A platinum-linked porphyrin trimer and a complementary aluminium tris[3-(4-pyridyl)acetylacetonate] guest

Lindsey G. Mackay, Harry L. Anderson and Jeremy K. M. Sanders *
Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

A cyclic trimeric porphyrin host has been synthesised with alkyne–platinum–alkyne linkages; binding of the octahedral aluminium tris[3-(4-pyridyl)acetylacetonate] guest ligand into the complementary cavity of the host induces an asymmetry which is readily detected by NMR spectroscopy. The ligand complementarity unambiguously establishes the structure of this complex artificial receptor, but did not lead to an effective templated synthesis. A platinum-linked tetramer was also tentatively identified, but the absence of a suitably complementary ligand reduces the confidence that can be placed in this larger, and highly flexible, structure. These results demonstrate the strengths, and limitations, of metal coordination chemistry for assembling supramolecular architectures.

Introduction

The first paper in this series set out a general design for model enzymes based on porphyrins;[1] it was an important part of our strategy that we should create a series of receptors of the same shape but with a range of cavity sizes, using the same diarylporphyrin monomer as a building block. In the first instance we used butadiyne linkers generated by Glaser coupling of a terminal alkyne [eqn. (1)].

$$\text{Ar–C}\equiv\text{C–H} + \text{H–C}\equiv\text{C–Ar} \longrightarrow \text{Ar–C}\equiv\text{C–C}\equiv\text{C–Ar} \quad (1)$$

The resulting trimer has an open, flexible cavity with a mean Zn–Zn distance of *ca.* 15 Å.[1-3] In this paper we describe the synthesis of a platinum-linked analogue which was designed to exhibit the same topology but with a larger cavity. Several possible linker groups were considered and the variation in cavity size that would be available in such a series was determined by energy minimisation of these structures using the MM2 forcefield in Macromodel.[4] A platinum centre was modelled as a constrained carbon atom with bond lengths and angles suitable for a square planar –(C≡C)–Pt(PR$_3$)$_2$–(C≡C)– centre (obtained from analysis of analogous structures in the Cambridge Structural Database). The trimer resulting from the linkage chemistry in eqn. (2) was predicted to have a mean Zn–Zn distance of *ca.* 18 Å.

$$\text{Ar–C}\equiv\text{C–H} + \text{Cl–Pt(PEt}_3)_2\text{–Cl} + \text{H–C}\equiv\text{C–Ar} \longrightarrow \text{Ar–C}\equiv\text{C–Pt(PEt}_3)_2\text{–C}\equiv\text{C–Ar} \quad (2)$$

Hagihara and Takahashi had developed this chemistry in their investigation of rigid platinum-containing polymers.[5] Use of an amine as solvent and as base in the presence of a catalytic quantity of cuprous halide in an inert atmosphere gave a rapid and efficient coupling between terminal acetylenes and metal halides and allowed formation of high molecular weight polymers. Cuprous iodide is the catalyst of choice by virtue of its stability in air,[6] and diethylamine was found to be the most effective amine. An inert atmosphere is required to avoid undesired oxidative Glaser coupling to give the butadiyne.

Our previous work on cyclic porphyrin oligomers demonstrated the utility of complementary multidentate ligands, both for probing geometry, by selective strong binding, and also for facilitating synthesis, by acting as templates. We therefore designed and synthesised the ligand **(Pyacac)$_3$Al** as a complementary structure to the desired platinum-linked trimer **Zn$_3$-c-Tri2a**. The size of this ligand can be estimated from examination of X-ray structural data for aluminium tris(acetylacetonate) complexes[7] and from the known dimensions of the pyridine ring. This gives a N–N distance of *ca.* 13 Å in **(Pyacac)$_3$Al** which is appropriate for the 18 Å Zn–Zn distance in **Zn$_3$-c-Tri2a**. This ligand should therefore be able to complex to the trimer to give very stable adducts, and we hoped to use it as a template to provide an efficient trimer synthesis. Some of these results have been reported previously in preliminary form.[8]

Results and discussion

Synthesis

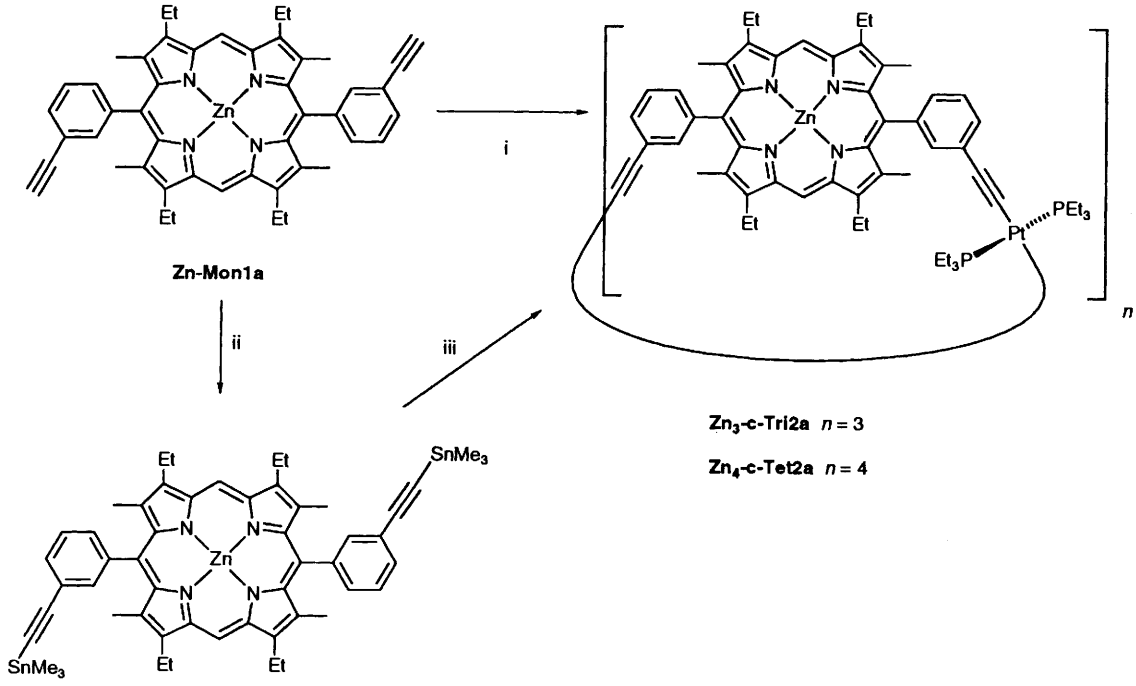
The choice of which platinum complex should be used as linker was not obvious. Despite its relative instability, triethylphosphine was chosen as the platinum ligand: molecular modelling indicated excessive congestion of the trimer cavity with the more stable tributylphosphine-substituted linkers which had been employed in much of Hagihara's work.[5] Furthermore, *trans*-[Pt(PEt$_3$)$_2$Cl$_2$] is readily separated from the *cis*-isomer and is easy to handle.[9]

Porphyrin monomer **Zn-Mon1a** and *trans*-[Pt(PEt$_3$)$_2$Cl$_2$], each 0.5 mmol dm^{-3} in diethylamine, were allowed to react together using Hagihara's coupling conditions[10] with 0.04 mol equivalent of CuI catalyst (Scheme 1). After 7 h at 50 °C no starting material was present and chromatography yielded four components: a product in 3% yield which appears to be a linear porphyrin dimer joined by a central platinum linker (FAB M$^+$ 1914);† the trimer **Zn$_3$-c-Tri2a** (16% yield); a third band tentatively assigned to tetramer **Zn$_4$-c-Tet2a**; and a highly polar/insoluble residue.

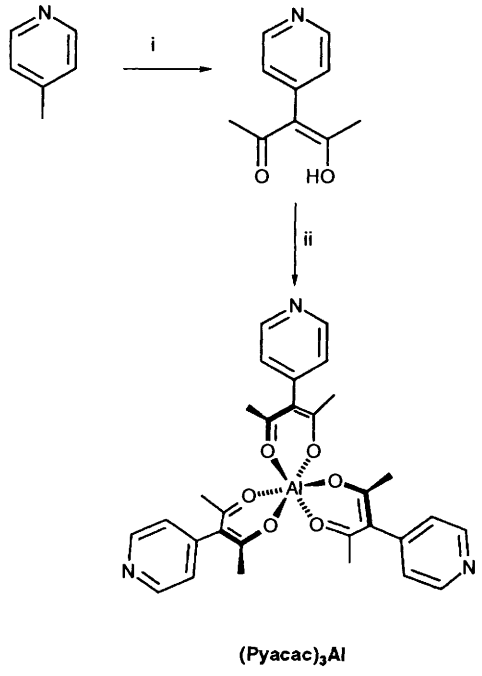
Although the platinum-linked porphyrin trimer could be prepared by this reaction, it was hoped that much higher yields might be achieved using a template-directed synthesis. A templating amine considerably larger than tri(4-pyridyl)triazine **Py$_3$T** was required and thus the new tripyridyl ligand **(Pyacac)$_3$Al** was prepared (Scheme 2). For the synthesis of this

* E-mail: jkms@cus.cam.ac.uk.

† The linear dimer proved difficult to purify and was not characterised fully.



Scheme 1 i, *trans*-$[Pt(PEt_3)_2Cl_2]$, $NHEt_2$, CuI, 50 °C; ii, Me_2NSnMe_3, THF, room temp.; iii, *trans*-$[Pt(PEt_3)_2Cl_2]$, CuI, toluene, 50 °C, 22 h



Scheme 2 i, CH_3COCl, $CHCl_3$, −20 °C; ii, $Al(NO_3)_3$, $NaHCO_3$, MeOH aq, room temp.

ligand 3-(4-pyridyl)pentane-2,4-dione was complexed to aluminium trinitrate in the presence of sodium hydrogen carbonate. After removal of the undesired aluminium hydroxide the pyridylacetylacetonate complex could be simply precipitated out by the addition of ethyl acetate and hexane (1:1, v/v). The pyridylpentanedione ligand was prepared in a modification of Nozawa's procedure,[11] coupling 4-methylpyridine with acetyl chloride at low temperature. The ligand itself is relatively unstable, readily undergoing reverse-Claisen condensation, but the complex appears to be indefinitely stable.

Characterisation of trimer

The trimeric product **Zn_3-c-Tri2a** had a positive ion FAB mass spectrum containing the expected M^+ and M^{2+} at m/z 3516 and 1756. The electrospray mass spectrum of the free base version **H_6-c-Tri2a**, run in 0.2% trifluoroacetic acid in methanol contained peaks for the multiply charged ions MH_2^{2+} (1661), MH_3^{3+} (1109) and MH_4^{4+} (832). The IR spectrum contained the expected ν(C≡C) band at 2064 cm^{-1}, and the UV spectrum had the three bands corresponding to the *trans*-(C≡C–Pt–C≡C)–moiety at 342, 292 and 260 nm, as well as a Soret band at 409 nm and Q bands at 563 and 572 nm.

The ^1H NMR spectrum of the trimer supported a cyclic structure in which each porphyrin nucleus was equivalent. The spectrum was virtually identical with the butadiyne-linked trimer[1] **Zn_3-c-Tri1a** with the addition of two complex signals resulting from the ethyl-substituted phosphines. The ^1H NMR spectra of square planar bis(triethylphosphine)platinum complexes have been well investigated:[12] the methyl signal in the *cis* complexes is a simple 1:2:1 triplet, whereas the *trans* isomers give rise to a 1:4:6:4:1 quintet. This results from the triplet coupling to the methylene being split further into a 1:2:1 triplet as a result of virtual coupling of the two phosphorus atoms.‡

In this case the two phosphorus atoms behave this way if $\delta P_1 = \delta P_2$ and $J(P_1\text{-}P_2) \geqslant J(P\text{-}X)$, the outer lines of the triplet produced from this coupling being separated by $|J(P_1\text{-}X)| + |J(P_2\text{-}X)|$. As the long range $^5J_{P,H}$ is expected to be very small, this separation will correspond to the shorter three-bond coupling which is *ca.* 14 Hz and so accidentally twice the magnitude of the $^3J_{H,H}$ coupling to the methylene protons. This 1:4:6:4:1 pattern was clearly seen in the methyl resonance and

‡ Virtual coupling appears when a group of k nuclei have such strong coupling that they behave as a single system of spin angular momentum $(I_1 + I_2 \ldots + I_k)h/2\pi$ rather than separate nuclei of individual spin angular momentum $(I_1h/2\pi + I_2h/2\pi \ldots + I_kh/2\pi)$. A nucleus coupled to one or more of the k nuclei set, and chemically shifted from the entire set, will effectively be coupled to all of them, *i.e.* there will exist a virtual coupling between pairs of nuclei i,j despite the fact that J_{ij} may be zero.

was further evidence for the retention of the *trans* platinum structure. The methylene signal presumably also displayed virtual coupling but in this case a $^2J_{P,H}$ and $^4J_{P,H}$ coupling is involved, the sum of which is no longer equal to twice the $^3J_{H,H}$ coupling and hence the coupling pattern is not simple. The signal was further complicated by coupling to the platinum nucleus ($I = \frac{1}{2}$, 33.8% abundance) which will result in broad satellites of relative intensity $\frac{1}{4}$.[13]

The ^{31}P NMR spectrum of the trimer confirmed equivalence of the phosphorus atoms, containing only a singlet at −130.4 ppm (relative to trimethyl phosphite) with platinum satellites having a $^1J_{Pt,P}$ value of 2370 Hz. The corresponding coupling in a dinuclear μ-ethyndiylplatinum phosphine complex has been reported as 2520 Hz.[14]

Assignment of the *J*-modulated spin echo ^{13}C spectrum of the trimer **Zn$_3$-c-Tri2a** was made by comparison with the acetylene-linked trimer **Zn$_3$-c-Tri1a** and with literature reports of similarly α-, β- and *meso*-substituted porphyrins.[15] The methylene carbon on the phosphorus appeared as a triplet, again as a result of virtual coupling of the two phosphorus nuclei. The outer lines of the triplet were separated by 34.5 Hz, corresponding to $\Sigma|^1J_{P,C}| + |^3J_{P,C}|$. In simple phosphines these two couplings are approximately −14 and +12 Hz, respectively,[16] in reasonable accord with the observed splitting. The acetylenic carbon attached to the platinum centre could not be identified; its intensity will be greatly reduced by the absence of any ^{1}H NOEs as the nearest proton is four bonds away. In addition, the signal intensity will be reduced by the 1:4:1 splitting from the coupling to the 33.8% abundance, spin-$\frac{1}{2}$ ^{195}Pt nucleus and the satellite signals will be broadened as a result of the large chemical shift anisotropy of this inorganic nucleus.[13] Taken together, these spectroscopic properties all support the expected trimer structure. This structure was further confirmed by the ligand binding studies described below.

The positive ion FAB mass spectrum of the product tentatively identified as the tetramer **Zn$_4$-c-Tet2a** contained peaks corresponding to M^+ at *m/z* 4686 and M^{2+} at 2345, but also contained a peak at 3515, which is consistent with the trimer. As the sample appeared by TLC to be free of trimer, the *m/z* 3515 ion may have resulted from loss of one platinum–porphyrin unit *via* cleavage of alkyne–Pt bonds.§ The ^{1}H NMR spectrum of the product suggests that a single porphyrin species is present, but the host resonances are broadened by at least 10 Hz, presumably due to the presence of multiple conformers as in the butadiyne-linked analogue.[2] However, heating of the sample to 373 K gave no significant improvement. Addition of tetrapyridylporphyrin did not help, the ligand presumably being too small to hold the host in the all-*cis* conformation. A larger ligand may have been be able to achieve this but none was to hand and the design and synthesis of a suitable candidate was not pursued.

Binding properties

The tridentate aluminium-centred ligand **(Pyacac)$_3$Al** was titrated against the platinum-linked trimer in $CDCl_3$ and ^{1}H NMR spectra were recorded at 250 MHz. The shifts in the host and guest signals indicated the formation of the 1:1 complex shown (Fig. 1). This system is in slow exchange on the NMR timescale at room temperature and the ligand binds extremely strongly. Sharp signals are seen for the bound ligand until more than 1 equivalent has been added and after this they broaden slightly and broad signals from free ligand appear; these are shifted slightly upfield and broadened as a result of the very weak binding to the external faces of the trimer *via* six-coordinate zinc. The shifts observed on complexation of the ligand are given in Table 1. The porphyrin ring currents shifted the guest H_α resonances of the pyridyl ring upfield by 6.5 ppm2 and the H_β-pyridyl doublet by 2.3 ppm; these shifts are consistent with those observed in our other complexes[2] and confirm that all three pyridines are bound simultaneously. The guest methyl, Me_g, shifted upfield by 1.5 ppm on binding to the trimer. All of the host resonances are shifted upfield except for the internal aromatic proton which experiences a downfield shift of 0.09 ppm; this arises because it is in a position to experience the ring-current of the guest molecule. Remarkably, the chirality of the remote propeller-shaped, octahedral guest ligand is sensed by the host, and the porphyrin methyl and ethyl side chain resonances are each split into two signals of equal intensity, as the adjacent side chains (a and a′, b and b′) are now in different environments in the complex. The *meso* singlet, which is shifted upfield from 10.11 to 9.90 ppm in the complex, is not split as both of these protons are still equivalent as expected from the molecular symmetry shown in Fig. 1.

A NOESY spectrum of the complex, Fig. 2, acquired in the

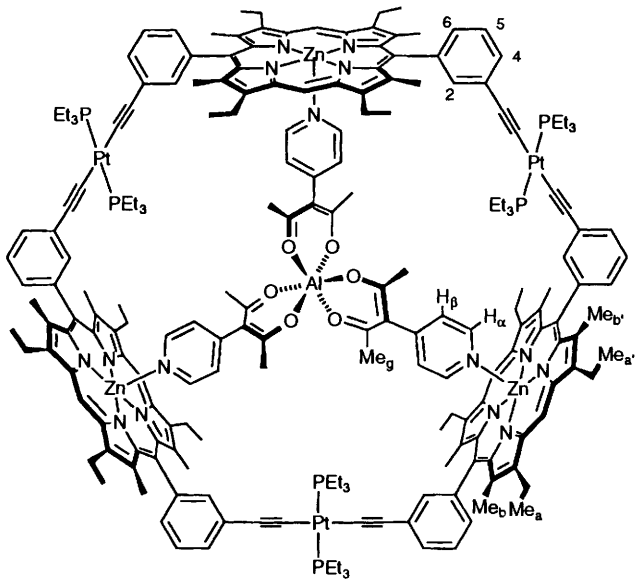


Fig. 1 The complex between **Zn$_3$-c-Tri2a** and **(Pyacac)$_3$Al**

Table 1 Free and bound ^{1}H NMR shifts observed for **(Pyacac)$_3$Al** and **Zn$_3$-c-Tri2a**

Resonance	Free (ppm)	Bound (ppm)
Ligand		
α-Pyridyl	8.63	2.12
β-Pyridyl	7.17	4.83
Methyl	1.90	0.40
Host		
Meso	10.11	9.90
Aromatic 2-H	7.85	7.94
Aromatic 6-H	7.79	7.70
Aromatic 4-H	7.67	7.56
Aromatic 5-H	7.54	7.41
Porph-CH_2CH_3	3.93	3.87, 3.77
Porph-CH_3	2.49	2.49, 2.40
Porph-CH_2CH_3	1.68	1.64, 1.54

§ The FAB mass spectrum of a porphyrin monomer terminated by two $Pt(PBu_3)_2Cl$ groups contained the molecular ion and an intense peak at 741 resulting from loss of the two platinum moieties, showing that cleavage of the two Pt–C bonds is not difficult under these conditions. Recently Diederich *et al.* have also reported a surprisingly easy Pt–C bond cleavage in a related system.[17]

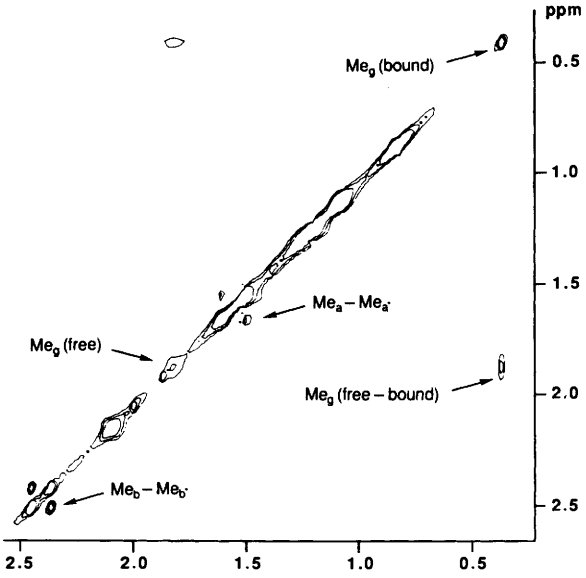


Fig. 2 Part of the 400 MHz ^{1}H NOESY spectrum of the **Zn$_3$-c-Tri2a-(Pyacac)$_3$Al** complex in the presence of a 10% excess of free ligand; the mixing time was 300 ms, temperature 293 K

presence of a 10% excess of the ligand, confirmed the above assignments by showing a rapid free-bound exchange of the ligand on the relaxation timescale. Chemical exchange cross peaks were observed between the free and bound guest and host resonances. The exchange of the two diastereotopic triplets (Me$_a$ with Me$_{a'}$) at δ 1.64 and 1.54, and of the singlets (Me$_b$ with Me$_{b'}$) at δ 2.49 and 2.40 is clearly shown in Fig. 2. This exchange process corresponds to an apparent inversion of configuration at the chiral aluminium centre but it presumably results from intermolecular exchange of the host with the two enantiomers of the racemic guest.

A strong host–guest complex thus forms in this system and a more quantitative assessment of the strength of this association was desired. A lower limit of the association constant was estimated from a UV titration at very low host concentration.[2] A value of 1.0×10^{10} dm^3 mol^{-1} was obtained for the binding of the tripyridylaluminium ligand to the platinum-linked trimer in dichloromethane at 293 K. For comparison, tripyridyltriazine[2] binds to the platinum trimer much more weakly with a binding constant of only 3.6×10^7 dm^3 mol^{-1}; this result suggests that this much smaller ligand can only coordinate to two of the porphyrin units in this trimer.

Attempted templating

The reaction conditions for the cyclisation needed to be altered to allow the **(Pyacac)$_3$Al** template to be employed: an amine solvent would compete for the zinc porphyrin binding sites. Thus, the proportion of diethylamine utilised in the coupling reaction was reduced to 10% by volume in toluene. Heating of the mixture at 50 °C for 24 h under these conditions gave a 22% yield of the isolated trimer, the most efficient synthesis which had been obtained so far. The reaction was repeated in the presence of 2 equivalents of the tripyridylaluminium template, **(Pyacac)$_3$Al** but with no improvement in yield, perhaps because the concentration of diethylamine was still too high.

The alternative coupling sequence shown in Scheme 1 *via* the bis(trimethylstannane)[18] was therefore investigated; this has the attraction that no amine is needed, and it has been used successfully to prepare alkyne–platinum–alkyne polymers.[19] The porphyrin monomer **Zn-Mon1a** could be converted almost quantitatively into the corresponding bis(trimethylstannane)-acetylide, and this activated monomer was then coupled with *trans*-[Pt(PEt$_3$)$_2$Cl$_2$], but there was no improvement in yield over the direct route and no significant success in templating with **(Pyacac)$_3$Al** using a range of different conditions. The most effective way to prepare **Zn$_3$-c-Tri2a** remains the direct coupling of **Zn-Mon1a** in 10% (v/v) diethylamine in toluene to give the trimer in 22% yield.

Conclusions

The spacious platinum-linked trimer can be readily prepared *via* simple coupling but templating of the reaction by the **(Pyacac)$_3$Al** ligand proved ineffective despite the strong affinity of this ligand for the cyclic trimeric product. In retrospect, the poor templating observed in this system is not entirely surprising, given that we now realise that our most effective templates exhibit only millimolar effective molarities for the reactive ends in a linear porphyrin intermediate.[20] At the slightly higher concentrations required for the condensation of the two monomeric subunits that comprise the platinum-linked trimer the apparent effect of a template will be decreased. In addition to this a template of this kind can hold the trimeric linear intermediate in the correct orientation to react but has no control over the freely rotating reactive ends. In the platinum-linked trimer case this is even more of a problem as the linear trimer must be 'caught' with the correctly substituted end groups before they have the chance to react further. The fact that this coupling must be carried out at elevated temperature also decreases the efficiency of the template as its binding constants for the various intermediates will be inherently lower.

A major disadvantage of the Pt-linked host is its lower stability by comparison with the smaller butadiyne-linked and the larger octatetrayne-linked structures.[21] The more robust molecules may be readily interconverted between the metallated and free base porphyrins in almost quantitative yield and may also be chromatographed repeatedly. In contrast, the platinum-linked trimer appears to be sensitive to the acidic conditions which are required for demetallation and to decompose on repeated chromatography. This is disappointing in light of the apparent stability of the reported polymeric structures containing similar platinum–alkyne linkages.[22]

An important principle concerning the characterisation of very large receptors can be seen to emerge from this work, *i.e.* that the use of complementary hosts and guests provides powerful evidence for the correct structures of each because the binding constants will be very high and the resulting NMR spectra will be firmly in slow exchange. This is best illustrated by the complementary results obtained with the large and small trimers and tri-ligands: the complementary pairs provide excellent evidence for the correct structures of both hosts. By contrast, the failure to find a suitable ligand for the spacious platinum-linked tetramer highlights the problem of identifying the exact nature of large receptors without a complementary guest.

Finally, the newly designed **(Pyacac)$_3$Al** ligand has the potential for creating a wide range of new heterometallic complexes with tunable properties.

Experimental

General directions are as given in the first paper of this series.[1]

3-(4-Pyridyl)pentane-2,4-dione

A mixture of 4-methylpyridine (18.2 cm^3, 17.4 g, 186 mmol) and $CHCl_3$ (50 cm^3) was cooled to −20 °C (carbon tetrachloride–solid CO_2) and acetyl chloride (10.6 cm^3, 11.7 g, 149 mmol) was added dropwise to the stirred solution over 75 min. An intense green colouration developed and stirring was continued at −20 °C for 3 h. The $CHCl_3$ and excess of starting material were

distilled off at reduced pressure (35 °C, 20 mmHg) and the brown residue was triturated with toluene to give a yellow solution and solid 4-methylpyridine hydrochloride. After removal of the precipitate, the solvent was removed from the filtrate under reduced pressure and the residue chromatographed. Elution with hexane–EtOAc (5:4, v/v) afforded a yellow band which yielded the unstable product (3.48 g, 26%) on solvent removal; δ_H(250 MHz) 1.90 (s, 6 H, CH_3), 7.14 (d, *J* 6, 2 H, β-Py), 8.65 (d, *J* 6, 2 H, α-Py) and 16.75 (s, 1 H, COCHCO).

Tris[3-(4-pyridyl)acetylacetonato]aluminium(III)

Aluminium trinitrate (120 mg, 0.32 mmol) and 3-(4-pyridyl)-pentane-2,4-dione (250 mg, 1.4 mmol) were dissolved in MeOH–H_2O (1 : 1; 3 cm^3) and $NaHCO_3$ (89 mg, 1.1 mmol) was added to the orange solution; the resulting suspension was then stirred for 5 min. After solvent removal under reduced pressure the residue was extracted with $CHCl_3$ (10 cm^3) and the precipitated aluminium hydroxide then filtered off. The solution was concentrated to 2 cm^3 and the product then precipitated by the addition of EtOAc–hexane (1 : 1, v/v). This cream solid was dried *in vacuo* to give the aluminium complex (134 mg, 75%) as a powdery solid, mp > 290 °C; δ_H(250 MHz) 1.90 (s, 18 H, CH_3), 7.17 (d, *J* 6, 6 H, β-Py) and 8.63 (d, *J* 6, 6 H, α-Py); [*m/z* (EI MS) 555 (M^+) $C_{30}H_{30}AlN_3O_6$ requires 555.5].

Platinum-linked porphyrin trimer Zn_3-c-Tri1a

The porphyrin monomer (50 mg, 67 μmol) and *trans*-dichlorobis(triethylphosphine)platinum(II) (34 mg, 67 μmol) were dissolved in diethylamine (125 ml) and the solution thoroughly deoxygenated. Copper(I) iodide (0.5 mg, 2.6 μmol) was added to the solution which was then heated under reflux under an argon atmosphere for 7 h; it was then stored at room temperature overnight. After solvent removal from the mixture under reduced pressure the residue was separated by chromatography, using initially CH_2Cl_2–hexane (6:4, v/v) as eluent; the polarity of the eluent was then gradually increased. The first band gave a 3% yield of crude linear dimeric platinum-linked porphyrin; FAB MS: *m/z* 1914 (M^+), $C_{108}H_{116}N_8P_2PtZn_2$ requires 1913.9; $\lambda_{max}(CH_2Cl_2)$/nm 271, 328, 410, 537 and 572. The second fraction yielded the cyclic trimeric product (13 mg, 16%); $\nu_{max}(CCl_4)/cm^{-1}$ 2105 (C≡C), 1598, 1475 and 1459 (C=C); δ_H(400 MHz) 1.11 (m, 54 H, PCH_2CH_3), 1.68 (t, *J* 7.5, 36 H, CH_2CH_3), 2.11 (m, 36 H, PCH_2CH_3), 2.49 (s, 36 H, CH_3), 3.93 (q, *J* 7.5, 24 H, CH_2CH_3), 7.54 (t, *J* 7.7, 6 H, 5-H Ar), 7.67 (d, *J* 7.9, 6 H, 4-H Ar), 7.79 (d, *J* 7.3, 6 H, 6-H Ar), 7.85 (s, 6 H, 2-H Ar) and 10.09 (s, 6 H, *meso*); δ_C(100 MHz) 8.2 (PCH_2CH_3), 15.1 (CH_2CH_3), 16.3 (t, *J* 17, PCH_2CH_3), 17.4 (CH_3), 19.8 (CH_2), 96.9 (*meso* CH), 119.3 (*meso* CAr), 127.0 (CH, Ar), 128.0 (*C*–C≡C, Ar), 130.1 (CH, Ar), 130.4 (CH, Ar), 135.8 (CH, Ar), 136.7 (*C-meso*, Ar), 143.1 (β-C), 144.4 (β-C), 145.8 (α-C) and 147.6 (α-C); δ_P(162 MHz) −130.4 (s and satellite d, *J* 2370) [Found: *m/z* (FAB) 3516 (M^+) and 1756 (M^{2+}) $C_{180}H_{216}N_{12}P_6Pt_3Zn_3$ requires 3514.9 and 1757.4]; $\lambda_{max}(CH_2Cl_2)$/nm 260, 292, 342, 409, 536 and 572. The third fraction gave what appears to be tetrameric product (7 mg, 9%); δ_H(250 MHz) 1.16 (m, PCH_2CH_3), 1.72 (br t, CH_2CH_3), 2.14 (m, PCH_2CH_3), 2.53 (br s, CH_3), 3.97 (br q, CH_2CH_3), 7.53 (br Ar), 7.67 (br Ar), 7.75 (br Ar), 7.95 (br Ar) and 10.14 (br, *meso*); δ_P(162 MHz) −130.4 (s and satellite d, *J* 2367) [Found: *m/z* (FAB) 4686 (M^+) and 2345 (M^{2+}) $C_{240}H_{288}N_{16}P_8Pt_4Zn_4$ requires 4686.5 and 2343.3]; $\lambda_{max}(CH_2Cl_2)$/nm 263, 290, 334, 410, 537 and 572.

Acknowledgements

We thank the Association of Commonwealth Universities, the New Zealand Vice-Chancellors' Committee, Magdalene College Cambridge and the SERC for financial support, the SERC mass spectrometry service (Swansea) for FAB mass spectra, Dr S. Anderson for electrospray mass spectra, Dr J. Mackay for the NOESY spectrum and Dr M. S. Khan for useful advice.

References

1 H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1*, 1995, 2223.
2 S. Anderson, H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1*, 1995, 2231.
3 H. L. Anderson, A. Bashall, K. Henrick, M. McPartlin and J. K. M. Sanders, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 429.
4 W. C. Still, F. Mohamadi, N. G. J. Richards, W. C. Guida, M. Lipton, R. Liskamp, G. Chang, T. Hendrickson, F. DeGunst and W. Hasel, MacroModel V2.5, Department of Chemistry, Columbia University, New York, NY 10027.
5 K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1978, **145**, 101.
6 S. Takahashi, M. Kariya, T. Yatake, K. Sonogashira and N. Hagihara, *Macromolecules*, 1978, **11**, 1063.
7 E. A. Shugam and L. M. Shkol'nikova, *Doklady Akad. Nauk SSSR*, 1960, **133**, 386.
8 L. G. Mackay, H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1992, 43; H. L. Anderson, R. P. Bonar-Law, L. G. Mackay, S. Nicholson and J. K. M. Sanders, *Supramolecular Chemistry*, eds. V. Balzani and L. de Cola, Kluwer, 1992, 359.
9 F. R. Hartley, *Organometallic Chem. Rev. A*, 1970, **6**, 119.
10 K. Sonogashira, S. Kataoka. S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1978, **160**, 319.
11 M. Nozawa, Jpn. Kokai Tokkyo Koho JP 61 69,760, 1986 (*Chem. Abstr.*, 1986, **105**, 97336m).
12 M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1968, 3074; E. W. Randall and D. Shaw, *Mol. Phys.*, 1965, **10**, 41.
13 J. K. M. Sanders and B. K. Hunter, *Modern NMR Spectroscopy*, 2nd edn, ch. 7, Oxford University Press, 1993.
14 H. Ogawa, K. Onitsuka, T. Joh and S. Takahashi, *Organometallics*, 1988, **7**, 2257.
15 K. M. Smith (ed.), *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1975, ch 10; K. Wüthrich and R. Baumann, *Helv. Chim. Acta*, 1973, **56**, 585.
16 H. Kalinowski, *Carbon-13 NMR Spectroscopy*, Wiley, Chichester, 1988, p.588.
17 F. Diederich, R. Faust, V. Gramlich and P. Seiler, *J. Chem. Soc., Chem. Commun.*, 1994, 2045.
18 K. Jones and M. F. Lappert, *J. Organomet. Chem.*, 1965, **3**, 295.
19 J. Lewis, M. S. Kahn, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittmann, R. H. Friend and A. E. Dray, *J. Organomet. Chem.*, 1992, **425**, 165.
20 S. Anderson, H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1995, preceding paper.
21 H. L. Anderson, C. J. Walter, A. Vidal-Ferran, R. A. Hay, P. A. Lowden and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1995, following paper.
22 R. Nast and J. Moritz, *J. Organomet. Chem.*, 1976, **117**, 81.

Paper 5/01075F
Received 22*nd February* 1995
Accepted 1*st June* 1995