Review Article

Highlights of Carbaporphyrin Chemistry

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Nilsen, H. J. and Ghosh, A., 1998. Highlights of Carbaporphyrin Chemistry. – Acta Chem. Scand. 52: 827–830. © Acta Chemica Scandinavica 1998.

The chemistry of a new class of ligands comprising inverted and carbaporphyrins is briefly reviewed, with a focus on the ability of these molecules to form organometallic complexes.

The study of porphyrin isomers and analogs is now an exciting subfield of tetrapyrrole chemistry.[1] Here we will briefly review the chemistry of inverted or *N*-confused porphyrins and carbaporphyrins which have turned out to be molecules of exceptional interest. The former undergo a remarkable activation of the central C–H bond to yield organometallic compounds (Fig. 1).[2] These compounds are also of great interest on account of their conceptual relationship to nucleophilic carbenes and their ability to stabilize high-valent transition metals.[3] We considered it useful to briefly review the chemistry of inverted and carba-porphyrins, a field that has seen many exciting developments since inverted porphyrins were first synthesized in 1994.

The inverted porphyrins were discovered accidentally as by-products of the well known acid-catalyzed pyrrole–aldehyde cyclocondensation route to porphyrins (Fig. 2).[2,4] Both protons and Lewis acids can be used to catalyze the reaction. Rational multistep approaches to inverted porphyrins have appeared recently. Dolphin *et al.* have reported a route involving acid-catalyzed McDonald-type [2+2] condensation of an α,β-dipyrro-methane and an α,α-dipyrromethane dialdehyde (Fig. 3).[5] Lee and coworkers have reported a [3+1] approach to porphyrin analogs with an inverted pyrrole ring and a thiophene or furan (Fig. 4).[6] True carbapor-
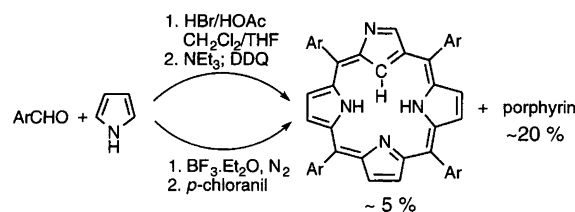

Fig. 2. The first preparations of inverted porphyrins.

phyrins, which lack one nitrogen relative to normal porphyrin, have also been synthesized via condensation of a tripyrrane and various cyclopentadiene aldehydes (Fig. 5).[7–10]

Figure 6 shows some possible tautomeric forms of inverted porphyrins. The most stable tautomeric form (A in Fig. 6) has three central hydrogens, one of which is attached to the central methine carbon and the other two to the nitrogens closest to the central methine unit. Both the central NH groups are hydrogen-bonded, which presumably stabilizes this tautomer relative to the one with an exocyclic NH group (B in Fig. 6) by a margin of about 5 kcal mol^{-1}.[11] There is also no [18]annulene substructure in the nonionic resonance form of B. Two tautomeric forms of a true carbaporphyrin are also shown in Fig. 6. The tautomer in which the two nitrogens closest to the central CH are protonated is the one observed experimentally,[7] presumably because both central NH groups in this form are hydrogen-bonded. This may be contrasted with the other tautomer.

Perhaps the most interesting property of *N*-confused porphyrins is that their central C–H bond can be activated by metals such as Ni^{II} to form organometallic complexes (i.e. with direct metal–carbon bonds).[2] One proposed reason for this, based on theoretical calculations,[12] is that the ligand in metal-complexed inverted porphyrins may be regarded as a nucleophilic singlet carbene (Fig. 7). For the carbenic tautomer of the free
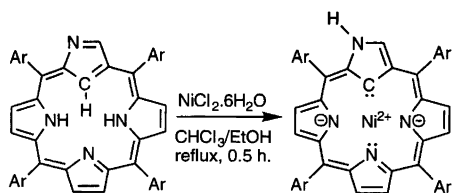

Fig. 1. Facile formation of nickel–carbon bond by an inverted porphyrin.

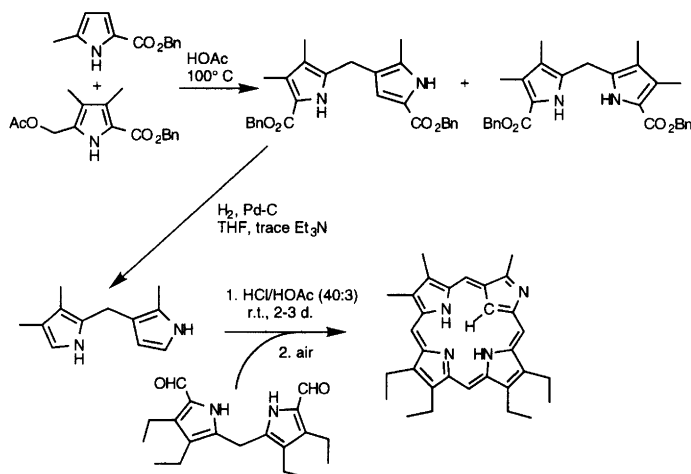* To whom correspondence should be addressed.

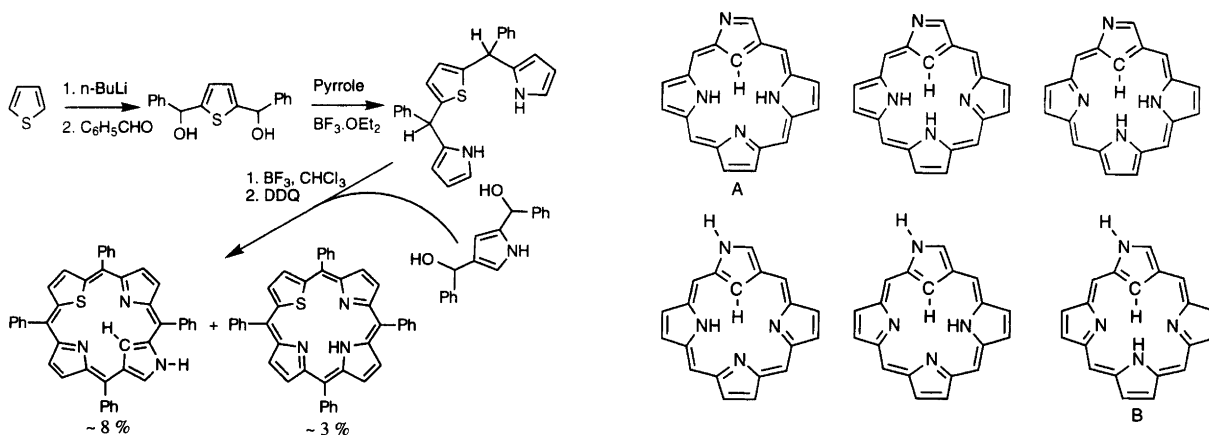Fig. 3. A directed synthesis of an inverted porphyrin by Dolphin *et al.*

Fig. 4. A directed synthesis of a porphyrin analog with an inverted pyrrole and a thiophene. See also Ref. 6 for a comment on this figure.
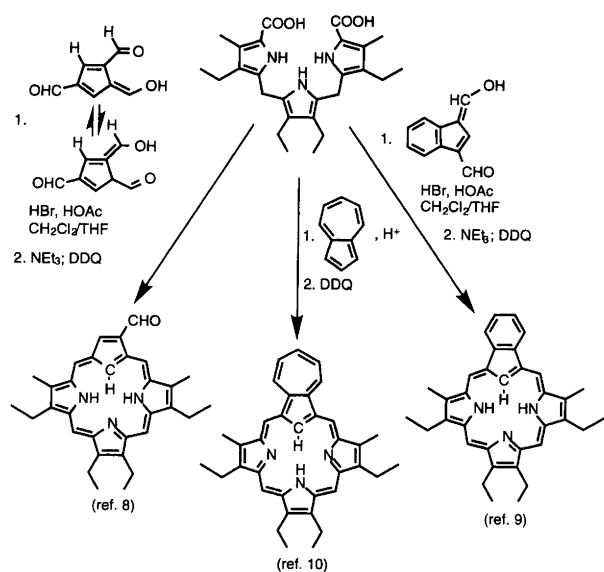

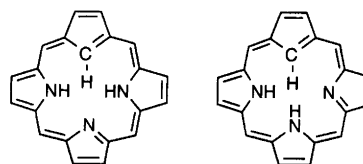Fig. 5. Some syntheses of carbaporphyrins.

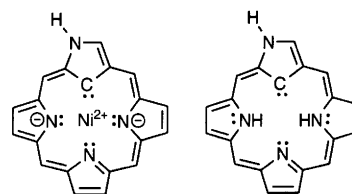Fig. 6. Some tautomeric forms of inverted and carba-porphyrins.

Fig. 7. Inverted porphyrins as masked carbenes.

inverted porphyrin ligand (Fig. 7), the energy required to excite an electron from the carbenic lone-pair into the LUMO roughly equals the singlet–triplet splitting in CF_2 (ca. 41 kcal mol^{-1}), a typical nucleophilic singlet carbene.[12] Another factor possibly contributing to the ease of insertion of Ni^{II} is the highly favorable covalent interaction between the carbenic lone pair and the empty

d_σ orbital of the d^8 Ni^{2+} ion. To estimate the energetic importance of this orbital interaction, it will be interesting to compare the enthalpies of complexation of Ni^{II} and Zn^{II} to the inverted porphyrin ligand.

In the above examples, the inverted porphyrins act as dianionic ligands, but they are potentially also trianionic ligands. Other trianionic ligands such as corrole can stabilize high-valent transition metals, and it was interesting to see whether inverted porphyrins can behave in the same manner.[13] Latos-Grazynski and co-workers succeeded in preparing Ni^{III} inverted porphyrins by oxidizing Ni^{II} inverted porphyrin with different one-electron oxidizing agents, such as Br_2, I_2 and $(PyH)_2Cr_2O_7$.[3] However, the ligand in these high-valent Ni^{III} complexes turned out to be dianionic instead of trianionic, with an axial monoanionic ligand such as Cl^- or OH^- balancing the extra positive charge on the nickel.

True carbaporphyrins have not yet been observed to form metal complexes.[7] Apparently, unlike corrole, carbaporphyrins do not readily act as trianionic ligands, possibly because carbaporphyrin ligands with N_3C cores are less electronegative than the corrole ligand with an N_4 core. This is also consistent with the finding of Latos-Grazynski et al. of a dianionic inverted porphyrin ligand in the Ni^{III} complexes mentioned above.[3] Synthetic routes for metal complexes of true carbaporphyrins remain to be explored, perhaps involving the use of an appropriately strong base.

Methylation of nickel complexes of inverted porphyrins with methyl iodide provides access to a number of new ligands (Fig. 8) in their complexed forms.[14] Free base 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin, $CTPPH_2$, methylates at the exocyclic 2-N position, giving 5,10,15,20-tetraphenyl-2-methyl-2-aza-21-carbaporphyrin, $2-NCH_3CTPPH$. Note that $2-NCH_3CTPPH$, which has two central hydrogens, has a different tautomeric structure (similar to B in Fig. 6) than $CTPPH_2$, which has three central hydrogens. Like $CTPPH_2$, NCH_3CTPPH can act as a dianionic ligand toward Ni^{II} (Fig. 8). In contrast, methylation of $CTPPNi^{II}$ starts at the inner carbon of the inverted pyrrole ring and continues to the 2-N position, giving three products: diamag-
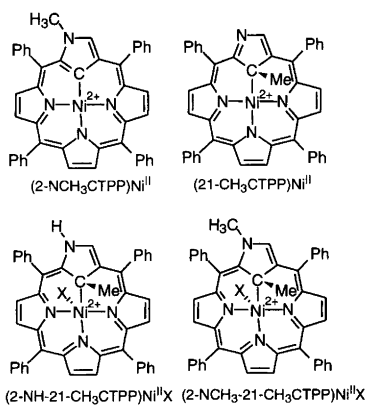
netic $(21-CH_3CTPP)Ni^{II}$ and paramagnetic $(2-NH-21-CH_3CTPP)Ni^{II}X$ and $(2-NCH_3-21-CH_3CTPP)Ni^{II}X$ (Fig. 8). For details of this somewhat complicated chemistry, the reader is referred to Ref. 14. Here we will only comment briefly on $(21-CH_3CTPP)Ni^{II}$. The nickel lies in the plane of the three central nitrogens, while the methylated pyrrole in this compound is tilted out of this plane by $42.2°$. The inner carbon may be regarded as a carbanionic center that is stabilized both by interaction with the empty Ni^{II} d_σ orbital and by delocalization into the macrocycle π system.

Nitration of $CTPPH_2$ under relatively mild conditions was found to yield $21-NO_2CTPPH$, a molecule with two central hydrogens (Fig. 9), in a regiospecific manner.[15] This suggests that the central C–H bond is considerably more susceptible to electrophilic substitution than the peripheral ones, for which a possible rationale may be as follows. As shown in Fig. 9, the cationic intermediate involved in the electrophilic substitution at the 21-position has many highly favorable [18]annulenic resonance forms. In contrast, a cationic intermediate from electrophilic substitution of any of the β-C–H groups has a number of relatively unfavorable resonance forms with cross-conjugated non-[18]annulenic structures (Fig. 9). It will be interesting to examine the regioselectivity of other electrophilic substitution reactions of inverted porphyrins.

In summary, we have given a brief overview of the preparation, tautomeric structures and chemical reactivity of inverted porphyrins and carbaporphyrins. In particular, we have used insights from theoretical calcula-
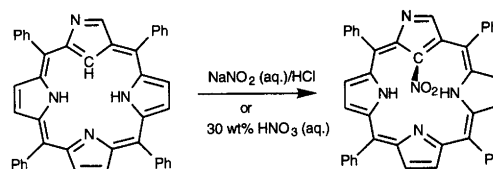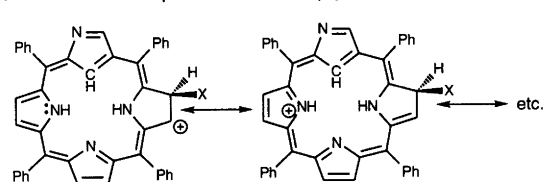

Fig. 8. Products of methylation of CTPPNi. X = halide.
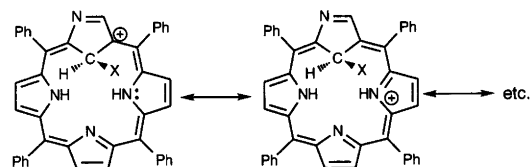
Fig. 9. Nitration of $CTPPH_2$.

tions to provide a unified perspective of the organometallic chemistry of these compounds.[16]

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