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A Convenient Synthesis of 2-Alkyl-5,10,15,20-tetraphenylporphyrins: Reaction of Metallo-2-nitro-5,10,15,20-tetraphenylporphyrins with Grignard and Organolithium Reagents

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A new synthesis of 2-alkylporphyrins is reported. Treatment of metallo-2-nitro-5,10,15,20-tetraphenylporphyrins (M = Cu, Ni, Zn) **2**–**4** with alkylmagnesium halides affords the corresponding metallo-2-alkyl-5,10,15,20-tetraphenylporphyrins (alkyl = Me, i-Pr, Bu) **6**–**12** in moderate to good yield. The reaction proceeds by initial nucleophilic attack of the Grignard reagent at the β-pyrrolic carbon next to that bearing the nitro group. The intermediate is protonated in workup to generate metallo-2-alkyl-3-nitro-2,3-dihydro-5,10,15,20-tetraphenylporphyrin **5**, which eliminates nitrous acid to give the corresponding 2-alkylporphyrin. The results of deuterium labeling experiments support this mechanism. The use of *tert*-butylmagnesium bromide and phenylmagnesium bromide as reagents does not lead to the corresponding 2-*tert*-butyl- or 2-phenylporphyrins but rather gives products from reductive processes. The reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) (**2**) with *tert*-butylmagnesium bromide results in reductive denitration to give the parent porphyrin **13**, presumably due to elimination of isobutylene and nitrous acid from an intermediate 2-*tert*-butyl-3-nitro-2,3-dihydroporphyrin. Reaction of **2** with phenylmagnesium bromide leads to a complicated mixture of products, the major one being the 2-(phenylamino) derivative **14** which results from reductive arylation of the nitro group. Preliminary studies show that butyllithium also reacts with **2**, but the reaction is difficult to control and a complex mixture of over-reacted products results; in this case, 2-butylporphyrin **10** is at best isolated in 10% yield which compares unfavorably with the 56% yield of **10** from the reaction involving the corresponding Grignard reagent.

In the course of our work on bond orders,[1] electron delocalization pathways, and tautomerism in porphyrin systems,[2,3] a range of 2-alkyl-5,10,15,20-tetraphenylporphyrins were required. While efficient methods for the introduction of a range of functional groups in the β-pyrrolic position of 5,10,15,20-tetraphenylporphyrins have been developed,[4-9] no convenient route for the preparation of 2-alkyl-5,10,15,20-tetraphenylporphyrins was available. The preparation of β-alkyldeuterioporphyrins and *meso*-alkyloctaethylporphyrins has been reported via modification of acyl functionalities.[10-13] The application of these methods to the synthesis of 2-alkyl-5,10,15,20-tetraphenylporphyrins requires a multistep process that is complicated by the additional steric component afforded by the phenyl rings and by the fact that intramolecular Friedel–Crafts acylation and alkylation reactions have been shown to occur readily at the adjacent phenyl ring of 2-formyl- and 2-(hydroxymethyl)-5,10,15,20-tetraphenylporphyrins under acidic conditions.[14,15]

Our observation[16] that metallo-2-nitro-5,10,15,20-tetraphenylporphyrins are converted into 2,3-dihydro-2-nitro-5,10,15,20-tetraphenylporphyrins, in a process involving conjugate addition to the nitro ene, by reaction with borohydride ion followed by aqueous workup, suggested that an analogous route involving organoalkyls might be used to prepare the corresponding 2,3-dihydro-2-alkyl-3-nitroporphyrins. As elimination of nitrous acid from 2,3-dihydro-2-nitro-5,10,15,20-tetraphenylporphyrins is a facile process,[16] it appeared that similar elimination of nitrous acid from a 2,3-dihydro-2-alkyl-3-nitroporphyrin should also occur easily and thus provide a straightforward route to 2-alkylporphyrins. This paper reports the development of such a route to 2-alkyl-5,10,15,20-tetraphenylporphyrins by reaction of readily available metallo-2-nitro-5,10,15,20-tetraphenylporphyrins with Grignard reagents.

Results and Discussion

The reactions of the Grignard reagents RMgX (R = Me, i-Pr, Bu, t-Bu, Ph) and the organolithium reagent butyllithium with (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (**2**),[7,9] -nickel(II) (**3**),[7,9,16] and -zinc(II) (**4**)[9]

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Scheme 1

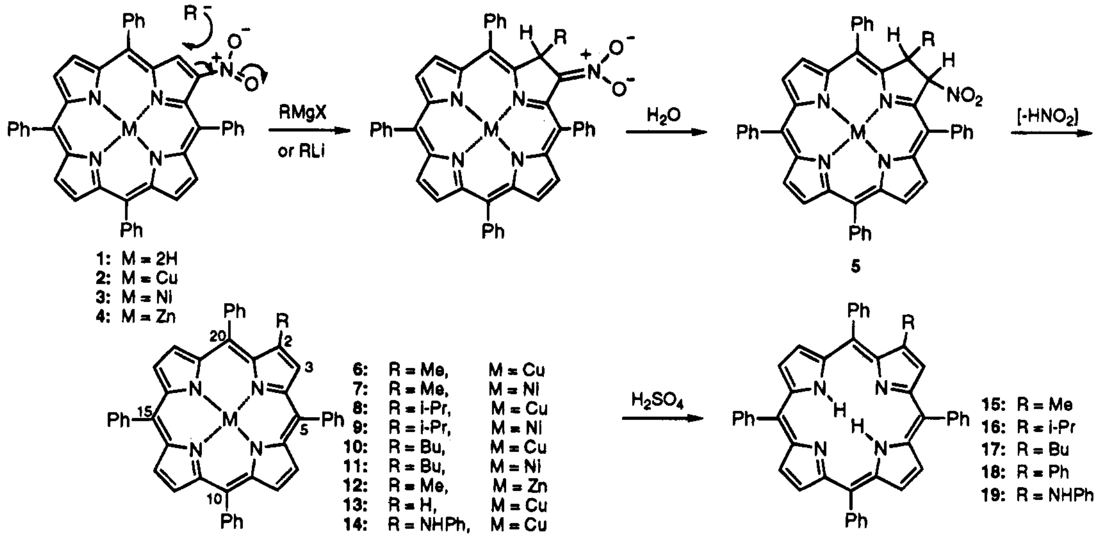

Table 1. Product Formed (Isolated Yield, %) from the Reaction of Metallo-2-nitro-5,10,15,20-tetraphenylporphyrins with Organometallic Reagents

starting porphyrin	organometallic reagent					
M =	MeMgI	i-PrMgI	BuMgI	t-BuMgBr	PhMgBr	BuLi
Cu **2**	**6** (57)	**8** (80)	**10** (56)	**13** (43)[a]	**14** (17)[b]	**10** (10)
Ni **3**	**7** (46)	**9** (23)	**11** (48)			trace
Zn **4**	**12** (41)					

[a] None of the alkylated porphyrin was formed. [b] No C-arylation was observed; see text.

were studied (Scheme 1). The general procedure involved treatment of a THF solution of the metallo-2-nitro-5,10,15,20-tetraphenylporphyrin with an ethereal solution of the alkylmagnesium iodide (or bromide) at room temperature, followed by aqueous quench to give the intermediate 2,3-dihydroporphyrin (chlorin) **5**. In most cases, these compounds were blue green solids and had a strong visible absorption at 650 nm, which is characteristic of a 2,3-dihydroporphyrin.[17] Attempts to purify these compounds on silica led to decomposition to the corresponding metalloporphyrin which was generally red in color.

The results are summarized in Table 1. In the case of reactions involving the methyl, isopropyl, and butyl Grignard reagents, good yields (45–80%) of the corresponding alkylated porphyrins **6**, **7**, **8**, and **10** were obtained, with porphyrin **9** obtained in a lower yield of 23%. Demetalation of these porphyrins afforded the free-base derivatives **15**–**17**. In the case of *tert*-butylmagnesium bromide, the expected 2-*tert*-butylporphyrin was not obtained, and the denitrated product, (5,10,15,20-tetraphenylporphyrinato)copper(II) (**13**), was isolated in 43% yield.

In the case of phenylmagnesium bromide, the reaction with (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**3**) gave variable results but each time resulted in formation of a large number of green products in low overall yield. When 2-nitro-(5,10,15,20-tetraphenylporphyrinato)copper(II) (**2**) was used the reaction gave small quantities of two green compounds which possessed electronic spectra characteristic of chlorins and a small amount (17%) of (2-(phenylamino)-5,10,15,20-tetraphenylporphyrinato)copper(II) (**14**), which was demetalated in 96% yield to give the (phenylamino)porphyrin (**19**). The *N*-arylation/reduction observed in this reaction has been noted previously in the reaction of Grignard reagents with aromatic nitro compounds.[18] The chlorin-like compounds could not be fully identified due to their instability toward demetalation reaction conditions; as the 2-phenylporphyrin (**18**) would be expected to result from loss of nitrous acid from a 3-nitro-2-phenylchlorin under the demetalation conditions but was not found, we conclude that direct C-arylation of the porphyrin nucleus did not occur.

The reactions proved to be extremely sensitive to the reaction conditions. Optimal conditions for the generation of the intermediate **5** were not investigated as varying reaction time or rate of addition of the reagent failed to give reproducible results. Dark green byproducts formed in all reactions, presumably due to further alkylation or from attack at other positions, as well as considerable amounts of base-line material. Structural analysis of these products was not attempted because of the difficulty in obtaining suitable quantities.

The reaction was also performed with butyllithium, to examine the possibility of using other sources of carbanions for the reaction. 2-Butyl-5,10,15,20-tetraphenylporphyrin (**17**) was prepared via the copper(II) derivative **10** although in reduced yield (10%) compared with the Grignard reactions (Table 1). The reaction was more difficult to control using BuLi, although the reaction pathway appeared similar to that occurring in the Grignard reaction, i.e, the initial formation of a blue green adduct which decomposed on silica to afford the alkylporphyrin. The alkylated porphyrin **11** was detected only in trace amounts in the reaction of butyllithium with (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**3**).

Effect of the Central Metal Ion. Reactions were carried out on metalloporphyrins **2-4** in order to avoid deactivation of the ring system toward nucleophilic attack that would be caused by deprotonation of the inner nitrogens in the free-base porphyrin. Chelated electronegative metal ions have also been shown to direct attack of nucleophiles away from the meso-position of porphyrins and toward the β-pyrrolic positions.[9] Copper(II) has

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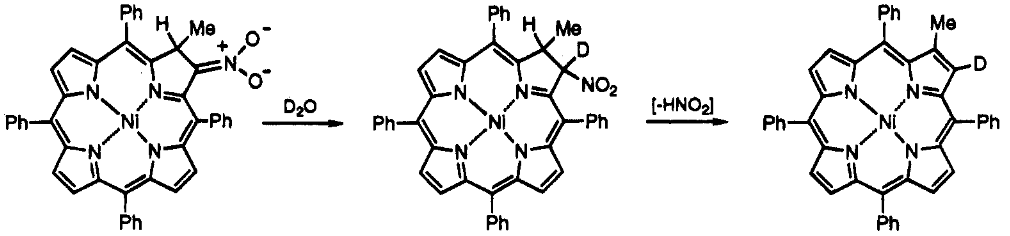
Scheme 2



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been shown to be the metal ion of choice in this respect and has the further advantage of being readily removed. Several reactions were carried out on the corresponding nickel and zinc porphyrins to enable NMR studies to be carried out and to investigate the generality of these reactions.

The reaction with Grignard reagents with the copper nitroporphyrin **2** gave better yields of alkylporphyrins than corresponding reactions with the nickel nitroporphyrin **3**. The difference was especially pronounced when isopropylmagnesium iodide was used with an 80% yield of isopropylporphyrin **8** being obtained from **2** while only 23% of the corresponding isopropylporphyrin **9** was obtained from **3**. As nickel directs substitution to the β-position,[9] it is unlikely that the poor yield is due to products formed by alkylation of the meso-positions. Compared to copper(II) porphyrins, nickel(II) porphyrins are somewhat buckled in shape due to the size and properties of the nickel(II) ion. The reduced yield may be a result of the combined increase in strain that occurs, due to both the steric size of the isopropyl group and the buttressing that is present in nickel(II) porphyrins, that prevents easy attack of the nucleophile.

Nickel alkylporphyrins also proved more difficult to demetalate cleanly than the corresponding copper chelates. Treatment of the copper methyl-, isopropyl-, and butylporphyrins **6**, **8**, and **10** with sulfuric acid gave the corresponding free-base alkylporphyrins **15**, **16**, and **17** in quantitative yield in each case. Demetalation of the corresponding nickel chelates **7**, **9**, and **11** with sulfuric acid gave the corresponding free-base alkylporphyrins **15**, **16**, and **17** in 66%, 64%, and 70% yield, respectively.

The reaction of methylmagnesium iodide with (2-nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II) (**4**) and subsequent demetalation gave the corresponding methylporphyrin **12**, but in poor yield. This is not surprising, as significant attack at the meso-positions leading to ring-opened products is expected. These results confirm our previous general conclusions regarding the use of the central metal ion to direct reaction to either the meso- or the β-position.

Mechanism of the Reaction. The alkylporphyrins obtained in this work are consistent with initial nucleophilic addition of the Grignard at the β-carbon adjacent to that bearing the nitro group, to give the intermediate chlorin **5**, which, in contact with silica, eliminates nitrous acid to yield the monoalkylated porphyrin (Scheme 1). The proposed intermediate **5** has UV absorbance characteristic of chlorins. The rapid elimination of nitrous acid from chlorin intermediates such as **5** has been observed previously in several related reactions involving nitrochlorins.[8,16] This process also has precedence in other systems; elimination of nitrous acid from nitroalkanes has been shown to proceed via an antiperiplanar transition state[19] and has also been observed in the reactions of alkyl-Grignard reagents on aromatic nitro compounds.[20]

Support for the proposed mechanism was obtained by deuterium labeling experiments. Quenching the reaction between methylmagnesium iodide and (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**3**) with deuterium oxide gave, after treatment with silica, (2-methyl-3-deuterio-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**20**) (Scheme 2), conclusive evidence that α attack is involved. The proton NMR spectrum of the intermediate from this reaction, compared with the NMR from normal aqueous quench, showed the absence of a proton signal at δ 6.23, assigned as being H 17, geminal to the nitro group. A doublet due to the methyl group at C 18 (δ 1.20, J = 7.2 Hz), and a quartet due to H 18, the proton geminal to the methyl (δ 4.86, J = 7.2 Hz), were clearly visible in both spectra. The absence of coupling between H 17 and H 18 indicates the *trans* arrangement of the protons. Similar systems have been described previously.[16]

Reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (**2**) with *tert*-butylmagnesium bromide produced a blue-green intermediate identified as a chlorin by its visible spectrum. Passage through silica gave the unalkylated, denitrated product, (5,10,15,20-tetraphenylporphyrinato)copper(II) (**13**). The initial adduct in the reaction is sterically very congested, and elimination of isobutylene and nitrous acid is consistent with formation of the denitrated product. Alternatively, the initial product of the reaction may have been the chlorin (2,3-dihydro-2-nitro-5,10,15,20-tetraphenylporphyrin)copper(II) which was oxidized on silica treatment. Such an intermediate could arise via a single electron transfer (SET) pathway leading to a porphyrin radical anion, followed by loss of nitrite ion, and radical capture. This reaction has been observed in the denitration of *meso*- and β-nitroporphyrins,[21] and may occur as the result of the steric impediment associated with attack by the *tert*-butyl carbanion. The reaction of Grignard reagents with aromatic ketones proceeds at least in part through a SET pathway.[22,23] Formation of nitronate adducts from the conjugate addition of Grignards to mononitroarenic systems has been reported,[24-26] and there is evidence for a single electron transfer mechanism in the 1,6-conjugate addition of 5-hexynylmagnesium bromide to 2-methoxy-

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1-nitronaphthalene where at least 36% of the products arise by a SET mechanism.[27] However, this mechanism is unlikely in the reaction outlined above, given the absence of any denitrated porphyrin in the other Grignard reactions.

Conclusion

The addition of alkylmagnesium halides to the copper(II) and nickel(II) chelates of 2-nitro-5,10,15,20-tetraphenylporphyrins provides direct entry to 2-alkyl-5,10,15,20-tetraphenylporphyrins. From the systems studied, the reaction appears to proceed by nucleophilic attack of the Grignard reagent on the β-pyrrolic carbon α to that bearing the nitro group. The intermediate chlorin, which possesses trans geometry about the saturated bond, is unstable to silica and eliminates nitrous acid to regenerate the fully delocalized alkylporphyrin.

Experimental Section

General experimental and instrument details are the same as those reported previously.[16] High-resolution mass spectra were determined with a Kratos MS902 mass spectrometer with a double-focusing magnet using a VG Micromass 3D8 data handling system.

Porphyrins **2**, **3**, and **4** were prepared by the literature methods.[7,9,16,28]

General Procedure for Demetalation of Porphyrins. A chloroform solution of the porphyrin (*ca.* 10 mg/100 mL) was added to sulfuric acid (18 M, 1 mL/10 mL of solution) and vigorously stirred for 2–3 min. The mixture was poured onto ice and extracted with chloroform. The combined organic extracts were washed with a saturated solution of sodium hydrogen carbonate and water and dried over sodium sulfate and the solvent removed to give the free base porphyrin. Occasionally it was necessary to filter the product through a small amount of silica to remove base-line material.

2-Methyl-5,10,15,20-tetraphenylporphyrin (15). Method A: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (2). Porphyrin **2** (893 mg, 1.24 mmol) in dry THF (800 mL) was treated with a freshly prepared ethereal solution of methylmagnesium iodide (0.5 M) until no starting material remained by TLC. The mixture was diluted with water, the product extracted into ether and dried over sodium sulfate, and the solvent removed. TLC showed the presence of a blue band (R_f 0.6) and a less polar red band (R_f 0.8). Chromatography (dichloromethane/light petroleum (1:1)) resulted in conversion of the blue band to the red band. The red band was collected, the solvent removed, and the residue recrystallized from dichloromethane/pentane to yield (2-methyl-5,10,15,20-tetraphenylporphyrinato)copper(II) (**6**) (485 mg, 57%) as a red powder: mp > 300 °C; UV λ_{max} (log ϵ) 411 (5.52), 541 (4.10), 577 (3.21) nm; MS *m/z* 691 (17), 689 (29), 677 (10), 675 (17), 57 (100). Anal. Calcd for $C_{45}H_{30}N_4Cu$: C, 78.3; H, 4.4; N, 8.1. Found: C, 78.4; H, 4.2; N, 7.9.

Demetalation of **6** afforded the crude free base porphyrin quantitatively. Recrystallization from dichloromethane/pentane gave 2-methyl-5,10,15,20-tetraphenylporphyrin (**15**) as shiny purple crystals: mp > 300 °C; IR υ_{max} 1600, 1730, 2855, 2940 cm^{-1}; UV λ_{max} (log ϵ) 417 (5.61), 519 (5.22), 552 (4.68), 591 (4.57), 648 (4.47) nm; MS *m/z* 628 (M$^+$, 100), 314 (10), 149 (21); ^{1}H NMR δ -2.89 (bs, 2H), 2.58 (d, 3H, J = 1.2 Hz), 7.68–7.80 (m, 12H), 8.07 (m, 2H), 8.18–8.24 (m, 6H), 8.61 (q, 1H, J = 1.2 Hz), 8.63 and 8.75 (ABq, 2H, J = 4.8 Hz), 8.75 and 8.80 (ABq, 2H, J = 4.8 Hz), 8.85 and 8.87 (ABq, 2H, J = 4.9 Hz). Anal. Calcd for $C_{45}H_{32}N_4$: C, 86.0; H, 5.1; N, 8.9. Found: C, 86.0; H, 5.5; N, 8.4.

Method B: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (3). Treatment of porphyrin **3** (200 mg, 0.28 mmol)) with an ethereal solution of methylmagnesium iodide and workup as above gave (2-methyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**7**) (89 mg, 46%) as a red powder: mp > 300 °C; UV λ_{max} (log ϵ) 417 (5.34), 530 (4.16) nm; ^{1}H NMR δ 2.39 (d, 3H, J = 1.2 Hz), 7.59-7.69 (m, 12H), 7.85 (m, 2H), 7.94–8.01 (m, 6H), 8.44 (q, 1H, J = 1.2 Hz), 8.66–8.75 (m, 6H); MS *m/z* 684 (M$^+$, ^{58}Ni, 100), 670 (11), 606 (10), 77 (16). Porphyrin **7** (10 mg) was demetalated to give **15** (6 mg, 66%), spectroscopically and chromatographically identical with that obtained in method A.

Method C: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II) (4). Treatment of porphyrin **4** (50 mg) with ethereal methylmagnesium iodide and workup as above gave (2-methyl-5,10,15,20-tetraphenylporphyrinato)zinc(II) (**12**) (19.5 mg, 41%) as a red powder: mp > 300 °C. The porphyrin **12** (10 mg) was demetalated to give **15** (5.4 mg, 59%), spectroscopically and chromatographically identical with that obtained by method A.

(2-Methyl-3-deuterio-5,10,15,20-tetraphenylporphyrinato)nickel(II) (20). Treatment of porphyrin **3** (50 mg) with an ethereal solution of methylmagnesium iodide followed by quenching with deuterium oxide and workup as in method A above gave (2-methyl-3-deuterio-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**20**) (20 mg, 40%) as a red powder: mp > 300 °C; UV λ_{max} (log ϵ) 417 (5.34), 530 (4.16) nm; ^{1}H NMR δ 2.39 (s, 3H), 7.59–7.69 (m, 12H), 7.85 (m, 2H), 7.94–8.01 (m, 6H), 8.66–8.75 (m, 6H); MS *m/z* 685 (M$^+$, ^{58}Ni, 100), 671 (8), 607 (11). The material was chromatographically identical with the nonlabeled analog **7** obtained in method B above.

2-Isopropyl-5,10,15,20-tetraphenylporphyrin (16). Method A: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (2). Porphyrin **2** (147 mg, 0.20 mmol) in dry THF (80 mL) was treated with a freshly prepared ethereal solution of isopropylmagnesium bromide (0.4 M) until no starting material remained. The mixture was diluted with water, the product extracted into ether and dried over sodium sulfate, and the solvent removed. TLC showed the presence of a blue band and a less polar red band. Chromatography on silica (dichloromethane/light petroleum (2:3)) resulted in conversion of the blue band to the red band. The red product was collected and recrystallized from dichloromethane/pentane to yield (2-isopropyl-5,10,15,20-tetraphenylporphyrinato)copper(II) (**8**) (117 mg, 80%) as a fine red powder: mp > 300 °C; IR υ_{max} 1000 s, 1065 sh, 1250, 1355 w, 1440 w, 1590 cm^{-1}; UV λ_{max} (log ϵ) 416 (5.62), 540 (4.24) nm; MS *m/z* 717 (M$^+$, 100), 702 (13), 687 (16), 610 (26). Demetalation afforded the free-base porphyrin quantitatively. Recrystallization from hexane gave 2-isopropyl-5,10,15,20-tetraphenylporphyrin (**16**) as shiny purple rhomboids: mp > 300 °C; IR υ_{max} 965 s, 990, 1180, 1350, 1445, 1465, 1600 cm^{-1}; UV λ_{max} (log ϵ) 419 (5.63), 516 (4.25), 551 (3.77), 590 (3.74), 644 (3.51) nm; ^{1}H NMR δ −2.90 (bs, 2H), 1.37, 1.39 (2s, 6H), 3.11 (septet, 1H, J = 6.7 Hz), 7.69–7.83 (m, 12H), 8.17 (m, 2H), 8.22 (m, 6H), 8.61 and 8.73 (ABq, 2H, J = 4.7 Hz), 8.73 and 8.79 (ABq, 2H, J_{AB} 4.7 Hz), 8.78 (s, 1H), 8.88 and 8.90 (ABq, 2H, J = 4.6 Hz); MS *m/z* 656 (M$^+$, 100), 641 (8), 627 (14), 613 (9). Anal. Calcd for $C_{47}H_{30}N_4$: C, 86.0; H, 5.5; N, 8.5. Found: C, 85.8; H, 5.4; N, 8.5.

Method B: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (3). Treatment of porphyrin **3** (100 mg, 0.14 mmol) with isopropylmagnesium iodide as above gave (2-isopropyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**9**) (23 mg, 23%) as a red powder: mp > 300 °C; IR υ_{max} 1009, 1074, 1347, 1523, 3016 cm^{-1}; UV λ_{max} (log ϵ) 418 (5.33), 533 (4.13) nm; ^{1}H NMR δ 1.15 (d, 6H, J = 6.7 Hz), 2.95 (septet, 1H, J = 6.7 Hz), 7.50–7.77 (m, 12H), 7.88–8.05 (m, 8H), 8.53–8.75 (m, 7H); MS *m/z* 712 (M$^+$, 100), 670 (28), 605 (26), 302 (21). The porphyrin **9** (12 mg) was demetalated to give 2-isopropyl-5,-10,15,20-tetraphenylporphyrin (**16**) (7 mg, 64%) as a red powder with spectroscopic and chromatographic properties identical to the sample prepared by method A.

2-Butyl-5,10,15,20-tetraphenylporphyrin (17). Method A: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (2) by Reaction with BuMgBr. Porphyrin **2** (20 mg, 0.03 mmol) in dry THF (50 mL) was treated with a freshly

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prepared ethereal solution of butylmagnesium iodide (0.5 M) until no starting material remained by TLC. The mixture was diluted with water, the product extracted into chloroform and dried over sodium sulfate, and the solvent removed. Chromatography (dichloromethane/light petroleum (1:1)) gave a red band which yielded (2-butyl-5,10,15,20-tetraphenylporphyrinato)copper(II) (**10**) (11 mg, 56%) as an amorphous red solid: mp > 300 °C; UV λ_{max} (log ϵ) 416 (5.59), 540 (4.23), 618 (3.20) nm; MS (relative intensity) *m/z* 731 (M^+, 100), 689 (16), 675 (12), 610 (24), 539 (20). Demetalation of porphyrin **10** afforded the free-base porphyrin quantitatively. Recrystallization from methanol gave 2-butyl-5,10,15,20-tetraphenylporphyrin (**17**) as fine purple crystals: mp > 300 °C; UV λ_{max} (log ϵ) 418 (5.50), 515 (4.15), 550 (3.67), 588 (3.64), 644 (3.45) nm; ^{1}H NMR δ −2.80 (bs, 2H), 0.84 (t, 3H, $J = 7.4$ Hz), 1.25 (m, 2H), 1.75 (m, 2H), 2.82 (m, 2H), 7.65−7.78 (m, 12H), 8.08 (m, 2H), 8.17−8.22 (m, 6H), 8.59 and 8.71 (ABq, 2H, $J = 4.8$ Hz), 8.62 (bs, 1H), 8.71 and 8.77 (ABq, 2H, J_{AB} 4.8 Hz), 8.83 and 8.85 (ABq, 2H, $J = 5.0$ Hz); MS *m/z* 670 (M^+, 100), 627 (15), 614 (30). Anal. Calcd for $C_{48}H_{38}N_4$: C, 85.9; H, 5.7; N, 8.4. Found: C, 85.6; H, 5.8; N, 8.0.

Method B: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (2) by Reaction with BuLi. Porphyrin **2** (300 mg, 0.42 mmol) in dry THF (100 mL) was stirred under nitrogen. Butyllithium (1.6 M solution in hexane, 0.3 mL) was added at approximately 3-h intervals until no starting material remained. The mixture was diluted with water, the product extracted into ether and dried over sodium sulfate, and the solvent removed. Chromatography (dichloromethane/light petroleum (1:3)) afforded **10** (31 mg, 10%) as an amorphous red solid with spectroscopic and chromatographic properties identical to the sample prepared by method A. Demetalation of porphyrin **10** gave a quantitative yield of the free-base porphyrin **17** with identical spectroscopic and chromatographic properties to the sample prepared by method A.

Method C: From (2-Nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (3). Treatment of porphyrin **3** (100 mg, 0.14 mmol) with ethereal butylmagnesium iodide followed by the usual workup gave (2-butyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) (**11**) (49 mg, 48%) as a red powder: mp > 300 °C; IR v_{max} 1009, 1074, 1220, 1350, 2926 cm^{-1}; UV λ_{max} (log ϵ) 417 (5.30), 532 (4.14) nm; ^{1}H NMR δ 0.82 (t, 3H, $J = 7.2$ Hz), 1.20 (m, 2H), 1.68 (m, 2H), 2.69 (m, 2H), 7.54−7.67 (m, 12H), 7.85 (m, 2H) 7.95−8.00 (m, 6H), 8.49 (bs, 1H), 8.64−8.70 (m, 6H); MS *m/z* 726 (M^+, 100), 683 (26), 670 (13), 605 (36), 301 (32), 77 (13). Demetalation of **11** gave 2-butyl-5,10,15,20-tetraphenylporphyrin (**17**) as a red powder in quantitative yield, mp > 300 °C, with spectroscopic and chromatographic properties identical to the compound prepared in method A.

2-(Phenylamino)-5,10,15,20-tetraphenylporphyrin (19). (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (**2**) (131 mg, 0.18 mmol) in dry THF (100 mL) was treated with a freshly prepared ethereal solution of phenylmagnesium bromide (0.4 M) until no starting material remained by TLC. The mixture was diluted with water, the product extracted into dichloromethane and dried over sodium sulfate, and the solvent removed. Chromatography of the residue on silica (dichloromethane/light petroleum (1:1)) afforded (2-(phenylamino)-5,10,15,20-tetraphenylporphyrinato)copper(II) (**14**) (23 mg, 0.03 mmol, 17%) as a purple solid: mp > 300 °C; IR v_{max} 979, 1029, 1363, 3450 cm^{-1}; UV λ_{max} (log ϵ) 405 (5.13), 548 (4.05), 582 (3.99), 600 sh (3.83) nm; MS *m/z* 766 (M^+, 100); HRMS calcd for $C_{50}H_{33}N_5Cu$ requires 766.2032, found 766.2029 ($\pm 3\sigma$). Demetalation of **14** (18 mg, 0.023 mmol) using standard conditions afforded 2-(phenylamino)-5,10,15,20-tetraphenylporphyrin (**19**) (16 mg, 97%) as a purple solid: mp > 300 °C; UV λ_{max} (log ϵ) 410 (5.30), 447 (4.76), 528 (4.23), 570 (3.92), 600 (3.90), 656 (3.60) nm; ^{1}H NMR δ −2.57 (bs, 1H), −2.05 (bs, 1H), 6.60 (s, 1H), 6.94 (t, 1H, $J = 7.0$ Hz), 7.02 (d, 2H, $J = 7.0$ Hz), 7.28 (t, 2H, $J = 7.0$ Hz), 7.70−7.78, 7.80−7.93, 8.15−8.20 (m, m and m, 20H), 8.28 (s, 1H), 8.55−8.81 (m, 6H); MS *m/z* 705 (M^+, 90), 704 (100); HRMS calcd for $C_{50}H_{35}N_5$ requires 705.2892, found 705.2886 ($\pm 3\sigma$). Anal. Calcd for $C_{50}H_{35}N_5$: C, 85.1; H, 5.0; N, 9.9. Found: C, 84.7; H, 4.8; N, 9.7.

Reductive Denitration of (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) (2) with t-BuMgBr. Porphyrin **2** (130 mg, 0.18 mmol) in dry THF (200 mL) was treated with a freshly prepared ethereal solution of *tert*-butylmagnesium bromide (0.4 M, 2 mL) and stirred under nitrogen for 4 h, before more Grignard solution was added, the reaction stirred for 12 h and quenched with water, the product extracted into ether and dried over sodium sulfate, and the solvent removed. Chromatography (dichloromethane/light petroleum (1:1)) resulted in conversion to a red product which was collected and recrystallized from dichloromethane/pentane to yield (5,10,15,20-tetraphenylporphyrinato)copper(II) (**13**) (52 mg, 43%) as a red powder, with spectroscopic and chromatographic properties identical to those of an authentic sample.

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