

Investigation of the synthesis of $\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}^+$ fragments partnered with the monoanionic carboranes $[\textit{closo}\text{-CB}_{11}\text{H}_{11}\text{Br}]^-$, $[\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]^-$ and $[\textit{closo}\text{-HCB}_{11}\text{Me}_{11}]^-$ by silver salt metathesis and hydride abstraction †

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

Department of Chemistry, University of Bath, Bath, BA2 7AY. E-mail: a.s.weller@bath.ac.uk

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Abstraction of iodide from $[\text{Cp}(\text{CO})_3\text{MoI}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) using the silver salt of the weakly coordinating anion $[\textit{closo}\text{-CB}_{11}\text{H}_{11}\text{Br}]^-$, initially affords an intermediate dimeric complex, $[\text{MoCp}(\text{CO})_3\text{I}\cdot\text{Ag}(\text{CB}_{11}\text{H}_{11}\text{Br})]_2$, which has a central $\{\text{AgI}\}_2$ core appended by two carborane anions in the solid state. Prolonged reaction does result in elimination of AgI to form $[\text{MoCp}(\text{CO})_3(\text{CB}_{11}\text{H}_{11}\text{Br})]$, but not cleanly. This complex can be isolated in good yield by hydride abstraction from $[\text{Cp}(\text{CO})_3\text{MoH}]$ using the new trityl salt $[\text{CPh}_3][\textit{closo}\text{-CB}_{11}\text{H}_{11}\text{Br}]$. Similarly, reaction of this hydride source with $[\text{CPh}_3][\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]$ in CD_2Cl_2 results in hydride abstraction, but a mixture of products is formed, suggested to consist of the hydride bridged dimer, $[\{\text{Cp}(\text{CO})_3\text{Mo}\}_2(\mu\text{-H})][\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]$, the anion coordinated complex $[\text{Cp}(\text{CO})_3\text{Mo}(\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6)]$ and the solvent adduct $[\text{Cp}(\text{CO})_3\text{Mo}(\text{ClCD}_2\text{Cl})][\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]$. Reaction of $\text{Ag}[\textit{closo}\text{-HCB}_{11}\text{Me}_{11}]$ with $[\text{Cp}(\text{CO})_3\text{MoX}]$ ($\text{X} = \text{Cl}, \text{I}$) results in an intermediate complex which has a $[\text{Cp}(\text{CO})_3\text{MoX}]_2\text{Ag}_2$ central core (crystallographically characterised for $\text{X} = \text{I}$) with no interactions from the permethylated carborane anions. Prolonged reaction does result in partial AgX elimination to form the halide-bridged dimers $[\{\text{CpMo}(\text{CO})_3\}_2(\mu\text{-X})][\textit{closo}\text{-HCB}_{11}\text{Me}_{11}]$. Hydride abstraction from $[\text{Cp}(\text{CO})_3\text{MoH}]$ using the new trityl salt $[\text{CPh}_3][\textit{closo}\text{-HCB}_{11}\text{Me}_{11}]$ resulted in the clean formation of the hydride-bridged dimer $[\{\text{Cp}(\text{CO})_3\text{Mo}\}_2(\mu\text{-H})][\textit{closo}\text{-HCB}_{11}\text{Me}_{11}]$. The two anions $[\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]^-$ and $[\textit{closo}\text{-HCB}_{11}\text{Me}_{11}]^-$ have been compared with $[\text{B}(\text{Ar}_F')_4]^-$ [$\text{Ar}_F' = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$] in Bullock's ionic hydrogenation of 3-pentanone using $[\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}]^+$ catalysts. The permethylated anion slightly outperforms its hexabrominated congener in catalysis, but is still slower than $[\text{B}(\text{Ar}_F')_4]^-$.

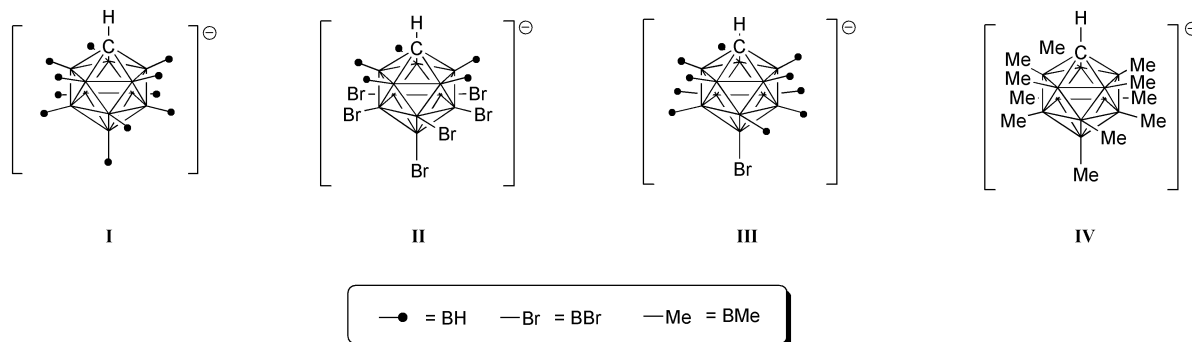
Introduction

Cationic transition-metal fragments partnered with weakly coordinating anions are becoming ubiquitous in contemporary organometallic chemistry. In the majority of cases the counterion is used to enhance a metal centre's activity as a catalyst by providing the "virtual"¹ vacant site(s) necessary in very many catalytic cycles. The use of perfluoroarylborates, such as $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{B}(\text{Ar}_F')_4$), as co-catalysts in single-site metallocene polymerisation is perhaps the best example of this.² The influence of the counterion has also been exploited in catalytic systems based around half sandwich $\{\text{CpL}_n\text{M}\}^+$ fragments.³ Kundig has reported that $[\text{B}(\text{Ar}_F')_4]^-$ salts significantly increase

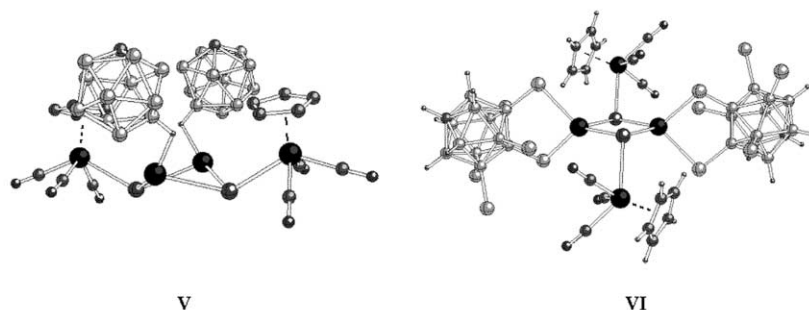
the catalytic efficiency of $\{\text{CpML}_2\}^+$ ($\text{M} = \text{Fe}, \text{Ru}, \text{L} = \text{electron withdrawing phosphine}, \text{Cp} = \eta^5\text{-cyclopentadienyl}$) in Diels–Alder reactions, compared with $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ and $[\text{OTf}]^-$ ($\text{OTf} = \text{triflate}$) counterions.⁴ Bullock and co-workers have recently reported on the use of $\{\text{Cp}(\text{CO})_2\text{LM}\}^+$ fragments ($\text{M} = \text{Mo}, \text{W}, \text{L} = \text{PCy}_3, \text{PPh}_3$) as ionic hydrogenation catalysts for ketones in which the greatest activity is observed for $[\text{B}(\text{Ar}_F')_4]^-$ salts [$\text{Ar}_F' = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$] when compared with complexes containing other anions such as $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ or $[\text{OTf}]^-$.^{5–7}

Although $[\text{B}(\text{Ar}_F')_4]^-$ type anions have received the most attention, anions based around $[\textit{closo}\text{-CB}_{11}\text{H}_{12}]^-$ I and its more weakly coordinating hexahalogeno congeners, such as $[\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]^-$, II, have also shown promise as counterions that reveal enhanced activity at metal centres (Scheme 1). For example, the chemistry of these robust, icosahedral anions has been developed by Reed and co-workers in order to stabilise highly reactive species such as protonated arenes,⁸ free $[\text{SiR}_3]^{+9}$ and $[\text{AlR}_2]^+$ cations.¹⁰ Fully halogenated (I, Br, Cl) examples have been synthesised by Xie *et al.*,¹¹ Strauss and co-workers have reported the perfluorinated analogs, used to stabilise

† Electronic supplementary information (ESI) available: Crystal data, bond lengths and angles and CIF files. X-Ray structures of $[\text{Cp}(\text{CO})_3\text{MoI}\cdot\text{Ag}(\textit{closo}\text{-CB}_{11}\text{H}_{11}\text{Br})]_2$, IA (Fig. S1) and IB (Fig. S2), $[\text{Cp}(\text{CO})_3\text{Mo}(\text{OH}_2)][\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]$ (Fig. S3) and $[\{\text{Cp}(\text{CO})_3\text{Mo}\}_2(\mu\text{-Cl})][\textit{closo}\text{-HCB}_{11}\text{Me}_{11}]$, 5-Cl (Fig. S4); Fig. S5: Relative rates of transfer hydrogenation of 3-pentanone to 3-pentanol using $[\text{Co}(\text{CO})_3(\text{PPh}_3)\text{Mo}][\text{Y}]$ $\text{Y} = [\text{B}(\text{Ar}_F')_4]^-$, $[\textit{closo}\text{-CB}_{11}\text{H}_6\text{Br}_6]^-$, $[\textit{closo}\text{-CB}_{11}\text{Me}_{11}\text{H}]^-$. See <http://www.rsc.org/suppdata/dt/b3/b303537a/>



Scheme 1



Scheme 2

exotic organometallic complexes such as non-classical carbonyls,¹² while Michl and co-workers have reported alkyl shrouded $[closo-CB_{11}H_{12}]^-$ derivatives.¹³ We have recently reported on the transition metal chemistry associated with anions such as $[closo-CB_{11}H_{12}]^-$, **I**, and $[closo-CB_{11}H_6Br_6]^-$, **II**, being interested in both the synthesis of new transition metal complexes partnered with these anions and the influence they have on selected catalytic transformations mediated by cationic transition metal fragments. For example we have demonstrated that when $[closo-CB_{11}H_6Br_6]^-$ is partnered with either $\{Ag(PPh_3)\}^+$ or $\{Rh(PPh_3)_2\}^+$ fragments, very efficient catalysts result for hetero-Diels–Alder^{14,15} and olefin hydrogenation¹⁶ reactions respectively, outperforming traditional counterions such as $[BF_4]^-$ or $[OTf]^-$.

Half sandwich complexes partnered with carborane counterions have also been synthesised. Reed and co-workers first reported the synthesis and structure of $[Cp(CO)_2Fe(closo-CB_{11}H_{12})]$ some time ago,¹⁷ and the analogous $[closo-CB_9H_{10}]^-$ complex has also been reported,^{18,19} while we have recently reported the synthesis of the equivalent group 6 complex: $[Cp(CO)_3Mo(closo-CB_{11}H_{12})]$.²⁰ All these compounds are prepared by silver-salt metathesis reactions from the corresponding organometallic halide (iodide, chloride) precursors and silver salt of $[closo-CB_{11}H_{12}]^-$. We have also described the intermediate in these reactions, namely a dimer that contains an $\{AgI\}_2$ central core: $[Cp(CO)_3MoI \cdot Ag(closo-CB_{11}H_{12})]_2$, **V** (Scheme 2).²¹ When the silver salt of more weakly coordinating (less nucleophilic) anion $[closo-CB_{11}H_6Br_6]^-$ is used with molybdenum fragments, the metathesis does not proceed to completion, but stops at the “intermediate” dimer stage, forming $[Cp(CO)_3MoI \cdot Ag(closo-CB_{11}H_6Br_6)]_2$, **VI**, where the low nucleophilicity of the anion is suggested to kinetically thwart the metathesis.²⁰ In contrast, the reaction of $[Cp(CO)_2FeI]$ with $Ag[closo-CB_{11}H_6Br_6]$ has been suggested to result in complete metathesis to afford $[Cp(CO)_2Fe(closo-CB_{11}H_6Br_6)]$, although this complex was not structurally characterised.¹⁸ Silver salt metathesis reactions have been halted in other cases, although these contain direct $[metal] \rightarrow Ag$ bonds in the solid state.²²

We were interested in extending the chemistry of the $\{Cp(CO)_3Mo\}$ fragment partnered with carborane mono-anions by expanding the range of anions used, to include the $[closo-12-BrCB_{11}H_{11}]^-$ **III**²³ and $[closo-1-HCB_{11}Me_{11}]^-$ **IV**¹³ anions. The former, mono-brominated, anion has been previously synthesised²³ but not used in transition metal chemistry, and this is of particular interest to us as it provides a comparative link between the relatively tightly binding $[closo-CB_{11}H_{12}]^-$ and the weakly coordinating hexabromo $[closo-CB_{11}H_6Br_6]^-$ anions. The latter, highly methylated, anion lies at the far end of the nucleophilic scale and thus should interact less well with metal centres than $[CB_{11}H_6Br_6]^-$. In general catalytic terms this may result in complexes that are more active (although this must always be balanced with the possibility that a more reactive catalyst is also potentially more active to catalyst decomposition). Concurrently, we are also interested in other methods of introducing the carborane anion into a metal's coordination sphere given that silver-salt metathesis is ineffec-

tual for the $[CB_{11}H_6Br_6]^- / [Cp(CO)_3MoX]$ ($X = I, Cl$) system. Trityl salts $\{trityl = [CPh_3]^+\}$ are particularly appealing as they have been used extensively by Beck *et al.* as hydride abstraction reagents to synthesise closely-related complexes with weakly coordinated anions, such as $[Cp(CO)_3Mo(FBF_3)]$,^{24,25} and Bullock and co-workers have recently reported a kinetic study on hydride abstraction reactions to give $[BF_4]^-$ coordinated complexes of $\{CpMoL_3\}^+$ fragments.⁵ The following paper describes our efforts towards these two goals.

Experimental

General

All manipulations were performed under an inert atmosphere of argon, using standard Schlenk-line and glove-box techniques. Glassware was dried in an oven at 130 °C overnight and flamed with a blowtorch, under vacuum, three times before use. CH_2Cl_2 and CH_3CN were distilled from CaH_2 . Toluene, diethyl ether and hexanes were distilled from sodium/benzophenoneketyl. CD_2Cl_2 was distilled under vacuum from CaH_2 . Microanalyses were performed by the University of Bath Microanalytical Service. The starting materials $Ag[closo-CB_{11}H_{11}Br]$,²³ $Ag[closo-HCB_{11}Me_{11}]$,²⁶ $MoCp(CO)_3Cl$,²⁷ $MoCp(CO)_3I$,²⁷ $CPh_3[closo-CB_{11}H_6Br_6]$,¹⁸ $MoCp(CO)_3H$,²⁸ were all prepared by published literature methods or slight variations thereof. All other chemicals were used as purchased from Aldrich, Acros or Fluka and used as received.

Spectroscopy

1H , $^1H\{^{11}B\}$, ^{11}B , $^{11}B\{^1H\}$ and ^{13}C NMR spectra were recorded on a Varian 400 MHz, Bruker Avance 300 MHz or JEOL 270 MHz FT-NMR spectrometers at room temperature, unless otherwise noted. Residual protio solvent was used as reference for 1H and $^1H\{^{11}B\}$ NMR spectra (CD_2Cl_2 : $\delta = 5.33$, d_6 -acetone: $\delta = 2.06$). ^{11}B and $^{11}B\{^1H\}$ NMR spectra were referenced against $BF_3 \cdot OEt_2$ (external). Coupling constants are quoted in Hz. Infrared spectra were recorded on a Nicolet NEXUS FT-IR spectrometer as solution spectra using a 0.1 mm path-length cell or as KBr pellets.

[MoCp(CO)₃I·Ag(closo-CB₁₁H₁₁Br)]₂ (1). $MoCp(CO)_3I$ (0.051 g, 0.14 mmol) and $Ag[closo-CB_{11}H_{11}Br]$ (0.046 g, 0.14 mmol) were stirred in CH_2Cl_2 (10 cm^3) for one hour. This solution was cannula filtered and solvent removed *in vacuo* to yield 0.061 mg (0.073 mmol) of $[MoCp(CO)_3I \cdot Ag(closo-CB_{11}H_{11}Br)]_2$ as a red solid. Red crystals suitable for an X-ray diffraction study were grown by re-dissolving the solid in minimum CH_2Cl_2 , layering with hexane, and placing in the freezer overnight at -30 °C.

Yield: 53%. $\delta^1H\{^{11}B\}$ (CD_2Cl_2): 5.77 (5H, s, C_5H_5), 2.45 (1H, s, CH_{cage}), 2.07 (5H, s, BH), 1.78 (5H, s, BH). $\delta^{11}B$ (CD_2Cl_2): -3.4 (1B, s), -13.1 [5B, d, $J(BH)$ 139 Hz], -16.3 [5B, d, $J(BH)$ 157 Hz]. IR (CH_2Cl_2/cm^{-1}): 2574 (m, BH), 2053 (s, CO), 1972 (br s, CO). Elemental analysis: Calc. for $C_9H_{16}O_3B_{11}BrIAgMo$: C, 15.4; H, 2.28. Found: C, 14.9; H, 2.36%.

[CPh₃][*closo*-CB₁₁H₁₁Br] (2). Ag[*closo*-CB₁₁H₁₁Br] (0.337 g, 1.0 mmol) and CPh₃Br (0.337 g, 1.0 mmol) were stirred in a 1:3 toluene/CH₃CN (5:15 cm³) mixture for one hour, then cannula filtered. The supernatant was removed *in vacuo* and the resulting oil stirred in hexane (2 × 20 cm³) overnight. Hexane was removed by decantation, and the yellow–orange solid formed was dried *in vacuo* to yield 0.410 g (0.88 mmol) of CPh₃[*closo*-CB₁₁H₁₁Br]. Yield: 86%. δ¹H{¹¹B} (d₆-acetone): 7.32–7.17 (15H, m, CH₃^{phenyl}), 2.26 (1H, s, CH₃^{cage}), 1.90 (5H, s, BH), 1.64 (5H, s, BH). δ¹¹B (C₃D₆O): –3.0 (1B, s), –15.7 [5B, d, *J*(BH) 142], –17.3 [5B, d, *J*(BH) 153]. Elemental analysis: Calc. for C₂₀H₂₆BrB₁₁: C, 15.4; H, 2.28. Found: C, 15.5; H, 2.43%.

[MoCp(CO)₃(*closo*-CB₁₁H₁₁Br)] (3). MoCp(CO)₃H (0.030 g, 0.12 mmol) was dissolved in CH₂Cl₂ (5 cm³) and added dropwise to a Schlenk charged with CPh₃[*closo*-CB₁₁H₁₁Br] (0.057 g, 0.12 mmol). The solution was stirred for one hour, cannula filtered, and the supernatant removed *in vacuo* to leave a red solid. This was redissolved in the minimum CH₂Cl₂, layered with hexanes and then placed in a freezer at –30 °C to yield 0.031 g (0.066 mmol) of MoCp(CO)₃(*closo*-CB₁₁H₁₁Br) as dark red crystals. Yield: 54%. δ¹H{¹¹B} (CD₂Cl₂): 5.92 (5H, s, C₅H₅), 2.43 (1H, br s, CH₃^{cage}), 1.86 (5H, br s, BH), 1.76 (5H, br s, BH). δ¹¹B (CD₂Cl₂): –1.6 (1B, s), –13.9 [5B, d, *J*(BH) 144 Hz], –16.9 [5B, d, *J*(BH) 158 Hz]. IR (CH₂Cl₂/cm^{–1}): 2577 (m, BH), 2071 (s, CO), 1999 (br s, CO). IR (KBr/cm^{–1}): 2560 (m, BH), 2069 (s, CO), 1982 (s, CO). Elemental analysis: Calc. for C₉H₁₆B₁₁O₃Mo₁Br₁: C, 23.2; H, 3.43. Found: C, 22.9; H, 3.49%.

NMR Tube reactions of [MoCp(CO)₃H] with [CPh₃][*closo*-CB₁₁H₆Br₆]. In a typical reaction: A Young's NMR tube was charged with MoCp(CO)₃H (0.032 g, 0.13 mmol) and [CPh₃][*closo*-CB₁₁H₆Br₆] (0.112 g, 0.13 mmol) and CD₂Cl₂ (0.4 cm³) added at –78 °C. The reaction was allowed to warm slowly to room temperature and NMR measurements taken immediately. The product(s) are poorly soluble in CD₂Cl₂ and forms a pink–lilac solid. Attempts to grow crystals of products *via* CD₂Cl₂–hexane layers were unsuccessful, while their high reactivity thwarted attempts to cleanly isolate them in analytically pure form.

δ¹H (CD₂Cl₂): 7.31–7.11 [m, Ph₃CH], 6.07 [s, {MoCp(CO)₃-(CH₂Cl₂)}{CB₁₁H₆Br₆}], 6.02 [s, MoCp(CO)₃(CB₁₁H₆Br₆)], 5.81 [s, ({MoCp(CO)₃}{μ-H})(CB₁₁H₆Br₆)], 5.55 [s, Ph₃CH], 2.81 [br s, CH₃^{cage}], 2.88 [br s, CH₃^{cage}], 2.70 [br s, CH₃^{cage}], –21.09 [s, ({MoCp(CO)₃}{μ-H})(CB₁₁H₆Br₆)]. δ¹¹B (CD₂Cl₂): –2.0 (1B, s), –10.2 (5B, s), –20.5 [5B, d, *J*(BH) 164 Hz]. IR (CD₂Cl₂/cm^{–1}): 2608 (m, BH), 2073 (s, CO), 1990 (br, s, CO).

[{CpMo(CO)₃I₃·Ag}₂][*closo*-HCB₁₁Me₁₁]₂ (4). The compounds [MoCp(CO)₃I] (0.027 g, 0.07 mmol) and Ag[1-H-CB₁₁Me₁₁] (0.029 g, 0.07 mmol) were stirred in CH₂Cl₂ (10 cm³) in the dark for one hour. The dark red solution was filtered to remove a small amount of material and the solvent removed *in vacuo* to leave a dark red light-sensitive oil. Crystals suitable for X-ray diffraction were grown by dissolving the solid in minimum CH₂Cl₂, layering with hexanes and placing in a –30 °C freezer overnight. This yielded a dark red crystals and some dark red powder. δ¹H{¹¹B} (CD₂Cl₂): 5.76 (30 H, s, Cp), 1.15 (2 H, s, CH₃^{cage}), –0.18 (30 H, s, BCH₃), –0.43 (30 H, s, BCH₃) and –0.55 (6 H, s, BCH₃). δ¹¹B (CD₂Cl₂): –0.9 (1B, s), –8.9 (5B, s) and –12.2 (5B, s). IR (CH₂Cl₂/cm^{–1}): 2055sh, 2043s and 1966s br.

[{CpMo(CO)₃}{μ-I}][*closo*-HCB₁₁Me₁₁] (5). A Young's NMR tube was charged with Ag[*closo*-HCB₁₁Me₁₁] (0.024 g, 0.06 mmol) and [Cp(CO)₃MoI] (0.022 g, 0.06 mmol) and dissolved in 0.3 ml of CD₂Cl₂ to give a deep red solution. The reaction was periodically monitored by ¹H{¹¹B} NMR spectroscopy until there was primarily only one Cp resonance (10 days total time). The solution was transferred to a Young's tube and

layered with *n*-hexanes to give dark red crystals (0.014 g, 0.02 mmol) of [{CpMo(CO)₃}{μ-I}][*closo*-HCB₁₁Me₁₁]. Yield 53%. δ¹H{¹¹B} (CD₂Cl₂): 5.82 (5H, s, Cp), 1.15 (1H, s, CH₃^{cage}), –0.18 (15H, s, BCH₃), –0.43 (15H, s, BCH₃) and –0.55 (3H, s, BCH₃). δ¹¹B (CD₂Cl₂): –0.9 (1B, s), –8.9 (5B, s) and –12.2 (5B, s). IR (CH₂Cl₂/cm^{–1}): 2066s, 2054s, 1992br, 1981br and 1963sh.

[Ph₃C][*closo*-HCB₁₁Me₁₁] (6). Cs[1-HCB₁₁Me₁₁] (0.500 g, 1.16 mmol) was dissolved in 20 cm³ CH₂Cl₂ and added in one portion to a CH₂Cl₂ solution of Ph₃CBr (0.375 g, 1.16 mmol) resulting in the immediate formation of a deep brown solution which was stirred for a further two hours. The solution was filtered and the solvents removed *in vacuo* to leave a brown oil that was redissolved in a minimum of CH₂Cl₂ and layered with *n*-hexanes to yield 0.468 g (0.87 mmol) of a dark brown crystalline solid, [Ph₃C][*closo*-HCB₁₁Me₁₁]. Yield 75%. δ¹H{¹¹B} (CD₂Cl₂): 8.25–7.6 (15H, m), 1.00 (1H, s, CH₃^{cage}), –0.30 (15H, s, BCH₃), –0.50 (15H, s, BCH₃) and –0.65 (3H, s, BCH₃). δ¹¹B (CD₂Cl₂): –0.9 (1 B, s), –8.9 (5 B, s), –12.2 (5 B, s). MS (FAB, NOBA matrix): *m/z* 243 (M⁺). Despite numerous attempts with crystalline samples that were pure by NMR spectroscopy a satisfactory microanalysis for **6** could not be obtained.

X-Ray crystallography

The crystal structure data for compounds **1**, **3**, **4** and **6** 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.²⁹ Data for **6** are of moderate rather than exceptional quality, and this is reflected in the associated *R*_{int} and *R*(sigma) values. The asymmetric unit for compound **4** was seen to consist of one carborane anion plus one half of a dication with the latter located proximate to a crystallographic two-fold rotation axis implicit in the space group symmetry. Hydrogens were included at calculated positions throughout.

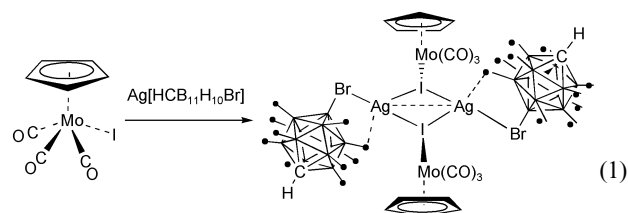
CCDC reference numbers 207303–207310.

See <http://www.rsc.org/suppdata/dt/b3/b303537a/> for crystallographic data in CIF or other electronic format.

Results and discussion

[*closo*-CB₁₁H₁₁Br][–]

Addition of one equivalent of Ag[*closo*-CB₁₁H₁₁Br] to [Cp(CO)₃MoI] in CH₂Cl₂ resulted in a clear red solution, which after one hour showed no noticeable precipitation of AgI. The CO stretching region of the IR spectrum of this solution showed that the bands due to starting material (2044 and 1966 cm^{–1}) had been cleanly replaced by two new peaks at higher frequency (2053 and 1972 cm^{–1}). These stretching bands are very close to those observed for **V** and **VI** (2054, 1973 cm^{–1} and 2055, 1975 cm^{–1}, respectively).²⁰ Addition of hexanes to this solution resulted in the isolation of red crystals suitable for a solid-state structural X-ray determination, which confirmed that this new compound was the silver–iodide dimer [Cp(CO)₃MoI·Ag(*closo*-CB₁₁H₁₁Br)]₂, compound **1** (eqn. (1)).



The asymmetric unit for **1** contains two crystallographically independent dimer halves, both of which have approximately similar bond lengths, angles and structural motifs. Fig. 1 (Tables 1 and 2 also) shows one of these independent molecules, **1A** (see

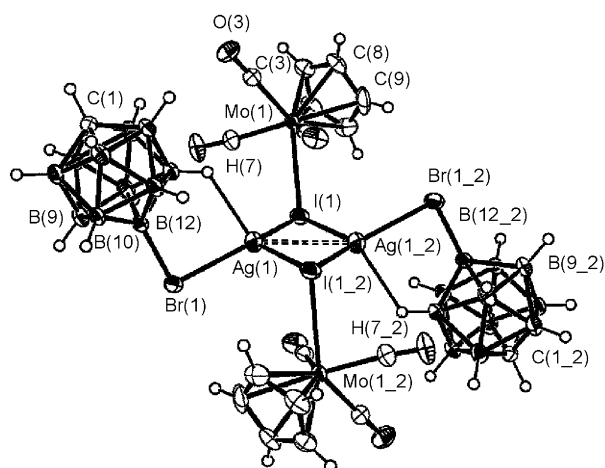
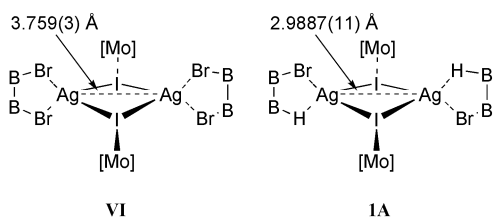


Fig. 1 Structure of one of the independent molecules in the asymmetric unit for complex **1A**. Thermal ellipsoids are shown at the 30% probability level. Equivalent atoms were generated by the operation: $-x + 1, -y + 1, -z + 1$.

ESI[†] for both structures). The centrosymmetric dimer contains a central planar $\{AgI\}_2$ core straddling a crystallographic inversion centre, to which is appended two $\{Cp(CO)_3Mo\}$ fragments and two $[closo-CB_{11}H_{11}Br]^-$ anions. This structure is grossly similar to that previously observed for “intermediate” structures for $[closo-CB_{11}H_{12}]^-$ and $[closo-CB_{11}H_6Br_6]^-$ anions, **V** and **VI**.²⁰ The two $\{Cp(CO)_3Mo\}$ fragments are orientated trans with respect to the planar $\{AgI\}_2$ core, as seen for **VI** (Scheme 3). Each carborane anion in **1A** ligates in a bidentate manner



Scheme 3

with a silver centre through one Ag–Br [2.6456(8) Å] and one Ag \cdots {HB} [B(7)–Ag(1) 3.159(3) Å, H(7)–Ag(1) 2.43(2) Å] interaction. The Ag–H distance in **1A** is longer than the average Ag–H distance (2.24 Å) found in $[Ag(CB_{11}H_{11}Br)_2] \cdot C_6H_6$,²³ although the Ag–Br distance is similar (2.642 Å). Compared with the analogous structure containing the unsubstituted $[closo-CB_{11}H_{12}]^-$ anion, **V**,²¹ the Ag–{HB} interactions in **1A** are significantly longer [Ag–H 1.96 Å, Ag–B 2.659(11) Å]. The only major difference between the two independent molecules in **1** is that for dimer **1B** there is a shorter Ag–{HB} distances [2.13(2) Å, Ag–B 2.861(3) Å] and a corresponding longer Ag–Br distance [2.7147(10) Å] than **1A**. The Ag–Br distances in **1A** and **1B** are shorter than those found in **VI** [2.803(3), 2.771(3) Å]. The Ag \cdots Ag separation is very similar [2.9887(11) Å in **1A**, 2.9816(10) Å in **1B**] in both independent molecules in **1**, being significantly shorter than that found in **VI** [3.759(3) Å]. The corresponding I–Ag–I angles reflect this difference in metal–metal separation by being more open in **1** than **VI** [116.56(3)° and 98.59(8)°, respectively]. The Ag \cdots Ag distances lie well inside the sum of van der Waals radii for two silver atoms [3.44 Å³⁰] and are close to that found in metallic silver [2.889 Å], which suggests that there are significant d¹⁰–d¹⁰ Ag \cdots Ag interactions present in **1**. Silver–silver (argentophilic) interactions are now well documented,³¹ and have been suggested to principally arise as a consequence of electron correlation effects,^{32,33} complementing the more established Au–Au, auriphilic, interactions. The fact that Ag–Ag interactions are observed in **1** but not **VI** shows that it is not the geometric constraints *per se* of the $\{AgI\}_2$ core that forces the two Ag

centres into close proximity, as both have essentially planar Ag–I–Ag–I motifs. However, whether the difference in the Ag \cdots Ag distance between these two closely related compounds is due to electronic, *i.e.* Br/Br vs. Br/BH interactions with Ag, or crystal packing influences on the $\{AgI\}_2$ core is not clear. In the gold complexes $[R_3PAuX]$ (X = halogen) it has been demonstrated both experimentally³⁴ and theoretically³² that the relative hardness of the halide ligand X has a pronounced effect on the degree of Au \cdots Au interaction, with softer iodide promoting significantly more auriphilic interaction than fluoride. However as we will show later, a {BH} vertex donates a similar amount of electron density as {BBr} (albeit by the rather crude measure of CO stretching frequencies of the coordinated $\{Cp(CO)_3Mo\}$ fragment) and we thus suggest that steric factors (*i.e.* crystal packing) may be dominant in determining the Ag \cdots Ag separation in the instance of compound **1**.

The solution ¹H NMR spectrum of **1** shows a single Cp environment at δ 5.75 ppm, with no low-field resonances due to Ag \cdots {HB} interactions observed, contrary to the solid-state structure. We have previously noted that such interactions are often not observed by ¹H NMR spectroscopy¹⁴ and that ¹¹B NMR spectroscopy provides a more reliable indicator of the extent of the [metal] \cdots carborane interaction, principally by an upfield shift of the interacting vertices.³⁵ In the ¹¹B{¹H} NMR spectrum of **1** the borane anions are equivalent and have C_{5v} symmetry, as shown by three peaks being observed at δ –3.4 (1 B), –13.1 (5 B) and –16.3 (5 B) ppm. There is a small upfield shift of the former two peaks [B(12) and B(7–11), respectively] compared with Cs[*closo-CB₁₁H₁₁Br*] (δ –2.4 and –11.9 ppm, respectively)²³ while the upper pentagonal belt [B(2–6)] is essentially unchanged. The values of ¹¹B–¹H coupling constants are also very similar in **1** and Cs[*closo-CB₁₁H₁₁Br*]. This all suggests that the B–H \cdots Ag interactions observed in the solid state are, at best, minimal in CD₂Cl₂ solution.

Compound **1** represents the intermediate structure on the pathway of replacement of iodide in $[Cp(CO)_3MoI]$ with $[closo-CB_{11}H_{11}Br]^-$ by silver salt metathesis. Continued stirring of a CH₂Cl₂ solution of **1** results in the gradual appearance of two new CO stretching bands in the IR spectrum at 2070 and 1998 cm^{–1} and the precipitation of AgI. These CO stretching frequencies are very similar to those observed for $[Cp(CO)_3Mo(closo-CB_{11}H_{12})]$ (2071 and 2001 cm^{–1}).²⁰ After nine days stirring these stretching bands represented the main carbonyl containing product in solution, but the ¹H NMR spectrum of the resulting isolated solid showed a multitude of products in the Cp region. Use of $[CpMo(CO)_3Cl]$, for which we have previously reported results in significantly faster metathesis when using Ag[*closo-CB₁₁H₁₂*],²⁰ only resulted in decomposition (by IR spectroscopy) to unidentified products after one day of stirring. An alternative route to introduce the mono-bromo anion into the coordination sphere of $\{Cp(CO)_3Mo\}$ was thus required.

Hydride abstraction, by using the corresponding trityl $[CPh_3]^+$ salt, from $[CpMo(CO)_3H]$ and related fragments has been used by Beck *et al.*,^{24,25} and more recently Bullock and Voges,⁷ to introduce weakly coordinating anions such as $[BF_4]^-$, $[PF_6]^-$ and $[B(Ar_F')_4]^-$. The trityl salt of $[closo-CB_{11}H_{11}Br]^-$ is unknown, but was readily prepared in an identical manner to that reported by Reed and co-workers for $[CPh_3][closo-CB_{11}H_6Br_6]$, by reaction of the silver salt with Ph₃CBr.¹⁸ $[CPh_3][closo-CB_{11}H_{11}Br]$, **2**, was characterised by ¹H, ¹¹B NMR spectroscopy and microanalysis, and its spectroscopic data are fully consistent with the formulation. Reaction of $[Cp(CO)_3MoH]$ with **2** in CH₂Cl₂ resulted in a red solution that showed CO stretching bands in the IR spectrum at 2071 and 1999 cm^{–1}, as found for the extended reaction with Ag[*closo-CB₁₁H₁₁Br*] and $[Cp(CO)_3MoI]$. Unlike the reaction with the silver salt, however, ¹H NMR spectroscopy demonstrated that hydride

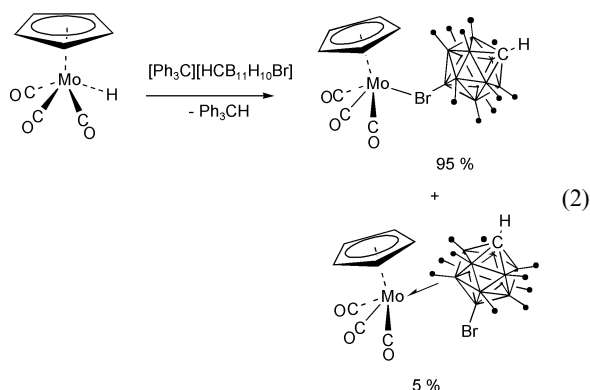
Table 1 Crystal data and structure refinement for compounds **1**, **3**, **4** and **6**

Compound	1	3	4	6
Empirical formula	C ₁₉ H ₃₄ Ag ₂ B ₂₂ Br ₂ Cl ₂ I ₂ Mo ₂ O ₆	C ₉ H ₁₆ B ₁₁ BrMoO ₃	C ₃₆ H ₄₆ AgB ₁₁ I ₃ Mo ₃ O ₉	C ₃₁ H ₄₉ B ₁₁
<i>M_r</i>	1488.42	466.98	1518.03	540.61
<i>T</i> /K	150(2)	173(2)	150(2)	150(2)
<i>λ</i> /Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	12.779(3)	7.6410(1)	33.8420(3)	9.5600(8)
<i>b</i> /Å	13.530(3)	10.9320(2)	14.9470(2)	22.7370(14)
<i>c</i> /Å	13.725(3)	11.3340(2)	26.1920(3)	15.3050(13)
<i>a</i> ^o	99.47(3)	104.8390(10)	90	90
<i>β</i> ^o	101.09(3)	100.4580(10)	128.5200(10)	96.048(3)
<i>γ</i> ^o	98.31(3)	90.2010(10)	90	90
<i>V</i> /Å ³	2258.6(8)	898.72(3)	10365.8(2)	3308.3(4)
<i>Z</i>	2	2	8	4
<i>D_c</i> /Mg m ⁻³	2.189	1.726	1.949	1.085
<i>μ</i> /mm ⁻¹	4.686	2.956	2.914	0.056
<i>F</i> (000)	1388	452	5792	1160
Crystal size/mm	0.20 × 0.10 × 0.08	0.50 × 0.40 × 0.20	0.20 × 0.15 × 0.10	0.20 × 0.15 × 0.15
<i>θ</i> Range for data collection ^o	3.09–27.48	3.59–30.00	3.56–26.72	3.60–27.54
Reflections collected	36486	20929	55789	11411
Independent reflections (<i>R_{int}</i>)	10316 (0.0414)	5224 (0.0523)	10970 (0.0780)	6020 (0.1147)
Reflections observed [<i>I</i> > 2σ(<i>I</i>)]	8863	4596	8784	3073
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	1.045, 0.933	0.81, 0.66	0.79, 0.64	1.00, 0.91
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	10316/2/543	5224/0/227	10970/0/563	6020/0/391
Goodness-of-fit on <i>F</i> ²	1.051	1.041	1.041	1.002
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0294, <i>wR</i> ₂ = 0.0635	<i>R</i> ₁ = 0.0278, <i>wR</i> ₂ = 0.0670	<i>R</i> ₁ = 0.0333, <i>wR</i> ₂ = 0.0713	<i>R</i> ₁ = 0.0758, <i>wR</i> ₂ = 0.1720
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0380, <i>wR</i> ₂ = 0.0670	<i>R</i> ₁ = 0.0346, <i>wR</i> ₂ = 0.0701	<i>R</i> ₁ = 0.0504, <i>wR</i> ₂ = 0.0781	<i>R</i> ₁ = 0.1688, <i>wR</i> ₂ = 0.2194
Largest diff. peak, hole/e Å ⁻³	1.234, −1.518	0.855, −0.912	0.814, −1.161	0.284, −0.234

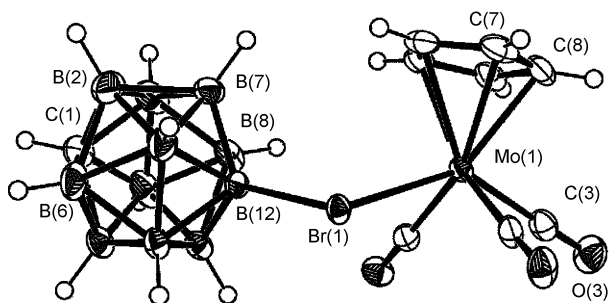
Table 2 Selected bond lengths (Å) and angles (°) for **1A**

Mo(1)–C(3)	1.997(4)	Mo(1)–C(2)	2.015(4)
Mo(1)–C(4)	2.017(4)	Mo(1)–C(8)	2.281(4)
Mo(1)–C(7)	2.287(4)	Mo(1)–C(9)	2.325(4)
Mo(1)–C(6)	2.347(4)	Mo(1)–C(5)	2.357(4)
Mo(1)–I(1)	2.8793(10)	Ag(1)–Br(1)	2.6456(8)
Ag(1)–H(7)	2.43(3)	Ag(1)–I(1_2)	2.9024(8)
Ag(1)–I(1)	2.7789(9)	Ag(1)–B(7)	3.159(3)
Ag(1)–Ag(1_2)	2.9887(11)	Br(1)–B(12)	2.005(4)
C(3)–Mo(1)–C(2)	76.85(15)	C(3)–Mo(1)–C(4)	76.06(15)
C(2)–Mo(1)–C(4)	113.29(14)	Br(1)–Ag(1)–I(1)	133.82(2)
Br(1)–Ag(1)–I(1_2)	103.42(3)	I(1)–Ag(1)–I(1_2)	116.56(3)
Ag(1)–I(1)–Ag(1_2)	63.44(3)	Br(1)–Ag(1)–Ag(1_2)	150.36(2)
Mo(1)–I(1)–Ag(1_2)	106.745(19)	Ag(1)–I(1)–Mo(1)	101.81(3)

abstraction proceeded cleanly, with one major and one minor product formed (*vide infra*) along with Ph_3CH (δ 5.56 ppm). Crystals were obtained by slow diffusion of a CH_2Cl_2 solution into hexanes at -30°C and a subsequent X-ray study revealed these to be $[\text{Cp}(\text{CO})_3\text{Mo}(12\text{-}\mu\text{-Br-closo-CB}_{11}\text{H}_{11})]$, **3** (eqn. (2)).



The solid-state structure of **3** is shown in Fig. 2 with selected bond lengths and angles given in Table 3. The molybdenum centre adopts a pseudo-piano stool structure where the carborane anion interacts with the $\{\text{Cp}(\text{CO})_3\text{Mo}\}^+$ fragment through a bromine atom [$\text{Mo}(1)\text{--Br}(1)$ 2.6759(2) Å]. This distance is only slightly longer than those observed in the bromide complexes $[\text{Cp}(\text{CO})_3\text{MoBr}]$ [2.651(1) Å]³⁶ and $[\{\text{Cr}(\text{CO})_3\text{--}(\text{C}_6\text{H}_5\text{--C}_3\text{H}_4)\}(\text{CO})_3\text{MoBr}]$ [2.640(1) Å],³⁷ indicating that the cage is bound quite tightly with the metal centre. Nonetheless, the $\text{B}(12)\text{--Br}$ bond length [2.028(2) Å] is only marginally lengthened compared with the corresponding distance found in simple ionic salt $\text{Cs}[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]$ [1.995(3) Å] and in $\text{Ag}[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]$ [1.998(9) Å] in which there is an Ag–Br interaction.²³ It is instructive to compare **3** and $[\text{Cp}(\text{CO})_3\text{Mo}(\text{closo-CB}_{11}\text{H}_{12})]$ with regard to the relative electron density donated by the $[\text{closo-CB}_{11}\text{H}_{12}]^-$ and $[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]^-$, given that both complexes have very similar structures, differing only in the coordinated anion. $[\text{Cp}(\text{CO})_3\text{Mo}(\text{closo-CB}_{11}\text{H}_{12})]$ and **3** also have almost identical CO stretching bands in the IR spectrum [2071, 1999 and 2071, 2001 cm^{-1} respectively], thus

**Fig. 2** Structure of complex **3** in the solid state. Thermal ellipsoids are shown at the 30% probability level.**Table 3** Selected bond lengths (Å) and angles (°) for **3**

Mo(1)–C(3)	2.005(2)	Mo(1)–C(2)	2.013(2)
Mo(1)–C(4)	2.035(2)	Mo(1)–Br(1)	2.6759(2)
O(2)–C(2)	1.136(2)	Br(1)–B(12)	2.028(2)
O(4)–C(4)	1.131(2)	O(3)–C(3)	1.137(3)
C(3)–Mo(1)–C(2)	76.51(9)	C(3)–Mo(1)–C(4)	77.56(8)
C(2)–Mo(1)–C(4)	109.95(8)	C(2)–Mo(1)–Br(1)	76.32(6)
C(3)–Mo(1)–Br(1)	134.96(6)	C(4)–Mo(1)–Br(1)	78.87(6)
B(12)–Br(1)–Mo(1)	116.42(7)	B(7)–B(12)–Br(1)	120.90(14)
B(11)–B(12)–Br(1)	114.93(14)	B(8)–B(12)–Br(1)	125.30(15)
B(10)–B(12)–Br(1)	115.38(14)	B(9)–B(12)–Br(1)	121.80(14)

suggesting that the electron density on the Mo centre in each complex is also very similar, and thus that $\{\text{BBr}\}$ can be considered as binding as strongly with the $\{\text{Cp}(\text{CO})_3\text{Mo}\}^+$ fragment as $\{\text{BH}\}$ in this system.

The solution NMR spectra of a crystalline sample of **3** indicates that there are two isomeric species present in solution. By far the major component (*ca.* 95%) is assigned to $[\text{Cp}(\text{CO})_3\text{Mo}(12\text{-}\mu\text{-Br-closo-CB}_{11}\text{H}_{11})]$, as found in the solid state, and assuming facile libration or rotation around the Mo–Br bond in **3** these data are fully consistent with the solid-state structure. A single peak is observed for the Cp ligand in the ^1H NMR spectrum at δ 5.92 ppm and three peaks in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum at δ -1.6 , -13.9 and -16.9 ppm in the ratio 1 : 5 : 5, respectively, indicating C_{5v} symmetry for the cage anion. As for **1**, there is a small ($\Delta\delta$ 0.8 ppm, this time downfield) chemical shift change of the unique brominated vertex compared with $\text{Cs}[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]$. These shifts of the B--Br--Mo linkage are not as pronounced as those observed for to B--H--Mo interactions,³⁵ suggesting that they do not provide an unambiguous spectroscopic marker for B--Br--Mo linkages. However, the cage C–H resonance does show a small downfield shift (*ca.* $\Delta\delta$ 0.2 ppm) on coordination compared with $\text{Cs}[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]$. The presence of a minor isomer in solution is indicated by a small Cp resonance observed at δ 5.96 ppm with approximately 5% of the intensity of the major isomer, along with a high-field partially collapsed quartet at δ -15.08 ppm of relative intensity 1H that shows a reduced $J(\text{BH})$ coupling constant (89 Hz), indicative of a Mo–H–B interaction.³⁸ This minor component is assigned to the linkage isomer $[\text{Cp}(\text{CO})_3\text{Mo}(7\text{-}\mu\text{-H-CB}_{11}\text{H}_{10}\text{Br})]$, and the ^1H NMR data are very similar to those previously observed for $[\text{Cp}(\text{CO})_3\text{Mo}(x\text{-}\mu\text{-H-CB}_{11}\text{H}_{11})]$ ($x = 7, 12$), in which the 12-isomer is the major component of the mixture.²⁰ The fact that signals corresponding to the minor isomer of **3** are not observed in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum is due to the low relative concentration coupled with the predicted number of low intensity broad signals, meaning that they are likely to be lost in spectral noise.

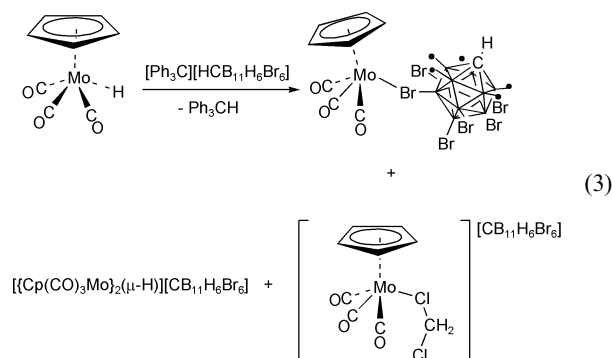
The $[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]^-$ cage in **3** is not displaced by weak nucleophiles such as H_2O or diethyl ether (by ^1H NMR). This lack of reactivity is as found for $[\text{Cp}(\text{CO})_3\text{Mo}(\text{CB}_{11}\text{H}_{12})]$ ²⁰ but is in contrast to the highly reactive complexes $[\text{Cp}(\text{CO})_3\text{Mo}(\text{FBF}_3)]$ and $[\text{Cp}(\text{CO})_3\text{Mo}(\text{FPF}_5)]$,²⁵ as well as those

described below which are tentatively suggested to have a coordinated [*closo*-CB₁₁H₆Br₆]⁻ cage anion.

[*closo*-CB₁₁H₆Br₆]⁻

Reaction of [CPh₃][*closo*-CB₁₁H₆Br₆]¹⁸ with one equivalent of [Cp(CO)₃MoH] in CH₂Cl₂ at -78 °C and warming to room temperature resulted a sensitive lilac / pink solution and a mixture of products as evidenced by ¹H NMR spectroscopy. Variation of conditions (temperature, relative molar concentrations, order of addition, *in situ* monitoring of the reaction by variable temperature NMR spectroscopy) did not result in cleaner samples, and the following discussion relates to the optimum conditions found (-78 °C warming to room temperature, 1 : 1 stoichiometry).

In the ¹H NMR spectrum of the reaction products three major resonances are assigned to Cp-containing complexes (eqn. (3), Fig. 3), along with a resonance at δ 5.56 ppm due to



Ph₃CH, resulting from hydride abstraction. The highest field Cp peak at δ 5.82 ppm is assigned to the hydride bridged dimer [$\{Cp(CO)_3Mo\}_2(\mu-H)[closo-CB_{11}H_6Br_6]$], with a corresponding hydride resonance, at one tenth of the relative intensity, observed at δ -21.09 ppm. The analogous [PF₆]⁻ complex has very similar spectral features (Cp: δ 5.93, Mo-H-Mo: δ -20.80, CD₃NO₃ solvent) and has been isolated from reaction of [Cp(CO)₃MoH] with half an equivalent of [Ph₃C][PF₆].^{39,40} This complex results from the reaction of a 16-electron cationic {Cp(CO)₃Mo}⁺ fragment, formed as a result of hydride abstraction, with an equivalent of [Cp(CO)₃MoH]. In our hands, with this system, we observed that this dimeric cation was always formed irrespective of reaction conditions.

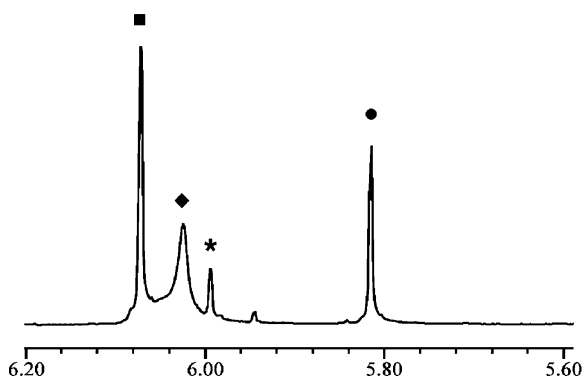


Fig. 3 Cp region of the room-temperature ¹H NMR spectrum of the reaction between [Cp(CO)₃MoH] and [CPh₃][*closo*-CB₁₁H₆Br₆]. Tentative assignments are as follows: [Cp(CO)₃Mo(ClCD₂Cl)][*closo*-CB₁₁H₆Br₆]⁻ (■); [Cp(CO)₃Mo(*closo*-CB₁₁H₆Br₆)] (◆); [$\{Cp(CO)_3Mo\}_2(\mu-H)[closo-CB_{11}H_6Br_6]$] (●). The asterisk denotes an unassigned peak.

The other two major Cp peaks are observed at δ 6.09 and 6.03 ppm in an approximate 1 : 1 ratio (Fig. 3), the latter significantly broader, while both are close to that reported by Bullock

and Beck for the coordinated dichloromethane complexes [Cp(CO)₃W(CD₂Cl₂)] [B(Ar_F'₄)] (δ 6.12 ppm)⁵ and [Cp(CO)₃Mo(ClCD₂Cl)] [PF₆]⁻ (δ 6.06 ppm).⁴¹ For the latter complex solvent coordination is favoured at low temperature while at higher temperatures the [PF₆]⁻ coordinated complex predominates. We tentatively suggest that the lower field, sharp, Cp resonance is due to the dichloromethane complex [Cp(CO)₃Mo(ClCD₂Cl)][*closo*-CB₁₁H₆Br₆]⁻ with the broader, higher field, Cp resonance due to the anion coordinated compound [Cp(CO)₃Mo(*closo*-CB₁₁H₆Br₆)]⁻. In the absence of a solid-state structure we suggest that the carborane anion bonds to the metal centre through a lower pentagonal belt bromine, as is found in the small number of crystallographically characterised examples of [*closo*-CB₁₁H₆Br₆]⁻ interacting with an electrophile.^{10,42} At low temperature (CD₂Cl₂, -65 °C), in our system, the ratio of these two respective Cp resonances changes to 2 : 1 with the tentatively assigned CD₂Cl₂ complex favoured (as reported for the [PF₆]⁻ complex), while at higher temperature (C₂D₄Cl₂, +60 °C) the reverse is observed, with the anion coordinated complex now favoured (relative ratios 1 : 2), although at this temperature some decomposition to unidentified products is also observed. At room temperature, *two* quadrupolar broadened resonances for the cage C-H proton are observed at room temperature in the product mixture, at δ 2.82 and 2.76 ppm, suggesting two different cage environments. On addition of a Lewis base (L) MeCN, acetone or H₂O to the reaction mixture, the Cp resonances at δ 6.09 and 6.03 ppm disappear immediately (<2 min) to give a unique Cp peak at δ 5.92 (D₂O),⁴⁰ 5.94 (MeCN) and 6.10 ppm (acetone).²⁵ Moreover, the cage C-H region is now observed as a *single* broad peak at δ 2.76 ppm. These products are therefore assigned as [Cp(CO)₃Mo(L)][*closo*-CB₁₁H₆Br₆]⁻ in which the cage anion does not coordinate with the 18-electron metal center. The H₂O adduct has been characterised crystallographically and shows the expected four legged piano stool geometry (see ESI †). Both the solvent and carborane-coordinated complex would be expected to react rapidly with external Lewis bases to give a single compound, as is observed. The two cage C-H peaks observed are assigned to coordinated [*closo*-CB₁₁H₆Br₆]⁻ (δ 2.82 ppm) and the uncoordinated cage present in both the dichloromethane complex and the hydride-bridged dimer (δ 2.76 ppm) (eqn. (3)). That the peak at δ 2.76 ppm is the one that persists on addition of a Lewis base is further evidence for the lower field signal arising from coordinated cage anion. Weakly coordinating anion complexes and dichloromethane complexes are highly labile and often characterised only spectroscopically, although crystallographically characterised CH₂Cl₂ complexes do exist.⁴³ To our knowledge, no Lewis base-free complexes of very weakly coordinating anions of the general formula [Cp(CO)_mM(anion)]⁻ (anion = [BF₄]⁻, [PF₆]⁻, [B(Ar_F'₄)]⁻) have been crystallographically characterised. ¹³C NMR spectroscopy at low temperatures (-80 °C) has been used to characterise CH₂Cl₂ complexes by the characteristic downfield shift of the methylene signal.⁴⁴ Unfortunately, the low solubility of the complexes described here at temperatures much below -40 °C frustrated attempts to record a meaningful ¹³C spectrum. The ¹¹B NMR spectrum of the reaction mixture showed three resonances at -2.0 (1B), -10.2 (5B), -20.5 [5B, J(BH) 164 Hz] not shifted significantly for those observed for Cs[*closo*-CB₁₁H₆Br₆]⁻, while the IR spectrum showed just two CO stretching bands at 2073 and 1990 cm⁻¹, which is very similar to that reported for [Cp(CO)₃MoF₂BF₃]⁻ (2071, 1988 cm⁻¹).⁴⁰

[*closo*-HCB₁₁Me₁₁]⁻

The highly methylated anion [*closo*-HCB₁₁Me₁₁]⁻, **IV**, developed by Michl and co-workers,¹³ can be considered to be one of the least coordinating of the carborane monoanions, shrouded as it is by methyl groups. However, the coordination chemistry of this class of anion is not well developed, with

Table 4 Selected bond lengths (Å) and angles (°) for **4**

I(3)–Ag(1)	2.7872(4)	I(3)–Mo(3)	2.8537(5)
I(2)–Ag(1)	2.8171(4)	I(2)–Mo(2)	2.8578(5)
I(1)–Mo(1)	2.8704(5)	I(1)–Ag(1_2)	2.8918(4)
I(1)–Ag(1)	2.9123(4)	Ag(1)–I(1_2)	2.8918(4)
Ag(1)–Ag(1_2)	3.0376(6)		
Ag(1)–I(3)–Mo(3)	105.866(13)	Ag(1)–I(2)–Mo(2)	115.421(15)
Mo(1)–I(1)–Ag(1_2)	124.805(14)	Mo(1)–I(1)–Ag(1)	108.507(13)
I(3)–Ag(1)–I(1_2)	120.361(15)	I(3)–Ag(1)–I(2)	109.145(14)
I(3)–Ag(1)–I(1)	108.417(14)	I(2)–Ag(1)–I(1_2)	109.977(14)
I(1_2)–Ag(1)–I(1)	104.342(13)	I(2)–Ag(1)–I(1)	103.137(14)
I(1)–Ag(1)–Ag(1_2)	58.114(12)	I(3)–Ag(1)–Ag(1_2)	100.863(9)

only two examples reported.^{45,46} We were thus interested in investigating silver salt and hydride abstraction reactions using {Cp(CO)₃Mo} fragments, in an attempt to introduce the anion into the metal's coordination sphere. We discuss the reactions of [Cp(CO)₃MoI] here, but very similar observations result from the use of [Cp(CO)₃MoCl] (*vide infra*).

Addition of one equivalent of Ag[*closo*-HCB₁₁Me₁₁] to [Cp(CO)₃MoI] in CH₂Cl₂ solution resulted in an IR spectrum that showed a number of CO stretching bands at 2055, 2043 and 1966 cm⁻¹, different from those observed for the “intermediate” complexes with [*closo*-CB₁₁H₁₂]⁻, [*closo*-CB₁₁H₆Br₆]⁻ and [*closo*-CB₁₁H₁₁Br]⁻ all of which contain central {AgI}₂ cores with appended with cage anions. Given that the permethylated anion would be expected to interact only lightly, if at all, with any metal centre, the structure of this new complex was of interest. Suitable crystals for a X-ray diffraction study were grown from a CH₂Cl₂/hexane layer at -30 °C. Fig. 4 shows the result of this study, while Table 4 lists selected bond lengths and angles.

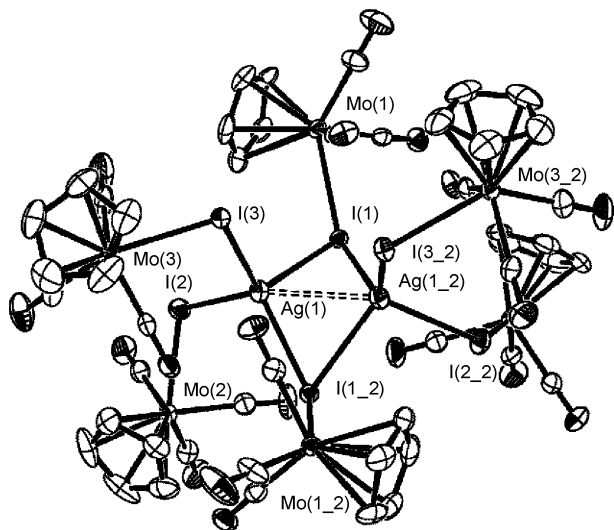


Fig. 4 Structure of the dicationic component of complex **4** in the solid state. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Equivalent atoms were generated by the operation: $-x + 1, y, -z + 1/2$

In the solid-state, complex **4** has a central {AgI}₂ core, in common with the other “intermediate” carborane anion containing structures reported in this work, or previously.²⁰ In contrast to **V**, **VI** and **1**, in which silver is also ligated with carborane anions, each silver in **4** is surrounded by three [Cp(CO)₃MoI] units, one of which bridges the two silver centres. This gives the ratio of Ag : [Cp(CO)₃MoI] as 1 : 3 and gives the molecule an overall dicationic charge. There are two [*closo*-HCB₁₁Me₁₁]⁻ anions associated with the dication in the solid state, but these are not located proximate to the metal fragment in the lattice. As the initial reaction stoichiometry was 1 : 1 in Ag[*closo*-HCB₁₁Me₁₁] : [Cp(CO)₃MoI], the unused carborane presumably remains in solution as the simple ionic

salt and does not crystallise. In accord with this, **4** may be cleanly synthesised by using a 1 : 3 ratio of reagents, respectively. Each silver atom in **4** is approximately tetrahedrally coordinated by four iodines (Fig. 5). The {AgI}₂ central core is not planar, as found for **1**, but hinged around the Ag(1)–Ag(1)' vector by 63.1°, similar to that observed in **V**.²⁰ The Ag ⋯ Ag separation [3.0376(6) Å] is slightly longer than that observed in **1**, but still well within the combined van der Waals radii of Ag–Ag (3.44 Å), suggesting a significant Ag ⋯ Ag interaction. The structure of **4** is also reminiscent of that seen for [Cp(CO)₃WI₄Ag][BF₄], in which the silver atom is tetrahedrally coordinated by four metal-iodide fragments.⁴⁷

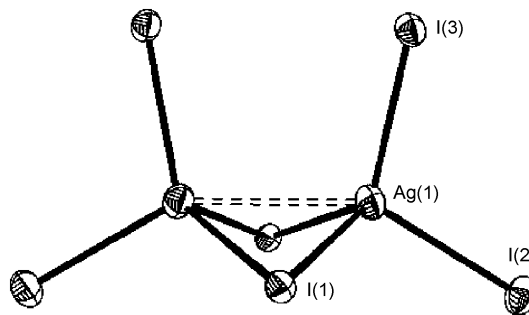
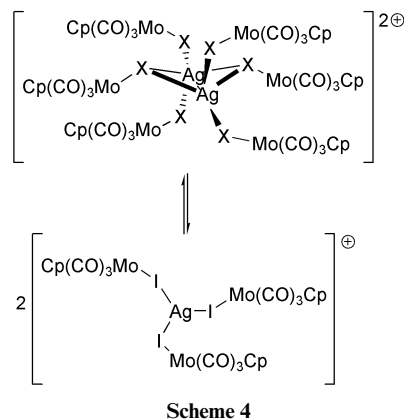


Fig. 5 Core structure of complex **4** showing the coordination motif around Ag.

The ¹H NMR spectrum of a crystalline sample of **4** taken immediately on dissolution in CD₂Cl₂ shows a single Cp peak at δ 5.76 ppm, demonstrating that all the [Cp(CO)₃MoI] fragments are equivalent in solution, contrary to that observed in the solid state. Some fluxional processes must thus be occurring, however this is not arrested on cooling to -60 °C (300 MHz), with the single Cp peak remaining sharp at this temperature. As it is unlikely that such a process would involve the breaking of a Mo–I bond at room temperature we suggest a mechanism for this that involves splitting the {AgI}₂ core to form two [Cp(CO)₃MoI₃Ag]⁺ fragments, which on recombination scramble the positions of the molybdenum fragments (Scheme 4). In many respects this is similar to the



fluxional processes that occur in related silver phosphine complexes.⁴⁸ Precedent for a monomeric complex such as $[\{\text{Cp}(\text{CO})_3\text{MoI}\}_3\text{Ag}]^+$ comes from the synthesis of $[\{\text{Cp}(\text{CO})_3\text{WI}\}_4\text{Ag}]^+$, which has a central Ag^+ surrounded by four $[\text{Cp}(\text{CO})_3\text{WI}]$ "ligands".⁴⁷ The ^{11}B NMR spectrum of **4** shows 3 peaks in the ratio 1 : 5 : 5 with chemical shifts very similar to that observed for $[\text{NBu}_4][\text{closo-HCB}_{11}\text{Me}_{11}]$.⁴⁶

If the reaction between $\text{Ag}[\text{closo-HCB}_{11}\text{Me}_{11}]$ and $[\text{Cp}(\text{CO})_3\text{MoI}]$ is not stopped at the intermediate stage, continued stirring for 10 days results in a gradual disappearance of CO stretching bands in the IR spectrum due to **4**, to eventually be completely replaced by more complex new stretching bands between 2066 and 1963 cm^{-1} . A precipitate, which we assign as AgI , is also formed. The ^1H NMR spectrum showed the presence of a single Cp containing product at δ 5.77 ppm. A single crystal X-ray diffraction study using material derived from $[\text{Cp}(\text{CO})_3\text{MoCl}]$ (prepared in exactly the same manner as the iodide) identified this product as the halide bridged dimer $[\text{Cp}(\text{CO})_3\text{Mo}(\mu\text{-Cl})\text{Mo}(\text{CO})_3\text{Cp}][\text{closo-HCB}_{11}\text{Me}_{11}]$, **5-Cl**. This has been previously reported as the $[\{\text{Cp}(\text{CO})_3\text{Mo}\}_2(\mu\text{-I})][\text{BPh}_4]$ salt and the observed spectra are in full accordance with those previously reported.⁴⁹ Mattson and Graham have also reported that $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-I})\text{Fe}(\text{CO})_2\text{Cp}][\text{BF}_4]$ is formed on reaction of $[\text{Cp}(\text{CO})_2\text{FeI}]$ with $\text{Ag}[\text{BF}_4]$.⁵⁰ Complex **5-I** is presumably formed in a similar manner, by halide abstraction from $[\text{Cp}(\text{CO})_3\text{MoI}]$ using $\text{Ag}[\text{closo-HCB}_{11}\text{Me}_{11}]$ to give a 16-electron $\{\text{Cp}(\text{CO})_3\text{Mo}\}^+$ fragment, which then reacts rapidly with remaining $[\text{Cp}(\text{CO})_3\text{MoI}]$. Intermediate **4** and subsequently complexes **5** are formed even if a large excess of $\text{Ag}[\text{closo-HCB}_{11}\text{Me}_{11}]$ is used. That **4** is the intermediate on the pathway to **5** is demonstrated by following the reaction by ^1H NMR spectroscopy. Fig. 6 shows the resulting time vs. mole fractions of **4** and **5-I** (calculated by integrating their respective Cp resonances to a internal standard). This shows that **4** rapidly forms (*ca.* 1 h) and then gradually decays to afford **5-I**. No other Cp containing products were observed and the mass balance remains constant showing that **4** smoothly converts to **5**. If crystalline **4** is redissolved in CD_2Cl_2 (or an initial 3 : 1 ratio of $[\text{Cp}(\text{CO})_3\text{MoI}] : \text{Ag}[\text{closo-HCB}_{11}\text{Me}_{11}]$ is used) and monitored over a period of days then metathesis proceeds to afford **5** and AgI , but as there is no longer sufficient $\text{Ag}[\text{closo-HCB}_{11}\text{Me}_{11}]$ in the solution to complete the metathesis, then half an equivalent of $[\text{Cp}(\text{CO})_3\text{MoI}]$ is also formed (Scheme 5) by ^1H NMR spectroscopy. If an excess (10-fold) of $\text{Ag}[\text{closo-HCB}_{11}\text{Me}_{11}]$ is used, then **5** is the only observed product.

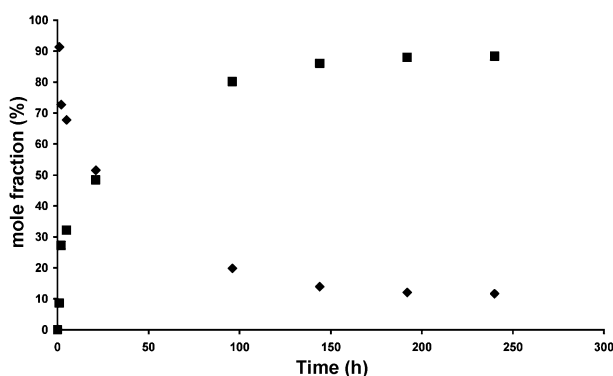
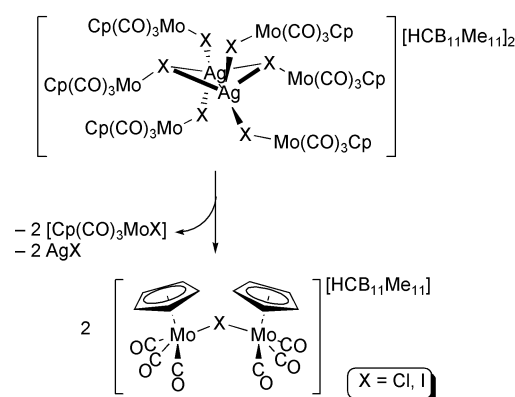


Fig. 6 Plot of mole fraction (determined by relative Cp integrals in ^1H NMR spectrum) of $[\{\text{Cp}(\text{CO})_3\text{MoI}\}_6\text{Ag}_2][\text{closo-HCB}_{11}\text{Me}_{11}]_2$ (◆) and $[\{\text{Cp}(\text{CO})_3\text{Mo}\}_2][\text{closo-HCB}_{11}\text{Me}_{11}]$ (■) against time. The mole fraction of the intermediate at time $t = 0$ is zero.

We were surprised to observe any metathesis, given that $[\text{closo-HCB}_{11}\text{Me}_{11}]$ is notionally less coordinating than $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^-$, and the hexabromo anion halts at the intermediate stage, forming a tight dimer **VI**, in which this anion coordinates to the silver centre through two Br–B interactions, and the $[\text{Cp}(\text{CO})_3\text{MoI}]$ fragments are locked into the $\{\text{AgI}\}_2$



Scheme 5

core. Metathesis halts presumably because the anion is not nucleophilic enough and too sterically crowded to participate in an associative mechanism that results in elimination of AgI , as addition of the more nucleophilic $[\text{closo-CB}_{11}\text{H}_{12}]$ immediately results in the onset of metathesis.²⁰ For **4**, the reduced nucleophilicity of the permethylated anion results in the coordination sphere of the silver being taken up by the next most Lewis basic component of the reaction mixture, *i.e.* $[\text{Cp}(\text{CO})_3\text{MoI}]$, rather than the carborane anion, which remains distal. Presumably, for **4**, the extra, Ag-bound, $[\text{Cp}(\text{CO})_3\text{MoX}]$ is nucleophilic enough to consummate metathesis, thus forming the observed halide bridged dimer and AgI in the process. A similar halide-bridged product has recently been reported, arising from elimination of AgCl from a well characterised metathesis intermediate, the dinuclear cation $[(\text{Me})(\text{N}-\text{N})\text{Pt}(\mu\text{-Cl})\text{Ag}(\mu\text{-Cl})\text{Pt}(\text{N}-\text{N})(\text{Me})][\text{BF}_4]$ ($\text{N}-\text{N}-\text{Ar} = \text{NC}(\text{Me})\text{C}(\text{Me})=\text{NAr}$, $\text{Ar} = 2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3$).⁵¹ In this case, it is suggested that the initial metathesis intermediate is isolated due to the steric bulk of the bis-imine ligand inhibiting the associative process.

In the manner of $[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]^-$ and $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^-$ we have also investigated hydride abstraction from $[\text{Cp}(\text{CO})_3\text{MoH}]$ and $[\text{CPh}_3][\text{closo-HCB}_{11}\text{Me}_{11}]$, **6**. This new trityl salt is easily synthesised from $\text{Cs}[\text{closo-HCB}_{11}\text{Me}_{11}]$ and BrCPh_3 in good yield, and can be isolated as a crystalline solid. The solid-state structure of **6** is presented in Fig. 7 (Table 5), and it shows a trigonal planar carbocation core, with the closest approach of the highly methylated anion being 3.66 \AA [$\text{C}(7)-\text{C}(13)$], which is just inside the sum of the van der Waals radii of carbon and methyl (3.70 \AA).³⁰ There is also an equivalent $[\text{C}(5)^+-\text{C}(13)]$ 3.70 \AA approach of a symmetry related carborane anion to opposite side of the trityl cation. We rationalise these relatively close distances as efficient crystal packing of the globular

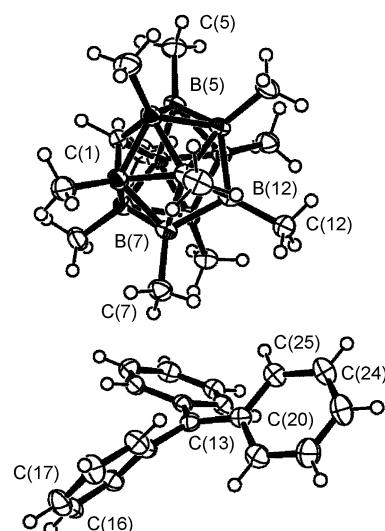


Fig. 7 Solid-state structure of complex **6**. Thermal ellipsoids are shown at the 30% probability level.

Table 5 Selected bond lengths (Å) and angles (°) for **6**

C(12)–B(12)	1.599(5)	C(13)–C(20)	1.440(4)
C(13)–C(14)	1.449(4)	C(13)–C(26)	1.433(5)
C(26)–C(13)–C(20)	121.7(3)	C(26)–C(13)–C(14)	119.3(3)
C(20)–C(13)–C(14)	119.0(3)		

carborane anion and propeller-shaped trityl cation, rather than any specific close cation–anion interactions, such as have been observed for isoelectronic [Bu₃Sn][*closo*-HCB₁₁Me₁₁].⁴⁵

Reaction of **6** with one equivalent of [CpMo(CO)₃H] in CD₂Cl₂ resulted in the isolation, in good yield based on Mo, of the hydride bridged dimer [{Cp(CO)₃Mo}₂(μ-H)][*closo*-HCB₁₁Me₁₁], with half an equivalent of unreacted **6** remaining in the reaction. Some cage methyl decomposition (*ca.* 10% in the ¹H and ¹¹B NMR spectra) is also observed. Hydride abstraction results in a reactive 16-electron {Cp(CO)₃Mo}⁺ complex, but this quickly reacts with unreacted hydride in solution to afford the observed dimer. Presumably this reaction to form the stable hydride bridged dimer is so rapid in the absence of any stabilisation afforded to the cation by the permethylated anion, that no solvent (CD₂Cl₂) or anion-coordinated complex is observed, in contrast to [*closo*-CB₁₁H₆Br₆][−]. This places [*closo*-HCB₁₁Me₁₁] beneath [*closo*-CB₁₁H₆Br₆][−] in terms of coordinating ability, as we have demonstrated previously in {Ag(PPh₃)⁺ systems.⁴⁶ Hydride abstraction in the presence of a good Lewis base (acetone) immediately formed [Cp(CO)₃Mo(O=CM₂)] [*closo*-HCB₁₁-Me₁₁] as the only Cp containing product (by ¹H NMR spectroscopy).²⁵

Catalysis

We have also briefly investigated the use of [*closo*-CB₁₁H₆Br₆][−] and [*closo*-HCB₁₁Me₁₁][−] in a catalytic system. In the catalytic transfer hydrogenation of 3-pentanone to 3-pentanol using the {Cp(CO)₂(PPh₃)Mo}⁺ fragment and H₂ recently reported by Voges and Bullock, the [B(Ar_F)₄][−] anion generally gave the best turnover rate for the reaction compared to other counterions such as [OTf][−] and [BF₄][−].^{6,7} We were interested to not only compare [*closo*-CB₁₁H₆Br₆][−] and [*closo*-HCB₁₁Me₁₁][−] with each other in this reaction, but also with [B(Ar_F)₄][−]. Thus, following the published protocol closely, [Cp(CO)₂(PPh₃)MoH] was treated with [*closo*-CB₁₁H₆Br₆][CPh₃] or [*closo*-HCB₁₁Me₁₁][CPh₃] in a CD₂Cl₂ solution containing ten equivalents of Et₂CO. The NMR tube was pressurised with H₂ (<4 atm) and the reaction monitored periodically for the appearance of hydrogenated product: 3-pentanol. With the anion [*closo*-HCB₁₁Me₁₁][−] a faster turnover rate was observed (8 turnovers after 12 days), while with [*closo*-CB₁₁H₆Br₆][−] the rate was slower (5 turnovers after 12 days). However these turnover rates do not match the [BAr₄][−] anion, which gave 10 turnovers after 5 days.⁷

Summary

The results presented in this study confirm that the mono anionic carborane anions **I** through **IV** can be ranked in a decreasing order of nucleophilicity: [*closo*-CB₁₁H₁₂][−] ≈ [*closo*-CB₁₁H₁₁Br][−] > [*closo*-CB₁₁H₆Br₆][−] > [*closo*-HCB₁₁Me₁₁][−]. The comparison between monobromo [*closo*-CB₁₁H₁₁Br][−] and [*closo*-CB₁₁H₆Br₆][−] is particularly revealing. The former forms a metal complex that has a strong Mo–Br bond (complex **3**), which is not displaced by acetone or water. The latter only weakly interacts with the {Cp(CO)₃Mo}⁺ fragment, being displaced rapidly by Lewis bases. This reiterates¹⁸ that the weakly coordinating properties of [*closo*-CB₁₁H₆Br₆][−] are not due to an intrinsically weak bond between bromine and a metal centre, but that the steric effect of six closely associated bromine atoms on the polyhedral surface must predominate.

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