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Construction of Multiporphyrin Arrays via Selective Cross-Metathesis

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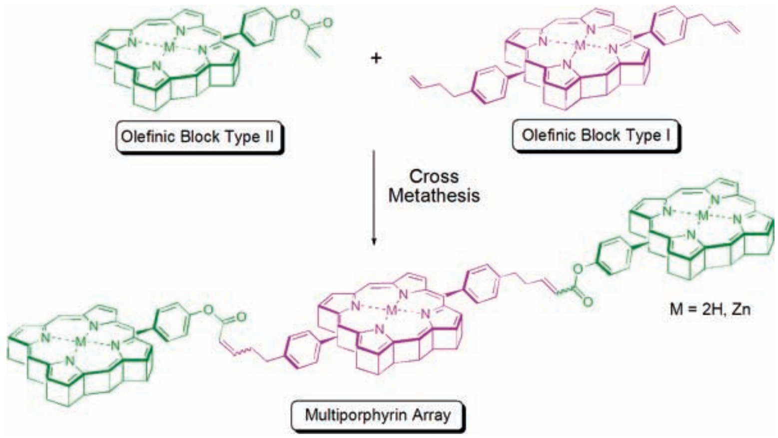
ABSTRACT



Selective cross-metathesis of type I and type II *meso*-functionalized porphyrin olefins afforded alkenyl-coupled dimeric and trimeric porphyrin systems in good yield with excellent *E*/*Z* selectivity. The synthetic utility of the method is demonstrated through the preparation of mixed metalated (M = 2H, Zn) porphyrin dimer and trimer.

The linking of porphyrin chromophores by covalent bonds in a simple and systematic way to form stable, multiporphyrin architectures and well-defined arrays is important for creating novel molecular wires, light-harvesting systems, energy transduction devices, and catalytic scaffolds and in molecular recognition applications.[1] Many successful porphyrin-to-porphyrin coupling techniques have been developed,[2] yet alternative methods suitable for forming regiospecifically mixed metal systems and systems containing sensitive pendant functional groups are still sought. The olefin cross-metathesis (CM) reaction has developed into an extremely useful coupling technique due to its mild reaction conditions and exceptional tolerance toward a variety of functional groups. Recently, metathesis conditions have been utilized in porphyrin modifications[3] and the covalent capture of supramolecular assemblies using Grubbs' first- or second-generation catalyst.[4] To the best of our knowledge, in all of the supramolecular examples the CM was performed using a homocoupling strategy. Targeting mixed-olefin CM products should improve selectivity and specificity, allowing greater functional flexibility to the synthesis and better control of the products formed by virtue of the different

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[1] Some recent topical reviews include: (a) Imahori, H. *J. Phys. Chem. B* **2004**, *108*, 6130. (b) Drain, C. M.; Hupp, J. T.; Suslick, K. S.; Wasielewski, M. R. *J. Porph. Phthal.* **2002**, *6*, 243. (c) Imahori, H. *Org. Biomol. Chem.* **2004**, *2*, 1425. (d) Satake, A.; Kobuke, Y. *Tetrahedron* **2005**, *61*, 13.

[2] (a) Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751 and references therein. (b) Frampton, M. J.; Akdas, H.; Cowley, A. R.; Rogers, J. E.; Slagle, J. E.; Fleitz, P. A.; Drobizhev, M.; Rebane, A.; Anderson, H. L. *Org. Lett.* **2005**, *7*, 5365. (c) Arnold D. P. *Synlett* **2000**, 296.

[3] Liu, X.; Sternberg, E.; Dolphin, D. *Chem. Commun.* **2004**, 57, 852.

[4] (a) Kim, Y.; Mayer, M. F.; Zimmerman, S. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 1121. (b) van Gerven, P. C. M.; Johannes, J. A. A. W.; Gerritsen, J. W.; Speller, S.; Nolte, R. J. M.; Rowan, A. E. *Chem. Commun.* **2005**, 28, 3535. (c) Ikeda, C.; Satake, A.; Kobuke, Y. *Org. Lett.* **2003**, *5*, 4935. (d) Cao, Y.; Wang, L.; Bolt, M.; Vysotsky, M. O.; Bohmer, V. *Chem. Commun.* **2005**, *58*, 3132. (e) Guidry, E. N.; Cantrill, S. J.; Stoddart, J. F.; Grubbs, R. H. *Org. Lett.* **2005**, *7*, 2129. (f) Bakker, J. M.; Langford, S. J.; Latter, M. J.; Lee, K. A.; Woodward, C. P. *Aust. J. Chem.* **2005,** 58, 757.

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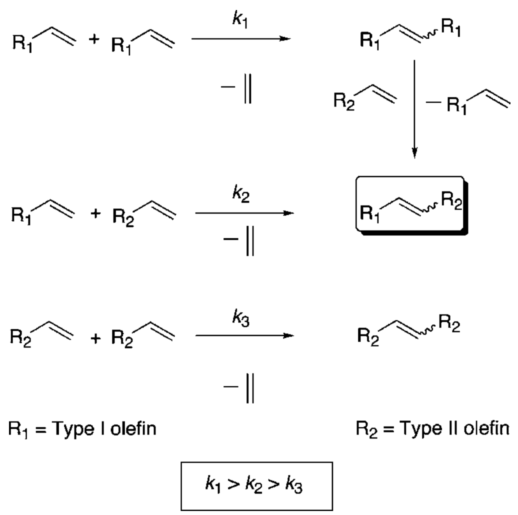
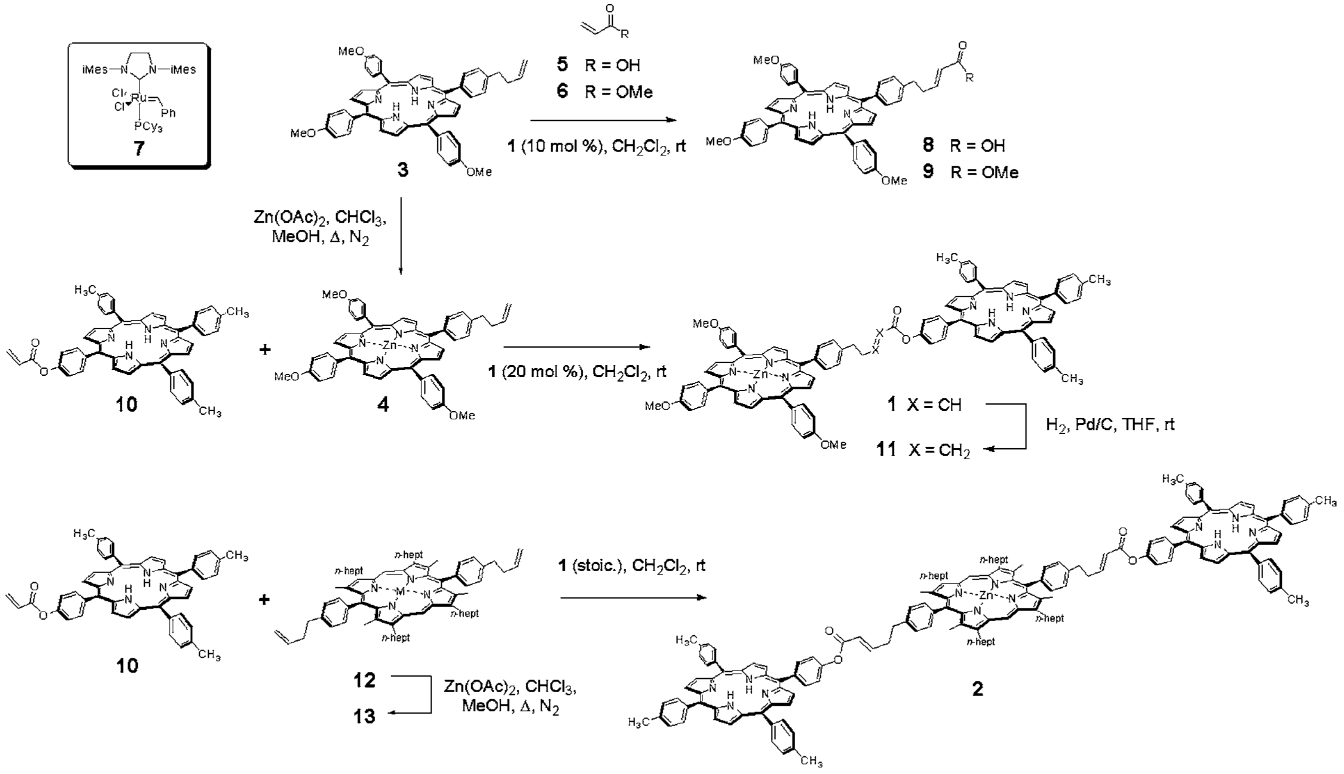


Figure 1. Schematic representation of the CM reaction involving type I and type II olefins.

kinetics associated with type I and type II olefins.[5] In a reaction mixture containing type I and type II olefins (Figure 1), two type I olefins readily homodimerize under metathesis conditions. The olefinic product of this reaction can undergo a subsequent CM with the type II olefin to yield an unreactive heterodimer with good selectivity and yield.[6] Homodimerization of type II olefins is slow and does not compete favorably with k_1 or k_2. Here, we demonstrate the use of olefin CM reactions for generating multiporphyrin systems[7] and demonstrate its versatility by synthesizing the dimer **1** and trimer **2** bearing mixed-metal (free-base and Zn(II)) species.

Porphyrin **3** containing a type I olefin was purified from a statistical mix using the Adler method,[8] condensing 4 equiv of pyrrole with a 2.5:1.5 ratio[9] of *p*-methoxybenzaldehyde and *p*-butenylbenzaldehyde in acidic media. The zinc(II) adduct **4** was prepared via the acetate metalation method in near-quantitative yield.[10] We began our investigation by conducting a model involving porphyrin **3** and the acryloyl olefins **5** and **6**. Using 10 mol % loading of catalyst **7** (Grubbs' second-generation catalyst), we were able to prepare the porphyrins **8** and **9** in 36 and 54% yield, respectively (Scheme 1).[11] The *E*/*Z* selectivity of the reaction was heavily biased toward the *Z*-isomer, with only trace amounts of the sterically less favored *E*-isomer identified. With the models in hand, the metalloporphyrin **4** was reacted under similar conditions (20 mol % loading of catalyst **7**, 24 h) with the free-base acrylate porphryin **10**[12] in a 1:2 ratio to bias the products toward the mixed species **1** (Scheme 1).[13] The reaction proceeded well as after 24 h all of **4** had been comsumed and a new, major band was detected from TLC monitoring. The heterodimer **1** was isolated in a 43% yield[14] after column chromatography and characterized by high-resolution ^{1}H and ^{13}C NMR spectroscopy as well as MALDI-TOF mass spectrometry (see the Supporting Information). Under this CM strategy, the dimer **1** is able to be further metalated/transmetalated utilizing the lability of the Zn(II) metalloporphyrin without the statistical complications as-

Scheme 1. Olefin Cross-Metathesis Reactions Using Second-Generation Grubb's Catalyst Form Porphyrin Dimers and Trimers



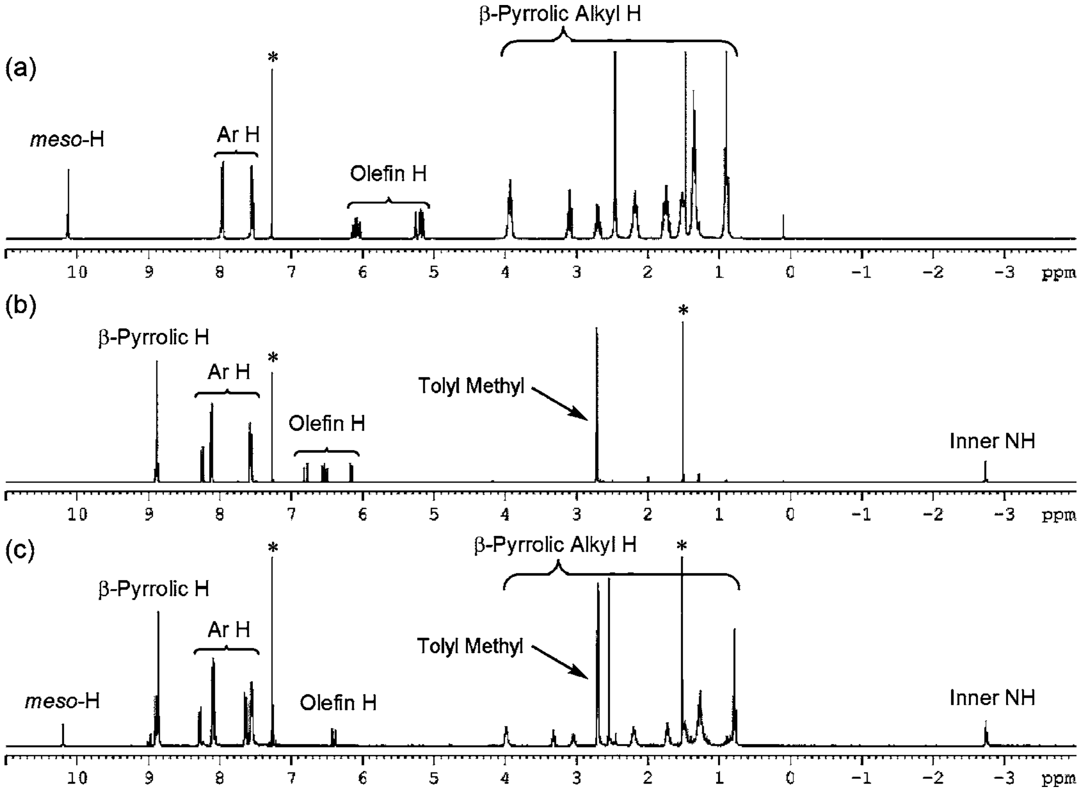


Figure 2. ^{1}H NMR spectroscopic comparison of (a) zinc porphyrin **13**, (b) free base monoalkenylporphyrin **10**, and (c) resulting trimer **2**. Resonances are annotated as per assigned protons and * indicates residual solvent resonances.

sociated with the bis-free-base analogue of **1**. Catalytic hydrogenation of the alkene **1** (H_2/Pd/C/THF/48 h) gave the bisporphyrin **11** in 96% yield (Scheme 1),[15] as evinced by the loss of alkenyl resonances and formation of upfield triplets within the ^{1}H NMR spectrum of **11**.[16]

Cross-metathesis of the 5,15-dialkenylporphyrin **13** bearing type I olefins, prepared by Zn(II) metalation of **12**,[17] with the type II-containing olefin **10** (4 equiv), was achieved in 48% yield using a stoichiometric amount of **7** (Scheme 1).[18] The trimer product **2** comprising a central dibutenylzinc porphyrin **13** capped by two free base acrylate porphyrins **10** was characterized by ^{1}H and ^{13}C NMR spectroscopies and MALDI TOF mass spectrometry (m/z = 2477.9 [M^+]). A comparison of the ^{1}H NMR spectra of **10**, **13**, and **2**

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(5) This is especially important in regioselective mixed metalloporphyrins systems, which are otherwised formed through statistical metalations post-multiporphyrin synthesis.

(6) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.

(7) This procedure has obvious uses with other olefins. For example, we have reacted **3** with allylglycine, which acts like a type-II olefin, to form a porphyrin α-amino acid in good yield. Conversely, we have reacted type-I olefins such as resin-bound undecenoate esters with protoporphyrin IX, which in our hands acts as a type-III olefin. These results and their applications will be published at a later date.

(8) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(9) Mainly tetra(*p*-methoxyphenyl)porphyrin and only a small amount of the desired monobutenyl porphyrin **2** was isolated using a 3:1 aldehyde ratio due to the greater reactivity of the *p*-methoxybenzaldehyde under the conditions used.

(10) Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1A, p 389.

(11) The lower yield observed for carboxylic acids over esters in CM has been recently discussed; see: Elaridi, J.; Jackson, W. R.; Robinson, A. J. *Tetrahedron: Asymmetry* **2005**, *16*, 2025.

(12) The acrylate porphyrin **10** was produced in 84% yield by reaction of an acrylate ester and 5,10,15-tris(*p*-tolyl)-20-(*p*-hydroxyphenyl)porphyrin. See: Nowakowska, M.; Karewicz, A.; Loukine, N.; Guillet, J. E. *Polymer* **2002**, *43*, 2003.

(13) The alternative synthesis of **1** employing an esterification procedure by reacting **5** or **6** and 5,10,15-tris(*p*-tolyl)-20-(*p*-hydroxyphenyl)porphyrin leads to in situ demetalation of the metalloporphyrin.

(14) The reduced yields are thought to result from the formation of a coordination product between catalyst **7** and porphyrin **4**.

(15) Previous reports on the reduction of alkyne porphyrins utilized palladium on carbon in THF with good effect; see: Bampos, N.; Marvaud, V.; Sanders, J. K. M. *Chem. Eur. J.* **1998**, *4*, 335.

(16) The success of the hydrogenation is important in instances where both geometric isomers are formed by CM. While not yet attempted, this last result opens up the possiblity of performing a CM/hydrogenation tandem reaction to produce flexibly linked porphyrin systems in one pot.

(17) The synthesis of **12** was recently reported by us; see ref 4f. We have since been able to grow crystals of **12** suitable for X-ray structural determination by slow diffusion of MeOH into a $CHCl_3$ solution of **12**. Crystal data for **12**: $C_{72}H_{98}N_4$, $M = 1019.54$, crystal dimensions $0.60 \times 0.08 \times 0.05$ mm^3, $a = 8.675(6)$ Å, $b = 9.849(10)$ Å, $c = 19.648(16)$ Å, $\alpha = 97.46(4)°$, $\beta = 96.67(3)°$, $\gamma = 100.67(4)°$, triclinic P-1, $Z = 1$, $V = 1619(2)$ Å^3, $D_c = 1.046$ g/cm^3, $F_{000} = 558$, $\lambda = 0.71073$ Å, $T = 123(2)$ K, $\mu = 0.060$ mm^{-1}, Nonius Kappa CCD diffractometer, ϕ scan data, 11123 data collected, corrected for Lorenz and polarization effects, 4557 unique ($R_{int} = 0.1261$) and 2886 observed [$I > 2\sigma(I)$], 471 refined parameters, $R = 0.0851$, $R_w = 0.2339$, $w = (\sigma^2(F))^{-1}$. Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 603983 for structure of **12**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

(18) The formation of oligomers of **13** is possibile and no doubt contributes to the reduced yield obtained. For a previous study in this regard, see ref 4b.

(Figure 2) provides clear evidence for formation of the trimer as well as to the *E*/*Z* selectivity of the CM reaction. Of most significance is the disappearance of the olefinic proton resonances of porphyrins **10** and **13** (Figure 2a and b, respectively) and only equal intensity resonances assignable to the *two* internal *Z* olefin protons of **2** seen at approximately δ 6.4 and 7.6 (hidden) in Figure 2c, indicating that both terminal alkenes of **13** had reacted with the acrylate unit of **10**. In addition to this, the remaining proton resonances (β-pyrrolic and inner periphery protons of **10**, *meso*-protons of **13**, *meso*-aromatic and alkyl protons of **10** and **13**) are all present in the spectrum of **2** at chemical shifts similar to their respective isolated spectra and of correct integration.

In conclusion, we have shown that the CM reaction is suitable as a construction protocol for porphyrinic arrays which exhibit a high degree of *E*/*Z* selectivity in the products. Removal of the alkene linkage has also been shown to be possible by catalytic hydrogenation in the case of **1**. The application of this synthesis strategy to more elaborate arrays is an active research area within our laboratory, and further results will be reported in due course.

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Supporting Information Available: Synthetic procedures for compounds for all new compounds and X-ray data for **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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