Tetrahedron Vol. 46, No. 15, pp. 5253-5262, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

UNEXPECTED ROUTES TO NAPHTOPORPHYRIN DERIVATIVES

H.J. Callot*, E. Schaeffer,[1a] R. Cromer[1b] and F. Metz.[1c]

Laboratoire de Chimie Organique des Substances Naturelles (U.A. 31 du C.N.R.S.), Département de Chimie, Université Louis Pasteur, 1, rue Blaise Pascal, 67008 Strasbourg, France.

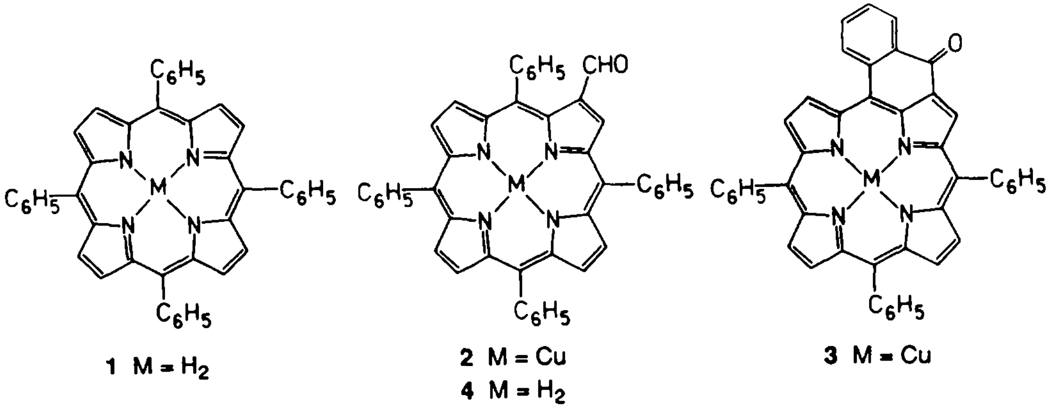
(*Received in France* 7 *May* 1990)

Abstract: Substituted α-styrylcobalt(III)tetraphenylporphyrins rearrange to naphto(*a,t*)porphyrin derivatives, one carbon atom of the styryl fragment being bound to a pyrrolic position and an *ortho* carbon atom of a vicinal phenyl group. This unexpected result led us to reinvestigate the acid-catalyzed cyclization of 2-formyltetraphenylporphyrins, which produces the same naphtoporphyrin framework.

INTRODUCTION

The most widely used models for natural porphyrins are the *meso*-tetraarylporphyrins.[2] They are easily prepared, usually in a single step, and, due to their inertness, their aryl substituents do not interfere with reactions performed at other sites, pyrrolic positions or central metal. A variety of simple tetraarylporphyrins substituted at the pyrrolic β positions, have also been prepared in order to study the possibility of side-chain extension,[3] redox potentials variations,[4] N-H tautomerism,[5] reactivity of the macrocycle as a function of the central metal,[7] etc. Despite the fact that the phenyl groups of H_2TPP **1** or its metal complexes and the substituents of the pyrrolic positions are in *peri* situation, which implies very short distances,[7] only one example of reaction between these groups appeared in the literature.[8] This reaction involved 2-formylTPP copper complex **2** (M = Cu) (Scheme 1), a product which is a useful intermediate for the extension of functionalized side-chains.[3] An acid catalyzed condensation of an aldehyde with the vicinal phenyl group produced, in very low yield, an additional six-membered ring containing a keto group. The structure of this naphtoporphyrin derivative **3** (M = Cu) was confirmed by an X-ray diffraction study.[8] The same reaction was observed during an attempted demetallation of the nickel complex of the same aldehyde but the products were not fully characterized.[6] It is interesting to note that the corresponding free-base, 2-formyl-*meso*-tetraphenylporphyrin **4** (M = H_2), could be obtained upon acid treatment of either the aldehyde iron(III) complex[3d] or an intermediate iminium salt[9,3a] (in all cases the formyl group was introduced by a Vilsmeier reaction).

In this article we first describe an experiment, starting with a styrylcobalt(III)porphyrin, which led to the formation of an additional six-membered ring followed by a necessary reinvestigation of the cyclization of 2-formyl-*meso*-tetraphenylporphyrin metal complexes, in order to confirm our structural hypotheses. In the light of these results and a few complementary reactions, the mechanism of the styrylcobalt(III)porphyrin rearrangement will then be discussed.



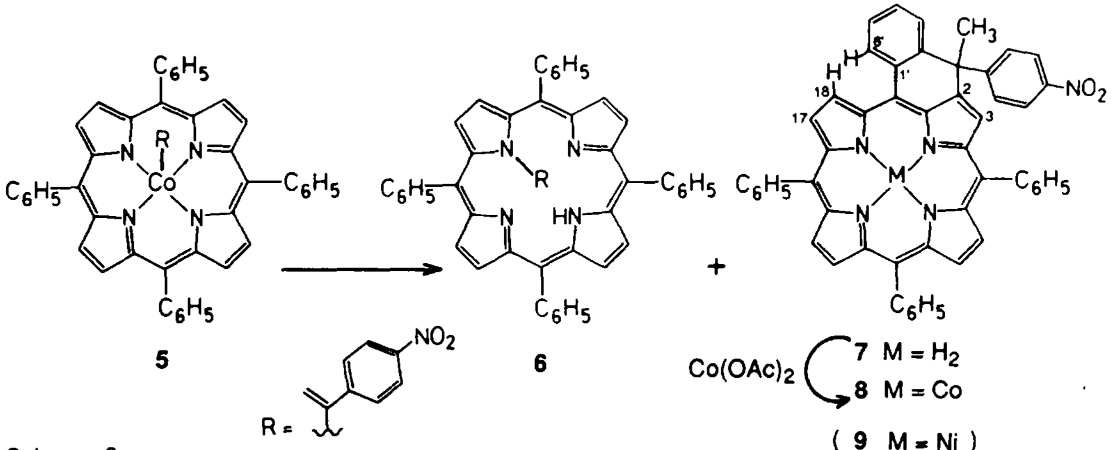
Scheme 1

RESULTS AND DISCUSSION.

Solution rearrangements of *p*-nitrostyrylcobalt(III)TPP 5 .

When *p*-nitrostyrylcobalt(III)TPP **5** was treated, in the presence of oxygen, with trifluoroacetic acid (TFA) in large excess, the green "normal" product **6** was produced, according to the well-documented metal - pyrrolic nitrogen migration reaction.[10,11] However, on decreasing the amount of TFA (from > 25×10^3 to $\leq 5 \times 10^3$ mol / mol of porphyrin) the complexity of the resulting mixture increased and two additional products, violet **7** and reddish-brown **8**, were isolated (Scheme 2). The relative proportions of the products seemed to be very sensitive to the acid concentration and the timing of the reaction (acid addition rate, reaction time, neutralization step). Similar results were also observed using the *p*-acetyl- and *m*-nitrostyrylcobalt(III)TPP's as starting materials.[11]

Compound **7** is a typical free-base porphyrin as shown by its spectral data: multiple long-wavelength visible absorptions, highly shielded N-H NMR signal. The absence of N-substituent was demonstrated by the position of the visible absorptions, the low basicity of the product and the absence of any high-field aromatic or olefinic signal. Of interest were the abnormal shift measured for proton H-C-18 (9.74 ppm) and the spreading of the signals from one *meso*-phenyl group (see experi-



Scheme 2

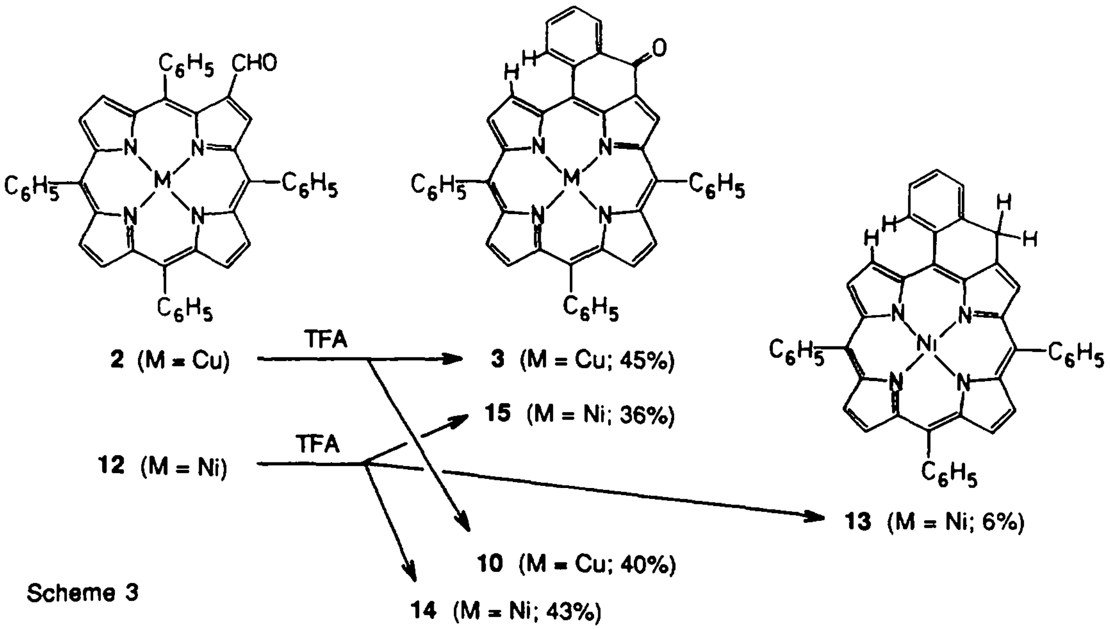
mental section for the full assignments). The only structural hypothesis compatible with the spectral and analytical data was **7**, where the linkage between phenyl and pyrrole units forces a quasi-flat geometry as in **3**. The unsubstituted pyrrole next to the modified phenyl group is now in the deshielding region induced by the phenyl and H-18 will experience the largest effect (*ca* 0.9 ppm in both **7** and the corresponding nickel(II) complex **9**).

Compound **8** showed an unresolved and shifted set of NMR resonances characteristic for a paramagnetic complex. Its polarity and mass spectral data suggested structure **8** and the metallation of **7** with cobalt(II) acetate confirmed this hypothesis.

Cyclization of 2-formylTPP's.

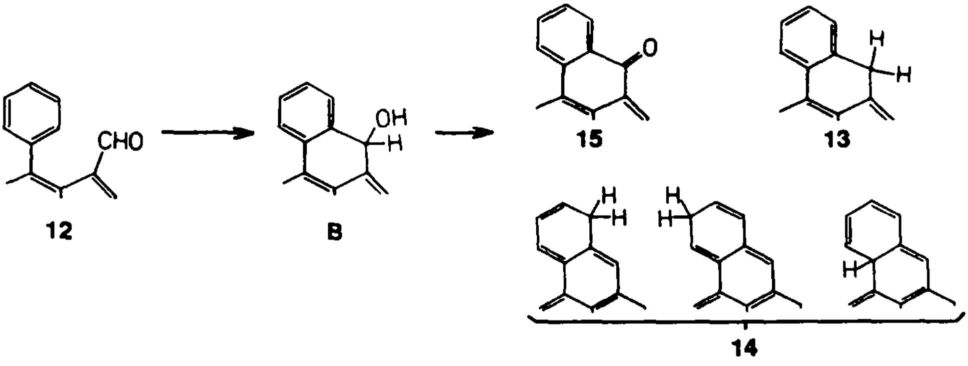
At this stage a comparison with the spectral data of the products derived from aldehyde **2** was necessary. However the literature[8] was not of much help since: (a) only the paramagnetic copper complex **3** was characterized, (b) the yield of the cyclization step was despairingly low (0.1%!)

We first repeated the **2** → **3** reaction. In fact, not only did ketone **3** form when **2** was dissolved in CH_2Cl_2 / TFA but its yield was good (45% after 1 h at 20°C) and it was accompanied by a fraction **10** of lower polarity (40%). Ketone **3** was demetallated in H_2SO_4 into the corresponding free-base **11** whose NMR data confirmed the effect of the cyclization (*ca* 0.6 ppm deshielding of the pyrrolic H-18 adjacent to the modified phenyl ring). The composition of **10** corresponds to **2** - 1 oxygen atom. Attempted demetallation of **10** led to extensive decomposition.



Scheme 3

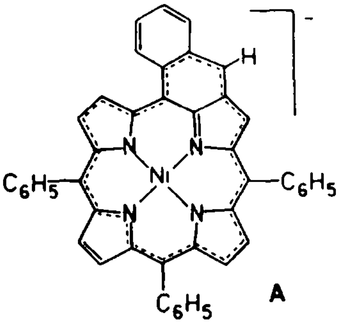
To obtain NMR informations about the primary cyclization products we replaced paramagnetic copper(II) by nickel(II) and treated similarly aldehyde **12** with TFA. We now obtained three fractions: red **13** and olive-green **14** followed by the more polar green ketone **15** (total yield **13** + **14** + **15** *ca* 75-77%) (Scheme 3). Ketone **15** was prepared independently from the reaction of **11** with Ni(acac)$_2$. The structure of **13**, whose composition corresponded to (**12** - 1 oxygen atom) was deduced from its NMR spectrum which was very similar to that of **7** and its nickel(II) complex **9**.



Scheme 4: Dismutation of hypothetical intermediate alcohol **B** (shown in the nickel complex series).

The nature of **14** (and by consequence that of the similar product **10**), could not be fully clarified. Its NMR spectrum is complex and points to a mixture of 3 isomeric products. Several signals appear in the 5-7 ppm olefinic range (J = 7-10Hz) indicating dearomatization of a phenyl ring. Some hypothetical structures are displayed in Scheme 4.

When left in the presence of air, either in solution or adsorbed on silicagel, both **13** and **14** slowly transformed into ketone **15**. Base treatment (triethylamine; pyridine was not basic enough) of **13** gave a blue-green solution (strong absorption at 666 nm, in addition to the Soret band), believed to be that of 22π (or 26π, *via* the modified phenyl group) anion **A**.



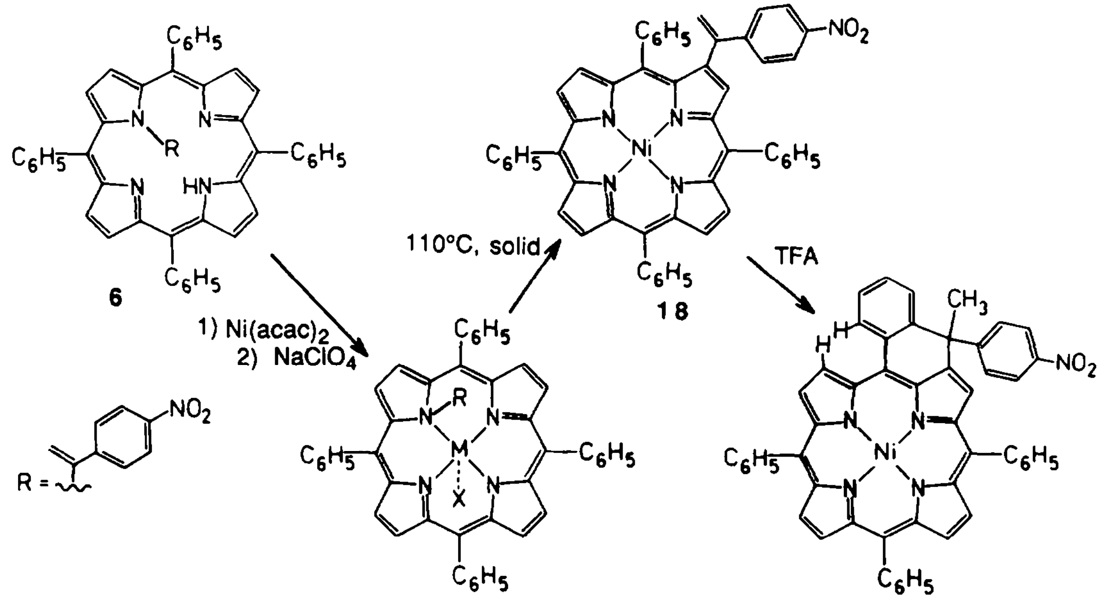
A

The first step of the cyclization of 2-formylTPP's can be seen as an electrophilic attack of the protonated carbonyl group on the vicinal phenyl. The resulting alcool **B** suffers a dismutation which gives ketone **15** and reduced products **13** and **14** (Scheme 4). The fact that the reduced products are found mostly in the form of the isomeric mixture **14** illustrates the dramatic H...H interaction in **13**, and suggests that the reduction step occurs at several sites of an intermediate delocalized cation, the loss in aromaticity being compensated by the loss of the H...H interaction.

Nature of the 5 → 7 transformation; solid state results.

In the presence of TFA and air, alkyl- and arylcobalt(III)porphyrins are oxidized into the corresponding π-cation-radicals which suffer a reductive elimination followed by demetallation to N-substituted porphyrins like **6**.[10b] The nature of the oxidizing species is still unknown but its "efficiency" is dependent on the acid nature and concentration (for example the reaction was slowed down when TFA was replaced by trichloroacetic acid). At low acid concentration there will remain, for some time, large amounts of untouched and electron-rich starting material **5** which might react with either the cation-radical or one of its cleavage products like an α-styryl radical or cation (the rearrangement yield never exceeded 40-45%, the balance being cleavage products H_2TPP **1** and the corresponding cobalt complex). A transfer of the styryl fragment to the pyrrolic β-carbon would result in an olefinic intermediate able to undergo Friedel-Crafts reaction with the adjacent phenyl group. The metal is partially lost, as expected under acidic conditions, to yield free base **7** in addition to **8**.

A strong support in favor of this interpretation was obtained fortuitously when we studied a series of related nickel(II) complexes (Scheme 5). Base **6** was metallated with nickel(II) acetate to the



Scheme 5

16 M = Ni, X = ClO$_4$
(CoCl complex = **19**)

cationic complex **16**, which was accidentally heated in the crystalline state at 110° for 120h. The resulting product was a mixture which consisted in NiTPP **17** (71%) and a pyrrole substituted nickel-porphyrin **18** (29%). When run in solution the same reaction gave very little **18** (< 5%) and NiTPP **17** (> 90%). Under similar conditions, solid and solution, the corresponding cobalt(II) complex **19** was stable. We suggest that the tendency of nickel(II) to favor a square planar environment, when inserted in a porphyrin core (and perhaps a different packing geometry for **16** *vs* **19** in the crystals) may be the driving force of the reaction. The expulsion of the styryl group as an electrophilic species (cation or radical ?) is then followed, inside the crystal, by an efficient trapping at a reactive pyrrolic position. This proximity effect does not exist in solution explaining the yield drop. A similar solid / solution effect was observed earlier when an acetic chain followed the same route .[13] The NMR data for **18** illustrate the *peri* interaction between the *p*-nitrostyryl group and the vicinal *meso*-phenyl group: the rotation of both groups is blocked and the phenyl is maintained in an orientation perpendicular to the macrocycle. The protons of the unsubstituted pyrrole experience the full shielding effect of the aromatic ring. This effect is virtually symmetrical - with regard to the normal resonance position of the pyrrolic protons - to that observed for **7**, **13**, **15** or similar cyclized compounds.

The last step of the correlation consisted in an acid treatment (TFA) which gave the cyclized nickel porphyrin **9**. The same compound was obtained when **7** was metallated with Ni(acac)$_2$. Alternatively, under more vigorous conditions (H_2SO_4), **18** was directly transformed into **7**.

EXPERIMENTAL SECTION

Nmr spectra were obtained in $CHCl_3$ at 200MHz and 400MHz on Bruker WP-200 SY and Bruker AM 400 respectively. Chemical shifts are expressed in ppm (δ) from TMS internal standard. Coupling constants of pyrrolic and aromatic (phenyl) protons are in the normal 5 or 8 Hz range and will not be specified. Visible spectra were taken in CH_2Cl_2 on a Hewlett-Packard 8451 A spectophotometer. Mass spectra were recorded on Thomson-Houston THN 208 or LKB 9000 S spectrometers (70 eV, direct inlet unless otherwise specified). Elemental analyses were performed by the "Service de Microanalyse de l'Institut de Chimie de Strasbourg". Chromatographic separations were obtained using Merck 60 (70-230 or 230-400 mesh) silicagel or Merck alumina 90 columns. Reactions were followed by using Merck F-250 silicagel TLC plates. Yields are for crystallized products.

Acid treatment of *p*-nitrostyrylcobalt(III)TPP 5.

To a solution of **5**[14] (200 mg) in CH_2Cl_2 (5 mL) was added dropwise TFA (0.5 mL over 1 min). The red solution turned green and after 5 min it was poured into a large excess aqueous ammonium carbonate. The aqueous phase was extracted (CH_2Cl_2) and the organic phase dried (Na_2SO_4) and evaporated. Chromatography on silicagel (eluent hexane + increasing % toluene) gave successively some CoTPP and H_2TPP, followed by brownish-red **8** (59 mg; 29%; crystallized from CH_2Cl_2-MeOH) and violet **7** (36 mg; 20%; crystallized from CH_2Cl_2-MeOH). Further elution with CH_2Cl_2-MeOH gave green **6**[10b] (37 mg; 20%; crystallized from CH_2Cl_2-MeOH containing a few drops NEt_3).

7: ^{1}H NMR 9.74 and 9.03 (2 x1H, 2d AB, resp. H-C-18 and H-C-17), 8.9-8.8 (4H, m, pyrrole), 8.62 (1H, d, H-C-6'), 8.44 (1H, s, H-C-2), 8.4-8.1 and 7.8-7.6 (16H, 2m, phenyl), 8.16 and 7.71 (2 x 2H, 2d, nitrophenyl), 7.63 (1H, d, H-C-3'), 7.47 (1H, t, H-C-4'), 2.58 (3H, s, CH_3), -1.66 (2H, broad s, NH); ^{13}C NMR (coupled, selected signals, reference TMS) 31.74 (q, CH_3), 47.93 (s, saturated quaternary carbon); visible λ_{max} 434 nm (rel. int. 1), 500 (0.024), 537 (0.042), 577 (0.065), 610 (0.02), 675 (0.018). Anal. Calcd for $C_{52}H_{35}N_5O_2$: C, 81.98; H, 4.63; N, 9.19. Found: C, 81.41; H, 4.93; N, 8.95.

We confirmed the assignments of the two doublets at 8.16 and 7.71 by preparing 7 from H_2TPP d_{20} (fully deuterated *meso*-phenyls) to eliminate the aromatic multiplets from the spectrum, and we also give below the full assignments for the corresponding nickel(II) complex **9**.

8: paramagnetic; visible λ_{max} 422 nm (rel. int. 1), 534 (0.087); MS (chemical ionisation, NH_3) 820 (100%). Anal. Calcd for $C_{52}H_{35}N_5O_2Co$: C, 76.07; H, 4.30; N, 8, 53. Found: C, 75.99; H, 4.04; N, 7.65.

When base **7** was metallated with Co(OAc)$_2$ in CH_2Cl_2-MeOH, the product obtained was found identical to **8** (TLC, visible spectrum).

Acid catalyzed cyclization of copper(II)-2-formylTPP 1.

Aldehyde **2**[8] (964 mg) was dissolved in $CHCl_3$ (150 mL) under argon. After addition of TFA (10 mL) the solution was kept at 20°C and the reaction followed by TLC (ca 1 h). The solution was washed (aq. Na_2CO_3, then H_2O), dried (Na_2SO_4) and evaporated to dryness. Chromatography (alumina, 350 mL, toluene) gave an olive-green fraction **10** (435 mg; 40%; crystallized from CH_2Cl_2-MeOH) followed by some starting material (43 mg, 4.5%) and ketone **3** (eluted with CH_2Cl_2; 365 mg; 38%; crystallized from CH_2Cl_2-MeOH).

3[7]: visible λ_{max} 460 nm (rel. int. 1), 592 (0.074), 651 (0.14), 695 (0.105); MS 701 (100%).

10: visible λ_{max} 421 nm (rel. int. 1), 571 (0.17), 608 (0.15), 678 (0.092); MS 687 (100%). Anal. Calcd for $C_{45}H_{28}N_4Cu$: C, 78.53; H, 4.10; N, 8.14. Found: C, 79.10; H, 4.17; N, 7.97.

Demetallation of ketone 3.

Ketone **3** (50 mg) was dissolved in H_2SO_4 (3 mL). After 10 min the resulting red solution was poured into a large excess aq. ammonia, extracted twice with CH_2Cl_2, washed (H_2O), dried (Na_2SO_4) and evaporated to dryness. Base **11** was crystallized from CH_2Cl_2-MeOH (41 mg; 91%). NMR 9.34 (1H, d, H-C-18), 9.24 (1H, s, H-C-3), 8.65, 8.60, 8.57, 8.53 and 8.50 (5H, 5d, pyrrole), 8.39 (1H, d, phenyl), 8.1 and 7.8 (18H, 2m, phenyl), 7.51 (1H, t, phenyl), -0.6 (2H, broad s, NH); visible λ_{max} 466 nm (rel. int. 1), 590 (0.052), 650 (0.079), 745 (0.089). No satisfactory analytical data could be obtained for base **11**.

The same procedure was applied to nickel(II) ketone **15** and gave base **11** in more than 90% yield.

Acid treatment of nickel(II)-2-formylTPP 12.

To a solution of aldehyde **12**[3a] (362 mg) in CH_2Cl_2 (100 mL) was added TFA (5 mL). After completion of the reaction (*ca* 0.5 h) the solution was washed (excess aq. Na_2CO_3, followed by H_2O), dried and evaporated. Chromatography (silicagel in 1:1 toluene : hexane) gave red **13** (20 mg; 6%; crystallized from CH_2Cl_2-MeOH), olive-green fraction **14** (156 mg; 43%; crystallized from CH_2Cl_2-MeOH) and green **15** (eluted with pure toluene; 130 mg; 36%; crystallized from CH_2Cl_2-MeOH). A general observation is that the recovery of the more polar and soluble **15** was less efficient than that of **13** and **14**.

13: NMR 9.48 and 8.85 (2 x 1H, 2d AB, resp. H-C-18 and H-C-17), 8.65 (5H, m, pyrrole), 8.09, 7.79, 7.60 and 7.43 (4 x 1H, d + d + t + t, cyclized phenyl, resp. H-C-6', 3', 5' and 4'), 8.0 and 7.7 (15H, 2m, phenyl), 5.17 (2H, s, CH_2); visible λ_{max} 434 nm (rel. int. 1), 550 (0.080), 588 (0.043); MS 682 (100%). Anal. Calcd for $C_{45}H_{28}N_4Ni$: C, 78.08; H, 4.13; N, 8.20. Found: 78.75; H, 3.62; N, 8.68.

14: NMR ; visible λ_{max} 432 nm (rel. int. 1), 562 (0.094), 600 (0.091), 674 (0.072); MS 682 (100%). Anal. Calcd for $C_{45}H_{28}N_4Ni$: C, 79.08; H, 4.13; N, 8.20. Found: C 79.53; H, 3.77; N, 8.33.

15: NMR 9.25 and 8.67 (2 x 1H, 2d AB, resp. H-C-18 and H-C-17), 9.16 (1H, s, H-C-3), 8.49, 8.46, 8.38 and 8.36 (4 x 1H, 4d, pyrrole), 8.46, 7.96, 7.70 and 7.48 (4 x 1H, d + d + t + t, cyclized phenyl, resp. H-C-3', 6', 5' and 4'), 7.9 and 7.7 (15H, 2m, phenyl); visible λ_{max} 462 nm (rel. int. 1), 650 (0.15), 686 (0.083, sh.); MS 696 (100%). Anal. Calcd for $C_{45}H_{26}N_4ONi$: C, 77.5; H, 3.76; N, 8.03. Found: C, 77.89; H, 3.91; N, 7.96.

Further transformations of 13 and 14.

When absorbed on silicagel (dry state; TLC spots) **13** and **14** slowly transformed into **15**. In the presence of bases (triethylamine, morpholine, but not pyridine) **13** gave a blue-green solution [λ_{max} 442 nm (rel. int. 1), 580 (0.060, sh.), 614 (0.73), 666 (0.184)] which reverted to the starting material upon neutralization (i.e. silicagel TLC or addition of acetic acid) but on standing turned slowly into a green solution of ketone **15**.

Nickel(II)-N-*p*-nitrostyrylTPP perchlorate 16.

To a refluxing solution of base **6** (113 mg) in CH_2Cl_2 (60 mL) was added $Ni(OAc)_2$ (300 mg) in MeOH (25 mL). After ca 10 min CH_2Cl_2 was evaporated and the product crystallized by addition of aq. $NaClO_4$. The green product was dissolved in CH_2Cl_2, filtered and crystallization was induced by addition of hexane (103 mg; 86%). Visible λ_{max} 452 nm (rel. int. 1), 564 (0.081), 628 (0.111), 684 (0.061). Anal. Calcd for $C_{52}H_{34}ClN_5O_6Ni$: C, 67.96; H, 3.73; N, 7.62. Found: C, 68.07; H, 3.74; N, 7.69.

Thermolysis of salt 16.

The solid salt (102 mg) was kept in an oven at 110° for 5 days after which it was dissolved in toluene and chromatographed on silicagel (60 g in toluene-hexane 6:3). Elution gave NiTPP **17** (53 mg; 71%) followed by a red band which after evaporation and crystallization from CH_2Cl_2-MeOH furnished red crystals of **18** (26 mg; 29%). NMR 8.73-8.75 (4H, m, pyrrole), 8.70 (1H, d, pyrrole), 8.59 and 8.27 (2x1H, 2d AB, H-C-17 and H-C-18), 8.0 and 7.7 (19H, 2m,), 7.73 and 6.86 (2x2H, 2d AB, nitrophenyl), 7.46 (1H, t, phenyl), 5.80 and 5.83 (2H, 2s, olefin); visible λ_{max} 420 nm (rel. int. 1), 514 (0.063), 552 (0.070), 590 (0.046), 644 (0.011). Anal. Calcd for $C_{52}H_{33}N_5O_2Ni$: C, 76.32; H, 4.06; N, 8.56. Found: C, 74.45; H, 3.89; N, 8.23.

Acid-catalyzed cyclization of nickel complex 18.

In CH_2Cl_2-TFA (9:1) complex **18** was rapidly converted (1 h) into **9**, while demetallation in H_2SO_4 (see procedure above) gave quantitatively base **7**. Nickel complex **9** was independently prepared from **7** (12 h reflux in CH_2Cl_2 with an excess $Ni(acac)_2$, filtration through an alumina bed and crystallization from CH_2Cl_2-MeOH).

9: NMR 9.50 and 8.88 (2 x 1H, 2d AB, resp. H-C-18 and H-C-17), 8.67 and 8.56 (2 x 1H, 2d AB, pyrrole), 8.63 and 8.62 (2 x 1H, 2d AB, pyrrole), 8.27 (1H, s, H-C-3), 8.15 and 7.86 (2 x 2H, 2d AB, nitrophenyl), 7.97, 7.85, 7.60 (15H, 3m, phenyl), 8.12, 7.59, 7.41 and 7.35 (4 x 1H, d + t + d + t, cyclized phenyl, resp. H-C-6', 5', 3' and 4'), 2.52 (3H, s, CH_3); visible λ_{max} 435 nm (rel. int. 1), 552 (0.078), 592 (0.041). Anal. Calcd for $C_{52}H_{33}N_5O_2Ni$: C, 76.32; H, 4.06; N, 8.56. Found: C, 75.08; H, 4.10; N, 8.62.

Acknowledgments. We wish to thank E. Krempp, P. Wehrung, R. Huber and G. Teller for technical assistance. This work was supported by the C.N.R.S. and Université Louis Pasteur.

REFERENCES AND NOTES

(1) Present address: (a) Institut Pasteur, Paris; (b) Syntex, Palo Alto, Cal., U.S.A.; (c) Rhône-Poulenc, Centre de Recherches des Carrières, St Fons.

(2) Kim, J.B.; Adler, A.D.; Longo, F.R. In The Porphyrins; Dolphin, D., Ed.; Academic Press: New York, NY, 1978; Vol. 1, pp 85-100.

(3) (a) Callot, H.J. *Tetrahedron* **1973**, *29*, 899-901. (b) Callot, H.J. *Bull. Soc. Chim. Fr.* **1973**, 3413-3416 and **1974**, 1492-1496. (c) Callot, H.J.; Castro, B.; Selve, C. *Tetrahedron Lett.* **1978**, 2877-2880. Selve, C.; Niedercorn, F.; Nacro, M., Castro, B.; Gabriel, M. *Tetrahedron* **1981**, *37*, 1893-1901 and 1903-1912. (d) Momenteau, M.; Loock, B.; Bisagni, E.; Rougée, M. Can. J. Chem. 1979, 57, 1804-1813. (e) More, K.M.; Eaton, S.S.; Eaton, G.R. *Inorg. Chem.* **1981**, *20*, 2641-2647. (f) Baldwin, J.E.; Crossley, M.J.; DeBernardis, J. *Tetrahedron* **1982**, *38*, 685-692. (g) Crossley, M.J.; Gosper, J.J.; King, L.G. *Tetrahedron Lett.* **1988**, *29*, 1597-1600.

(4) Callot, H.J.; Giraudeau, A.; Gross, M. *J. Chem. Soc. Perkin Trans. II* **1975**, 1321-1324. Giraudeau, A.; Callot, H.J.; Gross, M. *Inorg. Chem.* **1979**, *18*, 201-206. Giraudeau, A.; Callot, H.J.; Jordan, J.; Ezhar, I.; Gross, M. *J. Am. Chem. Soc.* **1979**, *101*, 3857-3862. Giraudeau, A.; Louati, A.; Gross, M.; Callot, H.J.; Rhodes, R.K.; Kadish, K.M.; Hanson, L.K. *Inorg. Chem.* **1982**, *21*, 1581-1586. Kadish, K.M.; Boisselier-Cocolios, B.; Simonet, B.; Chang, D.; Ledon, H.; Cocolios, P. *Inorg. Chem.* **1985**, *24*, 2148-2156. Lin, X.Q.; Boisselier-Cocolios, B.; Kadish, K.M. *Inorg. Chem.* **1986**, *25*, 3242-3248; El Kahef, L.; Gross, M.; Giraudeau, A. *J. Chem. Soc. Chem. Comm.* **1989**, 963 and preceding articles. Donohue, R.J.; Atamian, M.; Bocian, D.F. *J. Am. Chem. Soc.* **1987**, *109*, 5593-5599.

(5) Crossley, M.J.; Harding, M.M.; Sternhell, S. *J. Am. Chem. Soc.* **1986**, *108*, 3608-3613. Crossley, M.J.; Field, L.D.; Harding, M.M.; Sternhell, S *J. Am. Chem. Soc.* **1987**, *109*, 2335-2341.

(6) Buchler, J.W.; Dreher, C.; Herget, G. *Justus Liebigs Ann. Chem.* **1988**, 43-54.

(7) Although a large number of simple β-substituted TPP's have been prepared, no X-ray structure of any of these compounds was ever determined to our knowledge. However, the distance between the first carbon of a single-bonded substituent attached to a pyrrole and the plane of the adjacent phenyl ring should be in the order of 2.5Å.

(8) Henrick, K.; Owston, P.G.; Peters, R.; Tasker, P.A.; Dell, A. *Inorg. Chim. Acta* **1980**, *45*, L161-L163.

(9) Ponomarev, G.V.; Maravin, G.B. *Khim. Geterotsikl. Soedin.* **1982**, 59-64; *Chem. Abstr.* **1982**, *97*, 38727.

(10) (a) Dolphin, D.; Halko, D.J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348-4351. (b) Callot, H.J.; Metz, F. *J. Chem. Soc. Chem. Comm.* **1982**, 947-948. Callot, H.J.; Metz, F.; Cromer, R. *Nouv. J. Chim.* **1984**, *8*, 759-763.

(11) Callot, H.J.; Schaeffer, E. unpublished results.

(12) Battersby, A.R.; Jones, K.; Snow, R.J. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 734-735.

(13) Callot, H.J.; Tschamber, T. *Bull. Soc. Chim. Fr.* **1973**, 3192-3198.

(14) Callot, H.J.; Schaeffer, E. *J. Organomet. Chem.* **1980**, *193*, 111-115.