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Synthetic routes to porphyrins bearing fused rings

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1. Introduction

Since the early work of Fischer, porphyrin chemistry has evolved dramatically allowing many exotic macrocycles to be synthesised.[1] Few boundaries restrict the porphyrin chemist, as the field overlaps with organic, inorganic and physical chemistry, as well as with many areas of biology and medicine. Within this diversity of porphyrin chemistry, there has been much interest in the synthesis of porphyrins bearing fused rings, whether as extensions of the conjugated macrocycle or fused alicyclic ring systems. They have proved to be valuable research tools and a fruitful area for the development of synthetic methodology. These fused rings can affect porphyrins by altering their optical properties, both ground and excited state, coordination chemistry and redox behaviour, and it is this potential that has captured the attention of many scientists.

The formation of porphyrins with 'exocyclic' rings fused to the macrocycle can be achieved by a variety of reactions, which will be discussed further. Generally, porphyrins bearing fused rings can be divided into two categories. Namely those formed by intramolecular cyclisation reactions and those formed by intermolecular cyclisation reactions. An extensive discussion of methods for the formation of porphyrins with fused rings from non-porphyrin starting materials is outside the scope of this review and these will only be mentioned if they give access to starting materials for further modification of the fused rings. Finally, examples of the formation of arrays in which porphyrins are fused to one another and the use of porphyrins bearing fused rings to synthesise heterodimers will be covered briefly.

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2. Porphyrins with fused rings formed via intramolecular cyclisations

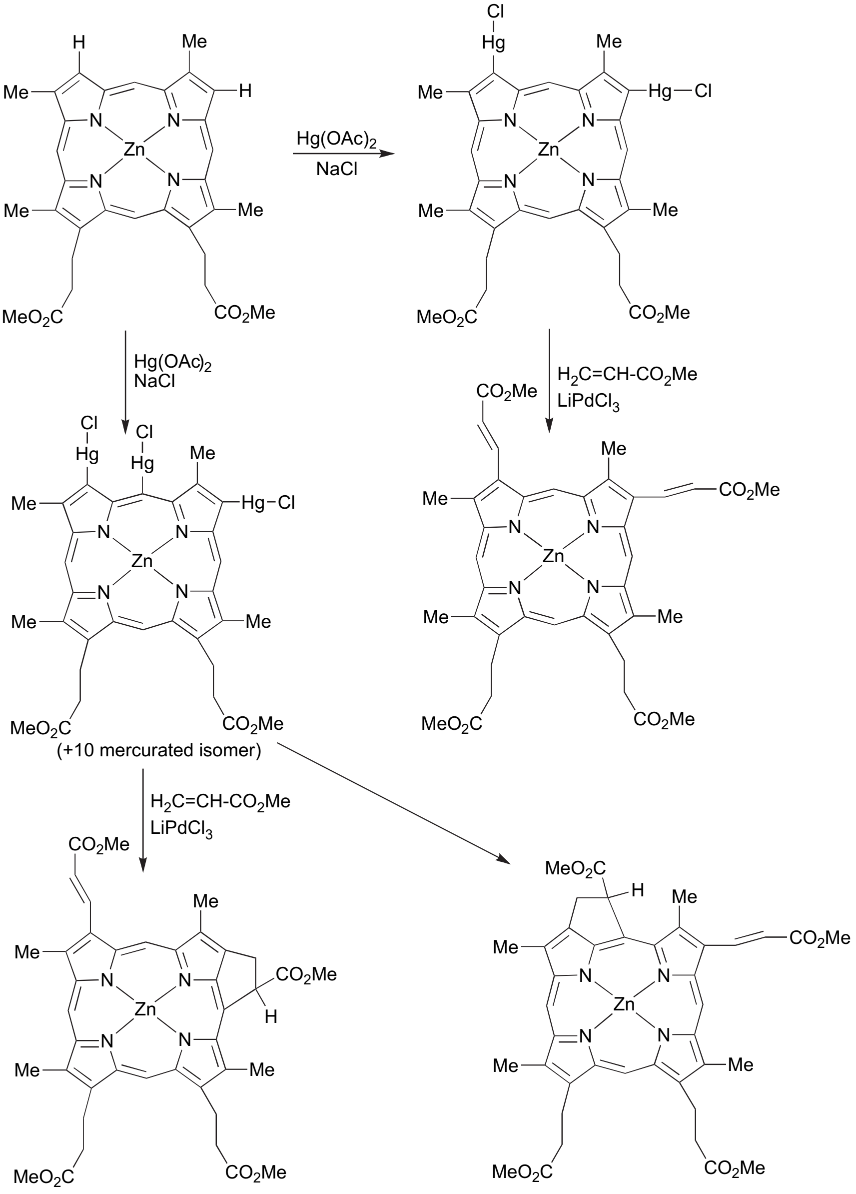
2.1. Metal-mediated cyclisations

In the 1980s, Smith et al. described a palladium-catalysed method that could be used to attach a number of unsaturated substituents directly to the periphery of mercurated porphyrins.[2–4] The first step was the mercuration of zinc(II) deuteroporphyrin IX dimethyl ester. Subsequent treatment with methyl acrylate and $LiPdCl_3$ gave the expected bis-acrylate, along with an unexpected by-product, which could be separated into two isomers (Scheme 1).

It was postulated that the bis-chloromercurated porphyrin product was contaminated with a tris-mercurated by-product in which mercuration had occurred at the 5- or 10-position. Subjecting these isomers to palladium-coupling conditions led to the formation of two products bearing fused five-membered exocyclic rings.[5] This synthetic method was then exploited to synthesise deoxyerythroetioporphyrin and deoxophylloerythrin methyl ester (Scheme 2).

Recently, Fox and Boyle[6] have developed a method for intramolecular cyclisation based on palladium-catalysed coupling of *meso*-(2-iodophenyl) porphyrins, which gives access to a variety of porphyrins in which the *meso*-phenyl rings are fused to adjacent β-positions (Scheme 3).

It is well documented that organozinc reagents can be easily prepared from organic bromides utilising metallic zinc.[7] Using this technique Chen et al.[8] discovered that treating 2-bromo-5,10,15,20-tetraphenylporphyrinatozinc with activated zinc metal[9] in DMSO at 60 °C for 30 min, resulted in the formation of a fused five-membered ring, similar to those accessed earlier by Fox and Boyle using intramolecular palladium coupling.



Scheme 1. Palladium-catalysed cross-couplings and cyclisations.