Annex

(Treballs pendents de publicació)

Synthesis and characterization of new phosphine η^5-Ru(II) complexes containing monoanionic charge compensated ligands

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Ruthenacarborane complexes of formula [3-H-3,3-$(PPh_3)_2$-8-L-3,1,2-$RuC_2B_9H_{10}$)] (L = SMe_2 (**2a**), SEt_2 (**2b**), $S(CH_2)_4$ (**2c**), SEtPh (**2d**)) and [1-Me-3-H-3,3-$(PPh_3)_2$-8-L-3,1,2-$RuC_2B_9H_9$)] (L = SMe_2 (**2e**), SEt_2 (**2f**)) were 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 [$RuCl_2(PPh_3)_3$]. Similary, complexes [3-H-3,3,8-$(PPh_3)_3$-3,1,2-$RuC_2B_9H_{10}$)] (**4a**) and [3-H-3,3-$(PPh_3)_2$-8-PPh_2Me-3,1,2-$RuC_2B_9H_{10}$)] (**4b**) were prepared from 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 **4a** 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 C_2B_3 open face, two PPh_3 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

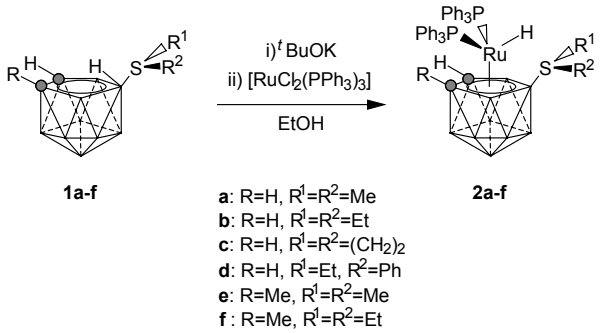
First examples of metallacarboranes were prepared about 35 years ago by Hawthorne et *al*., using the dicarbollide, $[C_2B_9H_{11}]^{2-}$ as ligand to form *closo*-M-C_2B_9 icosahedral clusters.[i] This ligand has been compared to $[C_5H_5]^-$, as both behave as formal 6-electron donors[ii] to metal atoms via η^5-face bonding. Thus, a great number of researchers from a variety of scientific backgrounds have developed this field.[iii] 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 $[LC_2B_9H_{10}]^-$ (L = pyridine, THF, SR_2, PPh_3, etc) have been described.[iv] Many transition metal (Rh, Fe, Rh, Pd, Mo, etc) complexes of these monoanionic carboranes have been prepared and fully characterized.[iiic,iv,v,vi,vii] The majority of these charge-compensated complexes contain the carborane ligands with the substituent at the 9 position, [9-L-7,8-*nido*-$C_2B_9H_{10}]^-$ or [9-L-7,8-R_2-*nido*-$C_2B_9H_8]^-$. Ligands with the substituent at the 10 position, [10-L-7,8-*nido*-$C_2B_9H_{10}]^-$,[ivc,vg] have been much less studied. The preparation of *closo* metallic complexes with monoanionic charge-compensated carborane ligands bearing an SR_2 or PR_3 group at the B(9) atom has been accomplished using two methods. The first one, generally used for [9-SMe_2-*nido*-7,8-R_2-7,8-$C_2B_9H_8]^-$ ligands, consists in the addition of the thallium salts of the ligand to a solution of the metallic complex in CH_2Cl_2.[vi] 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.[iiic,v,viia-b] The latter has also been used to prepare the few known complexes of [10-L-*nido*-7,8-$C_2B_9H_{10}]^-$ ligands with Co, Mo and Fe.[ivc,g,vg]

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*-$C_2B_9H_9]^-$ (L = SMe_2, SEt_2, $S(CH_2)_4$, SEtPh, PPh_3, PPh_2Me; 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 potential use as catalytic precursors for cyclopropanation, controlled radical polymerization, ATRP and Kharasch addition reactions. Some results about their catalytic activity have already been published by us.[viii] Crystal structures of [3-H-3,3-$(PPh_3)_2$-8-SMe_2-3,1,2-$RuC_2B_9H_{10}$] and [3-H-3,3,8-$(PPh_3)_3$-3,1,2-$RuC_2B_9H_{10}$] are also described. Some aspects of this work have been previously reported as a communication.[ix]

Results

Synthesis and Characterization of [3-H-3,3-$(PPh_3)_2$-8-L-3,1,2-$RuC_2B_9H_{10}$)] and [1-Me-3-H-3,3-$(PPh_3)_2$-8-L-3,1,2-$RuC_2B_9H_9$)] (L = SMe_2, SEt_2, $S(CH_2)_4$, SEtPh)

The reaction of 10-L-7,8-$C_2B_9H_{11}$ (L = SMe_2 (**1a**), SEt_2 (**1b**), $S(CH_2)_4$ (**1c**), SEtPh (**1d**)) with *t*-BuOK and [$RuCl_2(PPh_3)_3$] in 1.5:1.5:1 ratio in EtOH, at 50 ºC for one hour, resulted in the formation of yellow solids of general formula [3-H-3,3-$(PPh_3)_2$-8-L-3,1,2-$RuC_2B_9H_{10}$)] (L = SMe_2 (**2a**), SEt_2 (**2b**), $S(CH_2)_4$ (**2c**) and SEtPh (**2d**)), in yields ranging 85-95%. For the asymmetric ligands, 7-Me-10-L-7,8-$C_2B_9H_{10}$ (L = SMe_2 (**1e**), SEt_2 (**1f**)), orange compounds of general formula [1-Me-3-H-3,3-$(PPh_3)_2$-8-L-3,1,2-$RuC_2B_9H_9$)] (L = SMe_2 (**2e**), SEt_2 (**2f**)) were obtained. The reaction is depicted in Scheme 1.



Scheme 1 Formation of [1-R-3-H-3,3-$(PPh_3)_2$-8-SR^1R^2-3,1,2-$RuC_2B_9H_9$].

[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**.

Complex	δ_H (ppm)[a]		
	CH_3	S-CH_2-	CH_2
2a	2.28 (6H)	–	–
2b	1.21 (6H)	2.67 (2H) 3.09 (2H)	–
2c	–	2.82 (2H) 3.31 (2H)	1.82 (2H) 2.18 (2H)
2d	0.84 (3H)	2.95 (2H)	–
2e	1.79 (3H) 2.64 (3H)	–	–
2f	0.91 (3H) 1.50 (3H)	2.35 (2H) 2.93 (1H) 3.77 (1H)	–

[a] 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 ν(B-H) absorption, between 2520 and 2551 cm^{-1}. Low intensity bands were observed in the region 1960-2100 cm^{-1} attributable to ν(Ru-H).[vc] The absorptions at 1433, 1096, 744 and 695 cm^{-1} are typical of PPh_3 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.[ivd] 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 ($^2J(PH)$= 33-34 Hz) (Fig. 1a), however for the asymmetric compounds **2d-f** the signal appears as a doublet of doublets with two different $^2J(PH)$ (Fig. 1b).[vc,e] In addition, resonances attributable to aromatic hydrogen atoms from the phenyl groups, Ccarborane-H (Cc-H), and hydrogen atoms on the sulfonium groups are found for **2a-f.** The Cc-H resonances for compounds **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-CH_2 protons in complexes **2b-d,f** are magnetically non-equivalent, showing two J(HH) coupling constants, one for the geminal protons ($^2J(HH)$ = 13.4 Hz) and a second one for the neighbor CH_3 or CH_2 protons ($^3J(HH)$ = 7.4 Hz).

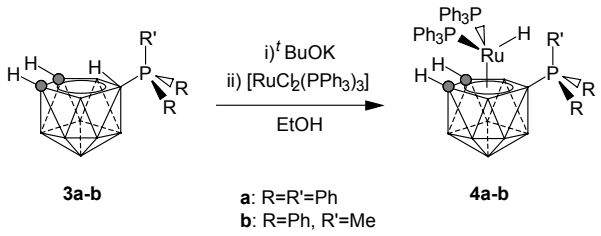
The $^{13}C\{^1H\}$ NMR spectra for **2a-f** display peaks corresponding to the organic groups bonded either to the sulfur and/or phosphorus atoms. The $^{11}B\{^1H\}$ spectra for **2a-f** was in agreement with the proposed symmetry; in all complexes the resonance at lower field was assigned to the sulfur-bearing atom B(8) by comparison with the ^{11}B NMR spectra. The $^{31}P\{^1H\}$ 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 ^{31}P NMR spectra with $^2J(PH)$ *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 $^2J(PP)$, ranging 25-30 Hz (Table 2).

Table 2 ^{31}P chemical shifts reported in ppm, $^2J(PH)$ values and $^2J(PP)$ values expressed in Hz for compounds **2a-f**.

Complex	δ_P	$^2J(PH)$	$^2J(PP)$
2a	55.88	33	-
2b	55.77	33	-
2c	55.80	34	-
2d	58.18 / 53.01	31/30	31
2e	52.31 / 46.72	40/30	25
2f	51.98 / 46.71	40/31	26

Synthesis and Characterization of [3-H-3,3,8-(PPh_3)$_3$-3,1,2-$RuC_2B_9H_{10}$] and [3-H-3,3-(PPh_3)$_2$-8-PPh_2Me-3,1,2-$RuC_2B_9H_{10}$]

Following a similar procedure as for the preparation of **2a-f**, the reaction of the potassium salts of [10-PPh_3-7,8-$C_2B_9H_{10}$]$^-$ (**3a**) and [10-$PMePh_2$-7,8-$C_2B_9H_{10}$]$^-$ (**3b**) with [$RuCl_2(PPh_3)_3$] led to the formation of complexes [3-H-3,3,8-(PPh_3)$_3$-3,1,2-$RuC_2B_9H_{10}$] (**4a**) and [3-H-3,3-(PPh_3)$_2$-8-PPh_2Me-3,1,2-$RuC_2B_9H_{10}$] (**4b**), respectively (see Scheme 2).



Scheme 2 Formation of [3-H-3,3-(PPh_3)$_2$-8-PR_2R'-3,1,2-$RuC_2B_9H_{10}$].

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 ($^2J(PH)$ = 33 Hz, $^3J(PH)$ = 11-12 Hz) (Fig. 1c), the latter splitting being due to coupling to phosphorus of the phosphonium moiety, B-PPh_3. Resonances due to the two Cc-H protons are observedd as a singlet around 3 ppm, and those due to the phenyl groups are found in the 6.90-7.50 ppm region.

The $^{31}P\{^1H\}$ NMR spectra of **4a**, at room temperature, has shown a singlet at 58.59 ppm, attributed to two equivalent PPh_3 ancillary ligands, and a tetraplet at 12.70 ppm due to the B-PPh_3 group ($^1J(BP)$ = 126 Hz). The equivalent resonances for **4b** are observed at 57.98 ppm, for PPh_3, and 2.17 ppm, for the B-PPh_2Me group ($^1J(BP)$ = 140 Hz). the resonances at 58.59 ppm for 4a and 57.98 ppm for 4b become a doublet with $^2J(P,H)$ = 33 Hz in the ^{31}P NMR spectra. A doublet is observed both in the $^{11}B\{^1H\}$ and ^{11}B NMR spectra at -5.3 ppm for **4a** and -7.6 ppm for **4b**, due to the B-P coupling.

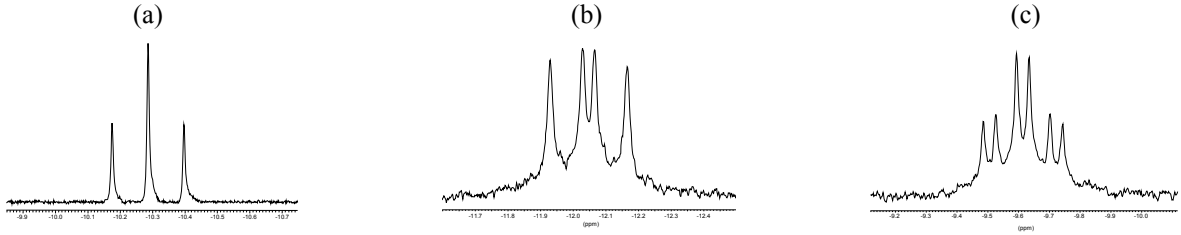


Fig. 1 Selected ^1H NMR portion corresponding to the hydride region in (a) compound **2b**, (b) compound **2d** and (c) compound **4a**.

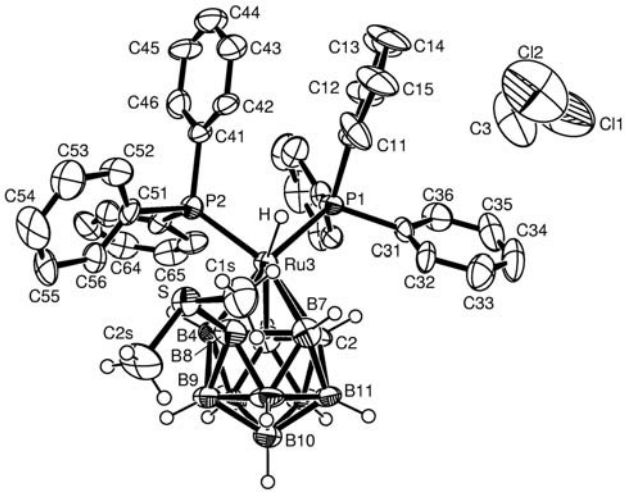


Fig. 2 Thermal ellipsoid plot (50% probability) of **2a**·CH_2Cl_2 (phenyl hydrogen atoms are omitted for clarity).

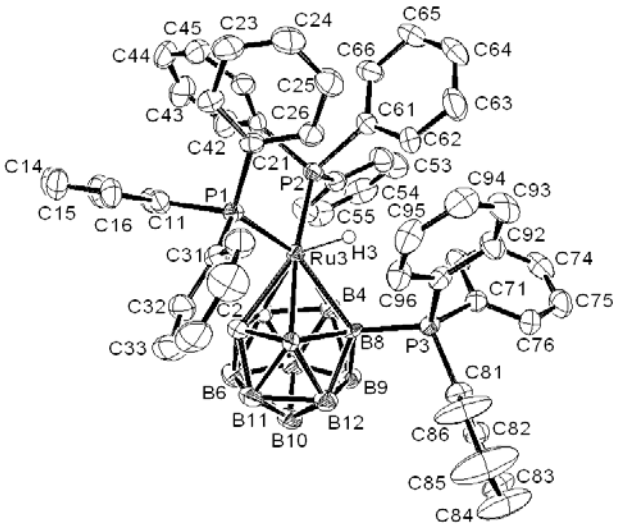


Fig. 3 Thermal ellipsoid plot (50% probability) of **4a** (phenyl hydrogen atoms removed for clarity).

Table 3 Crystallographic data for complexes **2a**·CH_2Cl_2 and **4a**.

	2a·CH_2Cl_2	**4a**
Formula	$C_{41}H_{49}B_9Cl_2P_2RuS$	$C_{56}H_{56}B_9P_3Ru$
Formula Weight	905.06	1020.2
Temperature/K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	P 21/c
Z	2	4
a/Å	11.483(4)	11.632
b/Å	12.888(2)	11.523
c/Å	15.220(12)	38.514
α/º	97.31(3)	90
β/º	97.65(4)	92.76
γ/º	100.65(2)	90
V/ Å^3	2167(2)	5156.3
μ(Mo-Kα)/mm^{-1}	0.638	0.435
Reflections collected	9123	15413
Independent reflections	8721	15209
Decay	1%	—
Max. and min. transmission	0.9577 and 0.6972	—
R_1 (I>2σ(I))	0.082	0.0852
wR_2 (all data)	0.232	0.227

Table 4 Selected interatomic distances (Å), angles (º) and torsion angles (º) for **2a**·CH_2Cl_2.

Ru(3)-B(4)	2.203(11)	Ru(3)-P(1)	2.321(3)
Ru(3)-C(2)	2.234(9)	Ru(3)-P(2)	2.298(3)
Ru(3)-B(8)	2.239(13)	Ru(3)-H	1.60(9)
Ru(3)-B(7)	2.304(12)	C11···C42	3.166(13)
Ru(3)-C(1)	2.307(10)	C16···C42	3.236(16)
Ru(3)-S	3.435(3)		
P(2)-Ru(3)-P(1)	96.12(10)	C(2)-Ru(3)-C(1)	40.9(4)
P(2)-Ru(3)-H	88 (3)	C(1)-Ru(3)-P(1)	106.2(2)
P(1)-Ru(3)-H	72 (3)	C(2)-Ru(3)-P(1)	91.5(3)
P(2)-Ru(3)-C(1)	111.3(3)	B(4)-B(8)-S	126.9(8)
C(2)-Ru(3)-P(2)	152.0(3)	B(7)-B(8)-S	119.4(8)
B(4)-B(8)-S-S(lone pair)	-36.8(1.5)		

X-ray Diffraction Studies of [3-H-3,3-(PPh_3)$_2$-8-SMe_2-3,1,2-$RuC_2B_9H_{10}$)] (2a)

Yellow crystals of **2a** crystallized from a 1:1 CH_2Cl_2/hexane solution, under nitrogen, to give yellow crystals adequate for X-Ray diffraction analysis. The ORTEP[x] view of **2a**·CH_2Cl_2 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

Table 5 Selected interatomic distances (Å) and angles (º) for **4a**.

C(1)-C(2)	1.570(7)	B(8)-P(3)	1.942(5)
C(1)-Ru(3)	2.318(4)	B(8)-Ru(3)	2.312(4)
C(2)-Ru(3)	2.285(4)	P(1)-Ru(3)	2.3146(12)
B(4)-Ru(3)	2.293(5)	P(2)-Ru(3)	2.3360(13)
B(7)-Ru(3)	2.288(5)		
C(2)-C(1)-Ru(3)	68.9(2)	C(2)-Ru(3)-P(2)	138.61(13)
B(6)-C(1)-Ru(3)	128.9(4)	P(1)-Ru(3)-P(2)	95.26(4)
B(7)-C(2)-Ru(3)	67.9(2)	C(1)-Ru(3)-P(2)	105.01(14)
C(2)-Ru(3)-P(1)	90.25(14)	B(7)-B(8)-P(3)	124.7(3)
C(2)-Ru(3)-C(1)	39.87(19)	B(4)-B(8)-P(3)	126.6(3)
P(1)-Ru(3)-C(1)	119.59(14)	B(9)-B(8)-P(3)	111.2(3)

three formal coordination sites occupied by the C_2B_3 open face, two by the PPh_3 ligands and the remaining site by the hydride. The present coordination is similar to that observed in [3-H-3,3-(PPh_3)$_2$-3,1,2-$RhC_2B_9H_{11}$],[xi] 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 C_2B_9, 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[viic] instead of phosphine ligands. The τ parameter,[iiic] 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-SMe_2-3,1,2-*closo*-$RuC_2B_9H_{10}$] and similar compounds,[viic] this conformation can be explained by steric repulsion between the SMe_2 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-(PPh_3)$_3$-3,1,2-$RuC_2B_9H_{10}$)] (4a)

Crystals of **4a** suitable for a single-crystal X-ray study were obtained by slow evaporation of a CH_2Cl_2/hexane/PPh_3 solution of the complex. A drawing of the compound may be seen in Figure 3, with crystal data and selected interatomic dimensions

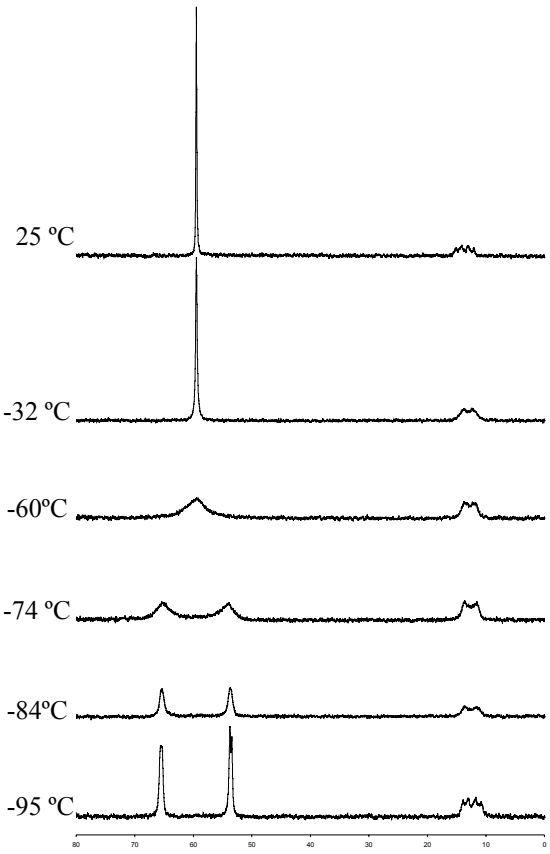


Fig. 4 Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra of complex **4a**.

being listed in Table 3 and 5, respectively. Compound **4a** is revealed to be a *closo*-ruthenacarborane in which a PPh_3 sgroup is bonded to the B(8) atom of the upper face, and the other two PPh_3 ligands are coordinated to Ru(II) placed on the C_2B_3 open face, in a similar way to that observed in complex **2a**. However, in complex **4a** the distance from Ru3 to the open face of C_2B_9, 1.777(2) Å, is longer to that found in **2a** (1.735(5) Å); in the same way the distances of Ru3 to the open face atoms C1, C2, B4, B7 and B8 are found in the ranging between 2.285(4) Å to 2.318(4) Å, and are slightly longer than those observed in complex **2a**. In the latter, the distance Ru3-B8 is 2.239(13) Å, shorter to that for **4a** (2.312(4) Å), probably due to the presence of a less crowded sulfonium substituent, instead of the phosphonium one. In both complexes, **2a** and **4a**, the large P1-Ru(3)-P2 angle, 96.12(10)º and 95.26(4)º respectively, and the short C···C distances between different rings have been found (C21···C46 = 3.157(7), 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 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-$C_2B_9H_{10}$]$^-$ 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-$C_2B_9H_{10}$]$^-$ 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 decarbonylation of alcohols.[xii] These reaction conditions produce **2a** impurified with a complex of the type $[RuH(CO)_x(PPh_3)_y]$. 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.

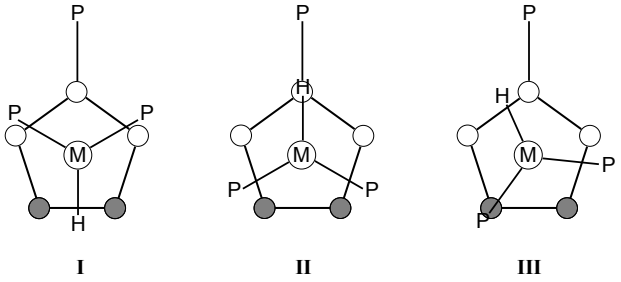


Fig. 2 Thermal ellipsoid plot (50% probability) of **2a**·CH_2Cl_2 (phenyl hydrogen atoms removed for clarity).

The room temperature $^{31}P\{^{1}H\}$ NMR of all symmetric complexes (**2a-c** and **4a,b**) 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 $^{31}P\{^{1}H\}$ NMR dynamic study for **2a-c** and **4a,b** was carried out so as to investigate the rotational behavior of these complexes. Interestingly, the $^{31}P\{^{1}H\}$ NMR spectra for compounds **2a-c** were invariant from 25 ºC to -95 ºC. 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 $^{31}P\{^{1}H\}$ NMR spectra of **4a** at room temperature is considered, only a singlet at 58.59 ppm is found. Near -60 ºC the decoalescence of this resonance takes place and two different phosphorus signals were clearly observed at -95 ºC. These resonances consist of two doublets with a $^{2}J(PP)$ = 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.[vc] 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 $PRPh_2$ 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.[xiii,xiv] For instance, $[CpRuL_2Cl]$ and $[Cp^*RuL_2Cl]$ can be easily converted into

$[CpRuL_2(D)]$ and $[Cp^*RuL_2(D)]$, in methanol-d_4/ sodium methoxide-d_3 at reflux and at room temperature, respectively. The latter occurs at room temperature, apparently due to the better electron donating properties of Cp* vs Cp.[xiii] The monoanionic charge-compensated carborane ligands reported here are also electron-donating ligands resembling, therefore, the Cp*, and are able to react in the same way. Thus, although we have not enough data to explain the reaction pathways, we propose the formation of a first species containing a Cl^- ligand, which quickly react under mild conditions to give the corresponding hydride complex. The reaction would take place in few minutes which have prevented to isolate the chloride species.

All these ruthenium complexes have been already tested as catalytic precursors in radical reactions such as Kharasch addition of CCl_4 to olefins and cyclopropanation, where have shown to be very efficient catalysts.[viii,ix]

Conclusion

These results demonstrate the preparation of ruthenacarborane complexes from 7-R-10-L-7,8-$C_2B_9H_{10}$ charge-compensated ligands, through a very simple one-pot reaction of the ligands with $[RuCl_2(PPh_3)_3]$ after deprotonation with K[*t*-BuO]. The new *closo*-complexes have shown, after full characterization, to posses two PPh_3 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 (Fluorochem) were freeze-pump-thawed three times under N_2 and transferred to the NMR tube using standard vacuum line techniques. The reagents **1a-c**,[ive] **1d-f**,[ivc] **3a**,[vd] **3b**,[xv] and $[RuCl_2(PPh_3)_3]$[xvi] 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), $^{13}C\{^1H\}$ (75.47 MHz), ^{11}B, $^{11}B\{^1H\}$ NMR (96.29 MHz) ^{31}P and $^{31}P\{^1H\}$ 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 ºC. Chemical shift data for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to $SiMe_4$, those for $^{11}B\{^1H\}$ and ^{11}B RMN spectra were referenced to external $BF_3{\cdot}Et_2O$ and those for $^{31}P\{^1H\}$ RMN spectra were referenced to external 85 % H_3PO_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).

Synthesis of the complex [3-H-3,3-$(PPh_3)_2$-8-SMe_2-3,1,2-$RuC_2B_9H_{10}$] (2a)

Method I) To a deoxygenated solution of ethanol (10 mL) containing **1a** (100 mg, 0.514 mmol) was added K[*t*-BuO] (58 mg, 0.514 mmol). The mixture was heated at 50 ºC, and $[RuCl_2(PPh_3)_3]$ (493 mg, 0.514 mmol) was added. The mixture was stirred for one hour at 50 ºC, 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 resulted 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.

Method II) 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 $[RuCl_2(PPh_3)_3]$ (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. 70. $C_{40}H_{47}B_9P_2SRu$ requires C, 58.58; H, 5.77; S, 3.91% *M* 819.28); ν_{max}/cm^{-1} 2555 (B-H), 1963 (Ru-H); δ_H ($CDCl_3$): -10.37 [t, 1H, ^2J(PH) 33, Ru-H], 2.17 (s, 2H, C_c-H), 2.28 (s, 6H, S-CH_3) and 6.98-7.92 (m, 30H, C_6H_5); $\delta_{P\{H\}}$ ($CDCl_3$): 55.88 (s); δ_P ($CDCl_3$): 55.88 [d, ^2J(PH) 33]; δ_B NMR ($CDCl_3$): -2.3 (1B), -10.1 [d, 1B, ^1J(BH) 128], -14.2 (1B), -16.5 [d, 3B, ^1J(BH) 147) and -25.1(3B); δ_C ($CDCl_3$): 26.04 (s, S-CH_3) and 127.25-138.67 (C_6H_5).

Synthesis of the complex [3-H-3,3-$(PPh_3)_2$-8-SEt_2-3,1,2-$RuC_2B_9H_{10}$] (2b)

The process was the same as for compound **2a** using 100 mg (0.448 mmol) of **1b**, 50 mg (0.448 mmol) of K[*t*-BuO] and 286 mg (0.299 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of deoxygenated ethanol (Method II). The mixture was stirred for 1 h at 50 ºC 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. $C_{42}H_{51}B_9P_2SRu$ requires C, 59.47; H, 6.06; S, 3.78% *M* 847.28); ν_{max}/cm^{-1} 2536 (B-H), 2029 (Ru-H); δ_H ($CDCl_3$): -10.29 [t, 1H, ^2J(PH) 33, Ru-H], 1.21 [t, ^3J(HH) 7.4, 6H, CH_3), 2.17 (br s, 2H, C_c-H), 2.67 [dq, 2H, ^2J(HH) 13.4, ^3J(HH) 7.4, S-CH_2], 3.09 [dq, 2H, ^2J(HH) 13.4 ^3J(HH) 7.4, S-CH_2] and 7.73-7.00 (m, 30H, C_6H_5); $\delta_{P\{H\}}$ ($CDCl_3$): 55.77 (s); δ_P ($CDCl_3$): 55.77 [d, ^2J(PH) 33]; δ_B ($CDCl_3$): 0.5 (1B), -8.0 [d, 1B, ^1J(BH) 132], -11.9 (1B), -14.4 [d, 3B, ^1J(BH) 134] and -23.0(3B); δ_C ($CDCl_3$): 13.30 (s, CH_3), 35.90 (s, S-CH_2) and 127.16-138.74 (C_6H_5).

Synthesis of the complex [3-H-3,3-$(PPh_3)_2$-8-$S(CH_2)_4$-3,1,2-$RuC_2B_9H_{10}$] (2c)

The process was the same as for compound **2a** using 100 mg (0.452 mmol) of **1c**, 61 mg (0.452 mmol) of K[*t*-BuO] and 289 mg (0.300 mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of deoxygenated ethanol. The mixture was stirred for 1 h at 50 ºC to form yellow solid. The solid was filtered and washed as described above to give **2c** (230 mg, 91%), (Found: C, 58.83; H, 5.77; S, 3.61. $C_{42}H_{49}B_9P_2SRu$ requires C, 59.61; H, 5.84; S, 3.79% *M* 845.28); ν_{max}/cm^{-1} 2576, 2551, 2522 (B-H), 2052 (Ru-H); δ_H ($CDCl_3$): -10.29 [t, 1H, ^2J(PH) 34, Ru-H], 1.82 (m, 2H, CH_2), 2.18 (m, 2H, CH_2), 2.21 (br s, 2H, C_c-H), 2.82 (m, 2H, S-CH_2), 3.31 (m, 2H, S-CH_2) and 7.00-7.73 (m, 30H, C_6H_5); $\delta_{P\{H\}}$ ($CDCl_3$): 55.80 (s); δ_P ($CDCl_3$): 55.80 [d, ^2J(PH) 34 Hz]; δ_B ($CDCl_3$): -1.5 (1B), -9.3 [d, 1B, ^1J(BH) 129], -14.1 (1B), -16.1 [d, 3B, ^1J(BH) 126) and -25.1 (3B); δ_C ($CDCl_3$): 30.30 (s, CH_2), 44.25 (s, S-CH_2) and 127.16-138.72 (C_6H_5).

Synthesis of the complex [3-H-3,3-$(PPh_3)_2$-8-SEtPh-3,1,2-$RuC_2B_9H_{10}$] (2d)

The process was the same as for compound **2a** using 100 mg (0.369 mmol) of **1d**, 41 mg (0.369 mmol) of K[*t*-BuO] and 236 mg (0.246mmol) of $[RuCl_2(PPh_3)_3]$ in 10 mL of deoxygenated ethanol. The mixture was stirred for 1 h at 50 ºC to obtain a yellow solid. The solid was filtered and washed as described above to give **2d** (194 mg, 88%), (Found: C, 61.12; H, 5.54; S, 3.60. $C_{46}H_{51}B_9P_2SRu$ requires C, 61.66; H, 5.69; S, 3.57% *M* 895.28); ν_{max}/cm^{-1} 2576, 2524 (B-H), 2064 (Ru-H); δ_H ($CDCl_3$): -10.38 [dd, 1H, ^2J(PH) 30.5, ^2J(PH) 30.4, Ru-H], 0.84 [t, 3H, ^3J(HH) 7.4, CH_3], 2.56 (s, 1H, C_c-H), 1.75 (s, 1H, C_c-H), 2.95 (m, 2H, S-CH_2) and 6.98-7.77 (m, 35H, C_6H_5); $\delta_{P\{H\}}$ ($CDCl_3$): 58.19 [d, ^2J(PP) 31], 53.01 [d, ^2J(PP) 31); $\delta_{B\{H\}}$ ($CDCl_3$): 0.02 (1B), -9.8 (1B), -12.2 (3B), -21.1(3B) and -26.2 (1B); δ_C

($CDCl_3$): 12.93 (s, CH_3), 38.15 (s, S-CH_2) and 127.70-139.90 (C_6H_5).

Synthesis of the complex [1-Me-3-H-3,3-(PPh_3)$_2$-8-SMe_2-3,1,2-$RuC_2B_9H_9$] (2e)

The process was the same as for compound **2a** using 100 mg (0.479 mmol) of **1e**, 54 mg (0.479 mmol) of K[*t*-BuO] and 306 mg (0.320 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. $C_{41}H_{49}B_9P_2SRu$ requires C, 59.05; H, 5.88; S, 3.84% M 833.28); ν_{max}/cm^{-1} 2551, 2517 (B-H), 2029 (Ru-H); δ_H ($CDCl_3$): -12.16 [dd, ^{2}J(PH) 40, ^{2}J(PH) 30, Ru-H], 1.79 (s, 3H, S-CH_3), 2.00 (br s, 1H, C_c-H), 2.21 (s, 3H, Cc-CH_3), 2.64 (s, 3H, S-CH_3) and 7.00-7.73 (m, 30H, C_6H_5); $\delta_{P\{H\}}$ ($CDCl_3$): 52.31 [d, ^{2}J(PP) 25 and 46.72 ^{2}J(PP) 25); δ_B ($CDCl_3$): -1.5 (1B), -10.5 (2B), -13.2 [d, 1B, ^{1}J(BH) 141], -16.3 (3B), -19.7 [d, 1B, ^{1}J(BH) 126] and -26.1 (1B); δ_C ($CDCl_3$): 24.86 (s, Cc-CH_3), 28.53 (s, S-CH_3) and 127.86-140.03 (C_6H_5).

Synthesis of the complex [1-Me-3-H-3,3-(PPh_3)$_2$-8-SEt_2-3,1,2-$RuC_2B_9H_9$] (2f)

The process was the same as for compound **2a** using 100 mg (0.423 mmol) of **1f**, 48 mg (0.423 mmol) of K[*t*-BuO] and 270 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 obtain a 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, 3.77. $C_{43}H_{53}B_9SP_2Ru$ requires C, 59.91; H, 6.15; S, 3.72% *M* 861.28); ν_{max}/cm^{-1}: 2557, 2522 (B-H), 2042 (Ru-H); δ_H ($CDCl_3$): -12.04 [dd, 1H, ^{2}J(PH) 40, ^{2}J(PH) 31, Ru-H], 0.91 [t, 3H, ^{3}J(HH) 7.4, CH_3], 1.50 [t, 3H, ^{3}J(HH) 7.4 Hz, CH_3], 2.01 (br s, 1H, C_c-H), 2.23 (s, 3H, C_c-CH_3), 2.35 (m, 2H, S-CH_2), 2.93 [dq, 1H, ^{2}J(HH) 13.4, ^{3}J(HH) 7.4, S-CH_2], 3.77 [dq, 1H, ^{2}J(HH) 13.4, ^{3}J(HH) 7.4, S-CH_2] and 7.00-7.73 (m, 30H, C_6H_5); $\delta_{P\{H\}}$ ($CDCl_3$): 51.98 [d, ^{2}J(PP) 26] and 46.71 [d, ^{2}J(PP) 26]; δ_B ($CDCl_3$): -1.5 (1B), -10.4(2B), -12.8 (1B), -16.7 (3B), -20.4 [d, 1B, ^{1}J(BH) 136] and -26.1 (1B); δ_C ($CDCl_3$): 13.74 (s, CH_3), 22.42 (s, Cc-CH_3), 34.23 (s, S-CH_2) and 127.85-139.72 (C_6H_5).

Synthesis of the complex [3-H-3,3,8-(PPh_3)$_3$-3,1,2-$RuC_2B_9H_{10}$] (4a)

The process was the same as for compound **2a** using 204 mg (0.516 mmol) of **3a**, 64mg (0.516 mmol) of K[*t*-BuO] and 330 mg (0.344 mmol) of [$RuCl_2(PPh_3)_3$] in 10 mL of deoxygenated ethanol (Method II). The mixture was stirred for 2 days at 50 ºC obtaining a yellow suspension. The solid was filtered and washed as described above to give **4a** (333 mg, 95%) (Found: C, 65.78; H, 5.73. $C_{56}H_{56}B_9P_3Ru$ requires C, 65.92; H, 5.53% *M* 1019.18); ν_{max}/cm^{-1} 2543, 2575 (B-H), 2102 (Ru-H); δ_H ($CDCl_3$): -9.61 [dt, 1H, ^{2}J(PH) 33, ^{3}J(PH) 12, Ru-H], 3.17 (br, 2H, Cc-H) and 6.91-7.36 (m, 45H, C_6H_5); $\delta_{P\{H\}}$ (CD_2Cl_2): 58.59 (s) and 12.70 [tp, ^{1}J(PB) 126]; δ_P (CD_2Cl_2): 58.59 [d, ^{2}J(PH) 33] and 12.70 [br tp, ^{1}J(PB) 126];δ_B (CD_2Cl_2): -5.3 [d, ^{1}J(PB) 126], -9.3, -14.9, -20.9, and -25.5.

Synthesis of the complex [3-H-3,3-(PPh_3)$_2$-8-PPh_2Me-3,1,2-$RuC_2B_9H_{10}$] (4b)

The process was the same as for compound **4a** using 50 mg (0.150 mmol) of **3b**, 18 mg (0.169 mmol) of K[*t*-BuO] and 96 mg (0.100 mmol) of [$RuCl_2(PPh_3)_3$] in 10 mL of deoxygenated ethanol. The mixture was stirred overnight at 50 ºC to give a yellow solid which was filtered and washed as described above to give **4b** (85 mg, 89%) (Found: C, 63.34; H, 5.66. $C_{51}H_{54}B_9P_3Ru$ requires C, 63.92; H, 5.68% *M* 957.18); ν_{max}/cm^{-1} 2543 (B-H), 2056 (Ru-H); δ_H ($CDCl_3$): -9.97 [dt, 1H, ^{2}J(PH) 33, ^{3}J(PH) 11, Ru-H], 1.39 [d, 3H, ^{3}J (PH) 11, CH_3], 3.14 (br, 2H, Cc-H) and 6.98-7.48 (m, 40H, C_6H_5); $\delta_{P\{H\}}$ (CD_2Cl_2): 57.98 (s) and 2.17 [tp, ^{1}J(PB) 140]; δ_P (CD_2Cl_2): 57.98 [d, ^{2}J(PH) 33] and 2.17 [br tp, ^{1}J(PB) 140];δ_B (CD_2Cl_2): -7.6 [d, ^{1}J(PB) 140 Hz], -15.1, -21.7 and -26.4.

X-Ray crystallography

Single crystal data collection was performed on an Enraf Nonius CAD4 diffractemeter using MoKα radiation. Cell parameters from 16 reflections with 10º < θ < 13º randomly searched for **2a**[ix] and 25 reflections with 11º < θ <13º for **4a**. Data were collected using ω/2θ scans. The WinGX program[x] was used for applying Lorentz-polarisation, and ψ-scan absorption corrections. For **4a** the structure was solved by direct methods using SIR2002[xvii] and refined by full-matrix, least squares method on F^2 using the SHELX97 programs[xviii]. All the hydrogen atoms were situated in calculated positions and refined riding on their bonded atom. Non-hydrogen atoms were anisotropically refined. Isotropic thermal vibration for the hydrogen atoms was fixed to 1.2-1.5 times U_{iso} of the bonded atom. The final refinement statistics and crystallographic information are shown in Table 3.

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Formation of new η^5-Rh(III) complexes from η^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-$RhC_2B_9H_{10}$)] (L = SMe_2 (**2a**), SEt_2 (**2b**), $S(CH_2)_4$ (**2c**), SEtPh (**2d**)) and [1-Me-3,3-$(PPh_3)_2$-8-L-3,1,2-$RhC_2B_9H_9$)] (L = SMe_2 (**2e**), SEt_2 (**2f**)) has 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 [$RhCl(PPh_3)_3$]. Complex [3,3'-cod-8-SMe_2-3,1,2-$RhC_2B_9H_{10}$] (**3**) has also been prepared by reaction of K[10-SMe_2-7,8-$C_2B_9H_{10}$] with [$(RhCl_2cod)_2$]. Rh(I). Complexes **2a-d** may be easily oxidized to the corresponding Rh(III) complexes **4a-d** 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-d** to **4a-d** 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.

Introduction

To date, a large number of metallacarboranes using the $[C_2B_9H_{11}]^{2-}$ dianionic dicarbollide ligand have been developed to form *closo*-M-C_2B_9 icosahedral clusters.[1,2] Also a few transition metal complexes[2c,3,4,5,6] with monoanionic charge-compensated ligands of the type $[LC_2B_9H_{10}]^-$ (L = pyridine, THF, SR_2, PPh_3, OEt_2, NR_3, etc) have been reported.[3b,4d,7] In general, all these complexes have been designed to establish detailed comparisons with their analogous cyclopentadienyl-metal complexes.[8] The main difference between both type of dicarbollide ligands is the total charge. In this respect, it is generally accepted that the dianionic $[C_2B_9H_{11}]^{2-}$ cluster stabilizes higher oxidation states than the monoanionic $[LC_2B_9H_{10}]^-$ 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.[7c] We have recently reported a series of charge-compensated monoanionic ligands with general formula [10-R_2S-7,8-$C_2B_9H_{10}]^-$, which seem to be capable to stabilize two consecutive oxidation states in a metal. This can be very relevant in different steps of a catalytic process.[9] In fact, ruthenium complexes [3-H-3,3'-PPh_3-8-L-3,1,2-$RuC_2B_9H_{10}$] of these ligands, analogous to [$RuClCp'(PR_3)_2$] (Cp'= Cp, substituted Cp), have been proven to be very active in cyclopropanation, radical polymerization and Kharasch addition catalytic reactions.[9,10]

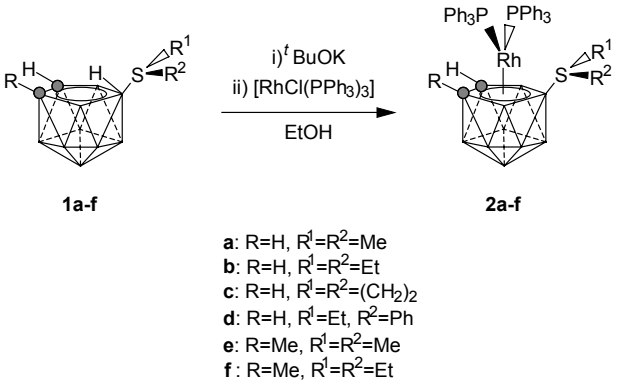
On the other hand, half-sandwich rhodium complexes containing a Cp' ligand, such as [$Cp'Rh(PPh_3)Cl_2$] and [$Cp'Rh(PPh_3)_2$], have demonstrated to be efficient catalysts for olefin hydrogenation, among other.[11] Nevertheless, until now, few Rh(I) [3e-f,4c-d] and Rh(III)[4g,6] complexes with dicarbollide 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 [$Cp'Rh(PPh_3)_2$] and [$Cp'Rh(PPh_3)Cl_2$], respectively, in which the Cp' has been replaced by the dicarbollide charge-compensated ligand [10-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.

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-$RhC_2B_9H_9$] (L = SMe_2, SEt_2, $S(CH_2)_4$, SEtPh)

The neutral charge-compensated *nido*-carboranes of general formula 7-R-10-L-7,8-$C_2B_9H_{10}$ (R = H; L = SMe_2 (**1a**), SEt_2 (**1b**), $S(CH_2)_4$ (**1c**), SEtPh (**1d**), and R = Me; L = SMe_2 (**1e**), SEt_2 (**1f**)) react quantitatively with K[*t*-BuO] in degassed ethanol to form the corresponding anionic species. The reaction of any of the anionic ligands with [$RhCl(PPh_3)_3$], in a 1:1 ratio, afforded dark-yellow solids formulated as [1-R-3,3-$(PPh_3)_2$-8-L-3,1,2-$RhC_2B_9H_9$)] (R = H; L = SMe_2 (**2a**), SEt_2 (**2b**), $S(CH_2)_4$ (**2c**), SEtPh (**2d**) and R = Me; L = SMe_2 (**2e**), SEt_2 (**2f**)). The reaction is shown in Scheme 1.



Scheme 1 Formation of [1-R-3,3-$(PPh_3)_2$-8-SR^1R^2-3,1,2-$RhC_2B_9H_9$].

[†] O.Tutusaus is enrolled in the UAB PhD program.

Table 1 Proton chemical shift data for the alkyl substituent on B(10) sulfonium moiety.

	$\delta(^1H)$ (ppm)[a]		
Complex	CH_3	S-CH_2-	CH_2
2a	2.33 (6H)	–	–
2b	1.30 (6H)	2.77 (2H) 3.05 (2H)	–
2c	–	2.96 (2H) 3.31 (2H)	1.87 (2H) 2.19 (2H)
2d	0.78 (3H)	3.00 (2H)	–
2e	2.36 (3H) 2.73 (3H)	–	–
2f	1.05 (3H) 1.61 (3H)	2.45 (1H) 2.59 (1H) 2.96 (1H) 3.30 (1H)	–

[a] The number between brackets corresponds to the protons area.

Table 2 ^{31}P chemical shifts reported in ppm, $^1J(Rh, P)$ values and $^2J(P_a, P_b)$ values expressed in Hz for compounds **2a-f**.

Complex	$\delta(^{31}P)$	$^1J(Rh, P)$	$^2J(P_a, P_b)$
2a	43.91	192	-
2b	42.47	192	-
2c	43.86	192	-
2d	42.97	192	-
2e	43.14 / 33.93	202 / 181	43
2f	42.12 / 33.33	199 / 182	47

The ^1H NMR, ^{31}P NMR and ^{11}B NMR spectra of complexes **2a-d** are consistent with a C_s symmetry molecule, while complexes **2e** and **2f** exhibit a C_1 symmetry. In the ^1H NMR spectra, the two distinct methylene protons in complexes **2b**, **2c** and **2f** exhibit an ABC_3 spin system with $^1J(H_a, H_b)$ = 13.4 Hz and $^3J(H_{a,b}, H_c)$ = 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 $^{11}B\{^1H\}$ 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 $^{31}P\{^1H\}$ 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 $^2J(P_a, P_b)$ 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 $^{31}P\{^1H\}$ NMR at room temperature. The variable temperature $^{31}P\{^1H\}$ NMR spectra of **2d** in CD_2Cl_2, are displayed in Figure 1. It can be interpreted as an A_2M spin system at room temperature which coalesces at –40 ºC. At –90 ºC the spectrum features two doublets of doublets corresponding to an ABM spin system. These details are in agreement with the hindered rotation of the $Rh(PPh_3)_2$ moiety about the metal-carborane ligand axis.[3f]

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.

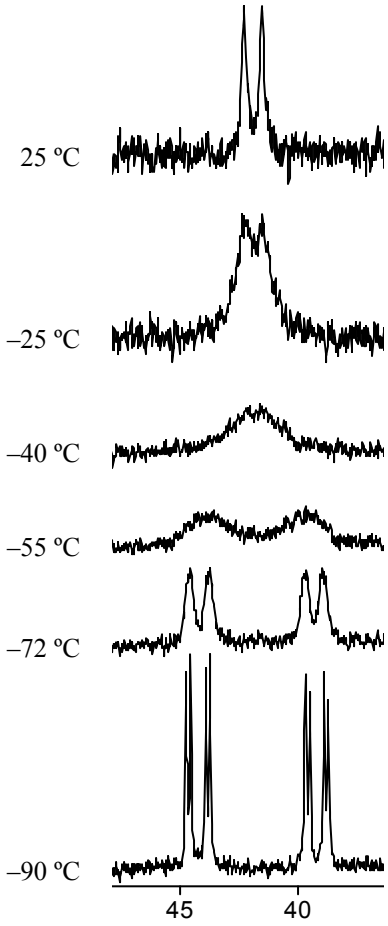


Fig. 1 Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex **2d**.

Synthesis and characterization of [3,3-cod-8-SMe_2-3,1,2-$RhC_2B_9H_{10}$]

In a similar way, the reaction of a degassed ethanolic solution of $K[10\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]$ 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 C_s symmetry. The ^1H NMR spectrum displays resonances at 2.25, 2.43, and 4.37 ppm attributable to the cycloocta-1,5-diene ligand,[4c] and a broad resonance at 3.12 ppm due to the Cc-H protons. The ^{11}B NMR resonances appear in the region between 3.2 to –25.0 ppm, common for *closo* compounds.

Complex **3** crystallized from $CHCl_3$ 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 1.736(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 CH_2Cl_2 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 $CHCl_3$, CCl_4, $CHBr_3$ or $ClCH_2CH_2Cl$, a change of colour from dark-yellow to red takes place under N_2, at room temperature, to form the new complexes **4a-d**. Contrarily, solutions of **2e-f** in the latter solvents are unstable, even under N_2, leading to total decomposition of the

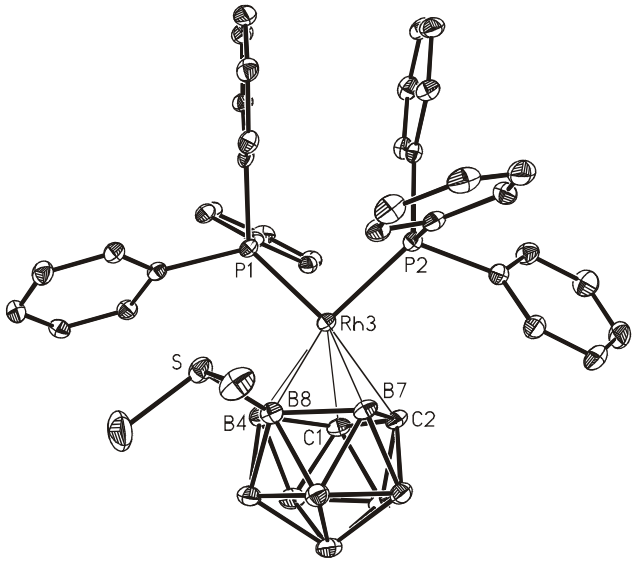


Fig. 2 Molecular structure of **2a**·0.912CH_2Cl_2 (hydrogen atoms removed for clarity). Displacement ellipsoids are drawn at 30% probability.

Table 3 Selected bond lengths (Å) and angles (º) for **2a**·0.912CH_2Cl_2.

Rh3-C1	2.422(4)	Rh3-P1	2.2461(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)

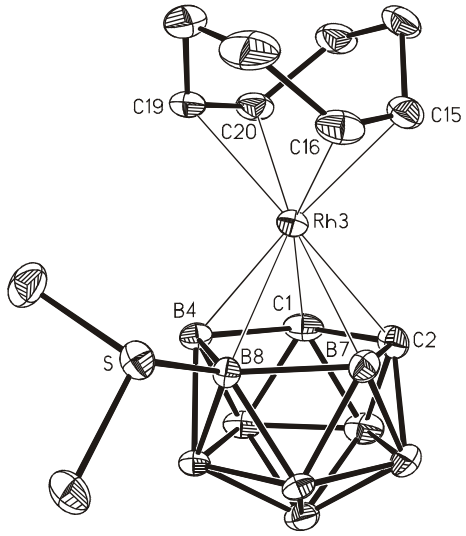
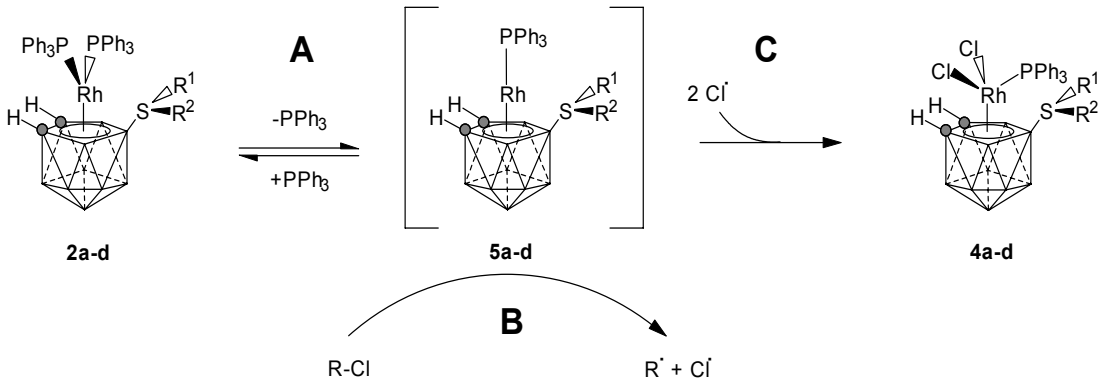


Fig. 3 Molecular structure of **3** (hydrogen atoms are omitted for clarity). Displacement ellipsoids are drawn at 20% probability.

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)		



a: R^1=R^2=Me
b: R^1=R^2=Et
c: R^1=R^2=$(CH_2)_2$
d: R^1=Et, R^2=Ph

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

product. 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_2Cl_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**.

From 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 ^1H NMR spectrum shows a singlet in the aliphatic region (2.28 ppm)

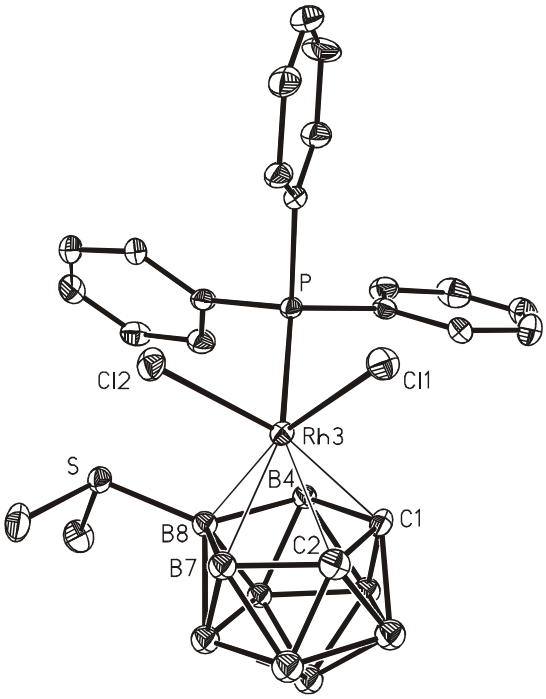


Fig. 4 Molecular structure of **4a**·$CHCl_3$ (hydrogen atoms removed for clarity). Displacement ellipsoids are drawn at 20% probability.

Table 5 Selected bond lengths (Å) and angles (º) for **4a**·$CHCl_3$.

Rh3-C1	2.161(9)	Rh3-Cl1	2.433(3)
Rh3-C2	2.210(11)	Rh3-Cl2	2.386(3)
Rh3-B4	2.164(11)	Rh3-P	2.357(3)
Rh3-B7	2.239(13)	C1-C2	1.649(18)
Rh3-B8	2.204(10)	S-B8	1.909(11)
B7-B8-S	121.4(7)	S-B8-Rh3	114.2(5)
B4-B8-S	126.9(9)		

attributed to the SMe_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 $^{11}B\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR spectrum features a doublet at 33.50 ppm, with a coupling constant $^1J(Rh, P) = 124$ 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-$RhC_2B_9H_{10}$] **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

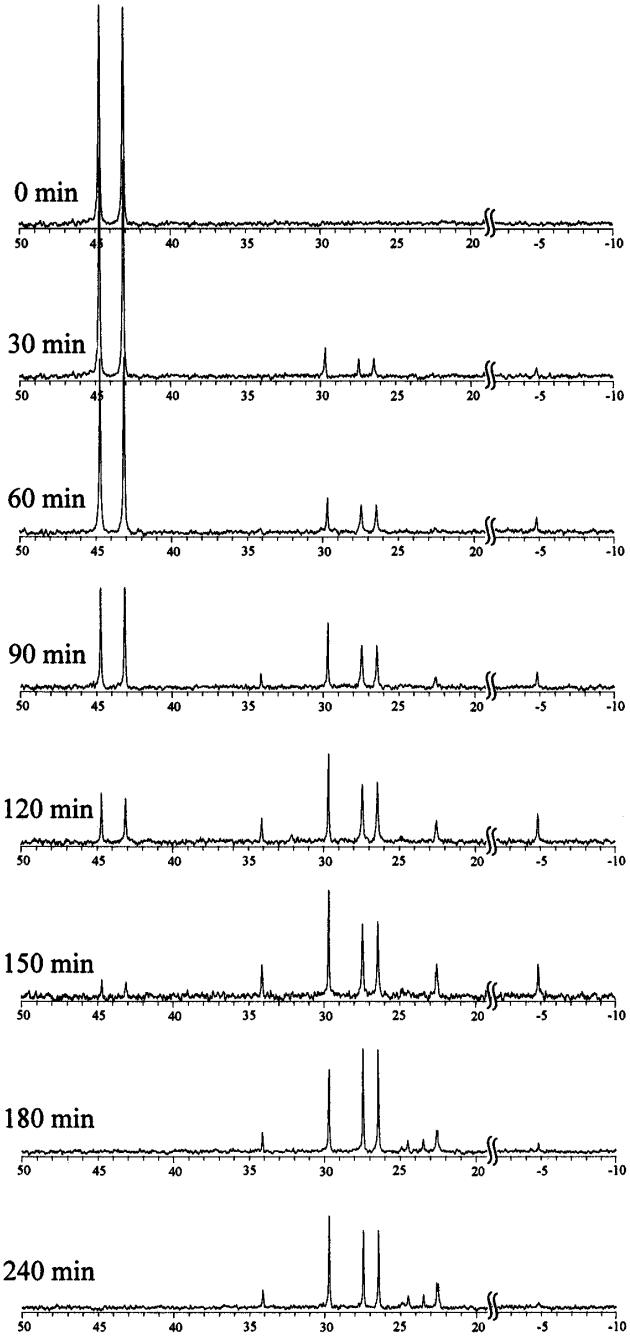


Fig. 5 $^{31}P\{^1H\}$ NMR spectra of **2a** in $CDCl_3$ showing the conversion to **4a**.

techniques. Firstly, the importance of the release of the phosphane ligand was evaluated by $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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

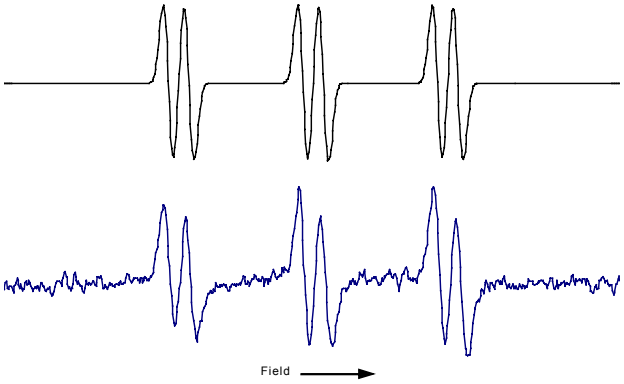


Fig. 6 Simulated and experimental EPR spectrum of PBN adducts observed in a $CHCl_3$ solution of **2a**.

90 minutes, two new and unidentified phosphorous containing species, with resonances at δ(^{31}P) 22.55 and 34.15 ppm, were also observed. After 3 hours, complex **2a** was no longer present and had been transformed into **4a**, as confirmed by the absence of the signal at 43.91 ppm and the presence of an intense doublet at 26.93 ppm. The ^{1}H NMR also supported a mixture of **2a** and **4a** after 30 minutes time, displaying two singlets in the aliphatic region attributed to the SMe_2 protons and two broad resonances at 2.05 and 3.87 ppm, due to the Cc-H protons. The ^{11}B{^{1}H} NMR spectrum also showed the formation of new species.

The dynamic study indicates that the release of PPh_3 occurs during the first step (step A, Scheme 2), and phosphorus containing by-products are formed in subsequent steps. We interpret that by-products are the result of the interaction of intermediate species with liberated PPh_3. Contrarily to the reaction with $CHCl_3$ or CCl_4, we had noticed that **2a** in $ClCH_2CH_2Cl$ only afforded **4a**, PPh_3 and $OPPh_3$. This suggested a radical mechanism, caused by **5a** that implies the homolytic cleavage of the halogenated solvent (see step B in Scheme 2). Homolytic cleavage of $ClCH_2CH_2Cl$ would lead to a birradical species $^{\bullet}CH_2CH_2^{\bullet}$, which would be removed from the solution as ethylene, allowing no further reaction with free PPh_3. In order to detect the presence of such free radicals, the EPR spectrum of a $CHCl_3$ solution of **2a** containing an excess of the spin-trap N-*tert*-butyl-α-phenylnitrone (PBN) was recorded. Figure 6 presents the EPR spectrum, as well as the EPRFTSM simulated spectrum,[13] showing a set of three equally spaced doublets centered at g = 2.0054 due to the coupling with one *N* and one *H* nuclei. The hyperfine splitting constants derived from the fitting procedure are a_N = 14.6 G and a_H = 2.26 G and are attributable to the PBN trapped $CHCl_2^{\bullet}$ radical following comparison with literature values.[14] The PBN trapped $Cl^{\bullet}$ radical is also generated but is not detected at the EPR spectrum due to its very short lifetime. No reddening of the solution was observed in the presence of the spin-trap PBN which indicates that the PBN had trapped the $Cl^{\bullet}$ radicals, preventing the oxidation of **5a**. Consequently, the cleavage of the solvent was conducted by **5a** (step B, Scheme 2) prior to its oxidation to **4a**; later on, in a reaction in which PBN had not been added, **5a** would capture the $Cl^{\bullet}$ radicals to yield **4a** (step C, Scheme 2). This analysis clearly evidences the formation of free radicals as intermediates in the evolution of **2a** to **4a**.

No such behaviour has been mentioned in the previously reported and structurally analogous Rh(I) complexes with isomeric charge-compensated ligands. Examples included [3,3-$(PPh_3)_2$-4-C_5H_5N-3,1,2-$RhC_2B_9H_{10}$], [3-PPh_3-3-CO-4-C_5H_5N-3,1,2-$RhC_2B_9H_{10}$],[3e-f] [3,3-$(CO)_2$-4-SMe_2-3,1,2-$RhC_2B_9H_{10}$] and [1-Ph-3,3-$(CO)_2$-7-SMe_2-3,1,2-$RhC_2B_9H_{10}$].[4d-e] The only reported example in which oxidation was accomplished, was by direct reaction of [3,3-$(CO)_2$-4-SMe_2-3,1,2-$RhC_2B_9H_{10}$] with iodine in ether to afford [3-(CO)-3,3-$(I)_2$-4-SMe_2-3,1,2-$RhC_2B_9H_{10}$].[4g]

Conclusions

In view of the results, we can deduce that Rh(I) complexes containing the charge-compensated cluster [10-L-7,8-$C_2B_9H_{10}]^-$ and PPh_3 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,[9] 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-$C_2B_9H_{10}]^-$.[9] 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 ^{1}H NMR (300.13 MHz), ^{11}B, ^{11}B{^{1}H} NMR (96.29 MHz) and ^{31}P{^{1}H } 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 ºC. Chemical shift data for ^{1}H and ^{13}C {^{1}H} NMR spectra were referenced to $SiMe_4$, those for ^{11}B{^{1}H} and ^{11}B RMN spectra were referenced to external BF_3 Et_2O and those for ^{31}P{^{1}H} RMN spectra were referenced to external 85 % H_3PO_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).

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 N_2 and transferred to the NMR tube using standard vacuum line techniques. **1a-c**[7d] were synthesized as is described in the literature. **1d-f**[7f] were also freshly prepared. $[RhCl(PPh_3)_3]$[15] and $[\{Rh(cod)Cl\}_2]$[16] 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-$(PPh_3)_2$-8-SMe_2-3,1,2-$RhC_2B_9H_{10}$] (2a)

To a deoxygenated solution of ethanol (15 mL) containing carborane zwitterion **1a** (110 mg, 0.565 mmol) and K[*t*-BuO] 67 mg, 0.597 mmol) was added $RhCl(PPh_3)_3$ (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 %). ^{1}H NMR ($CDCl_3$): δ 2.05 (br s, 2H,C_c-*H*), 2.33 (s, 6H, S-CH_3), 6.90-7.92 (m, 30H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 43.91 (d, ^1J(P, Rh) = 192 Hz). ^{11}B NMR ($CDCl_3$): δ 1.3 (s, 1B), -16.8 (d, ^1J(B, H)= 129 Hz, 4B), -22.1 (4B). FTIR (KBr), ν (cm^{-1}): 2545 (B-H). Anal. Calcd for $C_{40}H_{46}B_9P_2RhS$: C, 58.52; H, 5.65; S, 3.91 %. Found: C, 58.49; H, 5.77; S, 3.79.

Synthesis of [3,3-$(PPh_3)_2$-8-SEt_2-3,1,2-$RhC_2B_9H_{10}$] (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[*t*-BuO] and 537

mg (0.580 mmol) of $RhCl(PPh_3)_3$ 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. [3,3-$(PPh_3)_2$-8-SEt_2-3,1,2-$RhC_2B_9H_{10}$] (**2b**). (Yield: 376 mg, 76%). ^{1}H NMR ($CDCl_3$): δ 1.30 (t, 6H, ^3J(H, H) = 7.4 Hz, CH_3), 2.10 (br s, 2H,C_c-*H*), 2.77 (m, 2H, S-CH_2), 3.05 (m, 2H, S-CH_2), 7.08-7.54 (m, 30H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 42.47 (d, ^1J(P, Rh) = 192 Hz). ^{11}B NMR ($CDCl_3$): δ 1.8 (s, 1B), -16.6 (d, ^1J(B, H) = 126 Hz, 4B), -22.4 (4B). FTIR (KBr), ν (cm^{-1}): 2535 (B-H). Anal. Calcd for $C_{42}H_{50}B_9P_2RhS$: C, 59.41; H, 5.94; S, 3.78 %. Found: C, 58.40; H, 5.62; S, 3.48.

Synthesis of [3,3-$(PPh_3)_2$-8-$S(CH_2)_4$-3,1,2-$RhC_2B_9H_{10}$] (2c)

The process was the same as for compound **2a** using 125 mg (0.566 mmol) of **1c**, 67 mg (0.597 mmol) of K[*t*-BuO] and 552 mg (0.564 mmol of $RhCl(PPh_3)_3$ 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. [3,3-$(PPh_3)_2$-8- $S(CH_2)_4$-3,1,2-$RhC_2B_9H_{10}$] (**2c**). (Yield: 412 mg, 86%). ^{1}H NMR ($CDCl_3$): δ 1.87 (m, 2H, CH_2), 2.03 (br s, 2H,C_c-*H*), 2.19 (m, 2H, CH_2), 2.96 (m, 2H, S-CH_2), 3.31 (m, 2H, S-CH_2), 7.10-7.65 (m, 30H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 43.86 (d, ^1J(P, Rh) = 192 Hz). ^{11}B NMR ($CDCl_3$): δ 1.1 (1B), -16.8 (d, ^1J(B, H) = 119 Hz, 4B), -21.7 (2B), -23.9 (2B). FTIR (KBr), ν (cm^{-1}): 2541 (B-H). Anal. Calcd for $C_{42}H_{48}B_9P_2RhS$: C, 59.55; H, 5.71; S, 3.79 %. Found: C, 58.89; H, 5.60; S, 3.55.

Synthesis of [3,3-$(PPh_3)_2$-8-SEtPh-3,1,2-$RhC_2B_9H_{10}$] (2d)

The process was the same as for compound **2a** using 125 mg (0.461 mmol) of **1d**, 54 mg (0.481 mmol) of *t*-BuOK and 425 mg (0.459 mmol) $RhCl(PPh_3)_3$ 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 [3,3-$(PPh_3)_2$-8-SEtPh-3,1,2-$RhC_2B_9H_{10}$] (**2d**). (Yield: 311 mg, 76%). ^{1}H NMR ($CDCl_3$): δ 0.78 (t, 3H, ^3J(H, H) = 7.4 Hz, CH_3), 2.93 (br s, 2H,C_c-*H*), 3.00 (q, 2H, ^3J(H, H) = 7.4 Hz, S-CH_2), 6.99-7.57 (m, 35H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 42.97 (d, ^1J(P, Rh) = 192 Hz). ^{11}B NMR ($CDCl_3$): δ 0.6 (1B), -11.9 (d, ^1J(B, H) = 118 Hz, 1B), -16.5 (2B), -21.9 d, ^1J(B, H) = 109 Hz, 5B). FTIR (KBr), ν (cm^{-1}): 2565, 2533, 2513 (B-H). Anal. Calcd for $C_{46}H_{49}B_9P_2RhS$: C, 61.66; H, 5.51; S,3.58 %. Found: C, 61.67; H, 5.51; S, 3.65.

Synthesis of [1-Me-3,3-$(PPh_3)_2$-8-SMe_2-3,1,2-$RhC_2B_9H_9$] (2e)

The process was the same as for compound **2a** using 125 mg (0.599 mmol) of **1e**, 70 mg (0.623 mmol) of K[*t*-BuO] and 551 mg (0.595 mmol) $RhCl(PPh_3)_3$ 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. [1-Me-3,3-$(PPh_3)_2$-8-SMe_2-3,1,2-$RhC_2B_9H_9$] (**2e**). (Yield: 388 mg, 78%). ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 3H, C_c-CH_3), 2.36 (s, 3H, S-CH_3), 2.73 (s, 3H, S-CH_3), 7.10-7.53 (m, 30H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 43.14 (dd, ^1J(P, Rh) = 202 Hz, ^2J(P, P) = 43 Hz), 33.93 (dd, ^1J(P, Rh) = 181 Hz, ^2J(P, P) = 43 Hz). ^{11}B NMR ($CDCl_3$): 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), ν (cm^{-1}): 2516, 2550 (B-H). Anal. Calcd for $C_{41}H_{48}B_9P_2RhS$: C, 58.97; H, 5.79; S, 3.84 %. Found: C, 58.26; H, 5.53; S, 3.41.

Synthesis of [1-Me-3,3-$(PPh_3)_2$-8-SEt_2-3,1,2-$RhC_2B_9H_9$] (2f)

The process was the same as for compound **2a** using 113 mg (0.477 mmol) of **1f**, 56 mg (0.499 mmol) of K[*t*-BuO] and 440 mg (0.475 mmol) $RhCl(PPh_3)_3$ 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. [1-Me-3,3-$(PPh_3)_2$-8-SEt_2-3,1,2-$RhC_2B_9H_9$] (**2f**). (Yield: 280 mg, 68%). ^{1}H NMR (CD_2Cl_2): δ 1.05 (t, 3H, ^3J(H, H) = 7.3 Hz, CH_3), 1.61 (t, 3H, ^3J(H, H) = 7.3 Hz, CH_3), 1.29 (br s, 1H, C_c-*H),* 1.69 (s, 3H, CH_3), 2.45 (m, 1H, SCH_2,), 2.59 (m, 1H, SCH_2), 2.96 (m, 1H, SCH_2), 3.30 (m, 1H, SCH_2), 7.05-7.90 (m, 30H, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.12 (dd, ^1J(P, Rh) = 199 Hz; ^2J(P, P) = 47 Hz), 33.33 (dd, ^1J(P, Rh) = 182 Hz; ^2J(P, P) = 47 Hz). ^{11}B NMR (CD_2Cl_2): 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), ν (cm^{-1}): 2519, 2551, 2573 (B-H). Anal. Calcd for $C_{43}H_{52}B_9SP_2Rh$: C, 59.84; H, 6.07; S,3.71 %. Found: C, 59.36; H, 5.87; S, 3.22.

Synthesis of [3,3'-cod-8-SMe_2-3,1,2-$RhC_2B_9H_{10}$] (3)

To a deoxygenated solution of ethanol (15 mL) containing carborane zwitterion **1a** (100 mg, 0.515 mmol) and K[*t*-BuO] (64 mg, 0.540 mmol) was added [{RhClcod}$_2$] (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 filtered and washed 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 %). ^{1}H NMR ($CDCl_3$): δ 2.25 (m, 4H, CH_2), 2.43 (m, 4H, CH_2), 2.63 (s, 6H, S-CH_3), 3.12 (br s, 2H, C_c-*H*), 4.37 (m, 4H, CH_2). ^{11}B NMR ($CDCl_3$): δ 3.2 (1B), -14.4 (d, ^1J(B, H)= 143 Hz, 3B), -16.4 (d, ^1J(B, H)= 181 Hz, 2B) -22.1 (d, ^1J(B, H)= 155 Hz, 2B), -24.9 (d, ^1J(B, H)= 166 Hz, 1B). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.4, 32.3, 38.4, 75.6 (d, ^1J(C_c, Rh) = 13 Hz). FTIR (KBr), ν (cm^{-1}): 2543, 2504, 2679 (B-H). Anal. Calcd for $C_{12}H_{28}B_9RhS$: C, 35.62; H, 6.98; S, 7.93 %. Found: C, 35.39; H, 6.78; S, 7.69.

Synthesis of [3-PPh_3-3,3-Cl_2-8-SMe_2-3,1,2-$RhC_2B_9H_{10}$] (4a)

When compound **2a** was dissolved in CHX_3; 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 $CHCl_3$. (85 %). ^{1}H NMR (acetone-d^6): δ 2.28 (s, 6H, S-CH_3), 3.87 (br s, 2H, C_c-*H*), 7.35-8.02 (m, 15H, C_6H_5). ^{31}P{^{1}H} NMR (acetone-d^6): δ 33.50 (d, ^1J(P, Rh) = 124 Hz). ^{11}B NMR ($CDCl_3$): δ 10.8 (d, ^1J(B, H) = 141 Hz, 1B), 5.7 (3B), -3.2 (d, ^1J(B, H) = 139 Hz, 2B), -10.8 (1B), –14.2 (d, ^1J(B, H) = 159 Hz, 2B). ^{13}C{^{1}H} NMR: δ 26.5, 128.4, 130.5, 132.0, 133.6, 134.9. FTIR (KBr), ν (cm^{-1}): 2553 (B-H). Anal. Calcd for $C_{22}H_{31}B_9Cl_2PRhS{\cdot}0.7CHCl_3$: C, 38.32; H, 4.63; S, 4.13 %. Found: C, 38.23; H, 4.45; S, 4.49.

Synthesis of [3-PPh_3-3,3-Cl_2-8-SEt_2-3,1,2-$RhC_2B_9H_{10}$)] (4b)

Complex **4b** was formed from a solution of compound **2b** in 5 mL of $CDCl_3$. The formation of this complex was only monitored by NMR in solution, but **4b** was not isolated. ^{1}H NMR ($CDCl_3$): δ 1.12 (t, 6H, CH_3), 2.46 (m, 2H, S-CH_2), 3.04 (m, 2H, S-CH_2), 3.85 (br s, 2H, C_c-*H*), 7.35-8.02 (m, 15H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 25.12 (d, ^1J(P, Rh) = 121 Hz). ^{11}B NMR ($CDCl_3$): δ 6.4 (d, ^1J(B, H) = 125 Hz, 1B), 0.4 (3B), -8.5 (d, ^1J(B, H) = 128 Hz, 2B), -15.5 (1B), -19.3 (d, ^1J(B, H) = 143 Hz, 2B). ^{13}C{^{1}H} NMR: δ 12.2, 36.5, 128.4, 130.5, 132.0, 133.8.

Synthesis of [3-PPh_3-3,3-Cl_2-8-tht-3,1,2-$RhC_2B_9H_{10}$)] (4c)

The procedure was the same as for compound **4b** using compound **2c** in 5 mL of $CDCl_3$. ^{1}H NMR ($CDCl_3$): δ 1.28 (m, 2H, CH_2), 1.99 (m, 2H, CH_2), 2.85 (m, 2H, S-CH_2), 3.01 (m, 2H, S-CH_2), 3.87 (br s, 2H, C_c-*H*), 7.37-8.07 (m, 15H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 25.54 (d, ^1J(P, Rh) = 121 Hz). ^{11}B NMR ($CDCl_3$): δ 6.3 (d, ^1J(B, H) = 125 Hz, 1B), 1.6 (1B), -0.3 (2B), -8.3 (d, ^1J(B, H) = 128 Hz, 2B), -15-3 (1B), –19.2 (2B).

Table 6 Crystallographic parameters for **2a**·0.912CH_2Cl_2, **3** and **4a**·$CHCl_3$.

	2a·0.912CH_2Cl_2	**3**	**4a**·$CHCl_3$
Empirical Formula	$C_{40}H_{46}B_9P_2RhS$·0.912CH_2Cl_2	$C_{12}H_{28}B_9RhS$	$C_{22}H_{31}B_9Cl_2PRhS$·$CHCl_3$
Formula Weight	898.25	404.60	748.97
Crystal System	Triclinic	Monoclinic	Monoclinic
Crystal habit, color	Prism, Pale Yellow	Prism, Yellow	Plate, Red
Space Group	*P*-1 (no. 2)	$P2_1/c$	$P2_1$
a (Å)	9.2945(4)	7.086(3)	9.014(2)
b (Å)	12.2403(5)	14.502(9)	18.608(3)
c (Å)	19.7289(7)	18.208(6)	10.060(2)
α(deg)	105.032(3)	90	90
β (deg)	96.062(2)	90.56(3)	100.676(17)
γ (deg)	101.274(2)	90	90
V (Å^3)	2096.72(14)	1871.0(15)	1658.2(6)
Z	2	4	2
Temperature (K)	-100	20	21
ρ (g cm^{-3})	1.423	1.436	1.500
μ (cm^{-1})	6.81	10.13	10.45
GOF[a] on F^2	1.012	1.017	1.082
R[b] [$I > 2\sigma(I)$]	0.0468	0.0353	0.0445
R_w[c] [$I > 2\sigma(I)$]	0.0976	0.0758	0.0947

[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$, [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [c] $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Synthesis of [3-PPh_3-3,3-Cl_2-8-SEtPh-3,1,2-$RhC_2B_9H_{10}$)] (4d)

The process was the same as for compound **4b** using compound **2d** in 5 mL of $CDCl_3$. ^{1}H NMR ($CDCl_3$): δ 1.13 (t, 3H, CH_3), 2.83 (br s, 1H, C_c-*H*), 3.24 (m, 1H, S-CH_2), 3.22 (m, 1H, S-CH_2), 4.57 (br s, 1H, Cc-*H*), 7.08-8.02 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 24.84 (d, ^1J(P, Rh) = 118 Hz). ^{13}C{^{1}H} NMR: δ 12.2, 36.5, 128.4, 130.5, 132.0, 133.8. ^{11}B NMR ($CDCl_3$): δ 5.6 (1B), 0.8 (1B) –1.7 (2B), -5.9(2B), -10.3 (d, ^1J(B, H) = 123 Hz, 1B), –18.4 (2B).

Kinetic Experiments

A weighed amount of **2a** was placed in a small container, 0.5 mL of $CDCl_3$ added, and the time counter was resent. The mixture was stirred until dissolution and the solution was transferred to an NMR tube. The NMR spectrometer was configured to obtain the ^{1}H{^{11}B}, ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectra at preselected time intervals. After the experiment was finished the spectra were integrated and the percent composition of the mixture was calculated.

X-ray crystallography:

Single-crystal data collection for **2a**·0.912CH_2Cl_2 was performed at –100º with an Enraf Nonius KappaCCD diffractometer while the collections for **3** and **4a**·$CHCl_3$**,** were performed at ambient temperature with a Rigaku AFC5S diffractometer using graphite monochromatized Mo Kα radiation. A total of 7347, 3306 and 3026 unique reflections were collected for **2a**·0.912CH_2Cl_2, **3** and **4a**·$CHCl_3$**,** respectively.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[17] For **2a**·0.912CH_2Cl_2 and **3**, all non-hydrogen atoms were refined with anisotropic displacement parameters. For **4a**·$CHCl_3$, boron atoms were refined with isotropic but rest of the non-hydrogen atoms with anisotropic displacement parameters. For all structures, the hydrogen atoms were treated as riding atoms using the SHELX97 default parameters. **4a**·$CHCl_3$ crystallizes in a non-centrosymmetric space group, and absolute configuration of **4a**·$CHCl_3$ was determined by refinement of Flack x parameter. Crystallographic parameters for **2a**·0.912CH_2Cl_2, **3** and **4a**·$CHCl_3$ are gathered in Table 6.

Acknowledgement

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Highly stable neutral and positively charged dicarbollide sandwich complexes

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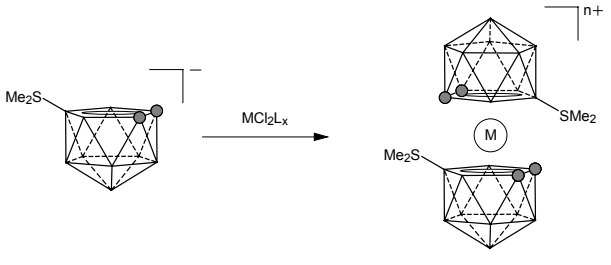
Introduction

Boron cluster ligands provide structural and bonding possibilities distinct of conventional organic ligands.[1] The best known of the η^5 boron ligands is the dicarbollide anion [7,8-$C_2B_9H_{11}]^{2-}$, $[Dcb]^{2-}$. The synthesis and properties of first metallacarborane sandwich complexes analogous to metallocenes employing the dicarbollide $[C_2B_9H_{11}]^{2-}$ ligand, $[Dcb]^{2-}$, were reported 35 years ago.[2] The $[Dcb]^{2-}$ ligand is formally equivalent to the cyclopentadienyl $[Cp]^-$ and both are able to coordinate in a η^5-π-bonding fashion. Sandwich complexes entirely made with the dicarbollide moiety with first row transition metals such as Fe(II),[3] Co(III),[3,4] Ni(III),[3,5] Ni(IV),[3,6] Cu(II),[7] Cu(III),[7] Cr(III) [8] and more recently Co(II) [9] have been synthesized and fully characterized. However, the differences between both ligands are the capacity of the dicarbollide to stabilize higher oxidation states than Cp, and the out of plane disposition of the open face substituents.[10,11] While Cp is a monoanionic species, $[C_2B_9H_{11}]^{2-}$ is a dianion. This has lead to the preparation of a new type of charge compensating monoanionic clusters in which a charge compensated group is located on an open face atom. The [X-L-7,8-$C_2B_9H_{10}]^-$ (X = 9,10) and [10-L-7,9-$C_2B_9H_{10}]^-$ ligands have been the most studied,[12] however a very few transition metal sandwich complexes of these monoanionic carborane ligands have been isolated and charaterized,[12d,13] such as the ferracarborane *commo*-[3,3'Fe{4-(SMe_2)-1,2-$C_2B_9H_{10}\}_2$] and isomers which present potential applications as novel molecular materials.[14] In this respect we report here on the preparation of new sandwich complexes using the charge-compensated *nido*- [10-SMe_2-7,8-$C_2B_9H_{10}]^-$ with different transition metals such as Co(II), Co(III), Ni(II), Ru(II) and Fe(II). We study their spectroscopic properties, crystal structure, and electrochemical behaviour and are compared to other analogous sandwich complexes with $[Dcb]^{2-}$ or $[Cp]^-$ anions.



1: M = Ni, L = H_2O, x = 6, n = 0
2: M = Co, x = 0, n = 1
4: M = Ru, L = dmso, x = 4, n = 0
5: M = Fe, L = dppe, x = 1, n = 0

Scheme 1. Formation of *commo*-[3,3'-M{8-(SMe_2)-1,2-$C_2B_9H_{10}\}_2]^{n+}$.

Results and Dicussion

Synthesis and structures

Reaction of $NiCl_2{\cdot}6H_2O$ with an ethanolic solution of K[10-SMe_2-7,8-$C_2B_9H_{10}$] (prepared by deprotonation of the neutral charge-compensated ligand with ^{t}BuOK)[15] at room temperature yielded a yellow suspension from which the paramagnetic complex *commo*-[3,3'-Ni{8-(SMe_2)-1,2-$C_2B_9H_{10}\}_2$], **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-$C_2B_9H_{11})_2]^{2-}$ obtained with the dicarbollide dianion which rapidly oxidized to a Ni(III) complex.[3] 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 ν(B-H). Since **1** is paramagnetic the $^{11}B\{^1H\}$ 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 ^{11}B 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.

Compound	λ_{max}, (ε)
1	217[a] (11300) 257[a] (6700) 351 (12000) 495 (85) 745 (54)
2·Cl	215[a] (5900) 250[a] (6100) 300 (23700) 464 (280)
3	222 (17800) 265 (11400) 339 (9500) 442 (220)
4	198 (54000) 223 (37000) 336[a] (30) 362 (610) 481 (60)
5	221 (32200) 268[a] (8900) 383 (130) 520 (180)

[a] 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 as 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-(SMe_2)-1,2-$C_2B_9H_{10}\}_2$] complex unit, with the metal lying on a C_2 axis, which coincides with the crystallographic *c* axis. The two C_2B_3 bonding faces have a staggered conformation and theC1-C2 and C1_2-C2_2 vectors have a *gauche* configuration. This configuration has never been observed on a sandwich bis-dicarbollyl nickel complex,[16] for which a *cisoid* ([3,3'-Ni(1,2-$C_2B_9H_{10})_2]^-$)[6] *transoid* ([3,3'-Ni(1,2-$C_2B_9H_{10})_2]^-$)[5c] or 'slipped' *transoid* ([3,3'-Ni(1,2-$C_2B_9H_{10})_2]^{2-}$)[7b] have been previously reported.

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

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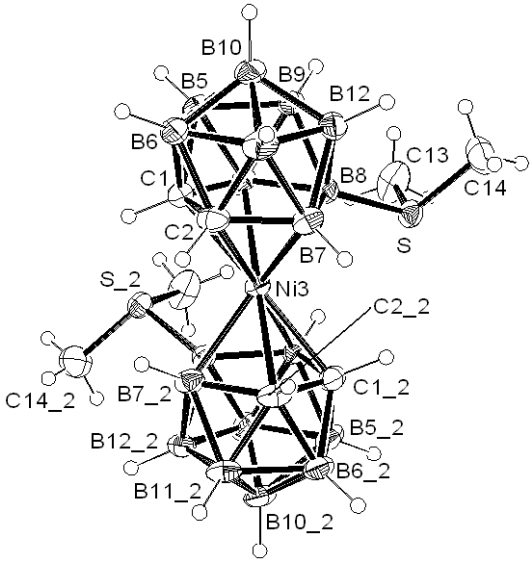

Fig. 1 Thermal ellipsoid plot (40% probability) of complex **1**.

Table 2 Selected bond lengths (Å), angles (º) and torsion angles (º) for **1**.

Ni3-C1	2.233	C1-C2	1.586
Ni3-C2	2.228	C1-B4	1.669
Ni3-B7	2.194	C2-B7	1.691
Ni3-B8	2.194	B4-B8	1.771
Ni3-B4	2.197	B7-B8	1.767
B8-S	1.902		
B4-B8-S	123.7	Ni3-B8-S	109.0
B7-B8-S	122.9	B7-B8-S-C13	172.8

atom is located 1.671 Å above the mean C_2B_3 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-$C_2B_9H_{10})_2]^-$ anion for which an 0.6 Å shift was observed and the analogous Ni(II) [3,3'-Ni(1,2-$C_2B_9H_{10})_2]^{2-}$ dianion for which a 0.6 Å shift was estimated,[7b] the present structure seems to belong to the π-sandwich rather then π-allyl classification. This irregular behaviour was already observed for the d^8 Ni(II) [3,3'-Ni(1,2-$C_2B_9H_{10})_2]^{2-}$ dianion for which a 0.15 Å shift was reported.[17]

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 an B10_2-Ni3-B10 angle of 172.9º, moving the B4 and B4_2 atoms further apart than the C2 and C2_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 zwitterionic B(8)-B(8') substituted sandwich complexes. The rotamer **A**, in which a cluster is

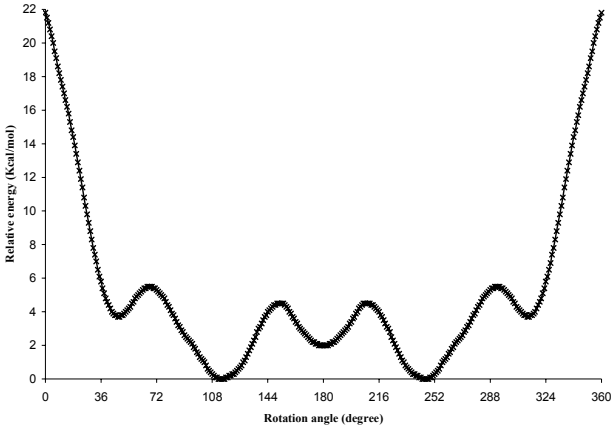

Fig. 3 Calculated energy profile for complex **1** by ZINDO/1 method.

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 electronical 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 mimima 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-$C_2B_9H_{10}$] 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_2O to yield *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}\}_2$]Cl, **2**·Cl. As observed in the synthesis of other cobaltacarborane sandwich complexes,

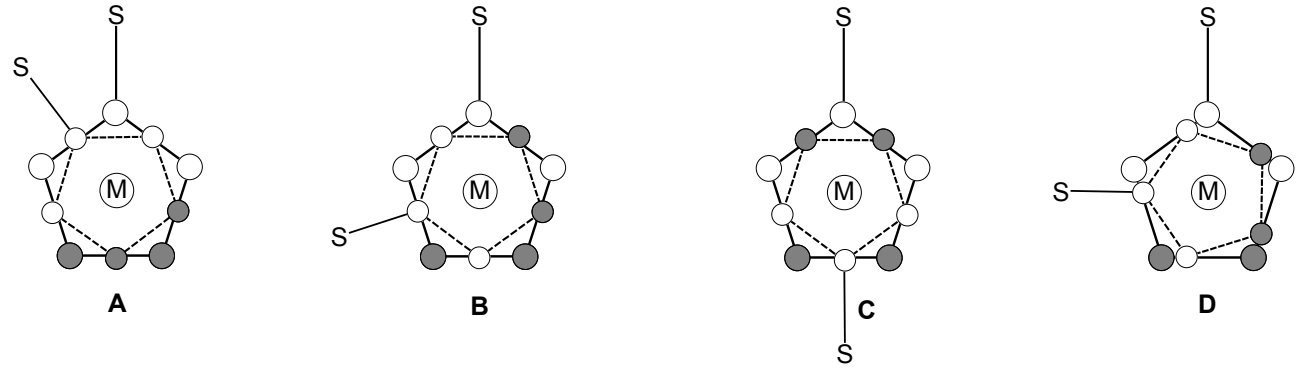

Fig. 2 Mutual configuration of monoanionic ligands in complexes **1-5**.

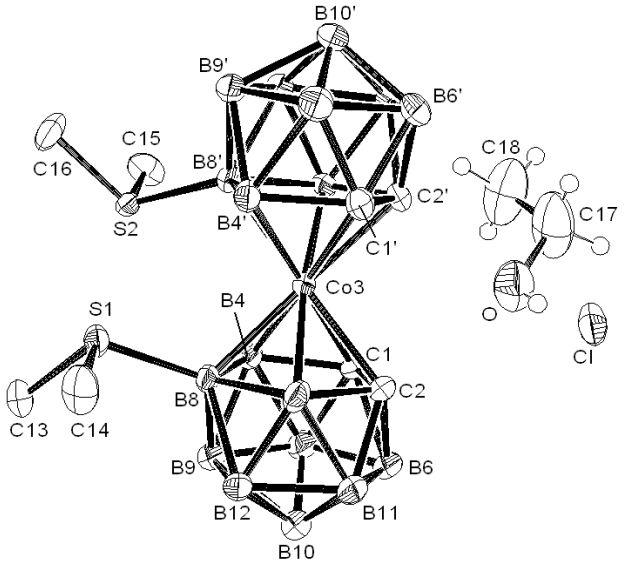

Fig. 4 Thermal ellipsoid plot (50% probability) of complex **2**·Cl·EtOH (cluster hydrogen atoms removed for clarity).

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

Co3-C1	2.050	Co3-C1'	2.050
Co3-C2	2.053	Co3-C2'	2.049
Co3-B7	2.116	Co3-B7'	2.109
Co3-B8	2.119	Co3-B8'	2.117
Co3-B4	2.085	Co3-B4'	2.097
C1-C2	1.611	C1'-C2'	1.610
C1-B4	1.714	C1'-B4'	1.713
C2-B7	1.700	C2'-B7'	1.705
B4-B8	1.801	B4'-B8'	1.811
B7-B8	1.778	B7'-B8'	1.782
B8-S1	1.925	B8'-S2	1.917
B4-B8-S1	126.4	B4'-B8'-S2	123.7
B7-B8-S1	120.1	B7'-B8'-S2	122.1
Co3-B8-S1	115.7	Co3-B8'-S2	115.0

the formation of complex **2** was accompanied of a black residue of Co^0 indicating the formation of an initial Co(II) complex, which disproportionates to Co(III) and cobalt metal. In this case, the monoanionic ligand $[10\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ acts in a similar way to the dianionic $[1,2\text{-}C_2B_9H_{11}]^{2-}$ towards Co(II), leading to the formation of the cationic Co(III) complex, **2**. Complex **2**·Cl was characterized in solution by ^1H and ^{11}B NMR spectroscopy. The $^1H\{^{11}B\}$ NMR spectrum shows a singlet at 4.96 ppm assigned to the CH_{cage} and a signal at 2.84 ppm due to the SMe_2 group protons. The $^{11}B\{^1H\}$ NMR spectrum displays a 1:1:4:2:1 pattern in a range between +13 and -17 ppm. The lower field resonance is not split into a doublet in the ^{11}B NMR, being assigned to the substituted B(8) of the cluster. The electronic spectrum data for **2**·Cl is displayed in Table 1 and remember those observed for other bis-dicarbollyl cobalt(III) derivatives.[3]

In order to effect an easy isolation of the cationic complex **2**, the $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ anion was chosen as a precipitating anion, yielding **2**·$[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$, in good yield (65%). Complex **2**·$[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ was fully identified by elemental analysis, IR and NMR spectroscopy. The IR spectrum shows an intense broad band centred at 2535 cm^{-1} assigned to the B-H stretching vibrations. In solution the $^1H\{^{11}B\}$ NMR spectrum of **2**·$[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ shows broad resonances at 4.96 and 3.95 ppm attributable to CH_{cage} for both cationic and anionic sandwiches. The resonances at 2.83 ppm are due to the SMe_2 group. Resonances due to {BH} groups are observed between 1.0 and 4.0 ppm. The $^{11}B\{^1H\}$ NMR spectrum consists of 1:1:1:1:8:2:2:1:1 pattern and is in agreement with the presence of two sandwiches of Cs symmetry with a 1:1:4:2:1 pattern each. The resonance at 9.61 ppm was assigned to the sulfur-bearing 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 [*commo*-3,3'-$Co\{4\text{-}(4\text{-}(C_5H_4N)CO_2CH_3)\text{-}3,1,2\text{-}CoC_2B_9H_{10}\}_2]^+$ synthesized by Hawthorne *et* al.[12d] 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.

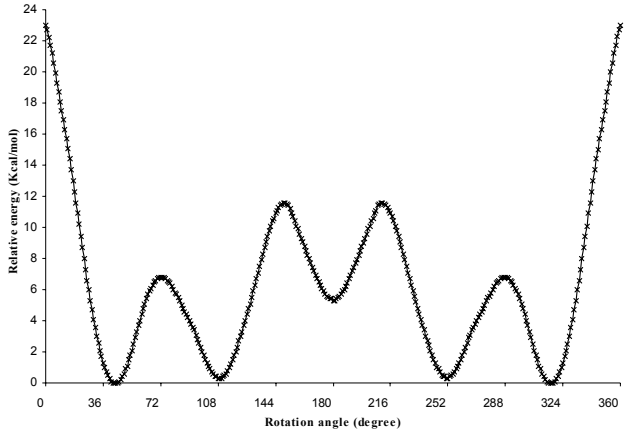

Fig. 5 Calculated energy profile for complex **2** by ZINDO/1 method.

The air stable diamagnetic Co(III) complex **2**·Cl·EtOH crystallized from a EtOH/H_2O 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 unint 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 $[3,3'\text{-}Co\{8\text{-}(SMe_2)\text{-}1,2\text{-}C_2B_9H_{10}\}_2]^+$ unit with distances of 2.390 and 2.644 Å.

The structure of **2** consists of two $[10\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{11}]^-$ 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 $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ complex, the *cosane* anion.[4b,18]. Any potential steric crowding from the SMe_2 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 SMe_2 substituents, because a similar distortion is apparent in the *cisoid* rotamer of the *cosane* anion.[4b] Thus, it appears that the SMe_2 moieties exert minimal steric influence on the overall structural details of $[3,3'\text{-}Co\{8\text{-}(SMe_2)\text{-}1,2\text{-}C_2B_9H_{10}\}_2]^+$, 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 energy minima are found for rotation angles of 45º and 110º, which could be assigned to rotamers **A** and **B** (Figure 2) with minor angle discrepancies, whereas a highly energetic relative energy minimum is located precisely for a rotation angle of 180 º (rotamer **C**). Two rotational barriers are detected with energies

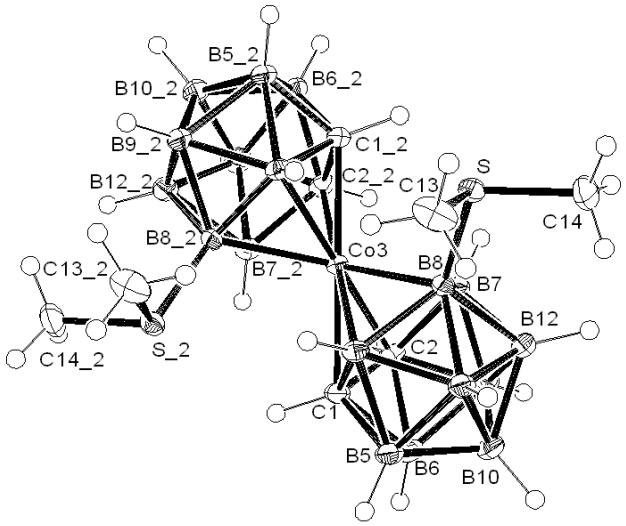

Fig. 6 Thermal ellipsoid plot (50% probability) of complex **3**.

Table 4 Selected bond lengths (Å), angles (º) and torsion angles (º) for **3**.

Co3-C1	2.170	C1-C2	1.592
Co3-C2	2.092	C1-B4	1.684
Co3-B7	2.140	C2-B7	1.717
Co3-B8	2.166	B4-B8	1.805
Co3-B4	2.132	B7-B8	1.749
B8-S	1.908		
B4-B8-S	122.7	Co3-B8-S	112.2
B7-B8-S	123.1	B7-B8-S-C13	176.0

of 11.5 and 6.8 Kcal·mol^{-1}. Thus, a clear difference has been found for the energy calculation in compound **1** and **2**, because in the latter, rotamer **A** is as energetically stable as rotamer **B**. Besides, if we observe the X-ray crystal structure for **2**, we found a *cisoid* conformation, with a rotational angle of about 40º, in very good agreement with the energy minimum found at 45º.

The reaction of a MeOH/H_2O solution of **2**·Cl with metallic Zn leads to the reduction of metal center affording the neutral air-sensitive complex *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$], **3** in a 60% yield. This reduced species is a formal Co(II) complex, in which the cobalt atom have a d^7 electronic configuration and the complex being paramagnetic. The $^{11}B\{^1H\}$ NMR spectrum appears in the range δ +63 to -35 ppm, in contrast to diamagnetic **2** which has peaks in the region δ +10 to -23 ppm. Contrarily to the previous Ni(II) complex **1**, in this case coupling of some boron atoms with the protons bonded to their is observed in the ^{11}B NMR spectrum. The ^1H NMR is extended from + 26 to -60 ppm. This range of resonances is very similar to that found for the Co(II) dianion $[Co(C_2B_9H_{11})_2]^{2-}$ reported by Chamberlin et *al*.[9] Until now, a large number of Co(III) bis(dicarbollide) complexes have been structurally characterized,[18] however only the d^7 Co(II) complex $[Cs_2(DME)_4][Co(C_2B_9H_{11})_2]$ has recently been fully study by X-ray analysis.[9] In our case, despite the ease of oxidation of **3** in solid state and in solution, the complex was recrystallized in a CH_2Cl_2/hexane solution, under inert atmosphere, and isolated as good crystals suitable for single crystal X-ray diffraction analysis. A simplified drawing of the complex is depicted in Figure 6 and selected geometrical parameters are collected in Table 4. In complex **3** the orientation of the carbon atoms in the cages is rotated from the *cisoid* geometry of the d^6 complex **2** to the *gauche* previously observed for the Ni(II) complex.

Asymmetric unit of complex **3** consists of half of *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$] complex unit, with the metal lying on a C_2 axis, which coincides with the crystallographic *c* axis. The two C_2B_3 ligating rings have a staggered conformation and the mutual orientation of the two coordinating cages assumes a *gauche* configuration.

The mean planes defined by the atoms of the two ligating rings are practically parallel, being inclined at 2.1º to each other. The vector distance from cobalt to both C_2B_3 planes is 1.571 Å, a displacement that is considerably longer from that found in the "parent" dianion $[Co(C_2B_9H_{11})_2]^{2-}$ (1.512 Å).[9] Similar structural perturbations are noted in the bond distance comparison (Table 5) between **2** and **3** cobalt complexes and its related Co(II) and Co(III) parent bis(dicarbollide) sandwich complexes.

The five ligating atoms in **3** are, in fact, not exactly coplanar : the face is folded about C1···B8 in an "envelope" conformation, with the C1-C2-B7-B8/C1-B4-B8 dihedral angle being 6.6º. The distortion is higher than the one reported previously in other charge compensated sandwich complexes such as [3,3'-Fe{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$],[19] and comparable to that of [3,3'-Fe{8-(NEt_3)-1,2-$C_2B_9H_{10}$}$_2$].[12d] Geometrical parameters associated with the pendant SMe_2 groups are close to those expected, and to those observed in [3,3'-Fe{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$].[19]

The analysis of the calculated energy profiles for compound **3** is very similar to that observed for the Ni(II) complex **1** (Figure 3). Three relative energy minima (at 46º, 115º and 180º, respectively) and two equal rotational barriers of 5.8 Kcal·mol^{-1} are observed. As for compound **1**, the lowest energy minimum corresponds to a rotation angle of about 115º, which could correspond to a *gauche* conformation represented by the a slightly distorted rotamer **B**. This result is in very good agreement with the X-ray results for complex **3** (Figure 6), in which a rotation angle of about 112º is inferred.

The reaction of complex $[RuCl_2(dmso)_4]$ with K[10-SMe_2-7,8-$C_2B_9H_{10}$] in EtOH at reflux overnight leads to the formation of a brown solid, which was partially dissolved in acetone to give a yellow solution, from which a yellow solid *commo*-[3,3'-Ru{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$], **4**, precipitated with hexane (Scheme 1). This compound was characterized by IR and NMR spectroscopy and elemental analysis. The infrared spectrum exhibits an intense broad absorption at 2559 cm^{-1} due to the B-H stretching vibrations, the C-H stretching absorption of the SMe groups occurs near 2920 cm^{-1}. The $^1H\{^{11}B\}$ NMR spectrum shows a singlet at 2.47 ppm assigned to the SMe protons and a broad signal at 3.59 ppm attributed to the CH_{cage} protons, resonances due to B-H protons are also observed in the region between 1.0 and 3.5 ppm. The 96 MHz $^{11}B\{^1H\}$ NMR spectrum of **4** at room temperature exhibits six resonances with area ratio 1:1:2:2:2:1, only the resonance at lower field (δ = 1.96 ppm) remains as a singlet in the ^{11}B spectrum, being assigned to the SMe_2-B(8) atom. The ^{11}B NMR pattern indicate the presence of a mirror plane of symmetry in the molecule, which suggests that the two 4-substitutes dicarbollides ligands are equivalent and in rapid rotation which respect to one another on the NMR time scale. The UV/Vis spectral data for complex **4** are given in Table 1.

Table 5 Comparison of average lengths (Å) in unsubstituted and charged-compensated cobalt bis(dicarbollide) sandwich complexes.

Complex	C(1)-C(2)	C(1,2)-B(4,7)	B(8)-B(4,7)	Co-C(1,2)	Co-B(4,7)	Co-B(8)
Unsusbstituted[4b,9]						
[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$	1.624	1.699	1.798	2.046	2.093	2.104
[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$]$^{2-}$	1.573	1.710	1.770	2.117	2.120	2.183
Charge-compensated						
[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$]$^+$ (**2**)	1.611	1.707	1.790	2.052	2.100	2.119
[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$] (**3**)	1.592	1.700	1.777	2.131	2.136	2.166

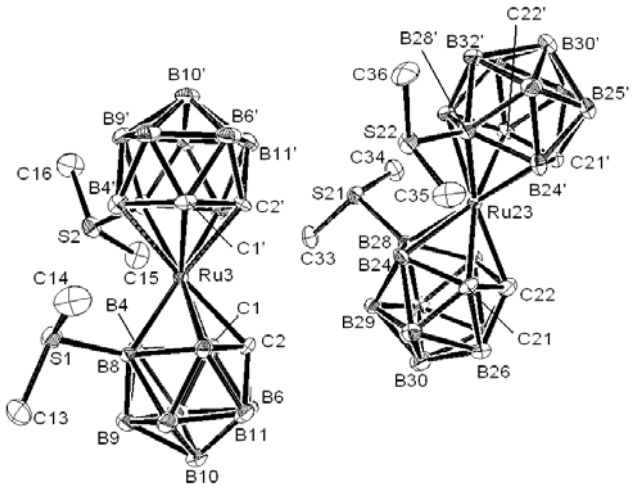

Fig. 7 Thermal ellipsoid plot (50% probability) of complex **4** (cluster hydrogen atoms removed for clarity).

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

Ru3-C1	2.180	Ru23-C21	2.170
Ru3-C2	2.181	Ru23-C22	2.181
Ru3-B7	2.223	Ru23-B27	2.219
Ru3-B8	2.218	Ru23-B28	2.234
Ru3-B4	2.201	Ru23-B24	2.212
Ru3-C1'	2.170	Ru23-C21'	2.178
Ru3-C2'	2.172	Ru23-C22'	2.172
Ru3-B7'	2.214	Ru23-B27'	2.210
Ru3-B8'	2.233	Ru23-B28'	2.215
Ru3-B4'	2.204	Ru23-B24'	2.213
C1-C2	1.628	C21-C22	1.610
C1-B4	1.723	C21-B24	1.734
C2-B7	1.703	C22-B27	1.710
B4-B8	1.781	B24-B28	1.782
B7-B8	1.791	B27-B28	1.798
C1'-C2'	1.641	C21'-C22'	1.630
C1'-B4'	1.734	C21'-B24'	1.709
C2'-B7'	1.714	C22'-B27'	1.735
B4'-B8'	1.780	B24'-B28'	1.798
B7'-B8'	1.798	B27'-B28'	1.785
B8-S1	1.925	B28-S21	1.915
B8'-S2	1.918	B28'-S22	1.920
B4-B8-S1	121.8	B24-B28-S21	121.0
B7-B8-S1	125.0	B27-B28-S21	127.0
Ru3-B8-S1	116.2	Ru23-B28-S21	113.5
B4'-B8'-S2	120.1	B24'-B28'-S22	123.7
B7'-B8'-S2	126.4	B27'-B28'-S22	122.7
Ru3-B8'-S2	116.4	Ru23-B28'-S22	115.0
B7-B8-S1-C14	8.9	B27-B28-S21-C34	-4.0
B27'-B28'-S22-C35	153.6	B7'-B8'-S2-C15	3.7

The crystal structure determination by X-ray diffraction corroborated the formation of *commo*-[3,3'-Ru{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$], **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 *hkl* 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 *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,[20] for which

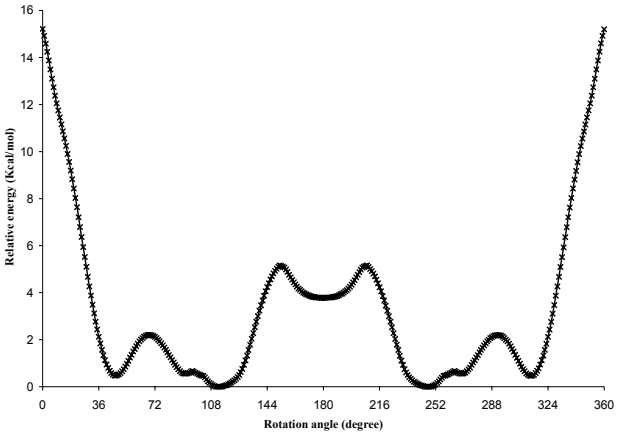

Fig. 8 Calculated energy profile for complex **4** by ZINDO/1 method.

cisoid, *gauche* and *transoid* configurations had been previously defined and reported.[16,18]

The C_2B_3 mean planes of the coordinating faces are nearly parallel, being inclined at 4.1º and 3.5º to each other for ismoers A and B, respectively. The distance of the Ru atom from the mean C_2B_3 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'-Ru23-B30 of 174º for rotamer B, approaching the C2 (C21') to the C2' (C22) atoms for isomer A(B). This phenomenon has been already 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.

Although complex *commo*-[3,3'-Fe{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$] (**5**) had been previously prepared by Plesek *et* al.,[19] using [10-SMe_2-7,8-$C_2B_9H_{10}$]$^-$ and $FeCl_2{\cdot}4H_2O$, 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-SMe_2-7,8-$C_2B_9H_{10}$] in thf with $FeCl_2$(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 *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 η^5 sandwich complexes redox couples and gas-phase ionization potentials (IP_j, eV) of the corresponding metals.

Complex	E° , V			Ref.
	M^{IV}/M^{III} (IP_4)	M^{III}/M^{II} (IP_3)	M^{II}/M^{I} (IP_2)	
[3,3'-Ni(8-SMe_2-1,2-$C_2B_9H_{10}$)$_2$ (**1**)	1.29 (54.9)	0.38 (35.2)	-1.06 (18.2)	This work
[3,3'-Ni(1,2-$C_2B_9H_{10}$)$_2$]	0.25	-0.59	-2.10	3, 21
Cp_2Ni	0.81[c]	0.01[c]	-1.85[c]	22
[3,3'-Co(8-SMe_2-1,2-$C_2B_9H_{10}$)$_2$] (**3**)	–	-0.35 (33.5)	-1.23 (17.1)	This work
[3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$	1.57 (51.3)	-1.46	-2.24	3, 21
Cp_2Co	3.15[b]	-0.90[c]	-1.91[c]	22
[3,3'-Ru(8-SMe_2-1,2-$C_2B_9H_{10}$)$_2$] (**4**)	–	1.04 (28.5)	–	This work
Cp_2Ru	–	0.88[d]	–	[23]
[3,3'-Fe(8-SMe_2-1,2-$C_2B_9H_{10}$)$_2$] (**5**)	–	0.54 (30.6)	–	This work
[3,3'-Fe(1,2-$C_2B_9H_{10}$)$_2$]	–	-0.42	–	3
Cp_2Fe	–	0.42	–	22

[a] $E^o = (E_p^a + E_p^c)/2$ *vs.* SCE. [b] In SO_2. [c] In THF. [d] 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte in THF.

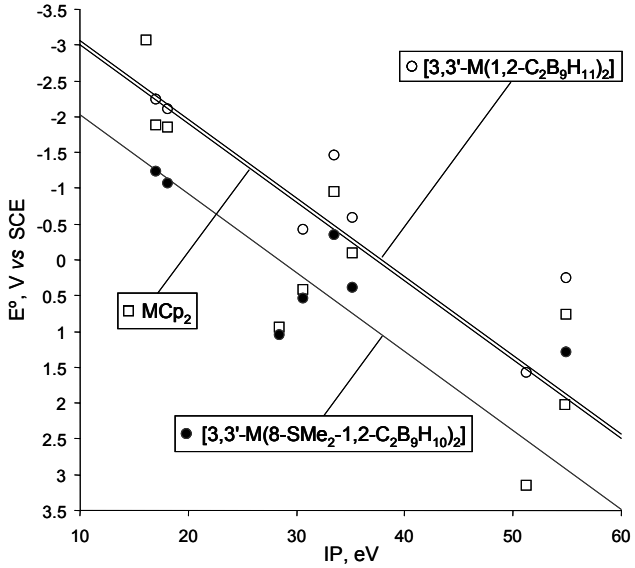

Fig. 9 Dependence of E° values for the redox transitions in the series of metallocenes and metallacarboranes on the corresponding IP_i of the metal.

Electrochemical studies

Up to now, on the basis of the presented complexes, it has been noted for the ligand [10-SMe_2-$C_2B_9H_{10}$]$^-$ a general tendency toward the formation of sandwich complexes in which the metal center is in lower oxidation states when comparing to its parent dicarbollide system $[C_2B_9H_{12}]^{2-}$. The study of the redox behaviour of the new complexes will allow a more detailed quantification of this electronic effect.

Cyclic voltammetry measurements were conducted on **1**, **3**, **4**, and **5**, in acetonitrile using NBu_4PF_6 as the supporting electrolyte. The inspected range, corresponding to the potential window between –2.0 and +2.0 V vs SCE, gave rise to fully reversible diffusion-controlled processes for all metal complexes. All heterogeneous electron transfer reactions showed similar ΔE_p values as for the $Cp_2Fe^{+/0}$ couple under same conditions, hence we inferred a quasi-Nerstian behaviour. Each process was assumed to have one-electron stoichiometry, as determined indirectly by comparison of their CV peak heights and ΔE_p values.

At first sight, data on Table 7 shows that each electrochemical process of the new sandwich compounds is shifted *ca.* +1 V to more positive values when compared to the equivalent process of the parent bis(dicarbollide) analogues. This considerable shift accounts for the possibility for this ligand to form air-stable Ni(II) and Fe(II) sandwich complexes, as well as the smooth preparation of the Co(II) complex. Moreover, the $E_{1/2}$ values are shifted a significant amount of +0.15 to +0.8 V comparing to their metallocenes analogues. Consequently it follows that the monoanionic carborane possess an enhanced electronic stabilizing ability for low oxidation states when compared to the dicarbollide or cyclopentadienyl systems. A similar increase in oxidation stability was previously found for the sandwich complexes of other monoanionic heteroborane ligands, such as $[MeC_3B_7H_9]^-$ and $[CB_9H_{10}PMe]^-$.

A more general view was taken by analysing the already established linear relationship between the standard potential values (E^o_j) of all possible redox reactions of sandwich complexes and metal ionization potentials (IP_j). The equation

$$E^o_j \text{ (V vs SCE)} \approx a_i + 0.11 \cdot IP_j$$

is valid for Cp_2M and $[C_2B_9H_{11}]_2M$ complexes among others, where a_i is a constant characteristic of each ligand (-4.16 for Cp^- and –4.10 for $[C_2B_9H_{11}]^{2-}$) and j=1,2,.... The a_i constant gives an approximate idea of the electronic stabilizing effect of the π-ligand, making it useful for comparison purposes. As expected, the E^o_j vs IP_j plot for **1**, **3**, **4**, and **5** revealed that the ligand [10-SMe_2-$C_2B_9H_{10}$]$^-$ also displays a similar linear behaviour with a slope of –3.12 (Figure 9). On the other hand, the E° value for the $\mathbf{1}^{2+/+}$ (+1.29 V) and the $\mathbf{3}^{0/+}$ (-0.35 V) couples deviated from the linear correlation in the direction of negative potentials (-0.91 V and –1.63 V, respectively), according to the particular features of the $d^{6/7}$ electron transfer reactions for the metallacarboranes. In addition, the $\mathbf{4}^{+/0}$ couple is unexpectedly moved -1.03 V away from the expected value, for which we still haven't found any suitable explanation.

The a_i value found for [10-SMe_2-$C_2B_9H_{10}$]$^-$ corresponds to a +1 V comparative inductive effect when compared to both the dicarbollide and cyclopentadienide 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 $^{11}B\{^{1}H\}$ NMR (96.29 MHz), and $^{31}P\{^{1}H\}$ 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 ºC. Chemical shift data for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to $SiMe_4$, those for $^{11}B\{^{1}H\}$ and ^{11}B RMN spectra were referenced to external $BF_3{\cdot}Et_2O$ and those for $^{31}P\{^{1}H\}$ RMN spectra were referenced to external 85 % H_3PO_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). The carborane 10-SMe_2-7,8-$C_2B_9H_{10}$ was prepared following the literature procedure[24] and $RuCl_2(dmso)_4$ was prepared according to the literature.[25] All other chemical were purchased from Fluka or Aldrich and used as received.

Electrochemical procedures

Cyclic voltammograms were recorded on a EG&G PAR273A potentiostat-galvanostat. Electrochemical measurements were performed in a standard double-compartment three-electrode cell. A 4-mm^2 platinum plate and a platinum wire were used as working and counter electrode, respectively. For standard cyclic voltammetric measurements, a silver wire was utilized as a quasi-reference electrode, and potentials were calibrated versus SCE by the addition of ferrocene as an internal standard using $E°(FeCp_2/FeCp_2^{+}) = 0.424$ V. All measurements were performed on 1 mM of complex in acetonitrile with tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte. Cyclic voltammograms were recorded with a scan rate of 50 $mV{\cdot}s^{-1}$.

Preparation of *commo*-[3,3'-Ni{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$] (1)

A solution of $NiCl_2{\cdot}6H_2O$ (162 mg, 0.682 mmol) in 2 mL of EtOH was added dropwise to a Schlenck charged with a solution of 10-SMe_2-7,8-$C_2B_9H_{11}$ (26.6 mg, 0.137 mmol) and ^{t}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 ºC, a yellow solid was isolated by filtration, washed with cold EtOH (2 x 2 mL) and dried in vacuo to afford 20 mg (66%) of **1**. Yellow crystals suitable for an X-ray diffraction study were grown by slow evaporation of an acetonitrile solution of the product at room temperature.

$^{1}H\{^{11}B\}$ (22 ºC): δ 84.3, 24.4, 6.9, -134.4, -156.7, -170.0; $^{11}B\{^{1}H\}$ (22 ºC): δ 139.2, 72.6, 71.5, -26.2, -116.3. IR(KBr): ν = 2560, 2537, 2528 (m, BH); elemental analysis calcd (%) for $C_8H_{32}B_{18}NiS_2$: C 21.6, H 7.2, S 14.4; found: C 21.7, H 7.3, S 13.6.

Preparation of *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$]·Cl (2·Cl)

A solution of $CoCl_2$ (57.0 mg, 0.439 mmol) in 4 mL of MeOH was added dropwise to a Schlenck charged with a solution of 10-SMe_2-7,8-$C_2B_9H_{11}$ (51.4 mg, 0.265 mmol) and ^{t}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_2O (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 filtered to give a yellow solid. This filtrate was combined with the yellow solution resulted 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 *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$]·Cl suitable for an X-ray diffraction study were grown by slow evaporation of this solution at room temperature.

$^{1}H\{^{11}B\}$ (22 ºC): δ 4.9 (br s, 4 H, CH_{cage}), 2.84 (s, 12 H, SCH_3); $^{11}B\{^{1}H\}$ (22 ºC): δ 9.7 (2B), 4.3 (2B), -5.4 (8B), -13.8 (4B), -19.8 (2B). ^{11}B (22 ºC): δ 9.7 (2B), 4.3 (d, 2B, J(HB) = 135 H), -5.4 (8B), -13.8 (d, 4B, J(HB) = 157 H), -19.8 (2B).

Preparation of *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$]·[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$] (2·[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$])

A solution of [Cs{3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$}] (90.0 mg, 0.197 mmol) in 10 mL of MeOH/H_2O (60:40) was added. The pale orange solid was filtered off and washed with 10 mL of MeOH/H_2O (60:40) to afford 66 mg of **2**·[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$] (65 %).

$^{1}H\{^{11}B\}$ (22 ºC): δ = 4.96 (br s, 4H; CH_{cage}), 3.95 (br s, 4H, CH_{cage}), 2.83 (s, 12 H; SCH_3); $^{11}B\{^{11}H\}$ (22 ºC): δ = 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 ºC): δ = 9.6 (s, 2B), 7.1 (d, 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 (d, 2B, J(HB) = 173 Hz). IR(KBr): ν = 2589, 2557, 2535, 2501 (m, BH); elemental analysis calcd (%) for $C_{12}H_{54}B_{36}Co_2S_2$: C 18.7, H 7.0, S 8.3; found: C 19.0, H 6.97, S 7.2.

Preparation of *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$] (3)

The synthetic procedure was the same as for **2** using $CoCl_2$ (418 mg, 3.22 mmol) in 8 mL of MeOH and 10-SMe_2-7,8-$C_2B_9H_{11}$ (125 mg, 0.644 mmol) and ^{t}BuOK (152 mg, 1.287 mmol) in 10 mL of MeOH. The workup was followed up to get a solution of *commo*-[3,3'-Co{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$]Cl in 100 mL of MeOH/H_2O (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_2Cl_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_2Cl_2/hexane (1:1), under N_2 atmosphere.

$^{1}H\{^{11}B\}$ (22 ºC): δ 26.6, 3.43, 2.87, 2.10, 7.50, 7.80, -37.55, -44.76, -59.43; $^{11}B\{^{1}H\}$ (22 ºC): δ 62.8 (4B), 51.2 (2B), 11.8 (2B), -30.6 (4B), -34.4 (6B). ^{11}B (22 ºC): δ 62.8 (4B), 51.2 (2B), 11.8 (d, 2B, J(HB) = 138 Hz), -30.6 (d, 4B, J(HB) = 143 Hz), -34.4 (d, 6B, J(HB) = 129 Hz).IR(KBr): ν = 2621, 2578, 2548, 2518 (m, BH); elemental analysis calcd (%) for $C_8H_{32}B_{18}CoS_2$: C 21.6, H 7.2, S 14.4; found: C 21.7, H 7.3, S 13.6.

Preparation of *commo*-[3,3'-Ru{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$] (4)

To a solution of 10-SMe_2-7,8-$C_2B_9H_{10}$ (25 mg, 0.129 mmol) and ^{t}BuOK (16 mg, 0.135 mmol) in 5 mL of EtOH was added $RuCl_2(dmso)_4$ (60 mg, 0.129 mmol) to yield a yellow solution. After refluxing for 30 minutes the colour changed to orange, however the reflux was continued overnight. The brown solid was filtered off and partially dissolved in acetone. The yellow solution was reduced in volume and treated with an excess amount of hexane. The resulting yellow solid was collected by filtration to yield 22 mg of **4** (70 %). Crystals suitable for an X-ray diffraction study were grown by redissolving the product up in acetone/$CHCl_3$.

$^{1}H\{^{11}B\}$ (22 ºC): δ = 3.59 (br s, 4H, CH_{cage}), 2.47 (s, 12 H; SCH_3); $^{1}B\{^{11}H\}$ (22 ºC): δ = 1.9 (1B), -5.4 (1B), -9.5 (2B), -15.0 (2B), -22. 7 (2B), -24.7 (1B); ^{1}B (22 ºC): δ =. 1.9 (s, 1B), -5.4 (d, 1B, J(HB) = 141 Hz), -9.5 (d, 2B, J(HB) = 145 Hz), -15.0 (d, 2B, J(HB) = 135 Hz), -22. 7 (d, 2B, J(HB) = 159 Hz), -24.7 (d, 1B, J(HB) = 189 Hz). IR(KBr): ν = 2611, 2559, 2522, 2491 (m, BH); elemental analysis calcd (%) for $C_8H_{32}B_{18}RuS_2$: C 19.6, H 6.6, S 13.1; found: C 19.7, H 6.7, S 13.1.

Preparation of *commo*-[3,3'-Fe{8-(SMe_2)-1,2-$C_2B_9H_{10}$}$_2$] (5)

To a solution of 10-SMe_2-7,8-$C_2B_9H_{10}$ (48.7 mg, 0.251 mmol) and BuLi (0.15 mL, 0.270 mmol) in 2 mL of thf was added $FeCl_2$(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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Neutral *nido*-heteroboranes with non ionisable hydrogen as arenes in coordination

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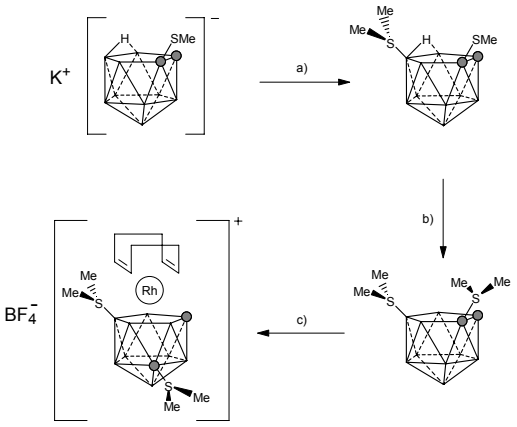
Designed ligands have been synthesised to produce the first arene-like metallacarborane. For arene-like coordination the number of electronegative elements on the coordinating site must be kept to a minimum. Choosing ligands with bulky substituents on the heteroatom allows easy rearrangement and arene-like coordination. This is more hampered the higher the number of hetereoatoms 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.[1-4] 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*-$B_{11}H_{15}$ ($[B_{11}H_{11}]^{4-}$), $C_2B_9H_{13}$ ($[C_2B_9H_{11}]^{2-}$) and $C_4B_7H_{11}$, in which the nature of the cluster skeleton elements is changed while its number is kept constant.[5] Some examples of neutral heteroboranes with non-ionisable hydrogen atoms are $C_4B_7H_{11}$,[2a] $P_3CB_7H_8$,[2f] $P_2C_2B_7H_9$,[2e] 7-Ph-7,8,10-$PC_2B_8H_{10}$ [2d] and *arachno*-$C_6H_6B_6Et_6$.[2c,4] These species either have a substitutent R (R=H, organic group) or a lone pair at each cluster vertex. While metal coordination by anionic boranes and heteroboranes is common,[6] no example has been reported of a metal coordinated to a neutral *nido* or *arachno* species with non-ionisable hydrogen atoms.[7] 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[8] 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* C_2B_9 skeletal cluster with no bridging hydrogen atoms, in which the necessary extra electrons to conform with the Polyhedral Skeletal Electron Pair (PSEP)[5,9] theory are given by Lewis bases moieties. In this aim $[(SMe_2)_2C_2B_9H_9]$,[10] which can exist as different isomers, was chosen as a suitable arene-like heteroborane neutral species. Reasons to choose the 7,10-$(SMe_2)_2$-7,8-$C_2B_9H_9$ (**1**) 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 **1** is isoelectronic and isostructural to 11-vertex triheteroborane species such as 7,10,11-$SC_2B_8H_{10}$,[3c] 7-R-7,10,11-$PC_2B_8H_{10}$,[3c] 7,8,9-$As_2SB_8H_8$, 7,8,9-$As_2SeB_8H_8$,[11,12] 8,1,2-$SC_2B_8H_{10}$ [13] and 8,1,2-$SeC_2B_8H_{10}$.[14] Therefore, we have treated **1** as a triheteroborane-like neutral molecule where the three heteroatoms would be C-SMe_2, C-H, and B-SMe_2.

Reaction of [Rh(acac)(cod)] (30.5 mg, 98.3 μmol) in 1 mL of THF with 13 μL (104 μmol) of HBF_4 (8.0 M solution in water) yielded a solution containing $[Rh(cod)]^+$.[15] To this solution was added **1** (25 mg, 98.3 μmol) in 4 mL of CH_2Cl_2, the mixture 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 $CHCl_3$ was added, and the mixture cooled to 0 ºC followed by filtration affording a green-yellowish solid, 48.8 mg (90 %) having the formula $[Rh(cod)\{(SMe_2)_2C_2B_9H_9\}][BF_4]$, **[2][BF$_4$]**.



Scheme 1. Synthetic procedure to yield the compounds **1** and **2**. a) $S(CH_3)_2$, CH_3CHO, H^+ in toluene. b) NaOH, MeI in CH_3OH. c) [Rh(acac)(cod)], HBF_4in THF.

Compound **1** has a C_1 symmetry, and it was expected that this would be preserved in **[2][BF$_4$]**. Indeed this is the case, and the ^{11}B-NMR in CD_3COCD_3 shows 8 resonances at δ -0.2 (1B, BF_4), -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 $[C_3B_8H_{11}]^-$ tricarbaborane ligand with either {C-C-C} or {C-C-B-C} strings in the C_3B_2 open face result from either an isomerization of at least one open face carbon atom to the second layer[16] or from a deboronation yielding a "C_3B_7" cluster, with three carbon atoms coordinated to the metal.[17] A similar process was expected to the triheteroborane-like **1**.

Good quality crystals of **[2][BF$_4$]** were grown by slow evaporation of a heptane layered acetone solution. Crystal structure analysis[18] confirmed isomerization of the carborane ligand **1** during complexation. The SMe_2 group of ligand **1**, connected to cluster carbon C(7) at the upper belt of the *nido* cage, has moved during complexation to lower belt to produce $[2\text{-cod-}8,11\text{-}(SMe_2)_2\text{-}2,1,8\text{-}RhC_2B_9H_9]^+$, $[\mathbf{2}]^+$. A perspective view of $[\mathbf{2}]^+$ is shown in Fig. 1**.**

‡ O.T. is enrolled in the PhD program of the UAB.

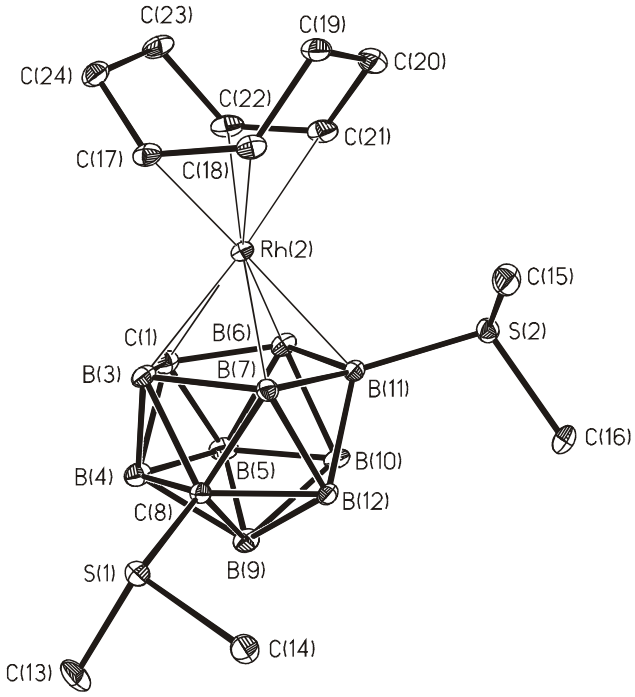
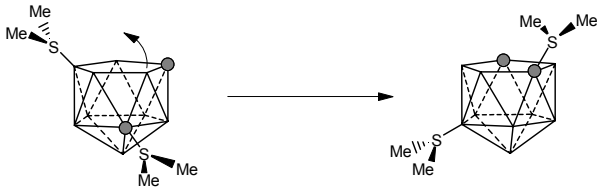


Fig. 1 Perspective view of $[\mathbf{2}]^+$ with 30% probability ellipsoids. H atoms are omitted for the sake of clarity. Selected bond lengths (Å): Rh(2)-C(1) 2.301(2), Rh(2)-B(3) 2.159(3), Rh(2)-B(6) 2.198(3), Rh(2)-B(7) 2.193(3), Rh(2)-B(11) 2.231(3), Rh(2)-C(17) 2.154(2), Rh(2)-C(18) 2.150(2), Rh(2)-C(21) 2.199(2), Rh(2)-C(22) 2.186(2), S(1)-C(8) 1.804(2), S(2)-B(11) 1.896(3).

Identical cluster rearrangement did take place when the reaction was carried out at -63 ºC. This was interpreted as evidence that the existence of a large number of heteroatoms in the ligand's coordinating site does not facilitate coordination. The fact that the bulky heteroatoms-like, C-SMe_2 and B-SMe_2, are in the cluster's coordinating site makes easier the re-arrangement. The tendency is to have the atoms more prone to coordination in the open face. This re-arrangement takes place even if the cluster's isomer in the complex does not correspond to the most stable isomer of the free ligand. Calculations by both semiempirical PM3 and *ab* initio HF/3-21G methods[19] on [2,10-$(SMe_2)_2$-2,8-$C_2B_9H_9$], which is the actual isomer in **[2][BF_4]**, support this conclusion. Scheme 2 shows the geometry optimization of [2,10-$(SMe_2)_2$-2,8-$C_2B_9H_9$] which transforms to [2,8-$(SMe_2)_2$-8,10-$C_2B_9H_9$] to have carbon atoms in the less coordinated positions, as would be predicted by geometrical systematics.[5,9]



[2,10-$(SMe_2)_2$-2,8-$C_2B_9H_9$] [2,8-$(SMe_2)_2$-8,10-$C_2B_9H_9$]

Scheme 2 Isomerization of the free ligand [2,10-$(SMe_2)_2$-2,8-$C_2B_9H_9$] to [2,8-$(SMe_2)_2$-8,10-$C_2B_9H_9$].

When a triheteroborane is synthesized the most electronegative elements are on the open face. [2a,d, 3a-b,20] According to the former data this heteroatoms arrangement does not appear to be the most suitable for cluster coordination. Heteroatoms should occupy more inner positions to leave enough electron density in the open face to coordinate to metal. This implies rearrangement 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 arene-like metallacarboranes can be produced with purposedly designed ligands, and that the absence of metallacarboranes with neutral polyheteroborane ligands is significant and meaningful.

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