

Rational Control of Heavier Main Group Carbene Analogue Reactivity



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Aims

The project consisted of using two major chemical reaction steps to synthesise new additions to a class of tin-containing molecule known as **stannylenes**, helping to further understand bonding interactions in molecules. The two primary steps were:

- Developing new **ligand systems** which will help stabilise **air-sensitive** compounds.
- Attaching these ligands to a **tin metal centre**, and characterising the resulting **stannylenes** by analytical chemical techniques.

Background

- Stabilising stannylenes using phosphine ligands is difficult, and requires development of specific sets of ligands.
- There is a high energy barrier for the phosphorus atom to achieve the right shape to stabilise the tin metal centre¹ (cf. NHCs - Figure 1).
- The steric (size) and electronic properties of the ligands must be manipulated and fine-tuned in order for them to give the stabilising effect we want.²

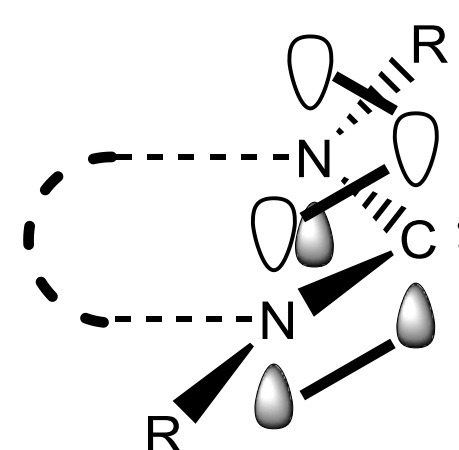
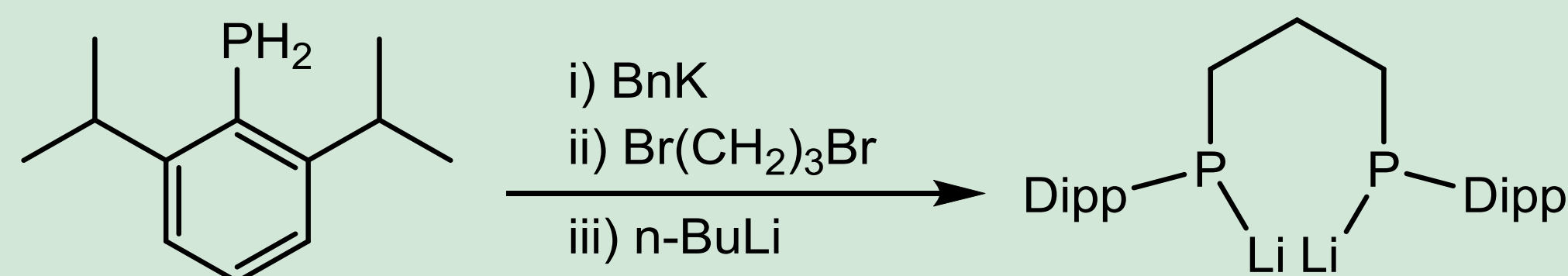


Figure 1: Donation of electron density in N-heterocyclic carbenes

1. Synthesis and Structure of (DippPLi)₂(CH₂)₃



By joining two primary phosphine molecules with an alkyl bridge and lithiating them, a bulky phosphide ligand is generated. The structure of this compound in solution can be analysed by a technique known as NMR spectroscopy, which shows signals corresponding to certain atoms in the molecule.

The ³¹P NMR spectrum shows that at low temperatures the single signal resolves into two separate peaks, suggesting multiple interactions between the phosphorus and lithium atoms in the molecule (Figure 2).

The crystal structure of the molecule can be determined by a technique known as X-ray crystallography, and the result pictorially shows the appearance of the atoms and bonds within the molecule (Figure 3).

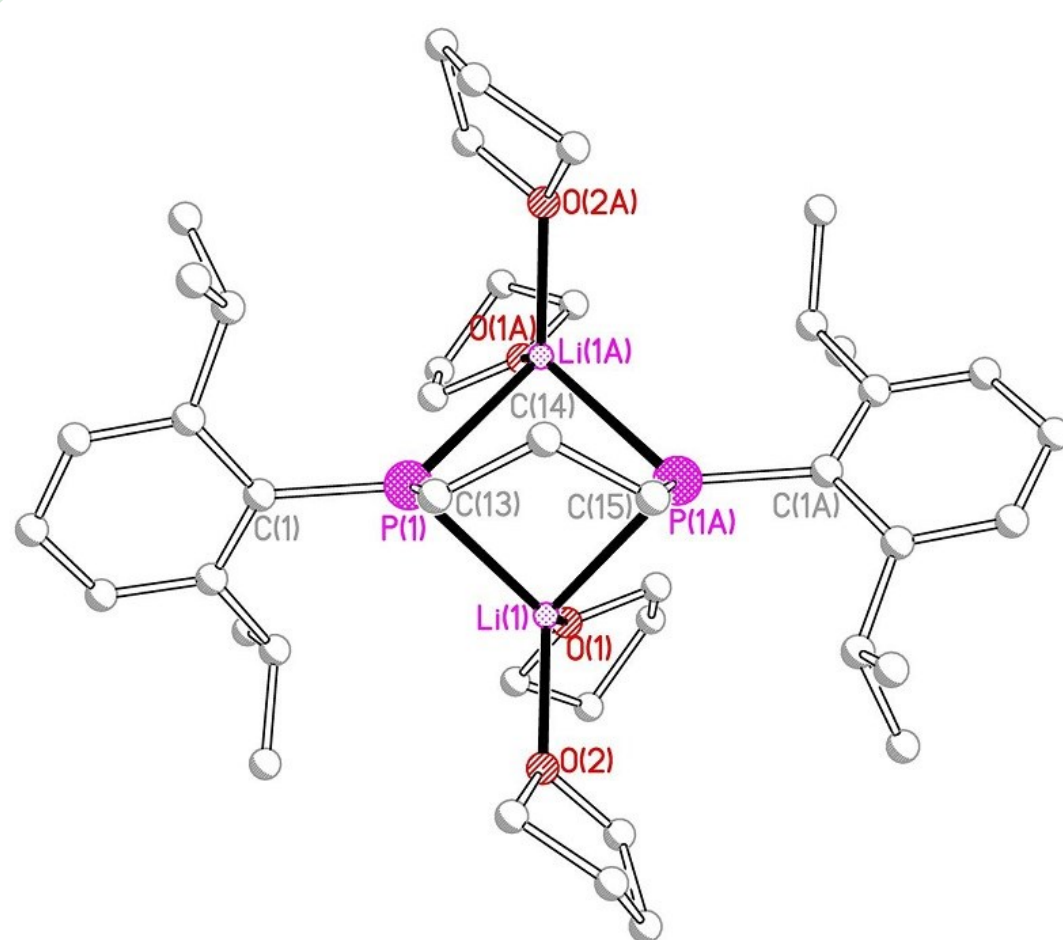


Figure 3: Crystal structure of (DippPLi)₂(CH₂)₃

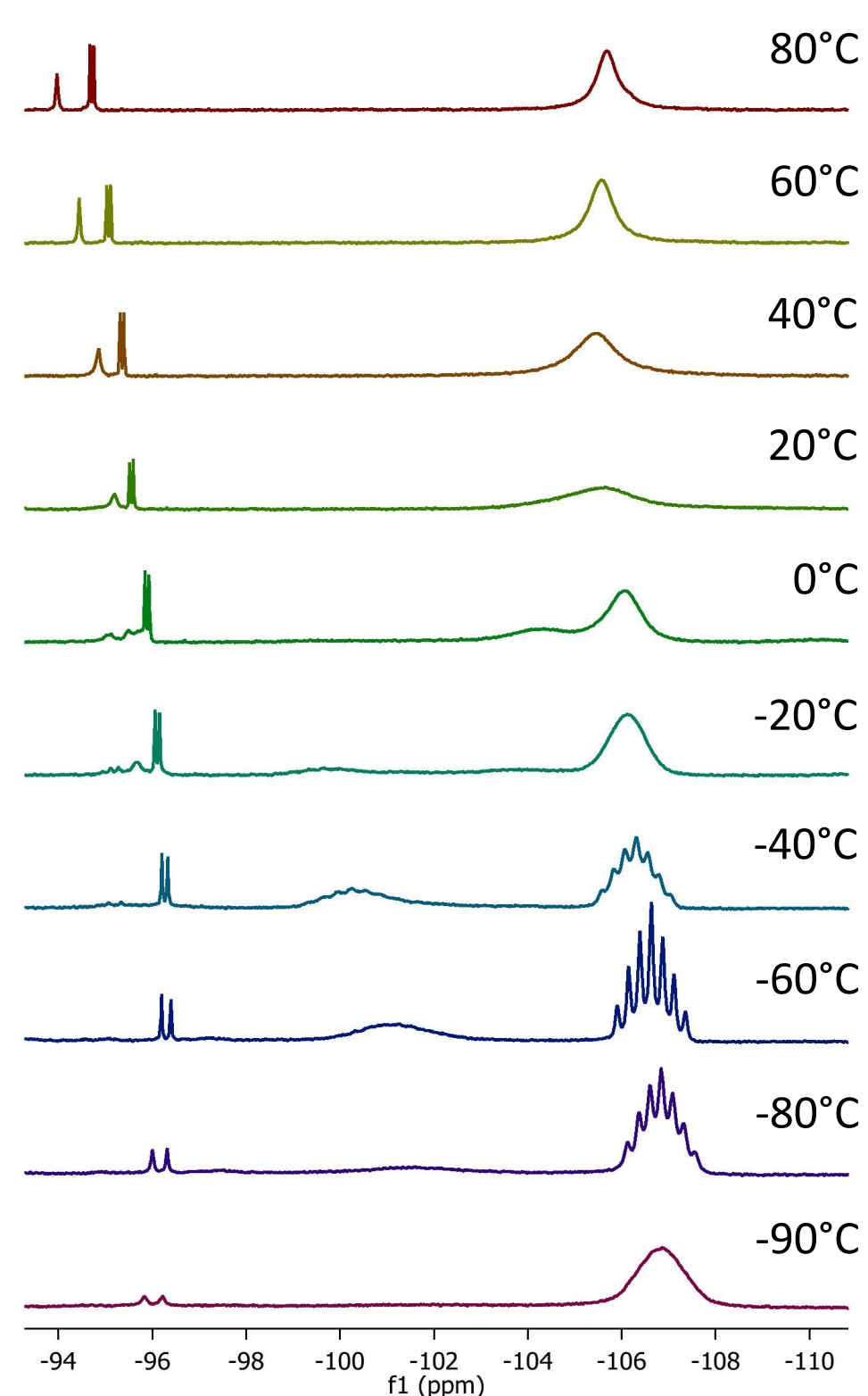
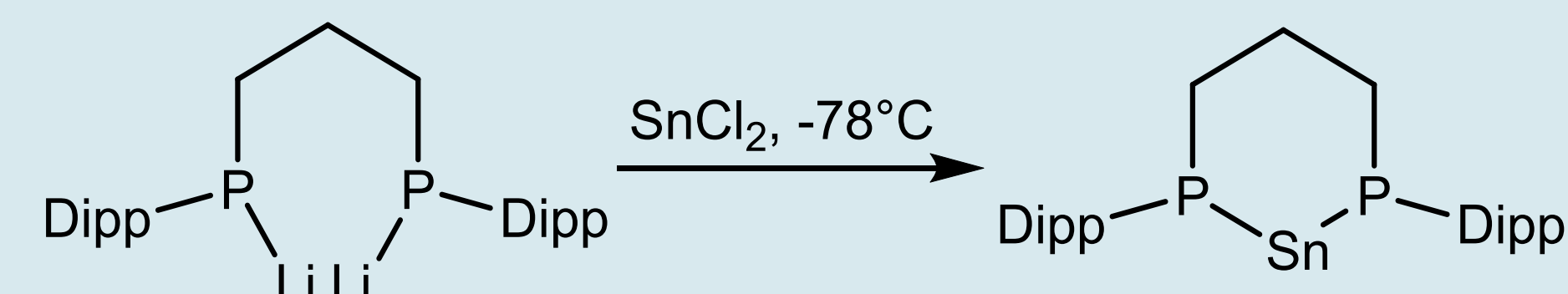


Figure 2: ³¹P VT NMR spectrum for (DippPLi)₂(CH₂)₃

2. Synthesis and Structure of [(Sn(DippP)₂(CH₂)₃)₂]



Reacting the phosphide ligand with SnCl₂ at low temperatures successfully generates the stannylene, showing that the bulky ligand system stabilises the tin metal centre, with a distinct structure.

This is corroborated by the determination of the crystal structure, which shows that in the solid state the stannylene has adopted a dimeric structure (Figure 5).

The ³¹P NMR spectrum has two separate peaks (doublets of doublets), suggesting the phosphorus atoms have different chemical environments (Figure 4). This would be consistent with a dimeric structure (i.e. two of the molecules combine into one molecular system).

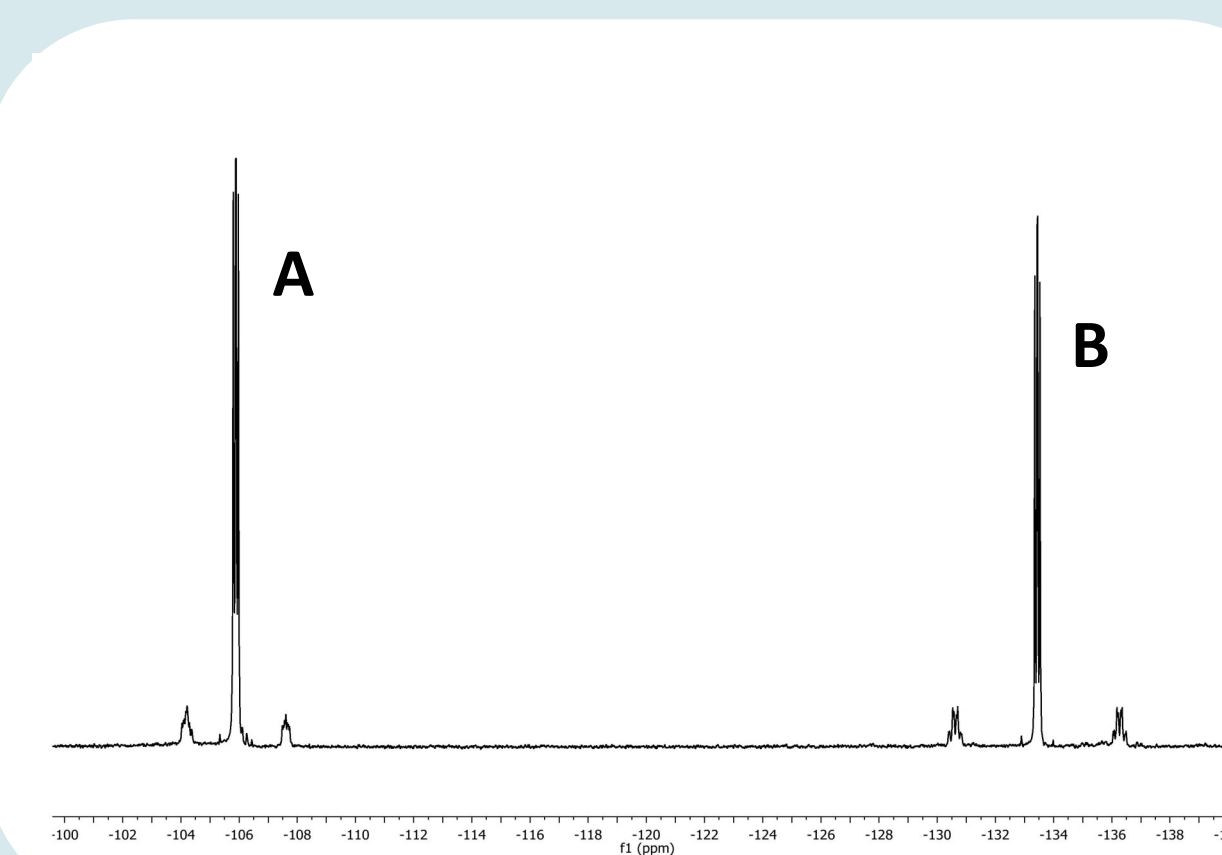


Figure 4: ³¹P NMR spectrum for [(Sn(DippPLi)₂(CH₂)₃)₂]

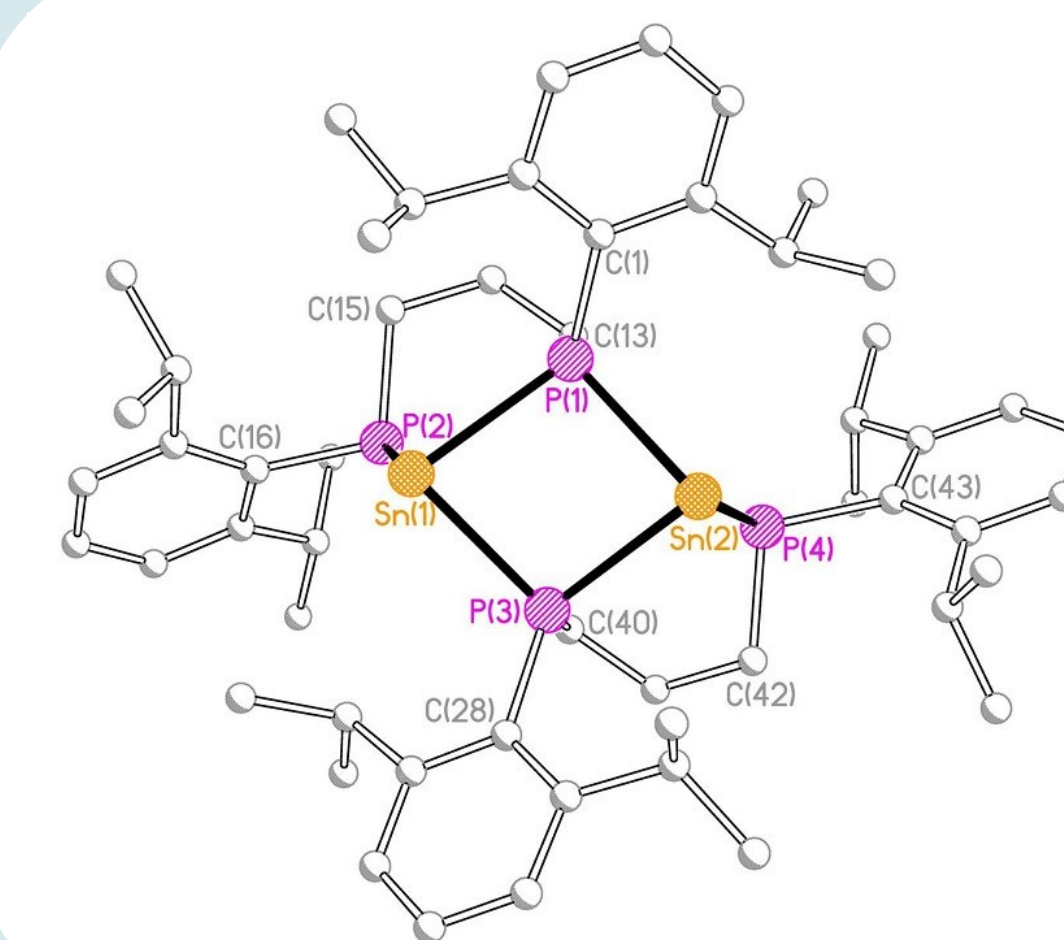


Figure 5: Crystal structure of [(Sn(DippPLi)₂(CH₂)₃)₂]

Conclusion

The project successfully resulted in the synthesis of new molecular systems, contributing to ongoing research into bonding interactions in novel compounds. The existence and structure of these molecular systems were fully confirmed and characterised by use of analytical techniques (NMR spectroscopy and X-ray crystallography).

Further research can be done by striving to develop more sterically-hindered ligand systems, which would allow the stannylene to be generated in a monomeric form in order to demonstrate similar π -bonding interactions as in other existing compounds.

References

1. K. Izod, D. G. Rayner, S. M. El-Hamruni, R. W. Harrington and U. Baisch, *Organometallics*, 2014, **33**, 378-386
2. K. Izod, P. Evans, P. G. Waddell, M. R. Probert, *Inorganic Chemistry*, in press.