Appendix A – The Synthetic Route Towards Carbon Phosphide

In 1921 E. de Mahler[1] reported that he had produced a solid containing only carbon and phosphorus. As this is the first report of a compound containing only carbon and phosphorus it was thought that it may be useful to make it and try to crystallise it, either by annealing or by finding a compatible solvent.

As the original text of the journal was in French, it was translated into English by myself, using translation software. The proposed reaction scheme is shown in Figure A.1:

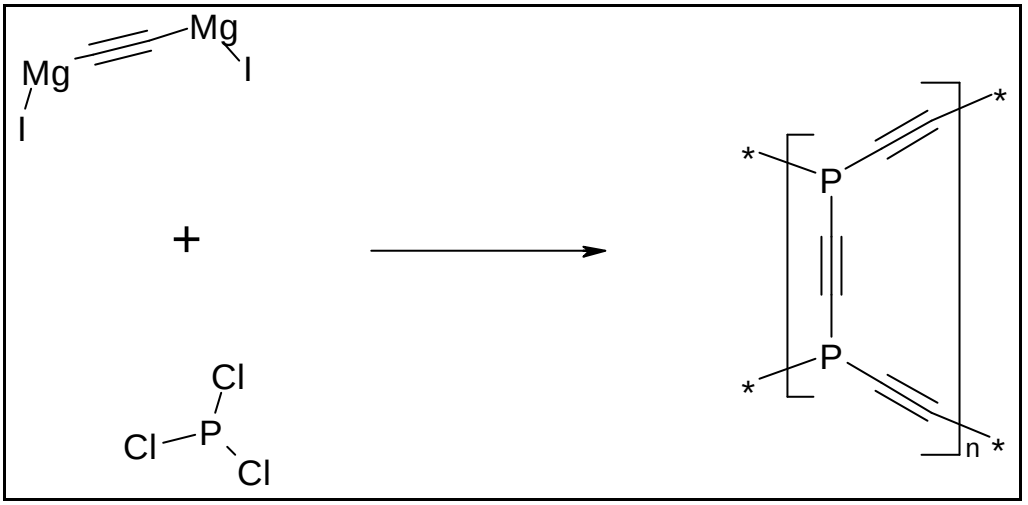

Figure A.1: Reaction performed by de Mahler *et al*. The product is the logical product from that reaction.

The product of this reaction was said to be a white waxy solid that is insoluble in all solvents, acids and bases (in the 1920s there were far less solvents, acids and bases available than there are today). It was said to burn rather well though. The experiment has not been repeated in any literature.

In order to repeat this experiment (or a similar one) the Grignard Reagent had to be prepared (Grignard Reagents are extremely sensitive to moisture so are generally prepared when they need to be used). The Grignard reagent was prepared as follows:

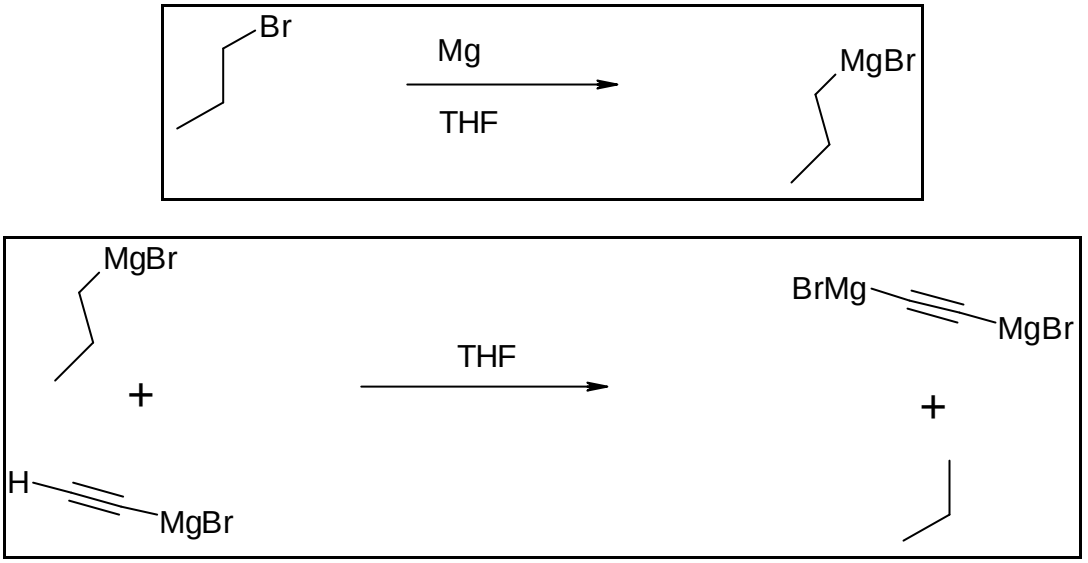

Figure A.2: The preparation of the Grignard Reagent

The acetylinic Grignard Reagent shown in the reagents of the second reaction step was obtained from Aldrich Chemicals. The reaction works because the acetylinic hydrogen is very loosely bound, the MgBr group attached to the propyl group is also loosely bound so they swap very easily. The reverse reaction does not occur as one of the products is propane, which is gaseous and is easily removed. The rest of the reaction is the same as in Figure A.1 apart from the iodine groups are substituted with bromine groups.

The reaction was carried out in a dry Schlenk line arrangement pumped with dry nitrogen to prevent air or moisture affecting the reaction. The glassware was dried with a heat gun prior to use, and the Mg was dried in an oven overnight.

When PCl_3 was added to the reaction mixture a brown solid appeared very quickly (the flask got very hot). This was washed and dried under high vacuum. This was sent to solid state NMR for analysis by ^{13}C and ^{31}P nuclei. As all P atoms should be equivalent in the structure a single strong peak was expected and in the ^{13}C NMR a single strong peak was expected. The spectra obtained were very noisy with several peaks.

Investigations on this compound were ceased due to lack of time.

References

1 E. de Mahler, Bull. Soc. Chim **29,** 1071 (1921).