Semi-Rigid Bis-Phosphane Ligands for Metallamacrocycle Formation

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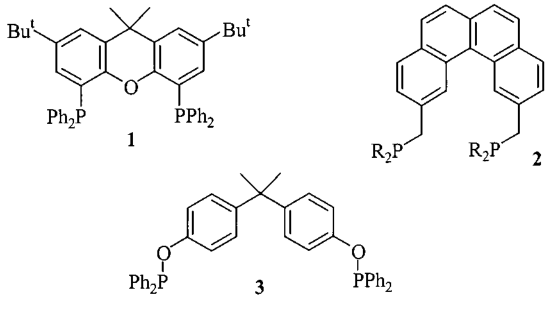
Efficient syntheses are described for the new bridging bis-phosphanes DPPN (**4**) and DPEN (**5**) built around the restricted rigidity of a 2,7-dialkoxynaphthalene backbone. These show marked preference for bridging pairs of metal atoms (Pt^{II}, Mo^0) to form metallamacrocycles or oligomers. Single-crystal X-ray structure determinations of four dimeric complexes with Pt^{II} and Mo^0 are reported. The dimeric platinum complexes can be obtained as the kinetically favoured *trans,trans* products, which isomerise to the *cis,cis* forms in the presence of free ligand. *cis,cis*-$[Pt_2Cl_4(DPEN)_2]$ (**12**) shows marked hydroformylation catalytic activity.

Introduction

Wide bite-angle and bridging phosphane ligands and their metal complexes have recently undergone a marked resurgence of interest. Some bis-phosphanes, like van Leeuwen's "xantphos" **1** (Scheme 1) and related ligands with calculated bite angles around 110−115°, are well suited to *cis* chelation in a trigonal bipyramidal complex.[1,2] The xanthene skeleton imposes a well-defined bite angle on such ligands, which has been linked to the high activity of hydroformylation catalysts derived from them, particularly rhodium and platinum derivatives.[3,4] *trans*-Spanning bis-phosphane ligands and their metal complexes have recently been reviewed.[5] *trans*-Spanning has been reliably achieved by, among others, Venanzi and co-workers, who used the rigid benzo[c]phenanthrene skeleton in ligands **2** (Scheme 1).[6] More flexible long-chain bis-phosphanes occasionally coordinate *trans*, though these are often in equilibria with other geometries[7] unless constrained by other ligands. An alternative strategy has been to synthesise some *trans*-spanning ligands in situ.[8,9] Ditopic bis-phosphanes are designed for coordination to two metal centres, with[10] or without (e.g. Faraone's ligand **3**[11]) metal−metal bonding. A further class of ligands involves monophosphanes on solid supports, whose coordination geometry is subject to different controls.[12,13]

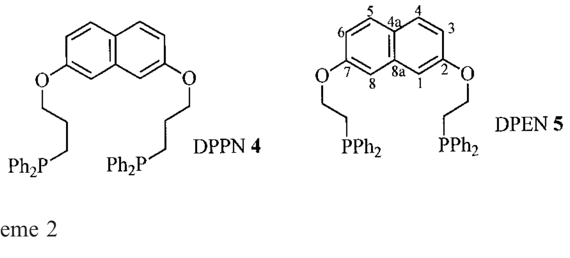


Scheme 1

We were interested to study the complexation behaviour of novel phosphanes, designed to be wide-angle chelators or bridging, and the catalytic activity of their transition metal complexes. For a ligand to be widely used, it must be readily available, with a short and high-yielding synthesis. We report here the efficient syntheses and complexing properties of two new semi-rigid, ditopic bis-phosphane ligands which further explore the relationship between ligand geometry and the structures of their transition metal complexes. The work extends recent reports on the formation of metallamacrocycles using related ligand types.[11]

Results and Discussion

Two new bis-phosphane ligands, 2,7-bis(3-diphenylphosphanylpropoxy)naphthalene (DPPN) **4** and 2,7-bis(2-diphenylphosphanylethoxy)naphthalene (DPEN) **5** (Scheme 2), were designed to allow similar separation be-



Scheme 2

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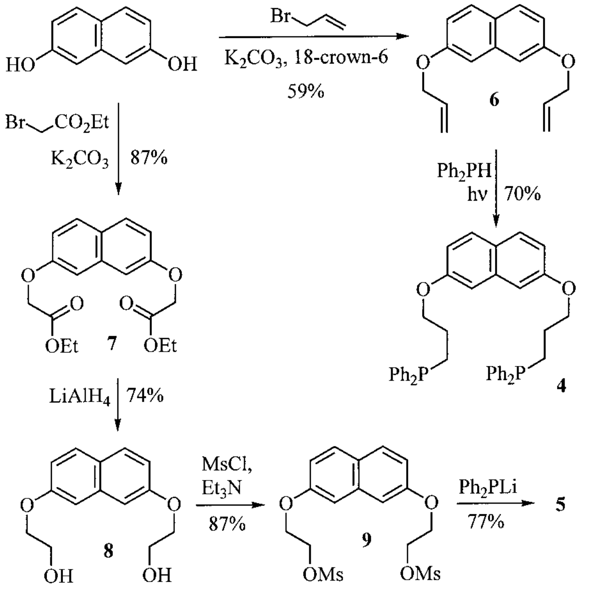
tween the P atoms to that found in the Venanzi ligands of type **2**, but with a more flexible ligand backbone. Bisphosphanes **2** suffer from lengthy and low-yielding synthetic approaches. By contrast, we sought ligands which could be synthesised by short, straightforward routes.

Ligand Synthesis

For the synthesis of DPPN **4** (Scheme 3), 2,7-dihydroxynaphthalene was alkylated with allyl bromide to give bis-allyl ether **6** by a modification of the literature procedure. Addition of 18-crown-6 to the reaction mixture, and improved purification methods, enabled us to improve the published yield of 45% crude[14] or 27% pure[15] to a relatively good 59% of recrystallised product. Ultraviolet irradiation of bis-ether **6** and diphenylphosphane in the absence of solvent gave the bis-phosphane DPPN (**4**) in an overall yield for this two-step synthesis of 41%. DPPN is a very viscous colourless oil which oxidises slowly in air (more rapidly in solution). In the synthesis of DPEN (**5**), the same starting material was alkylated with ethyl bromoacetate to give bis-ester **7**, which was reduced to the corresponding diol **8**[16] and then converted into bis-mesylate **9**. Treatment of **9** with lithium diphenylphosphide gave the bis-phosphane DPEN (**5**) in an overall yield of 49%. DPEN is a white, crystalline air-stable solid which oxidises slowly in solution.

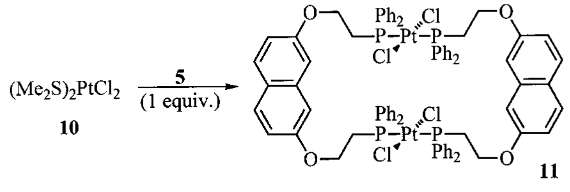


Scheme 3

Platinum(II) Complexes

The formation of square-planar platinum(II) complexes is known to be dependent on a number of factors, both kinetic and thermodynamic, including solvent polarity,[17] the *trans* effect of resident ligands, and the order of adding the reagents.[18,19] In addition, when polydentate ligands are involved, solution concentration exerts an effect, with high dilution favouring monomers whilst higher concentrations can promote dimer or oligomer formation. With suitable magnetic nuclei, the geometry of the products can often be determined from the magnitude of the coupling constants to ^{195}Pt. These are greatly dependent on the *trans* influence of the ligands opposite. For example, a phosphane *trans* to chloride has $^{1}J_{\text{P-Pt}}$ about 3500 Hz whereas a phosphane *trans* to another phosphane has $^{1}J_{\text{P-Pt}}$ near 2500 Hz.[20]

The geometry of the platinum complexes formed from DPEN (**5**) was dependent on the reaction conditions. Addition of up to one equivalent of **5** in dichloromethane to a solution of $[\text{PtCl}_2(\text{SMe}_2)_2]$ (**10**; *cis*/*trans* mixture) in the same solvent produced a complex mixture of products (Scheme 4). The ^{31}P{^{1}H} NMR spectrum of this mixture consisted of about ten signals, of varying intensities, with their associated ^{195}Pt satellites. Analysis of the ^{31}P-^{195}Pt coupling constants showed that it contained signals due to both *cis*- and *trans*-coordinated phosphanes. Only one compound, significantly less polar than the rest, could be isolated from the mixture by column chromatography. The ^{31}P{^{1}H} NMR spectrum of this complex gave $J_{\text{Pt-P}}$ = 2562 Hz indicating *trans* coordination of the ligand. A FAB mass spectrum indicated that the complex was dimeric. Slow diffusion of diethyl ether into a concentrated dichloromethane solution of the complex produced yellow prisms, and a single crystal X-ray analysis (Figure 1) showed the complex to be the metallamacrocycle *trans,trans*-$[\text{Pt}_2\text{Cl}_4(\text{DPEN})_2]$ (**11**). The yield of **11** was only 10%, however, and the remainder of the products in the mixture could not be separated; their behaviour on chromatography and on attempted crystallisation suggested facile interconversion.



Scheme 4

Figure 1 shows that complex **11** forms a centrosymmetric dimer with the DPEN ligand bridging between Pt centres in a mutually *trans,trans* arrangement, as expected from the colour and the NMR evidence. The four ligating P and Cl atoms form a slightly distorted square planar arrangement (these four atoms deviate from their least-squares plane by ±0.03 Å). The nearly linear PtCl_2 unit is displaced towards the centre of the metallamacrocyclic ring and towards the other centrosymmetrically related Pt atom [Pt(1)···Pt(1)^{ii} = 10.691(1) Å]. The space-filling diagram of **11** (Figure 2) shows the hetero-ring system to have a central hydrophobic cavity of radius ≈5 Å.

When this experiment was repeated using **4**, an intractable mixture of complexes was again produced. The ^{31}P{^{1}H} NMR spectrum of the crude product again showed a mixture of signals, of varying intensities, with their associated ^{195}Pt satellites. Analysis of the ^{31}P-^{195}Pt coupling constants showed that it contained signals due to both *cis*- and

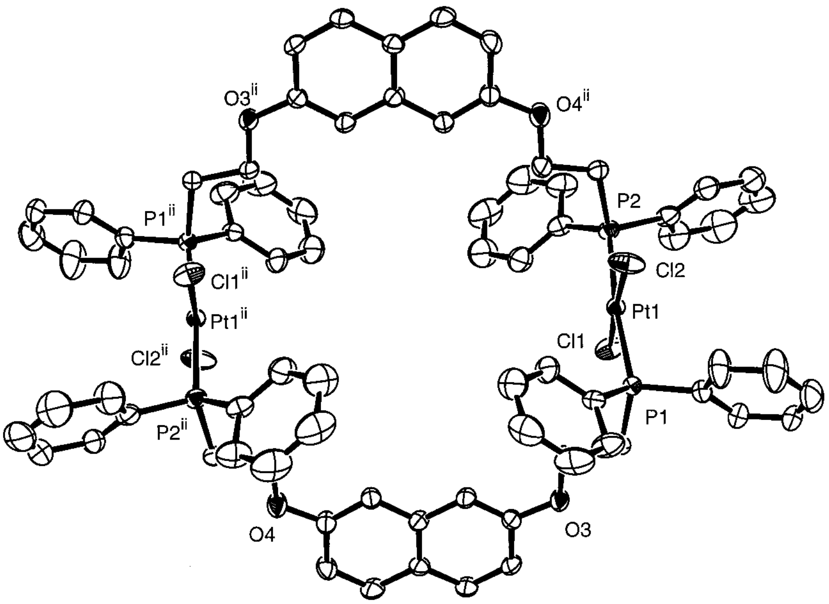


Figure 1. Ortep plot of compound **11** with thermal ellipsoids shown at the 30% probability level; atoms with primed labels are related to unprimed atoms by the symmetry operation ($1 - x$, $2 - y$, $1 - z$); selected bond lengths (Å) and angles (°): Pt−Cl(1) 2.2982(15), Pt−Cl(2) 2.2879(16), Pt−P(1) 2.3113(14), Pt−P(2) 2.3057(15), Pt···Pt^{ii} 10.692(1) ; Cl(1)−Pt−P(1) 92.02(5); Cl(1)−Pt−P(2), 88.70(6); Cl(2)−Pt−P(1) 87.75(6), Cl(2)−Pt−P(2) 91.27(6), Cl(1)−Pt−Cl(2) 177.29(8), P(1)−Pt−P(2) 174.32(5)

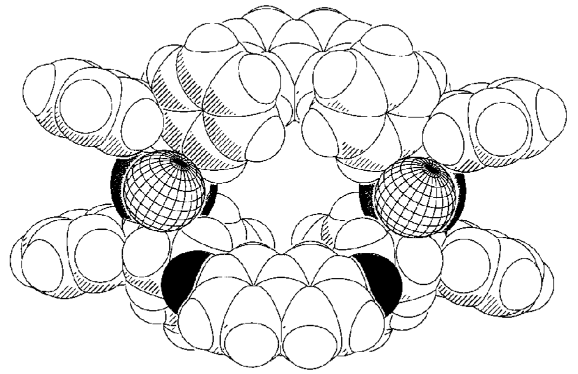
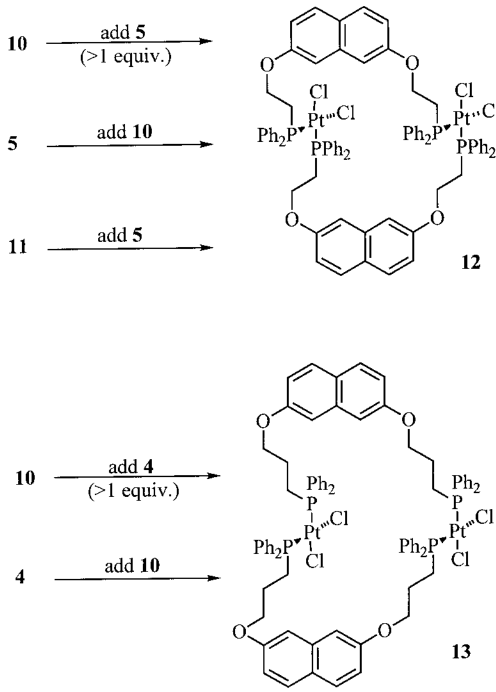


Figure 2. Space-filling plot of compound **11** showing the central cavity of the metallamacrocycle

trans-coordinated phosphanes, but in this case no single complex could be isolated by either chromatography or crystallisation.

Other methods of treating either **4** or **5** with Pt^{II} complex **10** produced a quite different outcome. The major products in almost all cases were the *cis,cis* complexes **12** (of DPEN) and **13** (of DPPN) (Scheme 5). These complexes show $J_{\text{Pt-P}}$ of 3627 Hz and 3646 Hz respectively, indicating exclusively *cis* coordination of the phosphanes. They were shown to be dimeric by FAB-MS, and to be *cis,cis*-dimers by single crystal X-ray analysis (Figures 3 and 4). Complex geometry was independent of precursor concentration over a range of 1.5−39 mmol l^{-1}, and apparently independent of solvent polarity (20% CH_2Cl_2 in toluene gave identical results to chloroform). Use of an excess of the bis-phosphane invariably resulted in formation of *cis,cis* complexes **12** or **13** as the sole or overwhelmingly major product. Similarly on inverse addition, i.e. addition of **10** to the bis-phosphane, the *cis,cis* complexes were the only products visible by ^{31}P NMR spectroscopy. These results led us to conclude that *cis,cis* complexes **12** and **13** were the thermodynamic products, and equilibration to them was catalysed by an excess of the phosphane, either by adding an excess of the ligand, or by having the excess present during the (inverse) addition of the platinum precursor. The mixture formed on "normal" addition of one equivalent of phosphane appeared to be a mixture of kinetic and thermodynamic products, of which the *trans,trans*-dimer **11** was the only one isolated. We tested this hypothesis by treating such mixtures with an excess of the bis-phosphane ligand **4** or **5** and in both cases the *cis,cis* complexes **12** and **13** became the only products observed by ^{31}P NMR spectroscopy.

Figure 3 shows that complex **12** forms a centrosymmetric dimer, this time with the DPEN ligand bridging between Pt centres in a mutually *cis,cis* arrangement. The geometry about the Pt centre shows a slight tetrahedral distortion away from a regular square planar environment. The "twist" angle between the $PtCl_2$ plane and the PtP_2 plane is 12.7°. The Pt−P bonds are shorter and Pt−Cl bonds longer than observed for **11**, consistent with the differing *trans* influences. The $PtCl_2$ groups lie exterior to the metallamacrocycle and the 2,7-dialkoxynaphthalene rings of the DPEN ligands are approximately parallel to each other and nearly in van der Waals contact, as shown in Figure 5. Figure 4 shows that complex **13** forms another centrosymmetric dimer, with the DPPN ligand bridging between Pt centres again in a mutually *cis,cis* arrangement. The geometry about the Pt centre is a more regular square-planar



Scheme 5

environment than found in **12** – the "twist" angle between the $PtCl_2$ plane and the PtP_2 plane is only 3.3°. The Pt–P and Pt–Cl bond lengths are very similar to those observed for **12**. The longer "reach" of the DPPN ligands allows the two $PtCl_2$ groups to lie interior to the metallamacrocycle so that the $Cl(1)\cdots Cl(1)^{ii}$ non-bonded distance is 3.942 Å, about 0.4 Å longer than the sum of van der Waals radii. This is shown in Figure 6.

It was observed by $^{31}P\{^{1}H\}$ NMR spectroscopy that treatment of a solution of pure *trans,trans*-dimer **11** with a small amount of **5** at room temperature rapidly converted it to the *cis,cis*-dimer **12** in the few minutes taken to obtain a spectrum. At lower temperatures, however, it was possible to observe the isomerisation process (Figure 7). A $^{31}P\{^{1}H\}$ NMR spectrum (Figure 7, trace a) was obtained from a solution of *trans,trans*-dimer **11** before cooling to 203 K. A few crystals of **5** were then added to the sample tube which was briefly shaken before being immediately frozen in liquid nitrogen and returned to the NMR probe. Over two hours at 203 K (traces b and c), little change was observed to the signal with $J = 2530$ Hz ($\delta = 6.4$) representing *trans,trans*-dimer **11**, although a few signals for intermediates did appear at $\delta = 10.7$ and $\delta = 5.7$. On warming to 223 K, the signal with $J = 2530$ Hz rapidly broadened and eventually vanished (trace d). On warming to 243 K, it was replaced by a signal with $J = 3624$ Hz ($\delta = 6.1$) representing the *cis,cis*-dimer **12**. After 40 minutes at this temperature, the broad signals representing intermediates had disappeared, and the only significant species present were the *cis,cis*-dimer **12** and free phosphane at $\delta = -24$ (trace e). No further change was observed after 19 h at room temperature (trace f). The broadness of the signals (traces b–d) did not allow identification of the intermediate fluxional five-coordinate platinum complexes.

Other Metal Complexes

In view of the interesting metallamacrocycles **11–13** formed by DPEN (**5**) and DPPN (**4**) with Pt^{II}, and their isomerisation behaviour, a brief investigation was made of the complexation of these new ligands with a wider range of transition metals. The results were, however, harder to obtain and interpret than with platinum.

Stirring an equimolar mixture of **5** and $[PdCl_2(MeCN)_2]$ overnight in dichloromethane produced a yellow solid, the $^{31}P\{^{1}H\}$ NMR spectrum of which consisted of several singlets. All attempts to isolate a pure complex from the mixture were unsuccessful, although a FAB mass spectrum suggested that the main species present was again dimeric and corresponded to $[Pd_2Cl_4(DPEN)_2]$. Attempts to prepare rhodium complexes of DPEN were unsuccessful. Reactions with (acetylacetonato)Rh(norbornadiene), (1,5-cyclooctadiene)$_2$Rh$_2$Cl$_2$, $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(PPh_3)_3]$ all produced intractable mixtures from which no complexes could be isolated.

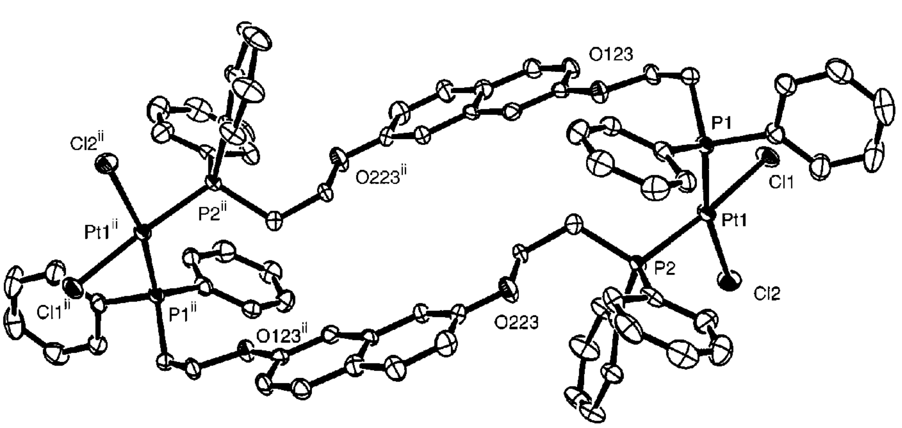


Figure 3. Ortep plot of compound **12** with thermal ellipsoids shown at the 50% probability level; atoms with primed labels are related to unprimed atoms by the symmetry operation $(1 - x, 1 - y, -z)$; selected bond lengths (Å) and angles (°): Pt–Cl(1) 2.3495(19), Pt–Cl(2) 2.3566(18), Pt–P(1) 2.2567(18), Pt–P(2) 2.2479(19), $Pt\cdots Pt^{ii}$ 14.174(1); Cl(1)–Pt–Cl(2) 87.56(7), P(1)–Pt–P(2) 97.54(7)

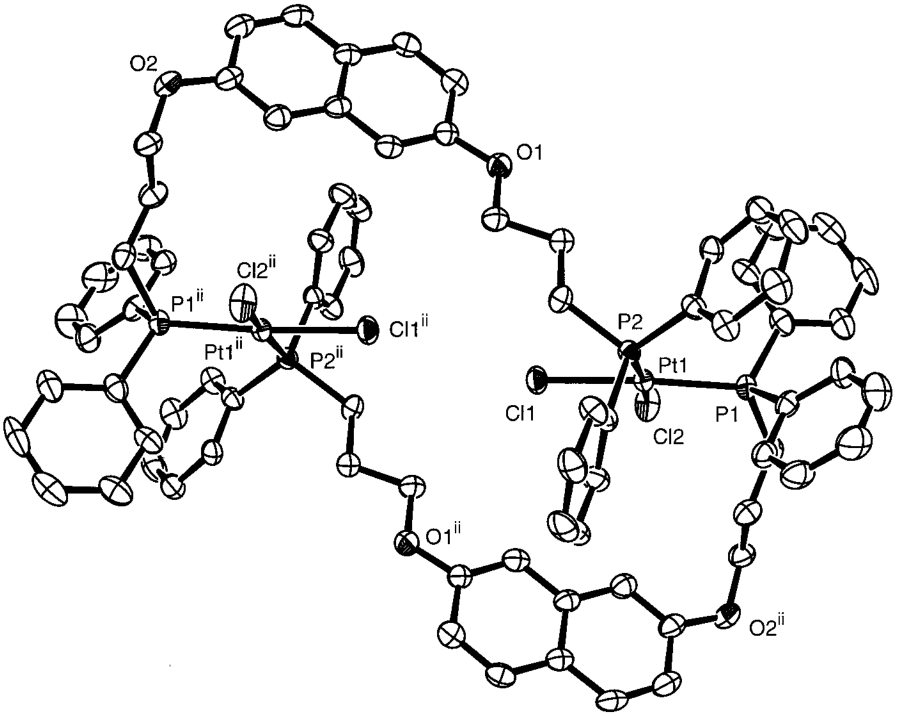


Figure 4. Ortep plot of compound **13** with thermal ellipsoids shown at the 50% probability level; atoms with primed labels are related to unprimed atoms by the symmetry operation (−*x*, −*y*, 1 − *z*); selected bond lengths (Å) and angles (°): Pt−Cl(1) 2.3500(9), Pt−Cl(2) 2.3467(10), Pt−P(1) 2.2544(9), Pt−P(2) 2.2510(9), $\mathrm{Pt}\cdots\mathrm{Pt}^{ii}$ 8.369(1); Cl(1)−Pt−Cl(2) 86.20(7), P(1)−Pt−P(2) 98.41(7)

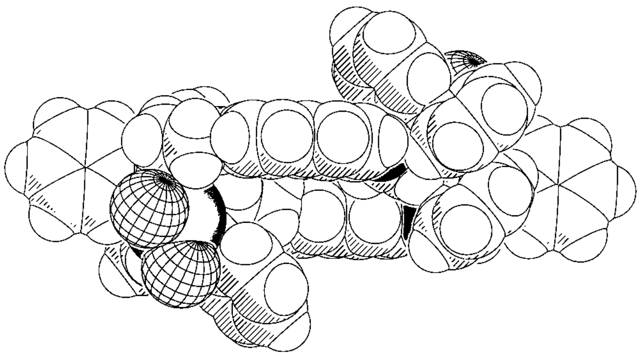


Figure 5. Space-filling plot of compound **12** showing the parallel close packing of the 2,7-dialkoxynaphthalene rings

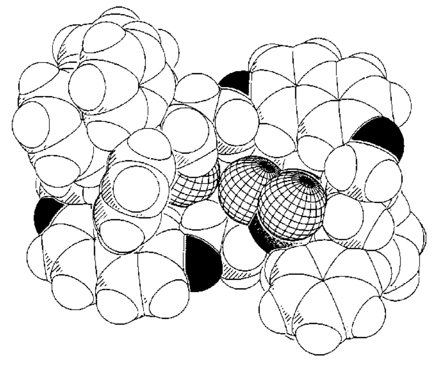


Figure 6. Space-filling plot of compound **13** showing the close Cl···Cl contact

Refluxing a suspension of **5**, molybdenum hexacarbonyl and sodium borohydride in ethanol[21] produced a pale-yellow solid, shown by single crystal X-ray analysis to be the *cis,cis*-dimer [$Mo_2(CO)_8(DPEN)_2$] (**14**) (Scheme 6 and Figure 8). The DPEN ligand adopts a similar conformation to that observed in **12**. The phosphane ligands coordinate in a *cis* fashion to the Mo centres and the two $Mo(CO)_4$ moieties lie exterior to the metallacyclic ring. The 2,7-dialkoxynaphthalene rings of the DPEN are approximately parallel to each other, as seen in **12**.

Catalytic Application

Recent work by van Leeuwen and co-workers on the catalytic hydroformylation of alkenes has highlighted an important application of phosphanes with wide bite angles.[1] They have reported excellent linear/branched product selectivity in the hydroformylation of terminal alkenes when the wide-angle bis-phosphane "xantphos" (**1**) or the corresponding bis-arsane is used in a Pt/Sn catalyst system. With this in mind, we set out to investigate whether our bridging bis-phosphanes would give similar catalytic activity. We note that the dimeric complex *cis,cis*-[$Pt_2Cl_4(DPEN)_2$] (**12**) has a P−Pt−P angle (97.5°) in the normal range for a complex having two *cis*-coordinated monophosphane ligands.[22−24] The ditopic ligands in a dimeric complex cannot, however, be expected to behave exactly as independent monodentate phosphanes, nor yet as the two phosphanes of a chelating ligand such as **1**. We applied van Leeuwen's procedure to the hydroformylation of 1-octene with *cis,cis*-[$Pt_2Cl_4(DPEN)_2$] (**12**) as the catalyst.

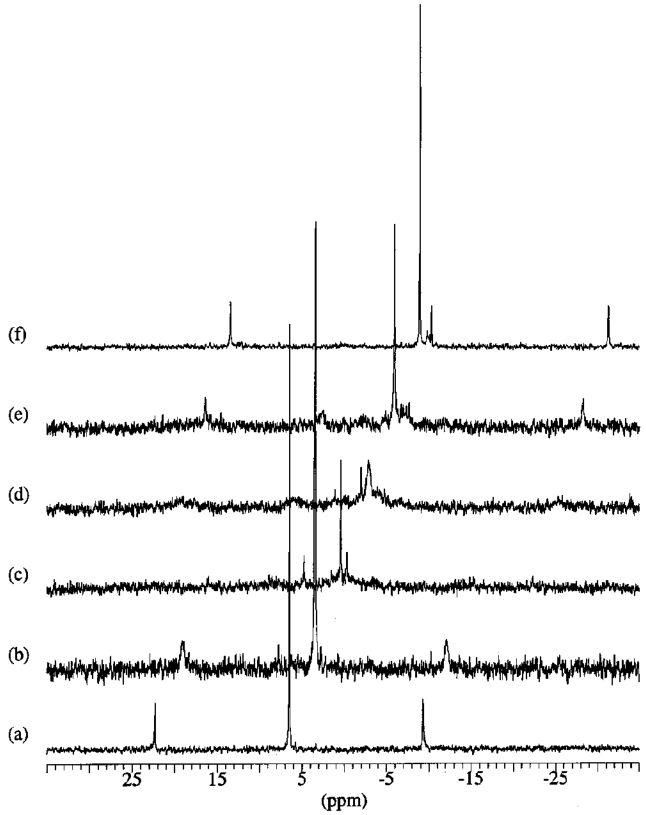
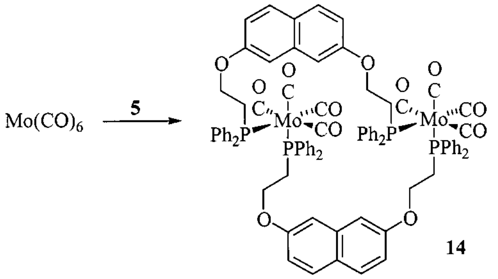
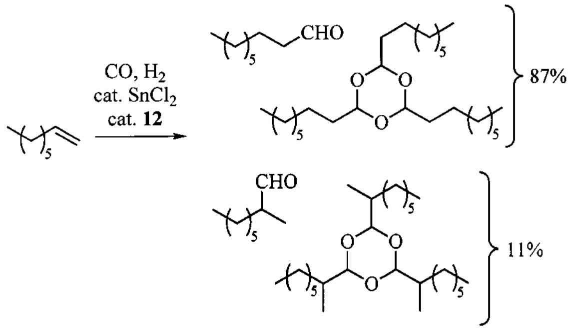


Figure 7. Stacked ^{31}P NMR spectra showing the changing Pt−P coupling constant on warming the mixture of complex **11** and DPEN **5** from 203 K; the spectra have been normalised to take account of the number of scans, but were run unlocked. They are plotted with an increment of 3 ppm between traces, and with traces (a) and (f) plotted at half the vertical intensity of the intervening spectra. Traces: (a) 298 K before commencing experiment; (b) 203 K after 35 min; (c) 203 K after 160 min; (d) 223 K after 210 min; (e) 243 K after 290 min; (f) 298 K after 24 h

The substrate was heated to 60 °C under an atmosphere of CO (20 bar) and H_2 (20 bar) in the presence of **12** (0.4 mol %) and $SnCl_2$ (0.8 mol %). After 18 hours, GCMS and ^1H NMR analysis of the mixture showed complete conversion of 1-octene to nonanal (87%) and 2-methyloctanal (11%) (both of which tended to trimerise in solution) with 2% of an unidentified by-product (Scheme 7). This activity and selectivity compares reasonably well with previously reported, monomeric, hydroformylation catalysts.



Scheme 6



Scheme 7

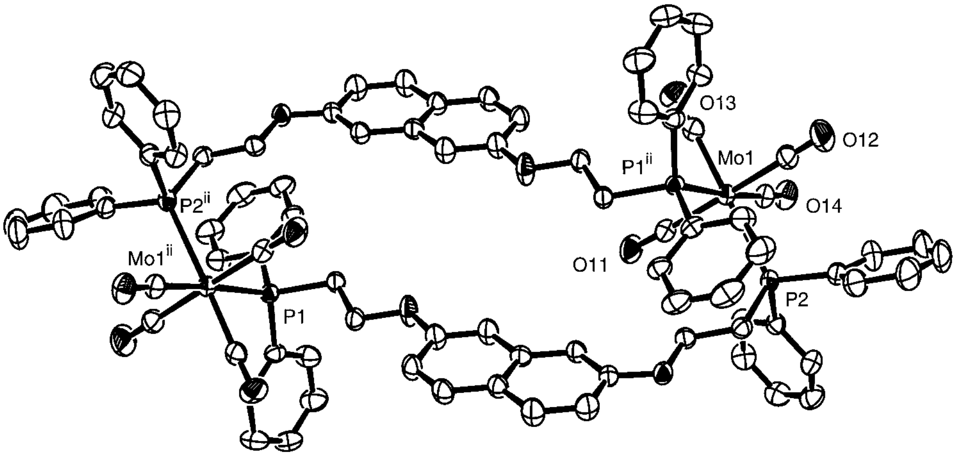


Figure 8. Ortep plot of compound **14** with thermal ellipsoids shown at the 50% probability level; atoms with primed labels are related to unprimed atoms by the symmetry operation ($-x$, $-y$, $1 - z$); selected bond lengths (Å) and angles (°): Mo−P(1) 2.5434(9), Mo−P(2) 2.5536(9), Mo···Mo^{ii} 13.720(1); P(1)−Mo−P(2) 98.75(3)

Conclusion

Short, straightforward and efficient syntheses of two new bis-phosphane ligands, DPPN (**4**) and DPEN (**5**), have been developed. Both ligands are ditopic: in transition metal complexation, dimeric or oligomeric complexes are greatly favoured. No monomeric complexes have been observed using Pt^{II}, Pd^{II} or Mo^0.

In the case of platinum, although kinetic conditions lead to a mixture of products, employing an excess of ligand to catalyse isomerisation allows clean formation of the 28-membered metallamacrocycle **12** from DPEN (**5**) and the 32-membered metallamacrocycle **13** from DPPN (**4**). These complexes feature *cis* coordination at both square-planar metal centres. The synthesis of a 28-membered molybdenum macrocycle **14** also revealed a preference for *cis* coordination, in this case as part of an octahedral geometry. The very strong preferences of these ligands for forming metallamacrocyclic complexes is interesting, particularly when contrasted with the strong preference for *trans*-chelation shown by Venanzi's related ligands **2**: clearly, formation of monomers with *trans*-coordinated phosphanes is not favoured by ligands of this general shape and size unless rigid steric constraints prevent bridging.

The potential importance of ditopic bis-phosphanes and their macrocyclic transition metal complexes is demonstrated by the activity and linear selectivity of platinum complex **12** as a hydroformylation catalyst.

Experimental Section

General Remarks: All reactions were carried out using oven-dried glassware under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. THF and CH_2Cl_2 were freshly distilled from sodium/benzophenone and calcium hydride respectively. Pet. ether refers to petroleum ether boiling between 40 and 60 °C. $PtCl_2(SMe_2)_2$ was prepared by the literature method.[18] Other reagents and starting materials were used as supplied without further purification. Column chromatography was carried out using silica gel (finer than 230 mesh ASTM) and reagent grade solvents which were not purified further before use.

All NMR spectra were obtained from $CDCl_3$ solutions unless stated otherwise. ^1H and ^{13}C NMR spectra were recorded using a Bruker DPX 400 spectrometer operating at 400 and 100 MHz, respectively. ^{31}P NMR spectra were recorded using a Bruker WP 200 SY spectrometer operating at 81 MHz. Chemical shifts (δ) are given in ppm relative to residual $CHCl_3$ (δ = 7.27) for ^1H, $CDCl_3$ (δ = 77.0) for ^{13}C, and 85% H_3PO_4 (δ = 0.0, external) for ^{31}P. Coupling constants (*J*) are given in Hz. Infra-red spectral analysis was performed on a Jasco 410 spectrometer, using KBr discs; absorbances are quoted in wavenumbers (cm^{-1}). Mass spectra were obtained using a JMS 700 spectrometer operating, unless stated otherwise, in FAB mode for coordination complexes, whose isotope patterns matched calculated patterns in all cases,[25] and in EI mode for their organic precursors. GC-MS was carried out using a Hewlett Packard 5890 Series II model GC, with a mass selective detector type 5971.

2,7-Bisallyloxynaphthalene (6): Potassium carbonate (3.80 g, 27.5 mmol) and 18-crown-6 (496 mg, 1.88 mmol) were added to a solution of 2,7-dihydroxynaphthalene (2.00 g, 12.5 mmol) in acetone (30 mL) under air. The mixture was refluxed for 1 h and then allyl bromide (2.7 mL, 31 mmol) was added and the mixture refluxed for a further 15 h. The reaction mixture was allowed to cool, filtered and then concentrated. The crude product was purified by column chromatography (silica, 5% EtOAc/hexane) and recrystallised from hexane to give bis-ether **6** as colourless plates (1.76 g, 59%): m.p. 60−62 °C [ref.[15] 62.5−63 °C (MeOH)]. ^1H NMR: δ = 4.65 (dt, *J* = 5.3, 1.4 Hz, 4 H, CH_2O), 5.33 (dq, *J* = 10.5, 1.4 Hz, 2 H, $CH_AH_B{=}CH$), 5.48 (dq, *J* = 17.3, 1.5 Hz, 2 H, $CH_AH_B{=}CH$), 6.13 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 2 H, $CH_2{=}CH$), 7.02−7.05 (m, 4 H, $C_{3,6}$ H, $C_{1,8}$ H), 7.66 (d, *J* = 8.6 Hz, 2 H, $C_{4,5}$ H). ^{13}C NMR: δ = 68.8 (CH_2O), 106.5 (C_3, C_6), 116.4 (C_1, C_8), 117.7 ($CH_2{=}CH$), 124.4 (C_{4a}), 129.1 (C_4, C_5), 133.2 ($CH_2{=}CH$), 135.8 (C_{8a}), 157.1 (C_2, C_7). IR: $\tilde{\nu}$ = 3084 w, 2921 w, 2866 w, 1631 m, 1514 m, 1425 m, 1387 m, 1250 m, 1209 s, 1017 m, 936 m, 823 m. MS: *m/z* (%) = 240 (100) [M^+], 212 (13) [$M^+ - CO$], 199 (24) [M^+ − allyl], 185 (39), 171 (94) [M^+ − allyl − CO], 143 (25), 128 (35), 102 (26).

DPPN (4): Bisallyloxynaphthalene **6** (500 mg, 2.08 mmol) was dissolved in diphenylphosphane (0.90 mL, 5.2 mmol) and the resulting solution was irradiated with ultraviolet light from a medium-pressure mercury lamp for 18 h. The gelatinous mass was then washed with pentane, dissolved in ethyl acetate and concentrated. The crude product was purified by column chromatography (silica, 5% EtOAc/pet. ether) to give DPPN **4** as a very viscous colourless oil (891 mg, 70%). ^1H NMR: δ = 1.99−2.05 (m, 4 H, CH_2CH_2P), 2.27−2.31 (m, 4 H, CH_2P), 4.13 (t, *J* = 6.3 Hz, 4 H, CH_2O), 6.97−7.00 (m, 4 H, $C_{1,8}$ H, $C_{3,6}$ H), 7.32−7.38 (m, 12 H, Ph), 7.44−7.50 (m, 8 H, Ph), 7.64 (d, *J* = 9.6 Hz, 2 H, $C_{4,5}$ H). ^{13}C NMR: δ = 24.5 (d, *J* = 12 Hz, CH_2CH_2P), 25.8 (d, *J* = 17 Hz, CH_2P), 68.2 (d, *J* = 14 Hz, CH_2O), 106.1 (s, C_3, C_6), 116.2 (s, C_1, C_8), 124.2 (s, C_{4a}), 128.4−128.6 (m, Ph *p*-C and Ph *m*-C), 129.0 (s, C_4, C_5), 132.7 (d, *J* = 18 Hz, Ph *o*-C), 135.9 (s, C_{8a}), 138.4 (d, *J* = 13 Hz, Ph *i*-C), 157.4 (s, C_2, C_7). $^{31}P\{^1H\}$ NMR: δ = −16.4 (s, PPh_2). IR (neat): $\tilde{\nu}$ = 3069 m, 2944 m, 1627 s, 1514 s, 1434 s, 1387 s, 1253 m, 1210 s, 1159 m, 1026 m, 832 m, 751 s, 699 s. MS: *m/z* (%) = 612 (11) [M^+], 582 (13) [$M^+ - CH_2O$], 496 (64) [$M^+ - C_6H_{12}O_2$], 227 (29) [$Ph_2P(CH_2)_3^+$], 199 (100) [$CH_2PPh_2^+$], 183 (50). HRMS: calculated for $C_{40}H_{38}O_2P_2$: 612.2347; found 612.2347.

2,7-Bis(ethoxycarbonylmethoxy)naphthalene (7): Potassium carbonate (34.5 g, 250 mmol) and ethyl bromoacetate (6.1 mL, 55 mmol) were added to a solution of 2,7-dihydroxynaphthalene (4.00 g, 25.0 mmol) in acetone (100 mL) under air and the mixture was refluxed for 21 h. The reaction mixture was allowed to cool, filtered and then concentrated to give diester **7** (7.19 g, 87%). A portion was recrystallised from ethanol to give diester **7** as a white microcrystalline solid: m.p. 124−125 °C [ref.[26] 126 °C (EtOH)]. ^1H NMR: δ = 1.31 (t, *J* = 7.1 Hz, 6 H, CH_3CH_2O), 4.30 (q, *J* = 7.1 Hz, 4 H, CH_3CH_2O), 4.72 (s, 4 H, $CH_2C{=}O$), 6.98 (d, *J* = 2.5 Hz, 2 H, $C_{1,8}$ H), 7.10 (dd, *J* = 8.9, 2.5 Hz, 2 H, $C_{3,6}$ H), 7.69 (d, *J* = 8.9 Hz, 2 H, $C_{4,5}$ H). ^{13}C NMR: δ = 14.1 (CH_3CH_2O), 61.4 (CH_3CH_2O), 65.4 ($CH_2C{=}O$), 106.7 (C_3, C_6), 116.4 (C_1, C_8), 125.2 (C_{4a}), 129.4 (C_4, C_5), 135.3 (C_{8a}), 156.5 (C_2, C_7), 168.8 ($C{=}O$). IR: $\tilde{\nu}$ = 2993 w, 2916 w, 1760 s, 1629 m, 1203 s, 1076 m, 847 w, 834 w. MS: *m/z* (%) = 332 (100) [M^+].

2,7-Bis(2′-hydroxyethoxy)naphthalene (8): A solution of lithium aluminium hydride (0.85 g, 22 mmol) in THF (50 mL) was cooled to 0 °C and a solution of diester **7** (6.84 g, 20.6 mmol) in THF (85 mL) was added. The resulting mixture was stirred for 60 min and then allowed to warm to room temperature and stirred overnight. Further portions of $LiAlH_4$ (1.3 g in total) were added until the reaction had gone to completion as indicated by TLC. The reaction mixture was quenched with EtOAc and then satd. aq. potassium sodium tartrate solution was added. The mixture was filtered, extracted with EtOAc, dried (Na_2SO_4) and concentrated to give diol **8** (3.79 g, 74%). A portion was recrystallised from methanol to give diol **8** as a white microcrystalline solid: m.p. 151−152 °C [ref.[16] 152−153 °C]. ^1H NMR: $\delta = 2.04$ (t, $J = 6.1$ Hz, 2 H, OH), 4.03 (td, $J = 4.2, 5.3$ Hz, 4 H, $C\mathit{H}_2OH$), 4.20 (t, $J = 4.5$ Hz, 4 H, $C\mathit{H}_2CH_2OH$), 7.03 (dd, $J = 8.8, 2.5$ Hz, 2 H, $C_{3,6}$ H), 7.07 (d, $J = 2.4$ Hz, 2 H, $C_{1,8}$ H), 7.68 (d, $J = 8.9$ Hz, 2 H, $C_{4,5}$ H). ^{13}C NMR: $\delta = 61.5$ (CH_2OH), 69.2 ($\mathit{C}H_2CH_2OH$), 106.3 (C_3, C_6), 116.3 (C_1, C_8), 125.2 (C_{4a}), 129.3 (C_4, C_5), 135.4 (C_{8a}), 157.2 (C_2, C_7). IR: $\tilde{\nu} = 3334$ br, 2931 w, 2882 w, 1631 s, 1387 m, 1213 s, 1081 m, 838 m. MS: *m*/*z* (%) = 248 (77) [M^+], 204 (35), 160 (100).

2,7-Bis(2′-hydroxyethoxy)naphthalene bis(methanesulfonate)ester (9): Methanesulfonyl chloride (1.6 mL, 21 mmol) and triethylamine (2.9 mL, 21 mmol) were added to a solution of diol **8** (2.17 g, 8.75 mmol) in THF (100 mL) and the mixture was stirred for 30 min at room temperature. The reaction mixture was then filtered and the solvent removed. The residue was dissolved in EtOAc, washed with water, dried (Na_2SO_4) and concentrated. The crude product was recrystallised from dichloromethane and methanol to give dimesylate **9** as colourless plates (3.09 g, 87%): m.p. 134−135 °C. ^1H NMR: $\delta = 3.12$ (s, 6 H, CH_3S), 4.36−4.38 (m, 4 H, $C\mathit{H}_2CH_2OS$), 4.64−4.66 (m, 4 H, CH_2OS), 7.01−7.05 (m, 4 H, $C_{3,6}$ H, $C_{1,8}$ H), 7.70 (d, $J = 8.7$ Hz, 2 H, $C_{4,5}$ H). ^{13}C NMR: $\delta = 37.8$ (CH_3SO_2), 65.8 (CH_2), 67.9 (CH_2), 106.5 (C_3, C_6), 116.3 (C_1, C_8), 125.0 (C_{4a}), 129.5 (C_4, C_5), 135.5 (C_{8a}), 156.7 (C_2, C_7). IR: $\tilde{\nu} = 3025$ w, 2941 w, 1629 s, 1517 m, 1353 s, 1256 m, 1216 s, 1171 s, 1069 m, 1024 m, 981 s, 930 s, 822 s. MS: *m*/*z* (%) = 404 (57) [M^+], 123 (100) [$C_2H_4OMs^+$], 79 (28) [$SO_2CH_3^+$]. $C_{16}H_{20}O_8S_2$ (404.45): calcd. C 47.51, H 4.98; found C 47.49, H 4.88.

DPEN (5): *n*-Butyllithium (2.5 M solution in hexanes, 2.3 mL, 5.75 mmol) was added to a solution of diphenylphosphane (1.0 mL, 5.75 mmol) in THF (6 mL). After stirring at room temperature for 15 minutes, a solution of dimesylate **9** (1.04 g, 2.57 mmol) in THF (60 mL) was added and the mixture stirred overnight. The solvent was removed and the residue dissolved in dichloromethane, washed with water, dried ($MgSO_4$) and concentrated. The crude product was recrystallised from ethyl acetate and pet. ether and washed with pentane to give DPEN (**5**) as white needles (1.15 g, 77%): m.p. 137−138 °C. ^1H NMR: $\delta = 2.65$ (t, $J = 7.7$ Hz, 4 H, CH_2P), 4.22 (q, $J = 7.5$ Hz, 4 H, CH_2O), 6.80 (d, $J = 2.2$ Hz, 2 H, $C_{1,8}$ H), 6.90 (dd, $J = 8.9, 2.3$ Hz, 2 H, $C_{3,6}$ H), 7.35−7.42 (m, 12 H, Ph), 7.51−7.55 (m, 8 H, Ph), 7.60 (d, $J = 8.9$ Hz, 2 H, $C_{4,5}$ H). ^{13}C NMR: $\delta = 28.3$ (d, $J = 13$ Hz, CH_2P), 65.2 (d, $J = 27$ Hz, CH_2O), 106.0 (s, C_3, C_6), 116.3 (s, C_1, C_8), 124.3 (s, C_{4a}), 128.6 (d, $J = 7$ Hz, Ph *m*-C), 128.8 (s, Ph *p*-C), 129.0 (s, C_4, C_5), 132.7 (d, $J = 19$ Hz, Ph *o*-C), 135.7 (s, C_{8a}), 137.9 (d, $J = 12$ Hz, Ph *i*-C), 156.9 (s, C_2, C_7). $^{31}P\{^1H\}$ NMR: $\delta = -22.8$ (s, PPh_2). IR: $\tilde{\nu} = 3066$ w, 2914 w, 1630 s, 1514 m, 1433 s, 1211 s, 1168 m, 1018 m, 834 m, 741 s, 697 s. MS: *m*/*z* (%) = 584 (4) [M^+], 553 (5) [$M^+ - CH_3O$], 371 (23) [$M^+ - C_2H_4PPh_2$], 341 (42) [$M^+ - C_2H_4PPh_2$], 328 (21), 212 (83) [$C_2H_3PPh_2^+$], 183 (100) [$C_{13}H_{11}O^+$]. HRMS: calculated for $C_{38}H_{34}O_2P_2$: 584.2034; found 584.2037.

***trans,trans*-[$Pt_2Cl_4(DPEN)_2$] (11):** A solution of DPEN (**5**; 250 mg, 0.43 mmol) in dichloromethane (8 mL) was added dropwise over 5 minutes to a solution of [$PtCl_2(SMe_2)_2$] (**10**; 167 mg, 0.43 mmol) in dichloromethane (5 mL). The mixture was stirred at room temperature for 5 min and then the solvent was removed. Column chromatography (silica, CH_2Cl_2) of the crude product mixture gave **11** as a yellow solid (37 mg, 10%). Slow diffusion of Et_2O into a CH_2Cl_2 solution of **11** produced yellow prisms suitable for X-ray analysis. ^1H NMR: $\delta = 3.08{-}3.15$ (m, 8 H, CH_2P), 4.00−4.05 (m, 8 H, CH_2O), 6.70 (d, $J = 2.3$ Hz, 4 H, $C_{1,8}$ H), 6.85 (dd, $J = 8.8, 2.4$ Hz, 4 H, $C_{3,6}$ H), 7.42 (t, $J = 7.6$ Hz, 16 H, Ph *o*-H), 7.50 (t, $J = 7.4$ Hz, 8 H, Ph *p*-H), 7.54 (d, $J = 8.9$ Hz, 4 H, $C_{4,5}$ H), 7.81 (dt, $J = 7.0, 5.6$ Hz, 16 H, Ph *m*-H). ^{13}C NMR: $\delta = 28.9$ (CH_2P), 62.4 (t, $J = 4$ Hz, CH_2O), 105.0 ($C_{3,6}$), 115.8 ($C_{1,8}$), 123.6 (C_{4a}), 127.6 (t, $J = 5$ Hz, Ph *m*-C), 128.3 ($C_{4,5}$) 128.8 (Ph *ipso*-C), 130.1 (Ph *p*-C), 133.0 (t, $J = 6$ Hz, Ph *o*-C), 134.9 (C_{8a}), 156.1 ($C_{2,7}$). $^{31}P\{^1H\}$ NMR: $\delta = 9.00$ ($J = 2563$ Hz). IR: $\tilde{\nu} = 3053$ w, 2919 w, 1631 s, 1513 m, 1435 s, 1253 m, 1209 s, 1158 m, 1101 m, 740 m, 691 s. MS: *m*/*z* (%) = 1701 (1.8) [$Pt_2Cl_4(DPEN)_2^+$], 1665 (1.3) [$M^+ - Cl$], 1628 (0.8) [$M^+ - 2Cl$]. HRMS: calculated for $C_{76}H_{69}Cl_4O_4P_4Pt_2$: 1701.2200; found 1701.2217.

***cis,cis*-[$Pt_2Cl_4(DPEN)_2$] (12). By Addition of an Excess of Phosphane:** A solution of DPEN (**5**; 150 mg, 0.26 mmol) in dichloromethane (8 mL) was added dropwise to a solution of [$PtCl_2(SMe_2)_2$] (**10**; 67 mg, 0.17 mmol) in toluene (90 mL) and dichloromethane (15 mL) and the mixture was stirred for 18 h at room temperature. The white precipitate formed was collected by filtration to obtain *cis,cis*-[$Pt_2Cl_4(DPEN)_2$] (**12**; 104 mg, 72%). Recrystallisation from a concentrated chloroform solution of **12** gave colourless prisms. ^1H NMR: $\delta = 2.88{-}2.94$ (m, 8 H, CH_2P), 4.56 (quintet, $J = 6.4$ Hz, 8 H, CH_2O), 6.76 (d, $J = 2.2$ Hz, 4 H, $C_{1,8}$ H), 6.83 (dd, $J = 8.8, 2.3$ Hz, 4 H, $C_{3,6}$ H), 7.22 (br t, $J = 6.9$ Hz, 16 H, Ph *o*-H), 7.37 (t, $J = 7.3$ Hz, 8 H, Ph *p*-H), 7.48 (d, $J = 8.9$ Hz, 4 H, $C_{4,5}$ H), 7.57, (dd, $J = 8.1, 10.7$ Hz, 16 H, Ph *m*-H). ^{13}C NMR: $\delta = 30.3$ (5-line m,[27] $J_{P-C} = 22$ Hz, CH_2P), 64.8 (CH_2O), 107.2 ($C_{3,6}$), 116.3 ($C_{1,8}$), 124.9 (C_{4a}), 128.8 (t, $J = 5$ Hz, Ph *m*-C), 129.4 ($C_{4,5}$), 130.1 (4 line m,[27] $J_{P-C} = 32$ Hz, Ph *i*-C), 131.5 (br. s, *p*-C), 133.7 (t, $J = 5$ Hz, *o*-C), 135.9 (C_{8a}), 156.6 (C_2). $^{31}P\{^1H\}$ NMR: $\delta = 6.49$ (PPh_2, $J_{Pt\text{-}P} = 3627$ Hz). IR: $\tilde{\nu} = 1631$ s, 1436 m, 1209 m, 694 m. MS: *m*/*z* (%) = 1701 (2.5) [$Pt_2Cl_4(DPEN)_2^+$], 1665 (13) [$M^+ - Cl$], 1629 (2) [$M^+ - 2Cl$]. HRMS: calculated for $C_{76}H_{68}Cl_3O_4P_4Pt_2$: 1665.2433; found 1665.2432. $C_{76}H_{68}Cl_4O_4P_4Pt_2$ (1701.3): calcd. C 53.7, H 4.03; found C 52.9, H 3.97.

***cis,cis*-[$Pt_2Cl_4(DPEN)_2$] (12). By Inverse Addition:** A solution of [$PtCl_2(SMe_2)_2$] (**10**; 167 mg, 0.43 mmol) in dichloromethane (5 mL) was added dropwise over 5 minutes to a stirred solution of DPEN (**5**; 250 mg, 0.43 mmol) in dichloromethane (8 mL). After 7 minutes, the solvent was removed to give a white solid (414 mg) consisting largely of *cis,cis*-[$Pt_2Cl_4(DPEN)_2$] (**12**; identified by ^1H and ^{31}P NMR spectroscopy and by MS) together with small quantities of higher oligomers.

***cis,cis*-[$Pt_2Cl_4(DPPN)_2$] (13):** A solution of [$PtCl_2(SMe_2)_2$] (**10**; 128 mg, 0.33 mmol) in dichloromethane (4 mL) was added dropwise over 5 minutes to a solution of DPPN (**4**; 200 mg, 0.33 mmol) in dichloromethane (4.5 mL). After 7 minutes the solvent was removed to give *cis,cis*-[$Pt_2Cl_4(DPPN)_2$] (**13**) as a white solid (281 mg, 97%) which contained small quantities of a closely similar compound, presumed from NMR and MS evidence to be a *cis,cis,cis*-trimer. Recrystallisation from dichloromethane produced **13** as colourless prisms suitable for X-ray analysis. ^1H NMR (CD_2Cl_2): $\delta = 2.20{-}2.30$ (m, 8 H, $C\mathit{H}_2CH_2P$), 2.45−2.55 (m, 8 H, CH_2P), 4.15 (t, $J = 6.1$ Hz, 8 H, CH_2O), 6.91 (dd, $J = 2.4, 8.8$ Hz, 4 H, $C_{3,6}$ H), 7.10−7.14 (m, 16 H, Hs *meta* to P), 7.21 (s, 4 H, $C_{1,8}$-H), 7.29 (t, $J = 7.0$ Hz, 8 H, Hs *para* to P), 7.41 (dd, $J = 8.2, 10.0$ Hz, 16 H, Hs *ortho* to P), 7.62 (d, $J = 8.9$ Hz, 4 H, $C_{4,5}$ H). $^{31}P\{^1H\}$ NMR: $\delta = 7.18$ ($J = 3646$ Hz). MS: *m*/*z* (%) = 1757 (1.3) [$Pt_2Cl_4(DPPN)_2^+$], 1721 (9.5) [$Pt_2Cl_3(DPPN)_2^+$], 1685 (2.5) [$Pt_2Cl_2(DPPN)_2^+$].

NMR Study of the Isomerisation of *trans,trans*-[Pt_2Cl_4(DPEN)$_2$] (11) to *cis,cis*-[Pt_2Cl_4(DPEN)$_2$] (12): A solution of *trans,trans*-[Pt_2Cl_4(DPEN)$_2$] (**11**; approx. 10 mg) in $CDCl_3$/CH_2Cl_2 was placed in an NMR tube and cooled to 203 K within the NMR machine. A ^{31}P NMR spectrum was taken. A microspatula was then used to add the minimum quantity of DPEN (**5**; approx. 0.5 mg) to the sample, which was briefly shaken then immediately frozen in liquid nitrogen and returned to the NMR machine. The sample was warmed to 298 K over 27 hours, during which time the sample was converted into *cis,cis*-[Pt_2Cl_4(DPEN)$_2$] (**12**). ^{31}P{^{1}H} NMR: initial: $\delta = 6.94$ ($J = 2530$ Hz); final: $\delta = 6.12$ ($J = 3624$ Hz). See Figure 7 for details.

[$Mo_2(CO)_8$(DPEN)$_2$] (14): $Mo(CO)_6$ (50 mg, 0.19 mmol) and $NaBH_4$ (13 mg, 0.35 mmol) were added to a suspension of DPEN (**5**; 100 mg, 0.17 mmol) in ethanol (5 mL). The mixture was refluxed for 15 h then allowed to cool to room temperature, by which time the initial white precipitate had become yellow. Water (10 mL) was added, the mixture filtered and the product washed from the resulting solid with dichloromethane. The solvent was then removed to give a pale-yellow solid (71 mg). Colourless prisms of complex **14** grown from a CH_2Cl_2 solution were suitable for X-ray analysis. ^{1}H NMR: $\delta = 2.50-2.55$ (m, 8 H, CH_2P), $4.08-4.13$ (m, 8 H, CH_2O), $6.85-6.95$ (m, 8 H, $C_{3,6}$ H and $C_{1,8}$ H) $7.27-7.45$ (m, 40 H, PPh_2), 7.62 (d, $J = 9$ Hz, 4 H, $C_{4,5}$ H). ^{31}P{^{1}H} NMR: $\delta = 19.39$. MS: *m*/*z* (%) = 1586 (0.28) [$Mo_2(CO)_8$(DPEN)$_2^+$], 1530 (0.18) [$Mo_2(CO)_6$(DPEN)$_2^+$], 1474 (0.21) [$Mo_2(CO)_4$(DPEN)$_2^+$], 1446 (0.23) [$Mo_2(CO)_3$(DPEN)$_2^+$], 1411 (0.57).

Hydroformylation of 1-Octene using *cis,cis*-[Pt_2Cl_4(DPEN)$_2$] (12): A solution of *cis,cis*-[Pt_2Cl_4(DPEN)$_2$] (**12**; 54 mg, 0.03 mmol), $SnCl_2$ (12 mg, 0.06 mmol) and 1-octene (1.38 mL, 8.1 mmol) in dichloromethane (25 mL) in a reaction vessel was placed in a stainless steel autoclave. The reaction mixture was placed under 20 bar of CO and 20 bar of H_2 at 60 °C for 18 h. GCMS showed 100% conversion of 1-octene; this was confirmed by ^{1}H NMR spectoscopy. GC: t_R = 7.07 minutes (11.1%, 2-methyloctanal), 8.73 minutes (87.3%, nonanal), 50.11 minutes (1.6%, unidentified). Due to aldehyde trimerisation the ^{1}H NMR spectrum showed two sets of signals associated with nonanal, and two associated with 2-methyloctanal. Nonanal monomeric form: ^{1}H NMR: $\delta = 0.89$ (m, 3 H, CH_3), 1.29 [m, 12 H, $CH_3(CH_2)_6$], 2.43 (td, $J = 1.8$, 7.3 Hz, 2 H, CH_2CHO), 9.67 (s, 1 H, CHO). Nonanal cyclic trimer form: ^{1}H NMR: $\delta = 0.89$ (m, 9 H, 3 × CH_3), 1.29 [m, 36 H, $CH_3(CH_2)_6$], 1.57 (m, 6 H, 3 × $OCHCH_2$), 4.84 (t, $J = 5.3$ Hz, 3 H, 3 × OCH). 2-Methyloctanal monomeric form: ^{1}H NMR: $\delta = 0.89$ (m, 3 H, CH_3CH_2), 1.01 (d, $J = 7.0$ Hz, 3 H, CH_3CH), 1.29 [m, 10 H, $CH_3(CH_2)_5$], 2.25 (m, 1 H, $CHCH_3$), 9.51 (d, 1 H, CHO). 2-Methyloctanal cyclic trimer form: ^{1}H NMR: $\delta = 0.86$ (m, 9 H, 3 × CH_3CH_2), 0.89 (d, J =

Table 1. Experimental details of the crystallographic study

	11	**12**	**13**	**14**
Formula	$C_{76}H_{68}Cl_4O_4P_4Pt_2$	$C_{76}H_{68}Cl_4O_4P_4Pt_2$ $\cdot 6CHCl_3$	$C_{80}H_{76}Cl_4O_4P_4Pt_2$ $\cdot 7CH_2Cl_2$	$C_{84}H_{68}Cl_4Mo_2O_{12}P_4$ $\cdot 4CH_2Cl_2$
Colour	pale yellow	colourless	colourless	colourless
M_r	1701.2	2417.4	2351.8	1924.9
Space group	*P*1bar	*P*1bar	$P2_1/n$	*P*1bar
Crystal system	triclinic	triclinic	monoclinic	triclinic
a (Å)	9.9438(9)	10.8061(4)	14.5506(1)	10.6251(2)
b (Å)	14.7383(13)	11.1389(5)	23.0337(2)	12.0645(3)
c (Å)	15.132(2)	20.6078(8)	15.0485(1)	21.4369(6)
α (°)	71.990(11)	81.450(2)		87.325(1)
β (°)	89.553(9)	77.570(2)	98.0901(6)	87.773(1)
γ (°)	83.186(7)	76.863(2)		65.051(1)
V (Å^3)	2093.1(4)	2345.97(16)	4993.37(6)	2488.2(1)
Z	1	1	2	1
$D_{calcd.}$ (g·cm^{-3})	1.35	1.71	1.564	1.285
F(000)	840	1188	2332	980
μ(Mo-K_α)	3.583	3.720	3.390	0.583
Crystal size	0.35 × 0.25 × 0.10	0.5 × 0.15 × 0.10	0.5 × 0.45 × 0.4	0.4 × 0.3 × 0.25
Transmission coefficients (range)	0.584–0.261	0.717–0.461	0.160–0.119	0.868–0.800
T (K)	298	173	150	150
θ angle (°)	2.7–26.0	3.4–26.0	2.1–30.0	2.9–27.6
No. of data collected	9714	24638	62058	19519
No. of unique data	8220	9021	14472	11202
h, *k*, *l* range	$-1 \rightarrow 12$	$-12 \rightarrow 13$	$-20 \rightarrow 20$	$-13 \rightarrow 13$
	$-18 \rightarrow 18$	$-13 \rightarrow 13$	$-32 \rightarrow 32$	$-15 \rightarrow 15$
	$-18 \rightarrow 18$	$-25 \rightarrow 25$	$-15 \rightarrow 21$	$-25 \rightarrow 27$
R_{int}	0.0312	0.0567	0.0442	0.0348
No. of data in refinement	8220	9021	14472	11202
No. of refined parameters	358	515	515	514
Final *R* [$I \geq 2\sigma(I)$] (all data)	0.0385 (0.0681)	0.0575 (0.0840)	0.0351 (0.0508)	0.0541 (0.0758)
*wR*2 [$I \geq 2\sigma(I)$] (all data)	0.0862 (0.0929)	0.117 (0.1277)	0.0933 (0.0980)	0.1353 (0.1455)
Goodness of fit *S*	0.949	1.062	1.032	1.019
Largest remaining feature in electron density map, max./min. e·Å^{-3}	0.72/–1.16	2.75/–1.98	1.50/–1.37	0.80/–0.57
Max shift/esd in last cycle	0.002	0.002	0.001	0.005

8.0 Hz, 9 H, 3 × CH_3CH), 1.29 [m, 30 H, 3 × $CH_3(CH_2)_5$], 1.57 (m, 3 H, 3 × OCHC*H*), 4.82 (m, 3 H, 3 × OCH).

Crystallographic Structure Determinations: Details of data collection procedures and structure refinements are given in Table 1. Single crystals of suitable size were attached to glass fibres using acrylic resin, and mounted on a goniometer head in a general position. All samples suffered solvent loss, this being particularly severe for compounds **12** and **13**, which required that these crystals were glued to the glass fibre under solvent and transferred as rapidly as possible to the cold stream of the Oxford Instruments Cryostream. For compounds **12**, **13** and **14**, low temperature data were collected on a Bruker-Nonius KappaCCD diffractometer, running under the Collect software, while data for compound **11** were collected on a Enraf−Nonius Turbo-CAD4 diffractometer at ambient temperature. Graphite monochromated X-radiation ($\lambda = 0.71073$ Å) was used for all studies. Precise unit cell dimensions for the CAD4 dataset were determined from 25 high-angle reflections which were flagged during data collection. Precise unit cell dimensions for the KappaCCD data-sets were determined by post-refinement using the Scalepack[28] program. Frame images were integrated using Denzo-SMN[28] and the resultant raw intensity files processed using a locally modified version of DENZOX[29] and then sorted and merged using SORTAV.[30] Empirical absorption corrections by the method of Blessing[31] for compounds **12**, **13** and **14** and Stuart and Walker[32] for **11** were applied to the data. No significant crystal decay was noted for any sample. The structures were solved by DIRDIF-99,[33] SIR-92[34] or SHELXS-97.[35] All non-H atoms were allowed anisotropic thermal motion. Aliphatic and aromatic C−H hydrogen atoms were included at calculated positions, with C−H = 0.96 Å, and were refined with a riding model and with U_{iso} set to 1.2 times that of the attached C atom. Refinement was with SHELXL97−2[35] using full-matrix least-squares on F^2 and all the unique data. All samples showed the presence of disordered solvent molecules, and the SQUEEZE procedure of Spek and van der Sluis[36] was used to model this extra electron density where appropriate. For compound **11** an extra 47 e/cell were indicated, this being potentially due to CH_2Cl_2, H_2O or Et_2O. For compound **12** three independent ordered molecules of $CHCl_3$ per asymmetric unit were found, and only a small residual solvent accessible void totalling ≈40 Å^3 was left. The SQUEEZE was not considered necessary in this case. For compound **13**, two ordered and one disordered CH_2Cl_2 molecules per asymmetric unit were found, along with indications of a further 1/2 molecule. An extra 83 e/cell were recovered by the SQUEEZE procedure, consistent with a 1/2 molecule of CH_2Cl_2. This was thus included in the cell contents. For compound **14** two ordered molecules of CH_2Cl_2 were observed as well as large voids containing further disordered solvent. The SQUEEZE procedure recovered 38 e/cell, consistent with a further 1/2 molecule of CH_2Cl_2. Neutral atom scattering factors, coefficients of anomalous dispersion and absorption coefficients were obtained from reference.[37] Thermal ellipsoid plots were obtained using the program ORTEP-3 for Windows.[38] All calculations were carried out using the WinGX package[39] of crystallographic programs.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165290 (**11**), CCDC-165291 (**12**), CCDC-165292 (**13**) and CCDC-165293 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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