Peripherally Metallated Porphyrins: the First Examples of *meso*-η¹-Palladio(II) and -Platinio(II) Complexes with Chelating Diamine Ligands

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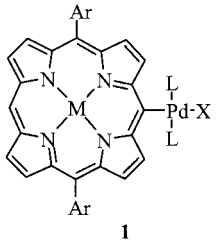
The oxidative addition of bis(dibenzylideneacetone)platinum(0) to *meso*-bromo-5,15-diarylporphyrins in the presence of PPh_3 has been shown to be an effective way of synthesising η¹-organoplatinum porphyrins in high yields. This methodology has been extended to synthesise various palladio- and platinioporphyrins that utilise bidentate nitrogen donor ligands [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) and 2,2′-bipyridyl (bpy)] in order to enforce a *cis* configuration at the metal centre. The products were characterised by multinuclear NMR and UV-Vis spectroscopy as well as fast-atom bombardment and high-resolution electrospray ionisation mass spectroscopy.

Introduction

There has been considerable interest in the investigation of the synthesis and properties of various types of organometallic porphyrins. Traditionally the "organometallic" fragment of the molecule involves a metal−carbon bond between the metal bound in the central cavity of the porphyrin macrocycle and either an alkyl or aryl moiety that has either σ- or π-bonding character.[1] These investigations have often been directed towards the catalytic activation of small molecules, usually in a biomimetic sense. The recent discovery and investigation of porphyrinoid macrocycles with modified cavities, such as inverted or "N-confused" porphyrins[2] and azuliporphyrins,[3] has somewhat increased the number of examples in this area; however, the centrally coordinated metal is still intimately involved in the organometallic character of the molecule. There are also several examples of porphyrinoid compounds covalently bound to organometallic fragments such as metallocenes,[4] or with one of the porphyrin pyrrole rings participating in an η⁵-pyrrolyl−metal arrangement.[5]

Besides the examples discussed above, there is also a small group of peripherally metallated η¹-organometallic porphyrins. Examples in this area include mercurated porphyrins,[6] *meso*-tellurium trichloride appended porphyrins,[7] porphyrinyl boronates[8] and the recent Grignard-like metalloporphyrin of Therien.[9] Our publications have been the only reports of isolated η¹-organopalladio- and organoplatinioporphyrins[10−13] and these are the only examples with transition metals directly bonded to porphyrin carbons. Compounds of type **1** are involved in the catalytic reactions for the coupling of *meso*-haloporphyrins with simple terminal alkynes, alkynylstannanes or alkynylzincs and alkenylorganometallics.[14−17] The key initial step in these couplings is the oxidative addition of the *meso*-carbon−halogen bond to a zerovalent palladium species, usually a bis(phosphane) moiety. Several years ago, we serendipitously isolated the resulting *meso*-η¹-organopalladium(II) porphyrin from one of these reactions[12] and have recently embarked on a systematic study of this type of palladium compound and their more robust organoplatinum(II) analogues. One possible area of interest in *meso*-η¹-platinioporphyrins relates to the combination of the cytotoxicity of the *cis*-platinum centre and the tumour selectivity and photodynamic effect of the porphyrin.[18−20] In this paper we report our synthesis for the first time of *meso*-η¹-organometallic porphyrins of palladium(II) and platinum(II) with chelating nitrogen ligands, namely *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) and 2,2′-bipyridyl (bpy).



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Results and Discussion

Syntheses of Palladio- and Platinioporphyrins

As part of our ongoing investigation of η¹-organometallic *meso*-platinio- and palladioporphyrins, we were very

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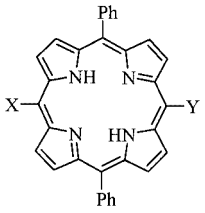
keen to synthesise platinioporphyrins with chelating ligands, in order to enforce a *cis* arrangement of the platinum fragment. This had been achieved for the palladioporphyrins by the use of various diphosphanes, for example, 1,2-bis(diphenylphosphanyl)ethane (dppe), 1,3-bis(diphenylphosphanyl)propane (dppp) and 1,1′-bis(diphenylphosphanyl)ferrocene (dppf).[13] These η^1-organometallic *meso*-palladioporphyrins were readily synthesised by the oxidative addition of a zerovalent palladium species into a 10-bromo-5,15-diarylporphyrin. The zerovalent palladium species is usually prepared in situ by the addition of the convenient palladium precursor, $Pd_2(dba)_3$ (dba = dibenzylideneacetone, 1,5-diphenylpenta-1,4-dien-3-one) to the bidentate phosphane in degassed toluene at 105 °C, to which the bromoporphyrin is later added. Under these conditions, the reaction is usually completed within 30 minutes. After removal of the solvent and recrystallisation, the desired η^1-organometallic *meso*-palladioporphyrin is obtained in high yields (> 80 %).

Having developed this efficient methodology for our palladioporphyrin analogues, we naturally sought to prepare the analogous platinioporphyrin species. After several attempts it was soon apparent that the intervening zerovalent platinum species that is formed in situ from $Pt(dba)_2$ and a diphosphane (dppe or dppp) is too stable to undergo the oxidative addition step with the haloporphyrin. This appears to be because the redistribution of ligands on Pt favours the apparently inert $18e^-$ species [e.g. $Pt(dppe)_2$]. The analogous reaction was also attempted several times with less stable, more sterically hindered zerovalent platinum species prepared from larger bidentate diphosphanes, namely 2,2′-bis(di-*p*-tolylphosphanyl)-1,1′-binaphthyl (tol-BINAP) and dppf. However, these also failed to undergo the oxidative addition step with a haloporphyrin to give the desired platinioporphyrin. In order to ensure that the $Pt(dba)_2$ substance that was being used throughout the investigations above was of high quality and not the cause of problematic side-reactions, we carried out a control reaction between monodentate triphenylphosphane, $Pt(dba)_2$ and a bromoporphyrin **2** (Table 1 shows the structures of compounds **2**−**14**). This reaction proceeded smoothly, as evident from TLC that the $Pt(dba)_2$ was consumed to form either $Pt(PPh_3)_3$ or $Pt(dba)(PPh_3)_2$ in situ and that **2** was being converted into a much more polar compound. Continual TLC analysis showed that the initial more polar compound was slowly being converted into a slightly more mobile product. This observation is in line with previous reports[10,11] that the initially formed product of the oxidative addition step is the *cis* isomer **3**, which with continued heating, isomerises slowly (ca. 6 hours) to the *trans* isomer **4**. This method has the distinct advantage over the previous method[10,11] that it avoids the use of air- and moisture-sensitive $Pt(PPh_3)_3$, which if not freshly prepared may be of doubtful quality.

With the viability of the dba-ligand method proven, as explained above, a different tactic was attempted in order to prepare the desired *cis*-orientated organoplatinum porphyrins. It is well-known that aromatic iodo groups undergo palladium(0)-catalysed coupling reactions at a much greater rate than those of bromo analogues.[21] This has also been shown to be true for 5-bromo-15-iodo-10,20-diarylporphyrins, which are found to undergo palladium(0)-catalysed coupling reactions at the iodo-substituted position preferentially over the bromo-substituted position.[17,22] With this in mind, the oxidative addition reactions of the platinum(0) diphosphane precursors were repeated with a range of iodoporphyrins; unfortunately, these also failed to give the desired η^1-organometallic porphyrins.

Table 1. Correspondence of compound numbers and structures



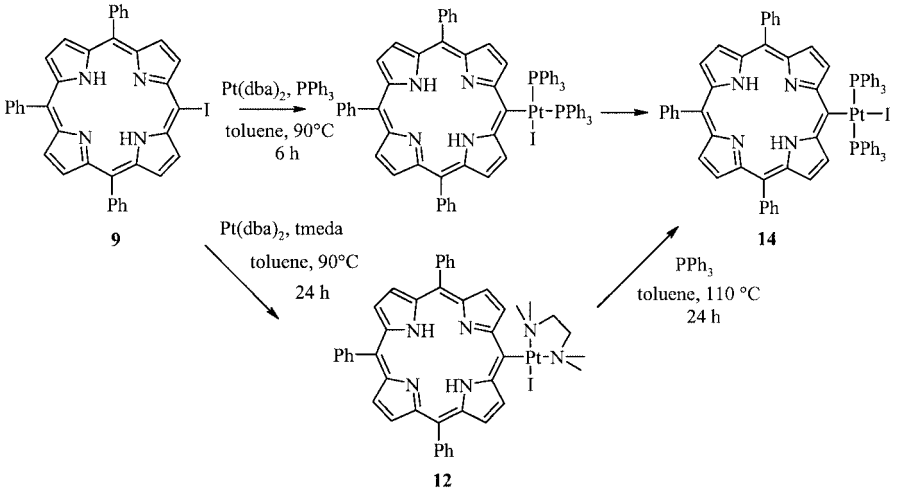
Compound	X	Y
2	H	Br
3	H	*cis*-$Pt(PPh_3)_2Br$
4	H	*trans*-$Pt(PPh_3)_2Br$
5	H	Pd(tmeda)Br
6	H	Pd(bpy)Br
7	Br	Br
8	Pd(tmeda)Br	Pd(tmeda)Br
9	Ph	I
10	H	H
11	Ph	H
12	Ph	Pt(tmeda)I
13	Ph	Pt(bpy)I
14	Ph	*trans*-$Pt(PPh_3)_2I$

After these disappointing results with bidentate diphosphanes, a new methodology that utilises bidentate nitrogen donor ligands was developed in order to approach the desired *cis*-orientated organoplatinum porphyrins. This reaction was initially attempted with palladium, since it is known to undergo oxidative addition reactions much more readily than platinum analogues. These reactions are well-known from the work of Canty and co-workers, who have used these N-ligands to make interesting Pd^{IV} complexes.[23] Thus, when $Pd_2(dba)_3$ was treated with an excess of tmeda and an equivalent of bromoporphyrin **2** in degassed toluene at 105 °C, it was soon evident that the starting material was being consumed and converted into a much more polar compound. The reaction was completed after approximately one hour and the solution was filtered to remove any palladium metal resulting from decomposition of the Pd^0 precursors. After two recrystallisations from $CHCl_3$/cyclohexane, product **5** was obtained in high yield as an air- and moisture-stable dark purple solid. This procedure was similarly carried out with 2,2′-bipyridine as the nitrogen donor ligand to produce a high yield of the similar η^1-organometallic porphyrin **6**. Unlike the porphyrinyl-palladium bidentate diphosphane analogues,[12,13] it

was found that these compounds are relatively stable towards silica and thus may be purified by column chromatography if required; as long as efforts are taken to ensure that any solvents used during the purification process are thoroughly free from acid. The reaction was repeated with the dibromoporphyrin species (**7**), tmeda and $Pd_2(dba)_3$ in order to prepare the bis(palladated) species. TLC analysis suggested that the desired double oxidative addition had occurred analogously; however, the product precipitated from the hot toluene solution. The precipitate was collected but it was found to be extremely insoluble in all common organic solvents and thus was not amenable to further purification. Other attempts at producing a bis(palladated) porphyrin system using the more soluble 5,15-bis(3′,5′-di-*tert*-butylphenyl)porphyrin also gave insoluble products that were difficult to purify thoroughly. FAB mass spectra of **8** (see below) indicated that the desired bis(palladium) porphyrin was formed. Initial thoughts were that the bidentate tmeda fragment could be flexible enough to act as a bridging group between two η^1-palladioporphyrin macrocycles, thus forming an oligomeric or polymeric species. However, the same result was seen with the less flexible 2,2′-bipyridine ligand, which suggests that they are not forming oligomers and that these examples of bis(palladiated) porphyrin species with bidentate nitrogen ligands are inherently insoluble.

Attempts at preparing the analogous platinioporphyrin systems with bromoporphyrin **2** failed, so the reactions were repeated with an iodoporphyrin. The iodoporphyrin chosen was 5-iodo-10,15,20-triphenylporphyrin (H_2TrPP-I) (**9**). This porphyrin was chosen due to its ease of synthesis in high yields, from the readily available starting material diphenylporphyrin (H_2DPP) (**10**).[11,24] The one free *meso*-position of triphenylporphyrin (H_2TrPP) (**11**) lends itself ideally to selective iodination.[17,22] This method avoids the tedious chromatographic separation procedures required to remove other iodoporphyrins that would be present if **10** itself were iodinated by similar procedures. Thus, when the more reactive iodoporphyrin **9** was utilised, the desired platinioporphyrins with bidentate nitrogen ligands were formed in good yields. As expected the formation of platinioporphyrins **12** and **13** was somewhat slower than the analogous palladioporphyrins **5** and **6**. The latter were formed in high yields within one hour, whilst **12** and **13** required overnight heating in degassed toluene with an excess of the platinating agent, but were eventually formed in good yields (ca. 80 %). Platinioporphyrins **12** and **13** were purified by column chromatography on silica support in order to remove a trace of the starting iodoporphyrin **9** and no degradation was seen during this procedure. It is important to note that even though these oxidative addition reactions are carried out on the free-base porphyrins, no metallation of the central porphyrin cavity is seen in any of these reactions, even after prolonged heating at 105 °C in toluene. This has been a general observation in all our metallation reactions. Moreover, Pd-catalysed couplings on free base porphyrins are readily carried out, as has been shown by several groups.[15,16,25] Indeed, we have found from qualitative reactivity comparisons of Pt insertions, that the bromo free bases react faster than either Ni^{II} or Zn^{II} substrates.[26] For all of these free-base η^1-organometallic porphyrins, it was found that the addition of a small amount of base (1 % triethylamine) to the mobile phase used during any of the chromatographic procedures greatly improved the tractability of these species. If base was omitted, it was found that the porphyrin macrocycle tended to protonate very readily on the column due to the strong electron donating properties of the η^1-organometallic fragment,[10−13] further enhanced by the electron-donating properties of the bidentate nitrogen ligands.

With metalloporphyrins **12** and **13** in hand, we investigated the substitution of the bidentate nitrogen donor ligands by chelating diphosphane ligands whose coordination to the soft Pt^{II} centre is expected to be favoured.



Scheme 1

Unfortunately, both **12** and **13** failed to undergo any ligand exchange reactions with a variety of bis(phosphanyl) ligands (dppe, dppp and dppf). It was surprising that the ligand exchange did not occur at all even with excess phosphane ligand, elevated temperatures, and prolonged reaction times. In all cases, the bis(N-donor)-chelated species was quantitatively recovered with no noticeable decomposition detectable by ^{1}H NMR spectroscopy. However, it is encouraging to observe that these species are quite stable and unlikely to decompose under a variety of different solvents and reaction conditions, so their use for the construction of multiporphyrin arrays with Pt^{II} connectors should be possible. The ligand exchange did occur with the simple monophosphane, PPh_3 to yield **14** in approximately 50 % yield, implying that the problems may be steric in origin. However, it was observed that H_2TrPP (**11**) was also produced in an approximately equal amount. Clearly, the organometallic platinioporphyrin **14** is best prepared by using our original, direct oxidative addition of a zerovalent Pt bis(phosphane) species (see Scheme 1), as discussed above.[10−13]

NMR Spectra of Palladio- and Platinioporphyrins

There are several aspects of interest in the NMR spectra of these η^1-organometallic porphyrins. The first observation is the facial asymmetry of the porphyrin due to the favoured, approximately orthogonal disposition of the N−Metal−N plane of the organometallic fragment and the plane of the porphyrin macrocycle. This arrangement gives rise to two different signals for the *o*-hydrogens of the phenyl groups in the 5,15-positions of the porphyrin. The unequal faces of the porphyrin are also clearly evident in the case of **5** where different nonequivalent *m*-hydrogens on the 5,15-phenyl groups are also seen. This feature was less apparent in our previous compounds with bidentate aryl diphosphanes because of overlap of many aryl signals.[12,13] The porphyrin β-hydrogens appear as four doublets (^1J = 4.7 Hz), typical of substituted porphyrins of this symmetry and all peaks are shifted from those encountered in the corresponding parent haloporphyrins. The biggest shifts are understandably experienced by the peaks arising from the 3,7-β-hydrogens adjacent to the organometallic fragment, which are shifted downfield by approximately δ = 0.8 ppm. In the case of **5** and **6**, this peak appears to be shifted even more downfield than the 20-*meso*-proton which is observed as a sharp singlet at about δ = 9.8 ppm. In those species containing a 2,2′-bipyridyl ligand, namely **6** and **13**, the peaks arising from the bipyridine unit appear as a series of eight mutually coupled signals over a δ = 4 ppm range (see Figure 1). The signals from the protons that are above the porphyrin plane are somewhat shielded by the macrocycle and this is demonstrated by large upfield shifts of about δ = 1 ppm from corresponding signals in the free ligand. Interestingly, the signals arising from the 6′-proton of the bipyridine moiety in **6** and **13** are strongly shifted downfield to δ = 9.7 and 10.4 ppm, respectively, demonstrating the effect of the halogen as a neighbouring electronegative centre. In NOESY experiments on **6** and **13**, a strong cross-peak is seen that represents the NOE between the 3,7-β-hydrogens of the porphyrin and the 6′′-proton of the bipyridine fragment. All peaks in these spectra have been assigned by careful examination of the 1-D spectra and a series of DQF-COSY and NOESY 2-D NMR experiments (see Figure 2). Similar spectra are observed for **5** and **12**, with signals for the tmeda fragment appearing in the upfield region between δ = 1.6 and 3.2 ppm. It is clear that the metallo-substituent is rotating slowly on the NMR timescale, mostly orthogonal to the plane of the porphyrin to give two singlets for the methyl groups corresponding to those that are *cis* and those that are *trans* to the porphyrin. A dipolar coupling cross-peak from one of these methyl singlets to the 3,7-β-hydrogens of the porphyrin reveals that the more upfield peak around δ = 1.6 ppm arises from the methyl groups that are *cis* to the porphyrin.

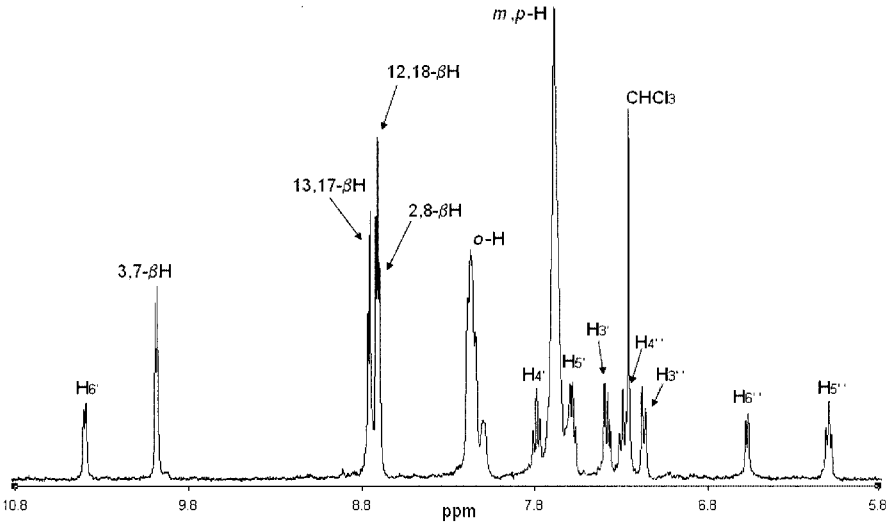


Figure 1. ^{1}H NMR spectrum of [PtI(H_2TrPP)(bpy)] (**13**) in $CDCl_3$ at 293 K

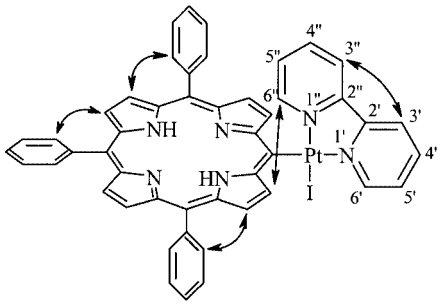


Figure 2. Numbering scheme for the bpy fragment and through-space correlations revealed by the NOESY spectrum of **13**

Mass and UV-Visible Absorption Spectra of Palladio- and Platinioporphyrins

All species gave mass spectra (ESI high-resolution for **5** and **6** and FAB for **12** and **13**) that displayed either the molecular ions of the respective complexes or their halide-exchanged analogues. For example, **6** did not give any molecular ion signal peaking at m/z = 805.0744 for the bromo complex, rather the most abundant peak in the spectrum corresponded extremely well with that for the iodo complex (calculated m/z = 851.0622; found m/z = 851.0722), which indicates that iodide from the NaI internal calibration standard had induced exchange. Also present in the spectra were the analogous chloro complexes from CH_2Cl_2 used in the introduction of the samples into the mass spectrometer. For platinioporphyrins **12** and **13**, the FAB mass spectra displayed the desired molecular ions for the appropriate parent compounds. In line with our observations that the halogen is less labile on the platinioporphyrins than on the palladioporphyrins, **13** displayed only a very small (< 10 %) cluster for the chloro-complex, whilst **12** did not display any analogous peak at all. In all mass spectra, fragmentation occurred and appropriate masses were recognised. These included fragments corresponding to the parent porphyrin macrocycle and fragments after loss of the halide. On the other hand, the MALDI-TOF spectra of all compounds displayed no parent molecular ions, but only clusters representing the porphyrin macrocycle, indicating that considerable fragmentation occurs during laser-induced ionisation. Bis(palladated)porphyrin **8** gave a strong parent molecular ion (calculated m/z = 1065.1; found m/z = 1065.2) as well as peaks corresponding to the loss of either one or both of the organometallic fragments. Peaks for the chloro analogues were also detected.

The UV-Visible spectra of these organometallic porphyrins are quite typical for di- and triphenylporphyrin derivatives. The wavelengths of the principal visible absorption bands for all complexes and the precursors are displayed in Table 2. Some trends can be distinguished, even with this limited number of examples. All groups other than H in the *meso* positions cause a red-shift, which is usual for these and related porphyrinic systems.[15] It can be seen that the *meso*-η^1-organometallic fragment exerts a similar effect on the electronic spectra to that of a simple halo substituent. There is a red-shift of the Soret band of approximately 10−15 nm and similar shifts for the Q bands relative to the base porphyrin macrocycles, after formation of the organometallic species. The nature of the nitrogen-donor ligands has very little effect on the electronic absorption spectrum for similar metallated species, for example, compare **5** and **6** or **12** and **13** to phosphane-ligated species like **14** and those previously reported.[10−13] They all have very similar electronic spectra although the phosphane-coordinated species displays slightly more red-shifted bands. The bis(palladated) species **8** continues the trend seen with mono-(palladated) **5**; the spectrum of **8** displays an even larger red-shift of all bands. This could be a sign of greater macrocycle distortion in order to cope best with the electronic and steric demands of the two organometallic fragments as well as the expected electron donating effect on the energy of the HOMO.

Table 2. Wavelengths for the principal UV-Visible absorption bands for the *meso*-metalloporphyrins and their precursors (in CH_2Cl_2)

Compound	λ_{max} (nm)				
Soret	IV	III	II	I	
2	420	510	545	587	642
5	417	518	551	588	642
6	418	516	550	589	640
8	427	529	567	607	665
9	421	519	554	595	651
10	405	502	535	575	630
11	411	508	542	583	637
12	426	527	564	599	655
13	426	526	563	597	653
14	434	528	567	601	659

Conclusion

The combination of $Pt(dba)_2$ and monodentate phosphane ligands with various haloporphyrins has been shown to be an effective way of synthesising η^1-organoplatinum porphyrins in high yields. An advantage of this method over previous methods is that it avoids the use of unstable Pt^0 phosphane complexes. This method has also been extended for the first time to synthesise various palladio- and platinioporphyrins that utilise bidentate nitrogen donor ligands in order to enforce a *cis* configuration of the metal centre. The availability of these stable *cis*-orientated organometallic porphyrins will allow for variation of architectures when incorporated with other suitable tectons in self-assembled supramolecular systems.

Experimental Section

General Remarks: Syntheses involving zerovalent metal precursors were carried out under high-purity argon using conventional Schlenk techniques. Porphyrin starting materials 10-bromo-5,15-diphenylporphyrin (**2**)[17] and 5,10,15-triphenylporphyrin (**11**)[11] were prepared by literature procedures and $Pt(dba)_2$ by the method of Cherwinski and co-workers.[27] All other reagents and ligands were

used as received from Sigma−Aldrich. Toluene was AR grade, stored over sodium wire, and degassed by heating and purging with argon at 105 °C. All other solvents were AR grade, and dichloromethane and chloroform were stored over anhydrous sodium carbonate. Analytical TLC was performed using Merck silica gel 60 F_{254} plates and column chromatography was performed using Merck silica gel (230−400 mesh). NMR spectra were recorded on Bruker Avance 400 MHz or Varian Unity 300 MHz instruments in $CDCl_3$ solutions, using $CHCl_3$ as the internal reference at δ = 7.26 ppm for ^1H spectra, and external 85 % H_3PO_4 as the reference for proton-decoupled $^{31}P\{^1H\}$ spectra. UV-Vis spectra were recorded on a Cary 3 spectrometer in dichloromethane. High resolution ESI mass spectra were recorded on a Bruker BioApex 47e FTMS fitted with an Analytica Electrospray Source. The samples were dissolved in dichloromethane and diluted with either dichloromethane/methanol (1:1) or methanol, and solutions were introduced into the source by direct infusion (syringe pump) at 60 μL/h, with a capillary voltage of 80 V. The instrument was calibrated using internal NaI. Positive ion FAB mass spectra were recorded on a Kratos Concept instrument at the Central Science Laboratory, University of Tasmania. Samples were dissolved in dichloromethane, and dispersed in a 4-nitrobenzyl alcohol matrix. In the data below, masses given are for the strongest observed peak in the molecular ion spectrum. In all compounds, this *m*/*z* value agreed with the predicted molecular mass, although in most cases it represented a mixture of M and M + 1 due to partial protonation of the free base porphyrin. Elemental analyses were carried out by the Microanalytical Service, The University of Queensland.

***trans*-[PtBr(H_2DPP−)(PPh_3)$_2$] (4):** Toluene (25 mL) was added to a Schlenk flask and degassed by bubbling argon through the solution at 90 °C. Bromoporphyrin **2** (20 mg, 0.037 mmol) was added and stirred for 5 min. Pt(dba)$_2$ (29 mg, 0.044 mmol) and triphenylphosphane (35 mg, 0.132 mmol) were added and the solution stirred at 105 °C. TLC analysis (50 % $CHCl_3$/*n*-hexane/1 % Et_3N) of the reaction mixture clearly showed disappearance of the starting material after about 30 min and that the initially formed *cis* isomer was slowly being converted into the *trans* isomer. After about 6 h the isomerisation was considered complete and the reaction mixture was cooled to room temperature and the solvent removed in vacuo. The residue (now air stable) was purified on a SiO_2 column and eluted with 50 % $CHCl_3$/*n*-hexane/1 % Et_3N; the major purple fraction was collected and the solvent removed in vacuo. The residue was recrystallised from $CHCl_3$/*n*-hexane to give **4** as dark purple crystals in 94 % yield. The data (^1H and ^{31}P NMR spectroscopy) of this compound agreed well with those of a genuine sample prepared previously using Pt(PPh_3)$_3$.[13]

General Procedure for the Preparation of Compounds 5, 6 and 8: As an example of this method, tmeda (35 μL, 0.25 mmol) and $Pd_2(dba)_3$ (43 mg, 0.046 mmol) were added sequentially to a stirred solution of bromoporphyrin **2** (25 mg, 0.046 mmol) in dry toluene (15 mL) that had been degassed at 90 °C. The reaction was maintained at 90 °C under an argon atmosphere and monitored by TLC (50 % $CHCl_3$/*n*-hexane/1 % Et_3N). When the reaction was considered to be complete by the total disappearance of starting material; the solution (now air stable) was filtered through a fine glass frit and the solvent removed in vacuo. The residue was recrystallised twice from $CHCl_3$/cyclohexane to give a dark purple solid that was dried thoroughly under high vacuum.

[PdBr(H_2DPP−)(tmeda)] (5): The desired complex **5** (34 mg) was obtained in 93 % yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = −2.78 (br. s, 2 H, NH), 1.50 [s, 6 H, (CH_3)$_2$N], 2.37 (m, 2 H, NCH_2CH$_2$N), 2.43 (m, 2 H, NCH$_2$$CH_2$N), 2.70 [s, 6 H, ($CH_3$)$_2$N], 7.65−7.75 (m, 2 H, one pair *m*-H on 10,20-phenyl), 7.75−7.85 (overlapping m, 4 H, one pair *m*-H on 10,20-phenyl and *p*-H on 10,20-phenyl), 8.05−8.10 (m, 2 H, *o*-H on 10,20-phenyl), 8.25−8.35 (m, 2 H, *o*-H on 10,20-phenyl), 8.82, 8.90, 9.18, 10.04 (each d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-H), 9.92 (s, 1 H, *meso*-H) ppm. UV-Vis: λ_{max} (ε/10^3 M^{-1}·cm^{-1}) = 417 (356), 518 (16.9), 551 (13.0), 588 (8.6), 642 (11.5) nm. High-resolution ESI MS: $[M]^+$ accurate mass calculated for $C_{38}H_{38}BrN_6Pd(+1)$: 765.1375; found: 765.1385.

[PdBr(H_2DPP−)(bpy)] (6): The desired complex **6** (36 mg) was obtained in 91 % yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = −2.93 (br. s, 2 H, NH), 5.95 (t, $^3J_{H,H}$ = 6.5 Hz, 1 H, 5′′-H), 6.02 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H, 6′′-H), 7.05 (t, $^3J_{H,H}$ = 6.5 Hz, 1 H, 4′′-H), 7.13 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H, 3′′-H), 7.32 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H, 3′-H), 7.48 (t, $^3J_{H,H}$ = 6.5 Hz, 1 H, 5′-H), 7.62 (t, $^3J_{H,H}$ = 6.5 Hz, 1 H, 4′-H), 7.65−7.75 (m, 6 H, *m*,*p*-H on 10,20-phenyl), 8.05−8.15 (m, 2 H, *o*-H on 10,20-phenyl), 8.20−8.25 (m, 2 H, *o*-H on 10,20-phenyl), 8.79, 8.92, 9.17, 10.25 (each d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-H), 9.70 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H, 6′-H), 9.91 (s, 1 H, *meso*-H) ppm. UV-Vis: λ_{max} (ε/10^3 M^{-1}·cm^{-1}) = 418 (492), 516 (15.2), 550 (9.9), 589 (6.3), 640 (7.0) nm. High-resolution ESI MS: I/Br exchanged product $[M]^+$ accurate mass calculated for $C_{42}H_{30}IN_6Pd(+1)$: 851.0622; found: 851.0722.

Bis(palladio)porphyrin (8): This was prepared by a similar procedure as above, but using dibromoporphyrin (**7**) and the appropriate amounts of tmeda and $Pd_2(dba)_3$. The crude yield was quantitative, however, the product is not sufficiently soluble for further purification and ^1H NMR analysis. UV-Vis: λ_{max} (rel. int.) = 427 (37.8), 529 (3.3), 567 (5.6), 607 (1.0), 665 (4.9) nm. FAB MS: $[M]^+$ mass calculated for $C_{44}H_{52}Br_2N_8Pd_2(+1)$: 1065.2; found: 1065.2.

H_2TrPP-I (9): Pyridine (250 μL), iodine (24 mg, 0.1 mmol) and bis(trifluoroacetoxy)iodobenzene (40 mg, 0.1 mmol) were added to a solution of triphenylporphyrin (**13**) (50 mg, 0.093 mmol) dissolved in $CHCl_3$ (25 mL). The reaction vessel was protected from light and stirred at room temperature. Periodically, the progress of the reaction was checked by TLC (30 % CH_2Cl_2/*n*-hexane). After 36 h it was found that there was total consumption of the starting material and the presence of a faster-moving spot. The solvent was removed in vacuo and the residue purified by column chromatography on SiO_2 and eluted with 50 % CH_2Cl_2/*n*-hexane. The major fraction was collected and the solvent removed and the residue recrystallised from CH_2Cl_2/*n*-pentane. The desired haloporphyrin (**9**) was collected as bright purple crystals in a 97 % yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = −2.71 (br. s, 2 H, NH), 7.7−7.8 (m, 9 H, *m*,*p*-H on 10,15,20-phenyl), 8.1−8.2 (m, 6 H, *o*-H on 10,15,20-phenyl), 8.78, 8.80 (overlapping d), 8.87, 9.68 (each d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-H) ppm. UV-Vis: λ_{max} (ε/10^3 M^{-1}·cm^{-1}) = 421 (433), 519 (19.7), 554 (11.6), 595 (5.5), 651 (4.9) nm. High-resolution ESI MS: $[M + H]^+$ accurate mass calculated for $C_{38}H_{26}IN_4(+1)$: 665.1202; found: 665.1212. $C_{38}H_{25}IN_4$: calcd. C 68.68, H 3.79, N 8.43; found C 68.54, H 3.70, N 8.27.

General Procedure for the Preparation of Compounds 12 and 13: As an example of this method, tmeda (28 μL, 0.19 mmol) and Pt(dba)$_2$ (125 mg, 0.19 mmol) were added sequentially to a stirred solution of iodoporphyrin (**9**) (25 mg, 0.038 mmol) in dry toluene (15 mL) that had been degassed at 90 °C. The reaction was maintained at 90 °C under an argon atmosphere and monitored by TLC (50 % $CHCl_3$/*n*-hexane/1 % Et_3N). When the reaction was considered complete (after 24 h by the total disappearance of starting material), the solution (now air stable) was filtered through a fine glass frit and the solvent removed in vacuo. The residue was dissolved in $CHCl_3$, loaded onto a SiO_2 column, and eluted with $CHCl_3$/1 %

Et_3N; the major purple/green band was collected. The solvent was removed in vacuo and the residue recrystallised from $CHCl_3$/cyclohexane to give a dark purple solid that was dried thoroughly under high vacuum.

[PtI(H_2TrPP−)(tmeda)] (12): The desired complex **12** (31 mg) was obtained in 83 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = −2.40 (br. s, 2 H, NH), 1.87 [s, 6 H, $(CH_3)_2$N], 3.27 (overlapping m, 4 H, NCH_2CH_2N), 3.27 [s, 6 H, $(CH_3)_2$N], 7.60−7.80 (m, 9 H, *m*,*p*-H on 10,15,20-phenyl), 8.00−8.10 (m, 3 H, *o*-H on 10,15,20-phenyl), 8.25−8.35 (m, 3 H, *o*-H on 10,15,20-phenyl), 8.67, 8.72, 8.78, 10.12 (each d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-H) ppm. UV-Vis: λ_{max} (ε/10^3 M^{-1}·cm^{-1}) = 426 (395), 527 (8.9), 564 (10.5), 599 (2.8), 655 (8.1) nm. FAB MS: $[M]^+$ mass calculated for $C_{44}H_{41}IN_6Pt(+1)$: 976.2; found: 976.0. $C_{44}H_{41}IN_6Pt$: calcd. C 54.16, H 4.23, N 8.61; found C 54.47, H 4.13, N 8.39.

[PtI(H_2TrPP−)(bpy)] (13): The desired complex **13** (30 mg) was obtained in 78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = −2.39 (br. s, 2 H, NH), 6.10 (t, $^3J_{H,H}$ = 6.2 Hz, 1 H, 5′′-H), 6.58 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, 6′′-H), 7.19 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, 3′′-H), 7.30 (t, $^3J_{H,H}$ = 6.2 Hz, 1 H, 4′′-H), 7.41 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, 3′-H), 7.60 (t, $^3J_{H,H}$ = 6.2 Hz, 1 H, 5′-H), 7.60−7.75 (m, 9 H, *m*,*p*-H on 10,15,20-phenyl), 7.80 (t, $^3J_{H,H}$ = 6.2 Hz, 1 H, 4′-H), 8.10−8.25 (m, 6 H, *o*-H on 10,15,20-phenyl), 8.70, 8.75, 8.80, 10.00 (each d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-H), 10.40 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, 6′-H) ppm. UV-Vis: λ_{max} (ε/10^3 M^{-1}·cm^{-1}) = 426 (379), 526 (13.0), 563 (14.1), 597 (5.9), 653 (8.6) nm. FAB MS: $[M]^+$ mass calculated for $C_{48}H_{33}IN_6Pt(+1)$: 1016.2; found: 1016.1. $C_{48}H_{33}IN_6Pt$: calcd. C 56.76, H 3.27, N 8.27; found C 56.53, H 4.38, N 8.34.

***trans*-[PtI(H_2TrPP)(PPh_3)$_2$] (14)**

Method A: The phosphane PPh_3 (5.2 mg, 0.02 mmol) was added to a refluxing solution of complex **13** (10 mg, 0.01 mmol) in toluene. The solution was refluxed under argon for 24 h. The solvent was removed in vacuo and the residue purified by column chromatography on SiO_2, and eluted with 50 % $CHCl_3$/*n*-hexane/1 % Et_3N to remove the by-product (**11**). The solvent was removed and the residue recrystallised from toluene/*n*-pentane to give the desired complex **14** in a 52 % yield.

Method B: Toluene (50 mL) was added to a Schlenk flask and degassed by bubbling argon through the solvent at 90 °C. Iodoporphyrin **9** (50 mg, 0.075 mmol) was added and stirred for 5 min. $Pt(dba)_2$ (59 mg, 0.090 mmol) and triphenylphosphane (47 mg, 0.18 mmol) were added and the solution stirred at 90 °C. TLC analysis (50 % $CHCl_3$/*n*-hexane/1 % Et_3N) of the reaction mixture clearly showed disappearance of the starting material after about 30 min and that the initially formed *cis* isomer was slowly being converted into the *trans* isomer. After about 6 h the isomerisation was considered complete; the reaction mixture was cooled to room temperature and the solvent removed in vacuo. The residue (now air stable) was purified by column chromatography and eluted with 50 % $CHCl_3$/*n*-hexane/1 % Et_3N; the major purple fraction was collected and the solvent removed in vacuo. The residue was recrystallised from $CHCl_3$/*n*-pentane to give 90 mg of **14** as dark purple crystals in 87 % yield. Some I/Cl exchange was found to occur when left in chlorinated solvents for extended periods. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = −3.13 (br. s, 2 H, NH), 6.40−6.60 (m, 18 H, PPh_3), 7.20−7.30 (m, 12 H, PPh_3), 7.60−7.70 (m, 9 H, *m*,*p*-H on 10,15,20-phenyl), 8.05−8.15 (m, 4 H, *o*-H on 10,20-phenyl), 8.20−8.25 (m, 2 H, *o*-H on 15-phenyl), 8.26, 8.63, 8.65 (overlapping d), 9.65 (each d, $^3J_{H,H}$ = 4.7 Hz, 2 H, β-H) ppm. ^{31}P NMR: δ = 24.0 (s, $^1J_{Pt-P}$ = 2976 Hz), UV-Vis: λ_{max} (ε/10^3 M^{-1}·cm^{-1}) = 434 (299), 528 (11.0), 567 (13.8), 601 (7.2), 659 (12.4) nm. High-resolution ESI MS: $[M]^+$ accurate mass calculated for $C_{74}H_{55}IN_4P_2Pt(+1)$: 1385.2690; found: 1385.2690.

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