

Unexpected formation of porphyrinic enyne under Sonogashira conditions

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Abstract—Reaction of 5-iodo-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin with excess trimethylsilylacetylene under Sonogashira conditions gives an unexpected porphyrinic enyne suitable for further transformations. The NMR spectrum and structural analysis of the porphyrin enynes show that the substituent on the acetylene group is positioned above the porphyrin ring. This structural characteristic makes the microenvironment of the porphyrin center in a controllable fashion.

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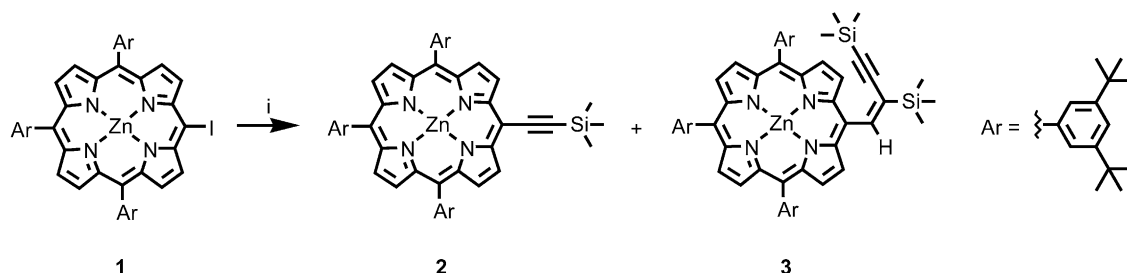
The synthesis of porphyrin-based multichromophoric assemblies continues to attract attention because of their unique photophysical and electrochemical properties.^{1–5} For example, a variety of porphyrin-containing dyads and triads have been synthesized for the studies of electron transfer reactions.¹ Recently, numerous nanometer-sized multiporphyrin assemblies have been prepared for the potential application in electronic and photonic devices.² In these multichromophore systems, a wide variety of spacers such as aryl, vinyl, acetylenic, and alkyl units have been utilized to bridge the chromophores.³ Previous work has shown that acetylenic substituents are the ideal linkers to enable strong interchromophore electronic communication.³ In the course of our studies of the highly conjugated porphyrin systems, we found that the reaction of iodoporphyrin **1** with trimethylsilylacetylene catalyzed by palladium complex and CuI gave porphyrin **2** and the unexpected product **3** (Scheme 1). Similar results were observed when 10,20-diphenyl-5-iodoporphyrin or 10,20-bis(3,5-di-*tert*-butylphenyl)-5-iodoporphyrin was employed as the starting material.

The structure of porphyrin **3** was characterized by various spectroscopic methods.⁶ The mass spectrum shows an intense peak at m/z 1132 ($M+H^+$). The presence of a carbon–carbon triple bond was indicated by IR

absorption at 2119 cm^{-1} . The coupling reaction shows both regio- and stereoselectivity as evidenced by the ^1H NMR spectrum. The downfield shift of the vinylic hydrogen (δ 9.45 ppm) is consistent with its being deshielded by the porphyrin ring current. The peak corresponding to the trimethylsilyl group attached to the acetylene is upfield shifted to -0.61 ppm, indicating that the protecting group is positioned above the porphyrin ring. This is further confirmed by the X-ray crystal structure (Fig. 1). The structure of porphyrin **3** shows that the vinyl plane twists out the porphyrin ring by 48.03° due to the van der Waals strain between the vinyl and β hydrogen atoms. This is larger than the analogous dihedral angle (36.1°) reported by Therien in a *meso*-substituted divinylporphyrin.⁷ The vinylic acetylene is slightly deviated from linearity, with bond angles at C(23) and C(24) of 174.70° and 172.52° , respectively. The bond distances of 1.350 for C(21)–C(22) and 1.204 Å for C(23)–C(24) fall into the normal range of the double and triple bonds, respectively. The three phenyl groups have dihedral angles of 57.92° , 66.18° , and 75.16° with respect to the porphyrin mean plane. The porphyrin framework is nearly planar, as indicated by the fact that the root-mean-square deviation of fitted atoms is 0.080 Å. The Zn^{2+} center is five-coordinated to an axial methanol molecule with a Zn–O(1) distance of 2.112 Å and a Zn–O(1)–C(73) angle of 130.57° . As a consequence of being five-coordinated, the Zn^{2+} ion is pulled out of the porphyrin mean plane by 0.289 Å. There is a solvated methanol molecule hydrogen-bonded to the coordinated methanol with a O(1)–O(2) distance

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Scheme 1. Reagents and conditions: (i) Pd catalyst, CuI, NEt_3 , THF.

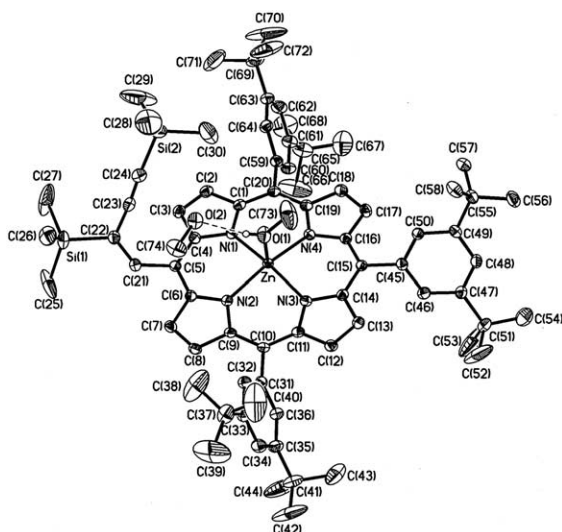


Figure 1. ORTEP drawing of compound **3** drawn at the 50% probability thermal ellipsoids. Hydrogen atoms omitted for clarity.

of 2.653 Å. The solvated methanol shows a short $\text{O}(2) \cdots \pi$ contact of 3.116 Å with the acetylene group.

The self- and cross-coupling reactions of terminal alkynes by various transition metals have been intensively studied.⁸ Generally, the key step of alkyne coupling reactions has been proposed to involve the migration of a σ -bonded metal acetylide to a coordinated alkyne. To gain some insight into the formation of porphyrin **3**, we first examined the coupling reaction between porphyrin **2** and trimethylsilylacetylene. However, the cross-coupling reaction under various conditions did not proceed. In another control experiment, porphyrin **2** was added to the mixture of the coupling reaction between **1** and trimethylsilylacetylene. The yield of porphyrin **3** remains unchanged. Based on these results, the possibility of porphyrin **3** being produced via **2** can be ruled out. We next examined the reaction under various conditions. **Table 1** gives the summary of the coupling reactions. Yields for porphyrin **3** are modest but it is anticipated that improvements can be made in future. In general, the coupling reactions between aryl halides and terminal acetylenes are accomplished by using palladium catalyst and copper cocatalyst. In 1998 Echavarren and co-workers reported that the reactions of aryl halides having a bulky *peri* or *ortho* substituent with terminal acetylenes gave the corresponding arylenyne along with arylalkynes.⁹ They found that the use of

Table 1. Summary for cross-coupling of porphyrin **1** with trimethylsilylacetylene under various conditions

Entry ^a	HCCTMS (equiv)	Pd catalyst (equiv)	Ligand (equiv)	Time (h)	Yield (%) (2 : 3)
1	10	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.36)	—	0.5	55:13
2 ^b	10	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.18)	—	0.5	58:16
3	10	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.05)	—	4.5	21:19
4	10	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10)	—	3.5	28:25
5	10	$\text{Pd}_2(\text{dba})_3$ (0.10)	AsPh_3 (0.8)	0.5	69:0
6	10	$\text{Pd}(\text{PPh}_3)_4$ (0.10)	AsPh_3 (0.4)	4	38:28
7 ^c	10	$\text{Pd}(\text{PPh}_3)_4$ (0.10)	—	22	79:0
8	20	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.36)	—	0.5	62:13
9	30	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10)	—	1.5	28:51
10	30	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10)	AsPh_3 (0.4)	1.5	31:22
11	30	$\text{Pd}(\text{PPh}_3)_4$ (0.10)	AsPh_3 (0.8)	3.5	31:50
12	30	$\text{Pd}(\text{PPh}_3)_4$ (0.10)	AsPh_3 (2.0)	3.5	24:50
13	50	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10)	—	1	38:25
14 ^{d,e}	30	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10)	—	12	15:28
15 ^d	30	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10)	—	24	0:0
16 ^{d,f}	30	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10)	—	24	0:0

^a Unless otherwise indicated, the reactions were carried out at room temperature in THF in the presence of Et_3N , Pd catalyst, and CuI. The ratio of Pd catalyst and CuI was 1:1.

^b The ratio of Pd catalyst and CuI was 1:2.

^c Base = Et_2NH .

^d Ag_2O was used instead of CuI.

^e Temperature = 60 °C.

^f Base = pyrrolidine.

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