Solvent-dependent ambident nucleophilicity of phenoxide ion towards nitroporphyrins: synthesis of 2-hydroxyaryl- and 2-aryloxy-5,10,15,20-tetraphenylporphyrins by displacement of a nitro group

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The reaction of phenoxide ion with the copper(II), nickel(II) and free-base 2-nitro-5,10,15,20-tetraphenylporphyrins, 1–3 respectively, has been investigated as a means of introducing inwards-directed functionality to the periphery of pre-existing porphyrin systems. It has been found that phenoxide ion shows highly selective solvent-dependent ambident nucleophilicity towards the nitroporphyrin system. Porphyrins 1–3 react with phenoxide ion in refluxing phenol to afford the corresponding 2-(*o*-hydroxyphenyl)- and 2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrins in good yields; in each case the *ortho* isomer is the major product and none of the *meta* isomer is detected. The scope of the reaction has been extended by the use of the substituted phenols which are blocked from reaction *para* to the hydroxy (*p*-cresol and 2,4-dimethylphenol) or blocked from reaction in the *ortho*-positions (2,6-dimethylphenol). In this way the copper(II) 2-(2-hydroxy-5-methylphenyl)porphyrin 14 (86%), 2-(2-hydroxy-5-methylphenyl)-porphyrin 15 (65%), copper(II) 2-(2-hydroxy-3,5-dimethylphenyl)porphyrin 16 (77%), 2-(2-hydroxy-3,5-dimethylphenyl)porphyrin 17 (69%) and 2-(4-hydroxy-3,5-dimethylphenyl)porphyrin 19 (63%) have all been obtained in good yields by reaction of the appropriate 2-nitroporphyrin 1 or 3 with the requisite substituted phenolate in the corresponding phenol. Reaction of the metalloporphyrins 1 and 2 with phenoxide ion in refluxing $HCONMe_2$ in contrast gives the corresponding 2-phenoxy-metalloporphyrins 10 and 11 in good yield. The results of mechanistic studies using the deuteriated compound, nickel(II) 2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]porphyrin, 37, suggest that both sets of products (from phenoxide as a *C*-nucleophile and as an *O*-nucleophile) can arise from *ipso*-substitution of the nitro group.

In the course of work on synthetic porphyrin-based model systems for cytochrome P450 and other haemoproteins, we required a means of introducing inwards-directed functionality to the periphery of pre-existing 5,10,15,20-tetraarylporphyrin systems. Substituents (ligands or substrates L) subsequently attached to the new functionality would thereby be directed towards the porphyrin centre (metal-ion binding site M) where the proximity of the attached groups was required (Fig. 1).

Collman *et al.* have shown that ligands attached by a short chain to a *meso o*-aminophenyl substituent complex effectively with an appropriate central metal ion in metalloporphyrin chemical models for haemoproteins,[1] but the possibility of functionalising a *meso*-aryl ring regioselectively in a pre-existing porphyrin was not attractive. Accordingly, our attention focused on the introduction of a substituent at a β-pyrrolic position. Use of a flexible substituent would not impose the required inwards orientation of an attached substrate or ligand. As the initial bond with a β-pyrrolic carbon is directed away from the porphyrin centre, the introduced substituent needs to have a rigid framework of bonds that loops back towards the porphyrin centre.

In order to reduce the degrees of freedom of the bonds linking the functional group to the porphyrin, we sought to append an *ortho*-substituted ring to the β-pyrrolic position on the porphyrin periphery. Buttressing of this substituent by a nearby *meso*-aryl group and biphenyl-like interactions with the porphyrin ring were both expected to orient such a substituted ring in an orthogonal plane to the porphyrin. Further elaboration of the ring substituent by attachment of a ligand or substrate would provide a means to direct such groups towards the metal site (M).

Nitroporphyrins have proved to be versatile starting materials for the synthesis of porphyrins with other functionalities.[2–14] In this paper we report in full our studies of the reaction of

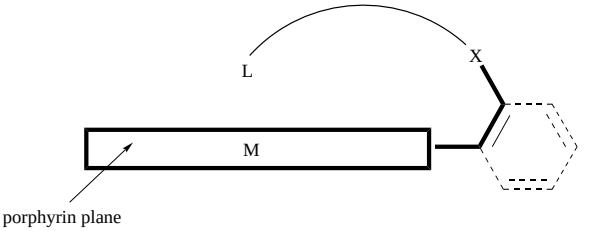


Fig. 1 Design for covalent attachment of an inward-directed ligand L to the porphyrin periphery

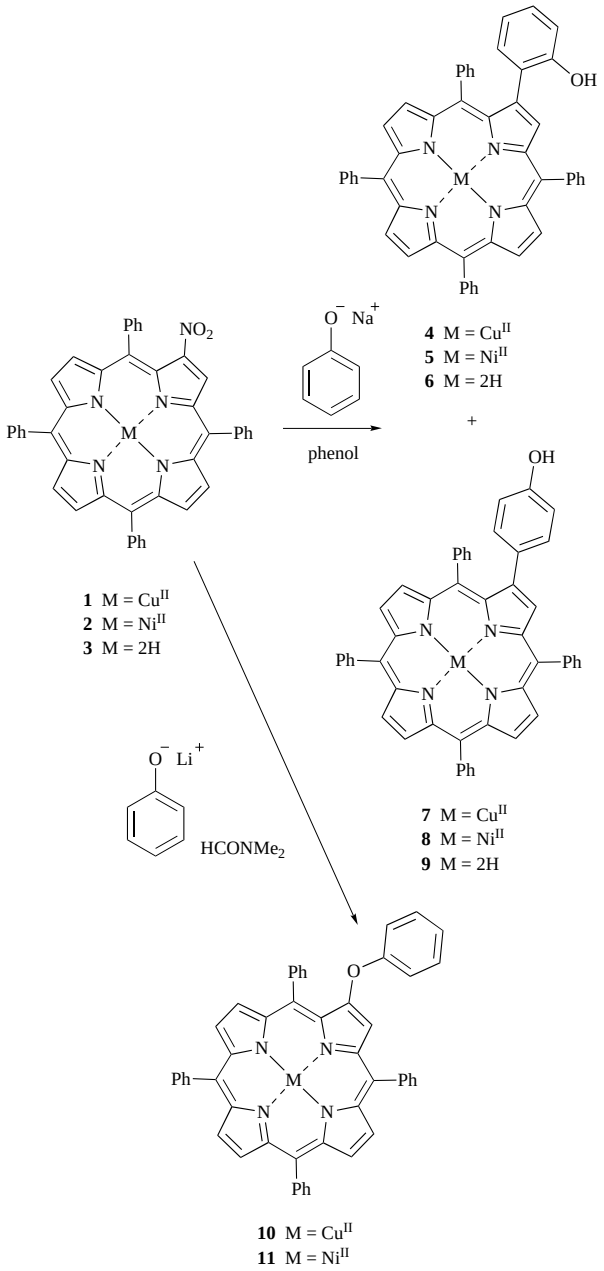
aryloxide nucleophiles with 2-nitroporphyrins that lead to the development of conditions which afford corresponding 2-(*o*-hydroxyaryl)porphyrins efficiently;[7] this hydroxy group thereby provides a site for attachment of an inwards-directed side-chain with an appended ligand, substrate or substrate recognition site.

Results and discussion

Nucleophilic substitution reactions at the β-pyrrolic positions of porphyrins are most efficient when the porphyrin inner periphery is metallated with a relatively electron-withdrawing metal ion.[2–14] In this work, the reactions of the copper(II), nickel(II) and free-base 2-nitro-5,10,15,20-tetraphenylporphyrins,[15] **1**–**3** respectively, were investigated.

Synthesis of 2-(hydroxyaryl)-5,10,15,20-tetraphenylporphyrins

Reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) **1** with sodium phenoxide (8–12 equiv.) in refluxing phenol for 4 to 7 h afforded the isomeric (hydroxyaryl)porphyrins, [2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **4** (52–54%) and [2-(*p*-hydroxyphenyl)-5,10,15,



Scheme 1

20-tetraphenylporphyrinato]copper(II) **7** (31–35%) along with a 2% yield of (2-phenoxy-5,10,15,20-tetraphenylporphyrinato)-copper(II) **10** (Scheme 1). Similar treatment of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **2** afforded [2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) **5** (66%) and [2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) **8** (24%) along with (2-phenoxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) **11** (5%) (Scheme 1). The generation of a new C–C bond in these products requires the phenoxide ion to have acted as a carbon-centred nucleophile. The ambident nucleophilicity of phenoxide has been known for some time;[16] carbon-centred rather than oxygen-centred reactions have been found to be favoured in polar, protic solvents.

The structures of the two nickel(II) hydroxyphenylporphyrins, **5** and **8** were assigned on the basis of 400 MHz ^{1}H NMR spectral data. The less polar and major of these two nickel(II) porphyrin products, **5**, was established as the 2-(*o*-hydroxyphenyl)porphyrin on the basis of the four-proton resonances (δ 6.61–7.08) of an *ortho*-disubstituted phenyl, together with the seven-proton β-pyrrolic resonances (δ 8.47–8.76) and the one-proton singlet at δ 5.00 corresponding to the hydroxy. The ^{1}H NMR spectrum of the more polar isomer, **8**, showed a four-proton AA′XX′ pattern (δ 6.50 and 7.04) of a *para*-disubstituted phenyl, together with one-proton hydroxy (δ 4.83) and seven-proton β-pyrrolic resonances (δ 8.41–8.74). Both isomers showed a parent peak in the mass spectrum [*m*/*z* 762 (M, 100)]. The structures of the two copper(II) 2-hydroxyphenylporphyrins, **4** and **7**, [*m*/*z* 767 (M, 100)] were definitively established by metallation of each of the free-base porphyrin isomers **6** and **9** which were prepared and characterised subsequently, as described below. The 2-phenoxyporphyrins **10** and **11** can be prepared in high yield by the route outlined later and their characterisation is discussed then.

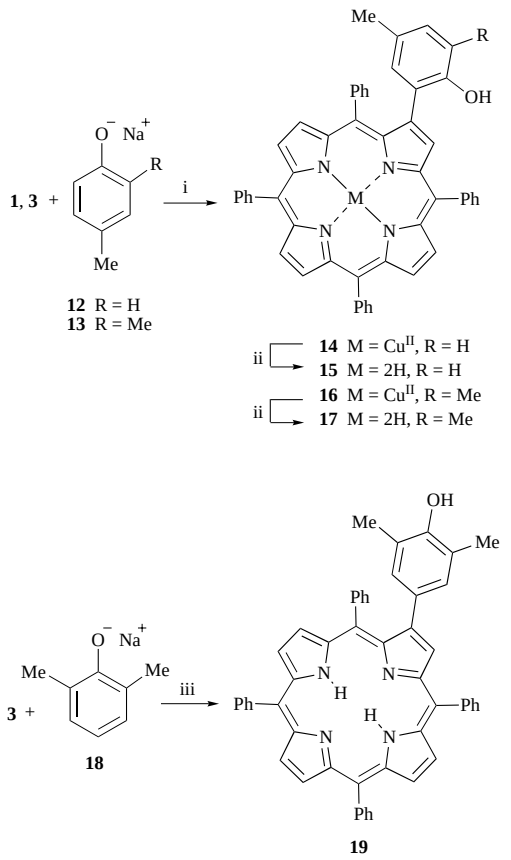
The reaction of nitroporphyrins with phenoxide ion in phenol provides non-basic conditions for nucleophilic attack on the porphyrin. Under these conditions the free-base 2-nitro-5,10,15,20-tetraphenylporphyrin **3** can also be used as a substrate for nucleophilic reaction without the formation of a deactivated porphyrin anion, which has been observed for the reaction of **3** with alkoxides in neutral solvents.[3,12] Thus, treatment of 2-nitro-5,10,15,20-tetraphenylporphyrin **3** with sodium phenoxide (1.2 equiv.) in refluxing phenol for 4.5 h afforded free-base 2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrin **6** in 38% yield and 2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrin **9** in 20% yield (Scheme 1). These yields are not optimised and might be improved by the use of a larger excess of nucleophile.

As was found for the nickel(II) 2-hydroxyphenylporphyrins, **5** and **8**, the less polar of these two free-base porphyrins proved to be the 2-(*o*-hydroxyphenyl)porphyrin isomer **6** [*ortho*-disubstituted phenyl proton resonances (δ 6.63–7.17)] and the more polar isomer proved to be 2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrin **9** [AA′XX′ system (δ 6.50 and 7.17)]. Metallation of **6** with cupric acetate afforded [2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **4** and similar metallation of **9** afforded [2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato)copper(II) **7**, each identical with the respective products isolated from the reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **1** and phenoxide ion in phenol (Scheme 1).

An (*o*-hydroxyaryl)-5,10,15,20-tetraphenylporphyrin was prepared regiospecifically by blocking the *para*-position of the aryloxide nucleophile. Thus, the reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **1** with sodium *p*-cresolate **12** (7 equiv.) in refluxing *p*-cresol afforded after 6 h [2-(2-hydroxy-5-methylphenyl)-5,10,15,20-tetraphenylporphyrinato]-copper(II) **14** [*m*/*z* 781 (M, 100)] in 86% yield (Scheme 2). Demetallation of **14** using strong acid gave the corresponding free-base porphyrin **15** in 54% yield; porphyrin **15** was also prepared in 65% yield by direct reaction of the free-base 2-nitroporphyrin **3** with sodium *p*-cresolate (Scheme 2).

We also sought to prepare a 2-(2-hydroxy-3-substituted-aryl)porphyrin. A substrate or ligand attached through the hydroxy site would be further limited in degree of freedom, and should be constrained to be directed towards the porphyrin centre, because of the vicinal substituent which should prevent conformations that allow the attached group to turn outwards again. Such porphyrins were readily prepared by reaction of a nitroporphyrin with sodium 2,4-dimethylphenoxide **13** in 2,4-dimethylphenol. In this way [2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **16** was obtained in 77% yield from the copper(II) 2-nitroporphyrin **1**, and the corresponding free-base porphyrin **17** was obtained in 69% yield from 2-nitroporphyrin **3** (Scheme 2). Free-base porphyrin **17** was also prepared in 57% yield by demetallation of the copper(II) porphyrin **16** under acidic conditions (Scheme 2) thereby providing additional evidence for the structure of the paramagnetic copper(II) compound. Extension of this idea to include reactions of even more hindered phenols and naphthols with more encumbered porphyrins will be described elsewhere.

A *p*-hydroxyaryl substituent could be introduced regio-

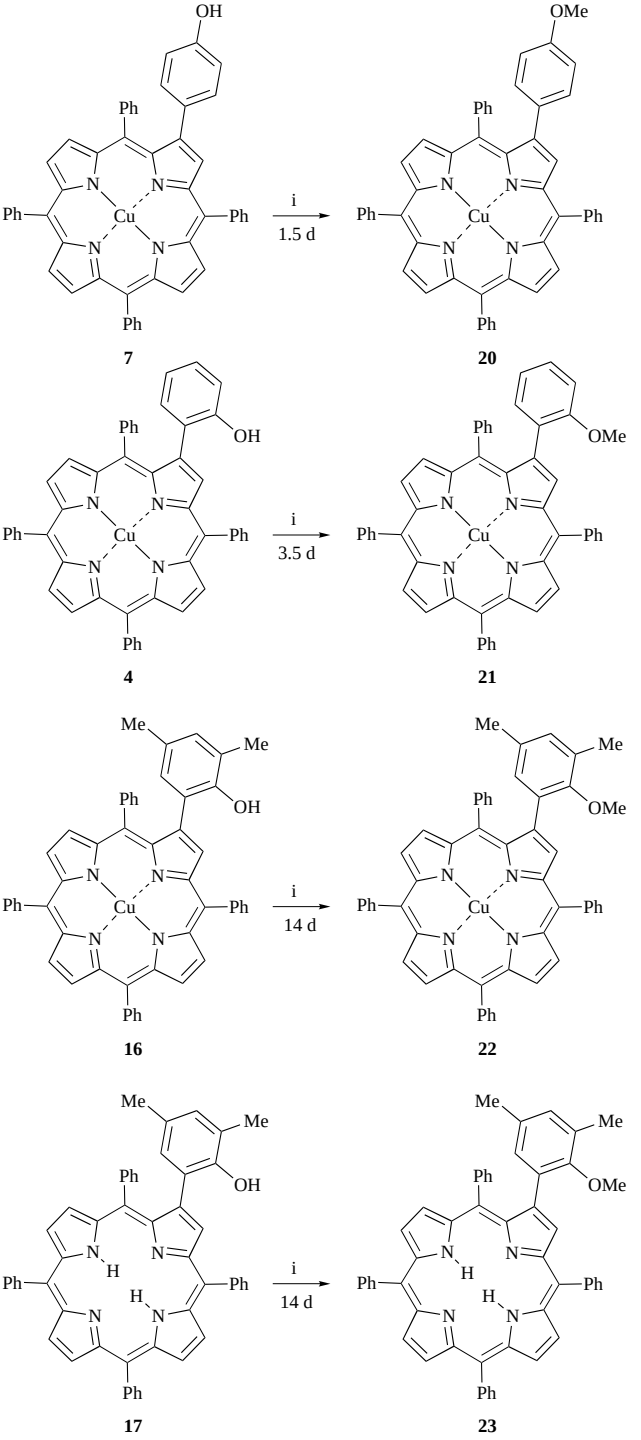


Scheme 2 *Reagents and conditions:* i, *p*-cresol, reflux; ii, H_2SO_4 (18 mol dm^{-3}), CH_2Cl_2, stir, 5 min; iii, 2,6-dimethylphenol, reflux, 2 h

selectively to the porphyrin periphery by using a phenol in which both the positions vicinal to the hydroxy group were blocked from reaction. Treatment of the free-base 2-nitroporphyrin **3** with sodium 2,6-dimethylphenoxide **18** in 2,6-dimethylphenol gave 2-(4-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrin **19** in 63% yield (Scheme 2).

It is evident that *o*-hydroxyaryl substituents potentially represent an excellent solution to the problem of producing an appropriately directed attachment point for the connection of chains bearing ligands or substrates for porphyrin-based model haemoprotein systems. An alkyl chain attached to the aryl hydroxy group would be expected to be directed toward the porphyrin centre at a well-defined angle and from a well-defined distance due to the rigidity of the sp^2 bonds connecting the linking oxygen atom back to the porphyrin periphery, and to the restricted rotation of the aryl substituent (Fig. 1).

The feasibility of attaching an alkyl chain to the aryl hydroxy groups in these molecules was demonstrated by the methylation of the phenolic hydroxys of copper(II) 2-(hydroxyaryl)-tetraphenylporphyrins **4**, **7** and **16** and free-base compound **17** (Scheme 3). The relative rate of the methylation parallels the degree of crowding about the hydroxy site. Thus, treatment of a solution of [2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **7** in acetone with methyl iodide and potassium carbonate afforded [2-(*p*-methoxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **20** [*m*/*z* 781 (M, 100)] after 1.5 days in 98% yield. Under identical conditions the more hindered [2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **4** afforded [2-(*o*-methoxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **21** in 84% yield after 3.5 days (Scheme 3). Reaction of the even more hindered [2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **16** was only partially completed after 14 days to give the methylation product **22** in 59% yield and the corresponding free-base porphyrin **17** yielded a 44% yield of 2-(2-



Scheme 3 *Reagents and conditions:* i, acetone, anhydrous K_2CO_3, MeI

methoxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrin **23** after 14 days reaction time.

Synthesis of 2-phenoxy-5,10,15,20-tetraphenylporphyrins

An efficient synthesis of 2-phenoxyporphyrins was also sought. It was envisaged that metallo-2-aryloxy-5,10,15,20-tetraphenylporphyrins might be prepared by reaction of a metallo-2-nitro-5,10,15,20-tetraphenylporphyrin with aryloxide ion at room temperature using solvents other than the corresponding phenol. By analogy to the reaction with alkoxides,[3,12] it was expected that the reaction of 2-nitroporphyrin with phenoxide would initially afford a metallo-2,2-diaryloxy-3-nitro-2,3-dihydroporphyrin which could then undergo reductive radical denitration and subsequent elimination of 1 equiv. of phenol. Copper(II) and nickel(II) 2-nitro-5,10,15,20-tetraphenylporphyrin, **1** and **2**, were each treated with phenoxide ion under

similar conditions to those used for alkoxide addition. This reaction, however, did not follow this course and 2-phenoxyporphyrins were obtained directly.

Initial experiments led to the formation of only trace amounts (<1%) of copper(II) and nickel(II) 2-phenoxy-5,10,15,20-tetraphenylporphyrin, **10** and **11**, and the return of the corresponding unreacted starting porphyrin **1** or **2**. These experiments involved the use of sodium phenoxide in *N*,*N*-dimethylformamide and in dimethyl sulfoxide at room temperature for periods of 1 to 4 days, and also involved the same experiments with lithium phenoxide. Phenoxide ion thus appeared to be much less reactive than alkoxide ions in this reaction.

Increasing the reaction temperature further increased the yield of 2-phenoxyporphyrins. Thus addition of lithium phenoxide (3 equiv.) to a refluxing solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **1** in $HCONMe_2$ (10 mmol dm^{-3}) afforded the required (2-phenoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** in 71% yield after 4 h. Similar treatment of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **2** afforded (2-phenoxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) **11** in 52% yield (Scheme 1). In each case, at elevated temperature, the formation of many minor products were also observed; similar side-products arose in the reactions of alkoxides with the porphyrins in these solvents at elevated temperature. It seemed likely that a number of these minor products arose from the reaction of the metallo-2-nitro-5,10,15,20-tetraphenylporphyrin **1** or **2** with decomposition products from the solvent. *N*,*N*-Dimethylformamide in particular is known to be unstable at reflux, especially in the presence of base, such as phenoxide.[17]

The structure of (2-phenoxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) **11** was evident from the 400 MHz ^{1}H NMR spectrum [δ 6.88–6.93 (2 H, m, *o*-PhO), 7.04 (1 H, m, *p*-PhO), 7.20–7.26 (2 H, m, *m*-PhO)] and the mass spectrum [*m*/*z* 762 (M, 100)]. The structure of the paramagnetic copper(II) complex **10** is supported by the mass spectrum [*m*/*z* 767 (M, 100)], elemental analysis and by TLC analysis [which showed **10** and **11** to have similar polarity and to be much less polar than the corresponding starting 2-nitroporphyrins and the 2-(hydroxyphenyl)porphyrin products] and visible spectrum comparison with **11**.

The direct introduction of a phenoxy group to the porphyrin ring is thus achieved in good yield by this elevated temperature reaction. In this respect the behaviour of phenoxide ion is similar to that of alkoxide ions[12] in that both types of nucleophile display increased tendency to effect apparent direct displacement of the porphyrin nitro group with increased reaction temperature in *N*,*N*-dimethylformamide solutions. Unlike alkoxide ions,[12] however, phenoxide does not undergo Michael addition with 2-nitroporphyrins at room temperature nor does it appear to effect significant porphyrin denitration in refluxing *N*,*N*-dimethylformamide.

This reaction represents the only synthesis of 2-aryloxyporphyrins currently available and is applicable, in principle, to the synthesis of other 2-aryloxyporphyrins. The application of this method to the preparation of aryloxyporphyrins with a free hydroxy group on the aryloxy substituent, however, was not pursued as the 2-hydroxyphenylporphyrins provide a more rigid anchor for attaching inwards-directed substituents.

Mechanistic considerations

A number of mechanisms can operate in reactions of nitroporphyrins. Attack of a nucleophile on metallo-2-nitroporphyrins **24** can occur either at the carbon bearing the nitro group (*ipso*-attack) to give the σ-anionic adduct **25** (*Path* a, Scheme 4), or at the adjacent β-pyrrolic position (α-attack) to give the alternate σ-anionic adduct **28** (*Path* b, Scheme 4). Reaction of **24** with 'soft' aldoximate and thiolate nucleophiles results in *ipso*-substitution of the nitro group to give the product **27** by loss of nitrite from the intermediate **25**; the overall process is similar to that of an S_NAr reaction.[5] While such an intermediate has not yet been isolated, protonation of the σ-anionic adduct **25** to give the chlorin **26**, which would afford **27** on elimination of nitrous acid, is also possible by analogy to processes that occur following α-attack of the nucleophile. With 'hard' nucleophiles (such as hydride,[9] alkoxides,[12] hydroxide,[9] acylamide ions[13] and carbanion equivalents from Grignard reagents and organolithium reagents[10]) α-attack occurs to initially afford the σ-anionic adduct **28**. Protonation of **28** gives the chlorin **29** which can eliminate nitrous acid to give the product of cine-substitution **30** or undergo oxidation to the α-substitution product **31** which is formally the vicarious nucleophilic substitution of hydrogen.[16] Subsequent nucleophilic addition to **31** affords the second σ-adduct **32** which can be trapped as the chlorin **33** by protonation.[12] Chlorins **33** have been exploited in a step-wise synthesis of **30** by denitration and elimination steps.[3,12] The products **27** and **30** are equivalent but the hydrogen at the 3-position of the starting porphyrin **24** has also been replaced in compound **30**, the product of cine-substitution. Without labelling a position on the porphyrin or isolating an intermediate compound, the two paths cannot be distinguished.

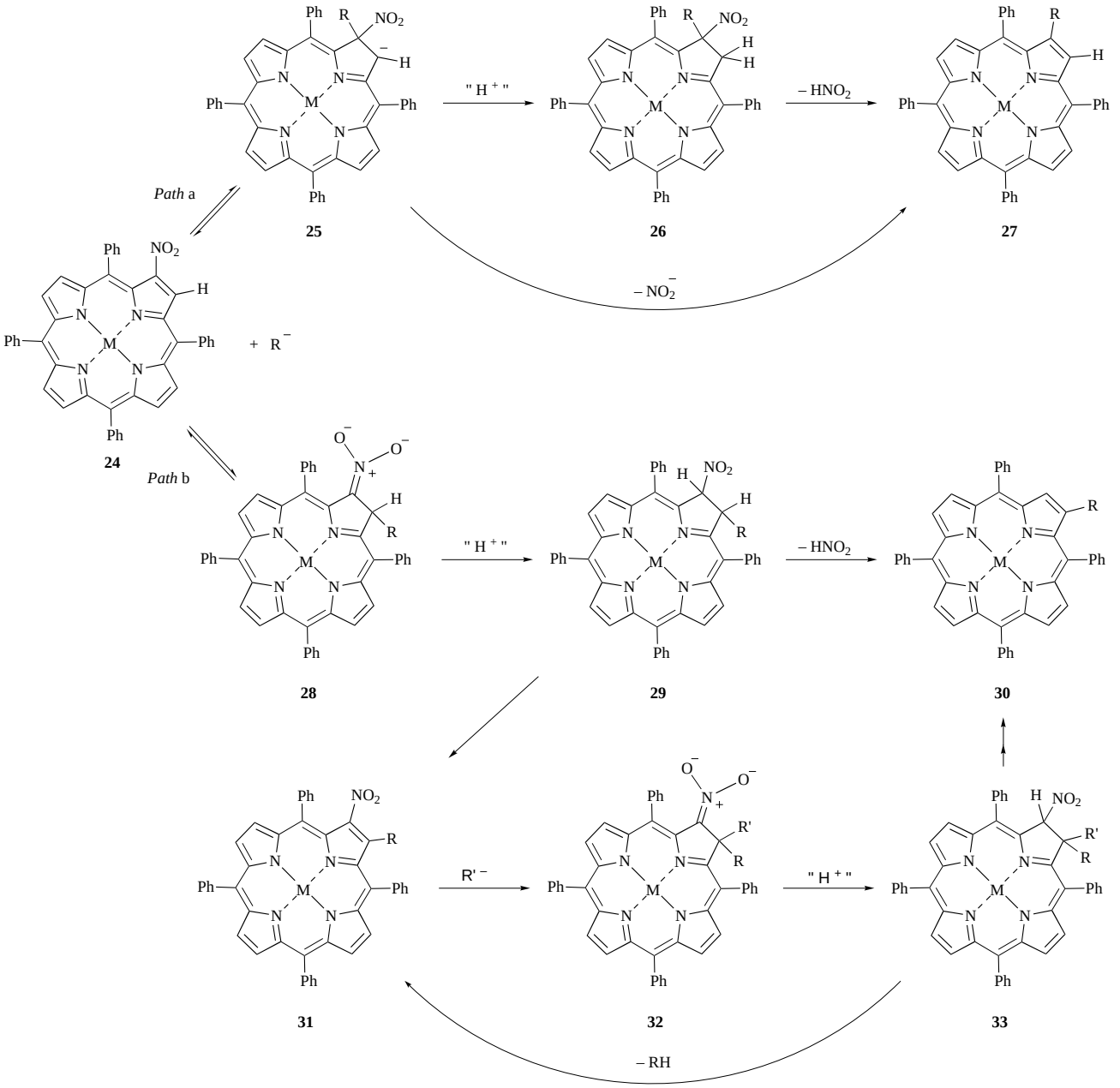
Reactions involving radical intermediates are also possible. Single electron transfer (SET) would give the nitroporphyrin radical anion **34** and then the porphyrinyl radical **35** by loss of nitrite (Scheme 5). The radical **35** can then be trapped by hydrogen abstraction to give **36** or possibly by reaction with another radical to give a substitution product **27**. Radical denitration occurs in reactions with single electron donors in the presence of an extractable hydrogen atom; these reactions are seen in reactions of nitroporphyrins with a 2-aminobenzenethiolate–2-aminobenzenethiol system[18] and with methoxide at elevated temperature.[12] The operation of a radical mechanism giving rise to either set of reaction products was considered unlikely as the highly reactive porphyrinyl radical **35** putatively generated in these mechanisms might be anticipated to abstract a hydrogen atom from the solvent (especially in the case of phenol) in competition with reaction leading to the phenoxy or hydroxyphenylporphyrin products. No denitrated product was observed, however, in any of these reactions.

The possibility that both phenoxyporphyrin and hydroxyphenylporphyrin products arise from nucleophilic reactions is supported by the known ability of phenoxide ion to act as an ambident nucleophile toward nitroaromatic systems. Thus phenoxide ion has been shown to form *C*-bonded Meisenheimer complexes with trinitrobenzene and the 'superelectrophiles' 4,6-dinitrobenzofuran and 4,6-dinitro-2-(2′,4′,6′-trinitrophenyl)benzotriazole 1-oxide through both the *ortho*- and *para*-carbons.[19–21] Further, 2,6-di-*tert*-butylphenoxide has been reported to react with nitrobenzenes, *via* C-4 attack, to give 4-hydroxy-4′-nitrobiphenyls.[22] The closely related anilines have also been reported to form *C*-bonded Meisenheimer complexes through both *ortho*- and *para*-carbons.[23–25]

In order to distinguish between the two mechanisms involving nucleophilic substitution, the reactions of phenoxide in phenol and in *N*,*N*-dimethylformamide were repeated with the vicinally deuteriated (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]-porphyrinato)nickel(II)[9] **37** as the substrate.

A solution of (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato)nickel(II) **37** in refluxing phenol (11 mmol dm^{-3}) was reacted with sodium phenoxide (11 equiv.) for 1 h and afforded {2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato}nickel(II) **38** (34%), {2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato}nickel(II) **39** (12%) and unreacted starting material **37** (13%) (Scheme 6). The deuterium content of the two hydroxyphenylporphyrins, **38** and **39**, was found to be 40 ± 5%. The recovered starting material **37** retained 100% deuterium content.

Treatment of (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]por-

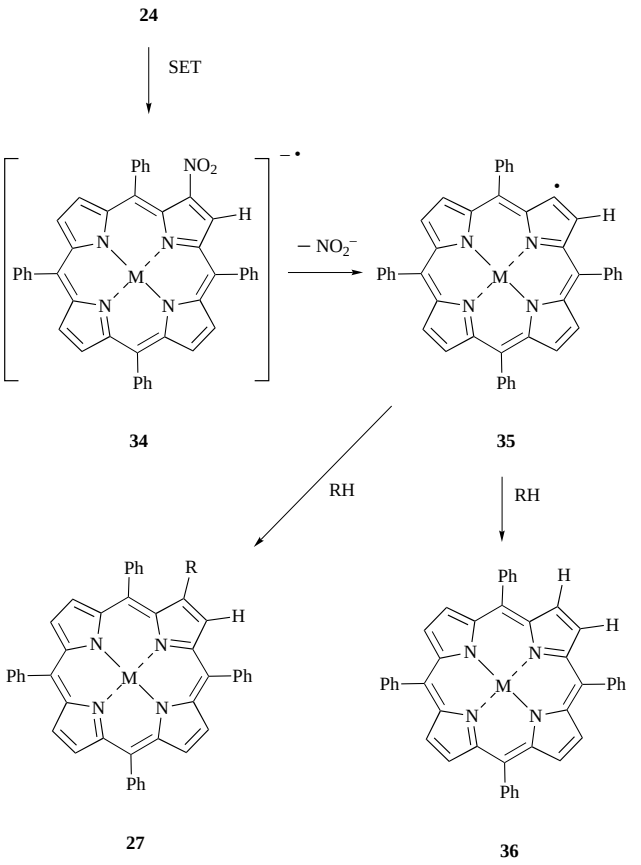


Scheme 4

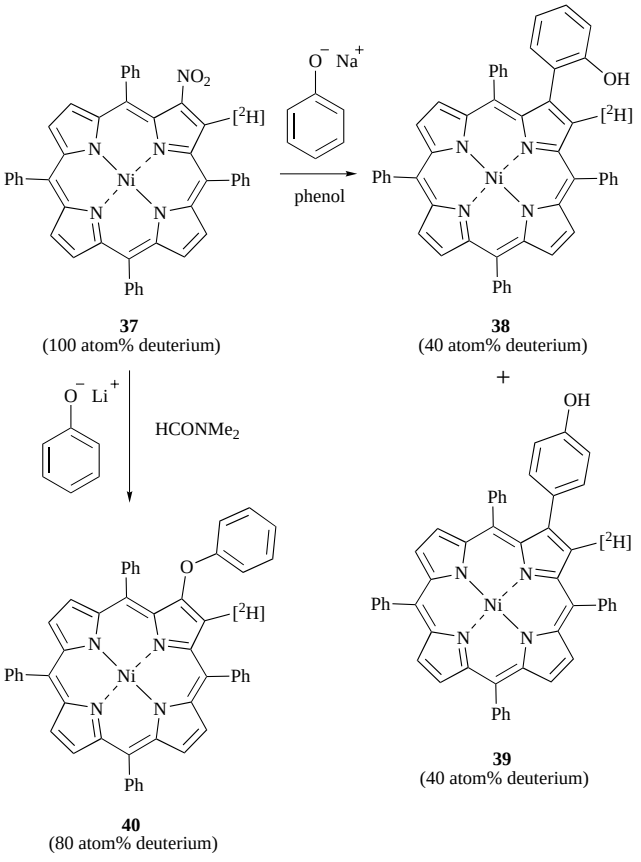
phyrinato)nickel(II) **37** in refluxing *N*,*N*-dimethylformamide with lithium phenoxide afforded deuterium labelled (2-phenoxy-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato)nickel(II) **40** (33%). The deuterium content of **40** was determined by 400 MHz ^{1}H NMR and mass spectrometry to be 80 ± 5%.

It is clear from the retention of some deuterium label in the products of both these reactions that each reaction proceeds, at least to a significant extent, by an *ipso*-substitution mechanism. The source of the variation in the products formed is therefore not simply the adoption of an *ipso* mechanism in one solvent and a cine mechanism, with different requirements for attack of the nucleophile, in the other.

The loss of deuterium label in the products (approximately 20% in the formation of **40** and 60% in the formation of **38** and **39**) from the reactions in *N*,*N*-dimethylformamide and phenol, respectively, could simply indicate that some reaction also occurs by a cine-substitution mechanism. Alternately, the loss of label could arise from protonation of the σ-anionic adduct **25** (Scheme 4). Protonation from either face of the porphyrin would give a diastereomeric mixture of chlorins **26** which then undergo *syn*-elimination of nitrous or [^{2}H]nitrous acid, the latter process affording non-deuteriated product. The trapping of the alternate σ-anionic adduct (arising from α-attack) is commonplace in the reaction of 2-nitroporphyrins with 'hard' nucleophiles such as alkoxide, hydride and the carbanions derived from Grignard reagents and organometallics.[3,9,10] The low amount of deuterium loss in the formation of phenoxyporphyrin **40** would then reflect a small amount of protonation of the σ-anionic adduct **25**, presumably from the water present even in rigorously dried *N*,*N*-dimethylformamide.[26] A much higher degree of protonation of the σ-anionic adduct **25** would be expected for the reaction carried out in phenol; complete, non-diastereoselective protonation of the anion **25**, however, and subsequent nitrous or [^{2}H]nitrous acid elimination can only account for a maximum 50% loss of label in hydroxyphenylporphyrins **38** and **39**, as [^{2}H]nitrous acid is lost by a *syn*-elimination process.[10,12] The reason for the 60% label loss in **38** and **39** is not known but may involve an extent of diastereoselective protonation of σ-anionic adduct resulting from intramolecular proton transfer from the adjacent hydroxyphenyl group in the initially formed dienone tautomer or may indicate competing cine-substitution. Labelling of the 2-, 4- and 6-positions of phenol with deuterium would unravel the detail of the mechanism. The alternate possible source of label loss



Scheme 5



Scheme 6

from **38** and **39**, exchange under the reaction conditions after formation of the product, was discounted since no further label was lost when **38** was heated at reflux in phenol for 3 h. Similarly, the fact that recovered nitroporphyrin **37** was still fully labelled ruled out loss of the label from intermediates in equilibrium with the starting nitroporphyrin.

Conclusions

The products arising from reaction of 2-nitroporphyrins with phenoxide ion can be controlled by choice of solvent. Reaction in phenol as solvent affords 2-(*o*- and *p*-hydroxyphenyl)-porphyrins while reaction in *N*,*N*-dimethylformamide yields 2-phenoxyporphyrins. Blocking the *para*-position of a phenol with a substituent forces the reaction of the corresponding phenoxide in the phenol to yield only the 2-(*o*-hydroxyaryl)-porphyrin. The products from both sets of reactions arise mainly, if not wholly, from *ipso*-substitution of the nitro group, a process seen in the reactions of 2-nitroporphyrins with other 'soft' nucleophiles such as aldoximate and thiolate. Compared with simple nitroarenes, the ease with which 2-nitroporphyrins react with nucleophiles is probably because of the fact the aromaticity is maintained in the macrocycle by a chlorin-like delocalisation pathway in all of the intermediates in the reaction.

In ongoing work we have found that the reaction of 2-nitroporphyrins with aryloxide ions to yield 2-(hydroxyaryl)-porphyrins to be a general one which may find useful application in the design of haemoprotein model systems. The synthesis, study of conformation and epoxidation reactions of arachidonic and oleic acid adducts of 2-(hydroxyaryl)porphyrins which illustrate this point will be reported in full shortly.

This work is a further illustration of the fact that 2-nitroporphyrins are versatile starting materials for introduction of other functionality to the porphyrin periphery.[2–14]

Experimental

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. Elemental analyses were performed by the Australian Microanalytical Service, Melbourne, Australia. Infrared spectra were recorded on a Perkin-Elmer 221 spectrometer. Visible spectra were recorded on a Hitachi 150-20 spectrophotometer. ^{1}H NMR spectra were recorded at 300 K on a Bruker WM400 (400 MHz) spectrometer with tetramethylsilane as the internal standard. *J* Values are given in Hz. Electron impact (EI) mass spectra were recorded on an AEI MS 902 spectrometer at 70 eV which was attached to a DS 30 data handling system for high-resolution mass spectra. Matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectra were recorded on a VG TofSpec spectrometer. Mass spectra recorded using this instrument are obtained as an envelope of the isotope peaks of the molecular ion. The mass corresponding to the envelope's maxima is reported and was compared with the maxima of a simulated spectrum. The MALDI-TOF mass spectra were accurate to ±1 amu (*ca*. 0.10%).

Flash chromatography was performed on Merck Type 9385 silica gel. Zinc-free silica gel refers to Merck Type 7754 (70–230 mesh) and was used for gravity-feed column chromatography. The chromatotron is a preparative, thin layer, centrifugally accelerated, chromatograph supplied by Harrison Research. Chromatotron separations were carried out on 4 mm thick plates prepared with Merck silica gel 60 PF_{254}. All reagents were purchased from commercial sources and used as received unless otherwise noted. All solvents were redistilled prior to use. *N*,*N*-Dimethylformamide ($HCONMe_2$) was dried over calcium hydride and distilled under reduced pressure.

The reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) 1 and sodium phenoxide in phenol

A mixture of (2-nitro-5,10,15,20-tetraphenylporphyrinato)-

copper(II)[15,27] **1** (265 mg, 0.368 mmol), sodium phenoxide (500 mg, 4.31 mmol) and phenol (10 g) was heated under reflux for 7 h. Upon cooling, the mixture was poured into aqueous sodium hydroxide (2 mol dm^{-3}; 100 cm^3). The aqueous suspension was extracted with dichloromethane (100 cm^3, 2 × 50 cm^3) and the combined extracts were washed with aqueous sodium hydroxide (2 mol dm^{-3}; 50 cm^3) and water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (4 cm diameter, 200 g) eluted with dichloromethane to yield three red fractions. The front running, non-polar band on evaporation afforded (2-phenoxy-5,10,15,20-tetraphenylporphyrinato)-copper(II) **10** (6.5 mg, 2%) which was identical with material prepared and fully characterised in an experiment described below.

The second fraction, on evaporation afforded [2-(o-*hydroxyphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*copper*(II) **4** (147 mg, 52%), mp 239–242 °C (from dichloromethane and light petroleum) (Found: C, 78.3; H, 4.3; N, 7.4. $C_{50}H_{32}CuN_4O$ requires C, 78.2; H, 4.2; N, 7.3%); ν_{max}(KBr)/cm^{-1} 3450br (OH), 1580, 1435, 1330, 1165, 1070 and 990; λ_{max}($CHCl_3$)/nm 419 (log ε 5.65), 505 (3.56), 542 (4.29) and 576 sh (3.53); *m*/*z* (EI) 770 (30%), 769 (67), 768 (60) and 767 (M, 100).

The third fraction yielded, on evaporation [2-(p-*hydroxyphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*copper*(II) **7** (100 mg, 35%), mp 295–298 °C (from dichloromethane and light petroleum) (Found: C, 78.7; H, 4.2; N, 7.2. $C_{50}H_{32}CuN_4O$ requires C, 78.2; H, 4.2; N, 7.3%); ν_{max}(Nujol)/cm^{-1} 3450br (OH), 1595, 1260, 1160, 1065 and 995; λ_{max}($CHCl_3$)/nm 419 (log ε 5.64), 504 (3.61), 543 (4.33) and 578 sh (3.53); *m*/*z* (EI) 770 (30%), 769 (67), 768 (60) and 767 (M, 100).

The reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) 2 and sodium phenoxide in phenol

A mixture of (2-nitro-5,10,15,20-tetraphenylporphyrinato)-nickel(II)[9,15] **2** (110 mg, 0.154 mmol), sodium phenoxide (110 mg, 0.948 mmol) and phenol (5 g) was heated at reflux for 3.5 h. Upon cooling, the mixture was diluted with dichloromethane (80 cm^3), washed with aqueous sodium hydroxide (3 mol dm^{-3}; 3 × 100 cm^3) and water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (2 cm diameter, 100 g) eluted with dichloromethane–light petroleum (1:1) until the first red band was eluted, thence with dichloromethane–light petroleum (4:1) to yield three fractions. The first band afforded on evaporation (2-phenoxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) **11** (6 mg, 5%) as a red solid which was identical with material prepared and fully characterised in an experiment described below.

The second, major, red band on evaporation yielded [2-(o-*hydroxyphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*nickel*(II) **5** (78 mg, 66%) as a red powder, mp 315–317 °C (from dichloromethane and light petroleum) (Found: C, 79.2; H, 4.3; N, 7.5. $C_{50}H_{32}N_4NiO$ requires C, 78.7; H, 4.2; N, 7.3%); ν_{max}(Nujol)/cm^{-1} 3350br (OH), 1580 and 1000; λ_{max}($CHCl_3$)/nm 420 (log ε 5.38), 496 sh (3.62), 534 (4.24) and 567 sh (3.68); δ_H(400 MHz; CD_2Cl_2) 5.00 (1 H, s, OH), 6.61 (1 H, dd, *J* 1 and 8, 3′-H), 6.72 (1 H, dt, *J* 1 and 7.5, 5′-H), 7.03 (1 H, ddd, *J* 1.5, 7.5 and 8, 4′-H), 7.08 (1 H, dd, *J* 1.5 and 7.5, 6′-H), 7.17 (2 H, m, 20-H_m), 7.22 (1 H, m, 20-H_p), 7.56–7.78 (11 H, m, 5-, 10-, 15-$H_{m,p}$ and 20-H_o), 7.96–8.05 (6 H, m, 5-, 10- and 15-H_o), 8.47 and 8.63 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.72–8.76 (4 H, m, β-pyrrolic H) and 8.73 (1 H, s, 3-H); *m*/*z* (EI) 766 (18%), 765 (29), 764 (56), 763 (60) and 762 (M, 100).

The third, red fraction afforded on evaporation [2-(p-*hydroxyphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*nickel*(II) **8** (28 mg, 24%) as an amorphous red solid, mp 278–285 °C (from dichloromethane and light petroleum) (Found: H, 4.2; N, 7.5. $C_{50}H_{32}N_4NiO$ requires H, 4.2; N, 7.3%) (Found: *m*/*z* 762.1942. $C_{50}H_{32}N_4{}^{58}NiO$ requires *m*/*z* 762.1930) (Found: *m*/*z* 764.1935. $C_{50}H_{32}N_4{}^{60}NiO$ requires *m*/*z* 764.1908) (Found: *m*/*z* 766.1942. $C_{50}H_{32}N_4{}^{62}NiO$ requires *m*/*z* 766.1859) (Found: *m*/*z* 768.1919. $C_{50}H_{32}N_4{}^{64}NiO$ requires *m*/*z* 768.1856); ν_{max}(Nujol)/cm^{-1} 3450br (OH), 1245, 1155, 1060 and 955; λ_{max}($CHCl_3$)/nm 421 (log ε 5.30), 536 (4.17) and 570 sh (3.66); δ_H(400 MHz; CD_2Cl_2) 4.83 (1 H, s, OH), 6.50 (2 H, m, spacing 1.5 and 8, 2-H_m), 7.04 (2 H, m, spacing 1.5 and 8, 2-H_o), 7.19 (2 H, m, 20-H_o), 7.30 (1 H, m, 20-H_p), 7.60 (2 H, m, 20-H_o), 7.64–7.76 (9 H, m, 5-, 10- and 15-$H_{m,p}$), 7.95–8.05 (6 H, m, 5-, 10- and 15-H_o), 8.41 and 8.62 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.61 (1 H, s, 3-H), 8.70 and 8.74 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.71 and 8.73 (2 H, ABq, J_{AB} 5, β-pyrrolic H); *m*/*z* (EI) 766 (15%), 765 (29), 764 (57), 763 (58) and 762 (M, 100).

The reaction between 2-nitro-5,10,15,20-tetraphenylporphyrin 3 and sodium phenoxide in phenol

A mixture of 2-nitro-5,10,15,20-tetraphenylporphyrin[2] **3** (64 mg, 0.097 mmol), sodium phenoxide (12 mg, 0.10 mmol) and phenol (5 g) was heated under reflux for 4.5 h. Upon cooling, the mixture was taken up in dichloromethane (60 cm^3), washed with aqueous sodium hydroxide (3 mol dm^{-3}; 2 × 50 cm^3), and water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on zinc-free silica, eluted with dichloromethane–light petroleum (7:3) until the first band eluted, thence with dichloromethane. The first band afforded 2-nitro-5,10,15,20-tetraphenylporphyrin **3** (5 mg, 8%).

The second band afforded 2-(o-*hydroxyphenyl*)-5,10,15,20-*tetraphenylporphyrin* **6** (26 mg, 38%) as an amorphous brown solid, mp 205–210 °C (from dichloromethane and hexane) (Found: C, 84.6; H, 4.7; N, 8.1. $C_{50}H_{34}N_4O$ requires C, 85.0; H, 4.9; N, 7.9%); ν_{max}(Nujol)/cm^{-1} 3500br, 3300br, 1600, 1180 and 970; λ_{max}($CHCl_3$)/nm 403 sh (log ε 4.04), 422 (5.55), 487 (3.59), 519 (3.59), 554 (4.23), 594 (3.82) and 650 (3.56); δ_H(400 MHz; CD_2Cl_2) −2.67 (2 H, br s, NH), 6.63 (1 H, dd, *J* 1 and 8, 2′-H), 6.74 (1 H, dt, *J* 1 and 7.5, 5′-H), 7.03 (1 H, ddd, *J* 2, 7.5 and 8, 4′-H), 7.17 (1 H, dd, *J* 2 and 7.5, 6′-H), 7.19–7.30 (3 H, m, 20-$H_{m,p}$), 7.68–7.81 (10 H, m, 5-, 10-, 15-$H_{m,p}$ and 20-H_o), 7.98 (1 H, m, 20-H_o), 8.18–8.25 (6 H, m, 5-, 10- and 15-H_o), 8.66 and 8.78 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.81 (1 H, s, 3-H), 8.83 and 8.85 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.87 and 8.88 (2 H, ABq, J_{AB} 5, β-pyrrolic H); *m*/*z* (EI) 770 (15%), 769 (31), 768 (27), 767 (M + [^{63}Cu], 43), 708 (24), 707 (67) and 706 (M, 100).

The third band yielded 2-(p-*hydroxyphenyl*)-5,10,15,20-*tetraphenylporphyrin* **9** (14 mg, 20%) as a brown amorphous solid, mp 191–195 °C (from dichloromethane and hexane) (Found: C, 84.8; H, 5.2; N, 7.7. $C_{50}H_{34}N_4O$ requires C, 85.0; H, 4.9; N, 7.9%); ν_{max}(Nujol)/cm^{-1} 3300br, 1590, 1260, 1170 and 960; λ_{max}($CHCl_3$)/nm 402 sh (log ε 4.90), 422 (5.52), 488 (3.58), 520 (4.23), 555 (3.83), 594 (3.73) and 649 (3.47); δ_H(400 MHz; CD_2Cl_2) −2.70 (2 H, br s, NH), 6.50 (2 H, m, spacing 1.5 and 8, 2-H_m), 7.17 (2 H, m, spacing 1.5 and 8, 2-H_o), 7.25 (2 H, m, 20-H_m), 7.33 (1 H, m, 20-H_p), 7.69–7.81 (9 H, m, 5-, 10- and 15-$H_{m,p}$), 7.84–7.89 (2 H, m, 20-H_o), 8.19–8.25 (6 H, m, 5-, 10- and 15-H_o), 8.67 and 8.73 (2 H, ABq, J_{AB} 4.5, β-pyrrolic H), 8.81 and 8.84 (2 H, ABq, J_{AB} 4.5, β-pyrrolic H), 8.86 and 8.88 (2 H, ABq, J_{AB} 4.5, β-pyrrolic H); *m*/*z* (EI) 770 (29%), 769 (54), 768 (58), 767 (M + [^{63}Cu], 86), 708 (18), 707 (58) and 706 (M, 100).

The reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) 1 and sodium *p*-cresolate 12

A mixture of (2-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) **1** (246 mg, 0.342 mmol), sodium *p*-cresolate **12** (300 mg, 2.31 mmol) and *p*-cresol (7 g) was heated at reflux for 6 h. Upon cooling, the mixture was diluted with dichloromethane (100 cm^3), washed with aqueous sodium hydroxide (3 mol dm^{-3}; 2 × 50 cm^3) and water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue

was chromatographed on a chromatotron eluted with dichloromethane to afford [2-(2-*hydroxy*-5-*methylphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*copper*(II) **14** (230 mg, 86%) as a red amorphous solid, mp 260–270 °C (from dichloromethane and hexane) (Found: C, 78.3; H, 4.5; N, 7.5. $C_{51}H_{34}CuN_4O$ requires C, 78.3; H, 4.4; N, 7.2%); ν_{max}(Nujol)/cm^{-1} 3400br (OH), 1585, 1335 and 985; λ_{max}($CHCl_3$)/nm 394 sh (log ε 4.56), 419 (5.66), 477 sh (3.66), 506 (3.61), 542 (4.33) and 578 sh (3.58); *m*/*z* (EI) 784 (32%), 783 (62), 782 (59) and 781 (M, 100).

The reaction between porphyrin 3 and sodium *p*-cresolate 12 to give 2-(2-hydroxy-5-methylphenyl)-5,10,15,20-tetraphenylporphyrin 15

Method 1. To a refluxing mixture of sodium *p*-cresolate **12** (200 mg, 1.54 mmol) and *p*-cresol (15 g) was added 2-nitro-5,10,15,20-tetraphenylporphyrin **3** (317 mg, 0.48 mmol). The mixture was heated at reflux for 3.5 h and upon cooling it was diluted with dichloromethane (150 cm^3), washed with aqueous sodium hydroxide (3 mol dm^{-3}; 2 × 50 cm^3) and water (100 cm^3). It was then dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:2), and the major band was collected and evaporated to dryness to afford 2-(2-*hydroxy*-5-*methylphenyl*)-5,10,15,20-*tetraphenylporphyrin* **15** (226 mg, 65%), mp 225–230 °C (from dichloromethane and methanol) (Found: C, 84.7; H, 5.3; N, 7.4. $C_{51}H_{36}N_4O$ requires C, 85.0; H, 5.0; N, 7.8%); ν_{max}($CHCl_3$)/cm^{-1} 3547m br (OH), 3062m, 3011m, 1599m, 1495s, 1474s, 1442m, 1350m, 1074w, 1032w, 1003m and 984m; λ_{max}($CHCl_3$)/nm 420 (log ε 5.63), 484 sh (3.59), 517 (4.28), 552 (3.84), 592 (3.45) and 648 (3.58); δ_H(400 MHz; $CDCl_3$) −2.63 (2 H, br s, inner NH), 2.21 (3 H, s, CH_3), 5.04 (1 H, s, OH), 6.66 (1 H, d, *J* 7.3, 3′-H), 6.85 (1 H, d, *J* 7.3, 4′-H), 6.87 (1 H, s, 6′-H), 7.19–7.36 (3 H, m, 20-H$_{m,p}$), 7.68–7.80 (9 H, m, 5-, 10- and 15-H$_{m,p}$), 7.85 (1 H, d, *J* 7, 20-H$_o$), 7.96 (1 H, d, *J* 7, 20-H$_o$), 8.20–8.23 (6 H, m, 5-, 10- and 15-H$_o$), 8.68 and 8.80 (2 H, ABq, J_{AB} 5, 12- and 13-H), 8.82 (1 H, s, 3-H), 8.81 and 8.83 (2 H, ABq, J_{AB} 5, 7- and 8-H), 8.85 and 8.87 (2 H, ABq, J_{AB} 5, 17- and 18-H); *m*/*z* (MALDI-TOF) 722 (M + H requires 722).

Method 2. [2-(2-Hydroxy-5-methylphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **14** (100 mg, 0.13 mmol) was dissolved in dichloromethane (50 cm^3) and concentrated sulfuric acid (98%; 10 cm^3) was added. The mixture was stirred for 5 min and then poured onto ice (150 g). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 50 cm^3). The combined organic layers were washed with aqueous sodium hydroxide (3 mol dm^{-3}; 50 cm^3), water (50 cm^3) and then dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:3) to yield 2-(2-hydroxy-5-methylphenyl)-5,10,15,20-tetraphenylporphyrin **15** (48 mg, 54%). This product was identical in all respects with the sample prepared by Method 1.

The reaction between porphyrin 1 and sodium 2,4-dimethylphenoxide 13 to give [2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) 16

To a refluxing mixture of sodium 2,4-dimethylphenoxide **13** (400 mg, 2.78 mmol) and 2,4-dimethylphenol (20 g) was added (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **1** (614 mg, 0.852 mmol). The mixture was heated at reflux for 2.5 h, cooled, then extracted into dichloromethane (100 cm^3). This was washed with aqueous sodium hydroxide (3 mol dm^{-3}; 150 cm^3), water (100 cm^3) and dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:3). The red band on evaporation yielded [2-(2-*hydroxy*-3,5-*dimethylphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*copper*(II) **16** (521 mg, 77%), mp > 320 °C (from dichloromethane and methanol) (Found: C, 78.2; H, 4.5; N, 7.1. $C_{52}H_{36}CuN_4O$ requires C, 78.4; H, 4.6; N, 7.0%); ν_{max}($CHCl_3$)/cm^{-1} 3548m (OH), 3014s, 1600s, 1491m, 1480m, 1442s, 1344s, 1073m, 1005s and 996s; λ_{max}($CHCl_3$)/nm 418 (log ε 5.58), 505 sh (3.50) and 542 (4.23); *m*/*z* (EI) 799 (6%), 798 (18), 797 (65), 796 (75) and 795 (M, 100).

The reaction between porphyrin 3 and sodium 2,4-dimethylphenoxide 13 to give 2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrin 17

Method 1. A mixture of 2-nitro-5,10,15,20-tetraphenylporphyrin **3** (160 mg, 0.24 mmol), sodium 2,4-dimethylphenoxide **13** (200 mg, 1.39 mmol) and 2,4-dimethylphenol (14 g) was heated at reflux for 10 h and cooled. It was then extracted into dichloromethane (100 cm^3), washed with aqueous sodium hydroxide (3 mol dm^{-3}; 2 × 100 cm^3), water (2 × 100 cm^3), dried over anhydrous sodium sulfate and evaporated to dryness. The residue was chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:1). The major band was collected and evaporated to dryness to afford 2-(2-*hydroxy*-3,5-*dimethylphenyl*)-5,10,15,20-*tetraphenylporphyrin* **17** (126 mg, 69%), mp 220–224 °C (from dichloromethane and methanol) (Found: C, 85.2; H, 5.5; N, 7.7. $C_{52}H_{38}N_4O$ requires C, 85.0; H, 5.2; N, 7.6%); ν_{max}($CHCl_3$)/cm^{-1} 3550w br (OH), 3331w (NH), 1599w, 1475m, 1442w, 1350w, 1074w, 1003w and 966s; λ_{max}($CHCl_3$)/nm 420 (log ε 4.61), 486 sh (3.59), 517 (4.29), 552 (3.83), 592 (3.74) and 647 (3.56); δ_H(400 MHz; $CDCl_3$) −2.64 (2 H, br s, inner NH), 2.14 (3 H, s, CH_3), 2.18 (3 H, s, CH_3), 4.94 (1 H, br s, OH), 6.72 (1 H, d, *J* 2.5, 4′-H), 6.80 (1 H, d, *J* 2.5, 6′-H), 7.22–7.27 (3 H, m, 20-H$_{m,p}$), 7.67–7.77 (9 H, m, 5-, 10- and 15-H$_{m,p}$), 7.82 (1 H, br m, 20-H$_o$), 7.95 (1 H, br m, 20-H$_o$), 8.18–8.22 (6 H, m, 5-, 10- and 15-H$_o$), 8.67 and 8.76 (2 H, ABq, J_{AB} 7.4, 12- and 13-H), 8.83 (1 H, s, 3-H), 8.81 and 8.84 (2 H, ABq, J_{AB} 6.3, 7- and 8-H) and 8.85 (2 H, ABq, J_{AB} 6.3, 17- and 18-H); *m*/*z* (EI) 736 (4%), 735 (30), 734 (M, 52), 659 (12), 658 (57) and 657 (100).

Method 2. To a stirred solution of [2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **16** (129 mg, 0.16 mmol) in dichloromethane (50 cm^3) was added concentrated sulfuric acid (98%; 10 cm^3). The mixture was stirred for 5 min, then poured onto ice (50 g). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 50 cm^3). The combined organic layers were washed with aqueous sodium hydroxide (3 mol dm^{-3}; 75 cm^3), water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:2) to afford 2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrin **17** (68 mg, 57%). This product was identical in all respects with the sample prepared by Method 1.

The reaction between porphyrin 3 and sodium 2,6-dimethylphenoxide 18 to give 2-(4-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrin 19

To a refluxing mixture of 2,6-dimethylphenol (15 g) and sodium hydroxide (200 mg) was added 2-nitro-5,10,15,20-tetraphenylporphyrin **3** (200 mg, 0.30 mmol). The mixture was heated at reflux for 2 h, cooled, then extracted into dichloromethane (100 cm^3). This was washed with aqueous sodium hydroxide (3 mol dm^{-3}; 150 cm^3), water (100 cm^3) and dried over sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:3). The major band gave 2-(4-*hydroxy*-3,5-*dimethylphenyl*)-5,10,15,20-*tetraphenylporphyrin* **19** (140 mg, 63%) as purple crystals, mp >300 °C (Found: C, 84.6; H, 5.4; N, 7.3. $C_{52}H_{38}N_4O$ requires C, 84.5; H, 5.2; N, 7.0%); ν_{max}($CHCl_3$)/cm^{-1} 3610w br (OH), 3310w br (NH), 3062w, 3009m, 2924w, 2382w, 1598m, 1484s, 1442m, 1350w, 1196w and 1165s; λ_{max}($CHCl_3$)/nm 412 (log ε 5.60), 486 sh (3.61), 517

(4.32), 553 (3.86), 592 (3.77) and 647 (3.49); δ_H(400 MHz; $CDCl_3$) −2.64 (2 H, br s, inner NH), 2.17 (6 H, s, 2 × CH_3), 4.55 (1 H, br s, OH), 6.94 (2 H, s, 2′- and 6′-H), 7.23 (3 H, m, 20-$H_{m,p}$), 7.68–7.78 (9 H, m, 5-, 10- and 15-$H_{m,p}$), 7.87 (1 H, d, *J* 2.5, 20-H_o), 7.89 (1 H, d, *J* 2.5, 20-H_o), 8.19–8.25 (6 H, m, 5-, 10- and 15-H_o), 8.67 and 8.72 (2 H, ABq, J_{AB} 4.9, β-pyrrolic H), 8.74 (1 H, s, 3-H), 8.78 and 8.81 (2 H, ABq, J_{AB} 4.7, β-pyrrolic H), 8.84 and 8.86 (2 H, ABq, J_{AB} 4.8, β-pyrrolic H); *m*/*z* (MALDI-TOF) 735 (M + H requires 736).

Methylation of porphyrin 7 to give [2-(*p*-methoxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) 20

[2-(*p*-Hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]-copper(II) **7** (51 mg, 0.066 mmol) in acetone (10 cm^3) was stirred with anhydrous potassium carbonate (48 mg, 0.35 mmol) and methyl iodide (0.5 cm^3, 8.0 mmol) for 1.5 days, by which time the product had precipitated from solution. The solvent was removed by rotary evaporation. The residue was taken up in chloroform (30 cm^3), washed with water (50 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (1 cm diameter, 50 g) eluted with dichloromethane–light petroleum (1:1) to yield [2-(p-*methoxyphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*copper*(II) **20** (51 mg, 98%) as a red powder, mp > 350 °C (from dichloromethane and methanol) (Found: C, 78.5; H, 4.2; N, 6.9. $C_{51}H_{34}CuN_4O$ requires C, 78.3; H, 4.4; N, 7.2%); ν_{max}(KBr)/cm^{-1} 1595, 1480, 1420, 1335, 1230, 1165, 1060 and 985; λ_{max}($CHCl_3$)/nm 389 sh (log ε 3.94), 418 (5.55), 504 (3.56), 542 (4.27) and 574 sh (3.49); *m*/*z* (EI) 785 (15%), 784 (38), 783 (68), 782 (68) and 781 (M, 100).

Methylation of porphyrin 4 to give [2-(*o*-methoxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) 21

A solution of [2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **4** (54 mg, 0.070 mmol) in acetone (10 cm^3) was stirred with anhydrous potassium carbonate (48 mg, 0.35 mmol) and methyl iodide (0.5 cm^3, 8.0 mmol) for 3.5 days, by which time the product had precipitated from solution. The solvent was removed by rotary evaporation. The residue was taken up in chloroform (30 cm^3), washed with water (50 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (1 cm diameter, 50 g) eluted with dichloromethane–light petroleum (1:1) to yield [2-(o-*methoxyphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*copper*(II) **21** (46 mg, 84%) as a red powder, mp 298–303 °C (from dichloromethane and methanol) (Found: C, 78.3; H, 4.5; N, 7.1. $C_{51}H_{34}CuN_4O$ requires C, 78.3; H, 4.4; N, 7.2%); ν_{max}(KBr)/cm^{-1} 1590, 1425, 1335, 1240 and 985; λ_{max}($CHCl_3$)/nm 396 sh (log ε 4.49), 417 (5.50), 474 sh (3.60), 504 (3.55), 541 (4.28) and 575 sh (3.45); *m*/*z* (EI) 785 (13%), 784 (36), 783 (61), 781 (M, 100), 691 (14), 690 (13) and 689 (21).

Methylation of porphyrin 16 to give [2-(2-methoxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) 22

A solution of [2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrinato]copper(II) **16** (106 mg, 0.13 mmol) in acetone (20 cm^3) was stirred with methyl iodide (1 cm^3, 16 mmol) and anhydrous potassium carbonate (220 mg) for 7 days. Further methyl iodide (2 cm^3, 32 mmol) was added and the mixture was stirred for a further 7 days. The solvent was removed by rotary evaporation and the residue was dissolved in dichloromethane (50 cm^3), washed with water (50 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was then chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:2) to yield [2-(2-*methoxy*-3,5-*dimethylphenyl*)-5,10,15,20-*tetraphenylporphyrinato*]*copper*(II) **22** (64 mg, 59%), mp >320 °C (Found: C, 78.9; H, 4.5; N, 7.2. $C_{53}H_{38}CuN_4O$ requires C, 78.6; H, 4.7; N, 6.9%); ν_{max}($CHCl_3$)/cm^{-1} 3014s, 1600m, 1491m, 1442m, 1344s, 1151m, 1073m, 1006s and 997s; λ_{max}($CHCl_3$)/nm 417 (log ε 5.63), 504 sh (3.58) and 540 (4.30); *m*/*z* (EI) 812 (26%), 811 (73), 810 (60) and 809 (M, 100).

Methylation of porphyrin 17 to give 2-(2-methoxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrin 23

A solution of 2-(2-hydroxy-3,5-dimethylphenyl)-5,10,15,20-tetraphenylporphyrin **17** (104 mg, 0.14 mmol) in acetone (20 cm^3) was stirred with methyl iodide (3 cm^3, 48 mmol) and anhydrous potassium carbonate (150 mg) for 7 days. Further methyl iodide (5 cm^3, 80 mmol) was added and the mixture was stirred for a further 7 days. The solvent was removed by rotary evaporation and the residue was extracted into dichloromethane (100 cm^3), washed with water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was then chromatographed on a silica column, eluted with dichloromethane–light petroleum (1:2) to yield 2-(2-*methoxy*-3,5-*dimethylphenyl*)-5,10,15,20-*tetraphenylporphyrin* **23** (47 mg, 44%), mp 201–205 °C (from dichloromethane and light petroleum) (Found: C, 84.7; H, 5.5; N, 7.3. $C_{53}H_{40}N_4O$ requires C, 85.0; H, 5.4; N, 7.5%); ν_{max}($CHCl_3$)/cm^{-1} 3314m (NH), 3061m, 3009s, 1598s, 1474s, 1442s, 1349m, 1073m, 1015m, 1003s, 981m and 966s; λ_{max}($CHCl_3$)/nm 420 (log ε 5.64), 516 (4.29), 552 (3.84), 591 (3.74) and 647 (3.47); δ_H(400 MHz; $CDCl_3$) −2.64 (2 H, br s, inner NH), 2.12 (3 H, s, CH_3), 2.28 (3 H, s, CH_3), 3.04 (3 H, s, OCH_3), 6.78 (1 H, d, *J* 2, 4′-H), 7.05 (1 H, d, *J* 2, 6′-H), 7.16–7.31 (3 H, m, 20-$H_{m,p}$), 7.71–7.77 (6 H, m, 5-, 10- and 15-$H_{m,p}$), 8.06 (1 H, d, *J* 7, 20-H_o), 8.18–8.25 (7 H, m, 5-, 10-, 15- and 20-H_o), 8.63 and 8.72 (2 H, ABq, J_{AB} 5, 12- and 13-H) and 8.80–8.85 (5 H, m, 3-, 7-, 8-, 17- and 18-H); *m*/*z* (EI) 752 (3%), 751 (16), 750 (61), 749 (M, 100) and 748 (3).

The reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) 1 and lithium phenoxide in *N*,*N*-dimethylformamide

To a refluxing solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **1** (53 mg, 0.074 mmol) in dry HCONMe$_2$ (7 cm^3), under nitrogen, was added solid lithium phenoxide (20 mg, 0.20 mmol) and the mixture was heated at reflux under nitrogen for 4 h. On cooling, the mixture was diluted with dichloromethane (30 cm^3), washed with water (6 × 50 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (1 cm diameter, 50 g), eluted with dichloromethane–light petroleum (1:1). The front running red band was collected and evaporated to dryness to yield (2-*phenoxy*-5,10,15,20-*tetraphenylporphyrinato*)*copper*(II) **10** (37 mg, 65%, 71% based on consumed starting material) as an amorphous red solid, mp 316–318 °C (from benzene and methanol) (Found: C, 78.6; H, 4.1; N, 7.3. $C_{50}H_{32}CuN_4O$ requires C, 78.2; H, 4.2; N, 7.3%); ν_{max}(Nujol)/cm^{-1} 1585, 1545, 1205, 1160, 1060 and 985; λ_{max}($CHCl_3$)/nm 394 sh (log ε 4.59), 416 (5.68), 472 sh (3.64), 502 (4.34), 540 (3.54) and 604 sh (2.97); *m*/*z* (EI) 770 (30%), 769 (64), 768 (63), 767 (M, 100) and 675 (10). A second, reddish-green band contained starting porphyrin **1** (4 mg, 8%).

The reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) 2 and lithium phenoxide in *N*,*N*-dimethylformamide

To a refluxing solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **2** (53 mg, 0.074 mmol) in dry HCONMe$_2$ (30 cm^3) under nitrogen was added lithium phenoxide (48 mg, 0.48 mmol) and the mixture was heated at reflux for 3.5 h. On cooling, the mixture was diluted with dichloromethane (50 cm^3), washed with water (6 × 100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a chromatotron eluted with dichloromethane–light petroleum (3:2) to yield two major frac-

tions. The first, red fraction afforded on evaporation (2-*phenoxy*-5,10,15,20-*tetraphenylporphyrinato*)*nickel*(II) **11** (26 mg, 44%, 52% based on consumed starting material), mp 174–176 °C (Found: *m*/*z* 762.1927. $C_{50}H_{32}N_4NiO$ requires *M*, 762.1929); ν_{max}(Nujol)/cm^{-1} 1596, 1579, 1485, 1220 and 1070; λ_{max}($CHCl_3$)/nm 417 (log ε 5.35), 491 (3.72), 531 (4.21) and 565 sh (3.69); δ_H(400 MHz; CD_2Cl_2) 6.88–6.93 (2 H, m, 2-H$_o$), 7.04 (1 H, m, 2-H$_p$), 7.20–7.26 (2 H, m, 2-H$_m$), 7.44–7.54 (3 H, m, 20-H$_{m,p}$), 7.58–7.75 (9 H, m, 5-, 10- and 15-H$_{m,p}$), 7.79–7.83 (2 H, m, 20-H$_o$), 7.91–7.98 (2 H, m, 5-H$_o$), 7.99–8.04 (4 H, m, 10- and 15-H$_o$), 8.06 (1 H, s, 3-H), 8.64 and 8.69 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.66 and 8.73 (2 H, ABq, J_{AB} 5, β-pyrrolic H) and 8.73 (2 H, ABq, J_{AB} 5, β-pyrrolic H); *m*/*z* (EI) 766 (16%), 765 (30), 764 (61), 763 (61), 762 (M, 100), 673 (12), 672 (25), 671 (26) and 670 (52). A more polar, reddish-green fraction yielded starting porphyrin **2** (6 mg, 11%).

The reaction between (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]-porphyrinato)nickel(II) 37 and sodium phenoxide

A mixture of (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato)nickel(II) **37** (100 atom% deuterium, 39 mg, 0.054 mmol), sodium phenoxide (70 mg, 0.60 mmol) and phenol (5 g) was heated at reflux for 1 h. Upon cooling, the mixture was diluted with dichloromethane (50 cm^3), washed with aqueous sodium hydroxide (3 mol dm^{-3}; 2 × 80 cm^3) and water (100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a chromatotron eluted with dichloromethane–light petroleum (1:1) until the major red band was eluted thence with dichloromethane–light petroleum (3:1) to yield three major fractions. The first, reddish-green band on evaporation yielded (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato)nickel(II) **37** (100 atom% deuterium, 5 mg, 13%), identical ^{1}H NMR and EI mass spectrum with authentic starting material and co-chromatographed with authentic unlabelled compound **2**.

The second, red fraction afforded {2-(*o*-hydroxyphenyl)-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato}nickel(II) **38** (40 atom% deuterium, 14 mg, 34%), δ_H(400 MHz; CD_2Cl_2) 5.00 (1 H, s, OH), 6.61 (1 H, dd, *J* 1 and 8, 3′-H), 6.72 (1 H, dt, *J* 1 and 7.5, 5′-H), 7.03 (1 H, ddd, *J* 1.5, 7.5 and 8.0, 4′-H), 7.08 (1 H, dd, *J* 1.5 and 7.5, 6′-H), 7.17 (2 H, m, 20-H$_m$), 7.22 (1 H, m, 20-H$_p$), 7.56–7.78 (11 H, m, 5-, 10-, 15-H$_{m,p}$ and 20-H$_o$), 7.96–8.05 (6 H, m, 5-, 10- and 15-H$_o$), 8.47 and 8.63 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.72–8.76 (4 H, m, β-pyrrolic H) and 8.73 (0.6 H, s, 3-H); *m*/*z* (EI) 767 (12%), 766 (28), 765 (52), 764 (80), 763 ([^{2}H]M, 100) and 762 ([^{1}H]M, 92).

The third, red fraction afforded {2-(*p*-hydroxyphenyl)-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato}nickel(II) **39** (40 atom% deuterium, 5 mg, 12%), δ_H(400 MHz; CD_2Cl_2) 4.83 (1 H, s, OH), 6.50 (2 H, m, spacing 1.5 and 8, 2-H$_m$), 7.04 (2 H, m, spacing 1.5 and 8, 2-H$_o$), 7.19 (2 H, m, 20-H$_m$), 7.30 (1 H, m, 20-H$_p$), 7.60 (2 H, m, 20-H$_o$), 7.64–7.76 (9 H, m, 5-, 10- and 15-H$_{m,p}$), 7.95–8.05 (6 H, m, 5-, 10- and 15-H$_o$), 8.41 and 8.62 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.61 (0.6 H, s, 3-H), 8.70 and 8.74 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.71 and 8.73 (2 H, ABq, J_{AB} 5, β-pyrrolic H); *m*/*z* (EI) 767 (15%), 766 (31), 765 (58), 764 (84), 763 ([^{2}H]M, 100) and 762 ([^{1}H]M, 86).

The reaction between (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]-porphyrinato)nickel(II) 37 and lithium phenoxide

To a refluxing solution of (2-nitro-5,10,15,20-tetraphenyl[3-^{2}H]porphyrinato)nickel(II) **37** (40 mg, 0.056 mmol) in dry, distilled $HCONMe_2$ (20 cm^3) under nitrogen was added lithium phenoxide (35 mg, 0.35 mmol) and the mixture was heated at reflux for 2 h. Upon cooling, the mixture was diluted with dichloromethane (50 cm^3), washed with water (6 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a chromatotron eluted with dichloromethane–light petroleum (1:1) to yield a major, red fraction of (2-phenoxy-5,10,15,20-tetraphenyl-[3-^{2}H]porphyrinato)nickel(II) **40** (80 atom% deuterium, 14 mg, 33%), δ_H(400 MHz; CD_2Cl_2) 6.88–6.93 (2 H, m, 2-H$_o$), 7.04 (1 H, m, 2-H$_p$), 7.20–7.26 (2 H, m, 2-H$_m$), 7.44–7.54 (3 H, m, 20-H$_{m,p}$), 7.58–7.75 (9 H, m, 5-, 10- and 15-H$_{m,p}$), 7.79–7.83 (2 H, m, 20-H$_o$), 7.91–7.98 (2 H, m, 5-H$_o$), 7.79–8.04 (4 H, m, 10- and 15-H$_o$), 8.06 (0.2 H, s, 3-H), 8.64 and 8.69 (2 H, ABq, J_{AB} 5, β-pyrrolic H), 8.66 and 8.73 (2 H, ABq, J_{AB} 5, β-pyrrolic H) and 8.73 (2 H, ABq, J_{AB} 5, β-pyrrolic H); *m*/*z* (EI) 767 (14%), 766 (28), 765 (50), 764 (63), 763 ([^{2}H]M, 100), 762 ([^{1}H]M, 29), 674 (14), 673 (27), 672 (24) and 671 (49).

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