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Complete reductive cleavage of CO facilitated by highly electrophilic borocations†

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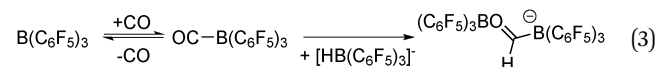
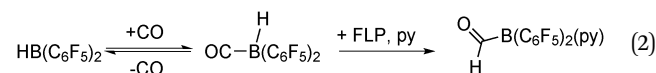
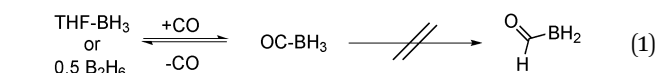
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The addition of CO to $[(R_3N)BH_2]_2(\mu-H)[B(C_6F_5)_4]$ leads to formation of trimethylboroxine $(MeBO)_3$ and $[(R_3N)_2BH_2][B(C_6F_5)_4]$. When $R = Et$, $[(Et_3N)H_2B(\mu-O)B(CH_3)NEt_3][B(C_6F_5)_4]$, is isolated and demonstrated to be an intermediate in the formation of $(MeBO)_3$.

The reduction of carbon monoxide is important for generating hydrocarbon feedstocks (e.g., Fischer–Tropsch) and potentially in the hydrogen economy.^{1,2} The reduction of CO generally requires transition metal catalysts,³ with metal free systems comparatively rare.⁴ Whilst boranes are ubiquitous reducing agents in chemical synthesis the reduction of CO with neutral B(H) species is more challenging. For example the combination of CO with diborane or THF $\rightarrow BH_3$ only leads to low equilibrium concentrations of borane-carbonyl ($OC \rightarrow BH_3$). No subsequent hydride migration from boron to carbon is observed in borane-carbonyl (eqn (1)),⁵ although external strong nucleophiles do react with $OC \rightarrow BH_3$ at carbon,^{6a,b} however, the addition of $NaBH_4$ to borane-carbonyl leads to reductive cleavage of CO and formation of trimethylboroxine.^{6c} Recently, Erker and co-workers utilised $HB(C_6F_5)_2$ in combination with frustrated Lewis pairs (FLPs) to reduce CO to the formyl level.⁷ Significantly, whilst the strongly electrophilic borane $HB(C_6F_5)_2$ reacts with CO to form the borane carbonyl adduct, $HB(CO)(C_6F_5)_2$, the CO reduction product, $B(HCO)(C_6F_5)_2$, was still considerably endergonic. Thus the use of a FLP in combination with $HB(C_6F_5)_2$ was essential for CO reduction to enable isolation of the unusual pyridine adduct of $B(HCO)(C_6F_5)_2$ (eqn (2)).^{7a,c} In related work Stephan and co-worker utilised mixtures of $B(C_6F_5)_3$ – $[HB(C_6F_5)_3]^-$ and $CO-H_2$ to synthesise a $B(C_6F_5)_3$ stabilised formyl borate (eqn (3)),^{8a} which reacts with further H_2 to cleave the CO bond.^{8b}

The novel metal free CO reduction chemistry recently reported with neutral boranes all utilise perfluoroarylboranes, with the multiple $-C_6F_5$ groups required to provide sufficient electrophilicity at boron.

However this requirement limits the number of hydrides available for delivery from B to C and can lead to $-C_6F_5$ transfer from boron to carbon. In contrast to neutral boranes the electrophilicity of borocations is provided by the unit positive charge and thus significant variation in structure is achievable whilst maintaining high electrophilicity at boron. Furthermore, it has been demonstrated that borocations enable transformations not achievable with neutral boranes due to their greater electrophilicity.⁹ We were interested in using borenium cations, such as $[(R_3N)BH_2]^+$ (or functional equivalents thereof), as more electrophilic analogues of BH_3 , surmising that enhanced electrophilic activation of CO would facilitate subsequent reduction steps and the presence of multiple B–H moieties will enable reduction of CO beyond the formyl level. Importantly for this study, previous calculations indicate that $[(Me_3N)BH_2]^+$ is considerably more electrophilic than BH_3 and even Me_3C^+ .^{10a} The exceptional electrophilicity of $[(R_3N)BH_2]^+$ is perhaps best exemplified by their ability to activate aliphatic C–H bonds.¹⁰ Herein we report the complete reductive cleavage of CO to afford $\{H_3C-BO\}$ containing species utilising these highly electrophilic borocations (eqn (4)).



This work



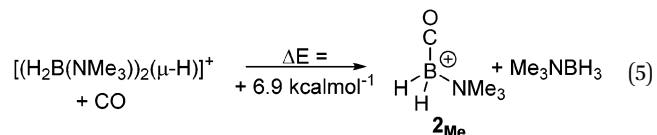
As previously reported the addition of $[Ph_3C][B(C_6F_5)_4]$ to two equivalents of Et_3NBH_3 in DCM leads to the formation of the hydride bridged dimer $[(Et_3N)BH_2]_2(\mu-H)[B(C_6F_5)_4]$, $\mathbf{1}[B(C_6F_5)_4]$ and Ph_3CH (by NMR spectroscopy).^{10d} In our hands minor resonances attributable to unreacted Et_3NBH_3 are also persistently present. Degassing this solution followed by the addition of ca. 2 atm. of CO led to no observable change in the 1H and ^{11}B NMR spectra. Furthermore, cooling this solution to -70°C did not result in the

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observation of any new species. This is consistent with the reaction of the Me_3N analogue of $\mathbf{1}^+$ with CO to form the cationic borane-carbonyl, $\mathbf{2}_{\text{Me}}$, and Me_3NBH_3 being calculated to be endothermic by $6.9 \text{ kcal mol}^{-1}$ (eqn (5), all calculations are at the M06-2X/6311G(d,p), PCM(DCM) level and are ΔE values unless otherwise indicated).



Despite no CO adduct being observable the slow growth of two new resonances in the ^{11}B NMR spectrum and two new Et_3N environments in the ^1H NMR spectrum was observed (combined representing *ca.* 25% of Et_3N after 20 h at 20°C) on standing a solution of $\mathbf{1}[\text{B}(\text{C}_6\text{F}_5)_4]$ under *ca.* 2 atm. of CO in DCM at 20°C . In the absence of CO $\mathbf{1}[\text{B}(\text{C}_6\text{F}_5)_4]$ shows no decomposition over this time-scale in DCM. Repeating the reaction with 2 atm. of CO and heating to 60°C for 18 h in *ortho*-dichlorobenzene (termed *o*-DCB) led to complete consumption of $\mathbf{1}[\text{B}(\text{C}_6\text{F}_5)_4]$ and the appearance of identical resonances to the 20°C DCM reaction as the major product (Et_3NBH_3 was observed throughout as a minor impurity). Notable new resonances included a three coordinate boron centre with $\delta_{11\text{B}} + 37.6$ and a new four coordinate boron resonance with $\delta_{11\text{B}} - 2.3$ (both broad and showing no observable coupling to H) along with the expected resonance for $[\text{B}(\text{C}_6\text{F}_5)_4]^-$. ^1H NMR spectroscopy revealed two new Et_3N environments formed in a 1 : 1 ratio along with a new resonance at $+0.66$ ppm consistent with a B-CH₃ moiety (integral 3H relative to each Et_3N). The $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum revealed an integral 2 (relative to each Et_3N) B-H resonance at 2.5 ppm overlapped with one set of amine CH₂ resonances. The use of isotopically enriched ^{13}CO confirmed formation of a new B-CH₃ moiety and that the carbon is derived from ^{13}CO , with the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum now showing a broad singlet at -2.5 ppm with enhanced intensity that appears as a quartet in the ^{13}C spectra with $^1J_{\text{C-H}}$ of 120 Hz. This is supported by ^1H NMR spectroscopy where the singlet observed using natural abundance CO at $+0.66$ ppm now appears as a doublet at 0.66 ppm with a $^1J_{\text{C-H}}$ coupling of 120 Hz. Therefore NMR spectroscopy confirms C-O cleavage and reduction to a B-CH₃ moiety.

The new CO derived compound could not be isolated analytically pure in bulk (due to the continued presence of varying amounts of $[\text{Et}_3\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$), however, crystals suitable for single crystal X-ray diffraction studies were obtained. This revealed the complex from CO reduction to be the oxo-bridged borocation $[(\text{Et}_3\text{N})\text{BH}_2(\mu\text{-O})\text{BCH}_3(\text{Et}_3\text{N})][\text{B}(\text{C}_6\text{F}_5)_4]$, $\mathbf{3}[\text{B}(\text{C}_6\text{F}_5)_4]$ (Fig. 1, left). This formulation is fully consistent with NMR spectroscopy, with the three coordinate boron centre in $\mathbf{3}[\text{B}(\text{C}_6\text{F}_5)_4]$ attributable to the major resonance at $\delta_{11\text{B}} = +37.6$ which is comparable with the $\delta_{11\text{B}}$ of a previously reported *N*-methyl oxazaborolidinium cation which contains a similar environment around boron.¹¹ The other major resonances observed *in situ* are assigned to the anion and the four coordinate boron centre. The structure of $\mathbf{3}[\text{B}(\text{C}_6\text{F}_5)_4]$ also confirms complete CO cleavage and transfer of three hydrides from boron to carbon. The angles around B1 ($\Sigma = 359.9^\circ$) confirm a trigonal planar environment consistent with the absence of any intermolecular contacts involving B1 in the extended structure (none $< 4 \text{ \AA}$ to either the anion or another B-O moiety). Whilst the B-N and C1-B1 bond distances are in the

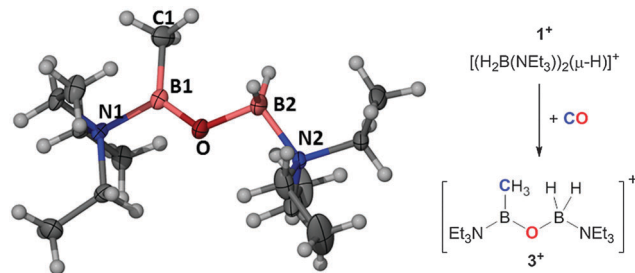


Fig. 1 Left, solid state structure of $\mathbf{3}^+$ (ellipsoids at 30% probability). Selected bond lengths (\AA) and angles ($^\circ$): B1-O = 1.302(4), B2-O = 1.507(5), B1-C1 = 1.561(5), N1-B1 = 1.583(5), N2-B2 = 1.630(5), B1-O-B2 = 123.5(3), N1-B1-O = 115.2(3), O-B1-C1 = 126.4(3), C1-B1-N1 = 118.3(3) and O1-B2-N2 = 105.6(3). Right, schematic for the formation of $\mathbf{3}^+$ from $\mathbf{1}^+$ and CO.

expected distance ranges,¹² the disparate B-O bond distances are notable. The extremely short B1-O (1.302(4) \AA) distance indicates a considerable degree of O \rightarrow B π donation and a degree of oxoborane character.¹³

With unambiguous characterisation of the CO reductive cleavage product $\mathbf{3}$ in hand possible mechanistic scenarios were investigated for the initial step in the reduction of CO. No intermediate compounds (*e.g.*, at a formyl reduction level) were observed at 60°C or at 20°C (by NMR spectroscopy), therefore computational methods were used to provide further insight. It is expected that cleavage of the hydride bridged dimer $\mathbf{1}^+$ with CO will form the $[\text{H}_2(\text{Et}_3\text{N})\text{B}(\text{CO})]^+$ cation, termed $\mathbf{2}_{\text{Et}}$. Therefore, the energetic feasibility of a subsequent intramolecular 1,2-hydride transfer step in the model complex containing Me_3N in place of Et_3N , termed $\mathbf{2}_{\text{Me}}$, was examined. Attempts to calculate a formyl borane structure derived from a B \rightarrow C 1,2-hydride transfer in $\mathbf{2}_{\text{Me}}$ led to minimisation to the cationic cyclic compound, $\mathbf{4}$ (Fig. 2). The formation of $\mathbf{4}$ is significantly endergonic, more so than that reported for formation of $(\text{C}_6\text{F}_5)_2\text{B}(\text{HCO})$ from $(\text{C}_6\text{F}_5)_2\text{HB}(\text{CO})$.⁴ Furthermore, the conversion of $\mathbf{2}_{\text{Me}} \rightarrow \mathbf{4}$ proceeds *via* a high energy transition state ($\text{TS}_{2 \rightarrow 4}$), precluding an intramolecular hydride transfer step proceeding from $\mathbf{2}_{\text{Me}}$. It should be also noted that whilst borocations are particularly strong Lewis acids towards hard nucleophiles¹⁴ the O-bound isocarbonyl derivative of $\mathbf{2}_{\text{Me}}$ was calculated to be $19.8 \text{ kcal mol}^{-1}$ higher in energy than the C bound isomer $\mathbf{2}_{\text{Me}}$, disfavouring a reduction mechanism proceeding *via* the isocarbonyl as previously calculated for CO reduction with a scandium cation.¹⁵ Instead the intermolecular reduction of $\mathbf{2}_{\text{Et}}$ is presumably occurring. This could proceed by a multitude of pathways including concerted or stepwise

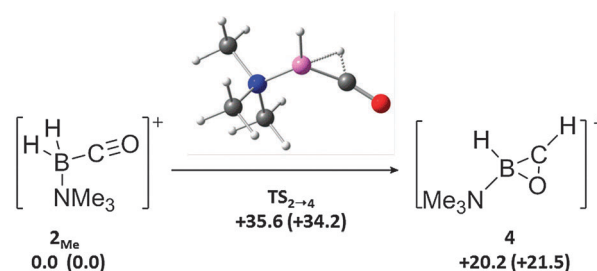
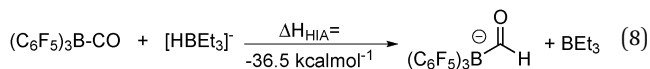
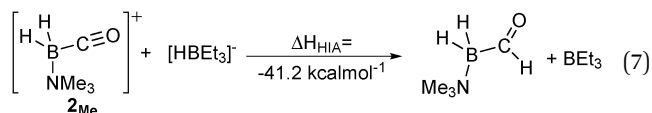
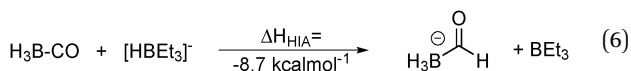


Fig. 2 Relative $E(\text{G}_{298})$ in CH_2Cl_2 (kcal mol^{-1}) for the conversion of $\mathbf{2}_{\text{Me}}$ to $\mathbf{4}$.

hydride transfer processes with a number of possible reductants such as Et_3NBH_3 (potentially forming 1^+ as a by-product) or 1^+ (potentially forming a dicationic $[(\text{Et}_3\text{NBH})_2(\mu\text{-H})_2]^{2+}$ species as by-product).^{10c} Attempts to reduce CO activated by borocation 1^+ at 60 °C using Et_3SiH as an alternative reductant led to no consumption of the silane (by ^1H and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy), although 3^+ was still formed in this reaction from B–H based reductive cleavage of CO. The necessity for borane based reductants may be due to the greater hydride nucleophilicity of amine boranes relative to silanes.¹⁶

The complete reduction of CO by $1[\text{B}(\text{C}_6\text{F}_5)_4]$ in the absence of strong reducing agents is in contrast to the reactivity of $\text{H}_3\text{B-CO}$, which does not undergo reduction with THF-BH_3 or $\text{Me}_3\text{N-BH}_3$.^{5,6} This suggests that coordination of CO to the borocation significantly enhances the electrophilicity at carbon in 2_{Et} , relative to that in $\text{H}_3\text{B-CO}$. To assess this hypothesis we performed hydride ion affinity (HIA) calculations following a previously reported protocol to determine the HIA of the CO adducts relative to BEt_3 .¹⁴ These calculations confirmed that the model cationic complex, 2_{Me} , is substantially more Lewis acidic towards hydride than $\text{OC} \rightarrow \text{BH}_3$ (by $>32 \text{ kcal mol}^{-1}$, eqn (6) and (7)). Furthermore, 2_{Me} was also computed to be more Lewis acidic towards hydride than the CO adduct of the archetypal neutral strong boron Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ (eqn (8)). These calculations clearly demonstrate the enhanced degree of activation provided on substrate coordination to highly electrophilic borocations even relative to strong neutral borane Lewis acids. Remarkably, the HIA of 2_{Me} is comparable to that calculated for $\text{B}(\text{C}_6\text{F}_5)_3$,¹⁴ indicating the considerable Lewis acidity of the carbon centre in 2_{Me} towards hydride which is presumably essential for subsequent CO reduction steps. The comparable HIAs of 2_{Me} and $\text{B}(\text{C}_6\text{F}_5)_3$ suggests a possible reduction pathway, as the reaction of Et_3NBH_3 and 0.5 eq. of $\text{B}(\text{C}_6\text{F}_5)_3$ results in hydride transfer to form $[(\text{Et}_3\text{N})\text{BH}_2](\mu\text{-H})[\text{HB}(\text{C}_6\text{F}_5)_3]$,¹⁷ indicating that 2_{Me} may also be capable of abstracting hydride from Et_3NBH_3 . It should be noted that heating $1[\text{HB}(\text{C}_6\text{F}_5)_3]$ under 2 atm of CO in *o*-DCB leads to anion decomposition and formation of $(\text{Et}_3\text{N})\text{BH}_2(\text{C}_6\text{F}_5)$ as the major product.¹⁷



Increasing the reaction temperature for the reductive cleavage of CO with $1[\text{B}(\text{C}_6\text{F}_5)_4]$ to 100 °C in *o*-DCB resulted in the formation of different products. The ^{11}B NMR spectrum now contained two major resonances (excluding that associated with the anion) at +32.0 and –6.7 ppm, whilst the ^1H NMR spectra only displayed a single Et_3N environment. The use of ^{13}CO again unambiguously confirmed the formation of a B–CH₃ moiety from complete reductive cleavage of CO. The compound associated with the $\delta_{^{11}\text{B}} = 6.7$ resonance was assigned as the boronium salt $[(\text{Et}_3\text{N})_2\text{BH}_2][\text{B}(\text{C}_6\text{F}_5)_4]$, $5[\text{B}(\text{C}_6\text{F}_5)_4]$, by independent synthesis and X-ray diffraction studies

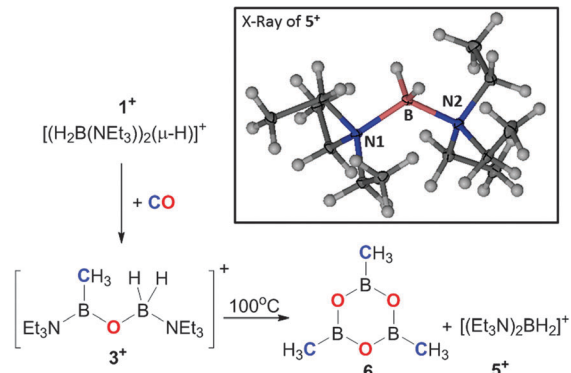
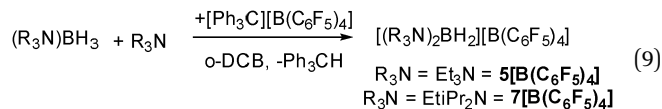


Fig. 3 Schematic for the formation of trimethylboroxine, **6** and 5^+ via intermediate 3^+ . Inset, solid state structure of 5^+ (ellipsoids at 30% probability). Selected bond lengths (Å) and angles (°): B–N1 = 1.631(3), B–N2 = 1.639(5) and N1–B–N2 = 120.8(2).

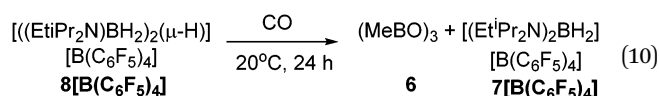
(Fig. 3, inset). The solid state structure of 5^+ has B–N distances (1.63–1.64 Å) indicating minimal bond elongation especially when compared to the B–N distances in the highly strained boronium cation [9-BBN(bis(dimethylamino)naphthalene)]⁺ (B–N = 1.73 Å, BBN = 9-borabicyclononane).¹⁸ It is notable, however, that there is a considerable opening of the N1–B–N2 bond angle to 120.8(2)° in 5^+ to accommodate the steric bulk of both Et_3N substituents (in less hindered $[\text{L}_2\text{BH}_2]^+$ comparable angles are in the region 105–110°).¹⁹ With formation of boronium $5[\text{B}(\text{C}_6\text{F}_5)_4]$ as one new boron containing species mass balance suggested trimethylboroxine, **6**, to be the other; comparison with an independently synthesised sample of **6** confirmed this. The formation of $5[\text{B}(\text{C}_6\text{F}_5)_4]$ and **6** could proceed *via* $3[\text{B}(\text{C}_6\text{F}_5)_4]$. Support for the intermediacy of 3^+ comes from heating $3[\text{B}(\text{C}_6\text{F}_5)_4]$ to 100 °C in *o*-DCB which leads to the formation of $5[\text{B}(\text{C}_6\text{F}_5)_4]$ and **6** (Fig. 3). This conversion could proceed by an associative mechanism (possibly involving two equivalents of **3** or reaction of Et_3NBH_3 and 3^+ to form 1^+ and $(\text{Et}_3\text{N})\text{B=O}$) or a dissociative mechanism (O–B bond cleavage on heating to form $(\text{Et}_3\text{N})\text{B=O}$ and $[(\text{Et}_3\text{N})\text{BH}_2]^+$). The oxoborane $(\text{Et}_3\text{N})\text{B=O}$ would rapidly oligomerise and subsequently dissociate Et_3N leading to **6**, with the released Et_3N then sequestered by the primary boronium salt, or 1^+ , to form boronium 5^+ . Calculations favour an associative mechanism as the formation of $\text{Et}_3\text{N}(\text{CH}_3)\text{B=O}$ and $[(\text{Et}_3\text{N})\text{BH}_2]^+$ from 3^+ at 100 °C was found to be endergonic ($\Delta E = +64.5$ and $\Delta G_{373} = 46.9 \text{ kcal mol}^{-1}$).

The significant distortion in the N–B–N bond angle observed in the solid state structure of boronium salt 5^+ suggested that the use of amines bulkier than Et_3N may destabilise the boronium. This could lead to amine dissociation and generation of $[(\text{amine})\text{BH}_2]^+$ or formation of the hydride bridged dimer (in the presence of excess $(\text{amine})\text{BH}_3$), with either species capable of enabling reduction of further equivalents of CO (with excess $(\text{amine})\text{BH}_3$). To this end we explored if the boronium cation $[(\text{Et}^t\text{Pr}_2\text{N})_2\text{BH}_2]^+$ was accessible. Following the same approach used for the independent synthesis of $5[\text{B}(\text{C}_6\text{F}_5)_4]$, specifically addition of one equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to a 1 : 1 mixture of amine/amineBH₃ in *o*-DCB (eqn (9)), led to the formation of a single new product with NMR data consistent with the boronium salt $[(\text{Et}^t\text{Pr}_2\text{N})_2\text{BH}_2][\text{B}(\text{C}_6\text{F}_5)_4]$, $7[\text{B}(\text{C}_6\text{F}_5)_4]$; this included an integral 2 B–H moiety in the $^1\text{H}\{^1\text{B}\}$

NMR spectrum at +1.67 ppm and a $\delta_{11\text{B}}$ resonance at -14.7 consistent with a four coordinate boron centre. The accessibility of boronium 7^+ does not preclude catalytic (in trityl salt) CO reduction,



as 7^+ is presumably extremely sterically congested at boron (confirmation by X-ray diffraction studies have been frustrated by the lack of suitable crystals) and therefore may react with CO by a $\text{S}_{\text{N}}2$ mechanism or *via* the borenium salt if reversible amine dissociation generates a low concentration of borenium salt. Activation of $(\text{Et}^i\text{Pr}_2\text{N})\text{BH}_3$ with 0.5 equivalents of $[\text{Ph}_3\text{C][B(C}_6\text{F}_5)_4]$ generated the hydride bridged dimer $[[(\text{Et}^i\text{Pr}_2\text{N})\text{BH}_2]_2(\mu\text{-H})][\text{B(C}_6\text{F}_5)_4]$, $\mathbf{8}[\text{B(C}_6\text{F}_5)_4]$, as previously reported.^{10c} Degassing an *o*-DCB solution of $\mathbf{8}[\text{B(C}_6\text{F}_5)_4]$ followed by the addition of *ca.* 2 atm. of CO led to no immediate change in the ^1H and ^{11}B NMR spectra. On standing at 20°C two new boron resonances were observed to increase in intensity at $\delta_{11\text{B}} = +31.9$ and -14.9 , which after 24 h were the major products with all $\mathbf{8}[\text{B(C}_6\text{F}_5)_4]$ consumed. The $\delta_{11\text{B}}$ chemical shifts indicate formation of the boronium salt $\mathbf{7}[\text{B(C}_6\text{F}_5)_4]$ and $\mathbf{6}$ (eqn (10)), with no intermediates observed. Thus the increased steric bulk of $\text{Et}^i\text{Pr}_2\text{N}$ relative to Et_3N is presumably destabilising the hydride and oxo bridged cations leading to lower reaction barriers and complete conversion to $\mathbf{6}$ at 20°C whereas with the Et_3N congeners this requires heating to 100°C . With the desired CO reductive cleavage proceeding from $\mathbf{8}[\text{B(C}_6\text{F}_5)_4]$ to form $\mathbf{6}$ and $\mathbf{7}[\text{B(C}_6\text{F}_5)_4]$ attempts were made to see if $\mathbf{7}[\text{B(C}_6\text{F}_5)_4]$ would be active for further CO reduction cycles with additional amine borane. However, the addition of a further 3 equivalents of $(\text{Et}^i\text{Pr}_2\text{N})\text{BH}_3$ (and recharging with *ca.* 2 atm. of CO) led to no further boroxine formation or consumption of $(\text{Et}^i\text{Pr}_2\text{N})\text{BH}_3$ even on heating to 60°C for 24 h and to 100°C for 24 h. Instead an unidentified resonance at +17.6 ppm was observed in the ^{11}B NMR spectrum as the major product.



In conclusion, we report a metal free system that results in the complete cleavage of the C–O bond in CO and reduction to B-CH_3 . The high electrophilicity of weakly stabilized borocations is essential to activate the coordinated CO sufficiently to transform CO into a strong Lewis acid towards hydride. We are currently investigating the reactivity of other highly electrophilic borocations towards CO.

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Notes and references

- For a recent review on Fischer–Tropsch chemistry see: P. M. Maitlis and V. Zanotti, *Chem. Commun.*, 2009, 1619.
- G. A. Olah, A. Goeppert and G. K. Surya Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, 2006.
- For recent reviews on CO reduction using transition metal catalysts see: (a) M. Gupta, M. L. Smith and J. J. Spivey, *ACS Catal.*, 2011, **1**, 641; (b) M. M. West, A. J. Miller, J. A. Labinger and J. E. Bercaw, *Coord. Chem. Rev.*, 2011, **255**, 881.
- For a review on the use of frustrated Lewis pairs for the reduction of main group oxides including CO see: D. W. Stephan and G. Erker, *Chem. Sci.*, 2014, **5**, 2625.
- For BH_3 carbonyl reactivity: (a) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, 1936, **59**, 780; (b) H. C. Brown, *Acc. Chem. Res.*, 1969, **2**, 65.
- (a) J. C. Carter and R. W. Parry, *J. Am. Chem. Soc.*, 1965, **87**, 2354; (b) R. Alberto, K. Ortner, N. Wheatley, R. Schibli and A. P. Schubiger, *J. Am. Chem. Soc.*, 2001, **123**, 3135; (c) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, 1966, **88**, 2606.
- (a) M. Sajid, L.-M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr and G. Erker, *Angew. Chem., Int. Ed.*, 2013, **52**, 2243; (b) M. Sajid, G. Kehr, C. G. Daniliuc and G. Erker, *Angew. Chem., Int. Ed.*, 2014, **53**, 1118; (c) M. Sajid, G. Kehr, C. G. Daniliuc and G. Erker, *Chem. – Eur. J.*, 2015, **21**, 1454.
- (a) R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 4974; (b) M. Finze, E. Bernhardt, A. Terheiden, M. Berkei, H. Wilner, D. Christen, H. Oberhammer and F. Aubke, *J. Am. Chem. Soc.*, 2002, **124**, 15385.
- For reviews on borocation chemistry see: (a) P. Koelle and H. Nöth, *Chem. Rev.*, 1985, **85**, 399; (b) W. E. Piers, S. C. Bourke and K. D. Conroy, *Angew. Chem., Int. Ed.*, 2005, **44**, 5016; (c) T. S. De Vries, A. Prokofjevs and E. Vedejs, *Chem. Rev.*, 2012, **116**, 4246; (d) M. J. Ingleson, *Top. Organomet. Chem.*, 2015, **49**, 39.
- For select studies on the reactivity of $[(\text{amine})\text{BH}_2]^+$ (or functional equivalents) see: (a) T. S. De Vries, A. Prokofjevs, J. N. Harvey and E. Vedejs, *J. Am. Chem. Soc.*, 2009, **131**, 14679; (b) A. Prokofjevs and E. Vedejs, *J. Am. Chem. Soc.*, 2011, **133**, 20056; (c) A. Prokofjevs, J. W. Kampf, A. Solovjev, D. P. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2013, **135**, 15686; (d) T. S. De Vries and E. Vedejs, *Organometallics*, 2007, **26**, 3079.
- E. Canales and E. J. Corey, *Org. Lett.*, 2008, **10**, 3271.
- For borenium cations containing hydrocarbyl groups see: (a) A. Prokofjevs, J. Jermaks, A. Borovika, J. W. Kampf and E. Vedejs, *Organometallics*, 2013, **32**, 6701; (b) I. A. Cade and M. J. Ingleson, *Chem. – Eur. J.*, 2014, **20**, 12874.
- A. Del Grosso, E. R. Clark, N. Montoutte and M. J. Ingleson, *Chem. Commun.*, 2012, **48**, 7589, and references therein.
- E. R. Clark, A. Del Grosso and M. J. Ingleson, *Chem. – Eur. J.*, 2013, **19**, 2462.
- A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron and O. Eisenstein, *J. Am. Chem. Soc.*, 2012, **134**, 10843.
- M. Horn, L. H. Schappele, G. Lang-Wittowski, H. Mayr and A. R. Ofial, *Chem. – Eur. J.*, 2013, **19**, 249.
- G. Menard and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 5447.
- A. Prokofjevs, J. W. Kampf and E. Vedejs, *Angew. Chem., Int. Ed.*, 2011, **50**, 2098.
- For solid state structure of relevant boronium salts see: (a) P. A. Fox, S. T. Griffin, W. M. Reichert, E. A. Salter, A. B. Smith, M. D. Tickell, B. F. Wicker, E. A. Cioffi, J. H. Davis Jr., R. D. Rogers and A. Wierzbicki, *Chem. Commun.*, 2005, 3679; (b) O. J. Metters, A. M. Chapman, A. P. M. Robertson, C. H. Woodall, P. J. Gates, D. F. Wass and I. Manners, *Chem. Commun.*, 2014, **50**, 12146.