

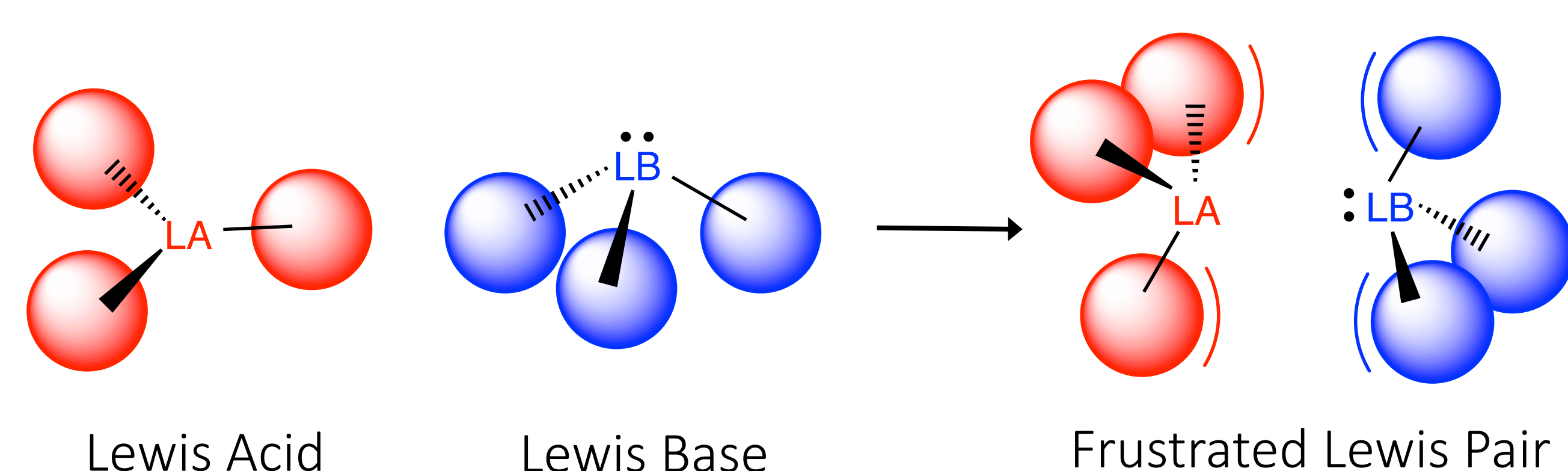


Frustrated Lewis Pairs in Ionic Liquids

Shannon McLaughlin, Małgorzata Swadźba-Kwaśny and John D. Holbrey

Email: smclaughlin52@qub.ac.uk

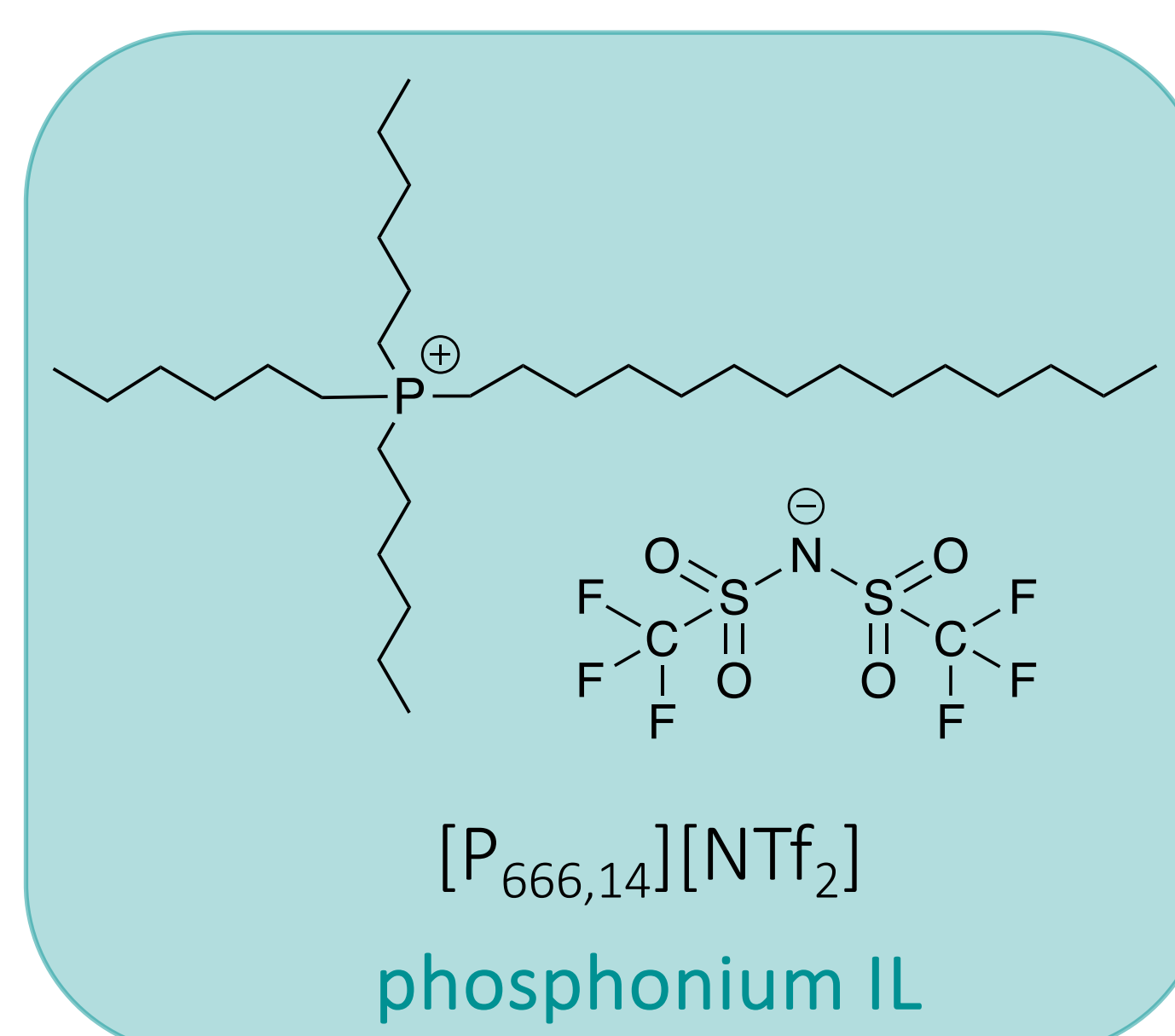
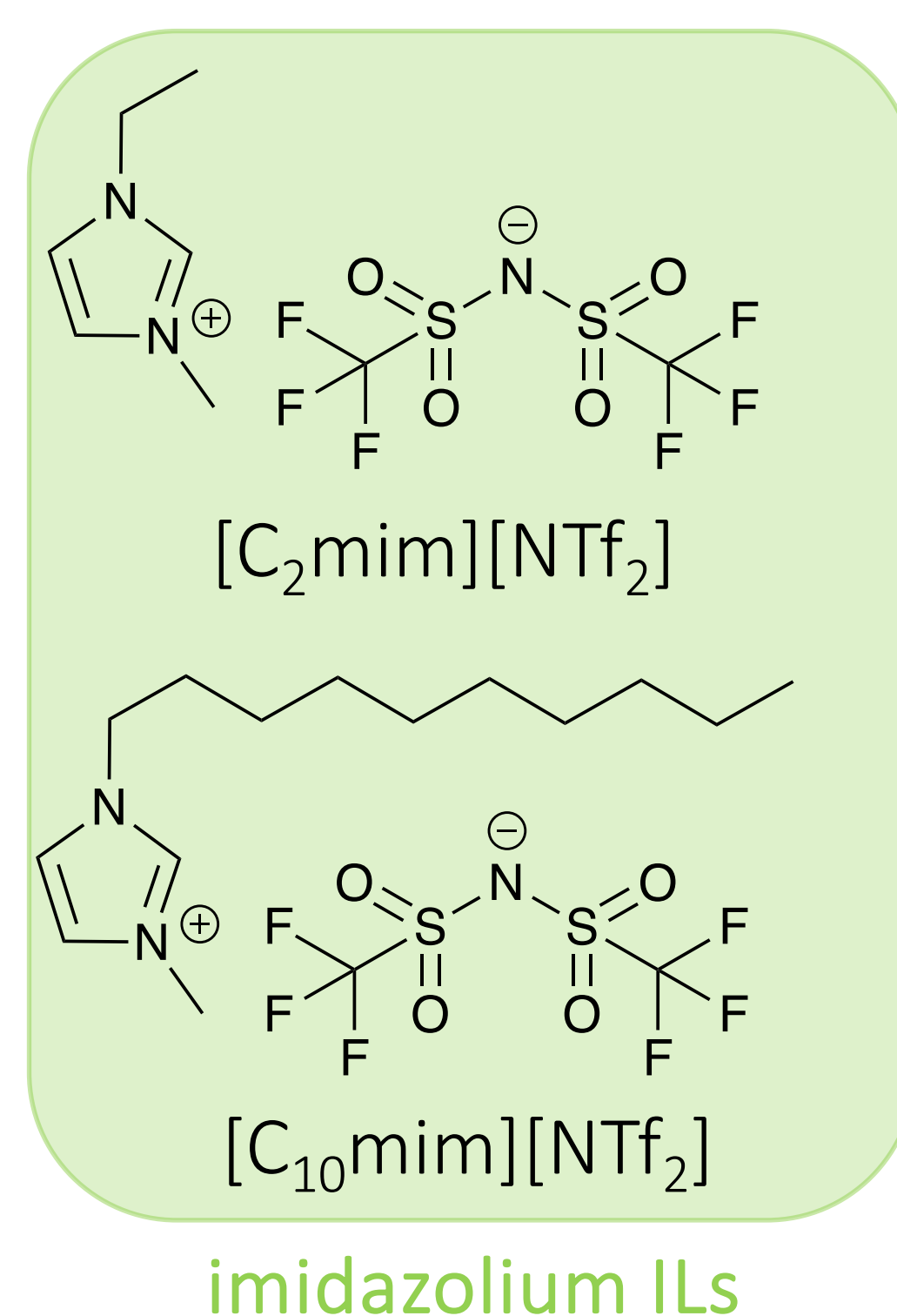
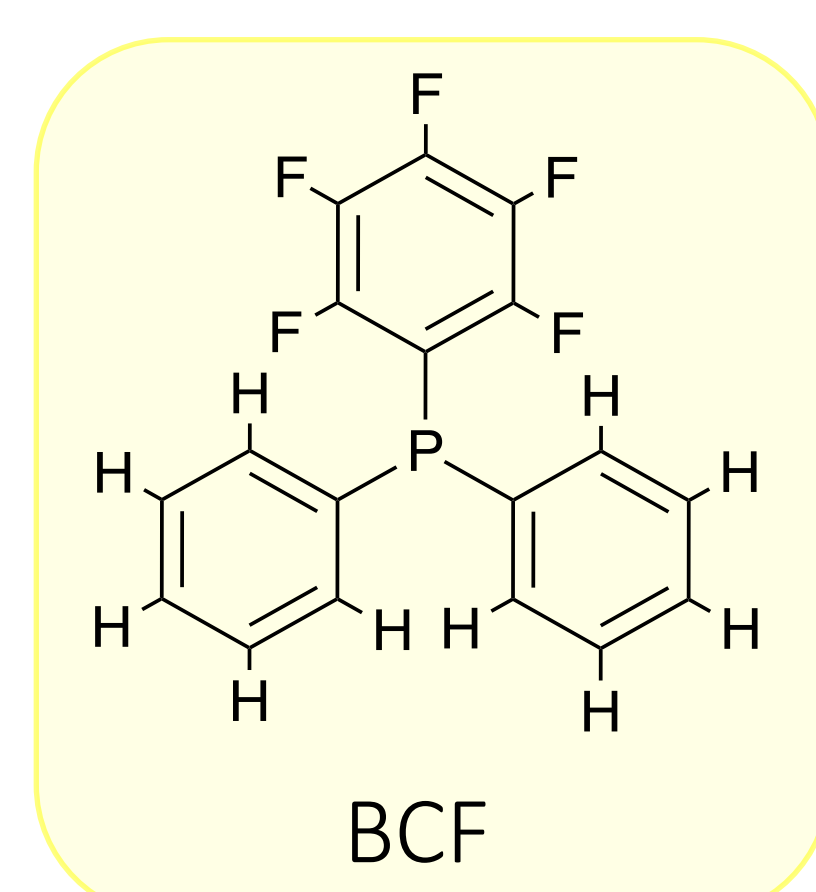
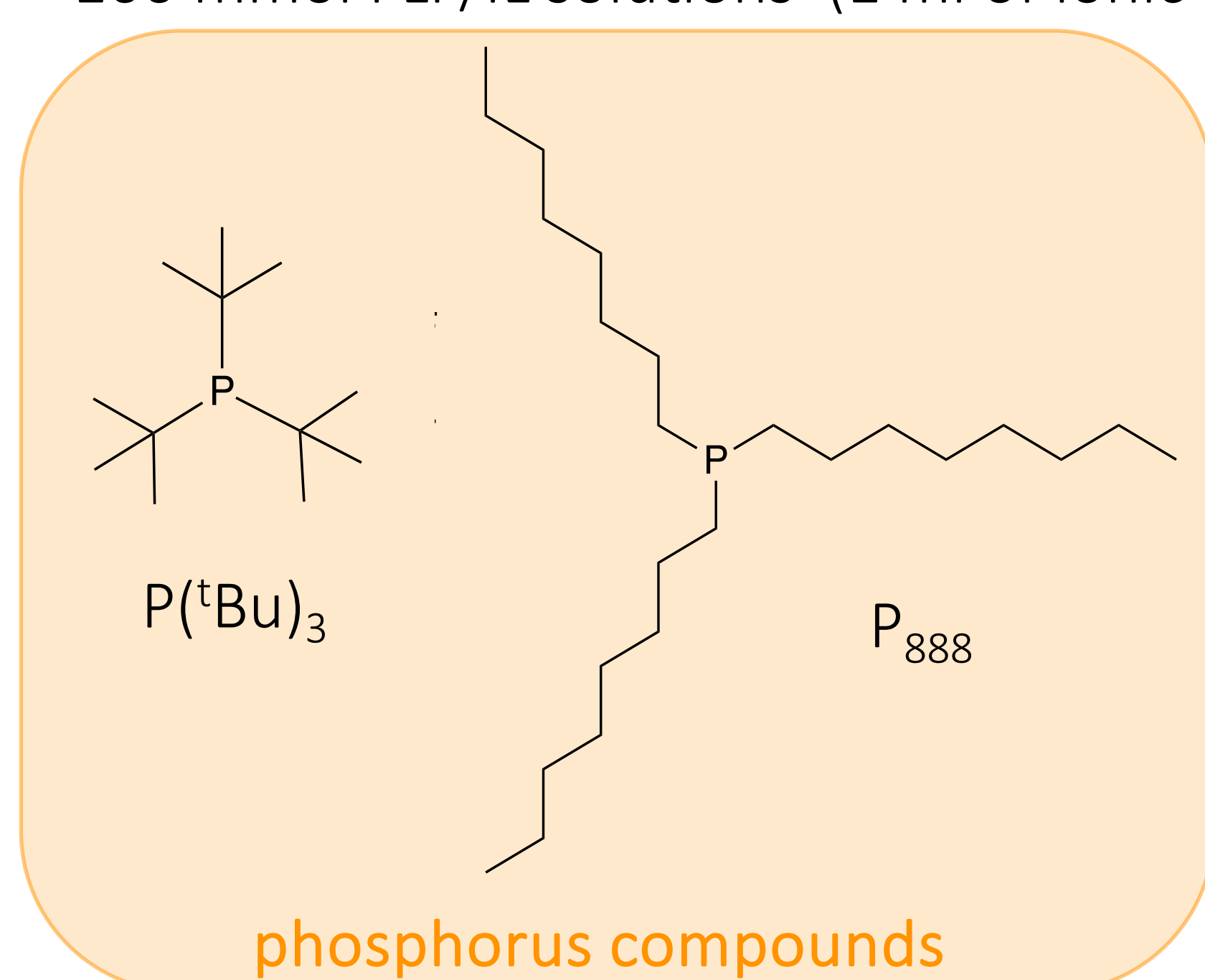
Frustrated Lewis Pairs



- FLPs are compounds or mixtures containing a Lewis acid and a Lewis base that cannot combine to form a classical adduct due to steric hindrance¹
- FLP chemistry has been used to allow main group compounds to activate small molecules, including metal-free H₂ splitting^{3,4}

Preparation of FLPs in Ionic Liquids

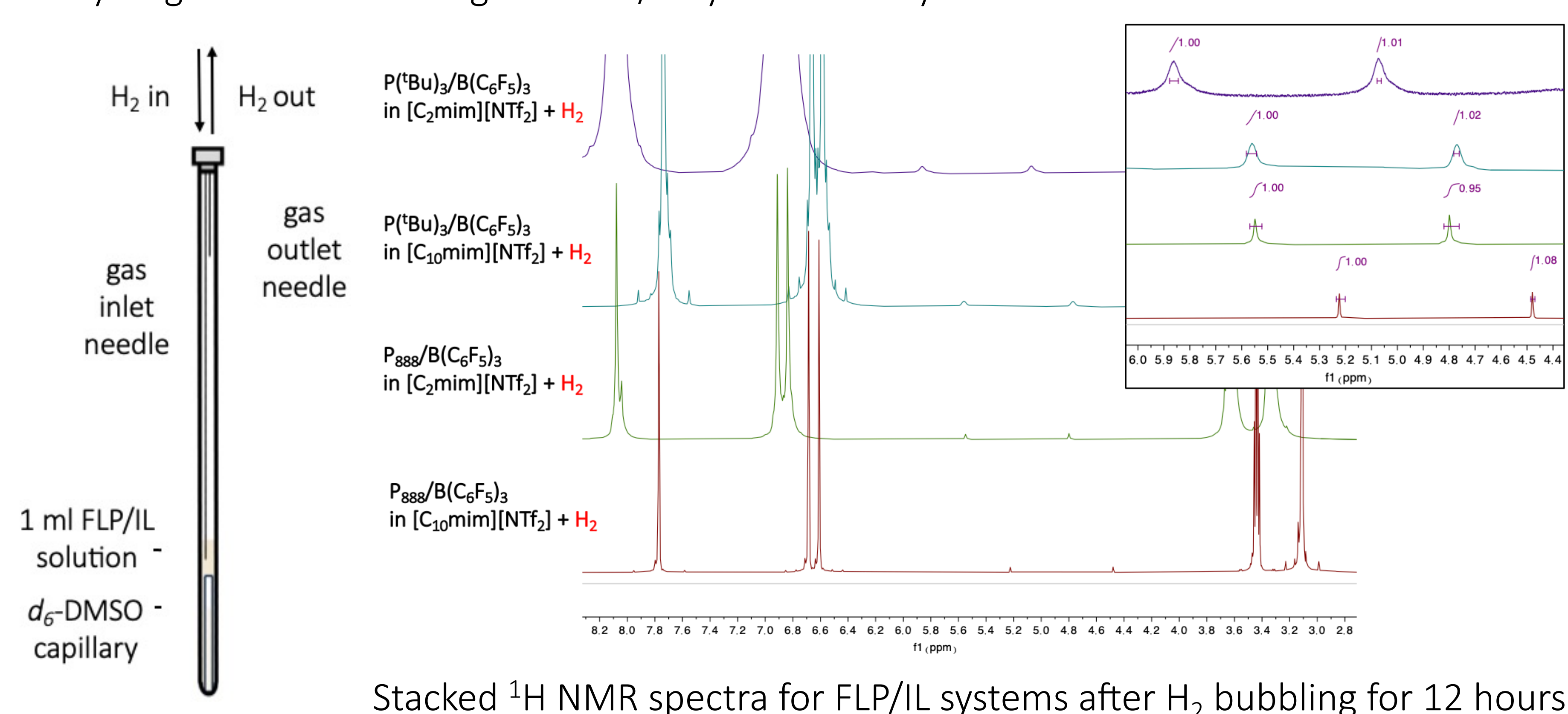
- Two sterically hindered phosphorus compounds were combined with BCF to form FLPs
- 160 mmol FLP/IL solutions (1 ml of ionic liquid)



Hydrogen splitting using FLPs

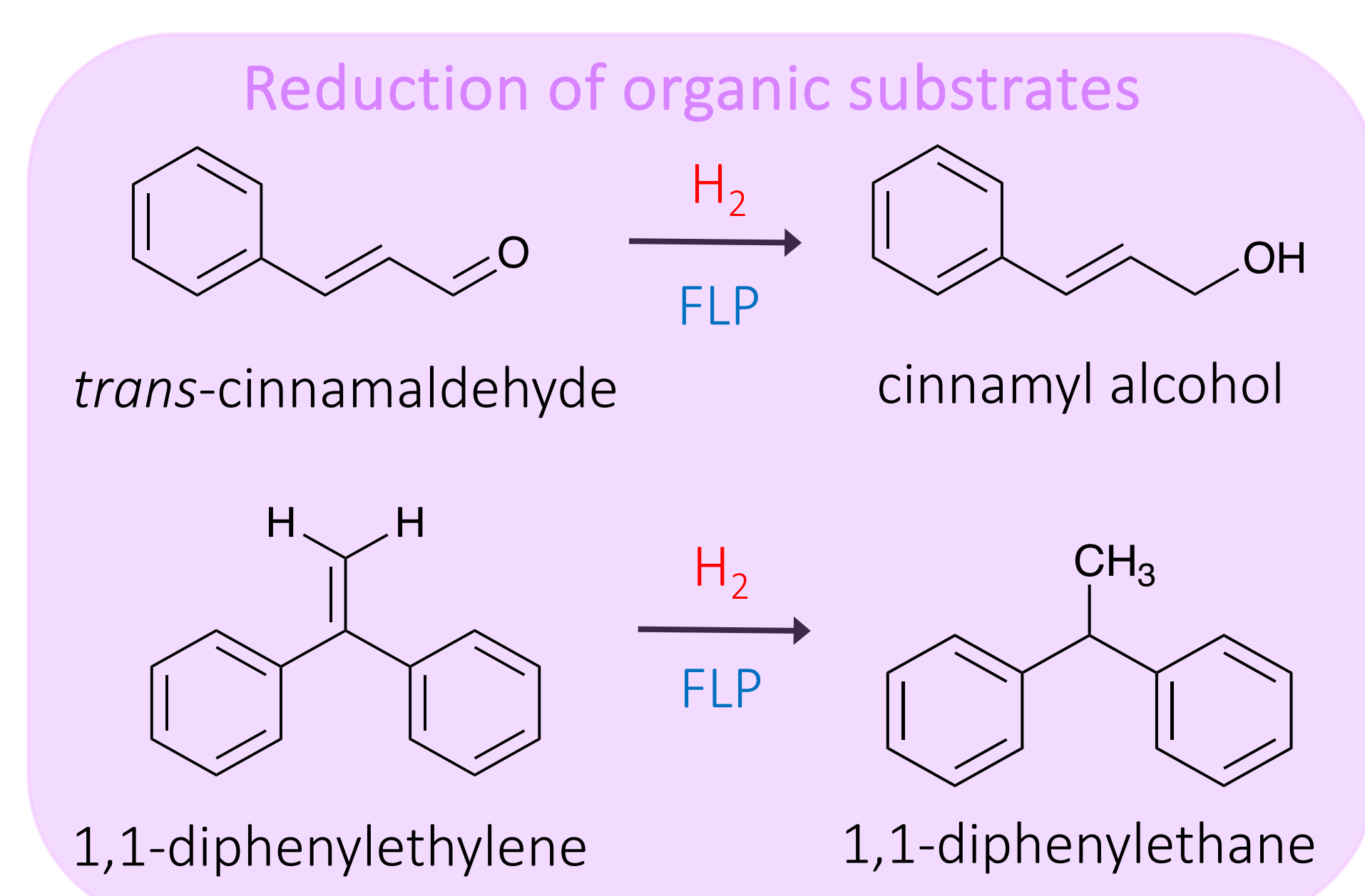
Monitored using ¹H NMR

- Hydrogen bubbled through the FLP/IL system directly in the NMR tube

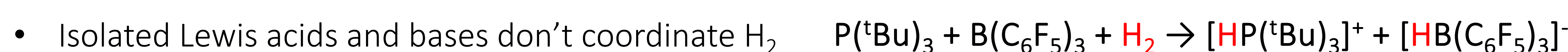


Future Work

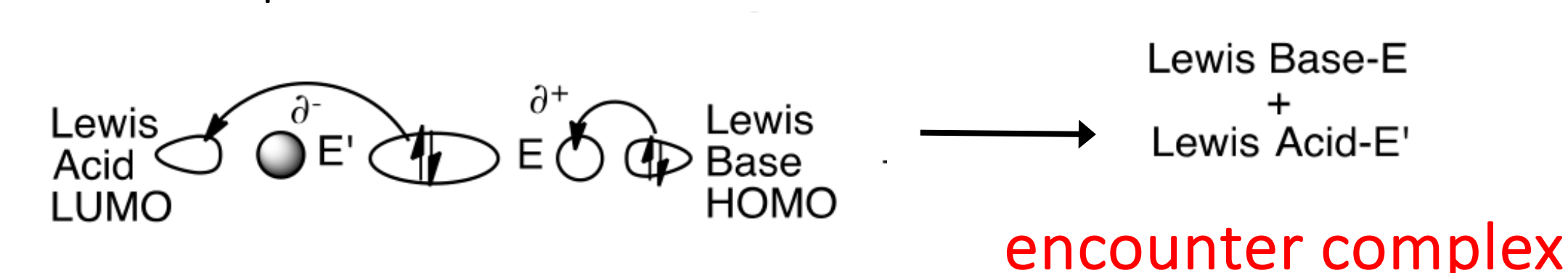
- Hydrogenation of organic substrates e.g. 1,1-diphenylethylene and *trans*-cinnamaldehyde
- Kinetic study of FLP catalysis
- SILPs and SILL



Mechanism of Hydrogen Splitting by an FLP



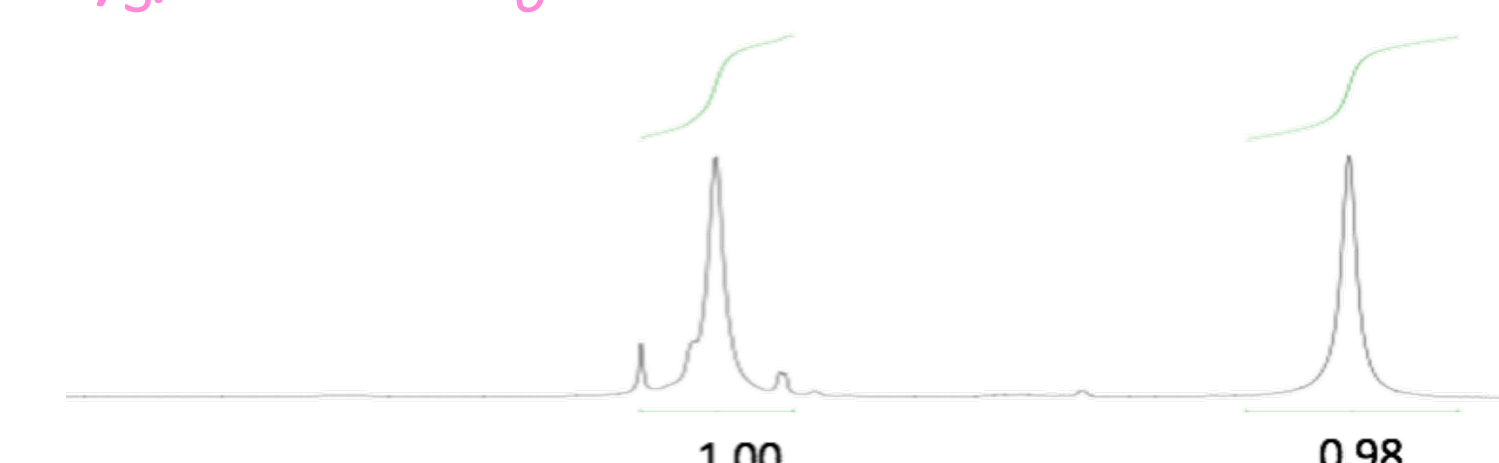
- Pre-organised acid-base **encounter complexes (EC)** must be present in solution



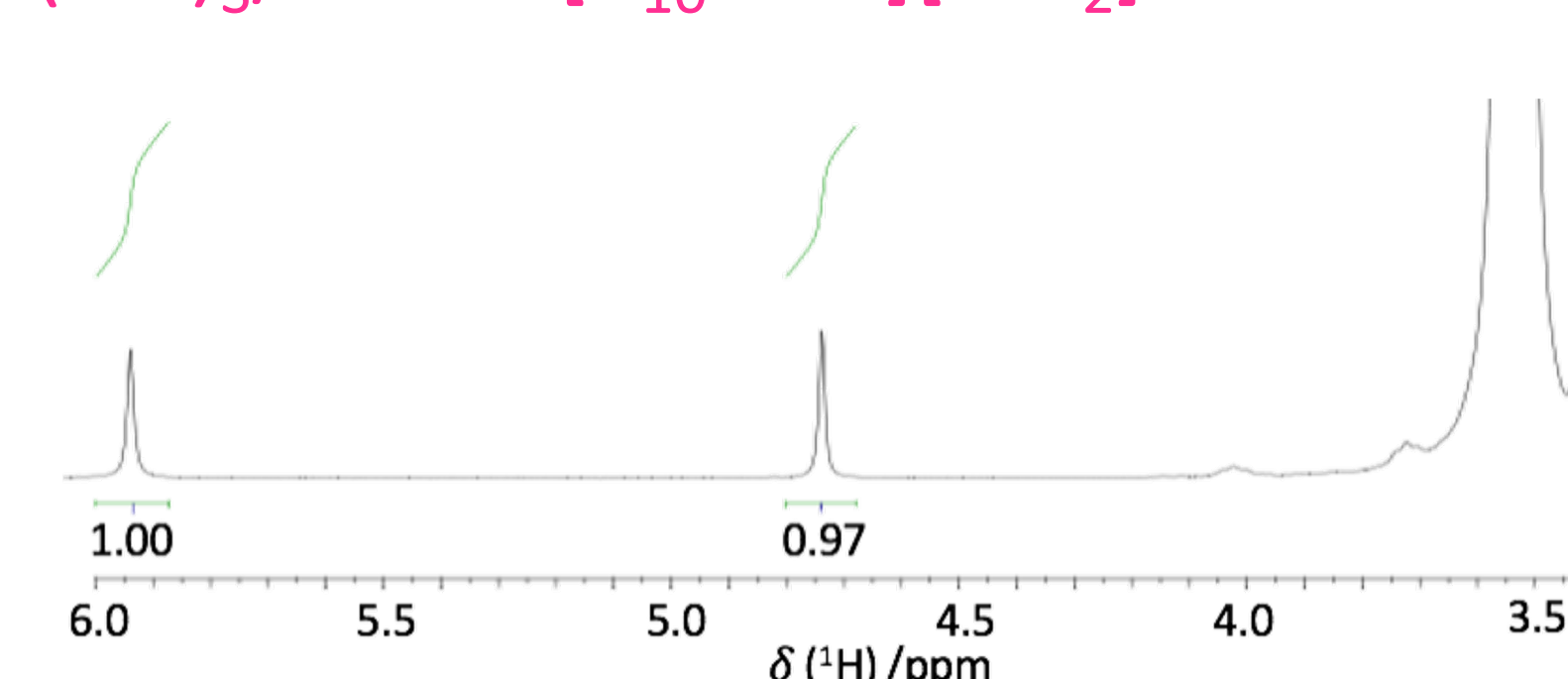
Orbital interactions in substrate cleavage (E-E') by an FLP

- Encounter complex in ionic liquid can be detected using ¹H NMR
- Only **5% of molecules in EC in d₆-benzene** compared to **20% of molecules in EC in [C₁₀mim][NTf₂]**
- This suggests both a higher degree of association and a longer lifetime of the EC in the ionic liquid

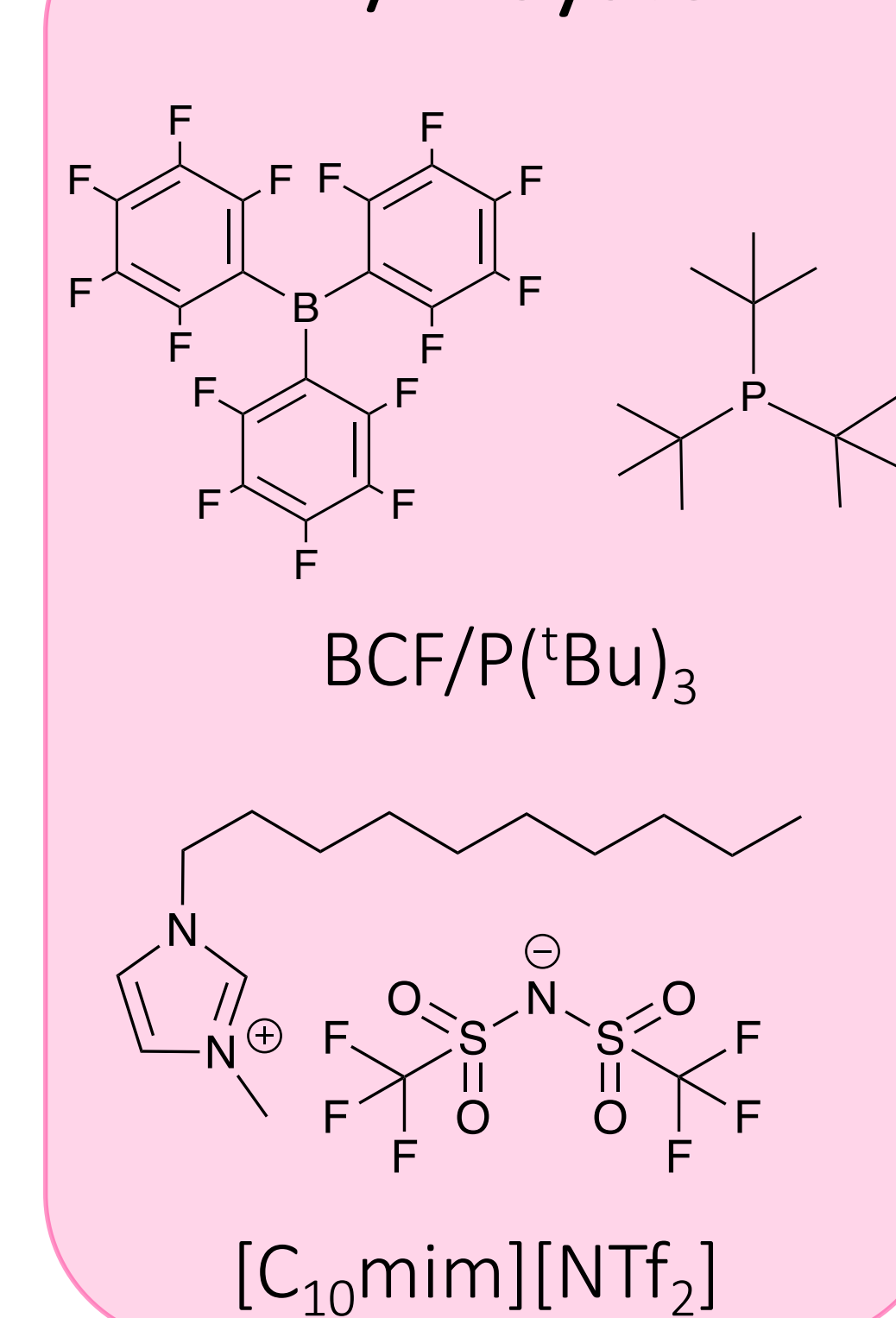
P(tBu)₃/BCF in d₆-benzene



P(tBu)₃/BCF in [C₁₀mim][NTf₂]



FLP/IL System



Advantages of ILs:

- Low volatility
- Comparable to molecular solvents (> 100 mM)
- Non-coordinating anion
- Good solubility of FLP components

Drawbacks of ILs:

- Expensive
- Not Lewis acidic

Experimental Matrix

	P(tBu) ₃	P ₈₈₈	
[C ₂ mim][NTf ₂]	✓	✓	BCF
[C ₁₀ mim][NTf ₂]	✓	✓	
[P _{666,14}][NTf ₂]	?	?	

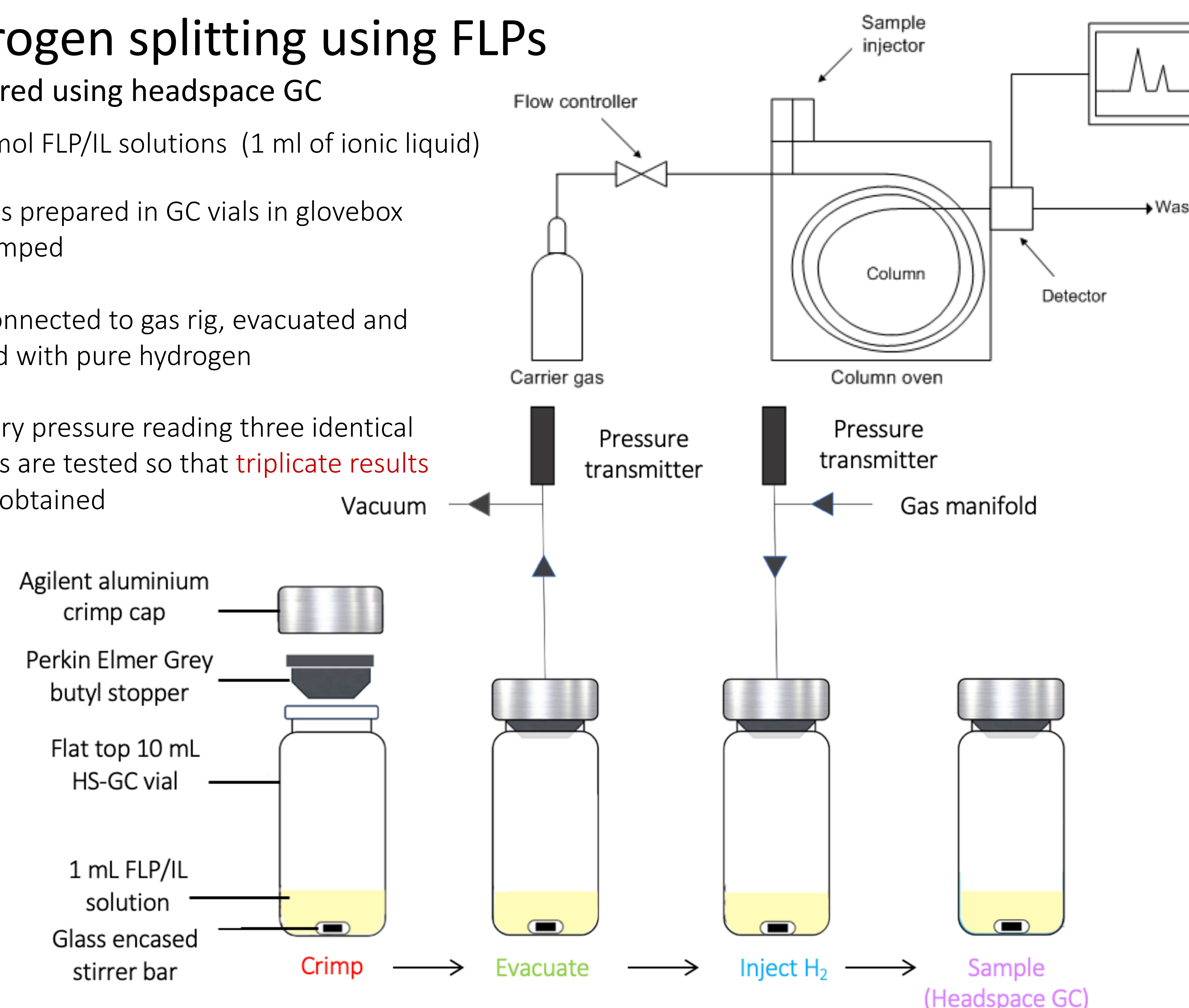
✓ Splits hydrogen

? Unknown

Hydrogen splitting using FLPs

Monitored using headspace GC

- 160 mmol FLP/IL solutions (1 ml of ionic liquid)
- Samples prepared in GC vials in glovebox and crimped
- Vials connected to gas rig, evacuated and injected with pure hydrogen
- For every pressure reading three identical samples are tested so that **triplicate results** can be obtained



Schematic diagram of the HS-GC method

References:

- Stephan, D. W. *et al.*, *Science*, 2006, **314**, 1124–1126.
- Erker G. *et al.*, *Angew. Chem., Int. Ed.*, 2010, **49**, 1402–1405.
- Stephan, D. W. *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 1880–1881.
- Swadźba-Kwaśny, M. *et al.*, *Chem. Commun.*, 2018, **54**, 8689–8692.
- J. M. Young *et al.*, *ACS Sustain. Chem. Eng.*, 2023, **11**, 17787–17796.

With thanks to:

Anne McGrogan Haris Amir
Mark Young Aloisia King
Sam McCalmont



Department for the
Economy

