Peripherally-metallated porphyrins: *meso*-η^1-porphyrinyl-platinum(II) complexes of 5,15-diaryl- and 5,10,15-triarylporphyrins

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ABSTRACT: Attempted metathesis reactions of peripherally-metallated *meso*-η^1-porphyrinylplatinum(II) complexes such as *trans*-[PtBr(NiDPP)(PPh_3)$_2$] (H_2DPP = 5,15-diphenylporphyrin) with organolithium reagents fail due to competitive addition at the porphyrin ring carbon opposite to the metal substituent. This reaction can be prevented by using 5,10,15-triarylporphyrins, e.g. 5,10,15-triphenylporphyrin (H_2TrPP) and 5-phenyl-10,20-bis(3',5'-di-*t*-butylphenyl)porphyrin (H_2DAPP) as substrates. These triarylporphyrins are readily prepared using the method of Senge and co-workers by addition of phenyllithium to the appropriate 5,15-diarylporphyrins, followed by aqueous protolysis and oxidation. They are convenient, soluble building blocks for selective substitutions and subsequent transformations at the remaining free *meso* carbon. The sequence of bromination, optional central metallation and oxidative addition of Pt(0) tris(phosphine) complexes generates the organoplatinum porphyrins in high overall yields. The bromo ligand on the Pt(II) centre can be substituted by alkynyl nucleophiles, including 5-ethynylNiDPP, to form the first examples of *meso*-η^1-porphyrinylplatinum(II) complexes with a second Pt-C bond. The range of porphyrinylplatinum(II) bis(tertiary phosphine) complexes was extended to the triethylphosphine analogues, by oxidative addition of H_2TrPPBr to $Pt(PEt_3)_3$, and the initially-formed *cis* adduct is only slowly thermally transformed to *trans*-[PtBr(H_2TrPP)(PEt_3)$_2$] **16**. The molecular structures of NiDAPP **9b**, *trans*-[Pt(NiDPP)(C_2NiDPP)(PPh_3)$_2$] **14** and **16** were determined by X-ray crystallography.

KEYWORDS: porphyrin, organometallic, platinum, crystal structure, phosphine

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INTRODUCTION

For the entire history of porphyrin chemistry, scientists have studied the coordination of metal ions in the central cavity of the macrocycle [1]. Until the recent discovery and investigation of modified porphyrinoids such as inverted or "N-confused" porphyrins [2] and azuliporphyrins [3], the coordination of metal ions in or near the macrocycle plane has involved metal-nitrogen bonding. While there are many examples of "organometallic" porphyrins, until recently almost all of these have also involved the metal atom being placed at the centre of the ring, with various types of metal-carbon bonds to out-of-plane organic fragments [4]. Reports of externally-bonded porphyrin carbon-metal bonded species are still quite rare. They include both σ- and π-bonded systems [5-8], and some examples are shown in Chart 1. We generally exclude from consideration species where the porphyrin is separated from the metal by an intervening substituent (such as ferrocenylporphyrins), although some interesting examples of such compounds with fused cyclopentadienyl rings appended to porphyrin pyrrole rings were recently reported by Smith and co-workers [9].

We entered this field as a result of our work on palladium-catalysed carbon-carbon couplings involving porphyrins. Our work on the coupling of alkynyl porphyrins with haloarenes and alkynes with bromoporphyrins [10] appeared almost simultaneously with that of Therien on *meso*-bromoporphyrin couplings [11]. The first work on palladium-catalysed couplings involved mercurated porphyrins studied by Smith's group [5a]. More recently, many workers have employed the haloporphyrin/alkyne coupling to prepare alkynylporphyrin monomers and oligomers [12]. This is now the simplest route to alkynylporphyrins of the 5,15-diaryl type. The initial step in the catalytic cycle of such a coupling is the oxidative addition of the bromoarene to a 14- or 16-electron Pd(0) entity introduced as such or produced *in situ* from a Pd(II) precursor [13]. Several years ago, we serendipitously isolated the resulting *meso*-η^1-organopalladium(II) porphyrin from one of these reactions [14].

Because such compounds had not previously been studied in their own right, we embarked on a systematic study of this type of palladium compound, and have also studied their more robust organoplatinum(II) analogues of the type shown on the right of Chart 1 [14-16]. Apart from our reports, there appear to be no other examples of compounds with direct transition metal to porphyrin M–C σ-bonds. The present paper reports the results of our recent work on (i) substitution reactions at the Pt(II) centre using simple carbon nucleophiles and (ii) extensions for the first time to tri*alkyl*phosphines as supporting ligands. These studies produced several new types of organometallic porphyrins and the molecular structures of two of these were determined by X-ray crystallography. We found it to be advantageous on the grounds of selectivity and solubility to use 5,10,15-triarylporphyrins as starting materials in some parts of the work, and we also report here their synthesis and the molecular structure of one example.

EXPERIMENTAL

General

Syntheses involving zerovalent metal precursors were carried out in an atmosphere of high-purity argon using conventional Schlenk techniques. Porphyrin starting materials 5,15-diphenylporphyrin (H_2DPP) **4a** and 5,15-bis-(3,5-di-*tert*-butylphenyl)porphyrin **4b** [11,17] and *trans*-[PtBr(NiDPP)(PPh_3)$_2$] **1** [15] and the zerovalent platinum precursors [18] were synthesised by literature methods. Phenyllithium was freshly prepared from bromobenzene and lithium metal in ether. 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°. Tetrahydrofuran was distilled from a dark blue solution of potassium/benzophenone under an atmosphere of argon immediately before use.

Diethylamine was distilled under anhydrous conditions and stored over Molecular Sieves. 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 7.26 ppm for ^1H spectra, and external 85% H_3PO_4 as the reference for proton-decoupled ^{31}P spectra. UV – vis spectra were recorded on a Cary 3 spectrometer in dichloromethane solutions. In some cases, both chloro and bromo analogues are known to be present in the products, but extinction coefficients are quoted using the molecular weight of the bromo species. Errors introduced by this will be small since the molecular weights differ by only about 4%. Positive ion FAB mass spectra were recorded on a VG-ZAB instrument at the Research School of Chemistry, The Australian National University, or 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 cluster. 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. Elemental analyses were carried out by the Microanalytical Service, The University of Queensland.

Synthesis

trans-*Bromo[15-butyl-10,20-diphenylporphyrinatonickel(II)-5-yl]bis(triphenylphosphine)platinum(II)* 3. To a solution of *trans*-[PtBr(NiDPP)(PPh_3)$_2$] **1** (20 mg, 0.015 mmol) in dry THF (20 cm^3) under an atmosphere of argon, BuLi (46 μL of a 1.6 M solution in hexanes) was added dropwise and stirred at room temperature for 1 hr. TLC analysis (40% $CHCl_3$/hexane) showed the presence of some starting material and a more mobile spot. The reaction was quenched by the addition of 50% aqueous THF and the solvent was removed *in vacuo*. The residue was loaded onto a column and eluted with 40% $CHCl_3$/hexane and the more mobile fraction was isolated. The solvent was removed and the residue recrystallised from $CHCl_3$/hexane to give red crystals of **3** in a 28% yield. ^1H-NMR: δ 0.88 (3H, t, J = 7.2 Hz, -$(CH_2)_3$-*CH_3*), 1.57 (2H, m, -$(CH_2)_2$-*CH_2*-CH_3), 2.30 (2H, m, -CH_2-*CH_2*-CH_2-CH_3), 4.48 (2H, br t, J = 7.2 Hz, por-*CH_2*-$(CH_2)_2$-CH_3), 6.50-6.70 (18H, m, PPh_3), 7.20-7.30 (12H, m, PPh_3), 7.60-7.70 (6H, m, *m,p*-H on 10,20-phenyl), 7.80-7.90 (4H, m, *o*-H on 10,20-phenyl), 7.80, 8.56, 9.12, 9.35 (each 2H, d, J = 4.7 Hz, β-H); ^{31}P-NMR: δ 23.20 (s, J_{Pt-P} 2942 Hz), FAB MS: 1373.3.

5,10,15-Triphenylporphyrin 5a and 5,15-bis(3',5'-di-t-butylphenyl)-10-phenylporphyrin 5b. As an example of this method, diphenylporphyrin **4a** (100 mg, 0.22 mmol) was dissolved in dry THF (50 cm^3) under an atmosphere of argon and the solution cooled to 0°. PhLi (1.4 cm^3 of 1.5 M solution in ether) was added dropwise and the reaction vessel was removed from the cooling bath and allowed to warm to room temperature and stirred for 30 min. To the reaction mixture 50% aqueous THF (1 cm^3) was added and stirring was continued for 10 min. DDQ (100 mg, 0.44 mmol as a DCM solution) was added and the solution was stirred for 15 min. The solvent was removed under vacuum and the residue dissolved in a minimum of DCM. This solution was passed through a short column eluting with DCM. The first major red fraction was collected and the solvent removed *in vacuo* and the residue recrystallised from DCM/methanol to give dark purple crystals in 96% yield. ^1H-NMR: δ -2.85 (2H, br s, NH), 7.8-7.9 (9H, m, *m,p*-H on 5,10,15-phenyl), 8.3-8.4 (6H, m, *o*-H on 5,10,15-phenyl), 9.01, 9.03, 9.10, 9.33 (each 2H, d, J = 4.7 Hz, β-H), 10.20 (1H, s, *meso*-H); UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 411 (383), 508 (17.3), 542 (5.5), 583 (5.4), 637 (2.3) nm; FAB MS: 539.2. Anal. Calcd. for $C_{38}H_{26}N_4$: C, 84.7; H, 4.9; N, 10.4. Found: C, 84.5; H, 4.9; N, 10.7.

A similar method was used for the synthesis of H_2DAPP **5b**, which was recrystallised from DCM/methanol to give dark purple crystals in 84% yield. ^1H NMR: δ -2.92 (2H, br s, NH), 1.57 (36H, s, *tert*-butyl-H on 5,15-aryl), 7.7-7.8

(3H, m, *m*,*p*-H on 10-phenyl), 7.84 (1H, t, J = 1.8 Hz, 4-H on 5,15-aryl), 8.14(2H, d, J = 1.8 Hz, 2,5-H on 5,15-aryl), 8.2-8.3 (2H, m, *o*-H on 10-phenyl), 8.88, 8.98, 9.10, 9.36 (each 2H, d, J = 4.7 Hz, β-H), 10.23 (1H, s, *meso*-H); UV – vis: λ_{max} ($\varepsilon/10^3$ M^{-1} cm^{-1}) 413 (409), 510 (16.2), 545 (6.1), 584 (4.9), 638 (2.6) nm; FAB MS: 762.9. Anal. Calcd. for $C_{54}H_{58}N_4 \cdot H_2O$: C, 83.0; H, 7.7; N, 7.2. Found: C, 82.5; H, 7.7; N, 7.0.

5-Bromo-10,15,20-triphenylporphyrin 6a and 5-bromo-10,20-bis(3',5'-di-t-butylphenyl)-15-phenylporphyrin 6b. Triphenylporphyrin **5a** (100 mg, 0.19 mmol) was dissolved in DCM (20 cm^3) and the solution was cooled to 0°. N-Bromosuccinimide (33 mg, 0.19 mmol) was added and the solution was stirred for 5 min, the progress of the reaction being checked by TLC (30% DCM/hexane). 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 washed with 50% aqueous methanol and collected by filtration in order to remove the succinimide. The solid was then recrystallised from DCM/methanol to give dark brown/purple crystals of **6a** in almost quantitative yield. ^{1}H-NMR: δ -2.77 (2H, br s, NH), 7.7-7.9 (9H, m, *m*,*p*-H on 10,15,20-phenyl), 8.2-8.3 (6H, m, *o*-H on 10,15,20-phenyl), 8.79, 8.80, 8.96, 9.70 (each 2H, d, J = 4.7 Hz, β-H); UV – vis: λ_{max} ($\varepsilon/10^3$ M^{-1} cm^{-1}) 419 (366), 517 (16.1), 552 (8.5), 594 (5.1), 651 (4.6) nm; FAB MS: 618.1. Anal. Calcd. for $C_{38}H_{25}BrN_4$: C, 73.9; H, 4.1; N, 9.1. Found: C, 73.4; H, 4.0; N, 8.8.

A similar method was used for the synthesis of H_2DAPPBr **6b**, which was recrystallised from DCM/methanol to give dark purple crystals in 90% yield. ^{1}H NMR: δ -2.65 (2H, br s, NH), 1.58 (36H, s, *tert*-butyl-H on 10,20-aryl), 7.75-7.85 (3H, m, *m*,*p*-H on 15-phenyl), 7.86 (1H, t, J = 1.8 Hz, 4-H on 10,20-aryl), 8.11 (2H, d, J = 1.8 Hz, 2,5-H on 10,20-aryl), 8.2-8.25 (2H, m, *o*-H on 15-phenyl), 8.83, 8.89, 8.99, 9.72 (each 2H, d, J = 4.7 Hz, β-H); UV – vis: λ_{max} ($\varepsilon/10^3$ M^{-1} cm^{-1}) 422 (383), 519 (15.8), 555 (9.3), 596 (4.8), 652 (5.1) nm; FAB MS: 842.5. Anal. Calcd. for $C_{54}H_{57}BrN_4$: C, 77.0; H, 6.8; N, 6.7. Found: C, 76.4; H, 7.0; N, 6.4.

5-Bromo-10,15,20-triphenylporphyrinatonickel(II) 7a and 5-bromo-10,20-bis(3',5'-di-t-butylphenyl)-15-phenylporphyrinatonickel(II) 7b. Bromoporphyrin **6a** (100 mg, 0.16 mmol) and $Ni(acac)_2$ (222 mg, 0.8 mmol) were dissolved in toluene (50 cm^3) and refluxed. The progress of the reaction was monitored by TLC (30% DCM/hexane) and was considered complete with the disappearance of the free base porphyrin after 4 h. The solvent was removed *in vacuo* and the residue redissolved in $CHCl_3$ and passed through a short column, eluting with $CHCl_3$. The first red fraction was collected and the solvent removed *in vacuo* and recrystallised from DCM/methanol to give dark red crystals of **7a** in 95% yield. ^{1}H-NMR: δ 7.65-7.75 (9H, m, *m*,*p*-H on 10,15,20-phenyl), 7.95-8.05 (6H, m, *o*-H on 10,15,20-phenyl), 8.69, 8.71, 8.79, 9.52 (each 2H, d, J = 4.7 Hz, β-H); UV – vis: λ_{max} ($\varepsilon/10^3$ M^{-1} cm^{-1}) 417 (256), 530 (17.2) nm; FAB MS: 673.9. Anal. Calcd. for $C_{38}H_{23}BrN_4Ni$: C, 67.7; H, 3.4; N, 8.3. Found: C, 67.4; H, 3.4; N, 8.3.

A similar method was used for the synthesis of NiDAPPBr **7b** which was recrystallised from DCM/methanol to give dark red crystals in 97% yield. ^{1}H NMR: δ 1.49 (36H, s, *tert*-butyl-H on 10,20-aryl), 7.65-7.70 (3H, m, *m*,*p*-H on 15-phenyl), 7.74 (1H, t, J = 1.8 Hz, 4-H on 10,20-phenyl), 7.85 (2H, d, J = 1.8 Hz, 2,5-H on 10,20-aryl), 7.9-8.0 (2H, m, *o*-H on 15-phenyl), 8.70, 8.74, 8.84, 9.52 (each 2H, d, J = 4.7 Hz, β-H); UV – vis: λ_{max} ($\varepsilon/10^3$ M^{-1} cm^{-1}) 431 (139), 541 (9.5), 576 (3.3) nm; FAB MS: 898.7. Anal. Calcd. for $C_{54}H_{55}BrN_4Ni \cdot CH_2Cl_2$: C, 67.2; H, 5.8; N, 5.7. Found: C, 66.9; H, 5.3; N, 5.3.

trans-*Bromo[10,15,20-triphenylporphyrinatonickel(II)-5-yl]bis(triphenylphosphine)-platinum(II) 8a and* trans-*bromo[10,20-bis(3',5'-di-t-butylphenyl)-15-phenylporphyrinato-nickel(II)-5-yl]bis(triphenylphosphine)platinum(II) 8b.* Toluene (50 cm^3) was added to a Schlenk flask and degassed at 105° under an atmosphere of argon. Bromoporphyrin **7a** (100 mg, 0.11 mmol) was added and stirred for 5 min. Zerovalent $Pt(PPh_3)_3$ (130 mg, 13.2 mmol) was added and the solution stirred at 105°. TLC analysis (50% $CHCl_3$/hexane) of the reaction mixture clearly showed disappearance of the starting material after *ca*. 30 min and that the initially-formed *cis* isomer was slowly being converted to the *trans* isomer. After *ca*. 6 hr the isomerisation was considered complete and the reaction mixture was

cooled to room temperature and the solvent removed under high vacuum. The residue was purified on a column eluting with 50% $CHCl_3$/hexane and the major red fraction was collected and the solvent removed *in vacuo*. The residue was recrystallised from $CHCl_3$/hexane to give **8a** as dark red crystals in 84% yield. ^{1}H-NMR: δ 6.60-6.75 (18H, m, PPh_3), 7.25-7.40 (12H, m, PPh_3), 7.60-7.70 (9H, m, *m*,*p*-H on 10,15,20-phenyl), 7.85-7.95 (4H, m, *o*-H on 10,20-phenyl), 8.0-8.05 (2H, m, *o*-H on 15-phenyl), 8.20, 8.53, 8.57, 9.48 (each 2H, d, J = 4.7 Hz, β-H); ^{31}P-NMR: δ 23.0 (s, J_{Pt-P} 2936 Hz), UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 431 (235), 541 (14.9), 573 sh (4.5) nm; FAB MS: 1393.3. Anal. Calcd. for $C_{74}H_{53}BrN_4NiP_2Pt{\cdot}0.5C_6H_{14}$: C, 64.4; H, 4.2; N, 3.9. Found: C, 64.5; H, 4.3; N, 3.9.

In one case the chloro analogue of **8a** was isolated by column chromatography by elution with 30% $CHCl_3$/hexane and its spectroscopic data follow. ^{1}H-NMR: δ 6.60-6.75 (18H, m, PPh_3), 7.25-7.40 (12H, m, PPh_3), 7.60-7.70 (9H, m, *m*,*p*-H on 10,15,20-phenyl), 7.80-7.90 (4H, m, *o*-H on 10,20-phenyl), 7.95-8.05 (2H, m, *o*-H on 15-phenyl), 8.16, 8.53, 8.56, 9.44 (each 2H, d, J = 4.7 Hz, β-H); ^{31}P-NMR: δ 24.2 (s, J_{Pt-P} 2961 Hz), UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 430 (226), 541 (15.3), 573 sh (4.8) nm; FAB MS: 1348.1. Anal. Calcd. for $C_{74}H_{53}ClN_4NiP_2Pt{\cdot}0.5C_6H_{14}$: C, 66.4; H, 4.3; N, 4.0. Found: C, 66.3; H, 4.4; N, 3.9.

A similar method was used for the synthesis of $PtBr(NiDAPP)(PPh_3)_3$ **8b**, which was recrystallised from $CHCl_3$/hexane to give dark red crystals in 78% yield. ^{1}H NMR: δ 1.42 (36H, s, *tert*-butyl-H on 10,20-aryl), 6.60-6.75 (18H, m, PPh_3), 7.20-7.30 (12H, m, PPh_3), 7.60-7.70 (3H, m, *m*,*p*-H on 15-phenyl), 7.60 (1H, t, J = 1.8 Hz, 4-H on 10,20-aryl), 7.72 (2H, d, J = 1.8 Hz, 2,5-H on 10,20-aryl), 7.95-8.05 (2H, m, *o*-H on 15-phenyl), 8.28, 8.53, 8.60, 9.40 (each 2H, d, J = 4.7 Hz, β-H); ^{31}P-NMR: δ 23.0 (s, J_{Pt-P} 2941 Hz); UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 432 (250), 542 (16.4), 576 (5.5) nm; FAB MS: 1618.3. Anal. Calcd. for $C_{90}H_{85}BrN_4NiP_2Pt$: C, 66.8; H, 5.3; N, 3.5. Found: C, 66.9; H, 5.4; N, 3.3.

[5,15-Bis(3',5'-di-t-butylphenyl)-10-phenylporphyrinatonickel(II) 9b. Free base porphyrin **5b** (50 mg, 0.065 mmol) and $Ni(acac)_2$ (80 mg, 0.32 mmol) were dissolved in toluene (20 cm^3) and refluxed. The progress of the reaction was monitored by TLC (30% DCM/hexane) and was considered complete with the total disappearance of the free base porphyrin after 4 h. The solvent was removed *in vacuo* and the residue redissolved in $CHCl_3$ and passed through a short column, eluting with $CHCl_3$. The first red fraction was collected and the solvent removed *in vacuo* and recrystallised from $CHCl_3$/pentane to give dark red crystals in 98% yield. ^{1}H NMR: δ 1.50 (36H, s, *tert*-butyl-H on 5,15-aryl), 7.6-7.7 (3H, m, *m*,*p*-H on 10-phenyl), 7.76 (1H, t, J = 1.8 Hz, 4-H on 5,15-aryl), 7.92 (2H, d, J = 1.8 Hz, 2,5-H on 5,15-aryl), 8.0-8.1 (2H, m, *o*-H on 10-phenyl), 8.79, 8.84, 8.96, 9.15 (each 2H, d, J = 4.7 Hz, β-H), 9.85 (1H, s, *meso*-H); UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 409 (243), 521 (16.9), 549 (4.8) nm; FAB MS: 818.3.

5-Butyl-10,15,20-triphenylporphyrinatonickel(II) 10 and 5,10,15,20-tetraphenylporphyrinatonickel(II) 11. To a stirred solution of triphenylporphyrin complex **8a** (20 mg, 0.014 mmol) in dry THF (20 cm^3) under an atmosphere of argon, BuLi (45 μL of a 1.6 M solution in hexanes) was added dropwise. The reaction mixture was stirred for 1 hr at room temperature. TLC analysis (40% $CHCl_3$/hexane) showed the consumption of most of the starting material and the appearance of a more mobile spot. The reaction was quenched by the addition of 50% aqueous THF and the solvent was removed *in vacuo*. The residue was purified on a column eluting with 40% $CHCl_3$/hexane and the fastest-moving major red band was collected. ^{1}H NMR analysis showed the loss of the phosphine-containing moiety and the spectrum agreed with that in the literature [19d]. A similar experiment using PhLi led to the isolation of NiTPP **11**, whose ^{1}H NMR spectrum agreed with that of an authentic sample.

trans-*Phenylethynyl[10,20-diphenylporphyrinatonickel(II)-5-yl]bis(triphenylphosphine)-platinum(II) 12.* To a degassed solution of *trans*-$[PtBr(NiDPP)(PPh_3)_2]$ **1** (20 mg, 0.015 mmol), CuI (*ca*. 2 mg) and $Pd(PPh_3)_2Cl_2$ (*ca*. 2 mg) in dry THF (5 cm^3) and Et_2NH (15 cm^3) under an atmosphere of argon, phenylacetylene (15 mg, 0.15 mmol) was added. The solution was stirred at 60° for 24 hr, after which TLC analysis (40% $CHCl_3$/hexane) showed the

disappearance of starting material and the appearance of a less polar spot. The solvent was removed *in vacuo* and the residue loaded on a column eluting with 40% $CHCl_3$/hexane. The major band was collected and the solvent removed and the residue recrystallised from $CHCl_3$/pentane to give dark red needles of **12** in a 80% yield. ^{1}H-NMR: δ 6.25-6.35 (2H, m, *o*-H on C_2Ph), 6.60-6.70 (18H, m, PPh_3), 6.90-6.95 (3H, m, *m,p*-H on C_2Ph), 7.25-7.35 (12H, m, PPh_3), 7.60-7.65 (6H, m, *m,p*-H on 10,20-phenyl), 7.85-7.95 (4H, m, *o*-H on 10,20-phenyl), 8.11, 8.67, 8.94, 9.19 (each 2H, d, J = 4.7 Hz, β-H), 9.54 (1H, s, *meso*-H); ^{31}P-NMR: δ 23.0 (s, J_{Pt-P} 2848 Hz), UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 424 (215), 532 (14.5), 563 sh (4.7) nm; FAB MS: 1338.0. Anal. Calcd. for $C_{76}H_{54}N_4NiP_2Pt$: C, 68.2; H, 4.1; N, 4.2. Found: C, 68.0; H, 4.0; N, 4.0.

trans-*{[10',20'-Diphenylporphyrinatonickel(II)-5'-yl]ethynyl}[10,20-diphenylporphyrinato-nickel(II)-5-yl]bis(triphenylphosphine)platinum(II) 14.* A similar method to that above was used to prepare **14**, namely *trans*-[PtBr(NiDPP)(PPh_3)$_2$] **1** (20 mg, 0.015 mmol) was reacted with NiDPP-C_2H **13** (9.2 mg, 0.015 mmol) in dry THF (10 cm^3) and Et_3N (10 cm^3) for 48 hr to give **14** in 38% yield. ^{1}H-NMR: δ 6.50-6.70 (18H, m, PPh_3), 7.50-7.60 (12H, m, PPh_3), 7.60-7.70 (12H, m, *m,p*-H on 10,10',20,20'-phenyl), 7.90-7.95 (8H, m, *o*-H on 10,10',20,20'-phenyl), 8.20, 8.21, 8.40, 8.67, 8.69, 8.94, 8.95, 9.41 (each 2H, d, J = 4.7 Hz, β-H), 9.55 (2H, s, *meso*-H of both porphyrins); ^{31}P-NMR: δ 22.85 (s, J_{Pt-P} 2850 Hz); UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 442 (267), 540 (23.7), 579 (19.0) nm; FAB MS: 1778.6. CHN analysis gave unusually high C and N results, but the crystal structure confirmed the composition.

cis-*Bromo(10,15,20-triphenylporphyrin-5-yl)bis(triethylphosphine)platinum(II) 15.* Toluene (20 cm^3) was added to a Schlenk flask and degassed at 105° under an atmosphere of argon. Bromoporphyrin **6a** (20 mg, 0.032 mmol) was added and stirred for 5 min. Zerovalent Pt(PEt_3)$_3$ (17 μL of a 0.18 M solution in toluene, 0.032 mmol) was added and the solution was stirred at 105°. TLC analysis (50% $CHCl_3$/hexane) of the reaction mixture after 5 min showed the disappearance of the starting material and the presence of a much more polar spot. The mixture was cooled to room temperature and the solvent removed under high vacuum. The residue was purified by column chromatography eluting with 50% $CHCl_3$/hexane and the major purple/green fraction collected and the solvent removed *in vacuo*. The residue was recrystallised from $CHCl_3$/hexane to give **7** as dark purple crystals in a 67% yield. ^{1}H-NMR: δ -2.45 (2H, br s, NH), 0.70-0.90 (9H, m, PEt_3 *trans* to Br), 1.05-1.25 (6H, m, PEt_3 *trans* to Br), 1.40-1.60 (9H, m, PEt_3 *trans* to porphyrin), 2.20-2.40 (6H, m, PEt_3 *trans* to porphyrin), 7.60-7.80 (9H, m, *m,p*-H on 10,15,20-phenyl), 8.00-8.10 (4H, m, *o*-H on 10,20-phenyl), 8.25-8.35 (2H, m, *o*-H on 15-phenyl), 8.70, 8.73, 8.79, 9.80 (each 2H, d, J = 4.7 Hz, β-H); ^{31}P-NMR: δ 1.7 (d, J_{P-P} 18 Hz, J_{Pt-P} *trans* to Br 3972 Hz), 7.3 (d, J_{P-P} 18 Hz, J_{Pt-P} *trans* to porphyrin 1791 Hz); UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 425 (226), 524 (13.9), 560 (11.8), 598 (5.1), 652 (8.0) nm; FAB MS: 1049.1 (chloro analogue also present at 1005.2).

trans-*Bromo(10,15,20-triphenylporphyrin-5-yl)bis(triethylphosphine)platinum(II) 16.* A solution of the *cis* isomer **10** [10 mg, 0.012 mmol in xylene (5 cm^3)] was degassed at 140° under an atmosphere of argon. The mixture was stirred for 4 hr, cooled to room temperature and the solvent removed under high vacuum. The residue was chromatographed on a short column eluting with 30% ethyl acetate/hexane in order to remove a minor impurity of unsubstituted porphyrin **4a**, apparently formed by thermolysis of the Pt-C bond. The major fraction was collected and the solvent removed *in vacuo*. The residue was recrystallised from ethyl acetate/pentane to give the *trans* isomer **11** in 90% yield. ^{1}H-NMR: δ -2.30 (2H, br s, NH), 0.70-0.90 (18H, m, PEt_3), 1.40-1.60 (12H, m, PEt_3), 7.60-7.80 (9H, m, *m,p*-H on 10,15,20-phenyl), 8.20-8.30 (6H, m, *o*-H on 10,15,20-phenyl), 8.70, 8.72, 8.79, 9.92 (each 2H, d, J = 4.7 Hz, β-H); ^{31}P-NMR: δ 10.04 (s, J_{P-Pt} 2611 Hz); UV – vis: λ_{max} (ε/10^3 M^{-1} cm^{-1}) 426 (207), 525 (10.0), 562 (8.4), 598 (4.2), 654 (5.6) nm; FAB MS: 1049.1 (chloro analogue also present at 1005.2).

Crystallography

Crystal Structure Determinations. The data collection, extraction, solution and refinement were all relatively routine although two of the crystals were very small, one a needle of 0.06 x 0.06 mm cross-section and the other a plate only 20 μm thick. Crystal data are summarized in Table 1. Data were collected on a Nonius Kappa CCD [20] diffractometer fitted with MoKα radiation using ϕ and ω scans. Data were integrated using the DENZO [21] package and a numerical absorption correction was applied [22]. Structure solutions were by direct methods [23] and refinement was by means of the CRYSTALS [24] program suite. For **9b** a highly disordered solvent region apparently occupied by pentane was subjected to the SQUEEZE routine of the PLATON suite [25] and the contribution of this region to the data was thereby eliminated. A solvent-accessible region was also evident in **14**, but the low electron density in this region was not suggestive of any significant solvent content. There is some disorder of the phosphine ethyl groups in **16** and this was modelled in terms of pairs of sites of fractional occupancy. Relatively high anisotropic displacement ellipsoids are also observed for the 10,20-phenyl groups, although no resolution of discrete disordered sites was apparent in a series of slant Fouriers through the groups. The single site high ADP model was therefore preferred over a disordered model.

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RESULTS AND DISCUSSION

Studies of the addition of carbon nucleophiles to porphyrinylplatinum(II) complexes

Our *meso*-η^1-organopalladium(II) and -platinum(II) porphyrins prepared by the oxidative addition of the bromoporphyrin to Pd(0) and Pt(0) phosphine complexes are the first reported examples of such compounds [14,15]. In the interests of studying the chemistry of such species in more detail, and in particular their possible use in preparing more elaborate structures based on the *meso*-metallo connection, we attempted alkylation/arylation at the metal(II) centre. Successful exchange of bromide at the metal would allow us to assess the stability of compounds possessing both the porphyrin-metal and another carbon-metal bond. Such compounds constitute a late intermediate along the carbon-carbon coupling pathway when palladium complexes are used as catalysts. Given the predicted instability of such compounds in the Pd series, these experiments were naturally carried out on the more robust Pt(II) analogues, beginning with our well-characterised complex *trans*-[PtBr(NiDPP)(PPh_3)$_2$] **1** (Scheme 1) [14,15].

Initially, ligand exchange of the halogen on the metal by an alkyl moiety was attempted with Grignard reagents. Unfortunately, a selective reaction was not found with a range of such reagents, under various stoichiometric ratios and reaction conditions. However when the reaction was repeated in THF with excess alkyllithium reagents (PhLi, BuLi) as the source of the nucleophilic species, TLC indicated that soon after the addition of RLi, a more mobile compound was present. This fraction was isolated by column chromatography and recrystallised. However, the ^{1}H NMR spectrum of the product isolated from the BuLi reaction displayed a broad, distorted triplet at 4.48 ppm which is characteristic of an alkyl chain directly bonded to the porphyrin's *meso* position. This assignment was supported by the disappearance of the *meso*-proton signal in the downfield region. It appeared therefore that the nucleophile had added to the opposite *meso* position of the porphyrin ring, rather than substituting the halide on Pt to give the desired **2**. Exposure to aerial oxygen during the work-up and chromatographic separation was sufficient to oxidise the porphodimethene back to the tetra-substituted porphyrin **3**. The FAB mass spectrum also supported this conclusion with the parent ion of **3** clearly evident. This behaviour recalled the recent extensive work of the Senge group on alkylation and arylation of porphyrins

using alkyl- and aryllithiums [19]. It seemed to be unlikely that we could escape this reaction, so with this in mind it was decided to synthesise porphyrin precursors that have no unsubstituted *meso*-positions available for attack by the alkyllithium reagent.

As shown in Scheme 2, triarylporphyrins **5a** (Ar = phenyl) and **5b** (Ar = 3,5-di-*t*-butylphenyl) were synthesised in high yields (>90%) from the respective 5,15-diarylporphyrins **4a** and **4b** using the method of Senge [19]. After the initial addition of an organolithium reagent to one *meso* position, quenching with aqueous THF gives the porphodimethene which is re-oxidised to the respective triarylporphyrin by the addition of dichlorodicyanoquinone (DDQ) to the reaction mixture. We use the abbreviations H_2TrPP (5,10,15-triphenylporphyrin, **5a**) and H_2DAPP ["diarylphenylporphyrin", 5,15-bis(3',5'-di-*t*-butylphenyl)-10-phenylporphyrin, **5b**] from now on. The structures of both triarylporphyrins can easily be deduced by inspection of the ^{1}H NMR spectra. In the case of H_2TrPP the hydrogens of the phenyl group on the 10-*meso* position understandably overlap with the signals arising from the phenyl groups on the 5,15-*meso* positions. The reduced symmetry of the molecule can be seen by the appearance of four doublets in the downfield region that correspond to the four unique sets of β-hydrogens. Both triarylporphyrins were brominated in almost quantitative yield using the standard procedure of N-bromosuccinimide in dichloromethane at 0° [11,12b]. These bromo-triarylporphyrins **6a** and **6b** offer an attractive entry into species elaborated at the remaining *meso* carbon. The selective bromination at the only available *meso*-position removes the need for the tedious chromatographic separation of the di-, mono- and non-brominated porphyrins that is required if the halogenation is carried out on the parent diarylporphyrins. Mono-halogenated derivatives of 5,15-diphenylporphyrin have been synthesised in moderate yields (66%), however these compounds tend to have limited solubilty in common organic solvents [11,12b]. In our hands, the large-scale separation of the bromination products of the more soluble bis(di-3,5-*tert*-butylphenyl)porphyrin is difficult and the use of these triarylporphyrins has now overcome this problem. Both mono-brominated porphyrins **6a** and **6b** are considerably more soluble than the parent diaryl analogues. This is especially the case with **6b**, since it is even partially soluble in hexane and methanol, in which the diaryl analogues have very limited solubility. Insertion of nickel into both **6a** and **6b** to give NiTrPPBr **7a** and NiDAPPBr **7b**, respectively, was readily carried out by standard metallation procedures, i.e. the action of Ni(II) acetylacetonate in refluxing toluene over 4 hours.

The metallation of H_2DAPP **5b** was also undertaken, and the product NiDAPP **9b** was characterised crystallographically (Fig. 1). This is the first crystal structure of a monomeric 5,10,15-triarylporphyrin, although two 5-*alkyl* DPP structures, namely 5-isopropyl-10,20-diphenylporphyrin free base and 5-*sec*-butyl-10,20-diphenylporphyrinatonickel(II) were reported by Senge and Feng [19b]. As shown in Fig. 1, the porphyrin ring is mildly ruffled as is typical for most Ni(II) porphyrins. The di-*t*-butylphenyl rings are almost orthogonal to the porphyrin mean plane, while the unique phenyl ring lies at a more oblique angle.

We have also used **6b** as an entry into conjugated bis(porphyrinyl) butadiynes based on the DAPP unit, and their availability enabled us to advance our research into the electrogenerated cations and anions from such bis(porphyrins) [26]. 5,10,15-Triarylporphyrins have been prepared before by other routes [27], but the present method is clean, high-yielding, and convenient. The only proviso is that the phenyllithium should be in good condition, preferably freshly prepared, as degraded solutions give poor results.

Bromometalloporphyrins **7a** and **7b** undergo the oxidative addition of zerovalent $Pt(PPh_3)_3$ in hot, degassed toluene [14,15] to give the η^1-organometallic platinioporphyrins **8a** and **8b**, respectively. The initial adduct is the *cis* isomer and its thermal conversion to the *trans* isomer can be monitored by TLC. Isomerisation is complete after approximately six hours. The identity of the final isomer is unambiguously determined by ^{31}P NMR, due to the presence of a sharp singlet at approximately 23 ppm and a P-Pt coupling constant of about 2400 Hz. It is known that these η^1-

organometallic porphyrins undergo some halogen exchange in chlorinated solvents [15]. In one case the chloro analogue of **8a** was separated from the bromo complex by column chromatography, and fully characterised.

With this new set of Pt(II) starting materials in hand, we returned to the alkylation reactions (Scheme 3). When the η^1-organometallic platinioporphyrin **8a** was treated with n-butyl- or phenyllithium in THF, the isolated products of the reaction were simply the corresponding butyltriphenylporphyrin [19d] and tetraphenylporphyrin nickel(II) complexes, **10** and **11**, respectively. This loss of the platinum fragment was evident in the ^{1}H NMR by the lack of resonances near 7 ppm that arise from the triphenylphosphine moieties, and the absence of any ^{31}P NMR signal. The products of these reactions can be rationalised by reductive elimination of the platinum fragment to yield the new C-C bond. This mechanism is analogous to the final step of several palladium-catalysed coupling reactions, such as the Stille and Suzuki reactions [13]. It therefore appeared that preparation of the desired alkyl(aryl)/porphyrinyl Pt(II) complexes would be frustrated by this reaction, so we turned our attention to less basic organic ligands, namely alkynyls, which allowed us to isolate the first examples of this class of compounds.

The alkynyl complexes **12** and **14** were obtained using the terminal alkynes and the bromoplatinum NiDPP complex **1** as shown in Scheme 4. Phenylethynyl **12** was prepared by the coupling of **1** with phenylacetylene in dry THF and diethylamine at 60° for 24 hours. TLC analysis showed the disappearance of starting material and the appearance of a less polar spot. After isolation of the latter compound, its ^{1}H NMR spectrum clearly showed the presence of the extra phenyl moiety. The peaks corresponding to this phenyl group are somewhat upfield of the usual aromatic region, presumably due to the shielding effects of the phenyl rings of the bulky triphenylphosphine ligands. Given this favourable result, we next applied this method to the 5-ethynylporphyrin **13**, resulting in the isolation of novel bis(porphyrin) **14**. Compound **13** was obtained by reaction of the corresponding trimethylsilylethynylporphyrin [12a] with fluoride ion. In the preparation of **14** the usual 2° amine solvent diethylamine was replaced with triethylamine in order to prevent consumption of the alkyne by the formation of the porphyrinylenamine [28]. The ^{1}H NMR spectrum of **14** clearly showed eight doublets in the downfield region that correspond to the eight unique sets of β-hydrogens distributed over the two porphyrin rings. Not unexpectedly, the visible absorption of **14** showed a broad but unsplit Soret band, indicating minimal ground state communication between the π-systems of the two rings and also small through-space coupling.

We determined the molecular structure of this unusual complex by X-ray crystallography (Fig. 2). It is the first example of a *meso*-η^1-platinioporphyrin with two carbon-bound ligands and represents a new type of bis(porphyrin) with a unique alkynylmetal spacer. As usual for Ni(II) porphyrins, both rings are slightly ruffled. The coordination geometry at Pt is almost ideally square-planar, with no bond angle deviating by more than 5° from 90°. The alkyne group is almost linear, the bond angles at the triply-bonded carbons being 176.2(6) (Pt-C42-C41) and 174.7(7)° (C42-C41-C25). There is one other published alkynyl NiDPP structure, namely that of 5-trimethylsilyl-10,20-diphenylporphyrinatonickel(II), and in that structure, the alkyne unit is slightly more distorted from linearity, with angles of 169.7(5) and 172.6(4)° [12a]. The triphenylphosphine ligands, as usual in this type of organometallic porphyrin, take up positions in which one phenyl group of each ligand overlies the adjacent porphyrin ring in a nearly eclipsed relationship along the P-Pt-P vector [15,16].

η^1-Platinioporphyrins with triethylphosphine ligands

The published structures of η^1-platinioporphyrins with triphenylphosphine ligands show the considerable steric demand of these ligands [14-16]. In some situations this may be desirable as a way of protecting the faces of the porphyrin, but we are naturally also interested in the preparation of analogues with different phosphine groups that may

leave these faces very open. As an entry point into this area the smaller triethylphosphine ligand was chosen. This phosphine is also much more electron-donating than triphenylphosphine, and $Pt(PEt_3)_3$ is much more reactive than $Pt(PPh_3)_3$, possibly allowing easier synthesis of bis(platinio)porphyrins, whose preparation has so far been somewhat difficult [16]. So bromo-triarylporphyrin free base **6a** was treated with $Pt(PEt_3)_3$ in hot, degassed toluene under an argon atmosphere (Scheme 5). Immediately after the addition of the zerovalent Pt complex, TLC showed the presence of a much more polar compound and almost complete consumption of the bromo starting material. The high basicity conferred by the electron-rich -$PtBr(PEt_3)_2$ moiety can be detected by TLC on silica gel, because the product appears as an almost stationary bright green spot. This is due to the protonation of the porphyrin nitrogens, and hence the addition of a base (e.g. Et_3N) to the TLC elution solvent is required in order to mobilise the spot (the colour also changes to purple). Such behaviour was also observed for the PPh_3 analogues [15]. The reaction was stopped at this point by the removal of the solvent under high vacuum in order to prevent conversion to the *trans* isomer. The structure of the *cis* isomer **15** was proved by ^{31}P NMR, which revealed two sets of doublets for the non-equivalent phosphines. These have a P-P coupling constant of 18 Hz, and P-Pt coupling constants of 3972 Hz for the phosphine *trans* to the Br, and 1791 Hz for that *trans* to the porphyrin. The inequivalence of the phosphine groups is also reflected in the ^1H NMR spectrum, which clearly shows two sets of ethyl signals in the upfield region.

By analogy with PPh_3-containing η^1-organometallic platinioporphyrins, isomerisation of the *cis* to the *trans* isomer was attempted by heating at 105° in degassed toluene. Even after four hours of this treatment, isomerisation was undetectable by ^{31}P NMR. In fact it was found by ^{31}P NMR that higher temperatures (four hours in xylene at 140°) were required to complete the isomerisation. The ^{31}P NMR spectrum of *trans* isomer **16** showed a sharp singlet at 10.0 ppm with a Pt-P coupling constant of 2611 Hz. This increased symmetry could also be seen in the ^1H NMR with only a single set of ethyl resonances visible in the upfield region. So the triethylphosphine ligand is advantageous if the *cis* isomer is the desired product, offering improved selectivity in comparison to triphenylphosphine. For the latter ligand, conversion to the *trans* adduct intervenes well before all the bromo starting material is consumed. These triethylphosphine complexes undergo halogen exchange in chlorinated solvents more readily than the triphenylphosphine analogues, and hence in the NMR spectra (both ^{31}P and ^1H) some peaks of the chloro complex are discernible close to those of the bromo complex. Parent ions of both bromo and chloro complexes are also visible in the FAB mass spectra, however no separation was possible by TLC in a variety of solvent systems.

The molecular structure of **16** was determined by X-ray crystallography and is shown in Fig. 3. As expected for a free base porphyrin without steric crowding on the periphery, the macrocycle is nearly planar, with the P-Pt-P vector almost orthogonal to that plane. The bond angles at the platinum atom are all 90 ± 2°. Although there is some disorder in the triethylphosphine alkyl groups, the ligands adopt an eclipsed relationship down the P-Pt-P direction as seen for the triphenylphosphine analogues. However the flexibility of the ethyl groups allows the methyls nearest the porphyrin to point directly away from that ring.

CONCLUSION

Triarylporphyrins of the 5,10,15 substitution pattern are formed in a clean and selective manner by the method of Senge and co-workers [19]. Bromination is then directed exclusively to the remaining *meso* position, enabling us to prepare the *meso*-η^1-platinioporphyrins in a convenient manner. This series of compounds is significantly more soluble in common solvents than the DPP analogues. The alkylation of complexes of the type *trans*-[$PtBr(porphyrin)(PPh_3)_2$] with strongly basic organometallic nucleophiles occurs at the opposite *meso* carbon, unless the latter is already substituted. In that case, butyl- or phenyllithium attacks at platinum, but reductive elimination occurs to extrude the Pt(0) moiety and form a new porphyrin-carbon bond. However, less basic nucleophiles produced by the combination

phenyl- or porphyrinylethyne with catalytic CuI form stable diorganoplatinum(II) bis(phosphine) complexes such as **12** and **14**. Oxidative addition of *meso*-bromoporphyrins to platinum(0) complexes of trialkylphosphines was demonstrated for the first time, and the smaller bulk of triethylphosphine compared with triphenylphosphine significantly increases the stability of the initial *cis* adduct. Our present work involves the use of these novel organoplatinum(II) porphyrins in the construction of supramolecular arrays and chirally-superstructured porphyrins, as well as studies of the effects of the metallo substituents on photophysical properties.

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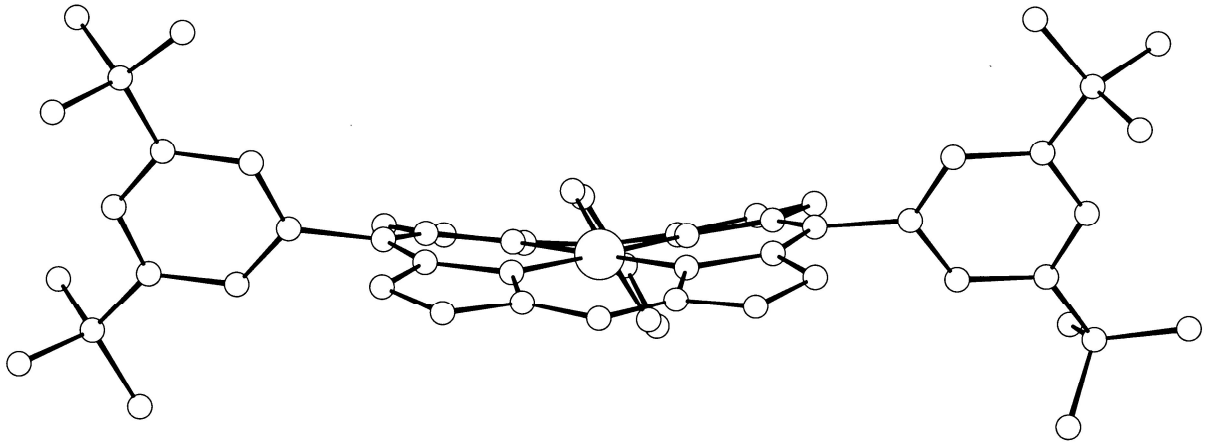


Fig. 1. Molecular structure of NiDAPP **9b** as determined by X-ray crystallography (hydrogen atoms have been omitted for clarity). For one of the *t*-butyl substituents, only one of the disordered sites is shown.

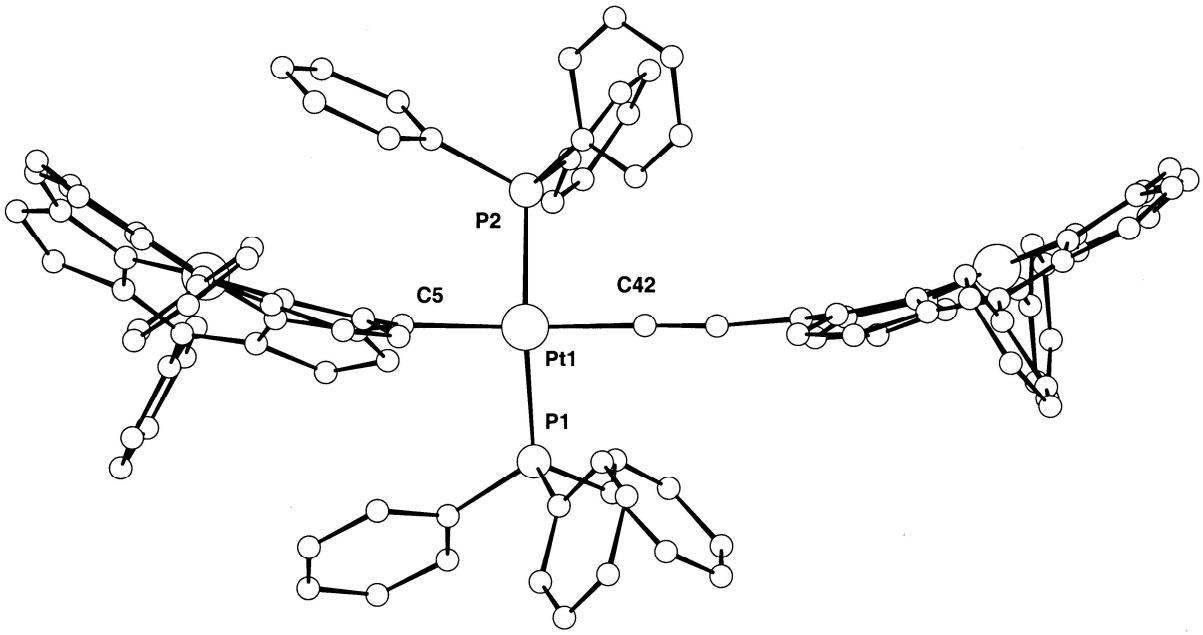


Fig. 2. Molecular structure of *trans*-[Pt(NiDPP)(C_2NiDPP)(PPh_3)$_2$] **14** as determined by X-ray crystallography (hydrogen atoms have been omitted for clarity).

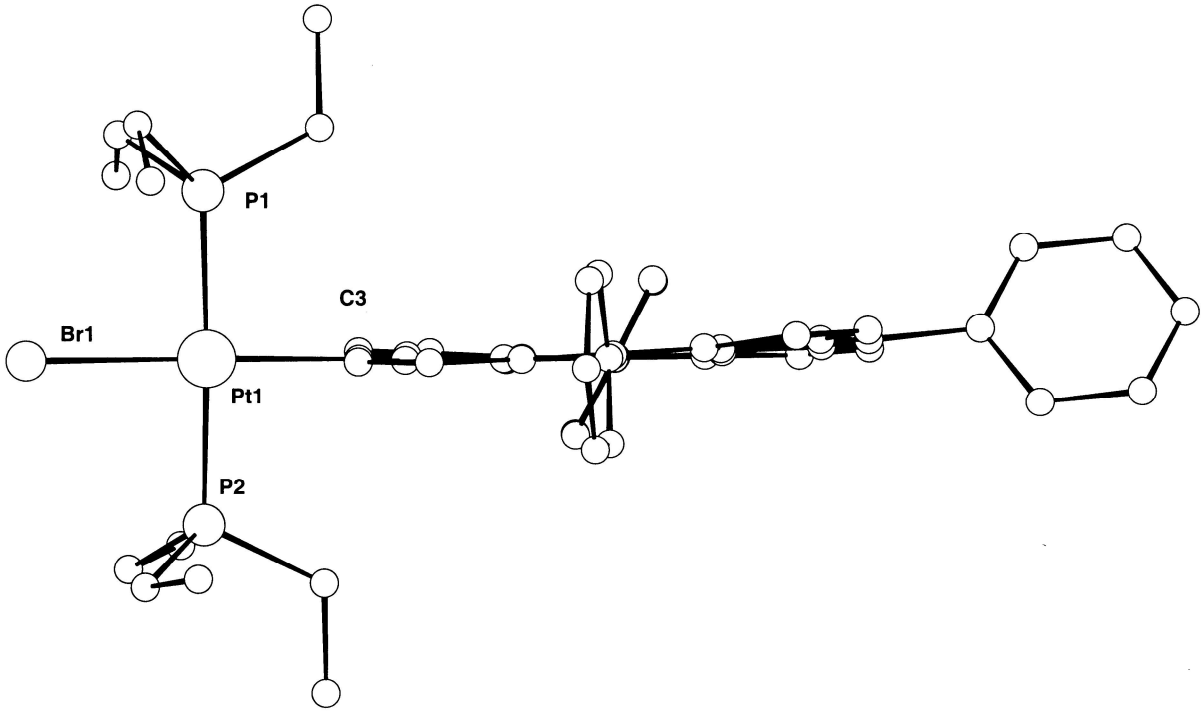
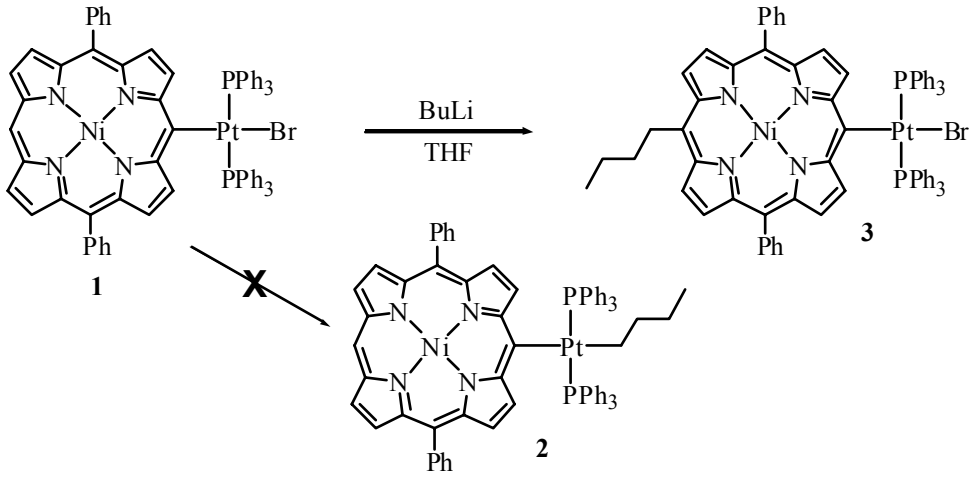
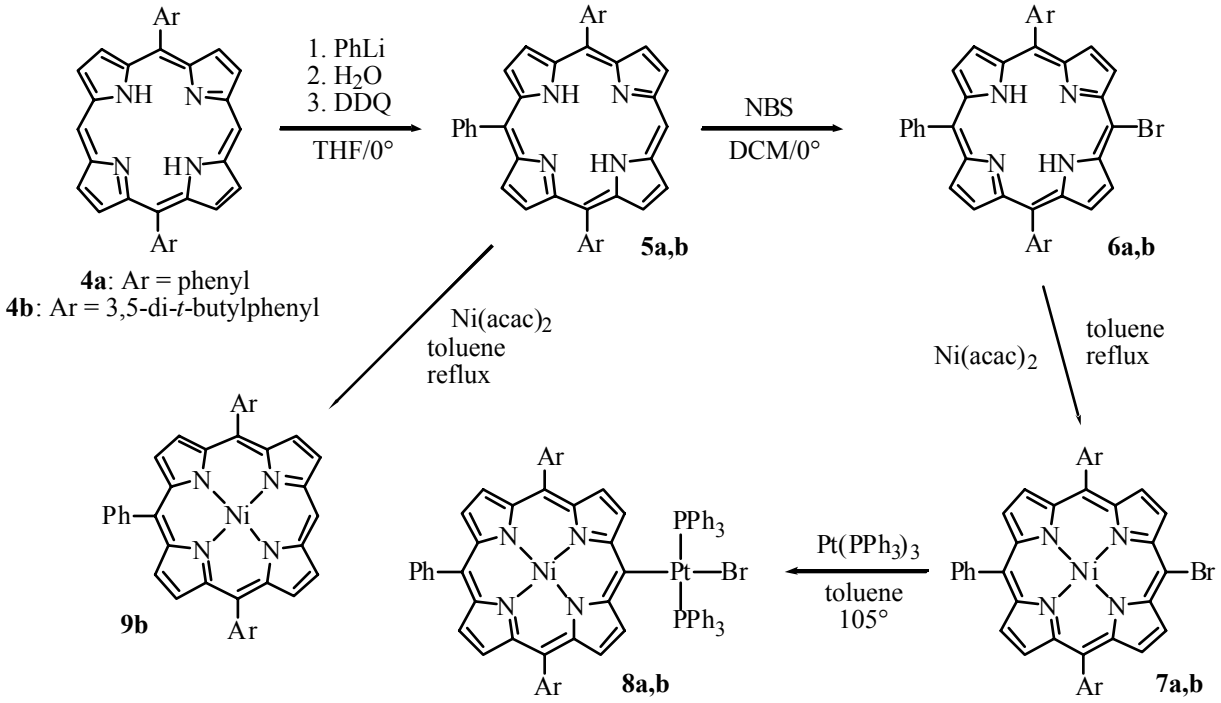


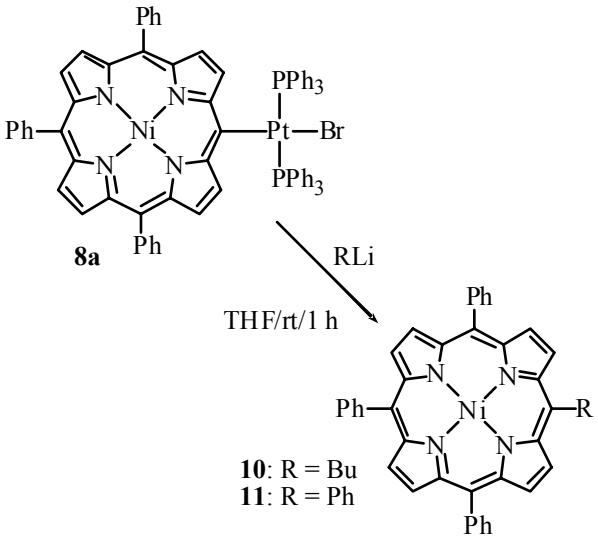
Fig. 3. Molecular structure of *trans*-[PtBr(H_2TrPP)(PEt_3)$_2$] **16** as determined by X-ray crystallography (hydrogen atoms have been omitted for clarity). For each of the three disordered carbons of the ethyl groups, only one position is shown.



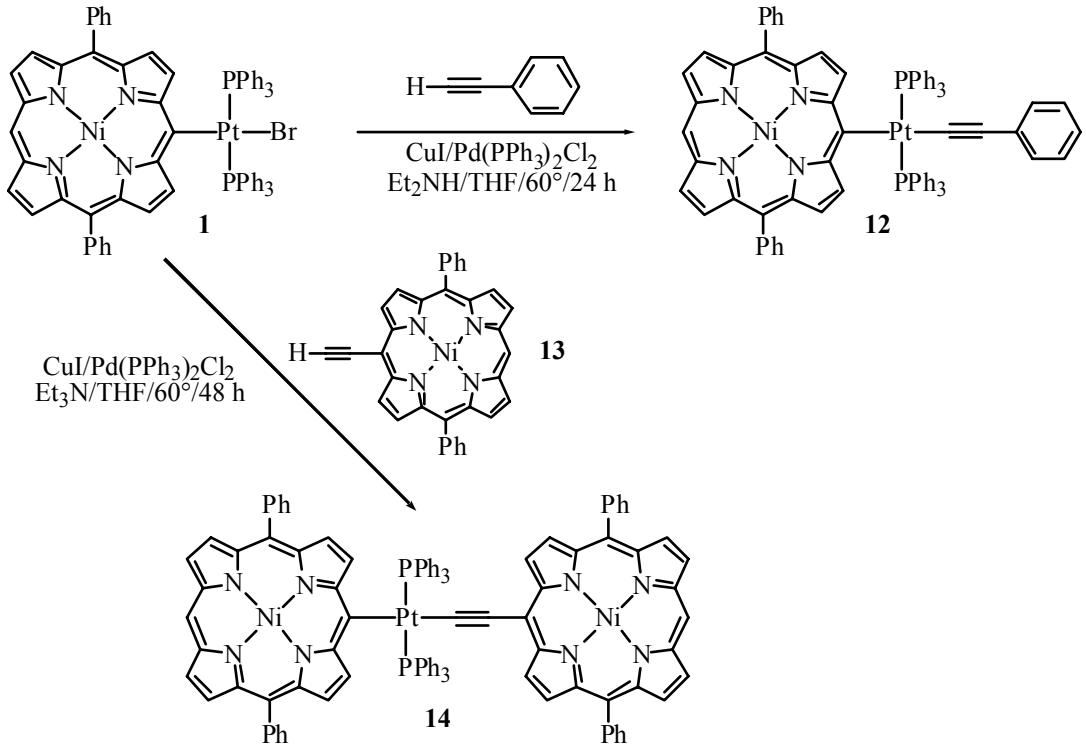
Scheme 1. Attempted alkylations at platinum in **1**.



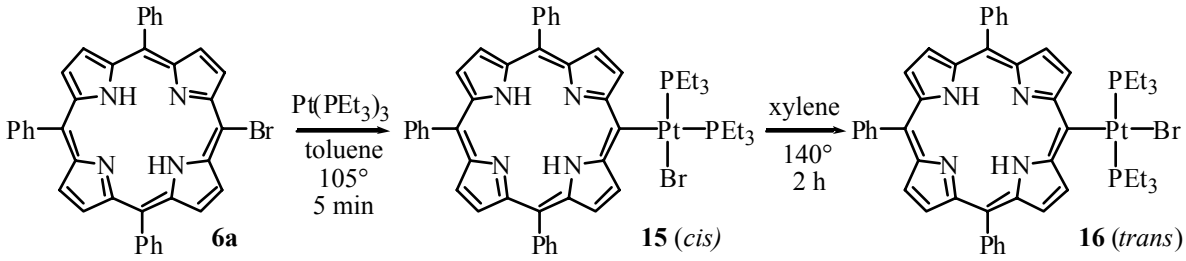
Scheme 2. Preparations of triarylporphyrins and their derived platinioporphyrins.



Scheme 3. Attempted alkylation at platinum in **8a**.



Scheme 4. Alkynylation at platinum in **1**.



Scheme 5. Formation of bis(triethylphosphine) complexes of H_2TrPP by oxidative addition.

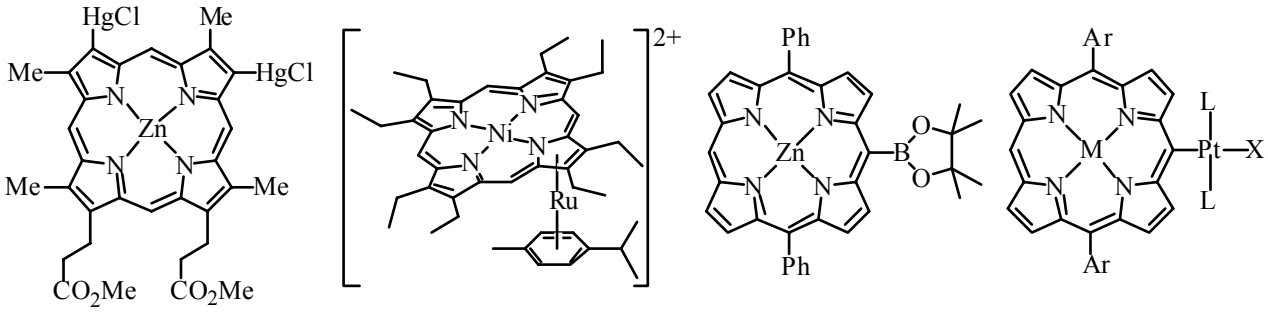


Chart 1. Some examples of peripherally-metallated porphyrins with direct porphyrin-metal bonds.

Table 1. Crystal data for NiDAPP **9b**, *trans*-[Pt(NiDPP)(C_2NiDPP)(PPh_3)$_2$] **14** and *trans*-[Pt(H_2TrPP)(PEt_3)$_2$] **16**.

	9b	**14**	**16**
a (Å)	11.3026(2)	14.2070(2)	13.90680(10)
b (Å)	11.3044(2)	16.5744(2)	14.78240(10)
c (Å)	21.0858(3)	20.6061(3)	23.3665(2)
α (deg)	105.0783(6)	90.2470(5)	90
β (deg)	97.7815(6)	101.7677(6)	102.6361(3)
γ (deg)	103.5210(6)	113.9458(6)	90
Cell volume (Å^3)	2473.40(7)	4320.73(10)	4687.24(6)
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	*P* $2_1/n$
R_{int}	0.060	0.050	0.049
R	0.041	0.047	0.051
R_w	0.047	0.050	0.056
S	1.064	0.987	1.026
θ limits	3 – 27.5^o	3-25.4^o	3 – 27.5^o
No. unique/ No. observed (obs. criterion)	11356/4648 (I>3σI)	15830/9484 (I>3σI)	10756/5606 (I>3σI)
Number refined parameters	525	1036	504
Crystal size (mm)	0.18 x 0.18 x 0.21	0.06 x 0.06 x 0.14	0.018 x 0.25 x 0.44