

Porphodimethene–porphyrinogen relationship: the generation of unprecedented forms of porphyrinogen†

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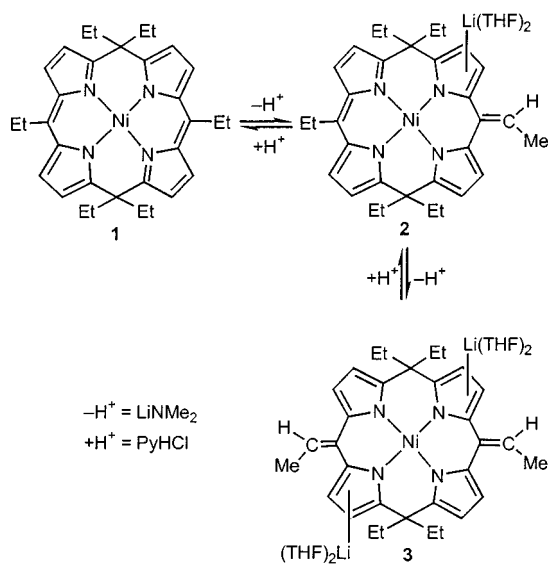
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The electrophilic reactivity of the porphodimethene skeleton towards nucleophiles led the establishment of a synthetic methodology to unprecedented forms of porphyrinogen containing the vinylidene substituents as well as other functionalities in the *meso*-positions

The intermediacy of porphodimethenes^{1,2} in the oxidation of porphyrinogen to porphyrin is well accepted. Work on the chemistry of the porphodimethene skeleton³ has suffered, however, for a long time from the absence of a real synthetic methodology, which is now available⁴ for exploring its reactivity. Porphodimethenes are the target molecules of this report, since they allow one to enter the field of unprecedented forms of porphyrinogen. The latter compounds have been obtained studying the reactivity of lithium and nickel hexaethylporphodimethenes (5,15-diethyl-*meso*-tetraethylporphyrin) towards nucleophiles. The synthetic sequences are displayed in Schemes 1 and 2.

Complex **1**⁴ underwent a stepwise deprotonation by LiNMe₂ to the monovinylidene porphodimethene complex **2**,⁵ containing a trianionic tetrapyrrolic derivative, which undergoes further deprotonation to the bisvinylidene porphyrinogen Ni derivative **3**. Both complexes **2** and **3** can be protonated back to the starting material by employing PyHCl.

The stepwise deprotonation of **1** to **3** requires the preliminary attack of a nucleophile, *i.e.* [NMe₂]⁻, at the mono-substituted *meso*-position of **1**. Such a pathway is supported by the reactivity of **1** with nucleophiles other than [NMe₂]⁻, namely

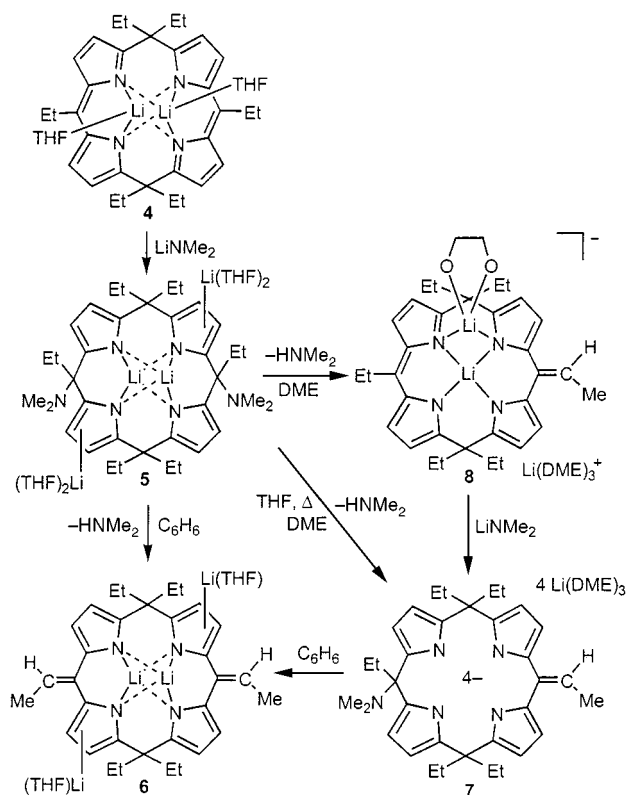


† Syntheses of complexes **2**, **3**, **5**, **6**, **7** and **8**, and complete ORTEP drawings of **3** and **7**, are available from the RSC web site, see <http://www.rsc.org/suppdata/cc/1999/2227/>

LiBu, LiHBEt₃ and LiCH₂CN, and by the reactions in Scheme 2, leading to *meso*-functionalized octaalkylporphyrinogens.⁶ Compounds **2** and **3** have been fully characterized including the X-ray analysis of **3**. The ¹H NMR of **3** revealed the presence of an equimolar mixture of the two possible isomers with two quartets and two doublets of equal intensity for the vinylidene groups and eight doublets for the β-protons to the pyrroles. This spectroscopic analysis has been confirmed with an X-ray structure revealing a statistical distribution of the Me and H groups around the vinylidene carbon, although not in the same ratio observed in solution. We should draw attention to the structural similarity of **3** with the 5,15-dioxoporphyrinogen.⁷

The structure of the anionic moiety of **3** is displayed in Fig. 1, with a selection of the structural parameters which support the proposed bonding scheme.† The presence of two *meso*-sp³ carbons gives rise to a saddle shape conformation of the porphyrinogen with nickel 0.011(3) Å above the N₄ plane. A relevant structural feature is the two short Ni–H contacts [Ni1...H15A and Ni1...H15A', 2.92 Å (prime denotes a symmetry operation $-x, y, -z + 1/2$)] with two *meso*-ethyl groups from the same face of the N₄ coordination plane.

Complex **3** contains a novel form of porphyrinogen, which may have considerable synthetic potential and may be available either from the demetalation or the transmetalation of **3**. We



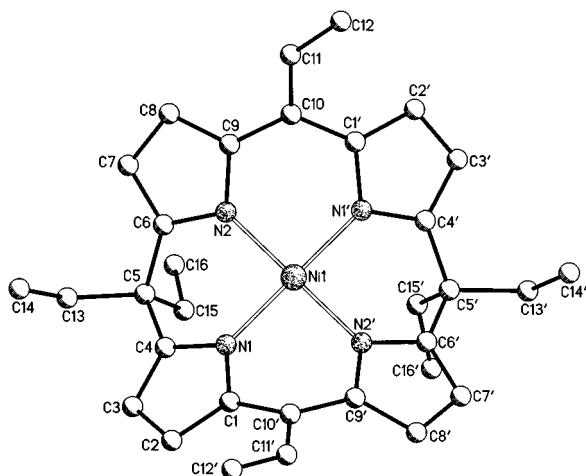


Fig. 1 A plot of the dianion of **3** [hydrogen atoms, Li(DME)₃⁺ cations and disorder have been omitted for clarity]. Selected bond distances (Å): Ni1–N_{av} 1.887(4) C10–C11 1.32(1). Prime indicates the following symmetry operation: $-x, y, \frac{1}{2}-z$.

found, however, a better access to the bisvinylidene porphyrinogen tetraanion bonded to Ni^{II} in **3** from the direct deprotonation of the *meso*-hexaethylporphodimethene dilithium derivative **4**⁴ (see Scheme 2).

In addition, such a reaction shed light on the deprotonation mechanism of the porphodimethene skeleton as a function of the metal and the reaction solvent. The addition of LiNMe₂ to **4**, regardless of the solvent (THF, DME or benzene), led to the formation of the bisdimethylamino porphyrinogen **5**, which upon heating underwent HNMe₂ elimination to give different porphyrinogen derivatives according to the solvent, namely to **6** in benzene, **7** in THF, and **8** in DME. Scheme 2 displays also the relationship between **6**, **7** and (preliminarily) **8**.⁵ Compounds in Scheme 2 have all been isolated and characterized. The X-ray structure is reported only for **7**. Those two structures, along with that of **3**, give the complete picture of the vinylidene porphyrinogen derivatives. The structure of the ion pair form of **7** is shown in Fig. 2 with some structural parameters which support the proposed bonding scheme.[‡] In the absence of a transition metal ion, the porphyrinogen skeleton does not display any well-defined conformation and **7** occurs either in the ion-separated or in the ion-pair form⁸ (Fig. 2). Lithium cations show different geometry: Li1 has a quasi-square planar

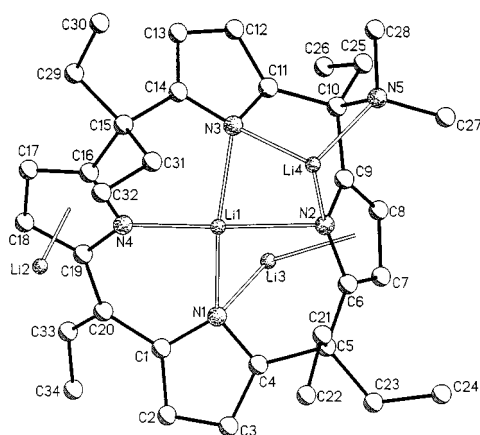


Fig. 2 A view of compound **7** (hydrogen atoms, DME and disorder have been omitted for clarity). Selected bond distances (Å): Li1–N1 2.050(6), Li1–N2 2.206(6), Li1–N3 2.136(6), Li1–N4 1.984(6), Li2–η⁵(Pyr) 1.904(6), Li3–η⁵(Pyr) 2.183(6), Li3–N1 2.110(7), Li4–N2 2.057(6), Li4–N3 2.070(6), Li4–N5 2.123(6), C30–C33 1.347(5), C10–N5 1.543(4). η⁵(Pyr) indicates the centroid.

arrangement [out-of-plane of 0.160(5) Å from the N₄ core], Li2 is η⁵-linked to one pyrrolyl moiety, Li3 links one nitrogen atom (N1) and is also η⁵-bonded to one pyrrole, while Li4 lies in between two pyrroles and is bonded to the nitrogen of the NMe₂ group. Each lithium cation (except Li1) competes its coordination sphere with DME.

The procedures reported here should be applicable to the synthesis of novel forms of porphyrinogen and functionalization of the *meso*-positions using the reactivity of the porphodimethene skeleton towards nucleophiles, in the case of both the transition metal and the lithium derivatives. Furthermore, the lithiated forms are of direct use for the synthesis of a variety of transition metal derivatives.

Notes and references

‡ *Crystal data for 3*: C₃₂H₃₆N₄Ni₂(C₁₂H₃₀LiO₆), *M* = 1089.96, monoclinic, space group *C2/c*, *a* = 12.269(3), *b* = 19.417(4), *c* = 26.192(5) Å, β = 103.49(3)°, *V* = 6067(2) Å³, *Z* = 4, *D_c* = 1.193 g cm⁻³, *F*(000) = 2360, λ (Mo–Kα) = 0.71070 Å, μ = 0.379 mm⁻¹; crystal dimensions 0.18 × 0.15 × 0.10. For 2120 observed reflections [*I* > 2σ(*I*)] and 351 parameters, the conventional *R* is 0.0689 (*wR2* = 0.2153 for 3664 independent reflections). For **7**: C₄₆H₇₃Li₄N₅O₆, *M* = 819.85, monoclinic, space group *P2₁/n*, *a* = 11.755(2), *b* = 20.644(4), *c* = 19.117(4) Å, β = 95.22(3)°, *V* = 4619.9(16) Å³, *Z* = 4, *D_c* = 1.179 g cm⁻³, *F*(000) = 1776, λ (Mo–Kα) = 0.71070 Å, μ = 0.076 mm⁻¹; crystal dimensions 0.17 × 0.15 × 0.13. For 4735 observed reflections [*I* > 2σ(*I*)] and 561 parameters, the conventional *R* is 0.0789 (*wR2* = 0.2481 for 7078 independent reflections). For both compounds the diffraction data were collected on a mar345 Imaging Plate at 143 K. The structures were solved with direct methods and refined using the full-matrix least-squares on *F*² with all non-H atoms anisotropically defined. CCDC 182/1416. See <http://www.rsc.org/suppdata/cc/1999/2227/> for crystallographic data in .cif format.

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