B-Substituted (Arene)ruthenacarborane–Sulfonium, –Thioether and –Mercaptan Complexes: Mild Single and Double Dealkylation and Structural Implications in the Antipodal Distance

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Reactions of $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = benzene, *p*-cymene) with *nido*-[7-R-10-L-7,8-$C_2B_9H_9$]$^-$ in THF at room temperature for 3 d give the (arene)ruthenacarborane complexes *closo*-[3-Ru(η^6-arene)-1-R-8-L-1,2-$C_2B_9H_9$]$^+$ {arene = benzene, R = H [L = Me_2S (**1a**), THT (**1b**), EtPhS (**1c**)], R = Me [L = Me_2S (**2a**)]; arene = *p*-cymene, R = H [L = Me_2S (**3a**)]} and mercaptan *closo*-[3-Ru(η^6-arene)-1-R-8-HS-1,2-$C_2B_9H_9$] [arene = benzene, R = H (**4**), Me (**5**); arene = *p*-cymene, R = H (**6**)] in yields of 20–40 % and 22–29 %, respectively. The asymmetric ligand *nido*-[9-Me_2S-7,8-$C_2B_9H_{10}$]$^-$ leads to the thioether complex *closo*-[3-Ru(η^6-benzene)-7-MeS-1,2-$C_2B_9H_{10}$] (**8**) in 34 % yield under the same reaction conditions. The crystal structure of **1a** is described and compared with those of **4** and **8**. The fully assigned ^{11}B NMR spectroscopic data for a whole series of ruthenacarboranes having *B*-substituted sulfonium, thioether and mercaptan groups are presented. These data show a relation between antipodal cluster atom distances (antipodal distance) and antipodal effect (AE) in the crystal structures of these complexes and for other families of heteroboranes such as *closo*-[$EB_{11}H_{11}$] and *closo*-[EB_9H_9].

Introduction

Metal complexes having the dicarbollide ligand *nido*-[7-R-8-R^1-7,8-$C_2B_9H_9$]$^{2-}$ constitute the most widely studied class of metallacarboranes since they were first reported by Hawthorne in the 1960s.[1] These dicarbollide ligands have planar binding faces and are isolobal and isoelectronic analogues of the cyclopentadienide ligand $[C_5H_5]^-$ (Cp), both behaving as 6-electron donors in transition metal complexes.[1,2] Introduction of substituents such as amines, ethers, sulfides and phosphanes etc. at the boron atoms reduces the cluster charge, thereby producing "charge-compensated" ligands such that a better comparison with the classical (Cp)metal complexes can be made.[3] In particular, sulfides are widely used as substituents in polyhedral *B*-substituted carboranes affording "charge-compensated" ligands of the type *nido*-[9- or 10-L-7,8-R$R^1$$C_2B_9H_8$]$^-$ (L = SR^2R^3).[4] Interestingly, whereas nearly 500 structures of icosahedral cages of the type *closo*-[3,1,2-MC_2B_9] have been determined by X-ray crystallography, only 33 of those contain a sulfur atom attached to a boron atom.[5] Of these, only 5 correspond to ruthenacarboranes all having a "charge-compensated" ligand, i.e. *closo*-[3-Ru(Cp*)-7-Me_2S-1-R-2-R^1-1,2-$C_2B_9H_8$] (R/R^1 = H/H, H/Ph, Ph/H),[3g] *closo*-[3-Ru(η^6-benzene)-7-Me_2S-1,2-$C_2B_9H_{10}$][6] and *closo*-[3-Ru-3-H-3,3-$(PPh_3)_2$-8-Me_2S-1,2-$C_2B_9H_{10}$].[3i] The latter type of (phosphane)ruthenacarborane complexes have proven to be very efficient catalysts in various types of olefin-related catalytic reactions surpassing, in some cases, the Cp-type complexes.[7] As part of our systematic work on monoanionic *o*-carboranes as alternatives to the cyclopentadienide ligand in transition metal complex catalysts,[7] we became interested in the synthesis of (arene)ruthenacarborane complexes. Here we report the syntheses and characterisation of the new symmetrically *B*-substituted (arene)ruthenacarborane–sulfonium complexes *closo*-[3-Ru(η^6-arene)-1-R-8-L-1,2-$C_2B_9H_9$]$^+$ {arene = benzene, R = H [L = Me_2S (**1a**), THT (**1b**), EtPhS (**1c**)], R = Me [L = Me_2S (**2a**)]; arene = *p*-cymene, R = H [L = Me_2S (**3a**)]} and of the unprecedented (arene)ruthenacarborane–mercaptan complexes *closo*-[3-Ru(η^6-arene)-1-R-8-HS-1,2-$C_2B_9H_9$] {arene = benzene, R = H (**4**), Me (**5**); arene = *p*-cymene, R = H (**6**)} and the asymmetric thioether complex *closo*-[3-Ru(η^6-benzene)-7-MeS-1,2-$C_2B_9H_{10}$] (**8**), formed by double and single dealkylation of the sulfonium groups in the starting *nido*-carboranes, respectively. A pathway for the dealkylation reaction is proposed. The structure for [**1a**]PF_6 is now reported and compared with those of complexes **4** and **8**

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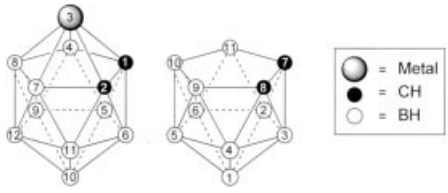
which were published in a preliminary communication.[8] We present here the fully assigned ^{11}B NMR spectroscopic data for a whole series of ruthenacarboranes having *B*-substituted sulfonium, thioether and mercaptan groups. The study reveals clear trends in the ^{11}B NMR spectra and the antipodal effect (AE)[9] which, to date, had only been related to NMR spectroscopic data. We have found that the AE can be clearly observed in the crystal structures for the new complexes and other previously reported heteroboranes of the type $EB_{11}H_{11}$ and EB_9H_9. We have adopted in this work the carborane numbering system shown in Scheme 1.



Scheme 1. Carborane numbering.

Results

1. Reactions of $[RuCl_2(\eta^6\text{-arene})]_2$ with Charge-Compensated Carboranes *nido*-[7-R-10-L-7,8-$C_2B_9H_9$]$^-$ and *nido*-[9-Me_2S-7,8-$C_2B_9H_{10}$]$^-$

According to protocols established in our group, *t*BuOK was employed as the base for in situ deprotonation of the neutral "charge-compensated" *o*-carboranes *nido*-[7-R-10-L-7,8-$C_2B_9H_{10}$] (R = H, L = Me_2S, THT, EtPhS; R = Me, L = Me_2S) (THT = tetrahydrothiophene) affording the potassium salt of the anionic "charge-compensated" *o*-carboranes *nido*-[7-R-10-L-7,8-$C_2B_9H_9$]$^-$.[10] Exclusive deprotonation of the bridge BHB proton is confirmed by disappearance of its resonance signal in the $^1H\{^{11}B\}$ NMR spectrum. The $^{11}B\{^1H\}$ NMR spectra show the typical highfield displacement of the antipodal boron B-1 signal after hydrogen bridge deprotonation (see Figure 1 for one example). Treatment of the *nido*-[7-R-10-L-7,8-$C_2B_9H_9$]$^-$ compounds with a suspension of the (arene)ruthenium complexes $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = benzene, *p*-cymene) in THF at room temperature for 3 d afforded the new cationic ruthenacarborane complexes *closo*-[3-Ru(η^6-arene)-1-R-8-L-1,2-$C_2B_9H_9$]$^+$ Cl^- (**1**–**3**) as insoluble solids (Scheme 2). A Cl^- exchange reaction in **1**–**3** using PF_6^- afforded the readily soluble complexes *closo*-[3-Ru(η^6-arene)-1-R-8-L-1,2-$C_2B_9H_9$][PF_6] (**1a**–**c** and **3a**) in yields of 20–40% but only traces of **2a** were obtained. Detailed analysis of the remaining solution showed, in all cases, the presence of starting anionic "charge-compensated" *o*-carboranes *nido*-[7-R-10-L-7,8-$C_2B_9H_9$]$^-$ which could be recovered. In addition, we unexpectedly found that (mercaptan)ruthenacarborane complexes of the type *closo*-[3-Ru(η^6-arene)-1-R-8-HS-1,2-$C_2B_9H_9$] (**4**–**6**) were also formed in yields of 22–29% (Scheme 2). Although yields for the latter complexes were low, their formation is remarkable since they are the result of double dealkylation of all sulfonium salt derivatives under very mild conditions regardless of the nature of the substituents at the sulfur atom. Small amounts of sandwich complexes of the type *closo*-[3,3′-Ru-(8-L-1,2-$C_2B_9H_{10})_2$] were also detected in the reaction mixtures in some cases. Synthesis of the latter has been reported in a separate paper.[11] As an example, the sandwich complex *closo*-[3,3′-Ru-(8-Me_2S-1,2-$C_2B_9H_{10})_2$] was obtained in 8% yield after workup of the reaction mixture of *nido*-[10-Me_2S-7,8-$C_2B_9H_{10}$]$^-$ with (benzene)ruthenium dichloride. Fortunately, the latter type of sandwich complexes could, in most cases, be easily removed by column chromatography (see Exp. Sect.). The reactions shown in Scheme 2 have been conclusively established by spectroscopic (^{11}B, ^1H and ^{13}C NMR) and analytical characterisation of all compounds and crystallographic characterisation of [**1a**]PF_6 and **4**.

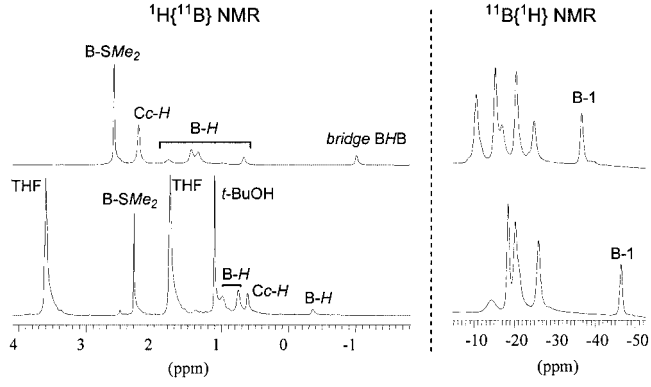
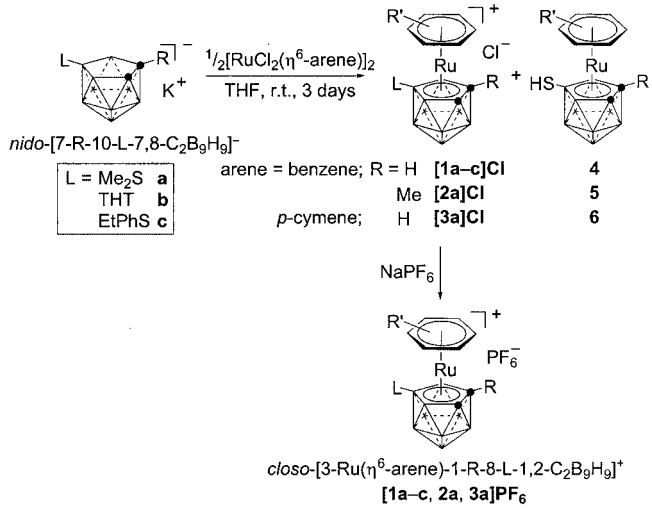


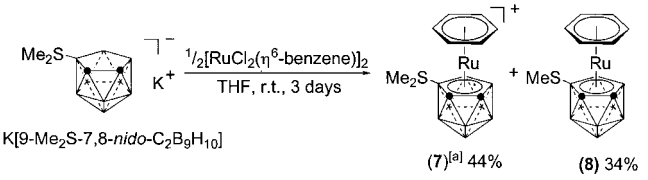
Figure 1. NMR monitoring for the deprotonation of *nido*-[10-Me_2S-7,8-$C_2B_9H_{11}$]: (top) NMR spectra before addition of *t*BuOK (1.0 M solution in THF); (bottom) after addition of 1 equiv. of *t*BuOK (>99% *nido*-K[10-Me_2S-7,8-$C_2B_9H_{10}$]).



Scheme 2. Syntheses of new (arene)ruthenacarborane complexes.

Interestingly, the asymmetric isomer of **1a**, namely *closo*-[3-Ru(η^6-benzene)-7-Me_2S-1,2-$C_2B_9H_{10}$]$^+$ (**7**), has been previously reported in an analogous reaction of $[RuCl_2(\eta^6$-benzene)]$_2$ with the anionic *nido*-[9-Me_2S-7,8-$C_2B_9H_{10}$][Na] in

44% yield but no other species were reported to be formed.[6] Based on our present results, we have examined this reaction in more detail in order to determine whether C–S bond cleavage of Me_2S was also possible in this case. We found that the new soluble neutral complex *closo*-[3-Ru(η^6-benzene)-7-MeS-1,2-$C_2B_9H_{10}$] (**8**) is formed, in addition to the previously reported **7**, in 34% yield [Equation (1)]. Complex **8** has been identified by ^{11}B, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and structurally characterised by X-ray diffraction.



K[9-Me_2S-7,8-*nido*-$C_2B_9H_{10}$] (**7**)[a] 44% (**8**) 34%

[a] From ref.[6]

(1)

2. Characterisation of the New Complexes

a. closo-[3-Ru(η^6-arene)-1-R-8-L-1,2-$C_2B_9H_9$]$^+$

The ^1H NMR spectra for all cationic complexes **1**–**3** (anion for all cationic complexes throughout the text is PF_6^-, unless otherwise noted) show diagnostic signals for coordinated (η^6-arene) fragments to Ru at δ = 6.62–6.82 ppm.[12] Signals for the cage C–H protons (C_c–H) appear as broad resonances at δ = 4.61–4.67 ppm for the unsubstituted carborane compounds (**1** and **3**) and at δ = 4.97 ppm for the methylcarborane complex **2a**, all data being consistent with those of other (arene)ruthenacarborane complexes.[6,13] The $^{13}C\{^1H\}$ NMR spectra for all complexes also show characteristic peaks for the benzene or *p*-cymene ligands, two cage-carbon vertices and the L groups (see Exp. Sect.). The $^{11}B\{^1H\}$ NMR spectra for all complexes are consistent with a *closo*-icosahedral geometry for the cage and are similar to those found for related metallacarborane species.[3i,11] The fully coupled ^{11}B NMR spectra of these complexes show a singlet for the L–B boron vertex whereas the rest of the boron atoms appear as doublets due to ^{11}B-^1H coupling. For example, complex **1a** displays six resonances in a 1:1:2:2:2:1 ratio in its ^{11}B NMR spectrum at δ = 7.1 (s, B-8), 1.9 (d, $^1J_{B,H}$ = 148 Hz, B-10), –6.9 (d, $^1J_{B,H}$ = 153 Hz, B-4,7), –9.8 (d, $^1J_{B,H}$ = 144 Hz, B-9,12), –17.5 (d, $^1J_{B,H}$ = 155.1 Hz, B-5,11), –22.0 (d, $^1J_{B,H}$ = 169 Hz, B-6) ppm. The assignments for each boron atom have been unequivocally determined by 2D $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ COSY for all complexes. These data are consistent with C_s symmetry for the complexes as shown in Scheme 2. However, the symmetry is disrupted in complexes **1c** and **2a** due the presence of the compensating EtPhS group at B(8) and a methyl group at one of the carbon cage vertexes. Thus, the $^{11}B\{^1H\}$ NMR spectrum for **1c** displays seven resonances with relative intensities of 1:1:2:1:1:2:1. The asymmetry can also be observed in the $^{13}C\{^1H\}$ NMR spectrum which shows two different C_c–H resonances (two broad singlets at δ = 49.2 and 49.9 ppm). The asymmetry of **2a** results in all the B signals being inequivalent such that extensive overlap can be observed. In addition, all cationic complexes [**1**–**3**]PF_6 show typical septuplets in their ^{31}P NMR spectra at $\delta \approx$ –143 to –146 ppm, due to $^1J_{P,F}$ coupling (ca. 710 Hz).

b. closo-[3-Ru(η^6-arene)-1-R-8-HS-1,2-$C_2B_9H_9$]

The ^{11}B NMR spectrum for the neutral mercaptan derivative **4** closely resembles that of **1a** with an even larger downfield resonance for the B–SH vertex (δ = 14.3 ppm). The corresponding ^1H NMR spectrum shows a broad resonance at δ = 0.87 ppm which is consistent with an SH group, a situation similar to that found in the related (mercaptan)cobaltacarborane complex *closo*-[3-Co(Cp)-8-HS-1,2-$C_2B_9H_{10}$].[14] In addition, the ^1H and $^{13}C\{^1H\}$ NMR signals for the η^6-benzene moiety and the cage C_c–H for this complex appear at higher field than in the cationic complex **1** and are consistent with other neutral ruthenacarborane complexes.[13a] Complexes **5** and **6** exhibited very similar NMR characteristics to **4** so that their multinuclear NMR spectroscopic data were assigned accordingly.

c. closo-[3-Ru(η^6-benzene)-7-MeS-1,2-$C_2B_9H_{10}$]

The resonance for the substituted B atom in the ^{11}B NMR spectrum is more shielded than in **4** (δ = 6.4 ppm) and, unlike the latter, a signal for an MeS fragment can be observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra. These data are in agreement with cleavage of only one of the C–S bonds of the Me_2S moiety affording the new neutral thioether complex **8** as outlined in Equation (1). The asymmetry of the complex is also evident in the ^1H and $^{13}C\{^1H\}$ NMR spectra which display two resonances for the C_c–H atoms.

3. Crystal Structures

The structures for [**1a**]PF_6, **4** and **8** have been unequivocally established by X-ray crystallography (Figures 2, 3 and 4). The Exp. Sect. contains the crystal and data collection parameters for [**1a**]PF_6. Figure 2 clearly shows that the ruthenium atom in **1a** is sandwiched between the benzene and *nido*-[10-Me_2S-7,8-$C_2B_9H_{10}$]$^-$ ligands giving the cluster the expected *closo*-[3,1,2-MC_2B_9] geometry. The Ru–(C_2B_3 plane) and Ru–(C_6 plane) distances are 1.629 and 1.724 Å, respectively, and these values are similar to those of the dicarbollide-containing neutral complex *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$].[13c] Interestingly, the C_6 benzene ring and C_2B_3 plane angle is 1.59° in **1a** which is significantly smaller than that for the related complex *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$] (4.1°).[13c] Notably the C1–C2 distance is 1.637(4) Å which is similar to that in other *closo* structures.[3] The B8–S1 distance of 1.899(2) Å is consistent with that in other *B*-substituted sulfonium salts.[15]

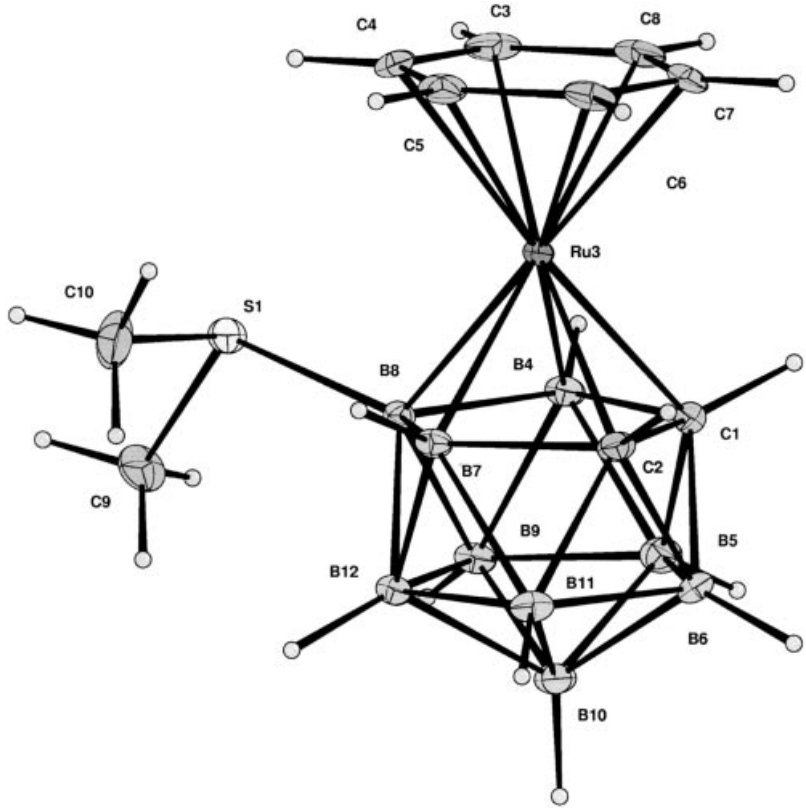


Figure 2. Molecular structure of [**1a**]PF_6 (thermal ellipsoids shown at the 50% probability level). The PF_6^- anion has been omitted for clarity. Selected interatomic distances [Å]: Ru3–C1 2.169(2), Ru3–C2 2.177(2), Ru3–B4 2.212(2), Ru3–B7 2.215(2), Ru3–B8 2.217(2), Ru3–C3 2.219(2), Ru3–C4 2.218(2), Ru3–C5 2.228(2), Ru3–C6 2.236(2), Ru3–C7 2.230(2), Ru3–C8 2.226(2), C1–C2 1.637(4), C2–B7 1.719(3), B7–B8 1.798(3), B4–B8 1.794(3), B8–S1 1.899(2).

The neutral complex **4** also displays a *closo*-[3,1,2-MC_2B_9] geometry for the cluster (Figure 3). The ruthenium atom is sandwiched between the benzene and *nido*-[10-HS-7,8-$C_2B_9H_{10}]^-$ ligands, thus supporting the structure for the complex in solution and confirming that double demethylation occurs from the starting charge-compensated ligand. The average Ru–(C_2B_3 plane) and Ru–(C_6 plane) distances are similar to those in **1a** (1.613 and 1.718 Å). The C_6 benzene ring and the C_2B_3 planes are nearly parallel, the dihedral angle of 2.74° is slightly larger than that for the sulfonium derivative **1a**. The C1–C2 distance is 1.644(4) Å and the B8–S1 bond [1.836(3) Å] is shorter than that of **1a** thereby being consistent with a thiol fragment attached to a boron atom.[16]

As can be seen in Figure 4, the structure of **8** exhibits a similar sandwich-type geometry with the ruthenium atom flanked both by the benzene ring and the C_2B_3 face of the *nido*-[9-MeS-7,8-$C_2B_9H_{10}]^-$ cage. The Ru–(C_2B_3 plane) and Ru–(C_6 plane) distances are 1.719 and 1.606 Å, respectively, the angle between planes of 3.68° is similar to that for the related complex *closo*-[3-Ru(η^6-benzene)-7-Me_2S-1,2-$C_2B_9H_{10}]^+$ (**7**) (4.4°).[6] The C1–C2 [1.627(3) Å] and B4–S1 distances [1.855(3) Å] are also consistent with the above data.

Discussion

1. Reactions of [$RuCl_2(\eta^6$-arene)]$_2$ with Charge-Compensated Carboranes *nido*-[7-R-10-L-7,8-$C_2B_9H_9]^-$ and *nido*-[9-Me_2S-7,8-$C_2B_9H_{10}]^-$

The yields of the new cationic (arene)ruthenacarborane complexes **1**–**3** (Scheme 2) and the reported **7**[6] [Equation (1)] are usually below 50% (Table 1). As demonstrated in this work, these low yields can be partially accounted for by the formation of the (mercaptan)ruthenacarborane complexes **4**–**6** in the case of the symmetric ligands *nido*-[7-R-10-L-7,8-$C_2B_9H_9]^-$ (*isomer-10*) or the thioether complex **8** for the related asymmetric ligand *nido*-[9-Me_2S-7,8-$C_2B_9H_{10}]^-$ (*isomer-9*). Since the starting (arene)ruthenium dichloride and *isomer-10* ligand were also detected during workup of the reactions, we initially thought that insolubility of the benzene(chloro)ruthenium dimer was responsible for the low yields of the complexes (Table 1, Entries 1–2 and 4–5). However, yields for the cationic complexes did not increase when using the more soluble chloro(*p*-cymene) ruthenium dimer (Table 1, Entry 3). Heating was avoided to minimise the formation of the unwanted sandwich complexes *closo*-[3,3′-Ru-(8-L-1,2-$C_2B_9H_{10})_2$] mentioned earlier.[11]

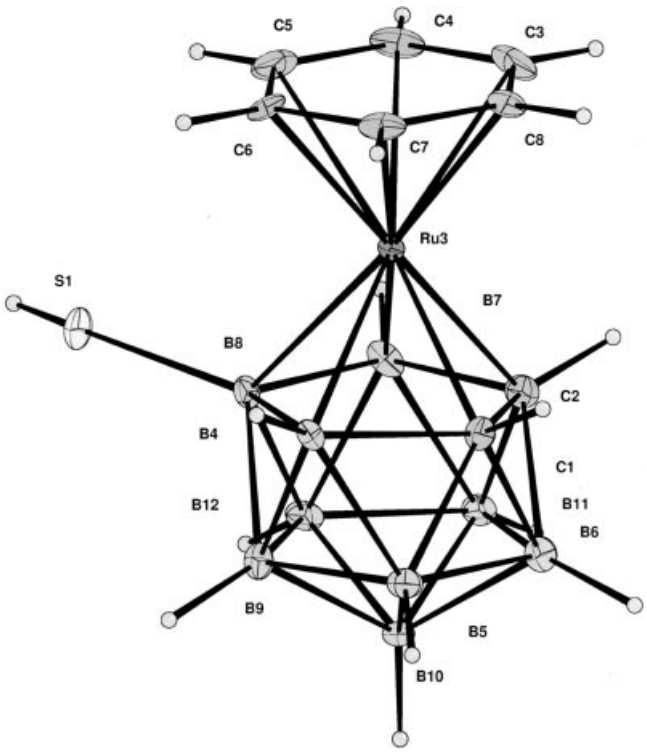


Figure 3. Molecular structure of **4** (thermal ellipsoids shown at the 50% probability level). Selected interatomic distances [Å]: Ru3–C1 2.157(3), Ru3–C2 2.164(3), Ru3–B4 2.202(3), Ru3–B7 2.198(3), Ru3–B8 2.215(3), Ru3–C3 2.242(3), Ru3–C4 2.229(4), Ru3–C5 2.206(3), Ru3–C6 2.197(3), Ru3–C7 2.221(4), Ru3–C8 2.238(3), C1–C2 1.644(4), C2–B7 1.727(4), B7–B8 1.810(4), B4–B8 1.808(4), B8–S1 1.836(3).

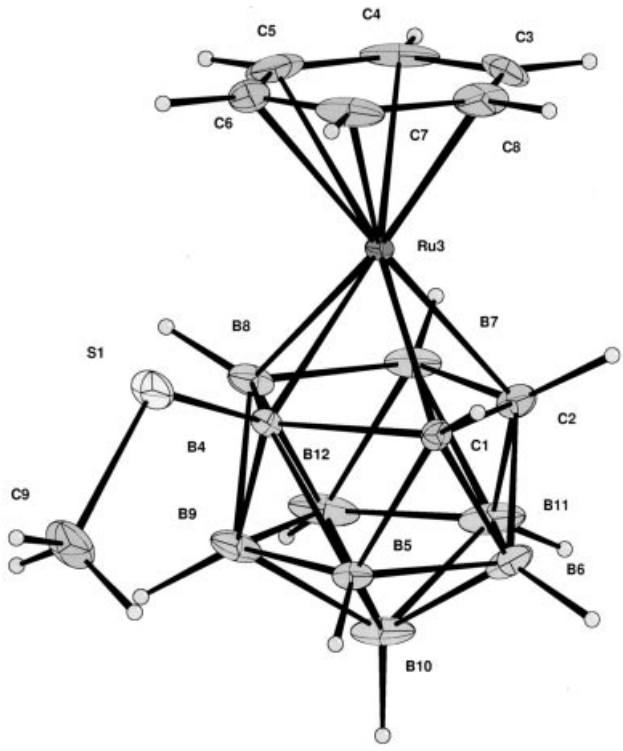


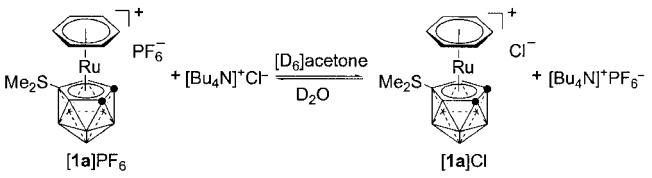
Figure 4. Molecular structure of **8** (thermal ellipsoids shown at the 50% probability level). Selected interatomic distances [Å]: Ru3–C1 2.153(2), Ru3–C2 2.163(2), Ru3–B4 2.202(3), Ru3–B7 2.198(3), Ru3–B8 2.215(3), Ru3–C3 2.228(3), Ru3–C4 2.199(3), Ru3–C5 2.188(3), Ru3–C6 2.199(3), Ru3–C7 2.214(3), Ru3–C8 2.235(3), C1–C2 1.627(3), C2–B7 1.721(4), B7–B8 1.801(4), B4–B8 1.815(4), B4–S1 1.855(3), C9–S1 1.810(3).

Table 1. Yield distribution of *closo*-[3-Ru(η^6-arene)-1-R-8-L-1,2-$C_2B_9H_9$]$^+$ (**1**–**3**) and *closo*-[3-Ru(η^6-arene)-1-R-8-HS-1,2-$C_2B_9H_9$] (**4**–**6**) formed for each reaction.

Entry	R	L	Arene	**1**–**3** [%]	**4**–**6** [%]
1	H	Me_2S	benzene	40 (**1a**)	22 (**4**)
2	Me	Me_2S	benzene	<1 (**2a**)	29 (**5**)
3	H	Me_2S	*p*-cymene	40 (**3a**)	–[a] (**6**)
4	H	THT	benzene	20 (**1b**)	26 (**4**)
5	H	EtPhS	benzene	17 (**1c**)	28 (**4**)

[a] Spectroscopically characterised (see Exp. Sect. for details).

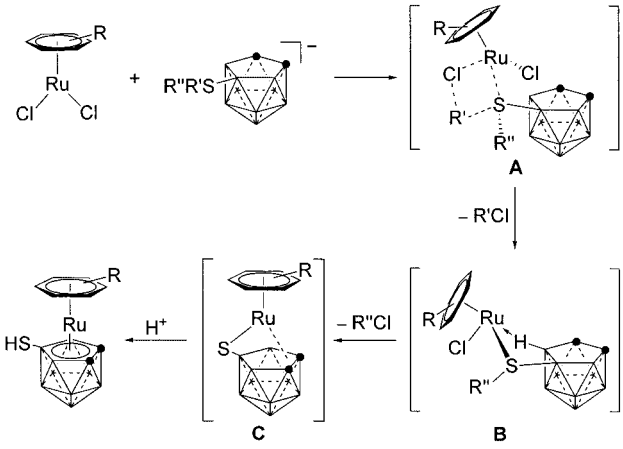
Formation of complexes **4**–**6** is remarkable since they are the result of double dealkylation of any of the sulfonium derivatives at room temperature regardless of the nature of the groups attached to the sulfur atom. This was further confirmed by detection of MeCl (Entry 1 in Table 1), $Cl(CH_2)_4Cl$ (Entry 4) or PhCl and EtCl (Entry 5) during the formation of **4**. Elimination of the alkyl or aryl halides suggests that C–S bond cleavage takes place by means of nucleophilic addition of Cl^- to the organic fragments of the L groups. Similar yields for complexes **4**–**6**, regardless of the starting sulfonium salt derivative, indicate that neither the electronic nor the steric nature of the carbon substituents at the sulfur atom have an important role in the C–S bond cleavage. Although this type of C–S bond activation has been previously reported in thioethers coordinated to electron-withdrawing W or Pt centres, cleavage of only one C–S bond (single dealkylation) was observed in those cases.[17] Double demethylation has only been observed in polyhedral boranes having the charge-compensated Me_2S group but, in this case, a large excess of Li was needed as the reducing agent.[18] Two crucial questions then arise: (i) Does the C–S bond cleavage take place prior to or after coordination of Ru to the open face of the monoanionic carboranes and (ii) does Ru participate in the double C–S bond cleavage? In order to address these points, we first attempted the reaction of complex [**1a**]PF_6 with a Cl^- source such as $[Bu_4N]Cl$. The latter did not cleave any C–S bond. The only reaction observed was a single anion exchange reaction as shown in Equation (2). On the other hand, addition of an excess of the same Cl^- source during the reaction of $[RuCl_2(\eta^6\text{-benzene})]_2$ with *nido*-[10-Me_2S-7,8-$C_2B_9H_{10}]^-$ (Scheme 2) did not affect the ratio of species formed. These two observations are consistent with the cationic complexes not being intermediates of the dealkylation reaction, a fact which is further supported by in situ NMR spectroscopic studies of the formation of [**1a**]Cl and **4** (see Exp. Sect.). In fact, the (arene)ruthenacarborane complexes are so stable that they could be subjected to heating under reflux or photolysis for days without alteration. This clearly suggests that the Cl^- anion itself is not the nucleophile and that Ru must play some role in the cleavage reaction.



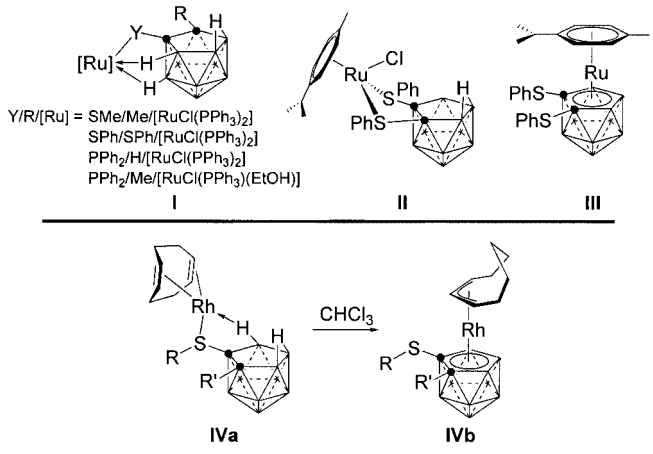
(2)

All the above data support the suggestion that cleavage of the C–S bond in the sulfonium fragments takes place prior to coordination of Ru to the open face of the cluster. Since addition of an external Cl^- source did not affect the dealkylation reaction, formation of alkyl halides could then only be explained by the occurrence of some type of nucleophilic addition of Cl^- bonded to Ru. Taking into account all experimental evidence, we propose the following pathway for the dealkylation reactions: thioether–*exo*-*nido*-carboranes could be formed first (Scheme 3, proposed intermediate **B**) with release of 1 equiv. of either an alkyl or aryl halide. In this way, only Cl^- anions attached to Ru are able to cleave the C–S bond by some type of sulfonium–Ru interaction like that proposed in **A**. The first stepwise single dealkylation is supported by the isolation and crystallographic characterisation of the neutral methyl thioether complex *closo*-[3-Ru(η^6-benzene)-7-MeS-1,2-$C_2B_9H_{10}$] (**8**). Observation of a resonance at δ = –4.27 ppm in the ^{1}H NMR spectrum during the double dealkylation reaction provides evidence for the participation of some type of B–H→Ru agostic interaction like that postulated in **B**.[19] We have previously reported a series of *exo*-cluster monothioether and monophosphanyl complexes having these types of B–H→M (M = Rh, Ru) agostic bonds (Scheme 4, **I** and **IVa**).[20] Carbon–sulfur bond cleavage in (thioether)Ru complexes, as could be the case in intermediate **B**, is known to happen by means of π-back-donation from the metal to the thioether C–S σ*-orbitals.[21] Thus, further dealkylation by C–S bond cleavage in the thioether **B** would follow liberation of a second equivalent of the halide and an *exo*-cluster *S*-bonded (thiolato)ruthenium intermediate like **C** could be formed (Scheme 3). Decoordination of the *S*-bonded thiolato complex **C** could then take place[22] thus forming the more stable (η^5-C_2B_3)ruthenacarborane complex which becomes protonated to give the mercaptan complex.

The stability of the thioether complex **8** towards further cleavage to the corresponding (mercaptan)ruthenacarborane derivative could be related to the different electronic nature of this isomer with regard to its symmetrical analogue. Calculation of Mulliken charges at the Hartree-Fock 3-21G level clearly confirms that charge distribution is affected by the position of C atoms in the C_2B_3 open face of the *nido*-[10-MeS-7,8-$C_2B_9H_9$]$^{2-}$ and *nido*-[9-MeS-7,8-$C_2B_9H_9$]$^{2-}$ carboranes as shown in Scheme 5. It is noteworthy that whereas both hydrogen atoms in the BH vertexes besides the BSMe group are negatively charged in *isomer-10* (both have hydridic B–H hydrogen atoms), those for the asymmetric *isomer-9* have different charges (a hydridic B–H and a protic C–H hydrogen atom). The necessary condition for B–H→M agostic interactions to take place is the existence of electron-enriched B–H bonds such as those in the open-face (C_2B_3) boron atoms of *nido*-C_2B_9 clusters.[20d] Therefore, existence of two hydridic B–H hydrogen atoms in the postulated *exo*-*nido* intermediate **B** (Scheme 3), which could interact indistinctly with Ru, might prevent fast isomerisation of **B** to the thioether and facilitate the second dealkylation to give the observed mercaptan complex **4** (Schemes 2 and 5 left). In the presence of only one hydridic hydrogen atom, the related *isomer-9* might isomerise faster from *exo*-*nido* to *closo* than its symmetrical analogue precluding the Ru from cleaving the second C–S bond (Scheme 5, right). Such isomerisation has been shown to take place in related Rh complexes of the type **IV** at room temperature in $CHCl_3$ solution (Scheme 3).[20d] Removal of the bridging H in the *nido*-carborane in **II** also favours the formation of the *closo* tautomer **III**.[23]



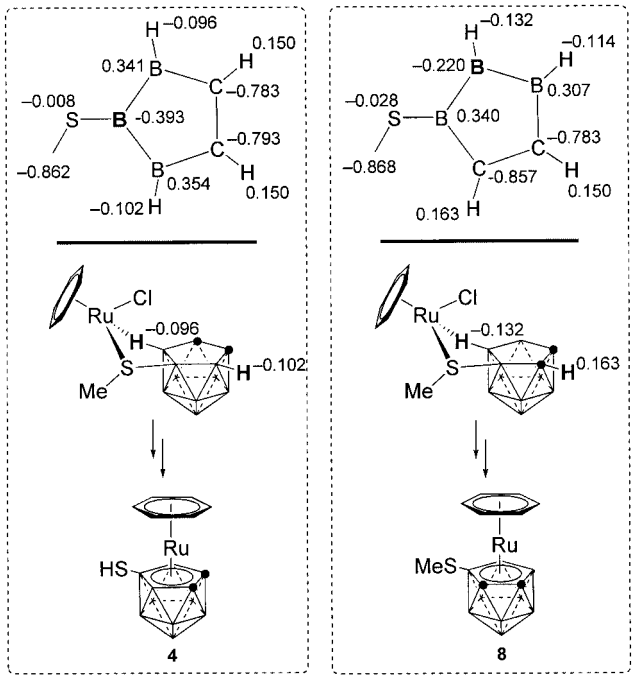
Scheme 3. Proposed pathway for the double dealkylation reaction.



Scheme 4. Other selected ruthenium complexes and reactions.

2. Trends in ^{11}B NMR Spectroscopy for the Ruthenacarboranes

All compounds reported in this paper exhibit a *closo*-[3,1,2-RuC_2B_9] geometry; thus, it is possible to compare the differences in the boron chemical shifts caused by the dif-



Scheme 5. Representation of the C_2B_3 faces of the *nido*-[10-MeS-7,8-$C_2B_9H_{10}]^{2-}$ (left) and *nido*-[9-MeS-7,8-$C_2B_9H_{10}]^{2-}$ ligands (right) and corresponding postulated *exo-nido* Ru species prior to the dealkylation reaction (below bold lines). Boron atoms in bold correspond to the B-8 vertex in the *closo*-ruthenacarborane complexes.

ferent substituents at the boron atoms. Cationic **1**–**3** and **7** as well as the neutral ruthenacarborane complexes **4**–**6** and **8** can be considered as resulting from substitution of a hydride ion in *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$] by sulfonium and thioether or thiol fragments, respectively. Figure 5 shows a comparison of the neutral *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$] which is taken as the reference, with substituted Me_2S and HS at B-8 (Table 2; Entries 1, 2 and 7).

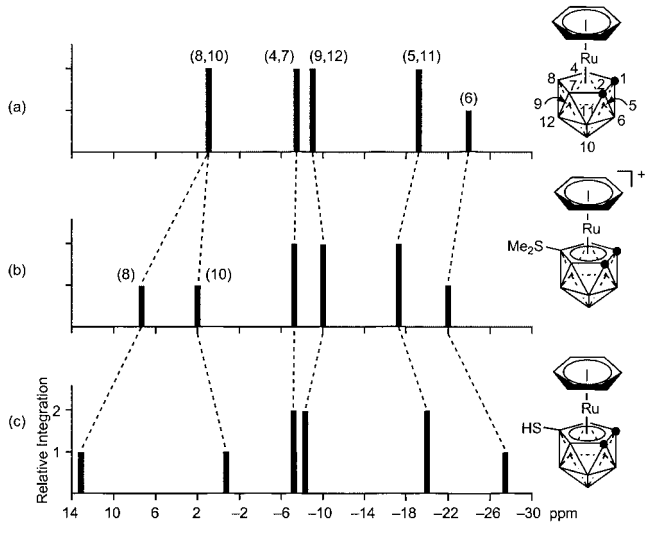


Figure 5. Representation of the $^{11}B\{^1H\}$ NMR spectra for complexes: (a) *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$] (showing boron assignment); (b) [**1a**]PF_6; (c) **4**.

{Although the ruthenacarborane complex *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$] has been previously reported,[13a] assignment of the cluster ^{11}B NMR spectroscopic data was not published; the present assignments were made by $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ COSY spectrosopy ([D_6]acetone): δ = 1.3 (m, 2 B, B-8 and -10), –7.4 (d, $^1J_{B,H}$ = 117 Hz, 2 B, B-4 and -7), –8.7 (d, $^1J_{B,H}$ = 117 Hz, 2 B, B-9 and -12), –18.9 (d, $^1J_{B,H}$ = 152 Hz, 2 B, B-5 and -11) and –23.7 [d, $^1J_{B,H}$ = 176 Hz, 1 B, B-6] ppm.} The most apparent effect observed in Figure 5 is a large downfield displacement of chemical shifts for the substituted B-8 with respect to our reference complex, that of the HS derivative being larger than that of the Me_2S derivative. Whereas the signal for the Me_2S–B boron atom in **1a** is shifted downfield by about 7 ppm, that for the HS-B boron atom in **4** is displaced by 13 ppm. A second significant effect apparent from Figure 5 is the so-called antipodal effect (AE)[9] to the substituted boron atom (B-6). Whereas the chemical shift for the boron atom antipodal to Me_2S has moved downfield (Figure 5b), that of the boron atom antipodal to HS is displaced upfield (Figure 5c). These two main effects have good precedent.[9,18] As expected, smaller antipodal effects can also be observed in the asymmetric complexes *closo*-[3-Ru(η^6-benzene)-7-Me_2S-1,2-$C_2B_9H_{10}]^+$ (**7**) and *closo*-[3-Ru(η^6-benzene)-7-MeS-1,2-$C_2B_9H_{10}$] (**8**) due to the lack of a plane of symmetry crossing both the substituted and antipodal vertex[9] {compound/δ(B-5): *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$]/–18.9 ppm, **7**/–18.7 ppm,[6] **8**/–17.0 ppm}.

Other minor effects include a downfield/upfield butterfly effect (BE)[9] analogous to the AE in our system (signals for B-5, -10 and -11 have moved downfield with respect to the reference in the case of the Me_2S-substituted species **1a** but those for the HS analogue **4** are displaced upfield) and the neighbouring effect (NE)[9] which only affects B-9 and -12 in the Me_2S-substituted **1a**.

3. Crystal Structures and Antipodal Effect

The empirically observed AE has been previously explained through cooperation of atomic orbitals on antipodally interacting vertices.[9] It is noteworthy that although the AE has been extensively studied using calculations[24] and by comparing various series of compounds,[9] the comparison has always been related to the ^{11}B chemical shifts as the only experimental evidence. Surprisingly, even though such a hypothesis involves the transfer of part of the electrons between antipodal boron atoms and, therefore, through some type of interaction between atomic orbitals, no other experimental evidence has ever been obtained apart from NMR chemical shifts.

We were curious to see whether the AE obtained by NMR spectroscopy, for neutral and cationic ruthenacarboranes, has any influence on their X-ray structures. A comparison of the X-ray structures of the complexes *closo*-[3-Ru(η^6-benzene)-1,2-$C_2B_9H_{11}$] (the reference compound) with *closo*-[3-Ru(η^6-benzene)-8-Me_2S-1,2-$C_2B_9H_{10}]^+$ (**1a**) and *closo*-[3-Ru(η^6-benzene)-8-HS-1,2-$C_2B_9H_{10}$] (**4**)

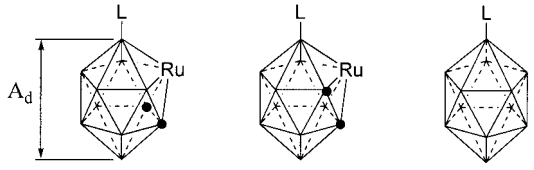
Table 2. Comparison of ^{11}B NMR chemical shifts for *closo*-[3-Ru(η^6-arene)-1-R-8-L-1,2-$C_2B_9H_{10}$][PF_6] (above bold line) and *closo*-[3-Ru(η^6-arene)-1-R-8-HS-1,2-$C_2B_9H_9$] (below bold line).[a]

Entry	Arene	L	R	Complex	B-8	B-10	B-4/B-7	B-9/B-12	B-5/B-11	B-6
1	benzene	H	H	–	1.3	1.3	–7.4	–8.7	–18.9	–23.7
2	benzene	Me_2S	H	1a	7.1	1.9	–6.9	–9.8	–17.5	–22.0
3	benzene	THT	H	1b	6.2	1.2	–8.0	–10.7	–19.0	–23.3
4	benzene	EtPhS	H	1c	7.1	2.1	–6.6	–9.2/–9.6	–17.6	–21.7
5	benzene	Me_2S	Me	2a	6.1	1.7		–4.5 to –18.5		–22.9
6	*p*-cymene	Me_2S	H	3a	7.2	1.2	–5.7	–9.8	–17.6	–21.6
7	benzene	HS	H	4	14.3	–1.1	–6.9	–8.5	–20.0	–27.5
8	benzene	HS	Me	5	15.0	0.0	–3.5 to –9.4		–15.1/-18.6	–22.0
9	*p*-cymene	HS	H	6	13.6	–2.9	–7.7	–7.7	–20.9	–27.9

[a] See Scheme 1 for numbering.

(Table 3, polyhedral type V) shows a significant shortening of the distance between the substituted B atom and its antipodal boron atom (A_d: antipodal distance) in the sulfonium salt derivative **1a** with respect to the reference complex (0.061 Å). A smaller shortening can be observed for the neutral complex **4** (0.023 Å). The same situation can be observed when comparing the structures of the related substituted polyhedral boranes *closo*-[1-L-$B_{12}H_{11}$]$^{z-}$ with the reference *closo*-[$B_{12}H_{12}$]$^{2-}$ molecule (Table 3, polyhedral type VII). In this case the shortening of A_d is slightly larger (0.093 Å) than in the related ruthenacarborane structures. In contrast, the shortening of A_d is hardly seen in the asymmetric *closo*-[3-Ru(η^6-benzene)-7-L-1,2-$C_2B_9H_{10}$]$^+$ (Table 3, polyhedral type VI) which is consistent with a smaller AE for these complexes as expected from the lack of symmetry.[9] It is remarkable that the shortening of the antipodal distance (A_d) is observed in those compounds having strong electron-attracting substituents attached to boron atoms. According to the accepted hypothesis,[9] such substituents are believed to decrease the electron density at the antipodal boron atom with the consequent downfield shift of the chemical shift of the signal of this boron atom. Although the magnitudes of both the downfield chemical shift and the shortening of A_d are quite small in our complexes, a relation between AE and the shortening of A_d can be clearly seen when analysing the X-ray structures for the polyhedral heteroboranes *closo*-$EB_{11}H_{11}$ and *closo*-EB_9H_9 (Table 4).[25] The latter complexes are known to exhibit AE of at least one order of magnitude larger than the examples in Table 3.[8] The data summarised in table 4 clearly show that the downfield AE and the shortening of A_d both follow the same order, E = $MeAl^{2-}$ < HB^{2-} < HC^- < HN, i.e. with decreasing electron density at the E vertex. The shortening of the antipodal distances A_d is really significant. The difference between the first compound in the *closo*-$EB_{11}H_{11}$ series ($MeAl^{2-}$) and the last (HC^-) is 0.637 Å (Table 4)! The shortening of A_d is clearly not driven by the charges on the clusters, since *closo*-[$MeAlB_{11}H_{11}$]$^{2-}$ and *closo*-[$B_{12}H_{12}$]$^{2-}$ already show a significant shortening. To the best of our knowledge, this correlation has not been previously observed.

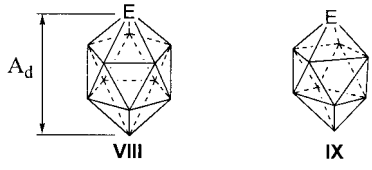
Table 3. Antipodal distances (A_d) for *closo*-[3-Ru(η^6-benzene)-8-L-1,2-$C_2B_9H_{10}$]$^+$ (polyhedral type V), *closo*-[3-Ru(η^6-benzene)-7-L-1,2-$C_2B_9H_{10}$]$^+$ (type VI) and *closo*-[$LB_{12}H_{11}$]$^{z-}$ (type VII).



Polyhedral type	L	Compound charge	A_d [Å]
V	H	0	3.439[a]
	HS (**4**)	0	3.416[b]
	Me_2S (**1a**)	+1	3.378[c]
VI	H	0	3.387[a]
	MeS (**8**)	0	3.405[b]
	Me_2S	+1	3.354[c]
VII	H	–2	3.391[d]
	MeS	–2	3.374[e]
	Me_2S	–1	3.298[f]

[a] Value measured from the structure in ref.[13c] [b] From ref.[8] [c] This work. [d] From ref.[26] [e] From ref.[18a] [f] From ref.[15a]

Table 4. Antipodal distances (A_d) for *closo*-$EB_{11}H_{11}$ (polydedral type VIII) and *closo*-EB_9H_9 (type IX).[a]



Polyhedral type	E	Cluster charge	δ[b]	A_d [Å]
VIII	MeAl	–2	–25.5	3.893
	HB	–2	–15.3	3.391
	HC	–1	–7.0	3.256
IX	HB	–2	–2.0	3.697
	HC	–1	28.4	3.387
	HN	0	61.0	3.303

[a] A_d values were measured from the structures in ref.[25] [b] ^{11}B NMR chemical shift for antipodal B atoms taken from ref.[9]

Conclusion

In this study, we describe the formation of cationic ruthenacarborane complexes *closo*-[3-Ru(η^6-arene)-1-R-8-L-

1,2-$C_2B_9H_9]^+$ (L = Me_2S, THT, EtPhS) (**1**–**3**) and neutral mercaptan *closo*-[3-Ru(η^6-arene)-1-R-8-HS-1,2-$C_2B_9H_9$] (**4**–**6**) and *closo*-[3-Ru(η^6-benzene)-7-MeS-1,2-$C_2B_9H_{10}$] (**8**). The neutral complexes are the result of double or single dealkylation of L groups in mono-anionic "charge-compensated" *o*-carborane derivatives at room temperature. Such facile C–S bond activations are unprecedented in polyhedral carborane chemistry and open a new route to mercaptan metallocarboranes. A pathway for the dealkylation reactions is proposed. The findings also show, for the first time, a relation between the empirical antipodal effect (AE) and the structural antipodal distance (A_d) in the crystal structures for the new complexes and other previously reported 12- and 10-vertex heteroboranes. We are currently working on an extension of this correlation to other *closo*-heteroboranes.

Experimental Section

General: All manipulations were carried out under N_2. Chemicals were prepared as follows: THF was distilled from Na/benzophenone; acetone was distilled from P_2O_5; *t*BuOK (95%, Aldrich or 1.0 M solution in THF) and $NaPF_6$ (98%, Aldrich) were used as received. The following were prepared by literature procedures: *nido*-[9-Me_2S-7,8-$C_2B_9H_{11}$],[4a] *nido*-[7-R-10-L-7,8-$C_2B_9H_{10}$] (R = H, L = Me_2S, THT, EtPhS; R = H, L = Me_2S)[4] and [$RuCl_2$(η^6-arene)]$_2$ (arene = benzene, *p*-cymene).[12] NMR spectra were acquired with a Bruker ARX 300 MHz spectrometer and referenced to the solvent (^{1}H, residual signals of [D_5]acetone, [D_2]acetonitrile or [D_7]THF; ^{13}C signals of [D_6]acetone or [D_3]acetonitrile),[26] BF_3·OEt_2 (^{11}B NMR) or PPh_3 (^{31}P NMR; a C_6D_6 solution in an internal sealed capillary, δ = –5.00 ppm). Chemical shifts are reported in ppm and coupling constants in Hz. Multiplet nomenclature is as follows: s, singlet; d, doublet; t, triplet; sept, septuplet; br., broad; m, multiplet. Chromatography was carried out using ACROS silica gel (0.035–0.070 mm, pore diameter ca. 6 nm). Microanalyses were conducted with a Carlo Erba EA1108 instrument. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF instrument [N_2 laser; λ_{exc} = 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.20 kV (Uis2)]. Photochemical reactions were performed in a quartz Schlenk vessel equipped with a magnetic bar and condenser. The unfiltered output of an in-house 76.8 W medium-pressure mercury lamp was used as a light source.

***closo*-[3-Ru(η^6-benzene)-8-Me_2S-1,2-$C_2B_9H_{10}$]$^+$ (1a) and *closo*-[3-Ru(η^6-benzene)-8-HS-1,2-$C_2B_9H_{10}$] (4). General Procedure:** A Schlenk flask was charged with *nido*-[10-Me_2S-7,8-$C_2B_9H_{11}$] (95.1 mg, 0.489 mmol), *t*BuOK (0.550 mL, 1.0 M) and THF (10 mL). The mixture was stirred at room temperature for 30 min giving a clear pale yellow solution. The flask was then charged with [$RuCl_2$(η^6-benzene)]$_2$ (122.4 mg, 0.245 mmol) and the resultant heterogeneous brown mixture was stirred at room temperature for 3 d. Workup for **1a** and **4** was as follows:

1a: A solid residue was separated from the supernatant orange solution and transferred into another Schlenk vessel for further isolation of **4** (vide infra). The solid residue remaining in the flask was dried by oil-pump vacuum to give **[1a]**Cl and KCl as a pale brown powder. Addition of an aqueous solution of $NaPF_6$ (176.7 mg, 1.052 mmol) to the heterogeneous brown mixture of **[1a]**Cl in ethanol (10 mL) resulted in the formation of a tan precipitate. After stirring for at room temperature for 1 h, the remaining ethanol was removed under reduced pressure and the resultant suspension was allowed to settle without stirring in the refrigerator for 1 h. The aqueous solution was separated by cannula and the residue was washed with H_2O (1 mL) and extracted with CH_2Cl_2 which was then evaporated and the residue dried by oil-pump vacuum to afford **[1a]**PF_6 as a tan powder (101.3 mg, 0.196 mmol, 40%). $C_{10}H_{22}B_9F_6PRuS$: calcd. C 23.20, H 4.28, S 6.19; found C 22.92, H 3.92, S 5.86. MALDI-TOF *m*/*z* (%) = 373.53 (100) [M], 311.46 (43) [M – Me_2S].

[1a]Cl: ^{1}H NMR ([D_3]acetonitrile): δ = 6.58 (s, 6 H, η^6-C_6H_6), 4.50 (br. s, 2 H, C_c-*H*), 2.45 (s, 6 H, Me_2S) ppm. ^{1}H{^{11}B} NMR ([D_3]acetonitrile; only signals due to B-H protons are given): δ = 2.92 (br. s, 2 H), 1.90–1.60 (m, 6 H) ppm. ^{11}B NMR ([D_3]acetonitrile): δ = 6.9 (s, 1 B, B-8), 1.7 (d, $^1J_{B,H}$ = 154 Hz, 1 B, B-10), –7.1 (d, $^1J_{B,H}$ = 150 Hz, 2 B, B-4 and -7), –10.0 (d, $^1J_{B,H}$ = 144 Hz, 2 B, B-9 and -12), –17.6 (d, $^1J_{B,H}$ = 162 Hz, 2 B, B-5 and -11), –22.0 (d, $^1J_{B,H}$ = 175, 1 B, B-6) ppm. ^{13}C{^{1}H} NMR ([D_3]acetonitrile): δ = 93.3 (s, η^6-benzene), 50.8 (br. s, C_c-H), 25.7 (s, Me_2S) ppm.

[1a]PF_6: ^{1}H NMR ([D_6]acetone): δ = 6.80 (s, 6 H, η^6-benzene), 4.64 (br. s, 2 H, C_c-*H*), 2.63 (s, 6 H, Me_2S) ppm. ^{1}H{^{11}B} NMR ([D_6]acetone; only signals due to B-H protons are given): δ = 3.40 (br. s, 1 H), 3.02 (br. s, 2 H), 1.86 (br. s, 2 H), 1.70 (m, 3 H) ppm. ^{11}B NMR ([D_6]acetone): δ = 7.1 (s, 1 B, B-8), 1.9 (d, $^1J_{B,H}$ = 148 Hz, 1 B, B-10), –6.9 (d, $^1J_{B,H}$ = 153 Hz, 2 B, B-4 and -7), –9.8 (d, $^1J_{B,H}$ = 144 Hz, 2 B, B-9 and -12), –17.5 (d, $^1J_{B,H}$ = 155 Hz, 2 B, B-5 and 11), –22.0 (d, $^1J_{B,H}$ = 169 Hz, 1 B, B-6) ppm. ^{13}C{^{1}H} NMR ([D_6]acetone): δ = 92.6 (s, η^6-benzene), 49.4 (br. s, C_c-H), 24.5 (s, Me_2S) ppm. ^{31}P NMR ([D_6]acetone): δ = –143.7 (sept, $^1J_{P,F}$ = 708 Hz, PF_6) ppm.

4: Concentration of the above-mentioned supernatant orange THF solution afforded a mixture of **4** and *closo*-[3,3′-Ru-(8-Me_2S-1,2-$C_2B_9H_{10}$)$_2$] as an orange residue. Chromatographic separation on silica gel using THF as the eluent afforded *closo*-[3,3′-Ru-(8-Me_2S-1,2-$C_2B_9H_{10}$)$_2$] (R_f = 0.63) as a yellow-orange solid (10.0 mg, 0.020 mmol, 8%) and **4** (R_f = 0.50) as a yellow solid after washing with cold CH_2Cl_2 (36.4 mg, 0.106 mmol, 22%). $C_8H_{17}B_9RuS$ (343.65): calcd. C 27.96, H 4.99, S 9.33; found C 28.09, H 4.74, S 8.39. ^{1}H NMR ([D_6]acetone): δ = 6.38 (s, 6 H, η^6-benzene), 4.31 (br. s, 2 H, C_c-*H*), 0.87 (br. m, 1 H, S*H*) ppm. ^{1}H{^{11}B} NMR ([D_6]acetone; only signals due to B-H protons are given): δ = 3.09 (br. s, 1 H), 2.91 (br. s, 2 H), 1.99 (br. s, 2 H), 1.53 (br. s, 2 H), 1.31 (br. s, 1 H) ppm. ^{11}B NMR ([D_6]acetone): δ = 14.3 (s, 1 B, B-8), –1.1 (d, $^1J_{B,H}$ = 140 Hz, 1 B, B-10), –6.9 (d, $^1J_{B,H}$ = 144 Hz, 2 B, B-4 and -7), –8.5 (d, $^1J_{B,H}$ = 160 Hz, 2 B, B-9 and -12), –20.0 [d, $^1J_{B,H}$ = 155 Hz, 2 B, B-5 and -11), –27.5 (d, $^1J_{B,H}$ = 170 Hz, 1B, B-6) ppm. ^{13}C{^{1}H} NMR ([D_6]acetone): δ = 92.1 (s, η^6-benzene), 46.2 (br. s, C_c-H) ppm.

The synthesis was repeated in a modified form to identify the volatile by-product MeCl. A Schlenk flask was charged with 10-Me_2S-7,8-*nido*-$C_2B_9H_{11}$ (294.0 mg, 1.513 mmol), *t*BuOK (1.65 mL, 1.0 M) and THF (20 mL). The mixture was stirred at room temperature for 30 min affording a clear pale-yellow solution. The flask was then charged with [$RuCl_2$(η^6-benzene)]$_2$ (369.9 mg, 0.740 mmol), closed with a rubber stopper and the resultant heterogeneous brown mixture was stirred at room temperature for 3 d. MeCl gas was detected using gas chromatography by comparing the retention time with that of an authentic sample. ^{1}H NMR identification was also carried out (see in situ NMR studies below).

***closo*-[3-Ru(η^6-benzene)-8-THT-1,2-$C_2B_9H_{10}$]$^+$ (1b) and 4:** The general procedure described above was applied using *nido*-[10-THT-7,8-$C_2B_9H_{11}$] (103.9 mg, 0.471 mmol), *t*BuOK (0.48 mL, 1.0 M),

THF (5 mL), $[RuCl_2(\eta^6\text{-benzene})]_2$ (116.9 mg, 0.234 mmol) and $NaPF_6$ (165 mg, 0.982 mmol) to give **[1b]PF_6** (51.0 mg, 0.094 mmol, 20%). The neutral complex **4** was separated and purified by chromatography as described above (41.7 mg, 0.121 mmol, 26%).

[1b]Cl: ^{1}H NMR ([D$_3$]acetonitrile): δ = 6.53 (s, 6 H, η^6-benzene), 4.42 (br. s, 2 H, C$_c$-*H*), 3.45 [m, 2 H, S(C*H*H′CH′′H′′′)$_2$], 3.03 [m, 2 H, S(CH*H*′CH′′H′′′)$_2$], 2.12 [br. t, $^3J_{H,H}$ = 7.5 Hz, 2 H, S(CHH′C*H*′′H′′′)$_2$], 2.10 ppm [br. t, $^3J_{H,H}$ = 7.8 Hz, 2 H, S(CHH′CH′′*H*′′′)$_2$]. ^{11}B NMR ([D$_3$]acetonitrile): δ = 7.4 (s, 1 B, B-8), 2.2 (d, $^1J_{B,H}$ = 144 Hz, 1 B, B-10), –6.7 [d, $^1J_{B,H}$ = 151 Hz, 2 B, B-4 and -7), –9.7 (d, $^1J_{B,H}$ = 145 Hz, 2 B, B-9 and -12), –17.8 (d, $^1J_{B,H}$ = 160 Hz, 2 B, B-5 and -11), –22.1 (d, $^1J_{B,H}$ = 183 Hz, 1 B, B-6) ppm. ^{13}C{^{1}H} NMR ([D$_3$]acetonitrile): δ = 93.4 (s, η^6-benzene), 51.0 (s, *C*$_c$-H), 44.5 [s, S(*C*H$_2$CH$_2$)$_2$], 30.4 [s, S(CH$_2$*C*H$_2$)$_2$] ppm.

[1b]PF_6: $C_{12}H_{24}B_9F_6PRuS$ (543.72): calcd. C 26.51, H 4.45, S 5.90; found C 26.72, H 4.46, S 6.00. MALDI-TOF: *m*/*z* (%) = 397.9 (74) [M + 1], 309.8 (100) [M + 1 – (CH$_2$)$_4$S]. ^{1}H NMR ([D$_6$]acetone): δ = 6.82 (s, 6 H, η^6-benzene), 4.67 (br. s, 2 H, C$_c$-*H*), 3.72 [m, 2 H, S(C*H*H′CH′′H′′′)$_2$], 3.20 [m, 2 H, S(CH*H*′CH′′H′′′)$_2$], 2.22 [br. t, $^3J_{H,H}$ = 7.5 Hz, 2 H, S(CHH′C*H*′′H′′′)$_2$], 2.20 ppm [br. t, $^3J_{H,H}$ = 6.6 Hz, 2 H, S(CHH′CH′′*H*′′′)$_2$]. ^{1}H{^{11}B} NMR ([D$_6$]acetone; only signals due to B-H protons are given): δ = 3.42 (br. s, 1 H), 3.06 (br. s, 2 H), 1.78 (br. s, 2 H), 1.68 (br. s, 3 H) ppm. ^{11}B NMR ([D$_6$]acetone): δ = 6.2 (s, 1 B, B-8), 1.2 (d, $^1J_{B,H}$ = 147 ppm, 1 B, B-10), –8.0 (d, $^1J_{B,H}$ = 152 Hz, 2 B, B-4 and -7), –10.7 (d, $^1J_{B,H}$ = 144 Hz, 2 B, B-9 and -12), –19.0 (d, $^1J_{B,H}$ = 156 Hz, 2 B, B-5 and -11), –23.3 (d, $^1J_{B,H}$ = 174 Hz, 1 B, B-6) ppm. ^{13}C{^{1}H} NMR ([D$_6$] acetone): δ = 92.4 (s, η^6-benzene), 49.3 (s, *C*$_c$-H), 45.7 [s, S(*C*H$_2$CH$_2$)$_2$], 43.2 [s, S(CH$_2$*C*H$_2$)$_2$] ppm. ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = –146.0 (sept, $^1J_{P,F}$ = 705 Hz, PF_6) ppm.

***closo*-[3-Ru(η^6-benzene)-8-EtPhS-1,2-$C_2B_9H_{10}$]$^+$ (1c) and 4:** The general procedure described above was applied using *nido*-[10-EtPhS-7,8-$C_2B_9H_{11}$] (116.6 mg, 0.431 mmol), *t*BuOK (0.47 mL, 1.0 M), THF (15 mL), $[RuCl_2(\eta^6\text{-benzene})]_2$ (107.9 mg, 0.216 mmol) and $NaPF_6$ (82.9 mg, 0.494 mmol) to afford **[1c]**PF_6 (44.0 mg, 0.074 mmol, 17%). The neutral complex **4** (41.7 mg, 0.121 mmol, 28%) was isolated by chromatography as in the previous procedure.

[1c]Cl: ^{1}H NMR ([D$_3$]acetonitrile): δ = 7.80–7.50 (m, 5 H, S*Ph*), 6.34 (s, 6 H, η^6-benzene), 4.35 (br. s, 2 H, C$_c$-*H*), 3.40–3.15 [m, 2 H, S(C*H*$_2$CH$_3$)], 1.14 [t, $^3J_{H,H}$ = 7.2 Hz, 3 H, S(CH$_2$C*H*$_3$)] ppm.[27] ^{11}B NMR ([D$_3$]acetonitrile): δ = 7.0 (s, 1 B, B-8), 2.1 (d, $^1J_{B,H}$ = 170 Hz, 1 B, B-10), –6.7 (d, $^1J_{B,H}$ = 139 Hz, 2 B, B-4 and -7), –9.4 (d, $^1J_{B,H}$ = 133 Hz, 1 B, B-9 or -12), –9.9 (d, $^1J_{B,H}$ = 122 Hz, 1 B, B-12 or -9), –17.6 (d, $^1J_{B,H}$ = 162 Hz, 2 B, B-5 and -11), –21.8 (d, $^1J_{B,H}$ = 190 Hz, 1 B, B-6) ppm. ^{13}C{^{1}H} NMR ([D$_3$]acetonitrile): δ = 134.2, 133.0, 131.7 (3 s, *o*-, *m*- and *p*-S*Ph*), 93.2 (s, η^6-benzene), 49.9 (s, *C*$_c$-H), 49.3 (s, *C*$_c$′-H), 38.7 [s, S(*C*H$_2$CH$_3$)], 11.5 [s, S(CH$_2$*C*H$_3$)] ppm.

[1c]PF_6: MALDI-TOF: *m*/*z* (%) = 448.95 (77) [M], 310.93 (100) [M – EtPhS]. ^{1}H NMR ([D$_6$]acetone): δ = 7.80 (d, $^3J_{H,H}$ = 6.9 Hz 2 H, *o*-S*Ph*), 7.80 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, *p*-S*Ph*), 7.73 (t, $^3J_{H,H}$ = 6.9 Hz, 2 H, *m*-S*Ph*), 6.62 (s, 6 H, η^6-benzene), 4.61 (br. s, 2 H, C$_c$-*H*), 3.50 [dq, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 7.3 Hz, 1 H, S(C*H*H′CH$_3$)], 3.41 [dq, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 7.3 Hz, 1 H, S(CH*H*′CH$_3$)], 1.27 [t, $^3J_{H,H}$ = 7.3 Hz, 3 H, S(CHH′C*H*$_3$)] ppm.[28] ^{11}B NMR ([D$_6$] acetone): δ = 7.1 (s, 1 B, B-8), 2.1 (d, $^1J_{B,H}$ = 148 Hz, 1 B, B-10), –6.6 (d, $^1J_{B,H}$ = 145 Hz, 2 B, B-4 and -7), –9.2 (d, $^1J_{B,H}$ = 141 Hz, 1 B, B-9 or -12), –9.9 (d, $^1J_{B,H}$ = 132 Hz, 1 B, B-12 or -9), –17.6 (d, $^1J_{B,H}$ = 154 Hz, 2 B, B-5 and -11), –21.7 (d, $^1J_{B,H}$ = 172 Hz, 1 B, B-6) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 133.3, 132.1, 130.7 (3 s, *o*-, *m*- and *p*-S*Ph*), 124.4 (s, *i*-S*Ph*), 92.5 (s, η^6-benzene), 49.9 (s, *C*$_c$-H), 49.2 (s, *C*$_c$′-H), 37.6 [s, S(*C*H$_2$CH$_3$)], 10.7 [s, S(CH$_2$*C*H$_3$)] ppm. ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = –142.7 (sept, $^1J_{P,F}$ = 708 Hz, PF_6) ppm.

The reaction was repeated in a modified fashion to identify the by-products PhCl and EtCl. 10-Me$_2$S-7,8-*nido*-$C_2B_9H_{11}$ (14.8 mg, 0.055 mmol), [D$_8$]THF (0.50 mL) and a THF solution of *t*BuOK (0.066 mL, 1.0 M) were placed into an NMR tube. The clear solution rapidly turned light yellow. After 20 min, the solution was transferred under N_2 by syringe to another NMR tube containing $[RuCl_2(\eta^6\text{-benzene})]_2$ (13.4 mg, 0.026 mmol). PhCl [δ = 7.34–7.18 (m) ppm] and EtPhS [δ = 7.30–7.35 (m, 5 H, *Ph*), 2.95 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, *Et*), 1.26 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, *Et*) ppm] were detected by ^{1}H NMR spectroscopy. Signals for THF prevented identification of EtCl due to overlapping of signals (proton resonances for terminal B-H groups appear as broad unresolved peaks in the range $\delta \approx$ 3.5–1.0 ppm).

***closo*-[3-Ru(η^6-benzene)-1-Me-8-Me$_2$S-1,2-$C_2B_9H_9$]$^+$ (2a) and *closo*-[3-Ru(η^6-benzene)-1-Me-8-HS-1,2-$C_2B_9H_9$] (5):** The general procedure described above was applied using *nido*-[10-Me$_2$S-7-Me-8-$C_2B_9H_{10}$] (104.8 mg, 0.502 mmol), *t*BuOK (0.55 mL, 1.0 M), THF (10 mL), $[RuCl_2(\eta^6\text{-benzene})]_2$ (125.7 mg, 0.251 mmol) and $NaPF_6$ (114.0 mg, 0.665 mmol) to afford traces of **[2a]**PF_6. The neutral complex **5** was purified by chromatography as described above (52.0 mg, 0.145 mmol, 29%).

[2a]PF_6: Selected NMR spectroscopic data are given: ^{1}H NMR ([D$_6$]acetone): δ = 6.82 (s, 6 H, η^6-benzene), 4.97 (br. s, 1 H, C$_c$-*H*), 2.25 (s, 3 H, C$_c$-*Me*), 2.66 (s, 3 H, S*Me*$_2$), 2.60 (s, 3 H, S*Me*$_2$) ppm. ^{11}B NMR ([D$_6$]acetone): δ = 6.1 (s, 1 B, B-8), 1.7 (d, $^1J_{B,H}$ = 156 Hz, 1 B, B-10), –4.5 to –18.5 (m, 6 B, B-4, -5, -7, -9, -11 and -12), –22.1 (d, $^1J_{B,H}$ = 177 Hz, 1 B, B-6) ppm. ^{31}P{^{1}H} NMR ([D$_6$] acetone): δ = –142.6 (sept, $^1J_{P,F}$ = 707 Hz, PF_6) ppm.

5: $C_9H_{19}B_9RuS$ (357.68): calcd. C 30.22, H 5.35, S 8.96; found C 30.15, H 5.20, S 9.10. ^{1}H NMR ([D$_6$]acetone): δ = 6.40 (s, 6 H, η^6-benzene), 4.60 (br. s, 1 H, C$_c$-*H*), 2.17 (s, 3 H, C$_c$-*Me*), 0.87 (br. m, 1 H, S*H*) ppm. ^{1}H{^{11}B} NMR ([D$_6$]acetone; only signals due to B-H protons are given): δ = 3.17 (br. s, 2 H), 3.02 (br. s, 1 H), 2.07 (br. s, 2 H), 1.82 (br. s, 1 H), 1.62 (br. s, 2 H) ppm. ^{11}B NMR ([D$_6$] acetone): δ = 15.0 (s, 1 B, B-8), 0.0 (d, $^1J_{B,H}$ = 143 Hz, 1 B, B-10), –3.5 to –9.4 (4 B, B-4, -7, -9 and -12) (these signals can be clearly observed in the ^{11}B{^{1}H } NMR spectrum as singlets for 1 B each at δ = –4.2, –5.5, –7.8, –8.6 ppm), –15.1 (d, $^1J_{B,H}$ = 155 Hz, 1 B, B-5 or -11), –18.6 (d, $^1J_{B,H}$ = 156 Hz, 1 B, B-11 or -5), –22.0 (d, $^1J_{B,H}$ = 172 Hz, 1 B, B-6) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 93.02 (s, η^6-benzene), 68.40 (br. s, *C*$_c$-Me), 55.03 (br. s, *C*$_c$-H), 35.15 (s, C$_c$-*Me*) ppm.

***closo*-[3-Ru(η^6-*p*-cymene)-8-Me$_2$S-1,2-$C_2B_9H_{10}$]$^+$ (3a) and *closo*-[3-Ru(η^6-*p*-cymene)-8-HS-1,2-$C_2B_9H_{10}$] (6):** The general procedure described above was applied using *nido*-[10-Me$_2$S-7,8-$C_2B_9H_{11}$] (90.5 mg, 0.466 mmol), *t*BuOK (0.51 mL, 1.0 M), THF (15 mL), $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (143.1 mg, 0.234 mmol) and $NaPF_6$ (78.8 mg, 0.469 mmol) to afford **[3a]**PF_6 (107.3 mg, 0.187 mmol, 40%). From the procedure described above, a brown-orange oily mixture, which was found to include the neutral complexes **6** (R_f = 0.69) and *closo*-[3,3′-Ru-(8-Me$_2$S-1,2-$C_2B_9H_{10}$)$_2$] (R_f = 0.63), was obtained and characterised spectroscopically.

[3a]Cl: ^{1}H NMR ([D$_3$]acetonitrile): δ = 6.38 (d, $^2J_{H,H}$ = 6.6 Hz, 2 H, *m*- of *p*-cymene), 6.33 (d, $^2J_{H,H}$ = 6.6 Hz, 2 H, *o*- of *p*-cymene), 4.30 (br. s, 2 H, C$_c$-*H*), 2.98 (sept, $^3J_{H,H}$ = 6.6 Hz, 1 H, MeC$_6$H$_4$C*H*Me$_2$), 2.46 (s, 6 H, *Me*$_2$S), 2.42 (S, 3 H, *Me*C$_6$H$_4$CHMe$_2$), 1.32 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, MeC$_6$H$_4$CH*Me*$_2$)

ppm. $^1H\{^{11}B\}$ NMR ([D$_3$]acetonitrile; only signals due to B-H protons are given): δ = 3.31 (br. s, 1 H), 2.64 (br. s, 2 H), 2.50–2.30 (m, 2 H), 1.79 (br. s, 1 H), 1.66 (br. s, 2 H) ppm. ^{11}B NMR ([D$_3$] acetonitrile): δ = 7.0 (s, 1 B, B-8), 1.0 (d, $^1J_{B,H}$ = 138 Hz, 1 B, B-10), –5.8 (d, $^1J_{B,H}$ = 146 Hz, 2 B, B-4 and 7), –9.9 (d, $^1J_{B,H}$ = 144 Hz, 2 B, B-9 and -12), –17.7 (d, $^1J_{B,H}$ = 165 Hz, 2 B, B-5 and -11), –21.7 (d, $^1J_{B,H}$ = 169 Hz, 1 B, B-6) ppm. $^{13}C\{^1H\}$ NMR ([D$_3$] acetonitrile): δ = 115.7 (s, *C*CHMe$_2$), 106.4 (s, Me*C*), 92.1 (s, *o*- of *p*-cymene), 89.5 (s, *m*- of *p*-cymene), 49.5 (s, C_c-H), 31.3 (s, MeC$_6$H$_4$*C*HMe$_2$), 24.8 (s, S*Me*$_2$), 21.8 (s, *Me*C$_6$H$_4$CHMe$_2$), 18.0 (s, MeC$_6$H$_4$CH*Me*$_2$) ppm.

[3a]PF$_6$: RuC$_{14}$H$_{30}$B$_9$SPF$_6$ (573.79): calcd. C 29.31, H 5.27, S 5.59; found C 29.56, H 5.29, S 5.47. MALDI-TOF: *m*/*z* (%) = 429.00 (100) [M], 363.97 (22) [M – Me$_2$S – 3 H]. ^1H NMR ([D$_6$]acetone): δ = 6.63 (d, $^2J_{H,H}$ = 6.6 Hz, 2 H, *m*- of *p*-cymene), 6.58 (d, $^2J_{H,H}$ = 6.6 Hz, 2 H, *o*- of *p*-cymene), 4.49 (br. s, 2 H, C_c-*H*), 3.11 (sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, MeC$_6$H$_4$C*H*Me$_2$), 2.65 (s, 6 H, *Me*$_2$S), 2.53 (S, 3 H, *Me*C$_6$H$_4$CHMe$_2$), 1.38 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, MeC$_6$H$_4$CH*Me*$_2$) ppm. $^1H\{^{11}B\}$ NMR ([D$_6$]acetone; only signals due to B-H protons are given): δ = 3.38 (br. s, 1 H), 2.80–2.50 (br. s, 2 H), 1.86 (br. s, 2 H), 1.69 (br. s, 3 H) ppm. ^{11}B NMR ([D$_6$] acetone): δ = 7.2 (s, 1 B, B-8), 1.2 (d, $^1J_{B,H}$ = 144 Hz, 1 B, B-10), –5.7 (d, $^1J_{B,H}$ = 146 Hz, 2 B, B-4 and -7), –9.8 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B-9 and -12), –17.6 (d, $^1J_{B,H}$ = 159 Hz, 2 B, B-5 and -11), –21.6 (d, $^1J_{B,H}$ = 195 Hz, 1 B, B-6) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 116.0 (s, *C*CHMe$_2$), 106.8 (s, Me*C*), 92.5 (s, *o*- of *p*-cymene), 89.9 (s, *m*- of *p*-cymene), 49.5 (s, C_c-H), 31.7 (s, MeC$_6$H$_4$*C*HMe$_2$), 24.9 (s, *Me*$_2$S), 22.1 (s, *Me*C$_6$H$_4$CHMe$_2$), 18.2 (s, MeC$_6$H$_4$CH*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = –145.6 (sept, $^1J_{P,F}$ = 708 Hz, PF$_6$) ppm.

6: ^1H NMR ([D$_6$]acetone): δ = 6.17 (d, $^2J_{H,H}$ = 6.5 Hz, 2 H, *m*- of *p*-cymene), 6.10 (d, $^2J_{H,H}$ = 6.5 Hz, 2 H, *o*- of *p*-cymene), 4.19 (br. s, 2 H, C_c-*H*), 3.02 (sept, $^3J_{H,H}$ = 7.2 Hz, 1 H, MeC$_6$H$_4$C*H*Me$_2$), 2.43 (s, 3 H, *Me*C), 1.35 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, MeC$_6$H$_4$CH*Me*$_2$) ppm. ^{11}B NMR ([D$_6$]acetone): δ = 13.6 (s, 1 B, B-8), –2.9 (d, $^1J_{B,H}$ = 143 Hz, 1 B, B-10), –7.7 (d, $^1J_{B,H}$ = 137 Hz, 4 B, B-4, -7, -9 and -12), –20.9 (d, $^1J_{B,H}$ = 154 Hz, 2 B, B-5 and -11), –27.9 (d, $^1J_{B,H}$ = 183 Hz, 1 B, B-6) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 113.2 (s, *C*CHMe$_2$), 104.1 (s, Me*C*), 92.9 (s, *o*- of *p*-cymene), 89.7 (s, *m*- of *p*-cymene), 46.1 (s, C_c-H), 31.5 (s, MeC$_6$H$_4$*C*HMe$_2$), 22.1 (s, *Me*C$_6$H$_4$CHMe$_2$), 18.0 (s, MeC$_6$H$_4$CH*Me*$_2$) ppm.

***closo*-[3-Ru(η^6-benzene)-7-MeS-1,2-C$_2$B$_9$H$_{10}$] (8):** A Schlenk flask was charged with *t*BuOK (52.5 mg, 0.408 mmol), *nido*-[9-Me$_2$S-7,8-C$_2$B$_9$H$_{11}$] (64.9 mg, 0.334 mmol), THF (10 mL) and CH$_3$CN (1.0 mL). The mixture was stirred at room temperature for 30 min giving a clear pale yellow solution. The flask was then charged with [RuCl$_2$(η^6-benzene)]$_2$ (81.5 mg, 0.167 mmol) and the resultant heterogeneous brown mixture was stirred at room temperature for 3 d. The supernatant orange solution was filtered using a cannula and transferred into another Schlenk vessel. The remaining solid residue was washed with further THF (2×5 mL) and combined with the orange solution. The orange residue obtained after evaporation of the THF was then filtered through a short silica gel column using CH$_2$Cl$_2$ as eluent. Concentration of the eluate gave a yellow-orange solid which was washed with Et$_2$O (2×5 mL) to eliminate of the remaining 9-Me$_2$S-7,8-*nido*-C$_2$B$_9$H$_{11}$ and complex **8** was obtained as a yellow solid (40.8 mg, 0.114 mmol, 34%). C$_8$H$_{17}$B$_9$RuS (343.65): calcd. C 30.22, H 5.35, S 8.96; found C 30.24, H 5.37, S 8.71. ^1H NMR ([D$_6$]acetone): δ = 6.34 (s, 6 H, η^6-benzene), 4.51 (br. s, 1 H, C_c-*H*), 4.30 (br. s, 1 H, C_c-*H*′), 1.87 ppm (s, 3 H, *Me*S). $^1H\{^{11}B\}$ NMR ([D$_6$]acetone; only signals due to B-H protons are given): δ = 3.22 (br. s, 1 H), 2.98 (br. s, 1 H), 2.49 (br. s, 1 H), 1.64 (br. s, 2 H), 1.38 (br. m, 3 H) ppm. ^{11}B NMR ([D$_6$]acetone): δ = 6.4 (s, 1 B, B-7), 4.91 (d, $^1J_{B,H}$ = 114 Hz; this resonance overlaps partially with the signal at δ = 6.36 ppm so that the coupling constant is an estimate, 1 B, B-8), 1.2 (d, $^1J_{B,H}$ = 127 Hz, 1 B, B-10), –6.6 (d, $^1J_{B,H}$ = 159 Hz, 2 B, B-4 and -12), –8.3 (d, $^1J_{B,H}$ = 171 Hz, 1 B, B-9), –17.0 (d, $^1J_{B,H}$ = 159 Hz, 1 B, B-5), –20.2 (d, $^1J_{B,H}$ = 169 Hz, 1 B, B-11), –22.1 (d, $^1J_{B,H}$ = 197 Hz, 1 B, B-6) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 91.0 (s, η^6-benzene), 51.0 (br. s, C_c-H), 47.3 (br. s, C'_c-H), 14.7 (s, *Me*S) ppm.

Reaction of *closo*-[3-Ru(η^6-benzene)-8-Me$_2$S-1,2-C$_2$B$_9$H$_{10}$][PF$_6$] ([1a]PF$_6$) with [Bu$_4$N]Cl: A 5-mm NMR tube was charged with solid [**1a**]PF$_6$ (22.9 mg, 0.044 mmol), [Bu$_4$N]Cl (13.6 mg, 0.046 mmol) and [D$_6$]acetone (0.50 mL). A beige precipitate was observed after a few minutes and a remaining pale yellow solution. After 1 h, ^1H and ^{11}B NMR spectra showed no change in the chemical shifts for all species but the ratio of [**1a**]$^+$/[Bu$_4$N]$^+$ was found to be 1:2. Addition of D$_2$O (0.50 mL) was followed by dissolution of the precipitate and the ratio between the latter species was restored to 1:1. Whereas [**1a**]PF$_6$ and [Bu$_4$N]Cl are readily soluble in [D$_6$]acetone, [**1a**]Cl is only partially soluble. The NMR experiment can be explained by a simple anion exchange reaction as shown in Equation (2).

Reaction of [RuCl$_2$(η^6-benzene)]$_2$ with *nido*-[10-Me$_2$S-7,8-C$_2$B$_9$H$_{10}$][K]. In situ NMR Studies: An analogous procedure for the deprotonation of the carborane was applied: *nido*-[10-Me$_2$S-7,8-C$_2$B$_9$H$_{11}$] (10.7 mg, 0.055 mmol), [D$_8$]THF (0.50 mL) and a THF solution of *t*BuOK (0.07 mL, 1.0 M) were mixed. The clear solution rapidly turned light yellow. After 20 min, ^1H and ^{11}B NMR spectra showed 100% conversion of *nido*-[10-Me$_2$S-7,8-C$_2$B$_9$H$_{11}$] to *nido*-K[10-Me$_2$S-7,8-C$_2$B$_9$H$_{10}$] with concomitant formation of *t*BuOH. The solution was then transferred by syringe to another NMR tube containing [RuCl$_2$(η^6-benzene)]$_2$ (13.7 mg, 0.028 mmol) under N$_2$. NMR spectra of the heterogeneous mixture were frequently recorded over a period of 6 d. Due to low solubility of the ruthenacarborane [**1a**]Cl, no quantitative measure of concentration of the species was obtained. However, the experiment clearly showed a gradual and constant increase in **1a** and **4**, whereas *nido*-K[10-Me$_2$S-7,8-C$_2$B$_9$H$_{10}$] decreased. A small amount of reprotonation of the latter was observed, probably due to moisture in the solvent. MeCl (δ = 3.06 ppm) was also detected by ^1H NMR spectroscopy and a broad resonance at low field (δ = – 4.27 ppm) was observed during the experiment which could be due to a B–H→Ru agostic interaction. NMR spectroscopic data for *nido*-K[10-Me$_2$S-7,8-C$_2$B$_9$H$_{10}$]: ^1H NMR ([D$_8$]THF): δ = 2.37 (s, 6 H, *Me*$_2$S), 0.85 (br. s, 2 H, C_c-*H*) ppm. $^1H\{^{11}B\}$ NMR ([D$_6$]acetone; only signals due to B-H protons are given): δ = 1.59 (br. s, 1 H), 1.0–0.6 (m, 6 H), –0.16 (br. s, 1 H) ppm. ^{11}B NMR ([D$_8$]THF, 96 MHz): δ = –14.1 (br. s, 1 B, B-8), –18.2 (d, $^1J_{B,H}$ = 135 Hz, 3 B), –19.6 (d, $^1J_{B,H}$ = 135 Hz, 2 B), –25.4 (d, $^1J_{B,H}$ = 132 Hz, 2 B), –45.9 (d, $^1J_{B,H}$ = 134 Hz, 1 B, B-10) ppm.

Photolysis of *closo*-[3-Ru(η^6-arene)-8-Me$_2$S-1,2-C$_2$B$_9$H$_{10}$][PF$_6$]: An acetonitrile solution (8.0 mL) of the benzene complex [**1a**]PF$_6$ (36.4 mg, 0.070 mmol) or *p*-cymene complex [**3a**]PF$_6$ (40.7 mg, 0.071 mmol) was irradiated with stirring for 3–5 d. Evaporation of the solvent afforded unreacted starting material.

Calculation Details: The geometries for *nido*-[10- and 9-MeS-7,8-C$_2$B$_9$H$_{10}$]$^{2-}$ were obtained from the X-ray structures of *nido*-[10- and 9-Me$_2$S-7,8-C$_2$B$_9$H$_{11}$].[4c,28] Geometries were then optimised with AM1 semiempirical methods and a single-point UHF calculation at the 3-21G level using Hyperchem Release 7 for Windows (Hypercube Inc.). A summary of selected charges is outlined in Scheme 5.

Crystallography: Colourless crystals of **[1a]**PF_6 were obtained from acetone at room temperature. Cell parameters and intensity data were collected with a Bruker Nonius Kappa CCD diffractometer mounted at the window of a molybdenum rotating anode according to standard procedures. Crystal data for **1a**: Colourless block, $0.38 \times 0.36 \times 0.20$ mm, $C_{10}H_{22}B_9F_6PRuS$, M_r = 517.67, T = 120(2) K, monoclinic, $P2_1/c$, a = 6.6900(3), b = 30.6880(14), c = 9.4050(3) Å, β = 92.916(2)°, V = 1928.37(14) Å^3, Z = 4, $\rho_{calcd.}$ = 1.783 g cm^{-3}, $2\theta_{max}$ = 27.47°, Mo-K_α (0.71073 Å) radiation, φ and ω scans used to fill the asymmetric unit, 13685 reflections measured, 4324 independent reflections used in the refinement, R_{int} = 0.0253, Lorentz polarisation corrections were made using Scalepack,[29] a multi-scan absorption correction was applied using SADABS[30] (μ = 1.054 mm^{-1}, min/max transmission factor ratio = 0.811856), the structure was solved by direct methods and refined using full-matrix least squares with SHELX-97,[31] 253 parameters were refined and hydrogen atoms were placed in calculated positions and refined using a riding model, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0267, wR_2 = 0.0818, R indices (all data): R_1 = 0.0323. wR_2 = 0.0860, largest difference peak/hole: 0.508/–0.486 e Å^{-3}. CCDC-264406 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) M. F. Hawthorne, D. C. Young, P. A. Wegner, *J. Am. Chem. Soc.* **1965**, *87*, 1818–1819; b) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., P. A. Wegner, *J. Am. Chem. Soc.* **1968**, *90*, 879–896; c) M. F. Hawthorne, *Pure Appl. Chem.* **1973**, *33*, 475; d) K. P. Callahan, M. F. Hawthorne, *Adv. Organomet. Chem.* **1976**, *14*, 145; e) R. N. Grimes, in: *Comprehensive Organometallic Chemistry*, vol. 1 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, New York, **1982**, pp. 459–537; f) R. N. Grimes, in: *Comprehensive Organometallic Chemistry II*, vol. 1 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, New York, **1995**, pp. 373–425.

[2] D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **1977**, 602–610.

[3] a) F. N. Tebbe, P. M. Garret, M. F. Hawthorne, *J. Am. Chem. Soc.* **1968**, *90*, 869–879; b) D. C. Young, D. V. Howe, M. F. Hawthorne, *J. Am. Chem. Soc.* **1969**, *91*, 859–862; c) J. Plešek, Z. Janousek, S. Heřmánek, *Collect. Czech. Chem. Commun.* **1978**, *43*, 2862–2868; d) H. C. Kang, S. S. Lee, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1991**, *30*, 2024–2031; e) G. M. Rosair, A. J. Welch, A. S. Weller, S. K. Zahn, *J. Organomet. Chem.* **1997**, *536*, 299–308; f) G. M. Rosair, A. J. Welch, A. S. Weller, *Organometallics* **1998**, *17*, 3227–3235; g) S. Dunn, R. M. Garrioch, G. M. Rosair, L. Smith, A. J. Welch, *Collect. Czech. Chem. Commun.* **1999**, *64*, 1013–1027; h) O. Tutusaus, R. Nuñez, C. Viñas, F. Teixidor, I. Mata, E. Molins, *Inorg. Chem.* **2004**, *43*, 6067–6074; i) R. Nuñez, O. Tutusaus, F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, *Organometallics* **2004**, *23*, 2273–2280.

[4] a) J. Plešek, Z. Janousek, S. Heřmánek, *Inorg. Synth.* **1983**, *22*, 239; b) J. Plešek, T. Jelínek, F. Mares, S. Heřmánek, *Collect. Czech. Chem. Commun.* **1993**, *58*, 1534–1547; c) Y.-K. Yan, D. M. P. Mingos, T. E. Müller, D. J. Willians, M. Kurmoo, *J. Chem. Soc., Dalton Trans.* **1994**, 1735–1741; d) O. Tutusaus, F. Teixidor, R. Núñez, C. Viñas, R. Sillanpää, R. Kivekäs, *J. Organomet. Chem.* **2002**, *657*, 247–255.

[5] A search of the February 2005 release of the Cambridge Structural Database revealed 498 examples of *closo*-[3-M-1,2-C_2B_9] metallacarboranes, 33 of those having a *B*-attached sulfonium group. With regards to the related ruthenacarboranes, 59 *closo*-[3-Ru-1,2-C_2B_9] structures were found, 5 of which have a *B*-attached sulfonium group.

[6] A. R. Kudinov, D. S. Perekalin, P. V. Petrovskii, G. V. Grintselev-Knyazev, *Russ. Chem. Bull.* **2002**, *51*, 1928–1930.

[7] a) O. Tutusaus, S. Delfosse, A. Demonceau, A. F. Noels, C. Viñas, F. Teixidor, *Tetrahedron Lett.* **2003**, *44*, 8421–8425; b) O. Tutusaus, S. Delfosse, F. Simal, A. Demonceau, A. F. Noels, R. Nuñez, C. Viñas, F. Teixidor, *Tetrahedron Lett.* **2002**, *43*, 983–987; c) C. Viñas, O. Tutusaus, R. Nuñez, F. Teixidor, A. Demonceau, S. Delfosse, A. F. Noels, I. Mata, E. Molins, *J. Am. Chem. Soc.* **2003**, *125*, 11830–11831.

[8] J. G. Planas, C. Viñas, F. Teixidor, M. B. Hursthouse, M. E. Light, *Dalton Trans.* **2004**, 2059–2061.

[9] See for example: a) S. Heřmánek, J. Plešek, B. Štíbr, 2nd IMEBORON, Leeds, 25–29 March **1974**, abstract no. 38; b) A. R. Siedle, G. M. Bodner, A. R. Garber, D. C. Beer, L. J. Todd, *Inorg. Chem.* **1974**, *13*, 2321–2324; c) F. Teixidor, C. Viñas, R. W. Rudolph, *Inorg. Chem.* **1986**, *25*, 3339–3345; d) S. Heřmánek, *Chem. Rev.* **1992**, *92*, 325–362; S. Heřmánek, *Inorg. Chim. Acta* **1999**, *289*, 20–44; e) J. M. Oliva, C. Viñas, *J. Mol. Struct.* **2000**, *556*, 33–42; f) C. Viñas, G. Barberà, J. M. Oliva, F. Teixidor, A. J. Welch, G. M. Rosair, *Inorg. Chem.* **2001**, *40*, 6555–6562.

[10] C. Viñas, J. Pedrajas, J. Bertran, F. Teixidor, R. Kivekäs, R. Sillanpää, *Inorg. Chem.* **1997**, *36*, 2482–2486.

[11] R. Núñez, O. Tutusaus, F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, *Chem. Eur. J.* **2005**, *11*, 1933–1941.

[12] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.

[13] a) T. P. Hanusa, J. C. Huffman, L. J. Todd, *Polyhedron* **1982**, *1*, 77–82; b) T. P. Hanusa, J. C. Huffman, T. L. Curtis, L. J. Todd, *Inorg. Chem.* **1985**, *24*, 787–792; c) M. P. Garcia, M. Green, F. G. A. Stone, R. G. Somerville, A. J. Welch, C. E. Briant, D. N. Cox, M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **1985**, 2343–2348.

[14] J. Plešek, S. Heřmánek, *Collect. Czech. Chem. Commun.* **1978**, *43*, 1325–1331.

[15] a) E. J. M. Hamilton, G. T. Jordan, E. A. Meyers, S. G. Shore, *Inorg. Chem.* **1996**, *35*, 5335–5341; b) S. Du, J. A. Kautz, T. D. McGrath, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **2001**, 2791–2800; c) A. Franken, C. A. Kilner, M. Thornton-Pett, J. D. Kennedy, *Collect. Czech. Chem. Commun.* **2002**, *67*, 869–912; d) O. Tutusaus, C. Vinas, R. Kivekäs, R. Sillanpää, F. Teixidor, *Chem. Commun.* **2003**, 2458–2459.

[16] a) W. Schwarz, H. D. Hausen, H. Hess, J. Mandt, W. Schmelzer, B. Krebs, *Acta Crystallogr., Sect. B* **1973**, *29*, 2029–2031; b) H. Nakai, M. Komura, M. Shiro, *Acta Crystallogr., Sect. C* **1987**, *43*, 1420–1422; c) H. Brunner, G. Gehart, B. Nuber, J. Wachter, M. L. Ziegler, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1021–1023; d) M. Ito, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 4314–4319.

[17] a) R. J. Angelici, *Polyhedron* **1997**, *16*, 3073–3088 and references cited therein; b) L. R. Hanton, K. Lee, *Inorg. Chem.* **1999**, *38*, 1634–1637.

[18] a) R. G. Kultyshev, J. Liu, E. A. Meyers, S. G. Shore, *Inorg. Chem.* **2000**, *39*, 3333–3341; b) R. G. Kultyshev, S. Liu, S. G. Shore, *Inorg. Chem.* **2000**, *39*, 6094–6099.

[19] a) R. T. Baker, R. E. King III, C. Knobler, C. A. O'Con, M. F. Hawthorne, *J. Am. Chem. Soc.* **1978**, *100*, 8266–8267; b) M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.* **1985**, 1778–1780; c) I. T. Chizhevsky, I. A. Lobanova, V. I. Bregadze, P. V. Petrovskii, V. A. Antonovich, A. V. Polyakov, A. I. Yanovskii, Y. T. Struchkov, *J. Chem. Soc. Mendeleev Commun.* **1991**, 47.

[20] a) F. Teixidor, C. Viñas, J. Casabó, A. M. Romerosa, J. Rius, C. Miravitlles, *Organometallics* **1994**, *13*, 914–919; b) F. Teixidor,

M. A. Flores, C. Viñas, R. Kivekas, R. Sillanpää, *Angew. Chem.* **1996**, *108*, 2388; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2251–2253; c) C. Viñas, R. Nuñez, M. A. Flores, F. Teixidor, R. Kivekäs, R. Sillanpää, *Organometallics* **1995**, *14*, 3952–3957; C. Viñas, R. Nuñez, M. A. Flores, F. Teixidor, R. Kivekäs, R. Sillanpää, *Organometallics* **1996**, *15*, 3850–3858; d) F. Teixidor, M. A. Flores, C. Viñas, R. Kivekäs, R. Sillanpää, *Organometallics* **1998**, *17*, 4675–4679; e) F. Teixidor, M. A. Flores, C. Viñas, R. Kivekäs, R. Sillanpää, *J. Am. Chem. Soc.* **2000**, *122*, 1963–1973.

[21] G. E. D. Mullen, M. J. Went, S. Wocadlo, A. K. Powell, P. J. Blower, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1205–1207.

[22] Y. Ohki, H. Sadohara, Y. Takikawa, K. Tatsumi, *Angew. Chem. Int. Ed.* **2004**, *43*, 2290–2293.

[23] F. Teixidor, C. Viñas, M. A. Flores, G. M. Rosair, A. J. Welch, A. S. Weller, *Inorg. Chem.* **1998**, *37*, 5394–5395.

[24] See for example: a) J. Plešek, D. Hnyk, Z. Havlas, *J. Chem. Soc., Chem. Commun.* **1989**, 1859–1861; b) T. P. Fehlner, P. T. Czech, R. F. Fenske, *Inorg. Chem.* **1990**, *29*, 3103–3109; c) M. Bühl, P. V. R. Schleyer, Z. Havlas, S. Heřmánek, *Inorg. Chem.* **1991**, *30*, 3107–3111.

[25] a) $MeAlB_{11}H_{11}$: T. D. Getman, S. G. Shore, *Inorg. Chem.* **1988**, *27*, 3439–3440 (GEZGEX); b) $B_{12}H_{12}$; A_d was taken from two structures (average of 10 B–B bonds): G. Shoham, D. Schomburg, W. N. Lipscomb, *Cryst. Struct. Commun.* **1980**, *9*, 429 (ETADCB); K. Hofmann, B. Albert, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1055 (VIRQOC); c) $HCB_{11}H_{11}$: A. S. Larsen, J. D. Holbrey, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2000**, *122*, 7264–7272 (IBEDUO, IBEGAX); d) $B_{10}H_{10}$; A_d is the average of 11 structures: E. S. Shubina, I. A. Tikhonova, E. V. Bakhmutova, F. M. Dolgushin, M. Yu. Antipin, V. I. Bakhmutov, I. B. Sivaev, L. N. Teplitskaya, I. T. Chizhevsky, I. V. Pisareva, V. I. Bregadze, L. M. Epstein, V. B. Shur, *Chem. Eur. J.* **2001**, *7*, 3783–3790 (ACERAB, ACEREF); Yu. N. Mikhailov, A. S. Kanishcheva, L. A. Zemskova, V. E. Mistryukov, N. T. Kuznetsov, K. A. Solntsev, *Zh. Neorg. Khim.* **1982**, *27*, 2343 (BOVRAF); Z. Yongmao, C. Zhaoping, C. Zhiwei, P. Kezhen, L. Jiaxi, Z. Guomin, Z. Hong, *Jiegou Huaxue* **1982**, *1*, 45 (BUBCUW); D. J. Fuller, D. L. Kepert, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1987**, *40*, 2097 (FUDHIV, FUDHOB); E. A. Malinina, K. A. Solntsev, L. A. Butman, N. T. Kuznetsov, *Koord. Khim.* **1989**, *15*, 1039 (JIJNUL); A. V. Virovets, N. N. Vakulenko, V. V. Volkov, N. V. Podberezskaya, *Zh. Strukt. Khim.* **1994**, *35*, 72 (POCHOE); S. Chitsaz, H. Folkerts, J. Grebe, T. Grob, K. Harms, W. Hiller, M. Krieger, W. Massa, J. Merle, M. Mohlen, B. Neumuller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **2000**, *626*, 775 (QEYKUA); A. M. Orlova, V. N. Mustyatsa, L. V. Goeva, S. B. Katser, K. A. Solntsev, N. T. Kuznetsov, *Zh. Neorg. Khim.* **1996**, *41*, 1956 (REBRUL); S. B. Katser, E. A. Malinina, V. N. Mustyatsa, K. A. Solntsev, N. T. Kuznetsov, *Koord. Khim.* **1992**, *18*, 387 (WAKXIP); e) $HCB_{10}H_{10}$: K. Nestor, B. Stibr, J. D. Kennedy, M. Thornton-Pett, T. Jelinek, *Collect. Czech. Chem. Commun.* **1992**, *57*, 1262–1268 (JOXCUU); f) $HNB_{10}H_{10}$: L. Schneider, U. Englert, P. Paetzold, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1191 (WIHKED).

[26] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

[27] P. M. Boorman, X. Gao, J. F. Fait, M. Parvez, *Inorg. Chem.* **1991**, *30*, 3886–3893.

[28] J. Cowie, E. J. M. Hamilton, J. C. V. Laurie, A. J. Welch, *Acta Crystallogr., Sect. C* **1998**, *54*, 1648–1650.

[29] Z. Otwinowski, W. Minor, "Processing of X-ray diffraction data collected in oscillation mode", in *Macromol. Crystallogr., Part A* **1997**, *276*, 307.

[30] *SADABS, Area-Detector Absorption Correction*, Siemens Industrial Automation, Inc., Madison, WI, **1996**.

[31] G M Sheldrick, *SHELX97, Programs for Crystal Structure Analysis*, release 97-2, Universität Göttingen, Germany, **1998**.

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