Novel Frustrated Lewis Pairs for Hydrogen Storage and Activation

Maastricht Science Programme

Harriet Kildahl and Marie C. Correia*

Maastricht University

Objectives

Hydrogen activation and storage is an important topic which has fostered much research interest. Frustrated Lewis pairs have been shown to be successful, but hydrogen release at low temperatures is still inefficient. This research uses the naturally occurring or renewable heterocyclic amines triazabicyclodec-5-ene, cytosine and guanine with the Lewis acid $B(C_6F_5)_3$ in an attempt to synthesize 3 frustrated Lewis pairs (FLPs) and test their catalytic behaviour.

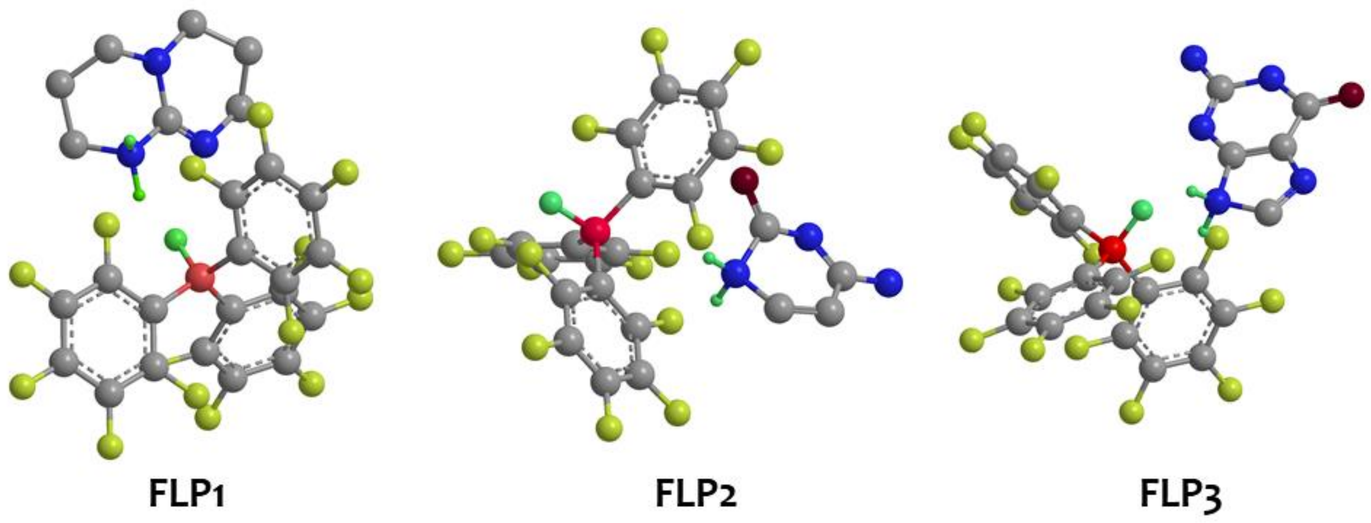

Figure 1. MM2 Energy Minimised 3D models of FLP1, FLP2 and FLP3

Methods

Tris(pentafluorophenyl)borane (0.5 mmol) and the Lewis base (0.5 mmol) were added to toluene (12 mL) followed by charging with H2 (1 atm) via cannula. The resulting solution was stirred at room temperature for 1.5 h then concentrated by half and hexane added to induce precipitation of a white solid. The solid was filtered and washed with hexane and allowed to dry before characterisation. [1]

Results

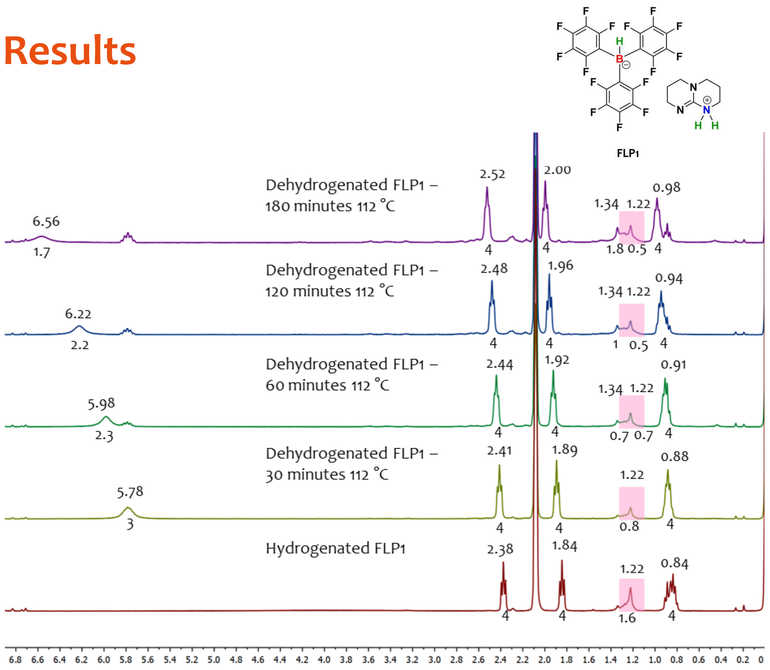

Figure 2. [1]HNMR showing the dehydrogenation of FLP1 at 112 °C

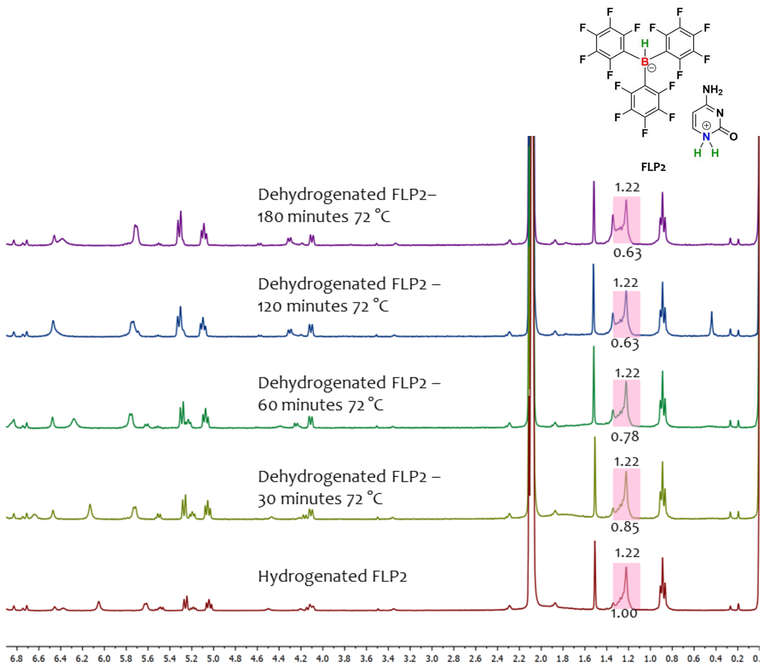

Figure 3. [1]HNMR showing the dehydrogenation of FLP2 at 72 °C

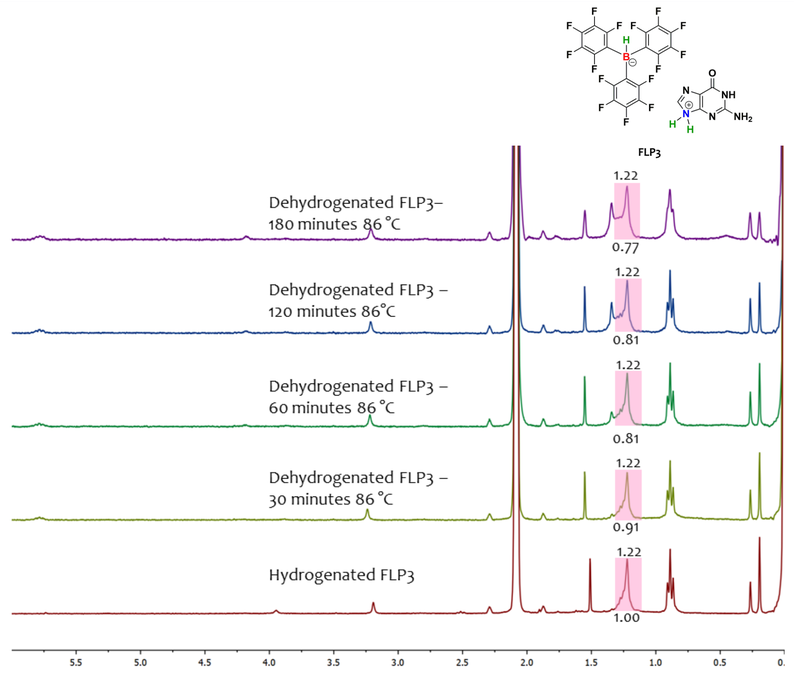

Figure 4. [1]HNMR showing the dehydrogenation of FLP3 at 86 °C

Table 1. Table showing UV-Vis wavelengths, Bond Lengths, IR peaks and [19]F NMR peaks for FLP1, FLP2 and FLP3

	UV-Vis (peak wavelength nm)			Bond Lengths (A°)			IR (cm^{-1})	^{19}F NMR (C_6D_6, ppm)					
								Hydrogenated			Dehydrogenated		
	Borane	Amine	FLP	B-H	N-H1	N-H2	N-H	*o-*	*p-*	*m-*	*o-*	*p-*	*m-*
1	262.8	205.7	257.5	1.352	1.045	1.045	3681.54	-135.59	-160.54	-165.08	-135.51 -139.12	-154.12 -160.64	-162.39 -165.16
2	262.8	272.0/237.4	279.2	1.361	1.047	1.044	3676.17	-133.62	-156.90	-163.31	-133.53 -135.33	-155.29 -157.03	-162.27 -163.34
3	262.8	190.4	259.2	1.347	1.038	1.044	3676.32	-135.02	-155.85	-163.37	-135.01 -139.12	-154.10 -155.10	-161.18 -162.48

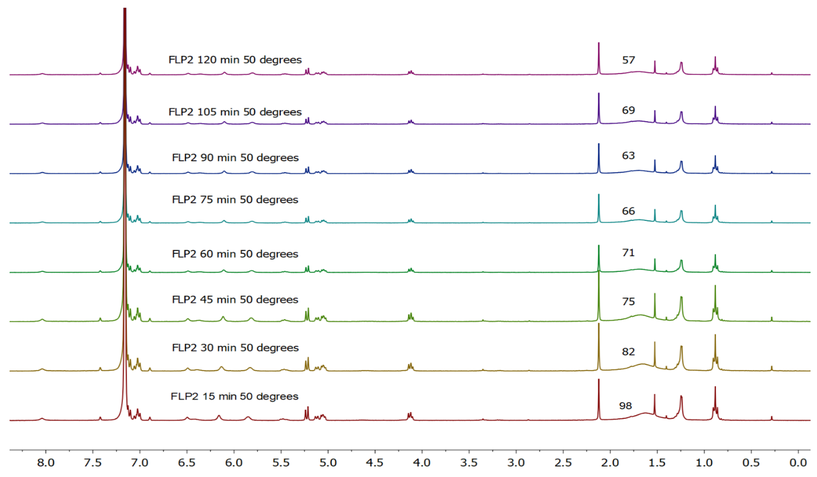

Figure 5. [1]HNMR showing the dehydrogenation of FLP2 at 50 °C

Conclusion

- 3 novel frustrated Lewis pairs were synthesised
- Facile activation of hydrogen occurred at room temperature and 1 atm
- Release of hydrogen from FLPs was observed at 50 °C, 72 °C , 86 °C and 112 °C
- Hydrogenation catalysis using FLP1 was observed with various substrates and conditions;
  - 50 °C and 5 bar H_2 hydrogenated acetophenone to 1-phenyl alcohol in 14.6 % yield after 22 hours
  - 50 °C and 50 bar H_2 hydrogenated acetophenone to 1-phenyl alcohol in 8.6 % yield after 22 hours
  - 50 °C and 5 bar H_2 hydrogenated benzyl furfurylimine to benzyl furfurylamine in 1.9 % yield after 22 hours
  - 50 °C and 50 bar H_2 hydrogenated furfural to furfuryl alcohol in 4.6 % yield after 22 hours

Table 2. Table showing GC area percentage hydrogenation of a substrate catalysed by 7.5 mol% FLP1

Substrates	Condition 1 50 °C and 5 bar H_2 22 hours	Condition 2 50 °C and 50 bar H_2 22 hours	Condition 3 25 °C and 5 bar H_2 22 hours
Acetophenone	14.6	8.6	–
Benzyl furfurylimine	1.9	0.7	–
Furfural	–	4.6	–
Trans-stilbene	–	–	–

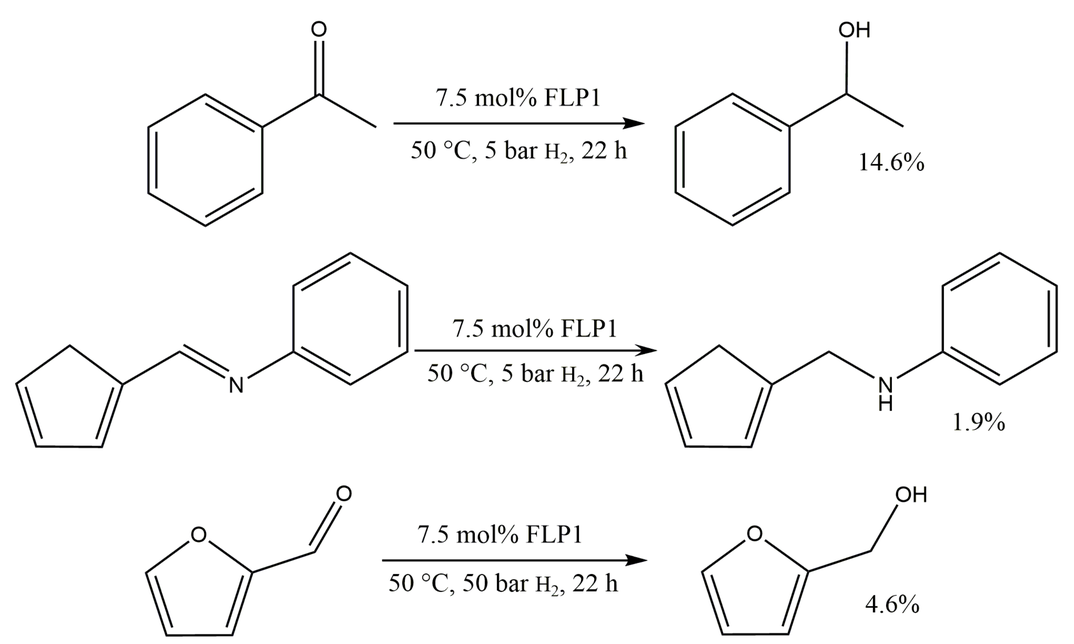

Figure 6. Hydrogenation pathways of the substrates showing optimal conditions and yield of hydrogenated product

Acknowledgements

- Christian van Slagmaat for help with hydrogenation reactions and access to hydrogen.
- Dr Thomas Defize for assistance with the variable temperature NMR
- Dr Burgert Blom for helpful discussions.

References

1. Jiang, C.; Blacque, O.; Fox, T.; Berke, H. Dalton Trans. 2011, 40 (5), 1091–1097.