Unusual Loss of Substituents in the Course of Cyclization of Tetrahydrobilines to Dihydroporphyrins

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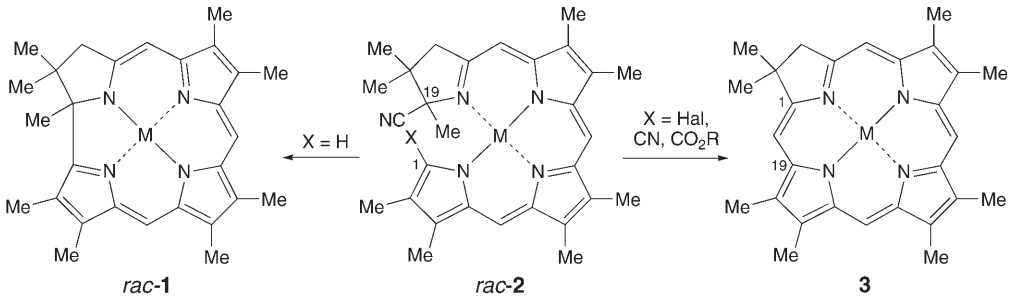
Metallo-tetrahydrobiline *rac*-**8** was prepared to investigate its cyclization directed to the formation of *N*-confused chlorins. To achieve the site-directed selectivity of the cyclization, the 2-position of *rac*-**2** was activated by an electron-withdrawing cyano function and its 1-position was blocked by a methyl group. In spite of this provision, the cyclization occurred at the apparently blocked 1-position with loss or migration of the methyl substituent.

Introduction. – Since the pioneering work of *Johnson* [1] and *Eschenmoser* [2], the cyclization of biline-type tetra(hydro)pyrroles became an important synthetic concept for the construction of porphyrinoid and corrinoid structures.

In our laboratory, cyclization of tetrahydrobilines *rac*-**2** were investigated with regard to the construction of hexadehydrocorrins *rac*-**1** [3] or dihydroporphyrins (chlorins) **3** [4]. Depending on functional groups or/and substituents at the cyclization positions, the tetrahydrobilines *rac*-**2** show different modes of reaction. Electron-withdrawing groups (X = Hal, CN, CO_2R) favor the formation of chlorins **3**, whereas the 1-unsubstituted biline (X = H) *rac*-**2** forms the corrin structure *rac*-**1** (*Scheme 1*)[1]).

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



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

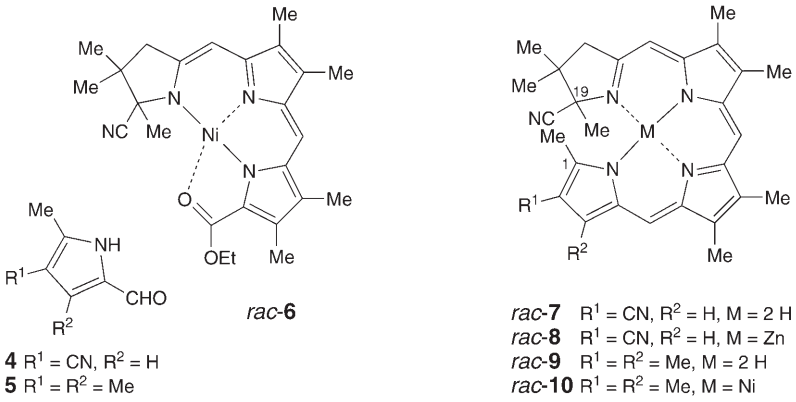
In the course of investigations directed to the synthesis of chlorins with the N-atom at the periphery of the chromophore (*N*-confused chlorins), we prepared tetrahydrobilines *rac*-**7** – *rac*-**10** with Me groups at C(1).

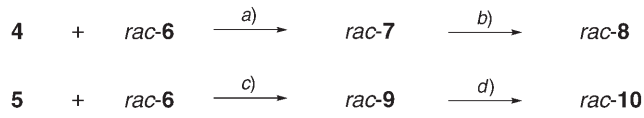
Here, we could demonstrate that, even with the tetrahydrobilines *rac*-**7** – *rac*-**10** which bear Me substituents at C(1), cyclization reactions occurred. During the cyclization processes whether migration or complete loss of the Me groups were observed.

Results and Discussion. – Tetrahydrobilines *rac*-**7** and *rac*-**10** were obtained starting from the Ni complex *rac*-**6**, which was previously prepared [4], and which was used in our laboratory for syntheses of numerous chlorins [5].

Alkaline hydrolysis of the ester function of the Ni complex *rac*-**6**, followed by acid-induced condensation with decarboxylation and decomplexation with the pyrrole carbaldehydes **4** and **5**, furnished the tetracyclic bilines *rac*-**7** and *rac*-**9**, respectively (*Scheme 2*).

Scheme 2





a) 1. 5N KOH, MeOH/H_2O 9:1, THF, reflux, 45 min; 2. 1.9 equiv. **4**, TsOH, $CHCl_3$, reflux, 20 min. *b*) $Zn(OAc)_2$, AcONa, r.t., Ar, 30 min, 35% (rel. to *rac*-**6**). *c*) 1. 5N KOH, MeOH/H_2O 9:1, THF, reflux, 45 min; 2. 1.9 equiv. **5**, TsOH, $CHCl_3$, reflux, 20 min; 64%. *d*) $Ni(OAc)_2$, AcONa, r.t., Ar, 30 min, chromatogr.; 92%.

Both tetrahydrobilines *rac*-**7** and *rac*-**9** were recomplexed with $Zn(OAc)_2$ or $Ni(OAc)_2$ to give *rac*-**8** and *rac*-**10**, respectively.

The tetracyclic metal complexes *rac*-**8** and *rac*-**10** were obtained as binary mixtures of diastereoisomers on account of the stereogenic centers at C(19) and because of the helicity of the tetrapyrrolic chromophore. The occurrence of these diastereoisomers

was clearly indicated by twofold sets of ^{1}H-NMR signals for each pair of diastereoisomers.

Interestingly, also with the metal-free biline *rac*-**9**, two diastereoisomeric structures in the ratio of 80:20 were observed in the crystal lattice (*Fig.*, *a*)[2]). In the major diastereoisomer *rac*-**9a**, the Me group at C(19) points to the ring D pyrrole of the tetracycle. The minor diastereoisomer *rac*-**9b** has the CN function at C(19) directed to ring D. As a consequence, the distance between C(1) and C(19) is 5.04 Å for the major diastereoisomer *rac*-**9a** and 5.61 Å for the minor diastereoisomer *rac*-**9b**.

Semiempirical PM3 calculations (*Fig.*, *b*) confirmed the major diastereoisomer *rac*-**9a** by 7.89 kJ/mol more stable than the more helical and distorted minor diastereoisomer *rac*-**9b**. In both diastereoisomers, the distortion leading to helicity occurs mainly around the C(10)–C(11) bond (according to the numbering of the X-ray structures) so that A–B and C–D subunits form more or less independent chromophores each stabilized by intramolecular H-bonds. In solution, free rotation around the C(10)–C(11) bond is possible so that the existence of diastereoisomers could not be detected in the ^{1}H-NMR spectrum of *rac*-**9**.

To achieve the cyclization of the tetrahydrobilines, their metal complexes *rac*-**8** and *rac*-**10** were simply heated in 1,2,4-trichlorobenzene. It can be seen with the Zn biline *rac*-**8** that the cyclization process is initiated by elimination of HCN from C(19)[1]), thus giving a tetrahydrobiline **11** with an exocyclic enamine C=C bond (*Scheme 3*, *Reaction A*). Biline **11** is formed in a mixture together with cyclized Zn chlorin **12**.

The cyclization occurs between the enamine C-atom C(19) and C(1), whereby the central metal ion exercises a template effect. The Zn chlorin **12**, which has lost the Me group at C(1) during the course of the reaction, and the tetrahydrobiline **11** were separated by chromatography.

When the separated pure biline **11** was heated again (*Scheme 3*, *Reaction B*), a mixture of uncyclized biline and a new chlorin **13** bearing a Me group at C(17) was formed. After separation of unreacted **11** from chlorin **13**, heating was repeated with **11** to give again the mixture of **11** and **13**.

For the Ni tetrahydrobiline *rac*-**10**, in which C(3) has already a Me substituent, only loss of the Me group at C(1) but no Me migration during the cyclization process was observed (*Scheme 4*).

A possible mechanistic interpretation of the experimental results is summarized in *Scheme 5*. It can be assumed that in all cases the primary cyclization product **A** is formed.

If a nucleophile is present in the reaction mixture, this nucleophile undergoes a nucleophilic attack at the Me group at C(19) with the whole macrotetracycle **B** as a leaving group. The macrotetracyclic chromophoric system of **B** should be able to stabilize the negative charge. The CN^- which is formed by elimination from C(19)

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[2]) The structures and calculations were performed with direct methods (*Siemens-P4*; SHELX Program Package). Crystallographic data (excluding structure factors) for the structure of *rac*-**9a** and *rac*-**9b** have been deposited with the *Cambridge Crystallographic Data Centre*. CCDC-658495 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif.

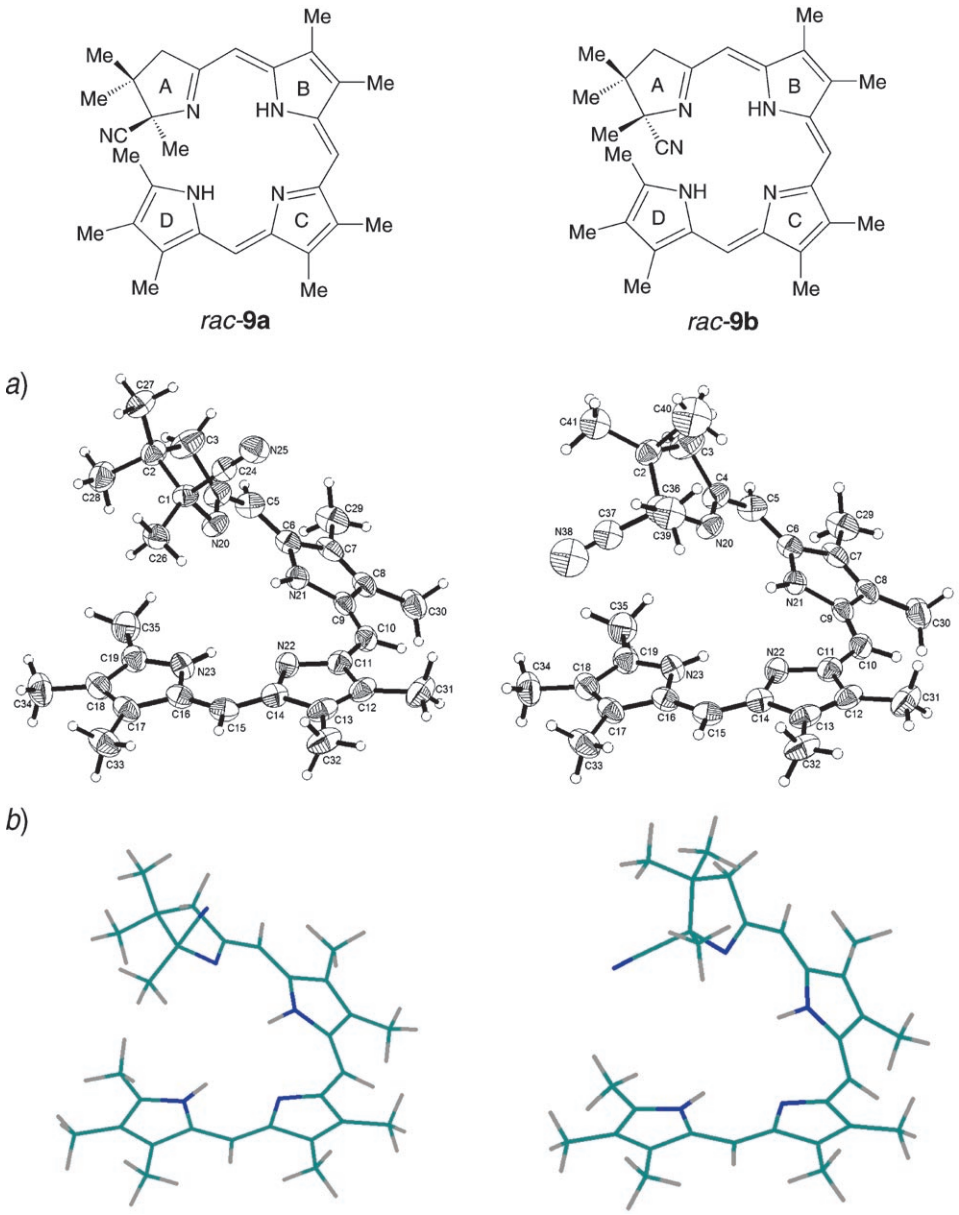
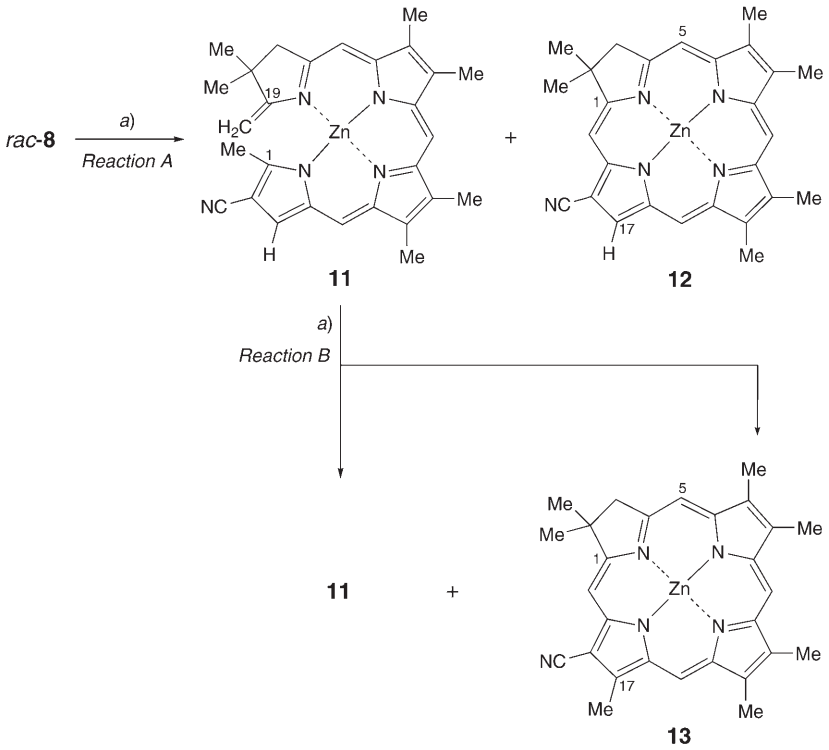


Figure. a) *X-Ray crystal-structure analysis of 17,18,19,23-tetrahydro-1,2,3,7,8,12,13,18,18,19-decamethyl-22*H-*biline-19-carbonitrile* (*rac*-**9a** and *rac*-**9b**; $C_{30}H_{37}N_5$, M_r 467.65, ball and stick representation). Arbitrary numbering. Monoclinic, space group $P2_1/c$, $D_c = 1.165$ mg/m^3, $Z = 4$, $a = 1907.6(2)$, $b = 1103.0(2)$, $c = 1284.3(2)$ pm, $\alpha = 90$, $\beta = 99.330(10)$, $\gamma = 90°$, $V = 2.6665(7)$ nm^3, $\mu(\mathrm{Mo}K_\alpha) = 0.070$ mm^{-1}, $wR_2 = 0.2155$. b) *Semiempirical PM3 calculations of structures* rac-**9a** *and* rac-**9b** (stick representation).

Scheme 3



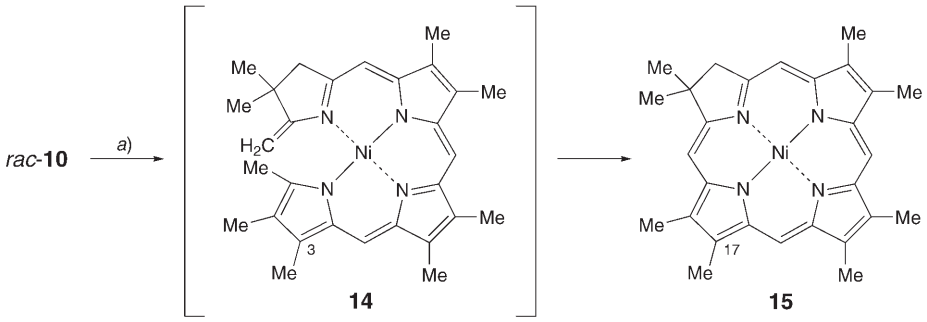
a) 1,2,4-Trichlorobenzene, 220°, Ar, 10 min (*Reaction A*), 30 min (*Reaction B*).

(*Scheme 3*, *Reaction A* and *Scheme 4*) acts as the nucleophile. Finally, oxidation of **B** leads to chlorins **12** or **15**.

If the nucleophile is not present during the reaction, intermediate **A** follows an alternative reaction path, namely sigmatropic shifts of the Me group at C(19) to the unsubstituted C(17). The absence of the nucleophilic CN^- is guaranteed when pure tetrahydrobiline **11** undergoes cyclization under heating (*Scheme 3*, *Reaction B*) to yield intermediate **C**. The anion **B** as well as the intermediate **C** are both finally oxidized in the presence of atmospheric O_2 to give the stabilized aromatic chlorins **12**, **13**, and **15**.

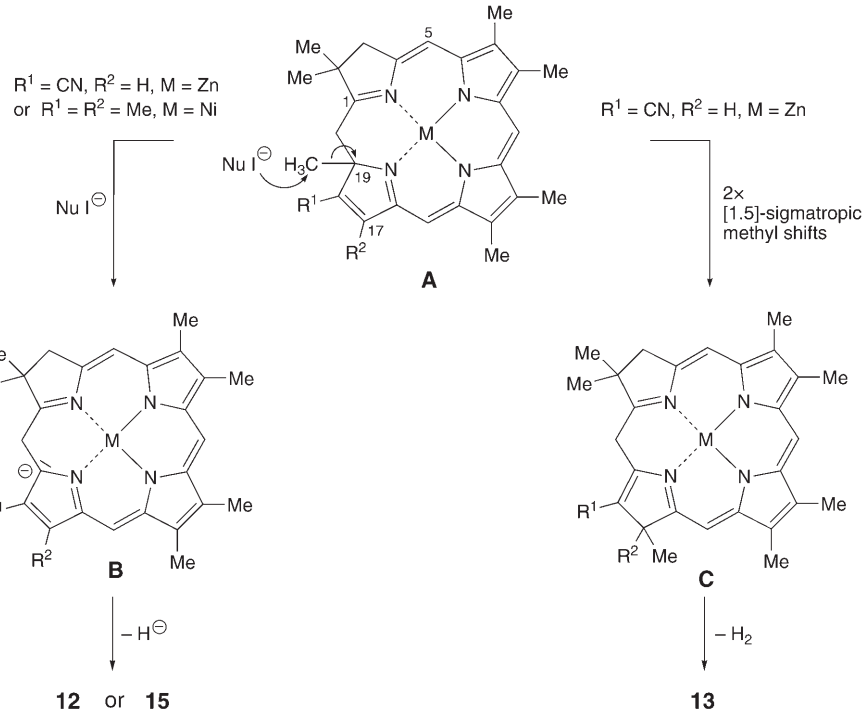
We thank Dr. *Enno Lork* (Institute of Inorganic Chemistry, University of Bremen) for X-ray crystal-structure determinations, *Johannes Stelten* (Institute of Organic Chemistry, University of Bremen) for NMR measurements, Dr. *Thomas Dülcks* and *Dorit Kemken* (Institute of Organic Chemistry, University of Bremen) for MS measurements, and Dr. *Tobias Borrmann* (Institute of Organic Chemistry, University of Bremen) for helpful assistance in the preparation of theoretical calculations. *L. L.-G.* thanks the *Alexander von Humboldt-Foundation* (D-Bonn) for granting him the *Alexander von Humboldt-Award*.

Scheme 4



a) 1,2,4-Trichlorobenzene, 220°, Ar, 30 min; 76% of **15**.

Scheme 5. *Possible Mechanistic Courses of Formation of Chlorins* **12**, **13**, *and* **15**



Experimental Part

General. Starting materials were either prepared according to literature procedures or were purchased from *Fluka*, *Merck*, or *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*, 32–63 μm (*ICN Biomedicals*). TLC: Precoated *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): *Perkin-Elmer Paragon-500* FT-IR spectrometer; KBr pellets, $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR Spectra: *Bruker DPX-200 Avance* spectrometer; δ in ppm rel. to TMS as internal standard, *J* in Hz; δ(H) from spectra in $CDCl_3$ at 23°, if not otherwise noted. MS and HR-MS: *Finnigan MAT-8200*, *Finnigan MAT-95*, or *Esquire* spectrometer (EI (70 eV) and ESI); in *m*/*z* (rel.%).

*5-Formyl-2-methyl-1*H*-pyrrole-3-carbonitrile* (**4**). For preparation of the *Vilsmeyer* reagent, $POCl_3$ (364 µl, 3.98 mmol) was added to dry DMF (636 µl) at 0° under Ar, and the mixture was stirred for 15 min. To a soln. of 2-Methyl-1*H*-pyrrole-3-carbonitrile [6] (77.2 mg, 0.727 mmol) in dry DMF (10 ml) cooled to 10°, the *Vilsmeyer* reagent (570 µl, 3 equiv.) was added dropwise under Ar, and the soln. was then heated for 2.5 h at 60°. The reaction was quenched by addition of sat. AcONa soln. (20 ml), and the mixture was stirred for further 20 min at 60°. The mixture was diluted with H_2O (20 ml), extracted four times with CH_2Cl_2, and dried by filtration through cotton wool. After removal of CH_2Cl_2 in a rotavapor, DMF was evaporated by a bulb-to-bulb distillation under reduced pressure. The residue was purified by CC (SiO_2 (10 g); CH_2Cl_2/AcOEt 13:1) to afford **4** (82.8 mg, 84.9%). Colorless solid. R_f (SiO_2; CH_2Cl_2/AcOEt 13:1) 0.25. M.p. 197°. IR (KBr): 3174 (NH), 2227 (CN), 1646 (C=O). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.55 (*s*, Me−C(2)); 7.15 (*d*, ^4J = 2.0, H−C(4)); 9.47 (*s*, CHO−C(5)); 10.01 (br. *s*, NH). EI-MS: (70 eV, direct inlet, *T* 107°): 133 (100, M^+), 105 (26, $[M - CHO]^+$), 78 (16), 51 (8). HR-MS: 134.04786 ($M^{+\bullet}$, $C_7H_6N_2O^{+\bullet}$; calc. 134.04801).

General Procedure for the Synthesis of Tetrahydrobilines rac-**8** *and* rac-**10**. A 5N soln. of KOH in MeOH/H_2O 9:1 (4 ml) was added to a soln. of *(ethyl 14-cyano-12,13,14,17-tetrahydro-2,3,7,8,13,13,14-heptamethyl-15*H*-tripyrrincarboxylato)nickel(II)* (*rac*-**6**) (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 extracted under vigorous shaking with CH_2Cl_2 (4 × 30 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 pyrroles **4** or **5** (6.9 or 7.7 mg, 51.7 µmol, 1.9 equiv.) in dry $CHCl_3$ (6 ml) and 0.4N TsOH in $CHCl_3$ (0.68 ml, 272 µmol, 10 equiv.) were successively added by a syringe through a septum to the degassed carboxylic acid under Ar. The mixture was refluxed with stirring for 20 min. The green mixture was diluted with CH_2Cl_2 (20 ml), poured into a separating funnel containing H_2O (30 ml), and extracted under vigorous shaking 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 bilines *rac*-**7** or *rac*-**9** were used without further purification for the next reaction step. Therefore, a soln. of dry $Zn(OAc)_2$ (60.0 mg, 327 µmol, 5 equiv.) or $Ni(OAc)_2$ (57.8 mg, 327 µmol, 5 equiv.), and AcONa (27 mg, 327 µmol, 5 equiv.) in dry MeOH (3 ml) was added to solns. of *rac*-**7** or *rac*-**9** in dry CH_2Cl_2 (6 ml). The mixture was reacted at r.t. for 30 min under Ar. The mixture was transferred into a separating funnel containing H_2O (20 ml) and extracted under vigorous shaking 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 (SiO_2; CH_2Cl_2/AcOEt 15:1) to yield *rac*-**8** or *rac*-**10** as green solids.

*(17,18,19,23-Tetrahydro-1,7,8,12,13,18,18,19-octamethyl-22*H*-biline-2,19-dicarbonitrilato)zinc(II)* (*rac*-**8**). Yield: 5 mg (9.5 µmol, 35%). R_f (SiO_2; CH_2Cl_2/AcOEt 9:1) 0.70. UV/VIS ($CHCl_3$): 615 (0.46), 574 (0.11, sh), 528 (0.08, sh), 396 (1), 386 (0.82, sh). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.08 (*s*, Me−C(19)); 1.25 (*s*, 2 Me−C(18)); 2.14, 2.16, 2.22, 2.29 (4*s*, Me−C(1), Me−C(7), Me−C(8), Me−C(12), Me−C(13)); 2.61, 2.94 (*AB*, *J* = 16.6, 2 H−C(17)); 5.49, 5.98, 6.80, 6.99 (4*s*, H−C(5), H−C(10), H−C(15), H−C(3)). EI-MS: (70 eV, direct inlet, *T ca.* 200°): 485 (64), 483 (100, $[M^+, {}^{64}Zn]$), 470 (20), 468 (40, $[M^+ - CH_3, {}^{64}Zn]$), 455 (22), 453 (42, $[M^+ - 2\ CH_3, {}^{64}Zn]$), 438 (9), 436 (3).

*(17,18,19,23-Tetrahydro-1,2,3,7,8,12,13,18,18,19-decamethyl-22*H*-biline-19-carbonitrilato)nickel(II)* (*rac*-**10**). Yield: 8.4 mg (16.1 µmol, 59%). R_f (SiO_2, CH_2Cl_2/MeOH 99:1) 0.74. UV/VIS ($CHCl_3$): 749 (0.38), 692 (0.12, sh), 466 (0.34, sh), 412 (0,70), 378 (0.51, sh). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.54, 1.19, 1.27 (3*s*, Me−C(19), 2 Me−C(18)); 1.88, 1.90, 2.19, 2.22, 2.24, 2.53 (6*s*, Me−C(1), Me−C(2), Me−C(3), Me−C(7), Me−C(8), Me−C(12), Me−C(13)); 5.69, 6.52, 6.99 (3*s*, H−C(5), H−C(10), H−C(15)). EI-MS: (70 eV, direct inlet, *T ca.* 200°): 525 (43), 523 (100, $[M^+, {}^{58}Ni]$), 510 (17), 508 (39, $[M^+ - CH_3, {}^{58}Ni]$), 497 (8), 481 (9), 466 (8), 451 (10), 439 (10).

*(17,18,19,23-Tetrahydro-1,7,8,12,13,18,18-heptamethyl-19-methylidene-22*H*-biline-2-carbonitrilato)-zinc(II)* (**11**). A carefully degassed soln. of *rac*-**8** (5 mg, 9.5 μmol) in dry 1,2,4-trichlorobenzene (5 ml) was heated at 220° for 10 min under Ar. After cooling to r.t., the solvent was removed by bulb-to-bulb distillation at 60° *in vacuo* of an oil pump. The dark-brown residue was purified by CC (SiO_2; CH_2Cl_2/MeOH 99:1) to yield **11** (2.1 mg, 4.1 mmol, 43%) as green solid, followed by a small blue fraction of chlorin **12** (R_f (SiO_2; CH_2Cl_2/MeOH 99:1) 0.68). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.15 (*s*, 2 Me–C(18)); 2.05, 2.06, 2.11, 2.18 (4*s*, Me–C(1), Me–C(7), Me–C(8), Me–C(12), Me–C(13)); 2.54, 2.87 (*AB*, *J* = 16,6, 2 H–C(17)); 2.89, 3.28 (*AB*, *J* = 15, CH_2=C(19)); 5.44, 5.96, 6.72, 6.94 (4*s*, H–C(5), H–C(10), H–C(15), H–C(3)). ESI-MS (pos. mode, CH_2Cl_2/MeOH 1:10): 499 (64, $M^{+\bullet}$). ESI-MS (neg. mode, CH_2Cl_2/MeOH 1:10): 498 (64, $[M-H]^-$), 534 (100, $[M+Cl]^-$).

(2,3-Dihydro-2,2,7,8,12,13-hexamethylporphyrin-18-carbonitrilato)zinc(II) (**12**). A carefully degassed soln. of *rac*-**8** (5 mg, 9.5 μmol) in dry 1,2,4-trichlorobenzene (5 ml) was heated at 220° for 10 min under Ar. After cooling to r.t., the solvent was removed by bulb-to-bulb distillation at 60° *in vacuo* of an oil pump. The brown residue was purified (SiO_2; CH_2Cl_2/MeOH 99:1) to yield **12** (0.6 mg, 1.2 mmol, 13%). Blue crystals. R_f (SiO_2; CH_2Cl_2/MeOH 99:1) 0.49. UV/VIS ($CHCl_3$): 615 (0.46), 574 (0.11, sh), 528 (0.08, sh), 396 (1), 386 (0.82, sh). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.01 (*s*, 2 Me–C(2)); 3.18 (*s*, Me–C(7)); 3.28 (*s*, Me–C(8)); 3.25 (*s*, Me–C(12)); 3.26 (*s*, Me–C(13)); 4.48 (*s*, 2 H–C(3)); 8.51 (*s*, H–C(5)); 8.66 (*s*, H–C(20)); 9.18 (*s*, H–C(10)); 9.27 (*s*, H–C(17)); 9.44 (*s*, H–C(15)). EI-MS: (70 eV, direct inlet, *T ca.* 200°): 485 (64), 483 (100, $[M^+, {}^{64}Zn]$), 470 (20), 468 (40, $[M^+ - CH_3, {}^{64}Zn]$), 455 (22), 453 (42, $[M^+ - 2\,CH_3, {}^{64}Zn]$), 438 (9), 436 (3). HR-MS: 483.13943 ($M^{+\bullet}$, $C_{27}H_{25}N_5{}^{64}Zn^{+\bullet}$; calc. 483.14014).

(2,3-Dihydro-2,2,7,8,12,13,17-heptamethylporphyrin-18-carbonitrilato)zinc(II) (**13**). A carefully degassed soln. of **11** (2.1 mg, 4.1 μmol) in dry 1,2,4-trichlorobenzene (5 ml) was heated at 220° for 30 min under Ar. After cooling to r.t., the solvent was removed by bulb-to-bulb distillation at 60° *in vacuo* of an oil pump. The brown residue was purified by CC (SiO_2; CH_2Cl_2/MeOH 99:1) to yield **13** (1.0 mg, 2.1 mmol, 50%) as blue crystals, followed by a small green fraction of starting material **11**. R_f (SiO_2; CH_2Cl_2/MeOH 99:1) 0.45. UV/VIS ($CHCl_3$): 629 (0.36), 586 (0.07), 546 (0.04), 409 (0.61). ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.05 (*s*, 2 Me–C(2)); 3.11 (*s*, Me–C(7)); 3.21 (*s*, Me–C(8)); 3.19 (*s*, Me–C(12)); 3.20 (*s*, Me–C(13)); 3.99 (*s*, Me–C(17)); 4.35 (*s*, 2 H–C(3)); 8.29 (*s*, H–C(5)); 8.98 (*s*, H–C(10)); 9.24 (*s*, H–C(20)); 9.26 (*s*, H–C(15)). EI-MS: (70 eV, direct inlet, *T ca.* 200°): 499 (6), 497 (100, $[M^+, {}^{64}Zn]$), 484 (10), 482 (18, $[M^+ - CH_3, {}^{64}Zn]$), 469 (25), 467 (50, $[M^+ - 2\,CH_3, {}^{64}Zn]$), 452 (10), 437 (2). HR-MS: 497.15419 ($M^{+\bullet}$, $C_{28}H_{27}N_5{}^{64}Zn^{+\bullet}$; calc. 497.15579).

(2,3-Dihydro-2,2,7,8,12,13,17,18-octamethylporphyrinato)nickel(II) (**15**). A carefully degassed soln. of *rac*-**10** (8.4 mg, 16.1 μmol) in dry 1,2,4-trichlorobenzene (10 ml) was heated at 220° for 30 min under Ar. After cooling to r.t., the solvent was removed by bulb-to-bulb distillation at 60° *in vacuo* of an oil pump. The brown residue was purified by CC (SiO_2; CH_2Cl_2/MeOH 99:1) to yield **15** (5.9 mg, 12.2 μmol, 76%). Blue crystals. M.p. 110–112°. R_f (SiO_2; CH_2Cl_2/AcOEt 9:1) 0.82. UV/VIS ($CHCl_3$): 614 (20109), 570 (3465), 522 (2066), 488 (2105), 396 (40796). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.81 (*s*, 2 Me–C(2)); 3.05, 3.07, 3.18 (5*s*, Me–C(7), Me–C(8), Me–C(12), Me–C(13), Me–C(17), Me–C(18)); 4.14 (*s*, 2 H–C(3)); 8.07 (*s*, 1 H), 8.19 (*s*, 1 H), 9.09 (2*s*, 2 H) (H–C(5), H–C(10), H–C(15), H–C(20)). DCI-MS (neg. mode): 483 (15, $[M^-, {}^{12}C, {}^{60}Ni, 1{}^{13}C]$), 482 (42, $[M^-, {}^{12}C, {}^{60}Ni]$), 481 (32, $[M^-, {}^{12}C, {}^{58}Ni, 1{}^{13}C]$), 480 (100, $[M^-, {}^{12}C, {}^{58}Ni]$). HR-MS: 480.18233 ($M^{+\bullet}$, $C_{28}H_{30}N_4{}^{64}Ni^{+\bullet}$; calc. 480.18239). The anal. data of **15** were in every respect identical with those of a sample obtained earlier by a slightly different route.

X-Ray Crystal-Structure Analysis. The data parameters of the crystal structure of *rac*-**9a** and *rac*-**9b** are summerized in the *Table*. Structural representations of *rac*-**9a** and *rac*-**9b** are displayed in the *Figure*. The data were collected on a *Siemens P4* apparatus equipped with a *LT-II* low-temp. device at 173 K. All calculations were performed using the SHELX Program Package. Pictures were prepared with the Diamond Program (Crystal Impact). Crystallographic data (excluding structure factors) for the structure of *rac*-**9a** and *rac*-**9b** have been deposited with the *Cambridge Crystallographic Data Centre*. CCDC-658495 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table. *X-Ray Crystal-Structure Analysis of* rac-*17,18,19,23-Tetrahydro-1,2,3,7,8,12,13,18,18,19-decamethyl-22*H-*biline-19-carbonitrile* (*rac*-**9**)

Crystallized from	CH_2Cl_2/hexane
Empirical formula	$C_{30}H_{37}N_5$
M_r [g·mol^{-1}]	467.65
Crystal color	green
Crystal dimensions [mm]	$0.60 \times 0.50 \times 0.25$
Temp. [K]	173(2)
Radiation, wavelength [pm]	MoK_α, 71.073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a [Å]	1.9076(2)
b [Å]	1.1030(2)
c [Å]	1.2843(2)
α [°]	90.00
β [°]	99.330(10)
γ [°]	90.00
V [nm^3]	2.6665(7)
Z	4
Density (calc.) [g cm^{-3}]	1.165
Absorption coefficient [mm^{-1}]	0.070
θ Range for data collection [°]	2.57 – 25.01
$F(000)$	1008
Index range	$-22 \le h \le 22,\ -13 \le k \le 1,\ -15 \le l \le 1$
Reflections collected	7291
Independent reflections	4641 [R(int) = 0.0445]
Observed reflections	2814
Completeness to $\theta = 25.01°$	98.8%
Absorption correction	None
Max. and min. transmission	0.9827 and 0.9593
Refinement method	Full-matrix least-squares on F^2
Data, restraints, parameters	4641, 12, 343
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0736$, $wR_2 = 0.1844$
	$R_1 = 0.1286$, $wR_2 = 0.2155$
Largest diff. peak and hole [e·Å^3]	0.214 and -0.275

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