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Small molecule activation by frustrated Lewis pairs†

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A series of frustrated Lewis pairs (FLPs) based on the Lewis acids tris(perchloroaryl)borane (BAr^{Cl}), and tris(2,2′,2″-perfluorobiphenyl)borane (PBB) and trialkylphosphines were prepared; their ability to effect the heterolytic cleavage of dihydrogen, insert carbon dioxide into the borohydride, and reduce the resulting formatoborate to methanol were studied. Additionally, the insertion of CO_2 into a B–OH bond is explored with the ultimate aim of developing a homogeneous, catalytic preparation of carbonates. The compound [PBB–OH][H–P(^{t}Bu)$_3$] was characterised by single crystal X-ray crystallography.

Introduction

The reduction of carbon dioxide to methanol by the $[B(C_6F_5)_3]$ (BAr^F)/2,2,6,6,-tetramethypiperidine (TMP) frustrated Lewis pair (FLP) system has been recently reported.[1] Protonolysis of fluoroaryl rings in the methoxyborate adduct, facilitated by mesomeric electron donation to the aryl ring by fluorine atoms with strong 2p–2p overlap, prevents dissociation of methanol to regenerate the FLP system, rendering the system non-catalytic. Subsequent work has focused on developing new Lewis acids and FLP systems capable of analogous reactivity, but without the susceptibility to decomposition, in an attempt to generate a system capable of catalytic CO_2 reduction at low temperature and pressure.[2,3] Electrochemical and solution Lewis acidity measurements indicate that electron density on the boron atom increases with increasing n for the series $[B(C_6Cl_5)_n(C_6F_5)_{3-n}]$ (where n = 1–3).[2] Although tris(perchloroaryl)borane, $(B(C_6Cl_5)_3 = BAr^{Cl})$, was found to be the most Lewis acidic borane, it experienced reduced reactivity with H_2 compared to the prototypic $[B(C_6F_5)_3]$, attributed to steric crowding of the boron by *ortho* chlorine atoms.

In an attempt to weaken the B–O bond of the methoxyborate species, and so facilitate its cleavage to evolve methanol and regenerate the FLP catalyst, the Lewis acid $[B\{C_6F_4(o\text{-}C_6F_5)\}_3]$, PBB, was synthesised – the rationale being that steric bulk at the *ortho* position alone could decrease the B–O bond strength.[3] The steric bulk of PBB reduces its reactivity in FLP chemistry, although in combination with the bulky nitrogen base 1,4-diazabicyclo[2.2.2]octane (DABCO), it forms formatoborates *via* heterolytic cleavage of H_2 followed by insertion of CO_2 (although no further reduction was observed). FLP mediated CO_2 reduction chemistry has so far been largely demonstrated with bulky amines,[1,4] despite the ready availability of hindered phosphines, their amenable study by $^{31}P\{^1H\}$ NMR spectroscopy, and their FLP activity.[5,6] Furthermore, the greater Lewis basicity of phosphines should lead to the formation of more activating FLPs.[8]

Herein we aim to detail the synthesis of frustrated Lewis pairs of BAr^{Cl} and PBB with appropriately selected phosphines and report their activation of small molecules.

Results and discussion

Synthesis of novel FLPs

The Lewis acids PBB (tris(2,2′,2″-perfluorobiphenyl)borane) and BAr^{Cl} tris(perchloroaryl)borane, were synthesised from adapted literature procedures (Fig. S1, ESI†) (Fig. 1).[2,3,9,10]

In an attempt to quantitatively account for the Lewis basicity of available phosphines, computational methods have been used to calculate the reaction enthalpy for the methyl detachment reaction.[11] Methyl Cation Affinity is chosen over

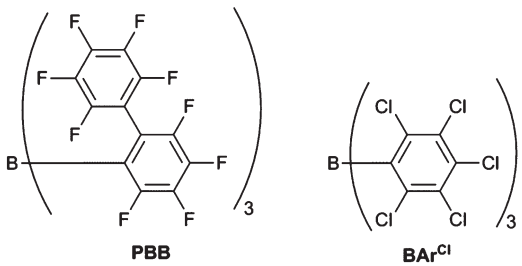

Fig. 1 (tris(2,2′,2″-perfluorobiphenyl)borane), $[B\{C_6F_4(o\text{-}C_6F_5)\}_3]$, PBB, and tris(perchloroaryl)borane, $[B(C_6Cl_5)_3]$, BAr^{Cl}.

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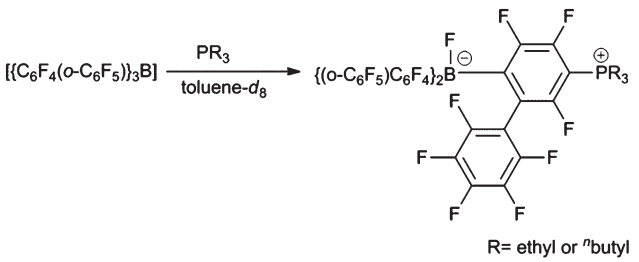
pK_a or analogous transition metal indices for ligand activity as a measure of the Lewis basicity of phosphines due to the closer correlation between the methyl cation and isoelectronic boron centre. Tris-*tert*-butylphosphine ($P(^tBu)_3$) has been used extensively in FLP chemistry to induce small molecule activation,[12–14] heterolytically cleave H_2.[15] Tricyclohexylphosphine ($P(Cy)_3$) has been used in FLP mediated ring opening of thf,[16] and in N_2O,[17] and H_2 activation.[18] Tris-*para*-tolylphosphine ($P(p\text{-tolyl})_3$), tri-*n*-butylphosphine ($P(^nBu)_3$) and triethylphosphine ($P(Et)_3$) have not, to the best of our knowledge, been shown to form FLP systems. Tri-*para*-tolylphosphine is selected due to its similarity to both triphenylphosphine and tri-*ortho*-tolylphosphine, which have been shown to successfully form FLPs capable of H_2 activation.[7,19] Triethylphosphine and Tri-*n*-butylphosphine have been selected due to their relatively low steric bulk, in the hope that they may be able to complement the two bulky Lewis acids.

The reactions using PBB were carried out in toluene-d_8 at room temperature. The change in chemical shift in $^{31}P\{^1H\}$ NMR upon reaction with PBB and the final $^{11}B\{^1H\}$ chemical shift are shown in Table S4.† Changes in chemical shift observed in $^{11}B\{^1H\}$ NMR spectra, from the 70.9 ppm recorded for PBB to 0.8 ppm and 0.2 ppm in PBB systems of tris-*para*-tolyphosphine and tricyclohexylphosphine respectively, are consistent with the formation of four coordinate boron species (Scheme 1).[20]

The formation of adducts is also suggested by the de-shielding of phosphorus environments by 22.1 ppm and 29.8 ppm from the free phosphine to the PBB system in the decoupled $^{31}P\{^1H\}$ NMR spectrum. Furthermore, nine resonances were observed in the ^{19}F NMR spectrum, replacing the seven observed in uncoordinated PBB. It would appear that the coordination of the phosphine to the central boron atom has restricted internal rotation between biphenyl rings, removing the degeneracy between fluorines in the *ortho* and *meta* positions of the C_6F_5 ring (Fig. S2†), as in the case of the [PBB–Me]$^-$ anion synthesised by Chen *et al.*[9]

In the case of systems containing triethylphosphine and tris-*n*-butylphosphine, resonances at 0.4 ppm and 0.5 ppm were observed in the $^{11}B\{^1H\}$ NMR spectra respectively upon addition of PBB, once again indicating the formation of a four coordinate boron species (Scheme 2). Additionally, in each case, the ^{19}F spectrum was considerably more complicated, with 18 fluorine environments, despite only one phosphorus resonance being observed by $^{31}P\{^1H\}$ NMR. FLP systems comprising phosphine and [$B(C_6F_4H)_3$] have been developed with a hydrogen atom in the *para* position in order to prevent nucleophilic attack.[5,19,20] In BAr^F, where the F *para* atom remained, all but the most sterically bulky phosphine Lewis bases



Scheme 2 Synthesis of [{C_6F_4(*o*-C_6F_5)}$_2$BF-*p*-{C_6F_3(*o*-C_6F_5)}PR_3] where R = ethyl or ^{n}butyl.

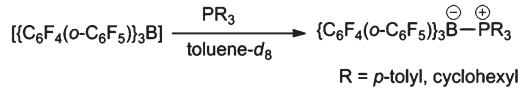
underwent nucleophilic aromatic substitution to give phosphinium borates.[21] Detailed inspection of the ^{19}F spectrum of the PBB/$P(Et)_3$ and PBB/$P(^nBu)_3$ systems show 17 resonances in the region typical of fluorine atoms directly bonded to the aromatic ring and one considerably further upfield, at −184.4 ppm in both cases. This shielded peak corresponds well with the literature reported values of the B–F fluorine resonance generated through the nucleophilic attack on BAr^F to form phosphonum borates,[21] and with [PBB–F][CPh_3].[22] Furthermore, in these systems more drastic de-shielding of phosphorus nuclei in $^{31}P\{^1H\}$ NMR was observed upon reaction with PBB (57.6 ppm and 64.4 ppm for triethylphosphine and tri-*n*-butylphosphine respectively), than with systems suspected to form adducts, an observation consistent with literature preparations of phosphonium borates.[21]

The tri-*tert*-butylphosphine system showed no observable change in the $^{11}B\{^1H\}$, $^{31}P\{^1H\}$ or ^1H NMR spectra compared to the starting materials, leading to the conclusion that this system had formed an FLP (Scheme 3).

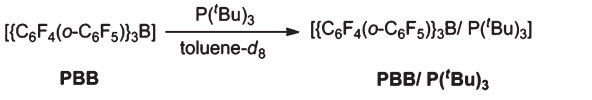
PBB is less vulnerable to nucleophilic attack than BAr^F, which forms phosphonium borates with all four phosphines PR_3 (R = cyclohexyl, phenyl, ethyl and ^{n}butyl).[21] Stephan and co-workers have shown the treatment of [R_3P-(C_6F_4)$BF(C_6F_5)_2$] species with Grignard reagents evolves [R_3P-(C_6F_4)$B(C_6F_5)_2]^+$ cationic phosphonium-boranes capable of H_2 activation.[23]

BAr^{Cl} has poor solubility in toluene at ambient temperature, and so heating to 80 °C was required to allow reaction monitoring by NMR. None of the five phosphines (PR_3, R = *p*-tolyl, ethyl, ^{n}butyl, ^{t}butyl and cyclohexyl) formed Lewis adducts or underwent nucleophilic substitution reactions, as evidenced by the lack of change in either $^{11}B\{^1H\}$ or $^{31}P\{^1H\}$ NMR, showing that all five the systems successfully formed FLPs (Scheme 4).

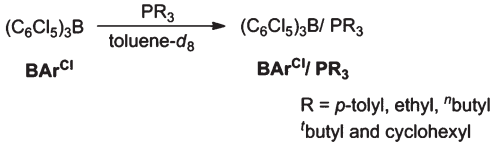
The formation of FLPs, even with phosphines of low steric bulk such as $P(Et)_3$ is unexpected, and reflective of the very sterically hindered boron centre in BAr^{Cl}.



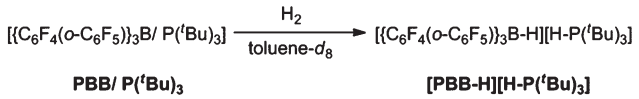
Scheme 1 Synthesis of the classical adduct [{C_6F_4(*o*-C_6F_5)}$_3$B–PR_3] where R = *p*-tolyl or cyclohexyl.



Scheme 3 Synthesis of the FLP system PBB/$P(^tBu)_3$.



Scheme 4 Synthesis of FLPs using BAr^{Cl} and PR_3 where R = *p*-tolyl, ethyl, ^{n}butyl, ^{t}butyl and cyclohexyl.



Scheme 5 H_2 splitting from the FLP system PBB/$P(^tBu)_3$.

H_2 activation using FLP and Lewis adducts

The FLPs and Lewis adducts were exposed to dihydrogen. Systems containing the classical adduct of PBB and the phosphines $P(Cy)_3$ and $P(p\text{-tolyl})_3$ did not split H_2 at room temperature or when heated at 120 °C for 48 hours.

The PBB/$P(^tBu)_3$ FLP underwent instantaneous reaction at room temperature upon the addition of H_2 at 1 atm (Scheme 5).

The $^{11}B\{^1H\}$ NMR spectrum of the PBB/$P(^tBu)_3$ reaction shows a broad singlet at 71 ppm (associated with residual, unreacted three co-ordinate PBB), as well as a new resonance, at −18.2 ppm (Fig. S3a†) which was shown to be a doublet in the ^{11}B NMR spectrum ($^1J_{B-H}$ = 87.2 Hz, Fig. S3b†), consistent with the formation of a new $[PBB–H]^-$ anion species. Both the chemical shift and coupling constants observed were within the literature range for $[PBB–H]^-$ salts.[3] In addition to the $[PBB–H]^-$ species, $[H–P(^tBu)_3]^+$ formation was also observed in the $^{31}P\{^1H\}$ NMR spectrum (60.0 ppm). The ^{31}P and ^1H NMR spectra showed the formation of doublets ($^1J_{P-H}$ = 438 Hz, $^3J_{P-H}$ = 16 Hz) consistent with literature values of the $[H–P(^tBu)_3]^+$ cation (Fig. 2).[19] In contrast with the $BAr^F/P(^tBu)_3$ analogue,[7] PBB required significant heating before it demonstrated H_2 activation to the point of completion, showing PBB to be less activating, despite its increased Lewis acidity.[2,3] This is attributed to the greater steric bulk around the boron centre which would be expected to hinder the H_2 entrance process, increasing the energetic barrier to reaction.

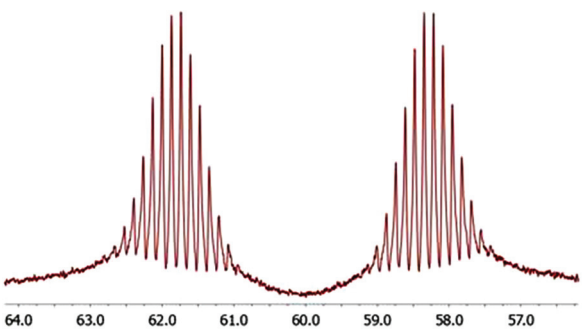
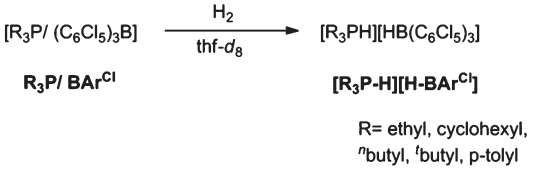


Fig. 2 ^{31}P NMR spectrum of the $[PBB–H][H–P(^tBu)_3]$ (toluene-d_8, 25 °C, 300 MHz).



Scheme 6 H_2 splitting using a BAr^{Cl} based FLP.

All the R_3P/BAr^{Cl} FLP systems (where R = ethyl, cyclohexyl, ^{n}butyl, ^{t}butyl or *p*-tolyl) have been used for the splitting of dihydrogen in thf-d_8 (Scheme 6). The reactivity is detailed below, and is summarised in Table S5.†

In the case of the tri-*para*-tolylphosphine system, no reaction occurred at room temperature. After heating at 90 °C for 24 hours in the presence of an H_2 atmosphere, a doublet became visible in the ^{11}B NMR at −8.37 ppm ($^1J_{B-H}$ = 83.0 Hz). The low yield of the $P(p\text{-tolyl})_3$ system is consistent with the low expected activity of the FLP with the phosphine of the lowest Metal Cation Affinity (MCA). In accordance with theoretical calculations detailed above, this system would be expected to have the lowest electric field strength, and hence lowest dihydrogen cleavage activity.[24]

The remaining BAr^{Cl}/phosphine systems were considerably more reactive, all showing doublets in ^{11}B NMR spectroscopy in thf-d_8. For the BAr^{Cl} FLP systems containing $P(Et)_3$ and $P(^nBu)_3$, $[H–BAr^{Cl}]^-$ was formed, observed by resonances characterised by ^{11}B NMR spectroscopy at −8.43 ppm ($^1J_{B-H}$ = 67.8 Hz) and −8.54 ppm ($^1J_{B-H}$ = 81.8 Hz) respectively, although initially in low yield. Heating both of the systems at 90 °C for 24 hours generated a new three coordinate species, visible in the $^{11}B\{^1H\}$ NMR spectrum as a broad resonance at approximately 27 ppm. Further heating at 90 °C for 24 hours ultimately led to high conversion of starting material to both $[R_3P–H][H–BAr^{Cl}]$ (where R = ethyl or ^{n}butyl). Conversion to the salt was observed in ^{11}B NMR spectrum at −8.19 ppm ($^1J_{B-H}$ = 55.8 Hz) after heating at 90 °C for 56 hours for $P(^tBu)_3$ and at −8.78 ppm ($^1J_{B-H}$ = 55.8 Hz) after 40 hours for $P(Cy)_3$.

Of all the phosphines which, in conjunction with BAr^{Cl}, successfully cleaved H_2 without thermal decomposition, $P(Cy)_3$ was the most active going to completion after only 40 hours at 90 °C. This correlates well with the initial hypothesis that increased phosphine MCA should induce a greater electric field, facilitating dihydrogen cleavage. Additionally, the FLPs with $P(Et)_3$ and $P(^nBu)_3$ showed complete disappearance of the starting material after only 48 hours at 90 °C, despite their lower MCA than $P(^tBu)_3$, which showed complete conversion only after 56 hours. Previous work suggested that, with one exception (the nitrogen base 1,4-diazabicyclo[2.2.2]octane, DABCO), BAr^{Cl} is too sterically bulky to allow sufficient proximity between Lewis pairs to successfully polarise H_2 enough to achieve cleavage.[10]

H_2O splitting using FLP

The synthesis of [PBB–OH][H–P(^{t}Bu)$_3$] was attempted for the purpose of investigating CO_2 insertion into the B–O bond. A drop of water was added to an ampoule containing an equimolar mixture of PBB and tris-*tert*-butylphosphine in toluene. The solution was stirred vigorously for 24 hours, resulting in the formation of a deep yellow solution; after which the solvent was removed *in vacuo*.

As with the hydride salts, the formation of [H–P(^{t}Bu)$_3$] was demonstrated with the emergence of a doublet at 59.1 ppm ($^1J_{P–H}$ = 433 Hz) in the ^{31}P NMR spectrum, and was also visible in the ^{1}H NMR spectrum at 5.02 ppm with the same coupling constant. The [PBB–OH]$^-$ resonance was the only visible resonance in the ^{11}B{^{1}H} NMR spectrum as a singlet at −3.90 ppm. The ^{19}F NMR spectrum exhibited nine resonances (Fig. S5†). The experiment was repeated with a drop of degassed D_2O. The ^{31}P{^{1}H} NMR spectrum highlighted a 1 : 1 : 1 triplet at 60.0 ppm, with a coupling constant $^1J_{P–D}$ of 71 Hz.

Colourless crystals suitable for a single crystal X-ray structural analysis were grown by slow evaporation of chloroform-d_1 solution at room temperature over a period of four days. The molecular structure of [PBB–OH][H–P(^{t}Bu)$_3$] is depicted Fig. 3.

As expected, coordination of $^-$OH deforms PBB away from the trigonal planar geometry around boron observed in PBB,[3] to a pseudotetrahedral arrangement, with C–B–C bond angles contracted to an average of 112.6°, and C–B–O angles widened to 106.2° (in comparison of 110.7° and 108.0° respectively in [BAr^F–OH]$^-$).[27] The significant structural change upon coordination is reflected in the average dihedral angle between the two perfluorophenyl rings of each perfluorobiphenyl group, which are 64.4° in PBB,[3] 74.3° [PBB–F][CPh$_3$],[22] rising to 82.4° in [PBB–OH][H–P^{t}Bu$_3$]. The steric congestion exacerbated by the coordination of an adduct appears to distort the perfluorobiphenyl groups away from an arrangement in which π stacking is maximised by forming a propeller like structure, as made evident by the space filling diagram (Fig. S6†).

The B–C bond lengths increase from an average of 1.581 Å in PBB to 1.642(3) Å in [PBB–OH]$^-$, reflecting the substantial steric strain in PBB exacerbated upon coordination of $^-$OH, similar to that observed upon the coordination of the bulkier nucleophiles to give [PBB–Me]$^-$ and [PBB–CN]$^-$ which exhibit average B–C bond lengths of 1.676 Å and 1.682 Å respectively.[25] At 1.463(7) Å the B–O bond is within the literature range for tetrahedral boron centres,[26] but shorter than for [BAr^F–OH]$^-$ (in the context of the literature example [BAr^F–OH][H–NEt$_3$])[28] reflecting PBB's greater Lewis acidity. Interestingly the cations and anions pack in a manner that that results in the P–H and B–OH fragments not orienting towards each other, contrary to what is observed in hydride salts of FLPs,[1] and in [BAr^F–OH]-[H–NEt$_3$].[28] In the [BAr^F–H][H–P(^{t}Bu)$_3$] salt, the BH–HP approach is 2.75 Å,[1] consistent with that of a non-traditional proton-hydride hydrogen bond.[29]

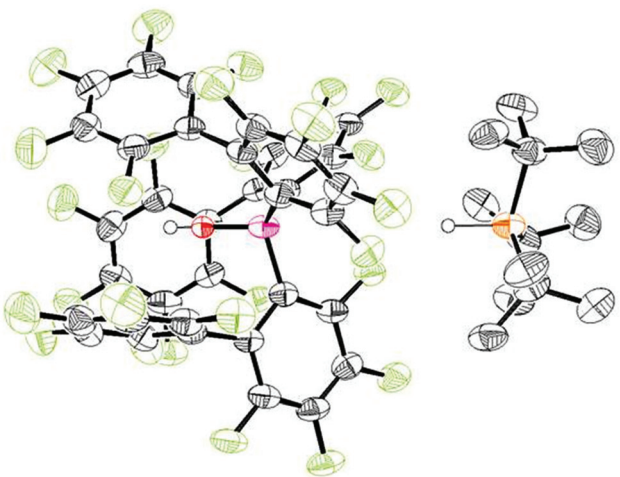
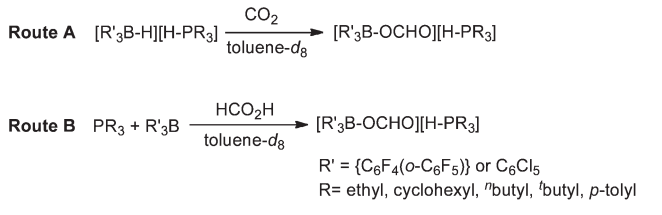


Fig. 3 Molecular structure of [PBB–OH][H–P(^{t}Bu)$_3$] with ellipsoids at 50% probability level. Methyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): B–O 1.463(7), B–C 1.642(3) and C–B–C 113.10(19). Green: fluorine, pink: boron, red: oxygen, orange: phosphorus, grey: carbon and white: hydrogen.

CO_2 insertion reactions

Formatoborate systems were prepared *via* the exposure of the hydride salts of FLPs to CO_2 (Route A in Scheme 7) and were compared to formatoborates independently synthesised through the facile association of formate ions to the Lewis acid (Route B in Scheme 7).

Preparation of the formatoborate [PBB–OC(O)H][H–P(^{t}Bu)$_3$] *via* route B was achieved by adding formic acid to equimolar amounts of PBB and P(^{t}Bu)$_3$ and stirring at room temperature for 16 hours, before removal of the solvent *in vacuo*. A singlet at −0.60 ppm in the ^{11}B{^{1}H} NMR spectrum, and nine resonances in ^{19}F demonstrated the synthesis of the formatoborate. Infrared spectroscopy showed a sharp absorption at 1681 cm^{-1}, consistent with carbonyl stretches observed in the literature for the preparation of formatoborates.[1,30] Preparation of the formatoborate through route A was subsequently attempted *via* the exposure of the [PBB–H][H–P(^{t}Bu)$_3$] salt to one atmosphere of CO_2. No initial reaction was observed at room temperature. Upon heating the system at 140 °C for 24 hours, a new resonance was observed in the ^{11}B{^{1}H} NMR spectrum as a broad singlet at −0.38 ppm, corresponding to the formation of a formatoborate. Further heating at 145 °C increased the intensity of the formatoborate resonance, while residual signals associated with the B–H starting material at −18.2 ppm decreased (Fig. S7†). The infrared spectrum revealed an absorption in the carbonyl stretching region of 1680 cm^{-1}, correlating well with the formatoborate synthesised



Scheme 7 Formation of formatoborate complexes using two different routes.

via route B. A solution of the formatoborate [PBB–OCHO][H–P(ᵗBu)₃] was exposed to a H_2 atmosphere and heated at 140 °C for 16 hours. The resonance attributed to the formatoborate group in the $^{11}B\{^1H\}$ NMR spectrum reduced in intensity, giving way to the appearance of a resonance at −18.15 ppm, which was shown to be a doublet with $^1J_{B-H}$ of 86.8 Hz (Fig. S8†). It was concluded that decarboxylation of the formatoborate was occurring at high temperatures, yielding the hydride salt, and that no further reduction occurred.

The analogous Route B preparation of the formatoborate [BAr^{Cl}–OCHO][HP(ᵗBu)₃] was successful, as evidenced by the appearance of a resonance at 3.77 ppm in the $^{11}B\{^1H\}$ spectrum and at 8.08 ppm in the ^1H NMR spectrum, both attributed to the coordinated formate group. Once again, a carbonyl stretch was observed at 1689 cm^{-1} in agreement with literature values for formatoborates.[1,30] Route A preparation was attempted with hydride salts of BAr^{Cl} previously synthesised. The subsequent reactivity is collated in Table S7.† No system showed the formation of formatoborate upon initial mixing, or after heating up to 120 °C.

This highlights the choice of the halogen on the aromatic rings, despite the importance of increased bulk, [B{C_6F_4(*o*–C_6F_5)}₃] demonstrated ability for CO_2 insertion; however, BAr^{Cl} showed no reactivity even after heating. Furthermore, Momming *et al.* have shown the insertion of CO_2 in [(C_6F_5)₃B]-[PᵗBu_3] frustrated Lewis pairs.[31]

Conclusions

Six novel frustrated Lewis pair systems using a range of phosphines with PBB and BAr^{Cl} were synthesised. Additionally, in combination with PBB, the phosphines triethylphosphine and tris-*n*-butylphoshpine formed phosphonium borates, and the phosphines tricyclohexylphosphine and tris-*para*-tolylphosphine showed the formation of classical adducts.

The PBB/P(ᵗBu)₃ FLP system caused the heterolytic cleavage of dihydrogen, giving the hydride salt [PBB–H][H–P(ᵗBu)₃] in good yield, and the formate [PBB–OC(O)H][H–P(ᵗBu)₃] upon subsequent insertion of CO_2. Further reduction to the methoxyborate was not observed. [PBB–OH][H–P(ᵗBu)₃] was synthesised and structurally characterised by single crystal X-ray structural analysis, but displayed no CO_2 insertion reactivity.

All BAr^{Cl} FLP systems displayed hydrogenation reactivity, with the BAr^{Cl}/P(ᵗBu)₃ and BAr^{Cl}/P(Cy)₃ systems showing near complete conversion to the hydride salt. Heterolytic activation of dihydrogen by FLPs with the phosphines P(ⁿBu)₃, P(Et)₃ and P(*p*-tolyl)₃ is recorded here. However, none of the BAr^{Cl} hydride salts showed CO_2 insertion.

Experimental

General procedure

Air and moisture sensitive reactions were performed on a dual-manifold vacuum/N_2 line using standard Schlenk techniques, or in a N_2 filled MBraun Unilab glovebox. Hexane and toluene were dried using a Braun SPS-800 solvent purification system. Et_2O and thf were dried at reflux over Na/benzophenone and distilled under N_2. Hexane and toluene were stored over K mirrors. thf and Et_2O were stored over activated 3 Å molecular sieves. H_2 gas (>99.95%) was obtained from Sigma Aldrich and passed directly into a dual manifold Schlenk. CO_2 gas (99.99%) was obtained from ARGO International Ltd. and passed into a Schlenk line. Toluene-d_8 (99.6%) was obtained from Cambridge Isotope Laboratories Inc., dried over K and freeze–pump–thaw degassed (×3). Benzene-d_6 (99%) and chloroform-d_1 (99%) were obtained from Goss Scientific, dried over K and preactivated 3 Å molecular sieves respectively, freeze–pump–thaw degassed three times before being vac transferred prior to use. thf-d_8 (Sigma–Aldrich) was dried over CaH_2, freeze–pump–thaw degassed three times before being vac transferred prior to use. Fe powder was purchased from East Anglia chemicals; $MgCO_3$, $Na_2S_2O_3$, conc. H_2SO_4 and $I_{2(s)}$ from Fischer Scientific; with the remaining chemicals utilised in the preparations below obtained from Sigma Aldrich. All were used as received. PBB and BAr^{Cl} were synthesised following literature procedure.[9,10]

Solution NMR samples were prepared in the glovebox under N_2 atmosphere in Young's tap NMR tubes, which were subsequently filled by H_2 or CO_2 as appropriate by freeze–pump–thaw cycles (×3). ^1H, $^{13}C\{^1H\}$, ^{11}B, $^{11}B\{^1H\}$, ^{19}F, ^{31}P and $^{31}P\{^1H\}$ NMR spectra were recorded on 300 MHz Varian VX-Works spectrometers. All chemical shifts were expressed as δ, in parts per million (ppm), ^1H and $^{13}C\{^1H\}$ relative to TMS ($\delta = 0$), and referenced internally to the residual proton shift in the deuterated solvent used. $^{11}B\{^1H\}$, ^{19}F and $^{31}P\{^1H\}$ were referenced externally to $BF_3{\cdot}OEt_2$, $CFCl_3$ and 85% H_3PO_4 ($\delta = 0$), respectively.

Crystals were mounted on MiTeGen MicroMants using perfluoropolyether oil, and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit.[32] Data collections were performed using an Enraf-Nonius FR590 KappaCCD diffractometer, utilising graphite-monochromated Mo K_α X-ray radiation (λ = 0.71073 Å). Raw frame data were collected at 150(2) K using a Nonius Kappa CCD diffractometer, reduced using DENZO-SMN[33] and corrected for absorption using SORTAV.[34] The structure was solved using SuperFlip[35] and refined using full matrix least-squares using CRYSTALS.[36,37] Dihedral angles were calculated using PLATON.[38,39]

Non-air sensitive infrared (IR) spectra were recorded on a Biorad FTS 6000 FTIR Spectrometer and air sensitive IR spectra were recorded on a Biorad FTS 7000 FTIR Spectrometer. Both are equipped with a high performance Dura-Samp1IR II diamond accessory of attenuated total reflection (ATR) mode in the range of 400–4000 cm^{-1} with 100 scans at 4 cm^{-1} resolution.

Crystallographic data of [PBB–OH][H–P(ᵗBu)₃]

Single crystals were grown from a chloroform-d_1 solution, $C_{48}H_{29}BF_{27}OP$, M_r = 1176.49, trigonal, R_3, a = 16.0095(3) Å, b = 16.0095(3) Å, c = 15.8189(4) Å, α = 90°, β = 90° γ = 120°, V =

3511.26(13) Å^3, Z = 3, T = 150 K, block, colourless, 3541 independent reflections, R(int) = 0.065, R_1 = 0.042 wR_2 = 0.106 [$I > 2\sigma(I)$].

Synthesis of FLP

Following literature preparation,[3] the synthesis of FLPs was attempted as follows: one equivalent of borane and one equivalent of phosphine were added to a Young's tap NMR tube, in 0.7 ml of toluene-d_8. Specific reactant amounts are listed in Tables S1 and S2.†

PBB/P(*p*-tolyl)$_3$. ^{19}F NMR (282.5 MHz): −129.3 (F_d, d, $^3J_{d–c}$ = 29.2 Hz, 1F), −140.5 ($F_{e/i}$, d, $^3J_{e/i–f/h}$ = 28.9 Hz), −141.5 ($F_{e/i}$, d, $^3J_{e/i–f/h}$ = 23.4 Hz), −141.7 (F_a, d, $^3J_{a–g}$ = 26.7 Hz), −158.1 ($F_{f/h}$, t, $^3J_{f/h–e/i,g}$ = 21.4 Hz), −158.6 ($F_{f/h}$, t, $^3J_{f/h–e/i,g}$ = 23.8 Hz), −162.2 (F_b, t, $^3J_{b–a}$ = 22.2 Hz), −165.8 (F_g, t, $^3J_{g–f,h}$ = 22.6 Hz), −167.6 (F_c, td, $^3J_{c–d/b}$ = 22.3 Hz, $^5J_{c–a}$ = 9.0 Hz) ppm; ^{11}B{^{1}H} NMR (96.2 MHz) 0.8 (br) ppm; ^{31}P{^{1}H} NMR (121.6 MHz): −19.3 (s), ^{1}H NMR: δ (ppm), 300.3 MHz 2.0 (s, 3H), 6.9 (m, 2H), 7.3 (m, 2H) ppm.

PBB/P(Et)$_3$. ^{19}F NMR (282.5 MHz): −130.3, −131.8, −137.4, −140.4, −141.9, −142.5, −149.1, −150.5, −154.8, −156.6, −157.3, −159.2, −160.6, −162.0, −165.7, −166.8, −184.4 ppm; ^{11}B{^{1}H} NMR (96.2 MHz): 0.4 (br) ppm; ^{31}P{^{1}H} NMR (121.6 MHz): 42.6 (s) ppm; ^{1}H NMR (300.3 MHz): 0.97 (dt, $^4J_{P–H}$ = 13.8 Hz, $^3J_{H–H}$ = 6.8 Hz, 3H), 1.18 (q, $^3J_{H–H}$ = 6.9 Hz, 2H) ppm.

PBB/P(^{n}Bu)$_3$. ^{19}F NMR (282.5 MHz): −130.5, −131.8, −139.2, −140.4, −141.0, −141.4, −142.4, −150.4, −154.8, −156.6, 157.4, −159.0, 160.6, −162.1, −166.1, 167.1, −168.6, −184.4 ppm; ^{11}B{^{1}H} NMR (96.2 MHz): 0.5 ppm; ^{31}P{^{1}H} NMR (121.6 MHz): 36.9 (s) ppm; ^{1}H NMR (300.3 MHz): 0.89 (t, $^3J_{H–H}$ = 6.8 Hz, 3H), 1.28 (m, 2H), 1.37 (m, 2H), 1.39 (m, 2H) ppm.

PBB/P(^{t}Bu)$_3$. ^{19}F NMR (282.5 MHz): −126.7 (F_d, d, $^3J_{Fd–Fc}$ = 23.4 Hz, 1F), −135.0 (F_a, d, $^3J_{Fa–Fb}$ = 22.7 Hz, 1F), −138.7 (F_e, d, $^3J_{Fe–Ff}$ = 26.5 Hz, 2F), −148.7 (F_c, td, $^3J_{Fc–Fb,d}$ = 22.5 Hz, $^5J_{Fc–Fa}$ = 5.1 Hz, 1F), −150.1 (F_g, tt, $^3J_{Fg–Ff}$ = 22.1 Hz, $^5J_{Fc–Fe}$ = 3.4 Hz 1F), −154.3 (F_b, td, $^3J_{Fb–Fa,c}$ = 22.3 Hz, $^5J_{Fb–Fd}$ = 4.5 Hz, 1F), −160.7 (F_f, m, 2F) ppm; ^{11}B{^{1}H} NMR (96.2 MHz): 70.9 ppm; ^{31}P{^{1}H} NMR (121.6 MHz): 61.0 (s) ppm; ^{1}H NMR (300.3 MHz) 1.25 (d, $^3J_{P–H}$ = 10.0 Hz) ppm.

PBB/P(Cy)$_3$. ^{19}F NMR (282.5 MHz): −124.8 (F_d, d, $^3J_{d–c}$ = 29.2 Hz), −135.3 ($F_{e/i}$, d, $^3J_{e/i–f/h}$ = 27.4 Hz), −135.7 ($F_{e/i}$, d, $^3J_{e/i–f/h}$ = 23.5 Hz), −136.5 (F_a, d, $^3J_{a–g}$ = 23.9 Hz), −152.5 ($F_{f/h}$, t, $^3J_{f/h–e/i,g}$ = 21.6 Hz), −154.1 ($F_{f/h}$, t, $^3J_{f/h–e/i,g}$ = 25.5 Hz), −156.9 (F_b, t, $^3J_{b–a}$ = 22.2 Hz), −160.6 (F_g, t, $^3J_{g–f,h}$ = 25.9 Hz), −162.1 (F_c, td, $^3J_{c–d/b}$ = 22.9 Hz, $^5J_{c–a}$ = 8.1 Hz) ppm; ^{11}B{^{1}H} NMR (96.2 MHz): −0.6 (br) ppm; ^{31}P{^{1}H} NMR (121.6 MHz): 44.6 (s) ppm; ^{1}H NMR (300.3 MHz) 0.97 (m), 1.59 (m) ppm.

BAr^{Cl}/P(*p*-tolyl)$_3$. ^{11}B{^{1}H} NMR (96.2 MHz): 71.2, (br) ppm; ^{31}P{^{1}H} NMR (121.6 MHz) −2.85 (s) ppm, ^{1}H NMR (300.3 MHz) 1.81 (s, 3H), 6.9 (m, 2H), 7.3 (m, 2H) ppm.

BAr^{Cl}/P(Et)$_3$. ^{11}B{^{1}H} NMR (96.2 MHz): 69.8 (br) ppm ^{31}P{^{1}H} NMR (121.6 MHz): −15.0 (s) ppm; ^{1}H NMR (300.3 MHz): 0.96 (dt, $^4J_{P–H}$ = 13.8 Hz, $^3J_{H–H}$ = 6.5 Hz, 3H), 1.19 (q, $^3J_{H–H}$ = 7.92 Hz, 2H) ppm.

BAr^{Cl}/P(^{n}Bu)$_3$. ^{11}B{^{1}H} NMR (96.2 MHz) 69.6 (br) ppm; ^{31}P{^{1}H} NMR (121.6 MHz): −27.4 (s) ppm; ^{1}H NMR (300.3 MHz): 0.89 (t, $^3J_{H–H}$ = 7.0 Hz, 3H), 1.29 (m, 2H), 1.37 (m, 2H), 1.39 (m, 2H) ppm.

BAr^{Cl}/P(^{t}Bu)$_3$. ^{11}B{^{1}H} NMR (96.2 MHz) 69.8 (br) ppm; ^{31}P{^{1}H} NMR (121.6 MHz): 61.0 (s); ^{1}H NMR (300.3 MHz): 1.24 (d, $^3J_{P–H}$ = 9.5 Hz) ppm.

BAr^{Cl}/P(Cy)$_3$. ^{11}B{^{1}H} NMR (96.2 MHz): 69.9 ppm, ^{31}P{^{1}H} NMR (121.6 MHz): −14.7 ppm; ^{1}H NMR (300.3 MHz): 1.71 (m, 6H), 1.25 (m, 5H) ppm.

Synthesis of hydride salts with PBB

In accordance with literature preparations,[1,3] NMR tubes containing FLPs were freeze–pump–thaw degassed three times and refilled with H_2. After heating at 90 °C for 22 hours, and 110 °C for 6 hours [PBB–H][H–P(^{t}Bu)$_3$] was produced (96% yield).

[PBB–H][H–P^{t}Bu$_3$]. ^{19}F NMR (282.5 MHz): −124.6 (m), −132.4 (s), −135.0 (dd), −136.9 (d), −137.4 (t), −144.0 (t), −145.5 (m), −150.8 (t), −152.1 (t), −154.1 (t), −155.6 (td), −156.6 (t), −158.2 (t), −159.1 (t), −160.3 (t) ppm; ^{11}B NMR (96.2 MHz): −18.2 (d, $^1J_{B–H}$ = 87.2 Hz) ppm, ^{31}P NMR (121.6 MHz): 60.0 (dm, $^1J_{P–H}$ = 437.7 Hz, $^3J_{P–H}$ = 10.1 Hz) ppm; ^{1}H NMR (300.3 MHz): 4.08 ppm (P–H, d, $^3J_{P–H}$ = 454.8 Hz), 0.75 ppm (^{t}Bu, d, $^3J_{P–H}$ = 15.6 Hz) ppm. ^{13}C{^{1}H} NMR (75.1 MHz): 29.0 ppm (^{t}Bu), Quaternary carbons unassigned.

Synthesis of hydride salts containing BAr^{Cl}

Conditions to which NMR tubes were subjected are listed in Table S3.†

[BAr^{Cl}–H][H–P(Cy)$_3$]. ^{11}B NMR (96.2 MHz): −8.78 (d, $^1J_{B–H}$ = 81.4 Hz) ppm; ^{31}P NMR (121.6 MHz): 30.5 (dm, $^1J_{P–H}$ = 438.0 Hz) ppm; ^{1}H NMR (300.3 MHz): 3.75 (d, $^1J_{P–H}$ = 435.8 Hz) 1.85 (m) 1.30 (m) ppm.

[BAr^{Cl}–H][H–P(^{t}Bu)$_3$]. ^{11}B NMR (96.2 MHz): −8.19 (d, $^1J_{B–H}$ = 77.9 Hz) ppm; ^{31}P NMR (121.6 MHz): 59.7 (d, $^1J_{P–H}$ = 445.0 Hz) ppm; ^{1}H NMR (300.3 MHz): 3.77 (d, $^1J_{P–H}$ = 433.4 Hz), 1.62 (d, $^1J_{P–H}$ = 15.5 Hz) ppm.

[BAr^{Cl}–H][H–P(^{n}Bu)$_3$]. ^{11}B NMR (96.2 MHz): −8.54 (d, $^1J_{B–H}$ = 81.8 Hz) ppm.

[BAr^{Cl}–H][H–P(Et)$_3$]. ^{11}B NMR (96.2 MHz): −8.62 (d, $^1J_{B–H}$ = 67.8 Hz) ppm.

[BAr^{Cl}–H][H–P(*p*-tolyl)$_3$]. ^{11}B NMR (96.2 MHz): −8.37 (d, $^1J_{B–H}$ = 83.0 Hz) ppm.

Synthesis of hydroborate salts

A drop of degassed H_2O was added to a mixture of PBB (60 mg, 62.8 μmol) and P(^{t}Bu)$_3$ (12.7 g, 62.8 μmol) in toluene in an ampoule. The solution was stirred for 16 hours at room temperature before the solvent was removed *in vacuo*.

[PBB–OH][H–P(^{t}Bu)$_3$]. ^{19}F NMR (282.5 MHz): −129.5 (F_d, dd, $^3J_{d–c}$ = 22.8 Hz, $^5J_{d–b}$ = 12.4 Hz), −140.3 ($F_{e/i}$, dd, $^3J_{e/i–f/h}$ = 24.3 Hz, $^5J_{e/i–g}$ = 7.9 Hz), −140.7 ($F_{e/i}$, dd, $^3J_{e/i–f/h}$ = 24.1 Hz, $^5J_{e/i–g}$ = 12.8 Hz), −141.6 (F_a, dd, $^3J_{a–b}$ = 25.3 Hz, $^5J_{a–c}$ = 8.8 Hz), −157.7 ($F_{f/h}$, t, $^3J_{f/h–e/i,g}$ = 21.9 Hz), −158.0 ($F_{f/h}$, t, $^3J_{f/h–e/i,g}$ = 23.6 Hz), −161.3 (F_b, t, $^3J_{b–a,c}$ = 22.7 Hz), −165.2 (F_g, tt, $^3J_{g–f,h}$ = 23.0 Hz, $^5J_{g/e,i}$ = 6.4 Hz), −167.3 (F_c, td, $^3J_{c–b,d}$ = 23.1 Hz, $^5J_{c–a}$ = 8.1 Hz) ppm; ^{11}B{^{1}H} NMR (96.2 MHz): −3.90 (s) ppm; ^{31}P NMR (121.6 MHz): 60.0 (dm, $^1J_{P–H}$ = 430.7 Hz, $^3J_{P–H}$ = 15.8 Hz) ppm; ^{1}H NMR (300.3 MHz): 4.21 (P–H, dm, $^1J_{P–H}$ = 433.2 Hz, $^3J_{P–H}$ =

15.8 Hz, 1H), 0.93 (^{t}Bu $^3J_{P-H}$ = 15.7 Hz, 27 H) ppm. $^{13}C\{^1H\}$ NMR (75.1 MHz): 30.2 ppm (^{t}Bu), Quaternary carbons unassigned.

Synthesis of formatoborates *via* route B

One equivalent of both Lewis acid and Lewis base were added to a Schlenk, (precise quantities are listed in Table S4†), before being dissolved in appropriate solvent. A single drop of formic acid was then added, before the mixture was stirred for 16 hours, after which the solvent was removed *in vacuo*.

[PBB–OC(O)–H][H–P(^{t}Bu)$_3$]. $^{19}F\{^1H\}$ NMR (282.5 MHz): −123.7 (s, 3F), −136.8 (s, 3F), −137.0 (d, J = 24.6 Hz, 3F), −137.6 (s 3F), −156.0 (t, J = 21.9 Hz, 3F), −156.4 (t, J = 23.7 Hz, 3F), −158.9 (t, J = 22.5 Hz 3F), −164.5 (br. s, 3F), −164.7 (t, J = 28.2 Hz, 3F) ppm; $^{11}B\{^1H\}$ NMR (96.2 MHz): −0.60 (br) ppm; $^{31}P\{^1H\}$ NMR (121.6 MHz) 61.8 (s) ppm; ^{1}H NMR (300.3 MHz): 8.02 (formate, s), 4.49 (P–H, $^1J_{P-H}$ = 444.6 Hz), 0.80 (^{t}Bu, $^3J_{P-H}$ = 15.2 Hz), $^{13}C\{^1H\}$ NMR (75.1 MHz): 29.1 ppm (^{t}Bu), Quaternary carbons unassigned. Infra-Red: 1681 cm^{-1} (s) ppm.

[BAr^{Cl}–OC(O)–H][H–P(^{t}Bu)$_3$]. $^{11}B\{^1H\}$ NMR (96.2 MHz): 3.8 (br) ppm; $^{31}P\{^1H\}$ NMR (121.6 MHz): 62.0 (s) ppm, ^{1}H NMR (300.3 MHz) 8.08 (s, formate) 1.09 (d, $^3J_{P-H}$ = 12.2 Hz, P–H) ppm, infra-red (neat): 1689 cm^{-1} (s).

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