First Synthesis of Azachlorins and Azacorrins with a N-Atom in β-Pyrrolic Positions

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Azachlorins **7** and **11**, and azahexadehydrocorrin *rac*-**10** are novel structural types of tetrapyrrolic macrocycles. Synthesis of the target structures bearing N-atoms in the β-periphery of the macrotetracycles could be achieved by attaching an imidazole moiety **4** to the tricyclic Ni complex *rac*-**5**, followed by cyclization. Depending on the central metal ion of the bilin intermediates *rac*-**6a** and *rac*-**6b**, chlorin- or corrin-type structures were formed by cyclization.

Introduction. – Since the discovery of '*N*-confused' porphyrins [1] which contain an N-atom in the β-periphery of the chromophore, several synthetic approaches were developed [2][3] aiming at porphyrin structures with an N-atom in peripheral β-positions. Among numerous structures devised according to the initial blueprint, hydroporphyrin- and corrin-like molecules are missing.

Based on the pioneering work of *Johnson* [4] and *Eschenmoser* [5], tetrahydrobilins such as *rac*-**2** were prepared and utilized for the construction of hexadehydrocorrins *rac*-**1** [6] or dihydroporphyrins (chlorins) **3** [7] by cyclization (*Scheme 1*)[1]). Depending on functional groups or/and substituents at the cyclization positions, the tetrahydrobilins *rac*-**2** show different modes of reactions. Electron-withdrawing groups (X = Hal, CN, CO_2R) and Me substituents (X = Me) favor the formation of chlorins **3**, whereas 1-unsubstituted bilin (X = H) *rac*-**2** leads to the corrin structure *rac*-**1** [8].

In the course of investigations directed to the synthesis of '*N*-confused' chlorins, we prepared tetrahydrobilins with an imidazole moiety instead of a normal pyrrole as ring *D* unit.

With different central metal ions in the bilin intermediates *rac*-**6a** and *rac*-**6b**, it was intended to control the course of the cyclization processes to achieve chlorin or corrin formation.

Results and Discussion. – Tetrayhydrobilins *rac*-**6a** and *rac*-**6b** were obtained starting from the Ni complex *rac*-**5**, which had been prepared in our laboratory for the synthesis of different chlorins [7][9].

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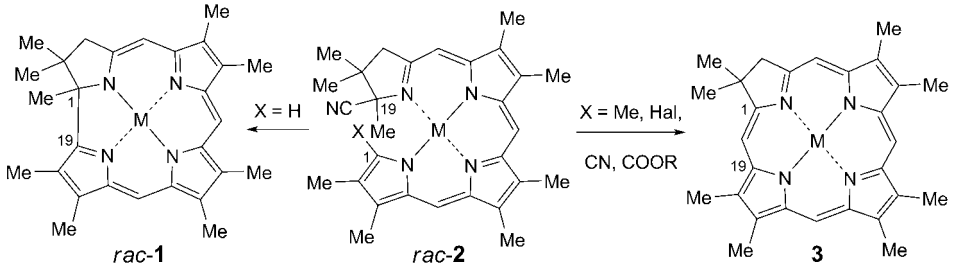
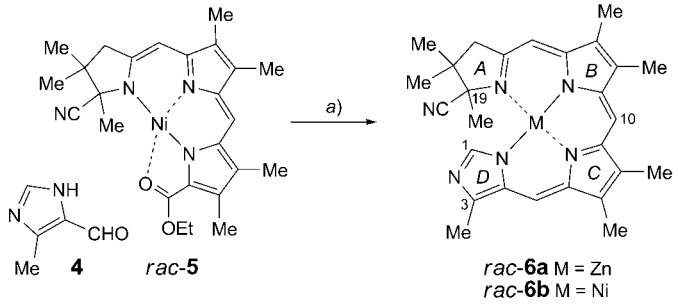
[1]) As a consequence of *IUPAC* nomenclature, the numbering of the C-framework of tetrahydrobilins is different from that of their cyclization products.

Scheme 1. *Cyclization of Tetrahydrobilins* rac-**2** *to Hexadehydrocorrinates* rac-**1** *or Dihydroporphyrinates* (*Chlorins*) **3**



Alkaline hydrolysis of the ester function of the Ni complex *rac*-**5**, followed by acid-induced condensation with decarboxylation and decomplexation [8] with the imidazole carbaldehyde **4** furnished a tetracyclic bilin intermediate. The latter was recomplexed with $Zn(OAc)_2$ or $Ni(OAc)_2$ to give the tetracyclic metal complexes *rac*-**6a** or *rac*-**6b**, respectively (*Scheme 2*).

Scheme 2



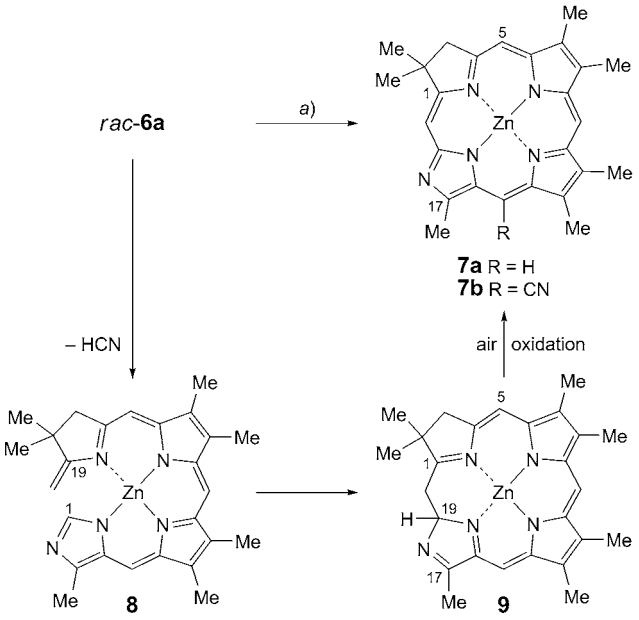
a) 1. 5N KOH, MeOH/H_2O 9:1, THF, reflux, 45 min; 2. 1.8 equiv. **4**, TsOH, $CHCl_3$, reflux, 30 min; 3. $Zn(OAc)_2$, AcONa, r.t., Ar, 20 min, 66% *rac*-**6a** (relative to *rac*-**5**), or $Ni(OAc)_2$, AcONa, r.t., Ar, 20 min, 67% *rac*-**6b** (relative to *rac*-**5**).

To achieve the cyclization, metallo-tetrahydrobilins *rac*-**6a** and *rac*-**6b** were heated in 1,2,4-trichlorobenzene.

The cyclization (*Scheme 3*) of Zn-bilin *rac*-**6a** forms Zn-azachlorin **7a** in almost quantitative yield. The process is initiated by HCN eliminiation to give the intermediate **8** with an exocyclic enamine-like C=C bond [8]. Attack of the nucleophilic enamine-like C=C bond at C(1) of the imidazole moiety led to ring closure and yielded, after oxidation of intermediate **9**, macrotetracycle **7a** together with a trace amount of 15-CN-substituted chlorin **7b**.

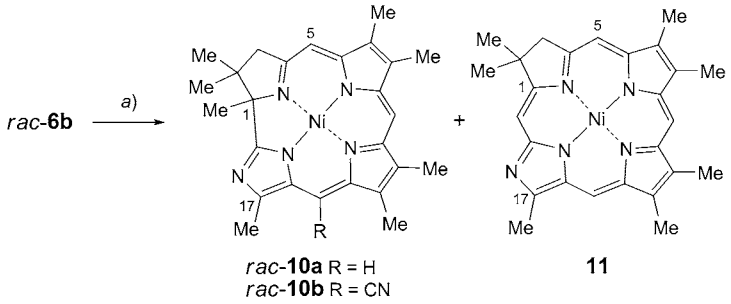
In contrast to Zn-azabilin *rac*-**6a**, Ni-azabiline *rac*-**6b** formed mainly Ni-hexadehydroazacorrin *rac*-**10a** (*Scheme 4*), together with a small amount (6.4%) of Ni-azachlorin **11** and traces of 15-CN-substituted hexadehydroazacorrin *rac*-**10b**. In both

Scheme 3



a) 1,2,4-Trichlorobenzene, 220°, Ar, 30 min; 51% **7a**, trace amount of **7b**.

Scheme 4

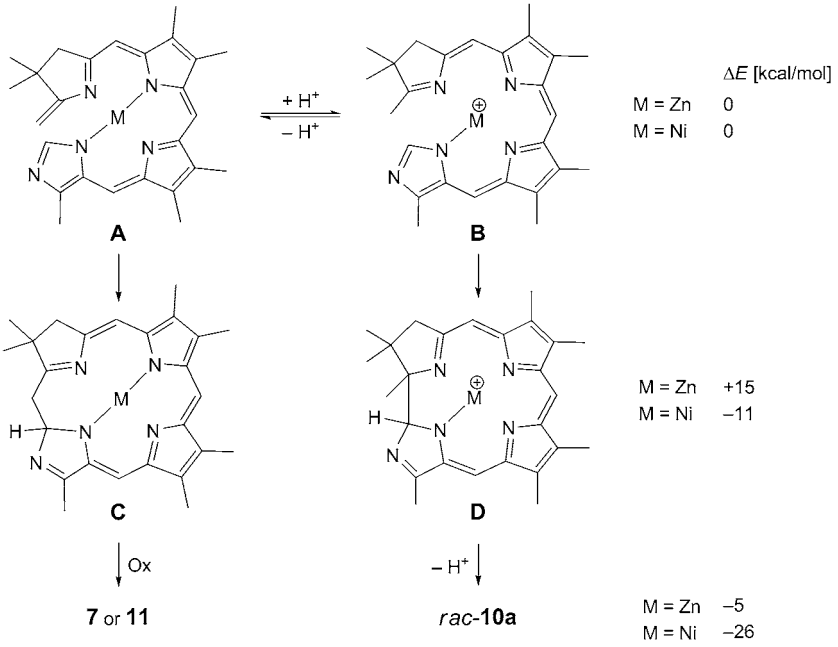


a) 1,2,4-Trichlorobenzene, 220°, 30 min; 50.5% *rac*-**10a**, 6.4% **11**, 4% *rac*-**10b**.

cyclization processes, the central metal ions exert template effects, which bring the reaction centers together. Zn as central metal ion favors ring closure *via* intermediate **A** with the enamine-like C=C bond, whereas Ni contracts the bilin ligand system so that the protonated structure **B** undergoes preferred cyclization to form the corrin *rac*-**10a** (*Scheme 5*).

These findings were confirmed by density-functional theory (DFT) calculations, which revealed that intermediate **A** with an exocyclic C=C bond and Zn was favored

Scheme 5. *Different Reaction Modes of Bilin Intermediates Yielding Corrin- and Chlorin-Type Macrocycles* (M = Zn, Ni)



for cyclization to yield chlorin due to orientation and distance of the reaction centers (*Fig. 1,a*). For the Ni-bilin, it was found that imine-like intermediate **B** formed from **A** by protonation was the preferred structure for cyclization to give the corrin-type product **D** (*Fig. 1,b*).

The calculations demonstrated as well that Ni-corrin intermediate Ni-**D** was formed exothermically, whereas Zn-**D** formation was an endothermic process almost to the same extent. Therefore, the reaction path for formation of Zn-corrin-type structures is energetically blocked. Energies for formation of chlorin intermediate **C** with Zn and Ni are very similar. From these findings, it becomes obvious that, from the protonation $\rightleftharpoons$ deprotonation equilibrium mixture of **A** and **B**, Zn as central metal ion favors chlorin formation, whereas with Ni the corrin-type intermediate **D** is preferred.

The low energy of the final Ni-corrin *rac*-**10a** obtained by deprotonation from intermediate **D** reflects again the stability of the Ni complex compared to the corresponding Zn compounds.

The UV/VIS spectra of Zn-chlorin **3** and Zn-18-azachlorin **7a** were almost identical (*Fig. 2,a* and *b*). Only minor bathochromic shifts compared to **3** could be observed for the *Soret* band (404 nm) and the Q band (620 nm) of **7a**. However, **7a** showed a significant hypsochromic shift of the Q-band on protonation, which was expected due to the electron-withdrawing function of protonated N(18) as part of the chromophore. With exception of a bathochromic shift of the Q-band, the electronic spectrum of **3**

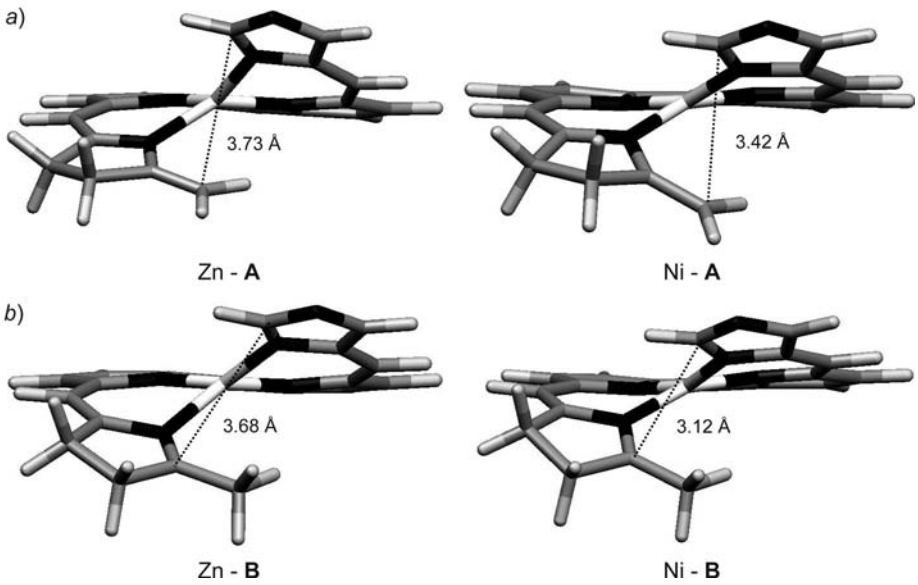


Fig. 1. a) *Calculated conformations* (side view) *of Zn- and Ni-**secochlorin** intermediates* **A**, *and distances between reaction centers.* b) *Calculated conformations* (side view) *of protonated Zn- and Ni-**secocorrin** intermediates* **B**, *and distances between reaction centers*

remained largely unchanged on protonation. On excitation of the *Soret* band, the Zn-azachlorin **10a** exhibited the expected emission (fluorescence) (*Fig. 2*, *c*).

The UV/VIS absorption spectra of the Ni-corrin *rac*-**1** and Ni-18-azacorrin *rac*-**10a** were very similar indicating that the N(18)-atom did not significantly influence the chromophore (*Fig. 3*, *a* and *b*).

A striking difference in the absorption spectra of *rac*-**1** and the aza analog *rac*-**10a** was observed for the protonated structures in acidic solutions. From investigations in the field of Ni-dehydrocorrins [5][10], it is known that protonation occurs at C(17) of the β-periphery, thus completely changing the electronic structure of ring *D* and, accordingly, the absorption spectra.

In contrast, the Ni-18-azacorrin *rac*-**10a** underwent protonation at N(18) preserving the chromophoric system. The absorption bands experience hypsochromic shifts, but the complete pattern of the absorption spectrum was retained.

Experimental Part

General. Starting materials were either prepared according to literature procedures, or were purchased from *Fluka*, *Merck*, or *Sigma–Aldrich*, and used without further purification. All solvents were purified and dried by standard methods. All reactions were carried out under Ar. Column chromatography (CC): silica gel *60* Å, 32–63 μm (*ICN Biomedicals*). TLC: Precoated silica-gel *Kieselgel 60 F_{254}* (*Riedel de Haen*) plates. M.p.: *Reichert Thermovar* hot-stage apparatus or on *Gallenkamp* apparatus; uncorrected. UV/VIS Spectra: *Varian Cary 50* spectrophotometer; λ_{max} (log ε) in nm, ε [$dm^3\ mol^{-1}cm^{-1}$]. IR Specra (KBr, cm^{-1}): *Perkin-Elmer Paragon 500* FT-IR spectrometer. ^{1}H-NMR Spectra: *Bruker DPX-200 Avance* spectrometer; δ in ppm rel. to TMS as internal standard, *J* in Hz. MS

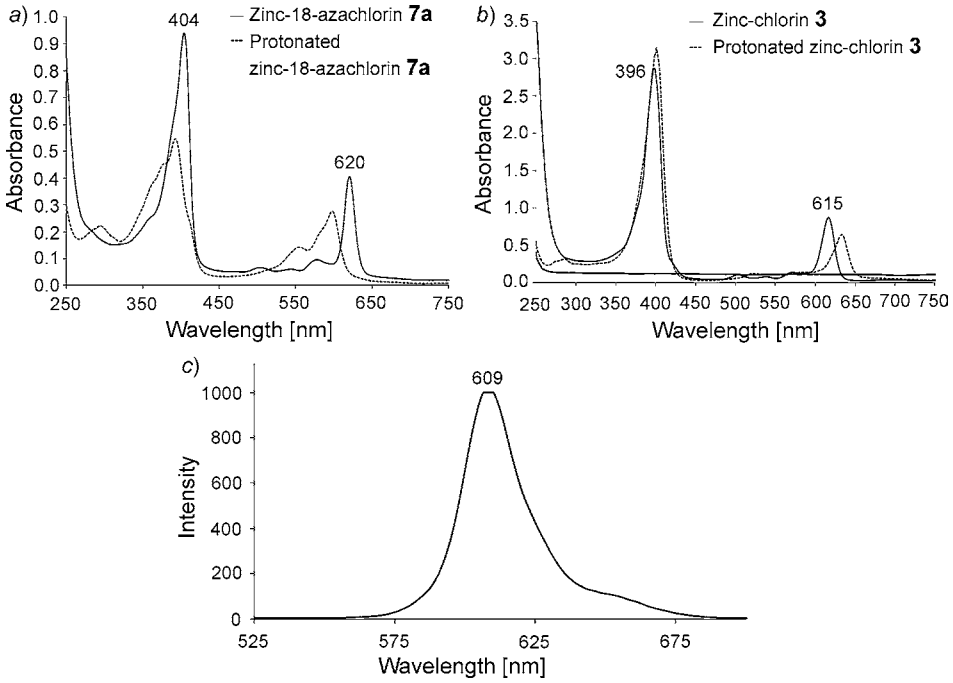


Fig. 2. a) *UV/VIS Spectrum* ($CHCl_3$) *of Zn-18-azachlorin* **7a** (—) *and protonated* ($CHCl_3$/TFA) *Zn-18-azachlorin* **7a** (---). b) *UV/VIS Spectrum* ($CHCl_3$) *of Zn-chlorin* **3** (—) *and protonated* ($CHCl_3$/TFA) *Zn-chlorin* **3** (---). c) *Fluorescence spectrum of* **7a** ($CHCl_3$, $c = 1.69 \times 10^{-5}$ mol/l), *excitation at 394 nm.*

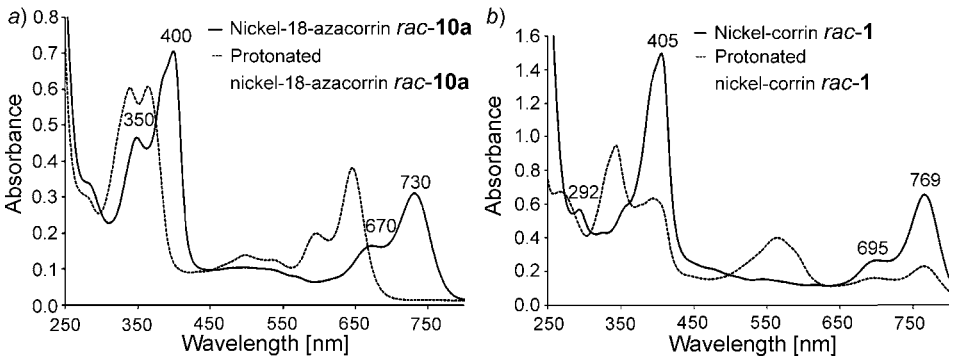


Fig. 3. a) *UV/VIS Spectrum* ($CHCl_3$) *of Ni-18-azacorrin* rac-**10a** (—) *and protonated (CHCl₃/TFA) Ni-18-azacorrin* rac-**10a** (---). b) *UV/VIS Spectrum* ($CHCl_3$) *of Ni-corrin* rac-**1** (—) *and protonated* ($CHCl_3$/TFA) *Ni-corrin rac-***1** (---). Picture in *b* represents a superposition of spectra of 'neutral' and protonated *rac-***1**.

and HR-MS: *Finnigan MAT 8200*, *Finnigan MAT 95*, or *Esquire* spectrometer (EI (70 eV) and ESI); in *m*/*z* (rel.%).

*4-Methyl-1*H*-imidazole-5-carbaldehyde* (**4**) was purchased from *Sigma–Aldrich* and used without further purification.

General Procedure for Synthesis of Tetrahydrobilins rac-**6a** *and* rac-**6b**. A 5N soln. of KOH in MeOH/H_2O 9:1 (4 ml) was added to a soln. of *rac*-**5** [7] (13.0 mg, 27.2 μmol) in dry THF (5 ml). The mixture was heated at 80° for 45 min under Ar. After cooling, the mixture was diluted with CH_2Cl_2 (20 ml) and washed with a $NaHCO_3$ soln. (20 ml). The aq. layer was vigorously extracted again with CH_2Cl_2 (4 × 10 ml), and the combined org. layers were dried by filtration through cotton wool and concentrated *in vacuo* to afford the free carboxylic acid of *rac*-**6**. Degassed solns. of **4** (7.5 mg, 68.1 μmol, 2.5 equiv.) in dry $CHCl_3$ (6 ml) and 0.4N TsOH in $CHCl_3$ (1.4 ml, 545 μmol, 20 equiv.) were successively added by a syringe through a septum to the degassed carboxylic acid under Ar. The mixture was heated at reflux with stirring for 40 min. The blue mixture was diluted with CH_2Cl_2 (20 ml), poured into a separating funnel containing H_2O (30 ml), and vigorously extracted with CH_2Cl_2 (3 × 20 ml). The combined org. layers were dried by filtration through cotton wool and concentrated *in vacuo*. The metal-free bilin was used without further purification for the next reaction step. A soln. of dry $Zn(OAc)_2$ (60.0 mg, 327 μmol, 12.1 equiv.) and AcONa (27 mg, 327 μmol, 12.1 equiv.) in dry MeOH (3 ml) was added to a soln. of crude metal-free bilin in dry CH_2Cl_2 (6 ml). The mixture was reacted at r.t. for 30 min under Ar, then it was transferred into a separating funnel containing H_2O (20 ml) and vigorously extracted with CH_2Cl_2 (3 × 20 ml). The org. layers were dried by filtration through cotton wool and concentrated under reduced pressure. The residue was purified by CC (*Alox N*; CH_2Cl_2/MeOH 15:1) to yield *rac*-**6a** as a blue solid.

The Ni-bilin *rac*-**6b**, also a blue solid, was obtained in the same way by using $Ni(OAc)_2$ (67.8 mg, 383 μmol, 14 equiv.).

*(17,18,19,24-Tetrahydro-3,7,8,12,13,18,18,19-octamethyl-22*H*-2-azabilin-19-carbonitrilato)zinc(II)* (*rac*-**6a**). Yield: 9.1 mg (18.1 μmol, 66%). R_f (SiO_2; CH_2Cl_2/MeOH 9:1) 0.45. UV/VIS ($CHCl_3$): 679 (10394), 619 (6485), 369 (17545), 270 (10212). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.79 (*s*, Me–C(18)), 0.98 (*s*, Me–C(18)), 1.27 (*s*, Me–C(19)), 2.04, 2.10, 2.20 (3*s*, Me–C(7), Me–C(8), Me–C(12), Me–C(13)), 2.40 (*s*, Me–C(3)), 2.65, 3.06 (*AB*, J = 15.7, CH_2(17)), 5.48 (*s*, H–C(15)), 6.00 (*s*, H–C(10)), 6.92 (*s*, H–C(5)), 7.75 (*s*, H–C(1)). EI-MS (70 eV, direct inlet, *T ca.* 200°): 504 (41), 502 (72, [M^+, ^{64}Zn]), 489 (11.5), 487 (20, [M^+ – Me, ^{64}Zn]), 477 (41), 475 (70, [M^+ – HCN, ^{64}Zn]), 462 (29), 460 (50, [M^+ – HCN – Me, ^{64}Zn]), 446 (17), 444 (30, [M^+ – HCN – 2 Me, ^{64}Zn]), 435 (6), 433 (10, [M^+ – HCN – 3 Me, ^{64}Zn]), 239 (7), 238 (12, [M^{2+} – HCN, ^{64}Zn]), 231 (3), 230 (5, [M^{2+} – HCN – Me, ^{64}Zn]), 223 (7), 222 (13, [M^{2+} – HCN – 2 Me, ^{64}Zn]). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 505 (57, [M + H]$^+$, ^{66}Zn), 503 (100, [M + H]$^+$, ^{64}Zn). HR-MS could not be recorded because of decomposition.

*(17,18,19,24-Tetrahydro-3,7,8,12,13,18,18,19-octamethyl-22*H*-2-azabilin-19-carbonitrilato)nickel(II)* (*rac*-**6b**). Yield: 9.1 mg (18.34 μmol, 67%). R_f (SiO_2; CH_2Cl_2/MeOH 6:1) 0.4. UV/VIS ($CHCl_3$): 692 (14466), 634 (7096), 400 (29649), 348 (13689). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.03, 1.63 (2*s*, 2 Me–C(18)), 1.45 (*s*, Me–C(19)), 2.23 (*s*, Me–C(8)), 2.24 (*s*, Me–C(13)), 2.26 (*s*, Me–C(12)), 2.33 (*s*, Me–C(7)), 2.66 (*s*, Me–C(3)), 2.69, 3.06 (*AB*, J = 17.3, CH_2(17)), 6.1 (*s*, H–C(15)), 6.46 (*s*, H–C(10)), 7.01 (*s*, H–C(5)), 7.51 (*s*, H–C(1)). EI-MS: (70 eV, direct inlet, *T ca.* 200°): 498 (1.5), 496 (4, [M^+, ^{58}Ni]), 471 (38), 469 (100, [M^+ – HCN, ^{58}Ni]), 456 (23), 454 (60, [M^+ – HCN – Me, ^{58}Ni]), 441 (15), 439 (38, [M^+ – HCN – 2 Me, ^{58}Ni]), 426 (12), 424 (32, [M^+ – HCN – 3 Me, ^{58}Ni]), 411 (3), 409 (6, [M^+ – HCN – 4 Me, ^{58}Ni]), 248 (3, [M^{2+} – Me, ^{58}Ni]), 235 (5), 234 (12, [M^{2+} – HCN, ^{58}Ni]), 220 (4), 219 (10, [M^{2+} – HCN – 2 Me, ^{58}Ni]), 213 (3), 212 (8, [M^{2+} – HCN – 3 Me, ^{58}Ni]). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 499 (38, [M + H]$^+$, ^{60}Ni), 497 (100, [M + H]$^+$, ^{58}Ni). HR-MS: 496.18756 (M^+, $C_{27}H_{30}N_6{}^{58}Ni^+$; calc. 496.18854).

(2,3-Dihydro-2,2,7,8,12,13,17-heptamethyl-18-azaporphyrinato)zinc(II) (**7a**) *and (2,3-Dihydro-2,2,7,8,12,13,18-heptamethyl-18-azaporhyrin-15-carbonitrilato)zinc(II)* (**7b**). A carefully degassed soln. of *rac*-**6a** (5 mg, 9.5 μmol) in dry 1,2,4-trichlorobenzene (5 ml) was heated at 220° for 20 min under Ar. After cooling to r.t., the solvent was removed by bulb-to-bulb distillation at 80° *in vacuo* (oil pump). The brown residue was purified by CC (SiO_2; CH_2Cl_2/MeOH 7:1). The first fraction consisted of a trace amount of **7b**, and the following main fraction of **7a** gave green violet crystals. Yield of **7a**: 2.63 mg (5.54 μmol, 51%). Yield of **7b** could not be determined.

Data for **7a**. R_f (SiO_2; CH_2Cl_2/MeOH 7:1) 0.35. UV/VIS ($CHCl_3$): 620 (24004), 574 (5554), 500 (3934), 404 (55625). ^{1}H-NMR ($CDCl_3$ + (D_5)pyridine, 600 MHz): 1.57 (*s*, 2 Me–C(2)); 2.76, 2.84, 2.86 (*s*, Me–C(7), Me–C(8), Me–C(12), Me–C(13)); 3.45 (*s*, Me–C(17)), 3.92 (*s*, CH_2(3)); 7.78 (*s*, H–C(5)); 8.24 (*s*, H–C(20)); 8.47 (*s*, H–C(10)); 8.87 (*s*, H–C(15)). EI-MS: (70 eV, direct inlet, *T ca.* 200°): 475 (74), 473 (100, [M^+, ^{64}Zn]), 460 (37), 458 (64, [M^+ – Me, ^{64}Zn]), 445 (14), 443 (24, [M^+ – 2 Me, ^{64}Zn]), 430 (5), 428 (8, [M^+ – 3 Me, ^{64}Zn]), 238 (9), 237 (15, [M^{2+}, ^{64}Zn]), 230 (7), 229 (12, [M^{2+} – Me, ^{64}Zn]), 223 (14), 222 (24, [M^{2+} – 2 Me, ^{64}Zn]), 215 (6), 214 (10, [M^{2+} – 3 Me, ^{64}Zn]). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 476 (57, [M + H]$^+$, ^{66}Zn), 474 (100, [M + H]$^+$, ^{64}Zn). HR-MS: 473.15688 (M^+, $C_{26}H_{27}N_5{}^{64}Zn^+$; calc. 473.15579).

Data of **7b**. R_f (SiO_2; CH_2Cl_2/MeOH 7:1) 0.68. UV/VIS ($CHCl_3$): 656 (0.5), 410 (0.85). EI-MS (70 eV, direct inlet, *T ca.* 200°): 500 (50), 498 (85, [M^+, ^{64}Zn]), 485 (37), 483 (64, [M^+ – Me, ^{64}Zn]), 470 (11), 468 (20, [M^+ – 2 Me, ^{64}Zn]), 250 (20), 249 (35, [M^{2+}, ^{64}Zn]), 243 (9), 242 (16, [M^{2+} – Me, ^{64}Zn]), 234 (15), 233 (26, [M^{2+} – 2 Me, ^{64}Zn]). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 501 (57, [M + H]$^+$, ^{66}Zn), 499 (100, [M + H]$^+$, ^{64}Zn).

*(7,8,12,13,18,19-Hexadehydro-1,2,2,7,8,12,13,17-octamethyl-18-aza-24*H*-corrinato)nickel(II)* (*rac*-**10a**), *(7,8,12,13,18,19-Hexadehydro-1,2,2,7,8,12,13,17-octamethyl-18-aza-24*H*-corrin-15-carbonitrilato)-nickel(II)* (*rac*-**10b**), *and (2,3-Dihydro-2,2,7,8,12,13,17-heptamethyl-18-azaporphyrinato)nickel(II)* (**11**). A carefully degassed soln. of *rac*-**6b** (5 mg, 10.05 μmol) in dry 1,2,4-trichlorobenzene (5ml) was heated at 220° for 20 min under Ar. After cooling to r.t., the solvent was removed by bulb-to-bulb distillation at 80° *in vacuo* (oil pump). The brown residue was purified by CC (SiO_2; CH_2Cl_2/MeOH 10:1) to yield **11** (0.3 mg, 1.1 μmol, 6.4%) as a green unpolar fraction, *rac*-**10b** (0.2 mg, 0.4 μmol, 4%) as a brown green fraction, and finally *rac*-**10a** (2.39 mg, 5.1 μmol, 50.5%) as a deep-green solid main product.

Data of **10a**. R_f (SiO_2; CH_2Cl_2/MeOH 9:1) 0.2. UV/VIS ($CHCl_3$): 730 (12663), 670 (6716), 400 (28936), 350 (18915), 282 (14097). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.98, 1.45 (2*s*, 2 Me–C(2)), 2.25, 2.29, 2.31, 2.32 (4*s*, Me–C(7), Me–C(8), Me–C(12), Me–C(13)), 2.87, 3.36 (*AB*, J = 16.6, CH_2(3)), 2.71 (*s*, Me–C(17)), 6.08 (*s*, H–C(5)), 6.63 (*s*, H–C(10)), 7.14 (*s*, H–C(15)). EI-MS (70 eV, direct inlet, *T ca.* 200°): 471 (38), 469 (100, [M^+, ^{58}Ni]), 456 (28), 454 (72, [M^+ – Me, ^{58}Ni]), 441 (14), 439 (36, [M^+ – 2 Me, ^{58}Ni]), 426 (10), 424 (26, [M^+ – 3 Me, ^{58}Ni]), 411 (1), 409 (4, [M^+ – 4 Me, ^{58}Ni]), 236 (10), 235 (24, [M^{2+}, ^{58}Ni]), 228 (2), 227 (6, [M^{2+} – Me, ^{58}Ni]), 221 (8), 219 (22) [M^{2+} – 2 Me, ^{58}Ni]), 213 (7), 212 (18, [M^{2+} – 3 Me, ^{58}Ni]), 206 (4), 205 (10, [M^{2+} – 4 Me, ^{58}Ni]). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 472 (38, [M + H]$^+$, ^{60}Ni), 470 (100, [M + H]$^+$, ^{58}Ni). HR-MS: 469.17877 (M^+, $C_{26}H_{29}N_5{}^{58}Ni^+$; calc. 469.17764).

Data of **10b**. R_f (SiO_2; CH_2Cl_2/MeOH 9:1) 0.48. UV/VIS ($CHCl_3$): 727 (0.3), 770 (0.18), 519 (0.23), 411 (0.98), 402 (0.99), 353 (0.83), 280 (0.6). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.96, 1.27 (2*s*, 2 Me–C(2)), 1.63 (*s*, Me–C(1)), 2.25, 2.31, 2.33, 2.55 (4*s*, Me–C(7), Me–C(8), Me–C(12), Me–C(13)), 2.89, 3.34 (*AB*, J = 16.6, CH_2(3)), 6.14 (*s*, H–C(5)), 6.62 (*s*, H–C(10)). EI-MS (70 eV, direct inlet, *T ca.* 200°): 496 (38), 494 (100) [M^+, ^{58}Ni]), 481 (28), 479 (75, [M^+ – Me, ^{58}Ni]), 466 (11), 464 (30, [M^+ – 2 Me, ^{58}Ni]), 451 (11), 449 (28) [M^+ – 3 Me, ^{58}Ni]), 436 (2), 434 (5, [M^+ – 4 Me, ^{58}Ni]), 248 (4), 247 (10, [M^{2+}, ^{58}Ni]), 433 (5), 432 (13) [M^{2+} – 2 Me, ^{58}Ni]), 256 (5), 225 (13, [M^{2+} – 3 Me, ^{58}Ni]). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 497 (38, [M + H]$^+$, ^{60}Ni), 495 (100, [M + H]$^+$, ^{58}Ni).

Data of **11**. R_f (SiO_2; CH_2Cl_2/MeOH 9:1) 0.5. UV/VIS ($CHCl_3$): 618 (22138), 398 (34913) , 381 (28208). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.79 (*s*, 2 Me–C(2)), 3.01 (*s*, Me–C(7)), 3.13 (*s*, Me–C(7), Me–C(12)), 3.15 (*s*, Me–C(13)), 4.15 (*s*, CH_2(3)), 8.16 (*s*, H–C(5)), 8.31 (*s*, H–C(10)), 8.93 (*s*, H–C(15)), 9.2 (*s*, H–C(20)). EI-MS (70 eV, direct inlet, *T ca.* 200°): 469 (38), 467 (100, [M^+, ^{58}Ni]), 454 (20), 452 (56, [M^+ – Me, ^{58}Ni]), 439 (9), 437 (24, [M^+ – 2 Me, ^{58}Ni]), 424 (3), 422 (8, [M^+ – 3 Me, ^{58}Ni]), 407 (2) [M^+ – 4 Me, ^{58}Ni]), 235 (6), 234 (16, [M^{2+}, ^{58}Ni]), 227 (4), 226 (10) [M^{2+} – Me, ^{58}Ni]), 220 (8), 219 (22, [M^{2+} – 2 Me, ^{58}Ni]), 212 (6), 211 (16, [M^{2+} – 3 Me, ^{58}Ni]), 204 (2), 203 (5, [M^{2+} – 4 Me, ^{58}Ni]). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 470 (38, [M + H]$^+$, ^{60}Ni), 468 (100, [M + H]$^+$, ^{58}Ni). HR-MS: 467.16057 (M^+, $C_{26}H_{27}N_5{}^{58}Ni^+$; calc. 467.16199).

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