

# Towards earth abundant replacements for precious metal

## catalysts:

### Can agostic interactions from phosphorus-borane complexes stabilise the formation of monomeric Sn(II) hydrides?

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#### Aims

- To investigate the reaction between a prepared phosphorus-borane complex, SnCl<sub>2</sub> and DIBAL-H and categorise the product formed using spectroscopic and diffraction techniques, namely NMR and single crystal x-ray diffraction.
- To determine the extent of agostic type interactions between the Sn centre and the borane ligand.

#### 1. Introduction

Common industrial catalysts typically are precious, non-earth abundant transition metals and the demand placed upon these scarce resources is continuing to increase, presenting a huge sustainability question. Modern research into main group compounds has led to the realisation that the chemistry can sometimes be parallel that of a transition metal. One type of compound that is thought to be capable of the activation of small molecules, such as hydrogen, is Sn(II) hydride. A Sn(II) hydride is a coordinately unsaturated molecule, meaning the Sn centre has sites available for coordination of additional ligands. All current isolated compounds of this type are dimeric<sup>1</sup>, where each Sn is bonded to 2 bridging hydrogens and an extended aromatic system. The Izod group have characterised a novel type of ligand system which contains previously unseen stabilising agostic interactions as a result of phosphorus-borane bonds. It is thought by combining both of these fields, the previously unseen monomeric Sn(II) hydride can be synthesised.

#### 2. Generation of the phosphorus-borane complex

The initial phosphorus-borane complex precursor was synthesised in line with previous literature.<sup>2</sup> The steps taken can be seen in the following scheme:

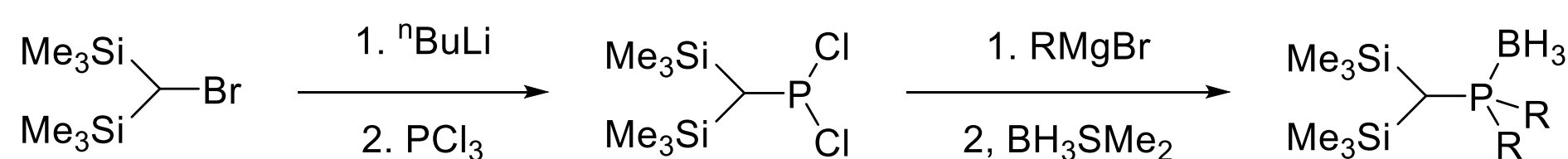


Fig 1: The two step reaction scheme used to prepare the phosphorus-borane ligands of study. Two different ligands were synthesised where R = Me or Ph in each case. In both cases the products were purified by recrystallizing in methylcyclohexane.

#### 3. Generation of the organotin complexes

The organotin chloride species was prepared by the deprotonation of the prepared phosphorus-borane complex and further reacted with dry SnCl<sub>2</sub>. The reaction scheme for the multi step process can be seen below.

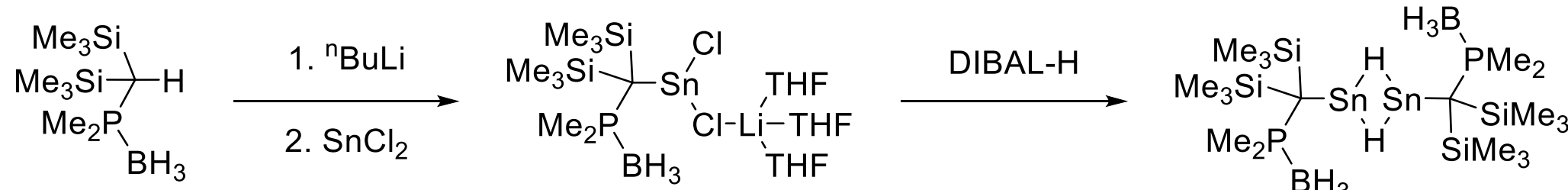


Fig 2: The two step reaction scheme used to prepare the organotin complexes.

The organotin chloride species was found to crystallise in the same methylcyclohexane solvent as the initial phosphorus-borane complex. The deduced crystal structure taken from single crystal x-ray diffraction can be seen in fig 3.

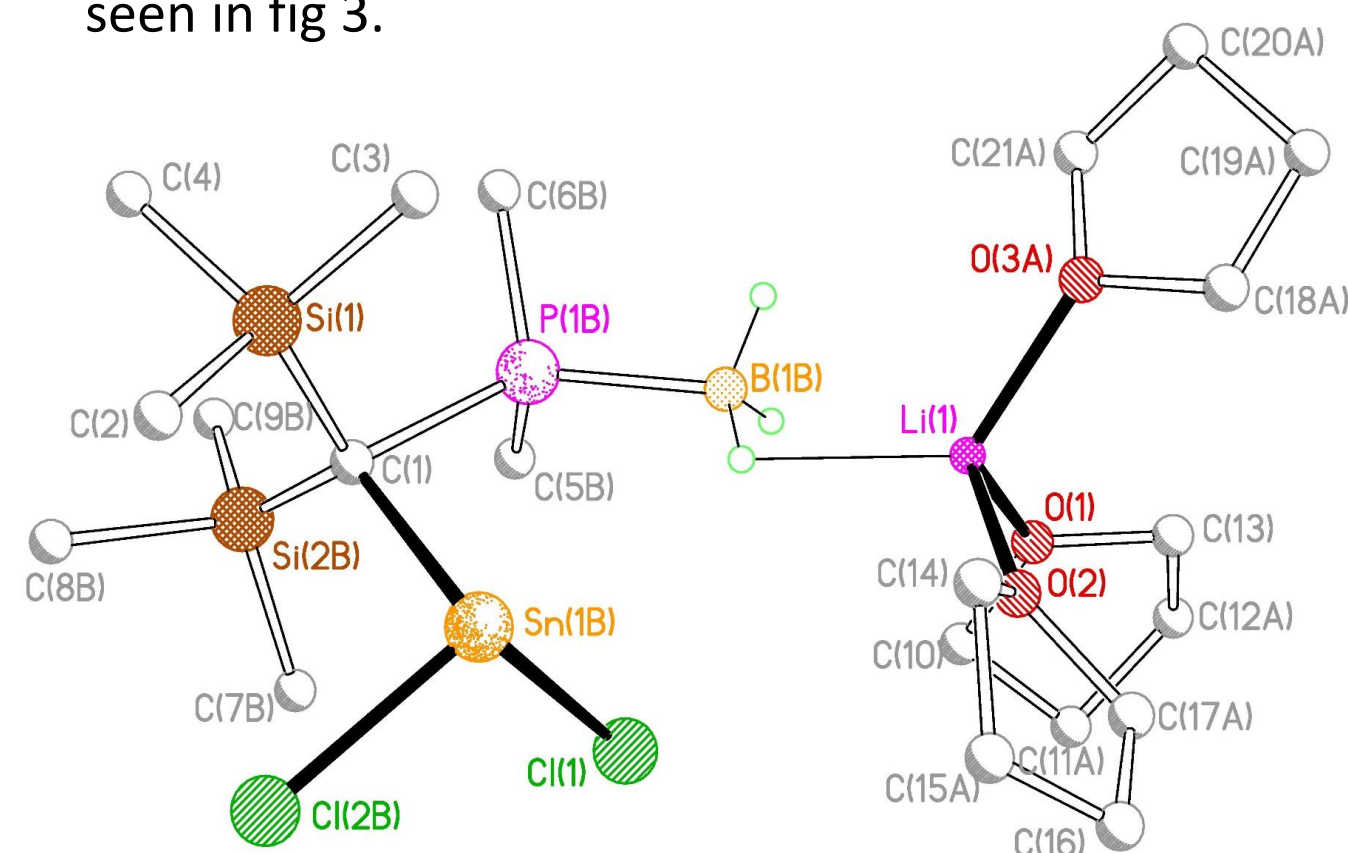


Fig 3: The crystal structure of the intermediate organotin chloride species as determined by Dr Paul G. Waddell.

It was found that the unsaturated Sn centre was being stabilised by a LiCl salt coordinated by THF solvent molecules forming an ate complex. Efforts to remove this additional stabilising force were in vain. This was the first indication of the lack of stabilising interaction between the metal centre and the B-H bonds from the ligand.

#### 4. Generation of a dimeric species

The organotin chloride species was reacted with known hydride transfer agent DIBAL-H to produce a dark coloured viscous oil. The resulting product was unable to be crystallised in available solvents because of the compound's high solubility, removing the possibility of crystallographic data. Despite this, spectroscopic data of compound was taken in the form of <sup>119</sup>Sn NMR data which can be seen in fig 4.

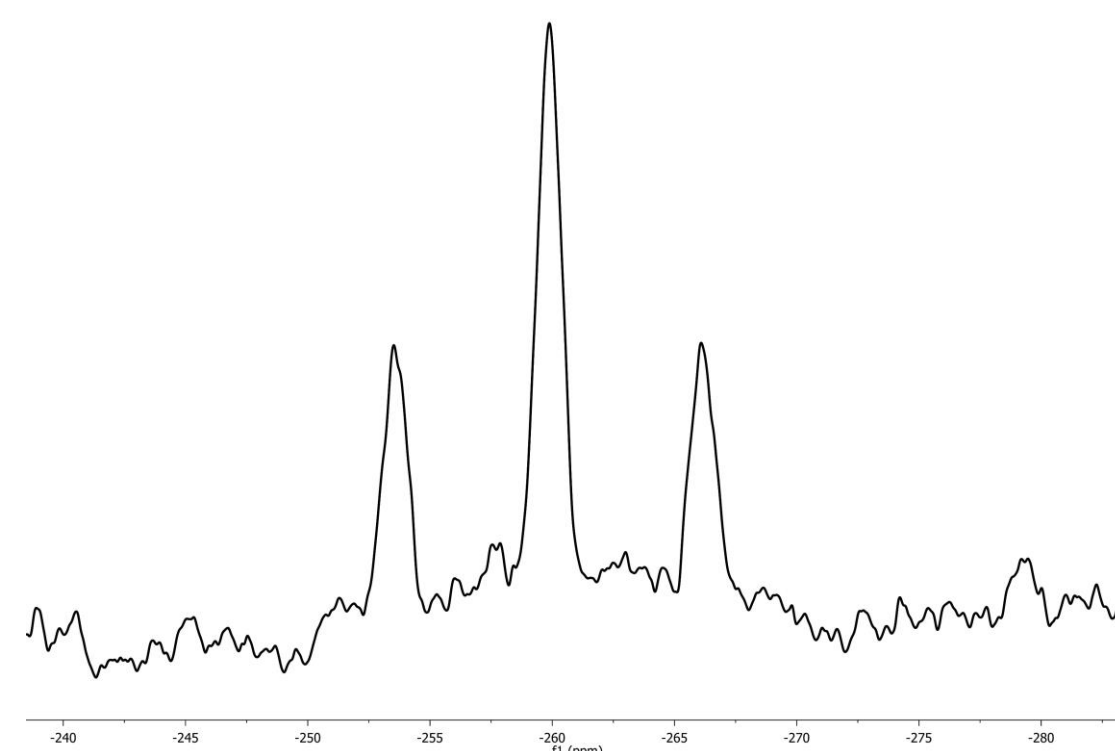


Fig 4: The recorded <sup>119</sup>Sn NMR data of the product of the reaction between the organotin chloride and DIBAL-H. The spectra was recorded on a 500 MHz magnet.

The recorded <sup>119</sup>Sn{<sup>1</sup>H} NMR spectrum provided two major developments in the project:

- The triplet splitting pattern demonstrates the formation of a hydride bridge system like those isolated previously by the Powers group with alkyl substituents being observed in this type of structure for the first time.
- The formation of a dimer suggests that either no stabilising agostic interactions were generated or the formation of a dimeric species is more highly favoured.

#### 5. A new approach

To dissuade the formation of the dimer, further categorise the role of agostic interactions on the structure and to decrease the solubility of the compound to attempt to collect crystallographic data, a new larger phosphorus-borane ligand was synthesised. Upon attempting to mount this new ligand onto the Sn centre in the same manner the smaller ligand, it was found that the new product was heavily sensitive to air, light and temperature suggesting an inherent instability. The increased bulk of the ligand preventing dimeric formation and the instability of the monomer categorically demonstrates the agostic type interactions present are insufficient to stabilise the Sn(II) hydride.

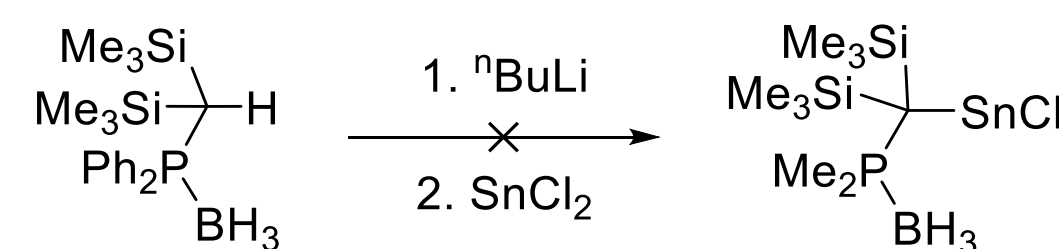


Fig 5: The proposed reaction scheme used to prepare the organotin chloride.

#### 6. Conclusion

Main group systems that mimic the chemistry of the transition metals are becoming an increasingly necessary to tackle the sustainability issue of using precious metals. The research completed as part of this project has presented interesting developments going forward. It has been found that:

- Stabilising agostic interactions are not solely sufficient in the formation of the ever elusive monomeric Sn(II) hydride.
- Dimeric Sn (II) are not exclusively formed with aryl substituents - alkyl analogues have been synthesised for the first time.

#### 7. Acknowledgements

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#### References

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