# Triphosphamacrocycle complexes of rhodium(III), iron(II) and ruthenium(II); crystal structure of trichloro[1,5,9-tris(2-propyl)-1,5,9-triphosphacyclododecane]rhodium(III) †

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The free macrocyclic 1,5,9-tris(2-propyl)-1,5,9-triphosphacyclododecane ($Pr^i_3[12]aneP_3$, L) has been used for the first time to prepare a range of metal complexes. Reaction of L with $RhCl_3 \cdot 3H_2O$ yields the six-co-ordinate *fac*-octahedral complex [$RhCl_3(L)$], which has been structurally characterised and is also used to prepare the analogous rhodium(III)–trihydrido and –triiodo complexes. The half-sandwich complex, [$Fe(\eta^5-C_5H_5)(L)$]$PF_6$ was prepared from [$Fe(\eta^5-C_5H_5)(\eta^6-C_6H_5)$]$PF_6$ and L. The ruthenium complexes [$RuCl_2(dmso)(L)$] (dmso = dimethyl sulfoxide) and [$Ru_2(\mu-Cl)_3(L)_2$]Cl were also formed from the reaction of L with [$RuCl_2(dmso)_4$] and [$RuCl_2(\eta^6-C_6H_4Me-4-Pr^i-1)$]$_2$ respectively.

Despite the substantial body of chemistry reported in the literature concerning phosphine and polyphosphine ligands and their metal complexes, there are few studies of the co-ordination chemistry of phosphorus macrocycle ligands. This is surprising in view of the relative control of ligand lability as well as structure that macrocycles can enable, as well as the importance of related nitrogen and chalcogenide macrocycles. Our interest in macrocyclic phosphines arises from the potential ability of these ligands to stabilise unusual oxidation states and co-ordination environments of transition metals. The control over the metal's co-ordination sphere that they may allow, with consequent influences upon reactivity, may be of considerable value in the development of applications of metal complexes such as in homogeneous catalysis. With this in mind, we have undertaken to study triphosphorus macrocycles since with appropriate macrocyclic ring sizes they should be ideally suited to facial co-ordination to a metal thus leaving remaining co-ordination sites mutually *cis*. This feature is desirable in the further study of the reactivity of phosphorus macrocycle complexes. As well as their potential as precursors to homogeneous catalysts, these compounds can act as cyclic, tridentate, six-electron donors with close similarities to the cyclopentadienyl family of ligands. Since they are formally neutral however, they may also lead to a range of chemistry that might otherwise not be accessible with negatively charged cyclopentadienyl and related ligands. The manipulation of functional groups at phosphorus is also straightforward and a wide variation in the nature of the substituents in tertiary phosphines is readily achievable. Thus as well as enabling the selective control and design of the steric and electronic properties of the ligands, the incorporation of other functions such as further pendant donors is also possible.

Triphosphorus macrocycles are rare, the only previously reported free (unco-ordinated) examples consist of unsymmetrical eleven-membered rings based on the 1,2-diphosphinobenzene unit and were prepared by high dilution methods.[1a] This synthetic route resulted in a mixture of stereoisomers and low yields of individual isomers following tedious separation procedures. Complexes of these triphosphorus macrocycles were subsequently reported with a range of metals [$Cr^0$, $Mo^0$, $W^0$, $Ni^{II}$ and $Cu^{II}$] where all three phosphorus atoms were co-ordinated;[1] the ligand is also known to be bidentate with the third phosphorus atom unco-ordinated.[2] Norman and co-workers[3] published the synthesis of the first 1,5,9-triphosphacyclododecane complex from the template coupling of the tris(allylphosphine)tricarbonyl molybdenum complex. This also constituted the only example of a symmetrical triphosphorus macrocycle. We have subsequently extended this chemistry to the analogous tungsten and chromium templates,[4] and also prepared a range of tritertiary phosphine complexes from the original molybdenum triphosphacyclododecane,[4b] and their oxidation to the corresponding molybdenum(II) complexes.[5] We have recently reported the first preparation of a free, symmetrical triphosphorus macrocycle from the molybdenum(II) template,[4a] and have demonstrated that this route is appropriate for the stereoselective synthesis of a range of 1,5,9-triphosphacyclododecanes, $R_3[12]aneP_3$ (R = H, methyl, ethyl, 2-propyl, 2-methylpropyl or trimethylsilylmethyl).[6]

The stereoselective synthesis of these ligands (for the *syn,syn* isomer) is important. The *syn,anti* stereoisomer might prefer either bidentate or bridging co-ordination modes whereas the *syn,syn* isomer would be better suited to act as a tridentate ligand in the manner observed for the analogous nitrogen and sulfur macrocyclic ligands. For example, 1,5,9-triazacyclododecane ([12]aneN_3) and 1,5,9-trithiacyclododecane ([12]aneS_3) complexes have been reported with $Cu^{II}$,[7] $Zn^{II}$,[8] $Ni^{II}$[9] and $Ru^{II}$.[10] It is perhaps significant however that the chemistry of these twelve-membered macrocycles has been studied to a considerably lesser extent than that of the corresponding nine-membered analogues, 1,4,7-triazacyclononane,[11] and 1,4,7-trithiacyclononane.[12]

The detailed insight into the nature of transition-metal tertiary phosphine complexes that the pioneering work of Geoffrey Wilkinson and others has provided has enabled the design of new ligand systems that may allow control of the properties of complexes to good effect. The unique properties of this macrocyclic ligand allow us to build upon this. This paper constitutes the first reported co-ordination study of a free triphosphacyclododecane ligand and in which we describe the synthesis and characterisation of complexes of $Pr^i_3[12]aneP_3$ (L) with a range of transition metals.

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† We dedicate this paper to Sir Geoffrey Wilkinson for whom we had great respect as an individual and as a scientist and whose loss was met with great sadness. We remember his support, encouragement and his style; he will be missed. It is a pleasure to be able to present this work which includes studies on what Sir Geoffrey referred to as 'the connoisseurs elements', rhodium and ruthenium. At least to an extent he lives on in some of his students.
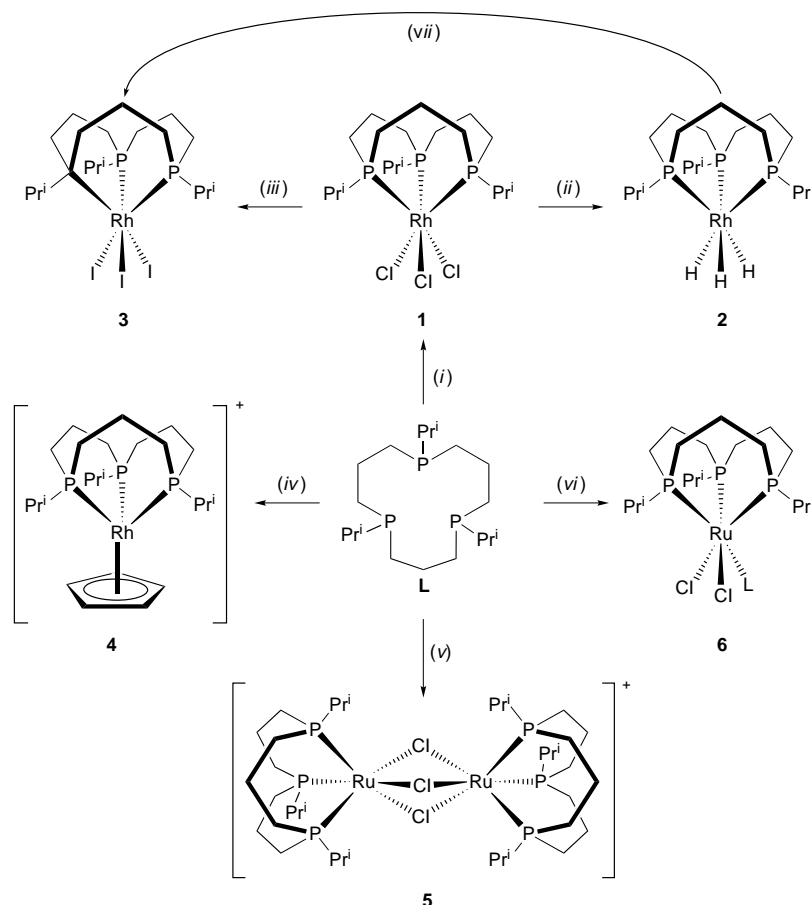
**Scheme 1** (*i*) $RhCl_3 \cdot H_2O$ in ethanol; (*ii*) $NaBH_4$ in ethanol; (*iii*) NaI in ethanol; (*iv*) $[FeCp(C_6H_6)]PF_6$ in thf; (*v*) $[RuCl_2(\eta^6\text{-}C_{10}H_{14})]_2$ in $CH_2Cl_2$; (*vi*) $[RuCl_2(dmso)_4]$ in $CH_2Cl_2$; (*vii*) MeI

## Results and Discussion

Synthetic routes to the new complexes described below are collected in Scheme 1. The NMR data are collected in Table 1; IR, mass spectroscopic and analytical data are in Table 2.

### Rhodium compounds

The reaction of L with $RhCl_3 \cdot 3H_2O$ in ethanol results in the formation of yellow $[RhCl_3(L)]$ **1** in good yield. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a doublet at $\delta$ 15.6 (due to coupling with Rh) which is unchanged at low temperature, consistent with facial co-ordination of the macrocycle in a half-sandwich structure. The $^1H$ NMR spectrum of **1** is similar to that of the free ligand; four resonances are observed in the $^{13}C\text{-}\{^1H\}$ NMR spectrum, again consistent with magnetically equivalent phosphorus atoms. Two weak $\nu$(Rh–Cl) bands were observed in the IR spectrum at 325 and 295 cm$^{-1}$, confirming a facial arrangement of ligands and that the solution and solid-state structures are related. Related trisphosphine trichloro complexes of Rh have long been known with both monodentate tertiary alkyl phosphines[13a] and with linear tridentate phosphines;[13b] in both cases meridional isomers were formed.

Reaction of **1** with $NaBH_4$ in ethanol at room temperature readily forms the trihydride complex $[RhH_3(L)]$ **2** in reasonable yield. The $^{31}P\text{-}\{^1H\}$ NMR spectrum again shows only one, temperature invariant resonance at $\delta$ 29.6. Analytical data are consistent with the formulation and a strong molecular ion ($m/z$ = 452) is observed in the mass spectrum. Two bands assigned to $\nu$(Rh–H) are observed in the IR spectrum at 1910 and 1820 cm$^{-1}$ indicating facially co-ordinated hydrides.

The formation of Rh$^{III}$–trihydride trisphosphine complexes is relatively rare; with monodentate phosphines, complex mixtures of uncharacterised products were reported from reactions with $BH_4^-$. With the tripodal triphosphine complexes, $[RhCl_3(L^1)]$ [where $L^1$ = $MeC(CH_2PPh_2)_3$, triphos or $EtC(CH_2PPh_2)_3$] however, reaction with $NaBH_4$ leads to the formation of the analogous *fac*-trihydride complexes.[14] Furthermore, these tripodal phosphine complexes react with CO to form complexes of the type $[RhH(CO)(L^1)]$, they also react with a range of co-ordinatively unsaturated metal fragments to form a family of bimetallic polyhydride complexes of the general formulae $[(L^1)Rh(\mu\text{-H})_3M(L^1)]^{n+}$ ($n$ = 1–3; M = Rh, Co or Ni; $L^1$ = triphos),[14] and $[(L^1)Rh(\mu\text{-H})_2\{Au(PPh_3)_m\}]^{n+}$ ($n$ = 1–3; $m$ = 1 or 2).[15]

The trihydride, **2**, is unstable in solution resulting in the slow decay of the hydride signal in the $^1H$ NMR spectrum ($t_{\frac{1}{2}}$, 27 °C in $C_6D_6 \approx$ 5 h). Again, similar behaviour has been observed for the related $[RhCl_3(triphos)]$ complexes. Solutions of **2** react with MeI during several days resulting in the quantitative conversion to a new orange crystalline material for which analytical data indicate the formula $[RhI_3(L)]$ **3**. The triiodide **3** is also formed as the major product from the reaction of **1** with NaI along with several unidentified minor by-products. Compound **3** also gives rise to one resonance in the $^{31}P\text{-}\{^1H\}$ NMR ($\delta$ −1.4) as would be expected for a facial isomer. Reactions of **1** and **2** are under investigation.

### Iron and ruthenium compounds

The reaction of $[FeCp(C_6H_5)]PF_6$ (Cp = $\eta^5\text{-}C_5H_5$) with L under thermal conditions did not result in substitution of the co-ordinated benzene; under UV irradiation (254 nm) however, yellow $[FeCp(L)]PF_6$ **4** was formed in good yield. Again, a single resonance was observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum ($\delta$ 37.0) suggesting a symmetrical, mixed-sandwich structure and $^1H$, $^{13}C\text{-}\{^1H\}$ NMR and analytical data are consistent with this formulation. Analogous complexes of this type are well known for both linear tridentate phosphines,[16] and tridentate

**Table 1** The NMR spectroscopic data for 1,5,9-triphosphacyclododecane complexes

| Complex | δ ($^1$H) | δ ($^{13}$C-{$^1$H}) | δ ($^{31}$P-{$^1$H}) |
|---|---|---|---|
| **1** [RhCl$_3$(L)]$^a$ | 1.80 (br m, PCH$_2$C$H_2$) | 29.1 (m, PCH$_2$) | 15.6 [d, $J$(RhP) 106 Hz] |
| | 1.50 (br m, PCH and CCH$_2$) | 25.5 (m, PCH$_2$C$H_2$) | |
| | 1.00 [dd, $^3J$(PH) + $^2J$(HH) 12 Hz and 9 Hz, CH$_3$] | 18.4 (s, CH$_3$) | |
| | | 17.0 (m, PCH) | |
| **2** [RhH$_3$(L)]$^b$ | 1.8 (br m, PCH$_2$C$H_2$) | $c$ | 29.6 [d, $J$(RhP) 90 Hz] |
| | 1.50 (br m, PCH and PCH$_2$) | | |
| | 0.97 (br s, CH$_3$) | | |
| | −9.42 (ddt, $^1J$(RhH) 127 Hz) | | |
| **3** [RhI$_3$(L)]$^d$ | 1.81 (br m, PCH$_2$C$H_2$) | 34.4 (br m, PCH$_2$) | −1.4 [d, $J$(RhP) 106 Hz] |
| | 1.48 (br m, PCH and PCH$_2$) | 20.7 (m, PCH$_2$C$H_2$) | |
| | 1.01 [dd, $^3J$(PH) and $^2J$(HH) 12 and 9 Hz, CH$_3$] | 18.7 (m, PCH) | |
| | | 17.3 (s, CH$_3$) | |
| **4** [FeCp(L)]PF$_6$$^b$ | 4.34 (q, $^3J$(PH) 2 Hz, C$_5$H$_5$) | 77.5 (s, C$_5$H$_5$) | 37.0 (s) |
| | 1.85 (br m, PCH$_2$C$H_2$) | 32.4 (br m, PCH$_2$) | −144.6 [spt, $J$(PF) 707 Hz] |
| | 1.60 (br m, PCH and PCH$_2$) | 21.7 (m, PCH$_2$C$H_2$) | |
| | 1.18 [dd, $^3J$(PH) 13 and $^2J$(HH) 7 Hz, CH$_3$] | 18.6 (m, PCH) | |
| | | 17.8 (s, CH$_3$) | |
| **5** [Ru$_2$(μ-Cl)$_3$(L)$_2$]Cl$^a$ | 1.79 (br m, PCH$_2$C$H_2$) | 31.9 (br m, PCH$_2$) | 25.0 (s) |
| | 1.49 (br m, PCH$_2$ and CCH$_2$) | 22.0 (m, PCH$_2$C$H_2$) | |
| | 1.00 (br s, CH) | 19.0 (m, PCH) | |
| | | 18.0 (s, CH$_3$) | |
| **6** [RuCl$_2$(dmso)(L)]$^a$ | 2.91 (s, SCH$_3$) | 48.0 (s, SCH$_3$) | 37.1 (s) |
| | 1.88 (br m, PCH$_2$C$H_2$) | 32.2 (br m, PCH$_2$) | |
| | 1.60 (br m, PCH and PCH$_2$) | 22.9 (m, PCH) | |
| | 1.08 (br s, PHC$H_3$) | 18.0 (s, CH$_3$) | |

$^a$ In CDCl$_3$ solution. $^b$ In CD$_3$OD solution. $^c$ Decomposes during data collection. $^d$ In CD$_2$Cl$_2$ solution.

**Table 2** Selected IR spectroscopic, analytical and mass spectrometry data for 1,5,9-triphosphacyclododecane complexes

| Complex | $\tilde{\nu}$(M–X)/cm$^{-1}$ | Analysis$^a$ (%) C | H | Mass spectrum |
|---|---|---|---|---|
| **1** | 325w, 295w | 38.45 (38.74) | 7.02 (6.99) | 558 ($M^+$, 5%) |
| | | | | 523 ([$M$ − Cl]$^+$, 12%) |
| **2** | 1910s, 1820vs $^b$ | 47.60 (47.58) | 9.84 (9.25) | 452 ($M^+$, 40%) |
| **3** | | 25.72 (25.96) | 5.25 (4.69) | 528 ([$M$ − I$_2$]$^+$, 10%) |
| **4** | | 44.18 (44.98) | 6.89 (7.17) | — |
| **5** | 270vw | 41.77 (41.54) | 7.66 (7.50) | — |
| **6** | 320w, 305w | 39.97 (40.13) | 7.71 (7.53) | 520 ([$M$-dmso]$^+$, 5%) |
| | 1160s (br), 920s (br) $^c$ | | | |

$^a$ Found (Calc.). $^b$ $\nu$(M–H). $^c$ $\nu$(S–O).

sulfur macrocycles,[17] although different synthetic routes were used in those cases.

As with rhodium–phosphine complexes, ruthenium–phosphine compounds are known to catalyse a number of different, homogeneous reactions. Also, a number of ruthenium(II)–tripodal phosphine complexes have been reported in the literature and shown to possess catalytic activity,[18] and ruthenium(II) complexes with triaza- and trithia-macrocycles are well known.[19] Clearly, an investigation of the co-ordination chemistry of R$_3$[12]aneP$_3$ ligands with ruthenium(II) is of interest.

Reaction of the dimeric ruthenium starting material di-μ-chloro-bis[chloro(η$^6$-1-isopropyl-4-methylbenzene)ruthenium(II)] {[RuCl$_2$(η$^6$-C$_{10}$H$_{14}$)]$_2$} with 2 equivalents of L at room temperature results in the displacement of the arene from the metal centre to afford a dark red-orange material for which analytical data indicate the formula [RuCl$_2$(L)] **5**. In CDCl$_3$ solution, **5** shows a singlet in its $^{31}$P-{$^1$H} NMR spectrum which is temperature invariant. Although a non-conductor in CH$_2$Cl$_2$ solution, **5** is, however, a 1:1 electrolyte in ethanol ($\Lambda_m$ = 88 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ based upon a binuclear cation). These data imply therefore that this complex is more correctly formulated as [Ru$_2$(μ-Cl)$_3$(L)$_2$]Cl. The ionic nature of **5** is confirmed by its conductivity in polar solvents whilst the presence of the chlorine bridge renders both ruthenium atoms symmetrical and all

phosphorus atoms magnetically equivalent giving rise to the singlet observed in the $^{31}$P-{$^1$H} NMR spectrum. Only one weak band is observed in the IR spectrum that may be assigned to $\nu$(Ru–Cl), the relatively low frequency of this band (270 cm$^{-1}$ cf. compound **6** below) is consistent with bridging chlorides. All other analytical data are consistent with this structure. Analogous ionic, triply bridged binuclear compounds are well known for ruthenium(II) complexed to tripodal ligands.[18a]

A different product is formed from [RuCl$_2$(dmso)$_4$] (dmso = dimethyl sulfoxide). Reaction at room temperature of [RuCl$_2$(dmso)$_4$] with 1 equivalent of L affords a yellow crystalline product for which analytical data indicate the formula [RuCl$_2$(dmso)(L)] **6**. Complex **6** is a non-conductor in polar organic solvents [EtOH or tetrahydrofuran (thf)] and as for **5**, a temperature invariant singlet is observed in the $^{31}$P-{$^1$H} NMR spectrum. Whilst this may be unexpected for the unsymmetrical structure of **6**, this type of behaviour is precedented for tripodal arsine ligands. Treatment of [RuCl$_2$(dmso)$_4$] with 1 equivalent of 'triars' [MeC(CH$_2$AsPh$_2$)$_3$] initially forms the complex [RuCl$_2$(dmso)(triars)], in which all three arsine functions appear equivalent in the $^1$H NMR spectrum; this observation was explained as being due to the facile lability of dmso in solution.[18b]

Complex **6** shows bands in the IR spectrum at 320 and 305 cm$^{-1}$ which are assigned to terminal $\nu$(Ru–Cl) absorbances consistent with **6** having a mononuclear structure. Further
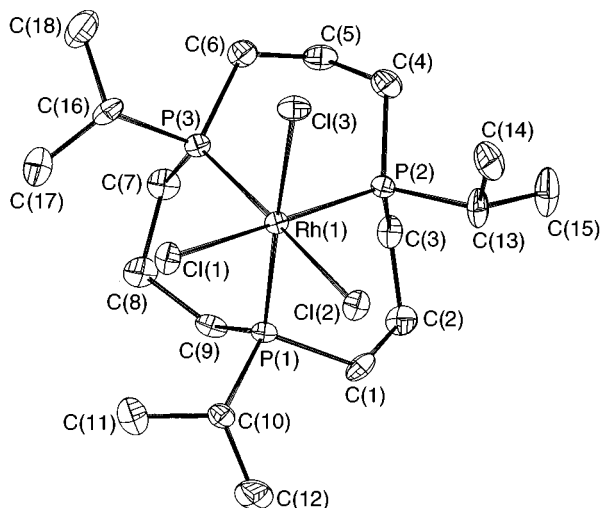
**Fig. 1** Molcular structure and atom labelling scheme of trichloro-[1,5,9-tris(2-propyl)-1,5,9-triphosphacyclododecane]rhodium(III) **1**. Selected bond lengths (Å) and angles (°): Rh–P(2) 2.288(2), Rh–P(3) 2.291(2), Rh–P(1) 2.292(2), Rh–Cl(1) 2.423(2), Rh–Cl(3) 2.449(2), Rh–Cl(2) 2.456(2), P(1)–C(9) 1.819(7), P(1)–C(1) 1.840(7), P(1)–C(10) 1.859(8), P(2)–C(4) 1.828(9), P(2)–C(3) 1.829(7), P(2)–C(13) 1.845(8), P(3)–C(7) 1.812(8), P(3)–C(6) 1.841(8), P(3)–C(10) 1.871(7), P(2)–Rh–P(3) 91.45(7), P(2)–Rh–P(1) 90.44(7), P(3)–Rh–P(1) 96.39(7), P(2)–Rh–Cl(1) 176.24(7), P(3)–Rh–Cl(1) 90.77(7), P(1)–Rh–Cl(1) 92.33(7), P(2)–Rh–Cl(3) 89.20(3), P(3)–Rh–Cl(3) 86.23(7), P(1)–Rh–Cl(3) 177.37(7), P(3)–Rh–Cl(22) 177.24(7), P(2)–Rh–Cl(2) 91.14(7), P(1)–Rh–Cl(2) 84.56(7), Cl(1)–Rh–Cl(2) 86.59(7), Cl(1)–Rh–Cl(3) 87.92(7), Cl(3)–Rh–Cl(2) 92.84(7)

absorptions are observed at 1160 and 920 cm$^{-1}$ corresponding to ν(S–O) implying that the complex contains both S- and O-bonded dmso in the solid state. In the $^1$H NMR spectrum, a resonance attributed to the methyl protons of dmso appears at δ 2.91. It has previously been shown that the reaction of [RuCl$_2$(dmso)$_4$] with tripodal ligands at elevated temperature forms triply-bridged dimers of the type [Ru$_2$(μ-Cl)$_3$(tripod)$_2$]Cl, rather than dmso-bonded complexes.[18c] The conversion of **6** into **5** however in refluxing toluene (24 h) is slow (resulting in approximately 5% conversion, $^{31}$P NMR spectroscopy); refluxing **5** in dmso (16 h) leaves it unchanged. It appears then that these d$^6$ Ru$^{II}$ complexes are significantly more kinetically inert than similar complexes with linear tridentate ligands.

### Solid-state structure of [RhCl$_3$(L)] 1

The crystal-structure determination of **1** (Fig. 1) shows a regular, octahedral arrangement of the six donor atoms with only slight distortions from idealised positions. As was seen for other crystal structures of d$^6$ triphosphacyclododecane metal complexes, e.g. [Mo(CO)$_3$(L)],[4] P–Rh–P angles are greater than, and Cl–Rh–Cl angles are less than 90°, presumably as a result of repulsions from the bulky isopropyl groups.

Comparison of **1** with data from the literature is restricted since there are relatively few structures of Rh(X)$_3$ complexes of tridentate phosphines and none with alkyl triphosphines.[20] There is, to our knowledge, only one reported crystal-structure determination of a complex of this type with a monodentate alkyl phosphine, [RhCl$_3${P(C$_2$H$_5$)$_2$Ph}$_3$] **7**,[21] despite the large number of [RhX$_3$(L$_3$)] (where L = phosphine, X = halide) known in the literature. There is also a report of the structure determination of [RhCl$_3${P(C$_4$H$_9$)$_3$}$_2${(MeO)$_3$P}] **8**.[22] Both of these complexes however adopt meridional octahedral structures; there are no crystallographically characterised facial [RhX$_3$(L$_3$)] complexes with phosphine ligands. For **7** there are two phosphorus environments, i.e. P trans to P and P trans to Cl, with only the latter suitable for a comparison with **1**; in **8** the

two phosphine groups are mutually trans, the phosphite is trans to Cl.

Although the angles vary over a range of about 6°, **1** attains a reasonably regular octahedral geometry with average P–Rh–P and Cl–Rh–Cl angles of 92.76(7) and 89.12(7)° respectively. The average Rh–P bond length in **1** [2.290(4) Å] is a little longer than that to the smaller P(OMe)$_3$ ligand trans to Cl in **8** (2.199 Å), but is shorter than that to the PEt$_2$Ph ligand trans to Cl in **7** [2.325(3) Å]. These variations presumably reflect the different relative steric constraints between the tertiary phosphines (in **1** and **7**). Since the macrocycle is quite flexible and can accommodate metals of widely varying radii, this difference is likely due to the relative bulk of three PEt$_2$Ph groups in comparison to L. There may also be an enhanced π-bonding contribution to the shortness of the Rh–P bond in **8**. The average Rh–Cl bond length in **1** [2.443(4) Å] is a little longer than Rh–Cl trans to P in **8** [2.418(4) Å] but similar to that (trans to P) in **7** [2.429(3) Å]. For **7**, with identical phosphines, the length of the Rh–P bond trans to Cl is significantly less than the length of the mutually trans Rh–P bonds [2.415(4) and 2.382(4) Å] confirming phosphine to have a greater trans influence than chloride in these complexes. This may well be a significant influence upon the reactivity of **1** and its analogues since clearly all halide or other anionic ligands are restricted to be trans to a phosphorus donor and thus will all be subjected to the relatively high trans effect of tertiary phosphines.

### Conclusion

The reactions of Pr$^i_3$[12]aneP$_3$ with d$^6$ Fe, Ru and Rh precursor complexes readily give rise to facially co-ordinated tris(phosphine) complexes in which other anionic or neutral ligands are restricted to a mutually cis co-ordination environment. The macrocyclic ligand is capable of forming halide, hydride or cyclopentadienyl complexes for metals of varying radii and which (for Rh) are relatively free from structural distortions.

### Experimental

All reactions were carried out in an atmosphere of dry nitrogen. All solvents were dried by boiling under reflux over standard drying agents. The compounds L [1,5,9-tris-(2-propyl)triphosphacyclododecane],[6] [FeCp(C$_6$H$_6$)]PF$_6$,[23] [RuCl$_2$(η$^6$-C$_{10}$H$_{14}$)]$_2$,[24] and [RuCl$_2$(dmso)$_4$][25] were prepared by literature methods. All other chemicals were obtained from the Aldrich Chemical Company. The NMR spectra were recorded on a Bruker WM360 instrument operating at 360.13 ($^1$H) or 90.53 ($^{13}$C) MHz, or a JEOL FX-90 instrument operating at 36.23 ($^{31}$P) MHz. All NMR spectra are quoted in ppm and were recorded in CDCl$_3$ solution except where noted, with the $^1$H and $^{13}$C NMR chemical shifts relative to solvent and $^{31}$P NMR chemical shifts relative to 85% external H$_3$PO$_4$ (δ = 0). Infrared spectra were recorded in Nujol on a Perkin-Elmer 783-IR spectrometer. Mass spectra (electron impact, EI) and microanalyses were obtained from within this department. Conductivities were measured at 25 °C on 0.5 × 10$^{-4}$ M solutions.

#### Preparations

**Trichloro[1,5,9-tris(2-propyl)triphosphacyclododecane]-rhodium(III) 1.** A solution of L (0.14 mmol) in ethanol (30 cm$^3$) was added dropwise to a solution of RhCl$_3$·3H$_2$O (0.14 mmol) in ethanol (15 cm$^3$) at room temperature. The mixture was stirred for 1 h and solvent removed in vacuo to give a pale orange residue. Dichloromethane (50 cm$^3$) was added and the mixture filtered through Celite to give a pale orange solution. The solvent was removed in vacuo and the residue recrystallised from dichloromethane–diethyl ether to give **1** as pale orange prisms (0.10 mmol, 70%).

**Trihydrido[1,5,9-tris(2-propyl)triphosphacyclododecane]-rhodium(III) 2.** Sodium tetrahydroborate (1.00 mmol, excess) was added to a suspension of complex **1** (0.10 mmol) in ethanol (10 cm³) and stirred at room temperature until effervescence had ceased. The solvent was removed *in vacuo* to give a grey residue. Toluene (20 cm³) was added and the mixture filtered through Celite to give a pale yellow solution. Solvent was removed *in vacuo* to give **2** as a pale yellow powder (0.06 mmol, 60%).

**Triiodo[1,5,9-tris(2-propyl)triphosphacyclododecane]-rhodium(III) 3.** A suspension of complex **2** (0.10 mmol) in MeI (10 cm³) was stirred at room temperature for 48 h. The mixture was allowed to settle and the supernatant solution removed by filtration to give **3** as an orange solid which was then washed with diethyl ether (2 × 10 cm³) (0.08 mmol, 78%).

Complex **3** was also prepared from **1** (0.10 mmol) by stirring with NaI (0.40 mmol) in ethanol (20 cm³) for 24 h. Evaporation *in vacuo* followed by recrystallisation from dichloromethane–ethanol gave orange prisms (0.09 mmol, 90%).

**($\eta^5$-Cyclopentadienyl)[1,5,9-tris(2-propyl)triphosphacyclo-dodecane]iron(II) hexafluorophosphate 4.** A solution of L (0.10 mmol) in thf (20 cm³) was added to a solution of [FeCp-($C_6H_6$)]PF$_6$ (0.10 mmol) in thf (30 cm³) and the mixture irradiated under UV radiation for 8 h. The solvent was removed *in vacuo* and recrystallisation from $CH_2Cl_2$–$Et_2O$ gave **4** as yellow prisms (0.06 mmol, 65%).

**Tri($\mu$-chloro)bis[1,5,9-tris(2-propyl)triphosphacyclo-dodecane]diruthenium(II) chloride 5.** A solution of L (0.10 mmol) in dichloromethane (10 cm³) was added dropwise to a solution of [RuCl$_2$($\eta^6$-$C_{10}H_{14}$)]$_2$ (0.05 mmol) in dichloromethane (10 cm³) and the resultant mixture stirred for 4 h at room temperature. Evaporation to dryness *in vacuo* gave a red residue which was recrystallised from hot toluene to give **5** as red crystals (0.06 mmol, 58%).

**Dichloro(dimethyl sulfoxide)[1,5,9-tris(2-propyl)triphospha-cyclododecane]ruthenium(II) 6.** A solution of L (0.10 mmol) in dichloromethane (10 cm³) was added dropwise to a solution of [RuCl$_2$(dmso)$_4$] (0.10 mmol) in dichloromethane (10 cm³) and the resultant mixture stirred for 4 h at room temperature. The solvent was removed to give a yellow solid which was recrystallised from hot toluene to give **6** as yellow crystals (0.06 mmol, 56%).

### X-Ray crystallography

**Crystal data.** $C_{19}H_{39}Cl_5RhP_3$: $M_r = 640.57$, triclinic, space group $P\bar{1}$, $a = 7.665(2)$, $b = 12.173(2)$, $c = 14.458(2)$ Å, $\alpha = 89.904(14)$, $\beta = 94.428(8)$, $\gamma = 100.102(11)°$, $U = 1324.0(4)$ Å³, $Z = 2$, $D_c = 1.607$ g cm⁻³, $F(000) = 656$, $\mu$(Mo-K$\alpha$) = 1.337 cm⁻¹.

Data for a crystal of approximate dimensions $0.07 \times 0.14 \times 0.14$ mm were collected at 150 K, on a FAST TV Area detector diffractometer at the window of a rotating anode generator, with a molybdenum target [$\lambda$(Mo-K$\alpha$) = 0.71069 Å] and driven by MADNES[26] software. 5655 Data were recorded ($2.20 < \theta < 25.00°$), index ranges $-8 < h < 7$; $-14 < k < 13$; $-14 < l < 16$, giving 3597 unique data [$R_{int} = 0.0847$ after absorption correction (DIFABS)[27] (min/max absorption correction factors = 0.851 and 1.044 respectively)].

The structure was solved *via* heavy atom methods (SHELXS)[28] and refined by full-matrix least squares based on $F_o^2$ (SHELXL 93).[29] The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. The final $R1$ [$= \Sigma(F_o - F_c)/\Sigma(F_o)$] and $wR2$ $\{= [\Sigma(F_o^2 - F_c^2)^2/\Sigma\{w(F_o^2)^2\}]^{\frac{1}{2}}\}$ values were 0.0624 and 0.1557 for 2832 data with $F_o > 4\sigma(F_o)$ and 259 parameters ($\rho_{max}, \rho_{min}$ 2.49, $-0.781$e Å⁻³). The corresponding values for all data were 0.0743 and 0.1606 respectively. Diagrams were drawn with SNOOPI.[30] Sources of scattering factor data are given in ref. 29.

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