

Synthesis and coordination chemistry of phosphinine-based hybrid ligands

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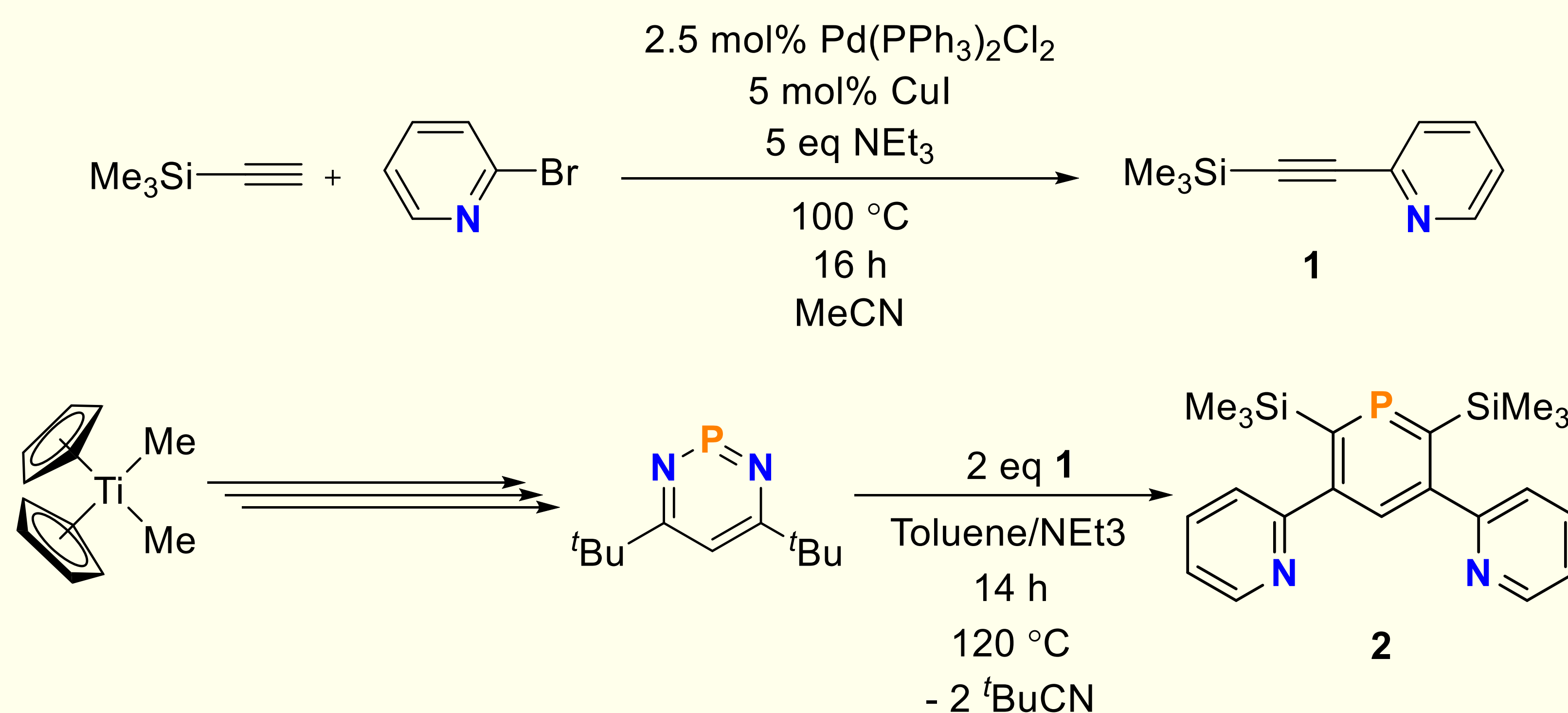
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1. Introduction

Hybrid ligands, as defined by Braunstein and Naud,¹ are ligands encompassing both a hard and soft binding motif. This can be used to exploit the binding properties of various metals and potentially extend the principle to synthesise complexes bearing differing metal centres. Phosphinines are an attractive candidate for this purpose as it is possible to synthesise highly functionalised molecules with the donor atoms separated, allowing for selective coordination. As phosphinines are known to be weak σ -donors this may also lead to being able to selectively target the various binding motifs with different metals.

2. Ligand synthesis

The synthesis of 2-(2-pyridyl)-1-trimethylsilylacetylene was adapted from the literature.² The work up was altered allowing for the isolation of a crystalline material suitable for SCXRD. The phosphinine is then synthesised using the procedure developed by Mathey *et al.*³ 1,3,2-diazaphosphinine is synthesised from Cp_2TiMe_2 and then reacted with two equivalents of **1** affording **2**.

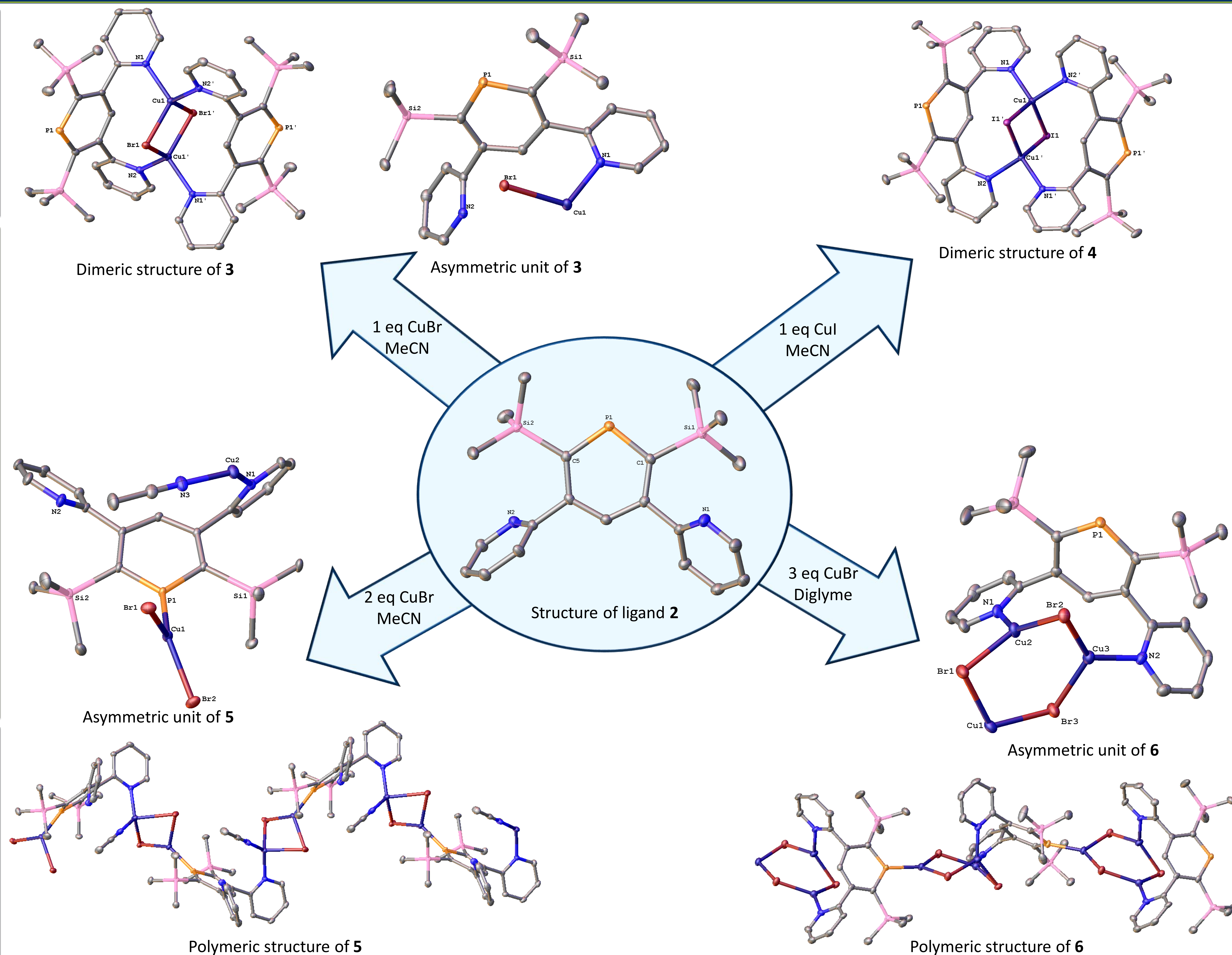


3. Complexation reactions

The asymmetric unit and dimeric/polymeric structures are given for all CuBr structures (**3**, **5** and **6**), only the dimer is given for structure **4**. Structures **3** and **4** were found to be isostructural in the solid state, with both compounds crystallising in $P2_1/n$, with half of the dimer in each asymmetric unit. **5** is a one-dimensional coordination polymer in the solid state consisting of a Cu_2Br_2 core with one equivalent of ligand **2** and one equivalent of MeCN. Performing the reaction in a less coordinating solvent (diglyme) allowed for the formation of **6**. This too is a one-dimensional coordination polymer but this compound features a Cu_3Br_3 core and just one equivalent of the ligand.

Conclusions

We have synthesised a number of Cu complexes by varying the amount of CuX salts and the solvents used in the reactions. Further work in this area will investigate what other metals can be coordinated to this ligand with a view to synthesising bimetallic species by selectively coordinating at the P or N atoms.



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References:

- 1) P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, 40, 680
- 2) Y. Lei, T. Hu, X. Wu, Y. Wu, H. Xian, H. Sun, Q. You, X. Zhang, *Tetrahedron Lett.* **2016**, 57, 1100
- 3) N. Avarvari, P. Le Floch, F. Mathey, *J. Am. Chem. Soc.* **1996**, 118, 11978