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New Heck-Type Reaction Applied to the Synthesis of Protoporphyrin-IX Derivatives

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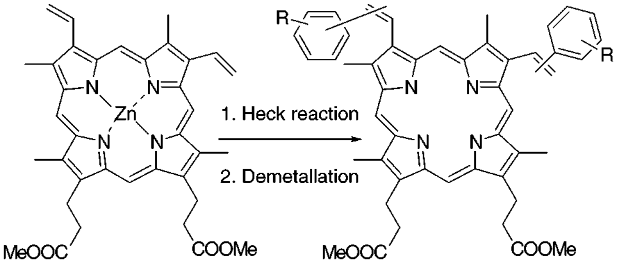
ABSTRACT



A new Heck-type reaction under catalysis by Pd for obtaining polysubstituted arylvinylydene derivatives of porphyrin systems is reported. The coupling between the Zn(II)-protoporphyrin-IX dimethylester Zn-2 and several bromo-aryl and iodo-aryl compounds in the presence of a new Pd catalyst has been studied. This coupling reaction, although providing moderate regioselectivity, gives quantitative conversion.

Porphyrin synthesis offers potential for a large number of research endeavors in organometallic chemistry,[1] biomimetic reactions,[2] photodynamic therapy,[3] and material sciences.[4] Most porphyrins are usually synthesized via routes that generate the macrocycles from monopyrroles, which normally entails low yield and tedious purifications. We prepared new polysubstituted porphyrins using a commercially available porphyrin, hemin **1**. We took advantage of the two vinyl groups of hemin **1**.

Several Heck-type reactions have been reported for the functionalization and linking of porphyrins.[5−12] In most cases these coupling reactions are between the halogenated por-

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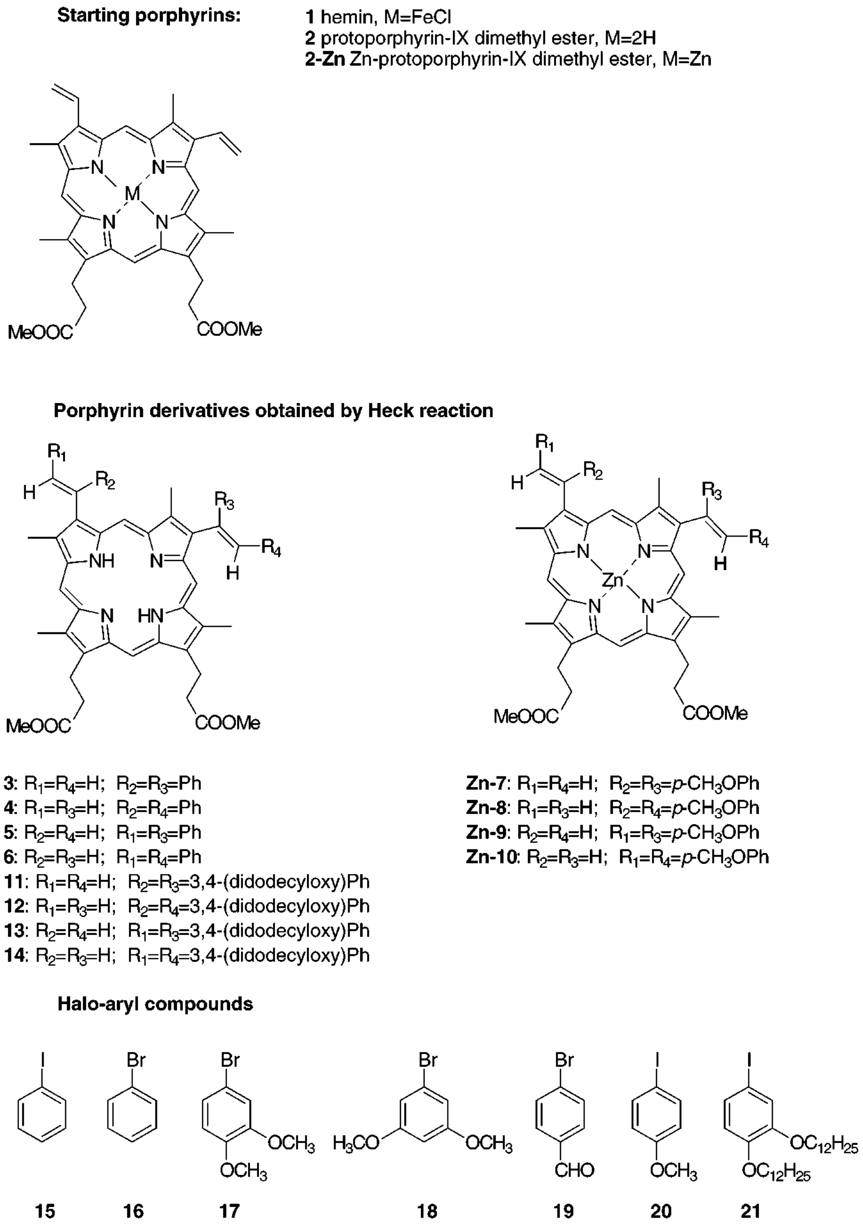
Scheme 1. Porphyrinic Systems and Halo-Aryl Compounds Here Reported



Starting porphyrins:

1 hemin, M=FeCl

2 protoporphyrin-IX dimethyl ester, M=2H

2-Zn Zn-protoporphyrin-IX dimethyl ester, M=Zn

Porphyrin derivatives obtained by Heck reaction

3: $R_1=R_4=H$; $R_2=R_3=Ph$

4: $R_1=R_3=H$; $R_2=R_4=Ph$

5: $R_2=R_4=H$; $R_1=R_3=Ph$

6: $R_2=R_3=H$; $R_1=R_4=Ph$

11: $R_1=R_4=H$; $R_2=R_3=$3,4-(didodecyloxy)Ph

12: $R_1=R_3=H$; $R_2=R_4=$3,4-(didodecyloxy)Ph

13: $R_2=R_4=H$; $R_1=R_3=$3,4-(didodecyloxy)Ph

14: $R_2=R_3=H$; $R_1=R_4=$3,4-(didodecyloxy)Ph

Zn-7: $R_1=R_4=H$; $R_2=R_3=p$-CH_3OPh

Zn-8: $R_1=R_3=H$; $R_2=R_4=p$-CH_3OPh

Zn-9: $R_2=R_4=H$; $R_1=R_3=p$-CH_3OPh

Zn-10: $R_2=R_3=H$; $R_1=R_4=p$-CH_3OPh

Halo-aryl compounds

15 **16** **17** **18** **19** **20** **21**

phyrin, either the iododerivative or the bromoderivative, and an alkene[5,6] or an acetylene[7−9] compound, which may be another porphyrin system.[10]

Normally, palladium(0)-catalyzed coupling has been performed either using phase transfer conditions, working with 5 mol % palladium(II) acetate in DMF and tetra-*n*-butylammomium bromide as the phase transfer agent,[5,6] or in homogeneous conditions, using either $PdCl_2(PPh_3)_2$, CuI in Et_3N,[7−9] or tris(dibenzylideneacetone)-dipalladium(0) ($Pd_2(dba)_3$) and the ligand $AsPh_3$ in the absence of any copper reagent.[10] Moreover, metal-mediated cross-coupling with brominated porphyrins and organic tin and zinc compounds has also been reported.[11] The yields described for these reactions range from 40% to 90%. Furthermore, the reaction between Zn-protoporphyrin-IX dimethylester **Zn-2** and phenylmercuric chloride in the presence of $LiPdCl_3$ produces 2,4-distyryldeuterioporphyrin-IX dimethyl ester **6** in about 60% yield.[12]

Here we present a Heck-type coupling reaction, in the presence of a palladium(II) catalyst, between the porphyrin system with two alkene units (**Zn-2** and **2**) and several halo-aryl derivatives. We examine the best conditions for this coupling and their influence on the yield and the regioselectivity of the halo-aryl compound.

The starting materials used in the study of the Heck-type reaction were the protoporphyrin-IX dimethyl ester **2** and

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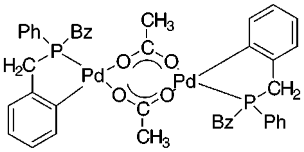
its Zn complex **Zn-2**, which were obtained from hemin **1** in the conditions described[13,14] with a global yield of 85% for **2** and 80% for **Zn-2**.

Reaction between Zn-protoporphyrin-IX dimethylester **Zn-2** and iodobenzene **15** applying the previously published conditions,[7−9] $PdCl_2(PPh_3)_2$, CuI in Et_3N, did not yield the desired final product, although under these conditions bromo- and iodo-porphyrins are described to react with acetylene compounds.

On the other hand, when the Zn-protoporphyrin dimethylester **Zn-2** and phenylmercuric chloride reacted in a preformed solution of $LiPdCl_3$[12] (2:1 molar ratio of $PdCl_2$ to phenylmercuric chloride; 1:2 molar ratio of $PdCl_2$ to LiCl), a mixture of disubstituted **3**, **4**, **5**, and **6** and even trisubstituted porphyrins was obtained as detected by MALDI-TOF mass spectrometry of the crude. This mixture was demetalated by brief treatment with TFA and partially purified by column on silica gel. After the purification we obtained 50% of the desired *anti-anti*-disubstituted porphyrin **6** and 25% of a mixture of disusbtituted porphyrins **3**, **4**, and **5**, which were determined by ^1H NMR spectroscopy. Taking into account these results, it seems that the reaction shows regioselectivity for the *anti-anti*-substitution.

The high toxicity of mercurated compounds and the large amount of catalyst that this method requires prompted us to search for safer conditions to achieve the preparation of polysubstituted arylvinilydene derivatives of porphyrin systems.



Here we describe the coupling reaction between halobenzene compounds with the vinyl groups of the porphyrins **Zn-2** and **2** using the new reported catalyst *syn*-di(μ-acetate)-bis[*o*-(benzylphenylphosphyno)benzyl]dipalladium(II). The synthesis of this catalyst was performed in the following way. To a 0.045 M solution of palladium acetate in toluene was added 1.3 equiv of dibenzylphenylphosphine, and the resulting mixture was stirred for 16 h at 50 °C. Afterward the solution was cooled to room temperature and concentrated. The addition of hexane caused the precipitation of the desired product in 85% yield.[15]

This catalyst has several advantages over other systems mentioned above.[5−10] The amount of catalyst required is much smaller than in other catalytic systems, which makes this reaction cheaper, and it avoids working with highly toxic mercury salts.[12]

We described our studies on the coupling between the porphyrin **Zn-2** and iodobenzene **15**. Factors such as temperature, time, and ratio between iodobenzene **15** and **Zn-2** were considered. Table 1 collects the results obtained in the coupling process. The temperature has a strong effect on the kinetics of the reaction. No coupling reaction took place below 100 °C. It was necessary to increase the temperature and the time of reaction until 120 °C and 72 h, respectively, to obtain an 88% yield of a mixture of disubstituted porphyrins **3**−**6** (entry 5, Table 1). However, MALDI-TOF mass spectrometry of the crude still revealed the presence of unreacted and monosubstituted porphyrins.

Table 1. Experimental Assays for the Coupling Reaction between Zn-Protoporphyrin Dimethylester **Zn-2** and Iodobenzene **15**

entry[a]	*T* (°C)	*t* (h)	**15** (equiv)	conversion[b] (%)	yield (%)	ratio[b] **3:4:5:6**
1	80	72	2.5	0	0	
2	100	24	2.5	15	*c*	
3	120	24	3	40	*c*	
4	120	24	4	70	*c*	
5	120	72	2.5	90	88	1:1:1:2
6	120	24	5	100	55	1:1:1:2

[a] Typical procedure: the porphyrin, the catalyst (0.011 equiv), the haloaryl derivative, and an excess of NaAcO were added into a Schlenk with a refrigerator, which had been previously purged with nitrogen. The system was purged again with N_2 and dissolved with nitrogen-saturated, dry DMF, giving a concentration in porphyrin of 0.018 M. The mixture was stirred and heated for several hours under nitrogen to avoid oxidation of the catalyst. Afterward, the crude was dissolved with CH_2Cl_2, washed three times in water, dried over anhydrous Na_2SO_4, and evaporated. The resulting solid was dissolved again in CH_2Cl_2, and TFA was added. The solution was stirred for 1 h at room temperature and then washed three times in water to eliminate the excess of TFA. The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated. The solid was purified by column either on silica gel or alumina. [b] Determined by ^1H NMR. [c] No separation of the crude was performed, although MALDI-TOF mass spectrometry revealed the mass peak of unreacted, monosubstituted, and disubstituted porphyrins.

Entry 6 (Table 1) shows similar experimental conditions for the coupling reaction. A quantitative conversion of the starting material **Zn-2** was detected giving a mixture of disubstituted porphyrins **3**−**6**. After demetalation of the mixture with TFA, it was purified by column either on silica gel (entry 5, Table 1) or on alumina (entry 6, Table 1). The purification on alumina allowed better separation. Thus, pure porphyrins **3**[16] and **6**[16] were isolated from the inseparable mixture of **4** and **5**, whereas the purificacion on silica gel let us separate only the porphyrin **6** from the mixture of **3**, **4**, and **5**. Although the conversion of the reaction into the disubstituted derivative was estimated as quantitative from the MALDI-TOF analyses, purification on alumina caused a degradation of around 30% of the material (entry 6, Table 1).

The reaction shows low regioselectivity for the *anti-anti* regioisomer, since we found no evidence of *anti-syn* or *syn-syn* products.

These best conditions found for the Heck-type reaction were also assayed for the metal-free porphyrin **2** and for **Zn-2**

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[15] $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ, ppm) 53.6 (s), 45.1 (d, $J = 4.2$ Hz); ^1H NMR ($CDCl_3$, δ, ppm) 2.23 (s, 6H, $\underline{\text{Me}}$); 2.6−3.2 (m, $C\underline{H}_2$, 8H), 6.0−7.7 (m, aromatic, 28H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ, ppm): 24, 5 (s, $\underline{\text{Me}}$), 33.6−37.2 (m, $\underline{C}H_2$), 180 (s,$\underline{C}OO$). Anal. Calcd for $C_{44}H_{42}O_4P_2Pd_2$: C, 58.10; H, 4.65. Found: C, 57.61; H, 4.54. IR (KBr, ν, cm^{-1}): 1559, 1409, 1096, 698.

with other halo-aryl derivatives with different substitution patterns, **15**−**21**.

To simplify the purification procedure, the Heck reaction was also assayed with the metal-free porphyrin **2**. Whereas the reaction using **Zn-2** was quantitatively accomplished (entry 6, Table 1), the use of porphyrin **2**, in the same conditions, gave only 20% conversion (entry 1, Table 2).

Table 2. Coupling Reaction Using Different Halo-Aryl Derivatives

entry[a]	porphyrin	aryl derivative	conversion[b] (%)	yield (%)	ratio[b]
1	**2**	**15**	20	[c]	
2	**Zn-2**	**20**	100	91	4:6:6:7[d]
3	**Zn-2**	**21**	100	49	4:7:7:8[e]

[a] The optimized conditions were used (entry 6, Table 1). [b] Determined by ^1H NMR. [c] No separation of the mixture was performed, although MALDI-TOF mass spectrometry revealed the mass peak of unreacted, monosubstituted and disubstituted porphyrins. [d] Ratio for the products **Zn-7:Zn-8:Zn-9:Zn-10**. [e] Ratio for the products **11:12:13:14**.

The Heck-type reaction also gave poor conversions, between 10 %and 20%, when a bromo-aryl derivative was used. We detected a 20% conversion when we performed the reaction of **Zn-2** with the bromobenzene **16**. Moreover, neither electron-donor groups, **17** or **18**, nor electron-withdrawing groups, **19**, in bromo-aryl derivatives improved the reaction yield.

The reaction between **Zn-2** and the iodo-aryl derivatives **20** and **21** were accomplished with quantitative conversions (entries 2 and 3, Table 2), although the regioselectivity for the *anti-anti* product decreases in both cases

The separation of the mixture of **Zn-10**[17] from **Zn-7**, **Zn-8**, and **Zn-9** was carried out by preparative TLC on silica, and in this case demetalation was not necessary. However, to obtain the isolated **14**,[18] the crude was first demetalated and then purified by preparative TLC on alumina, causing a degradation of approximately 40% of the material, which explains the low yields (entry 3, Table 2).

In summary, we have described a new method for the preparation of substituted arylvinilydene porphyrins from metalated protoporphyin derivatives and iodo-aryl compounds.

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(16) Characterization of **6** is reported in ref 12. Characterization **3**: mp 75−78 °C.; CCPA (Al_2O_3, CH_2Cl_2/hexà (6:4)) $R_f = 0.39$; IR (KBr, ν, cm^{-1}) 3317 (st NH), 2925 (vib asym methyls β), 2856 (vib sym methyls β), 1739 (st CO); ^1H NMR ($CDCl_3$, δ, ppm) 10.19; 10.09; 10.08; 9.96 (4s, H_{meso}, 4H); 7.70 (m, H_o, 4H); 7.36 (m, H_m and H_p, 6H); 6.69; 6.65 (2d, −CPh═$CH_{trans}H_{cis}$, $J_{gem} = 1, 6$ Hz, 2H); 6.03; 5.97 (2d, −CPh═$CH_{trans}H_{cis}$, $J_{gem} = 1, 6$ Hz, 2H); 4.44; 4.40 (2t, −CH_2−CH_2−COO−, $J = 8$ Hz, 4H); 3.68 (s, −$COOCH_3$, 6H); 3.66; 3.54; 3.43; 3.32 (4s, CH_3−ring, 12H); 3.28 (2t, −CH_2−CH_2−COO−, $J = 8$ Hz, 4H); −3.56 (s, −NH, 2H); ^{13}C NMR ($CDCl_3$, δ, ppm) 173.55 (CO); 143.53 (−CPh═CH_2); 142.38 (C_{ar}−porphyrin); 143.00−122.00 ($C_{\alpha,\beta}$); 128.54; 128.50; 127.40 (C_m and C_o); 119.61; 119.50 (−CPh═CH_2); 99.76; 99.03; 97.26; 96.13 (C_{meso}); 51, 71 (−$COOCH_3$); 36.97; 36, 90 (−CH_2−CH_2−COO−); 21.93; 21.86 (−CH_2−CH_2−COO−); 12.48, 12.24; 11.73; 11.48 (CH_3−ring); UV−vis (CH_2Cl_2, λ, nm) 404 (145500), 502 (11900), 536 (8000), 571 (5600), 625 (3600); fluorescence (CH_2Cl_2, $\lambda_{exc} = 400$ nm) λ_{em}(nm) = 627, 694; MS (MALDI-TOF, DHB/THF) M + H, 743.37. Anal. Calcd for $C_{48}H_{46}N_4O_4$: C, 77.60; H, 6.24; N, 7.54. Found: C, 77.35; H, 6.22; N, 7.21.

(17) Characterization of **Zn-10**: mp 272−275 °C; CCPA (SiO_2, CH_2Cl_2/MeOH (100:1.5)) $R_f = 0.26$; IR (KBr, ν, cm^{-1}) 2925 (vib asym methyls β), 2856 (vib sym methyls β), 1739 (st CO); ^1H NMR ($CDCl_3$, δ, ppm) 9.10; 9.05; 8.81; 8.57 (4s, H_{meso}, 4H); 7.87 (m, H_o and −CH═CH−$PhOCH_3$, 6H); 7, 23 (m, −CH═CH−$PhOCH_3$, 2H); 7.15 (m, H_m, 4H); 4.00 (m, −CH_2−CH_2−COO− and Ph−OCH_3, 10H); 3.66 (s, −$COOCH_3$, 6H); 3.40; 3.20; 3, 14 (3s, CH_3−ring, 12H); 3.00 (m, −CH_2−CH_2−COO−, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 173.60 (−CO); 159.50 (C_{ar}−OCH_3); 147.40−132.00 ($C_{\alpha,\beta}$); 146.77 (C_{ar}−porphyrin); 135.74 (−CH═CH−C_6H_4−OCH_3); 127.90 (C_o); 120.08 (−CH═CH−C_6H_4−OCH_3); 114.46 (C_m); 96.79 (C_{meso}); 55.51 (−C_6H_4−OCH_3); 51.65 (−$COOCH_3$); 36.87 (−CH_2−CH_2−$COOCH_3$); 21.65 (−CH_2−CH_2−$COOCH_3$); 12.55; 11.48 (CH_3-ring); UV−vis (CH_2Cl_2, λ, nm) 417 (167200), 547 (17200), 586 (31200); fluorescence (CH_2Cl_2, $\lambda_{exc} = 400$ nm) λ_{em} (nm) = 595, 648; MS (MALDI-TOF, DHB/THF) M − Zn, 803.63. Anal. Calcd for $ZnC_{50}H_{48}N_4O_6$: C, 69.32; H, 5.58; N, 6.47. Found: C, 69.12; H, 5.59; N, 6.38.

(18) Characterization of **14**: mp 83−85 °C; CCPA (Al_2O_3, CH_2Cl_2/hexà (6:4)) $R_f = 0.20$; IR (KBr, ν, cm^{-1}) 3317 (st NH), 2925 (vib asym methyls β), 2856 (vib sym methyls β), 1739 (st CO); ^1H NMR ($CDCl_3$, δ, ppm) 10.30; 10.23; 10.11; 10.05 (4s, H_{meso}, 4H); 8.53; 8.52 (2d, −CH═CH−Ph$(OC_{12}H_{25})_2$), $J_{trans} = 16.5$ Hz, 2H); 7.68; 7.67 (2d, −CH═CH−Ph$(OC_{12}H_{25})_2$), $J_{trans} = 16.5$ Hz, 2H); 7, 50 (m, H_o, 4H); 7.09 (d, H_m, $J_o = 8.4$ Hz, 2H); 4.42 (t, −CH_2−CH_2−COO−, $J = 7.5$ Hz, 4H); 4.25; 4.15 (2t, −OCH_2−, $J = 6.6$ Hz, 8H); 3.79; 3.72 (2s, −$COOCH_3$, 6H); 3.66; 3.65; 3.63 (3s, CH_3−ring, 12H); 3.29 (t, $J = 7.5$ Hz, −CH_2−CH_2−COO−, 4H); 1.95 (q, OCH_2−CH_2−, $J = 6.6$ Hz, 8H); 1.30−1.26 (m, −CH_2−, 72H); 0.88 (2t, −CH_2−CH_3, $J = 6.6$ Hz, 12H); −3.68 (s, −NH, 2H); ^{13}C NMR ($CDCl_3$, δ, ppm) 173.55 (CO); 154.00−126.00 ($C_{\alpha,\beta}$); 149.68 (C_{ar}−$OC_{12}H_{25}$); 135.43 (−CH═CH−Ph$(OC_{12}H_{25})_2$); 131.14 (C_{ar}−porphyrin); 120.20; 120.03 (−CH═CH−Ph$(OC_{12}H_{25})_2$), 114.22; 112.47 (C_o and C_m); 97.84; 96.94; 96.09 (C_{meso}); 69.76; 69.52 (−OCH_2−); 51.71 (−$COOCH_3$); 36.89 (−CH_2−CH_2−COO−); 31, 95 (−O−CH_2−CH_2); 29.70−26.15 (−CH_2−); 22.67 (−CH_2−CH_3); 21.82 (−CH_2−CH_2−COO−); 14.09 (−CH_2−CH_3); 12.96; 11.73 (CH_3−ring); UV−vis (CH_2Cl_2, λ, nm) 409 (175370), 508 (17400), 552 (18400), 582 (12700), 638 (9100); fluorescence (CH_2Cl_2, $\lambda_{exc} = 400$ nm) λ_{em} (nm) = 643, 694; MS (MALDI-TOF, DHB/THF) M, 1480.27. Anal. Calcd for $C_{96}H_{142}N_4O_8$: C, 77.90; H, 9.67; N, 3.78. Found: C, 77.95; H, 9.59; N, 3.88.