

## The Four-electron Oxidation of *meso*-Octaethylporphyrinogen *via* a Metal-mediated Dealkylation Process: Formation of [RuL(PhCN)<sub>2</sub>] [H<sub>2</sub>L = 5,15-dihydro-5,5,10,15,15,20-hexaethylporphyrin]

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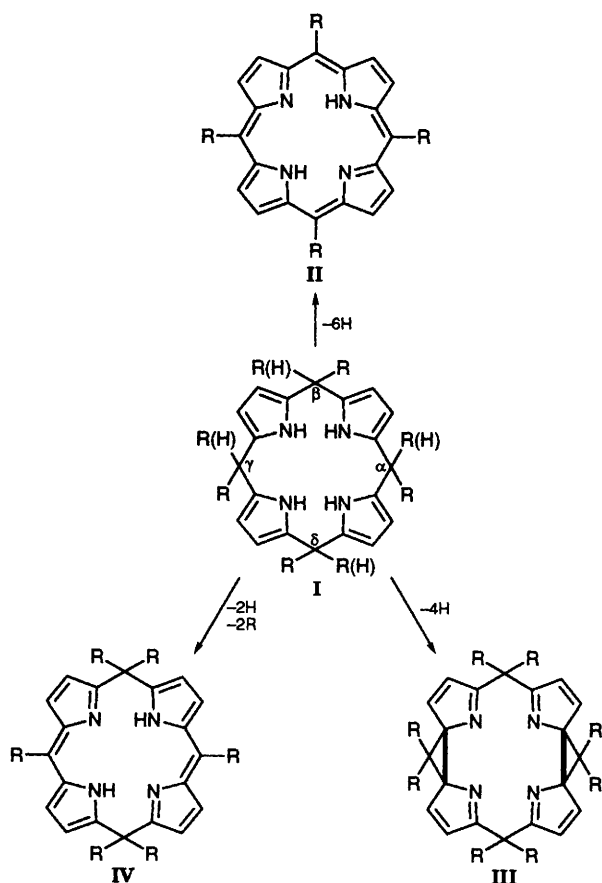
A four-electron oxidation of *meso*-octaethylporphyrinogen (H<sub>4</sub>L') involving the dealkylation of two *meso* carbons has been observed in the reaction between [Ru(Cl)<sub>2</sub>(PhCN)<sub>4</sub>] and [Li<sub>4</sub>L'(THF)<sub>4</sub>] leading to [RuL(PhCN)<sub>2</sub>] which contains two hemiporphyrin fragments joined by two sp<sup>3</sup> carbons, as shown by an X-ray analysis.

The absence of any hydrogen in the *meso*-position of *meso*-octaalkylporphyrinogen may provide information on the aromatization of porphyrinogen (I) to porphyrins<sup>1</sup> (Scheme 1) and simultaneously enable the generation of novel forms of the oxidized porphyrinogen. We have recently discovered that a four-electron oxidation of *meso*-octaalkylporphyrinogen mediated by transition metals<sup>2</sup> led to an unusual aromatization of the porphyrinogen skeleton with the loss of four hydrogens and the introduction of two cyclopropane units<sup>3</sup> (Scheme 1, III). An alternative four-electron oxidation of a *meso*-octaalkylporphyrinogen<sup>2c,4</sup> involving the unprecedented and unexpected loss of two alkyl groups from two *meso* positions and two hydrogen atoms (Scheme 1, IV) is reported here.

The reaction of [Li<sub>4</sub>L'(thf)<sub>4</sub>]<sup>2c</sup> [H<sub>4</sub>L' = *meso*-octaethylporphyrinogen] with [RuCl<sub>2</sub>(PhCN)<sub>4</sub>] [eqn. (1)] was carried out in dimethoxyethane, then the suspension was refluxed for 24 h. The resulting solution gave upon evaporation an oily residue which was recrystallized from toluene–heptane to give purple crystals of 3.†

The formation of 3 from 2 is an overall four-electron oxidation, involving the loss of two ethyl groups from two *meso*-positions. Several redox reactions occur when using different sources of ruthenium in the synthesis of porphyrin complexes,<sup>1,5</sup> though the mechanism is rather obscure and accounts in the present case for the low yield of 3.

We should note the previously unobserved C–C bond cleavage in the aromatization of the porphyrinogen skeleton.



Scheme 1

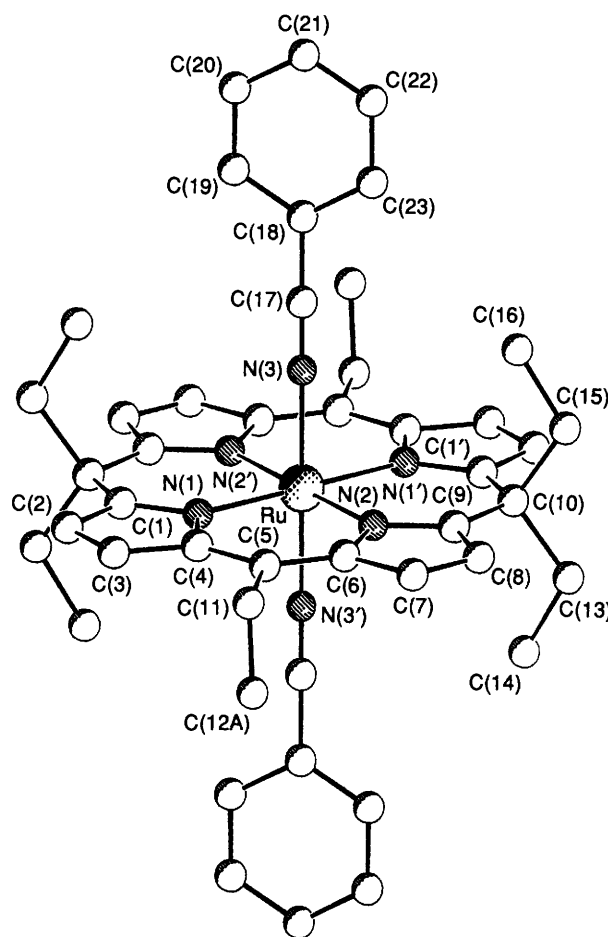
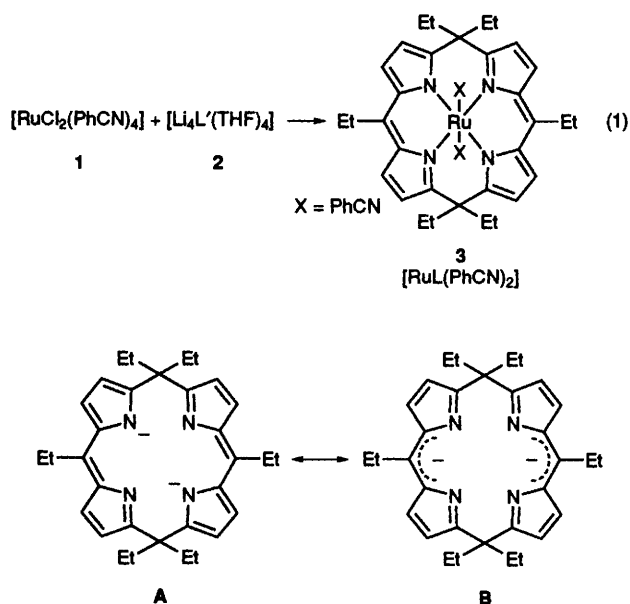


Fig. 1 SCHAKAL view of complex 3 (30% probability ellipsoids). Bond distances (Å): Ru–N(1) 2.074(3), Ru–N(2) 2.069(3), Ru–N(3) 1.996(3), N(1)–C(1) 1.345(5), N(1)–C(4) 1.405(5), N(2)–C(6) 1.410(5), N(2)–C(9) 1.335(5), N(3)–C(17) 1.143(5), C(1)–C(2) 1.413(8), C(1')–C(10) 1.477(7), C(2)–C(3) 1.333(8), C(3)–C(4) 1.432(7), C(4)–C(5) 1.377(7), C(5)–C(6) 1.383(7), C(6)–C(7) 1.419(7), C(7)–C(8) 1.324(9), C(8)–C(9) 1.430(7), C(9)–C(10) 1.501(7). Bond angles (°): N(2)–Ru–N(3') 88.9(1), N(2)–Ru–N(1') 89.3(1), N(2)–Ru–N(3) 91.1(1), N(1)–Ru–N(3') 89.1(1), N(1)–Ru–N(2') 89.3(1), N(1)–Ru–N(3) 90.9(1), N(1)–Ru–N(2) 90.7(1), Ru–N(3)–C(17) 178.0(3), N(3)–C(17)–C(18) 178.8(4). Prime denotes a transformation of 0.5 – x, 0.5 – y, – z



The proposed structure of **3** shows a bonding scheme in agreement with the presence of two halves of a porphyrin skeleton joined by an  $sp^3$  carbon. The X-ray analysis of **3**† gave significant insight on such a bonding scheme, providing, in addition, a support for another contributing form. The centrosymmetric structure of **3** is shown in Fig. 1 with a selection of structural parameters. The two hemiporphyrin fragments constitute the equatorial plane of the octahedron with the C(15)C(16) and C(13)C(14) ethyl groups pointing respectively above and below this plane. The *meso* carbons C(5) only show a slight deviation from the porphyrin-like skeleton [0.033(5) Å]. The structural parameters of the metal-coordination sphere do not deserve special comments, being very similar to those in a number of ruthenium porphyrin complexes.<sup>6</sup>

A careful analysis, however, of the bond distances within the porphyrin-like skeleton suggests two major contributing forms (A and B) for the dianion bonded to ruthenium(II), with a significant preference for the B form.

We wish to emphasize the relevance of this novel aromatization process of a *meso*-octaalkylporphyrinogen involving a metal-mediated dealkylation and the generation of a novel porphyrin-like ruthenium prototype in the context of the extremely varied nature of ruthenium porphyrin chemistry.<sup>1,3</sup>

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### Footnotes

† Satisfactory elemental analysis has been obtained. NMR for **3**: <sup>1</sup>H NMR (δ, 200 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature): 0.83 (t, 12 H), 1.47 (t,

6 H), 2.39 (q, 8 H), 3.19 (q, 4 H), 6.40 (m, 10 H), 6.94 (d, 4 H), 7.73 (d, 4 H). IR: ν (PhCN) (Nujol) 2211 cm<sup>-1</sup>.

‡ Crystal data: for **3**, C<sub>40</sub>H<sub>48</sub>N<sub>6</sub>Ru, *M* = 786.0, monoclinic, space group C2/c, *a* = 15.773(2), *b* = 19.019(2), *c* = 13.228(3) Å, β = 96.12(1), *V* = 3945.6(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.323 g cm<sup>-3</sup>, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 4.27 cm<sup>-1</sup>, crystal dimensions 0.21 × 0.23 × 0.37 mm. The structure was solved by the heavy-atom method and anisotropically refined for all non-hydrogen atoms. The C(12) methyl carbon was found to be statistically distributed over two positions (A and B) isotropically refined with site occupation factors of 0.7 and 0.3 respectively. The hydrogen atoms with the exception of those associated to the disordered C(11)C(12) ethylic chain, which were ignored, were located from a difference map and introduced in refinement as fixed contributors in the last stage of refinement (*U*<sub>iso</sub> = 0.10 Å<sup>2</sup>). For 2529 unique observed reflections [*I* > 2σ(*I*)] collected at room temperature (6 < 2θ < 56°) and corrected for absorption the final *R* value was 0.030 (unit weights). All calculations were carried out using SHELX-76 on an IBM AT personal computer equipped with an INMOS T800 transputer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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