

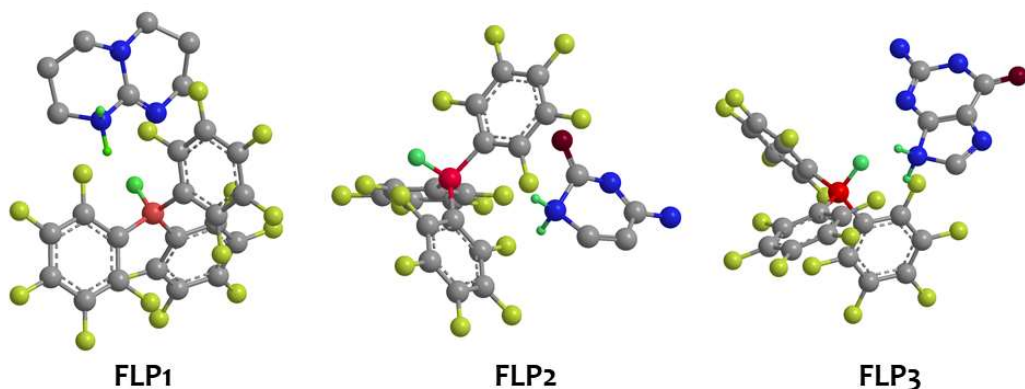
Novel Frustrated Lewis Pairs for Hydrogen Storage and Activation

Introduction

Hydrogen activation and storage is an important topic which has fostered much research interest. Frustrated Lewis Pairs (FLPs) 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 tris(pentafluorophenyl)borane to synthesize 3 FLPs.

Methodology

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 and Discussion

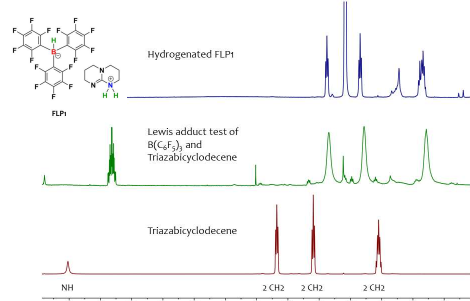


Figure 1. ¹H NMR showing FLP1, the Lewis adduct test of FLP1 and Triazabicyclodec-5-ene

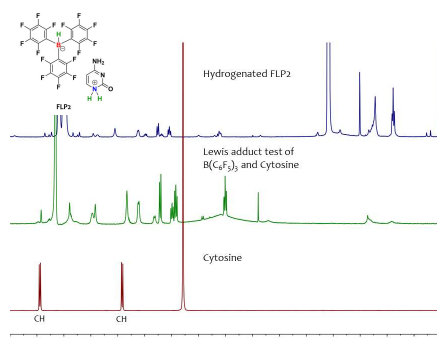


Figure 2. ¹H NMR showing FLP2, the Lewis adduct test of FLP2 and Cytosine

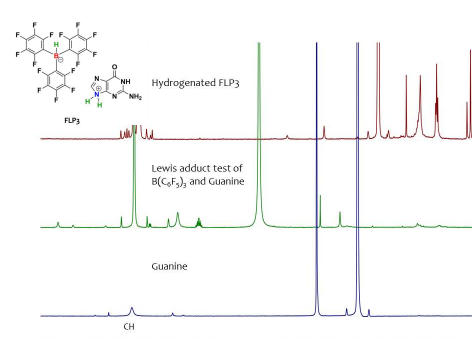


Figure 3. ¹H NMR showing FLP3, the Lewis adduct test of FLP3 and Guanine

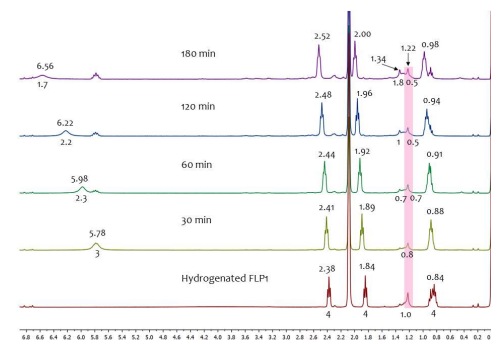


Figure 4. ¹H NMR showing the dehydrogenation of FLP1 at 112 °C

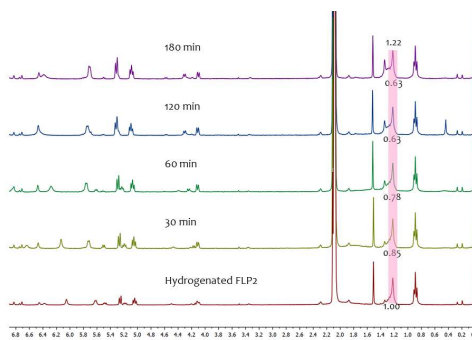


Figure 5. ¹H NMR showing the dehydrogenation of FLP2 at 72 °C

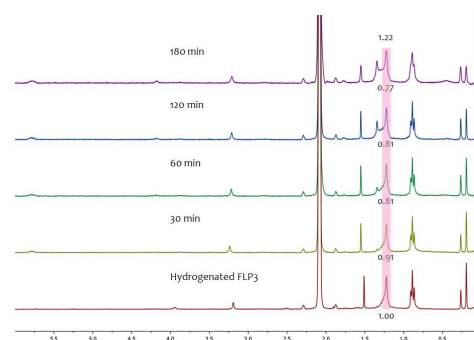


Figure 6. ¹H NMR showing the dehydrogenation of FLP3 at 86 °C

Table 1. Spectroscopic properties for FLP1, FLP2 and FLP3

FLPs	UV-Vis Wavelength (nm)			Bond Lengths (Å)			IR (cm ⁻¹)	¹⁹ F NMR (C ₆ D ₆ , ppm)					
	Borane	Amine	FLP	B–H	N–H1	N–H2	N–H	Hydrogenated			Dehydrogenated		
								<i>o</i> -	<i>p</i> -	<i>m</i> -	<i>o</i> -	<i>p</i> -	<i>m</i> -
1	262.8	205.7	257.5	1.352	1.045	1.045	3681.54	-135.59	-160.54	-165.08	-135.51	-154.12	-162.39
								-139.12	-160.64	-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	-155.29	-162.27
											-135.33	-157.03	-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	-154.10	-161.18
								-139.12	-155.10	-162.48			

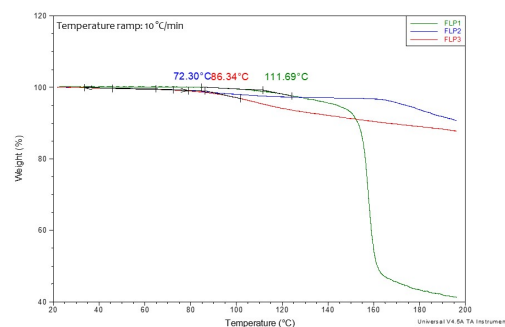


Figure 8. TGA of FLP1, FLP2 and FLP3 showing likely temperatures of dehydrogenation

Conclusion

- Three novel Frustrated Lewis Pairs were synthesized
- Hydrogen (1 atm) was easily activated at room temperature after 1 h.
- FLP1 released 50% of H₂ in 3 h at 112 °C
- FLP2 released 37% of H₂ in 3 h at 72 °C
- FLP3 released 23% of H₂ in 3 h at 86 °C

Acknowledgements

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- Dr Burgert Blom for helpful discussions.

References

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