The Heck reaction for porphyrin functionalisation: synthesis of *meso*-alkenyl monoporphyrins and palladium-catalysed formation of unprecedented *meso*–β ethene-linked diporphyrins

Oliver B. Locos and Dennis P. Arnold*

Received 1st December 2005, Accepted 22nd December 2005
First published as an Advance Article on the web 25th January 2006
DOI: 10.1039/b516989e

Palladium-catalysed coupling of the vinyl derivatives methyl acrylate, styrene and acrylonitrile with 5-bromo-10,15,20-triphenylporphyrin (MTriPPBr; M = 2H, Ni, Zn) and 5,15-dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin ($MDAPBr_2$) produced a series of mono- and disubstituted alkenylporphyrins, thus demonstrating the applicability of *meso*-haloporphyrins in Heck-type reactions. The same technique was also applied to *meso*-ethenylporphyrins and simple aryl halides, with mixed results. Only *meso*-vinyl nickel(II) porphyrins showed any reactivity under our conditions. A mixture of 1,1- and 1,2-disubstitution across the alkene was observed for 5-vinyl-10,15,20-triphenylporphyrinatonickel(II) (*meso*-vinylNiTriPP), whereas 5-vinyl-10,20-bis(3,5-di-*t*-butylphenyl)porphyrinatonickel(II) (*meso*-vinylNiDAP) produced a mixture of *meso*-1,1-, *meso*-1,2- and, surprisingly, β-1,2-disubstituted Heck products. Coupling *meso*-vinylNiDAP with MTriPPBr under similar Heck conditions led unexpectedly to *trans* β-*meso*-NiDAP-ethene-MTriPP dyads, affording the first members of a new class of alkenyl-linked diporphyrins. A mechanism for the unusual *meso* to β rearrangement is discussed. The electronic absorption spectra of the dyads have a red-shifted shoulder on the Soret (B) band, which is evidence of a moderate degree of electronic interaction between the porphyrins *via* the ethenyl bridge.

Introduction

The construction of novel porphyrins by palladium-catalysed couplings to the periphery of the macrocycle is a topic of considerable interest in the recent literature.[1] Most of the popular types of C–C couplings have been reported, such as aryl, vinyl and alkynyl organometallics, boronates and boronic acids, and terminal alkynes. However, apart from the use of the vinyl organometallics,[2–5] the coupling of alkenes directly to the porphyrin nucleus by Pd-catalysed methodologies has been rather restricted in scope. Smith and co-workers reported the first such reactions, using β-mercurioporphyrins and alkenes, and in one case, the β-vinylporphyrin plus phenylmercuric chloride.[6,7] Others have used β-bromoporphyrins of the natural substitution pattern in Heck couplings, including for the synthesis of dyads and triads linked by β-attached ethenyl–phenyl–ethenyl bridges,[8] and Odobel and co-workers have prepared dyads linked by *meso*-attached ethenyl–$(thienyl)_n$–ethenyl bridges using Heck-type coupling.[9]

Alkenyl-substituted porphyrins have been prepared by other means as well, for example, by vinylogous Vilsmeier substitution,[10] Wittig alkenation of formylporphyrins,[11–13] or dehydration of carbinols.[14] Burrell and Officer have linked tetraarylporphyrins through β-carbons *via* a variety of alkene-containing bridges using the Wittig reaction.[15] These reactions have mostly involved octaalkyl- or 5,10,15,20-tetraarylporphyrins as substrates. However, for the new generation of porphyrin substrates, the 5,15-diaryl (or alkyl)- and 5,10,15-triaryl (or alkyl)porphyrins, the *meso*-bromo derivatives are the ideal starting materials, as they can be formed in high yields and purities.[2] Alkenes that usually perform well in this type of coupling, namely α,β-unsaturated esters, nitriles, *etc.*, have the potential for further functional group interconversion, conjugation to biomolecules, or external coordination to metal ions or other metalloporphyrins. In addition, *vinylporphyrins* are possible Heck-type alkenes themselves, and they have been used to a very limited extent in this manner.[16,17] Moreover, by combining a vinylporphyrin with a bromoporphyrin, a novel entry into ethene-bridged bis- or oligoporphyrins may be possible. The unencumbered edges of the 5,15-diarylporphyrins would appear to offer the best chance of strong ground state interporphyrin coupling when linked *via* ethenyl bridges, in contrast to the sterically crowded octaalkylporphyrin building blocks.[18] The *trans*- and *cis*-*meso*,*meso*-bis(octaalkylporphyrinyl)ethenes have been studied rather extensively,[19] while the corresponding *meso*,*meso*-bis(5,15-diarylporphyrinyl)ethenes surprisingly are almost unknown.[3] Very recently, Anderson and co-workers have reported the crystal structure, electrochemistry and electronic spectral properties of the dizinc complex of a *meso*,*meso*-bis(5,10,15-triarylporphyrinyl)ethene, prepared by the CsF–CuI variation of the Stille coupling.[20] Odobel's group reported bis(5,10,15-triarylporphyrin)s linked by the octatetraenenyl unit, prepared by a combination of Stille and Wittig chemistry.[5]

We have now investigated the direct coupling of some typical Heck-type alkenes (methyl acrylate, styrene and acrylonitrile) with *meso*-bromoporphyrins. Palladium-catalysed couplings on porphyrins often behave differently depending on whether, and with which metal ion, the porphyrin is coordinated. Therefore,

Synthesis and Molecular Recognition Program, School of Physical and Chemical Sciences, Queensland University of Technology, G.P.O. Box 2434, Brisbane 40001, Australia. E-mail: d.arnold@qut.edu.au; Fax: 61 7 3864 1804; Tel: 61 7 3864 2482

 This journal is © The Royal Society of Chemistry 2006

each reaction was studied for three substrates: the free base porphyrin, the Ni(II) complex, and the Zn(II) complex. Both mono- and dibromo substrates were used as starting materials. Then we attempted to use the *meso*-vinylporphyrin as the alkene partner, in pursuit of the goals mentioned above. Here we report the successful use of the Heck reaction for preparing a range of mono- and bis(alkenyl) monoporphyrins, and the lack of success in applying the same chemistry to the formation of *meso*,*meso*-bis(arylporphyrinyl)ethenes. However, as is often the case with porphyrin chemistry, we discovered a very intriguing rearrangement reaction, and this serendipitously afforded entry into a new type of porphyrin dyad, namely *trans-meso*,β-bis(porphyrinyl)ethenes. In subsequent papers, we will report our success in applying the Suzuki coupling to obtain the original target *meso*,*meso*-bis(porphyrinyl)ethenes, together with molecular modelling and theoretical calculations of electronic spectra.[21]

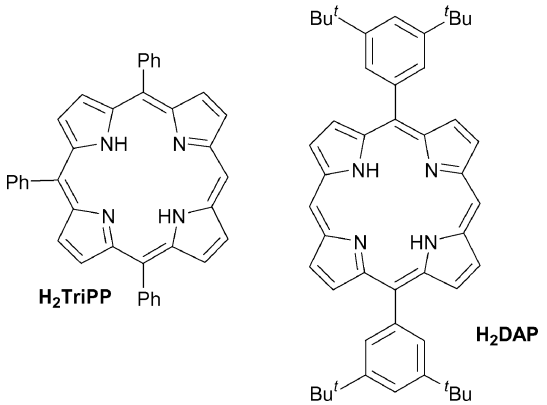


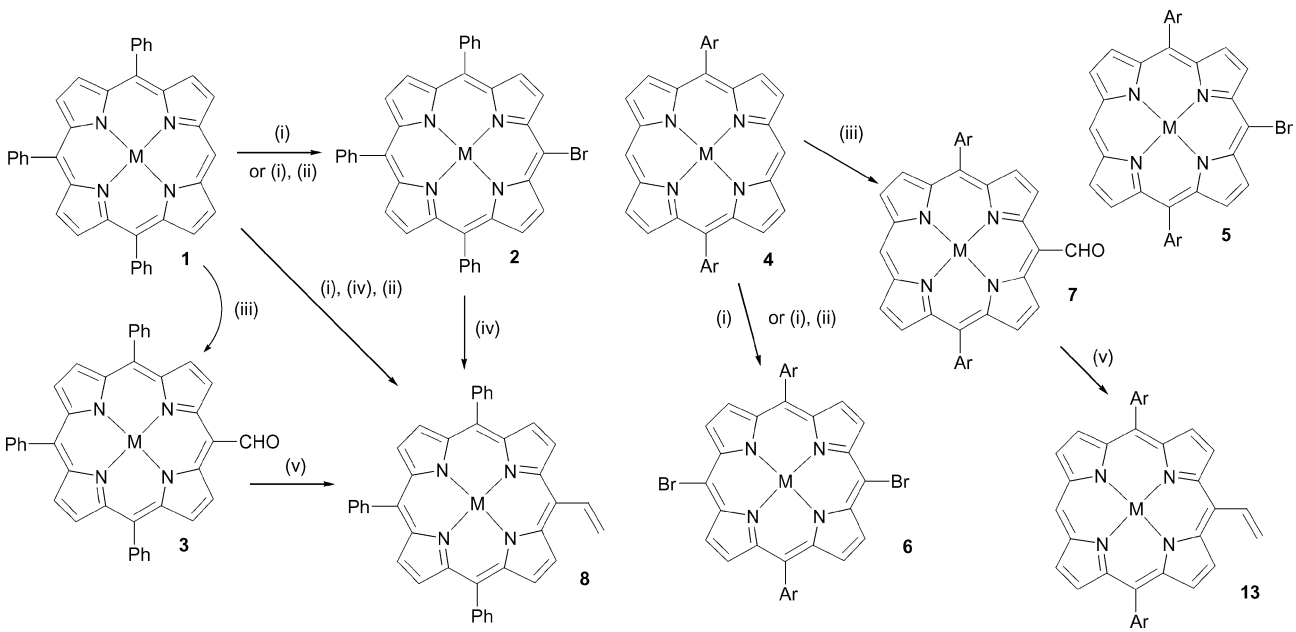
Fig. 1 Structures of the parent porphyrin nuclei 5,10,15-triphenylporphyrin (H_2TriPP) and 5,15-bis(di-*t*-butylphenyl)porphyrin (H_2DAPP).

Results and discussion

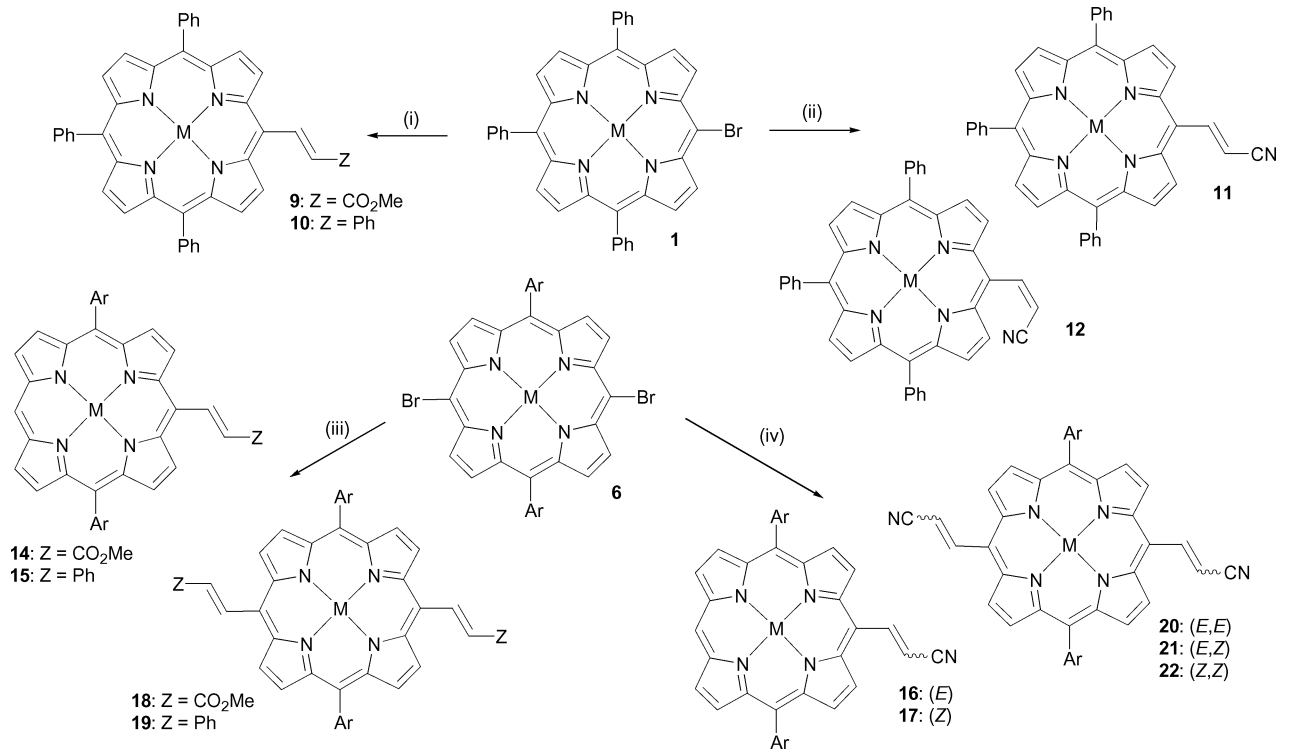
In this work, we used two porphyrins as scaffolds, 5,10,15-triphenylporphyrin (H_2TriPP, **$H_2$1**) and 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (H_2DAP, **$H_2$4**) (Fig. 1). The former, which we have used for selective mono-couplings, has advantages over the commonly used diphenylporphyrin. Its derivatives are much more soluble in common solvents and it has only one free *meso*-carbon. Bromination and other reactions that functionalise the *meso*-positions of porphyrins therefore give high yields of only one product, and the third phenyl group effectively blocks any adventitious processes during the coupling reactions. We employed the latter starting porphyrin for double couplings and also as a second porphyrin to demonstrate the use of Pd-catalysed coupling for the selective preparation of *heteronuclear* dyads.

Known bromination reactions with NBS produced the bromoporphyrins **$H_2$2** and **$H_2$6** in high yield (Scheme 1).[2] The bromination of **$H_2$4** to afford high yields of monobromo **$H_2$5** is made tedious by the lack of selectivity in the bromination and by the difficulty of chromatographic separation of **$H_2$4**, **$H_2$5** and **$H_2$6** on a large scale. We published a way around this problem using organopalladium porphyrins.[22] In the present work, we avoided the use of **$H_2$5** by making the vinyl starting material by the alternative route of Vilsmeier formylation and Wittig alkenation (see below). The nickel(II) and zinc(II) ions were inserted into the bromo starting materials by conventional reactions to yield **Ni2**, **Zn2**, **Ni6** and **Zn6**, thus allowing us to prepare the trio of coupling products for each alkene.

The Pd-catalysed coupling of large excesses of methyl acrylate, styrene and acrylonitrile with monobromoporphyrins **$H_2$2**, **Ni2** and **Zn2** proceeded successfully (Scheme 2). The palladium



Scheme 1 *Reagents and conditions*: (i) **$H_2$1** or **$H_2$4**, NBS, $CHCl_3$, 0 °C (**$H_2$2**: 98%; **$H_2$6**: 95%); (ii) **$H_2$1**, **$H_2$2**, **$H_2$4**, **$H_2$6** or **$H_2$8**, Ni(acac)$_2$, toluene, reflux (**Ni1**: 97%; **Ni2**: 98%; **Ni4**: 98%; **Ni6**: 99%; **Ni8**: 99%); **$H_2$2**, **$H_2$6** or **$H_2$8**, Zn(OAc)$_2$, $CHCl_3$, MeOH, reflux (**Zn2**: 90%; **Zn6**: 92%; **Zn8**: 91%); (iii) **Ni1** or **Ni4**, DMF, $POCl_3$, 1,2-DCE, 50 °C (**Ni3**: 71%; **Ni7**: 73%); (iv) **$H_2$2**, $CH_2CHSnBu_3$, $Pd_2(dba)_3$, $AsPh_3$, THF, 50 °C (**$H_2$8**: 88%); (v) **Ni3** or **Ni7**, CH_2PPh_3, THF, rt (**Ni8**: 65%; **Ni13**: 65%).



Scheme 2 *Reagents and conditions*: (i) **1**, methyl acrylate or styrene (50 eq.), $Pd(OAc)_2$, ligand, K_2CO_3, DMF, toluene, 105 °C (75–87%); (ii) **1**, acrylonitrile (50 eq.), $Pd(OAc)_2$, ligand, K_2CO_3, DMF, toluene, 105 °C (**11**, **12**: 78–85%); (iii) **6**, methyl acrylate or styrene (50 eq.), $Pd(OAc)_2$, ligand, K_2CO_3, DMF, toluene, 105 °C (**14** or **15**: *ca* 5%; **18** or **19**: *ca.* 70%); (iv) **6**, acrylonitrile (50 eq.), $Pd(OAc)_2$, ligand, K_2CO_3, DMF, toluene, 105 °C (**Ni20**, **Ni21**, **Ni22**: 75%; **Zn20**, **Zn21**, **Zn22**: 64%).

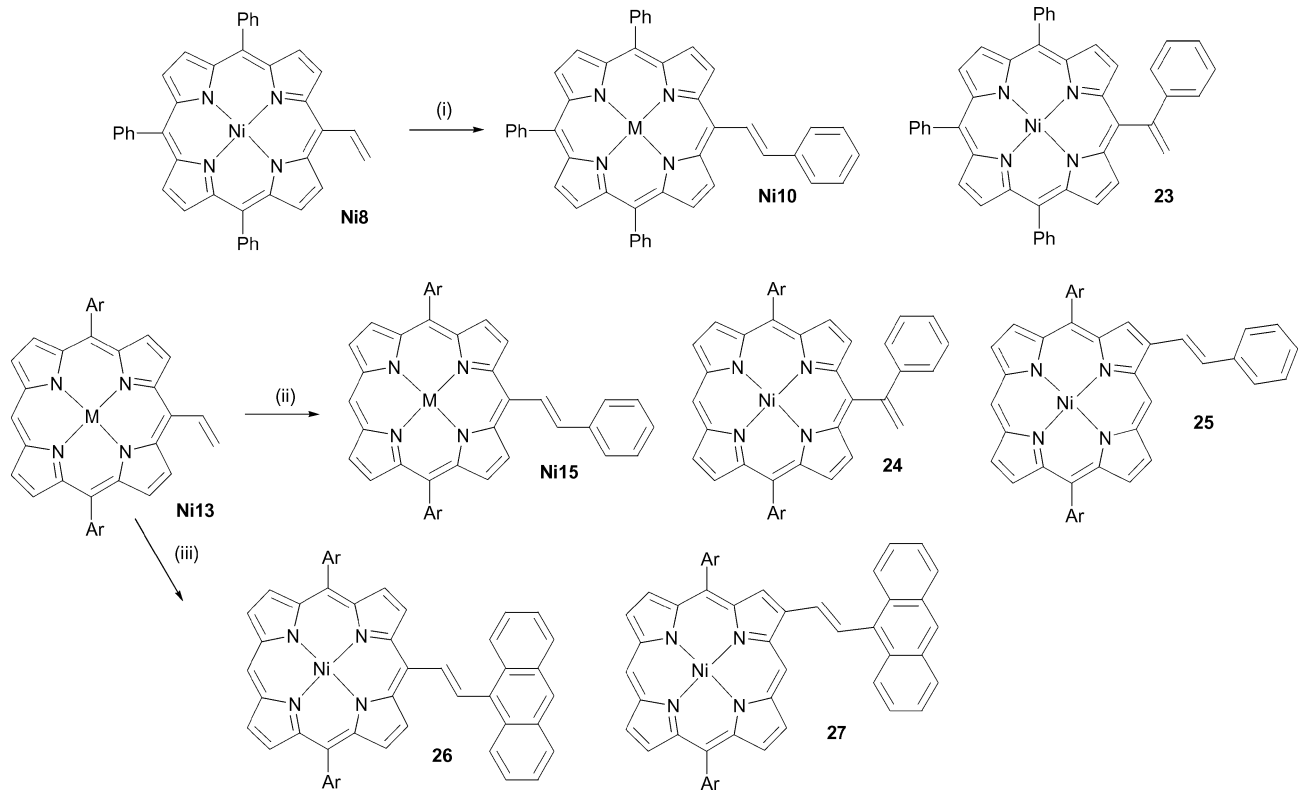
catalysts were prepared *in situ* by using $Pd(OAc)_2$ and a phosphine ligand. The conditions for these reactions were those optimised for the preparation of the porphyrin dyads to be described below, although extensive optimisation was not carried out separately for these alkene + bromoporphyrin reactions, as the yields in almost all cases were satisfactory. The main reaction competing with the Heck coupling was debromination of the starting material through adventitious protolytic cleavage and, in the case of the free-base porphyrins, metallation of the central core with palladium sometimes occurred to a small extent. Zinc porphyrins suffered from a small amount of demetallation and transmetallation (~5%). Initially these coupling reactions were carried out in dry, deoxygenated DMF, however, the solubility of the dibromoporphyrins proved to be extremely limited, even at high temperatures. The solvent was subsequently changed to a 50 : 50 mixture of DMF and toluene, which allowed the reactions to be carried out in conveniently small volumes of solvent, without appreciably affecting the yield of the desired product.

In all cases with methyl acrylate and styrene, the *trans*-alkenylporphyrins were isolated, but for acrylonitrile, the *cis* isomer also formed. This is presumably due to the small steric demand of the cyano substituent in comparison to the ester or phenyl group of methyl acrylate and styrene. Moreover, the ratio of the two isomers is somewhat dependent on the nature of the coordinated metal ion. The ratio *cis* : *trans* decreased in the order H_2 > Ni > Zn, within the triphenylporphyrin series.

The dibromo DAP substrates **$H_2$6**, **Ni6** and **Zn6** were subjected to the coupling with excess alkenes to form the corresponding bis(alkenyl) products (Scheme 2). All were successful, except the reaction of **$H_2$6** with acrylonitrile, which led to a low yield of the completely debrominated **$H_2$4**, and the formation of intractable material that was not eluted from the column even with polar solvents. Yields for the other reactions were consistently 60–70%. Small amounts of the mono(alkenyl) debrominated compounds **14–17** were also apparent, and were readily separated from the bis(alkenes) and identified by NMR spectroscopy. Once again, acrylonitrile also afforded the *cis* products, leading to inseparable mixtures of **20**, **21**, and **22** for the nickel analogues and **20** and **21** for the zinc analogues. In all these cases, the products were characterised by their ^{1}H NMR, accurate mass, and electronic absorption spectra, and in most cases by CHN analysis. The alkenyl substituent was represented by a pair of doublets with coupling constants near 16 Hz for *trans* isomers and 12 Hz for *cis* isomers. There were no unexpected features amongst these spectra.

Having shown initially that the Heck reaction works well for the above processes, we turned to the original aim of seeing if the *meso*-vinylporphyrin could be used as a "Heck alkene". Two alkenyl porphyrins were used, vinyl-NiTriPP (**Ni8**) and vinyl-NiDAP (**Ni13**) (Scheme 3). *meso*-Vinyl-substituted porphyrins have previously been prepared by three methods, dehydration of the methyl carbinol,[14] Wittig methylenation of the *meso*-formylporphyrin,[11,12] and more recently, by the Pd-catalysed Stille coupling of vinyltri(*n*-butyl)stannane with *meso*-haloporphyrins.[2,4] In this work, we tried the last two methods. As the Vilsmeier formylation is unsuitable for free bases and zinc complexes, **$H_2$8** was prepared using the Stille reaction and zinc was inserted to form **Zn8**, both in high

 This journal is © The Royal Society of Chemistry 2006



Scheme 3 *Reagents and conditions*: (i) iodobenzene, $Pd(OAc)_2$, triphenylphosphine, K_2CO_3, DMF, toluene, 105 °C (**Ni10**: 54%; **23**: 20%); (ii) iodobenzene, $Pd(OAc)_2$, triphenylphosphine, K_2CO_3, DMF, toluene, 105 °C (**Ni15**, **24**, **25** mixture: 68%); (iii) 9-bromoanthracene, $Pd(OAc)_2$, 2-P(*t*-Bu)$_2$biphenyl, K_2CO_3, DMF, toluene, 105 °C (**26** contaminated with **27** and other impurities, *ca.* 10%).

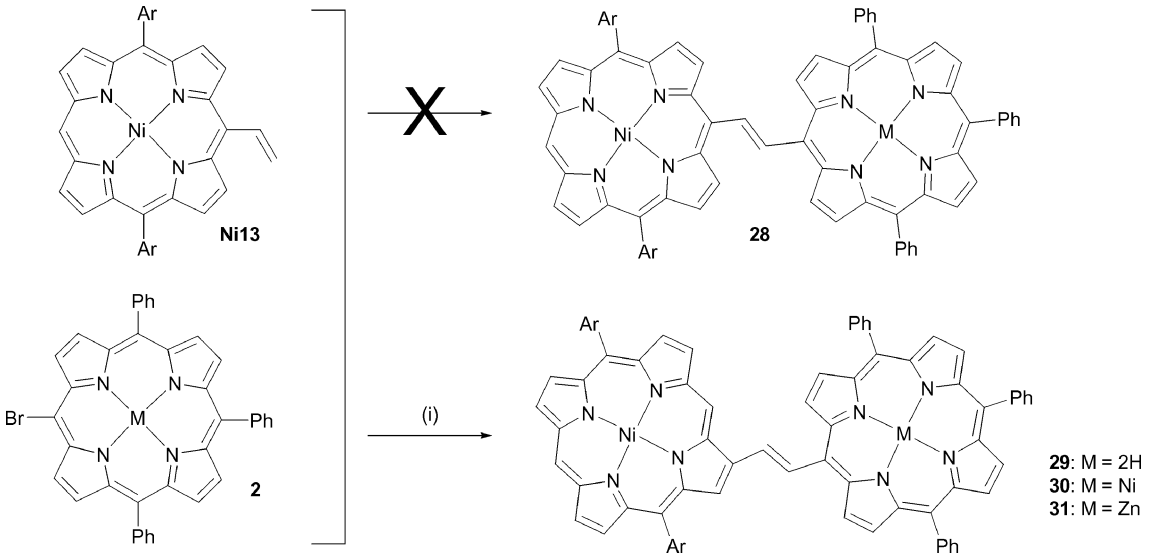
yield. The nickel analogue **Ni8** was obtained by both methods, *i.e.*, insertion of Ni(II) into **$H_2$8** and Wittig reaction with the Vilsmeier product **Ni3**. The former route gave a higher overall yield. The DAP analogue **Ni13** was prepared exclusively by the latter route *via* **Ni7** (Scheme 1).

The coupling of **Ni8** with a large excess of iodobenzene under catalytic conditions similar to those described above, led to two major products, isolable after extensive chromatography. The product eluted first was the 1,1-disubstituted ethene **23** and the second was the expected 1,2-disubstituted ethene **Ni10**. Although the porphyrin macrocycle is a very bulky substituent, 1,1-substitution in the Heck reaction is by no means unprecedented, and is well known for alkenes substituted with electron-donating groups and in reactions involving 1,2-disubstituted alkenes.[23] A third minor product also resulted from the reaction, and was identified as formyl-NiTriPP **Ni3**.

Heck coupling of vinyl-NiDAP **Ni13** with excess iodobenzene and PPh_3 as the ligand produced a far more curious result (Scheme 3). Three alkenyl products were identified by ^{1}H NMR studies, the expected 1,2-*meso*-styrylporphyrin **Ni15**, the 1,1-*meso*-styrylporphyrin **24** and a 1,2-β-styrylporphyrin. Formyl-NiDAP **Ni7** was also a minor side-product. Discussion of the possible mechanisms of this apparent *meso* to β rearrangement, and the NMR proof of the structure of the *β*-styrylporphyrin will be deferred until the porphyrin dyad formation has been presented (see below). The formation of the aldehydes **Ni3** and **Ni7** in these reactions is also unexpected, as the most common oxidation for alkenes in the presence of a palladium catalyst is the Wacker process, which in this case would lead to the porphyrinylacetaldehyde. No such "normal" oxidation product was detected.

Changing the phosphine ligand to the more bulky ligand, 2-(di-*t*-butylphosphino)biphenyl, apparently resulted in the palladium intermediate being too bulky to allow for 1,1-substitution, and only the *meso*- and β-2-styrylporphyrins were produced (from **Ni13**). Replacing iodobenzene with bromobenzene produced the same Heck-coupled products for both vinylporphyrins, but more sluggishly and with more unidentified side products. We also attempted the coupling of **Ni13** with 9-bromoanthracene as a model for the shape of the side of a *meso*-haloporphyrin. This reaction yielded both *meso*- and *β*-substituted anthracenylethenylporphyrins **26** and **27**, although we have been unable to purify these so far. Interestingly, the ratio of *meso*- to β-alkenyl porphyrins (by NMR) is greater for the coupling of bromoanthracene than for iodobenzene. To investigate the rearrangement further, we tried to couple 9-vinylanthracene with a bromoporphyrin, to see if migration occurred from the 9- to the 1-anthryl position, by analogy with the *meso*- and β-positions of a porphyrin. However, no Heck coupling was observed at all in any conditions tried. Perhaps these two results indicate that the anthracene "model" is a poor one for these processes.

Having proved that, at least under some conditions, *meso*-vinylporphyrins can act as the alkene partner in Heck couplings, we tried the target reactions, *i.e.*, the coupling of **Ni13** with bromoporphyrins to form the *meso*,*meso*-ethenyl dyads **28** (Scheme 4). Of course, in using these expensive starting materials, it was no



Scheme 4 *Reagents and conditions*: (i) $Pd(OAc)_2$, ligand, K_2CO_3, DMF, toluene, 105 °C (**29**: 23%; **30**: 33%; **31**: 15%).

longer feasible to use one partner or the other in large excess, as we had done so far for simpler substrates like styrene and iodobenzene. Not unexpectedly, the reaction was rather sluggish, and debromination of the starting material was a problem. In fact, the porphyrin **Ni1** was isolated as the major product as a consequence of this. However, the remarkable positive result is that the only dinuclear porphyrin isolated was not **28**, but rather the *meso*,β-ethenyl-linked dyad **30**. Not surprisingly, in view of the severe steric problems, there was no 1,1-coupled product.

Our first experiments were conducted with triphenylphosphine as the ligand, and in view of the low yields of dyad in our initial experiments, some optimization was attempted, examining catalyst concentration, temperature, phosphine ligand and base, using this coupling of **Ni13** with **Ni2** as a prototype. Although these experiments were not comprehensive, due to the expense of the two coupling partners, one significant result was that the bidentate chelating diphosphines dppe, dppp and dppf were almost completely unsuccessful in this reaction, and the hindered monodentate ligand 2-(di-*t*-butylphosphino)biphenyl gave the highest yield. Higher temperatures (>120 °C) favoured the debromination strongly, while potassium and caesium carbonates gave better yields than potassium phosphate. A catalyst loading of 20% was used.

These conditions were then applied to couplings of $\mathbf{H_2 2}$ and **Zn2**, using **Ni13** as the alkene, and the yields of **29**, **30**, and **31**, although only modest (33, 23 and 15%, respectively), were sufficient for characterisation and comparison. In each case, the only dyads detected were those linked to a 2-β-carbon on the NiDAP unit, and the 5-*meso*-carbon on the other partner. The rearrangement thus provided a new trio of *trans*-ethenyl-linked dyads, representing a new class of heterobis(porphyrin)s to add to the known β,β and *meso*,*meso* types.

The dinuclear structures were apparent from the mass spectra. Accurate mass measurements were possible using electrospray ionization for free base **29**, which exhibited a clear $[M + H]^+$ ion cluster. Laser desorption-TOF spectra gave molecular ion clusters at the expected m/z values for **30** and **31**. The position of substitution of the bridge in the dyads was established by their 1D and 2D (COSY and NOESY) ^{1}H NMR spectra. The obvious indicator of the 2-*ethenyl*-5,15-diarylporphyrin fragment in **29**, **30**, and **31** is the presence of 17 porphyrinic protons, distributed as three singlets, representing the two *meso*-Hs and the unique 3-β-H on the NiDAP side, six doublets for the inequivalent protons on the other three pyrrole rings of NiDAP, and a further four sets of doublets for the two pairs of equivalent rings on the MTriPP side. The two doublets for the *trans*-ethenyl protons (*J ca.* 15.5 Hz) were observed in all cases. There is a clear distinction between the chemical shifts of the β-attached and *meso*-attached alkene CH units; the CH protons next to the NiDAP appear at 8.92, 8.36 and 8.88 ppm for **29**, **30**, and **31**, respectively. Conversely, those adjacent to the *meso*-attached TriPP resonate at 10.30, 9.89 and 10.44 ppm for **29**, **30**, and **31**. These shifts are congruent with those for the CH protons adjacent to MTriPP in, for example, the *meso*-styryl derivatives $\mathbf{H_2 10}$, **Ni10** and **Zn10** (9.68, 9.31, 9.78 ppm). The only other examples of rearranged, *β*-alkenyl units for NiDAP are the styryl (**25**) and anthracenyl (**27**) derivatives. The alkenyl protons were not found for **27**, but in **25**, this signal appeared at 8.63 ppm.

The 2D NMR experiments (DQF COSY and gradient NOESY) were performed on the dyad **29** to assign the protons definitively (Fig. 2, 3). For the H_2TriPP fragment, the 2D spectra showed normal scalar couplings and NOEs for a triphenylporphyrin. The major points of interest were the resolution of the *ortho*-Hs on the inequivalent phenyl rings, 2e and 2f, highlighting the strong electronic effects of the alkenylporphyrin substituent at the *meso* position, and the observation of NOEs between both alkene protons and the *β*-Hs 2a.

For the NiDAP fragment, the starting point was the singlet arising from β-H 1b. By comparison with the monoporphyrins, this was logically assigned initially as the singlet with the lowest chemical shift (9.65 ppm), and an NOE resulting from an *ortho*-proton, 1k, confirmed this belief. It was hoped that an NOE would be seen between *meso*-H 1a and an alkenyl proton, which would readily distinguish between the two sides of the ring. This was

 This journal is © The Royal Society of Chemistry 2006

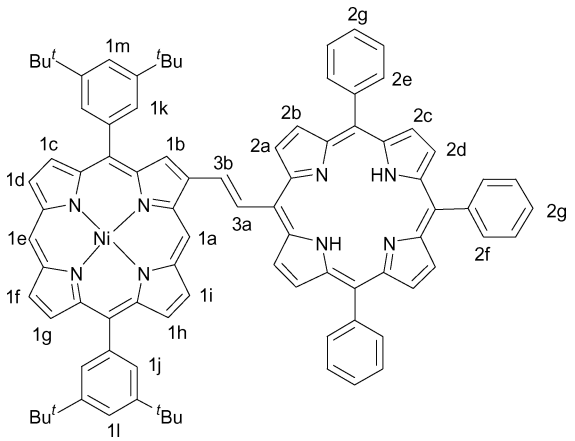


Fig. 2 Labelling of the proton positions in the *meso*,β-dyad **29** (see text and Fig. 3).

not the case; however, one of the *meso*-protons experienced only one NOE due to a neighbouring β-H, whereas the other *meso*-proton exhibited two NOEs arising from two neighbouring β-Hs. This allowed these two *meso*-protons to be distinguished as 1a and 1e, respectively. The NOEs between 1k and 1c and between 1j and 1g, together with the assistance of the COSY spectrum, confirmed the assignments of 1c, 1d, 1e, 1f and 1g. Although no NOE was observed between 1j and 1h, the assignment of 1a led to the confirmation of the chemical shift of 1i from the NOESY spectrum and subsequently 1h from its scalar coupling with 1i observed in the COSY. The chemical shifts of protons 1l and 1m were identified by COSY cross-peaks.

We note that while the *β*-Hs 2a gave observable NOEs from the alkenyl Hs, 3a and 3b, we could not resolve any dipolar couplings from the alkenyl protons to either the *meso*-H 1a or β-H 1b. It is understandable with the resolution of a 2D experiment that with the overlapping chemical shifts, no coupling can be observed between 3a and 1a. However, the lack of coupling of 1a and 1b with 3b remains unexplained at present. Thus the conformation of **29** drawn in Fig. 2 is for convenience only, and is not meant to imply that it is the preferred one.

The electronic absorption spectra of the novel dyads show evidence of interaction between the porphyrin transition dipoles across the potentially conjugated-CH=CH-bridge. In Fig. 4, we show the spectrum of the Ni_2 complex **30**, together with that of an analogous alkenyl-monoporphyrin, namely styryl-substituted **Ni10**, and the parent **Ni1**, for comparison. The intense Soret (B) band is almost split into two components, resulting in a strong shoulder on the red side. The lowest-energy Q band is significantly red-shifted with respect to the monoporphyrins. These features are consistent with a modest degree of interporphyrin ground state interaction *via* a partially conjugated bridge. Two features are likely to diminish this coupling, compared with dyads (such as those joined by *meso*,*meso*-alkyne bridges) with strong interporphyrin coupling: (i) the expected twisting of the alkene with respect to the porphyrin plane(s), which reduces π–π overlap *via* the bridge orbitals; (ii) the linkage through the β-carbon on one side. The former is due to steric interference between the alkene CHs and the peripheral porphyrin Hs, and is expected, from crystallographic studies on related mono- and di-porphyrins, to be less pronounced on the β-linked side.[15] The latter is a consequence of the smaller

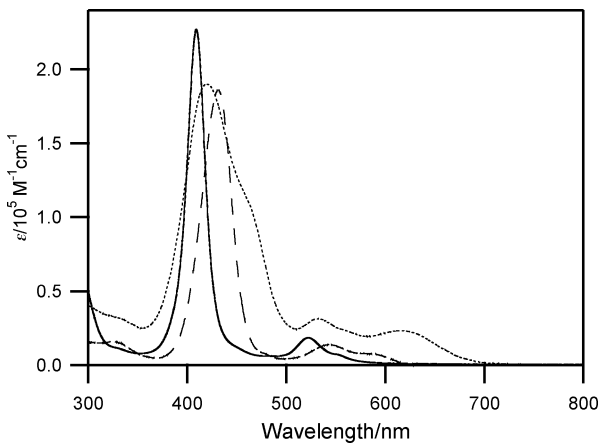


Fig. 4 UV–Visible absorption spectra of parent porphyrin **Ni1** (solid line), *meso*-styryl **Ni10** (dashed) and dinickel *meso*,β-dyad **30** (dotted) in $CHCl_3$.

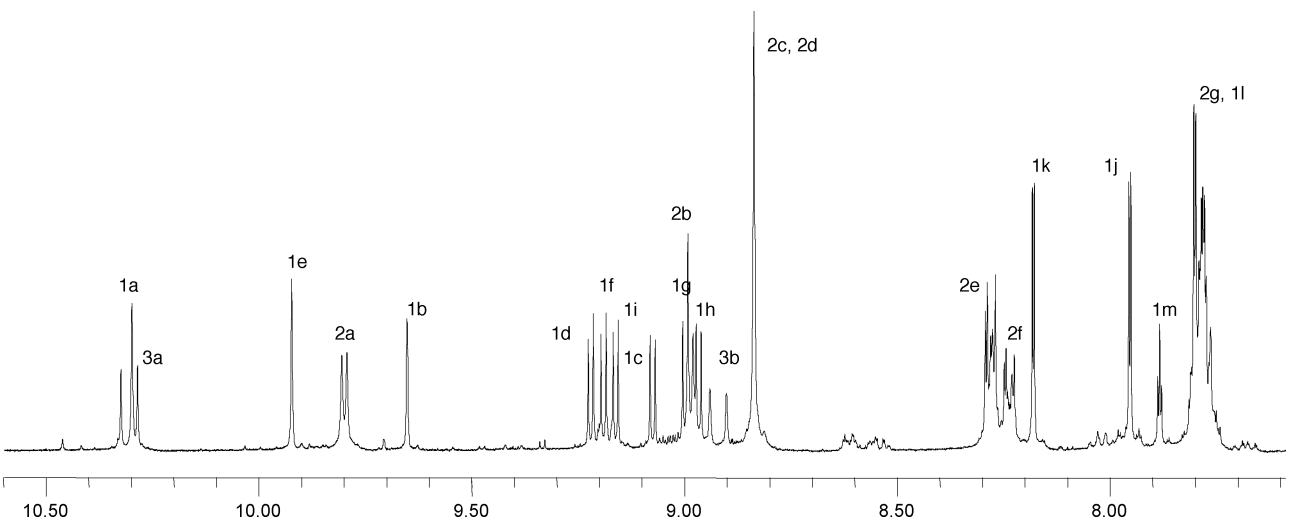
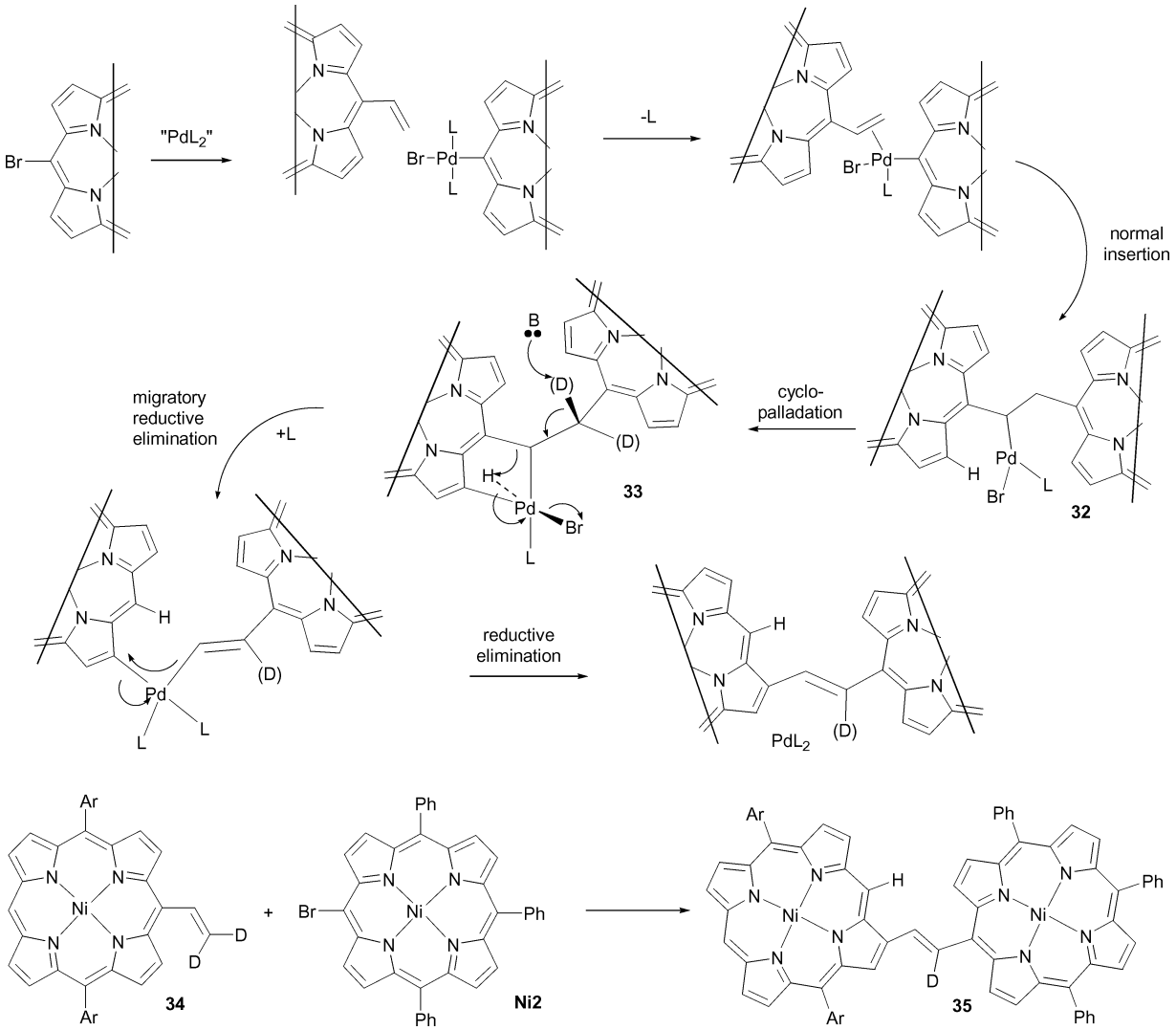


Fig. 3 Downfield region of the ^{1}H NMR spectrum of *meso*,β-dyad **29** in $CDCl_3$; the protons are labelled according to Fig. 2.



Scheme 5 Possible mechanism for the *meso* to β migration during the Pd-catalysed coupling of *meso*-vinylporphyrins with *meso*-bromoporphyrins.

orbital coefficients at the β-carbons than at the *meso*-carbons in the occupied frontier orbitals, and this feature has been described in some detail, especially for alkyne-linked dyads.[24] The *meso*,*meso* ethene-linked triarylporphyrin dizinc dyad recently described by Anderson and co-workers displays a split Soret band with maxima at 422 and 480 nm, which they compared with the corresponding *meso*,*meso* ethyne-linked dyad, whose Soret components have maxima at 408 and 483 nm.[20] Detailed discussions of equilibrium geometries, electronic spectra and theoretical comparisons with *meso*,*meso* ethenyl-linked dyads will be the topics of a subsequent paper.[21]

Mechanistic considerations

The fact that only the *meso*,β-dyads were isolated from the coupling of a *meso*-vinylporphyrin with a *meso*-bromoporphyrin is noteworthy, and so some consideration of the mechanism is warranted. The standard version of the Heck coupling cycle involves oxidative addition of the haloarene to a Pd(0)L_n fragment, followed by η^2-coordination of the alkene partner (Scheme 5). After insertion of the alkene into the Pd–C bond and then β-H elimination, the coupling product is extruded, and the Pd hydride collapses again to a catalytic Pd(0) species.[25] From our results, it seems that it is unfavourable for the bis(porphyrinyl)palladium(II) intermediate (Scheme 5, **32**) to reach a conformation that allows β-H elimination, namely with the palladium *syn* to that hydrogen. While this conformation can be achieved to some extent in the coupling of smaller haloarenes (*e.g.* iodobenzene) with vinylporphyrins, the hindrance due to the presence of two porphyrins makes the elimination of an ε-H from the β-position on the porphyrin a viable (albeit low-yielding) alternative. Another significant point is that the chelating diphosphines gave almost no coupling products, and moreover the bulkier phosphine gave somewhat better yields than triphenylphosphine. This suggests that the key steps occur on a species with either *trans*-directed phosphine ligands, or more likely, on Pd(II) [or Pd(IV)] intermediates that have only one coordinated phosphine ligand. Cyclopalladation onto the 2-carbon is an attractive proposition,

 This journal is © The Royal Society of Chemistry 2006

although this requires a Pd(IV) intermediate, *e.g.*, **33** (Scheme 5). A possible pathway for a migratory reductive elimination is shown, to give a Pd(II) intermediate that can collapse as expected to eliminate the *meso*,β-dyad.

It is desirable to obtain evidence of the fate of the various hydrogens that participate in the reaction, and the origin of the new *meso*-H in the rearranged dyad. The dideuterio-vinylporphyrin **34** was synthesised from deuterated ylide and **Ni8**, and coupled with **Ni2**. The product was confirmed to be monodeuterio **35**, by the absence of the 9.89 ppm doublet in its NMR spectrum, together with the observation of a broad singlet, rather than a doublet, at 8.36 ppm. However, the *meso*-H at 10.03 ppm was unchanged, so it does not arise specifically by migration from the terminal alkene carbon, but may come from the β-porphyrin carbon (*via* the Pd in our proposal) or from the DMF or toluene or adventitiously from trace impurities in the solvents. The coupling of undeuterated substrates in d_7-DMF afforded completely non-deuterated dyad. Without more detailed labelling experiments, we cannot make any more statements on mechanistic possibilities at this stage.

The bromoporphyrin **Ni2** and vinylporphyrin **Ni13** were separately subjected to Heck conditions without the complementary partner for 4 days at 105 °C. The bromoporphyrin was 30% debrominated over this time, while 5% of the vinylporphyrin had been converted to formylporphyrin. The latter reaction was repeated and left for 7 days and the amount of formylporphyrin increased to 8%. This incidentally rules out formation of the formylporphyrin *via* the bromoporphyrin, as well as indicating that apparently both partners have to be engaged on the palladium for the migration to occur.

Conclusions

meso-Bromo- and *meso*-ethenylporphyrins have been investigated as potential Heck synthons. While the bromoporphyrins proved efficient in Heck coupling with typical electron-deficient alkenes, namely methyl acrylate, acrylonitrile and styrene, to produce mononuclear alkenylporphyrins, ethenylporphyrins gave mixtures of 1,1-, 1,2-, and surprisingly, β-1,2-disubstituted alkenylporphyrins. In attempting to form *meso*,*meso*-ethenyl(bis)porphyrins through the same procedures, only *meso*,β-linked dyads were isolated. This has fortuitously enabled the study of the spectra of this new type of dyad in comparison with other conjugated or partially conjugated carbon-bridged dyads.

We offer a possible mechanism for the rearrangement, however, deuteration studies have so far not provided evidence for or against this mechanism. However, rearrangements accompanying metal-catalysed coupling may open new pathways for novel synthetic reactions in the *meso*,β-region of porphyrins. In our own work with β-mercurioporphyrins, we have seen other examples of substituents "walking" from one β-carbon to a neighbouring position during Pd-catalysed reactions.[26] We predict the development of a range of similar reactions that involve metal-induced C–H activations on porphyrins, and note the recent work of Boyle and Fox[27], and Cammidge *et al.*,[28] and the pioneering results of Smith *et al.*[6] on intramolecular cyclisations on porphyrins induced by palladium catalysts. Moreover, Osuka's group has recently reported Ir-induced β-boronation of porphyrins, a reaction that also involves transition metal-induced C–H activation on porphyrins.[29]

Experimental

General

All solvents were Analytical Reagent grade unless otherwise stated. The following solvents and reagents were distilled prior to use (under Ar): pyrrole; phosphorus oxychloride; THF from sodium/benzophenone; dichloromethane and 1,2-dichloroethane from calcium hydride; and triethylamine and pyridine from potassium hydroxide. Phosphine ligands were obtained from Sigma-Aldrich or Strem, and metal salts were obtained from Sigma-Aldrich. TLC was performed on Merck Silica Gel 60 F254 TLC plates. Preparative column chromatography was performed on silica gel (40–63μm), which was purchased from Qindao Haiyang Chemical Co. Ltd., China.

^{1}H, DQF COSY and NOESY NMR experiments were conducted on a Bruker Avance 400 spectrometer operating at 400.155 MHz. All samples were prepared in $CDCl_3$ and chemical shifts were referenced to $CHCl_3$ at 7.26 ppm. Coupling constants are given in Hz. Solutions of zinc porphyrins were prepared with the addition of 10 μL d_5-pyridine (*ca.* 1%). Microanalyses were performed by the Microanalytical Service, School of Molecular and Microbial Sciences, The University of Queensland. UV–Visible spectra were recorded on a Varian Cary 3 or Varian Cary 50 UV–visible spectrometer in $CHCl_3$.

Accurate Electrospray Ionisation (ESI) and Laser Desorption Ionisation (LDI) mass spectra were recorded at the School of Chemistry, Monash University, Melbourne. ESI measurements were performed using an Agilent 1100 Series LC attached to an Agilent G1969A LC-TOF system with reference mass correction using NaI clusters. An eluent of 50 : 50 CH_2Cl_2–MeOH with 0.1% formic acid was employed using a flow rate of 0.3 mL min^{-1}. For the ESI probe, solvent aspiration was achieved by nitrogen gas flowing at 8 L min^{-1}. The source temperature was set to 350 °C and the capillary voltage to 4.0 kV. LDI MS analyses were performed with an Applied Biosystems Voyager-DE STR BioSpectrometry Workstation. The instrument was operated in positive polarity in reflectron mode. Data from 500 laser shots employing a 337 nm nitrogen laser were collected, the signal was averaged, and processed with the instrument manufacturer's Data Explorer software.

Starting materials

The following parent porphyrins, *meso*-substituted porphyrins, and their complexes with Ni(II) and Zn(II), were prepared according to published procedures for these or similar compounds: **$H_2$1**,[30] **Ni1**,[30] **$H_2$2**,[31] **Ni2**,[31] **Zn2**,[32] **$H_2$4**,[33] **$H_2$6**,[34] **Zn6**[33] and **Zn8**.[4,35]

5-Formyl-10,15,20-triphenylporphyrinatonickel(II) (Ni3). The method was adapted from a procedure reported for similar porphyrins by Johnson and Oldfield.[36] A dry 100 cm^3 two neck flask was fitted with a dropping funnel and septum. The system was purged with argon, and dry DMF (4 cm^3, 50 mmol) was added and the mixture was chilled to 0 °C. Freshly distilled $POCl_3$ (4.6 cm^3, 49 mmol) was added dropwise *via* a syringe, with stirring. The Vilsmeier reagent was allowed to warm to room temperature and stirred for 30 min. The pale yellow reagent was heated to 50 °C before a solution of **Ni1** (380 mg, 0.64 mmol) in dry 1,2-dichloroethane (75 cm^3) was added dropwise over a period of

45 min. The progress of the reaction was monitored by TLC using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. After addition of the porphyrin, the reaction mixture was allowed to stir for a further 2 h by which time **Ni1** was no longer present. The heat source was removed and the mixture was transferred to a 1 L flask containing saturated NaOAc solution (380 cm^3) and allowed to stir overnight. The organic layer was separated, washed with deionised water (150 cm^3 × 2) and dried with Na_2SO_4. The solvent was evaporated and the dark purple residue was subjected to column chromatography using $CHCl_3$–*n*-hexane (75 : 25) as the eluent. Fractions containing **Ni3** were collected and recrystallised from $CHCl_3$–MeOH to yield purple crystals (282 mg, 71%). δ_H 12.04 (1 H, s, aldehyde), 9.80 (2 H, d, ^3J 5.1, β-H), 8.85 (2 H, d, ^3J 5.1, β-H), 8.64 (2 H, d, ^3J 4.9, β-H), 8.57 (2 H, d, ^3J 4.9, β-H), 7.95 (4 H, m, *o*-Ph–H), 7.68 (2 H, t, *m*,*p*-Ph–H); UV–vis: λ_{max} (log ε) 424 (5.15), 553 (3.84), 597 (4.00) nm. MS (LDI$^+$) $m/z = 622.08$. Calc. M$^+$ for $C_{39}H_{24}N_4NiO$ $m/z = 622.13$.

5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni4). The method was adapted from a procedure reported for similar porphyrins by Arnold *et al.*[37] Porphyrin **$H_2$4** (500 mg, 0.73 mmol) and nickel(II) acetylacetonate (205 mg, 0.8 mmol) were added to a 100 cm^3 flask equipped with a condenser, dissolved in toluene (50 cm^3) and refluxed for 3 h. The progress of the reaction was monitored by TLC using CH_2Cl_2–*n*-hexane (50 : 50). Upon completion of the reaction, the solvent was removed by vacuum and the product was isolated after passage through a plug of silica gel using $CHCl_3$ as the eluent. Recrystallisation of the dark red residue using $CHCl_3$–MeOH yielded a red crystalline material (535 mg, 98%). δ_H 9.94 (2 H, s, *meso*-H), 9.19 (4 H, d, ^3J 4.6, β-H), 9.00 (4 H, d, ^3J, β-H), 7.95 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.78 (2 H, t, ^4J 1.8, *p*-Ar–H), 1.52 (36 H, s, ^{t}Bu–H), −2.98 (2 H, s, N–H); UV–vis: λ_{max} (log ε) 403 (5.13), 515 (4.09), 546 (3.87) nm. HRMS (LSIMS$^+$) $m/z = 742.3533$. Calc. M$^+$ for $C_{48}H_{52}N_4Ni$ $m/z = 742.3545$. Although this porphyrin has been synthesised previously,[38,39] no spectroscopic data were reported.

5,15-Dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni6). This was prepared as described above for **Ni4**, using porphyrin **$H_2$6** (50 mg, 0.059 mmol) and Ni(acac)$_2$ (16 mg, 0.063 mmol). Recrystallisation of the product using $CHCl_3$–MeOH yielded a purple-red powder (53 mg, 99%). δ_H 9.45 (2 H, d, ^3J 4.9, *β*-H), 8.77 (2 H, d, ^3J 4.9, β-H), 7.80 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.74 (2 H, t, *p*-Ar–H), 1.56 (36 H, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 422 (5.13), 536 (4.08). The data were in agreement with previous work.[40]

5-Formyl-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel (II) (Ni7). This was prepared from **Ni4** as described above for **Ni3**. The dark purple crude product was subjected to column chromatography using $CHCl_3$–*n*-hexane (75 : 25) as the eluent. Fractions containing **Ni7** were collected and recrystallised from $CHCl_3$–MeOH to yield purple crystals (380 mg, 73%). δ_H 12.16 (1 H, s, aldehyde), 9.89 (2 H, d, ^3J 4.9, β-H), 9.75 (1 H, s, *meso*-H), 9.07 (2 H, d, ^3J 4.7, β-H), 8.97 (2 H, d, ^3J 4.9, β-H), 8.80 (2 H, d, ^3J 4.7, β-H), 7.86 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.79 (2 H, t, ^4J 1.8, *p*-Ar–H), 1.53 (36 H, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 420 (5.19), 545 (3.81), 590 (4.06). Although this compound has been synthesised previously,[39,41] no spectroscopic data were described.

5-Ethenyl-10,15,20-triphenylporphyrin ($H_2$8). The method was adapted from a procedure reported by Liebeskind *et al.*[4] Porphyrin **$H_2$2** (200 mg, 0.33 mmol), $Pd_2(dba)_3$ (15 mg, 0.016 mmol) and $AsPh_3$ (39 mg, 0.13 mmol) were added to a Schlenk flask which was evacuated and subsequently charged with argon. Dry, deoxygenated THF (20 cm^3) and tri-*n*-butyl(vinyl)tin (130 μL, 0.44 mmol) were added and the flask was sealed and heated to 50 °C. The progress of the reaction was monitored by TLC using CH_2Cl_2–*n*-hexane (50 : 50) as the eluent. After 2.5 h the reaction was complete and the solvent was removed under vacuum. The product was purified by passage through a plug of silica gel using CH_2Cl_2–*n*-hexane as the eluent (40 : 60) and recrystallised using CH_2Cl_2–MeOH to give purple crystals (163 mg, 88%). δ_H 9.50 (2 H, d, ^3J 4.9, β-H), 9.24 (1 H, dd, ^3J 17.1, ^3J 11.0, alkene-H), 8.91 (2 H, d, ^3J 4.9, β-H), 8.81 (4 H, br s, β-H), 8.21 (6 H, m, *o*-Ph–H), 7.76 (9 H, m, *m*,*p*-Ph–H), 6.54 (1 H, dd, ^3J 11.0, ^2J 1.8, alkene-H, *trans* to porphyrin), 6.15 (1 H, dd, ^3J 17.1, ^2J 1.8, alkene-H, *cis* to porphyrin), −2.68 (2 H, br s, N–H); UV–vis: λ_{max} (log ε) 421 (5.23), 519 (3.79), 554 (3.52), 651 (3.14) nm. HRMS (ESI$^+$) $m/z = 565.2389$. Calc. MH$^+$ for $C_{40}H_{29}N_4$ $m/z = 565.2392$.

Synthesis of alkenylporphyrins

5-Ethenyl-10,15,20-triphenylporphyrinatonickel(II) (Ni8).

Method 1[11]. Methyltriphenylphosphonium bromide (357 mg, 1.00 mmol) was added to a 100 cm^3 round-bottom flask equipped with a side-arm gas adapter and dried under vacuum before the vessel was purged with argon. Dry, deoxygenated THF (10 cm^3) was added and the mixture was allowed to stir for 5 min at room temperature to create a suspension of the phosphonium salt. Butyllithium (0.6 cm^3, 1.6 M) was added dropwise to the slurry *via* a syringe, resulting in a bright yellow solution. Porphyrin **Ni3** (200 mg, 0.32 mmol) was dissolved in dry, oxygen-free THF (20 cm^3) and added dropwise through a syringe to the freshly made ylide. The solution turned from purple to red over a period of 2 h and was monitored by TLC using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. Upon the complete consumption of the starting material, the reaction was quenched by the addition of H_2O, followed by extraction with $CHCl_3$. The $CHCl_3$ layer was washed with water (50 cm^3 × 2) and dried using Na_2SO_4 before being concentrated *in vacuo.* The red residue was purified by column chromatography using $CHCl_3$–*n*-hexane (50 : 50) as eluent. The fractions containing **Ni8** were collected, dried and recrystallised from $CHCl_3$–MeOH to yield red crystals (128 mg, 65%).

Method 2. Porphyrin **$H_2$8** (100 mg, 0.16 mmol) and Ni(acac)$_2$ (48 mg, 0.19 mmol) were added to a 50 cm^3 flask, dissolved in toluene (20 cm^3) and refluxed for 3 h. The progress of the reaction was monitored by TLC using CH_2Cl_2–*n*-hexane (50 : 50). Upon completion of the reaction, the solvent was removed by vacuum and the product was isolated after passage through a plug of silica gel using $CHCl_3$ as the eluent. Recrystallisation of the product from $CHCl_3$–MeOH yielded red crystals (109 mg, 99%). δ_H 9.35 (2 H, d, ^3J 5.1, β-H), 8.94 (1 H, dd, ^3J 17.4, ^3J 11.2, alkene-H), 8.81 (2 H, d, ^3J 4.9, β-H), 8.70 (2 H, d, ^3J 5.1, β-H), 8.68 (2 H, ^3J 4.9, β-H), 7.99 (6 H, m, *o*-Ph–H), 7.68 (9 H, m, *m*,*p*-Ph–H), 6.32 (1 H, dd, ^3J 11.2, ^2J 1.7, alkene-H, *trans* to porphyrin), 5.65 (1 H, dd, ^3J 17.4, ^2J 1.7, alkene-H, *cis* to porphyrin); UV–vis: λ_{max} (log ε) 418 (5.18), 532 (4.03) nm. MS (LDI$^+$) $m/z = 620.10$. Calc. M$^+$ for $C_{40}H_{26}N_4Ni$ $m/z = 620.15$.

This journal is © The Royal Society of Chemistry 2006

5-Ethenyl-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni13). This compound was prepared as described above for **Ni8**, starting with **Ni7**. The red residue was purified by column chromatography using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. The fractions containing **Ni13** were collected, dried and recrystallised from $CHCl_3$–MeOH to produce a red crystalline material (129 mg, 65%). δ_H 9.73 (1 H, s, *meso*-H), 9.39 (2 H, d, ^3J 4.8, β-H), 9.08 (2 H, d, ^3J 4.8, β-H), 8.99 (1 H, dd, ^3J 15.6 (*trans*), $^3J'$ 11.0 (*cis*), alkene-H), 8.89 (2 H, d, ^3J 4.8, β-H), 8.88 (2 H, d, ^3J 4.8, β-H), 7.88 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.74 (2 H, t, *p*-Ar–H), 6.34 (1 H, dd, ^3J 11.0, ^2J 1.8, *cis* alkene-H), 5.70 (1 H, dd, ^3J 15.6, ^2J 1.8, alkene-H), 1.50 (36 H, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 415 (5.21), 529 (4.07) nm. MS (LDI$^+$) $m/z = 768.39$. Calc. M$^+$ for $C_{50}H_{54}N_4Ni$ $m/z = 768.37$.

Synthesis of alkenyl porphyrins by Heck coupling

Several conditions were tested for Heck coupling involving *meso*-bromo and *meso*-ethenyl porphyrins (see text). The conditions that produced the optimum yield of the Heck-coupled dyads were also employed for the monoporphyrin couplings described below.

General procedure for mono(alkenyl)porphyrins

Bromoporphyrin (0.029 mmol), palladium acetate (1.5 mg, 0.0058 mmol, 20 mol%), 2-(di-*tert*-butylphosphino)biphenyl (4.3 mg, 0.015 mmol) and K_2CO_3 (6.5 mg, 0.036 mmol) were added to a Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (1.5 cm^3), dry toluene (1.5 cm^3) and the vinyl reagent (50-fold excess). The mixture was then degassed *via* three freeze–pump–thaw cycles before the vessel was purged with argon again. The Schlenk flask was sealed and heated to 105 °C and allowed to stir for 15 h. The progress of each reaction was monitored by TLC using CH_2Cl_2–*n*-hexane (50 : 50) for free-base porphyrins and $CHCl_3$–*n*-hexane (50 : 50) for metallated porphyrins. In monitoring the progress of the reactions, the heat source was removed for the duration of the sampling, and in the cases where highly volatile reagents were used, the reactions were chilled to 0 °C to prevent loss of the reagent. Upon the complete conversion of the starting material, the mixture was diluted with toluene (10 cm^3) and washed with water (10 cm^3 × 2). The organic layer was collected, dried and the residue was subjected to column chromatography. This procedure was used to produce the following compounds.

***E*-5-(2-Methoxycarbonylethenyl)-10,15,20-triphenylporphyrin ($H_2$9).** Produced from **$H_2$2** (17.8 mg) and methyl acrylate (130 μL). The product was purified by column chromatography using CH_2Cl_2–*n*-hexane (50 : 50) as the eluent. The first band from the column corresponded to **$H_2$1**, which resulted from debromination (1.1 mg, 7%). The second band contained the desired product **$H_2$9** which was recrystallised using CH_2Cl_2–MeOH to yield a purple semi-crystalline material (15.9 mg, 87%). δ_H 10.28 (1 H, d, ^3J 15.8, alkene-H), 9.49 (2 H, d, ^3J 4.8, β-H), 8.93 (2 H, d, ^3J 4.8, β-H), 8.81 (2 H, d, ^3J 4.8, β-H), 8.80 (2 H, d, ^3J 4.8, β-H), 8.20 (6 H, m, *o*-Ph–H), 7.78 (9 H, m, *m*,*p*-Ph–H), 6.84 (1 H, d, ^3J 15.8, alkene-H), 4.07 (3 H, s, CH_3), −2.54 (2 H, br s, N–H); UV–vis: λ_{max} (log ε) 424 (5.26), 518 (3.99), 558 (3.82), 589 (3.70), 651 (3.46) nm. HRMS (ESI$^+$) $m/z = 623.7283$. Calc. MH$^+$ for $C_{42}H_{30}N_4O_2$ $m/z = 623.7213$.

***E*-5-(2-Methoxycarbonylethenyl)-10,15,20-triphenylporphyrinatonickel(II) (Ni9).** Produced from **Ni2** (19.7 mg) and methyl acrylate (130 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. The first band from the column corresponded to **Ni1**, which resulted from debromination (1.4 mg, 8%). The second band contained the desired product **Ni9** which was recrystallised using $CHCl_3$–MeOH to yield dark red crystalline plates (17.5 mg, 89%). δ_H 9.90 (1 H, d, ^3J 15.6, alkene-H), 9.37 (2 H, d, ^3J 4.9, β-H), 8.81 (2 H, d, ^3J 4.9, β-H), 8.67 (2 H, d, ^3J 4.9, β-H), 8.63 (2 H, d, ^3J 4.9, β-H), 7.96 (6 H, m, *o*-Ph–H), 7.68 (9 H, m, *m*,*p*-Ph–H), 6.32 (1 H, d, ^3J 15.6, alkene-H), 3.97 (3 H, s, CH_3); UV–vis: λ_{max} (log ε) 430 (5.23), 545 (4.09), 589 (3.92); MS (LDI$^+$) $m/z = 678.27$. Calc. M$^+$ for $C_{42}H_{28}N_4NiO_2$ $m/z = 678.15$; Found: C, 74.0; H, 4.1; N, 8.25. Calc. for $C_{42}H_{28}N_4NiO_2$: C, 74.25; H, 4.15; N, 8.25%.

***E*-5-(2-Methoxycarbonylethenyl)-10,15,20-triphenylporphyrinatozinc(II) (Zn9).** Produced from **Zn2** (19.7 mg) and methyl acrylate (130 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (75 : 25) as the eluent. The first band from the column contained **Zn1** (2.6 mg, 15%), which resulted from debromination. The second band contained the desired product **Zn9** which was recrystallised using $CHCl_3$(1% pyridine)–MeOH, yielding bright purple plates (15.9 mg, 80%). δ_H 10.39 (1 H, d, ^3J 15.6, alkene-H), 9.53 (2 H, d, ^3J 4.6, β-H), 8.93 (2 H, d, ^3J 4.6, β-H), 8.81 (2 H, d, ^3J 4.6, β-H), 8.79 (2 H, d, ^3J 4.6, β-H), 8.16 (6 H, m, *o*-Ph–H), 7.72 (9 H, m, *m*,*p*-Ph–H), 6.78 (1 H, d, ^3J 15.6, alkene-H), 4.04 (3 H, s, CH_3); UV–vis: λ_{max} (log ε) 431 (5.28), 560 (3.97), 608 (3.80) nm. MS (LDI$^+$) $m/z = 684.31$. Calc. M$^+$ for $C_{42}H_{28}N_4O_2Zn$ $m/z = 684.15$; Found: C, 72.8; H, 4.7; N, 8.00. Calc. for $C_{42}H_{28}N_4O_2Zn$: C, 73.5; H, 4.1; N, 8.2%.

***E*-5-(2-Phenylethenyl)-10,15,20-triphenylporphyrin ($H_2$10).** Produced from **$H_2$2** (17.8 mg) and styrene (137 μL). The product was purified by column chromatography using CH_2Cl_2–*n*-hexane (50 : 50) as the eluent. Porphyrin **$H_2$10** eluted first and was recrystallised using CH_2Cl_2–MeOH (15.9 mg, 87%). δ_H 9.68 (1 H, d, ^3J 15.9, alkene-H), 9.51 (2 H, d, ^3J 4.9, β-H), 8.89 (2 H, d, ^3J 4.9, β-H), 8.80 (2 H, br s, β-H), 8.21 (6 H, m, *o*-Ph–H), 7.97 (2 H, d, ^3J 7.8, *o*-phenylethenyl-H), 7.77 (9 H, m, *m*,*p*-Ph–H), 7.60 (2 H, t, ^3J 7.3, *m*-phenylethenyl-H), 7.47 (1 H, t, ^3J 7.3, *p*-phenylethenyl-H), 7.41 (1 H, d, ^3J 15.9, alkene-H), −2.52 (2 H, br s, N–H); UV–vis: λ_{max} (log ε) 427 (5.26), 524 (3.88), 566 (3.94), 599 (3.54), 660 (3.58) nm. HRMS (ESI$^+$) $m/z = 641.4168$. Calc. MH$^+$ for $C_{46}H_{32}N_4$ $m/z = 641.2705$. A second fraction was collected, **$H_2$1**, which resulted from debromination of the starting material (1.6 mg, 10%).

***E*-5-(2-Phenylethenyl)-10,15,20-triphenylporphyrinatonickel(II) (Ni10).** Produced from **Ni2** (19.7 mg) and styrene (137 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (40 : 60) as the eluent. Porphyrin **Ni10** eluted first and was recrystallised from $CHCl_3$–MeOH to give a bright red crystalline material (17.1 mg, 85%). δ_H 9.38 (2 H, d, ^3J 4.9, β-H), 9.31 (1 H, d, ^3J 15.9, alkene-H), 8.79 (2 H, d, ^3J 4.9, β-H), 8.67 (2 H, d, ^3J 4.9, β-H), 8.65 (2 H, d, ^3J 4.9, β-H), 7.98 (6 H, m, *o*-Ph–H), 7.80 (2 H, d, ^3J 7.3, *o*-phenylethenyl-H), 7.67 (9 H, m, *m*,*p*-Ph–H), 7.51 (2 H, t, ^3J 7.3, *m*-phenylethenyl-H), 7.40 (1 H, t, ^3J 7.3, *p*-phenylethenyl-H), 6.87 (1 H, d, ^3J 15.9, alkene-H); UV–vis: λ_{max} (log ε) 431 (5.20), 544 (4.10), 586 (3.87) nm. MS

(LDI$^+$) m/z = 696.19. Calc. M$^+$ for $C_{46}H_{30}N_4Ni$ m/z = 696.18; Found: C, 79.0; H, 4.3; N, 7.8. Calc. for $C_{46}H_{30}N_4Ni$: C, 79.2; H, 4.3; N, 8.0%. A second fraction containing **Ni1**, resulting from debromination of the starting material, was also isolated (1.7 mg, 10%).

***E*-5-(2-Phenylethenyl)-10,15,20-triphenylporphyrinatozinc(II) (Zn10).** Produced from **Zn2** (19.7 mg) and styrene (137 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (30 : 70) as the eluent. Porphyrin **Zn10** eluted from the column first and was recrystallised using $CHCl_3$(1% pyridine)–MeOH to give bright purple plates (15.3 mg, 75%). δ_H 9.78 (1 H, d, ^3J 15.7, alkene-H), 9.55 (2 H, d, ^3J 4.6, β-H), 8.91 (2 H, d, ^3J 4.6, β-H), 8.81 (4 H, br s, β-H), 8.19 (4 H, m, *o*-Ph–H), 8.16 (2 H, m, *o*-Ph–H), 7.93 (2 H, d, ^3J 7.3, *o*-phenylethenyl-H), 7.71 (9 H, m, *m*,*p*-Ph–H), 7.57 (2 H, t, ^3J 7.3, *m*-phenylethenyl-H), 7.43 (1 H, t, ^3J 7.3, *p*-phenylethenyl-H), 6.78 (1 H, d, ^3J 15.7, alkene-H); UV–vis: λ_{max} (log ε) 430 (5.27), 559 (3.99), 605 (3.88) nm. MS (LDI$^+$) m/z = 702.21. Calc. M$^+$ for $C_{46}H_{30}N_4Zn$ m/z = 702.17. A second fraction containing **Zn1**, resulting from debromination of the starting material, was also isolated (2.2 mg, 12.5%).

***E*-5-(2-Cyanoethenyl)-10,15,20-triphenylporphyrin ($H_2$11) and *Z*-5-(3-cyanoethenyl)-10,15,20-triphenylporphyrin ($H_2$12).** Produced from **$H_2$2** (17.8 mg) and acrylonitrile (95 μL). The products were purified by column chromatography using CH_2Cl_2–*n*-hexane (50 : 50) as the eluent. Porphyrin **$H_2$2**, resulting from debromination, eluted first (1.2 mg, 8%). The second fraction was collected and recrystallised using CH_2Cl_2–MeOH, yielding a purple powder. NMR studies showed the presence of two compounds, **$H_2$11** (*ca.* 65%, NMR) and **$H_2$12** (*ca.* 35%), which could not be separated further (13.7 mg, 81%). HRMS (ESI$^+$) m/z = 590.2332. Calc. MH$^+$ for $C_{41}H_{27}N_5$ m/z = 590.2345. **$H_2$11** δ_H 10.01 (1 H, d, ^3J 16.4, alkene-H), 9.38 (2 H, d, ^3J 4.6, β-H), 8.95 (2 H, d, ^3J 4.6, β-H), 8.81 (4 H, br s, β-H), 8.20 (6 H, m, *o*-Ph–H), 7.78 (9 H, m, *m*,*p*-Ph–H), 6.25 (1 H, d, ^3J 16.4, alkene-H), −2.52 (2 H, br s, N–H); **$H_2$12** δ_H 9.77 (1 H, d, ^3J 11.5, alkene-H), 9.31 (2 H, d, ^3J 4.6, β-H), 8.96 (2 H, d, ^3J 4.6, β-H), 8.79 (4 H, br s, β-H), 8.20 (6 H, m, *o*-Ph–H), 7.78 (9 H, m, *m*, *p*-Ph–H), 6.69 (1 H, d, ^3J 11.5, alkene-H), −2.64 (2 H, br s, N–H).

***E*-5-(2-Cyanoethenyl)-10,15,20-triphenylporphyrinatonickel(II) (Ni11) and *Z*-5-(2-cyanoethenyl)-10,15,20-triphenylporphyrinatonickel(II) (Ni12).** Produced from **Ni2** (19.7 mg) and acrylonitrile (95 μL). The products were purified by column chromatography using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. Compound **Ni1**, resulting from debromination, eluted first (1.9 mg, 11%). The second fraction was collected and recrystallised using $CHCl_3$–MeOH, yielding an orange-red powder. NMR studies showed the presence of two compounds, **Ni11** (*ca.* 85%, NMR) and **Ni12** (*ca.* 15%), which could not be separated further (15.8 mg, 85%). HRMS (ESI$^+$) m/z = 668.1354. Calc. MNa$^+$ for $C_{41}H_{25}N_5Ni$ m/z = 668.1361; Found: C, 76.3; H, 4.6; N, 9.5. Calc. for $C_{41}H_{25}N_5Ni$: C, 76.2; H, 3.9; N, 10.8%. **Ni11** δ_H 9.58 (1 H, d, ^3J 16.4, alkene-H), 9.23 (2 H, d, ^3J 4.9, β-H), 8.82 (2 H, d, ^3J 4.9, β-H), 8.68 (2 H, d, ^3J 4.9, β-H), 8.63 (2 H, d, ^3J 4.9, β-H), 7.95 (6 H, m, *o*-Ph–H), 7.69 (9 H, m, *m*,*p*-Ph–H), 5.67 (1 H, d, ^3J 16.4, alkene-H); **Ni12** δ_H 9.47 (1 H, d, ^3J 11.5, alkene-H), 9.15 (2 H, d, ^3J 4.9, β-H), 8.83 (2 H, d, ^3J 4.6, β-H), 8.70 (2 H, d, ^3J 5.1, β-H), 8.66 (2 H, d, ^3J 5.1, β-H), 7.97 (6 H, m, *o*-Ph–H), 7.69 (9 H, m, *m*,*p*-Ph–H), 6.35 (1 H, d, ^3J 16.4, alkene-H).

***E*-5-(2-Cyanoethenyl)-10,15,20-triphenylporphyrinatozinc(II) (Zn11) and *Z*-5-(2-cyanoethenyl)-10,15,20-triphenylporphyrinatozinc(II) (Zn12).** Produced from **Zn2** (19.7 mg) and acrylonitrile (95 μL). The products were purified by column chromatography using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. Porphyrin **Zn1**, resulting from debromination, eluted first (3.1 mg, 18%). The second fraction was collected and recrystallised using $CHCl_3$(1% pyridine)–MeOH, yielding a bright purple powder. NMR studies showed the presence of two compounds, **Zn11** (*ca.* 90%, NMR) and **Zn12** (*ca.* 10%), which could not be separated further (14.7 mg, 78%). MS (LDI$^+$) m/z = 651.13. Calc. M$^+$ for $C_{41}H_{25}N_5Zn$ m/z = 651.14; **Zn11**: δ_H 9.94 (1 H, d, ^3J 16.1, alkene-H), 9.36 (2 H, d, ^3J 4.7, β-H), 8.97 (2 H, d, ^3J 4.7, β-H), 8.92 (2 H, d, ^3J 4.7, β-H), 8.89 (2 H, d, ^3J 4.7, β-H), 8.17 (6 H, m, *o*-Ph–H), 7.77 (9 H, m, *m*,*p*-Ph–H), 6.14 (1 H, d, ^3J 16.1, alkene-H); **Zn12**: δ_H 9.73 (1 H, d, ^3J 11.5, alkene-H), 9.31 (2 H, d, ^3J 4.7, β-H), 9.00 (2 H, d, ^3J 4.7, β-H), 8.92 (2 H, d, ^3J 4.7, β-H), 8.89 (2 H, d, ^3J 4.7, β-H), 8.16 (6 H, m, *o*-Ph–H), 7.72 (9 H, m, *m*,*p*-Ph–H), 6.65 (1 H, d, ^3J 11.5, alkene-H).

General procedure for bis(alkenyl)porphyrins using dihaloporphyrins

Dibromoporphyrin (0.029 mmol), palladium acetate (3.0 mg, 0.0104 mmol, 20 mol%), di-*tert*-butylbiphenylphosphine (8.6 mg, 0.03 mmol) and K_2CO_3 (13 mg, 0.072 mmol) were added to a Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (5 cm^3), dry toluene (10 cm^3) and the vinyl reagent (50-fold excess). The mixture was degassed *via* three freeze–pump–thaw cycles before the vessel was purged with argon again. The Schlenk flask was sealed and heated to 105 °C and allowed to stir for 15 h. The progress of each reaction was monitored by TLC using CH_2Cl_2–*n*-hexane (50 : 50) for free-base porphyrins and $CHCl_3$–*n*-hexane (50 : 50) for metallated porphyrins. In monitoring the progress of the reactions, the heat source was removed for the duration of the sampling, and in the cases where highly volatile reagents were used, the reactions were chilled to 0 °C to prevent loss of the reagent. Upon the complete conversion of the starting material, the mixture was diluted with toluene (20 cm^3) and washed with water (20 cm^3 × 2). The organic layer was collected, dried and the residue was purified by column chromatography. This procedure was used to produce the following compounds.

***E*-5-(2-Methoxycarbonylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin ($H_2$14) and *E*,*E*-5,15-bis(2-methoxycarbonylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin ($H_2$18).** Produced from the reaction between **$H_2$6** (24.5 mg) and methyl acrylate (260 μL). CH_2Cl_2–*n*-hexane (50 : 50) was used as the initial eluent and the first fraction was collected. This fraction corresponded to **$H_2$14** (1.1 mg, 5%), which resulted from debromination of the intermediate bromo(alkenyl)porphyrin. Once the first fraction was collected, the eluent was changed to neat CH_2Cl_2 and a second fraction (**$H_2$18**) was collected and recrystallised from CH_2Cl_2–MeOH to yield a dark powder (17.8 mg, 72%). **$H_2$14**: δ_H 10.36 (1 H, d, ^3J 15.9, alkene-H), 10.21 (1 H, s, *meso*-H), 9.54 (2 H, d, ^3J 4.9, β-H), 9.31 (2 H, d, ^3J 4.9, β-H), 9.04 (2 H, d,

This journal is © The Royal Society of Chemistry 2006

^3J 4.9, β-H), 9.02 (2 H, d, ^3J 4.9, β-H), 8.10 (4 H, d, ^4J 1.7, *o*-Ar–H), 7.85 (2 H, t, ^4J 1.7, *p*-Ar–H), 6.84 (1 H, d, ^3J 15.9, alkene-H), 4.07 (3 H, s, CH_3), 1.57 (overlapping H_2O, s, ^{t}Bu–H), −2.80 (2 H, br s, N–H). **$H_2$18**: found: C, 78.8; H, 7.3; N, 6.5. Calc. for $C_{56}H_{63}N_4O_4$: C, 78.6; H, 7.4; N, 6.5; HRMS (ESI$^+$) m/z = 855.4837. Calc. MH$^+$ for $C_{56}H_{63}N_4O_4$ m/z = 855.4849; δ_H 10.24 (2 H, d, ^3J 15.7, alkene-H), 9.44 (4 H, d, ^3J 4.9, β-H), 8.92 (4 H, d, ^3J 4.9, β-H), 8.06 (4 H, d, ^4J 1.7, *o*-Ar–H), 7.85 (2 H, t, *p*-Ar–H), 6.84 (1 H, d, ^3J 15.9, alkene-H), 4.06 (6 H, s, CH_3), 1.56 (overlapping H_2O, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 433 (5.24), 533 (3.79), 580 (4.03), 674 (3.75) nm.

***E*-5-(2-Methoxycarbonylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni14) and *E*,*E*-5,15-bis(2-methoxycarbonylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni18).** Produced from the reaction between **Ni6** (26.1 mg) and methyl acrylate (260 μL). $CHCl_3$–*n*-hexane (50 : 50) was used as the initial eluent and the first fraction was collected. This fraction corresponded to **Ni14** (1.2 mg, 5%), which resulted from debromination of the intermediate bromo(alkenyl)porphyrin. Once the first fraction was isolated, the eluent was changed to $CHCl_3$–*n*-hexane (80 : 20) and a second fraction (**Ni18**) was collected and recrystallised from $CHCl_3$–MeOH to give a dark powder (18.5 mg, 70%). **Ni14**: δ_H 9.77 (1 H, d, ^3J 15.6, alkene-H), 9.71 (1 H, s, *meso*-H), 9.40 (2 H, d, ^3J 4.8, β-H), 9.07 (2 H, d, ^3J 4.8, β-H), 8.91 (2 H, d, ^3J 4.8, β-H), 8.84 (2 H, d, ^3J 4.8, β-H), 7.85 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.75 (2 H, t, ^4J 1.8, *p*-Ar–H), 6.36 (1 H, d, ^3J 15.6, alkene-H), 3.97 (3 H, s, CH_3), 1.50 (36 H, s, ^{t}Bu–H), −2.80 (2 H, br s, N–H). **Ni18**: HRMS (ESI$^+$) m/z = 910.4014. Calc. M$^+$ for $C_{56}H_{60}N_4O_4Ni$ m/z = 910.3968; found: C, 73.75; H, 6.8; N, 6.2. Calc. for $C_{56}H_{60}N_4O_4Ni$: C, 73.8; H, 6.6; N, 6.1%; δ_H 9.81 (2 H, d, ^3J 15.6, alkene-H), 9.30 (4 H, d, ^3J 4.9, β-H), 8.78 (4 H, d, ^3J 4.9, β-H), 7.79 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.74 (2 H, t, ^4J 1.8, *p*-Ar–H), 6.30 (1 H, d, ^3J 15.6, alkene-H), 3.95 (6 H, s, CH_3), 1.49 (36 H, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 441 (5.18), 569 (3.97), 616 (4.20) nm.

***E*,*E*-5,15-Bis(2-methoxycarbonylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (Zn18).** Produced as the main product from the reaction between **Zn6** (26.3 mg) and methyl acrylate (230 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. After the first band, which consisted of a number of unidentified porphyrins (5.1 mg), eluted from the column, the solvent was changed to $CHCl_3$–MeOH (99 : 1), and the second fraction (**Zn18**) was collected and recrystallised from $CHCl_3$(1% pyridine)–MeOH as a dark green powder (18.4 mg, 69%). HRMS (ESI$^+$) m/z = 916.3996. Calc. MH$^+$ for $C_{56}H_{60}N_4O_4Zn$ m/z = 916.3906; found: C, 73.3; H, 6.6; N, 6.1. Calc. for $C_{56}H_{60}N_4O_4Zn$: C, 73.2; H, 6.6; N, 6.1%; δ_H 10.22 (2 H, d, ^3J 15.8, alkene-H), 9.53 (4 H, d, ^3J 4.8, β-H), 9.04 (4 H, d, ^3J 4.8, β-H), 8.08 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.95 (2 H, t, *p*-Ar–H), 6.73 (1 H, d, ^3J 15.8, alkene-H), 3.97 (6 H, s, CH_3), 1.57 (36 H, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 439 (5.28), 571 (2.76), 629 (4.04).

***E*-5-(2-Phenylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin ($H_2$15) and *E*,*E*-5,15-bis(2-phenylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin ($H_2$19).** Produced from the reaction between **$H_2$6** (24.5 mg) and styrene (275 μL). CH_2Cl_2–*n*-hexane (30 : 70) was used as the initial eluent and the first fraction was collected. This fraction corresponded to **$H_2$15**, which resulted from debromination of the intermediate bromo(alkenyl)porphyrin (1.6 mg, 7.5%). Once **$H_2$15** was isolated, the eluent was changed to CH_2Cl_2–*n*-hexane (70 : 30) and a second fraction (**$H_2$19**) was collected and recrystallised from CH_2Cl_2–MeOH as a dark powder (17.8 mg, 69%). **$H_2$15**: δ_H 10.15 (1 H, s, *meso*-H), 9.76 (1 H, d, ^3J 15.9, alkene-H), 9.60 (2 H, d, ^3J 4.6, β-H), 9.31 (2 H, d, ^3J 4.6, β-H), 9.06 (2 H, d, ^3J 4.6, β-H), 9.04 (2 H, d, ^3J 4.6, β-H), 8.16 (4 H, d, ^4J 1.5, *o*-Ar–H), 7.98 (2 H, d, ^3J 7.3, *o*-phenylethenyl-H), 7.87 (2 H, t, ^4J 1.5, *p*-Ar–H), 7.60 (2 H, t, ^3J 7.3, *m*-phenylethenyl-H), 7.48 (1 H, t, ^3J 7.3, *p*-phenylethenyl-H), 7.44 (1 H, d, ^3J 15.9, alkene-H), 1.56 (overlapping H_2O, s, ^{t}Bu–H), −2.69 (2 H, br s, N–H). **$H_2$19**: found: C, 86.2; H, 7.55; N, 6.3. Calc. for $C_{64}H_{66}N_4$: C, 86.25; H, 7.5; N, 6.3%. δ_H 9.63 (2 H, d, ^3J 15.9, alkene-H), 9.46 (4 H, d, ^3J 4.6, β-H), 8.89 (4 H, d, ^3J 4.6, β-H), 8.09 (4 H, d, ^4J 1.5, *o*-Ar–H), 7.96 (4 H, d, ^3J 7.6, *o*-phenylethenyl-H), 7.83 (2 H, t, *p*-Ar–H), 7.58 (4 H, d, ^3J 7.6, *m*-phenylethenyl-H), 7.46 (2 H, d, ^3J 7.6, *p*-phenylethenyl-H), 7.46 (1 H, d, ^3J 15.9, alkene-H), 1.56 (overlapping H_2O, s, ^{t}Bu–H), −2.20 (2 H, s, N–H); UV–vis: λ_{max} (log ε) 437 (5.31), 535 (3.79), 584 (4.16), 677 (3.83) nm.

***E*-5-(2-Phenylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni15) and *E*,*E*-5,15-bis(2-phenylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni19).** Produced from the reaction between **Ni6** (26.1 mg) and styrene (275 μL). $CHCl_3$–*n*-hexane (20 : 80) was used as the initial eluent and the first fraction was collected. This fraction corresponded to **Ni15**, which resulted from debromination of the intermediate bromo(alkenyl)porphyrin (1.2 mg, 5%). Once the first fraction was isolated, the eluent was changed to neat $CHCl_3$ and a second fraction was collected (**Ni19**), which was recrystallised from $CHCl_3$–MeOH as a dark powder (19.2 mg, 70%). **Ni15**: δ_H 9.77 (1 H, d, ^3J 16.1, alkene-H), 9.64 (1 H, s, *meso*-H), 9.44 (2 H, d, ^3J 4.9, β-H), 9.38 (2 H, d, ^3J 4.7, β-H), 9.07 (2 H, d, ^3J 4.9, β-H), 8.90 (2 H, d, ^3J 4.7, β-H), 7.89 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.82 (2 H, d, ^3J 7.6, *o*-phenylethenyl-H), 7.76 (2 H, t, ^4J 1.8, *p*-Ar–H), 7.52 (2 H, t, ^3J 7.6, *m*-phenylethenyl-H), 7.40 (1 H, ^3J 7.6, *p*-phenylethenyl-H), 6.94 (1 H, d, ^3J 16.1, alkene-H), 1.50 (overlapping H_2O, s, ^{t}Bu–H). **Ni19**: found: C, 81.3; H, 6.9; N, 5.9. Calc. for $C_{64}H_{64}N_4Ni$: C, 81.1; H, 6.8; N, 5.9%. δ_H 9.30 (4 H, d, ^3J 4.9, β-H), 9.23 (2 H, d, ^3J 16.1, alkene-H), 8.74 (4 H, d, ^3J 4.9, β-H), 7.82 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.78 (4 H, d, ^3J 7.6, *o*-phenylethenyl-H), 7.71 (2 H, t, ^4J 1.8, *p*-Ar–H), 7.49 (2 H, t, ^3J 7.6, *m*-phenylethenyl-H), 7.37 (2 H, t, ^3J 7.6, *p*-phenylethenyl-H), 6.84 (1 H, d, ^3J 16.1, alkene-H), 1.48 (36 H, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 447 (5.22), 569 (4.04), 616 (4.23) nm.

***E*,*E*-5,15-Bis(2-phenylethenyl)-10,20-(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (Zn19).** Produced as the main product from the reaction between **Zn6** (26.3 mg) and styrene (275 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (40 : 60) as the eluent. After the first band, which consisted of a number of unidentified porphyrins (7.5 mg), eluted from the column, the solvent was changed to pure $CHCl_3$, and the second fraction was collected and recrystallised from $CHCl_3$(1% pyridine)–MeOH to yield **Zn19** as a dark powder (16.6 mg, 60%). Found: C, 80.5; H, 6.8; N, 5.9. Calc. for $C_{64}H_{64}N_4Zn$: C, 80.5; H, 6.8; N, 5.9%; δ_H 9.69 (2 H, d, ^3J 15.8, alkene-H), 9.60 (4 H, d, ^3J 4.8, β-H), 9.02 (4 H, d, ^3J 4.8, β-H), 8.10 (4 H, d, ^4J 1.8, *o*-Ar–H),

7.96 (4 H, d, ^3J 7.7, *o*-phenylethenyl-H), 7.82 (2 H, t, *p*-Ar–H), 7.58 (4 H, t, ^3J 7.7, *m*-phenylethenyl-H), 7.46 (2 H, t, ^3J 7.7, *p*-phenylethenyl-H), 7.41 (1 H, d, ^3J 15.8, alkene-H), 1.52 (36 H, s, ^{t}Bu–H); UV–vis: λ_{max} (log ε) 440 (5.31), 569 (3.91), 621 (4.11) nm.

***E*-5-(2-Cyanoethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni16), *Z*-5-(2-cyanoethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni17), *E*,*E*-5,15-bis(2-cyanoethenyl) - 10,20 - bis(3,5 - di - *tert* - butylphenyl)porphyrinatonickel(II) (Ni20), *E*,*Z*-5,15-bis(2-cyanoethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (Ni21) and *Z*,*Z*-5,15-bis(2-cyanoethenyl) - 10,20 - bis(3,5 - di - *tert* - butylphenyl)porphyrinatonickel(II) (Ni22).** This mixture was produced from the reaction between **Ni6** (26.1 mg) and acrylonitrile (190 μL). The crude product was treated by column chromatography using $CHCl_3$–*n*-hexane (70 : 30) as the eluent. The first fraction was collected, and NMR showed it to be a mixture of **Ni16** and **Ni17**, resulting from debromination of the starting material. These two compounds could not be separated further. **Ni16** (*ca.* 75%, NMR): δ_H 9.73 (1 H, s, *meso*-H), 9.68 (1 H, d, ^3J 16.2, alkene-H), 9.30 (2 H, d, ^3J 5.0, β-H), 9.07 (2 H, d, ^3J 4.8, β-H), 8.93 (2 H, d, ^3J 5.0, β-H), 8.84 (2 H, d, ^3J 4.8, β-H), 7.82 (4 H, d, ^3J 1.7, *o*-Ar–H), 7.76 (2 H, overlapped, *p*-Ar–H), 5.75 (2 H, d, ^3J 16.2, alkene-H), 1.48 (overlapped, s, ^{t}Bu–H); **Ni17** (*ca.* 25%): δ_H 9.79 (1 H, s, *meso*-H), 9.58 (1 H, d, ^3J 11.6, alkene-H), 9.22 (2 H, d, ^3J 5.0, β-H), 9.11 (2 H, d, ^3J 4.8, β-H), 9.00 (2 H, d, ^3J 5.0, β-H), 8.88 (2 H, d, ^3J 4.8, β-H), 7.86 (4 H, d, ^3J 1.7, *o*-Ar–H), 7.76 (2 H, overlapped, *p*-Ar–H), 6.44 (2 H, d, ^3J 11.6, alkene-H), 1.48 (36 H, s, ^{t}Bu–H). The major second band was collected and the residue was recrystallised using $CHCl_3$–MeOH to yield a dark powder. NMR studies showed the presence of three isomers, **Ni20** (*ca.* 65%, NMR), **Ni21** (*ca.* 25%) and **Ni22** (*ca.* 10%), which could not be separated further (total 17.5 mg, 72%). HRMS (ESI$^+$) m/z = 844.3770, 845.3814, 867.3665. Calc. M$^+$, MH$^+$, MNa$^+$ for $C_{54}H_{54}N_6Ni$ m/z = 844.3763, 845.3842, 867.3661, respectively; **Ni20**: δ_H 9.50 (2 H, d, ^3J 16.2, alkene-H), 9.19 (4 H, d, ^3J 4.9, β-H), 8.80 (4 H, d, ^3J 4.9, β-H), 7.76 (4 H, overlapped, *o*-Ar–H), 7.74 (2 H, overlapped, *p*-Ar–H), 5.69 (2 H, d, ^3J 16.2, alkene-H), 1.48 (36 H, s, ^{t}Bu–H); **Ni21**: δ_H 9.55 (1 H, d, ^3J 16.2, alkene-H), 9.43 (1 H, d, ^3J 11.6, *cis*-alkene-H), 9.29 (2 H, d, ^3J 4.9, *β*-H), 9.12 (2 H, d, ^3J 4.9, β-H), 8.83 (2 H, d, ^3J 4.9, β-H), 8.79 (2 H, d, ^3J 4.9, β-H), 7.76 (4 H, overlapped, *o*-Ar–H), 7.74 (2 H, overlapped, *p*-Ar–H), 6.36 (1 H, d, ^3J 11.6, *cis*-alkene-H), 5.37 (1 H, d, ^3J 16.2, alkene-H), 1.48 (36 H, s, ^{t}Bu–H); **Ni22**: δ_H 9.44 (2 H, d, ^3J 11.9, alkene-H), 9.15 (4 H, d, ^3J 4.9, β-H), 8.77 (4 H, d, ^3J 4.9, β-H), 7.76 (4 H, overlapped, *o*-Ar–H), 7.74 (2 H, overlapped, *p*-Ar–H), 6.39 (2 H, d, ^3J 11.6, alkene-H), 1.48 (36 H, s, ^{t}Bu–H).

***E*-5-(2-Cyanoethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (Zn16), *E*,*E*-5,15-bis(2-cyanoethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (Zn21) and *E*,*Z*-5,15-bis(2-cyanoethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (Zn22).** Produced from the reaction between **Zn6** (26.3 mg) and acrylonitrile (190 μL). $CHCl_3$–*n*-hexane (60 : 40) was used as the initial eluent and the first fraction was collected. This fraction corresponded to **Zn16**, which resulted from debromination of the intermediate bromo(alkenyl)porphyrin (1.9 mg, 8%). **Zn16**: δ_H 10.29 (1 H, s, *meso*-H), 10.15 (1 H, d, ^3J 16.4, alkene-H), 9.55 (2 H, d, ^3J 4.9, β-H), 9.41 (2 H, d, ^3J 4.4, β-H), 9.17 (2 H, d, ^3J 4.9, β-H), 9.12 (2 H, d, ^3J 4.4, β-H), 8.09 (4 H, d, ^4J 2.0, *o*-Ar–H), 7.85 (2 H, d, ^3J 2.0, *p*-Ar–H), 6.29 (1 H, d, ^3J 16.4, alkene-H), 1.56 (overlapping H_2O, s, ^{t}Bu–H). Once **Zn16** was isolated, the eluent was changed to neat $CHCl_3$ and a second fraction was collected. NMR studies showed the presence of two isomers, **Zn21** (*ca.* 90%, NMR), and **Zn22** (*ca.* 10%), which could not be separated further. This fraction was recrystallised from $CHCl_3$(1% pyridine)–MeOH, yielding a dark powder (15.8 mg, 64%). MS (LDI$^+$) m/z = 850.25. Calc. M$^+$ for $C_{54}H_{54}N_6Zn$ m/z = 850.4. **Zn21**: δ_H 9.99 (2 H, d, ^3J 16.1, alkene-H), 9.36 (4 H, d, ^3J 4.7, β-H), 8.95 (4 H, d, ^3J 4.7, β-H), 8.09 (4 H, overlapped, *o*-Ar–H), 7.83 (2 H, overlapped, *p*-Ar–H), 6.04 (2 H, d, ^3J 16.1, alkene-H), 1.56 (overlapping H_2O, s, ^{t}Bu–H). **Zn22**: δ_H 10.02 (2 H, d, ^3J 16.4, alkene-H), 9.77 (1 H, d, ^3J 10.5, alkene-H), 9.39 (2 H, d, ^3J 4.6, β-H), 9.34 (2 H, d, ^3J 4.9, β-H), 8.96 (2 H, d, ^3J 4.6, β-H), 8.94 (2 H, d, ^3J 4.9, β-H), 7.94 (4 H, overlapped, *o*-Ar–H), 7.81 (2 H, overlapped, *p*-Ar–H), 6.66 (1 H, d, ^3J 10.5, alkene-H), 6.13 (1 H, d, ^3J 16.4, alkene-H), 1.56 (overlapped, s, ^{t}Bu–H).

General procedure for Heck coupling using vinylporphyrins

Vinylporphyrin (0.019 mmol), palladium acetate (1.0 mg, 0.004 mmol, 20 mol%), triphenylphosphine (2.6 mg, 0.01 mmol) and K_2CO_3 (4.3 mg, 0.024 mmol) were added to a Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (1 cm^3), dry toluene (1 cm^3) and the halogen reagent (50-fold excess). The mixture was degassed *via* three freeze–pump–thaw cycles before the vessel was purged with argon again. The Schlenk flask was sealed and heated to 105 °C and allowed to stir for 48 h. Each reaction was monitored by TLC using $CHCl_3$–*n*-hexane (50 : 50). After 48 h, the mixture was diluted with toluene (10 cm^3) and washed with water (10 cm^3 × 2). The organic layer was collected, dried and the residue was subjected to column chromatography. The bands containing the desired porphyrins were collected and recrystallised using $CHCl_3$–MeOH. This procedure was used to produce the following compounds.

5 - (1 - Phenylethenyl) - 10,15,20 - triphenylporphyrinatonickel(II) (23). Produced from the reaction between **Ni8** (11.9 mg) and iodobenzene (106 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (10 : 90). The first fraction contained unreacted starting material (2.0 mg, 17%). The second fraction contained the expected product **Ni10** (7.2 mg, 54%). The third fraction contained **23** (2.7 mg, 20%). HRMS (ESI$^+$) m/z = 696.1827. Calc. M$^+$ for $C_{46}H_{30}N_4Ni$ m/z = 696.1824; δ_H 9.10 (2 H, d, ^3J 5.1, β-H), 8.73 (2 H, d, ^3J 5.1, β-H), 8.73 (4 H, br s, β-H), 8.00 (6 H, m, *o*-Ph–H), 7.67 (9 H, m, *m*,*p*-Ph–H), 7.43 (2 H, m, *o*-phenylethenyl-H), 7.23 (3 H, m, *m*,*p*-phenylethenyl-H), 6.83 (1 H, d, ^2J 1.1, alkene-H (*cis* to porphyrin)), 5.91 (1 H, d, ^2J 1.1, alkene-H (*trans* to porphyrin)). Once **27** eluted from the column, the solvent was changed to neat $CHCl_3$ and a fourth fraction was collected. NMR studies showed it to be the aldehyde **Ni3** (<1 mg, ~5%).

5-(1-Phenylethenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (24) and *E*-2-(2-phenylethenyl)-5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (25). Produced from the reaction between **Ni13** (14.6 mg) and iodobenzene (106 μL). The product was purified by column chromatography using $CHCl_3$–*n*-hexane (10 : 90). The first fraction contained unreacted starting

This journal is © The Royal Society of Chemistry 2006

material **Ni13** (3.5 mg, 24%). The second and third fractions contained mixtures of **Ni15**, **24**, and **25**, which could not be separated further (9.2 mg, 68%). MS (LDI$^+$) m/z = 844.94. Calc. M$^+$ for $C_{56}H_{58}N_4Ni$ m/z = 844.40. **24**: 30% (estimated from NMR). δ_H 9.84 (1 H, s, *meso*-H), 9.16 (2 H, d, ^3J 4.9, β-H), 9.14 (2 H, d, ^3J 4.9, β-H), 8.93 (2 H, d, ^3J 4.9, β-H), 8.84 (2 H, d, ^3J 4.9, β-H), 7.88 (overlapped, *o*-Ar–H), 7.75 (overlapped, *p*-Ar–H), 7.42 (overlapped, *o*-phenylethenyl-H), 7.22 (3 H, m, *m*,*p*-phenylethenyl-H), 6.85 (1 H, d, ^2J 1.1, alkene-H (*cis* to porphyrin)), 5.94 (1 H, d, ^2J 1.1, alkene-H (*trans* to porphyrin)), 1.51 (36 H, s, ^{t}Bu–H); **25**: δ_H 10.13 (1 H, s, *meso*-H), 9.88 (1 H, s, *meso*-H), 9.21 (1 H, d, ^3J 4.7, β-H), 9.15 (2 H, d, ^3J 4.7, β-H), 9.11 (1 H, s, β-H), 8.98 (1 H, d, ^3J 4.7, β-H), 8.96 (1 H, d, ^3J 4.7, β-H), 8.94 (1 H, d, ^3J 4.7, β-H), 8.63 (1 H, d, ^3J 16.1, alkene-H), 7.97 (2 H, d, ^3J 1.7, *o*-Ar–H), 7.93 (2 H, d, ^4J 1.7, *o*-Ar–H), 7.83 (2 H, d, ^3J 7.6, *o*-phenylethenyl-H), 7.77 (1 H, t, ^4J 1.7, *p*-Ar–H), 7.52 (2 H, t, ^3J 7.6, *m*-phenylethenyl-H), 7.38 (2 H, t, ^3J 7.6, *o*-phenylethenyl), 1.54 (18 H, s, ^{t}Bu–H), 1.52 (18 H, s, ^{t}Bu–H). The solvent was changed to neat $CHCl_3$ and a fourth fraction was collected; NMR studies showed it to be **Ni7** (<1 mg, ~5%).

***E*-5-[2-(Anthracen-9-yl)ethenyl]-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (26) and *E*-2-[2-(anthracen-9-yl)-ethenyl]-5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II) (27).** Produced from the reaction between **Ni13** (14.6 mg) and 9-bromoanthracene (15 mg, 3.1-fold excess) using 2-P(*t*-Bu)$_2$biphenyl as phosphine ligand. The product mixture was isolated by column chromatography using $CHCl_3$–*n*-hexane (30 : 70) as the eluent. The first fraction contained unreacted starting material **Ni13** (7.3 mg, 50%), while the second fraction corresponded to **26**, with a minor amount of the *β*-substituted analogue **27** and other impurities that could not be removed by chromatography. This mixture was recrystallised twice from $CHCl_3$–MeOH to yield a dark red powder (2.0 mg, 11%). MS (LDI$^+$) m/z = 945.27. Calc. M$^+$ for $C_{56}H_{58}N_4Ni$ m/z = 945.43. **26**: δ_H 9.72 (1 H, s, *meso*-H), 9.61 (2 H, d, ^3J 4.9, β-H), 9.29 (1 H, d, ^3J 15.9, alkene-H), 9.09 (2 H, d, ^3J 4.9, β-H), 8.93 (2 H, d, ^3J 4.9, β-H), 8.89 (2 H, d, ^3J 4.9, β-H), 8.69 (2 H, m, anthracene-H), 8.53 (2 H, s, anthracene-H), 8.11 (2 H, m, anthracene-H), 7.89 (4 H, d, ^4J 1.8, *o*-Ar–H), 7.74 (2 H, d, ^4J 1.8, *p*-Ar–H), 7.53 (4 H, m, anthracene-H), 7.53 (1 H, d, ^3J 15.9, alkene-H), 1.49 (36 H, ^{t}Bu–H). The β-alkenylanthracene **27** could not be fully characterised by NMR because of the number of overlapping peaks in the spectrum.

Preparation of *meso*,β-porphyrin dyads by Heck coupling. Porphyrin **Ni13** (14.6 mg, 0.019 mmol), bromoporphyrin (0.015 mmol), palladium acetate (1.0 mg, 0.004 mmol, 20 mol%), di-*tert*-butylbiphenylphosphine (3.0 mg, 0.01 mmol) and K_2CO_3 (4.3 mg, 0.024 mmol) were added to a Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (1.5 cm^3), and dry toluene (1.5 cm^3). The mixture was degassed *via* three freeze–pump–thaw cycles before the vessel was purged with argon again. The Schlenk flask was sealed and heated to 105 °C and allowed to stir for 72 h. Each reaction was monitored by TLC using CH_2Cl_2–*n*-hexane (50 : 50) for free base bromoporphyrin and $CHCl_3$–*n*-hexane (50 : 50) for metallated bromoporphyrins. After 72 h, TLC showed the complete consumption of bromoporphyrin, so the mixture was diluted with toluene (10 cm^3) and washed with water (10 cm^3 × 2). The organic layer was collected, dried and the residue was subjected to column chromatography. This procedure was used to produce the following compounds.

***E*-1-[5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II)-2-yl]-2-[(10,15,20-triphenyl)porphyrin-5-yl]ethene (29).** Produced from **H$_2$2** (9.2 mg) as the bromoporphyrin partner. The product was purified using CH_2Cl_2–*n*-hexane (50 : 50) as the eluent. The first band contained unreacted starting material **Ni13** (10.5 mg, 71%). The second fraction contained the product **29**, which was recrystallised from CH_2Cl_2–MeOH to give a dark powder (4.4 mg, 23%). HRMS (ESI$^+$) m/z = 1305.4376. Calc. MH$^+$ for $C_{88}H_{79}N_8Ni$ m/z = 1305.4781; δ_H 10.30 (1 H, d, ^3J 15.4, 2-alkene-H), 10.30 (1 H, s, 20-*meso*-H, NiDAP), 9.92 (1 H, s, 10-*meso*-H, NiDAP), 9.80 (2 H, d, ^3J 4.7, β-H, H$_2$TriPP), 9.65 (1 H, s, β-H, NiDAP), 9.22 (1 H, d, ^3J 4.9, β-H, NiDAP), 9.19 (1 H, d, ^3J 4.9, β-H, NiDAP), 9.16 (1 H, d, ^3J 4.9, β-H, NiDAP), 9.07 (1 H, d, ^3J 4.9, β-H, NiDAP), 9.00 (1 H, d, ^3J 4.9, β-H, NiDAP), 8.99 (2 H, d, ^3J 4.7, β-H, H$_2$TriPP), 8.97 (1 H, d, ^3J 4.9, β-H, NiDAP), 8.92 (1 H, d, ^3J 15.4, β-H, 1-alkene-H), 8.84 (4 H, br s, β-H, H$_2$TriPP), 8.28 (4 H, m, *o*-Ph–H, H$_2$TriPP), 8.24 (2 H, m, *o*-Ph–H, H$_2$TriPP), 8.18 (2 H, d, ^4J 1.7, *o*-Ar–H, NiDAP), 7.95 (2 H, d, ^4J 1.7, *o*-Ar–H, NiDAP), 7.88 (1 H, t, ^4J 1.7, *p*-Ar–H, NiDAP), 7.79 (1 H, overlapped, *p*-Ar–H, NiDAP), 7.79 (9 H, m, *m*,*p*-Ph–H, H$_2$TriPP), 1.64 (18 H, s, ^{t}Bu–H, NiDAP), 1.52 (18 H, s, ^{t}Bu–H, NiDAP), −2.30 (2 H, br s, N–H, H$_2$TriPP); UV–vis: λ_{max} (log ε) 425 (5.30), 522 (4.45), 594 (4.55), 673 (4.23) nm. A third and fourth fraction were also collected, containing **H$_2$1** (5.8 mg, 72% from **H$_2$2**) and **Ni7** (<1 mg, ~5%), respectively.

***E*-1-[5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II)-2-yl]-2-[(10,15,20-triphenyl)porphyrinatonickel(II)-5-yl]ethene (30).** Produced from **Ni2** (10.1 mg) as the bromoporphyrin reagent. The product was purified by column chromatography using $CHCl_3$–*n*-hexane (50 : 50) as the eluent. The first band eluted contained unreacted starting material **Ni13** (10.1 mg, 69%). The second fraction contained the product **30**, which was recrystallised from $CHCl_3$–MeOH, yielding a dark powder (6.7 mg, 33%). MS (LDI$^+$) m/z = 1360.54. Calc. M$^+$ for $C_{88}H_{76}N_8Ni_2$ m/z = 1360.49; δ_H 10.03 (1 H, s, 20-*meso*-H, NiDAP), 9.90 (1 H, s, 10-*meso*-H, NiDAP), 9.89 (1 H, d, ^3J 15.7, 2-alkene-H), 9.67 (2 H, d, ^3J 4.9, β-H, NiTriPP), 9.54 (1 H, s, β-H, NiDAP), 9.19 (1 H, d, ^3J 4.9, β-H, NiDAP), 9.16 (1 H, d, ^3J 4.9, β-H, NiDAP), 9.05 (1 H, d, ^3J 4.9, β-H, NiDAP), 9.03 (1 H, d, ^3J 4.9, β-H, NiDAP), 8.96 (1 H, d, ^3J 4.9, β-H, NiDAP), 8.90 (1 H, d, ^3J 4.9, β-H, NiDAP), 8.89 (2 H, d, ^3J 4.9, β-H, NiTriPP), 8.70 (2 H, d, ^3J 4.9, β-H, NiTriPP), 8.68 (2 H, d, ^3J 4.9, β-H, NiTriPP), 8.36 (1 H, d, ^3J 15.7, 1-alkene-H, NiDAP), 8.13 (2 H, d, ^4J 1.7, *o*-Ar–H, NiDAP), 8.04 (4 H, m, *o*-Ph–H, NiTriPP), 8.01 (2 H, m, *o*-Ph–H, NiTriPP), 7.90 (2 H, d, ^4J 1.7, *o*-Ar–H, NiDAP), 7.88 (1 H, t, ^4J 1.7, *p*-Ar–H, NiDAP), 7.75 (1 H, t, *p*-Ar–H, NiDAP), 7.70 (9 H, m, *m*,*p*-Ph–H, NiTriPP), 1.64 (18 H, s, ^{t}Bu–H, NiDAP), 1.49 (18 H, s, ^{t}Bu–H, NiDAP); UV–vis: λ_{max} (log ε) 422 (5.29), 458 (5.09, shoulder on Soret band), 526 (4.53), 560 (4.40), 619 (4.47) nm. A third and fourth fraction were also collected, containing **Ni1** (5.2 mg, 65% from **Ni2**) and **Ni7** (<1 mg, ~5%), respectively.

***E*-1-[5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonickel(II)-2-yl]-2-[(10,15,20-triphenyl)porphyrinatozinc(II)-5-yl]ethene (31).** Produced from **Zn2** (10.2 mg) as the bromoporphyrin reagent. The product was purified by column chromatography using

$CHCl_3$–*n*-hexane (50 : 50) as the eluent. The first band eluted contained unreacted starting material **Ni13** (10.1 mg, 69%). The second fraction contained the product **31**, which was recrystallised from $CHCl_3$–MeOH to give shiny dark plates (3.1 mg, 15%). MS (LDI$^+$) m/z = 1367.38. Calc. MH$^+$ for $C_{88}H_{76}N_8NiZn$ m/z = 1367.49; δ_H 10.44 (1 H, d, ^3J 15.7, 2-alkene-H), 10.33 (1 H, s, 20-*meso*-H, NiDAP), 9.92 (1 H, s, 10-*meso*-H, NiDAP), 9.87 (2 H, d, ^3J 4.7, β-H, ZnTriPP), 9.63 (1 H, s, β-H, NiDAP), 9.23 (1 H, d, ^3J 4.7, β-H, NiDAP), 9.20 (1 H, d, ^3J 4.7, β-H, NiDAP), 9.17 (1 H, d, ^3J 4.7, β-H, NiDAP), 9.08 (1 H, d, ^3J 4.7, β-H, NiDAP), 9.02 (2 H, d, ^3J 4.7, β-H, ZnTriPP), 9.00 (1 H, d, ^3J 4.7, β-H, NiDAP), 8.98 (1 H, d, ^3J 4.7, β-H, NiDAP), 8.88 (1 H, d, ^3J 15.7, 1-alkene-H), 8.85 (4 H, br s, β-H, ZnTriPP), 8.26 (4 H, m, *o*-Ph–H, ZnTriPP), 8.21 (2 H, m, *o*-Ph–H, ZnTriPP), 8.18 (2 H, d, ^4J 1.7, *o*-Ar–H, NiDAP), 7.95 (2 H, d, ^4J 1.7, *o*-Ar–H, NiDAP), 7.87 (1 H, t, ^4J 1.7, *p*-Ar–H, NiDAP), 7.75 (1 H, overlapped, *p*-Ar–H, NiDAP), 7.75 (9 H, m, *m*,*p*-Ph–H, ZnTriPP), 1.63 (18 H, s, ^{t}Bu–H, NiDAP), 1.52 (18 H, s, ^{t}Bu–H, NiDAP); UV-vis: λ_{max} (log ε) 425 (5.26), 524 (4.33), 561 (4.39), 620 (4.43) nm. A third and fourth fraction were also collected, corresponding to **Zn1** (7.2 mg, 80% from **Zn2**) and **Ni7** (<1 mg, ~5%), respectively.

Acknowledgements

We thank Queensland University of Technology for a postgraduate scholarship for OBL, and DPA thanks Prof. H. L. Anderson for provision of data prior to publication.

References

1 For reviews, see: W. M. Sharman and J. E. van Lier, *J. Porphyrins Phthalocyanines*, 2000, **4**, 441–453; J. Setsune, *J. Porphyrins Phthalocyanines*, 2004, **8**, 93–102.
2 S. G. DiMagno, V. S.-Y. Lin and M. J. Therien, *J. Org. Chem.*, 1993, **58**, 5983–5993.
3 M. J. Therien and S. G. DiMagno, *US Pat.*, 5 371 199, 1994.
4 X. Shi, R. Amin and L. S. Liebeskind, *J. Org. Chem.*, 2000, **65**, 1650–1664.
5 E. Blart, F. Suzunet, J.-P. Quintard and F. Odobel, *J. Porphyrins Phthalocyanines*, 2003, **7**, 207–213.
6 K. M. Smith, K. C. Langry and O. M. Minnetian, *J. Org. Chem.*, 1984, **49**, 4602–4609.
7 X. Jiang, R. K. Pandey and K. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1607–1615; I. K. Morris, K. M. Snow, N. W. Smith and K. M. Smith, *J. Org. Chem.*, 1990, **55**, 1231–1236; O. H. Minnetian, I. K. Morris, K. M. Snow and K. M. Smith, *J. Org. Chem.*, 1989, **54**, 5567–5574.
8 R. Gauler, R. Keuper, A. Winter and N. Risch, *ARKIVOC*, 2004, 48–56; N. Risch, R. Gauler and R. Keuper, *Tetrahedron Lett.*, 1999, **40**, 2925–2926; R. Gauler and N. Risch, *Eur. J. Inorg. Chem.*, 1998, 1193–1200.
9 F. Odobel, S. Suresh, E. Blart, Y. Nicolas, J. P. Quintard, P. Janvier, J. Y. Le Questel, B. Illien, D. Rondeau, P. Richomme, T. Haupl, S. Wallin and L. Hammarstrom, *Chem.–Eur. J.*, 2002, **8**, 3027–3046.
10 M. G. H. Vicente and K. M. Smith, *J. Org. Chem.*, 1991, **56**, 4407–4418.
11 See, for example: D. P. Arnold, R. Gaete-Holmes, A. W. Johnson, A. R. P. Smith and G. A. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1660–1670.
12 H. J. Callot, *Bull. Soc. Chim. Fr.*, 1973, 3413–3416.
13 A. Ando, M. Yamazuki, M. Komura, Y. Sano, N. Hattori, M. Omote and I. Kumadaki, *Heterocycles*, 1999, **50**, 913–918.
14 D. P. Arnold, A. W. Johnson and M. Mahendran, *J. Chem. Soc., Perkin Trans. 1*, 1978, 366–370.
15 A. K. Burrell and D. L. Officer, *Synlett*, 1998, 1297–1307 and references cited therein.
16 M. Castella, F. Calahorra, D. Sainz and D. Velasco, *Org. Lett.*, 2001, **3**, 541–544.
17 M. Castella, F. López-Calahorra, D. Velsaco and H. Finkelmann, *Liq. Cryst.*, 2002, **29**, 559–565.
18 T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwick and H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 2002, 320–329.
19 See, for example: V. V. Borovkov, G. V. Ponomarev, A. Ishida, T. Kaneda and Y. Sakata, *Chem. Lett.*, 1993, 1409–1412; R. Kitagawa, Y. Kai, G. V. Ponomarev, K. Sugiura, V. V. Borovkov, T. Kaneda and Y. Sakata, *Chem. Lett.*, 1993, 1071–1074; G. V. Ponomarev, V. V. Borovkov, K. Sugiura, Y. Sakata and A. M. Shulga, *Tetrahedron Lett.*, 1993, **34**, 2153–2156; M. O. Senge, M. G. H. Vicente, K. R. Gerzevske, T. P. Forsyth and K. M. Smith, *Inorg. Chem.*, 1994, **33**, 5625–5638; H. Higuchi, K. Shimizu, J. Ojima, K. Sugiura and Y. Sakata, *Tetrahedron Lett.*, 1995, **36**, 5359–5362; D. P. Arnold, V. V. Borovkov and G. V. Ponomarev, *Chem. Lett.*, 1996, 485–486; M. Chachisvilis, V. S. Chirvony, A. M. Shulga, B. Källebring, S. Larsson and V. Sundström, *J. Phys. Chem.*, 1996, **100**, 13857–13866; M. Chachisvilis, V. S. Chirvony, A. M. Shulga, B. Källebring, S. Larsson and V. Sundström, *J. Phys. Chem.*, 1996, **100**, 13867–13873; H. Higuchi, K. Shimizu, M. Takeuchi, J. Ojima, K. I. Sugiura and Y. Sakata, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1923–1933.
20 M. J. Frampton, H. Akdas, A. R. Cowley, J. E. Rogers, J. E. Slagle, P. A. Fleitz, M. Drobizhev, A. Rebane and H. L. Anderson, *Org. Lett.*, 2005, **7**, 5365–5368.
21 O. B. Locos and D. P. Arnold, unpublished results.
22 A. Kato, R. D. Hartnell, M. Yamashita, H. Miyasaka, K.-i. Sugiura and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2004, **8**, 1222–1227.
23 R. F. Heck, in *Palladium Reagents in Organic Synthesis*, ed. R. F. Heck, Academic Press, London, 1982, pp. 345–389.
24 See, for example: V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105–1111; V. S. Y. Lin and M. J. Therien, *Chem.–Eur. J.*, 1996, **1**, 645–651; H. L. Anderson, *Chem. Commun.*, 1999, 2323–2330; J. J. Piet, P. N. Taylor, B. R. Wegewijs, H. L. Anderson, A. Osuka and J. M. Warman, *J. Phys. Chem. B*, 2001, **105**, 97–104; D. P. Arnold, G. A. Heath and D. A. James, *New J. Chem.*, 1998, **22**, 1377–1387; D. P. Arnold, G. A. Heath and D. A. James, *J. Porphyrins Phthalocyanines*, 1999, **3**, 5–31; G. J. Wilson and D. P. Arnold, *J. Phys. Chem. A*, 2005, **109**, 6104–6113.
25 S. Braese and A. De Meijere, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. E-i. Negishi, John Wiley & Sons, New York, 2002, vol. 1, pp. 1123–1132.
26 A. Kato, D. P. Arnold, H. Miyasaka, M. Yamashita and K.-i. Sugiura, manuscript in preparation.
27 S. Fox and R. W. Boyle, *Chem. Commun.*, 2004, 1322–1323.
28 A. N. Cammidge, P. J. Scaife, G. Berber and D. L. Hughes, *Org. Lett.*, 2005, **7**, 3413–3416.
29 H. Hata, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2005, **127**, 8264–8265.
30 M. O. Senge and X. D. Feng, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3615–3621.
31 R. D. Hartnell, A. J. Edwards and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2002, **6**, 695–707.
32 K. Tomizaki, A. B. Lysenko, M. Taniguchi and J. S. Lindsey, *Tetrahedron*, 2004, **60**, 2011–2023.
33 M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405–2413.
34 T. S. Balaban, R. Goddard, M. Linke-Schaetzel and J.-M. Lehn, *J. Am. Chem. Soc.*, 2003, **125**, 4233–4239.
35 S. N. Kuester, M. M. McGuire and S. M. Drew, *J. Electroanal. Chem.*, 1998, **452**, 13–18.
36 A. W. Johnson and D. Oldfield, *J. Chem. Soc. C*, 1966, 794–798.
37 D. P. Arnold, R. C. Bott, H. Eldridge, F. M. Elms, G. Smith and M. Zojaji, *Aust. J. Chem.*, 1997, **50**, 495–503.
38 T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono and A. Osuka, *Angew. Chem., Int. Ed.*, 1999, **38**, 176–179.
39 H. Imahori and Y. Sakata, *Chem. Lett.*, 1996, 199–200.
40 M. J. Hodgson, M. App. Sc. Thesis, Queensland University of Technology, 2005.
41 Y. Xu, L. Jaquinod, A. Wickramasinghe and K. M. Smith, *Tetrahedron Lett.*, 2003, **44**, 7753–7756.

This journal is © The Royal Society of Chemistry 2006