.8 (d, 4B, J(HB) = 157 Hz), -19.8 (2B).
Preparation of commo-[3,3’-Fe[8-(SMe2)-1,2-C2B6H10]2] (5)

To a solution of 10-SMe7,8-C2B6H10 (0.15 mg, 0.251 mmol) and BuLi (0.15 mL, 0.270 mmol) in 2 mL of thf was added FeCl3(dppe) (80 mg, 0.152 mmol) leading to a violet solution. After refluxing for 30 minutes, the solvent was evaporated and EtOH (5 mL) was added. The resulted violet precipitated was filtered off and washed with EtOH (5 mL). The solid is dried in vacuo to yield 35 mg of 5 (63%).

Acknowledgements

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References


Neutral nido-heteroboranes with non ionisable hydrogen as arenes in coordination

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Designed ligands have been synthesised to produce the first arene-like metallacarborane. For arene-like coordination the number of electronegative elements on the coordinating site must be kept to a minimum. Choosing ligands with bulky substituents on the heteroatom allows easy rearrangement and arene-like coordination. This is more hampered the higher the number of heteroatoms to be re-located.

In recent years, there has been great interest towards the synthesis and study of heteroboranes with a high heteroelement to boron ratio. The result are clusters with a lower number of bridging hydrogen atoms (ionisable hydrogen atoms), and with a lower negative charge. This can be exemplified with the sequence nido-B11H13 ([B11H11]4–), C2B9H13 ([C2B9H11]2–) and C6B6H6, in which the nature of the cluster skeleton elements is changed while its number is kept constant. Some examples of neutral heteroboranes with non-ionisable hydrogen atoms are C2B7H7,22 P,C-B-H,22 7-P,C-B-H,22 7-Pb-7,8,10-P2C6B7H19,22 and arachno-C,H,B8H13.22-24 These species either have a substituent R (R=H, organic group) or a lone pair at each cluster vertex. While metal coordination by anionic boranes and heteroboranes is common, no example has been reported of a metal coordinated to a neutral nido or arachno species with non-ionisable hydrogen atoms. This may be interpreted as if such process was not possible. On the other hand, considering the existence of bis(arene) and arene half-sandwich complexes it might be anticipated that the arene-like heteroborane neutral species should behave similarly; but, is it really as simple as this?

We have addressed this question by producing a neutral nido C2B7 skeletal cluster with no bridging hydrogen atoms, in which the necessary extra electrons to conform to the Polyhedral Skeletal Electron Pair (PSEP) theory are given by Lewis bases moieties. In this aim ([SMe2]C2B7H6),16 which can exist as different isomers, was chosen as a suitable arene-like heteroborane neutral species. Reasons to choose the 7,10-(SMe2)2-7,8-C2B9H9 (I) isomer were based on the synthetic routes available, and because it was expected that a high steric energy would built up upon complexation to metal facilitating rearrangements within the cluster. The reactions are shown in Scheme 1, steps a) and b). Compound I is isoelectronic and isostructural to 11-vertex triheteroborane species such as 7,10,11-SC2B9H7,23 7-R-7,10,11-PC2B7H13,3c 7,8,9-As,Sb,B9H7,29 7,8,9-As,Se,B9H95,12 8,1,2-SC2B9H1013 and 8,1,2-SeC2B9H1014. Therefore, we have treated I as a triheteroborane-like neutral molecule where the three heteroatoms would be C-SMe2, C-H, and B-SMe2.

Reaction of [Rh(acac)(cod)] (30.5 mg, 98.3 µmol) in 1 mL of THF with 13 µL (104 µmol) of HBF4 (8.0 M solution in water) yielded a solution containing [Rh(cod)].12 To this solution was added I (25 mg, 98.3 µmol) in 4 mL of CH3Cl, the mixture was stirred for an additional hour, and then refluxed for 30 minutes yielding a yellowish pale solid (Scheme 1, step c). After reducing the volume to approximately 1 mL, 10 mL of CHCl3 was added, and the mixture cooled to 0 ºC followed by filtration affording a green-yellowish solid, 48.8 mg (90 %) having the formula [Rh(cod)][(SMe2)2C2B9H9][BF4], [2][BF4].

Compound 2 has a C1 symmetry, and it was expected that this would be preserved in [2][BF4]. Indeed this is the case, and the 11B-NMR in CD3COCD3 shows 8 resonances at δ -0.2 (1B, BF4), -0.5(1B), -9.0 (1B), -11.6 (2B), -13.5 (1B), -14.3 (1B), -21.9 (1B), -23.2 (2B) with two resonances of intensity 2 arising from a coincidental overlap. This is the first cationic metallacarborane complex with a neutral carborane ligand, and thus the first example of arene-like type of coordination of a borane moiety. Metallacarboranes derived from the monoanionic [C2B7H13] tricarborane ligand with either [C-C-C] or [C-C-B-C] strings in the C2B7 open face result from either an isomerization of at least one open face carbon atom to the second layer or from a deboronation yielding a “C3B7” cluster, with three carbon atoms coordinated to the metal.6 A similar process was expected to the triheteroborane-like I.

Good quality crystals of [2][BF4] were grown by slow evaporation of a heptane layered acetone solution. Crystal structure analysis confirmed isomerization of the carborane ligand I during complexation. The SM25 group of ligand I, connected to cluster carbon C(7) at the upper belt of the nido cage, has moved during complexation to lower belt to produce [2-cod-8,11-(SMe2)2-2,1,8-RhC2B9H9], [2]†. A perspective view of [2]† is shown in Fig. 1.

Scheme 1. Synthetic procedure to yield the compounds 1 and 2. a) S(CH3)2, CH3CHO, H+ in toluene. b) NaOH, MeI in CH3OH. c) [Rh(acac)(cod)], HBF4 in THF.

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from the most stable isomer in the free ligand to the most suitable isomer for coordination. Choosing heteroatoms with bulky substituents has permitted low temperature re-arrangements. A further conclusion could most possibly be drawn: the larger the number of heteroatoms to re-locate the more hampered the coordination process would be.16

We have then demonstrated that arené-like metallocarboranes can be produced with purposely designed ligands, and that the absence of metallocarboranes with neutral polyheteroboroligand is significant and meaningful.

Notes and references


7. In some complexes like those containing (CH₃)₄C₄B₈H₈ or C₂B₁₀H₁₂, Me or Me₂ as ligands one could consider that the original number of atoms in the ligand had been preserved. In reality the two above cited species must be accounted as dianionic.


17. Crystal data: C₁₂H₁₂B₁₀F₄Rh₂S₄, monoclinic, space group P2₁/c, a = 18.0250(4), b = 9.7442(3), c = 13.7608(2) Å, V = 2324.82(8) Å³, T = 293 K, F(000) = 1120, 7399 reflections collected, 4109 unique (R(int) = 0.0211). The structure was solved by direct methods and refined on F² by the SHELX-97 program to R1 = 0.0239 (wR2 = 0.0497) with a goodness-of-fit of 1.040. CCDC reference number 212591. See http://www.ccdc.cam.ac.uk/structures/ce/c1/b12591/ for crystallographic data in CIF or other electronic format.
