

## The Preparation of Novel Porphyrins and Bis(Porphyrins) Using Palladium Catalysed Coupling Reactions

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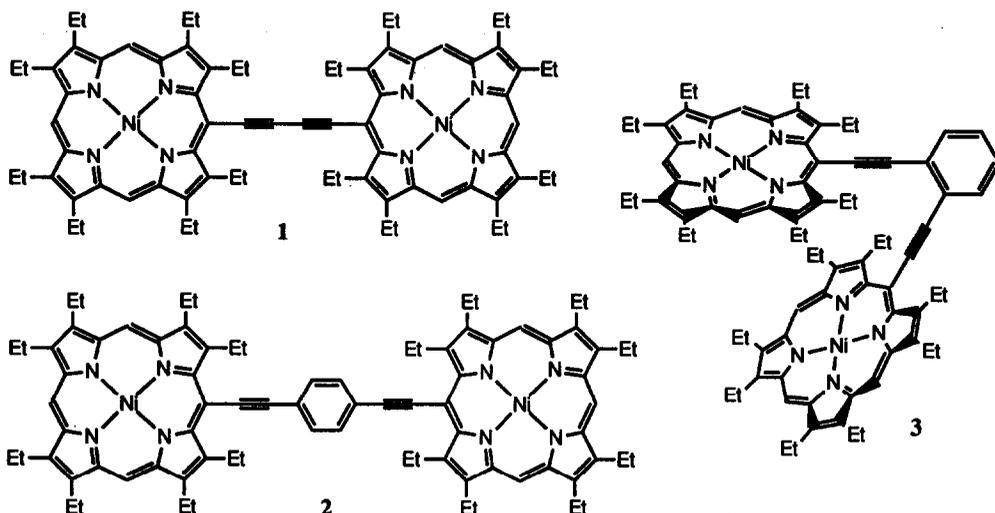
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**Abstract:** The palladium(0) catalysed coupling of alkynyl porphyrins with either aryl iodides or a  $\beta$ -bromovinylporphyrin leads to symmetrical and unsymmetrical bis(porphyrins) incorporating various unsaturated bridges. Some novel porphyrins bearing enyne and alkyne substituents are also described.

The preparation of arrays of covalently linked porphyrins is a popular area of research, not only for its possible application to the elucidation of natural photosynthetic mechanisms, but also for probing the fundamental physico-chemical properties of the porphyrin chromophore. The elegant studies directed to the former topic were recently reviewed.<sup>1</sup> Pandey *et al.*<sup>2</sup> recently described a novel and versatile approach to the preparation of unsymmetrical porphyrin dimers, in particular those linked by *p*-phenylene and *p,p'*-stilbenylene bridges. Other unsymmetrical hydrocarbon linked dimers are known.<sup>3,4</sup> We are concentrating on the properties of alkynyl-substituted porphyrins, and have found that the butadiyne 1 and complexes of the same ligand with other metals show strong inter-porphyrin interaction in their electronic absorption spectra.<sup>5-7</sup> The effects of *meso*-alkynyl substituents on porphyrin spectra have also been noted by Anderson.<sup>8</sup> Since the palladium catalysed coupling of terminal alkynes with alkenyl and aryl halides is a well tested and efficient process<sup>9</sup>, we sought to apply this chemistry to the synthesis of various dimeric porphyrins containing *meso*-alkynyl groups. We report herein our initial results, which show that this idea is indeed a fruitful one, enabling the preparation of symmetrical and unsymmetrical dimers containing various unsaturated bridges. Others<sup>10,11</sup> have reported porphyrin dimers or trimers incorporating alkyne bridges, but these examples contain *meso*-aryl groups between the porphyrin and the triple bonds.

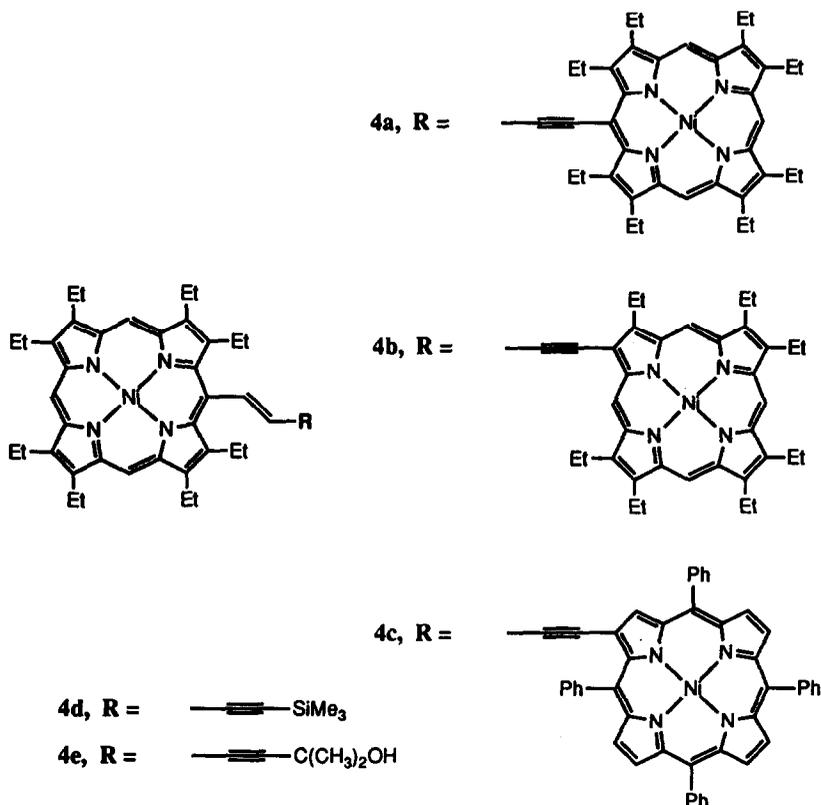
The coupling of a 50% excess of *meso*-(ethynyl)NiOEP (H<sub>2</sub>OEP = octaethylporphyrin)<sup>5,6</sup> with 1,4-diiodobenzene in the presence of PdCl<sub>2</sub> and triphenylphosphine in triethylamine as solvent, led to the isolation of the *p,p'*-diethynylphenylene bridged dimer 2.<sup>12</sup> The reaction was monitored by tlc, a challenging task, as the dimers 1 and 2, the intermediate *meso*-[(*p*-iodophenyl)ethynyl] species, and the alkyne starting material all display similar elution behaviour. The pure dimer 2 was obtained in 60% yield after passage through two silicagel columns. Its electronic absorption spectrum, perhaps surprisingly, appears to indicate that there is less conjugative interaction between the chromophores in 2, than exists in 1. Steric interactions involving the neighbouring ethyl substituents may be the cause of

this. The Soret band of **2** is split, but not to the same extent exhibited by **1**, and the longest wavelength band is red-shifted relative to the monomeric *meso*-ethynyl compound by only 4 nm.



The corresponding coupling reaction using 1,2-diiodobenzene, to form the dimer **3**, was more complicated, for two reasons. Firstly, steric constraints led to a more sluggish second coupling reaction. This enabled the isolation and characterisation of the mono-coupled *meso*-[(*o*-iodophenyl)ethynyl] derivative, a compound with potential uses in the synthesis of further novel structures. Secondly, although the desired product **3** appeared to be formed in moderate yield, chromatographic purification proved to be difficult. The compound decomposes to form more polar products, the structures of which are under investigation. Rearrangements of *o*-diethynylbenzenes and *cis*-enediynes are known.<sup>13</sup>

We have also achieved the formation of *unsymmetrical* porphyrin dimers by palladium catalysed coupling, using an alkynylporphyrin<sup>6</sup> and *meso*-( $\beta$ -bromovinyl)NiOEP.<sup>5,6</sup> Thus the dimers **4a** - **4c** were prepared. The first of these butenyne has not yet been separated from the by-product **1**, but has been characterised by its unmistakable <sup>1</sup>H and <sup>13</sup>C NMR spectra. The dimers **4b** and **4c** were obtained in 30% and 15% yields, respectively, after preparative tlc and recrystallization. These are the first examples of porphyrin dimers containing the butenyne linkage. As expected, the out-of-plane *trans*-alkene interrupts the conjugation, and the electronic spectra are simply the superimposition of the two chromophores. We have also prepared the protected enyne monomers **4d** and **4e** in high yields, since the readily available alkynes can be used in large excess. These last two compounds should be useful in the synthesis of dimers with longer bridges. Finally, we have illustrated coupling in the reverse sense, i.e. an alkyne with an iodoporphyrin, by preparing in good yield, the zinc complex of 2,4-bis(trimethylsilylethynyl)deuteroporphyrin IX dimethyl ester from the corresponding diiodoporphyrin complex, the free base of which was independently prepared by Bonnett *et al.*<sup>14</sup> and Minnetian *et al.*<sup>15a</sup> The Smith group used palladium catalysed coupling of mercurio- and haloporphyrins to form alkenyl and styryl substituted deuteroporphyrins, but were unable to introduce alkynes by their method.<sup>15</sup>



All compounds except 3 and 4a have been characterised by tlc, and <sup>1</sup>H and <sup>13</sup>C NMR, IR, electronic absorption and FAB mass spectra. The yields of the dimers have not yet been optimized. This methodology should be extendable to many other alkenyl, aryl and heteroaryl halides, and we are currently pursuing such studies.

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#### REFERENCES and NOTES

1. Wasielewski, R. *Chem. Rev.* **1992**, *92*, 435-461.
2. Pandey, R. K.; Forsyth, T. P.; Gerzevske, K. R.; Lin, J. J.; Smith, K. M. *Tetrahedron Lett.* **1992**, *33*, 5315-5318.
3. Maruyama, K.; Nagata, T.; Ono, N.; Osuka, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3167-3170.

4. Sessler, J. L.; Johnson, M. R.; Creager, S. F.; Fettingner, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9310-9329.
5. Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366-370.
6. Arnold, D. P.; Nitschinsk, L. I. *Tetrahedron*, **1992**, in press.
7. Arnold, D. P.; Heath, G. A. Unpublished results.
8. Anderson, H. L. *Tetrahedron Lett.* **1992**, *33*, 1101-1104.
9. Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd Ed.; Elsevier: Amsterdam. 1988; p. 214.
10. Maruyama, K.; Kawabata, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 170-175.
11. (a) Anderson, H. L.; Sanders, J. K. M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1400-1403. (b) Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1714-1715.
12. The method used to prepare **3** illustrates our typical experimental procedure: A mixture of *meso*-ethynylNiOEP (45 mg) and 1,4-diiodobenzene (8.3 mg) in NEt<sub>3</sub> (5 ml), was degassed by argon bubbling. PdCl<sub>2</sub> (10 mg) and PPh<sub>3</sub> (20 mg) were added, and the mixture was stirred and refluxed under argon for 4 h, then stirred overnight at room temperature. The solvent was removed under vacuum, the residue was extracted with CHCl<sub>3</sub>, the CHCl<sub>3</sub> layer was washed with 1M HCl, then water, dried, and evaporated. Column chromatography (silicagel 230-400 mesh; first column, 50/50 CHCl<sub>3</sub>/hexane; second column, 25/75 then 50/50 CHCl<sub>3</sub>/hexane) and recrystallisation from CHCl<sub>3</sub>/MeOH gave purple microcrystals of **3** in 60% yield. Brief data for **3**: <sup>1</sup>H NMR δ *ca.* 1.76 overlapping t, 36H; 1.87 t, 12H; *ca.* 3.8 overlapping q, 24H; 4.26 q, 8H; 7.82 s, 4H (phenyl); 9.40 s, 2H; 9.43 s, 4H; <sup>13</sup>C NMR δ 17.7, 18.2, 19.6, 22.0 (ethyl groups), 92.6, 93.0 (4° *meso* C and triply bonded C on porphyrin rings), 97.3 (2 x *meso* C), 97.6 (4 x *meso* C), 106.3 (triply bonded C on phenyl ring), 124.1 (4° phenyl C), 130.9 (phenyl CH), 137.7, 140.1, 140.2, 140.9, 143.0, 143.6, 145.2, 145.6 (porphyrin ring carbons); UV/Vis (CHCl<sub>3</sub>) λ<sub>max</sub> (ε x 10<sup>-3</sup>) 429 (164), 449 (164), 563 (27.6), 596 (38.1) nm; FAB MS m/z 1303, M+1 (<sup>58</sup>Ni<sup>58</sup>Ni).
13. See, for example, Nicolaou, K. C.; Zuccarello, G.; Riemer, C.; Estevez, V. A.; Dai, W.-M. *J. Am. Chem. Soc.* **1992**, *114*, 7360-7371.
14. Bonnett, R.; Champion-Smith, I. H.; Kozyrev, A. N.; Mironov, A. F. *J. Chem. Res. (M)* **1990**, 1015-1043.
15. (a) Minnetian, O. M.; Morris, I. K.; Snow, K. M.; Smith, K. M. *J. Org. Chem.* **1989**, *54*, 5567-5574. (b) Morris, I. K.; Snow, K. M.; Smith, N. W.; Smith, K. M. *J. Org. Chem.* **1990**, *55*, 1231-1236.

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