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Synthesis, spectroscopy and metallation of mixed carbaporphyrinoid systems†

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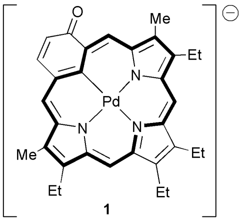
Modified tripyrranes incorporating furan and thiophene rings were found to condense with benzene, pyridine and indene dialdehydes to give a series of novel porphyrin analogues, including thia- and oxa-carbaporphyrins; the latter readily forms nickel(II) and palladium(II) organometallic complexes.

N-confused porphyrins have been shown to form diverse organometallic complexes[1,2] but until recently the coordination chemistry of closely related carbaporphyrinoid systems had not been explored.[3] Carbaporphyrinoids, porphyrin analogues where one or more of the pyrrole units are replaced by carbocyclic rings, clearly have great potential for generating organometallic derivatives[4,5] but it has only been very recently that this expectation has been demonstrated. Specifically, oxybenziporphyrin affords palladium(II) complexes **1**,[6] azuliporphyrins give nickel(II) and palladium(II) derivatives **2**,[7] benziporphyrin gives palladium(II) and platinum(II) chelates,[8] and true carbaporphyrins are easily converted to silver(III) derivatives **3**.[9] In addition, diphenyloxaoxybenziporphyrin has been shown to give a palladium(II) complex **4**.[10] This latter study shows that a CNON coordination core can effectly produce metallo-derivatives. The appearance of this paper prompts us to report our studies on a much more extensive suite of porphyrinoid macrocycles that are easily formed by the MacDonald '3 + 1' methodology.[11]



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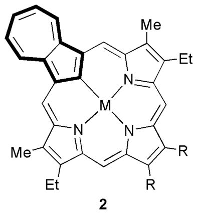

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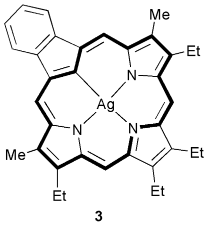
a. M = Ni; b. M = Pd



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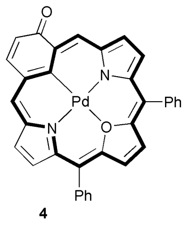

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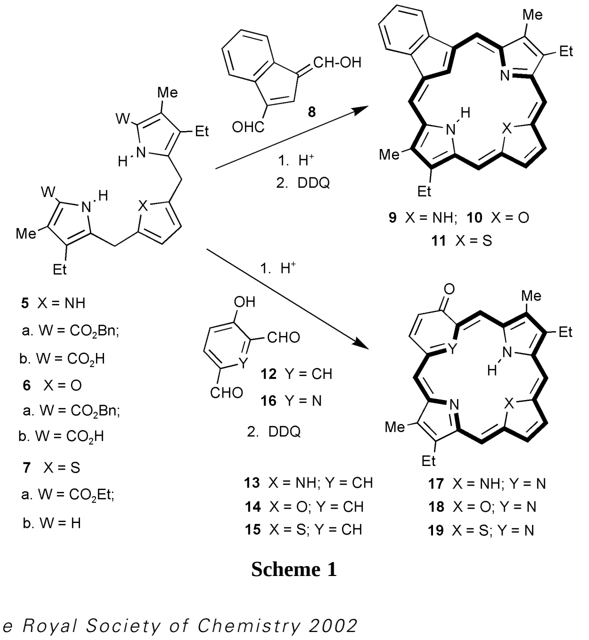
Porphyrin analogues can be conveniently synthesized from tripyrranes such as **5** and dialdehydes.[11] Modified tripyrranes with central furan and thiophene rings, **6a** and **7a**, were prepared by adaptation of literature methods[12] and the analogous tripyrrolic structure **5a** was generated to allow the synthesis of a matched set of porphyrinoid macrocycles (in our previous studies the central pyrrole ring was substituted). Deprotection of the benzyl esters **5a** and **6a** with hydrogen over Pd/C gave the related carboxylic acids **5b** and **6b**, respectively (Scheme 1). Diethyl ester **7a** was treated with TFA at 50 °C to give the α-unsubstituted tripyrrane **7b**. Condensation of **5b**, **6b** and **7b** with diformylindene **8** in the presence of TFA in dichloromethane, followed by oxidation with DDQ, gave the new carbaporphyrins **9–11** in 54, 41 and 31% yields, respectively. Similarly **5b**, **6b** and **7b** reacted with 5-formylsalicylaldehyde (**12**) to give oxybenziporphyrins **13–15** (38, 50 and 15% isolated yields, respectively), while 3-hydroxy-2,6-pyridinedicarbaldehyde (**16**) afforded oxypyriporphyrins **17–19** in 31, 40 and 10% yield, respectively. All of the new macrocycles were thoroughly characterized by ^{1}H and ^{13}C NMR, UV-vis spectroscopy and mass spectrometry. All nine of the porphyrin analogues gave UV-vis spectra with strong Soret bands and exhibited powerful diatropic ring currents in their proton NMR spectra. These properties are exemplified for oxa- and thia-carbaporphyrins **10** and **11**.‡ For **10**, the free base in 5% Et_3N–$CHCl_3$ shows a Soret band at 428 nm, while **11** shows the equivalent band at 431 nm. The oxacarbaporphyrin **10** was isolated as a monocation hydrochloride salt.[13] The proton NMR spectrum for **10**.HCl showed the internal CH at −6.45 ppm and the NHs at −1.5 ppm, while the external *meso*-protons gave rise to two 2H singlets at 10.1 and 10.3 ppm. The upfield region for the proton NMR spectrum for **11** in TFA–$CDCl_3$ showed a 1H singlet at −7.45 ppm for the internal CH and a broad 2H singlet at −5.86 ppm. The *meso*-protons again shifted downfield and gave two 2H singlets at 10.2 and 10.7 ppm.

Oxacarbaporphyrinoids **10** and **14** were considered to be the most promising candidates for metallation studies (**17–19** do not possess an internal carbon and consequently were of lesser interest). Reaction of **10** with nickel(II) or palladium(II) acetate in refluxing DMF gave a 53% isolated yield of the corresponding nickel(II) complex **20a** and 70% yield of the palladium(II) derivative **20b**.‡ However, oxaoxybenziporphyrin **14** failed to react under these conditions. It should be noted, however, that Chandrashekar and coworkers have been able to prepare a related palladium chelate **4** at elevated temperatures (refluxing



Scheme 1

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† Part 24 of the series 'Conjugated Macrocycles Related to the Porphyrins'. Part 23: D. A. Colby and T. D. Lash, *Chem. Eur. J.*, 2002, in press.

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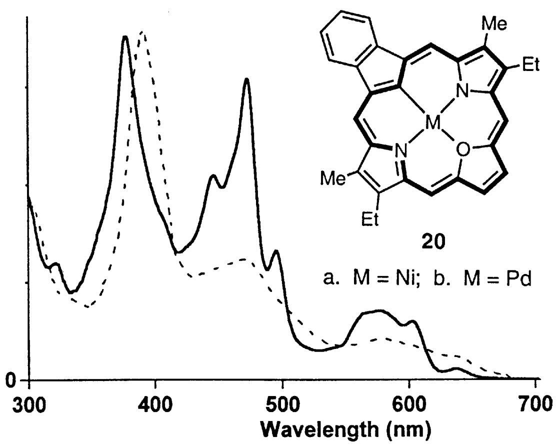

Fig. 1 UV-vis spectra of nickel(II) chelate **20a** (1.07×10^{-5} M; dotted line) and palladium(II) derivative **20b** (1.20×10^{-5} M; bold line) in chloroform.

benzonitrile).[10] Oxacarbaporphyrin derivatives **20a** and **20b**, which are formed under relatively mild conditions, were characterized by spectroscopic methods and mass spectrometry.‡ Both of these metallo-derivatives showed the disappearance of the upfield resonances but otherwise retained their aromatic characteristics as judged by the deshielding for the external protons. In nickel(II) complex **20a**, the *meso*-protons were observed at 9.74 and 9.86 ppm and the external furan gave a 2H resonance at 9.38 ppm. The equivalent signals for **20b** appeared at 9.88, 10.02 and 9.49 ppm, indicating that the palladium complex has a slightly larger diatropic ring current than the nickel(II) derivative. The uv-vis spectra for **20a** and **20b** were quite different from one another (Fig. 1), as was the case for nickel(II) and palladium(II) azuliporphyrins **2**.[7]

In conclusion, mixed macrocyclic systems consisting of different combinations of furan, thiophene and pyrrole, together with benzene, pyridine or indene rings, are easily prepared by the '3 + 1' methodology. These systems all retain porphyrin-like aromaticity, and the CNON cavity of the oxacarbaporphyrin system is shown to be particularly well suited for the synthesis of novel organometallic derivatives. Further studies are in progress to explore the metallation of these novel ligand systems.

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Notes and references

‡ *Selected spectroscopic data*: **10**·HCl: mp > 300 °C; UV-vis (5% Et_3N–$CHCl_3$; free base): λ_{max} ($\log_{10}\varepsilon$) 371 (4.65), 428 (4.85), 521 (4.15), 619 (3.81), 677 (3.40), 709 (3.16); UV-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 391 (4.79), 426 (4.70), 441 (4.70), 484 (4.47), 606 (4.01), 671 (3.19); ^1H NMR ($CDCl_3$): δ −6.45 (1H, s), −1.53 (2H, br s), 1.79 (6H, t, *J* 7.2 Hz), 3.56 (6H, s), 4.00 (4H, q, *J* 7.2 Hz), 7.63 (2H, m), 8.58 (2H, m), 9.78 (2H, s), 10.08 (2H, s), 10.32 (2H, s); ^{13}C NMR ($CDCl_3$): δ 11.8, 17.1, 19.9, 94.9, 105.1, 122.0, 128.8, 129.1, 129.6, 135.5, 137.0, 140.1, 140.6, 140.9, 142.6, 153.2; HRMS: calc. for $C_{31}H_{28}N_2O$: *m/z* 444.2202. Found: 444.2206. **11**: mp > 300 °C; UV-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 387 (4.60), 431 (4.89), 527 (4.14), 623 (3.80), 683 (3.22); UV-vis (0.01% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 428 (4.86), 617 (4.09), 667 (3.50); ^1H NMR (TFA–$CDCl_3$): δ −7.45 (1H, s), −5.86 (2H, br s), 1.81 (6H, t, *J* 7.6 Hz), 3.55 (6H, s), 4.02 (4H, q, *J* 7.6 Hz), 7.82 (2H, m), 8.72 (2H, m), 10.10 (2H, s), 10.21 (2H, s), 10.71 (2H, s); ^{13}C NMR ($CDCl_3$): δ 11.6, 17.0, 20.1, 105.0, 108.1, 122.1, 129.7, 135.8, 137.2, 138.5, 141.1, 141.4, 141.5, 144.8; EI HRMS: calc. for $C_{31}H_{28}N_2S$: *m/z* 460.1973. Found: 460.1967. **20a**: UV-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 392 (4.87), 470 (4.41), 580 nm (3.94); ^1H NMR ($CDCl_3$): δ 1.73 (6H, t), 3.41 (6H, s), 3.83 (4H, q), 7.46–7.48 (2H, m), 8.48–8.50 (2H, m), 9.38 (2H, s), 9.74 (2H, s), 9.86 (2H, s); HRMS: calc. for $C_{31}H_{26}N_2NiO$: *m/z* 500.1399. Found: 500.1405. **20b**: UV-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 322 (4.30), 378 (4.77), 447 (4.54), 473 (4.71), 496 (4.34), 576 (4.07), 603 (4.00), 639 nm (3.28); ^1H NMR ($CDCl_3$): δ 1.79 (6H, t), 3.49 (6H, s), 3.92 (4H, q), 7.51–7.53 (2H, m), 8.54–8.56 (2H, m), 9.49 (2H, s), 9.88 (2H, s), 10.02 (2H, s); HRMS: calc. for $C_{31}H_{26}N_2OPd$: *m/z* 548.1080. Found: 548.1074.

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13 The increased basicity of the furan-containing macrocycles **10**, **14** and **18** prevented the isolation of the free bases for these systems. However, the free bases appear to be reasonably stable in 5% Et_3N–$CHCl_3$ solutions.