Synthesis and structural characterisation of the first *N*-heterocyclic carbene ligand fused to a porphyrin†

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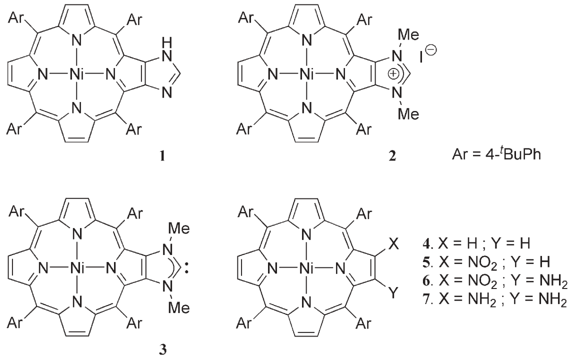
The functionalisation of two neighboring β-pyrrolic positions of a porphyrin by a fused *N*-heterocyclic carbene ligand, the subsequent metallation of this external coordination site by palladium(II) and the structural characterisation of the resulting compounds are presented.

The synthesis of multiporphyrin systems is of great interest because of their wide potential applications in catalysis,[1] molecular materials[2] and medicine.[3] A lot of synthetic strategies have been developed to build multiporphyrin systems through covalent[4] and non-covalent bonds.[5] The use of coordination bonds to link porphyrins together opened exciting opportunities to build systems with different shapes, such as linear,[6] cyclic,[7] 2-dimensional[8] and 3-dimensional[9] geometries. The classical building blocks employed for this strategy are porphyrins bearing one or more peripheral coordination sites, as is well illustrated by the examples of porphyrins linked to pyridyl derivatives.[8,10]

Surprisingly, the number of examples of porphyrins bearing *N*-heterocyclic carbene (NHC) ligands as external coordination site remains limited[11] and, to our knowledge, there is no example of NHC conjugated with the aromatic core of the porphyrin. Stable *N*-heterocyclic carbenes (NHCs), first isolated by Arduengo *et al.*,[12] are versatile ligands for transition metal complexes and remain very important in the field of organometallic chemistry and homogeneous catalysis.[13] Beyond catalysis, NHCs are emerging as relevant components in materials science.[14] It is obvious that there is a considerable potential for NHCs containing functional or tunable groups in conjugation with the carbene moiety.[15] Thus, we focused our attention on the design of the porphyrin **1** containing an imidazole ring fused across a β,β′-pyrrolic position and fully conjugated to the macrocycle. The formation of the imidazolium salt **2** gives a synthetic access to the porphyrin **3** fused to an NHC (Fig. 1).

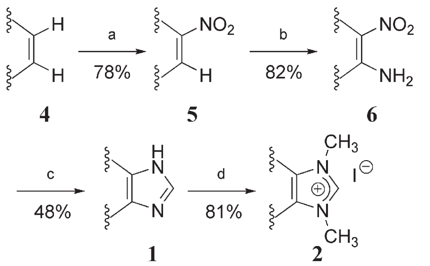


1 **2** **3**

Fig. 1 Structures of the complexes **1–7**.

The peripheral functionalisation of porphyrins is of great interest in order to access to new chromophores or to new multiporphyrin systems.[16] Crossley and co-workers prepared fused porphyrin-imidazole systems by the condensation of porphyrin-2,3-diones with an arylaldehyde in the presence of ammonia.[17] Following this procedure, the compounds obtained have a 2′-arylimidazole ring. Herein, we report another synthetic approach to obtain the fused porphyrin-imidazole **1** with a non functionalised 2′-imidazole carbon (Scheme 1).

The synthetic porphyrin used as starting material was the complex **4**.[18] First, a nitration reaction was realized according to the literature procedure to yield the β-nitroporphyrin **5**.[19] The electron withdrawing group NO_2 switched the reactivity of the neighboring pyrrolic β-carbon to an electrophilic center. Callot and co-workers showed that the 4-amino-4*H*-1,2,4-triazole is a powerful amination reagent for α,β-unsaturated ketones and aldehydes conjugated with the porphyrin core.[20] This can also be applied to **5** and it was possible to get the compound **6** in good yield (82%). The β-N*H*$_2$ ^{1}H NMR signal of **6** could be detected as a broad singlet at δ = 6.55 ppm in $CDCl_3$. Its UV-visible absorption bands were bathochromically shifted compared to **5**. The lowest energy absorption band of **6** shifted to 600 nm (587 nm for **5**). The diaminoporphyrin **7** was obtained by the reduction of



4 **5** **6** **1** **2**

Conditions:
(a) $LiNO_3$, $CHCl_3$/AcOH/Ac_2O, 45°C, 2h.
(b) 4-amino-4*H*-1,2,4-triazole, NaOH, toluene/EtOH, reflux, 1h.
(c) (i) $NaBH_4$, Pd/C, CH_2Cl_2/MeOH, 25°C, 1h.; (ii) HCO_2H, toluene, 110°C, 10 mn.; (iii) TFA, toluene, 110°C, 3h.
(d) MeI, K_2CO_3, 40°C, 24h.
Overall yields are indicated.

Scheme 1 Synthesis of the imidazolium salt **2**.

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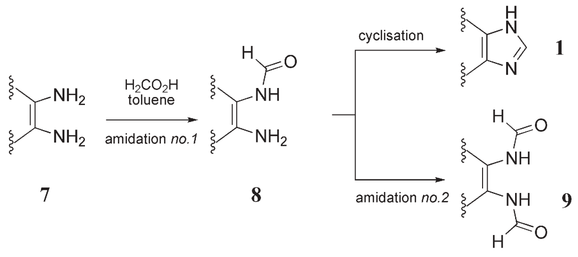
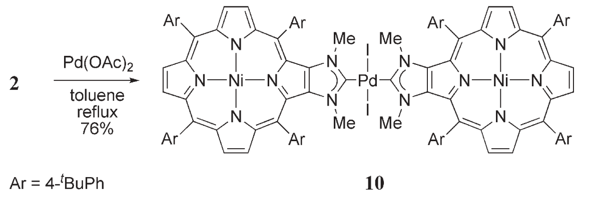


Scheme 2

the NO$_2$ group of **6** with NaBH$_4$ in the presence of methanol and Pd/C.[21] The porphyrin **7** was not isolated but used immediately for the formation of the imidazole ring.

The cyclisation reaction with formic acid was more challenging and realized in two steps compared to the classical procedure described for 2,3-diaminobenzene derivatives (one quantitative step).[22] First, the monoformamide **8** was obtained by the complete condensation reaction of **7** with formic acid in refluxing toluene (1 : 1 mixture) in less than 10 min, accompanied by two other compounds which appeared to be the imidazole **1** and the diformamide **9** (Scheme 2). The monoformamide **8** was stable enough to be purified by silica gel chromatography. The structure of **8** was clearly established by the usual characterisation techniques. In the ^{1}H NMR spectrum of **8** in CDCl$_3$, the two signals observed at δ = 4.59 and 6.75 ppm correspond respectively to β-N*H*$_2$ and β-N*H*CO. In the IR spectrum of **8** (KBr disc), the ν_{NH2} absorption bands are located at 3457 and 3389 cm^{-1}, and the $\nu_{C=O}$ is located at 1691 cm^{-1}. The right mass peak for **8** was obtained by FAB$^+$ mass spectrometry (m/z = 953). In the conditions described above, the intramolecular cyclisation of **8** to give the imidazole **1** occurred in competition with the formation of the diformamide **9** (Scheme 2). To prevent the formation of the undesirable diformamide **9**, it was preferable to remove the formic acid and to change the reaction conditions after the formation of the monoformamide **8**. The imidazole **1** was preferentially obtained by the slow addition of TFA to a refluxing solution of **8** in toluene. The overall yield from **6** to **1** was 48%. The ^{1}H NMR spectrum of **1** in CDCl$_3$ showed the broad signals due to the imidazole tautomerism that is slow on the ^{1}H NMR timescale.[17] The double *N*-alkylation of the imidazole ring of **1** with iodomethane yielded the corresponding imidazolium salt **2** in 81% yield. A sharp singlet at δ = 11.50 ppm corresponding to the iminium C*H* was observed in the ^{1}H NMR spectrum (C$_6$D$_6$) of **2**. This downfield chemical shift shows the highly electron-withdrawing nature of the metalloporphyrin macrocycle.

Then, we investigated the possibility of generating the carbene fused to the porphyrin **3**. As a proof of its existence, we performed the direct metallation of **2** with the basic metal precursor Pd(OAc)$_2$ in refluxing toluene.[23] This reaction proceeded smoothly leading to the formation of the complex **10** which was purified by chromatography on silica gel (Scheme 3). No signal corresponding to the iminium proton was observed by ^{1}H NMR spectroscopy (CDCl$_3$) showing the formation of the NHC–Pd(II) bond. The evidence of the formation of the complex **10** was also provided by FAB$^+$ mass spectrometry. The molecular peak corresponding to the dimer was observed at m/z = 2289. Two fragments were observed at m/z = 2162 and 1324 and correspond to the fragments of the complex **10** in which one ligand was removed, respectively the iodine and the porphyrin-NHC. The UV-visible absorption bands of **10** are slightly broadened and red-shifted compared to those of the imidazolium **2**. This result suggests that there is negligible ground state electronic communication between the prophyrins through the palladium center.



Scheme 3

The single-crystal X-ray analysis‡ unambiguously establishes the structure of the complex **10** and shows that the palladium atom lies on an inversion centre which ensures a *trans*-planar coordination (Fig. 2). The two porphyrin moieties show a combination of saddle and ruffle distorsions.[24] A maximum displacement of 0.909 Å (for C$_\beta$) and an average displacement of 0.386 Å of the core atoms from the porphyrin mean plane (based on a least-squares plane calculated for the 24 core atoms) are observed. The pyrrole rings exhibit twist angles of 16.3, 19.6, 21.2 and 22.6° (with respect to the porphyrin mean plan). Despite this distorted geometry of the aromatic core of the porphyrin, the additional imidazoylidene ring and the adjacent pyrrole are coplanar. The nickel(II) was found in a slightly distorted square planar geometry: the four Ni–N distances are almost equivalent (1.899(10), 1.907(10), 1.924(9), and 1.960(10) Å) and the four N–Ni–N *cis*-angles are close to 90° (88.5(4), 90.2(4), 91.1(4), and 91.2(4)°). In this square-planar *trans* palladium(II) complex, the Pd–C distances which are consistent with Pd–C single bonds (2.035(13) Å) are shorter than the Pd–I distances (2.5910(13) Å).[23] The two imidazoylidene rings are close to coplanarity and are tilted ~82° from the square planar central plane PdI$_2$C$_2$. This tilted conformation minimises the steric interactions between the methyl groups and the iodines linked to the palladium(II).

To conclude, we have presented here a new synthetic procedure to obtain a porphyrin with an additional imidazole ring fused across a β,β′-pyrrolic position. We have shown that it is possible to

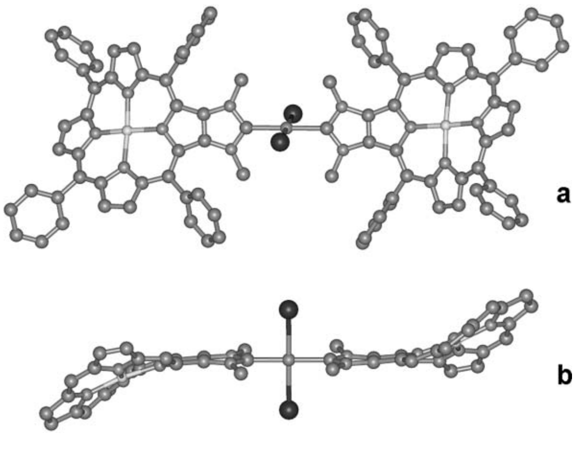


Fig. 2 Two views of the X-ray structure of the complex **10** (solvent molecules have been omitted for clarity). (a) *t*-Butyl groups and Hs omitted for clarity. (b) *meso*-Aryl groups and Hs omitted for clarity.

generate an NHC at the periphery of a porphyrin and to use it as a coordination site to built multiporphyrin assemblies. We are currently studying the tuning of the optical and redox properties of these NHC-porphyrin systems. The synthesis of bis-(NHC)porphyrins are also under investigation.

Notes and references

‡ Red-purple crystals have been obtained by vapour diffusion of acetone to a solution of the complex **10** in chloroform. Crystallographic data were recorded with an Xcalibur CCD camera (Oxford Diffraction) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å), 28 s per frame. The structure was solved using *ab initio* charge flipping methods[25] and refined using full-matrix least squares methods.[26] Hydrogen atoms (except one belonging to a chloroform molecule) were located from the Fourier difference map and refined with riding constraints. The other solvent molecules in the structure, *i.e.* acetone, were found to be highly disordered in channels along the *b* axis; they were modeled using the SQUEEZE procedure[27] as is implemented in CRYSTALS[25] and PLATON.[28] The crystal did not diffract well even at 175 K and only 18% of the available data could be used in the refinement on F. Thus, only the Ni, Pd, I and Cl atoms were refined anisotropically and all other non-H atoms were refined isotropically. Crystal data for **10**·4CHCl$_3$: $C_{130}H_{132}Cl_{12}I_2N_{12}Ni_2Pd$, M_W = 2765.48, monoclinic, space group $P2_1/c$ (no. 14), a = 22.1838(7) Å, b = 9.9174(4) Å, c = 31.4826(13) Å, β = 103.73(0)°, V = 6728.43(50) Å^3, Z = 2, D_c =1.365 g cm^{-3}, T = 173 K, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.128 mm^{-1}, 18567 reflns collected, 3351 unique reflns $I > 2\sigma(I)$, R_F = 0.263 and wR_F = 0.0887 for all reflections, R_F = 0.0764 and wR_F = 0.0521 for observed reflections. CCDC 642150. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704681b

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