meso-η¹-Metalloporphyrins: preparation of palladio- and platinioporphyrins and the crystal structure of 5-[bromo-1,2-bis(diphenylphosphino)-ethanepalladio(II)]-10,20-diphenylporphyrin

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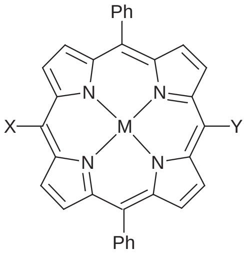
Received (in Cambridge, UK) 1st September 1998, Accepted 21st September 1998

***meso*-η¹-Palladio- and platinioporphyrins have been isolated for the first time by means of oxidative addition of bromoporphyrins to Pd(0) and Pt(0) complexes; the X-ray crystal structure of the title complex was determined.**

Palladium-catalysed coupling reactions have been employed by a number of research groups to prepare novel porphyrins. Mercuration/palladation was used by Smith and co-workers to introduce unsaturated substituents into mono-porphyrins,[1] and one of us first applied palladium/phosphine catalysis to the formation of bis(porphyrins).[2] Numerous coupling reactions of the Heck, Suzuki, Sonogashira, and Stille types have since been used to prepare substituted porphyrins and multi-porphyrin arrays linked by alkenes and alkynes, with or without accompanying aryl linkers.[3,4] The most direct entry to this chemistry is *via meso*-haloporphyrins,[4] which are readily prepared in the case of β-unsubstituted porphyrins of the 5,15-diaryl type, such as 5,15-diphenylporphyrin, DPP.[5] For example, 5-bromoDPP and 5-iodoDPP [as the nickel(II) or zinc(II) complexes], couple easily with terminal alkynes, organotin or organozinc compounds, in the presence of Pd(II) or Pd(0) phosphine complexes.[4,6] An essential process in these catalytic cycles appears to be the oxidative addition of the *meso*-carbon-to-halogen bond to a zerovalent palladium precursor. However, until now there were no examples of isolated and characterised *meso*-η¹-palladioporphyrins. Here we report the stoichiometric (rather than catalytic) preparations of a number of such novel organometallic porphyrins, and the single crystal X-ray structure of one example.



	M	X	Y
1	Ni	H	Pd(PPh_3)$_2$Br
2	H_2	H	Pd(PPh_3)$_2$Br
3	H_2	H	Pd($AsPh_3$)$_2$Br
4	Ni	Pd(PPh_3)$_2$Br	Pd(PPh_3)$_2$Br
5	H_2	H	Pd(dppe)Br
6	Ni	H	*cis*-Pt(PPh_3)$_2$Br
7	Ni	H	*trans*-Pt(PPh_3)$_2$Br
8	H_2	H	*cis*-Pt(PPh_3)$_2$Br
9	H_2	H	*trans*-Pt(PPh_3)$_2$Br
10	Ni	Pd(PPh_3)$_2$Br	*trans*-Pt(PPh_3)$_2$Br

The palladioporphyrins **1–5** were prepared by addition of the appropriate stoichiometric amount of palladium(0) precursor [Pd(PPh_3)$_4$ or Pd_2dba_3† + PPh_3, $AsPh_3$, or dppe] to 5-bromoDPP or 5,15-dibromoDPP or the corresponding nickel(II) complexes, in argon-purged toluene at 105 °C. The mono-adducts with the monodentate Group 15 ligands were formed quantitatively within a few minutes, while the double addition to form **4** required 40 minutes heating, and the dppe complex **5** required 8 hours heating. The complexes were readily isolated in high yield by evaporation of the toluene and trituration with ether. The palladioporphyrins are air-stable solids which undergo some Br/Cl exchange when dissolved in chlorinated solvents. We have also extended this chemistry to the analogous *meso*-platinioporphyrins. The addition of Pt(PPh_3)$_3$ to either 5-bromoDPPNi or 5-bromoDPP free-base in refluxing toluene initially leads within about 20 minutes to the *cis* adducts **6** and **8**, respectively, as shown by the characteristic ^1J(PtP) coupling constants in the ^{31}P NMR spectra [*e.g.* for **6**, *J trans* to porphyrin = 1790 Hz, *J trans* to Br = 4250 Hz, ^2J(PP) = 17 Hz]. These initial adducts isomerise over a period of 6 hours to the respective *trans* isomers **7** and **9**. The complexes were characterised by ^{1}H and ^{31}P NMR, electronic absorption, and FAB-mass spectra,‡ and in the case of the diphosphine derivative **5**, by X-ray crystallography.§ For all the Pd complexes except **5**, the ^{31}P NMR spectra showed that the Pd(II) centres have the *trans* geometry.

The crystal structure of **5** comprises two independent molecules in the asymmetric unit. Molecules A and B both display slightly distorted square-planar coordination about the Pd(II) atom, which is η¹-bonded to the *meso*-carbon of a weakly-ruffled porphyrin core (maximum deviation from the 24-atom mean plane = 0.28 Å in molecule A). Molecules A and B differ most markedly in the dihedral angles between the mean planes of the porphyrin and the 10,20-phenyl groups. In molecule A, these angles are 88 and 58°, and in molecule B, 56 and 59°. There is no obvious reason for the unique orthogonality of the phenyl ring in molecule A. Fig. 1 shows the coordination plane of the Pd atom for molecule A. The view from above the porphyrin ring, shown in space-filling form in Fig. 2, indicates how the phenyl groups of the diphosphine ligand shield the face of the porphyrin. This suggests immediately a use for this methodology in the engineering of cavities with tailored shape and hydrophobicity above and below a porphyrin ring, without the typically difficult and tedious synthetic work associated with ‘capping’ and ‘strapping’ opposite sides of a porphyrin. Moreover, the use of a chiral diphosphine may offer the intriguing possibility of generating chiral catalytic metalloporphyrins based on the present structural class.

The second insertion of the Pt(0) fragment into 5,15-dibromoDPPNi is so slow that the interesting compound **10** (containing all three members of the nickel triad) could be prepared by addition of Pt(PPh_3)$_3$, heating for 3 hours, followed by addition of Pd_2dba_3/PPh_3, and a further 3 hours heating. A similar but weaker deactivating effect of the Pt(II) fragment was noted by Stang and co-workers in their work on simpler arylene-bridged dipalladium and diplatinum organometallics, examples of which have also recently been reported by Kim *et al.*[7]

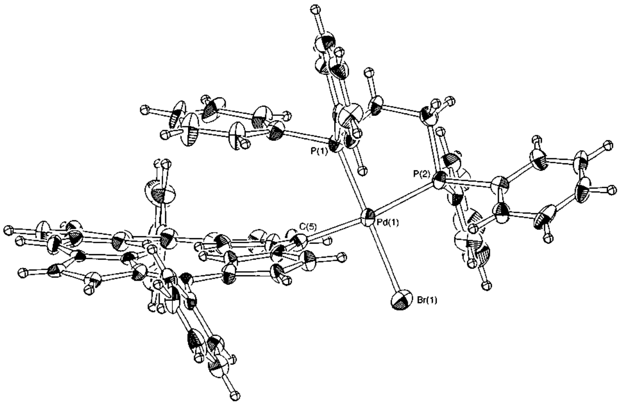


Fig. 1 Molecular structure of **5** (molecule A), showing the Pd coordination plane. Selected bond lengths and angles: Pd(1)–Br(1) 2.469(3), Pd(1)–P(1) 2.240(6), Pd(1)–P(2) 2.327(6), Pd(1)–C(5) 2.05(2) Å; P(1)–Pd(1)–P(2) 85.2(2), Br(1)–Pd(1)–P(2) 96.2(2), Br(1)–Pd(1)–C(5) 91.9(5), P(1)–Pd(1)–C(5) 87.2(6)°.

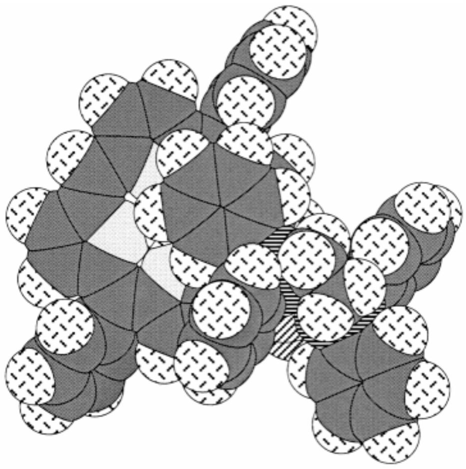


Fig. 2 Space-filling version of the molecular structure of **5**, viewed from normal to the porphyrin plane.

The electronic absorption spectra of our compounds are unexceptional, and the bromobis(phosphine/arsine)metallo moiety exerts a bathochromic effect of similar magnitude to that of a simple bromo substituent. The high polarizability of the heavy metal atoms(s) in direct communication with the porphyrin π-electrons may confer interesting third-order nonlinear optical properties on this new class of organometallic compound. We will be exploring their potential applications in this field, as well as in catalysis and for the construction of multi-porphyrin supramolecular arrays.[8]

We thank Q.U.T. for a Special Small Grant, and the Centre for Instrumental and Developmental Chemistry for financial support.

Notes and references

† dba = dibenzylideneacetone (1,5-diphenylpenta-1,4-dien-3-one).

‡ *Spectroscopic data* for **7**: NMR (CDCl$_3$) δ_H 9.52 (s, *meso*-H), 9.51, 8.92, 8.66, 8.21 (all d, β-H), 7.9, 7.65 (m, 10,20-Ph), 7.25, 6.65 (m, PPh); δ_P (*vs.* ext. 85% H$_3$PO$_4$) 28.5 [s with ^{195}Pt satellites, *J*(PtP) 2940 Hz]; UV–VIS (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 415 (5.36), 488 sh (3.57), 523 (4.20), 555 sh (3.67); FAB-MS maximum of cluster calc. for $C_{68}H_{49}BrN_4NiP_2Pt$ 1318.16, found 1318.1.

§ *Crystal data* for **5**: $C_{58}H_{45}N_4BrPdP_2$, M_r = 1046.27, monoclinic, space group $P2_1/c$, a = 17.006(6), b = 27.248(8), c = 22.13(1) Å, β = 91.18(5)°, V = 10254(6) Å^3, Z = 8, μ(Mo-Kα) = 12.47 cm^{-1}, D_c = 1.355 g cm^{-3}, T = 232(1) K, R = 0.075, R_w = 0.098 for 7246 reflections with $I > 3\sigma(I)$. CCDC 182/1024.

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Communication 8/06769D