A New Method for Regiospecific Deuteriation and Reduction of 5,10,15,20-Tetraphenylporphyrins: Nucleophilic Reaction of Borohydride Ion with 2-Nitro-5,10,15,20-tetraphenylporphyrins

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New methods for specific reduction and deuteriation of 5,10,15,20-tetraarylporphyrins are reported. Free-base and metalated 2-nitroporphyrins are converted into the corresponding nitrochlorins (2,3-dihydro-2-nitro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrins) by reaction with borohydride followed by aqueous workup. These nitrochlorins may be readily converted into the denitrated chlorin by treatment with tributyltin hydride or into the corresponding denitrated porphyrin by elimination of nitrous acid by heating or treatment with silica. Deuterium labeling studies show that the formation of nitrochlorin from nitroporphyrin involves attack by hydride at the β-pyrrolic carbon next to that bearing the nitro group followed by protonation of the resultant nitronate in aqueous workup. Specific deuteriation at the β-pyrrolic next to that previously occupied by a nitro group is readily achieved by borodeuteride ion reaction with a 2-nitroporphyrin (50 atom % deuterium incorporation) or with a 2-methoxy-3-nitroporphyrin (100 atom % deuterium incorporation).

The relationship between the various members of the porphyrin, chlorin, and bacteriochlorin macrocyclic family is principally one of oxidation level. The porphyrin macrocycle is fully unsaturated while the chlorin macrocycle contains one saturated C–C bond[1] and the bacteriochlorin and isobacteriochlorin macrocycles contain two saturated C–C bonds. The degree of saturation of the ring profoundly affects the spectral and redox properties of the macrocycle.[2-4] To extend our studies of tautomerism and aromaticity within this class of macrocycles,[5-9] we required a number of specifically reduced and substituted 5,10,15,20-tetraarylporphyrin derivatives.

Porphyrins are readily reduced to chlorins or bacteriochlorins in vitro by standard hydrogenation procedures;[10,11] however, mixtures of regioisomers are obtained and the method is prone to give over-reduced products. Smith and Simpson have reported that the photoreduction of several octa-substituted zinc(II) porphyrins to zinc(II) chlorins is ring specific depending on the substituents present.[12] In general, however, methods for the directed reduction of a porphyrin pyrrole ring have been lacking. Herein, we address this deficiency in the case of the 5,10,15,20-tetraarylporphyrins.

Borohydride ion is an effective nucleophile for conjugate addition to nitroene systems leading to reduction of the double bond.[13,14] As 2-nitroporphyrins show many similaries in their reactions to simpler nitroenes, we thought that a nitro group on a β-pyrrolic position of a porphyrin should direct the reduction of the porphyrin ring. Regioselective reduction of the pyrrolic β–β bond bearing the nitro group, by conjugate addition of hydride, in free-base and metalated 2-nitroporphyrin would afford the corresponding 2-nitro-2,3-dihydroporphyrins (2-nitrochlorins). Reductive denitration of 2,3-dihydro-2,2-dimethoxy-3-nitroporphyrins has been achieved using tributyltin hydride and 2,2′-azobis(isobutyronitrile) (AIBN),[15] and the successful application of this reaction seemed likely in the present case. A regiospecific route from 2-nitroporphyrin 1 to the corresponding chlorin 3 was envisaged (Scheme I). The realization of this procedure is reported herein. Use of deuteriated reagents and deliberate promotion of nitrous acid elimination from deuterium labeled 2-nitro-2,3-dihydroporphyrins intermediates also provides a new route for the regiospecific synthesis of deuteriated porphyrins and chlorins.

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[1] The IUPAC recommendations (Moss, G. P. *Pure Appl. Chem.* 1987, *59*, 779–832) propose that chlorins should be named as 2,3-dihydroporphyrins. This name implies that the inner hydrogens are on the nitrogen atoms at positions 21 and 22 in the free-base compounds. We (Crossley, M. J.; Harding, M. M.; Sternhell, S. *J. Org. Chem.* 1988, *53*, 1132–1137) and others (Schlabach, M.; Scherer, G.; Limbach, H.-H. *J. Am. Chem. Soc.* 1991, *113*, 3550–3558) have pointed out the actual structures of free-base chlorins are not consistent with this nomenclature as only one tautomer, that with the inner hydrogens on the other two nitrogens, can be directly detected in solution NMR studies. There is no difficulty in the 2,3-dihydroporphyrin name for a metalloporphyrin, as the issue of detectable tautomeric forms does not arise because there are no mobile inner hydrogens. Free-base chlorins, however, should be named either as a 7,8-dihydroporphyrin (just as bacteriochlorins are 7,8,17,18-tetrahydroporphyrins) or as 2,3-dihydro-22*H*,24*H*-porphyrins. In this paper and forthcoming papers, we prefer the later nomenclature as it maintains a link with the nomenclature of the starting porphyrins, rather than suggesting that it is the β-pyrrolic substituents that are moving positions rather than the inner hydrogens, and maintains consistency with the metallochlorin nomenclature.

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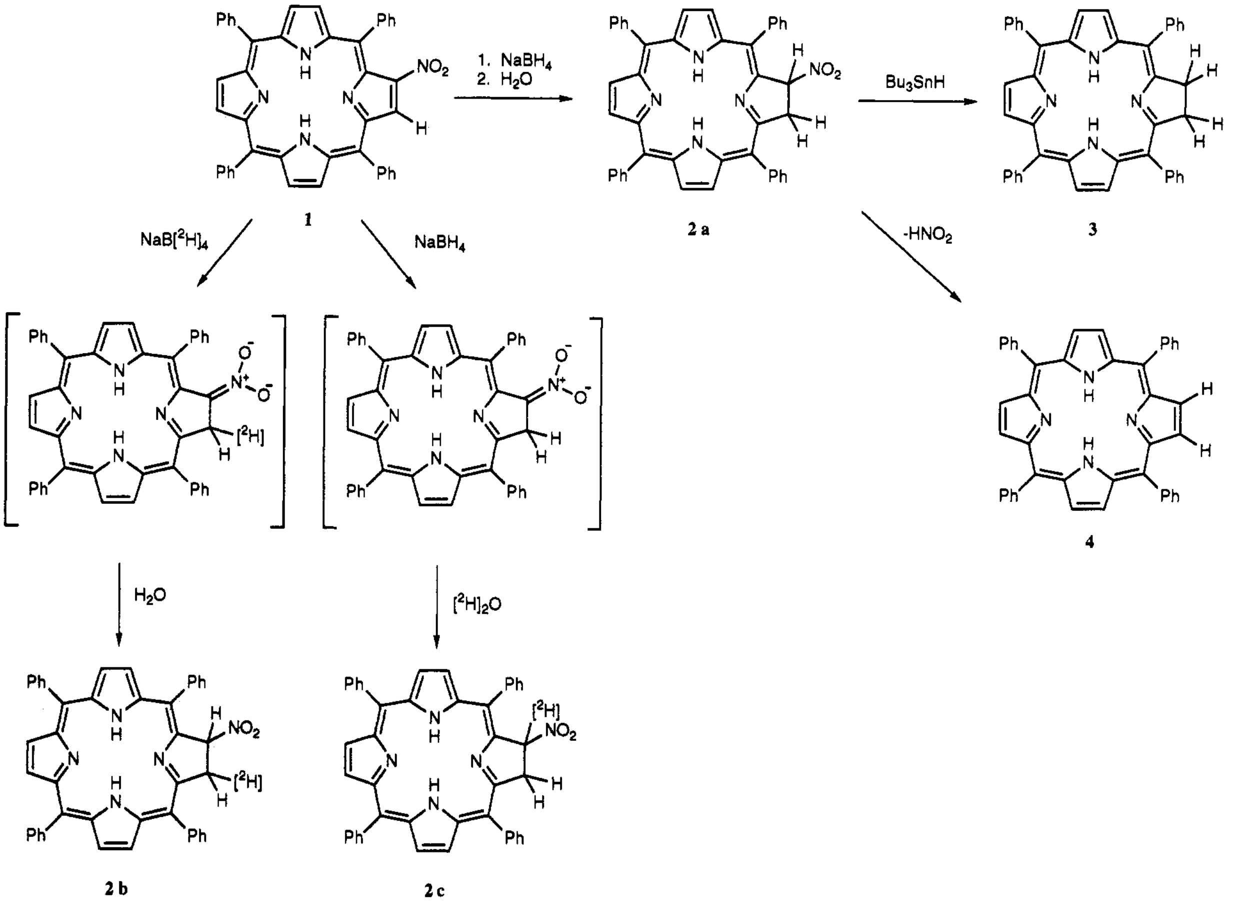
Scheme I



Results and Discussion

Treatment of a solution of 2-nitro-5,10,15,20-tetraphenylporphyrin (**1**) (3 mM) in dimethyl sulfoxide (Me_2SO) with sodium borohydride (2.4 equiv) for 15 min afforded the nitrochlorin, 2,3-dihydro-2-nitro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin (**2a**), in essentially quantitative yield after aqueous workup (Scheme I). A ^4J coupling (1 Hz) between the inner NH's and the protons at C-7, C-8, C-17, and C-18 confirms that the inner hydrogens reside on N-22 and N-24 as expected;[7,16,17] this tautomer has an 18-atom 18-π-electron aromatic delocalization pathway whereas the tautomer with the inner hydrogens on N-21 and N-23 has a less-stabilized 17-atom 18-π-electron aromatic delocalization pathway.[7]

The nitrochlorin **2a** proved unstable to warming and to chromatography as these processes caused the elimination of nitrous acid to afford the parent porphyrin **4**. The nitrochlorin **2a** was, therefore, reductively denitrated without further purification by a protocol involving sequential addition of AIBN (10 equiv), tributyltin hydride (51 equiv), and the nitrochlorin **2a** to a refluxing solution of benzene under nitrogen. This procedure afforded the parent chlorin, 2,3-dihydro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin[18] (**3**), in 81% yield with minimal formation of the byproduct **4**, formed by thermal elimination of nitrous acid.

The formation of the nitrochlorin **2a** from **1** could have involved initial hydride attack at either the carbon bearing the nitro group or at the adjacent β-pyrrolic position. The use of deuteriated reagents in NMR spectroscopy experiments clarified the mechanism of the reaction and suggested a new protocol whereby one or more deuteriums may be introduced regiospecifically to a β-pyrrolic ring of 5,10,15,20-tetraarylporphyrins and -chlorins. The NMR spectrum of the unlabeled nitrochlorin, 2,3-dihydro-2-nitro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin (**2a**), showed the C-2 and two C-3 hydrogens as a three-spin system. In d_6-Me_2SO solution, the C-2 hydrogen resonated at δ 7.42, consistent with it being in a geminal position to the 2-nitro group. It showed a 9.4-Hz coupling to hydrogen H_α (δ 4.94) at C-3, the two hydrogens being cis and in an essentially eclipsed relative orientation, and it showed a 1.4-Hz coupling to hydrogen H_β (δ 4.39). The two C-3 hydrogens showed a geminal coupling of 17.8 Hz. When the reaction was carried out using sodium borodeuteride and quenched with H_2O, one deuterium was introduced; it was evenly distributed ($\sim$50 atom %) at the two positions on C-3, and the 17.8 Hz geminal coupling seen in the ^1H NMR spectrum of unlabeled material was absent. The product was clearly **2b**. Quenching a reaction using $NaBH_4$ with $[^2H]_2O$ resulted in the regiospecific introduction of deuterium ($\sim$100 atom %) at C-2 (the resonance at δ 7.42 and the corresponding couplings to the vicinal hydrogens seen in unlabeled material were absent in the ^1H NMR spectrum of the reaction product). In this case the product was clearly **2c**. These data require a reaction mechanism (Scheme I) involving addition of hydride (or deuteride) to the porphyrin at the β-pyrrolic carbon adjacent to that bearing the nitro group thereby leading to an approximately planar nitronate which is quenched by protonation at C-2 from either face (with equal probability) of the

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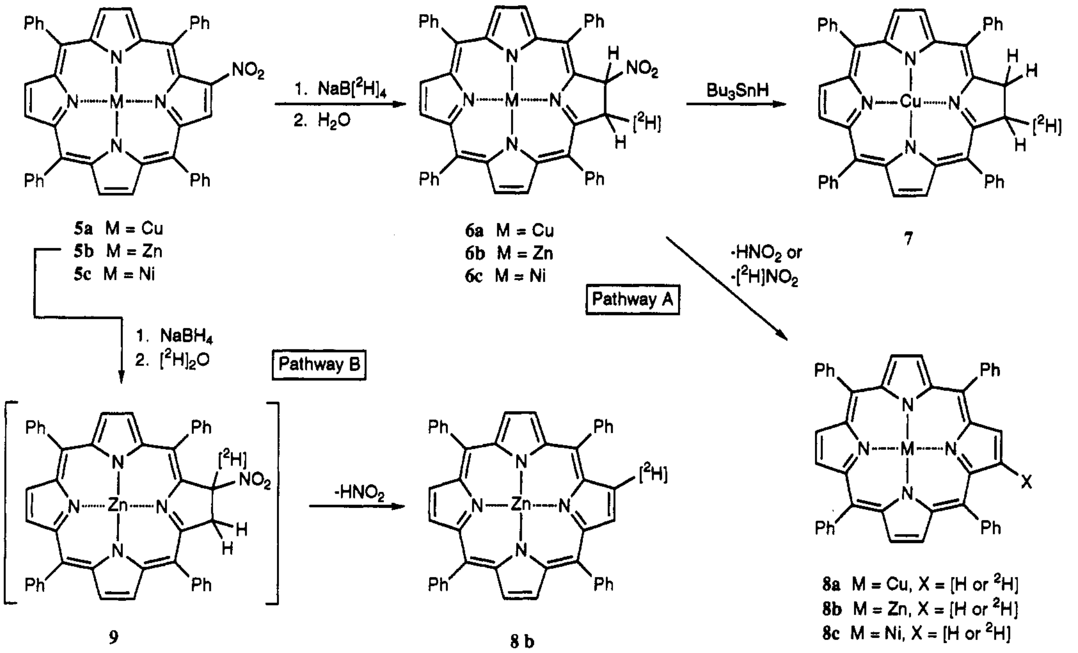
Scheme II



macrocycle. Appropriate use of unlabeled reagent or the deuteriated analogs of $NaBH_4$, H_2O, and Bu_3SnH would allow the parent chlorin, 2,3-dihydro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin (**3**), to be prepared as the $[2\text{-}^2H_1]$, $[2,2\text{-}^2H_2]$, $[2,3\text{-}^2H_2]$, or the $[2,2,3\text{-}^2H_3]$ derivative as desired.

The procedure was also amenable to the preparation of metallochlorins from the corresponding metallo-2-nitroporphyrins and once again allowed the regiospecific introduction of a deuterium atom into the reduced pyrrole ring of the chlorin (Scheme II). In this case, reactions of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II),[19,20] -zinc(II),[20,21] and -nickel(II) (**5a-c**) were investigated, the nickel porphyrin **5c** being obtained in 73% yield by nitration of (5,10,15,20-tetraphenylporphyrinato)nickel(II) using nitrogen dioxide.[20]

Thus, reaction of a solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (**5a**) in Me_2SO with sodium borodeuteride afforded (2,3-dihydro-2-nitro-5,10,15,20-tetraphenyl$[3\text{-}^2H_1]$porphyrinato)copper(II) (**6a**) in quantitative yield (Scheme II, pathway A). The blue-green nitrochlorin **6b** had a distinctive chlorin-like visible spectrum[3,18] and nitro stretch (ν_{max} 1550) in the infrared spectrum; however, no parent ion was able to be detected in the mass spectrum because of facile thermal elimination of nitrous acid. Subsequent reductive denitration with tributyltin hydride and AIBN gave (2,3-dihydro-5,10,15,20-tetraphenyl$[2\text{-}^2H_1]$porphyrinato)copper(II)[22] (**7**) in 76% yield with only a trace of the corresponding elimination product **8a**.

Deliberate promotion of nitrous acid elimination from deuterium labeled metallonitrochlorins provided access to regiospecifically deuterium labeled porphyrins. Both heat and chromatography of the nitrochlorin **6a** over silica promoted the elimination of nitrous acid and afforded (5,10,15,20-tetraphenyl$[2\text{-}^2H]$porphyrinato)copper(II) (**8a**) (67% yield overall from **5a**, 53 atom % deuterium). Similar treatment of (2-nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II) (**5b**) with borodeuteride followed by chromatography afforded (5,10,15,20-tetraphenyl$[2\text{-}^2H]$-porphyrinato)zinc(II) (**8b**) (51% yield, 47 atom % deuterium). Likewise, reaction of a suspension of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**5c**) with borodeuteride and subsequent chromatography gave (5,10,15,20-tetraphenyl$[2\text{-}^2H]$porphyrinato)nickel(II) (**8c**) (20% yield, 55 atom % deuterium) together with recovered starting nitroporphyrin **5c** (75%), the low conversion in this case being due to the low solubility of the starting porphyrin in the reaction mixture.

In these metalloporphyrin cases, the observation of approximately 50% deuterium incorporation is consistent with nonselective protonation of an intermediate nitronate ion to give an equimolar mixture of diastereomeric 2,3-dihydro-2-nitro-$[3\text{-}^2H_1]$porphyrins **6a-c**. Elimination of nitrous or deuterionitrous acid from the appropriate diastereomer will then give rise to the parent porphyrin **8a-c** with 50 atom % deuterium.

Use of a different combination of deuterium labeling in the reagents allowed regiospecific replacement of the nitro group of (2-nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II) (**5b**) by deuterium to give (5,10,15,20-tetraphenyl$[2\text{-}^2H]$porphyrinato)zinc(II) (**8b**) (>98 atom % deuterium) (Scheme II, pathway B). This was accomplished by performing the reaction with borohydride and quenching the reaction with D_2O; elimination of nitrous acid from the intermediate 2-deuterio-2-nitro-2,3-dihydroporphyrin **9**, facilitated by absorption onto silica, then gave the 2-deuterioporphyrin (**8b**).

While the reaction of 2-nitroporphyrin with borodeuteride (Scheme II, pathway A) provided a simple and convenient method for the partial (~50 atom %) incorporation of a deuterium atom into the β-pyrrolic site adjacent to that previously occupied by the nitro group,

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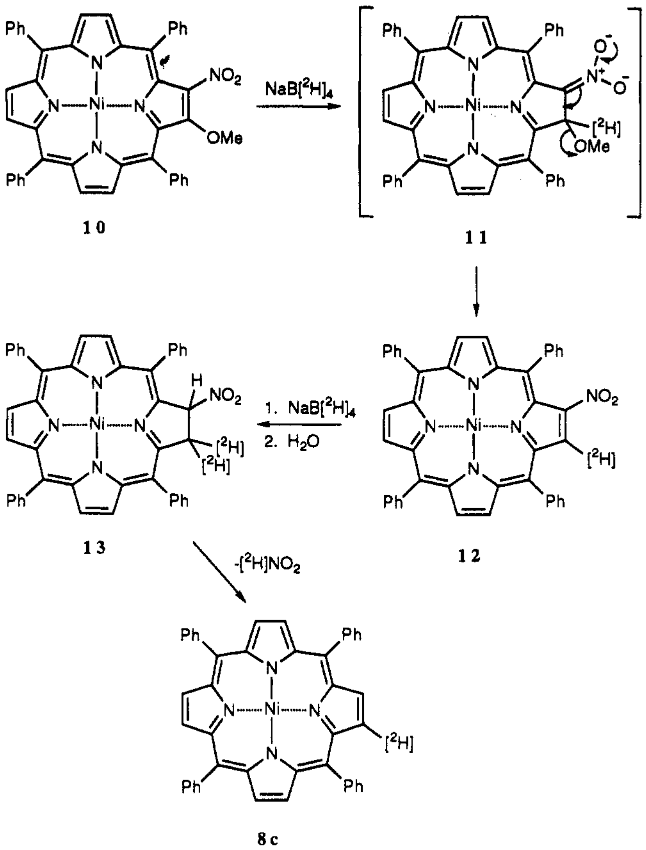
Scheme III



a method to fully deuteriate this site was required. We reasoned that this could be achieved if a leaving group other than hydrido was positioned at the site required to be deuteriated. This was accomplished by reaction of borodeuteride with 2-methoxy-3-nitroporphyrin **10** (Scheme III); the synthesis of **10** was achieved by treatment of **5c** with methoxide.[15]

The reaction of borodeuteride ion with (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**10**) was found to proceed with rapid substitution of a deuteron for the methoxyl to give the corresponding metallo-2-nitro-[3-^{2}H]porphyrin **12** that then underwent a slower second nucleophilic attack to give the metallo-2,3-dihydro-2-nitro-[2,2-$^{2}H_2$]porphyrin **13**. As was observed with the monodeuteriated nitrochlorins **6**, elimination of deuterionitrous acid then gave [2-^{2}H]porphyrin **8c**. Chromatography of the products of a reaction mixture quenched after 15 min by addition of water afforded nickel(II) [2-^{2}H]porphyrin **8c** (>98 atom % deuterium, 36%) and nickel(II) 2-nitro-[3-^{2}H]porphyrin **12** (>98 atom % deuterium, 55%). Compound **12** has proved very valuable in mechanistic studies of other reactions of 2-nitroporphyrins; these studies will be reported separately.

The reactivity of the borohydride nucleophile toward 2-nitroporphyrins parallels that of alkoxide nucleophiles[15] which also give conjugate addition. In contrast, the "soft" α-benzaldoximate nucleophile gives ipso substitution with nitroporphyrins,[23] as do reactions with thiolate nucleophiles.[24] While both the copper(II) and nickel(II) 2-nitroporphyrins **5a** and **5c** show all of these reactions, the relatively electron-rich zinc(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**5b**) only reacts with borohydride.

The facility of this conjugate addition on the periphery of an aromatic molecule is due to the nature of porphyrin aromaticity. The β–β bond bearing the nitro substituent can behave as a nitroene system without disrupting the aromaticity of the macrocycle. In the case of the free base **1**, the tautomer 2-nitro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin, in which there is an isolated nitroene system, is heavily favored in solution at tautomeric equilibrium.

Conclusion

The two step reduction of the easily accessible 2-nitro-5,10,15,20-tetraphenylporphyrin[20] to the corresponding chlorin via borohydride addition and reductive radical denitration provides a facile, high-yielding procedure which is both regiospecific and amenable to use in the presence of other reducible side chains, e.g. vinyl groups. Furthermore, this procedure is clearly adaptable to the preparation of chlorins with one to four deuterium (or tritium) atoms in the chlorin ring by a combination of choice of starting material (nitroporphyrin or 2-methoxy-3-nitroporphyrin) and/or the use of a D_2O quench and/or tributyltin deuteride at the appropriate stage in the sequence.

The regioselective β-deuteriation of a porphyrin ring at a site vicinal to that previously occupied by a nitro group is readily achieved with 50% deuterium incorporation by the reaction of borodeuteride ion with a 2-nitroporphyrin, an H_2O quench, followed by elimination of nitrous acid or deuterionitrous acid. Regioselective replacement of the nitro group by deuterium is readily achieved with 100% deuterium incorporation by the reaction of borohydride ion with a 2-nitroporphyrin and a D_2O quench, followed by elimination of nitrous acid. This deuteriation methodology complements the existing procedure for the deuteriation of the porphyrin ring involving *ipso* replacement of a nitro group with deuterium via the intermediacy of an (arylthio)porphyrin.[25]

This work is a further illustration of that 2-nitroporphyrins are versatile starting materials for introduction of other functionality to the porphyrin periphery.[15,23,25–29]

Experimental Section

Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 221 spectrometer or a Perkin-Elmer 710B spectrometer. Electronic spectra were recorded on a Hitachi 150-20 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WM 400 spectrometer (400 MHz), with tetramethylsilane as internal standard. Mass spectra were recorded at 70 eV on an A.E.I. MS 902 spectrometer. Deuterium content of deuteriated compounds was determined from their mass spectrum and checked by computer simulation of the spectrum. Microanalyses were performed by the Australian Mineral Development Laboratory, Melbourne, Australia.

Column chromatography was routinely carried out using the flash chromatography technique on Merck silica gel type 9385

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(230-400 mesh). All commercial solvents were redistilled prior to use. Light petroleum refers to the petroleum fraction of bp 60–80 °C. Where solvent mixtures are used, the proportions are given by volume.

2,3-Dihydro-2-nitro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin (2a). A solution of 2-nitro-5,10,15,20-tetraphenylporphyrin[20,21,28] (1) (49 mg, 0.074 mmol) in Me_2SO (25 mL) was stirred with sodium borohydride (7 mg, 0.18 mmol) for 15 min. The mixture was then diluted with dichloromethane (50 mL), washed with water (5 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by rotary evaporation at room temperature to afford chlorin **2a** as a brown solid in quantitative yield: mp >350 °C (decomposes with elimination of nitrous acid >50 °C); IR ν_{max} (Nujol) 3350 br (NH), 1545 cm^{-1} (unconjugated NO_2); UV and vis λ_{max} ($CHCl_3$) 367, 407sh, 418, 484sh, 517, 546, 591, 644 nm (log ϵ 4.55, 5.19, 5.32, 3.64, 4.17, 4.14, 3.84, 4.35); ^{1}H NMR δ (CD_2Cl_2) −1.84 (1 H, br s, interior NH), −1.77 (1 H, br s, interior NH), 4.55 (1 H, dd, $J_{2\alpha,3\beta}$ = 2.1 Hz, $J_{3\alpha,3\beta}$ = 18.4 Hz, H-3β), 4.76 (1 H, dd, $J_{2\alpha,3\alpha}$ = 9.6 Hz, $J_{3\alpha,3\beta}$ = 18.4 Hz, H-3α), 7.24 (1 H, dd, $J_{2\alpha,3\beta}$ = 2.1 Hz, $J_{2\alpha,3\alpha}$ = 9.6 Hz, H-2α), 7.61-7.83 (14 H, m, H_m and H_p of 4 phenyls and H_o of 1 phenyl), 8.01–8.11 (4 H, m, H_o of 2 phenyls), 8.13–8.24 (2 H, m, H_o of 1 phenyl), 8.30 and 8.68 (2 H, d of ABq, $^4J_{NH-H}$ = 1.0 Hz, $J_{7,8}$ = 4.8 Hz, H-7,8), 8.38 and 8.72 (2 H, d of ABq, $^4J_{NH-H}$ = 1.0 Hz, $J_{17,18}$ = 4.7 Hz, H-17,18), 8.48 and 8.51 (2 H, ABq, J = 4.8 Hz, H-12,13); MS *m/z* 614 (M – HNO_2, 100%). Attempts to prepare a sample for combustion analysis by an additional chromatography step or by recrystallization resulted in contamination of the product with 5,10,15,20-tetraphenylporphyrin (4) from a facile elimination of nitrous acid.

2,3-Dihydro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin- (3). To refluxing dry benzene (25 mL) under nitrogen were sequentially added AIBN (130 mg, 0.79 mmol), tributyltin hydride (1 mL), and a solution of 2,3-dihydro-2-nitro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin (**2a**), prepared by the method described above from 2-nitro-5,10,15,20-tetraphenylporphyrin (1) (49 mg, 0.074 mmol) in dry benzene (8 mL). The mixture was refluxed under nitrogen for 1.5 h and allowed to cool, and the solvent was removed by rotary evaporation. The residue was triturated with light petroleum (4 × 100 mL), and the soluble fractions were filtered through a silica column (6 cm diameter, 100 g) under vacuum. The process was repeated using successively more polar mixtures of dichloromethane/light petroleum (1:9, 100 mL), (1:4, 100 mL), (3:7, 100 mL) and (2:3, 250 mL). The first and major brown band to be eluted from the column was collected and evaporated to dryness to yield 2,3-dihyro-5,10,15,20-tetraphenyl-22*H*,24*H*-porphyrin (3) (37 mg, 81% from the nitroporphyrin **2a**): mp >350 °C; IR ν_{max} (nujol) 3300 br (NH), 1560 s cm^{-1}; UV and vis λ_{max} ($CHCl_3$) 372, 407sh, 420, 484, 520, 547, 598, 652 nm (log ϵ 4.49, 5.10, 5.29, 3.60, 4.14, 3.98, 3.72, 4.46) [lit.[18] λ_{max} (benzene) 419, 517, 542, 598, 652 nm (log ϵ 5.28, 4.20, 4.08, 3.79, 4.62)]; ^{1}H NMR δ ($CDCl_3$) −1.44 (2 H, br s, NH), 4.15 (4 H, s, 2 × CH_2), 7.64–7.71 (12 H, m, H_m and H_p), 7.84–7.90 (4 H, m, H_o at C-5,20), 8.08–8.13 (4 H, m, H_o at C-10,15), 8.17 and 8.56 (4 H, br ABq, J = 5 Hz, H-7,8,17,18), 8.41 (2 H, s, H-12,13); MS *m/z* 618 (15), 617 (52), 616 (M^+, 100%), 615 (30), 614 (M – 2H, 38).

(2,3-Dihydro-2-nitro-5,10,15,20-tetraphenyl[3-$^2H_1$]porphyrinato)copper(II) (6a) and (5,10,15,20-tetraphenyl-[2-^{2}H]porphyrinato)copper(II) (8a). A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II)[19,20] (**5a**) (97 mg, 0.13 mmol) in dry, distilled Me_2SO (50 mL) was stirred under nitrogen with sodium borodeuteride (50 mg, 1.2 mmol) for 20 min. The mixture was diluted with dichloromethane (100 mL), washed with water (6 × 200 mL), dried over anhydrous Na_2SO_4, and filtered, and the solvent was removed by rotary evaporation at room temperature to afford (2,3-dihydro-2-nitro-5,10,15,20-tetraphenyl[3-$^2H_1$]porphyrinato)copper(II) (**6a**) as a blue-green solid in quantitative yield: mp >350 °C (decomposes >50 °C); IR ν_{max} (Nujol) 1600, 1550 (NO_2), 1340 cm^{-1} (NO_2); UV and vis λ_{max} ($CHCl_3$) 414, 474sh, 508, 540, 574, 608 nm (log ϵ 5.42, 3.46, 3.64, 3.83, 3.89, 4.37); MS *m/z* 679 (25%), 678 (56), 677 (75), 676 (M-HNO_2, 100), 675 (M – [^{2}H]NO_2, 63).

Chromatography of crude **6a** on a silica column (4 cm diameter, 200 g) eluted with dichloromethane/light petroleum (1:1) afforded a major red band of (5,10,15,20-tetraphenyl[2-^{2}H]porphyrinato)copper(II) (**8a**) (53 atom % deuterium, 61 mg, 67%), MS *m/z* 680 (10%), 679 (25), 678 (57), 677 (75), 676 ([^{2}H]M^+, 100), 675 ([^{1}H]-M^+, 63). This product cochromatographed with and had the same electronic spectrum as the corresponding unlabeled (5,10,15,20-tetraphenylporphyrinato)copper(II).[30]

(2,3-Dihydro-5,10,15,20-tetraphenyl-[2-$^2H_1$]porphyrinato)-copper(II) (7). A solution of (2,3-dihydro-2-nitro-5,10,15,20-tetraphenyl[3-$^2H_1$]porphyrinato)copper(II) (**6a**) (79 mg, 0.11 mmol), AIBN (40 mg, 0.24 mmol), and tributyltin hydride (1.5 mL) in dry benzene (50 mL) was heated at reflux under nitrogen for 2 h. On cooling, the solvent was removed by rotary evaporation. The residue was triturated with light petroleum (2 × 50 mL) and filtered. The residue was triturated with dichloromethane/light petroleum (1:1, 2 × 50 mL) and filtered. The filtrate was chromatographed on a silica column (4 cm diameter, 250 g) eluted with dichloromethane/light petroleum (1:1) and the front running, major, blue-green band was collected, evaporated to dryness, and combined with the undissolved residue to yield (2,3-dihydro-5,10,15,20-tetraphenyl[2-$^2H_1$]porphyrinato)-copper(II) (7) (56 mg, 76%): mp >350 °C; IR ν_{max} (Nujol) 1560, 1045, 990 cm^{-1}; UV and vis λ_{max} ($CHCl_3$) 395sh, 416, 510, 542, 595, 618 nm (log ϵ 4.63, 5.38, 3.61, 3.84, 3.98, 4.30); MS *m/z* 681 (19%), 680 (44), 679 (58), 678 (M^+, 100), 677 (77), 676 (M – 2H, 96), 675 (M – ^{2}H, 58). The visible spectrum of this product was consistent with the visible spectra data of the corresponding unlabeled material and the two compounds cochromatographed.[22]

(5,10,15,20-Tetraphenyl[2-^{2}H]porphyrinato)zinc(II) (8b). Method A: Introduction of Deuterium Label at the β-Pyrrolic Position Adjacent to That Originally Occupied by the Nitro Group. A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II)[20,21] (**5b**) (83 mg, 0.11 mmol) in dry, distilled Me_2SO (40 mL) was stirred with sodium borodeuteride (98 atom % deuterium, 40 mg, 0.95 mmol) for 4 h. The mixture was then diluted with dichloromethane (100 mL), washed with water (6 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude nitrochlorin was chromatographed on a silica column (4 cm diameter, 200 g) eluted with dichloromethane/light petroleum (1:1) to yield (5,10,15,20-tetraphenyl[2-^{2}H]porphyrinato)zinc(II) (**8b**) (51 atom % deuterium, 35 mg, 47%): ^{1}H NMR δ ($CDCl_3$) 7.72–7.81 (12 H, m, *m* and *p*-Ph), 8.20–8.25 (8 H, m, *o*-Ph), 8.95 (7.5 H, s, β-pyrrolic H); MS *m/z* 682 (21%), 681 (38), 680 (48), 679 (66), 678 (67), 677 ([^{2}H]M^+, 100), 676 ([^{1}H]M^+, 64), 675 (30). This compound cochromatographed with and had a UV and vis spectrum essentially identical to that of an authentic sample of corresponding unlabeled compound.[30,31]

Method B: Introduction of Deuterium Label at the β-Pyrrolic Position Previously Occupied by the Nitro Group. To a solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II)[20,21] (**5b**) (100 mg, 0.14 mmol) in dry, distilled Me_2SO (25 mL) was added D_2O (100.0 atom % D, 0.25 mL) followed by sodium borohydride (100 mg, 2.4 mmol) and the mixture was stirred for 1 h. The mixture was then diluted with further D_2O (100.0 atom % deuterium, 2.25 mL) and the blue-green mixture was well stirred for 30 min. Dichloromethane (80 mL) was added and the organic layer was washed with water (6 × 50 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude nitrochlorin **9** was taken up in chloroform (20 mL) and adsorbed onto silica (Merck silica gel 60 HR, type 7744, 10 g), stirred at 50 °C for 30 min, during which time the color became purple-red, and then the solvent was removed on a rotary evaporator at 50 °C. The silica was added to the top of a short column (8 cm diameter × 8 cm length) of the same silica type and the whole was eluted with dichloromethane/light petroleum (1:1). Workup of the first (crimson-pink) band yielded (5,10,15,20-tetraphenyl[2-^{2}H]porphyrinato)zinc(II) (**8b**) as a crimson solid (>98 atom % deuterium, 39 mg, 42%), mp >350 °C; ^{1}H NMR δ ($CDCl_3$) 7.72–7.81 (12 H, m, *m* and *p*-Ph), 8.20–8.25 (8 H, m, *o*-Ph), 8.95 (7.0 H, s, β-pyrrolic H); MS *m/z* 683 (12%), 682 (35), 681 (60), 680 (55), 679 (76), 678 (70), 677 (M^+, 100). This

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compound also cochromatographed with the corresponding unlabelled (5,10,15,20-tetraphenylporphyrinato)zinc(II).[30,31]

(2-Nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (5c). To a stirred solution/suspension of (5,10,15,20-tetraphenylporphyrinato)nickel(II)[32] (500 mg, 0.75 mmol) in chloroform (1 L) was added a solution of nitrogen dioxide in light petroleum (0.5% (w/v), 15 mL) over a period of 6 h. The mixture was then evaporated to dryness. The residue was chromatographed over a silica column (10 cm diameter, 600 g) eluted with chloroform/light petroleum (1:1) to yield a red, front-running band of unreacted (5,10,15,20-tetraphenylporphyrinato)nickel(II) (43 mg, 9%) and a major, red-green band of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**5c**) (391 mg, 73%), which was recrystallized from chloroform/hexane as purple microcrystals: mp >350 °C; IR ν_{max} (Nujol) 1525 (NO_2), 1345 cm^{-1} (NO_2); UV λ_{max} ($CHCl_3$) 383, 431, 541, 585 nm (log ϵ 4.51, 5.16, 4.08, 3.98); ^1H NMR δ ($CDCl_3$) 7.56–7.77 (12 H, m, *m*- and *p*-Ph), 7.93–8.02 (8 H, m, *o*-Ph), 8.63 and 8.66 (2 H, ABq, J_{AB} 5 Hz, β-pyrrolic H), 8.64 and 8.72 (2 H, ABq, J_{AB} 5 Hz, β-pyrrolic H), 8.67 and 8.71 (2 H, ABq, J_{AB} 5 Hz, β-pyrrolic H), 8.99 (1 H, s, C(3)H); MS *m/z* 718 (10%), 717 (18), 716 (16), 715 (M^+, 31), 689 (19), 688 (32), 687 (50), 686 (55), 685 (M − NO, 100), 684 (18), 683 (28). Anal. Calcd for $C_{44}H_{27}N_5NiO_2$: C, 73.8; H, 3.8; N, 9.8. Found: C, 73.9; H, 3.6; N, 9.7.

(5,10,15,20-Tetraphenyl[2-^{2}H]porphyrinato)nickel(II) (8c). A slurry of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**5c**) (110 mg, 0.154 mmol) in dry, distilled Me_2SO (50 mL) was stirred with sodium borodeuteride (98 atom % deuterium, 55 mg, 1.31 mmol) under nitrogen for 5 h. The mixture was diluted with dichloromethane (200 mL), washed with water (6 × 200 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude nitrochlorin was chromatographed on a silica column (4 cm diameter, 300 g) eluted with dichloromethane/light petroleum (7:3) to yield a front running red band of (5,10,15,20-tetraphenyl[2-^{2}H]porphyrinato)nickel(II) (**8c**) (55 atom % deuterium, 20 mg, 20%), ^1H NMR δ ($CDCl_3$) 7.64–7.73 (12 H, m, *m*- and *p*-Ph), 7.99–8.04 (8 H, m, *o*-Ph), 8.75 (7.5 H, s, β-pyrrolic H); *m/z* 675 (10%), 674 (30), 673 (60), 672 (72), 671 ([^{2}H]M^+, 100), 670 ([^{1}H]M^+, 58). The compound cochromatographed with and had UV and vis essentially identical with that of the corresponding unlabeled compound, (5,10,15,20-tetraphenylporphyrinato)nickel(II).[30,32] A more polar red-green band afforded starting nitroporphyrin **5c** (82 mg, 75%), identical in all respects to authentic material.

(2-Methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (10). To a solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**5c**) (99 mg, 0.14 mmol) in DMF (20 mL) was added solid sodium methoxide (31 mg, 0.57 mmol), and the mixture was stirred under nitrogen for 16 h. The mixture was then diluted with dichloromethane (100 mL), washed with water (6 × 200 mL), dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The residue was chromatographed over silica. The second, red band gave (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **10** (16 mg, 16%) which recrystallized from dichloromethane/hexane as fine red microcrystals: mp 301–303 °C; IR ν_{max} (Nujol) 1570 cm^{-1} (NO_2); UV and vis λ_{max} ($CHCl_3$) 380sh, 425, 540, 578sh nm (log ϵ 4.30, 5.17, 4.15, 3.81); ^1H NMR δ ($CDCl_3$) 3.74 (3 H, s, OCH_3), 7.54–7.74 (12 H, m, *m*- and *p*-Ph), 7.83–7.88 (2 H, m, H_o at 20-Ph), 7.90–8.01 (6 H, m, H_o at 5-, 10- and 15-Ph), 8.54 and 8.66 (2 H, ABq, J_{AB} = 5 H, β-H), 8.62 (2 H, s, 12- and 13-H), 8.65 and 8.71 (2 H, ABq, J_{AB} = 5 Hz, β-H)); MS *m/z* 749 (13), 748 (26), 747 (54), 746 (55), 745 (M^+, 100), 717 (17), 716 (18), 715 (29), 703 (13), 702 (26), 701 (28), 700 (44), 699 (17), 698 (13), 697 (12), 688 (13), 687 (13), 686 (20), 685 (18), 684 (13), 683 (13), 668 (16). Anal. Calcd for $C_{45}H_{29}N_5NiO_3$: C, 72.4; H, 3.9; N, 9.4. Found: C, 72.6; H, 3.9; N, 9.4.

(5,10,15,20-Tetraphenyl[2-^{2}H]porphyrinato)nickel(II) (8c) and (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato)nickel(II) (12). A suspension of (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**10**) (40 mg, 0.054 mmol) in dry, distilled Me_2SO (40 mL) was stirred with sodium borodeuteride (98% deuterium content, 20 mg, 0.48 mmol) for 15 min. The mixture was then diluted with dichloromethane (50 mL), washed with water (6 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was chromatographed on a silica column (4 cm diameter, 200 g) eluted with dichloromethane/light petroleum (1:1). The front running, blue band gradually turned red on the column and was collected and evaporated to dryness to yield (5,10,15,20-tetraphenyl[2-^{2}H]porphyrinato)nickel(II) (**8c**) (<98 atom % deuterium, 13 mg, 36%): mp >350 °C; IR ν_{max} (Nujol) 1590, 1170, 1065, 995 cm^{-1}; UV and vis λ_{max} ($CHCl_3$) 416, 490s, 529, 614 nm (log ϵ 5.34, 3.51, 4.19, 2.69); ^1H NMR δ ($CDCl_3$) 7.64–7.73 (12 H, m, *m*- and *p*-Ph), 7.99-8.04 (8 H, m, *o*-Ph), 8.75 (7.0 H, s, β-pyrrolic H); MS *m/z* 675 (17%), 674 (28), 673 (58), 672 (60), 671 (M^+, 100).

The more polar, reddish-green band was collected to yield on evaporation (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato)nickel(II) (**12**) (>98 atom % deuterium, 21 mg, 54%), mp >350 °C; ^1H NMR δ ($CDCl_3$) 7.56–7.77 (12 H, m, *m*- and *p*-Ph), 7.93–8.02 (8 H, m, *o*-Ph), 8.64 and 8.71 (2 H, ABq, *J* 5 Hz, β-pyrrolic H), 8.65 (2 H, ABq, spacing 5 Hz, β-pyrrolic H), 8.67 and 8.72 (2 H, ABq, *J* 5 Hz, β-pyrrolic H); MS *m/z* 720 (17%), 719 (30), 718 (55), 717 (58), 716 (M^+, 100), 715 (18), 689 (20), 688 (36), 687 (58), 686 (72), 685 (79), 684 (36), 683 (48), 672 (14), 671 (18), 670 (24), 669 (18), 668 (11), 667 (12).

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