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Hydrogen Cleavage by Solid-Phase Frustrated Lewis Pairs

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We report the direct synthesis of a solid-phase frustrated Lewis pair (*s*-FLP) by combining a silica-supported Lewis acid (≡SiOB(C_6F_5)$_2$, *s*-BCF) with a Lewis base (tri-tert-butylphosphine, ^{t}Bu$_3$P) to give [≡SiOB(C_6F_5)$_2$][^{t}Bu$_3$P]. Reaction of this *s*-FLP with H_2 under mild conditions led to heterolytic H−H bond cleavage and the formation of [≡SiOB(H)(C_6F_5)$_2$][^{t}Bu$_3$PH].

Hydrogenation lies at the heart of many important chemical transformations. Such processes have been widely employed by industry, ranging from the upgrading of crude oil, to the synthesis of a variety of pharmaceutical and agricultural chemicals.[1] The majority of hydrogenation catalysts used by industry are metal based homogeneous or heterogeneous catalysts.[2,3] Non-biological metal-free systems that reversibly activate H_2 are rare.

The exploitation of frustrated Lewis pairs (FLPs) as a new class of metal-free hydrogenation catalyst stems from the pioneering work by Stephan *et al.* in 2006 on the unique reversible H_2 heterolysis exhibited by the phosphine-borane ($C_6H_2Mes_2$)$_2$P(C_6F_4)B(C_6F_5)$_2$.[4] Stephan further demonstrated that combination of bulky phosphines with B(C_6F_6)$_3$ lead to the formation of intermolecular FLP systems, which have also shown facile H_2 cleavage properties, while Erker *et al.* reported intramolecular FLP systems where the Lewis acid and base are linked by an ethylene bridge.[5] The unquenched acidic and basic counterparts in both inter- and intramolecular FLPs play essential roles in synergistic activation or fixation of a wide range of small molecules, including CO_2,[6–9] NO,[10] CO, H_2, N_2O, and SO_2.[11] Remarkably when activated with H_2 subsequent hydrogenation can take place on a variety of unsaturated bonds, ranging from imines, enamines, carbonyls to alkenes and alkynes, in a facile manner. Moreover, the tuneable structural properties of the acid and base components allow increased substrate selectivity, activation and broadening of the substrate scope, which further demonstrates the high versatility of FLP chemistry.[12–17]

FLPs have so far demonstrated extensive solution phase catalytic hydrogenation activity, however for the successful implementation of this technology in large-scale hydrogenation processes, heterogeneous catalysts will be required. This is due to the many well-documented industrial requirements including catalyst separation and the capability of using catalysts in continuous gas or liquid feed fixed bed reactors, or in slurry-phase reactors.[18,19] Silica has been the most commonly used supporting material for single-site polymerisation catalysts,[20] since it offers many advantages, including its inert properties and facile control of its surface hydroxyl content by simple thermo-treatments.[21–23] Silica supported B(C_6F_5)$_3$ (***s*-BCF**) has been reported as a co-catalyst for supported olefin polymerisations.[24,25]

Recently, Taoufik *et al.* reported the immobilisation of a 4-hydroxyphenyl)diphenyl phosphine on a tri-isobutyl aluminum modified silica support and the subsequent treatment with B(C_6F_5)$_3$ or HB(C_6F_5)$_2$ to produce surface bound FLPs. The former example showed highly Z-selective reduction of 3−hexyne at 98% under forcing conditions (40 bars, 80°C), whereas the latter only showed 9% reduction under the same conditions. The authors proposed that reduction of the alkyne occurred via a hydroboration reaction with HB(C_6F_5)$_2$ that was coordinated to the surface bound phosphine sites. However, the capability of H_2 activation of the latter example containing BCF as the Lewis acid was not reported. Furthermore, the preparation of their supported Lewis acid/base catalysts require multiple-stage synthesis, which may reduce the practicality of such systems.[26]

Here we report a facile preparation and extensive NMR characterisation of an ***s*-FLP** and its reactivity on exposure to hydrogen at low pressure. Reaction of silica-500 (pre-treated at 500 °C under vacuum for 4 h, BET surface area: 310 $m^2 g^{-1}$, containing 0.57 mmol g^{-1} of accessible ≡Si*OH*) with stoichiometric amount of HB(C_6F_5)$_2$ led to the formation of ***s*-BCF** (containing 6.8 wt. % C, 0.478 mmol of BCF per gram of silica).

Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, UK. E-mail: dermot.ohare@chem.ox.ac.uk † Electronic supplementary information (ESI) available: [General experimental and spectroscopic details].
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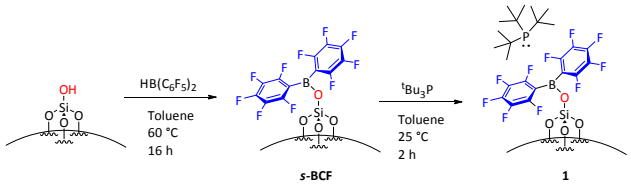

Scheme 1

Subsequent addition of a stoichiometric amount of $^{t}Bu_3P$ to the ***s*-BCF** afforded the ***s*-FLP** [≡SiOB(C_6F_5)$_2$][$^{t}Bu_3P$] (**1**), Scheme 1, which have been studied by FTIR (Fig. 1), solution- and solid-state NMR spectroscopy, (Fig. 2).

The IR spectrum of the unmodified silica-500 (Fig. 1a) contains a sharp absorption at 3746 cm^{-1} which is associated with accessible non-hydrogen bonded isolated hydroxyl groups on the silica surface, with a broad shoulder at 3680 cm^{-1} assigned to inaccessible silanols.[27] After modification with HB(C_6F_5)$_2$ (Fig. 1b), the sharp band disappeared, while the broad shoulder still remained, indicating that the surface hydroxyl groups have been converted to -OB(C_6F_5)$_2$. Several vibration modes are present in the range from 1325 to 1660 cm^{-1}, which are associated with B−O, B−C stretching, C−B−C wagging and C_6F_5 ring breathing modes. These results are consistent with the observations reported by Scott *et. al.*[24] After addition of $^{t}Bu_3P$ to the ***s*-BCF** in benzene slurry to afford **1** (Fig. 1c), new absorptions appeared at 2946 and 1466 cm^{-1} which are due to the ^{t}Bu groups on the Lewis base. In addition, the vibration bands which are associated with C_6F_5 ring breathing modes are both broaden and experience a 10 cm^{-1} red-shift of the 1524 cm^{-1} band. This is perhaps due to restricted C_6F_5 ring breathing motions caused by strong steric repulsions between the Lewis acid and base when they are in close proximity.

Solid-state NMR spectroscopic characterisations of **1** revealed weak B−P interactions, and this is consistent with the findings reported by Erker and co-workers.[28,29] This is evidenced by the isotropic chemical shifts (δ_{iso}) of the pair of core heteronuclei (^{11}B and ^{31}P), (Fig. 2). The $^{11}B\{H\}$-{F} DEPTH NMR spectrum of ***s*-BCF** (Fig. 2a) contains one broad resonance at 20 ppm with a shoulder at 10 ppm.

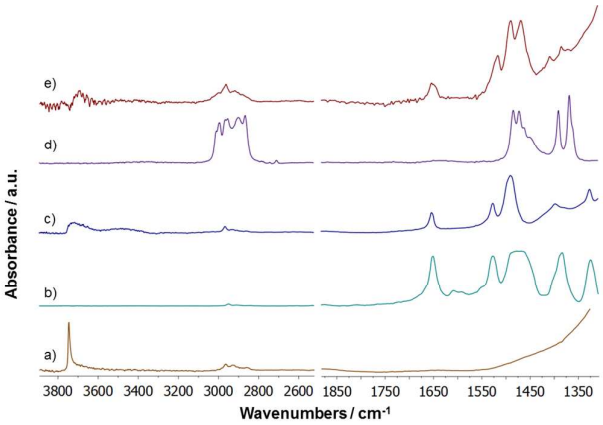

Fig. 1 DRIFT spectra of: a) silica-500. b) neat (C_6F_5)$_2$BH. c) silica-500 treated with (C_6F_5)$_2$BH (**s-BCF**). d) neat $^{t}Bu_3P$. e) addition of stoichiometric amount of $^{t}Bu_3P$ to form [≡SiOB(C_6F_5)$_2$][$^{t}Bu_3P$] (**1**).

The broad signal corresponds to the expected ***s*-BCF**, whereas the shoulder at 10 ppm is due to the formation of ≡(SiO)$_2$B(C_6F_5) caused by further side reaction of ≡SiOB(C_6F_5)$_2$ with nearby ≡SiOH groups. This finding is consistent with the results reported by Scott *et al.*.[24]

The solid state $^{11}B\{H\}$-{F} DEPTH spectrum of **1** features a narrow resonance and a broad shoulder with a complex line shape, (Fig. 2b). Coordination of $^{t}Bu_3P$ to ***s*-BCF** causes a downfield shift of 20 ppm to the ^{11}B nucleus. Furthermore, the increase from tri- to tetra-coordination results in a reduction in both the C_Q and η_Q value of the ^{11}B nucleus, hence a narrower resonance.[30] For instance, the narrow component at 1 ppm is consistent with a phosphine coordinated tetra-coordinated borate, whereas the broad shoulder at 10 ppm is assigned to tri-coordinate ≡(SiO)$_2$B(C_6F_5) which is essentially unaffected by the presence of $^{t}Bu_3P$. However, due to the amorphous nature of **1**, the exact C_Q and η_Q values are therefore difficult to extract.

The ^{31}P HPDEC MAS NMR spectrum of **1** also contains several resonances, (Fig. 2c). The sharp resonance at 48 ppm corresponds to phosphine coordinated to the Lewis acidic sites. The underlying broad resonance at 48 ppm is also attributed to phosphine associated with the Lewis acidic sites, which is perhaps broadened due to hindered motion. Although we observe phosphine coordination to the Lewis acid sites in the solid-state NMR, suggesting the formation of Lewis adducts, free unbound $^{t}Bu_3P$ can be observed in the solution-state ^{31}P and ^{1}H NMR of a suspension of **1**. This indicates that the coordination between the Lewis acid and base must be relatively weak, and that the steric repulsion may be sufficient to establish a dissociative equilibrium between the bound and unbound phosphine in a solvent suspension of **1**. Furthermore, washing **1** with generous amounts of toluene on a fritted glass disc resulted in the removal of $^{t}Bu_3P$ from **1** indicating that **1** is a genuine FLP. Similar observations of weak Lewis adduct formation in FLPs in the solid-state structure have also been reported by Erker *et al.*[28]

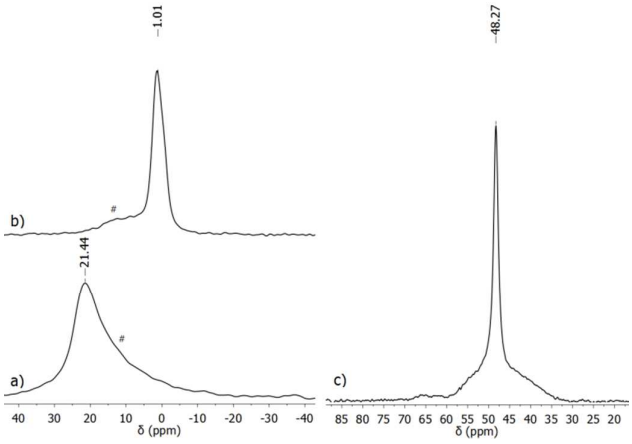

Fig. 2 Solid state ^{11}B {H}-{F} DEPTH MAS NMR spectra at 24 kHz spinning rate of: a)[≡SiOB(C_6F_5)$_2$] (**s-BCF**) and b) formation of [≡SiOB(C_6F_5)$_2$][$^{t}Bu_3P$] (**1**). c) Solid state ^{31}P HPDEC MAS NMR spectrum of [≡SiOB(C_6F_5)$_2$][$^{t}Bu_3P$] (**1**) at 24 kHz spinning rate.

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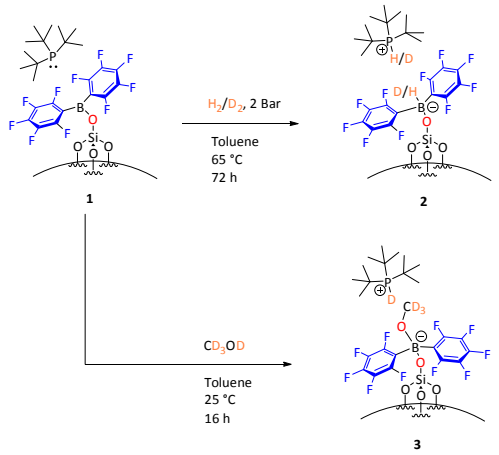


Scheme 2

Reaction of a suspension of **1** in toluene with H_2 occurs more slowly than the analogous solution phase system, nonetheless after 72 h at 65 °C, we observe the formation of **2.** Evidence for the formation of **2** is supported by the solid-state ^{11}B and ^{31}P NMR spectra, (Fig. 3). In particular, the ^{11}B-^{1}H CP MAS spectrum of **2** (Fig. 3a) contains a single narrow resonance at −2.3 ppm. This result is consistent with the solution state ^{11}B NMR spectrum of a silsesquioxane mimic **5** (*vide infra*). Moreover, in the ^{11}B-^{1}H CP MAS spectrum, the ^{11}B nuclei needs to be in close proximity to a ^{1}H nucleus in order for it to be observable in the spectrum, therefore this result supports the formation of a B−H bond. Furthermore, the ^{31}P-^{1}H CP MAS spectrum of **2** (Fig. 3b) contains a major signal at 54 ppm, which is assigned to a protonated phosphine environment as the result of H_2 cleavage reaction. This result is also in good agreement with the literature[31] as well as with the solution state ^{31}P NMR spectrum of **5**. The ^{2}H DPMAS spectrum of deuterated **2** (prepared by the reaction of **1** with D_2) showed a broad signal with complex line shape at the range between 1 to 10 ppm. This result is also in good agreement with the P−H signal observed in the solution-state ^{1}H NMR spectrum of **5**, indicating D_2 incorporation and further supporting the formation of **2**, (Fig. S2).

1 has also been found to activate polar OD bonds. Reaction of **1** with deuterated methanol (CD_3OD) at room temperature yielded [≡SiOB(OCD_3)(C_6F_5)$_2$][$^{t}Bu_3PD$] **3**. The DRIFT spectrum of

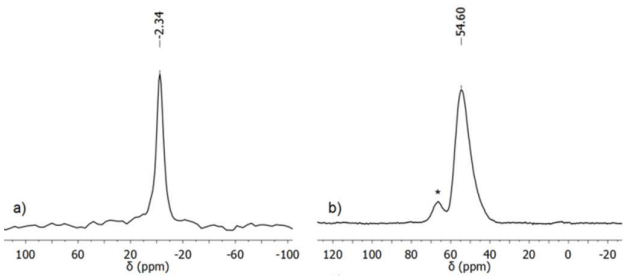


Fig. 3 a) Solid state ^{11}B-^{1}H CP MAS NMR spectrum of **2** at 10 kHz spinning rate, b) Solid state ^{31}P-^{1}H CP MAS NMR spectrum of **2** at 10 kHz spinning rate (*unreacted $^{t}Bu_3P$)

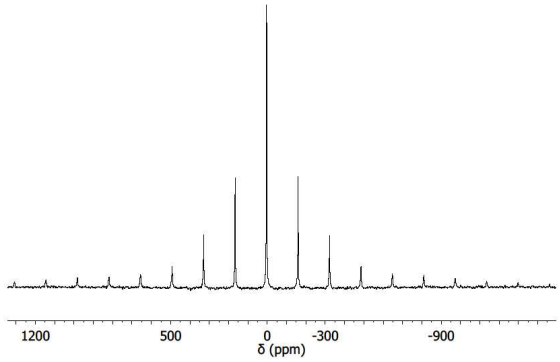
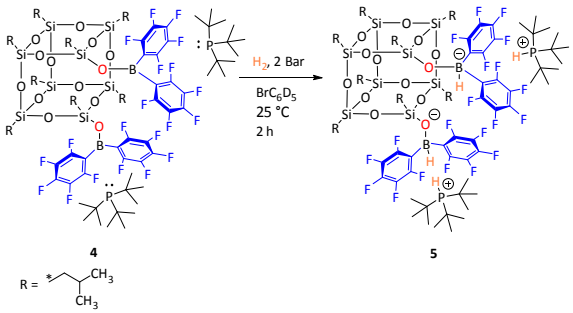


Fig. 4 Solid state ^{2}H DPMAS NMR spectrum of **3** at 10 kHz spinning rate.

3 has shown a characteristic absorption at 2083 cm^{-1} which corresponds to OCD_3 moiety, (Fig. S1).[32] The solid state ^{2}H MAS NMR spectrum of **3** showed a deuterium signal with a central band at δ_{iso} = 3.21 ppm, (Fig. 4). This signal was assigned to the –OCD_3 group and this finding is consistent with the solution phase NMR result of [(C_6F_5)$_3$B(OCH_3)][TMPH] reported by Ashley *et al.* (–OCH_3 at 3.12 ppm in CD_2Cl_2).[9] Furthermore, the shape of the spinning side bands is the characteristics of mobile D atoms within the sample, perhaps due to rapid rotation of the CD_3 group about the O–C bond.[33] The solid-sate NMR spectra of the pair of core heteronuclei (^{11}B and ^{31}P) both exhibit a narrow signal, and the δ_{iso} of both nuclei are very similar to the values found for **2**, (Fig S2 and Fig S3).

Further to our studies, we have prepared a solution phase mimic of **1** and studied its H_2 activation ability, Scheme 3. The solution state NMR results we obtained for this mimic system was highly consistent with the solid state NMR results of **2**. *endo*-3,7-di{[bis(pentafluorophenyl)boryl]oxy}-1,3,5,7,9,11,14-octaisobutyltetracyclo[7.3.3.1]heptasiloxane (T_8(OB(C_6F_5)$_2$)$_2$) formed via the reaction of HB(C_6F_5)$_2$ with the corresponding silsesquioxanediol was subsequently combined with two equivalents of $^{t}Bu_3P$ to form [T_8(OB(C_6F_5)$_2$)$_2$][($^{t}Bu_3P$)$_2$] (**4**) (see Fig. S5-S7). After 2 h of reaction at 25 °C under 2 bars of H_2, formation of **5** was observed. Evidence for the formation of **5** was supported by the observation of a protonated phosphine in the ^{31}P and ^{1}H NMR (Fig. S8 and S9). The doublet signal at 4.4 ppm in the ^{1}H NMR spectrum accompanied by a doublet of multiplet signal at 58 ppm in the ^{31}P NMR spectrum with a J coupling constant of 444 Hz, is in good agreement with the literature findings.[31]



Scheme 3

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Furthermore, in the ^{11}B NMR spectrum, the initial broad signal at 40 ppm which corresponds to a tri-coordinate borate **4** has narrowed greatly and shifted to 2.75 ppm in the ^{11}B NMR spectrum (Fig. S10). This finding is consistent with formation of the four coordinate hydridoborate **5**. In contrast, combination of **4** with more sterically hindered trimesitylphoshine Mes_3P also indeed forms an FLP, however, no reaction was observed when exposed to H_2 even under prolonged heating. This perhaps is due to steric factors causing reduced FLP reactivity.

We have demonstrated a simple straightforward preparation of a solid-phase FLP system. Solid-state NMR revealed Lewis adduct formation in the solid structure. The resulting ***s*-FLP** (**1**) is the first solid that has been spectroscopically shown to heterolytically cleave H_2. Preliminary work indicates that **1** is a solid-phase hydrogenation catalyst for unactivated alkenes but further work is in progress to optimise the reaction that will be reported at a later date. Furthermore, making improvements of our current system and expanding the scope of ***s*-FLPs** will continue to be the focus of our future studies.

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