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ARTICLE

Frustrated Lewis pairs incorporating the bifunctional Lewis acid 1,1'-fc{B(C_6F_5)$_2$}$_2$: reactivity towards small molecules

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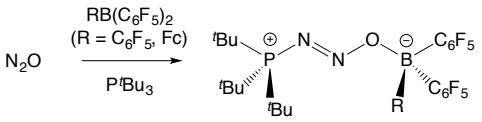
Applications of the bifunctional ferrocene-diyl Lewis acid 1,1'-fc{B(C_6F_5)$_2$}$_2$ in frustrated Lewis pair (FLP) chemistry are described. The coordination (or otherwise) of a range of sterically encumbered C-, N- and P-centred Lewis bases has been investigated, with lutidine, tetramethylpiperidine, PPh_3, P^tBu_3 and the expanded ring carbene 6Dipp being found to be sterically incapable of coordinate bond formation. The chemistry of a range of these FLPs in the presence of H_2O, NH_3, CO_2 and cyclohexylisocyanate (CyNCO) has been investigated, with the patterns of reactivity identified including simple coordination chemistry, E-H bond cleavage and C-B insertion.

Introduction

The exploitation of frustrated Lewis pairs (FLPs) constitutes a significant development in the fields of small molecule activation and catalysis over the past decade.[1-3] The cooperative use of sterically unquenched Lewis acid and Lewis basic sites facilitates transformations more typically associated with transition metal complexes.[3] Since the first example of their use in the heterolytic cleavage of H_2 was described in 2006,[2] numerous applications have been reported in the activation of other E-H bonds (e.g. E = B, C, N, O, Si), and in the binding of small molecules, including atmospheric oxides (such as CO, CO_2, NO, N_2O, and SO_2).[3] While the Lewis acid component of a large number of these FLP systems is the commercially available perfluoroaryl borane B(C_6F_5)$_3$, examples featuring other neutral boranes,[4] heavier Group 13 analogues,[5] borenium cations,[6] and Lewis acids from the *d*-block have also emerged.[7]

FLPs that contain a ferrocenyl reporter unit offer the possibility for inducing a measurable electrochemical and/or colorimetric response on small molecule capture,[8,9] and therefore have potential uses in detection. Two approaches in this area are exemplified by the Fe(η^5-C_5Ph_5)(η^5-$C_5H_4P^tBu_2$)/B(C_6F_5)$_3$ system in which the Lewis basic phosphine unit contains a ferrocenyl substituent,[10] and by recent work from our laboratory utilizing the ferrocenyl borane Fe(η^5-C_5H_5){η^5-C_5H_4B(C_6F_5)$_2$} [= FcB(C_6F_5)$_2$, **1**],[11] a compound which was previously reported by Piers and co-workers.[12a] In terms of small molecule capture, the P^tBu_3/**1** FLP binds N_2O intact to generate the ambiphilic adduct $^tBu_3P{\cdot}N_2O{\cdot}$**1** (Scheme 1); while similar chemistry also occurs with P^tBu_3/B(C_6F_5)$_3$, the formation of $^tBu_3P{\cdot}N_2O{\cdot}$**1** is signalled by a maroon-to-amber colour change and a shift of 300 mV in the $Fe^{II/III}$ redox potential.[11,13]



Scheme 1 Binding of N_2O by FLPs featuring P^tBu_3 and either B(C_6F_5)$_3$ or **1**.[11,13]

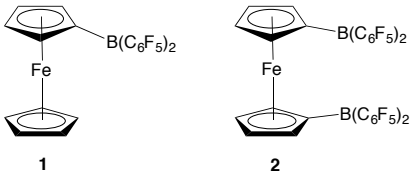


Figure 1 Ferrocenyl and ferrocene-diyl based Lewis acids FcB(C_6F_5)$_2$ (**1**) and 1,1'-fc{B(C_6F_5)$_2$}$_2$ (**2**) [Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4); 1,1'-fc = Fe(η^5-C_5H_4)$_2$].

Although this N_2O detection protocol illustrates the potential of ferrocenyl boranes in FLP chemistry, we wanted to probe the broader scope of this approach, by exploiting other boranes incorporating metallocene scaffolds. In particular, we hypothesized that 1,1'-fc{B(C_6F_5)$_2$}$_2$ (**2**) might be of interest, due to (i) its potential to act as a bifunctional (potentially chelating) Lewis acid to trap substrates bearing geometrically divergent Lewis basic sites; and (ii) its stronger Lewis acidity, in comparison to monofunctional **1** (Figure 1).[12] This observation reflects the π electron-withdrawing nature of the additional -B(C_6F_5)$_2$ group, and the fact that through-space donation from the electron-rich iron centre to the individual pendant borane function(s) is less pronounced when there are two such groups.[12]

With this in mind, we set out to explore the potential for **2** to act as the Lewis acid component in FLPs featuring a range of

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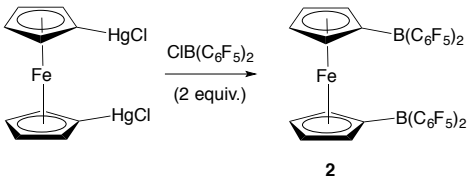
Electronic Supplementary Information (ESI) available: CIFs relating to the X-ray crystal structures; these are also available from the CCDC, reference numbers 954137, 1576950-1576952 and 1582718. See DOI: 10.1039/x0xx00000x

C-, N- and P-donors, and subsequently to probe the use of such systems in the activation of small molecules such as H_2O, NH_3 and CO_2. We report the results of these studies in this manuscript.

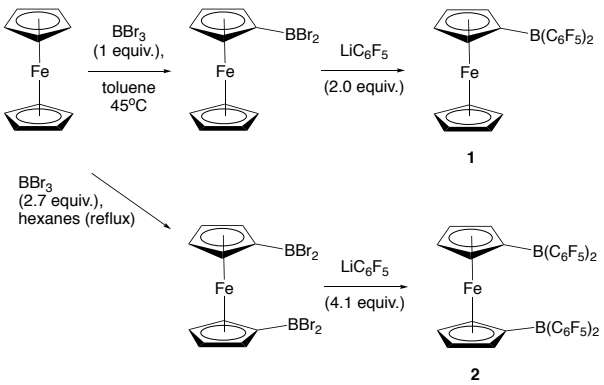
Results and discussion

Alternative synthesis of 1,1'-fc{B(C$_6$F$_5$)$_2$}$_2$ (2)



Scheme 2 Literature synthesis of 1,1'-fc{B(C$_6$F$_5$)$_2$}$_2$ (**2**).[12b]

Piers and co-workers have reported the synthesis of **2** from 1,1'-fc(HgCl)$_2$ and ClB(C$_6$F$_5$)$_2$ (Scheme 2).[12b] Generation of the ClB(C$_6$F$_5$)$_2$ precursor involves the synthesis of Me$_2$Sn(C$_6$F$_5$)$_2$ from LiC$_6$F$_5$, and its subsequent reaction with BCl$_3$ at elevated temperature/pressure.[12c] With this in mind, a more direct synthesis from LiC$_6$F$_5$ was targeted, drawing on the route which we have previously developed to prepare **1** from FcBBr$_2$ (Scheme 3).[14] The one-pot literature synthesis of bifunctional 1,1'-fc(BBr$_2$)$_2$ from ferrocene and BBr$_3$,[15] is followed by reaction with slightly greater than four equivalents of LiC$_6$F$_5$, generated *in situ* from ^{n}BuLi and C$_6$F$_5$Br. Although LiC$_6$F$_5$ is notoriously explosive above -40°C, the synthetic protocol that we employ means that [as in the synthesis of Me$_2$Sn(C$_6$F$_5$)$_2$] it never warms above -78°C, and so can be safely and reproducibly used in the synthesis of **2**. Following this procedure, **2** can be isolated after extraction into hot hexane with a yield (*ca.* 50%) broadly comparable to that reported by Piers (up to 40%).[12b]



Scheme 3 (upper) Synthesis of **1** from FcBBr$_2$, and (lower) modification for the synthesis of **2** from 1,1'-fc(BBr$_2$)$_2$. **Caution: the reaction temperature must be kept below -40°C at all times when handling LiC$_6$F$_5$.**

Interaction of Lewis Bases with 2

The sterically unencumbered tertiary phosphine Me$_3$P is known to form a 2:1 adduct with **2**, through the formation of two P→B coordinate bonds.[12b] The donor/acceptor chemistry of **1** has been explored in greater depth,[11a] and the combination with the much bulkier P^{t}Bu$_3$, for example, is known to constitute an FLP. With this in mind, the interaction of **2** with a range of bulky C-, N- and P-donor Lewis bases was investigated, with the aim of identifying FLP systems for further reactivity studies.

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(a) N-heterocyclic carbenes. **1** has previously been shown to form classical Lewis acid-base adducts with the bulky N-aryl substituted imidazolylidene donors IMes and IDipp, together with the less strongly donating, backbone-chlorinated carbene IMesCl$_2$ (Figure 2).[11a] These NHCs were therefore thought to provide a suitable comparative starting point for the exploration of the coordination behaviour of **2**. In addition, the behaviour of **2** in the presence of the more sterically encumbered (and more strongly σ-donating) expanded ring systems 6Mes and 6Dipp was also to be probed.[17]

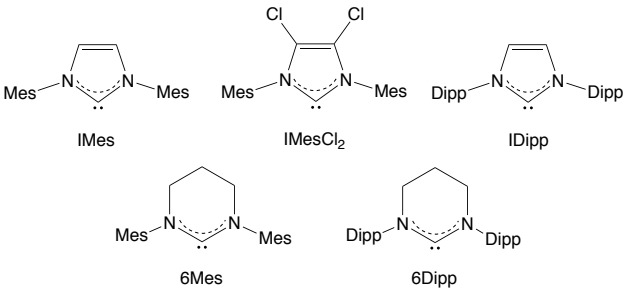


Figure 2 N-heterocyclic carbenes (NHCs) utilized in the current study.

The addition of IMes to **2** in a 2:1 molar ratio results in an immediate colour change from violet to orange, and the appearance of a ^{11}B NMR resonance at δ_B = -14 ppm, consistent with the formation of a tetra-coordinate borate through coordination of the IMes donor.[11a] ^{1}H NMR spectroscopy suggests that two molecules of NHC have been assimilated and that the 'normal' C2-mode of carbene binding pertains, with signals at δ_H = 7.46 and 7.59 ppm corresponding to the backbone N(CH)$_2$N protons (albeit with loss of the plane of symmetry). The formation of a low symmetry adduct is also consistent with the observation of ten distinct signals in the ^{19}F NMR spectrum (indicating that the equivalence between the *ortho*, *meta* and *para* fluorines of the two perfluorophenyl rings had been lost); a similar pattern of ^{19}F signals is observed in the ^{19}F spectrum of the corresponding monofunctional adduct **1**·IMes, and has been ascribed to restricted rotation about the sterically congested B-C bonds on the timescale of the NMR experiment.[11a]

In the case of **2**, the molecular structure derived from X-ray crystallography confirms the formulation of the adduct as 1,1'-fc{B(C$_6$F$_5$)$_2$·IMes}$_2$ (**2**·(IMes)$_2$, Figure 3). The solid-state structure possesses approximate (non-crystallographic) C_2 symmetry, and the fact that this adduct displays the same number of ^{19}F NMR resonances as **1**·IMes presumably reflects a similar symmetry relationship between the two -B(C$_6$F$_5$)$_2$·IMes functions in solution. Bond metrics associated with the borate functions (for example B-C distances) are essentially identical to those measured for **1**·IMes,[11a] reflecting the fact that there is relatively little

geometric perturbation around the boron centre induced by the presence of the second borate function.

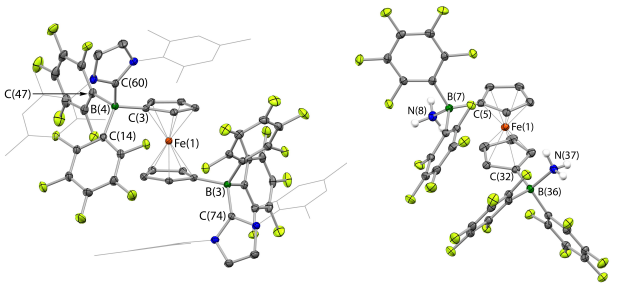


Figure 3 Molecular structures of (left) 1,1'-fc{$B(C_6F_5)_2$·IMes}$_2$, **2**·$(IMes)_2$ and (right) 1,1'-fc{$B(C_6F_5)_2$·NH_3}$_2$, **2**·$(NH_3)_2$, with thermal ellipsoids set at the 35% probability level. Selected hydrogen atoms and solvate molecules omitted and mesityl groups shown in wireframe format for clarity. Selected bond lengths (Å) and angles (°): [for **2**·$(IMes)_2$] B(4)-C(60) 1.675(5), B(4)-C(3) 1.638(5), B(4)-C(14) 1.666(5), B(4)-C(47) 1.676(5), C(3)-B(4)-C(14) 113.9(3), C(3)-B(4)-C(47) 106.0(3), C(14)-B(4)-C(47) 111.2(3); [for **2**·$(NH_3)_2$] B(7)-N(8) 1.624(2), B(7)-C(5) 1.601(2), B(7)-C(9) 1.648(2), B(7)-C(20) 1.639(2), B(36)-N(37) 1.627(2), B(36)-C(32) 1.600(2), B(36)-C(38) 1.649(2), B(36)-C(49) 1.638(2), C(5)-B(7)-C(9) 115.9(1), C(5)-B(7)-C(20) 113.3(1), C(9)-B(7)-C(20) 106.5(1), C(32)-B(36)-C(38) 114.4(1), C(32)-B(36)-C(49) 114.4(1), C(38)-B(36)-C(49) 108.9(1).

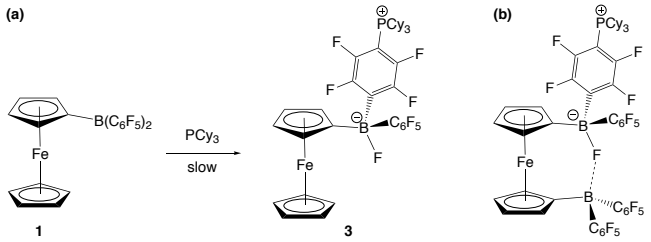
The reaction between IMes and **2** was also examined in a 1:1 molar ratio. However, monitoring by ^{19}F NMR suggests that this results in the formation of a mixture of the 1:1 adduct, the 2:1 adduct [i.e. **2**·$(IMes)_2$], and unreacted borane starting material. Ten resonances due to **2**·$(IMes)_2$ are observed, alongside signals corresponding to the free Lewis acid and further signals, presumed to be derived from the 1:1 adduct. This inference is supported by the ^{11}B NMR spectrum, which features a sharp signal at -13.7 ppm, consistent with the borate functions in the 2:1 adduct, alongside a broad signal consistent with uncomplexed three-coordinate borane centres. The observation of a mixture of products suggests that IMes binding at the two borane functions is essentially independent, consistent with the conformationally flexible nature of the ferrocene-diyl core.

Given the diagnostic nature of the ^{11}B and ^{19}F signals associated with adduct formation, these measurements were then used to determine the course of the reactions of **2** with other NHCs. Thus, signals in the range δ_B = -10 to -13 ppm were observed on addition of two equivalents of $IMesCl_2$, IDipp or 6Mes (with the solution in each case turning an orange colour), with the respective ^{19}F NMR spectra displaying a similar ten-resonance pattern to that measured for **2**·$(IMes)_2$. By contrast, on addition of 6Dipp to **2**, the deep maroon colour of the solution is retained, and ^{1}H, ^{11}B and ^{19}F NMR spectra could be used to establish that no substantive reaction has taken place. In particular, the ^{11}B and ^{19}F signals are unshifted from those of the starting material **2**, and the ^{1}H NMR spectrum consists of the superposition of the signals due to 6Dipp and **2**. In this case *alone* it appears that the NHC and **2** constitute an unquenched FLP, an observation consistent with the larger steric demands of the 6Dipp ligand (%V_{bur} = 50.8 *vs.* 36.5, 44.5 and 42.2 for IMes, IDipp and 6Mes).[18,19]

(b) Nitrogen and phosphorus-centred donors. We have also probed the interactions of a range of tertiary phosphines and bulky N-donor Lewis bases with **2**. Both lutidine (2,6-dimethylpyridine) and tetramethylpiperidine give rise to FLPs in benzene-d_6 solution, as do PPh_3 and P^tBu_3, the latter two being characterized by unchanged ^{31}P resonances at -5.4 and 61.9 ppm, respectively. By contrast, the combination of **2** and P^nBu_3 can be shown to result in an immediate reaction, and multinuclear NMR studies are consistent with classical adduct formation. The single broad peak at δ_B = -11.0 ppm is indicative of a four-coordinate borate centre, and the signal at δ_P = -2.9 ppm is consistent with the ^{31}P shift measured for the known compound $^nBu_3P{\cdot}B(C_6F_5)_3$.[20] The chemical shift difference between the *meta* and *para* ^{19}F NMR signals, $\Delta\delta_{m,p}$ is known to decrease on quaternization at boron, and has therefore been widely used to probe the interactions of Lewis bases with boranes containing the $B(C_6F_5)$ moiety.[21] In this case, the decrease in the value of $\Delta\delta_{m,p}$ determined from ^{19}F NMR (from 10.7 ppm for **2** to 5.8 ppm) also supports the idea that a classical phosphine-borane adduct has been formed.

The combination of PCy_3 and **1** has previously been shown by *in situ* NMR measurements to result in the formation of an FLP in benzene-d_6 solution.[11a] However, evidence can also be obtained for the formation of a minor co-product over a period of *ca.* 2 weeks at room temperature (Scheme 4a). Although the overwhelmingly dominant species present in solution at this point are still **1** and PCy_3, the minor product can be crystallized and shown by X-ray crystallography to be the zwitterion Fc{B(F)$(C_6F_5)$$(C_6F_4PCy_3$-4)} (**3**), derived from S_NAr attack by the phosphine at the *para* position of one of the perfluorophenyl rings of the Lewis acid, with accompanying migration of fluoride to the boron centre (Figure 4). Spectroscopically, this chemistry is characterised by diagnostic signals in the ^{11}B and ^{19}F NMR spectra at δ_B = 2.0 ppm and δ_F = – 193.7 ppm associated with the boron-bound fluoride, and a shift in the ^{31}P NMR spectrum from the free phosphine at δ_P = 9.7 ppm to 39.9 ppm. Very similar NMR signals are observed for the related system derived from the analogous activation of $B(C_6F_5)_3$, *i.e.* B(F)$(C_6F_5)_2(C_6F_4PCy_3$-4) (δ_B = -0.7 ppm, δ_P = 41.6 ppm).[22]

The combination of PCy_3 with **2** was therefore investigated in a 2:1 molar ratio. While there was no immediate colour change on mixing, ^{1}H, ^{11}B, ^{19}F and ^{31}P NMR spectra measured



Scheme 4 (a) Minor reaction pathway of PCy_3 with **1**, proceeding via nucleophilic attack at the para C-F bond of a C_6F_5 group to give **3**. (b) Proposed structure of the product of the reaction of **2** with PCy_3.

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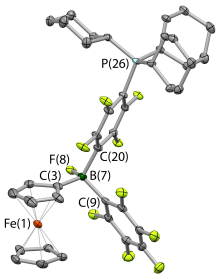

Figure 4 Molecular structure of Fc{B(F)(C_6F_5)($C_6F_4PCy_3$-4)}, **3**, with thermal ellipsoids set at the 35% probability level; hydrogen atoms for clarity. Selected bond lengths (Å) and angles (°): B(7)-F(8) 1.426(2), B(7)-C(3) 1.613(3), B(7)-C(9) 1.660(3), B(7)-C(20) 1.682(3), C(3)-B(7)-C(9) 110.1(2), C(3)-B(7)-C(20) 114.0(2), C(9)-B(9)-C(20) 108.2(2).

after 1 h show that a reaction has taken place. A broad upfield-shifted resonance is observed in the ^{11}B NMR spectrum at δ_B = 2.6 ppm, and a signal at δ_P = 40.1 ppm in the ^{31}P NMR spectrum; both are suggestive of an S_NAr type reaction similar to that observed for PCy_3/**1**. The ^{19}F NMR spectrum is more complex. In the case of Fc{B(F)(C_6F_5)($C_6F_4PCy_3$-4)} (**3**), six resonances are observed, corresponding to the boron-bound fluoride, the *ortho*, *meta* and *para* fluorines of the unreacted -C_6F_5 moiety, and two signals for the *para* -$C_6F_4PCy_3$ moiety. If analogous reactivity were to take place at both borane functions in **2**, then either six or twelve signals might be expected, depending on whether the two borate units are symmetry-related on the NMR timescale. On the other hand, if reaction were to take place at only one of the two borane units, then (superficially) nine signals would be expected, with the additional three arising from the perfluoroaryl rings associated with the unreacted borane centre. In this case twelve ^{19}F signals are observed, but paradoxically, the ^{1}H and ^{31}P NMR data are consistent with the take-up of only one phosphine unit. Half of the added PCy_3 remains unreacted.

Of the twelve ^{19}F resonances observed, six can readily be assigned to fluorine environments analogous to those in **3**, on the basis of their very similar pattern of chemical shifts (including a resonance at -194.9 ppm, indicative of a boron-bound fluoride). The additional six signals, come in three pairs, suggesting that they arise from the *ortho*, *meta* and *para* fluorines of an unreacted -B(C_6F_5)$_2$ moiety, in which the equivalence of the two perfluoroaryl rings has been lost. Such inequivalence is presumably caused by restricted rotation about the B-C_{Cp} bond, which might arise either as a result of the increased steric bulk of the peripheral borate centre, or due to an interaction between the borane and the boron-bound fluoride (Scheme 4b). Some evidence for the latter comes from analysis of the magnitude of the $\Delta\delta_{m,p}$ splittings derived from the ^{19}F NMR data (using in the case of the -B(C_6F_5)$_2$ unit, the mean chemical shift difference between *meta* and *para* resonances). $\Delta\delta_{m,p}$ has a value of 10.7 ppm for starting material **2**, this being reduced to 4.4 ppm for the C_6F_5 group of the borate function (*cf*. 3.6 ppm for the analogous C_6F_5 unit in **3**). That determined for the –B(C_6F_5)$_2$ group is 7.2 ppm (*i.e.* intermediate between borate and 'free' borane), and is therefore potentially suggestive of a weak secondary donor/acceptor interaction (Scheme 4b).[23]

Interestingly, and in contrast to PCy_3/**1**, NMR data for PCy_3/**2** show no evidence of unreacted **2** (*i.e.* FLP formation does not occur) - an observation consistent with the enhanced electrophilicity of **2** compared to **1**. It is also noteworthy that (despite the 2:1 molar ratio) PCy_3 does not appear to react at the second B(C_6F_5)$_2$ unit in **2**. Potentially, this can be attributed to the reduced electrophilicity of the remaining -B(C_6F_5)$_2$ unit on conversion of the first to an electron-donating fluoroborate function.[9h]

Reactions of small molecules with FLPs derived from 2

With the potential for **2** to function as an FLP in conjunction with sterically encumbered bases established, we focussed on exploring the chemistry of such systems in small molecule activation. In common with **1**, we find that combinations of **2** with any of PPh_3, P^tBu_3, or 6Dipp (or for that matter the N-donors lutidine or tetramethylpiperidine) do not activate H_2 either under ambient conditions or on heating to 350 K. Such observations are consistent with the electron-donating nature of the ferrocene-diyl substituent and the consequently reduced Lewis acidity at boron compared to B(C_6F_5)$_3$.[17,24] As such, we hypothesized that the bifunctional nature of Lewis acid **2** might be better suited to the cleavage (or capture) of small molecules which yield Lewis bases that can be bound in a chelating fashion (Figure 5). We therefore examined the reactivity of **2** towards H_2O, NH_3 and CO_2 (plus CO_2 surrogates of the type RNCO).

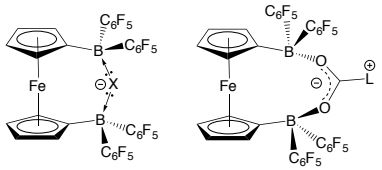

Figure 5 Postulated binding motifs in small molecule capture/activation using FLPs containing **2**.

The combination of **2** and P^tBu_3 reacts very readily with water via O-H bond cleavage. The dark maroon colour of **2** in benzene-d_6 solution turns to a yellow-orange, and over 24 hours the formation of a yellow crystalline product is observed. *In situ* ^{1}H, ^{11}B, ^{19}F and ^{31}P NMR studies give an indication as to the nature of the reaction taking place. Thus, the ^{31}P spectrum shows a single peak at δ_P = 58.3 ppm corresponding to the phosphonium cation, $[HP^tBu_3]^+$, and the ^{19}F NMR spectrum shows three resonances, shifted from those in the starting material, and with a significant decrease in $\Delta\delta_{m,p}$ compared to **2** (4.4 *cf.* 10.7 ppm). A large upfield shift in the ^{11}B NMR signal is also observed (to δ_B = 2.0 ppm), characteristic of the transformation of a three-coordinate borane to a four-coordinate borate. Moreover, single crystals suitable for X-ray crystallography could be obtained by recrystallization from chloroform. The solid-state structure so obtained confirms the nature of the product as $[HP^tBu_3]$[1,1'-fc{B(C_6F_5)$_2$}$_2$(μ-OH)] (i.e. $[HP^tBu_3]$[**2**·(μ-OH)]), featuring a

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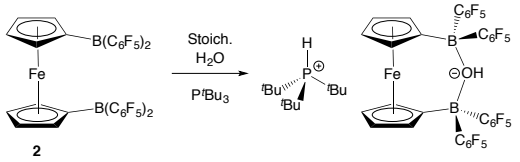
hydroxide ion bridging symmetrically between the two boron centres in the anionic component. (Scheme 5 and Figure 6).[25,26] From a geometric perspective, the hydroxide binding motif is similar to that observed in the zwitterionic cobaltocenium system $Co(C_5H_4BF_2)_2(\mu\text{-}OH)$ reported by Herberich and co-workers, with the B-O bond distances being comparable for the two adducts [1.569(2)/1.563(2) vs. 1.521(3)/1.556(3) Å, respectively].[27]



Scheme 5 Reaction of P^tBu_3/**2** with water.[24]

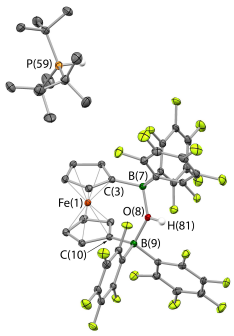


Figure 6 Molecular structure of $[HP^tBu_3][1,1'\text{-}fc\{B(C_6F_5)_2\}_2(\mu\text{-}OH)]$, $[HP^tBu_3][\mathbf{2}^-(\mu\text{-}OH)]$, with thermal ellipsoids set at the 35% probability level; hydrogen atoms (except those originating from H_2O) and solvate molecules omitted for clarity. Selected bond lengths (Å) and angles (°): B(7)-O(8) 1.569(2), B(9)-O(8) 1.563(2), B(7)-C(3) 1.596(2), B(7)-C(37/48) 1.660(2)/1.664(2), B(9)-C(10)1.593(2), B(9)-C(15/26) 1.652(2)/1.662(2), B(7)-O(8)-B(9) 139.9(1), C(3)-B(7)-C(37) 109.1(1), C(3)-B(7)-C(48) 116.2(1), C(37)-B(7)-C(48) 105.7(1), C(10)-B(9)-C(15) 109.4(1), C(10)-B(9)-C(26) 114.7(1), C(15)-B(9)-C(26) 107.4(1).

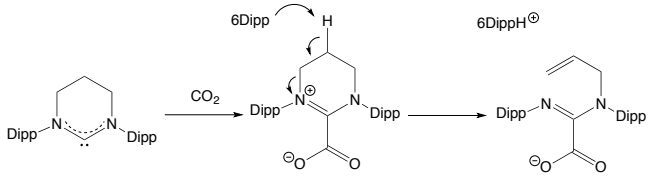
Given the vast disparity in the pK_as of H_2O and $[HP^tBu_3]^+$ (*ca.* 31.2 and 11.4, respectively in DMSO)[28,29] the cleavage of water by P^tBu_3/**2**, presumably relies very heavily from a thermodynamic viewpoint on the role of **2** as a chelating Lewis acid to sequester OH^-. With this in mind, we were also interested in examining the behaviour of this FLP in the presence of ammonia (pK_a *ca*. 41 in DMSO),[28] hypothesizing that a similar mode of binding might be possible with NH_2^-. Thus, a 'free-pump-thaw' degassed solution of P^tBu_3/**2** was exposed to NH_3 (at 1 atm. pressure) and stirred for 4 hours. The resulting yellow crystalline product was crystallized from a concentrated diethyl ether solution. However, the isolated material does not give rise to any ^{31}P NMR signals, and *in situ* measurements of the reaction mixture show a single peak at δ_P = 61.9 corresponding to free P^tBu_3. The ^{11}B NMR spectrum of the isolated product shows a single sharp resonance at δ_B = -8.7 ppm, and the ^{19}F NMR spectrum shows three signals at δ_F =-133.3, -156.2 and -162.7 ppm ($\Delta\delta_{m,p}$ = 6.5 ppm), diagnostic of a binding event occurring at both borane centres. The ^1H NMR signal corresponding to the NH unit integrates for six protons, suggesting formation of the bis-ammonia adduct, 1,1'-fc$\{B(C_6F_5)_2\cdot NH_3\}_2$ [i.e. **2**$\cdot(NH_3)_2$]. In order to confirm the formation of this adduct structurally, a higher yielding synthesis was developed via condensation of liquid ammonia onto solid **2**. An immediate colour change was observed from deep purple to pale yellow, and (after venting the excess ammonia) crystals suitable for X-ray crystallography could be grown from diethyl ether solution. The structure so obtained (Figure 3) confirms the formation of **2**$\cdot(NH_3)_2$. Geometrically the structure has much in common with that of **2**$\cdot(IMes)_2$ (also Figure 3), with the slightly less pyramidalized nature of the BC_3 fragments [$\Sigma(\angle$C-B-C) = 336.7° (mean) cf. 330.0° (mean) for $\mathbf{2}^-(IMes)_2$] presumably reflecting the differing donor capabilities of ammonia and IMes.

Clearly this phosphine-based FLP system does not have sufficient unquenched reactivity to deprotonate ammonia. On the other hand, NHCs have been shown to be basic enough to deprotonate the adduct $H_3N\cdot B(C_6F_5)_3$.[30] Imidazolylidene donors form (unreactive) classical donor/acceptor adducts with **2**, but the combination with the bulkier expanded ring NHC 6Dipp constitutes an FLP. Attempts were therefore made to activate ammonia using the 6Dipp/**2** system: however, these also resulted in the isolation of **2**$\cdot(NH_3)_2$. Presumably the 2:1 adduct is formed very rapidly, and essentially irreversibly, on exposure of the FLP to ammonia; in the absence of the possibility for chelation (due to 'blocking' of the second Lewis acid function by NH_3), 6Dipp is not sufficiently basic to deprotonate the bound NH_3. Given that ItBu will deprotonate $H_3N\cdot B(C_6F_5)_3$,[30] and that expanded ring NHCs are typically more basic than their imidazolylidene counterparts,[31] this observation again reflects the weaker intrinsic Lewis acidity of the individual boron centres in **2** compared to $B(C_6F_5)_3$.[12a]

FLP systems featuring **1** as the Lewis acid component are not able to bind/activate CO_2 (in contrast to $P^tBu_3/B(C_6F_5)_3$, for example).[31] With this in mind, analogous FLPs containing **2** were targeted, it being not only a stronger Lewis acid, but also bifunctional, and hence potentially complementary to the Lewis basic component formed in the reaction of a phosphine/NHC with CO_2 (Figure 5). However, benzene solutions containing either the P^tBu_3/**2** or tetramethylpiperidine/**2** FLP, show no propensity to bind CO_2, either at room temperature or 350 K. Both tertiary phosphines and secondary amines have previously been shown to be capable of binding CO_2 in conjunction with $B(C_6F_5)_3$, and the failure of systems containing **2** to act in a similar manner presumably also reflects its weaker Lewis acidity.[32]

The 6Dipp/**2** FLP features the strongest Lewis base under investigation, and it was postulated that this system might therefore be capable of binding CO_2. In our hands, however, we find that this reaction does not proceed cleanly, and when using benzene as the solvent, significant precipitate is formed. In previous examples of CO_2 capture by NHC-containing FLPs, an initial activation step is observed involving nucleophilic attack by the carbene at the carbon atom of CO_2, before trapping of the resulting betaine derivative by the Lewis acid component.[32c] The reaction of 6Dipp with CO_2 was therefore investigated *in the absence of* **2** in an attempt to shed light on the course of the reaction. Exposure of a benzene solution of

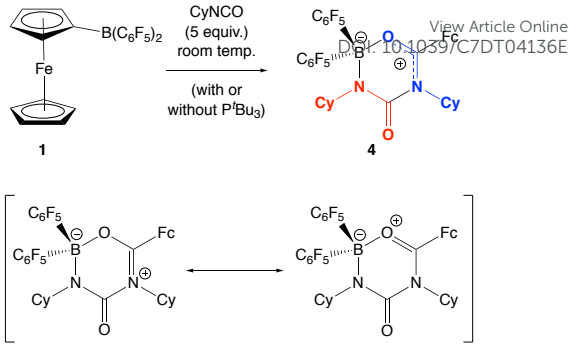
6Dipp to CO_2 (at *ca.* 1 atm. pressure), results in immediate formation of an off-white precipitate. Moreover, investigation of this material by ^{1}H NMR (in bromobenzene-d_5), reveals signals characteristic of the formamidinium cation $[(6Dipp)H]^+$, together with three multiplet resonances at 6.15, 5.14 and 5.10 ppm (integrating to 1H each), corresponding to the alkenic protons of an RCH=CH_2 unit. These observations are consistent with ring opening of the 6Dipp heterocycle via deprotonation at the C5 position (Scheme 6), in a manner analogous to that observed previously for 6Dipp in the presence of other electrophiles (e.g. H^+, $[LAu]^+$).[33] Although the product in this case could not be crystallographically characterized, peak envelopes at *m/z* = 405 and 447 in the positive and negative ESI-MS spectra, respectively, are consistent with the formation of the proposed cationic and anionic components.



Scheme 6 Ring opening of 6Dipp in the presence of CO_2.

In the absence of clean reactivity leading to the trapping of carbon dioxide by FLPs containing **2**, attention was turned to more reactive CO_2 surrogates, such as isocyanates. The reaction of P^tBu_3/**2** with CyNCO gives a complex mixture of products, and so to simplify matters, the analogous chemistry employing monofunctional **1** was probed. However, as in the case of the P^tBu_3/**2** system, the ^{31}P NMR spectrum measured *in situ* implies no net involvement of the phosphine, with an unshifted resonance being observed at δ_P = 61.9 ppm. A control reaction (without P^tBu_3) generates the same product (albeit more slowly), which gives rise to signals in the ^{11}B and ^{19}F NMR spectra consistent with the formation of a four-coordinate boron centre. In addition, a peak envelope centred at *m/z* = 780 in the ESI-MS spectrum is consistent with the assimilation of two molecules of CyNCO (Scheme 7). Crystals of the product, **4**, were obtained by slow cooling of a solution in benzene-d_6, and X-ray crystallography was used to unambiguously determine the connectivity associated with insertion of two molecules of CyNCO into the C_{Cp}-B bond of **1** (Figure 7).

The molecular structure is based around a non-planar six-membered CNCNBO heterocycle featuring a pendant carbonyl function. Analysis of the bond lengths within the heterocycle suggest that there is some degree of delocalized π character within the O(13)-C(12)-N(17) unit [*d*{C(12)-O(13)} = 1.288(2) Å] and also within the amido function defined by N(15)-C(16)-O(24) [*d*{N(15)-C(16)} = 1.332(3) Å]. The relatively long C(16)-N(17) distance [1.475(2) Å], on the other hand, suggests less significant delocalization *between* these two fragments.



Scheme 7 Reaction of CyNCO with the P^tBu_3/**1** FLP (or with **1** alone), leading to the formation of **4**.

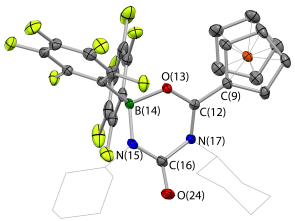
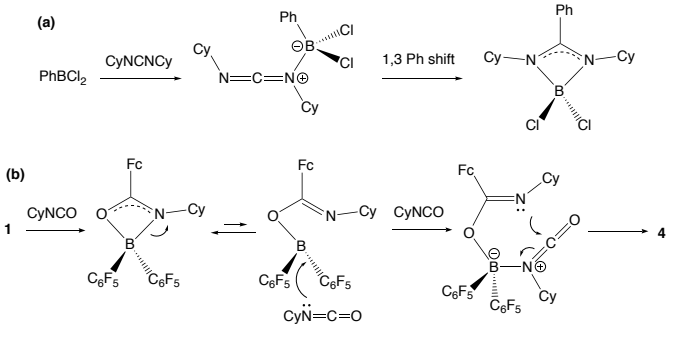


Figure 7 Molecular structure of **4**, with thermal ellipsoids set at the 35% probability level; hydrogen atoms and solvate molecules omitted, and cyclohexyl groups shown in wireframe format for clarity. Selected bond lengths (Å): C(9)-C(12) 1.452(2), C(12)-O(13) 1.288(2), O(13)-B(14) 1.534(2), B(14)-N(15) 1.533(3), N(15)-C(16) 1.332(3), C(16)-N(17) 1.475(2), C(12)-N(17) 1.340(3), C(16)-O(24) 1.215(3).

The insertion of heterocumulenes of this sort into reactive B-C bonds is by no means unprecedented. Cowley and co-workers have reported the insertion of dicyclohexyl carbodiimide into the B-C bond of $PhBCl_2$ to give the benzamidinate system $\{PhC(CyN)_2\}BCl_2$ (Scheme 8a),[34,35] and a similar initial step in the reaction of **1** with CyNCO would generate a closely-related BNCO four-membered ring via migration of the more nucleophilic ferrocenyl fragment (*cf.* C_6F_5; Scheme 8b). The more electrophilic nature of the boron centre in this intermediate then presumably facilitates nucleophilic attack by a second equivalent of the isocyanate, with subsequent ring-closure generating the observed 6-membered heterocyclic product.



Scheme 8 (a) Mechanism for the insertion of a carbodiimide into the B-C bond of $PhBCl_2$ as reported by Cowley and co-workers;[34] (b) potential mechanism for the double insertion of cyclohexyl isocyanate into the B-C_{Cp} bond of **1** to give **4**.

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Experimental

CAUTION: SOLUTIONS CONTAINING LiC_6F_5 ARE KNOWN TO EXPLODE AT TEMPERATURES IN EXCESS OF -40°C.

General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen, respectively. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS. NMR spectra were recorded in chloroform-d, benzene-d_6, bromobenzene-d_5 or THF-d_8, which were dried over molecular sieves, potassium, calcium hydride or calcium hydride respectively, and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury-VX-300 or Bruker AVII-500 spectrometers and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{11}B, ^{19}F and ^{31}P NMR spectra were referenced with respect to $Et_2O{\cdot}BF_3$, $CFCl_3$ and 85% aqueous H_3PO_4, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. UV-vis spectra were collected on a Scintio UV S-2100 UV/Vis spectrometer. Elemental analyses were carried out at London Metropolitan University. BrC_6F_5, ^{n}BuLi, P^tBu_3, PPh_3, lutidine, tetramethylpiperidine, ammonia and carbon dioxide were sourced commercially. 1,1'-fc$(BBr_2)_2$, $FcB(C_6F_5)_2$ (**1**), and NHCs (IMes, IDipp, $IMesCl_2$, 6Mes and 6Dipp) were prepared by literature routes.[14,15,36]

Syntheses of novel compounds

1,1'-fc{$B(C_6F_5)_2$}$_2$ (2): To a solution of bromopentafluorobenzene (5.89 mL, 47.5 mmol) in hexane (30 mL) at -78˚C, was added dropwise ^{n}BuLi (29.7 mL of a 1.6 M solution, 47.5 mmol) and the mixture stirred at -78˚C for 45 min. **CAUTION: LiC_6F_5 IS KNOWN TO EXPLODE AT TEMPERATURES ABOVE -40°C.** A solution of 1,1'-fc$(BBr_2)_2$ (6.10 g, 11.6 mmol) also in hexane (150 mL), was then added dropwise at -78°C, and the resulting mixture allowed to warm slowly to room temperature over a period of 12 h. After removal of volatiles *in vacuo* the product was extracted into hot hexane. Further removal of the volatiles *in vacuo*, and washing of the resulting solid with pentane, yielded a dark purple solid which was dried thoroughly, and found to be of sufficient purity for subsequent chemistry without further recrystallization. Yield: 5.45 g, 54%. ^{1}H, ^{11}B and ^{19}F NMR data agree with literature values.[12b]

General procedure for investigating the formation of Lewis base adducts of 2: The procedure is exemplified for the case of IMes in a 2:1 molar ratio. This and other Lewis bases were probed in both 2:1 and 1:1 molar ratios. In the case of 1,1'-fc{$B(C_6F_5)_2{\cdot}$IMes}$_2$, **2**·$(IMes)_2$, the product was isolated and characterized by standard spectroscopic, analytical and crystallographic methods. For other Lewis bases, *in situ* ^{11}B and ^{19}F NMR data (based on those measured for **2**·$(IMes)_2$) were used to determine whether or not a classical Lewis acid/base adduct was formed. IMes (0.035 g, 0.116 mmol) and **2** (0.100 g, 0.058 mmol) were dissolved in the minimum benzene required to dissolve all solid material (*ca.* 5 mL), and the reaction mixture stirred for 24 h at room temperature. Volatiles were then removed *in vacuo*, and the product recrystallized from THF/hexane as single crystals suitable for X-ray crystallography. Yield: 0.056 g, 65%.

Characterizing data for 2·$(IMes)_2$: ^{1}H NMR (500 MHz, THF-d_8, 20°C) : δ 7.59, 7.46 (d, $^2J_{H\text{-}H}$ = 2.1 Hz, each 2H, backbone CH of IMes), 6.99, 6.90, 6.70, 6.45 (s, each 2H, IMes aromatic CH), 3.80, 3.55, 3.22, 2.77 (br s, each 2H, CH of Cp), 2.40, 2.24, 2.20, 2.18, 1.98, 1.81 (s, each 6H, Me of IMes). ^{11}B NMR (128 MHz, THF-d_8, 20°C): δ -14 (sharp). ^{19}F NMR (377 MHz, THF-d_8, 20°C): δ -117.8 (d, $^3J_{FF}$ = 24.5 Hz, *ortho*-CF of C_6F_5), -119.0 (d, $^3J_{FF}$ = 24.5 Hz, *ortho*-CF of C_6F_5), -123.9 (d, $^3J_{FF}$ = 24.5 Hz, *ortho*-CF of C_6F_5), -128.1 (d, $^3J_{FF}$ = 24.5 Hz, *ortho*-CF of C_6F_5), -163.3 (t, $^3J_{FF}$ = 19.5 Hz, *para*-CF of C_6F_5), -164.1 (t , $^3J_{FF}$ = 20.0 Hz, *para*-CF of C_6F_5), -167.1 (t, $^3J_{FF}$ = 22.1 Hz, *meta*-CF of C_6F_5), -167.4 (t, $^3J_{FF}$ = 22.1 Hz, *meta*-CF of C_6F_5), -167.9 (t, $^3J_{FF}$ = 22.1 Hz, *meta*-CF of C_6F_5), -168.6 (t, $^3J_{FF}$ = 22.1 Hz, *meta*-CF of C_6F_5). Elemental microanalysis: calc. (for $C_{76}H_{56}B_2F_{20}FeN_4$) C 61.53, H 3.81, N 3.78; meas. C 61.88, H 4.01, N 3.66. Crystallographic data: **2**·$(IMes)_2{\cdot}{}^3/_2(THF){\cdot}{}^3/_2$(pentane), $C_{88}H_{83}B_2F_{20}FeN_4O_{1.5}$, M_r = 1678.05, orthorhombic, *P* 2ac 2ab, *a* = 11.4405(1), *b* = 22.3759(2), *c* = 32.0362(2) Å, *V* = 8201.0(1) Å^3, *Z* = 4, ρ_c = 1.359 Mg m^{-3}, *T* = 150 K, λ = 1.54180 Å. 17080 reflections collected, 16778 independent [R(int) = 0.029] used in all calculations. R_1 = 0.0421, wR_2 = 0.1252 for observed unique reflections [I>2σ(I)] and R_1 = 0.0428, wR_2 = 0.1263 for all unique reflections. Max. and min. residual electron densities 0.84 and -0.49 e Å^3. CCDC reference: 1582718.

***In situ* NMR data for 2·$(IMesCl_2)_2$**: ^{11}B NMR (128 MHz, benzene, 20°C): δ -13 (sharp). ^{19}F NMR (377 MHz, benzene, 20°C): δ -117.0 (d, $^3J_{FF}$ = 16.0 Hz, *ortho*-CF of C_6F_5), -118.9 (d, $^3J_{FF}$ = 16.0 Hz, *ortho*-CF of C_6F_5), -122.3 (d, $^3J_{FF}$ = 16.0 Hz, *ortho*-CF of C_6F_5), -128.5 (d, $^3J_{FF}$ = 16.0 Hz, *ortho*-CF of C_6F_5), -159.3 (d, $^3J_{FF}$ = 22.5 Hz, *para*-CF of C_6F_5), -162.0 (d, $^3J_{FF}$ = 22.5 Hz, *para*-CF of C_6F_5), -164.3 (d, $^3J_{FF}$ = 20.9 Hz, *meta*-CF of C_6F_5), -165.4 (d, $^3J_{FF}$ = 20.9 Hz, *meta*-CF of C_6F_5), -166.3 (d, $^3J_{FF}$ = 20.9 Hz, *meta*-CF of C_6F_5), -166.5 (d, $^3J_{FF}$ = 20.9 Hz, *meta*-CF of C_6F_5).

***In situ* NMR data for 2·$(6Mes)_2$**: ^{11}B NMR (128 MHz, benzene, 20°C): δ -11 (sharp). ^{19}F NMR (377 MHz, benzene, 20°C): δ -112.6 (d, $^3J_{FF}$ = 29.7 Hz, *ortho*-CF of C_6F_5), -118.8 (d, $^3J_{FF}$ = 27.4 Hz, *ortho*-CF of C_6F_5), -119.9 (d, $^3J_{FF}$ = 24.5 Hz, *ortho*-CF of C_6F_5), -123.0 (d, $^3J_{FF}$ = 25.4 Hz, *ortho*-CF of C_6F_5), -153.3 (t, $^3J_{FF}$ = 19.4 Hz, *para*-CF of C_6F_5), -158.3 (t , $^3J_{FF}$ = 19.4 Hz, *para*-CF of C_6F_5), -161.2 (t, $^3J_{FF}$ = 21.3 Hz, *meta*-CF of C_6F_5), -163.6 (t, $^3J_{FF}$ = 23.6 Hz, *meta*-CF of C_6F_5), -164.2 (t, $^3J_{FF}$ = 23.9 Hz, *meta*-CF of C_6F_5), -165.6 (t, $^3J_{FF}$ = 21.4 Hz, *meta*-CF of C_6F_5).

***In situ* NMR data for 2·$(P^nBu_3)_2$**: ^{11}B NMR (128 MHz, benzene, 20°C): δ -11 (broad). ^{19}F NMR (377 MHz, benzene, 20°C): δ -126.2 (broad s, *ortho*-CF of C_6F_5), -157.9 (t, $^3J_{FF}$ = 20.3 Hz, *para*-CF of C_6F_5), -163.7 (t, $^3J_{FF}$ = 20.3 Hz, *meta*-CF of C_6F_5). ^{31}P NMR (162 MHz, benzene, 20°C): δ -2.9.

In situ NMR data from the reaction of 2 with PCy_3: (500 MHz, chloroform-d, 20°C): δ 4.42, 4.38, 4.22, 4.09, 3.65, 3.29, 3.11, 3.08 (broad s, each 1H, C_5H_4B), 2.65 (m, 3H, Cy), 2.10-1.22 (overlapping m, 30 H, Cy). ^{11}B NMR (128 MHz, benzene-d_6,

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20°C): δ 32 (very broad), 3 (broad). ^{19}F NMR (377 MHz, benzene-d_6, 20°C): δ -123.4 (s, 2F, C_6F_4), -129.3 (s, *ortho*CF of $B(C_6F_5)_2$), -123.0 (s, *ortho*CF of $B(C_6F_5)_2$), -131.4 (s, 2F, C_6F_4), -131.9 (s, *ortho*CF of $BF(C_6F_4PCy_3)(C_6F_5)$), -156.3 (broad s, *para*-CF of $B(C_6F_5)_2$), -156.7 (broad s, *para*CF of $B(C_6F_5)_2$), -160.1 (s, *para*CF of $BF(C_6F_4PCy_3)(C_6F_5)$), -163.5 (s, *meta*CF of $B(C_6F_5)_2$), -163.9 (s, *meta*CF of $B(C_6F_5)_2$), -164.5 (s, *meta*CF of $BF(C_6F_4PCy_3)(C_6F_5)$), -194.9 (s, BF). ^{31}P NMR (162 MHz, benzene-d_6, 20°C): δ 40.1.

3: A mixture of PCy_3 (0.053 g, 0.19 mmol) and **1** (0.100 g, 0.19 mmol) were dissolved in benzene-d_6 (2 mL) at which point analysis by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy revealed an unquenched mixture of Lewis acid and Lewis base components. After stirring for 10 d, a brown oil formed at the bottom of the reaction vessel; volatiles were removed *in vacuo*, and the resulting residue dissolved in chloroform-d (5 mL) and layered with hexane. A very small quantity of orange crystals was formed, which was isolated by filtration and dried *in vacuo*. Yield: <5%. ^{1}H NMR (500 MHz, chloroform-d, 20°C): δ 4.42 (broad s, 2H, C_5H_4B), 4.18 (broad s, 5H, Cp), 3.35 (broad s, 2H, C_5H_4B), 2.90 (m, 3H, PCH of Cy), 2.13-1.27 (overlapping m, 30 H, CH_2 of Cy). ^{11}B NMR (96 MHz, chloroform-d, 20°C): δ 2 (broad). ^{19}F NMR (282 MHz, chloroform-d, 20°C): δ -124.7 (m, 2F, C_6F_4), -132.0 (m, 2F, C_6F_4), -133.3 (d, $^3J_{FF}$ = 20.9 Hz, *ortho*-CF of C_6F_5), -162.2 (t, $^3J_{FF}$ = 20.9 Hz, *para*-CF of C_6F_5), -165.8 (m, *meta*-CF of C_6F_5), -193.7 (broad s, BF). ^{31}P NMR (121 MHz, chloroform-d, 20°C): δ 39.9. Crystallographic data: **3**·$CHCl_3$, $C_{41}H_{43}BCl_3F_{10}FeP$, M_r = 929.76, triclinic, *P*-1, *a* = 11.7155(3), *b* = 12.6410(4), *c* = 15.6649(3) Å, α = 83.830(2), β = 79.824(2), γ = 66.833(3)º, *V* = 2097.4(1) Å^3, *Z* = 2, ρ_c = 1.472 Mg m^{-3}, *T* = 150 K, λ = 1.54180 Å. 8635 reflections collected, 8635 independent [R(int) = 0.019] used in all calculations. R_1 = 0.0357, wR_2 = 0.0824 for observed unique reflections [I>2σ(I)] and R_1 = 0.0374, wR_2 = 0.0838 for all unique reflections. Max. and min. residual electron densities 0.54 and -0.51 e Å^3. CCDC reference: 954137.

[HP^{t}Bu$_3$][2·(μ-OH)]: **2** (0.100 g, 0.114 mmol) was dissolved in minimal benzene and combined with P^{t}Bu$_3$ (0.023 g, 0.114 mmol). One drop of deionized water was added and the mixture stirred for 1 h. Volatiles were removed *in vacuo* and single crystals of the product obtained from a concentrated chloroform solution stored at -30 °C. Yield: 0.097 g, 78%. ^{1}H NMR (500 MHz, chloroform-d, 20 °C): δ 5.46 (broad s, 1H, OH), 4.06 (d, $^1J_{PH}$ = 461 Hz, 1H, PH), 3.91 (s, 4H, Cp), 3.68 (s, 4H, Cp), 1.55 (d, $^3J_{PH}$ = 15.2 Hz, 27H, ^{t}Bu). ^{11}B NMR (128 MHz, chloroform-d, 20°C): δ 1 (broad). ^{19}F NMR (377 MHz, chloroform-d, 20°C): δ -132.4 (d, $^3J_{FF}$ = 10.7 Hz, *ortho*-CF of C_6F_5), -160.4 (t, $^3J_{FF}$ = 20.4 Hz, *para*-CF of C_6F_5), -164.8 (t, $^3J_{FF}$ = 19.5 Hz, *meta*-CF of C_6F_5). ^{31}P NMR (121 MHz, chloroform-d, 20°C): δ 58.3. ESI-MS (*m*/*z*): (pos) 203.2 [HP^{t}Bu$_3$]$^+$; (neg) 921.0 [2·(μ-OH)]$^-$. Elemental microanalysis: calc. (for $C_{55}H_{46}B_2F_{20}FeOP$) C 54.49, H 3.83%; meas. C 54.88, H 4.01%. Crystallographic data: [HP^{t}Bu$_3$][**2**·(μ-OH)]·$^3/_2$(benzene), $C_{55}H_{46}B_2F_{20}FeOP$, M_r = 1211.37, triclinic, *P*-1, *a* = 11.8245(4), *b* = 13.6477(4), *c* = 15.8558(4) Å, α = 84.214(2), β = 88.541(2), γ = 87.111(3)º, *V* = 2542.0(1) Å^3, *Z* = 2, ρ_c = 1.583 Mg m^{-3}, *T* = 150 K, λ = 1.54180 Å. 27110 reflections collected, 10487 independent [R(int) = 0.026] used in all calculations. R_1 = 0.0326, wR_2 = 0.804 for observed unique reflections [I>2σ(I)] and R_1 = 0.0351, wR_2 = 0.0822 for all unique reflections. Max. and min. residual electron densities 0.31 and -0.39 e Å^3. CCDC reference: 1576950.

2·(NH$_3$)$_2$: A Schlenk flask containing **2** (0.100 g, 0.114 mmol) was cooled to -60 °C and sufficient NH_3 condensed to allow all of the solid material to dissolve. The solution was stirred, and allowed to warm to 20°C, while ammonia gas was vented to waste. The resulting yellow solid was isolated, and single crystals suitable for X-ray crystallography were obtained from a concentrated ether solution stored at -30°C. Yield: 0.089 g, 86%. ^{1}H NMR (500 MHz, benzene-d_6, 20°C): δ 3.89 (s, 4H, C_5H_4), 3.55 (s, 4H, C_5H_4) 3.41 (b s, 6H, NH). ^{19}F NMR (377 MHz, benzene-d_6, 20°C): δ -133.3 (d, $^3J_{FF}$ = 9.2 Hz, *ortho*-CF of C_6F_5), -156.2 (t, $^3J_{FF}$ = 20.4 Hz, *para*-CF of C_6F_5), -162.7 (t, $^3J_{FF}$ = 22.4 Hz, *meta*-CF of C_6F_5). ^{11}B NMR (128 MHz, benzene-d_6, 20°C): -9 (sharp). Elemental microanalysis: calc. (for $C_{34}H_{14}B_2F_{20}FeN_2$) C 44.94, H 1.55, N 3.08%; meas. C 44.89, H 1.56, N 3.28%. MS (ESI): 908.1. Crystallographic data: **2**·$(NH_3)_2$·$^3/_2(C_6H_6)$, $C_{43}H_{23}B_2F_{20}FeN_2$, M_r = 1025.10, triclinic, *P*-1, *a* = 10.4515(3), *b* = 13.5721(3), *c* = 14.2616(4) Å, α = 94.087(2), β = 93.027(3), γ = 100.948(2)°, *V* = 1976.6(1) Å^3, *Z* = 2, ρ_c = 1.722 Mg m^{-3}, *T* = 150 K, λ = 1.54180 Å. 41166 reflections collected, 8188 independent [R(int) = 0.021] used in all calculations. R_1 = 0.0259, wR_2 = 0.0656 for observed unique reflections [I>2σ(I)] and R_1 = 0.0270, wR_2 = 0.0664 for all unique reflections. Max. and min. residual electron densities 0.32 and -0.34 e Å^3. CCDC reference: 1576951.

Reaction of 6Dipp with CO_2: 6-Dipp (0.100 g, 0.247 mmol) was dissolved in minimal benzene, the solution freeze-pump-thaw degassed, and the evacuated headspace backfilled with CO_2 to 1 bar pressure. The reaction mixture was stirred for 4 h, and the resulting precipitate then isolated by filtration, washed with pentane and dried *in vacuo.* The product was dissolved in 0.6 mL of bromobenzene-d_5 and transferred to a J. Young's tube for analysis by multinuclear NMR. ^{1}H NMR (500 MHz, bromobenzene-d_5, 20°C): (signals due to cation) δ 7.19 (m, 6H, aromatic CH of Dipp), 3.61 (m, 4H, NCH_2), 3.10 (sept, $^3J_{HH}$ = 7.1 Hz, 4H, CH of ^{i}Pr), 2.39 (m, 2H, CH_2), 1.38 (d, $^3J_{HH}$ = 7.1 Hz, 24H, Me of ^{i}Pr); (signals due to anion) 7.19 (m, 6H, Ar), 6.15 (m, 1H, alkene CH), 5.14 (m, 1H, alkene CH_2), 5.10 (broad s, 1H, alkene CH_2), 4.35 (d, $^3J_{HH}$ = 6.5 Hz, 2H, CH_2), 3.10 (m, 4H, CH of ^{i}Pr), 1.24 (d, 24H, Me of ^{i}Pr). ESI-MS (*m*/*z*): (pos) 405 [6-DippH]$^+$; (neg) 447 [$C_{29}H_{39}N_2O_2$]$^-$.

4: **1** (0.100 g, 0.189 mmol) and excess (>5 equiv.) of CyNCO were dissolved in benzene-d_6 and the resulting solution transferred to a Young's NMR tube, for spectroscopic analysis over a period of one week. Storage at 6°C resulted in the formation of orange-red crystals. ^{1}H NMR (500 MHz, chloroform-d, 20°C): δ 4.89 (t, $^3J_{HH}$ = 2.1 Hz, 2H, Cp), 4.80 (t, $^3J_{HH}$ = 2.1 Hz, 2H, Cp), 4.18 (s, 5H, Cp), 4.02 (tt, $^3J_{HH}$ = 12.0 Hz, $^4J_{HH}$ = 3.4 Hz, 1H, CH of Cy), 3.04 (tt, $^3J_{HH}$ = 12.0 Hz, $^4J_{HH}$ = 3.4 Hz, 1H, CH of Cy), 2.70–1.05 (20H, CH_2 of Cy). ^{19}F NMR (282 MHz, chloroform-d, 20°C): δ -133.2 (d, $^3J_{FF}$ = 25.2 Hz, *ortho*-CF of C_6F_5), -156.0 (t, $^3J_{FF}$ = 20.9 Hz, *para*-CF of C_6F_5), -163.1 (td, $^3J_{FF}$ = 21.9 Hz, $^4J_{FF}$ = 9.6 Hz, *meta*-CF of C_6F_5). ^{11}B NMR (96 MHz,

chloroform-d, 20°C): δ 1. ^{13}C NMR (126 MHz, chloroform-d, 20°C): 178.1 (CO), 149.4 (Fc quaternary C), 148.1 (d, $^{1}J_{CF}$ = 243.5 Hz, C_6F_5), 140.3 (d, $^{1}J_{CF}$ = 254.2 Hz, C_6F_5), 137.0 (d, $^{1}J_{CF}$ = 255.6 Hz, C_6F_5), 75.0 (C_5H_4), 72.8 (C_5H_4), 70.7 (Cp), 61.8 (CH of Cy), 50.0 (CH of Cy), 31.2, 30.1, 28.9, 27.9, 26.5, 24.9 (CH_2 of Cy). ESI-MS (*m/z*): (pos) 780 $[M]^+$; accurate mass: calc. (for $C_{36}H_{31}BF_{10}FeN_2O_2$, $[M]^+$) 781.1747; meas. 781.1748. Crystallographic data: **4**·C_6H_6, $C_{42}H_{37}BF_{10}FeN_2O_2$, M_r = 858.41, triclinic, *P*-1, *a* = 10.9221(1), *b* = 11.1191(1), *c* = 17.0196(2) Å, α = 94.976(1), β = 95.697(1), γ = 112.976(1)°, *V* = 1875.7(1) Å^3, *Z* = 2, ρ_c = 1.520 Mg m^{-3}, *T* = 150 K, λ = 1.54180 Å. 55367 reflections collected, 8562 independent [R(int) = 0.030] used in all calculations. R_1 = 0.0389, wR_2 = 0.0842 for observed unique reflections [I>2σ(I)] and R_1 = 0.0648, wR_2 = 0.0926 for all unique reflections. Max. and min. residual electron densities 0.67 and -0.57 e Å^3. CCDC reference: 1576592.

Crystallography

Data for **2**·(IMes)$_2$, [HP^{t}Bu$_3$][**2**·(μ-OH)], **2**·(NH$_3$)$_2$, **3** and **4** were collected on a Oxford Diffraction Supernova diffractometer at 150 K. Data collection and reduction were carried out using CrysAlisPro or Denzo/Scalepack, structure solution using Superflip, and refinement using CRYSTALS or SHELXT-2014/7.[37] Complete details of all structures are contained within the respective CIFs which have been deposited with the CCDC (reference numbers: 954137, 1576950-1576952 and 1582718).

Conclusions

The bifunctional Lewis acid 1,1'-fc{B(C_6F_5)$_2$}$_2$ (**2**) is shown to form frustrated Lewis pairs with the sterically encumbered N-donor bases lutidine and tetramethylpiperidine, together with PPh_3, P^{t}Bu$_3$ and the expanded ring carbene 6Dipp. In the case of PCy_3, attack at the *para*-CF bond of one of the C_6F_5 groups leads to nucleophilic aromatic substitution with accompanying migration of fluoride to boron. The more facile nature of this chemistry in comparison to that observed for the mono-functional analogue Fc$B(C_6F_5)_2$ (**1**) can be attributed to the more electron deficient nature of the -$B(C_6F_5)_2$ functions in **2**.

The P^{t}Bu$_3$/**2** FLP can be shown to cleave one of the O-H bonds in water to give a tertiary phosphonium salt in which the anion features a symmetrically bound 'inverse-chelated' B-O(H)-B unit. Attempts to bring about analogous N-H bond activation with ammonia are frustrated by the weaker Brønsted acidity of the N-H bond and/or the inability to generate a similar B-$N(H)_2$-B motif due to the (less reversible) formation of strong H_3N→B donor/acceptor bonds. Neither P^{t}Bu$_3$/**1** or P^{t}Bu$_3$/**2** shows any propensity to activate carbon dioxide, in contrast to the combination of P^{t}Bu$_3$ and the stronger Lewis acid $B(C_6F_5)_3$. Attempts to use the stronger Lewis base 6Dipp lead to ring opening of the carbene brought about by coordination to the electrophilic C-atom of CO_2, while the use of the more reactive heterocumulene CyNCO can be shown to lead to insertion into the C-B bond linking the borane function to the ferrocene backbone.

Conflicts of interest

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There are no conflicts to declare.

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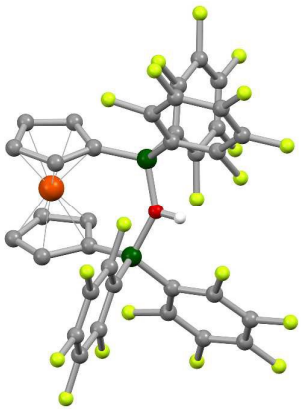

Applications of the bifunctional Lewis acid 1,1'-fc{$B(C_6F_5)_2$}$_2$ in FLP chemistry are described, including reactions towards H_2O, NH_3, CO_2 and cyclohexylisocyanate.