Polyethyl substituted weakly coordinating carborane anions: a sequential dehydrogenative borylation–hydrogenation route†

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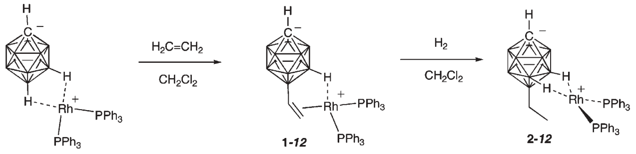
Received (in Cambridge, UK) 5th April 2005, Accepted 16th May 2005
First published as an Advance Article on the web 9th June 2005
DOI: 10.1039/b504630k

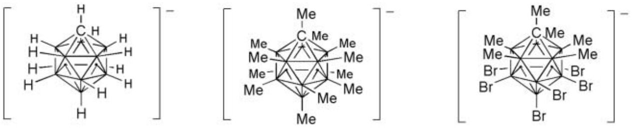
Polyethylated carborane monoanions based on [*closo*-$CB_{11}H_{12}$]$^-$ with up to five *B*-ethyl groups can be prepared by a sequential Rh-catalysed dehydrogenative borylation then hydrogenation.

Functionalised carborane monoanions based upon [*closo*-$CB_{11}H_{12}$]$^-$ (Fig. 1) are an important subset of the "least coordinating anions",[1] and find application in catalysis,[2] the stabilisation of reactive species such as naked protons or unsaturated main-group cations,[3] and complexes that show intermolecular [M]···H_3C interactions.[4] Given this interest, reliable synthetic routes to poly-functionalise the B–H periphery of the anion are few: methylation using MeOTf,[5] halogenation (*e.g.* using Br_2)[6] and sequential iodination/Pd-catalysed cross-coupling with aryl Grignards.[7] We report here an extension of a route that has been previously shown to be useful in effecting the clean mono and bis-functionalisation of boranes—transition metal catalysed hydroboration[8–11]—to sequentially, and regioselectively, functionalise [*closo*-$CB_{11}H_{12}$]$^-$ with up to 5 alkyl groups under mild conditions. Perethylation of [*closo*-$CB_{11}H_{12}$]$^-$ has previously been reported[12] using relatively harsh conditions (sealed tube, 220 °C).

Treatment of $(PPh_3)_2$Rh(*closo*-$CB_{11}H_{12}$)[13] in CH_2Cl_2 solution with ethene (excess) in a sealed J. Young's tube at room temperature affords mono-substituted $(PPh_3)_2$Rh(*x*-(C_2H_3)-*closo*-$CB_{11}H_{11}$) (*x* = 12, 7) **1** in quantitative yield (Scheme 1). Compound **1** is characterised as having a *B*-vinyl substituted cage anion in the 12- or 7-positions, with the metal fragment bound to the vinyl and one B–H group. In particular two sets of vinylic protons are observed in the ^{1}H NMR spectrum in the ratio 7 : 3, while a ^{11}B–^{11}B COSY NMR experiment (on the [Rh$(PPh_3)_2$(nbd)]$^+$salt) indicates the formation of both 12- and 7-isomers. Compound **1** results from dehydrogenative borylation of ethene by [*closo*-$CB_{11}H_{12}$]$^-$ mediated by *exo*-coordinated {Rh$(PPh_3)_2$}$^+$ (no reaction is observed between ethene and [*closo*-$CB_{11}H_{12}$]$^-$). Transition metal mediated catalytic dehydrogenative borylation of alkenes using simple boron sources {*e.g.* $B_2(OR)_4$} is well established,[14] and Sneddon has previously commented on such a process occurring during mono-functionalisation of boranes, carboranes and borazines with 1-alkenes using $PtBr_2$ as the hydroboration catalyst.[8,11,15]



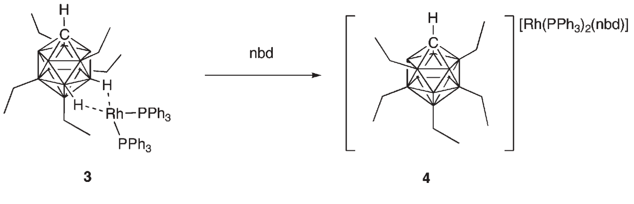
Scheme 1 (Only 12-isomer shown.)



[*closo*-$CB_{11}H_{12}$]$^-$ [*closo*-$CB_{11}Me_{12}$]$^-$ [*closo*-$CB_{11}Br_6Me_6$]$^-$

Fig. 1 Representative carborane monoanions based upon [*closo*-$CB_{11}H_{12}$]$^-$.

Compound **1** does not react further with ethene, presumably due to the firmly bound cage vinyl group. Treatment with H_2 results in the {Rh$(PPh_3)_2$}$^+$ mediated hydrogenation of the vinyl group to form $(PPh_3)_2$Rh(*x*-C_2H_5-*closo*-$CB_{11}H_{11}$) (*x* = 12, 7) **2** in which the ratio of the two isomers remains the same as in **1**. NMR data are fully consistent with the metal fragment remaining coordinated *exo* to the cage anion, in particular two quadrupolar broadened peaks at δ −0.84 and δ −2.11 ppm are observed—indicative of Rh–H–B interactions in each isomer.[16] With the vinyl group removed, **2** now reacts with ethene, resulting in further dehydrogenative borylation. However a number of products are formed, which by FAB-mass spectrometry are identified as having polysubstituted cages (*n* = 2–5). Cycling the dehydrogenative borylation–hydrogenation process a further 4 times (6 in total) results in a single compositionally pure product that has been identified by NMR spectroscopy as the penta-ethyl substituted cage anion complex, $(PPh_3)_2$Rh($(C_2H_5)_5$-*closo*-$CB_{11}H_7$) **3** (Scheme 2). Addition of nbd (nbd = norbornadiene) to **3** affords the separated ion-pair [$(PPh_3)_2$Rh(nbd)][$(C_2H_5)_5$-*closo*-$CB_{11}H_7$)] **4**, which has been characterised by NMR spectroscopy and an X-ray diffraction



Scheme 2

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† Electronic supplementary information (ESI) available: full experimental data and details of X-ray diffraction experiments. See http://www.rsc.org/suppdata/cc/b5/b504630k/

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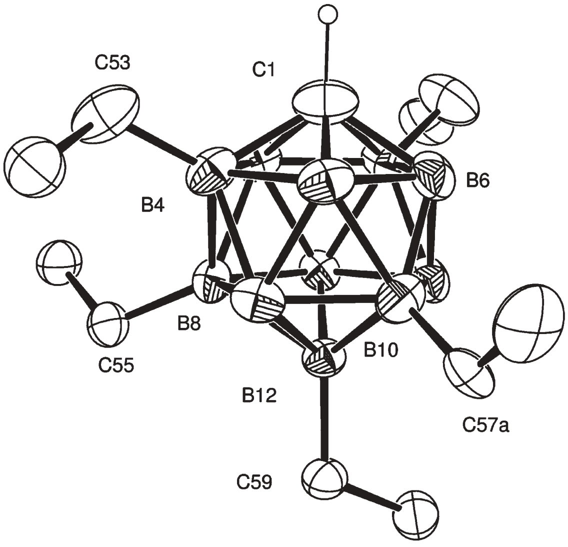


Fig. 2 Crystal structure of the anionic portion of $[Rh(PPh_3)_2(nbd)][(C_2H_5)_5\text{-}closo\text{-}CB_{11}H_7)]$ **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms, apart from the cage C–H, are omitted for clarity.

study. In our hands gram (~ 1.5 g) quantities of **4** can be prepared using this method in good yield (75% isolated yield).

The solid-state structure of the substituted anion in salt **4** is shown in Fig. 2.‡ This demonstrates five-fold B–H substitution has occurred: at the antipodal (B12) vertex, two vertices on the lower pentagonal belt and two on the upper belt. On the basis of charge distribution in the $[closo\text{-}CB_{11}H_{12}]^-$ cage substitution of all the lower-hemisphere B–H vertices would be expected to occur first.[17] However, the combination of steric bulk of the $\{(PPh_3)_2Rh\}^+$ fragment and the cage-bound ethyl groups results in vertices that are distal from one another to be substituted preferentially. This steric bulk (Fig. 3) presumably also disfavours further substitution of B–H vertices beyond 5-substitution under the mild conditions used. The substitution pattern observed in the solid state is supported by ^{11}B–^{11}B COSY NMR experiments in solution.

The degree of ethyl substitution can be modulated by introducing a methyl group onto the cage carbon atom. This has the effect of retarding substitution on the upper pentagonal belt so that after six successive dehydrogenative borylation–hydrogenation cycles the tri-substituted cage anion complex $(PPh_3)_2Rh(1\text{-}Me\text{-}(C_2H_5)_3\text{-}closo\text{-}CB_{11}H_8)$ **5** results as the major (~ 90%) product. **5** has been characterised by NMR spectroscopy, X-ray crystallography and mass spectrometry.‡ Addition of MeCN to **5** affords the separated ion-pair $[(PPh_3)_2Rh(MeCN)_x][1\text{-}Me\text{-}(C_2H_5)_3\text{-}closo\text{-}CB_{11}H_8]$ **6**, as characterised by NMR spectroscopy. Compounds **5** and **6** were not formed as compositionally pure materials, a small amount (*ca.* 10%) of another cage anion was always present, which FAB-mass spectroscopy suggests to be $[1\text{-}Me\text{-}(C_2H_5)_4\text{-}closo\text{-}CB_{11}H_7]^-$.

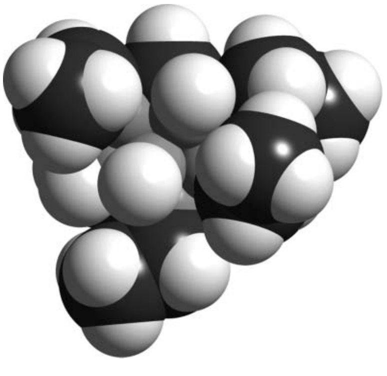
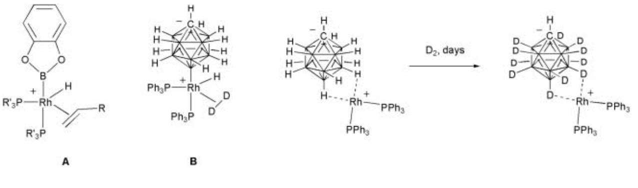


Fig. 3 Space filling representation (van der Waals radii) of the anionic portion of $[Rh(PPh_3)_2(nbd)][(C_2H_5)_5\text{-}closo\text{-}CB_{11}H_7)]$ **4**.

Fig. 4 shows the solid-state structure of **5** and demonstrates both the three fold-substitution and coordination of the $\{(PPh_3)_2Rh\}^+$ fragment through two Rh–H–B 3-centre 2-electron interactions, similar to that observed for $(PPh_3)_2Rh(closo\text{-}CB_{11}H_{12})$.[13] These Rh–H–B interactions are retained in solution as shown in the ^1H NMR spectrum by the observation of a characteristic, integral 2-H, quadrupolar broadened, signal at $\delta - 4.64$ ppm.[16] This signal disappears on addition of excess MeCN, consistent with the formation of the separated ion-pair **6**. ^1H, and ^{11}B NMR spectra are consistent with the C_s symmetry observed in the solid-state being retained in solution for **5** and **6**.

The mechanism of alkene (dehydrogenative) borylation has been discussed for both mono borane sources[9,14] and cluster species,[8] with the first step of such transformations being insertion of a low valent metal fragment into a B–H bond to give a metal–boryl intermediate such as **A** (Scheme 3). For the systems under discussion here H/D exchange experiments are fully consistent with a similar mechanism operating. Thus treatment of $(PPh_3)_2Rh(closo\text{-}CB_{11}H_{12})$ with D_2 (1 atm) in CD_2Cl_2 solution slowly (days) results in perdeuteration of all the B–H vertices (by ^1H and ^{11}B NMR spectroscopy). Moreover HD *and* H2 are also observed in the ^1H NMR spectrum, fully consistent with a putative Rh(III)–boryl intermediate **B** for this H/D exchange process. Replacement of D_2 for an alkene in structure **B** would afford an intermediate closely related to **A**. Similar Rh(III)–boryl intermediates have been proposed for the mono-functionalisation of a $\{nido\text{-}C_2B_9\}$ cage using a $\{Rh(PPh_3)_2\}^+$ catalyst, although in this case activated alkenes (acrylates) needed to be used.[10] Noteworthy is that by ^{11}B and $^1H\{^{11}B\}$ NMR spectroscopy H/D exchange occurs in the order B(12)/B(7–11) and finally B(2–6), consistent with the charge distribution in the $[closo\text{-}CB_{11}H_{12}]^-$ cage,[17] with the $\{Rh(PPh_3)_2\}^+$ fragment preferentially inserting into the B–H vertices carrying the most negative charge. As indicated by the sequence of compounds **1** → **5** → **4** a similar order of substitution occurs in the hydroboration of ethene.



Scheme 3

With the bulkier alkene 1-hexene, dehydrogenative borylation is suppressed to the extent that the hydroboration product represents ~90% of the isolated product (by ^1H NMR) and polyalkyl-functionalised cages result directly from addition of excess 1-hexene to $(PPh_3)_2Rh(1\text{-}Me\text{-}closo\text{-}CB_{11}H_{11})$ at 40 °C followed

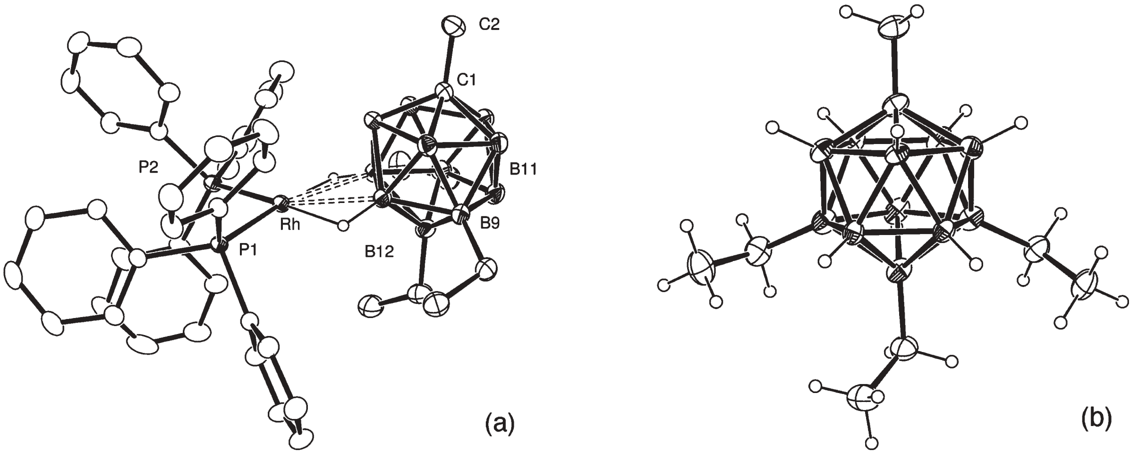
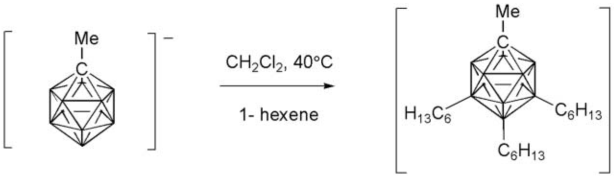


Fig. 4 (a) Crystal structure of complex **5**. Hydrogen atoms, apart from those associated with the Rh–H–B interaction are omitted for clarity. (b) The anion without the $\{Rh(PPh_3)_2\}^+$ fragment. Thermal ellipsoids are shown at the 30% probability level.



Scheme 4

by workup with MeCN (Scheme 4). NMR spectroscopy and FAB-mass spectrometry demonstrate that, as for ethene, 3-fold substitution takes place to afford [1-Me-$(C_6H_{13})_3$-*closo*-$CB_{11}H_8$][$(PPh_3)_2Rh(MeCN)_x$] **7**. Interestingly, the reaction with $(PPh_3)_2Rh$(1-H-*closo*-$CB_{11}H_{11}$) under the same conditions is much slower, suggesting that the cage-bound methyl group plays a role in activating the cage towards hydroboration of unactivated 1-hexene. In our hands **7** has been difficult to isolate in analytically pure form as it readily forms oily material on recrystallisation—a consequence of the increased length of the alkyl groups surrounding the cage. Nevertheless $^{11}B\{^1H\}$ NMR spectroscopy shows a very similar pattern compared with the ethyl counterparts (*e.g.* **6**) and we thus suggest a similar substitution pattern.

In summary, we have demonstrated that polyalkyl-functionalised monocarborane anions can be synthesised by multiple hydroboration of alkenes by a single [*closo*-$CB_{11}H_{12}]^-$ cage anion. Efforts are currently directed to using this, and related routes, to produce compositionally pure *per*-alkyl substituted carborane monoanions in synthetically useful quantities.

We acknowledge the EPSRC (GR/S42750/01) and the Royal Society for funding. Professor Larry Sneddon (University of Pennsylvania, USA) for useful discussions at the beginning of this project which were enabled by a Royal Society of Chemistry/J. W. T. Jones travelling fellowship awarded to A.S.W. Dr Adem Rifat is thanked for preliminary experiments.

Notes and references

‡ *Crystallographic data.* Intensity data were collected at 150 K on a Nonius Kappa CCD diffractometer, using graphite monochromated MoKα radiation (λ = 0.71073 Å). **4** $C_{54}H_{70}B_{11}P_2Rh$, M = 1002.86, $P2_1/c$, a = 16.7380(2) Å, b = 18.0910(2) Å, c = 18.5710(2) Å, β = 111.6180(10)° V = 5227.88(10) Å^3, Z = 4, μ = 0.424 mm^{-1}, unique reflections = 11940 [R(int) = 0.0545], R_1 = 0.0498, wR_2 = 0.1095 [$I > 2\sigma(I)$]. CCDC 268853. **5** $C_{44}H_{56}B_{11}P_2Rh$, M = 868.65, $P\bar{1}$, a = 9.8660(2) Å, b = 13.3420(4) Å, c = 17.7310(6) Å, α = 83.5920(10)°, β = 75.7420(10)°, γ = 78.438(2)° V = 2211.41(11) Å^3, Z = 2, μ = 0.491 mm^{-1}, unique reflections = 9894 [R(int) = 0.0741], R_1 = 0.0491, wR_2 = 0.0905 [$I > 2\sigma(I)$]. CCDC 268854. See http://www.rsc.org/suppdata/cc/b5/b504630k/ for crystallographic data in CIF or other electronic format.

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