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Synthesis of Nickel(II) Azacorroles by Pd-Catalyzed Amination of α,α′-Dichlorodipyrrin Ni^{II} Complex and Their Properties

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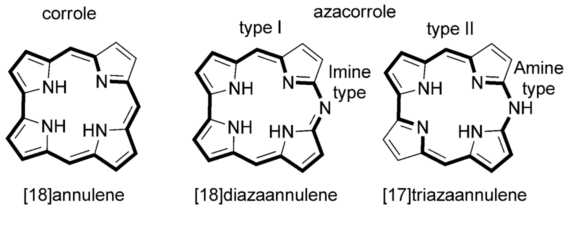
Abstract: Synthesis of nickel(II) complexes of *meso*-aryl-substituted azacorroles was performed by Buchwald–Hartwig amination of a dipyrrin Ni^{II} complex with benzylamine through C–N and C–C coupling. The highly planar structure of Ni^{II} azacorroles was elucidated by X-ray diffraction analysis. ^{1}H NMR analysis and nucleus independent chemical shift (NICS) calculation on Ni^{II} azacorrole revealed its distinct aromaticity with [17]triaza-annulene 18π conjugation. In addition, acylation of azacorrole selectively afforded N- and C-acylated azacorroles depending on the reaction conditions, showing the dual reactivity of azacorroles.

Keywords: amination • aromaticity • C–C coupling • palladium • porphyrinoids

Introduction

Porphyrinoids have attracted considerable attention due to their remarkable properties. Importantly, such properties can be drastically altered by change of the porphyrinoid skeleton. For instance, corrole, in which one methine carbon of porphyrin is missing, shows quite different properties from porphyrin, particularly in view of coordination chemistry.[1] Corrole skeleton can stabilize high-valent metal species, such as Fe^{IV}, Co^{V}, Mn^{V}, and Mn^{VI}.[2] As observed in the corrole chemistry, creation of a novel skeleton eventually leads to a novel properties. Various porphyrinoid skeletons have been developed and their unique properties have been unveiled. However, azacorrole, in which one of the *meso*-carbon atoms of corrole is replaced with nitrogen, remained almost unexplored despite its quite simple structure shown in Scheme 1.[3] In fact, there was no precedent report on the synthesis of *meso*-aryl azacorroles.



Scheme 1. Corrole and two possible tautomeric structures of azacorrole. The bold lines indicate the aromatic 18π conjugation circuit.

Introduction of one nitrogen atom at the *meso*-position of free-base corrole allowed us to draw two possible tautomeric structures of type I and type II (see below; the bold lines indicate the aromatic 18π-conjugation circuit, Scheme 1). The former has three inner NH protons and an imine-type outer nitrogen atom, which is a part of an [18]diaza-annulene structure. In contrast, the latter has two inner NH protons and the outer nitrogen is amine type, lone pair of which participates in the 18π aromatic conjugation pathway of a [17]triaza-annulene. Due to the number of inner NH protons, type I and type II azacorroles should serve as trivalent and divalent ligands, respectively. In other words, different valence states of central metal ions would alter the structure and π conjugation of azacorroles. These potential variations in azacorroles owing to the outer nitrogen atom would add novel functions to corrole, thus expanding the porphyrinoid chemistry. However, there was only one example of synthesis of an azacorrole with β-alkyl substituents.[4] Unfortunately, neither ^{1}H NMR spectrum nor X-ray data of the azacorrole were described; hence, the structure and aromaticity of azacorrole are still in question. Moreover, there was no precedent report on the synthesis of *meso*-aryl-substituted azacorroles. Herein, we report the synthesis and properties of Ni^{II} azacorroles by Buchwald–Hartwig amination of a dipyrrin precursor.[5]

The key of the present synthetic protocol of Ni^{II} azacorroles is transition-metal catalysis. Recently, we have demonstrated that α,α′-dichlorodipyrrin derivatives are good precursors for construction of porphyrinoids by combination with metal-mediated reactions.[6] Syntheses of porphyrinoids have largely relied on acid-promoted condensation–oxidation of pyrroles with aldehydes. However, metal-mediated reactions offer us an opportunity to access novel porphyrinoids, which are difficult to synthesize by the conventional porphyrin synthesis.

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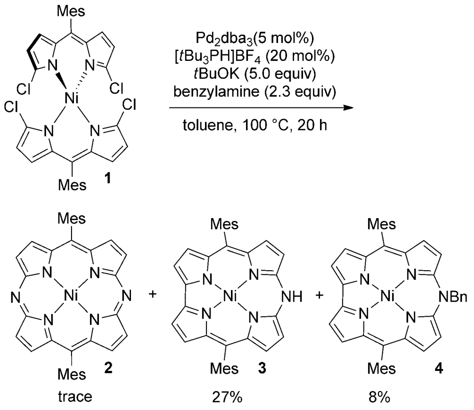
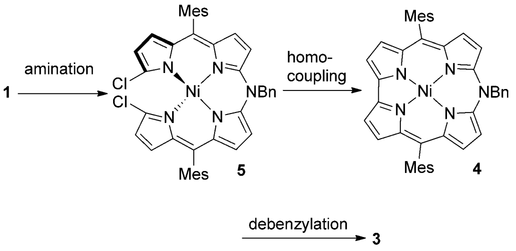
Results and Discussion

The synthetic protocol is shown in Scheme 2, in which α,α′-dichlorodipyrrin Ni^{II} complex **1** was employed as a precursor. We attempted Buchwald–Hartwig amination of **1** with expectation of the formation of diazaporphyrin Ni^{II} complex **2**.[7,8] We observed the formation of two green spots by TLC analysis. High resolution MS (ESI-TOF) analysis suggested that the products were nickel azacorrole **3** and N-benzylazacorrole **4** (Scheme 2). After separation by silica-gel chromatography, azacorroles **3** and **4** were isolated in 27 and 8% yields as black solids, respectively. In addition, a trace amount of Ni^{II} 5,15-diazaporphyrin **2** was also obtained.



Scheme 2. Buchwald–Hartwig amination of dipyrrin Ni^{II} complex **1**.

As a plausible reaction mechanism for the formation of nickel azacorrole **3**, we propose double C−N coupling of **1** with benzylamine to provide the tetrapyrrole intermediate **5**, reductive homocoupling to form N-benzylazacorrole **4**, and debenzylation to azacorrole **3** (Scheme 3). A trace amount of the intermediary open-chain tetrapyrrole **5** was also isolated from the reaction mixture. Presumably, the benzyl group was cleaved in situ by the action of Pd^0 species. In fact, we confirmed debenzylation of **4** to azacorrole **3**. Thus, treatment of benzylazacorrole **4** under the same reaction conditions resulted in formation of **3** in 40% yield. Interestingly, the use of a different catalyst combination of [Pd(OAc)$_2$-X-Phos] afforded diazaporphyrin **2** in 20% yield along with the formation of azacorrole **3** in a lower yield (13% yield). This result indicates that the product distribution depends on the reaction conditions including the choice of the phosphine ligands.



Scheme 3. Proposed reaction pathway for formation of **3** from **1**.

Compound **2** was easily identified to be Ni^{II} 5,15-diazaporphyrin based on its highly symmetric ^{1}H NMR spectrum and MS (ESI-TOF) analysis. The assignment was further supported by the X-ray structure analysis (Figure 1a and b). On the other hand, the ^{1}H NMR spectrum of **3** in CDCl$_3$ displayed rather broad peaks in the aromatic region from $\delta =$

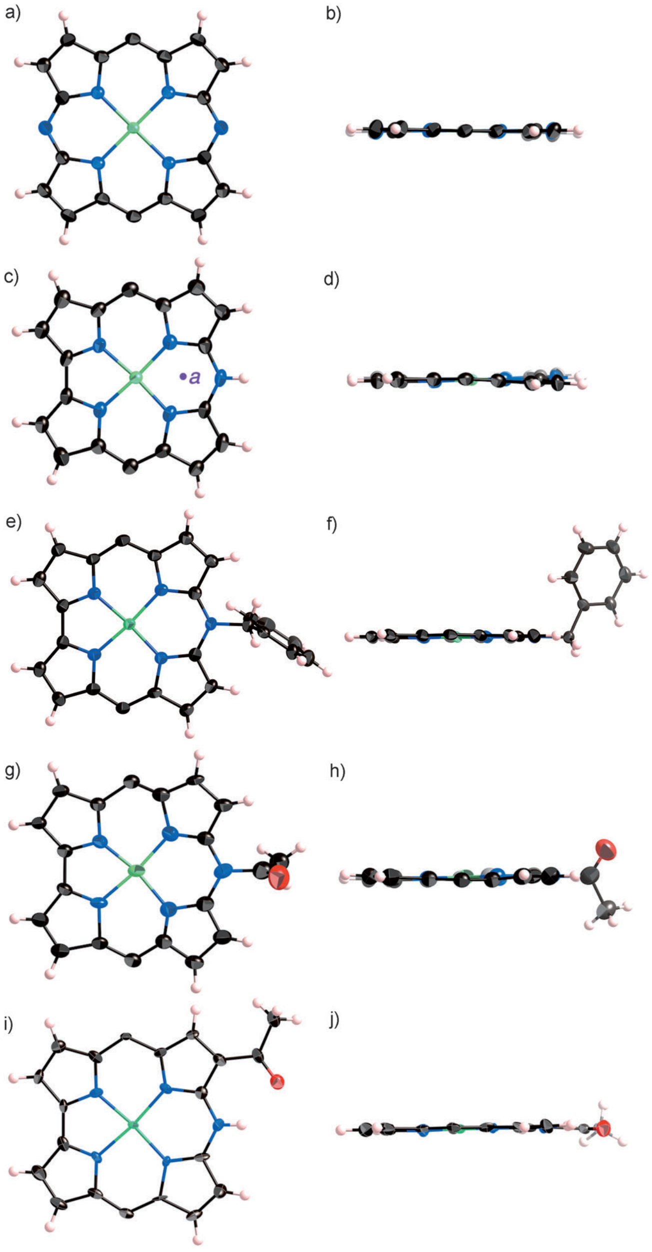


Figure 1. X-ray crystal structures: a) top view and b) side view of **2**; c) top view and d) side view of **3**; e) top view and f) side view of **4**; g) top view and h) side view of **6**; i) top view and j) side view of **7**. *meso*-Aryl substituents are omitted for clarity. The thermal ellipsoids are scaled to the 50% probability level.

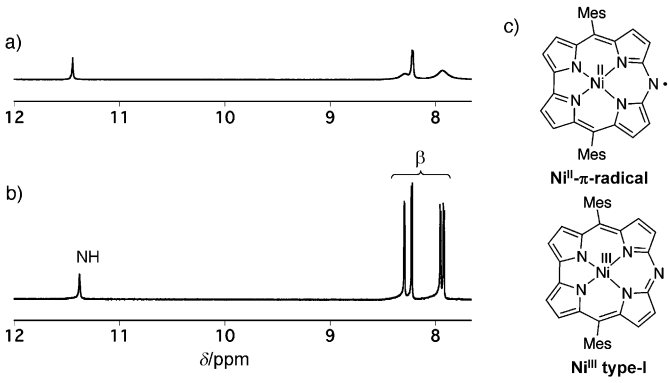
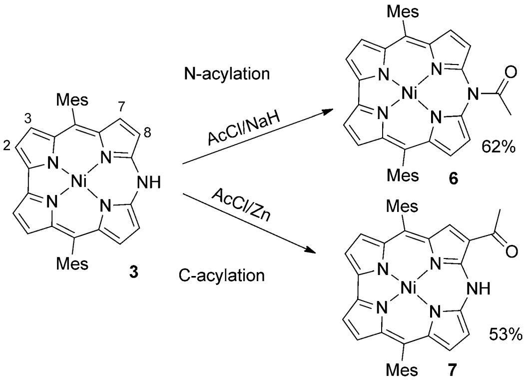


Figure 2. a) ^{1}H NMR spectrum of **3** in $CDCl_3$ and ^{1}H NMR spectrum of **3** after the addition of hydroquinone. b) Possible structures of paramagnetic species in the solution of **3**.

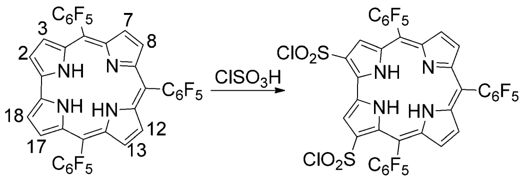
7.5 to 8.5 ppm (Figure 2a). In addition, the ESR spectrum of the solution of **3** exhibited a weak signal probably due to some organic radicals ($g=2.0047$), but the temperature-dependent magnetic susceptibility by the superconducting quantum interference device (SQUID) magnetometer negated the existence of paramagnetic species in the solid sample of **3** (Figure S14 the Supporting Information). On the basis of these findings, we assigned **3** as a Ni^{II} complex with type II structure, in which the nickel takes a low-spin state in a square-planar geometry. The highly planar structure of azacorrole **3** was unambiguously elucidated by the X-ray crystallographic analysis (Figure 1c and d).

The presence of some radical species in solution of **3** is probably because of adventitious oxidation of azacorrole **3** under ambient conditions. The paramagnetic species could be a delocalized π radical or a π-radical cation of **3**, because the observed g value and broad shape of the ESR signal match with ligand radicals rather than Ni^{III} complex of type I azacorrole (Figure 2c).[9] In the presence of a small amount of hydroquinone as antioxidant, the ^{1}H NMR spectrum of **3** exhibited distinct four doublet peaks for β-pyrrolic protons (Figure 2b). Moreover, outer NH proton appeared in the substantially downfield at $\delta=11.39$ ppm. Therefore, azacorrole **3** is concluded to be a distinctly aromatic [17]triaza-annulene. The nucleus independent chemical shift (NICS) value at the point a (indicated in Figure 1c) is calculated to be $\delta=-17.9$ ppm, suggesting strong aromatic character of **3**.[10] The aromaticity of **3** clearly indicates that the lone pair on the outer nitrogen actually participates in the 18π conjugation. Only a few examples of such large aza-annulenic macrocycles with odd-numbered rings are reported due to synthetic difficulty.[11] Furthermore, a porphyrinoid with the amine-type nitrogen atom on the π conjugation is also rare.

Ni^{II} azacorrole **3** has an acidic N−H bond at the *meso*-position, which should be more reactive than the corresponding C−H bond of corrole. This feature can be employed as an effective foothold for functionalization of azacorrole by such as simple acylation. For example, treatment of **3** with acetyl chloride in the presence of NaH as a base gave N-acetylated azacorrole **6** in 62% yield. In contrast, C-acylation occurred exclusively at the C8 position proximal to the NH group to give β-acetylazacorrole **7** in 53% yield through electrophilic substitution in the presence of zinc metal.[12] Importantly, no other regioisomers were detected in the reaction mixture. This regioselectivity to the C8 position is notable, because electrophilic substitution toward regular corroles predominantly occurs in the C2 and C17 positions (Schemes 4 and 5).[13] X-ray diffraction analysis of N- and C-acylated corroles **6** and **7** revealed their structures (Figure 1 g–j). Whereas the acetyl moiety in **6** stands perpendicularly to the macrocycle, which adopts coplanar conformation in **7** due to intramolecular hydrogen-bonding interaction between the *meso*-NH proton, which is supported by the downfield-shifted NH peak at $\delta=13.94$ ppm. The pyrrolic protons of **6** still appeared in the aromatic region around $\delta=8$ ppm, indicating no significant loss of aromaticity by *N*-acylation of Ni^{II} azacorrole. The observed dual reactivity toward an electrophile highlights some similarity to that of pyrrole.



Scheme 4. Site-selective functionalization of azacorrole **3** by acylation.



Scheme 5. Electrophilic substitution of normal corrole.[12a]

The shapes of the UV/Vis absorption spectra of azacorrole **3**, *N*-acetylazacorrole **6**, and *C*-acetylazacorrole **7** are similar to those of regular corroles and exhibit Soret bands and Q-like bands, which are attributable for aromatic porphyrinoids (Figure 3). A substantial redshift of the Q-like band observed for **7** resulted from effective expansion of conjugation due to the coplanar carbonyl group. Similar redshift was also observed in formyl-substitued corroles.[14] Electrochemical properties of **3**, **6**, and **7** were also studied by cyclic voltammetry in CH_2Cl_2 containing 0.1 M Bu_4NPF_6

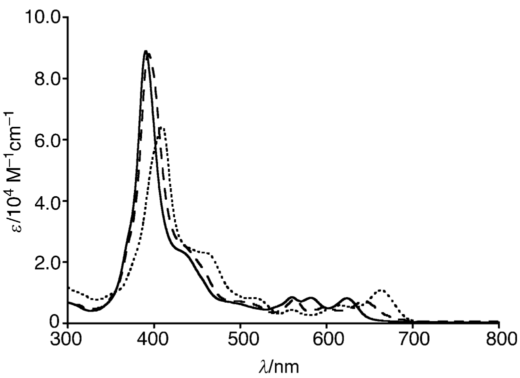


Figure 3. UV/Vis absorption spectra of azacorrole **3** (——), *N*-acetylazacorrole **6** (– – –), and *C*-acetylazacorrole **7** (-----), in CH_2Cl_2.

(Figure S15 in the Supporting Information). The first oxidation wave for azacorrole **3** was observed at relatively low potential [0.13 V (vs. ferrocene/fecrrocenium (Fc/Fc$^+$))] because of electron donation from the outer nitrogen atom. The low oxidation potential of azacorrole **3** is in sharp contrast to that of diazaporphyrin **2** (0.81 V). Although both *N*-acetyl- and *C*-acetylazacorroles **6** and **7** exhibited higher oxidation potentials (0.24 V for **6** and 0.32 V for **7**) due to the electron-withdrawing acyl group, C-acylation was more influential. Thus, the electronic feature of azacorrole can be effectively manipulated by regioselective functionalization at either β-C or *meso*-N positions.

Conclusion

We have achieved the first synthesis of *meso*-aryl azacorrole Ni^{II} complexes by Buchwald–Hartwig amination of a bis(α,α′-dichlorodipyrrinato) Ni complex **1**. Azacorrole Ni^{II} complex **3** can be recognized as a [17]triaza-annulene with distinct aromaticity. We have also accomplished regioselective functionalization of Ni^{II} azacorrole both at the *meso*-nitrogen and β-carbon atoms. Further investigation on the synthesis of free-base azacorrole and metal-coordination behavior is currently ongoing in our laboratory.

Experimental Section

Synthesis of 3 by Buchwald–Hartwig amination of 1: A Schlenk tube equipped with a septum rubber containing **1** (143 mg, 0.200 mmol), $[Pd_2(dba)_3{\cdot}CHCl_3]$ (dba = dibenzylideneacetone; 10.4 mg, 10.0 μmol), $[t\mathrm{Bu}_3\mathrm{P{\cdot}HBF_4}]$ (11.6 mg, 40.0 μmol), and KO*t*Bu (112.2 mg, 1.00 mmol) was evacuated and then refilled with N_2. Dry toluene (5 mL) and benzylamine (50.0 μL, 0.460 mmol) were added by syringes. The reaction mixture was stirred at 100 °C for 20 h. The resulting mixture was filtered through a pad of Celite (CH_2Cl_2 as an eluent) and the solvent was evaporated in vacuo. The crude product was purified by silica-gel column chromatography (CH_2Cl_2/hexane as an eluent) to give **3** (32.0 mg, 54.1 μmol) and **4** (10.3 mg, 15.1 μmol) in 27 and 8 % yields, respectively, along with a trace amount of **2**.

Ni^{II} 5,15-diazaporphyrin 2: ^{1}H NMR ($CDCl_3$): $\delta = 9.13$ (d, $J = 4.8$ Hz, 4H, β), 8.77 (d, $J = 5.1$ Hz, 4H, β), 7.28 (s, 4H, mesityl), 2.59 (s, 6H, mesityl), 1.78 ppm (s, 12H, mesityl); ^{13}C NMR ($CDCl_3$): $\delta = 150.5$, 144.0, 139.0, 138.5, 135.2, 134.2, 133.6, 128.0, 120.9, 21.5, 21.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 375 (63000), 391 (82000), 573 nm (61000 $\mathrm{M^{-1}cm^{-1}}$); HRMS (ESI): *m/z* calcd for $C_{36}H_{30}N_6Ni^+$: 605.1943 $[M{+}H^+]$; found: 605.1958. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of CH_3CN into a chloroform solution of **2**. Crystallographic data: $C_{36}H_{30}N_6Ni$; $M_w = 605.37$ g mol^{-1}; monoclinic; *C*2/*c* (No. 15); $a = 42.05(3)$, $b = 11.585(7)$, $c = 19.735(12)$ Å; $\beta = 115.179(10)°$; $V = 8700(9)$ Å^3; $Z = 12$; $\rho_{calcd} = 1.387$ g cm^{-1}; $T = 153(2)$ K; $R_1 = 0.0466$ $[I > 2.0\sigma(I)]$, $R_w = 0.1439$ (all data); GOF = 1.024 $[I > 2.0\sigma(I)]$.

Ni^{II} 10-azacorrole 3: ^{1}H NMR ($CDCl_3$): $\delta = 11.39$ (s, 1H, NH), 8.30 (d, $J = 4.5$ Hz, 2H, β), 8.23 (d, $J = 4.5$ Hz, 2H, β), 7.96 (d, $J = 4.5$ Hz, 2H, β), 7.93 (d, $J = 4.5$ Hz, 2H, β), 7.17 (s, 4H, mesityl), 2.55 (s, 6H, mesityl), 1.93 ppm (s, 12H, mesityl); ^{13}C NMR ($CDCl_3$): $\delta = 144.3$, 140.4, 138.5, 137.4, 135.1, 132.7, 132.3, 127.7, 127.6, 124.9, 116.7, 111.4, 21.3, 20.9 ppm (one peak was not observed probably because of overlapping); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 391 (89000), 560 (8000), 581 (8000), 624 nm (8000 $\mathrm{M^{-1}cm^{-1}}$); HRMS (ESI-TOF): *m/z* calcd for $C_{36}H_{30}N_5Ni^-$: 590.1860 $[M{-}H^-]$; found: 590.1860. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of hexane into a 1,2-dichloroethane solution of **3**. Crystallographic data: $C_{36}H_{31}N_5Ni$; $M_w = 592.37$ g mol^{-1}; monoclinic; $P2_1$ (No. 4); $a = 8.2257(18)$, $b = 13.707(3)$, $c = 13.050(3)$; $\beta = 101.556(4)°$; $V = 1441.5(5)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.365$ g cm^{-1}; $T = 153(2)$ K; $R_1 = 0.0672$ $[I > 2.0\sigma(I)]$; $R_w = 0.1830$ (all data); GOF = 1.068 $[I > 2.0\sigma(I)]$.

Ni^{II} *N*-benzyl-10-azacorrole 4: ^{1}H NMR ($CDCl_3$): $\delta = 8.25$ (d, $J = 4.3$ Hz, 2H, β), 8.14 (d, $J = 4.8$ Hz, 2H, β), 7.96 (d, $J = 4.8$ Hz, 2H, β), 7.87 (d, $J = 4.3$ Hz, 2H, β), 7.28 (m, 3H, Ph), 7.18 (m, 2H, Ph), 7.14 (s, 4H, mesityl), 6.98 (s, 2H, methylene), 2.52 (s, 6H, mesityl), 1.93 ppm (s, 12H, mesityl); ^{13}C NMR ($CDCl_3$): $\delta = 145.3$, 144.3, 139.1, 138.5, 138.1, 135.8, 133.7, 133.6, 133.1, 129.7, 128.8, 128.7, 128.3, 126.0, 125.7, 117.6, 112.2, 57.7, 22.0, 21.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 395 (75000), 564 (8000), 589 (6000), 639 nm (7000 $\mathrm{M^{-1}cm^{-1}}$); HRMS (ESI): *m/z* calcd for $C_{43}H_{37}N_5Ni^-$: 716.2100 $[M{+}Cl^-]$; found: 716.2096. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of EtOH into a 1,2-dichloroethane solution of **4**. Crystallographic data: $C_{88}H_{78}Cl_2N_{10}Ni_2$; $M_w = 1463.92$ g mol^{-1}; monoclinic; $P2_1$ (No. 4); $a = 11.5914(10)$, $b = 24.867(2)$, $c = 13.6500(11)$ Å; $\beta = 112.4730(10)°$; $V = 3635.8(5)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.337$ g cm^{-1}; $T = 153(2)$ K; $R_1 = 0.0491$ $[I > 2.0\sigma(I)]$; $R_w = 0.1274$ (all data); GOF = 1.042 $[I > 2.0\sigma(I)]$.

Procedure for N-acylation: Sodium hydride (8.0 mg, 0.20 mmol) was washed with dry hexane (3 × 3 mL) before adding dry THF (2 mL) under nitrogen atmosphere. A solution of **3** (14.8 mg, 25 μmol) in THF (5 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 30 min, and acetyl chloride (15.0 μL, 0.21 mmol) was added dropwise. The reaction mixture was stirred at RT for 5 h. The mixture was poured into water and extracted with AcOEt. The organic layer was dried with Na_2SO_4 and evaporated in vacuo. The crude product was purified by silica-gel column chromatography ($CHCl_3$/hexane as an eluent) to give **6** in 62 % yield (9.8 mg, 16 μmol) as a black solid.

***N*-Acetylazacorrole 6**: ^{1}H NMR ($CDCl_3$): $\delta = 8.20$ (d, $J = 4.3$ Hz, 2H, β), 8.15 (d, $J = 4.8$ Hz, 2H, β), 7.85 (d, $J = 4.2$ Hz, 2H, β), 7.79 (d, $J = 4.5$ Hz, 2H, β), 7.15 (s, 4H, mesityl), 3.28 (s, 3H, -C(O)CH_3), 2.53 (s, 6H, mesityl), 1.93 ppm (s, 12H, mesityl); ^{13}C NMR ($CDCl_3$): $\delta = 176.21$, 145.4, 138.4, 138.3, 137.6, 134.8, 133.1, 132.9, 132.4, 129.7, 127.7, 127.6, 125.8, 117.3, 110.8, 21.3, 20.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 394 (88000), 563 (8000), 596 (5000), and 645 nm (7000 $\mathrm{M^{-1}cm^{-1}}$); HRMS (ESI-MS): *m/z* calcd for $C_{38}H_{33}N_5NiO^-$: 633.2006 $[M^-]$; found: 633.2033. Single crystals suitable for X-ray analysis were obtained by slow vapor diffusion of hexane into a dichloromethane solution of **6**. Crystallographic data: $C_{38}H_{33}N_5NiO$; $M_w = 634.40$ g mol^{-1}; monoclinic; *C*2 (No. 5); $a = 26.602(11)$, $b = 11.237(5)$, $c = 11.071(4)$ Å; $\beta = 90.687(8)°$; $V = 3309(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.273$ g cm^{-1}; $T = 153(2)$ K; $R_1 = 0.0627$ $[I > 2.0\sigma(I)]$; $R_w = 0.1539$ (all data); GOF = 1.095 $[I > 2.0\sigma(I)]$.

Procedure for C-acylation: A mixture of **3** (14.8 mg, 25 μmol) and zinc powder (5.0 mg, 76.5 μmol) was evacuated and then refilled with N_2. Dry toluene (3 mL) was added by syringe and the reaction mixture was stirred at 110 °C for 10 min. Then, acetyl chloride (3.0 μL, 42.2 μmol) was added by syringe and the mixture was stirred for 16 h. The resulting mixture was quenched with saturated sodium dicarbonate solution and extracted with AcOEt. The organic layer was dried with Na_2SO_4 and evaporated in vacuo. The residue was purified by silica-gel column chromatography ($CHCl_3$/hexane as an eluent). Recrystallization from $CHCl_3$/MeOH afforded **7** in 53 % yield (8.4 mg, 13.3 μmol) as a green solid.

***C*-Acetylazacorrole 7**: ^{1}H NMR ($CDCl_3$): $\delta = 13.94$ (s, 1 H, NH), 8.31 (s, 1 H, β), 8.16 (m, 3 H, β), 7.94 (d, $J = 4.5$ Hz, 1 H, β), 7.84 (d, $J = 4.5$ Hz, 1 H, β), 7.74 (d, $J = 4.5$ Hz, 1 H, β), 7.18 (s, 2 H, mesityl), 7.14 (s, 2 H, mesityl), 2.83 (s, 3 H, $-C(O)CH_3$), 2.55 (s, 3 H, mesityl), 2.52 (s, 3 H, mesityl), 1.95 (s, 6 H, mesityl), 1.94 ppm (s, 6 H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 197.1$, 148.8, 143.2, 142.8, 139.9, 138.4, 138.2, 137.9, 137.7, 134.7, 134.5, 134.4, 134.2, 134.0, 133.9, 130.5, 128.4, 127.8, 127.7, 123.9, 119.6, 119.0, 117.1, 114.2, 27.6, 21.4, 21.3, 20.9 ppm (two peaks were not observed probably because of overlapping); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 410 (64 000), 515 (8000), 559 (4000), 663 nm (11 000 $M^{-1}cm^{-1}$); HRMS (ESI): *m/z* calcd for $C_{38}H_{33}N_5NiO^-$: 632.1975 [$M-H^-$]; found: 632.1966. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of MeOH into a toluene solution of **7**. Crystallographic data: $C_{38}H_{33}N_5NiO$; $M_w = 634.40$ g mol^{-1}; monoclinic; *Cc* (No. 9); $a = 8.6358(18)$, $b = 45.858(10)$, $c = 8.3877(18)$; $\beta = 110.372(4)°$; $V = 3113.9(11)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.353$ g cm^{-1}; $T = 93(2)$ K; $R_1 = 0.0982$ [$I > 2.0\sigma(I)$]; $R_w = 0.2215$ (all data); GOF = 1.281 [$I > 2.0\sigma(I)$].

CCDC-861381 (**2**), CCDC-861382 (**3**), CCDC-861383 (**4**), CCDC-861384 (**6**), and CCDC-861385 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] For excellent reviews on corrole chemistry, see: a) D. T. Gryko, *Eur. J. Org. Chem.* **2002**, 1735; b) Z. Gross, H. B. Gray, *Adv. Synth. Catal.* **2004**, *346*, 165; c) A. Ghosh, E. Steene, *J. Inorg. Biochem.* **2002**, *91*, 423; d) I. Aviv-Harel, Z. Gross, *Chem. Eur. J.* **2009**, *15*, 8382; e) D. T. Gryko, *J. Porphyrins Phthalocyanines* **2008**, *12*, 906; f) R. Paolesse, *Synlett* **2008**, 2215; g) D. T. Gryko, J. P. Fox, D. P. Goldberg, *J. Porphyrins Phthalocyanines* **2004**, *8*, 1091; h) I. Aviv-Harel, Z. Gross, *Coord. Chem. Rev.* **2011**, *255*, 717.

[2] a) S. Will, J. Lex, E. Vogel, V. A. Adamian, E. Van Caemelbecke, K. M. Kadish, *Inorg. Chem.* **1996**, *35*, 5577; b) E. Vogel, S. Will, A. S. Tilling, L. Neumann, J. Lex, E. Bill, A. X. Trautwein, K. Wieghardt, *Angew. Chem.* **1994**, *106*, 771; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 731; c) A. Kumar, I. Goldberg, M. Botoshansky, Y. Buchman, Z. Gross, *J. Am. Chem. Soc.* **2010**, *132*, 15233; d) Z. Gross, G. Golubkov, L. Simkhovich, *Angew. Chem.* **2000**, *112*, 4211; *Angew. Chem. Int. Ed.* **2000**, *39*, 4045.

[3] Corroles in which all *meso*-carbons are replaced with nitrogen atoms are known as corrolazines, synthesis of which was achieved in 2001, and the intriguing reactivity based on central metals has been revealed, see: a) B. Ramdhanie, C. L. Stern, D. P. Goldberg, *J. Am. Chem. Soc.* **2001**, *123*, 9447; b) S. Fukuzumi, H. Kotani, K. A. Prokop, D. P. Goldberg, *J. Am. Chem. Soc.* **2011**, *133*, 1859; c) A. J. McGown, W. D. Kerper, H. Fujii, D. P. Goldberg, *J. Am. Chem. Soc.* **2009**, *131*, 8040; d) B. Ramdhanie, J. Telser, A. Caneschi, L. N. Zakharov, A. L. Rheingold, D. P. Goldberg, *J. Am. Chem. Soc.* **2004**, *126*, 2515.

[4] W. Johnson, I. T. Kay, R. Rodrigo, *J. Chem. Soc.* **1963**, 2336. *meso*-Arylazacorrole has not been synthesized.

[5] a) J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805; b) J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154; *Angew. Chem. Int. Ed.* **1998**, *37*, 2046; c) J. F. Hartwig, *Acc. Chem. Res.* **2008**, *41*, 1534; d) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 6438; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338.

[6] T. Sakida, S. Yamaguchi, H. Shinokubo, *Angew. Chem.* **2011**, *123*, 2328; *Angew. Chem. Int. Ed.* **2011**, *50*, 2280.

[7] For diazaporphyirins, see: a) N. Kobayashi in *The Porphyrin Handbook, Vol. 2* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, p. 301; b) J. P. Singh, L. Y. Xie, D. Dolphin, *Tetrahedron Lett.* **1995**, *36*, 1567; c) S. Neya, H. Hori, K. Imai, Y. Kawamura-Konishi, H. Suzuki, Y. Shiro, T. Iizuka, N. Funasaki, *J. Biochem.* **1997**, *121*, 654; d) H. Shinmori, F. Kodaira, S. Matsugo, S. Kawabata, A. Osuka, *Chem. Lett.* **2005**, *34*, 322; e) O. G. Khelevina, N. V. Chizhova, P. A. Stuzhin, A. S. Semeikin, B. D. Berczin, *Russ. J. Coord. Chem.* **1996**, *22*, 811; f) G. Khelevina, N. V. Chizhova, P. A. Stuzhin, A. S. Semeikin, B. D. Berczin, *Russ. J. Phys. Chem.* **1997**, *71*, 74.

[8] Matano et al. have independently developed an efficient synthetic procedure for the synthesis of 5,10-diazaporphyrin from dipyrrin metal complexes. Y. Matano, T. Shibano, H. Nakano, H. Imahori, *Chem. Eur. J.* **2012**, *18*, DOI:10.1002/chem.201200463.

[9] For a paramagnetic Ni corrole, see: S. Will, J. Lex, E. Vogel, H. Schmickler, J. P. Gisselbrecht, C. Haubtmann, M. Bernard, M. Gross, *Angew. Chem.* **1997**, *109*, 367; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 357.

[10] The NICS value has been successfully used as a measure of aromaticity, see: a) Z. Chen, C. S. Wannere, C. Corminboeuf, P. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842; b) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[11] For annulenes with odd numbered rings, see: a) S. Hayashi, E. Tsurumaki, Y. Inokuma, P. Kim, Y. M. Sung, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2011**, *133*, 4254; b) Y.-H. Lai, P. Chen, *J. Org. Chem.* **1997**, *62*, 6060; c) R. H. Mitchell, V. S. Iyer, *J. Am. Chem. Soc.* **1996**, *118*, 722; d) R. H. Mitchell, R. Zhou, *Tetrahedron Lett.* **1991**, *32*, 6319; e) T. D. Lash, A. D. Lammer, G. M. Ferrence, *Angew. Chem. Int. Ed.* **2011**, *50*, 9718; f) K. Fujino, Y. Hirata, Y. Kawabe, T. Morimoto, A. Srinivasan, M. Toganoh, Y. Miseki, A. Kudo, H. Furuta, *Angew. Chem.* **2011**, *123*, 6987; *Angew. Chem. Int. Ed.* **2011**, *50*, 6855.

[12] For acylation of pyrrole with zinc powder, see: J. S. Yadav, B. V. S. Reddy, G. Kondaji, R. Srinivasa Rao, S. Praveen Kumar, *Tetrahedron Lett.* **2002**, *43*, 8133.

[13] a) A. Mahammed, I. Goldberg, Z. Gross, *Org. Lett.* **2001**, *3*, 3443; b) Z. Gross, A. Mahammed, *J. Porphyrins Phthalocyanines* **2002**, *6*, 553.

[14] a) I. Saltsman, A. Mahammed, I. Goldberg, E. Tkachenko, M. Botoshansky, Z. Gross, *J. Am. Chem. Soc.* **2002**, *124*, 7411; b) J. J. Weaver, K. Sorasaenee, M. Sheikh, R. Goldschmidt, E. Tkachenko, Z. Gross, H. B. Gray, *J. Porphyrins Phthalocyanines* **2004**, *8*, 76; c) K. Sorasaenee, P. Taqavi, L. M. Henling, E. Tkachenko, H. B. Gray, A. Mahammed, Z. Gross, *J. Porphyrins Phthalocyanines* **2007**, *11*, 189.

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