APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 388–392

Bi- and tri-metallic {Cp*RhCl} fragments partnered with carborane monoanions $[CB_{11}H_6Y_6]^-$ (Y = H, Br): control of nuclearity by choice of anion†

Nathan J. Patmore, Mary F. Mahon and Andrew S. Weller*

Department of Chemistry, University of Bath, Bath BA2 7AY, UK

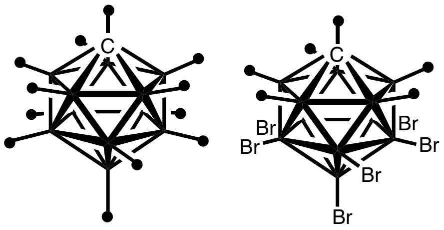
Received 11 December 2002; Revised 6 January 2003; Accepted 24 January 2003

Reaction of $[Cp^*RhCl_2]_2$ (Cp* = pentamethylcyclopentadienyl) with Ag[*closo*-$CB_{11}H_{12}$] affords the dinuclear salt $[Cp^*RhCl]_2[CB_{11}H_{12}]_2$ (1), which in the solid state reveals a single carborane anion interacting with two {Cp*RhCl} fragments, *via* two B–H–Rh interactions. With Ag[*closo*-$CB_{11}H_6Br_6$] the trimetallic complex $[\{Cp^*Rh(\mu_2\text{-}Cl)\}_3(\mu_3\text{-}Cl)]$[*closo*-$CB_{11}H_6Br_6$]$_2$ (2) results. In the solid state, three metal fragments and four chloride ligands form seven-corners of a cube, and the eighth vertex is completed by a cage C–H unit hydrogen bonded to three bridging chloride ligands. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: carborane; weakly coordinating; rhodium; hydrogen bond

INTRODUCTION

Carborane monoanions based on $[CB_{11}H_{12}]^-$ (**I**) are among the most robust weakly coordinating anions currently available, especially when the polyhedral surface is halogenated, *e.g.* $[CB_{11}H_6Br_6]^-$ (**II**).[1] Their transition metal chemistry has been investigated over the last decade or so[2–7] by others, with more recent results from ourselves.[8–13] Many of these reports involve well-defined monometallic complexes (excluding the simple salts such as Ag^+), in which the carborane anion satisfies electronic and coordinative unsaturation at the metal centre through B–H–M or B–X–M (X = halogen) interactions. Given that there is current recent interest in bimetallic systems that can potentially show cooperative effects in binding substrates and catalysis,[14,15] the synthesis of systems containing two proximate Lewis acidic transition metal cations stabilized by a weakly coordinating anion are of some interest. Herein we report some preliminary results to this end.



I **II**

EXPERIMENTAL

General

All manipulations were carried out under an atmosphere of argon using standard Schlenk line techniques. Solvents were dried according to standard procedures and distilled under nitrogen. NMR solvents were dried over CaH_2 for at least 24 h, vacuum distilled and freeze–pump thawed prior to use. NMR spectra were recorded on either a Brüker 300 MHz or a Varian 400 MHz spectrometer. ^1H NMR spectra were referenced using residual protio solvents, $^{11}B\{^1H\}$ NMR spectra were referenced to $BF_3{\cdot}OEt_2$ (external). All NMR spectra were recorded at room temperature in CD_2Cl_2. Coupling constants are quoted in hertz. Ag[$CB_{11}H_{12}$], Ag[$CB_{11}H_6Br_6$],[16] and $[Cp^*RhCl_2]_2$[17] were prepared by the published procedures.

*$[Cp^*RhCl]_2$[*closo*-$CB_{11}H_{12}$]$_2$ (**1**)*

$[Cp^*RhCl_2]_2$ (0.100 g, 0.162 mmol) and Ag[*closo*-$CB_{11}H_{12}$] (0.081 g, 0.324 mmol) were stirred in CH_2Cl_2 (10 cm^3)

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*Correspondence to: Andrew S. Weller, Department of Chemistry, University of Bath, Bath BA2 7AY, UK.
E-mail: a.s.weller@bath.ac.uk

†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

Contract/grant sponsor: Royal Society.

overnight. Filtration and recrystallization from CH_2Cl_2–hexanes afforded X-ray quality crystals, 0.107 g, yield 75% (based on rhodium).

^1H NMR (300 MHz, CD_2Cl_2): 2.52 (br, 2H, $C_{cage}H$), 1.96 (br, 16H, BH) 1.82 (s, 30H, Cp*), 0.22 (5H, BH, partially collapsed quartet, J(BH) 159 Hz), −3.30 (1H, BH, partially collapsed quartet, J(BH) 94 Hz). $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2): −7.90 (1B), −11.8 (5B), −15.1 (11B), −16.0 (sh 5B). Anal. Found: C, 31.4; H, 5.75. $C_{22}H_{54}B_{22}Cl_2Rh_2$ requires: C, 31.7; H, 6.48%.

$[\{Cp^*Rh(\mu_2\text{-}Cl)\}_3(\mu_3\text{-}Cl)][closo\text{-}CB_{11}H_6Br_6]_2$ (2)

$[Cp^*RhCl_2]_2$ (0.100 g, 0.162 mmol) and Ag[*closo*-$CB_{11}H_6Br_6$] (0.235 g, 0.324 mmol) were stirred in CH_2Cl_2 (10 cm^3) overnight. Filtration and recrystallization from CH_2Cl_2–hexanes afforded X-ray quality crystals, 0.129 g, yield 51% (based on rhodium).

^1H NMR (300 MHz, CD_2Cl_2): 2.59 (br, 2H, $C_{cage}H$), 2.25 (br, 10H, BH) 1.68 (s, 45H, Cp*). $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2): −1.9 (1B), −10.1 (5B), −20.5 (5B, br, B–Br). Anal. Found: C, 18.5; H, 2.62. $C_{35}H_{63}B_{22}Br_{12}Cl_{10}Rh_3$ requires: C, 17.9; H, 2.60%.

X-ray crystallography

The crystal structure data for compounds **1** and **2** were collected on a Nonius KappaCCD diffractometer. Structure solution, followed by full-matrix least-squares refinement was performed using the SHELX suite of programs throughout.[18] For compound **2**, the asymmetric unit consists of half of one cation, two independent anion halves and 1.5 molecules of dichloromethane, where the cation, anion and half of dichloromethane reside on a mirror plane implicit in the space group symmetry. The hydrogen atoms on the cage carbon atom were located and refined subject to distance restraints. Crystallographic data files for **1** (199562) and **2** (199563) have been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; tel.: (+44) 1223-336-408; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for 1

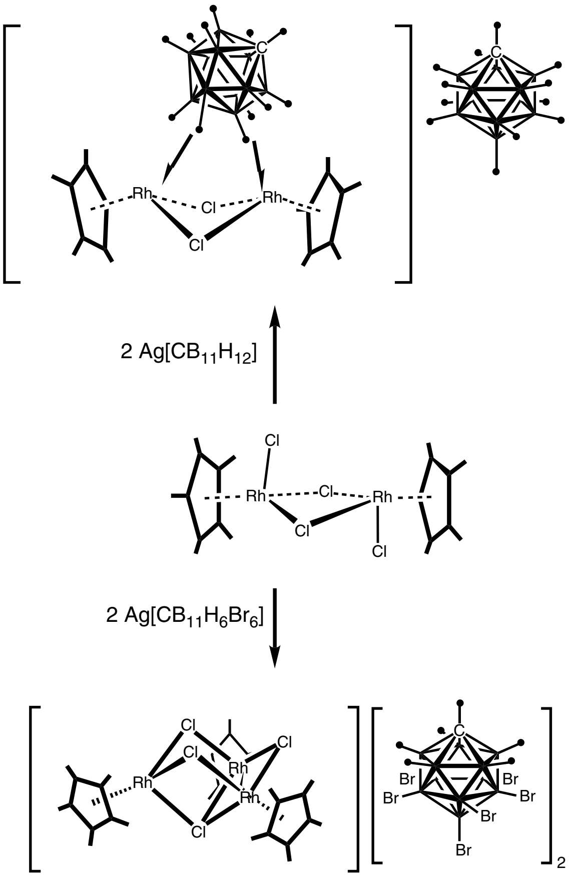
$C_{22}H_{54}B_{22}Cl_2Rh_2$, $M = 833.19$, $\lambda = 0.71070$ Å, monoclinic, space group $C2/c$, $a = 33.831(1)$, $b = 8.2008(1)$, $c = 29.545(1)$ Å, $\beta = 92.629(1)°$, $U = 8188.57(19)$ Å^3, $Z = 8$, $T = 170(2)$ K, $D_c = 1.352$ g cm^{-3}, $\mu = 0.954$ mm^{-1}, $F(000) = 3360$, crystal dimensions $0.10 \times 0.20 \times 0.20$ mm^3, 8474 unique reflections ($R_{int} = 0.0337$), $R_1 = 0.027$ $wR_2 = 0.087$ $[I > 2\sigma(I)]$.

Crystallographic data for 2

$C_{35}H_{63}B_{22}Br_{12}Cl_{10}Rh_3$, $M = 2343.82$, $\lambda = 0.71073$ Å, orthorhombic, space group $Pmcn$, $a = 16.969(1)$, $b = 18.050(1)$, $c = 24.071(2)$ Å, $U = 7372.72(9)$ Å^3, $Z = 4$, $T = 150(2)$ K, $D_c = 2.112$ g cm^{-3}, $\mu = 7.560$ mm^{-1}, $F(000) = 4432$, crystal dimensions $0.20 \times 0.40 \times 0.50$ mm^3, 7208 unique reflections ($R_{int} = 0.0973$), $R_1 = 0.031$ $wR_2 = 0.073$ $[I > 2\sigma(I)]$.

RESULTS AND DISCUSSION

Addition of two equivalents of Ag[$CB_{11}H_{12}$] to dimeric $[Cp^*RhCl_2]_2$ ($Cp^* = \eta^5 - C_5Me_5$) in a CH_2Cl_2 solution results in the precipitation of AgCl and the formation of the new complex $[Cp^*RhCl]_2[CB_{11}H_{12}]_2$ (**1**) in good yield after recrystallization from CH_2Cl_2–hexanes (Scheme 1). The solid-state structure of **1** is shown in Fig. 1. The structural motif reveals that one cage anion interacts intimately with a dicationic $\{Cp^*Rh(\mu\text{-}Cl)\}_2^{2+}$ fragment [Rh(1)–B(1) 2.924(2), Rh(2)–B(3) 2.894(2) Å] and that the second anion does not (closest Rh–B distances 5.617 Å). The coordinated anion interacts through two, three-centre–two-electron Rh–H–B bonds, one to each metal centre, bridging the Rh–Rh vector, making each metal centre formally rhodium(III) and 18 electron. The Rh–Rh distance (3.5559(2) Å) demonstrates that no metal–metal bond exists. The cage carbon vertices in both anions were located by a combination of thermal parameters and bond lengths, suggesting that the cage interacts through two B–H vertices on the lower pentagonal belt in the coordinated anion. Interestingly, this leaves the antipodal vertex free, in contrast to all the other structurally characterized examples of $[CB_{11}H_{12}]^-$ interacting with transition metal fragments.[2–4,9,11,13,19] However, as the energy difference between the two most likely coordination



Scheme 1.

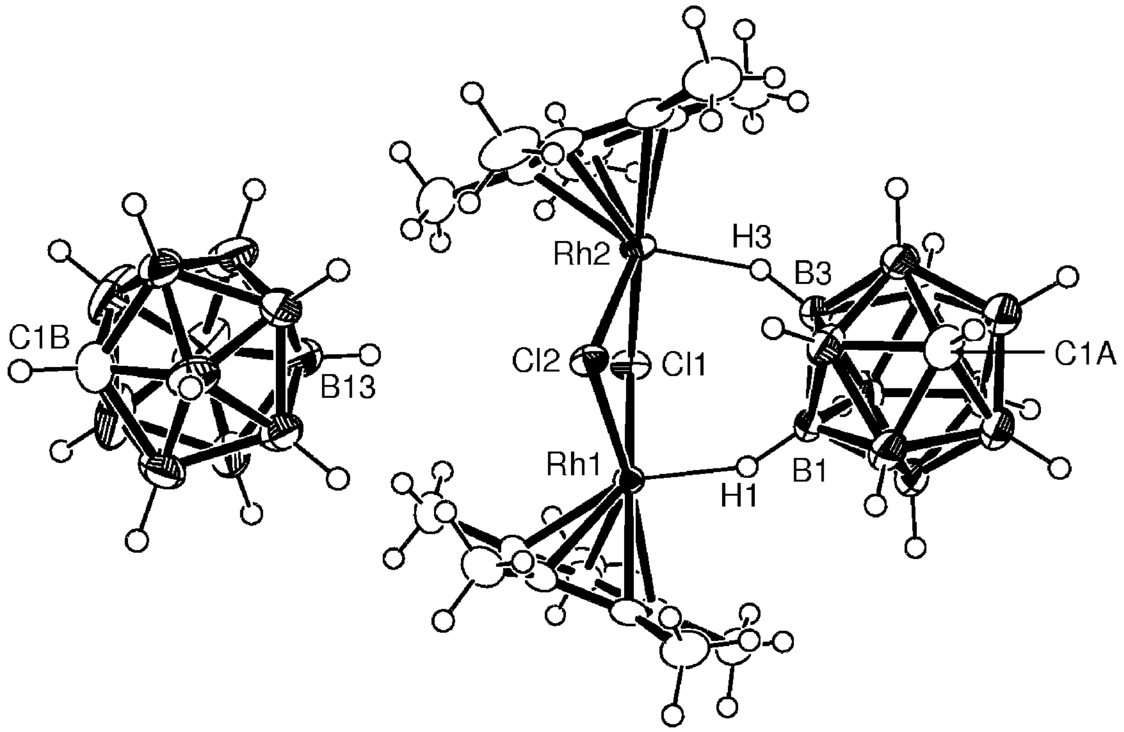
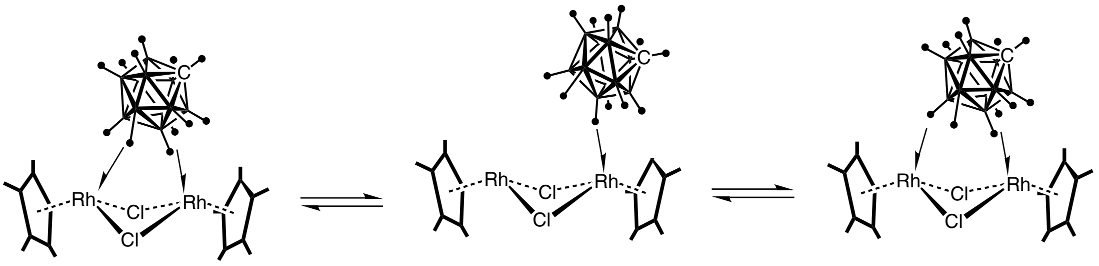


Figure 1. Solid-state structure of compound **1**. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Rh1–Rh2 3.5559(2), Rh(1)–Cl(1) 2.4355(5), Rh(1)–Cl(2) 2.4032(5), Rh(2)–Cl(1) 2.4473(5), Rh(2)–Cl(2) 2.4081(5), Rh(1)–B(1) 2.924(2), Rh(2)–B(3) 2.894(2); Rh(1)–Cl(1)–Rh(2) 93.479(17), Rh(1)–Cl(2)–Rh(2) 95.301(17).

isomers (*i.e.* interaction *via* the antipodal vertex and one lower pentagonal belt vertex or through two lower pentagonal belt B–H vertices) is likely to be small (indeed two isomers of $[CB_{11}H_{12}]^-$ coordinated to a metal fragment have previously been observed spectroscopically[5,11]) and the unambiguous differentiation between boron and carbon by X-ray diffraction can be problematic, the precise coordination mode of the carborane anion is, at best, tentative. Although a good number of monometallic transition metal complexes of $[CB_{11}H_{12}]^-$ are known,[2–4,9,11,13,19] compound **1** is the first example of a bimetallic congener in which the $[CB_{11}H_{12}]$ cage also acts to bridge two metal centres in the same molecule. However, solid-state coordination polymers that show a similar motif have been described,[8,20] and the solid-state structure that shows a $[CB_{11}H_{12}]^-$ anion bridging two separate $\{Ag(PPh_3)_2\}^+$ fragments has also been reported.[12] Although not interacting with the metal centre, the remaining anion in **1** is in close proximity to the metal fragment in the lattice, coming close to the rear of the $[Cp^*Rh(\mu\text{-}Cl)]_2$ fragment (closest B–C distance is 4.05 Å), presumably to maximize coulombic attraction between the complex cation and carborane anion.

The solution ^1H NMR spectrum for **1** shows a single Cp* environment (δ 1.82 ppm) in a 1 : 1 ratio with the $[CB_{11}H_{12}]^-$ anion, consistent with the solid-state structure. Interaction of a carborane monoanion with a transition metal centre is often shown by diagnostic upfield shifts for those B–H vertices involved in bonding with the metal centres in both the ^1H and ^{11}B NMR spectra.[3–5,9,11,21] In the case of **1**, three distinct areas are observed for the B–H vertices in the ^1H NMR spectrum: centred at δ 1.96 (16H), 0.22 (5H) and −3.30 ppm (1H). This latter resonance also shows a greatly reduced H–B coupling constant [*J*(BH) 94 Hz] indicating a weakened B–H bond, further indicative of an Rh–H–B interaction. The ^{11}B NMR spectrum shows four environments in the ratio 1 : 5 : 11 : 5. It is essentially a superposition of the NMR spectrum of 'free' $[CB_{11}H_{12}]^-$ (1 : 5 : 5 ratio of ^{11}B environments[22]) on top of that of $[CB_{11}H_{12}]^-$ interacting with a metal centre through both antipodal and lower pentagonal belt vertices (11B, coincident signal representing $1 + 5 + 5B$). The latter spectrum resembles the ^{11}B NMR spectrum observed for $(COD)Rh(CB_{11}H_{12})$, in which one carborane anion interacts with the rhodium centre in a bidentate mode through two Rh–H–B three-centre–two-electron bonds, and rapidly exchanges lower pentagonal belt Rh–H–B interactions on the NMR time scale.[9] Overall, this suggests that, in solution, one of the $[CB_{11}H_{12}]^-$ anions interacts with the metal centres whereas the other remains distal with no Rh–H–M interactions, fully consistent with the solid-state structure. Furthermore, as the solution NMR spectra suggest that *both* the five lower pentagonal belt boron vertices *and* the antipodal boron vertex interact with the metal centres, this means that some fluxional process must be occurring to make equivalent the lower pentagonal belt boron atoms on the NMR time scale and to invoke



Scheme 2.

an interaction between the antipodal vertex and the metal centres, contrary to the solid-state structure. That this process is a low energy one is demonstrated by the observation that the ^{1}H NMR spectrum does not change when a sample of **1** is cooled to low temperature (−60 °C, CD_2Cl_2, 400 MHz). It is likely that the fluxional process involves breaking one Rh−H−B bond, rotation of the cage around the remaining interaction, followed by subsequent formation of an alternative Rh−H−B bond (Scheme 2), similar to that suggested for (COD)Rh($CB_{11}H_{12}$).[9] Given that superimposed spectra are observed in the ^{11}B NMR spectrum, this fluxional process does not exchange the two cages on the NMR time scale at room temperature, similar to that observed for the complex [{^{t}Bu$_2$P(CH$_2$)$_3$P^{t}Bu$_2$}Pd($CB_{11}H_{12}$)][$CB_{11}H_{12}$],[3] which shows that the metal-bound anion is held strongly by the dication. Addition of excess Ag[$CB_{11}H_{12}$] to **1** did not result in any observable change in ^{1}H or ^{11}B NMR spectra, suggesting that the two remaining chloride ligands are unwilling to be further substituted.

The anion $[CB_{11}H_6Br_6]^-$ is considered to be significantly less coordinating than $[CB_{11}H_{12}]^-$,[1] and the transition metal chemistry of both can often be usefully contrasted, with the hexa-halogenated congener often forming significantly looser ion pairs with metal centres, which can result in enhanced catalytic activity.[12,13] Addition of two equivalents of Ag[$CB_{11}H_6Br_6$] to [Cp*RhCl$_2$]$_2$ did not result in the formation of a dimeric complex such as **1**, but the trimeric complex [{Cp*Rh(μ_2-Cl)}$_3$(μ_3-Cl)][*closo*-$CB_{11}H_6Br_6$]$_2$ (**2**) was formed instead, in moderate yield after recrystallization. Compound **2** has been characterized by NMR spectroscopy and X-ray crystallography (Fig. 2).

In the solid state, compound **2** presents an [Rh_3Cl_4] core that forms seven vertices of a cube, reminiscent of the cubic tetramer [Cp*RuCl]$_4$ with a metal vertex missing.[23] The molecule sits on a crystallographic mirror plane, which bisects Cl(1), Cl(3) and Rh(2). Three of the chlorides in **2** bridge two metal centres, and the fourth [Cl(1)] bridges all three (chemically equivalent) {Cp*Rh} fragments. There are two $[CB_{11}H_6Br_6]^-$ anions associated with this dicationic fragment, making each metal centre formally rhodium(III) and 18 electron. While one of the anions is well distant from the cation, the other forms a trifurcated hydrogen bond[24] between the cage C−H and the three μ_2-chlorides (H···Cl(2), 2.707 Å; H···Cl(3), 2.6956 Å). This interaction completes the eighth vertex of the cube. In solution, only one Cp* environment is observed in the ^{1}H NMR spectrum, which is consistent with the solid-state structure; the hydrogen bond is probably not retained, as both anions are equivalent on the NMR time scale (the ^{11}B NMR spectrum shows essentially 'free' [$CB_{11}H_6Br_6$]) and only one cage C−H environment is observed in the ^{1}H NMR spectrum, which is not significantly shifted from that found in Cs[$CB_{11}H_6Br_6$].[16]

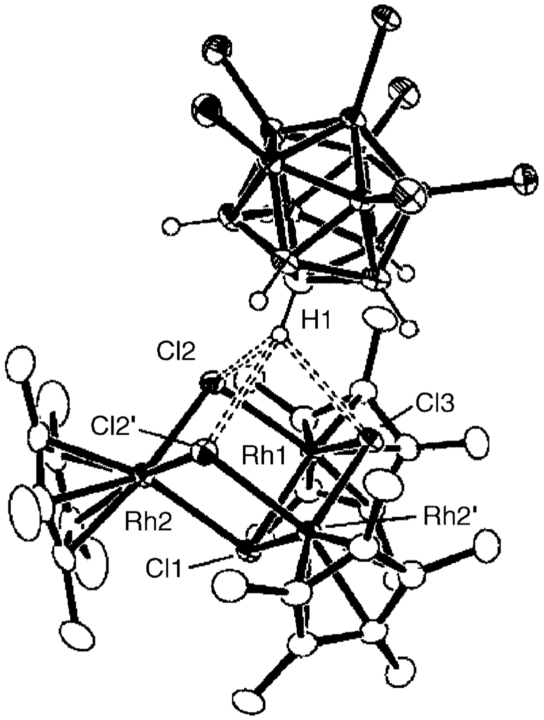


Figure 2. Solid-state structure of the cationic component of compound **2**. Thermal ellipsoids shown at the 30% probability level. Equivalent (primed) atoms were generated by the operation $-x + 1/2$, y, z. Hydrogen atoms (apart from those on the cage anion), the distal $[CB_{11}H_6Br_6]^-$ anion and solvent of crystallization (CH_2Cl_2) are not shown for clarity. Selected bond lengths (Å) and angles (°): Rh(1)−Cl(1) 2.5456(9), Rh(1)−Cl(2) 2.4464(10), Rh(1)−Cl(3) 2.4179(9), Rh(2)−Cl(1) 2.5124(14), Rh(2)−C(2) 2.4290(10), H(1)−Cl(2) 2.70, H(1)−Cl(3) 2.69; Cl(2)−Rh(1)−Cl(3) 91.87(4), Rh(1)−Cl(2)−Rh(2) 98.13(4).

The difference in structural motifs between **1** and **2** can be traced back to the anion involved in metathesis. Fast halide abstraction presumably forms the dication $[Cp^*Rh(\mu\text{-}Cl)]_2^{2+}$ and AgCl in both cases, which for compound **1**, having the relatively strongly coordinating $[CB_{11}H_{12}]^-$, is stabilized by two Rh–H–B interactions. In contrast, the more weakly coordinating $[CB_{11}H_6Br_6]^-$ is reluctant to interact with the metal centres, and the transient $[Cp^*Rh(\mu\text{-}Cl)]_2^{2+}$ dication rapidly reacts with another half equivalent of $[Cp^*RhCl_2]_2$ to form the observed product, **2**.

Acknowledgements

ASW thanks the Royal Society for financial support and Johnson Mathhey Chemicals Ltd for the generous loan of rhodium salts.

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