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The Synthesis of Dimeric Porphyrins Linked by a Ferrocene

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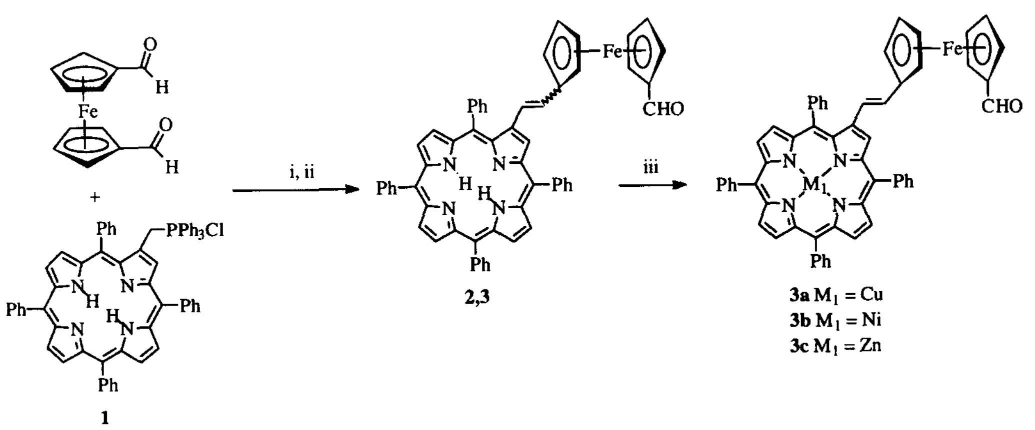
Abstract: The synthesis and characterisation of dimeric porphyrins linked *via* a ferrocene are reported. The porphyrins are prepared using a Wittig reaction of a tetraphenylporphyrin-derived phosphonium salt and 1,1'-diformylferrocene. The reaction can be carried out in a stepwise manner to enable the preparation of heterobimetallic complexes. © 1997, Elsevier Science Ltd. All rights reserved.

The combination of redox-active moieties, such as ferrocene, covalently linked to macrocycles has been of considerable interest for some time. In particular, porphyrin-ferrocene conjugates[1-6] have great potential in such areas as chemical sensors, porphyrin-assisted electron transfer, solar energy conversion, small molecule activation and molecular devices. Also dimeric porphyrins have attracted attention as models for electron transfer[7-10] and in the activation of small molecules[11-12]. We report herein the selective synthesis of dimeric porphyrins that are linked by a conjugated connection to a ferrocene.

Treatment of 1,1'-diformylferrocene with one equivalent of the tetraphenylporphyrin-derived phosphonium salt **1**[13] in the presence of a base results in the formation of a *cis*:*trans* mixture of the ferrocene functionalised compounds **2** and **3**[14] in 70% yield.

Scheme 1 : Synthesis of ferrocene porphyrins conjugates.

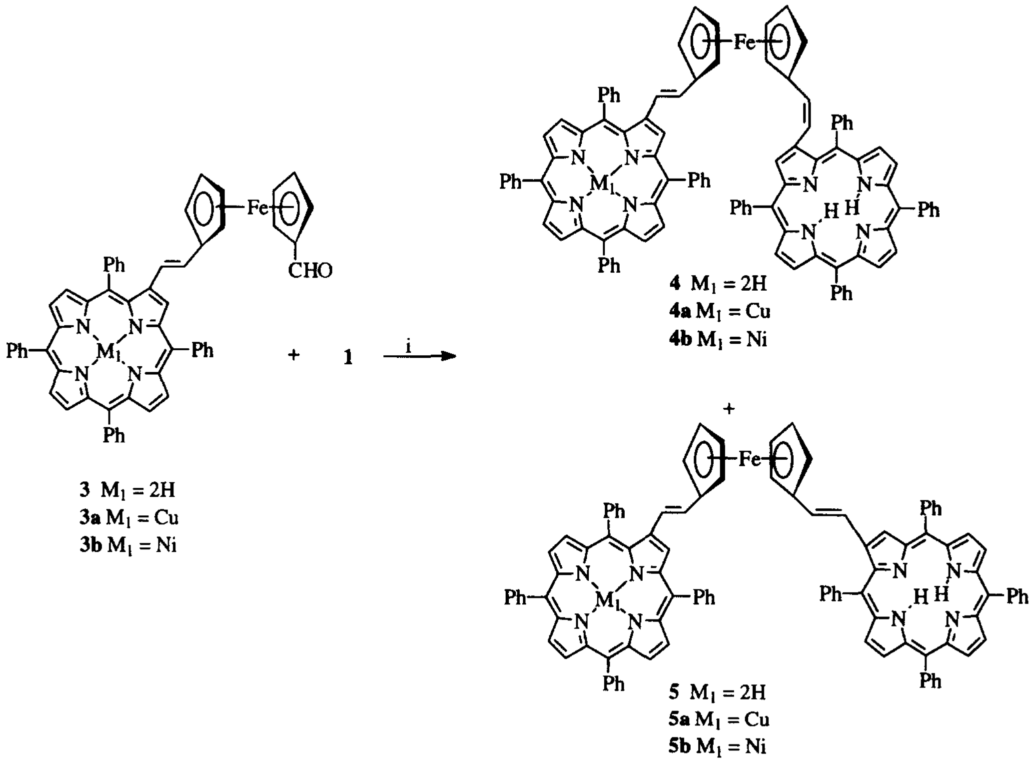


Reagents: i, DBU, CH_2Cl_2, RT; ii, I_2, CH_2Cl_2; iii, $M_1(OAc)_2$, CH_2Cl_2:MeOH, reflux.

The coupling constants for the olefinic protons, in the ^{1}H NMR spectra, enable unambiguous assignment of isomers **2** (*cis* $^3J_{HH}$ = 11 Hz) and **3** (*trans* $^3J_{HH}$ = 16 Hz). The two isomers can be separated by careful chromatography and are obtained as a 5:95 *cis*:*trans* (**2**:**3**) ratio. In practice it is more convenient to treat the *cis*:*trans* mixture with iodine which converts **2** to **3** enabling the isolation of **3** in 68% yield overall. Metallation of the **3** with Zn, Cu, and Ni, can be achieved using standard conditions[15] in near quantitative yields (scheme 1).

Reaction of **3** with a second equivalent of **1** in the presence of a base results in the formation of the dimeric compounds **4** and **5**[14] in 56% yield (Scheme 2). Once again **4** and **5** are isomers, formed in a 20:80 (**4**:**5**) ratio, where the newly formed double bond is either *cis* **4** or *trans* **5**. As before the isomers *cis*:*trans* **4** and *trans*:*trans* **5** can be separated by chromatography.

Scheme 2 : Synthesis of dimeric porphyrins.



Reagents: i, DBU, toluene, reflux.

The ^{1}H NMR of **4** is shown in Figure 1 with the signals for both the *cis* and *trans* olefins apparent as separate resonances[14]. The cyclopentadienyl protons give rise to four signals which is further evidence of the unsymetrical nature of **4**. In contrast to the complex ^1H NMR spectrum produced by **4,** the spectrum obtained for **5** is simple. For example, only two resonances are observed for the protons of cyclopentadienyl rings, as is expected for a symmetrical dimer.

Reaction of **3a** or **b**, with **1** results in the formation of compounds containing both a free base porphyrin and a metalloporphyrin (**4a**, **4b**) without loss of metal or the formation of **4**. The *cis*:*trans* ratios are generally 5:95 and yields range from 50-70%. The free base porphyrin can be metallated using standard conditions. Thus, treatment of **5b** with $Cu(OAc)_2$ results in the formation of the Ni-Cu heterobimetallic complex. Other systems prepared are Cu-Cu, Cu-Zn, Zn-Zn, Zn-Ni, and Ni-Ni. The yields for the insertion of the second metal are essentially quantitative.[15] This selective metallation should enable fine tuning of the properties of the dimeric porphyrins. More extensive investigations of these compounds will be reported elsewhere.

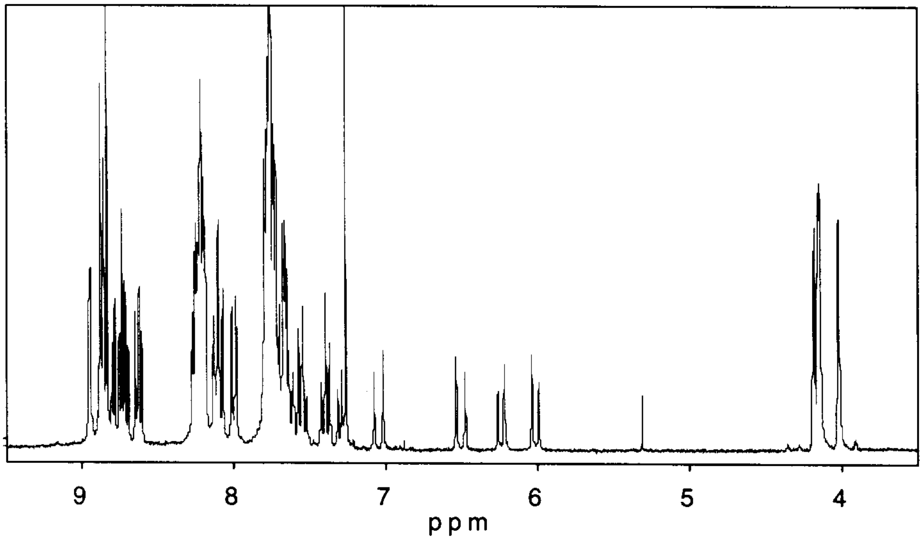


Figure 1. ^1H NMR spectra of **4**.

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References and Notes.

1. Loim, N. M.; Abramova, N. V.; Sokolov, V. I. *Mendeleev Commun.* **1996**, 46-47.
2. Beer, P. D.; Drew, M. G.; Hesek, D.; Jagessar, R. *J. Chem. Soc., Chem. Commun.* 1995, 1187-1189.
3. Beer, P. D.; Kurek, S. S. *J. Organomet Chem.* **1987,** *336*, C17-C21.
4. Beer, P. D.; Kurek, S. S. *J. Organomet. Chem.* **1989,** *366*, C6-C8.
5. Wagner, R. W.; Brown, P. A.; Johnson, T. E.; Lindsey, J. S. *J. Chem. Soc., Chem. Commun.* **1991**, 1463-1466.

6. Sessler, J. L.; Johnson, M. R.; Creager, S. E.; Fettinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1990,** *112*, 9310.
7. Osuka, A.; Kobayashi, F.; Nakajima, S.; Maruyama, K.; Yamazaki, I.; Nishimura, Y. *Chem. Lett.* **1993,** 161-165.
8. Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron Lett.* **1993,** *34*, 693-696.
9. Lin, V. S. Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994,** *264*, 1105-1111.
10. Senge, M. O.; Vincente, M. G. H.; Gerzevske, K. R.; Forsyth, T. P.; Smith, K. M. *Inorg. Chem.* **1994,** *33*, 5625-5638.
11. Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Tabard, A.; Guilard, R.; Seok, W. K.; Ibers, J. A.; L'Her, M. *J. Am. Chem. Soc.* **1992,** *114*, 9869-9877.
12. Collman, J. P.; Herrmann, P. C.; Boitrel, B.; Zhang, X.; Eberspacher, T. A.; Fu, L *J. Am. Chem. Soc.* **1994,** *116*, 9783-9784.
13. Bonfantini, E. E.; Officer, D. L. *Tetrahedron Lett.* **1993,** *34*, 8531-8534.
14. Selected spectroscopic data:

    for **3**, ^{1}H NMR (270 MHz, $CDCl_3$) (ppm) δ = 9.96 (s, 1H, C*H*O), 8.97-8.67 (m, 7H, β-pyrrolics), 8.29-8.20 (m, 8H, Ph*H*), 7.94-7.73 (m, 12H, Ph*H*), 7.00 (d, *J* = 16 Hz, 1H, *trans* C=C*H*–), 6.62 (d, *J* = 16 Hz, 1H, *trans* C=C*H*–),4.80 (d, *J* = 2 Hz, 2H, Cp*H*), 4.62 (d, *J* = 2 Hz, 2H, Cp*H*), 4.34 (d, *J* = 2 Hz, 2H, Cp*H*), 4.40 (d, *J* = 2 Hz, 2H, Cp*H*), -2.60 (br s, 2H, N*H*). UV-Vis : λ_{max} (nm) (ε M^{-1} cm^{-1}) ($CHCl_3$) 655 (2730), 601 (11900), 568 (15500), 524 (23900), 424 (264000). MS(FAB) 853 (MH^+, 100). MSHR calcd. for MH^+ ($C_{57}H_{41}N_4OFe$) : 853.2669 Found : 853.2629.

    for **4**, ^{1}H NMR (270 MHz, $CDCl_3$) (ppm) δ = 8.94-8.60 (m, 14H, β-pyrrolics), 8.27-7.98 (m, 12H, Ph*H*), 7.79-7.32 (m, 28H, Ph*H*), 7.04 (d, *J* = 16 Hz, 1H, *trans* C=C*H*–), 6.50 (d, *J* = 16 Hz, 1H, *trans* C=C*H*–), 6.23 (d, *J* = 11 Hz, 1H, *cis* C=C*H*–), 6.01 (d, *J* = 11 Hz, 1H, *cis* C=C*H*–), 4.18-4.14 (m, 6H, Cp*H*), 4.02 (m, 2H, Cp*H*) -2.63 (br s, 4H, N*H*). UV-Vis : λ_{max} (nm) (ε M^{-1} cm^{-1}) ($CHCl_3$) 605 (24172), 570 (21528), 521 (37098), 423 (408591). MS(FAB) 1464 (MH^+, 100). MSHR calcd. for MH^+ ($C_{102}H_{71}N_8Fe$) : 1463.5151 Found : 1463.5134.

    for **5**, ^{1}H NMR (270 MHz, $CDCl_3$) (ppm) δ = 8.87-8.62 (m, 14H, β-pyrrolics), 8.29-8.13 (m, 14H, Ph*H*), 7.91-7.73 (m, 22H, Ph*H*), 7.49 (d, *J* = 7 Hz, 2H, Ph*H*), 7.23 (t, *J* = 7 Hz, 2H, Ph*H*), 7.18 (d, *J* = 16 Hz, 2H, *trans* C=C*H*–), 6.91 (t, *J* = 7 Hz, 2H, Ph*H*), 6.63 (d, *J* = 16 Hz, 2H, *trans* C=C*H*–), 4.35 (d, *J* = 1 Hz, 4H, Cp*H*), 4.27 (d, *J* = 2 Hz, 4H, Cp*H*), -2.54 (br s, 4H, N*H*). UV-Vis : λ_{max} (nm) (ε M^{-1} cm^{-1}) ($CHCl_3$) 646 (10035), 601 (22954), 519 (42112), 421 (539581). MS(FAB) 1464 (MH^+, 100). MSHR calcd. for MH^+ ($C_{102}H_{71}N_8Fe$) : 1463.5151 Found : 853.2629
15. Smith, K. M. (Ed.) *Porphyrins and Metalloporphyrins*, **1975**, Elsevier, Amsterdam.

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