Effect of a Rigid Backbone on the Stability and Reactivity of Main Group Carbene Analogues

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1. Aims

- To synthesis and characterise a suitable starting material
- To synthesise and characterise a new compound – a cyclic phosphorus-substituted heavier group 14 carbene analogue
- To investigate the effect of a rigid backbone on the planarity of phosphorus centres

2. Introduction

The development of, e.g. new drugs and electronic materials is frequently dependent on the chemist's skill on discovering new molecules. One of the aims of a chemist is to synthesise entirely new classes of molecule, which possess new and exploitable properties.

The isolation in the early 1990s of stable N-heterocyclic carbenes (NHCs) (**1**) have had an immense impact on chemistry and catalysis. The corresponding heavier group 14 analogues have a much longer history and it is perhaps surprising that the corresponding phosphorus-substituted species are rather less well established.[1] This, at least in part, may be attributed to the high energetic barrier to achieving a planar configuration at phosphorus.

The Izod group has recently prepared the first examples of heavier group 14 carbene analogues (**2**) with a planar phosphorus centre.[2,3]

This project focuses on the synthesis of a suitable starting material to allow the synthesis of cyclic analogues of (**2**) and if successful, the synthesis of these cyclic analogues (**8**), in order to explore the impact of a rigid backbone on the planarity of phosphorus centres.
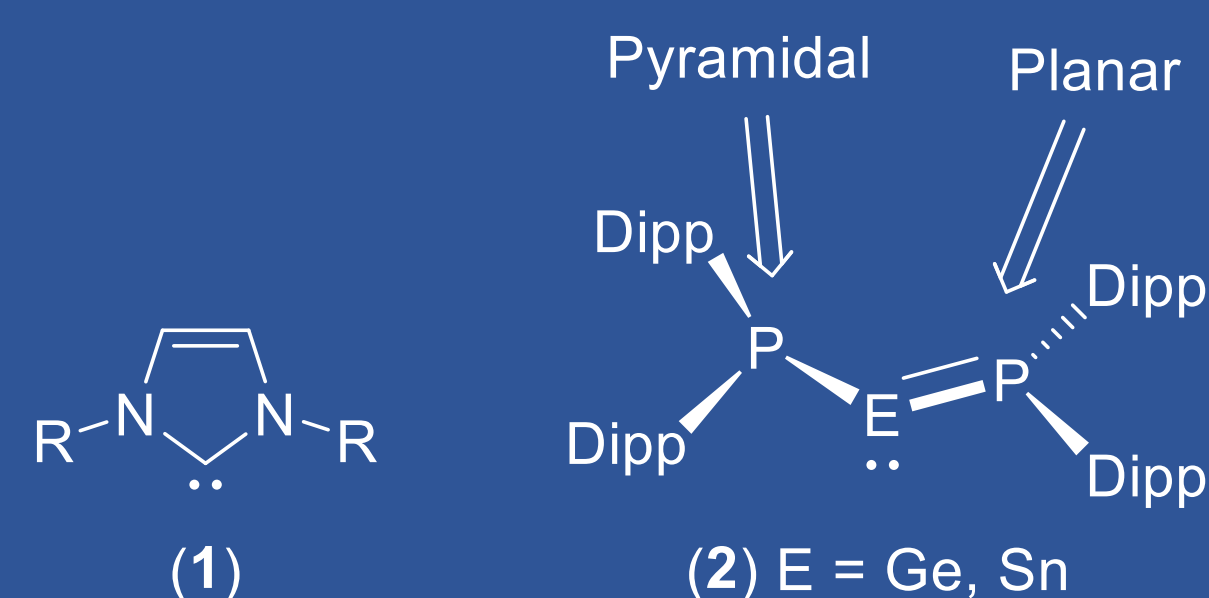
Figure 1: (**1**) An N-heterocyclic carbene (NHC). (**2**) The first example of a phosphorus-substituted heavier group 14 carbene analogue with a planer phosphorus centre.

3. Synthesis

Almost all compounds used are air and moisture sensitive, therefore all synthesis was carried out under an argon atmosphere, in air and moisture free conditions, using Schlenk line techniques.

The synthesis of various suitable starting materials was attempted, however the majority of time was spent on the synthesis of 1,2-bis(dichlorophosphino)benzene (**7**) from 1,2-dibromobenzene (**4**) using a modified synthesis of that reported by Reetz et al[4,5] and Xia and Ding et al.[6] Unfortunately the first step, the transformation from (**4**) to (**5**) proved particularly challenging and required low temperature conditions. A methylcyclohexane/liquid nitrogen cooling bath was used to preform this reaction at -126 °C. This transformation was only successful on a very small scale and all attempts to scale up proved unsuccessful. It is suspected that benzyne, shown in figure 2(C), was formed during the transformation, which was detrimental and prevented the synthesis of (**5**). The synthesis of bis(diethylamino)chlorophosphine (**3**) used in the reaction and the proposed synthesis of a cyclic phosphorus-substituted heavier group 14 carbene analogue (**8**) is shown in figure 2.
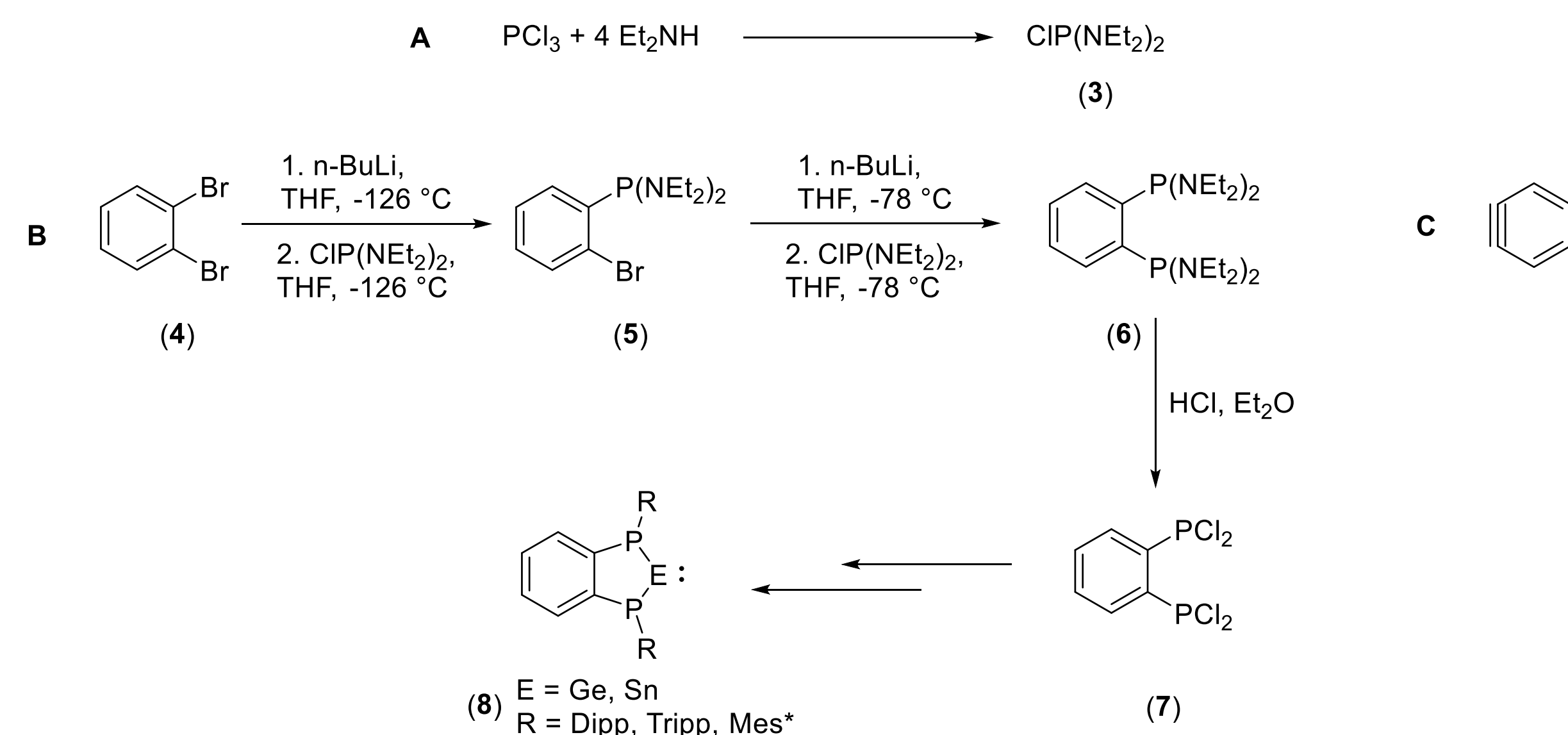
Figure 2 (**A**) Scheme showing the synthesis of bis(diethylamino)chlorophosphine (**3**). (**B**) Scheme showing the proposed synthesis of a cyclic phosphorus-substituted heavier group 14 carbene analogue (**8**). (**C**) Benzyne.

4. Characterisation

Nuclear magnetic resonance (NMR) is a technique used to obtain structural information of molecules, by looking at the chemical shifts of the peaks in the spectrum. If the NMR data for a particular molecule is known, then the experimental chemical shift value can be compared to the reported value, to see if the correct product has been made. In this project ^{31}P and ^{1}H MNR was used to obtain information about the molecules synthesised.

The expected chemical shift of compound (**5**) was expected to be around 97.4 ppm as reported by Xia and Ding et al.[6] However, in most attempts of the transformation from (**4**) to (**5**), the ^{31}P NMR spectrum of the product obtained showed a peak around 134.8 ppm, shown in figure 3(A), which meant that the correct product had not be formed. This transformation, was however, successful on a very small scale and the ^{31}P MNR spectrum of the product showed a peak at 95.6 ppm, shown in figure 3(B).
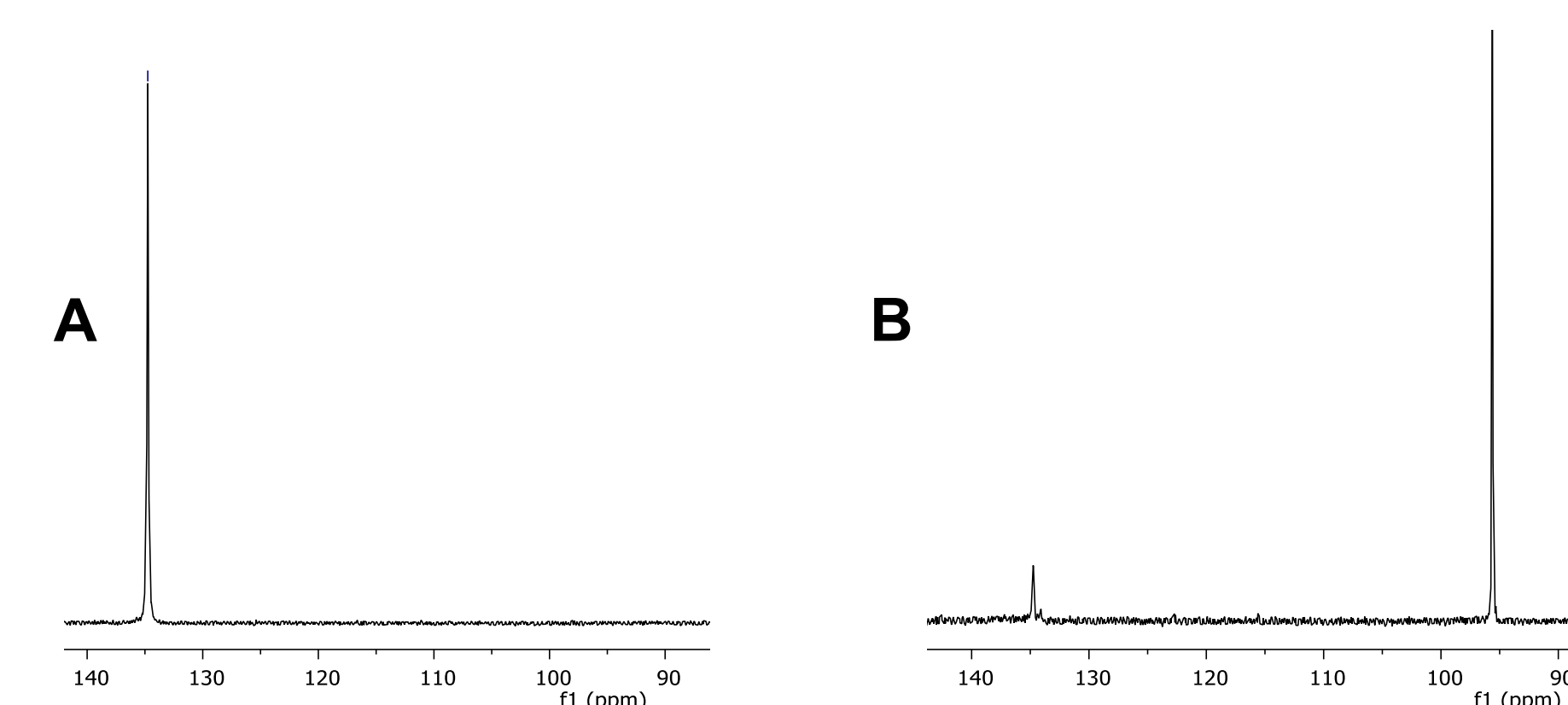
Figure 3 (**A**) ^{31}P NMR spectrum of the product from an unsuccessful transformation from (**4**) to (**5**). (**B**) ^{31}P MNR spectrum of (**5**).

5. Conclusion

Although a cyclic phosphorus-substituted heavier group 14 carbene analogue was unable to be synthesized during this project, much was learned about potential routes for this synthesis, which will be useful as others continue this project. I am confident that this new class of compound will be synthesized and that this will have a significant impact on the field of main group chemistry.

References

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