Nonaromatic Corroles: Regioselectivity of Electrophilic Substitution

Romain Ruppert, Christophe Jeandon, and Henry J. Callot*

Institut de Chimie, UMR CNRS 7177, Université Louis Pasteur, 1 rue Blaise Pascal,
67000 Strasbourg, France

callot@chimie.u-strasbg.fr

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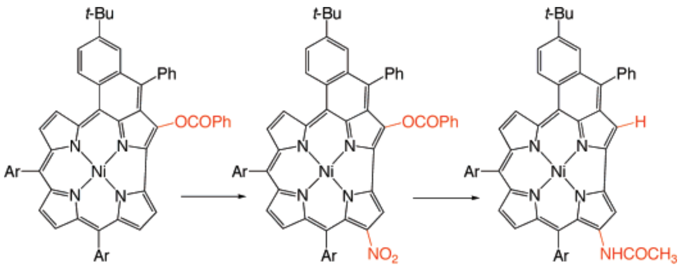


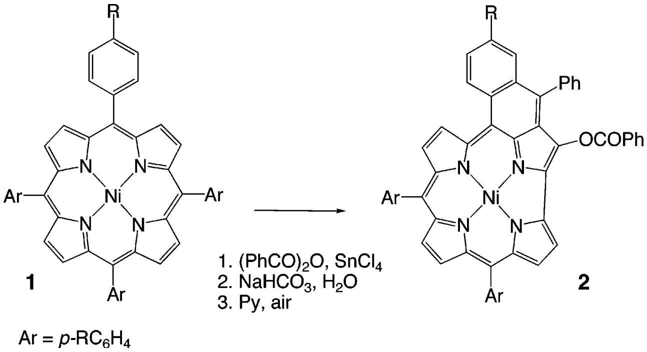
Ring contraction of nickel *meso*-tetraarylporphyrins produced nonaromatic divalent corroles bearing a benzoyloxy function. We investigated their reactivity under electrophilic conditions: formylation, halogenation, nitration. We also found that the benzoate function could be eliminated to afford deoxocorroles, and we tested the formylation and nitration in this deoxo series. These corroles were generally very stable under the reaction conditions, and in both series, the directly bonded pyrroles were the most reactive. The nitration reaction produced a series of corrole dimers via electron transfer initiated coupling.

Introduction

We recently described[1] the ring contraction of nickel *meso*-tetraarylporphyrins **1** to corroles and proposed a mechanism for this highly unusual reaction (Scheme 1). This reaction produced a series of new corroles **2** that significantly differed from classical corroles in that they were divalent, nickel complexes were neutral, and that they did not show aromaticity, though they were fully unsaturated. This last feature was well-illustrated by their NMR data, which show pyrrole resonances between 5 and 7 ppm. Another feature that seemed unexpected was the very high stability of these corroles as nickel complexes, contrasting with the moderate stability of many aromatic corroles.

In recent years, many research groups explored the chemistry of aromatic corroles and their metal complexes and described numerous new reactions: synthesis, peripheral functionalization, catalytic activity of metal complexes.[2−6] Having developed an efficient synthesis of corroles, we wished to explore their chemistry, in particular, their peripheral substitution, because one would expect a significant regioselectivity due to the low symmetry of these compounds. A high regioselectivity has been observed with aromatic corroles, as free bases or metal complexes, in the case of bromination,[7,8] formylation,[9,10] nitration,[9] sulfonation,[9,11,12] chlorocarbonylation,[13] deuteration,[12] and borylation.[14] Electrophilic substitutions on porphyrins often do not show such a high selectivity.[15] Also, the replacement of

SCHEME 1. Ring Contraction of *meso*-Tetraarylporphyrins



1

2

Ar = *p*-RC$_6$H$_4$

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[1] Jeandon, C.; Ruppert, R.; Callot, H. J. *J. Org. Chem.* **2006**, *71*, 3111−3120.

[2] Paolesse, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 2, pp 201−232.

[3] Gryko, D. T. *Eur. J. Org. Chem.* **2002**, 1735−1743.

[4] Ghosh, A. *Angew. Chem., Int. Ed.*, **2004**, *43*, 1918−1931.

[5] Gryko, D. T.; Fox, J. P.; Goldberg, D. P. *J. Porphyrins Phthalocyanines* **2004**, *8*, 1091−1105.

[6] Aviv, I.; Gross, Z. *Chem. Commun.* **2007**, 1987−1999.

10.1021/jo702321h CCC: $40.75

the very inert nickel ion could lead to various metal complexes and possibly to catalytic applications.

In this paper, we describe several successful peripheral substitution reactions, as well as attempts to demetalate these corroles. The benzoyloxy substituent resulting from the ring contraction appeared initially as a drawback since one would expect it to be labile, but we will show that it could be reductively disposed of, providing an entry to the unfunctionalized series.

Results and Discussion

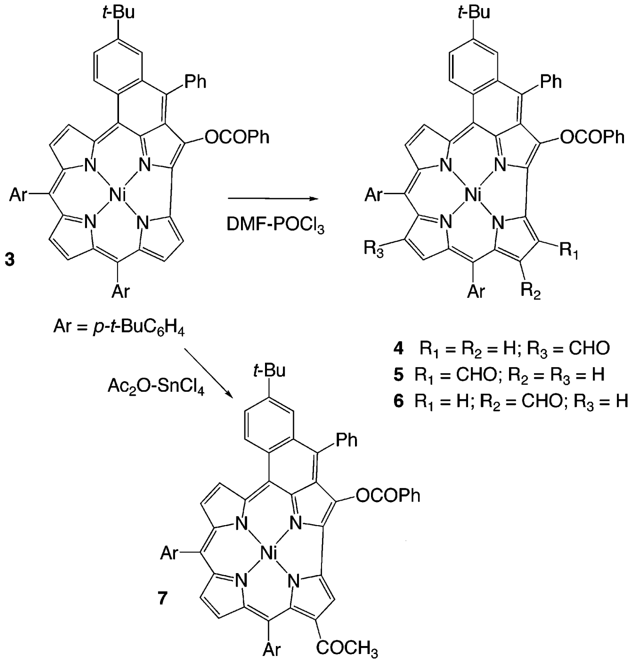
Four reactions often used in metallotetrapyrrole chemistry were tested: acylation (Vilsmeier−Haack formylation and Friedel−Crafts acetylation), halogenation (chlorination and bromination), nitration, acid-catalyzed demetalation. The products of these reactions should give entries to a wide array of corroles by either condensation (Wittig and related reactions), substitution of halogen atoms (palladium-catalyzed reactions), reduction of nitro groups to reactive aminated intermediates, metal replacement, etc. Also, such reactions should allow comparisons to the reactivity of aromatic corroles to be drawn.

The structure of the functionalized corroles was mostly deduced from their rather simple NMR data, including COSY and ROESY experiments, and in addition, three compounds gave crystals suitable for X-ray diffraction studies (see Supporting Information).

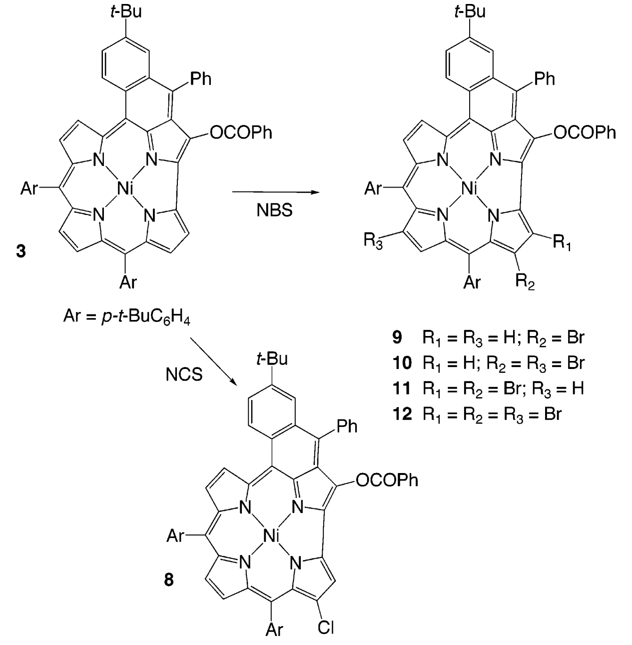
Formylation of corrole **3** (Scheme 2) proceeded rapidly (full conversion within 20 min at 20 °C) and gave two minor monoaldehydes **4** (3%) and **5** (4%) and a major one **6** (86%). Acetylation of corrole **3** gave acetylcorrole **7** in low yield (11%) as the only isolable product because overreaction occurred and produced a very complex mixture of corroles (as proven by the UV−visible spectra of the chromatographic fractions) showing a wide range of polarity.

Chlorination of **3** with NCS proceeded slowly to give monochlorocorrole **8** (35% accompanied by 40% recovered starting material). At variance with most experiments involving aromatic corroles,[7] we used low amounts of reagent in order to identify the initial reaction sites. Reaction of corrole **3** with NBS (1.2 molar equiv) gave monobromocorrole **9** as the major product (62%), but two dibromocorroles **10** (traces) and **11** (12%) were also present (Scheme 3). Higher NBS/corrole ratio (2 or 3 molar equiv) gave the same dibromocorroles **10** (10%) and **11** (62%) or tribromocorrole **12** (56%). Traces of minor bromination products were also detected (TLC) but were not isolated.

SCHEME 2. Formylation of Benzoyloxycorrole 3



SCHEME 3. Halogenation of Benzoyloxycorrole 3



Under mild nitration conditions ($LiNO_3$, AcOH, Ac_2O), corrole **3** was converted into nitrocorrole **13** (55%), but four minor compounds of lower polarity, **14** (7%), **15**, **16** (7%), and **17**, were also isolated (Scheme 4). Compounds **15** and **17** were obtained as a 1:1 mixture from which pure **15** and slightly

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(7) (a) Paolesse, R.; Nardis, S.; Sagone, F.; Khoury, R. G. *J. Org. Chem.* **2001**, *66*, 550−556. (b) Golubkov, G.; Bendix, J.; Gray, H. B.; Mahammed, A.; Goldberg, I.; DiBilio, A.J.; Gross, Z. *Angew. Chem., Int. Ed.* **2001**, *40*, 2132−2134.

(8) Nardis, S.; Mandoj, F.; Paolesse, R.; Fronczek, F. R.; Smith, K. M.; Prodi, L.; Montalti, M.; Battistini, G. *Eur. J. Inorg. Chem.* **2007**, 2345−2352.

(9) (a) Paolesse, R.; Jaquinod, L.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1997**, *62*, 6193−6198. (b) Saltsman, I.; Mahammed, A.; Goldberg, E.; Tkachenko, E.; Botoshansky, M.; Gross, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7411−7420. (c) Sorasaenee, K.; Taqavi, P.; Henling, L. M.; Gray, H. B.; Tkachenko, E.; Mahammed, A.; Gross, Z. *J. Porphyrins Phthalocyanines* **2007**, *11*, 189−197. (d) Stefanelli, M.; Mastroianni, M.; Nardis, S.; Licoccia, S.; Fonczek, F. R.; Smith, K. M.; Zhu, W.; Ou, Z.; Kadish, K. M.; Paolesse, R. *Inorg. Chem.* **2007**, *46*, 10791−10799.

(10) Paolesse, R.; Nardis, S.; Venanzi, M.; Mastroianni, M.; Russo, M.; Fronczek, F. R.; Vicente, M. G. H. *Chem.*−*Eur. J.* **2003**, *9*, 1192−1197.

(11) Mahammed, A.; Golberg, I.; Gross, Z. *Org. Lett.* **2001**, *3*, 3443−3446.

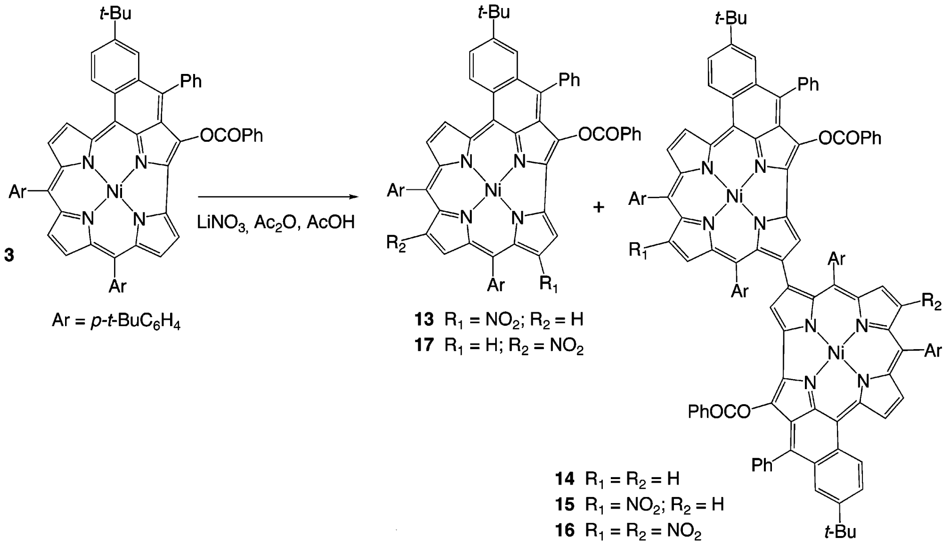
(12) Gross, Z.; Mahammed, A. *J. Porphyrins Phthalocyanines* **2002**, *6*, 553−555.

(13) Saltsman, I.; Goldberg, I.; Gross, Z. *Tetrahedron Lett.* **2003**, *44*, 5669−5673.

(14) Hiroto, S.; Hisaki, I.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6763−6766.

(15) (a) Vicente, M. G. H. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 1, pp 149−199. (b) Jaquinod, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 1, pp 201−237.

SCHEME 4. Nitration of Benzoyloxycorrole 3



impure **17** could be isolated (estimated yields were ca. 3% each). Three compounds, **14**, **15**, and **16**, were dimers, bearing zero, one, or two nitro groups, respectively, while the last one was an isomeric mononitrocorrole **17**. Monomeric corrole **17** (see Supporting Information) and dimer **14** (Figure 1) gave crystals suitable for an X-ray diffraction study.

In order to test whether a reduction followed by an acylation of nitropyrrole **13** was compatible with the benzoate function, **13** was successively treated with sodium borohydride in the presence of nickel chloride, then acetic anhydride (Scheme 5). To our surprise, the ^{1}H NMR spectrum of product **18** (47%) did not show the benzoate moiety any more but an additional singlet, as well as the expected signals for an acetylamino group. Suitable crystals of **18** were subjected to an X-ray diffraction study which showed that the benzoate group had been replaced by a hydrogen (Figure 2).

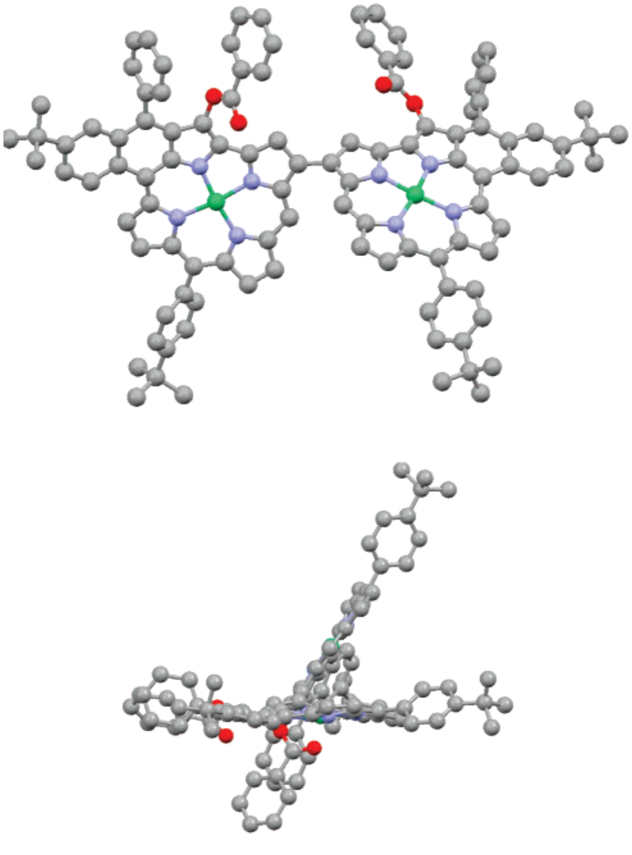
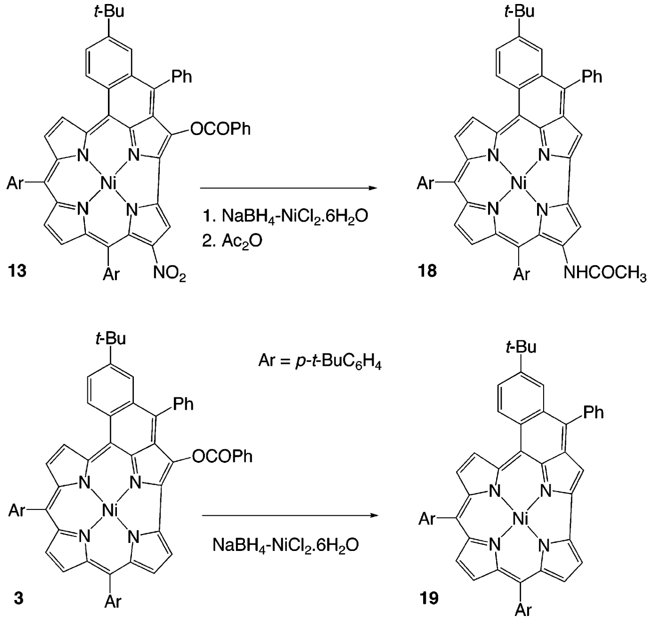


FIGURE 1. Structure (front and side views) of dimer **14**. All hydrogen atoms and two *meso*-aryl groups have been omitted for clarity.

We suspect that, under the basic conditions generated by sodium borohydride, the benzoate function was hydrolyzed to an enol whose keto tautomer was reduced to the corresponding alcohol. Simultaneously, the nitro group was reduced and the resulting amine acylated in the second step. That the dehydration to **18** occurred in the last step is strongly suggested by the observation of an intermediate polar brown product. It transformed spontaneously and quantitatively into **18** on attempted purification, and we suspect that this unstable intermediate was an acylaminoalcohol.

The structural data for deoxocorrole **18** are very similar to those of **3** and **14**. In particular, the planarity of the corrole

SCHEME 5. Reduction−Acylation of Nitrocorrole 13 and Corrole 3



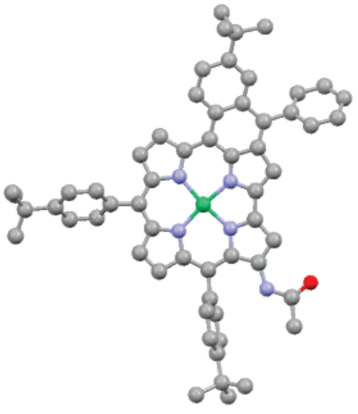
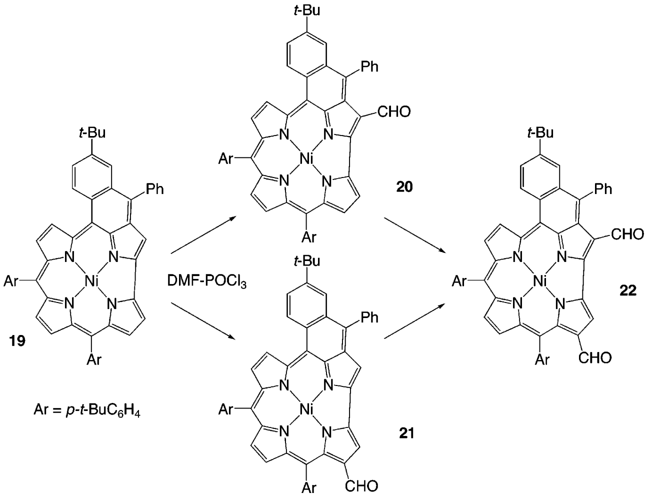


FIGURE 2. Structure of corrole **18**. All hydrogen atoms have been omitted for clarity.

SCHEME 6. Formylation of Deoxocorrole 19



core was conserved, as were the alternate carbon−carbon bond lengths in the vicinity of the C1−C2 cross-conjugated double bond.

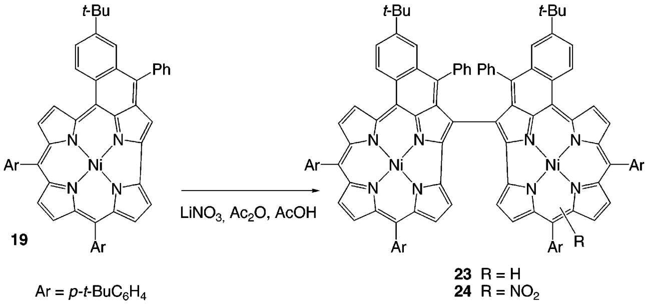
Having in hand a method for producing benzoate-free corroles, we tested the reduction step on corrole **3**, and indeed, the same reduction occurred and gave corrole **19** (yield 90%) (Scheme 5). This corrole was in turn subjected to formylation and nitration conditions in order to investigate whether such a structural change would modify the regioselectivity.

Formylation of **19** proceeded rapidly, and under dilute conditions, two monoaldehydes **20** (38%) and **21** (31%) were isolated. In the presence of a larger amount of reagent, monoaldehydes **20** and **21** (respectively, 14 and 35%) were accompanied by dialdehyde **22** (26%) (Scheme 6).

Under nitration conditions, **19** gave three fractions of low polarity in addition to polar mixtures (Scheme 7). Two were dimers **23** (14%) and **24** (11%), possessing the same carbon framework and a 2,2′ connexion, the more polar one bearing one nitro group. The third fraction could not be purified, due to its instability, but mass spectra indicated that a tetramer was the major constituent of this fraction. No monomer could be isolated from the nitration mixture.

The demetalation of corroles **3** and **19** failed, even under conditions leading to rapid and clean demetalation of nickel porphyrins. Corrole **3**, when treated with strong acids, gave complex mixtures that were not further investigated. An interference of the benzoyloxy function could be suspected. On the contrary, corrole **19** proved to be very stable, even in sulfuric or triflic acid for hours at 20 °C. Heating such solutions only resulted in decomposition.

SCHEME 7. Nitration of Deoxocorrole 19



These results demonstrate that electrophilic substitution at the periphery of nonaromatic corroles such as **3** shows a high regioselectivity: in all reactions, position 17 was favored versus all other pyrrolic carbon atoms (Figure 3). Second to position 17, positions 12 and 18 were functionalized in low yield under stoichiometric conditions and efficiently under forcing conditions. This high regiospecificity in favor of position 17 is similar to that observed[7−10] with classical aromatic corroles on monosubstitution (formylation, bromination, nitration). In contrast, some monosubstitution of the pyrroles nonadjacent to the pyrrole−pyrrole direct bond was also detected. The easy formation of vicinal 17,18-dibromocorroles is similar to the results observed in the aromatic series.[8]

The image changed with corrole **19**: elimination of the benzoate substituent revealed the high reactivity, on monosubstitution, of position 2, which is only the second in terms of reactivity in aromatic corroles.[9] Position 17 retained a similar level of reactivity.

Nitration of both **3** and **19** resulted in the production of, respectively, small or high yields of oligomers, possibly up to tetramer in the case of **19**. However, in the case of **3**, the major products were the mononitrocorroles **13** and **17**, in agreement with the reactivity pattern discussed above. The formation of corrole oligomers under such conditions reminds one of the—often serendipitous—oxidative coupling of corroles.[16−21] As in the literature examples, the coupling of our corroles occurred at the most reactive positions defined above. We propose that the nitrating reagent was able to transfer one electron from corrole **3** to give a cation radical whose reaction with the starting material or the coupling with another cation radical gave dimer **14**. A similar explanation was put forward in the case of the oxidative coupling of cobalt corrole complexes.[16] Subsequent nitration of dimer **14** yielded dimers **15** and **16**.

In order to test this hypothesis in the absence of nitrating reagents and competing nucleophiles, we oxidized electrochemically corrole **3** in a divided cell and obtained dimer **14** in

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(16) Mahammed, A.; Giladi, I.; Goldberg, I.; Gross, Z. *Chem.—Eur. J.* **2001**, *7*, 4259−4265.

(17) Luobeznova, I.; Simkhovich, L.; Goldberg, I.; Gross, Z. *Eur. J. Inorg. Chem.* **2004**, 1724−1732.

(18) Barata, J. F. B.; Silva, A. M. G.; Neves, M. G. P. M. S.; Tomé, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S. *Tetrahedron Lett.* **2006**, *47*, 8171−8174.

(19) Hiroto, S.; Furukawa, K.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2006**, *128*, 12380−12381.

(20) Sankar, J.; Rath, H.; Prabhuraja, V.; Gokulnath, S.; Chandrashekar, T. K.; Purohit, C. S.; Verma, S. *Chem.—Eur. J.* **2007**, *13*, 105−114.

(21) Koszarna, B.; Gryko, D.T. *Chem. Commun.* **2007**, 2994−2996.

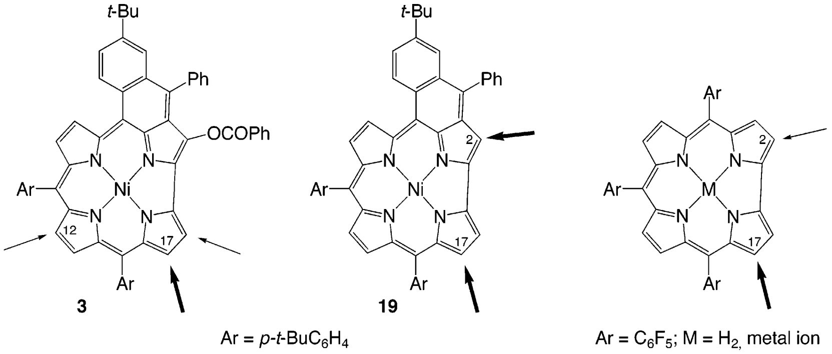

FIGURE 3. Summary of the regioselectivity of electrophilic substitution of corroles (bold arrow/light arrow, major vs minor pathways).

moderate yield (20%). We also measured the potential of the first oxidation wave for corroles **3** and **19** by cyclic voltammetry in 1,2-dichloroethane and found +0.25 and 0.15 V vs Fc/Fc^+, respectively. These data show that their first oxidation wave is very accessible and that these corroles, in particular, **19**, are good substrates for electron transfer, in agreement with the experimental results. For comparison, porphyrins bearing similar substituents, such as nickel *meso*-tetraphenylporphyrin, are oxidized at ca. +0.5 V more positive potentials.[22]

The stability and long wavelength absorptions of the corroles described in this work suggested that they could be tested for singlet oxygen production, but keeping in mind that the corresponding porphyrin nickel complexes are inactive. Corrole **3** was irradiated in the presence of a large excess of cholesterol, in order to trap any singlet oxygen produced, using a standard method.[23] However, both corrole and cholesterol were recovered intact, under conditions known to produce significant amounts of cholesterol oxidation products with porphyrinic photosensitizers.

Conclusion

Nonaromatic nickel corroles bearing a benzoate moiety produced by ring contraction of nickel tetraarylporphyrins are reactive molecules that can be acylated, halogenated, nitrated, or deoxygenated under very mild conditions. Under most conditions, good yield of corroles can be isolated, and X-ray data show that the typical planarity of these corroles was maintained. Electron transfer followed by oligomerization competed with nitration. Comparison with the similar reactions of aromatic corroles shows little difference: the reactivity of both series is high, the reactive positions are concentrated on the two pyrroles adjacent to the direct pyrrole−pyrrole bond, and coupling reactions triggered by electron transfer from the corrole were observed in both series. The remarkable stability of the nickel + tetrapyrrole core was exemplified by its lack of reactivity toward strong acids, dioxygen, light, as well as by the high recovery of corroles under most reaction conditions tested in this study.

Experimental Section

Formylation of Corrole 3. To a solution of corrole **3**[1] (22 mg) in 1,2-dichloroethane (5 mL) was added dropwise a solution of Vilsmeier−Haack reagent made from DMF (2 mL) and $POCl_3$ (0.3 mL) in 1,2-dichloroethane (5 mL) until no significant spot of starting material was detectable on silica gel by TLC. At this stage, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and poured into excess aqueous NaOAc. After 40 min, the organic phase was decanted, washed with water (3×), dried over Na_2SO_4, and evaporated. Chromatography of the residue (200 mL silica gel; toluene + cyclohexane 1:1) gave traces of starting material followed by aldehydes **4** (<1 mg, ca. 3%), **5** (1 mg, ca. 4%; slightly impure), and **6** (19.5 mg, 86%), crystallized from $CH_2Cl_2-CH_3OH$.

Aldehyde **4**: ^1H NMR ($CDCl_3$) $\delta = 7.95$ (s, 1H, aldehyde), 7.72 (d, 1H, $J = 9$ Hz, cyclized aryl), 7.6−6.9 (m, 21H, aryl + 1 pyrrole), 6.96 (s, 1H, pyrrole), 6.82 (d, 1H, $J = 5.1$ Hz, pyrrole), 6.30 and 6.05 (2d, 1+1H, AB, $J = 4.5$ Hz, pyrrole), 1.37, 1.34, 1.10 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 392$ nm ($\epsilon = 40000$), 430 (39000), 530 (43000), 588 (20000), 680 (9500), 740 (16000); HRMS calcd for $C_{64}H_{54}N_4O_3Ni + H^+$ 985.3627; found 985.3622.

Aldehyde **5**: ^1H NMR ($CDCl_3$) $\delta = 9.54$ (s, 1H, aldehyde), 7.80 (d, 1H, $J = 9$ Hz, cyclized aryl), 7.75−6.8 (m, 20H, aryl + 1 pyrrole), 7.62 and 6.98 (2d, 1+1H, AB, $J = 5.1$ Hz, pyrrole), 6.93 (d, 1H, $J = 2.2$ Hz, cyclized aryl), 6.57 and 6.24 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 1.39, 1.34, 1.10 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 398$ nm (relative intensity 1), 490 (0.71), 602 (0.45), 690 (0.26), 754 (0.38); HRMS calcd for $C_{64}H_{54}N_4O_3Ni$ 984.3549; found 984.3540.

Aldehyde **6**: ^1H NMR ($CDCl_3$) $\delta = 8.24$ (s, 1H, aldehyde), 7.84 (d, 1H, $J = 9$ Hz, cyclized aryl), 7.70 (d, 1H, $J = 5.4$ Hz, pyrrole), 7.6−6.95 (m, 20H, aryl), 7.05 (d, 1H, $J = 5.4$ Hz, pyrrole), 6.66 (s, 1H, pyrrole), 6.45 and 6.31 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 1.40, 1.34, 1.12 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 396$ nm ($\epsilon = 54000$), 496 (38000), 614 (24000), 708 (14000), 772 (23000); HRMS calcd for $C_{64}H_{54}N_4O_3Ni + H^+$ 985.3627; found 985.3601.

Acetylation of Corrole 3. A solution of corrole **3** (18 mg) in CH_2Cl_2 (5 mL) was treated with Ac_2O (0.2 mL) and $SnCl_4$ (0.1 mL). After 0.5 h, the starting material was no more detectable (TLC), and the solution was treated with an excess of saturated aqueous $NaHCO_3$, stirred for 15 min, washed with water (3×), dried over Na_2SO_4, and evaporated. TLC showed numerous spots, but compound **7** could be chromatographically isolated (200 mL silica gel; cyclohexane + CH_2Cl_2 1:1) and crystallized from $CH_2Cl_2-CH_3OH$ (2 mg, 11%).

Acetylcorrole **7**: ^1H NMR ($CDCl_3$) $\delta = 7.70$ (d, 1H, $J = 9$ Hz, cyclized aryl), 7.6−6.85 (m, 21H, aryl + 1 pyrrole), 6.86 (d, 1H, $J = 5.1$ Hz, pyrrole), 6.44 and 6.14 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 6.12 (s, 1H, pyrrole), 1.38, 1.31, 1.09 (3s, 9+9+9H, *t*-butyl), 1.28 (s, 3H, acetyl); UV−visible (CH_2Cl_2) $\lambda = 392$ nm ($\epsilon = 50000$), 494 (31000), 608 (22000), 706 (12000), 766 (19000); HRMS calcd for $C_{65}H_{56}N_4O_3Ni + H^+$ 999.3784; found 999.3779.

Chlorination of Corrole 3. A solution of corrole **3** (15 mg) and *N*-chlorosuccinimide (40 mg, 21 equiv) in CH_2Cl_2 (15 mL) was kept at 20 °C for 24 h. Evaporation of the solvent and

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[22] Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 8, pp 1−114.

[23] Fouchet, J.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Org. Lett.* **2005**, *7*, 5257−5260.

chromatography of the residue (60 mL of silica gel in cyclohexane/toluene 1:1) gave chlorocorrole **8**, crystallized from $CH_2Cl_2-CH_3OH$ (5.5 mg, 35%), followed by recovered starting material (6 mg, 40%).

Chlorocorrole **8**: ^{1}H NMR ($CDCl_3$) $\delta = 7.60$ (d, 1H, $J = 9$ Hz, cyclized aryl), 7.5−7.05 (m, 20H, aryl + 1 pyrrole), 6.80 (d, 1H, $J = 2$ Hz, cyclized aryl), 6.72 (d, 1H, $J = 5.2$ Hz, pyrrole), 5.98 and 5.92 (2d, 1+1H, AB, $J = 4.5$ Hz, pyrrole), 5.78 (s, 1H, pyrrole), 1.36, 1.32, 1.07 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 390$ nm ($\epsilon = 46000$), 468 (28000), 488 (29000), 598 (21000), 698 (10000), 760 (17000); HRMS calcd for $C_{63}H_{53}N_4O_2ClNi + H^+$ 991.3234; found 991.3283.

Bromination of Corrole 3. A solution of corrole **3** (20 mg) and *N*-bromosuccinimide (5 mg, 1.2 equiv) in CH_2Cl_2 (5 mL) was kept at 20 °C for 20 h. After evaporation of the solvent, the residue was chromatographed (150 mL of silica gel in cyclohexane + toluene 2:1) to give traces of **10** followed by **11** (3 mg, 12%) and **9** (15 mg, 62%).

When the amount of reagent was increased to 2 or 3 molar equiv, we isolated **10** (2 mg, 10%) followed by a mixed fraction containing products of further bromination (TLC; confirmed by MS) and **11** (13 mg, 62%) or tribromocorrole **12** (14 mg, 56%) accompanied by traces of other brominated corroles. All bromocorroles were crystallized from $CH_2Cl_2-CH_3OH$.

Monobromocorrole **9**: ^{1}H NMR ($CDCl_3$) $\delta = 7.65-6.8$ (m, 22H, aryl + 1 pyrrole), 6.77 (d, 1H, $J = 5.4$ Hz, pyrrole), 6.31 and 6.05 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 6.05 (s, 1H, pyrrole), 1.37, 1.32, 1.07 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 388$ nm ($\epsilon = 52000$), 466 (28000), 486 (28000), 602 (21000), 695 (10000), 758 (19000); HRMS calcd for $C_{63}H_{53}N_4O_2BrNi$ 1034.2705; found 1034.2699.

Dibromocorrole **10**: ^{1}H NMR ($CDCl_3$) $\delta = 7.60-6.95$ (m, 21H, aryl + 1 pyrrole), 6.81 (d, 1H, $J = 1.8$ Hz, cyclized aryl), 6.61 (d, 1H, $J = 5.2$ Hz, pyrrole), 6.14 and 5.98 (2s, 1+1H, pyrrole), 1.36, 1.32, 1.07 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 390$ nm ($\epsilon = 47000$), 474 (31000), 500 (34000), 598 (22000), 694 (11000), 752 (18000); HRMS calcd for $C_{63}H_{53}N_4O_2Br_2Ni + H^+$ 1113.1883; found 1113.1851.

Dibromocorrole **11**: ^{1}H NMR ($CDCl_3$) $\delta = 7.65-6.8$ (m, 23H, aryl + 2 pyrrole), 6.11 and 6.02 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 1.37, 1.32, 1.07 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 388$ nm ($\epsilon = 71000$), 478 (46000), 602 (32000), 698 (17000), 758 (27000); HRMS calcd for $C_{63}H_{52}N_4O_2Br_2Ni + H^+$ 1113.1883; found 1113.1874.

Tribromocorrole **12**: ^{1}H NMR ($CDCl_3$) $\delta = 7.65-6.8$ (m, 21H, aryl + 1 pyrrole), 6.79 (d, 1H, $J = 2.0$ Hz, cyclized aryl), 6.69 (d, 1H, $J = 5.1$ Hz, pyrrole), 6.26 (s, 1H, pyrrole), 1.37, 1.32, 1.07 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 390$ nm ($\epsilon = 48000$), 476 (31000), 496 (32000), 602 (22000), 696 (12000), 754 (19000); HRMS calcd for $C_{63}H_{51}N_4O_2Br_3Ni$ 1190.0910; found 1190.0925.

Nitration of Corrole 3. A solution of corrole **3** (28 mg) in CH_2Cl_2 (10 mL) was treated with 1 mL of a solution of $LiNO_3$ (50 mg) in AcOH (2.5 mL) and Ac_2O (1.5 mL) and the mixture heated under reflux. The reaction was followed by TLC. After 0.5 h, the starting material had disappeared and the solution was diluted with CH_2Cl_2 (50 mL), washed with water (3×), dried over Na_2SO_4, and evaporated. Chromatography of the residue (200 mL of silica gel in toluene) gave successively dimer **14** (2 mg, 7%), a mixed fraction containing monomer **17** and dimer **15** (2.6 mg, 1:1 molecular ratio as measured by ^{1}H NMR, estimated yield ca. 3% each; separated on 40 mL of silica gel in cyclohexane + toluene 1:1 to give **15** and slightly impure **17**), dimer **16** (2 mg, 7%), and monomer **13** (16 mg, 55%), all crystallized from $CH_2Cl_2-CH_3OH$. Crystals of **14** and **17** suitable for X-ray diffraction measurements were grown by slow diffusion of CH_3OH in CH_2Cl_2 and $CHCl_3-CH_2Cl_2$, respectively.

Nitrocorrole **13**: ^{1}H NMR ($CDCl_3$) $\delta = 7.88$ (d, 1H, $J = 9$ Hz, cyclized aryl), 7.77 and 7.11 (2d, 1H+1H, AB, $J = 5.5$ Hz, pyrrole), 7.6−7.15 and 7.1−7.0 (m, 20H, aryl), 6.71 and 6.39 (2d, 1+1H, AB, $J = 4.9$ Hz, pyrrole), 6.64 (s, 1H, pyrrole), 1.40, 1.33, 1.13 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 398$ nm ($\epsilon = 58000$), 502 (47000), 620 (30000), 712 (19000), 774 (29000); HRMS calcd for $C_{63}H_{53}N_5O_4Ni + H^+$ 1002.3529; found 1002.3477.

Dimer **14**: ^{1}H NMR ($CDCl_3$) $\delta = 7.67$ (d, 2H, $J = 8.8$ Hz, cyclized aryl), 7.7−7.05 and 6.5−6.6 (2m, 42H, aryl + 4 pyrrole), 6.77 (d, 2H, $J = 2$ Hz, cyclized aryl), 5.86 and 5.78 (d + broadened signal, 2+2H, AB, $J = 4.6$ Hz, pyrrole), 4.77 (s, 2H, pyrrole), 1.62, 1.34, 1.06 (3s, 18+18+18H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 398$ nm ($\epsilon = 84000$), 472 (54000), 502 (58000), 602 (41000), 706 (19000), 766 (30000); HRMS calcd for $C_{126}H_{106}N_8O_4Ni_2 + H^+$ 1911.7117; found 1911.7115.

Mononitrodimer **15**: ^{1}H NMR ($CDCl_3$) $\delta = 7.75-7.0$ and 6.55−6.65 (m, 44H, aryl + 4 pyrrole), 6.93 (d, 1H, $J = 2.1$ Hz, cyclized aryl), 6.79 (d, 1H, $J = 2.0$ Hz, cyclized aryl), 6.56 (s, 1H, pyrrole), 5.94 and 5.83 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 5.15 and 4.92 (2s, 1+1H, pyrrole), 1.66, 1.50, 1.36, 1.35, 1.11, 1.07 (6s, 9+9+9+9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 394$ nm ($\epsilon = 39000$), 446 (31000), 466 (3000), 550 (29000), 600 (22000), 754 (14000); HRMS calcd for $C_{126}H_{105}N_9O_6Ni_2 + H^+$ 1956.6968; found 1956.6992.

Dinitrodimer **16**: ^{1}H NMR ($CDCl_3$) $\delta = 7.79$ (d, 2H, $J = 9$ Hz, cyclized aryl), 7.6−7.5 and 7.1−7.3 (m, 36H, aryl), 7.50 and 7.06 (2d, 2+2H, AB, $J = 5.5$ Hz, pyrrole), 6.97 (d, 2H, $J = 2.1$ Hz, cyclized aryl), 6.68 (d, 2H, $J = 7.8$ Hz, aryl), 6.60 (s, 2H, pyrrole), 5.32 (s, 2H, pyrrole), 1.51, 1.36, 1.12 (3s, 18+18+18H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 399$ nm ($\epsilon = 25000$), 443 (29000), 548 (32000), 672 (8600), 737 (12000); HRMS calcd for $C_{126}H_{104}N_{10}O_8Ni_2 + H^+$ 2001.6818; found 2001.6816.

Nitrocorrole **17**: ^{1}H NMR ($CDCl_3$) $\delta = 7.73$ (d, 1H, $J = 8.9$ Hz, cyclized aryl), 7.55−7.0 (m, 20H, aryl + 1 pyrrole), 7.09 (d, 1H, $J = 5.2$ Hz, pyrrole), 6.95 (d, 1H, $J = 2.1$ Hz, cyclized aryl), 6.84 (s, 1H, pyrrole), 6.38 and 6.13 (2d, 1+1H, AB, $J = 4.6$ Hz, pyrrole), 1.35, 1.34, 1.11 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 388$ nm (relative intensity 0.74), 438 (0.79), 540 (1.00), 670 (0.25), 734 (0.41); HRMS calcd for $C_{63}H_{53}N_5O_4Ni + H^+$ 1002.3524; found 1002.3491.

Electrochemical Experiments on Corroles 3 and 19. A solution of corrole **3** (10 mg) and $n\text{-}Bu_4N^+PF_6^-$ (165 mg) in CH_2Cl_2 (10 mL) was placed in a divided cell and electrolyzed (measured current 60 mA) for 2.5 h. The solvent was evaporated and the residue chromatographed (50 mL of silica gel in cyclohexane + toluene 1:1) to give recovered starting material (1.5 mg) and dimer **14** (2 mg).

The half-wave first oxidation potentials of **3** and **19** were determined by cyclic voltammetry in 1,2-dichloroethane (0.0005 M solution; 0.05 M $n\text{-}Bu_4N^+PF_6^-$ as supporting electrolyte; scan rate 50 mV/s).

Reduction/Acetylation of Nitrocorrole 13. To a stirred solution of nitrocorrole **13** (7 mg) was added a suspension formed when $NaBH_4$ (5 mg) was added to a solution of $NiCl_2 \cdot 6H_2O$ (15 mg) in CH_3OH (0.5 mL). To this mixture was added after 0.5 h $NaBH_4$ (5 mg). The solution slowly turned reddish-brown. When the color did not change anymore, Ac_2O (0.5 mL) was added and the suspension was stirred for an additional 3 min. The suspension was diluted with CH_2Cl_2 (10 mL), washed with H_2O (3×), dried over Na_2SO_4, and evaporated. Chromatography (25 mL of silica gel in toluene) gave amide **18** (3 mg, 47%) crystallized from $CH_2Cl_2-CH_3OH$.

Amide **18**: ^{1}H NMR ($CDCl_3$) $\delta = 7.5-7.15$ (m, 14H, aryl), 7.11 and 6.53 (2d, 1+1H, AB, $J = 5.1$ Hz, pyrrole), 7.01 (dd, 1H, $J = 9$ and 1.8 Hz, cyclized aryl), 6.98 (d, 1 H, $J = 1.8$ Hz, cyclized aryl), 6.55 (s, 1H, pyrrole), 5.92 (br s, 1H, NH), 5.75 and 5.70 (2d, 1+1H, AB, $J = 4.6$ Hz, pyrrole), 5.53 (s, 1H, pyrrole), 1.43 (s, 3H, methyl), 1.34, 1.33, 1.11 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 384$ nm ($\epsilon = 52000$), 494 (46000), 596 (27000), 675 (11000), 736 (16000); HRMS calcd for $C_{58}H_{53}N_5ONi + H^+$ 894.3676; found 894.3686.

Reaction of Corrole 3 with Sodium Borohydride. To a solution of corrole **3** (50 mg) in CH_2Cl_2 (15 mL) and CH_3OH (10 mL) was added solid $NaBH_4$. Vigorous gas evolution started after 5 min, and the suspension was stirred until the starting material was no more detectable (TLC; less than 1 h). Excess $NaBH_4$ was quenched with AcOH (1 mL), and the solution was washed with H_2O (3×) and dried over Na_2SO_4. At this stage, TLC showed a very dark blue spot typical for corrole **19** and a slightly more polar reddish-brown spot. All attempts to isolate this compound failed due to its slow transformation into **19** (on silica gel as well as in solution or as a solid). All fractions were gathered, and the solution was kept at room temperature overnight to ensure the full conversion into **19** and evaporated. The black residue was crystallized from $CH_2Cl_2-CH_3OH$ to give corrole **19** (39.5 mg, 90%).

Corrole **19**: ^1H NMR ($CDCl_3$) $\delta = 7.57$ (d, 1H, $J = 9$ Hz, cyclized aryl), 7.45−7.3 and 7.25−7.15 (m, 13H, aryl + 1 pyrrole), 7.07 (dd, 1H, $J = 9$ and 1.8 Hz, cyclized aryl), 7.03 (d, 1H, $J = 1.8$ Hz, cyclized aryl), 6.65 (d, 1H, $J = 5.1$ Hz, pyrrole), 6.18 and 5.91 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 6.08 and 6.05 (2d, 1+1H, AB, $J = 4.5$ Hz, pyrrole), 5.56 (s, 1H, pyrrole), 1.36, 1.33, 1.13 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 384$ nm ($\epsilon = 87000$), 464 (47000), 490 (52000), 602 (39000), 678 (17000), 736 (26000); HRMS calcd for $C_{56}H_{50}N_4Ni + H^+$ 837.3462; found 837.3474.

Formylation of Corrole 19. A solution of corrole **19** (14 mg) was formylated under the same conditions as **3** (see above) until the starting material disappeared (less than 3 min at 20 °C). Chromatography of the product (150 mL of silica gel in toluene) gave monoaldehydes **20** (5.5 mg, 38%) and **21** (4.5 mg, 31%), both crystallized from $CH_2Cl_2-CH_3OH$. When a larger excess reagent (ca. 3 times) was used, the formation of a more polar product was observed. Under these conditions, corrole **19** (7 mg) gave monoaldehydes **20** (1 mg, 14%) and **21** (2.5 mg, 35%), followed by dialdehyde **22** (2 mg, 26%).

Aldehyde **20**: ^1H NMR ($CDCl_3$) $\delta = 7.97$ (s, 1H, aldehyde), 7.35−7.37 and 7.14−7.17 (2m, 3+2H, phenyl), 7.29, 7.22 and 7.00, 6.94 (4d, 2+2+2+2H, aryl), 7.08 (d, 1H, $J = 9$ Hz, cyclized aryl), 6.86 (dd, 1H, $J = 9$ and 2.1 Hz, cyclized aryl), 6.57 (d, 1H, $J = 2.1$ Hz, cyclized aryl), 6.50 and 5.96 (2d, 1+1H, AB, $J = 5.4$ Hz, pyrrole), 6.06 and 5.33 (2d, 1+1H, AB, $J = 4.5$ Hz, pyrrole), 5.42 and 5.15 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 1.29, 1.25, 1.02 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 388$ nm ($\epsilon = 91000$), 483 (68000), 631 (39000), 779 (34000); HRMS calcd for $C_{57}H_{50}N_4ONi + H^+$ 865.3411; found 865.3420.

Aldehyde **21**: ^1H NMR ($CDCl_3$) $\delta = 8.27$ (s, 1H, aldehyde), 7.81 (d, 1H, $J = 9$ Hz, cyclized aryl), 7.67 and 7.03 (2d, 1+1H, AB, $J = 5.2$ Hz, pyrrole), 7.50 and 7.44 (2m, 2+3H, phenyl), 7.43, 7.45 and 7.32 (3d, 2+2+4H, $J = 8.4$ Hz, aryl), 7.24 (d, 1H, $J = 1.8$ Hz, cyclized aryl), 7.21 (dd, 1H, $J = 9$ and 1.8 Hz, cyclized aryl), 6.87 (s, 1H, pyrrole), 6.44 and 6.29 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 5.89 (s, 1H, pyrrole), 1.39, 1.35, 1.18 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 390$ nm ($\epsilon = 86000$), 496 (62000), 620 (40000), 692 (24000), 752 (34000); HRMS calcd for $C_{57}H_{50}N_4ONi + H^+$ 865.3411; found 865.3410.

Dialdehyde **22**: ^1H NMR ($CDCl_3$) $\delta = 8.21$ (s, 1H, aldehyde), 7.89 (s, 1H, aldehyde), 7.4−7.0 (m, 17H, aryl + 2 pyrrole), 6.80 (d, 1H, $J = 2.0$ Hz, cyclized aryl), 6.42 (d, 1H, $J = 5.4$ Hz, pyrrole), 5.81 and 5.63 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 1.32, 1.28, 1.07 (3s, 9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 392$ nm ($\epsilon = 47000$), 496 (37000), 644 (20000), 696 (16000), 764 (21000); HRMS calcd for $C_{58}H_{50}N_4O_2Ni + H^+$ 892.3360; found 892.3323.

Nitration of Corrole 19. Corrole **19** (7 mg) in CH_2Cl_2 (5 mL) was treated with a solution of $LiNO_3$ in AcOH (0.5 mL) and Ac_2O (0.5 mL). After 40 min, the solution was diluted with CH_2Cl_2 (10 mL), washed with H_2O (3×), dried over Na_2SO_4, and evaporated. Chromatography (50 mL of silica gel in cyclohexane + toluene 2:1) gave dimer **23** (1 mg, 14%), a fraction (2.5 mg) containing an unstable tetramer as shown by MS (peak cluster (3339 to 3352) centered at 3343), followed by dimer **24** (0.8 mg, 11%), all precipitated from $CH_2Cl_2-CH_3OH$. Some impurities are present, as shown by the low UV−visible absorptions, but NMR and MS data strongly suggest that each fraction contained only one corrole. More polar products were not investigated.

Dimer **23**: ^1H NMR ($CDCl_3$, 50 °C) $\delta =$ ca. 8.15 (br signal, 2H, phenyl ?), 7.61 (t, 2H, $J = 7.2$ Hz, phenyl *p*-H ?), 7.50 (d, 2H, $J = 8.7$ Hz, cyclized aryl), 7.4−7.05 (m, 20H, aryl + 2 pyrrole), 7.02 (dd, 2H, $J = 8.7$ and 2 Hz, cyclized aryl), 7.00 (d, 2H, $J = 2$ Hz, cyclized aryl), ca. 6.9 (br signal, 2H, phenyl ?), 6.63 (d, 2H, $J = 5.1$ Hz, pyrrole), 6.20 and 5.95 (d + br signal, 2+2H, AB, $J = 4.8$ Hz, pyrrole), 6.09 and 6.05 (br signal + d, 2+2H, AB, $J = 4.2$ Hz, pyrrole), 1.38, 1.36, 1.11 (3s, 18+18+18H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 392$ nm (relative intensity 1.00), 500 (0.82), 606 (0.37), 796 (0.30); HRMS calcd for $C_{112}H_{98}N_8Ni_2$ 1670.6692; found 1670.6595.

Dimer **24**: ^1H NMR ($CDCl_3$) $\delta =$ ca. 8.3 (br signal, 1H, phenyl ?), 7.8 (d, 1H, $J = 8.7$ Hz, cyclized aryl), 7.74 and 7.11 (dd, 1+1H, AB, $J = 5.1$ Hz, pyrrole), 7.5−6.9 (m, 30H, aryl), 7.17 and 6.60 (2d, 1+1H, AB, $J = 5.1$ Hz, pyrrole), 6.83 (s, 1H, pyrrole), 6.75 and 6.42 (2d, 1+1H, AB, $J = 5.1$ Hz, pyrrole), 6.14 and 5.89 (2d, 1+1H, AB, $J = 4.8$ Hz, pyrrole), 5.93 and 5.79 (2d, 1+1H, AB, $J = 4.5$ Hz, pyrrole), 1.40, 1.36, 1.35, 1.31, 1.17, 1.07 (6s, 9+9+9+9+9+9H, *t*-butyl); UV−visible (CH_2Cl_2) $\lambda = 394$ nm (relative intensity 1), 504 (0.72), 620 (0.43), 794 (0.36); HRMS calcd for $C_{112}H_{97}N_9O_2Ni_2$ 1715.6467; found 1715.6386.

Attempted Demetalation of Corroles 3 and 19. Corrole **19** dissolved easily in CF_3CO_2H, H_2SO_4, or CF_3SO_3H to give purple solutions whose neutralization gave back the starting material. On prolonged reaction (24 h) or heating (80 °C), decomposition occurred. Under the same conditions, corrole **3** gave complex mixtures.

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Supporting Information Available: General experimental procedures, X-ray crystallographic information files (CIF) for compounds **14** and **18**, preliminary crystal structure report for compound **17**, ^1H NMR spectra for all new compounds, and 2D NMR assignments for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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