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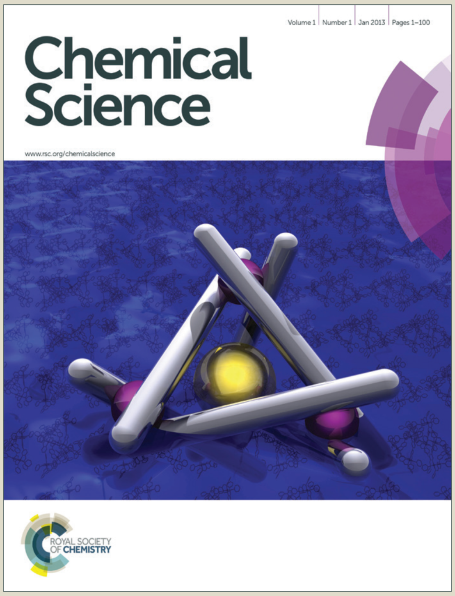

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Selective Reduction of CO_2 to a Methanol Equivalent by $B(C_6F_5)_3$-activated Alkaline Earth Catalysis

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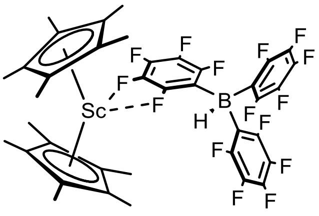
Abstract

Treatment of β-diketiminato Mg and Ca amidoborane compounds with $B(C_6F_5)_3$ *induces hydride elimination and formation of alkaline earth hydrido-tris(pentafluorophenyl)borate derivatives. Both species react with* CO_2 *to provide formate complexes, one of which has been structurally characterised, and may be applied to the highly selective reductive hydroboration of* CO_2 *with pinacolborane (HBpin) to provide the methanol equivalent,* CH_3OBpin*.*

Introduction

Atmospheric levels of carbon dioxide will continue to rise as industrial production outstrips the potential for its photosynthetic regulation. While the biological fixation of CO_2 is a vital process for the maintenance of life on Earth, the anaerobic conversion of resultant plant life to the fossil fuels so central to mankind's development requires geological timescales.[1] Consequently, the establishment of a 'methanol economy' through production of a transportable liquid fuel, methanol, by reductive recycling of CO_2 has been posited as a viable energy vector worthy of attention.[2] While a number of homogeneous catalytic methods have been devised for reduction of CO_2 to formic acid,[3] and a variety of protocols mediated by organo-[4] or transition metal[5] catalysis using silanes or boranes as oxygen scavengers have been described, sufficiently discriminative access to lower formal carbon oxidation states continues to present a significant challenge. The decamethylscandocenium hydrido-tris(pentafluorophenyl)borate species, **1**, for example, reacts with CO_2 to provide the formatoborate ion pair $[Cp^*_2Sc][HCO_2B(C_6F_5)_3]$,[6] which, in the presence of $B(C_6F_5)_3$ co-catalyst and excess triethysilane, effects the catalytic deoxygenative hydrosilylation of CO_2 to methane through a tandem process of metal-mediated silylformate production and posited frustrated Lewis pair-mediated reduction.



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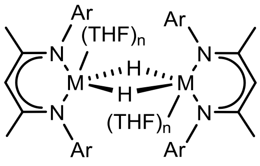
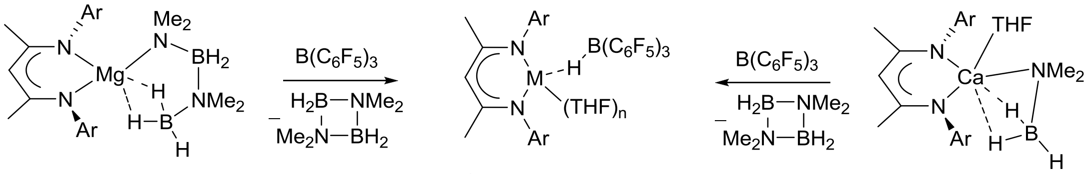


2 M = Mg, n = 0; **3** M = Ca, n = 1
Ar = 2,6-di-*iso*propylphenyl

While a majority of metal-catalysed processes providing CO_2 reduction, thus, require the use of complexes derived from either scarce heavy transition (e.g. crustal abundance, Ru 0.001 ppm) or rare earth (e.g. Sc, 16 ppm) metals, our own research efforts have focussed on the development of a homogeneous catalytic chemistry for complexes derived from the inexpensive and environmentally benign heavier alkaline-earth elements, in particular magnesium (29,000 ppm) and calcium (50,000 ppm). The synthesis of reactive magnesium and calcium hydride derivatives such as the β-diketiminato compounds, **2** and **3**,[7] has received particularly significant recent attention because of the use of these species in a range of reductive molecular catalyses.[8] In contrast, the sole precedents for hydrido ion paired group 2 species broadly analogous to compound **1**, the hetero- and homoleptic calcium derivatives, $[Ca\{C(SiHMe_2)_3\}\{HB(C_6F_5)_3\}(THF)_2]$ (**4**) and $[Ca\{HB(C_6F_5)_3\}_2(THF)_2]$ (**5**), have not been applied in any catalytic context.[9] We, thus, speculated that the catalytic reactivity of the alkaline earth-hydride partnership of **2** and **3** could be amplified through introduction of the commonly applied Lewis acid reagent, tris(pentafluorophenyl)borane. In this contribution we demonstrate that this is indeed the case and that magnesium and calcium hydrido-tris(pentafluorophenyl)borate derivatives can mediate the exquisitely selective hydroboration of CO_2 with pinacolborane (HBpin) to provide the methanol equivalent, MeOBpin.[10]

Results and Discussion

While our target compounds could be prepared through direct reaction of **2** and **3** with $B(C_6F_5)_3$, more convenient and high yielding syntheses were achieved with the previously described amidoborane derivatives, compounds **6** and **7** (Scheme 1).[11] Treatment of these species with a single molar equivalent of $B(C_6F_5)_3$ at room temperature induced δ- and β-hydride elimination to form the volatile cyclic borazane $[H_2BNMe_2]_2$ and the respective magnesium and calcium hydrido-tris(pentafluorophenyl)borate derivatives (**8** and **9**) in stoichiometric yield. The ^{11}B NMR spectra of compounds **8** and **9** comprised doublet resonances (**8**, $\delta_{11B} = -18.9$ ppm, $^1J_{BH} = 67$ Hz: **9**: –22.4 ppm, 86 Hz), congruent with analogous data reported for compounds **4** and **5**.[9] Although the ^{19}F NMR spectra of both compounds comprised three signals arising from the *o*-, *m*- and *p*-fluorine environments of equivalent fluoroaryl rings at temperatures >338 K, their spectra were more complex at reduced temperatures indicating the retention of ion paired interactions in solution. Notably, the onset of complete signal coalescense occurred at more elevated temperatures (ca. 338 *versus* 278 K) for compound **8**, consistent with more labile solution ion pairing in compound **9** containing the softer Lewis acidic calcium center. These deductions were supported by a single crystal X-ray diffraction analysis of compound **9**, which revealed the anticipated ion paired structure (Figure 1). The interaction of the hydridoborate anion with the calcium center, comprising contacts from the B-H unit and the *ortho*-fluorine atoms of two of the pentafluorophenyl rings, is completely analogous to the solid-state behaviour of **4** and **5** obviating further necessary comment.[9]



6 **Scheme 1** **8**: M = Mg, n = 0 **7**

9: M = Ca, n = 1

Ar = 2,6-di-*iso*propylphenyl

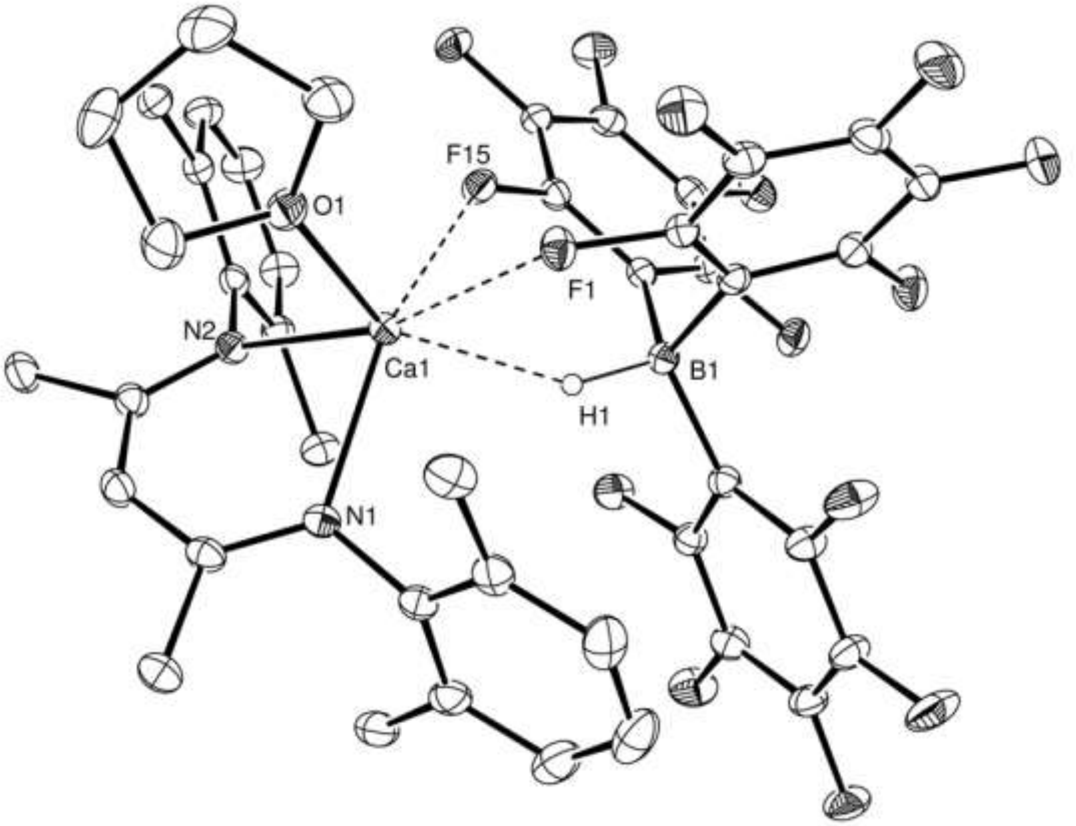
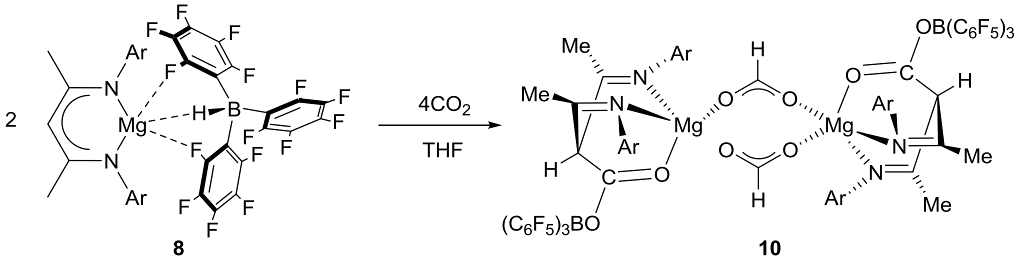


Figure 1: ORTEP representation of compound **9** (30% probability ellipsoids). *Iso*-propyl methyl groups, minor fractional-occupancy disordered atoms and hydrogen atoms except H(1) are removed for clarity. Selected bond lengths (Å) and angles (^{o}): Ca(1)-N(1) 2.3065(13), Ca(1)-N(2) 2.3194(13), Ca(1)-O(1) 2.3423(12), Ca(1)-F(15) 2.4259(9), Ca(1)-F(1) 2.4493(9), Ca(1)-H(1) 2.343(16), B(1)-H(1) 1.161(16): N(1)-Ca(1)-N(2) 81.28(5), N(1)-Ca(1)-O(1) 100.76(5), N(2)-Ca(1)-O(1) 99.48(4), N(1)-Ca(1)-F(15) 154.91(4), N(2)-Ca(1)-F(15) 91.75(4), O(1)-Ca(1)-F(15) 104.16(4), N(1)-Ca(1)-F(1) 114.86(4), N(2)-Ca(1)-F(1) 163.78(4), O(1)-Ca(1)-F(1) 76.81(4), F(15)-Ca(1)-F(1) 74.19(3), N(1)-Ca(1)-H(1) 96.0(4), N(2)-Ca(1)-H(1) 117.3(4), C(41)-B(1)-C(35) 114.55(13), C(41)-B(1)-C(47) 115.52(13), C(35)-B(1)-C(47) 106.49(12), C(41)-B(1)-H(1) 103.9(8), C(35)-B(1)-H(1) 108.7(8), C(47)-B-H(1) 107.4(8).



Scheme 2 (Ar = 2,6-di-*iso*-propylphenyl)

Compound **8** reacted with one atmosphere of CO_2 at room temperature to provide a single new species (**10**) characterised by the appearance of singlet resonances at 4.71 and 8.31 ppm in the resultant ^1H NMR spectrum (Scheme 2). The origin of this observation was confirmed through a further single crystal X-ray diffraction analysis of compound **10**, the results of which are displayed in Figure 2. Compound **10** is a centrosymmetric magnesium dimer in which the bridging formate groups arise from reduction of CO_2 through hydride transfer from the $[HB(C_6F_5)_3]^-$ anions. In a process reminiscent of reversible solution behaviour previously deduced for reactions of a cationic β-diketiminato methylscandium compound,[12] a further molecule of CO_2 is sequestered through C-C bond formation at the central methine center of the β-diketiminate ligand. In contrast to the precedent provided by the scandium-centered reactivity, however, the $B(C_6F_5)_3$ component engages with the exocyclic oxygen centre of what may be, thus, considered as a facially capping, tripodal carboxylatoborate ligand. An identical reaction performed with two molar equivalents of $^{13}CO_2$ indicated that the reaction to form compound **10** occurred sequentially with the appearance of the signal at 4.71 ppm as a doublet resonance ($^2J_{CH}$ = 6 Hz) prior to the signal ascribed to the formate residue at 8.31 ppm ($^1J_{CH}$ = 159 Hz) (Figures S1 – S4). Replacement of the atmosphere of this sample with $^{12}CO_2$ resulted in the conversion of the upfield doublet into a singlet resonance, indicating the reversibility of the transannular bonding of the β-diketiminate methine center to CO_2 (Figure S5). In contrast to this behaviour, reaction of compound **9** with $^{13}CO_2$ provided no indication of ligand-centered reactivity and evidenced only formate formation from observation of correlated (HMQC) resonances at 7.95 and 170.0 ppm in the respective ^1H and ^{13}C NMR spectra.

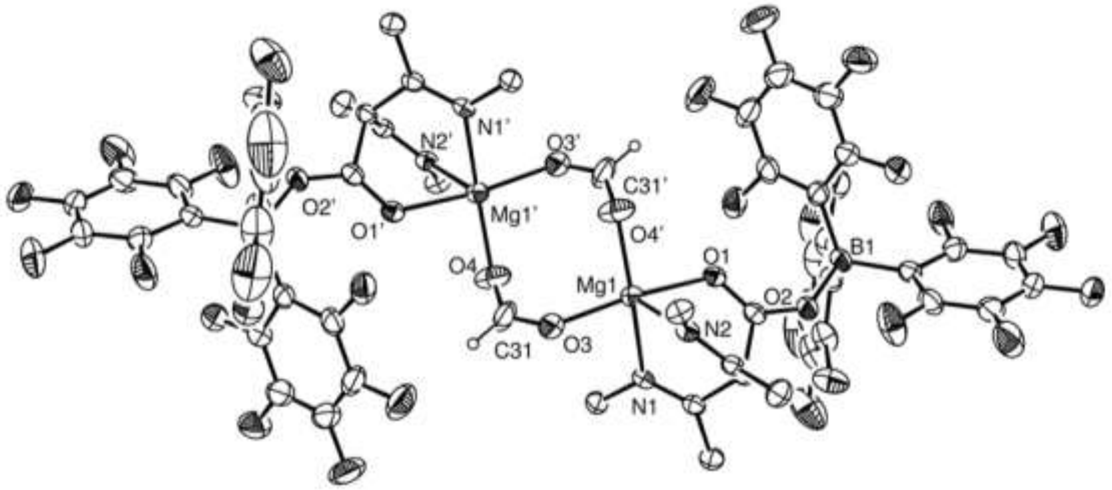


Figure 2: ORTEP representation of compound **10** (30% probability ellipsoids). For clarity, solvent has been omitted and only the hydrogen atom only that attached to C(31) has been displayed. For a similar reason, only the *ipso* carbon atoms from the di-*iso*propyl phenyl groups are illustrated. Selected bond lengths (Å) and angles (°): Mg(1)-O(1) 2.115(3), Mg(1)-O(3) 1.979(4), Mg(1)-N(1) 2.170(3), Mg(1)-O(3) 1.979(4), Mg(1)-O(4)' 1.935(3), O(1)-C(30) 1.229(5), O(2)-B(1) 1.540(6), O(3)-C(31) 1.218(6), O(4)-C(31) 1.203(6), O(4)'-Mg(1)-O(3) 99.55(16), O(4)'-Mg(1)-O(1) 87.20(14), O(3)-Mg(1)-O(1) 167.79(15), O(4)'-Mg(1)-N(2) 116.76(16), O(3)-Mg(1)-N(2) 101.45(15), O(1)-Mg(1)-N(2) 84.28(12), O(4)'-Mg(1)-N(1) 150.05(16), O(3)-Mg(1)-N(1) 87.41(14), O(1)-Mg(1)-N(1) 81.79(12), N(2)-Mg(1)-N(1) 89.85(13), (30)-O(1)-Mg(1) 118.2(3), C(30)-O(2)-B(1) 134.6(3). Symmetry transformations used to generate equivalent atoms: (') -*x*+1/2,-*y*+1/2,-z.

Encouraged by this alkaline earth-centred reactivity, compounds **8** and **9** (10 mol%) were employed in the catalytic hydroboration of one atmosphere of $^{13}CO_2$ with HBpin. Reactions performed at 60°C in THF required 6 and 4 days respectively to achieve 100% consumption of HBpin. Although slow in comparison to Sabo-Etienne's ruthenium polyhydride-based catalysis, which provided complete consumption of HBpin in 0.5 hours,[5f] these reactions proved to be exquisitely selective and provided $^{13}CH_3OBpin$ as the sole ^{13}C-containing product of CO_2 reduction. The formation of this methoxy derivative was evidenced by the development of a resonance at 52.6

ppm in the $^{13}C\{^1H\}$ NMR spectrum, which appeared as a binomial quartet ($^1J_{CH}$ = 143 Hz) in the corresponding ^{13}C-^1H gated spectrum (Figure 3). The formation of CH_3OBpin was also clearly apparent in the coincidental ^{11}B NMR spectra as a resonance at δ_{11B} 25.6 ppm, which appeared simultaneously, and in a 1:2 ratio of signal intensity, with a signal at δ_{11B} 24.8 ppm (Figure S6). This latter compound was identified as the known diboroxane, $(pinB)_2O$,[13] the formation of which provides the thermodynamic driving force for the overall reaction depicted in eq. 1. Notably, after removal of the CO_2 atmosphere and addition of further equivalents of HBpin, no further reduction of the methanol equivalent CH_3OBpin was observed.

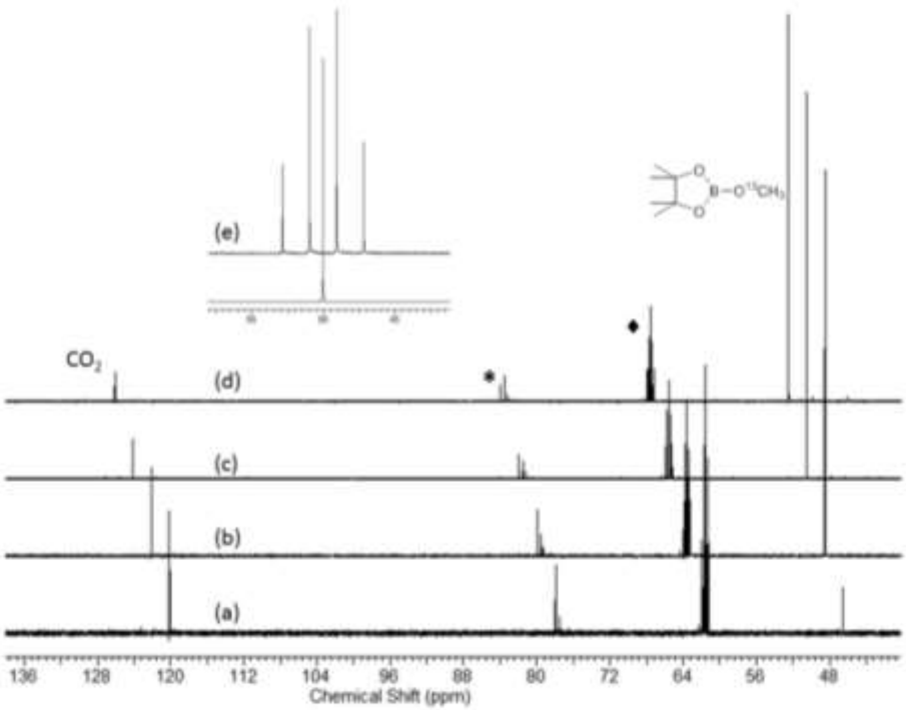
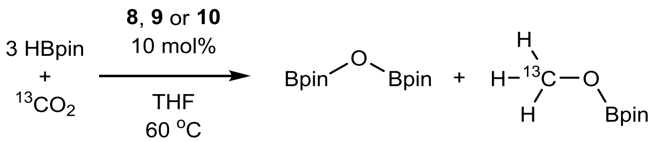
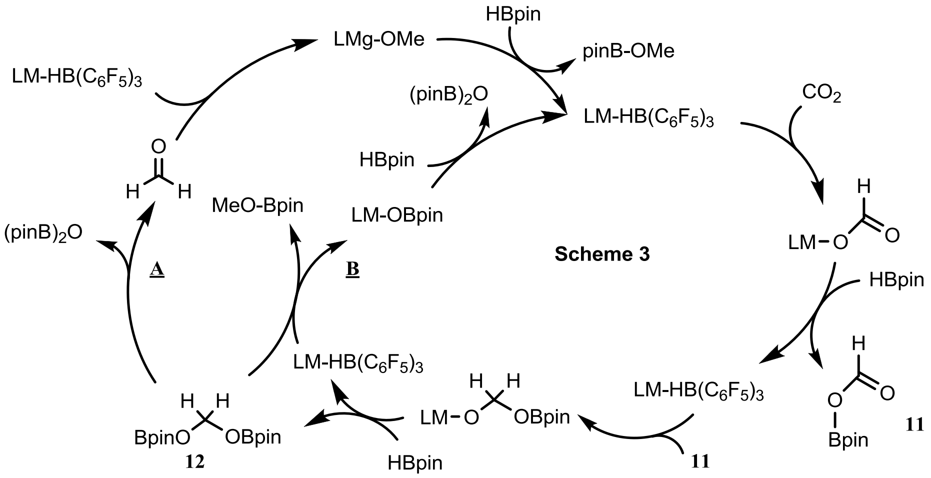


Figure 3: $^{13}C\{^1H\}$ NMR spectra recorded during the reaction of $^{13}CO_2$ and HBpin catalyzed by 10mol% **2** after (a) 0 hours; (b) 10 hours; (c) 20 hours; (d) 30 hours; (e) expansion of the $^{13}\underline{C}H_3Bpin$ signal showing the coupling to the three equivalent methyl protons (* signals attributed to various $B\{O\underline{C}(Me)_2\}_2$ environments; ♦ THF solvent).



(1)

Although no other C_1 organic compounds were observed among the final products of this catalysis, *in situ* monitoring of NMR scale reactions indicated the persistence of small quantities of the $[HB(C_6F_5)_3]^-$ anion throughout the reactions (Figure S6) and allowed the identification of $pinBO^{13}CHO$ (**11**) and $pinBO^{13}CH_2OBpin$ (**12**), which were formed in small quantities (<5%) before their ultimate consumption. The latter bis(bora)acetal species, assigned through comparison to the ^{1}H and ^{13}C NMR spectroscopic data described in a recent report of ruthenium-catalyzed CO_2 hydroboration (δ_{1H} 5.57; δ_{13C} 82.6 ppm),[5f] appeared alongside similarly correlated (HMQC) methylene signals (δ_{1H} 5.02; δ_{13C} 78.2 ppm), which were tentatively assigned as an alkaline earth-bound $[OCH_2OBpin]$ acetal residue.



Scheme 3

While the precise role of compound **10** could not be definitively delineated under catalytic conditions, it is notable that isolated samples of **10** provided comparable catalytic performance as compound **8** in providing complete conversion to CH_3OBpin within 4 days at 60°C. Scheme 3, thus, depicts a provisional reaction mechanism which accounts for these observations in which ‘LM’ describes the β-diketiminate Mg or Ca centre. Under this regime the electrophilic borane acts as a reagent for the delivery of a hydride anion during the alkaline earth-centred reductive processes and the formation of the bis(bora)acetal species **12** is predicated on a sequence of B-H/M-O metathesis and C=O/M-H insertion events. Although spontaneous or metal-centered breakdown of **12** to form $(pinB)_2O$ and formaldehyde, providing a direct and well-precedented pathway for the production of CH_3OBpin (Pathway **A** in Scheme 3),[14] has recently been implicated as a key process in Ru-catalyzed CO_2 hydroboration,[15] we cannot at present discount alternative possibilities. In pathway **B** (Scheme 3), for example, a C-O bond of **12** engages in metathesis with a further catalytic equivalent of an alkaline earth hydridoborate with the direct production of CH_3OBpin. In mitigation of this latter possibility, it is notable that magnesium-catalyzed ester hydroboration, involving the complete rupture of a C-O bond, has very recently been reported to take place via alkoxyborate intermediates.[16]

Conclusion

In summary, we have shown that the reactivity of simple alkaline earth hydride complexes in conjunction with well-precedented electrophilic borane reagents allows the completely selective reduction of CO_2 to the methanol equivalent, CH_3OBpin. We are continuing to explore the mechanistic possibilities presented by this process and to expand the use of CO_2 as a C_1 synthon in catalysis derived from these highly reactive but inexpensive alkaline earth reagents.

Methods

Details of the synthesis, characterisation data and the crystallographic protocols employed in this study are given in the Supporting Information. CCDC 986910-986911 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ca.ac.uk/data_request/cif.

Acknowledgements

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