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From alkaline earth to coinage metal carboranyls†

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The β-diketiminato calcium and magnesium complexes, [(BDI)Mg^{n}Bu] and [(BDI)CaH]$_2$ (BDI = HC{C(Me)NDipp}$_2$; Dipp = 2,6-di-isopropylphenyl), react with *ortho*-carborane (o-C$_2$B$_{10}$H$_{12}$) to provide the respective [(BDI)Ae(o-C$_2$B$_{10}$H$_{11}$)] (Ae = Mg or Ca) complexes. While the lighter group 2 species is a monomer with magnesium in a distorted trigonal planar environment, the heavier analogue displays a puckered geometry at calcium in the solid state due to Ca···H−B intermolecular interactions. These secondary contacts are, however, readily disrupted upon addition of THF to provide the 4-coordinate monomer, [(BDI)Ca(THF)(o-C$_2$B$_{10}$H$_{11}$)]. [(BDI)Mg(o-C$_2$B$_{10}$H$_{11}$)] was reacted with [NHC^{IPr}MCl] (NHC^{IPr} = 1,3-bis(isopropyl)imidazol-2-ylidene; M = Cu, Ag, Au) to provide [NHC^{IPr}M(o-C$_2$B$_{10}$H$_{11}$)], rare *C*-bonded examples of coinage metal derivatives of unsubstituted (o-C$_2$B$_{10}$H$_{11}$)$^-$ and confirming the alkaline earth compounds as viable reagents for the transmetalation of the carboranyl anion.

Introduction

The study of carboranes dates from the 1950s, with the intention of developing practical borane-based aircraft and rocket fuels that could exploit the higher energies generated by combustion of boron hydrides compared to hydrocarbons.[1] Since this time and pioneered by, among others, the wide ranging and influential studies of Hawthorne and coworkers,[2] the academic study of carborane and carboranyl derivatives has developed as a rich area of theoretical and practical study with impacts that run the gamut from weakly coordinating anions[3] to the creation of thermally-stable polymers.[4,5]

In more recent years, the practical potential of carboranes has begun to be realised, finding practical application within the fields of energy storage,[6] catalysis and medicine.[6,7] Within these disciplines, the introduction of different isomers of the C$_2$B$_{10}$H$_{12}$ icosahedron, *para*, *meta* and *ortho* (*p*, *m*, *o*), also impart variable electronic effects and thermal stabilities to the resultant compounds. The *o*-carborane (o-C$_2$B$_{10}$H$_{12}$) isomer for example, is more prominent in light-emitting applications, driven by the aggregation-induced emission that is typically observed for *o*-carborane containing materials.[8] Similarly, *o*-carborane has attracted significant attention in future antitumour therapeutics, specifically boron neutron capture therapy (BNCT).[9–11] Much research, therefore, has focused upon the

modification of carboranes as a means to enhance their biologically relevant properties, commonly *via* ligand or indeed metal functionalisation.[7,9,11] There has, for example, been specific recent interest directed toward the luminescent and/or antimicrobial properties of derivatives in which the carboranyl unit is *C*-functionalised by one of the coinage metals of group 11 (Cu, Ag, and Au).[12–14] In this latter regard, it is notable that a variety of routes to variously substituted Au(ɪ) compounds of this type have been described.[15–21] In contrast, there is a relative paucity of information relating to broadly analogous species comprising *C*-σ bonded carboranyl anions to either silver or copper. Indeed, the sole structurally characterised Ag(ɪ) species (**I**, Fig. 1) was obtained serendipitously and was further stabilised by a pendent N-heterocyclic carbene.[13] Similarly, treatment of CuCl with the *o*-dilithiocarborane (1,2-Li$_2$C$_2$B$_{10}$H$_{10}$) has been reported to provide an efficient method to enable the coupling of two carboranes and the synthesis of 1,1′-bis(*o*-carborane) through the sacrificial one electron reduction of the Cu(ɪ) centres to metallic copper, albeit the C–C coupled product may be further deprotonated and functionalised as the bis-Cu(ɪ) complex, [1,1′-2,2′-{Cu(toluene)}$_2$(o-C$_2$B$_{10}$H$_{10}$)$_2$] (**II**).[22]

Sodium and potassium hexamethyldisilazides have seen recent application in the generation of carbanionic intermediates for the *C*-vertex functionalisation of carboranes.[23] It is apparent, however, that the development of further less reducing and more kinetically discriminating sources of the parent carboranyl nucleophile would be a highly desirable addition to the armoury of reagents available for the preparation of further metal-functionalised complexes. A long-standing focal point of our own research has been the exploitation of

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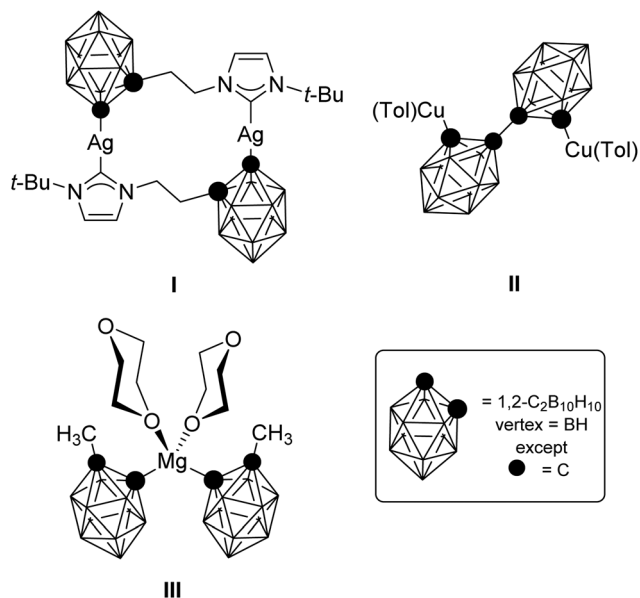
Fig. 1 The o-carboranyl derivatives **I**–**III**.

β-diketiminato magnesium and calcium complexes, [(BDI)Ae-X] (where BDI = HC{C(Me)NDipp}$_2$; Dipp = 2,6-di-isopropyl-phenyl; Ae = Mg or Ca; X = *e.g.* H or C-, Si-, Sn-, B-, Al-), for the kinetically discriminating delivery of potent *p*-block centred nucleophiles. Fully authenticated examples of carboranyl compounds comprising a group 2 atom are currently restricted to the *C*-methylated species, [Mg(2-Me-1,2-C$_2$B$_{10}$H$_{10}$)$_2$·2C$_4$H$_8$O$_2$] (**III**),[24] and two further derivatives of 1,1′-bis(o-carborane).[25] Examples comprising magnesium's heavier congeners, meanwhile, remain completely unrepresented as a class of organoalkaline earth compound. To address this lacuna, therefore, in this contribution we describe the facile syntheses of several alkaline earth *ortho*-carboranyl compounds. [(BDI)Ae(o-C$_2$B$_{10}$H$_{11}$)] (Ae = Mg, Ca), and an initial assessment of their potential as anion transfer reagents for the preparation of novel coinage metal carboranyl complexes.

Results and discussion

We have previously demonstrated that terminal alkynes are readily deprotonated by magnesium and calcium organo and amido bases to yield the corresponding *C*–Ca bonded acetylide derivatives.[26–29] The notably comparable pK_a values pertaining to the C–H bonds of *ortho*-carborane and terminal acetylenes (~23),[30,31] suggest that comparable treatment with *ortho*-carborane should similarly provide dehydrogenative access to the parent o-carboranyl group 2 complexes. We first attempted to prepare a magnesium derivative through the reaction of [(BDI)Mg^{n}Bu] with an equivalent of o-carborane. Although no reaction was observed at ambient temperature, heating for 7 days at 60 °C, induced 66% conversion to a new BDI-containing species which displayed a characteristic carborane methine signal (δ$_H$ 2.41 ppm) in the resultant ^{1}H NMR spectrum. The

evolution of *n*-butane and partial consumption of both [(BDI)Mg^{n}Bu] and o-carborane were also observed indicating [(BDI)Mg(o-C$_2$B$_{10}$H$_{11}$)] (**1**) was being formed, albeit slowly. The reaction was, therefore, repeated at 100 °C, a procedure that induced the stoichiometric conversion of the starting reagents to compound **1** within 16 hours. The structure of **1** was confirmed by X-ray diffraction analysis (Fig. 2), which demonstrated the magnesium centre is unambiguously 3-coordinate (∑Mg1^{CNN} = 359°) and co-planar with respect to both the BDI backbone and the (C30) *ipso*-carbon of the carboranyl anion. The reduced magnesium coordination number and the otherwise underivatised structure evidently impacts only marginally on the Mg–C bond distance [Mg1–C30 2.1288(13) Å] in comparison to analogous bond lengths within the 4-coordinate and *C*-methylated structure of **III** [Mg–C 2.156(5) Å].[24]

The dimeric β-diketiminato calcium hydride, [(BDI)CaH]$_2$,[32,33] has previously been utilised to prepare aliphatic organocalcium derivates *via* insertion reactions of terminal alkenes and as a reagent for the dehydrogenative reduction or catalytic coupling of a significant variety of protic and hydridic small molecule substrates.[34–41] Accordingly, reaction of [(BDI)CaH]$_2$ with a stoichiometric amount of *ortho*-carborane resulted in the effervescence of gaseous H$_2$ and consumption of the hydridic signal at δ$_H$ 4.27 ppm, which occurred with the simultaneous appearance of a new BDI methine resonance of [(BDI)Ca(o-C$_2$B$_{10}$H$_{11}$)] (**2**) at 4.52 ppm in the ^{1}H NMR spectrum (Scheme 1). The methine CH carboranyl signal of **2**, which integrated in a 1:1 ratio with the aforementioned methine resonance, was observed at 3.03 ppm, representing a downfield
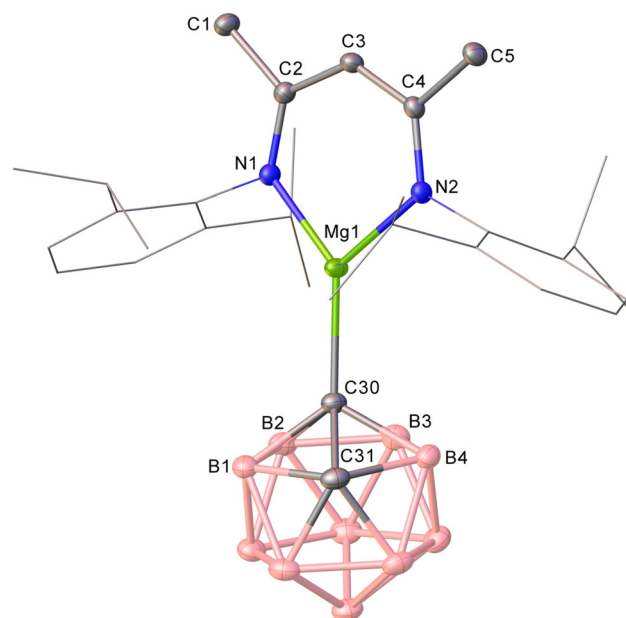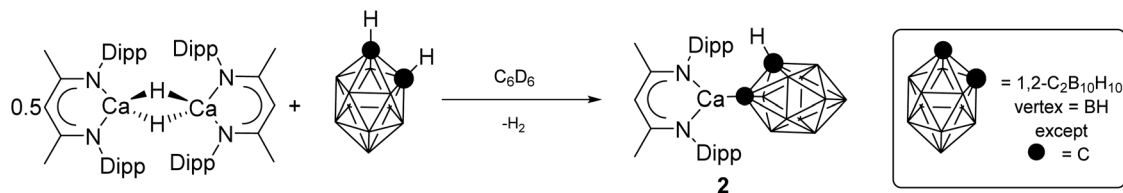

Fig. 2 Molecular structure of **1** with hydrogen atoms omitted and Dipp groups displayed as wireframe for clarity; displacement ellipsoids at 30%. Selected bond lengths (Å) and angles (°): Mg1–N1 2.0001(11), Mg1–N2 1.9954(11), Mg1–C30 2.1288(13), N2–Mg1–N1 96.45(4), N1–Mg1–C30 131.90(5), N2–Mg1–C30 130.65(5).

Scheme 1 Synthesis of [(BDI)Ca(o-C$_2$B$_{10}$H$_{11}$)] (**2**) through the dehydrogenative coupling of [(BDI)CaH]$_2$ and 1,2-C$_2$B$_{10}$H$_{12}$.

shift relative to free *ortho*-carborane (δ_H 2.04 ppm).[42] The identification of compound **2** as the calcium analogue of **1** was corroborated by the corresponding ^{13}C{^{1}H} and ^{11}B NMR data, with the latter spectrum comprising four doublet signals at δ_B −0.6, −5.4, −10.4 and −12.6 ppm, indicative of an *ortho*-carboranyl derivative. The structure of **2** was ultimately confirmed by crystallisation of the reaction product from hexane at −35 °C and subsequent single crystal X-ray diffraction analysis (Fig. 3).

Compound **2** provides Ca1 with two N–Ca contacts [2.290(5) and 2.307(4) Å] and a two-centre σ-*C*–Ca bond to the *o*-carboranyl anion of 2.572(6) Å. Although no direct precedent exists for this latter interaction, it is somewhat elongated in comparison to the sole example of a BDI-coordinated calcium centre featuring a terminal acetylide ligand, the 5-coordinate complex [(BDI)Ca{C≡CSi-iPr$_3$}(THF)$_2$] [Ca–C 2.4703(19) Å],[28] or the Ca–C distances (*ca.* 2.48 Å) typically observed in the similarly supported C–Ca bonds of various three-centre alkyl-bridged species.[32–35] In contrast to the distorted trigonal planar disposition of magnesium in **1**, the Ca1 centre in compound **2** is

situated *ca.* 1.508 Å above the least squares plane defined by the BDI backbone. Reminiscent of the structure of [(BDI)CaN(SiMe$_3$)$_2$],[43,44] in which a comparable deformation from planarity could be identified as a consequence of strong agostic-type Ca···MeSi contacts, similar Ca···H–B intermolecular interactions are observed between three of the B–H units of the adjacent molecule of **2** and Ca1 in the solid state [Ca1···H *ca.* 1.956(7) Å]. This solid-state assembly gives rise to a 1-dimensional polymer which, by virtue of the twofold screw symmetry intrinsic to the *Pca*2$_1$ space group, propagates along the crystallographic *c* axis.

The calcium centre of **2** can be readily saturated by addition of THF, affording [(BDI)Ca(o-C$_2$B$_{10}$H$_{11}$)(THF)] (**3**), which displays only marginally adjusted spectroscopic data in comparison to those provided by **2** (Fig. S13–S17†). This deduction was confirmed by X-ray diffraction analysis, which identified **3** as the THF adduct of compound **2** (Fig. 4), such that the intermolecular Ca···H interactions observed for **2** are prevented by coordination of the cyclic ether. The structure of **3**, thus, presents an unambiguously monomeric structure in which the
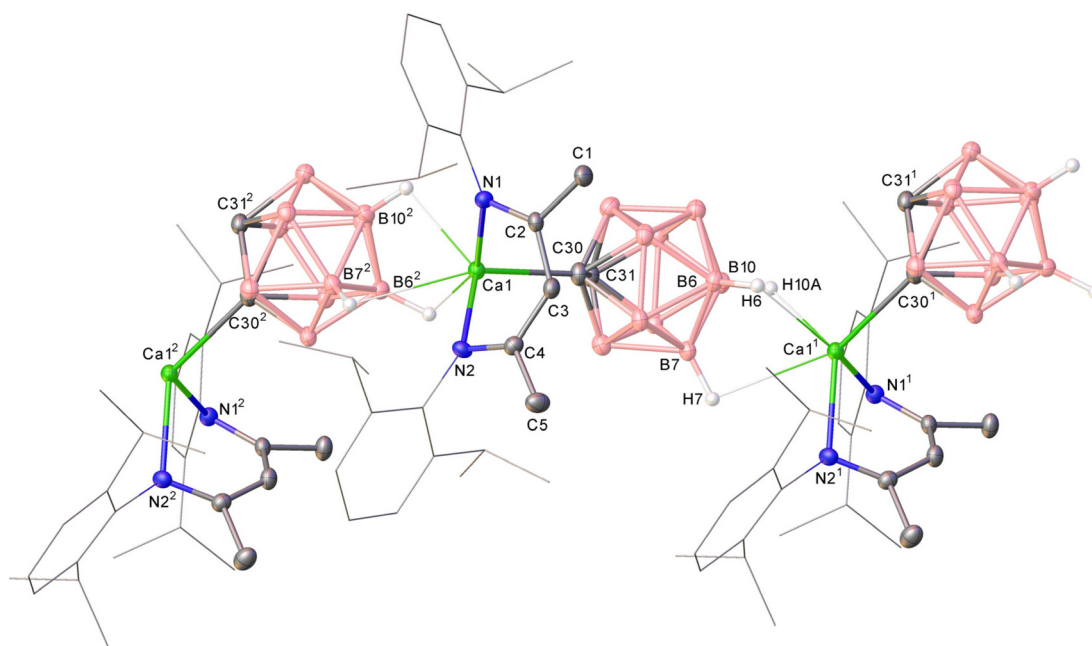
Fig. 3 Structure of compound **2** with most hydrogen atoms omitted and Dipp groups displayed as wireframe for clarity; displacement ellipsoids at 30%. Selected bond lengths (Å) and angles (°): Ca1–N1 2.290(5), Ca1–N2 2.307(4), Ca1–C30 2.572(6), N1–Ca1–N2 85.77(15), N1–Ca1–C30 113.66(18), N2–Ca1–C30 118.83(18). Symmetry operations to generate equivalent atoms: ^{1} $\frac{1}{2}$ − x, y, $\frac{1}{2}$ + z; ^{2} $\frac{1}{2}$ − x, y, −$\frac{1}{2}$ + z.
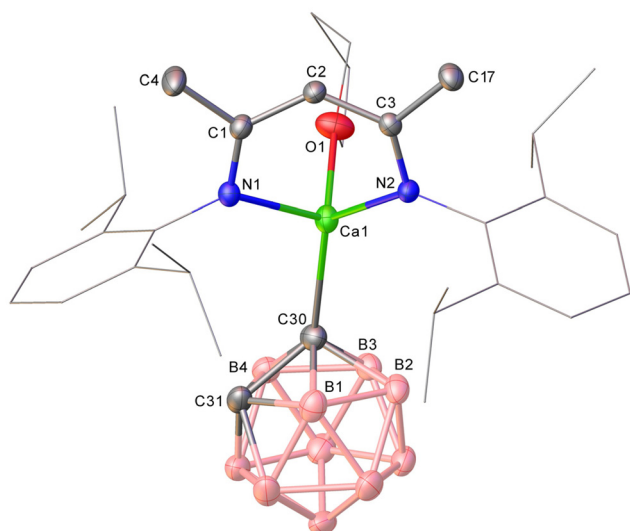
Fig. 4 Structure of compound **3**. Hydrogen atoms have been omitted for clarity while THF carbon atoms and Dipp substituents are displayed as wireframes, also for visual ease; displacement ellipsoids at 30%. Selected bond lengths (Å) and angles (°): Ca1−N1 2.304(3), Ca1−N2 2.301(3), Ca1−O1 2.299 (3), Ca1−C30 2.478(4), O1−Ca1−N1 112.76(10), O1−Ca1−N2 111.17(10), O1−Ca1−C30 100.34(11), N1−Ca1−C30 117.03 (11), N2−Ca1−N1 84.63(9), N2−Ca1−C30 130.88(11).

calcium atom now adopts a 4-coordinated distorted pseudo-tetrahedral geometry ($\tau_4 = 0.79$),[45] and with a Ca−C distance to the carboranyl anion that is surprisingly shorter [Ca1−C30 2.478(4) Å] than that observed in **2**.

With the alkaline earth carboranyl complexes **1**–**3** in hand, we turned our attention towards their use as carboranyl transfer reagents. In an initial assessment of their potential, com-

pound **1** was reacted with the respective group 11 chlorides, [NHC^{IPr}MCl] (NHC^{IPr} = 1,3-bis(isopropyl)imidazol-2-ylidene; M = Cu, Ag, Au) in benzene to provide the respective o-carboranyl derivatives, [NHC^{IPr}M(o-C$_2$B$_{10}$H$_{11}$)] [where M = Cu (**4**), Ag (**5**), Au (**6**)] (Scheme 2). The syntheses of both compounds **4** and **6** resulted in the immediate precipitation of [(BDI)MgCl]$_2$ from the solution, whereupon filtration and analysis by ^{1}H NMR spectroscopy provided spectra that displayed signals which could be assigned solely to NHC^{IPr} and a broadened singlet arising for the remaining methine C–H resonance of the group 11-bonded carboranyl anion (**4**, δ = 3.18 ppm; **6**, δ = 3.37 ppm). These data were also reflected in the corresponding ^{13}C{^{1}H} and ^{11}B NMR spectra, with the latter exhibiting four distinct boron environments as has been observed in a variety of previously reported σ-bound M–C carboranyl complexes (e.g. 1-[(CO)$_4$Mn=C(OCH$_3$)(CH$_3$)]-2-R-1,2-$closo$-C$_2$B$_{10}$H$_{10}$ (R = CH$_3$, C$_6$H$_5$); [2,6-(^{i}Pr$_2$PO)$_2$C$_6$H$_3$]Pt(1-o-carborane)).[46,47]

In contrast to the ready formation of compounds **4** and **6**, the reaction between compound **1** and NHC^{IPr}AgCl was less

Table 1 Selected bond distances (Å) and angles (°) for compounds **4** (Cu), **5** (Ag) and **6** (Au)

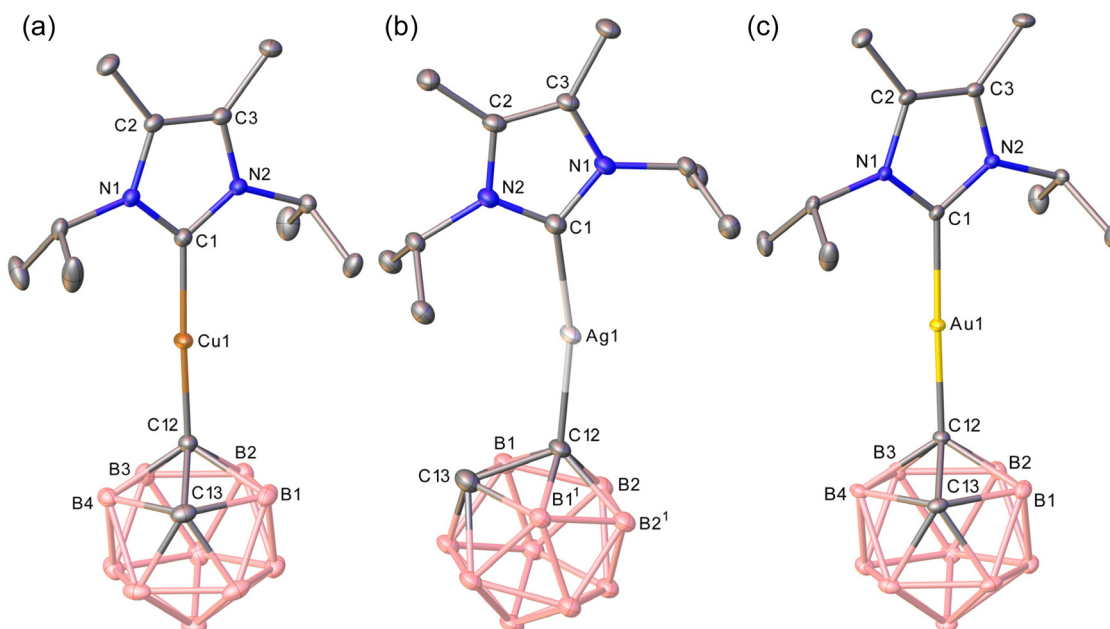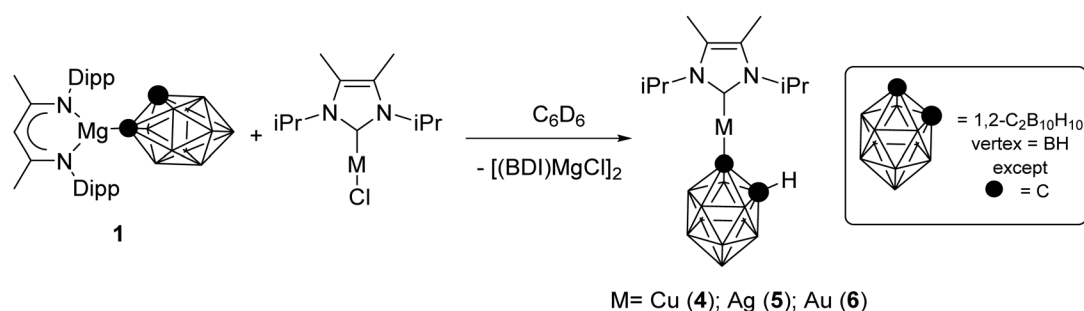|	**4**[a]	**5**[b]	**6**[c]
M1−C1	1.9001(13)	2.094(5)	2.023(3)
M1−C12	1.9192(13)	2.120(5)	2.045(3)
N1−C1	1.3565(16)	1.360(6)	1.348(3)
N2−C1	1.3546(16)	1.340(7)	1.355(3)
C1−M1−C12	176.97(6)	167.3(2)	177.84(11)
N1−C1−N2	104.20(10)	104.5(4)	105.2(2)

[a] M1 = Cu. [b] M1 = Ag. [c] M1 = Au.

Fig. 5 Structures of (a) **4**, (b) **5** and (c) **6** with displacement ellipsoids at 30%. Hydrogen atoms have been omitted for clarity. Symmetry operation to generate equivalent atoms in **5**, x, 3/2 − y, z.

Scheme 2 Synthesis of $[(NHC^{IPr})M(o\text{-}C_2B_{10}H_{11})]$ (M = Cu (**4**), Ag (**5**), Au (**6**)) using **1** as a carboranyl transfer reagent.

discriminating. Even with the exclusion of light, this reaction induced the instantaneous and persistent precipitation of Ag metal and the apparent formation of multiple species. The formation of $[(BDI)MgCl]_2$ could, however, still be identified and the implied formation of $[(NHC^{IPr})Ag(o\text{-}C_2B_{10}H_{11})]$ (**5**) was ultimately verified by X-ray diffraction analysis of a single crystal isolated by crystallisation of the crude reaction product from hexane solution. The resultant structure of **5** is presented in Fig. 5 alongside those of **4** and **6**, while selected bond distance and angle data for all three compounds are shown in Table 1.

The solid-state structures of compounds **4** and **6** each present an approximation to linear (*ca.* 177°) two-coordinate geometry, bearing an NHC ancillary ligand and a σ-bonded carboranyl unit. In contrast, compound **5** displays a more bent geometry at Ag1 [C1–Ag1–C12 167.3(2)°], but one which is still comparable with previously reported two-coordinate silver species, which also display a significant deviation from linearity.[13,48,49] The M–C_{NHC} bond lengths are representative of those observed in generic NHC–M(ɪ) (M = Cu, Ag and Au) complexes.[50–55] Although the data available for direct comparison are quite limited, the metal-to-carborane [M1–C12] bond lengths in compounds **4** [1.9192(13) Å] and **5** [2.120(5) Å] are effectively identical to the precedents provided by compounds **II** [2.128(3), 2.118(2) Å][22] and **I** [1.920(2) Å],[13] indicating that neither further *C*-substitution of the carborane anion nor the identity of the formally neutral co-ligand impact significantly on the M(ɪ)-to-carboranyl interaction. Similarly, the Au1–C12 bond length in **6** [2.045(3) Å] is entirely commensurate with analogous interactions within the variously substituted Au(ɪ) carboranyl species which have been described (*e.g.* [Ph₃PAu(2-*t*-BuMe₂Si-$C_2B_{10}H_{10}$)], 2.050(4) Å).[17]

Conclusion

The deprotonation of *ortho*-carborane by either $[(BDI)Mg^nBu]$ or $[(BDI)CaH]_2$ facilitates the efficient generation of the first alkaline earth complexes of the unfunctionalised *o*-carboranyl anion, $[(BDI)Ae(o\text{-}C_2B_{10}H_{11})]$. These group 2 carboranyl complexes can be utilised as efficient carboranyl transfer reagents, allowing the synthesis of coinage metal functionalised carborane complexes, $[(NHC^{IPr})M(o\text{-}C_2B_{10}H_{11})]$ (M = Cu, Ag, Au). We are continuing to elaborate this reactivity to related systems.

Data availability

See ESI† for complete synthetic, and crystallographic details. CCDC codes 2332977–2332982 contain the supplementary crystallographic data for this paper.†

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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