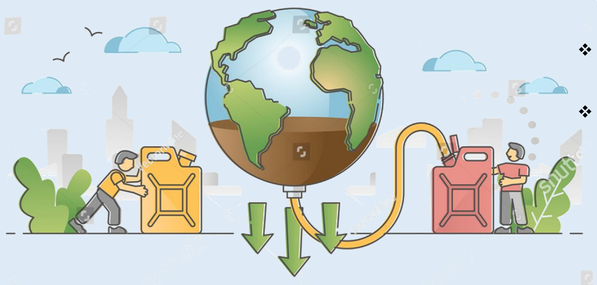
# Dual Functionality of Manganese Complexes in Catalysis: Transfer Hydrogenation of Nitriles and Dehydration of Ammonia Borane

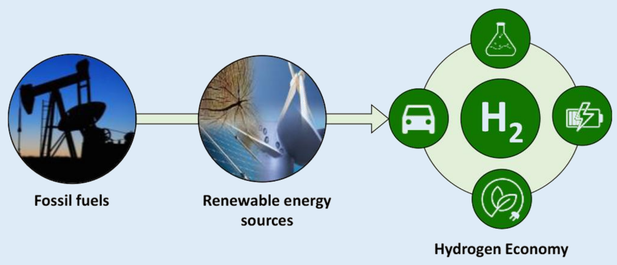
Tshegofatso Molapo and Andrew Swarts

*Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, 2050, South Africa*

## Problem statement

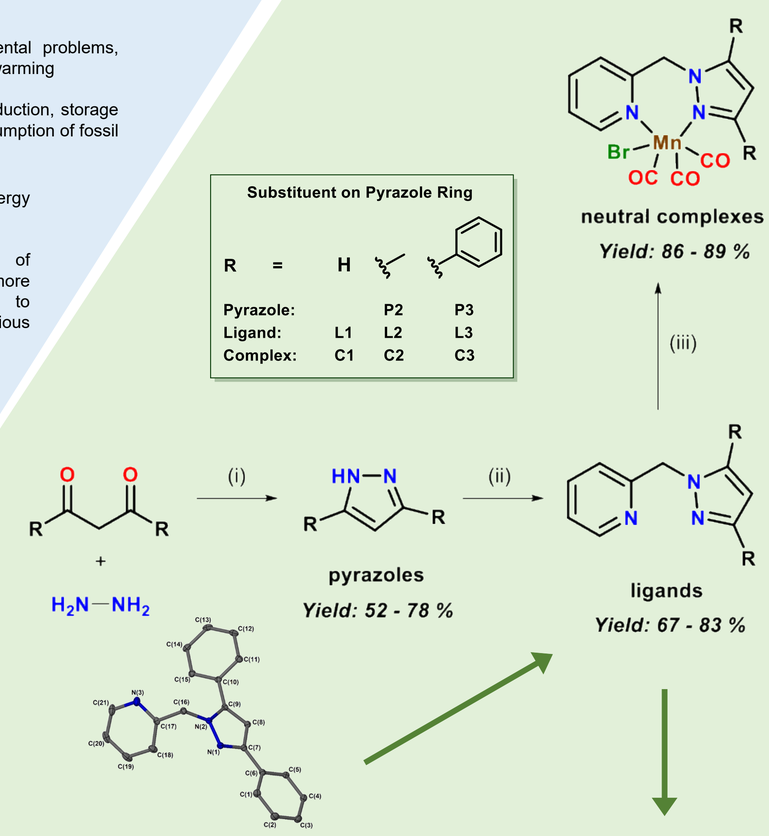


- Address current energy and environmental problems, including fossil fuel depletion and global warming
- Development of technologies for the production, storage and utilisation of energy without the consumption of fossil fuels has attracted growing interest
- Alternative: Conversion of natural energy into chemical-bonding
- Contribute to the advancement of sustainable catalysis by providing a more environmentally friendly alternative to traditional methods that may rely on precious metals or hazardous reducing agents.




## 1.Literature

## 2.Mn(I) complexes




The only octahedral species observed, confirmed by XRD and NMR spectroscopy

**Figure 1:** Crystal structure of **L3** drawn with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

**Conditions:**

**(i)** Hydrazine added in EtOH at r.t., 3hrs. **(ii)** 2-bromopyridine, NaOH (40% aq), TBAB (10 drops), toluene, reflux, 18 hrs. **(iii)** 1mol eq. $MnBr(CO)_5$, THF, r.t., 18hrs. **(iv)** 1mol eq. $MnBr(CO)_5$, THF, r.t., 18hrs; recrystallize at extended time periods from a THF/Hex solution

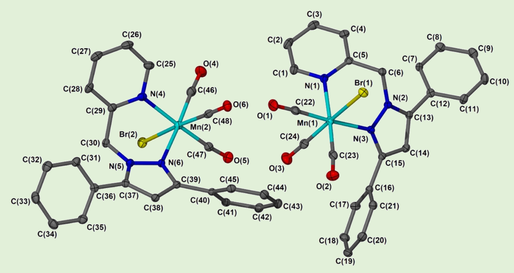
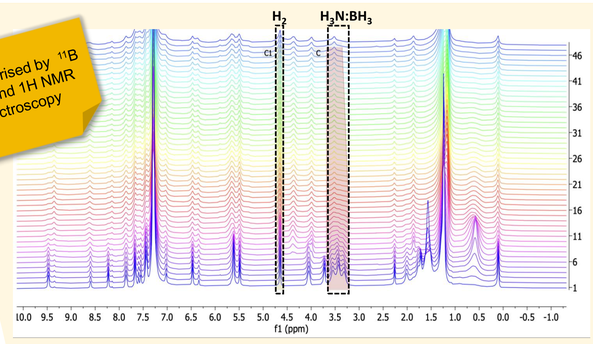


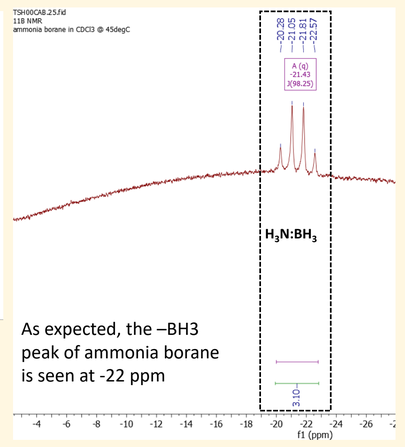
**Figure 2:** Crystal structure of **C3** drawn with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

## 3.Dehydrogenation of Ammonia Borane

Characterised by $^{11}B$ NMR and 1H NMR spectroscopy

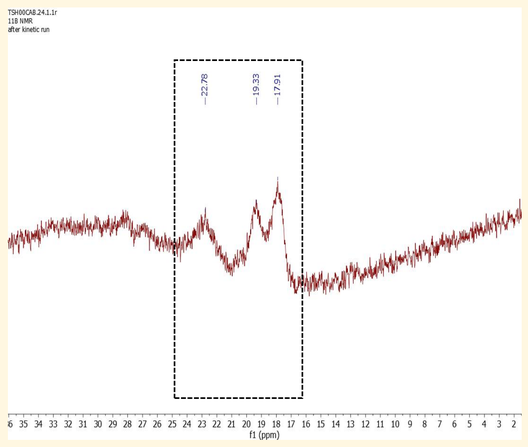



**Using a J Young NMR Tube** $^{11}H$ NMR (400 MHz, $CDCl_3$) spectrum of the reaction mixture after $NH_3BH_3$ (0.32 mmol) dehydrogenation with catalyst C1_Mn (5 mol%) in $CDCl_3$ after 24 hours at 45 °C. Chemical shifts originating from protons on $CDCl_3$, $H_2$ gas, and ammonia borane are indicated.




As expected, the –BH3 peak of ammonia borane is seen at -22 ppm

**Before Catalysis**




**After Catalysis**

**Key Result:** Decrease in the ammonia borane signal (typically a quartet around -20 to -25 ppm).

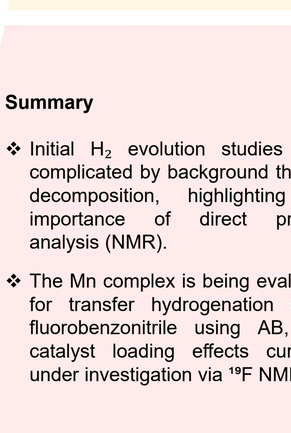
•*The appearance and growth* of new signals in the region (around +17.5 to +25 ppm).

## 4. Transfer Hydrogenation of Niriles


**Figure 4: $^{19}$ F NMR spectra (a)** Model substrate 4-fluorobenzonitrile **(b)** Transfer hydrogenation of 4-fluorobenzonitrile catalysed by Mn(I) complexes **C1 (3 mol%), 0.56 mmol substrate,1.12 mmol ammonia borane (2 eqi) at 45 °C in THF** and **(c)** Condition: Mn(I) complexes **C1 (3 mol%), 0.56 mmol substrate,1.12 mmol ammonia borane (2 eqi) at 45 °C in Isopropanol (d)** Condition: Mn(I) complexes **C1 (3 mol%), 0.56 mmol substrate,1.12 mmol ammonia borane (2 eqi) at 45 °C in EtOH.**

| Catalyst | Solvent | Catalyst Loading (mol%) | Temperature (°C ) | Conversion |
|---|---|---|---|---|
| **C1** | THF | 1 | 45 | 8 |
| **C1** | THF | 2 | 45 | 18 |
| **C1** | THF | 3 | 45 | 30 |
| **C1** | EtOH | 3 | 45 | 54 |
| **C1** | IPA | 3 | 45 | 56 |
| **C1** | EtOH | 3 | 65 | 67 |
| **C1** | IPA | 3 | 65 | 72 |
| **C1** | EtOH | 3 | 25 | 12 |
| **C1** | IPA | 3 | 25 | 15 |

Possible products expected from the catalysis Characterised using $^{19}$F NMR spectroscopy




## Aim

Investigate the catalytic activity of the Mn complex(es) towards the dual functionality of the dehydrogenation of ammonia borane and transfer hydrogenation of nitriles

## Objectives

1. Preparation of a series of Mn(I) complexes ligated by Pyridyl-pyrazole ligands
2. Evaluate the catalytic activity of the complex(s) towards the dehydrogenation of ammonia borane
3. Evaluate the catalytic activity of the complex(s) for the transfer hydrogenation of nitriles
4. Mechanistic studies

## Research question

What are the optimal reaction conditions (catalyst loading, solvent, temperature, and reaction time) for the efficient pyrazolyl-pyridine chelated Mn(I) complexes, in AB dehydrogenation and AB-mediated transfer hydrogenation of nitriles?

## 5.Conclusion and Future Prospects

### Conclusion

- ✓ Successfully synthesized and characterized new Mn(I/II) complexes ligated by pyrazolyl-pyridine ligands.
- ✓ Complex (**C1**) was active in the dehydrogenation of ammonia borane towards borazine derivatives.
- ✓ Complex (**C1**) was active in the transfer hydrogenation of nitriles

### Future work

- ➢ Preparation of Mn(I) complexes ligated by *bis*-(pyrazolyl) pyridine ligands.
- ➢ Optimise conditions and perform kinetics studies (gain insight into the transfer hydrogenation mechanism).

**Summary**

- ❖ Initial $H_2$ evolution studies were complicated by background thermal decomposition, highlighting the importance of direct product analysis (NMR).
- ❖ The Mn complex is being evaluated for transfer hydrogenation of 4-fluorobenzonitrile using AB, with catalyst loading effects currently under investigation via $^{19}$F NMR.

**Previous work in our group:** Swarts *et al.,* Sustainable Energy Fuels, **2021**, 5, 2771. **Key literature:** Weber *et al*., Catalysis Science & Technology, **2024**, 14, 17; Jurt, P., **2021**. Small Molecule Activation by Dirhodium and Rhodium-Platinum Complexes (Doctoral dissertation, ETH Zurich); Zhang, X., 2016. Ruthenium Catalysis for Ammonia Borane Dehydrogenation and Dehydrative Coupling (Doctoral dissertation, University of Southern California).

sasol reaching new frontiers · NRF National Research Foundation · WITS UNIVERSITY 1922 2022 · School of CHEMISTRY · SR Swarts Research Group Organometallic Chemistry | Spectroscopy | Catalysis