Multicarbocycle Formation Mediated by Arenoporphyrin 1,4-Diradicals: Synthesis of Picenoporphyrins**

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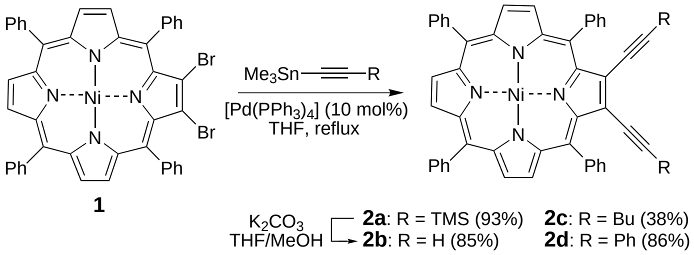
Porphyrin chromophores have received much attention, particularly as photoelectric devices and molecular wires[1–4] in materials science, as photosensitive drugs for singlet oxygen formation in photodynamic therapy,[5] and as models for the photosynthetic reaction center and antenna arrays.[6] Efficient π-electronic communication between porphyrin macrocycles is pivotal in various complex functions. Our recent work has concentrated on the synthesis of novel porphyrin compounds bearing extended π systems, establishment of novel synthetic methods for such π-extended porphyrins, and fine-tuning of their electronic networks.[7] In this connection we recently developed a novel synthesis of monobenzoporphyrins by the Diels–Alder reaction of a pyrroloporphyrin with dimethyl acetylenedicarboxylate.[8] This led us to investigate the chemistry of 2,3-dialkynylporphyrins to seek more general methodologies to access such benzoporphyrin derivatives. Adjacent acetylenic units on porphyrins **2a–d** (see Scheme 1) might be expected to behave as components of an "enediyne". Thus, they could undergo Bergman cyclization,[9] that is, thermal benzoannulation via a 1,4-dehydrobenzene system, to fashion a fused benzo ring onto the porphyrin periphery.

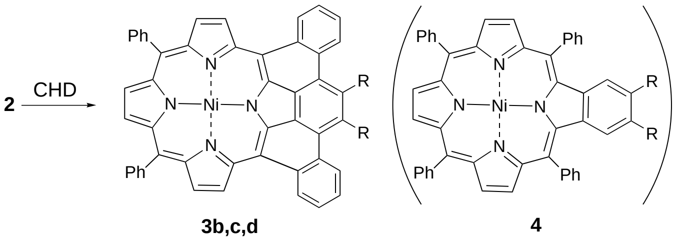
Herein we report unprecedented multicarbocycle formation on the porphyrin periphery by Bergman aromatization of vicinal dialkynylporphrins, to produce a new class of highly π-extended porphyrins. Precedents for the intramolecular cyclization of *meso*-aryl rings onto the porphyrin framework are limited to the acid-catalyzed condensations of 2-formyl- and 2-vinyl-tetra-arylporphyrins with a vicinal *meso*-aryl ring affording benzocyclohexenone porphyrins,[10] or naphthochlorins.[11]

Nickel(II) 2,3-dialkynyl-5,10,15,20-tetraphenylporphyrins **2a–d** were prepared by Pd^0-catalyzed cross-coupling reactions[12] of nickel(II) 2,3-dibromo-5,10,15,20-tetraphenylporphyrin (**1**)[13] with the corresponding alkynyl trimethylstannanes in good to excellent yields (Scheme 1). Refluxing **2b** (R = H, Table 1) in 5% 1,4-cyclohexadiene (CHD, as a hydrogen source)/chlorobenzene solution at 190 °C gave a greenish compound as a single product; in the absence of CHD the same reaction only produced a complex mixture of oligoporphyrins. Surprisingly, none of the expected monobenzoporphyrin **4** was obtained. The greenish compound was characterized by ^{1}H NMR spectroscopy, NOE experiments, and laser desorption/ionization time-of-flight (LDI-TOF) mass spectrometry (MS) as the highly π-extended porphyrin **3b**.[14]



Scheme 1. Preparation of 2,3-dialkynylporpyrins **2**. TMS = trimethylsilyl.

Table 1. Thermal annulation of 2,3-dialkynylporphyrins **2**.



Entry	R	Conditions	**2** (recovered)	**3**
1	TMS (**2a**)	190 °C, 12 h	quant.	–
2	H (**2b**)	190 °C, 8 h	–	89 %
3	Bu (**2c**)	190 °C, 60 h	44 %	50 %
4[a]	Ph (**2d**)	280 °C, 18 h	–	86 %

[a] 5 % CHD in 1,2,4-trichlorobenzene was used as solvent.

The ^{1}H NMR spectrum of **3b** clearly confirms the large structural and electronic changes of the porphyrin macrocycle as well as the disappearance of the characteristic terminal alkyne protons ($\delta = 3.49$) observed in 2,3-diethynylporphyrin **2b**. The resonance signal from the aromatic protons on the benzo ring formed by the Bergman annulation appeared at $\delta = 8.48$ as a sharp singlet. In addition, the absorption spectrum of **3b** is red-shifted (λ_{max} (CH_2Cl_2) = 450, 629 nm) relative to **2a**, a result of the extended π-conjugation in **3b**.

The new porphyrin obtained from this reaction is named as a "picenoporphyrin" after its [5]phenacene structure,[15] and specifically nickel(II) 10,15-diphenyl-piceno[20,1,2,3,4,5-*fghij*]-porphyrin (**3b**).

The molecular structure of **3b** is shown in Figure 1.[16] The porphyrin macrocycle exhibits a ruffled conformation with a 0.242 Å mean deviation of the 24 macrocyclic atoms from their least-squares plane. The piceno group is nearly planar with a 0.100 Å mean deviation of the 22 atoms from their least-squares plane. The Ni–N bond lengths are 1.988(4), 1.852(4), 1.970(4), and 1.934(4) Å for Ni(1) to N(1)–N(4) respectively. The Ni(1)–N(2) bond length is noteworthy because it is the shortest Ni–N bond length reported for any nickel(II) porphyrin crystal structure. This feature results from geometry imposed upon the porphyrin macrocycle by the

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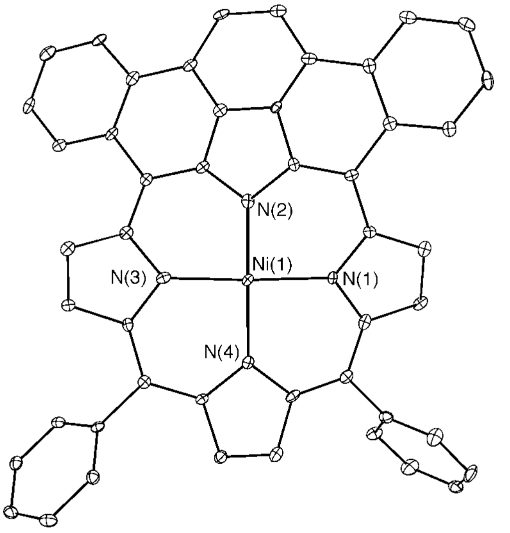

Figure 1. Molecular structure of picenoporphyrin **3b** (thermal ellipsoids at 30% probability). Hydrogen atoms have been omitted for clarity.

rigid piceno group. Of additional note in this regard were significant contractions of the fused C_α-C_{meso}-C_α bond angles and C_α–C_{meso} bond lengths along with expansions of the fused N-C_α-C_{meso} bond angles and C_β–C_β bond lengths in comparison to other reported nickel(II) porphyrin crystal structures.[17]

Compounds **2c** and **2d**, which have internal alkynyl substituents (R = Bu, Ph), undergo the same multicarbocycle formation to give the corresponding dibutylpicenoporphyrin **3c** in 50% yield, and diphenylpicenoporphyrin **3d** (86%), (Table 1, entries 3, 4). These transformations required a longer reaction period (60 h, for **3c**) or a higher temperature (280 °C, for **3d**). Compound **2a** (R = TMS) gave none of the corresponding picenoporphyrin, and was recovered quantitatively after the reaction.

A tentative mechanistic pathway to the picenoporphyrins is shown in Scheme 2. Thermal annulation of the 2,3-alkynyl moieties would produce a 1,4-diradical species **5**. This diradical then attacks the vicinal *meso*-phenyl groups yielding a planar diradical species **6**. Our experimental results indicate that the steric hindrance of the alkynyl substituents of **2** slows the thermal annulation. After two successive intermolecular hydrogen transfers from CHD, **6** affords tetrahydro species **7**, which is oxidized during the course of work-up to give picenoporphyrins **3b**–**d**. The absence of any monobenzoporphyrin **4** clearly indicates that intramolecular carbon–carbon bond formation via diradicals **5** is faster than intermolecular hydrogen transfer from CHD.

In conclusion, we have shown that neighboring acetylenic units on porphyrins provide a means for the efficient construction of aromatic superstructures triggered by Bergman reaction conditions, and give novel access to [*n*]phenacenoporphyrins.

Experimental Section

In a typical Bergman cyclization, 2,3-dialkynylporphyrins **3** (30 mg) was added to a Schlenk tube and dissolved in anhydrous 5% 1,4-cyclohexadiene (CHD) in chlorobenzene or 1,2,4-trichlorobenzene (20 mL). The reaction flask was sealed well and the mixture was then heated under reflux under appropriate conditions (see Table 1). After being cooled to room temperature, silica gel (ca. 1 g) was added to the flask, and the solvent was removed under vacuum. The resulting powder was loaded onto a silica gel column and eluted initially with 20% toluene in cyclohexane, and then with CH_2Cl_2. The major green band was collected and recrystallized from CH_2Cl_2/methanol. Compounds **3b**–**d** were soluble in common organic solvents despite their rigid piceno structures.

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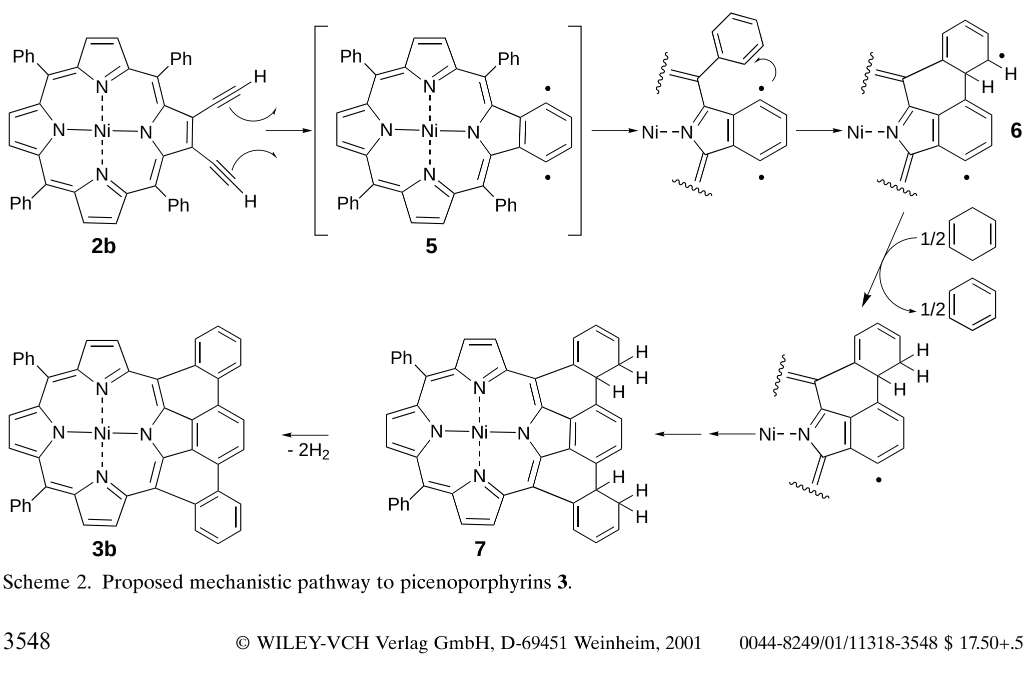

Scheme 2. Proposed mechanistic pathway to picenoporphyrins **3**.

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[14] Physical data for **3b**: m.p. > 300°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.67–7.79$ (m, 8H), 7.90 (dd, 2H, $J = 7.8$, 7.5 Hz), 8.05 (dd, 4H, $J = 7.8$, 1.8 Hz), 8.48 (s, 2H, β-H), 8.85 (d, 2H, $J = 5.0$ Hz, β-H), 8.96 (d, 2H, $J = 7.8$ Hz), 9.01 (s, 2H), 9.32 (d, 2H, $J = 8.1$ Hz), 9.58 (d, 2H, $J = 5.0$ Hz, β-H); UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-4}$) = 450 (2.1), 629 (0.4) nm; LDI-TOF MS: m/z (%) 717 (100).

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[16] Crystals of **3b** were grown from cyclohexane/$CHCl_3$ ($C_{48}H_{26}N_4Ni$, $M_w = 717.44$). The selected crystal (dimensions: $0.32 \times 0.14 \times 0.10$ mm) had an orthorhombic unit cell, space group $Pna2_1$, cell dimensions $a = 7.3143(6)$, $b = 21.296(2)$, $c = 20.154(2)$ Å, $V = 3139.2(4)$ Å^3, and $Z = 4$. Data were collected with ω-scans on a Bruker SMART 1000 diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å) at 90(2) K. A total of 40879 reflections were collected to $2\theta = 63°$. A 2θ cutoff of 55° was applied to afford 31351 total reflections: 7147 unique, 5573 observed ($I > 2\sigma$) ($R_{int} = 0.109$, $T_{min} = 0.82$, $T_{max} = 0.94$, $\rho_{calcd} = 1.518$ g cm^{-3}, $\mu = 0.665$ mm^{-1}). An empirical absorption correction was applied (SADABS 2.0, G. M. Sheldrick, **2000**). The structure was solved by direct methods and refined based on F^2 using all data by full-matrix least-squares methods with 479 parameters (Bruker SHELXS-97, SHELXL-97). A Flack x parameter of 0.06(2) was determined. Hydrogen atom positions were refined with a riding model. Final R factors were $R1 = 0.058$ (observed data) and $wR2 = 0.122$ (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-162682. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Olefin Metathesis with 1,1-Difluoroethylene[**]

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The recent development of ruthenium olefin-metathesis catalysts coordinated with N-heterocyclic carbene ligands is a significant advance because it extends the scope of the reaction to more challenging substrates, that is, those that are sterically hindered or that contain electronically deactivating groups, as well as monomers with low ring strain.[1–4] One set of substrates that has received relatively little attention, however, is the halogenated olefins;[5] the metathesis of allyl bromide, allyl chloride, and related substrates with the heterogeneous $Re_2O_7/Al_2O_3/Me_4Sn$ catalyst system are among the few examples.[6] Most recently, the cross metathesis of 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene with terminal olefin[4c] and the dimerization of vinyl *gem*-difluorocyclopropane derivatives[7] have been achieved using $[(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh]$ (**1**) (H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; Cy = cyclohexyl). In these cases, the substrates are challenging because of the electron-withdrawing nature of the pendent halogens.

A particularly interesting situation arises when the olefin is directly halogenated, because then the metathesis reaction will involve a monohalo $[M]{=}CXR$ or dihalo $[M]{=}CX_2$ carbene complex rather than the usual alkylidene $[M]{=}CR_2$. This possibility has been considered by Beauchamp and coworkers, who have speculated about the metathesis of directly fluorinated olefins with nickel or manganese complexes.[8] A tungsten dichlorocarbene complex $[W]{=}CCl_2$ has also been proposed as an active species in the $W(CO)_6/CCl_4/h\nu$ catalyst system.[9] To our knowledge, there has been only one report of metathesis involving directly halogenated olefins, namely the cross metathesis of 1-chloro- and 1-bromoethylene with propylene using $Re_2O_7/Al_2O_3/Me_4Sn$.[6e] Herein, we report the successful metathesis of 1,1-difluoroethylene with ruthenium catalyst **1**.

Under an atmosphere of 1,1-difluoroethylene, **1** reacts to form the corresponding methylidene $[(H_2IMes)(PCy_3)(Cl)_2Ru{=}CH_2]$ (**2**)[10] and difluorocarbene $[(H_2IMes)(PCy_3)(Cl)_2Ru{=}CF_2]$ (**3**) complexes [Eq. (1)].[11] When the reaction is performed at room temperature, the product mixture contains approximately 40% methylidene (**2**) and 60% difluorocarbene (**3**), as well as styrene and β,β-

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