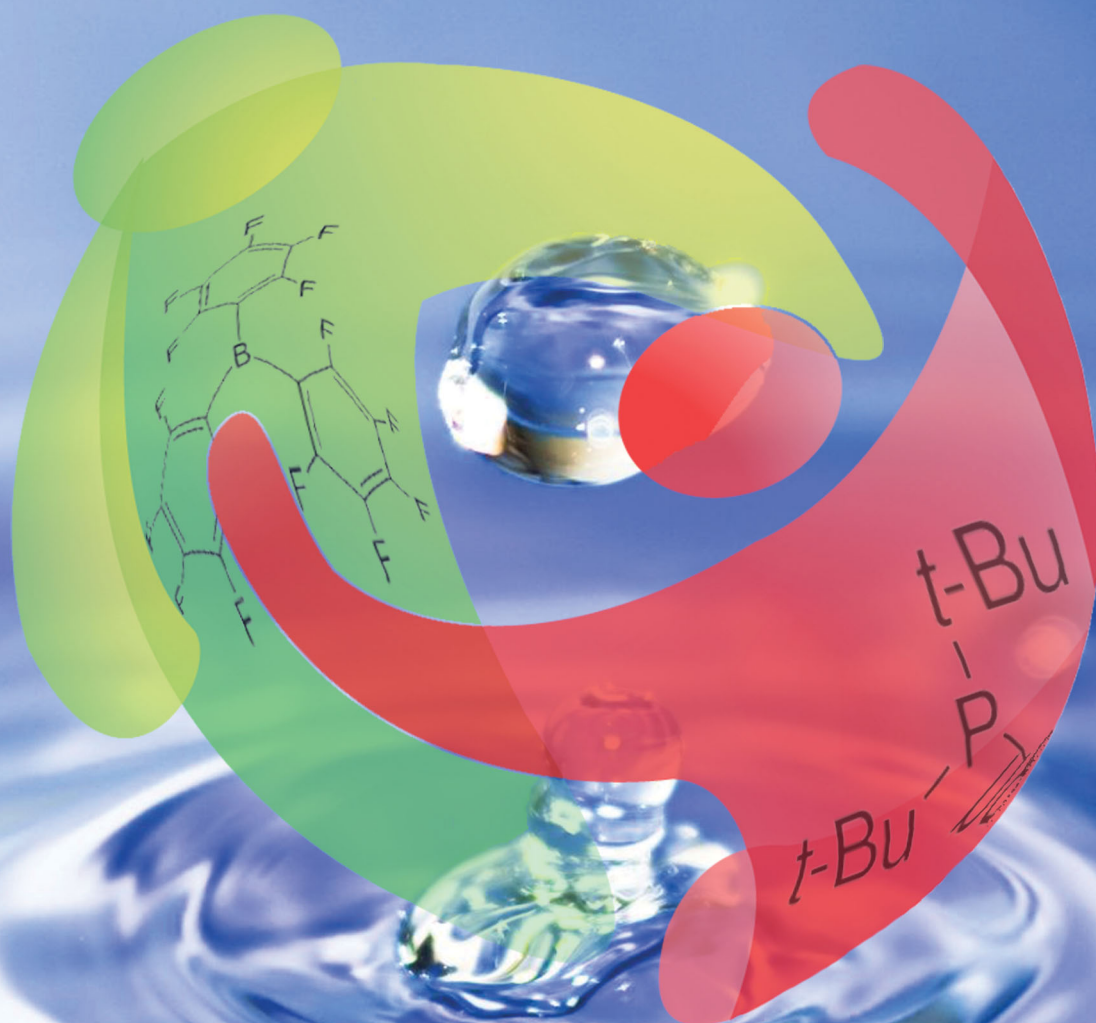


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Frustrated Lewis pairs in ionic liquids and molecular solvents – a neutron scattering and NMR study of encounter complexes†

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The presence of the weakly-associated encounter complex in the model frustrated Lewis pair solution (FLP): tris(*tert*-butyl)phosphine (P(*t*Bu)₃) and tris(pentafluorophenyl)borane (BCF) in benzene, was confirmed via P⋯B correlation analysis from neutron scattering data. On average, ca. 5% of dissolved FLP components were in the associated state. NMR spectra of the FLP in benzene gave no evidence of such association, in agreement with earlier reports and the transient nature of the encounter complex. In contrast, the corresponding FLP solution in the ionic liquid, 1-decyl-3-methylimidazolium bistriflamide, [C₁₀mim][NTf₂], generated NMR signals that can be attributed to formation of encounter complexes involving over 20% of the dissolved species. The low diffusivity characteristics of ionic liquids is suggested to enhance high populations of encounter complex. The FLP in the ionic liquid solution retained its ability to split hydrogen.

Frustrated Lewis pairs (FLPs) are combinations of a Lewis acid and a Lewis base, where adduct formation is prevented by steric hindrance.¹ The proximity of free Lewis acidic and Lewis basic sites gives rise to interesting reactivity, particularly in the activation of a range of small molecules – including metal-free H₂ splitting (Fig. 1).^{1,2} FLP catalysis is now a rapidly-growing field and the seminal paper reporting the metal-free hydrogen activation² has been cited over 900 times.

Although neither the isolated Lewis acids nor bases coordinate H₂, hydrogen activation by FLPs follows bimolecular reaction kinetics, despite three species being involved. This has led to the proposition that pre-organised acid–base encounter complexes must be present in solution, supported by kinetic analysis and computational studies.^{3–5} However conclusive experimental

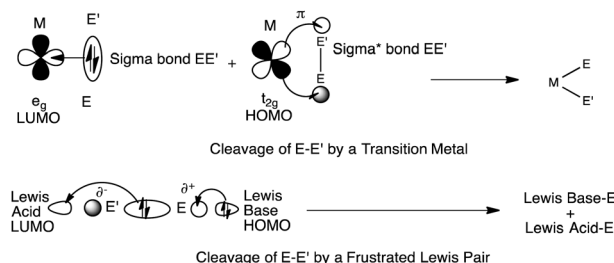


Fig. 1 Representation of the orbital interactions in substrate cleavage (E–E') by (i) a transition metal and (ii) an FLP.

evidence is limited.⁴ Solution state DFT simulation of P(*t*Bu)₃/BCF pairs in benzene indicates that the associate states have much lower thermodynamic stabilisation compared to previous gas phase calculations.⁵ Association through partial P–B dative bonding ($r_{P-B} < 4.2 \text{ \AA}$) is disfavoured due to reduction in conformational freedom, but associated states with larger P⋯B separation distances, including solvated “encounter pairs” ($r_{P-B} \sim 6.5 \text{ \AA}$) and solvent-separated pairs ($r_{P-B} \sim 8 \text{ \AA}$) have been identified. Associated state populations were estimated at very low levels, ca. 2% of the total amount of phosphine and borane in the system.

Conventional 1D NMR spectroscopy has failed to provide evidence for the encounter complex formation;⁵ however, the paucity of direct spectroscopic evidence could be a direct consequence of these low association energies and small dynamic populations. Rocchigiani *et al.*⁷ described ‘marginal shifts’ of the ¹⁹F NMR resonances upon saturating a highly concentrated phosphine solution in benzene with BCF, and no change to the ³¹P NMR spectra upon titration of concentrated BCF solutions with trimesitylphosphine. H/F association was identified from 2D ¹⁹F, ¹H HOESY NMR experiments, providing the first direct evidence for encounter complex in FLP solutions. Association via non-specific weak H/F dispersive forces was suggested, with the phosphine and borane in random relative orientations. Consistent with the DFT simulations,⁴ these diffusion NMR studies indicated that only a small fraction of the components in solution were associated.

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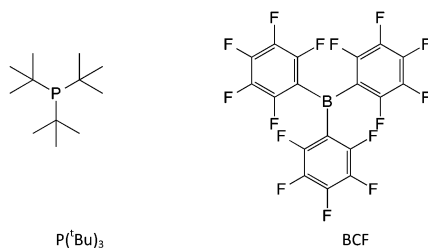


Fig. 2 The FLP components considered for this study.

Neutron diffraction is a powerful tool to study structure and solvation in both molecular^{8,9} and ionic¹⁰ liquids. Combined with H/D isotopic substitution,¹¹ multiple experimental data sets can be obtained with different scattering profiles associated with correlations from isotopically distinct sites. Using an approach such as empirical potential structure refinement (EPSR)¹² simulation models can be refined self-consistently to these multiple experimental scattering data sets. The resulting solution structure allows analysis of complex systems, even when the individual correlation functions are not accessible.

Here, we set out to examine concentrated equimolar solutions of BCF/ $P(tBu)_3$ (Fig. 2) in benzene, using the total neutron scattering data combined with EPSR analysis to isolate the $P \cdots B$ pair distribution function, and through this to provide experimental verification of the encounter complex. The Lewis acid/base pair was selected as a model system to compare with results from DFT simulation by Bakó *et al.*⁴ and NMR spectroscopy from Rocchigiani *et al.*⁷

Neutron scattering data were collected from equimolar solutions of $P(tBu)_3$ /BCF in benzene- h_6 , in benzene- d_6 and in 1:1 H/D mixture at 160 mmol concentration, which is equivalent to a 1:1:70 molar ratio of $P(tBu)_3$:BCF:benzene. The neutron scattering data was reduced, correcting for the instrumental parameters with Gudrun,¹³ and modelled using EPSR¹² with a cubic simulation box of sides 47.8 Å in length, containing 10 $P(tBu)_3$, 10 BCF and 700 benzene molecules (ESI†).

As expected, solvent/solute partial radial distribution functions from the EPSR model (Fig. S13, ESI†) show that most $P(tBu)_3$ and BCF molecules are solvated by benzene. The closest centre-of-mass correlation of BCF with benzene at ~ 4 Å, suggests π -donation from a solvent molecule aromatic system towards the vacant p-orbital on the Lewis acidic boron atom. The first shell benzene–phosphine correlation occurs at ~ 7 Å, consistent with first shell packing around the bulky *tert*-butyl substituents. Finally, the benzene–benzene correlation features first shell maxima at *ca.* 5.8–6.0 Å, consistent with the structure of bulk neat benzene.⁹

Formation of encounter complexes was expected to generate correlations in the $P \cdots B$ site–site distribution function, manifesting as peaks in the partial radial distribution function plot, accumulated over the time-frame of the structure simulation. Indeed, the $P \cdots B$ radial distributions generated from two independent data-driven simulations (Fig. 3) feature two signals which provide enticing evidence for the association of the phosphine and borane molecules. In both cases, a small

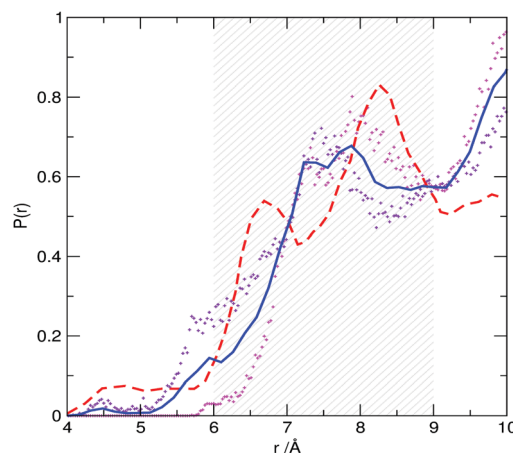


Fig. 3 The plot of the $P \cdots B$ pair partial radial correlation function (blue) between $P(tBu)_3$ and $B(C_6F_5)_3$ in benzene (1:1:70), averaged from two independent data-driven simulation models (purple and magenta data points), and compared to the equivalent correlation from DFT simulation⁴ of $P(tBu)_3$ and $B(C_6F_5)_3$ in toluene (red line). Correlation distances corresponding to the range of ‘solvent-separated’ pairs (6–9 Å) are indicated by the shaded region.

maximum at *ca.* 8 Å is followed by a second peak at *ca.* 10.5 Å, before the correlation reaches a probability of 1 (homogeneous distribution) beyond ~ 14 Å. The concentrations of BCF and $P(tBu)_3$ are low for neutron scattering experimental standards. This resulted in poor resolution for the specific site–site interactions, and thus in some variability in the refinement solutions, which is evident in the differences between the $P \cdots B$ distribution functions from the two refinement runs (Fig. 3). Nevertheless, both runs feature the peaks at *ca.* 8 and 10.5 Å.

From the running coordination number for $P \cdots B$ correlation lengths, $P(r)$, there is $< 1\%$ correlation at $P \cdots B$ separations of 5.7 Å, but this value increases at separation distances between 6–8 Å, to reach 4.9% at 8 Å. The 8 Å distance is of the same order as the “solvent-separated” pairs described by Bakó *et al.*⁴ and appears consistent with the H/F-contact interactions described by Rocchigiani *et al.*⁷ Slightly less than 5% of the borane and phosphine molecules contribute to the encounter complex, and of these, the majority are associated with a $P \cdots B$ separation of ~ 8 Å, which again is in agreement with DFT results.⁴ This strongly suggests that the small number (nearly 5%) of encounter complexes present in benzene solution of BCF/ $P(tBu)_3$ can be observed directly from the neutron total scattering data. In conclusion, the encounter complex can be detected, but our results corroborate with low concentration and transient nature of this association reported elsewhere.

The relative concentration of encounter complexes in solution is critical factor for enhancing the kinetics of FLP-promoted hydrogenation reactions.⁶ The second part of this study explored the opportunity to use the low diffusivity of solutes in ionic liquid media to stabilise encounter complexes of FLP. Solutions of BCF, $P(tBu)_3$ and BCF/ $P(tBu)_3$ in $[C_{10}mim][NTf_2]$ were prepared at 160 mmol concentrations, in keeping with concentrations used for neutron scattering experiments. No colour change was observed upon dissolution of the FLP components in $[C_{10}mim][NTf_2]$.

Table 1 ^{19}F and ^{31}P NMR signals of solutions of the BCF/ $\text{P}(\text{tBu})_3$ FLP and its individual components in benzene- d_6 and in an ionic liquid, $[\text{C}_{10}\text{mim}][\text{NTf}_2]$

| | ^{19}F signals/ppm | ^{31}P signals/ppm |
|---|--|-----------------------------|
| $\text{P}(\text{tBu})_3$ in benzene- d_6 | — | 61 |
| $\text{P}(\text{tBu})_3$ in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ | — | 60 |
| BCF in benzene- d_6 | -134, -149, -161 | — |
| BCF in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ | -133, -157, -166 | — |
| FLP in benzene- d_6 | -139, -152, -162 | 61 |
| FLP in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ | -134, -138, -140 -151, -156, -160 -164, -165, -166 | 53, 61 |

Solutions of the FLP and its individual components in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ were studied by ^{19}F and ^{31}P NMR spectroscopy. NMR spectra of isolated FLP components were nearly identical to NMR spectra of these components in benzene- d_6 , with a small discrepancy attributable to the solvent effect, but no indication of hydrolysis, oxidation, or strong interaction with the ionic liquid (Table 1). However, the solution containing both BCF and $\text{P}(\text{tBu})_3$ featured additional signals, absent from NMR spectra of the corresponding benzene- d_6 solution (Table 1). For the ease of comparison, ^{19}F and ^{31}P NMR spectra of the FLP in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ were overlaid with relevant spectra of its individual components in the same ionic liquid (Fig. 4).

Three ^{19}F NMR signals originating from BCF in the ionic liquid corresponded to averaged *ortho*-, *meta*- and *para*-fluorine environments in BCF (Fig. 2). Upon combination with $\text{P}(\text{tBu})_3$, very little change occur in their chemical shift (maximum $\Delta\delta_{19\text{F}} = 3$ ppm for the *meta*-fluorines). However, at least six new distinctive signals appeared at ^{19}F NMR chemical shifts very similar to the original peaks (Table 1). The most likely explanation for these signals is BCF entering a weak, but relatively long-lasting interaction with $\text{P}(\text{tBu})_3$, through which the three perfluorophenyl ligands cease to be identical in terms of their electronic environment. Peak area ratio of the signals from free BCF vs. the new smaller signals is 1 : 0.312, suggesting that *ca.* 24% of the BCF underwent a change of electronic environment upon contact with $\text{P}(\text{tBu})_3$.

The ^{31}P NMR spectrum of $\text{P}(\text{tBu})_3$ in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ features a single peak at 60 ppm, similar to the benzene- d_6 solution (Table 1).

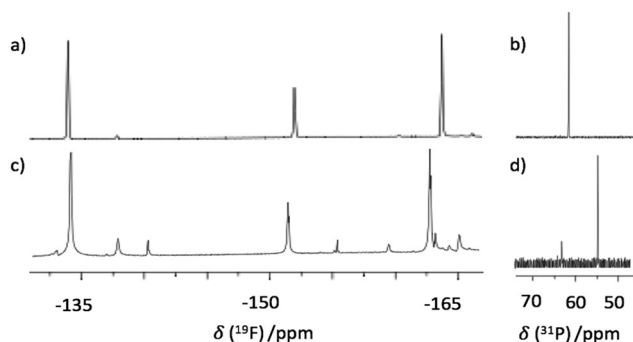


Fig. 4 Spectra of the FLP, BCF/ $\text{P}(\text{tBu})_3$, and its components, in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ (a) ^{19}F NMR spectrum of BCF, (b) ^{31}P NMR spectrum of $\text{P}(\text{tBu})_3$, (c) ^{19}F NMR spectrum of BCF/ $\text{P}(\text{tBu})_3$ and (d) ^{31}P NMR spectrum of BCF/ $\text{P}(\text{tBu})_3$.

In the spectrum of the FLP solution, this signal is slightly shifted due to solvent effect ($\Delta\delta_{31\text{P}} = +1$ ppm), but the main signal is a new upfield peak at 53 ppm ($\Delta\delta_{31\text{P}} = -8$ ppm). The measured peak area ratio between the free $\text{P}(\text{tBu})_3$ signal and the new signal is about 0.29 : 1, which indicates that *ca.* 78% of phosphines experienced a change in electronic environment. On average, when phosphines form adducts with strong Lewis acids, their ^{31}P NMR signal shifted downfield by about $\Delta\delta_{31\text{P}} = +20$ ppm;¹⁴ for example, triphenylphosphine adduct with BH_3 has $\Delta\delta_{31\text{P}} = +26$ ppm compared to free triphenylphosphine.¹⁵ Therefore, this change where the ^{31}P nuclei is slightly shielded, rather than deshielded, does not suggest adduct formation, but a different interaction mode.

The additional resonances observed for FLP in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ – but not for individual components – give clear evidence for interaction between the phosphine and borane. Furthermore, the fact that they are easily observed through NMR spectroscopy suggests stabilisation of these species in the ionic liquid medium. Interestingly, the stoichiometric ratio of species that seem to partake in this interaction is not equimolar, but *ca.* 3 : 1 for BCF : $\text{P}(\text{tBu})_3$. From these data, it is impossible to make definitive assignments to the nature of the association. However, it is clear that about 24% of BCF and 78% of $\text{P}(\text{tBu})_3$ are in different environments in the FLP solution which – in the absence of other factors – should be attributed to the interaction between the FLP components.

Direct acid–base interaction, with the Lewis base lone pair pointing in the direction of the Lewis acid empty orbital (and possibly partial orbital overlap) can be excluded, seeing as the ^{31}P NMR signal was shielded, rather than deshielded. This is in agreement with earlier results for FLPs in organic solvents by Bakó *et al.*⁴ (DFT) and Rocchigiani *et al.*⁷ (2D NMR spectroscopy), who suggested that FLPs form “solvent-separated pairs”, with many equally probable association orientations through H/F interactions. Results presented here, although not conclusive, align with this interpretation. However, in this work FLP components are solvated not by molecules, but by the ions of the ionic liquid, which appears to stabilise the encounter complex. This stabilisation can be attributed to high cohesive energy densities and internal pressure,¹⁶ combined with slow diffusivity¹⁷ in ionic liquids, which leads to matrix isolation. Ionic liquids may not promote the FLP formation, but are likely to reduce its tendency for disassociation when formed.

The extended life of encounter complex in the ionic liquid is of value only if the FLP retains its ability to activate H_2 .^{1,2} In a simple experiment, 160 mmol solutions of BCF/ $\text{P}(\text{tBu})_3$ in benzene and $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ were stirred under a flow of pure H_2 for 12 h, following which ^1H NMR spectra were recorded. In both cases, uptake of H_2 by the FLP system was confirmed by the formation of a new pair of broad peaks of equal integration (Fig. 5), demonstrating that the ability of the FLP to split H_2 in the ionic liquid medium, despite the very low solubility of molecular hydrogen in ionic liquids.¹⁸ In agreement with the literature, hydrogen could not be released from the benzene solution at ambient pressure; in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$, following heating to it was only released at 150 °C, under reduced pressure (1.0^{-3} mbar) however this was accompanied by decomposition of the FLP components.⁶

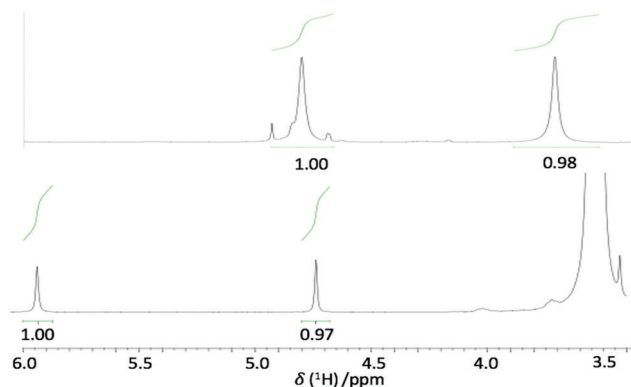


Fig. 5 Fragments of ^1H NMR spectra of the FLP solutions in benzene (top) and $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ (bottom) after saturation with H_2 , showing signals from split H_2 molecule.

These results inspire further investigation into potential use of ionic liquids in FLP chemistry, including detailed studies of encounter complex structure and exploring catalytic applications. In continuation of this work, neutron scattering data, analogous to that reported here in benzene solution, has already been collected and are currently being analysed.

In conclusion, experimental evidence for encounter complex formation of an intermolecular FLP was obtained in benzene solution by neutron scattering studies, and is consistent with prior DFT work. At any given time, *ca.* 5% of dissolved FLP remained associated as the encounter complex. In contrast to the benzene solution, the encounter complex in an ionic liquid, $[\text{C}_{10}\text{mim}][\text{NTf}_2]$, could be detected by a simple NMR spectroscopy experiment, suggesting both higher degree of association at any given time, and longer lifetime. It is postulated that the ionic liquid stabilises the encounter complex through matrix isolation, which may contribute to enhanced kinetics of hydrogenation. FLP dissolved in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ had the ability to split H_2 , as confirmed by ^1H NMR spectroscopy. On-going work in our groups is focused on interpretation of neutron scattering data recorded for the FLP in $[\text{C}_{10}\text{mim}][\text{NTf}_2]$. Furthermore, FLP-promoted hydrogenations in ionic liquids are under investigation, taking advantage of negligible vapour pressure in most ionic liquids, beneficial in handling gas-phase reactants. A supported ionic liquid layer (SILP) strategy gives promise of exploring continuous flow reaction,¹⁹ borenium ionic liquids,²⁰ developed by our group, are under investigation as dual role FLP components and solvents.

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Conflicts of interest

There are no conflicts to declare.

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