

Transition metal complexes of the weakly coordinating carborane anion $[\text{CB}_{11}\text{H}_{12}]^-$: the first isolation and structural characterisation of an intermediate in a silver salt metathesis reaction

Nathan J. Patmore,^a Jonathan W. Steed^b and Andrew S. Weller^{*a}

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

^b Department of Chemistry, Kings College London, The Strand, London, UK WC2R 2LS

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Reaction between $\text{CpMo}(\text{CO})_3\text{I}$ and $\text{Ag}[\text{CB}_{11}\text{H}_{12}]$ eventually affords $\text{CpMo}(\text{CO})_3(\eta^1\text{-CB}_{11}\text{H}_{12})$, via the dimeric compound $[\text{CpMo}(\text{CO})_3\text{I}\cdot\text{Ag}[\text{CB}_{11}\text{H}_{12}]]_2$ which represents the first structurally characterised intermediate in a silver salt metathesis reaction.

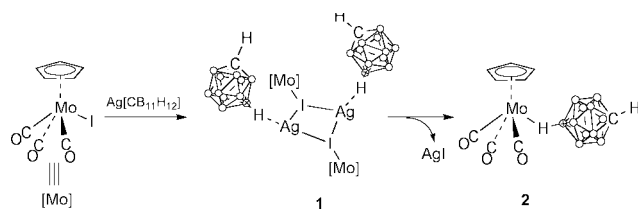
The ubiquitous silver halide metathesis reaction, used to generate vacant sites on a metal fragment, finds application in many transition metal-mediated reactions, especially *in situ* catalyst generation.¹ Typically, the counter ion paired in such transformations is triflate, $[\text{OTf}]^-$, $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$, and halide metathesis is considered to be rapid. Over ten years ago, Reed and coworkers reported² that very weakly coordinating anions, such as the monocarborane $[\text{closo-CB}_{11}\text{H}_{12}]^-$,³ could dramatically slow the rate of metathesis when paired with Ag^+ , suggesting that the exceptionally low nucleophilicity of the anion was a limiting factor in these reactions. Reaction between $\text{CpFe}(\text{CO})_2\text{I}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and $\text{Ag}[\text{CB}_{11}\text{H}_{12}]$ was proposed (by ¹H NMR and IR data) to proceed through an intermediate adduct, $\text{CpFe}(\text{CO})_2\text{I}\cdot\text{Ag}[\text{CB}_{11}\text{H}_{12}]$, similar to Mattson and Graham's⁴ proposed intermediate adduct, formed between $\text{CpFe}(\text{CO})_2\text{I}$ and $\text{Ag}[\text{BF}_4]$. However, neither of these transient species (or other related⁵ compounds) have been placed on a firm structural footing. Given the widespread use of the silver salt metathesis reaction, the identity of the intermediates in these reactions is of significant interest.

We have a current interest in the transition metal chemistry associated with carboranes such as $[\text{CB}_{11}\text{H}_{12}]^-$, and as part of this investigation have been studying the reactions of $\text{CpMo}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{I}$) with $\text{Ag}[\text{CB}_{11}\text{H}_{12}]$ and derivatives, with the anticipation of forming complexes *via* extrusion of AgX . We report here, the isolation and full characterisation, including the X-ray crystal structure, of the intermediate formed in this silver salt metathesis reaction.

Reaction between $\text{CpMo}(\text{CO})_3\text{Cl}$ and $\text{Ag}[\text{CB}_{11}\text{H}_{12}]$ in CH_2Cl_2 over 2 days resulted in the precipitation of AgCl and the isolation, in essentially quantitative yield, of $\text{CpMo}(\text{CO})_3(\eta^1\text{-CB}_{11}\text{H}_{12})$ **2** (Scheme 1). Compound **2** has been fully characterised by multinuclear NMR spectroscopy[†] and by an X-ray diffraction study⁶ and shows the expected² $3c\text{-}2e$ Mo–H–B agostic bonding. Compound **2** displays two CO stretching modes in its IR spectrum, at 2071 and 2001 cm^{-1} . Monitoring the reaction by IR spectroscopy showed that the reaction proceeded through an intermediate species [as found for $\text{CpFe}(\text{CO})_2\text{I}$], but at no time was there a single component

observed in the reaction mixture. Moving to $\text{CpMo}(\text{CO})_3\text{I}$ resulted in a slowing down of the reaction, so that formation of **2** now took 7 days, while after *ca.* 3 h of stirring there was only one component in the reaction mixture, which displayed IR stretches at 2054 and 1973 cm^{-1} , intermediate between the starting material and product. Monitoring this reaction by IR and ¹H NMR spectroscopies showed that this was indeed an intermediate species, continued stirring for 7 days resulting in the clean formation of **2**. Careful recrystallisation of this intermediate overnight at -30°C afforded small red crystals in reasonable isolated yield (50%), which were pure by IR, microanalysis and NMR spectroscopy,[‡] and shown by X-ray diffraction[§] to be $[\text{CpMo}(\text{CO})_3\text{I}\cdot\text{Ag}[\text{CB}_{11}\text{H}_{12}]]_2$ **1**: the first structurally characterised intermediate in a silver salt metathesis reaction.

The solid state structure of **1** is shown in Fig. 1. It is apparent that it adopts a centrosymmetric dimeric structure, with an I–Ag–I–Ag central core hinged around the Mo(1)–I(1)–I(1A)–Mo(1A) vector by 123.2° . The two Ag–I lengths are significantly different, Ag(1)–I(1) 2.9748(10) Å and Ag(1)–I(1A) 2.7599(9) Å. While similar central cores to **1** are known,^{7,8} the presence of two additional [M]–I–Ag bridges appended to such a motif is unprecedented. However, there are silver adduct species of transition metal halides that show similar features,⁹ such as the recently reported complex $[\{\text{TpRe}(\text{NC}_6\text{H}_4\text{Me-p})(\text{Ph})\text{I}\}_2\text{Ag}][\text{PF}_6]^{10}$ [Tp = tris(pyrazolyl)borate] in which silver bridges two $\{\text{Re}\text{-I}\}$ fragments. The carborane anion is intimately connected with silver, showing a short (1.96 Å) Ag–H–B interaction [Ag(1)–B(12) 2.659(10) Å]. The cages are orientated *syn* to one another with respect to the Mo–I–Mo vector, leaving the silver atoms with an apparent vacant coordination site. Inspection of the packing diagram for **1** reveals that this site is occupied by another short (1.96 Å) Ag–H–B interaction arising from an adjacent carborane cage in the lattice, meaning that each cage bridges two silver centres [through H(12) and H(7)]. This results in a chain-like structure



Scheme 1

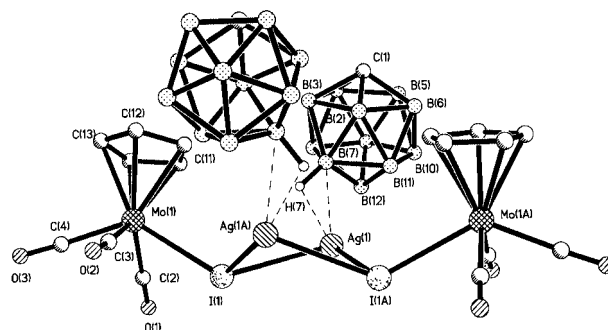


Fig. 1 Structure of the dimeric unit in complex **1**. Atom labels suffixed 'A' are generated crystallographically. Hydrogen atoms [except H(7)] are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Mo(1)–I(1) 2.8599(8), Ag(1)–I(1) 2.9748(10), Ag(1A)–I(1) 2.7599(9), Ag(1)–B(7) 2.659(10), Ag(1)–H(7) 1.96; Ag(1)–I(1)–Ag(1A) 71.19(3), I(1)–Ag(1)–I(1A) 97.10(3).

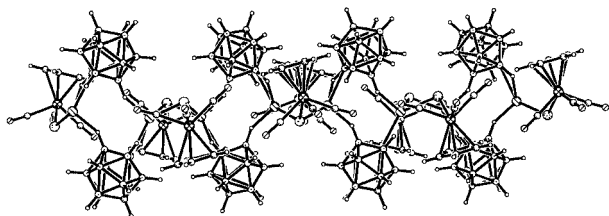


Fig. 2 Extended solid state structure of **1** viewed along the crystallographic 'a' axis.

along the 'a' axis in the crystal (Fig. 2). A similar bridging motif has been observed in the simple salt $\text{Ag}[\text{CB}_{11}\text{H}_{12}] \cdot 2\text{C}_6\text{H}_6$,² while dimeric structures formed from single Ag–H–B interactions have also been reported.^{11,12}

Although it is unlikely that this polymeric structure persists on dissolution in CH_2Cl_2 , evidence for coordination of the carborane cage to Ag in solution comes from inspection of the ^{11}B NMR spectra. The room temperature $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128 MHz) shows two peaks at $\delta -11.1$ and -14.6 in the ratio 1:10 (latter peak a 5 + 5 coincidence), significantly different from the free anion (*vide infra*), the unique boron resonance being shifted upfield by *ca.* 5.5 ppm with respect to $\text{Ag}[\text{CB}_{11}\text{H}_{12}]$ [$\delta_{^{11}\text{B}}$ -5.4 (1B), -10.6 (5B) and -12.3 (5B) in d_6 -acetone]. This chemical shift difference suggests sustained Ag–H–B interaction(s) in solution and is consistent with the observed Ag–H–B contacts in the solid state. In the room-temperature $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum the unique BH is observed at $\delta 2.12$ and shifts slightly to $\delta 1.92$ on cooling to -90°C , showing no Ag–H coupling, although such interactions are rarely observed. The ^{109}Ag NMR spectrum displayed a single sharp line at $\delta 1335$, shifted significantly downfield from the normal range ($\delta_{^{109}\text{Ag}}$ *ca.* 500) expected for Ag(I) centres.¹³

Overall metathesis can be dramatically suppressed in this system by moving to the less nucleophilic and sterically bulkier carborane anion $\text{Ag}[\text{CB}_{11}\text{H}_6\text{Br}_6]$. Stirring for 1 h results in the clean formation of the analogous intermediate complex to **1**,¹⁴ but, surprisingly, no subsequent metathesis was observed, even after extended stirring for 7 days. This result is in accord with the previous observation that the relative nucleophilicity of the conjugate anion in these reactions is rate determining.² Nevertheless, the cessation of this reaction at the intermediate stage is, to our knowledge, without precedent. It should be noted, however, that metathesis does not proceed to completion when Vaska's complex and $\text{Ag}[\text{CB}_{11}\text{H}_{12}]$ are combined, but in this system a strong Ag–Ir bond is formed instead,¹⁵ very different from the structure of **1**.

In summary, we have presented here the first fully characterised (NMR, X-ray diffraction) intermediate in a silver salt metathesis reaction, and found it to have a dimeric $\{[\text{Mo}]\text{--I}\}\text{--Ag}\text{--}\{[\text{Mo}]\text{--I}\}\text{--Ag}$ core in the solid state. This result leads us to speculate upon the motifs accessible using combinations of other CpML_nX_y fragments and monocarborane anions, and we are currently actively pursuing this. Moreover, the lack of metathesis consummation with $\text{Ag}[\text{CB}_{11}\text{H}_6\text{Br}_6]$ demonstrates that there is a significant degree of kinetic control in a reaction that is normally considered very facile. This has potential implications for the synthesis of transition metal complexes

bearing very weakly coordinating anions *via* silver salt metathesis.

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Notes and references

† *Spectroscopic data for 2*: $\delta_{\text{H}\{^{11}\text{B}\}}$ (400 MHz, CD_2Cl_2) 5.86* (5H, s), 2.53 (1H, s, $\text{C}_{\text{cage}}\text{H}$), 1.79 (5H, s, BH), 1.66 (5H, s, BH), -15.11 (1H, s, Mo–H–B). Selected δ_{H} : -15.11 [1H, partially collapsed quartet, $J(\text{BH})$ 90]. $\delta_{^{11}\text{B}}$ (128 MHz, CD_2Cl_2) -4.7^* , -10.4 (1B, d sh), -11.7 [5B, d, $J(\text{HB})$ 151 Hz], -13.9 [5B, d, $J(\text{HB})$ 151 Hz], -18.6^* (* indicates peaks relating to a minor isomer⁶). Found: C, 28.0; H, 4.4. Calc. for $\text{C}_9\text{H}_{17}\text{O}_3\text{B}_{11}\text{Mo}$: C, 27.9; H, 4.4%. IR (KBr, cm^{-1}): 2582m, 2549m, 2243w br, 2067s, 1991s, 1980s. (CH_2Cl_2): 2573m, 2230w, vbr, 2071s 2001s br.

‡ *Spectroscopic data for 1*: 273 K: $\delta_{\text{H}\{^{11}\text{B}\}}$ (CD_2Cl_2) 5.75 (5H, s), 2.56 (1H, s, $\text{C}_{\text{cage}}\text{H}$), 2.12 (1H, s, BH) and 1.86 (10H, s, BH). $\delta_{^{11}\text{B}}$ (CD_2Cl_2) -11.1 [1B, d, $J(\text{HB})$ 119 Hz], -14.6 [5B + 5B, app. d, $J(\text{HB})$ *ca.* 144 Hz]. 183 K: $\delta_{\text{H}\{^{11}\text{B}\}}$ (CD_2Cl_2) 5.76 (5H, s), 2.56 (1H, s, $\text{C}_{\text{cage}}\text{H}$), 1.92 (1H, s, BH), 1.73 (5H, s, BH) and 1.68 (5H, s, BH). $\delta_{^{11}\text{B}}$ (CD_2Cl_2) -10.1 (1B, br), -14.0 (10B, br). $\delta_{^{109}\text{Ag}}$ (18 MHz, CD_2Cl_2) 1335 (s). Found: C, 17.8; H, 2.8. Calc. for $\text{C}_9\text{H}_{17}\text{AgB}_{11}\text{IMoO}_3$: C, 17.4; H, 2.7%. IR (KBr, cm^{-1}) 2556m, 2531m, 2041s, 1971s, 1950s, (CH_2Cl_2): 2570m, 2054s, 1973s br.

§ *Crystal data for 1*: $\text{C}_9\text{H}_{17}\text{AgB}_{11}\text{IMoO}_3$, $M = 622.85$, $\lambda = 0.71073 \text{ \AA}$, orthorhombic, space group $Pnna$, $a = 13.8843(4)$, $b = 15.7193(4)$, $c = 18.1490(6) \text{ \AA}$, $U = 3961.0(2) \text{ \AA}^3$, $Z = 8$, $T = 120(2) \text{ K}$, $D_c = 2.089 \text{ g cm}^{-3}$, $\mu = 3.186 \text{ mm}^{-1}$, $F(000) = 2336$, crystal $0.20 \times 0.10 \times 0.08 \text{ mm}$, 3870 unique reflections ($R_{\text{int}} = 0.0476$), $R_1 = 0.0563$, $wR_2 = 0.1101$ [$I > 2 \sigma(I)$].

CCDC 182/1630. See <http://www.rsc.org/suppdata/cc/b0/b002585m/> for crystallographic files in .cif format.

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