5266 *J. Org. Chem.* **1995**, *60*, 5266−5273

Synthesis of Ethyne-Linked or Butadiyne-Linked Porphyrin Arrays Using Mild, Copper-Free, Pd-Mediated Coupling Reactions

Richard W. Wagner, Thomas E. Johnson, Feirong Li, and Jonathan S. Lindsey*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue,
Pittsburgh, Pennsylvania 15213

Received March 21, 1995[⊗]

The synthesis of multi-porphyrin light-harvesting arrays requires copper-free coupling reactions. Two studies of copper-free Pd-catalyzed coupling reactions are presented. First, we investigate the effects of different ligands in the Pd-catalyzed cross-coupling of a porphyrin bearing two aryl iodides with a porphyrin bearing an aryl ethyne. Triphenylarsine affords faster rates than triphenylphosphine or tri-2-furylphosphine when experiments are performed in conjunction with tris(dibenzylideneacetone)dipalladium(0) under anaerobic conditions. Reactions performed at 35 °C are relatively clean, fast (complete in 1−2 h), and afford the ethyne-linked porphyrin array in ~70% yield with a minimal amount of higher molecular weight byproducts. This reaction is ideal for preparing multi-porphyrin arrays. Second, treatment of a free base porphyrin−ethyne with a stoichiometric amount of $Pd(PPh_3)_2Cl_2$, or a catalytic amount of tris(dibenzylideneacetone)-dipalladium(0) and tri-2-furylphosphine, in toluene/triethylamine (5:1) in air at 50−60 °C affords the butadiyne-linked porphyrin dimer in ~70% yield. With $Pd(PPh_3)_4$ in toluene under anaerobic conditions at 100 °C, the porphyrin−ethyne reacts to give the head-to-tail enyne-linked dimer (29% yield). Size exclusion chromatography is effective in analyzing reaction mixtures and purifying the porphyrin arrays. These copper-free coupling reactions afford direct access to ethyne-, butadiyne-, or enyne-linked arrays of free base and/or zinc porphyrins from readily available porphyrin building blocks.

Modular synthetic approaches are of great attraction for the preparation of multicomponent systems. The syntheses of photosynthetic and related model systems require methods for joining large numbers of components into functional arrays. One modular approach employs porphyrin building blocks bearing peripheral functional groups that can be joined via specific coupling methods.[1] In this approach the inter-porphyrin linker is formed concomitantly with the joining step, thus the nature of the linker and the coupling method are closely intertwined. Among the various linkers that have been explored, ethynes,[1−7] butadiynes,[1,5−11] or polyynes[7,11] have many attractive design features.

Ethyne-linked porphyrin arrays have been constructed by the Pd-catalyzed cross-coupling reaction of a porphyrin aryl iodide and a porphyrin aryl ethyne.[1−4,6] This reaction, developed by Cassar,[12] Heck,[13] and Sonogashira,[14] has been used extensively in the synthesis of all-carbon-based acetylenic materials.[15] Though reaction conditions vary among workers, the general conditions for coupling aryl halides and ethynes employ a source of Pd(0), the PPh_3 ligand, an alkyl amine as a base, CuI co-catalysis, ethyne and aryl iodide concentrations > 0.1 M, and temperatures ranging up to 100 °C.

Butadiyne-linked porphyrin arrays have been synthesized by the oxidative homocoupling of ethynes using $Cu(OAc)_2$,[1,5,8] CuCl,[9] or $Pd(PPh_3)_4$ and CuI.[6,10] Because copper readily inserts into free base porphyrins, these butadiyne-forming reactions could only be employed with metalloporphyrins.

The goal of preparing multi-porphyrin arrays imposes stringent constraints on available coupling methods, including the Pd-coupling methods:[1]

(1) The desire to incorporate diverse metalloporphyrins into arrays rules out acidic conditions that cause demetalation and forcing conditions that give transmetalation. The Pd-coupling methods are attractive in part because

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1995.

(1) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941−8968.

(2) Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519−7520.

(3) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759−9760.

(4) Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron Lett.* **1993**, *34*, 693−696.

(5) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105−1111.

(6) Vidal-Ferran, A.; Müller, C. M.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2657−2658.

(7) Kawabata, S.; Tanabe, N.; Osuka, A. *Chem. Lett.* **1994**, 1797−1800.

(8) Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. I* **1978**, 366−370. Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron* **1992**, *48*, 8781−8792.

(9) Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1714−1715. Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 907−910. Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972−981. Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469−475.

(10) Gosper, J. J.; Ali, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1707−1708.

(11) Maruyama, K.; Kawabata, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 170−175.

(12) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253−257.

(13) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259−263.

(14) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

(15) For representative syntheses of high carbon materials, see: Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 268−269. Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489−2496. Praefcke, K.; Kohne, B.; Singer, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 177−179. Eaton, P. E.; Stössel, D. *J. Org. Chem.* **1991**, *56*, 5138−5142. Feldman, K. S.; Weinreb, C. K.; Youngs, W. J.; Bradshaw, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 9019−9026. Guo, L.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1994**, 243−244. Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354−1357. Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893−5894. Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2655−2656. Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227−4239. Diederich, F. *Nature* **1994**, *369*, 199−207. Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360−1363.

0022-3263/95/1960-5266$09.00/0

they are performed in neutral to basic conditions where demetalation does not occur.

(2) The desire to incorporate free base porphyrins into arrays rules out the presence of metals that can insert into porphyrins. Palladium does not insert into porphyrins unless high temperatures are employed (porphyrins are metalated with palladium(II) in refluxing dimethylformamide or benzonitrile),[16] thus the Pd-coupling methods can be used with free base porphyrins. Copper, however, readily inserts into free base porphyrins. Copper reagents have been used to effect transformations in porphyrin synthetic chemistry, but if the free base porphyrin is employed, the isolated product invariably is the porphyrin copper chelate. Copper can be removed from the porphyrin with 15% H_2SO_4 in trifluoroacetic acid.[17] Alternatively a metalloporphyrin can be used to suppress formation of the copper porphyrin, though under forcing conditions copper-transmetalation can occur with metalloporphyrins such as zinc porphyrins.[18] When copper porphyrins are formed, the copper porphyrins and other metalloporphyrins are separated with extreme difficulty. In spite of the superb advantages of copper reagents in select chemistries, these limitations of severe demetalation conditions or intractable mixtures have led to searches for methods to achieve the same transformations in porphyrin chemistry without copper.[19] The presence of small amounts of copper porphyrins is a nontrivial problem in porphyrin photochemistry, as copper porphyrins are generally nonfluorescent and can cause quenching of other porphyrins in photochemically excited states.[20] Since we are ultimately interested in the photochemical properties of synthetic light-harvesting arrays, and require arrays with porphyrins in precise states of metalation including free base porphyrins, synthetic chemistry in this domain has zero tolerance for copper reagents. The use of copper in conjunction with palladium severely limits the scope of application of the Pd-coupling methods in porphyrin chemistry.

(3) The intrinsic solubilities of the porphyrins require reactions to be performed in dilute solution, typically 0.001−0.01 M, which is as much as 100 times less concentrated than for typical coupling reactions. Maintaining solubility of the reactants, intermediates, and products is a key constraint since we want to extend the coupling methods developed with dimers or trimers to the synthesis of multi-porphyrin arrays. For syntheses of ethynes using Pd-coupling reactions, we have used toluene/triethylamine as solvent because toluene provides solubility of the mesityl-substituted porphyrins and triethylamine provides the requisite base. Triethylamine often can be used as a solvent for Pd-mediated coupling reactions, but triethylamine alone is not a suitable solvent for the porphyrins. Porphyrins bearing methoxy substituents are soluble in pyridine, and in these cases pyridine/triethylamine proved suitable.[1]

Previously we synthesized ethyne-linked porphyrin arrays using copper-free Pd(0)-catalyzed coupling conditions.[1−3] A similar approach was developed by Arnold and Nitschinsk.[4] Reactions were performed at ~3 mM total porphyrin concentration in a homogeneous solution containing $Pd(PPh_3)_4$ at 40−50 °C under an argon atmosphere. This method was applied to the preparation of arrays containing up to five porphyrins,[2] but reaction times of 2−10 days were required and significant amounts of higher molecular weight materials were formed. Xu and Moore have emphasized the superiority of low temperature (<40 °C) Pd-couplings in spite of the longer reaction times, as higher temperatures give even greater amounts of higher molecular weight byproducts.[21]

In this paper we reinvestigate the copper-free Pd-catalyzed cross-coupling reaction in an effort to achieve shorter reaction times while minimizing the amount of higher molecular weight material formed as byproducts. Because of the constraints on temperature, porphyrin concentration, and solvent, and given that we employ the iodo group which is the most reactive of the halogens, the only variables available to us for achieving increased rates of product formation are the nature of the ligand and the Pd reagent. Farina and Krishnan showed that triphenylarsine ($AsPh_3$) dramatically accelerated the Stille reaction.[22] Prompted by their results, we investigated the use of $AsPh_3$ and other ligands in the synthesis of multi-porphyrin arrays. We also have developed copper-free Pd-mediated conditions for the oxidative homocoupling of porphyrin−ethynes forming butadiyne-linked porphyrin dimers. We also have prepared an enyne-linked porphyrin dimer via a complementary Pd-coupling reaction.

Results and Discussion

Ethyne-Linked Porphyrin Trimer Formation. To investigate optimal coupling reactions, we selected the reaction involving a monoethynyl zinc-porphyrin (**Zn-1**) and a diiodo free base porphyrin (**2**)[23] as shown in Scheme 1. This reaction affords a product distribution that is easily examined by analytical size exclusion chromatography (SEC). The catalyst was formed *in situ* by the addition of tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), a convenient source of Pd(0), and a ligand to a deaerated solution of **Zn-1** (14.5 mg, 3.5 mM) and **2** (6.9 mg, 1.46 mM) in 5.0 mL toluene/triethylamine (5:1) in standard glassware with ground glass fittings (vide infra). The solution was then warmed at 35 °C under an argon atmosphere. The reactions performed at these concentrations remained homogeneous at all times.

The results obtained with various ligands are shown in Table 1. The ligand $AsPh_3$ gives the trimer **3** in 68% yield after 1 h with no further increase at 2 h (entries 1 and 2). The ligands tri-2-furylphosphine ($P(2\text{-furyl})_3$) and triphenylphosphine (PPh_3) gave very low yields of trimer **3** and significant amounts of unreacted starting materials (entries 3 and 4). $AsPh_3$ affords the highest yield of **3** and is clearly the superior ligand. Size exclusion chromatograms (Figure 1) from the reaction using $AsPh_3$ show the ethyne-linked trimer **3**, dimeric components, and small amounts of higher molecular weight material (defined as the components eluting in advance of the trimer). In most reactions, especially those at longer times (entries 2 and 9), monomeric porphyrin byproducts were formed.

In prior reactions we performed which were quite slow (and in which oxygen was introduced during monitor-

---

[16] Buchler, J. W. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed., Elsevier: Amsterdam, 1975; p 177.

[17] Smith, K. M.; Craig, G. W. *J. Org. Chem.* **1983**, *48*, 4302−4306.

[18] Barnes, J. W.; Dorough, G. D. *J. Am. Chem. Soc.* **1950**, *72*, 4045−4050. Grant, C., Jr.; Hambright, P. *J. Am. Chem. Soc.* **1969**, *91*, 4195−4198.

[19] Jeyakumar, D.; Snow, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 8562−8564.

[20] Yan, X.; Holten, D. *J. Phys. Chem.* **1988**, *92*, 5982−5986.

[21] Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246−248.

[22] Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585−9595.

[23] Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440.

Scheme 1. Pd(0)-Catalyzed Synthesis of Ethyne-Linked Porphyrin Trimer 3

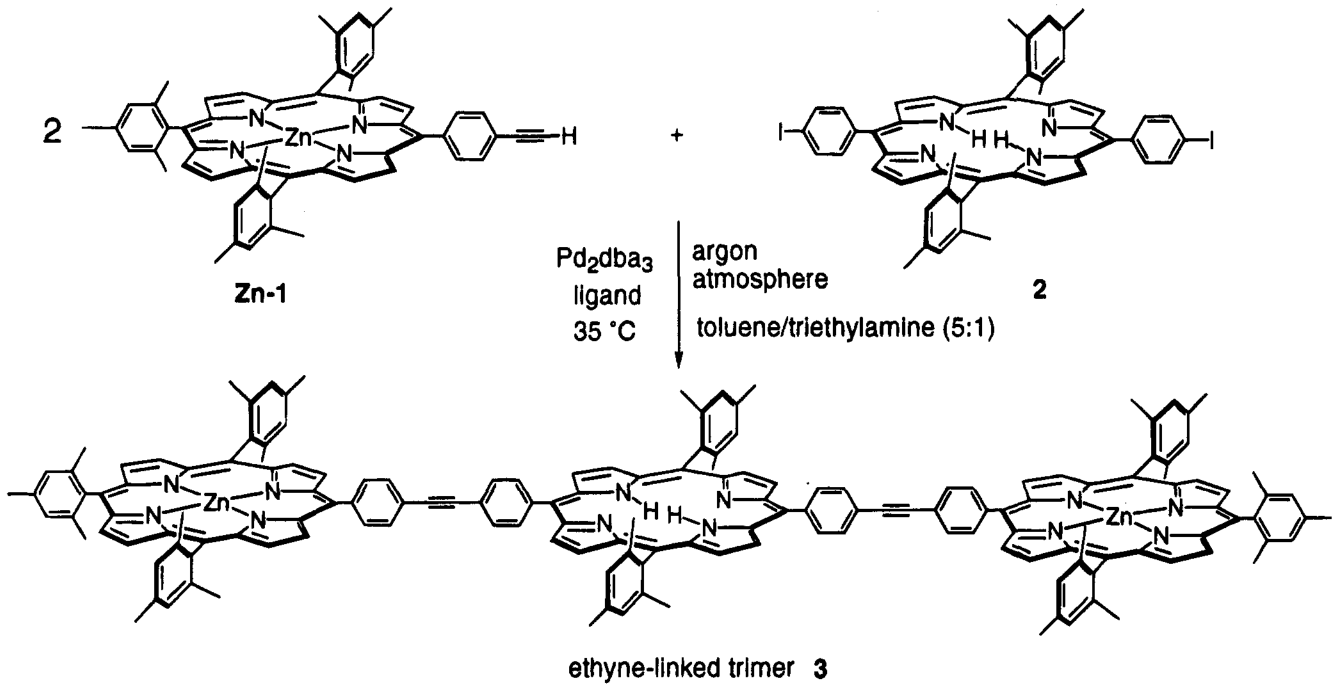


Table 1. Effects of Ligand and Concentration on the Formation of Ethyne-Linked Trimer 3[a]

entry	$[Pd_2(dba)_3]$ (mM)	ligand, [ligand] (mM)	[Pd]: [ligand]	time (h)	detection of dimer **4**[b]	HMWM: trimer **3**[c]	dimer(s): trimer **3**[d]	% unreacted porphyrins[e]	% yield of trimer **3**
1	0.44	$AsPh_3$, 3.5	1:4	1	−	0.08:1	0.29:1	17	68
2	0.44	$AsPh_3$, 3.5	1:4	2	−	0.1:1	0.34:1	0[f]	61
3	0.44	$P(2\text{-furyl})_3$, 3.5	1:4	2	+	no HMWM	3.2:1	60	7
4	0.44	PPh_3, 3.5	1:4	2	−	no HMWM	0.01:1[g]	96	0
5[h]	0.44	$AsPh_3$, 3.5	1:4	2	+	0.15:1	1.02:1	34	38
				5	+	0.25:1	0.94:1	25	40
				8	+	0.28:1	0.87:1	21	49
6	0.15	$AsPh_3$, 0.6	1:2	1	−	no HMWM	4.2 :1	76	1
7	0.15	$AsPh_3$, 1.2	1:4	1	−	0.14: 1	1.4:1	32	22
8	0.88	$AsPh_3$, 7.0	1:4	1	−	0.09:1	0.65:1	33	24
9[i]	0.44	$AsPh_3$, 3.5	1:4	2	−	0.08:1	0.26:1	0[f]	76

[a] All reactions were performed with 3.5 mM **Zn-1** and 1.46 mM **2** at 35 °C in toluene/triethylamine (5:1) under argon unless noted otherwise. Yields were determined by analytical SEC and calibration with authentic samples of **Zn-1**, **2**, and **3** (see Experimental Section). [b] Reaction samples were analyzed by TLC (silica, toluene/hexanes 3:2) for the presence of butadiyne-linked dimer **4**. [c] Integrated area of all higher molecular weight material (HMWM) relative to trimer peak area. [d] Integrated area of dimer peak (dimer formed by coupling of **Zn-1** and **2**, and butadiyne-linked dimer **4**, if any) relative to trimer peak area. [e] Sum of the integrated areas of peaks from starting materials **Zn-1** and **2**. Up to 14% of the unreacted porphyrins peaks is due to monomeric porphyrin byproducts. [f] Yield of monomeric porphyrin byproducts is 15%. [g] Relative to unreacted starting materials. [h] Reaction in the presence of air. [i] Preparative scale reaction.

ing),[1] the dimer peak derived in part from butadiyne-linked dimer (Scheme 2). Sonogashira *et al.* also reported finding butadiyne-linked dimer in their reaction mixtures.[14] The butadiyne-linked porphyrin dimer (**4**) and ethyne-linked porphyrin dimer (the dimer formed by coupling of **Zn-1** and **2**) co-chromatograph on SEC. Silica TLC analysis, which gives good separation of the butadiyne- and ethyne-linked porphyrin dimers, was used to assay for the presence of any butadiyne-linked dimer (**4**) in these reactions (Table 1). No butadiyne-linked dimer was observed with the reactions using $AsPh_3$ or PPh_3, but **4** was observed in the reaction using $P(2\text{-furyl})_3$. In the absence of any butadiyne **4**, the dimer peak is assigned to the ethyne-linked product of coupling of **Zn-1** and **2** (the precursor to **3**).

The reaction with $AsPh_3$ performed in the presence of air gave about half as much trimer after 2 h compared with the anaerobic reaction (entry 5, Table 1). Prolonged reaction (8 h) in air gave much more higher molecular weight material with only a slight increase in the yield of trimer. A significant amount of butadiyne-linked porphyrin dimer also formed. The palladium reagent, which is present at 30 mol %, rapidly loses activity in the presence of air and effectively functions for about one turnover. This experiment clearly shows the deleterious effects of air on this reaction.

We routinely perform the Pd-coupling reactions using standard glassware (without Schlenkware or sealed reaction vessels) on the benchtop and can achieve sufficiently anaerobic conditions to give good coupling yields. Removal of oxygen is accomplished by deaerating the reaction mixture with argon prior to the addition of catalyst and continuing deaeration throughout the 2 h reaction, during which no monitoring is performed. This approach is satisfactory and enables a large number of reactions to be performed on the benchtop without elaborate experimental apparatus.

Given the low concentration of substrates and reagents, we performed experiments with various concentrations of palladium reagents (entries 6−8, Table 1). Any increase or decrease in palladium reagent concentration gave lower product yields. The reaction with two ligands

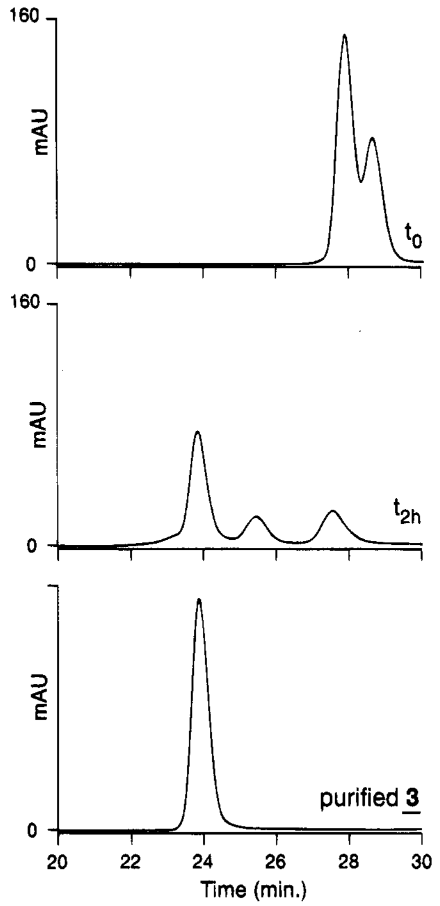


Figure 1. Size exclusion chromatograms of the reaction forming trimer **3** with AsPh$_3$ and Pd$_2$(dba)$_3$ (entry 2, Table 1). Top: The starting materials (**Zn-1**, t_R = 27.9 min, and **2**, t_R = 28.6 min) before the catalyst was added (10 μL reaction aliquot). Middle: the bands after 2 h correspond to higher molecular weight material (leading edge of trimer peak), ethyne-linked trimer **3** (t_R = 23.9 min), intermediate ethyne-linked dimer (t_R = 25.5 min), and a monomeric porphyrin byproduct (t_R = 27.7 min) (10 μL reaction aliquot). Bottom: purified trimer **3** (arbitrary quantity). Chromatograms are not corrected for different extinction coefficients of various components (see Experimental Section).

per Pd also gave a decrease in product yield. The highest yield of trimer **3** was obtained with the following molar ratio of components: ethyne (1.2), iodide (1), AsPh$_3$ (1.2), and Pd$_2$(dba)$_3$ (0.15).

The synthesis of ethyne-linked trimer **3** was scaled-up using these optimal conditions. The product distribution was nearly identical to that performed at the analytical scale (compare entries 9 and 2). The amount of higher molecular weight material was less than 10% of that of the trimer (assuming equal absorptivities per porphyrin). Preparative size exclusion chromatography (Bio-Beads SX-1, toluene) afforded 54 mg (79%) of **3**, which was confirmed by mass spectrometry, ^{1}H NMR spectroscopy, and absorption spectroscopy. In summary, rapid rates and good yields in Pd-mediated couplings can be achieved in dilute solution in the absence of copper by the appropriate selection of the ligand and reaction conditions. These results mirror those obtained by Farina *et al.* in the Stille reaction where the use of AsPh$_3$ gave large rate accelerations comparable to those provided by copper.[24]

Butadiyne-Linked Porphyrin Dimer Formation. Butadiyne-linked porphyrins have been synthesized by oxidative homocoupling of ethynes using Cu(OAc)$_2$,[1,5,8] CuCl,[9] or Pd(PPh$_3$)$_4$ and CuI.[6,10] In each case the presence of copper reagents necessitated the use of a metalloporphyrin to suppress copper insertion which would occur easily with a free base porphyrin. The oxidative coupling of terminal alkynes[25] can be employed with copper in stoichiometric (Eglinton reaction)[26] or catalytic (Glaser reaction)[27] amounts. Copper-mediated couplings are rapid and efficient. Recently, Pd-Cu co-catalysis was reported in the synthesis of aryl and alkyl diynes.[28-31] Though copper reagents have been the mainstay for forming butadiynes, the oxidatively-induced reductive elimination of butadiynes has been reported using ruthenium catalysts in the absence of copper.[32] During our prior work forming ethyne-linked porphyrins via copper-free Pd-mediated coupling reactions using reagents that gave slow reaction and conditions where reaction-monitoring admitted air to the reaction vessels, we observed butadiyne-linked porphyrins as a side product.[1,2] Butadiynes as side products in the ethyne-forming reactions are well-known.[14,21,28] We now have investigated the use of Pd(II) and Pd(0) as replacements for Cu(II) in the oxidative coupling of aryl ethynes in order that metalloporphyrins or free base porphyrins can be incorporated directly into butadiyne-linked arrays.

The synthesis of butadiyne-linked porphyrin dimers (Scheme 3) was explored via Pd(II)- or Pd(0)-mediated coupling of **Zn-1** in toluene/triethylamine (5:1) (Table 2). A zinc porphyrin was used in the Pd-mediated coupling so that direct comparisons could be made to a copper-mediated coupling reaction (which had to be performed using zinc porphyrins). Reactions were performed at 50 °C for 24 h in the presence of air and were monitored by analytical SEC. The identity of butadiyne-linked porphyrin dimer **4** was confirmed by comparison with an authentic sample prepared by the copper-mediated coupling of **Zn-1** in pyridine.[1]

Treatment of **Zn-1** with a stoichiometric amount of Pd(OAc)$_2$ afforded butadiyne-linked dimer **4** in 29% yield. In contrast, Pd(PPh$_3$)$_2$Cl$_2$, which is only sparingly soluble in the solvent and slowly came into solution, gave yields of 16% after 2 h, 51% after 6 h, and 73% after 24 h.

Reactions also were surveyed using a catalytic amount of Pd$_2$(dba)$_3$ and the three ligands examined in the formation of ethyne-linked porphyrins. P(2-furyl)$_3$ proved to be the best ligand, affording the highest yield and the cleanest reaction (Table 2). The yield increased with temperature from 35 °C (55%) to 60 °C (67%). Though the yields with AsPh$_3$ and P(2-furyl)$_3$ at 50 °C are comparable, the former gives a significant amount of higher molecular weight material and the latter gives much unreacted starting material. In contrast to ethyne formation with AsPh$_3$, butadiyne formation with P(2-furyl)$_3$ is relatively insensitive to slight changes in ligand/palladium ratios.

---

(24) Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905–5911.

(25) Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, pp 551–561.

(26) Eglinton, G.; Galbraith, A. R. *J. Chem. Soc.* **1959**, 889–896.

(27) Glaser, C. *Annalen* **1870**, *154*, 137–171.

(28) McGaffin, G.; de Meijere, A. *Synthesis* **1994**, 583–591.

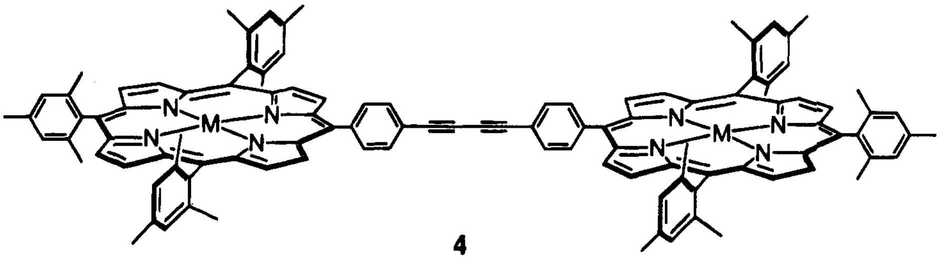
(29) Konishi, H.; Matsumura, C.; Okano, T.; Kiji, J. *J. Organomet. Chem.* **1989**, *364*, 245–248.

(30) Sabourin, E. T. *J. Mol. Catal.* **1984**, *26*, 363–373.

(31) Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett.* **1985**, *26*, 523–526.

(32) Pedersen, A.; Tilset, M.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 875–888.

Scheme 2. Butadiyne-Linked Porphyrin Dimer 4 (M = Zn)



4

Scheme 3. Pd(II)-Mediated Oxidative Coupling Yielding Butadiyne-Linked Porphyrin Dimers

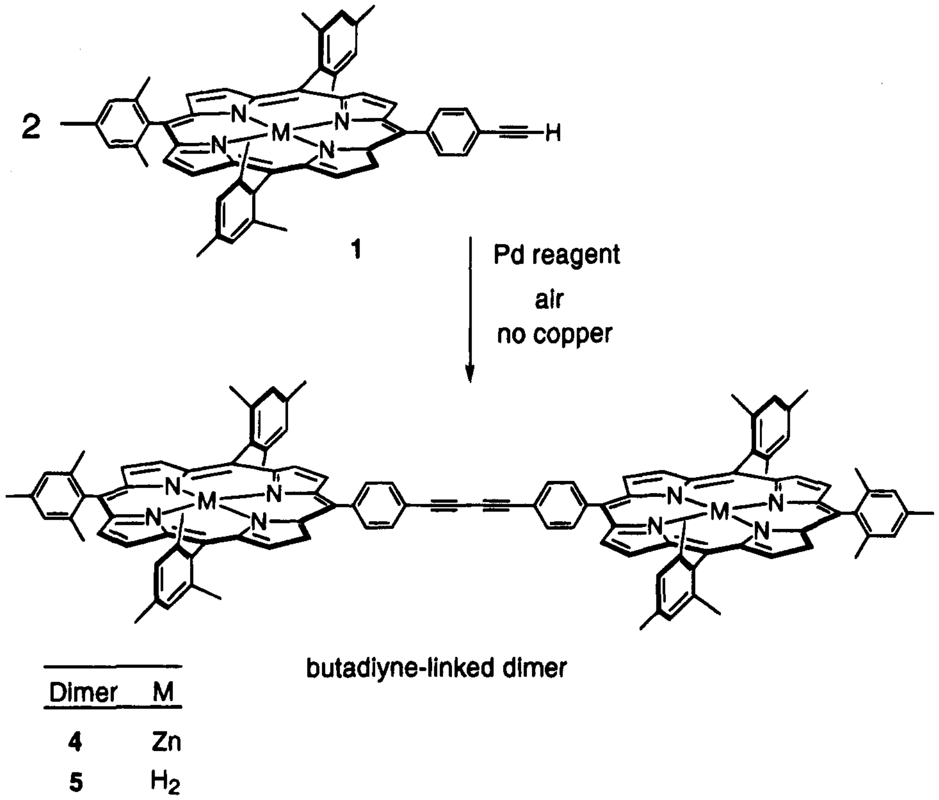


Table 2. Effect of Pd Reagents on the Formation of Butadiyne-Linked Dimer 4[a]

entry	Pd reagent	% unreacted **Zn-1**[b]	HMWM: dimer **4**[c]	% yield of dimer **4**
	Stoichiometric Pd(II)[d]			
1	$Pd(OAc)_2$	0[e]	3.30:1	29
2	$Pd(PPh_3)_2Cl_2$	0[e]	0.08:1	73
	Catalytic Pd(0)[f]			
3	$Pd_2(dba)_3 + AsPh_3$	28	0.80:1	56
4[g]	$Pd_2(dba)_3$ + P(2-furyl)$_3$	51	0.32:1	55
5	$Pd_2(dba)_3$ + P(2-furyl)$_3$	29	0.41:1	52
6[h]	$Pd_2(dba)_3$ + P(2-furyl)$_3$	17	0.26:1	67
7	$Pd_2(dba)_3 + PPh_3$	24	0.94:1	37
8[i]	$Pd_2(dba)_3$ + P(2-furyl)$_3$	22	0.30:1	67

[a] Reactions were performed with 5 mM **Zn-1** in toluene/triethylamine (5:1) at 50 °C for 24 h unless otherwise specified. Yields were determined at 24 h by analytical SEC and calibration with authentic samples of **Zn-1** and **4** (see Experimental Section). [b] 5–14% of **Zn-1** peak is due to monomeric porphyrin byproducts. [c] Integrated area of all higher molecular weight material (HMWM) relative to the dimer peak area. [d] 2.5 mM Pd reagent. [e] Yield of monomeric porphyrin byproducts is 5%. [f] 0.25 mM $Pd_2(dba)_3$ and 2.0 mM ligand. [g] Reaction at 35 °C. [h] Reaction at 60 °C. [i] 0.25 mM $Pd_2(dba)_3$ and 1.0 mM P(2-furyl)$_3$.

The optimal conditions for the Pd(0)-mediated oxidative homocoupling of porphyrin–ethynes were applied to the synthesis of the free base butadiyne-linked porphyrin dimer **5**. Free base porphyrin **1** (5 mM) was coupled using $Pd_2(dba)_3$ (0.25 mM) and P(2-furyl)$_3$ (2 mM) in a homogeneous solution of toluene/triethylamine (5:1) at 60 °C in air for 6 h. Very little higher molecular weight material was formed. The desired butadiyne–porphyrin dimer **5** was isolated in 63% yield (Figure 2). The identity of **5** was confirmed by mass spectrometry and ^1H NMR and absorption spectroscopy. No insertion of palladium into the free base porphyrin was observed. The ^1H NMR spectra of the butadiyne-linked porphyrins are devoid of any peaks in the 6–7 ppm region, as expected with these butadiyne-linked porphyrins (and unlike enyne-linked porphyrins; vide infra).

The generality of this coupling method was confirmed by synthesis of 1,4-diphenylbutadiyne (**6**) by reaction of phenylacetylene with $Pd_2(dba)_3$ and P(2-furyl)$_3$. The product (**6**) was identical with that prepared by Glaser coupling with CuCl and O_2 in pyridine.

The oxidative coupling reactions using catalytic Pd(0) were performed in solutions exposed to air. The catalytic oxidations employ 10 mol % $Pd_2(dba)_3$ per butadiyne linkage formed. Assuming O_2 serves as the stoichiometric oxidant and acts as a $4e^-$, 4 H^+ acceptor, then 0.25

---

(33) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993, p 293.

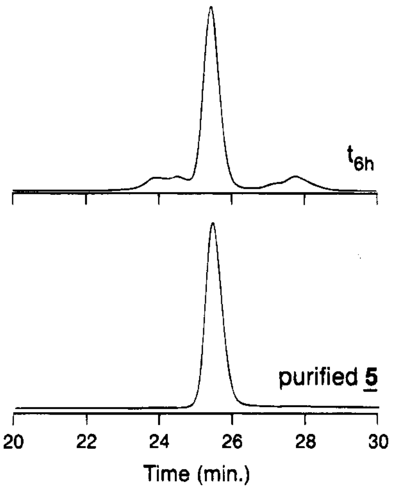


Figure 2. Size exclusion chromatograms of the reaction forming butadiyne-linked free base porphyrin dimer **5**. Top: The bands after 6 h correspond to higher molecular weight material (leading edge of dimer **5** peak), butadiyne-linked dimer **5** (t_R = 25.5 min), and monomeric porphyrin byproducts (t_R = 27.7 min). Bottom: purified butadiyne-linked dimer **5**.

mol of O_2 is required per ethyne. In the dimerizations of the porphyrin ethynes, the porphyrin concentrations (5 mM) are sufficiently dilute that continued aeration is not necessary. Under an air atmosphere the concentration of O_2 dissolved in toluene is substantial (2.1 mM at 25 °C),[33] which alone constitutes stoichiometric equivalents for reactions up to ~8 mM in ethyne. Oxidative dimerizations at much higher concentrations with catalytic Pd(0) would require continued aeration.

Enyne-Linked Porphyrin Dimer Formation. The reaction of terminal ethynes with cupric acetate under anaerobic conditions (Straus coupling) affords the enyne-linked dimer.[34] Enyne formation also has been observed with metal reagents based on Ir,[35] Ni,[36] Rh,[37] Ru,[38] Ti,[39] Zr[40] or Pd including $Pd(OAc)_2/CuI$,[30] $Pd(OAc)_2$ with a variety of ligands,[41] $Pd(PPh_3)_4$,[42] or $Pd(acac)_2/PPh_3 + Et_3Al$.[43] We sought to prepare enyne-linked porphyrin dimers for two reasons. First, this would establish a new linker for porphyrin arrays using the same starting materials as employed in butadiyne formation. Second, we wanted to obtain a sample of an enyne-linked porphyrin dimer and establish unequivocally the absence of enyne dimer in the Pd-coupling reaction forming butadiyne-linked porphyrin dimers.

Following the conditions of Ishikawa,[42] treatment of **Zn-1** in toluene with $Pd(PPh_3)_4$ in the absence of added ligand under anaerobic conditions at 100 °C for 24 h yielded a product distribution consisting of a large amount of higher molecular weight material, the enyne-linked dimer **7** (SEC t_R 25.7 min; to be compared with t_R 25.5 min for the butadiyne-linked dimer), and trace amounts of monomeric porphyrin byproducts (Scheme 4). Column chromatography afforded the enyne-linked dimer **7** in 29% yield. ^{1}H NMR showed two singlets in the 6−7 ppm region consistent with a head-to-tail linked enyne. The Pd-coupling methods for forming enynes usually afford the head-to-tail linked enyne. Ishikawa, however, has shown that with some special substrates the coupling with $Pd(PPh_3)_4$ or other metal affords the head-to-head-linked enyne.[44] In our case the porphyrin ethyne **Zn-1** gives the normal head-to-tail-linked enyne. This coupling method readily affords a clam-shell like architecture constructed with a pure hydrocarbon linker.

Conclusions

Ethyne-linked, butadiyne-linked, or enyne-linked porphyrin arrays can be synthesized from porphyrin building blocks in dilute solution, under mild, nonacidic, nonmetalating conditions using copper-free Pd-catalyzed coupling reactions. In the Pd(0)-catalyzed cross-coupling of a porphyrin aryl iodide and a porphyrin aryl ethyne, anaerobic conditions employing $AsPh_3$ and $Pd_2(dba)_3$ in toluene/triethylamine (5:1) at 35 °C gave the highest yield of ethyne-linked porphyrin array in 1−2 h. For the oxidative homocoupling of a porphyrin aryl ethyne, aerobic conditions employing a stoichiometric amount of $Pd(PPh_3)_2Cl_2$ or a catalytic amount of $Pd_2(dba)_3$ and $P(2\text{-furyl})_3$ in toluene/triethylamine (5:1) at 50−60 °C gave butadiyne-linked porphyrin dimer in 6−24 h. This reaction is slower than Glaser coupling, but the ability to perform the reaction in the absence of copper provides distinct advantages in porphyrin chemistry. The Pd(0)-mediated coupling of a porphyrin aryl ethyne under anaerobic conditions in the absence of a base at 100 °C afforded the enyne-linked porphyrin dimer. These three coupling methods are complementary. Neither palladium insertion into free base porphyrins nor transmetalation of zinc porphyrins was observed by absorption spectroscopy or mass spectral analysis of ethyne-linked, butadiyne-linked, or enyne-linked porphyrin arrays. These methods provide rapid and efficient means for covalently joining free base and metalloporphyrin building blocks in the absence of copper and should help broaden the scope of porphyrin model systems.

Experimental Section

General. ^{1}H NMR spectra (300 MHz, IBM FT-300) and absorption spectra (HP 8451A, Cary 3) were collected routinely. Toluene (Fisher, certified A.C.S.) was distilled from $LiAlH_4$. Triethylamine (Fluka, puriss) was distilled from CaH_2. All other reagents were obtained from Aldrich. Other solvents were used as received. All Pd-mediated porphyrin reactions were performed in the dark using routine glassware. No Schlenkware or sealed reaction vessels were employed.

Analytical Size Exclusion Chromatography. Analytical SEC columns (styrene−divinylbenzene copolymer) were purchased from Hewlett Packard and Phenomonex. Analytical SEC was performed with a Hewlett-Packard 1090 HPLC using 500 Å (300 × 7.8 mm), 500 Å (300 × 7.5 mm), and 100 Å (300 x 7.5 mm) columns (5 μm) in series eluting with THF (flow rate = 0.8 mL/min; void volume ~ 18.0 min). Reaction monitoring was performed by removing aliquots from the reaction mixture and diluting with THF (Fisher, HPLC).

---

(34) Straus, F. *Ann.* **1905**, *342*, 190−196. Carlton, L.; Read, G. *J. Chem. Soc., Perkin Trans. I* **1978**, 1631−1633.

(35) Jun, C.-H.; Lu, Z.; Crabtree, R. H. *Tetrahedron Lett.* **1992**, *33*, 7119−7120.

(36) Giacomelli, G.; Marcacci, F.; Caporusso, A. M.; Lardicci, L. *Tetrahedron Lett.* **1979**, 3217−3220.

(37) Singer, H.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 849−853.

(38) Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1976**, 841−842.

(39) Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480−487.

(40) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185−187.

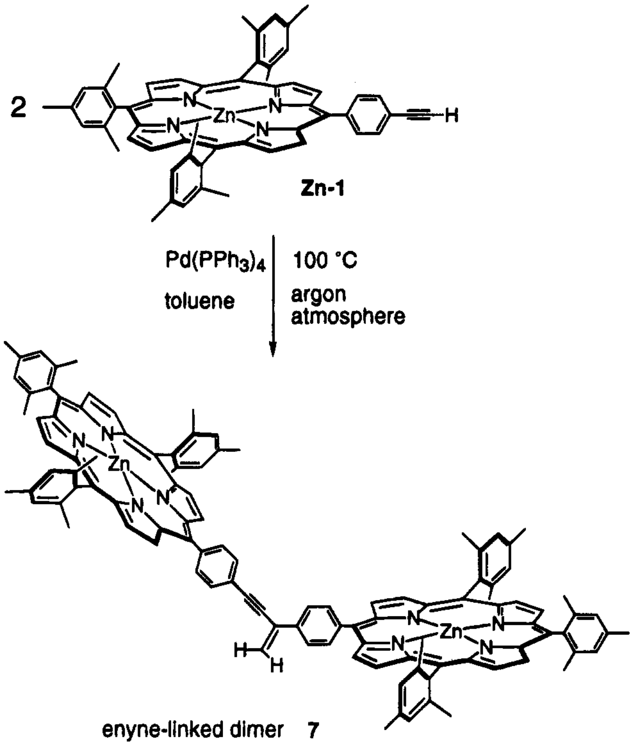
(41) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486−3487. Trost, B. M.; Matsubara, S.; Caringi, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 8745−8746.

(42) Ishikawa, M.; Ohshita, J.; Ito, Y.; Minato, A. *J. Organomet. Chem.* **1988**, *346*, C58−C60.

(43) Selimov, F. A.; Rutman, O. G.; Dzhemilev, U. M. *J. Org. Chem. USSR* **1984**, *19*, 1621−1623.

(44) Ohshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* **1990**, *55*, 3277−3280.

Scheme 4. Pd(0)-Mediated Formation of an Enyne-Linked Porphyrin Dimer (7)



Sample detection was achieved by absorption spectroscopy using a diode array detector with quantitation at 420 nm (±10 nm bandwidth), which best captures the peaks of monomeric and multimeric porphyrins.

In quantitation of the product distribution of the reactions forming trimer **3**, direct visual comparisons of the trimer and starting material peaks in a single chromatogram can be misleading because the porphyrin **Zn-1** has ϵ_{423} = 540 000 $M^{-1}cm^{-1}$ and fwhm 11.2 nm, while the trimer (**3**) has ϵ_{429} = 850 000 $M^{-1}cm^{-1}$ and fwhm = 19.6 nm. For quantitation, the yield of ethyne-linked trimer **3** is determined by comparison with known concentrations of authentic samples. The yield of unreacted porphyrins is determined by comparison with known concentrations of the starting porphyrins **Zn-1** and **2**. Peaks eluting after the dimers and before the sharp leading edge of **Zn-1** (26.5 to ~27.3 min) are ascribed to monomeric porphyrin byproducts. A working curve established the linearity of Beer's law for the concentrations of the samples investigated. The extinction coefficients and composition of higher molecular weight material are not known, so the integrated area of the peaks that precede the trimer is compared with that of the trimer. Similarly, the dimer peak in some cases consists of ethyne-linked dimer and butadiyne-linked dimer, and again the dimer(s):trimer ratio is simply tabulated. This method gives a rough quantitative picture of the types of product distributions from different coupling conditions. Assuming the higher molecular weight material has an absorption per porphyrin equal to that of the target molecule (and the ratio of higher molecular weight material to target molecule corresponds to a relative yield), then the total yield of all porphyrin components in a given chromatogram falls in the range of 100 ± 30%. This gives an indication of the accuracy of the yield values in Table 1. The same approach is used for the data concerning formation of butadiyne-linked dimer **4** (Table 2).

Zinc(II) 5,10,15-trimesityl-20-(4-ethynylphenyl)porphyrin (Zn-1). A sample of 5,10,15-trimesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin[1] (150 mg, 0.18 mmol) was dissolved in 50 mL of $CHCl_3$; then a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (79 mg, 0.36 mmol, 5 mL methanol) was added. The reaction mixture was stirred at room temperature and was monitored by fluorescence excitation spectroscopy. After being stirred overnight, the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated, affording 160 mg (100%) of the zinc chelate as a purple solid: ^1H NMR ($CDCl_3$) δ 0.39 (s, 9 H), 1.83 (s, 12 H), 1.84 (s, 6 H), 2.63 (s, 9 H), 7.27 (s, 6 H), 7.89 (AA'BB', 2 H), 8.19 (AA'BB', 2 H), 8.70 (s, 4 H), 8.77 (d, J = 4.5 Hz, 2 H), 8.83 (d, J = 4.5 Hz, 2 H); λ_{abs} (toluene) 428, 550 nm; λ_{em} (toluene) 598, 646 nm. Deprotection of the trimethylsilyl group could be achieved in two ways:

Method 1. The zinc chelate (102 mg, 0.11 mmol) was dissolved in 20 mL of anhydrous THF. Then 220 mg of tetrabutylammonium fluoride on silica gel (1.0–1.5 mmol F/g) was added and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was rotary evaporated to dryness, and the greenish-purple powder was dissolved in 50 mL of $CHCl_3$. The organic layer was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated to dryness. Column chromatography (silica, CH_2Cl_2/hexanes 1:1, 2.5 × 10 cm) afforded 83 mg (90%) of porphyrin.

Method 2. The zinc chelate (100 mg, 0.11 mmol) was dissolved in 13.5 mL of THF/methanol (3:1). K_2CO_3 (30 mg, 0.22) was added, and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated to dryness. Column chromatography (silica, CH_2Cl_2/hexanes 1:1, 2.5 × 10 cm) afforded 87 mg (95%) of porphyrin: ^1H NMR ($CDCl_3$) δ 1.83 (s, 12 H), 1.84 (s, 6 H), 2.63 (s, 9 H), 3.30 (s, 1 H), 7.27 (s, 6 H), 7.87 (AA'BB', 2 H), 8.18 (AA'BB', 2 H), 8.70 (s, 4 H), 8.76 (d, J = 4.5 Hz, 2 H), 8.82 (d, J = 4.5 Hz, 2 H); λ_{abs} (toluene) 423 (ϵ = 540 000 $M^{-1}cm^{-1}$, fwhm 11.2 nm), 550 nm; λ_{em} (toluene) 597, 646 nm.

Effects of Ligand in Ethyne-Linked Trimer 3 Formation. Compounds **Zn-1** (14.5 mg, 17.5 μmol) and 5,15-dimesityl-10,20-bis(4-iodophenyl)porphyrin[23] (**2**, 6.9 mg, 7.3 μmol) were added to a 15 mL one-neck round bottom flask and dissolved in 5.0 mL of toluene/triethylamine (5:1) with stirring. The flask was heated to 35 °C and was fitted with a 15 cm reflux condenser through which a drawn glass pipet was mounted for deaeration with argon. The reaction vessel headspace including the condenser was deaerated with a high flow rate of argon for 5 min. The solution was then deaerated by immersing the pipet in the solution and gently bubbling argon for 30 min. The condenser was then elevated, leaving the pipet in the solution, and the $Pd_2(dba)_3$ (2.1 mg, 2.2 μmol) and ligand solids were added simultaneously. The condenser was replaced and argon was bubbled through the solution for another 5 min. At this point the pipet was removed from the reaction mixture and positioned about 2 cm above the solution. The argon flow rate was turned up slightly, and the reaction was allowed to proceed. After 2 h the solvent volume had decreased by about 0.5 mL, and this volume was then replaced. Then samples (10 μL) were diluted in 2.0 mL of THF and 25 μL of this solution was injected into the HPLC and analyzed by SEC. Products were identified by comparison of their retention times with those of authentic samples of **Zn-1**, **2**, **3**, and **4**. Trimer yields were quantitated by calibration with an authentic sample of **3**. TLC analysis (silica, toluene/hexanes 3:2) of various reactions gave separation of the following components: **2**, R_f 0.88; **Zn-1**, R_f 0.77; butadiyne-linked dimer **4**, 0.55; intermediate ethyne-linked dimer, R_f 0.46; trimer **3**, R_f 0.28; unidentified porphyrin component, R_f 0.16, and black non-porphyrinic materials at the base line.

Trimer 3. Samples of **2**[23] (28 mg, 29 μmol) and **Zn-1** (58 mg, 70 μmol) were added to a 50 mL one-neck round bottom flask containing 20 mL of toluene/triethylamine (5:1). The flask was heated to 35 °C and was fitted with a 15 cm reflux condenser through which a drawn glass pipet was mounted for deaeration with argon. The reaction vessel headspace including the condenser was deaerated with a high flow rate of argon for 5 min. The solution was then deaerated by immersing the pipet in the solution and gently bubbling argon for 30 min. The condenser was then elevated, leaving the pipet in the solution, and $Pd_2(dba)_3$ (8.0 mg, 8.7 μmol) and $AsPh_3$ (21 mg, 70 μmol) were added. The condenser was replaced, and argon was bubbled through the solution for another 5 min. At this point the pipet was removed from the reaction mixture and positioned about 2 cm above the solution. The argon flow rate was turned up slightly, and the reaction was allowed to proceed. After 2 h the reaction mixture was concentrated to dryness, redissolved in 10 mL of toluene, and loaded onto a preparative size exclusion column (BioRad Bio-Beads SX-1 packed in toluene in a 4.8 × 60 cm glass gravity-flow column; flow rate 4 mL/min). Elution with toluene over 3 h yielded four major components (in order of elution): higher molecular weight material, trimer **3**, intermediate ethyne-linked dimer **4**, and a monomeric porphyrin byproduct. Five chromatographic fractions (15 mL each) containing trimer were combined and rechromatographed a second time in similar manner, affording 54 mg (79%). During the first chromatographic purification, a small amount of material precipitated at the top of the column (All of our previous mesityl-substituted multi-porphyrin arrays have high solubility in toluene.[1-3] This particular trimer, however, has limited solubility in toluene, though we note that the reaction mixture remained homogeneous.): ^{1}H NMR (CDCl$_3$) δ −2.65 (bs, 2 H), 1.87 (s, 36 H), 1.90 (s, 12 H), 2.64 (s, 6 H), 2.65 (s, 12 H), 2.67 (s, 6 H), 7.28 (s, 4 H), 7.30 (s, 8 H), 7.33 (s, 4 H), 8.06, 8.10 (m, 8 H), 8.30, 8.33 (m, 8 H), 8.73 (s, 8 H), 8.78 (d, 4 H, J = 4.8 Hz), 8.81 (d, 4 H, J = 4.8 Hz), 8.90 (d, 4 H, J = 4.8 Hz), 8.94 (d, 4 H, J = 4.8 Hz); $C_{160}H_{130}N_{12}Zn_2$ calcd avg mass 2351.6, obsd 2350.0; λ_{abs} (toluene) 429 (ϵ = 850 000 M^{-1}cm^{-1}, fwhm = 19.6 nm), 515, 550, 592, 650 nm.

Studies of Butadiyne-Linked Dimer 4 Formation. Porphyrin **Zn-1** (5.0 mM) was coupled in a 2 mL solution of toluene/triethylamine (5:1) in a 10 mL reaction vessel (at 35, 50, or 60 °C) equipped with a 15 cm reflux condenser open to the air. The Pd reagents varied depending on the reaction under investigation. A stoichiometric amount (2.5 mM) of Pd(II) was obtained by adding either Pd(OAc)$_2$ or Pd(PPh$_3$)$_2$Cl$_2$. For the reactions with Pd(0), additions were made of Pd$_2$(dba)$_3$ (0.5 mL of a fresh 1 mM stock solution in toluene/triethylamine (5:1), 0.25 mM) and ligand (0.04 mL of a 0.1 M stock solution, 2.0 mM). Reactions were monitored by removing 10 μL aliquots and diluting them in 2.0 mL of THF. Then 25 μL of this solution was injected into the HPLC and analyzed by SEC. Dimer yields were quantitated by calibration with an authentic sample of **4**.[1]

4,4′-Bis[5,10,15-trimesityl-20-porphinyl]diphenylbutadiyne (5). A solution containing 5,10,15-trimesityl-20-(4-ethynylphenyl)porphyrin[1] (**1**, 76.4 mg, 100 μmol), Pd$_2$(dba)$_3$ (4.6 mg, 5.0 μmol), and tri-2-furylphosphine (9.3 mg, 40 μmol) in 20 mL of toluene/triethylamine (5:1) in a 50 mL one-neck round bottom flask fitted with a reflux condenser open to the air was stirred at 60 °C for 6 h. After removal of the solvent, the reaction mixture was purified by column chromatography (silica, toluene/hexanes 3:2), affording 48 mg (63%). ^{1}H NMR (CDCl$_3$) δ −2.57 (bs, 4 H), 1.84 (s, 36 H), 2.61 (s, 6 H), 2.62 (s, 12 H), 7.26 (s, 4 H), 7.27 (s, 8 H), 7.97 (AA′BB′, 4 H), 8.22 (AA′BB′, 4 H), 8.62 (s, 8 H), 8.69 (d, J = 4.5 Hz, 4 H), 8.78 (d, J = 4.5 Hz, 4 H); $C_{110}H_{94}N_8$ calcd avg mass 1528.0, obsd 1528.3; λ_{abs} (toluene) 424, 516, 550, 592, 648 nm.

1,4-Diphenylbutadiyne (6). In a 250 mL one-neck round bottom flask was placed a stir bar, 200 mL of toluene/triethylamine (5:1), phenylacetylene (108 μL, 1 mmol, 5 mM), tri-2-furylphosphine (92 mg, 0.4 mmol), and Pd$_2$(dba)$_3$ (44 mg, 0.05 mmol). A reflux condenser open to the air was attached, and the flask was placed in an oil bath at 50 °C. At 19 h GC-MS analysis of the crude reaction mixture showed complete consumption of phenylacetylene, a peak at *m/e* = 202 due to 1,4-diphenylbutadiyne, and a peak with *m/e* = 248 (assigned to tri-2-furylphosphine oxide). The reaction mixture was concentrated to dryness under reduced pressure. Flash chromatography (silica, CH$_2$Cl$_2$/hexanes 1:1, 3.5 × 10 cm) gave the product as the first component eluting from the column. Evaporation of the solvent gave 71 mg (70% yield) of a light yellow solid. Recrystallization from ethanol gave 56 mg (55% yield) of a white solid: mp 84–86 °C (lit. mp 84–86 °C;[26] 88 °C[27]); ^{1}H NMR (CDCl$_3$) δ 7.32, 7.38 (m, 6 H), 7.52, 7.55 (m, 4 H). Anal. ($C_{16}H_{10}$) C, H. This product was identical to that obtained by Glaser coupling (CuCl + O$_2$ in pyridine).[45]

Zn$_2$–Porphyrin Enyne Dimer 7. In a 1-dram screw cap vial were placed 3 mL of toluene and a stir bar. Argon was bubbled through the toluene to effect deaeration. After 30 min **Zn-1** (15 mg, 0.018 mmol) and Pd(PPh$_3$)$_4$ (2.1 mg, 0.0018 mmol) were added at once. The argon bubbling was continued for another 5 min, at which point the vial was capped and placed in an oil bath at 100 °C. After 24 h analytical SEC showed higher molecular weight material, a new porphyrin component (t_R = 25.7 min), and unreacted **Zn-1**. The solvent was removed via rotary evaporation, and the crude reaction mixture was chromatographed on silica (hexanes/toluene 1:1, 3.5 × 10 cm). The product was the second porphyrin band to elute. Removal of the solvent gave 4 mg (29%): ^{1}H NMR (CDCl$_3$) δ 1.84 (s, 12 H), 1.85 (s, 12 H), 1.86 (s, 12 H), 2.62 (s, 6 H), 2.64 (s, 6 H), 6.15 (s, 1 H), 6.44 (s, 1 H), 7.28 (s, 8 H), 7.33 (s, 4 H), 8.03 (AA′BB′, 2 H), 8.24 (AA′BB′, 2 H), 8.27 (AA′BB′, 2 H), 8.32 (AA′BB′, 2 H), 8.70 (s, 4 H), 8.71 (s, 4 H), 8.78, 8.80 (m, 4 H), 8.89 (d, 2 H, J = 4.5 Hz), 8.96 (d, 2 H, J = 4.8 Hz); $C_{110}H_{92}N_8Zn_2$ calcd avg mass 1656.8, obsd 1655.7 and two unidentified peaks at 1932.3 and 2337.2 which constituted less than 5% of the integrated area; λ_{abs} (toluene) 424, 550 nm.

Acknowledgment. This work was supported by the NIH (GM36238). Laser desorption mass spectrometry was performed at Argonne National Laboratory. We thank Dr. Michael Wasielewski for mass spectrometry assistance.

Supporting Information Available: ^{1}H NMR spectra for **Zn-1**, **3**, **5**, and **7** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9505482

---

(45) Williamson, K. L. *Macroscale and Microscale Organic Experiments*; D. C. Heath and Company: Lexington, MA, 1989; pp 494–498.