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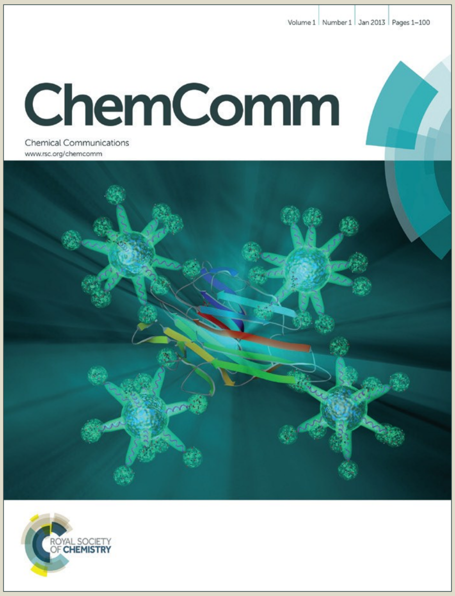

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# Complete reductive cleavage of CO facilitated by highly electrophilic borocations.

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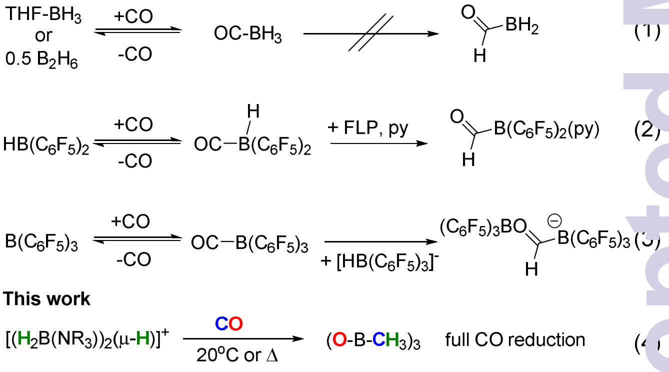
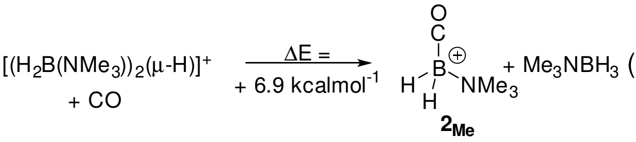
**The addition of CO to [((R$_3$N)BH$_2$)$_2$(μ-H)][B(C$_6$F$_5$)$_4$] leads to complete reductive cleavage of CO and formation of trimethylboroxine ((MeBO)$_3$) and [(R$_3$N)$_2$BH$_2$][B(C$_6$F$_5$)$_4$]. When R = Et the oxo bridged cation, [(Et$_3$N)H$_2$B(μ-O)B(CH$_3$)NEt$_3$][B(C$_6$F$_5$)$_4$], is isolated and demonstrated to be an intermediate in the formation of trimethylboroxine.**

The reduction of carbon monoxide is important for generating hydrocarbon feedstocks (e.g., Fischer-Tropsch) and potentially in the hydrogen economy (where reduced C$_1$ species act as hydrogen carriers).[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→BH$_3$ only leads to low equilibrium concentrations of borane-carbonyl (OC→BH$_3$). No subsequent hydride migration from boron to carbon is observed in borane-carbonyl (eq. 1),[5] although external strong nucleophiles such as amines and hydroxide do react with OC→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$_6$F$_5$)$_2$ in combination with frustrated Lewis pairs (FLPs) to reduce CO to the formyl level.[7] Significantly, whilst the strongly electrophilic borane HB(C$_6$F$_5$)$_2$ reacts with CO to form the borane carbonyl adduct, HB(CO)(C$_6$F$_5$)$_2$, the CO reduction product, B(HCO)(C$_6$F$_5$)$_2$, was still considerably endergonic (17 kcalmol$^{-1}$). Thus the use of a FLP in combination with HB(C$_6$F$_5$)$_2$ was essential for CO reduction to enable isolation of the unusual pyridine adduct of B(HCO)(C$_6$F$_5$)$_2$ (eq. 2) and the exploration of its chemistry.[7a, 7c] In related work Stephan and co-worker utilised mixtures of B(C$_6$F$_5$)$_3$ / [HB(C$_6$F$_5$)$_3$]$^-$ and CO/H$_2$ to synthesise a B(C$_6$F$_5$)$_3$ stabilised formyl borate (eq. 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$_6$F$_5$ 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$_6$F$_5$ 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$_3$N)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$_3$N)BH$_2$]$^+$ is considerably more electrophilic than BH$_3$ and even Me$_3$C$^+$.[10a] The exceptional electrophilicity of [(R$_3$N)BH$_2$]$^+$ suggested by these calculations has been confirmed experimentally and 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$_3$C-BO} containing species utilising these highly electrophilic borocations (eq. 4).

As previously reported the addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to two equivalents of Et$_3$NBH$_3$ in DCM leads to the formation of the hydride bridged dimer [((Et$_3$N)BH$_2$)$_2$(μ-H)][B(C$_6$F$_5$)$_4$], **1[B(C$_6$F$_5$)$_4$]** and Ph$_3$CH (by NMR spectroscopy).[10d] In our hands minor resonances attributable to unreacted Et$_3$NBH$_3$ are also persistently present. Degassing this solution followed by the addition of *ca.* 2 atm. of CO led to no observable change in the $^1$H and $^{11}$B NMR spectra. Furthermore, cooling this solution to -70°C did not result in the observation of any new species. This is consistent with the reaction of the Me$_3$N analogue of **1**$^+$ with CO to form the cation borane-carbonyl, **$2_{Me}$**, and $Me_3NBH_3$ being calculated to be endothermic by 6.9 kcalmol$^{-1}$ (eq. 5, all calculations are at the M06-2X/6311G(d,p), PCM(DCM) level and are ΔE values unless otherwise indicated).



$$[(H_2B(NMe_3))_2(\mu\text{-}H)]^+ + CO \xrightarrow[+\,6.9\ \text{kcalmol}^{-1}]{\Delta E\,=} H_2B(CO)(NMe_3)^{\oplus}\ (\mathbf{2_{Me}}) + Me_3NBH_3 \quad (5)$$

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 **1[B(C$_6$F$_5$)$_4$]** under *ca.* 2 atm. of CO in DCM at 20°C. In the absence of CO **1[B(C$_6$F$_5$)$_4$]** shows no decomposition over this timescale 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 **1[B(C$_6$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 $\delta_{11B}$ +37.6 and a new four coordinate boron resonance with $\delta_{11B}$ -2.3 (both broad and showing no observable coupling to H) along with the expected resonance for $[B(C_6F_5)_4]^-$. $^1H$ 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 $B\text{-}CH_3$ moiety (integral 3H relative to each $Et_3N$). The $^1H\{^{11}B\}$ NMR spectrum revealed an integral 2 (relative to each $Et_3N$) B-H resonance at 2.5 ppm overlapped with one set of amine $CH_2$ resonances. The use of isotopically enriched $^{13}CO$ confirmed formation of a new $B\text{-}CH_3$ moiety and that the carbon is derived from $^{13}CO$, with the $^{13}C\{^1H\}$ 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 $^1J_{C\text{-}H}$ 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 $^1J_{C\text{-}H}$ coupling of 120 Hz. Therefore NMR spectroscopy unambiguously confirms complete C-O cleavage and reduction of to a $B\text{-}CH_3$ moiety.

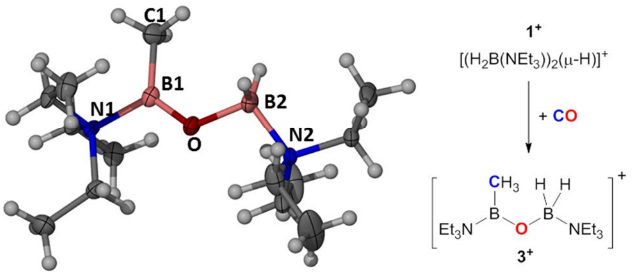


Figure 1. Left, solid state structure of **3$^+$** (ellipsoids at 30 % probability). Selected bond lengths (Å) and angles (°): B1-O = 1.302(4), B2-O = 1.507(5), B1-C1 = 1.561(5), N1-B1 = 1.583(5), N2-B2 = 1.630(5), B1-O-B2 = 123.5(3), N1-B1-O = 115.2(3), O-B1-C1 = 126.4(3), C1-B1-N1 = 118.3(3) and O1-B2-N2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

The new CO derived compound could not be isolated analytically pure in bulk (due to the continued presence of varying amounts of $[Et_3NH][B(C_6F_5)_4]$, presumably from reaction with adventitious water), 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 $[(Et_3N)BH_2(\mu\text{-}O)BCH_3(Et_3N)][B(C_6F_5)_4]$, **3[B(C$_6$F$_5$)$_4$]** (Figure 1, left). This formulation is fully consistent with NMR spectroscopy, with the three coordinate boron centre in **3[B(C$_6$F$_5$)$_4$]** attributable to the major resonance at $\delta_{11B}$ = +37.6 which is comparable with the $\delta_{11B}$ 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 **3[B(C$_6$F$_5$)$_4$]** also confirms complete CO cleavage and transfer of three hydrides from boron to carbon. The angles around B1 (Σ = 359.9°) confirm a trigonal planar environment consistent with the absence of any intermolecular contacts involving B1 in the extended structure (none < 4 Å to either the anion or another B-O moiety). Whilst the B-N and C1-B1 bond distances are in the expected distance ranges,[12] the disparate B-O bond distances are notable. The extremely short B1-O (1.302(4) Å) distance indicates a considerable degree of O→B π donation and a degree of oxoborane character.[13]

With unambiguous characterisation of the CO reductive cleavage product **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 **1$^+$** with CO will form the $[H_2(Et_3N)B(CO)]^+$ cation, termed **$2_{Et}$**. 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 **$2_{Me}$** was examined. Attempts to calculate a formyl borane structure derived from a B→C 1,2-hydride transfer in **$2_{Me}$** (analogous to that calculated for $(C_6F_5)_2B(HCO)$) led to minimisation to the cationic cyclic compound, **4** (Figure 2). The formation of **4** is significantly endergonic, more so than that reported for formation of $(C_6F_5)_2B(HCO)$ from $(C_6F_5)_2HB(CO)$.[4] Furthermore, the conversion of **$2_{Me}$→4** proceeds *via* a high energy transition state (**TS$_{2\to4}$**), precluding an intramolecular hydride transfer step proceeding from **$2_{Me}$**. It should be also noted that whilst borocations are particularly strong Lewis acids towards hard nucleophiles[14] the O-bound isocarbonyl derivative of **$2_{Me}$** was calculated to be 19.8 kcalmol$^{-1}$ higher in energy than the C bound isomer **$2_{Me}$**, disfavouring a reduction mechanism proceeding via the isocarbonyl as previously calculated for CO reduction with a scandium cation.[15] Instead the intermolecular reduction of **$2_{Et}$** is presumably occurring. This could proceed by a multitude of pathways including concerted or stepwise 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 $[(Et_3NBH)_2(\mu\text{-}H)_2]^{2+}$ 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 $^{29}Si\{^1H\}$ 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.[5]

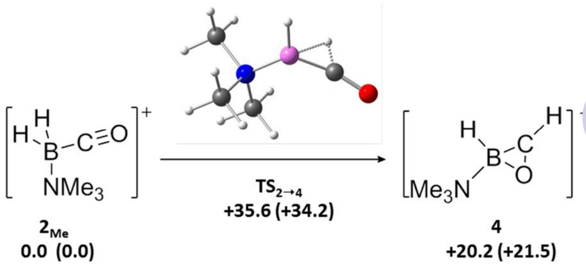
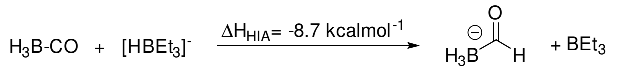


Figure 2: Relative E(G$_{298}$) in $CH_2Cl_2$ (kcal/mol) for the conversion of **$2_{Me}$** to **4**.

The complete reduction of CO by **1[B(C$_6$F$_5$)$_4$]** in the absence of strong reducing agents is in contrast to the reactivity of $H_3B$-CO, which does not undergo reduction with THF-$BH_3$ or $Me_3N$-$BH_3$.[5,6] This suggests that coordination of CO to the borocation significantly enhances the electrophilicity at carbon in **2$_{Et}$**, relative to that in $H_3B$-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 OC→$BH_3$ (by > 32 kcalmol$^{-1}$, eqs. 6 and 7). Furthermore, **2$_{Me}$** was also computed to more Lewis acidic towards hydride than the CO adduct of the archetypal neutral strong boron Lewis acid $B(C_6F_5)_3$ (eq. 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 $B(C_6F_5)_3$,[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 $B(C_6F_5)_3$ suggests a possible reduction pathway, as the reaction of $Et_3NBH_3$ and 0.5 eq. of $B(C_6F_5)_3$ results in hydride transfer to form $[((Et_3N)BH_2)_2(\mu\text{-}H)][HB(C_6F_5)_3]$,[17] indicating that **2$_{Me}$** may also be capable of abstracting hydride from $Et_3NBH_3$. It should be noted that heating **1[HB(C$_6$F$_5$)$_3$]** under 2 atm of CO in o-DCB leads to anion decomposition and formation of $(Et_3N)BH_2(C_6F_5)$ as the major product (by multinuclear NMR spectroscopy and comparison to the previously reported $Me_3N$ derivative).[17] With no CO reduction products observed using $[HB(C_6F_5)_3]^-$ the robust $[B(C_6F_5)_4]^-$ anion appears to be essential in this case to achieve CO reductive cleavage.



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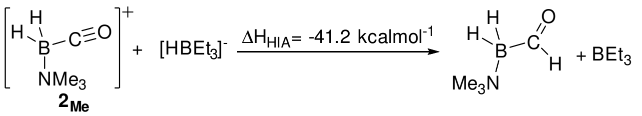

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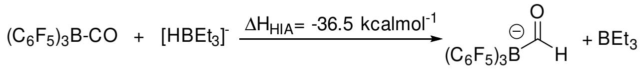

(8)

Increasing the reaction temperature for the reductive cleavage of CO with **1[B(C$_6$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 $^1$H NMR spectra only displayed a single $Et_3N$ environment. The use of $^{13}$CO again unambiguously confirmed the formation of a B-$CH_3$ moiety indicating complete reductive cleavage of CO. The compound associated with the $\delta_{11B}$ -6.7 resonance was assigned as the boronium salt $[(Et_3N)_2BH_2][B(C_6F_5)_4]$, **5[B(C$_6$F$_5$)$_4$]**, by independent synthesis and X-ray diffraction studies (Figure 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 $[L_2BH_2]^+$ comparable angles are in the region 105-110°).[19] With formation of boronium **5[B(C$_6$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[B(C$_6$F$_5$)$_4$]** and **6** could proceed *via* **3[B(C$_6$F$_5$)$_4$]**. Support for the intermediacy of **3$^+$** comes from heating **3[B(C$_6$F$_5$)$_4$]** to 100°C in o-DCB which leads to the formation of **5[B(C$_6$F$_5$)$_4$]** and **6** (Figure 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 $(Et_3N)B{=}O$) or a dissociative mechanism (O-B bond cleavage on heating to form the $(Et_3N)B{=}O$ and $[(Et_3N)BH_2]^+$). The oxoborane ($(Et_3N)B{=}O$) would rapidly oligomerise and subsequently dissociate $Et_3N$ leading to **6**, with the released $Et_3N$ then sequestered by the primary borenium salt, or **1$^+$**, to form boronium **5$^+$**. Calculations favour an associative mechanism as the formation of $Et_3N(CH_3)B{=}O$ and $[Et_3NBH_2]^+$ from **3$^+$** at 100°C was found to be endergonic (ΔE = + 64.5 and $\Delta G_{373}$ = 46.9 kcalmol$^{-1}$).

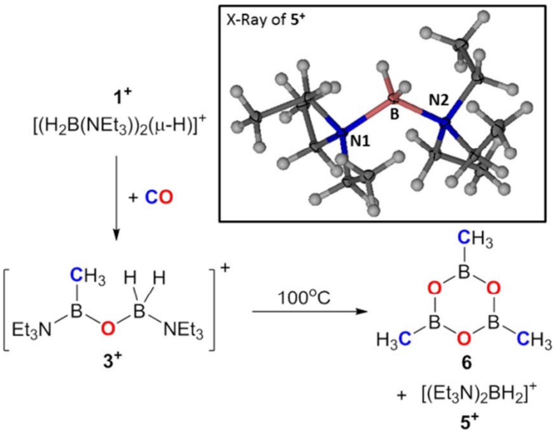

Figure 3. Schematic for the formation of trimethylboroxine, **6** and **5$^+$** via intermediate **3$^+$**. Inset, solid state structure of **5$^+$** (ellipsoids at 30 % probability). Selected bond lengths (Å) and angles (°): B-N1 = 1.631(3), B-N2 = 1.639(5) and N1-B-N2 = 120.8(2).

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 boronium formation. This could lead to amine dissociation and generation of $[(\text{amine})BH_2]^+$ or formation of the hydride bridged dimer (in the presence of excess (amine)$BH_3$), with either species capable of enabling reduction of further equivalents of CO (with excess (amine)$BH_3$). To this end we explored if the boronium cation $[(Et^iPr_2N)_2BH_2]^+$ was accessible. Following the same approach used for the independent synthesis of **5[B(C$_6$F$_5$)$_4$]**, specifically addition of one equivalent of $[Ph_3C][B(C_6F_5)_4]$ to a 1 : 1 mixture of amine / amineBH$_3$ in o-DCB (eq. 8), led to the formation of a single new product with NMR data consistent with the boronium salt $[(Et^iPr_2N)_2BH_2][B(C_6F_5)_4]$, **7[B(C$_6$F$_5$)$_4$]**; this included an integral 2 B-H moiety in the $^1$H{$^{11}$B} NMR spectrum at +1.67 ppm and a $\delta_{11B}$ resonance at -14 consistent with a four coordinate boron centre. The accessibility of boronium **7$^+$** does not preclude catalytic (in trityl salt) CO reduction

$$(R_3N)BH_3 + R_3N \xrightarrow[\text{o-DCB, -}Ph_3CH]{+[Ph_3C][B(C_6F_5)_4]} [(R_3N)_2BH_2][B(C_6F_5)_4] \quad (8)$$

$R_3N = Et_3N$ = **5[B(C$_6$F$_5$)$_4$]**
$R_3N$ = EtiPr$_2$N = **7[B(C$_6$F$_5$)$_4$]**

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 $S_N2$ mechanism or *via* the borenium salt if reversible amine dissociation generates a low concentrate of borenium salt. Activation of $(Et^iPr_2N)BH_3$ with 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ generated the hydride bridged dimer $[((Et^iPr_2N)BH_2)_2(\mu\text{-}H)][B(C_6F_5)_4]$, **8[B(C$_6$F$_5$)$_4$]**, as previously reported.[10c] Degassing an o-DCB solution of **8[B($C_6F_5$)$_4$]** followed by the addition of *ca*. 2 atm. of CO led to no immediate change in the $^1$H and $^{11}$B NMR spectra. On standing at 20$^o$C two new boron resonances were observed to increase in intensity at $\delta_{11B}$ = +31.9 and -14.9, which after 24 h were the major products with all **8[B($C_6F_5$)$_4$]** consumed. The $\delta_{11B}$ chemical shifts indicate formation of the boronium salt **7[B($C_6F_5$)$_4$]** and **6** (eq. 9), with no intermediates observed. Thus the increased steric bulk of Et$^i$Pr$_2$N relative to Et$_3$N is presumably destabilising the hydride and oxo bridged cations leading to lower reaction barriers and complete conversion to **6** at 20$^o$C whereas with the Et$_3$N congeners this requires heating to 100$^o$C. With the desired CO reductive cleavage proceeding from **8[B($C_6F_5$)$_4$]** to form **6** and **7[B($C_6F_5$)$_4$]** attempts were made to see if **7[B($C_6F_5$)$_4$]** would be active for further CO reduction cycles with additional amine borane. However, the addition of a further 3 equivalents of (Et$^i$Pr$_2$N)BH$_3$ (and recharging with ca. 2 atm. of CO) led to no further boroxine formation or consumption of (Et$^i$Pr$_2$N)BH$_3$ even on heating to 60$^o$C for 24 h and to 100$^o$C for 24 h. Instead an unidentified resonance at +17.6 ppm was observed in the $^{11}$B NMR spectrum as the major product.

$$\begin{array}{ccc} [((\mathrm{EtiPr_2N})\mathrm{BH_2})_2(\mu\text{-H})] & & (\mathrm{MeBO})_3 + [(\mathrm{Et^iPr_2N})_2\mathrm{BH_2}] \\ [\mathrm{B(C_6F_5)_4}] & \xrightarrow[20^o\mathrm{C},\ 24\ \mathrm{h}]{\mathrm{CO}} & \qquad\qquad [\mathrm{B(C_6F_5)_4}] \\ \mathbf{8[B(C_6F_5)_4]} & & \mathbf{6} \qquad\qquad \mathbf{7[B(C_6F_5)_4]} \end{array} \quad (9)$$

In conclusion, we report a rare example of a metal free system that results in the complete cleavage of the C-O bond in CO and full 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 and expect to uncover further unusual reactivity.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, compound characterisation data, NMR spectra and crystallographic data. CCDC 1058783 - 1058784 See DOI: 10.1039/c000000x/

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