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Complexes of 2,3-bis(diphenylphosphino)propene with Pt^{II}, Pd^{II} and Ru^{II}: synthesis, characterisation and rearrangements to complexes of *cis*-1,2-bis(diphenylphosphino)propene

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Treatment of $[PdCl_2(PhCN)_2]$ with 1 equivalent of 2,3-bis(diphenylphosphino)propene (2,3-dpppn) in CH_2Cl_2 gave [PdCl$_2$(2,3-dpppn)] **1** together with some [PdCl$_2$(1,2-dpppn)] **2** [1,2-dpppn = *cis*-1,2-bis(diphenylphosphino)propene]. Treatment of **1** with an excess of benzylamine did not lead to addition to the double bond, but resulted in complete isomerisation to **2**, as monitored by $^{31}P-\{^1H\}$ and ^1H NMR spectroscopy. Metathesis of **2** with NaI in acetone gave [PdI$_2$(1,2-dpppn)] **3**. Platinum(II) complexes [PtCl$_2$(2,3-dpppn)] **4** and [PtCl$_2$(1,2-dpppn)] **5** were prepared and characterised analogously. Treatment of **2** or **5** with an excess of MeLi gave [PdMe$_2$(1,2-dpppn)] **6** and [PtMe$_2$(1,2-dpppn)] **7** respectively, and treatment of **5** with hydrazine hydrate and an excess of HC≡CPh in ethanol gave [Pt(C≡CPh)$_2$(1,2-dpppn)] **8**. Treatment of $[PdCl_2(PhCN)_2]$ with 2 equivalents of $AgBF_4$ and 2 equivalents of 2,3-dpppn gave a mixture of at least four isomeric complexes, probably *cis*- and *trans*-[Pd(2,3-dpppn)$_2$][BF$_4$]$_2$ and *cis*- and *trans*-[Pd(1,2-dpppn)$_2$][BF$_4$]$_2$. On treatment with benzylamine, this mixture was converted into a *ca.* 1 : 1 mixture of two isomers, which NMR spectroscopic evidence suggested were *cis*- and *trans*-[Pd(1,2-dpppn)$_2$][BF$_4$]$_2$ **9**. Similarly, treatment of $[PtCl_2(PhCN)_2]$ with $AgBF_4$–2,3-dpppn gave *cis*- and *trans*-[Pt(1,2-dpppn)$_2$][BF$_4$]$_2$ **10**. A crystal structure determination was performed on the *trans* isomer, isolated on recrystallisation of the mixture from MeCN–Et_2O. Treatment of $[RuCl_2(PPh_3)_3]$ with 2 equivalents of 2,3-dpppn gave a very insoluble complex, *trans*-[RuCl$_2$(dpppn)$_2$] **11**. Treatment of [RuCl(η^5-C_5H_5)(PPh$_3$)$_2$] with 2,3-dpppn in refluxing benzene gave [RuCl(η^5-C_5H_5)(1,2-dpppn)] **12**. The formulation of **12** was confirmed by a single-crystal structure determination.

The chemistry of alkenyldiphosphines has been extensively investigated. For example, the readily synthesized 1,1-bis(diphenylphosphino)ethene[1] undergoes base-catalysed addition of P–H bonds, and this has been used to synthesize new multidentate phosphines such as 1,1,2-tris(diphenylphosphino)ethane and bis[2,2-bis(diphenylphosphino)ethyl]phenylphosphine.[2] In its chelate complexes the double bond of 1,1-bis(diphenylphosphino)ethene becomes greatly activated to nucleophilic addition,[3] probably because this reduces angle strain in the four-membered chelate rings. This is a convenient way of preparing complexes of functionalised diphosphine ligands,[4–6] and we have recently used such chemistry to synthesize redox-active ruthenium(II) complexes for anchoring to oxide surfaces[7,8] or for incorporation into electrochemically generated conjugated polymers.[9] Recently, gold(III)–methanide complexes have been synthesized by nucleophilic addition to $[Au(C_6F_5)_2Cl\{(Ph_2P)_2C{=}CH_2\}]$;[10] the latter chemistry is interesting as methanide complexes may be intermediates in the formation of co-ordinated $(Ph_2P)_2CHCH_2X$ (XH = nucleophile) in the earlier papers.

Convenient syntheses of diphosphines capable of forming five- or six-membered chelate rings, and bearing additional functionality, would be of considerable interest, but relatively few examples have been reported.[11] Efforts have been made to use co-ordinated alkenyldiphosphines and alkynylphosphines for this purpose. Complexes of $(Ph_2PCH_2)_2C{=}CH_2$ with Cr^0, Mo^0 and W^0 [12,13] and with Pt^{II} [14] have been described. Deprotonation of the complexed ligand gave resonance-stabilised co-ordinated bis(diphenylphosphino)allyl anions, which on treatment with electrophiles R–X gave complexes of the corresponding coordinated Z-$Ph_2PCH{=}CHMeCHRPPh_2$. Some time ago the addition of HPR'_2 (R′ = Ph or C_2H_4CN) or HP(Et)Ph to *cis*-$[MCl_2(Ph_2PC{\equiv}CR)_2]$ (M = Pd or Pt; R = Bu^t, Ph or CF_3) was reported to give complexes [MCl$_2$(*cis*-$Ph_2PCH{=}CRPR'_2$)], from which the free diphosphine could be displaced by treatment with an excess of CN^-.[15]

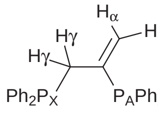
The ligand 2,3-bis(diphenylphosphino)propene (2,3-dpppn) has been described.[16] Complexes [M(2,3-dpppn)(CO)$_4$] (M = Cr, Mo or W) were found to undergo rearrangement to [M(1,2-dpppn)(CO)$_4$] [1,2-dpppn = *cis*-1,2-bis(diphenylphosphino)propene] on treatment with catalytic amounts of KOBu^t and $HPPh_2$. Nucleophilic addition to co-ordinated 2,3-dpppn would not be expected to be as favourable as addition to co-ordinated 1,1-bis(diphenylphosphino)ethene, as the relief of angle strain is unlikely to be an important consideration for the five-membered chelate ring. Nevertheless, *excess* of $HPPh_2$ was reported to undergo base-catalysed addition to [M(2,3-dpppn)(CO)$_4$] (M = Cr, Mo or W), to give η^2-co-ordinated 1,2,3-tris(diphenylphosphino)propane, whereas this reaction did not occur with free 2,3-dpppn.[16]

Previously, it was shown that the double bond of 1,1-bis(diphenylphosphino)ethene was activated to nucleophilic addition much more by co-ordination to metals in a higher oxidation state (*e.g.* Pd^{II}, Pt^{II}, Pt^{IV}) than by co-ordination to M^0 (M = Cr, Mo or W).[5,6] It was therefore of interest to investigate the co-ordination chemistry of 2,3-dpppn with Pd^{II}, Pt^{II} and Ru^{II}, and to investigate whether the co-ordinated ligand would undergo nucleophilic addition. In this paper, we report the syntheses and characterisation of neutral and cationic 2,3-dpppn complexes of these metals, and some chemistry of the co-ordinated ligand.

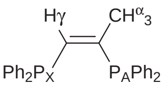
Results and Discussion

Neutral complexes of Pd^{II} and Pt^{II}

The ligand 2,3-dpppn was prepared by the literature route, reaction between 2,3-dichloropropene and $NaPPh_2$ in liquid ammonia.[16] Recrystallisation from CH_2Cl_2–EtOH is necessary to free the ligand from traces of *trans*-1,2-bis(diphenylphosphino)propene in the crude product. The latter is formed by base-catalysed allylic rearrangement of 2,3-dpppn, and has been independently synthesized using this reaction.[16]



2,3–dpppn



1,2–dpppn

Treatment of $[PdCl_2(PhCN)_2]$ with 1 equivalent of 2,3-dpppn in CH_2Cl_2 gave yellow $[PdCl_2(2,3\text{-dpppn})]$ **1**. This complex was insoluble in benzene, alcohols, acetone and thf, and only sparingly soluble in CH_2Cl_2 and $CHCl_3$. It was characterised by correct microanalyses (C and H; Experimental section), FAB mass spectrometry (Experimental section), which showed a cluster of peaks at *m*/*z* 553 corresponding to $[M - Cl]^+$, and by NMR spectroscopy (Experimental section; for convenience, we adopt the labelling scheme originally used for these ligands,[16] illustrated). The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed two doublets of equal intensity, at δ 56.9 and 42.0, with J_{PP} 12 Hz. As expected for a five-membered chelate ring diphosphine complex of Pd^{II}, the resonances are shifted considerably downfield from the free diphosphine values.[17] The $^{31}P\text{-}\{^1H\}$ NMR spectrum also revealed the presence of a second, minor species (4% total signal), giving two more doublets of equal intensity at δ 77.2 and 58.3 (J_{PP} 15 Hz). These parameters are comparable with those of the known complexes $[PtCl_2(cis\text{-}Ph_2PCH{=}CRPPh_2)]$ ($R = CF_3$, Ph or Bu^t),[15] suggesting that partial isomerisation had occurred to give $[PdCl_2(1,2\text{-dpppn})]$.†

We wished to examine whether amines would add to the double bond of co-ordinated 2,3-dpppn, in a similar fashion to the addition of $HPPh_2$ to complexes $[M(2,3\text{-dpppn})(CO)_4]$ (M = Cr, Mo or W),[16] or whether this would result in base-catalysed isomerisation to co-ordinated *cis*-1,2-bis(diphenylphosphino)propene. Accordingly, we treated **1** with a large excess of benzylamine in chlorobenzene, and monitored the progress of the reaction by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The only changes noted were that the proportion of the minor component in the spectrum increased. When the solution was refluxed overnight and re-examined the signals due to complex **1** had disappeared, and only the two doublets assigned to **2** were observed. The identity of **2** was confirmed by the isolation and characterisation of the complex. In particular, the microanalyses and FAB mass spectrum were consistent with it being an isomer of **1**. The ^1H NMR spectrum showed a doublet of doublets for the single alkenyl proton H_γ at δ 6.85, due to coupling to both phosphorus atoms (Experimental section), with a further small coupling to the protons of the methyl group, in turn seen at δ 2.11. This contrasts with the spectra of $[PdCl_2(cis\text{-}Ph_2PCH{=}CRPPh_2)]$ ($R = CF_3$, Ph or Bu^t) which were reported, somewhat surprisingly, to show only doublet resonances for the alkenyl protons where these were not obscured by the phenyl resonances.[15] The assignment of the more downfield $^{31}P\text{-}\{^1H\}$ resonance to P_A (Experimental section), as for the complexes $[M(CO)_4(1,2\text{-dpppn})]$,[16] was confirmed by recording the ^{31}P NMR spectrum; the resonance at δ 58.3 was simply broadened compared with the $^{31}P\text{-}\{^1H\}$ spectrum, but the resonance at δ 77.2 was a broad doublet (J_{PH} *ca.* 60 Hz), clearly due to the large coupling to the *trans* proton H_γ. Metathesis of **2** with LiI in hot acetone afforded yellow $[PdI_2(1,2\text{-dpppn})]$ **3**, characterised similarly (Experimental section).

Treatment of $[PtCl_2(PhCN)_2]$ in refluxing benzene with 2,3-dpppn gave $[PtCl_2(2,3\text{-dpppn})]$ **4**. The values of $^1J_{PtP}$ for both doublets in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4** are typical of P *trans* to Cl. The ^1H NMR spectrum, recorded in CD_2Cl_2, shows resonances characteristic of co-ordinated 2,3-dpppn (Experimental section). In particular, there are two multiplets for the two protons H_α and $H_{\alpha'}$ at δ 6.03 and 5.27 respectively (the latter partially obscured by the $CHDCl_2$ resonance). Coupling to ^{195}Pt was not resolved for these resonances. A multiplet with ^{195}Pt satellites at δ 3.16 is assigned to the H_γ protons. The $^{31}P\text{-}\{^1H\}$ NMR spectrum again showed the presence of a second complex, this time 10% of the total signal intensity, with two equally intense doublets at δ 53.1 and 35.3. The satellites due to coupling to ^{195}Pt were not resolved because of the poor signal-to-noise ratio in this case. That this was the isomer $[PtCl_2(1,2\text{-dpppn})]$ **5** was again confirmed when treatment of **4** with benzylamine in refluxing chlorobenzene resulted in a slow but total conversion into **5**, enabling **5** to be independently characterised. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **5** is similar to those of $[PtCl_2(cis\text{-}Ph_2PCH{=}CRPPh_2)]$ ($R = CF_3$, Ph or Bu^t),[15] except that whereas the J_{PP} for the latter complexes were reportedly too small to be observed we found that J_{PP} for **5** was 15 Hz. The phosphine *trans* to H_γ is again assigned as having the more downfield chemical shift (and therefore the larger value of $^1J_{PtP}$), by analogy with **2**, and with $[PtCl_2(cis\text{-}Ph_2PCH{=}CRPPh_2)]$ ($R = CF_3$, Ph or Bu^t).[15] The presence of an amine was essential; refluxing **4** in chlorobenzene alone (16 h) did not result in isomerisation. On the other hand, prolonged treatment of a CH_2Cl_2 solution of **4** with catalytic amounts of $KOBu^t$/18-crown-6, or 1,8-bis(dimethylamino)naphthalene, did not result in significant conversion into **5** either.

Treatment of complex **2** in dry diethyl ether with an excess of MeLi gave $[PdMe_2(1,2\text{-dpppn})]$ **6** in good yield, and treatment of **5** with MeLi gave $[PtMe_2(1,2\text{-dpppn})]$ **7**; characterising data are in the Experimental section. In the ^1H NMR spectra of **6** and **7** the alkenyl proton resonances are once again well resolved and clear of the aromatic resonances. The two methyl ligand resonances appear as deceptively simple triplets[18] (in the case of **7**, with satellites due to J_{PtH}) and occur at significantly different chemical shifts; we do not know which is which. Treatment of **5** with hydrazine hydrate and an excess of $HC{\equiv}CPh$ in ethanol gave $[Pt(C{\equiv}CPh)_2(1,2\text{-dpppn})]$ **8** in moderate yield. Although the alkenyl resonance is obscured by the phenyl resonances in the ^1H NMR spectrum of this complex the characteristic resonance for the methyl group is evident. Complexes **6**–**8** were significantly soluble in thf and toluene, facilitating spectroscopic characterisation.

Cationic complexes of Pd^{II} and Pt^{II}

Treatment of $[PdCl_2(PhCN)_2]$ with 2 equivalents of $AgBF_4$ and 2 equivalents of 2,3-dpppn in $MeCN\text{–}CH_2Cl_2$ gave a white solid on work-up. This had correct microanalyses (C and H) for a complex $[Pd(dpppn)_2][BF_4]_2$ and showed clusters of peaks at *m*/*z* 1013 ($[M - BF_4]^+$) and 926 ($[M - HBF_4 - BF_4]^+$) in the FAB mass spectrum. The complex was sparingly soluble in MeCN and the $^{31}P\text{-}\{^1H\}$ NMR spectrum, though noisy, was consistent with the presence of at least four isomeric complexes, probably *cis*- and *trans*-$[Pd(2,3\text{-dpppn})_2][BF_4]_2$ and *cis*- and *trans*-$[Pd(1,2\text{-dpppn})_2][BF_4]_2$ (*cis*- and *trans*-**9**, Scheme 1). The presence in the mixture of small amounts of additional isomers of the type $[Pd(1,2\text{-dpppn})(2,3\text{-dpppn})]^{2+}$ cannot be ruled out; their $^{31}P\text{-}\{^1H\}$ spectra, which one would expect to be very complex, may be lost in the noise. Prolonged treatment of this mixture with an excess of benzylamine resulted in conversion into a *ca.* 1 : 1 mixture of *cis*- and *trans*-**9**, as revealed by the $^{31}P\text{-}\{^1H\}$ spectrum (Fig. 1). Both isomers show AA′XX′ spectra as expected. The resonances of the *trans* isomer are 'virtual' triplets owing to the strong P-*trans*-P coupling, typical of palladium(II) complexes.[17] Although line shape analysis was not possible, an empirical simulation of peak positions and intensities was carried out using the program gNMR. The coupling constants used (Experimental section) are consistent with

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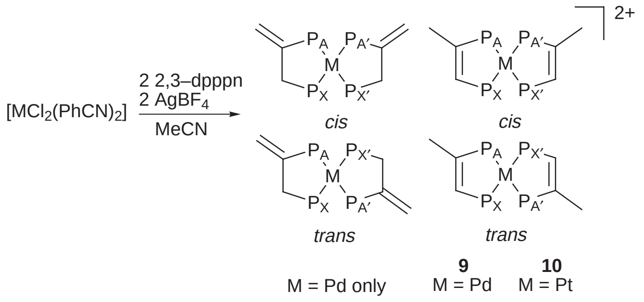
† Throughout this paper, the abbreviation 1,2-dpppn refers to the *cis* isomer of 1,2-bis(diphenylphosphino)propene as shown.



Scheme 1 Synthesis of isomers of cationic [Pd(dpppn)$_2$]$^{2+}$ complexes, and structures of *cis*- and *trans*-**9** and **10**, showing the labelling scheme for the ^{31}P nuclei used in the discussion of the NMR data and the assignments P$_A$ and P$_X$ in the Experimental section

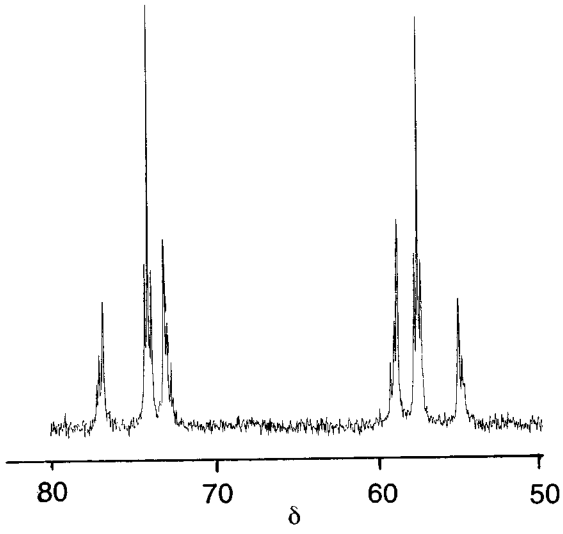


Fig. 1 The ^{31}P-{^{1}H} NMR spectrum (101 MHz, CD$_3$CN) of complex **10**, showing the mixture of the two isomers referred to in the text. The two 'virtual' triplets are due to the *trans* isomer

Table 1 Significant bond lengths (Å) and angles (°) for *trans*-[Pt(1,2-dpppn)$_2$][BF$_4$]$_2$ **10**

Pt–P(1)	2.326(3)	P(2)–C(19)	1.82(1)
Pt–P(2)	2.329(4)	P(2)–C(13)	1.82(1)
P(1)–C(1)	1.81(1)	P(2)–C(27)	1.83(1)
P(1)–C(25)	1.82(2)	C(25)–C(26)	1.41(3)
P(1)–C(7)	1.79(1)	C(25)–C(27)	1.32(2)
P(1)–Pt–P(1)	180.00	C(1)–P(1)–C(7)	105.7(6)
P(1)–Pt–P(2)	82.5(1)	C(7)–P(1)–C(25)	104.7(7)
P(1)–Pt–P(2*)	97.5(1)	Pt–P(2)–C(13)	118.9(4)
Pt–P(1)–C(25)	107.3(5)	Pt–P(2)–C(19)	112.9(4)
P(1)–C(25)–C(27)	120(1)	C(13)–P(2)–C(19)	107.5(6)
P(2)–C(27)–C(25)	116(1)	C(19)–P(2)–C(27)	104.4(6)
Pt–P(2)–C(27)	107.7(5)	C(13)–P(2)–C(27)	104.2(6)
Pt–P(1)–C(7)	117.3(5)	P(1)–C(25)–C(26)	123(1)
Pt–P(1)–C(1)	115.0(4)	C(1)–P(1)–C(25)	105.7(7)

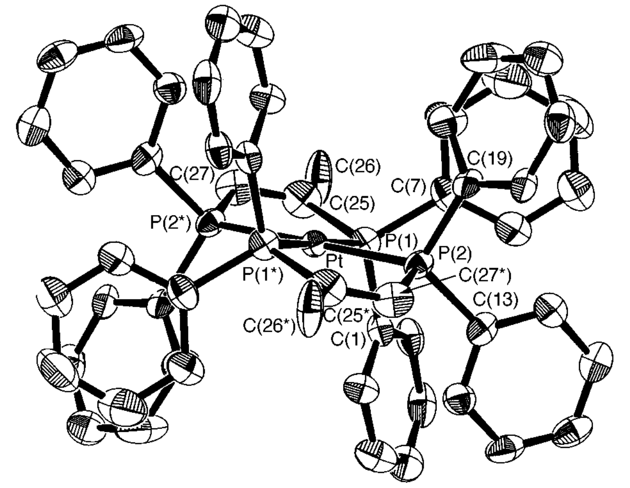


Fig. 2 Molecular structure of the dication *trans*-**10**. Ellipsoids are drawn at the 50% probability level

published values for related complexes.[15] The ^{1}H NMR spectrum (CD$_3$CN) showed two rather broad, overlapping multiplets at δ 2.15 and 2.09, assigned to the methyl groups of the different isomers; we do not know which is which. The resonances of the alkenyl protons could not be discerned, and are presumably obscured by the rather broad aromatic resonances.

Treatment of [PtCl$_2$(PhCN)$_2$] with 2 equivalents of AgBF$_4$ and 2 equivalents of 2,3-dpppn in MeCN–CH$_2$Cl$_2$ likewise gave a white solid on work-up, the microanalyses and FAB mass spectrum of which were consistent with the formulation [Pt(dpppn)$_2$][BF$_4$]$_2$. The ^{31}P-{^{1}H} NMR spectrum was consistent with the presence of only two isomers in this case. The ^{1}H NMR spectrum, though of poor quality owing to the limited solubility of the complex, suggested that these were *cis*- and *trans*-[Pt(1,2-dpppn)$_2$][BF$_4$]$_2$ (*cis*- and *trans*-**10**); a broad multiplet at δ 2.16 is assigned to the ligand methyl protons. Furthermore, no alkenyl proton resonances were observed. Whereas the single 1,2-dpppn alkenyl resonance is sometimes obscured by the phenyl resonances, this is most unlikely to be the case for the two more upfield alkenyl resonances characteristic of 2,3-dpppn. The ^{31}P-{^{1}H} NMR spectrum of a solution of the isomer mixture in MeCN–CD$_3$CN was recorded at regular intervals for 2 weeks; no change was observed. We do not know why Pt^{II} causes complete isomerisation to 1,2-dpppn whereas Pd^{II} gives a mixture of 1,2-dpppn and 2,3-dpppn complexes in these reactions.

Crystals of complex **10** were grown from MeCN–Et$_2$O by diffusion. That chosen for X-ray crystallographic analysis proved to be *trans*-**10**. In spite of the low-temperature (−120 °C) data collection, the final R and R' values are rather high, as is the residual electron density, which is localised around the BF$_4^-$ ions. Attempts to improve the weighting scheme, or model the residual electron density in terms of fractional amounts of solvent, or disordered BF$_4^-$, were unsuccessful. The structure is illustrated in Fig. 2, and significant bond lengths and angles are given in Table 1. The structure is similar to that of [Pt(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$][BPh$_4$]$_2$.[20] The centrosymmetric space group means that *trans*-**10** has a crystallographically imposed centre of symmetry, as does [Pt(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$][BPh$_4$]$_2$. The Pt–P bond lengths [mean 2.328(3) Å] are similar to those in [Pt(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$][BPh$_4$]$_2$ [mean 2.336(1) Å]. The complexes [PtCl$_2$(*cis*-Ph$_2$PCH=CHPPh$_2$)] and [Pt(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$][BPh$_4$]$_2$ have rigidly planar Pt–P–CH=CH–P units (within the e.s.d.s) and short C=C bonds [1.28(2), 1.315(5) Å respectively], and this was attributed to significant conjugation between the ligand backbone and the PtP$_2$ system.[20] However, although complex **10** has a C=C bond length [1.31(2) Å] comparable with that of [Pt(*cis*-Ph$_2$PCH=CHPPh$_2$)$_2$][BPh$_4$]$_2$, it also has a torsion angle Pt–P(1)–C(25)–C(27) of −13(1)°, so the PtP$_2$C$_2$ chelate atoms are not coplanar in **10**; this is also clear by inspection of Fig. 2. Thus, crystal packing forces are at least as significant as any additional π interactions due to the P–CH=CH–P chelate system in these complexes.[21]

It is apparent that co-ordination of 2,3-dpppn to Pd^{II} and Pt^{II} in complexes [M(2,3-dpppn)$_2$]$^{2+}$ activates it towards base-catalysed rearrangement to co-ordinated *cis*-1,2-dpppn more effectively than co-ordination to neutral [M(CO)$_4$] (M = Cr, Mo or W)[16] or MCl$_2$ (M = Pd or Pt). This suggests that deprotonation of complexes **9** and **10**, followed by treatment with

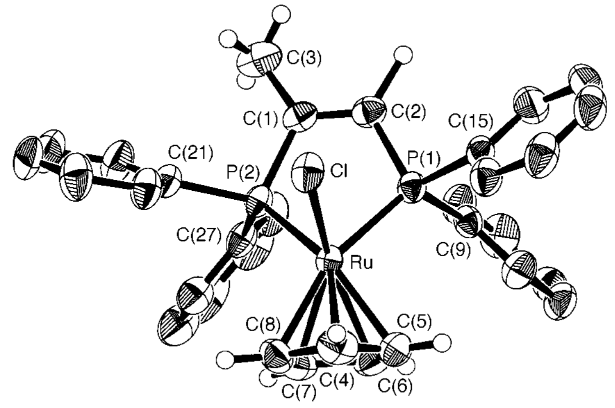


Fig. 3 Molecular structure of complex **12**. Ellipsoids are drawn at the 50% probability level

Table 2 Significant bond lengths (Å) and angles (°) for [RuCl(η^5-C_5H_5)(1,2-dpppn)] **12**

Ru–Cl	2.436(1)	Ru–C(7)	2.167(4)
Ru–P(1)	2.258(1)	Ru–C(8)	2.211(4)
Ru–P(2)	2.269(1)	P(1)–C(2)	1.825(4)
Ru–C(4)	2.236(5)	P(2)–C(1)	1.846(4)
Ru–C(5)	2.223(5)	C(1)–C(2)	1.334(5)
Ru–C(6)	2.166(5)	C(1)–C(3)	1.505(7)
Cl–Ru–P(1)	86.69(4)	P(2)–C(1)–C(2)	116.1(3)
Cl–Ru–P(2)	89.47(5)	Ru–P(2)–C(1)	109.2(1)
P(1)–Ru–P(2)	82.37(4)	P(2)–C(1)–C(3)	121.5(3)
Ru–P(1)C(2)	109.8(1)	C(2)–C(1)–C(3)	112.4(4)
P(1)–C(2)–C(1)	117.2(3)		

electrophiles, might afford functionalised five-membered chelate ring diphosphine complexes, and we are currently investigating this.

Complexes with Ru^{II}

Treatment of [$RuCl_2(PPh_3)_3$] with 2 equivalents of 2,3-dpppn in CH_2Cl_2 gave a yellow precipitate. The microanalytical data were consistent with the formulation [$RuCl_2$(dpppn)$_2$]·CH_2Cl_2 **11**. The FAB mass spectrum of **11** showed a molecular ion at *m*/*z* 992 together with peaks due to loss of Cl^- and (Cl^- + HCl), as observed for similar [$RuCl_2$(diphosphine)$_2$] complexes.[8] It proved difficult to characterise **11** further because of its limited solubility; after overnight accumulation in $CDCl_3$ the ^{31}P-{^1H} NMR spectrum (10 Hz line broadening) showed two broad peaks at δ 45.96 and 28.65. Although it has not so far been possible to determine whether **11** is a 1,2-dpppn or 2,3-dpppn complex, this spectrum does show that chemically different phosphorus atoms must be mutually *cis*, since P-*trans*-P coupling constants for ruthenium(II) complexes are typically 400 Hz.[22,23] Treatment of [$RuCl_2(PPh_3)_3$] with 2 equivalents of other five-membered ring chelate diphosphines under similarly mild conditions usually gives *trans*-[$RuCl_2$(diphosphine)$_2$].[24] It might be expected that **11** would also adopt this geometry, and that therefore it is either all-*trans*-[$RuCl_2$(1,2-dpppn)$_2$] or all-*trans*-[$RuCl_2$(2,3-dpppn)$_2$]. Recently, ruthenium(II) complexes of the related ligand *cis*-$Ph_2PCH{=}CHPPh_2$ have been described.[25] Treatment of [$RuCl_2(PPh_3)_3$] with 2 equivalents of *cis*-$Ph_2PCH{=}CHPPh_2$ in refluxing ethanol gave a mixture of *cis*- and *trans*-[$RuCl_2(Ph_2PCH{=}CHPPh_2)_2$]; the *trans* isomer was characterised crystallographically.

Treatment of [RuCl(η^5-C_5H_5)$(PPh_3)_2$] in refluxing benzene with 2,3-dpppn for 20 min gave a red solution. The ^{31}P-{^1H} NMR spectrum of this showed {in addition to free 2,3-dpppn, PPh_3 and unchanged [Ru(η^5-C_5H_5)Cl$(PPh_3)_2$]} two pairs of doublets, a more intense pair at δ 62.90 and 76.50 (J_{PP} 34 Hz) due to [RuCl(η^5-C_5H_5)(2,3-dpppn)], and a less intense pair at δ 87.08 and 73.3 (J_{PP} 35 Hz) due to [RuCl(η^5-C_5H_5)(1,2-dpppn)]. After prolonged reflux and work-up a single product was isolated, identified as [RuCl(η^5-C_5H_5)(1,2-dpppn)] **12** from the microanalytical and FAB mass spectral data (Experimental section), the ^{31}P-{^1H} NMR spectrum and, in particular, the ^1H NMR spectrum, which showed a singlet due to the cyclopentadienyl protons at δ 4.45 and a doublet of triplets at δ 2.22, clearly due to the methyl group. The alkenyl proton resonance was obscured by the aromatic resonances. However, crystals formed when the CD_2Cl_2 solution was set aside at room temperature, and the subsequent crystal structure determination (Fig. 3) confirms the identity of the complex. The structure of **12** has no remarkable features, and can be compared with that of (*S*)-[RuCl(η^5-C_5H_5){(*R*)-$Ph_2PCH_2CH(Me)PPh_2$}], with which it is in all key respects similar; significant bond lengths and angles are in Table 2. The alkenyl double bond in **12** [1.334(5) Å] is slightly longer than that in **10**.

Clearly, under these experimental conditions (prolonged reflux; complexation to Ru^{II}), isomerisation of the double bond has occurred without added base as a catalyst, in contrast to the behaviour of the platinum(II) complex **4**. It is possible that the displaced PPh_3 acts as a catalyst in the case of the ruthenium(II) complex. Whereas several reports of metal-promoted isomerisation of double bonds within alkenylmonophosphines exist,[26,27] these ligands chelate *via* both phosphorus and alkene, and the reaction probably occurs *via* allyl-metal formation; this is most unlikely with 2,3-dpppn.

Experimental

General methods were as described in previous papers from this laboratory.[6,8] Some fast atom bombardment mass spectra were run at the EPSRC National Mass Spectrometry Service (Swansea, UK). All reactions were performed under a nitrogen atmosphere. Light petroleum was of boiling range 40–60 °C. The ligand 2,3-dpppn was prepared from 2,3-dichloropropene (Aldrich Chemical Co.; used as supplied) and $NaPPh_2$ in liquid ammonia by the published route,[16] and was recrystallised from CH_2Cl_2–EtOH (1 : 3).

Preparations

[$PdCl_2$(2,3-dpppn)] 1. To a solution of [$PdCl_2(PhCN)_2$] (0.21 g, 0.55 mmol) in CH_2Cl_2 (20 cm^3) was added the diphosphine (0.23 g, 0.55 mmol). The mixture was refluxed with stirring for 30 min. A yellow solid precipitated. The mixture was cooled to room temperature and filtered. The solid was washed with MeOH (3 × 3 cm^3) and Et_2O (3 × 3 cm^3) and dried *in vacuo*. Yield 0.19 g, 59% (Found: C, 55.26; H, 4.10. $C_{27}H_{24}Cl_2P_2Pd$ requires C, 55.18; H, 4.12%) Mass spectrum (FAB, Xe^+): *m*/*z* 553 ([*M* − Cl]$^+$). ^{31}P-{^1H} NMR ($CDCl_3$, 101 MHz): δ 42.0 (d, P_X, J_{AX} 12 Hz) and 56.9 (d, P_A). Selected ^1H NMR ($CDCl_3$, 200 MHz): δ 3.20 [2 H, ddd, H_γ, $^3J(P_AH_\gamma)$ 25.5, $^2J(P_XH_\gamma)$ 12.9, $^4J(H_\alpha H_\gamma)$ 1.5], 5.19 [1 H, dd, br, $H_{\alpha'}$, $^3J(P_AH_{\alpha'})$ 15.4, $^4J(P_XH_{\alpha'})$ 5.5, $^2J(H_\alpha H_{\alpha'})$ 0] and 5.95 [1 H, ddt, H_α, $^3J(P_AH_\alpha)$ 32.0, $^4J(P_XH_\alpha)$ 5.2 Hz].

[$PdCl_2$(1,2-dpppn)] 2. To a solution of complex **1** (0.22 g, 0.374 mmol) in chlorobenzene (30 cm^3) was added benzylamine (2.0 cm^3). The mixture was refluxed for 24 h. An off-white solid was observed, and further solid precipitated on cooling to 4 °C. This was filtered off, washed with MeOH (3 × 3 cm^3) and Et_2O (3 × 3 cm^3) and dried *in vacuo*. Yield 0.21 g, 97% (Found: C, 55.16; H, 4.12. $C_{27}H_{24}Cl_2P_2Pd$ requires C, 55.18; H, 4.12%). Mass spectrum (FAB, Xe^+): *m*/*z* 553 ([*M* − Cl]$^+$) ^{31}P-{^1H} NMR ($CDCl_3$, 101 MHz): δ 58.3 (d, P_X, J_{AX} 15 Hz) and 77.2 (d, P_A). Selected ^1H NMR ($CDCl_3$, 200 MHz): δ 2.11 [3 H, dt, $^3J(P_AH_\alpha)$ 6.9, $^4J(P_XH_\alpha)$ 1.4, $^4J(H_\alpha H_\gamma)$ 1.4] and 6.85 [1 H, ddq, $^3J(P_AH_\gamma)$ 64.6, $^2J(P_XH_\gamma)$ 14.2 Hz].

$[PdI_2(1,2\text{-dpppn})]$ 3. To a solution of complex **2** (0.50 g, 0.852 mmol) in acetone (30 cm^3) was added sodium iodide (1.27 g, 8.52 mmol). The mixture was stirred for 1 h. The volume was reduced to *ca.* 3 cm^3 at the pump, and Et_2O (5 cm^3) was added. The yellow solid that precipitated was filtered off, washed with water (3 cm^3), EtOH (3 × 3 cm^3) and Et_2O (3 × 3 cm^3) and dried *in vacuo*. Yield 0.41 g, 63% (Found: C, 42.84; H, 3.36. $C_{27}H_{24}I_2P_2Pd$ requires C, 42.89; H, 3.34%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 770 (M^+) and 643 ($[M - I]^+$) ^{31}P-{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 55.3 (d, P_X, J_{AX} 15) and 75.9 (d, P_A). Selected ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.08 [3 H, ddd, $^3J(P_AH_\alpha)$ 7.8, $^4J(P_XH_\alpha)$ 1.9, $^4J(H_\alpha H_\gamma)$ 1.4] and 6.71 [1 H, ddq, $^3J(P_AH)$ 65.6, $^2J(P_XH_\gamma)$ 12.1 Hz].

$[PtCl_2(2,3\text{-dpppn})]$ 4. To a solution of $[PtCl_2(PhCN)_2]$ (0.60 g, 1.27 mmol) in benzene (30 cm^3) was added the diphosphine (0.52 g, 1.27 mmol). The mixture was refluxed for 1 h. A white solid precipitated. The mixture was cooled to room temperature and filtered. The solid was washed with a little cold benzene and Et_2O (3 × 3 cm^3), and dried *in vacuo*. Yield 0.63 g, 73% (Found: C, 48.30; H, 3.39. $C_{27}H_{24}Cl_2P_2Pt$ requires C, 47.96; H, 3.58%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 676 (M^+) and 641 ($[M - Cl]^+$) ^{31}P-{^{1}H} NMR (CDCl$_3$, 101 MHz) δ 21.2 (d, P_X, J_{AX} 13, $^1J_{PtP}$ 3566) and 34.7 (d, P_A, $^1J_{PtP}$ 3583 Hz). Selected ^{1}H NMR (CDCl$_3$, 200 MHz): δ 3.16 [2 H, ddd, H_γ, $^3J(P_AH_\gamma)$ 21.4, $^2J(P_XH_\gamma)$ 12.6, $^4J(H_\alpha H_\gamma)$ 1.4, $^3J(PtH_\gamma)$ 37.7], 5.27 [1 H, dd, br, $H_{\alpha'}$, $^3J(P_AH_{\alpha'})$ 15.4, $^4J(P_XH_{\alpha'})$ 3.8, $^2J(H_\alpha H_{\alpha'})$ 0] and 6.03 [1 H, ddt, H_α, $^3J(P_AH_\alpha)$ 33.5, $^4J(P_XH_\alpha)$ 4.9 Hz].

$[PtCl_2(1,2\text{-dpppn})]$ 5. To a suspension of complex **4** (0.52 g, 0.77 mmol) in chlorobenzene (40 cm^3) was added benzylamine (2.0 cm^3). The mixture was refluxed for 24 h. A white solid was observed, and further solid precipitated on cooling to 4 °C. This was filtered off, washed with MeOH (3 × 3 cm^3) and Et_2O (3 × 3 cm^3) and dried *in vacuo*. Yield 0.47 g, 91% (Found: C, 47.73; H, 3.60. $C_{27}H_{24}Cl_2P_2Pt$ requires C, 47.96; H, 3.58%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 641 ($[M - Cl]^+$). ^{31}P-{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 35.3 (d, P_X, J_{Ax} 14.5, $^1J_{PtP}$ 3582) and 53.1 (d, P_A, $^1J_{PtP}$ 3635 Hz). Selected ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.15 [3 H, dt, $^3J(P_AH_\alpha)$ 8.8, $^4J(P_XH_\alpha)$ 1.7, $^4J(H_\alpha H_\gamma)$ 1.7] and 6.87 [1 H, ddq, $^3J(P_AH_\gamma)$ 53.9, $^2J(P_XH_\gamma)$ 14.8 Hz].

$[PdMe_2(1,2\text{-dpppn})]$ 6. To a suspension of complex **2** (0.256 g, 0.44 mmol) in Et_2O (20 cm^3) was added MeLi (0.80 cm^3, 1.4 M in Et_2O; 1.12 mmol). The mixture was stirred for 16 h. Some white solid was observed suspended in an orange solution. The mixture was hydrolysed with MeOH (0.5 cm^3) whereupon the mixture faded to colourless. The solid was filtered off, washed with a little cold MeOH and dried *in vacuo*. More product was obtained from the mother-liquor by precipitation with MeOH. Yield 0.158 g, 66% (Found: C, 63.42; H, 5.39. $C_{29}H_{30}P_2Pd$ requires C, 63.72; H, 5.51%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 531 ($[M - Me]^+$) and 516 ($[M - CH_4 - Me]^+$) ^{31}P-{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 37.0 (d, P_X, J_{AX} 15) and 56.2 (d, P_A). Selected ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.30 [3 H, Pd–CH$_3$, $|J_{AH} + J_{XH}|$ 7.6), 0.42 (Pd–CH$_3$, $|J_{AH} + J_{XH}|$ 7.6), 2.13 [3 H, dt, $^3J(P_AH_\alpha)$ 5.5, $^4J(P_XH_\alpha)$ 1.4, $^4J(H_\alpha H_\gamma)$ 1.4] and 7.04 [1 H, ddq, $^3J(P_AH_\gamma)$ 51.4, $^2J(P_XH_\gamma)$ 4.4 Hz].

$[PtMe_2(1,2\text{-dpppn})]$ 7. To a suspension of complex **5** (0.205 g, 0.303 mmol) in Et_2O (20 cm^3) was added MeLi (0.76 cm^3, 1 M in Et_2O; 0.76 mmol). The mixture was stirred for 16 h. Some white solid was observed suspended in a pink solution. The mixture was hydrolysed with MeOH (0.5 cm^3) whereupon the mixture faded to colourless. The solid was filtered off, washed with a little cold MeOH and dried *in vacuo*. More product was obtained from the mother-liquor by precipitation with MeOH. Yield 0.142 g, 74% (Found: C, 54.78; H, 4.74. $C_{29}H_{30}P_2Pt$ requires C, 54.82; H, 4.76%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 620 ($[M - Me]^+$) and 604 ($[M - CH_4 - Me]^+$). ^{31}P-{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 42.35 (d, P_X, J_{AX} 14.6, $^1J_{PtP}$ 1772) and 61.2 (d, P_A, $^1J_{PtP}$ 1772 Hz). Selected ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.60 (3 H, Pt–CH$_3$, $|J_{AH} + J_{XH}|$ 7.4, $^3J_{PtH}$ 73.7), 0.75 (Pt–CH$_3$), $|J_{AH} + J_{XH}|$ 7.4, $^3J_{PtH}$ 71.4), 2.18 [3 H, d, br, $^3J(P_AH_\alpha)$ 6.1] and 7.11 [1 H, dd, br, $^3J(P_AH_\gamma)$ *ca.* 50, $^2J(P_XH_\gamma)$ 8 Hz].

$[Pt(C{\equiv}CPh)_2(1.2\text{-dpppn})]$ 8. To a suspension of finely ground **5** (0.202 g, 0.298 mmol) in EtOH (5 cm^3) was added $H_2NNH_2{\cdot}H_2O$ (57.8 µl, 1.18 mmol). The mixture was refluxed, and after 10 min PhC≡CH (249 µl, 2.36 mmol) was added. A further 15 min reflux resulted in the formation of a yellow solution. This was cooled to 0 °C and set aside for 1 h. The white crystalline solid that precipitated was filtered off, washed with a little cold EtOH and dried *in vacuo*. Yield 0.14 g, 59% (Found: C, 63.94; H, 4.24. $C_{43}H_{34}P_2Pt$ requires C, 63.95; H, 4.24%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 808 (M^+), 706 ($[M - C{\equiv}CPh]^+$) and 605 ($[M - C{\equiv}CPh{-}HC{\equiv}CPh]^+$). ^{31}P-{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 37.7 (d, P_X, J_{AX} 14.8, $^1J_{PtP}$ 2242) and 60.0 (d, P_A, $^1J_{PtP}$ 2244). Selected ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.28 [3 H, d, br, $^3J(P_AH_\alpha)$ 7.6 Hz].

***cis*- and *trans*-$[Pd(1,2\text{-dpppn})_2][BF_4]_2$ 9.** To a solution of $[PdCl_2(PhCN)_2]$ (0.51 g, 1.30 mmol) in MeCN (35 cm^3) and CH_2Cl_2 (25 cm^3) was added $AgBF_4$ (0.52 g, 2.7 mmol) and 2,3-dpppn (1.10 g, 2.7 mmol). The mixture was stirred for 30 min in the dark. The AgCl was filtered off using a Kieselguhr pad (3 cm depth) on a glass sinter, and solvent was removed *in vacuo*. The yellow solid was taken up in MeCN (2 cm^3) and Et_2O was added, precipitating a pale yellow solid. This was filtered off, washed with Et_2O and dried. Yield 1.08 g, 82%. This was shown to be a mixture of at least four complexes (Results and Discussion). The mixture was then refluxed overnight in chlorobenzene in the presence of benzylamine (2 cm^3). The solution was cooled to 4 °C, and the off-white solid was filtered off and dried *in vacuo*. Yield 1.05 g, 80% (Found: C, 48.63; H, 4.37. $C_{54}H_{48}B_2F_8P_4Pd$ requires C, 58.93; H, 4.39%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 1013 ($[M - BF_4]^+$) and 926 ($[M - HBF_4 - BF_4]^+$). ^{31}P-{^{1}H} NMR (CD$_3$CN, 101 MHz): δ 57.1, 74.9 (P_X, P_A respectively; *cis*-**9**, AA′XX′, $J_{AX'}$, 380, J_{AX} −24, $J_{AA'}$ −16, from simulation; see Results and Discussion), 57.7, 74.1 (P_X, P_A respectively; *trans*-**9**, AA′XX′, $J_{AA'}$ 380, J_{AX} −18, $J_{AX'}$ −20 Hz, from simulation; see Results and Discussion). Selected ^{1}H NMR (CD$_3$CN, 200 MHz): δ 2.09, 2.15 (br, m, H_α for different isomers).

***cis*- and *trans*-$[Pt(1,2\text{-dpppn})_2][BF_4]_2$ 10.** To a solution of $[PtCl_2(PhCN)_2]$ (0.52 g, 1.10 mmol) in MeCN (35 cm^3) and CH_2Cl_2 (25 cm^3) was added $AgBF_4$ (0.43 g, 2.2 mmol) and 2,3-dpppn (0.91 g, 2.2 mmol). The mixture was stirred for 30 min in the dark. The AgCl was filtered off using a Kieselguhr pad (3 cm depth) on a glass sinter, and solvent was removed *in vacuo*. The off-white solid was taken up in MeCN (10 cm^3), the solution was filtered and the volume was reduced to *ca.* 2 cm^3 *in vacuo*. On the addition of Et_2O a white solid precipitated. This was filtered off, washed with Et_2O and dried. Yield 0.75 g, 57% (Found: C, 54.51; H, 4.09. $C_{54}H_{48}B_2F_8P_4Pt$ requires C, 54.56; H, 4.07%). Mass spectrometry (FAB, Xe$^+$): *m*/*z* 1102 ($[M - BF_4]^+$) and 1015 ($[M - HBF_4 - BF_4]^+$). ^{31}P-{^{1}H} NMR (CD$_3$CN, 101 MHz): δ 48.9, 66.8 [P_X, P_A respectively; *cis*-**10**, AA′XX′, $J_{AX'}$ 300 Hz, $^1J(PtP_A)$ 2358, $^1J(PtP_X)$ 2295], 50.3, 65.4 [P_X, P_A respectively; *trans*-**10**, AA′XX′, $J_{AA'}$ 300, J_{AX} −10, $J_{AX'}$ −8 (from simulation; see Results and Discussion), $^1J(PtP_A)$ 2354, $^1J(PtP_X)$ 2303 Hz]. Selected ^{1}H NMR (CD$_3$CN, 200 MHz); δ 2.16 (br, m, H_α for different isomers).

$[RuCl_2(dpppn)_2]{\cdot}CH_2Cl_2$ 11. To $[RuCl_2(PPh_3)_3]$ (0.50 g, 0.52 mmol) in CH_2Cl_2 (20 cm^3) was added 2,3-dpppn (0.43 g, 1.04 mmol) in CH_2Cl_2 (5 cm^3). The mixture was set aside overnight, yielding a yellow precipitate. This was filtered off, washed with Et_2O and dried *in vacuo.* Yield 0.44 g, 78% (Found: C, 60.98; H, 4.65. $C_{54}H_{48}Cl_2P_4Ru{\cdot}CH_2Cl_2$ requires C, 61.29; H, 4.68%). Mass spectrometry (FAB, Xe^+): *m*/*z* 992 (M^+), 957 ($[M - Cl]^+$) and 921 ($[M - HCl - Cl]^+$). $^{31}P-\{^1H\}$ NMR ($CDCl_3$, 101 MHz); δ 28.6, 46.0 (m, br).

[RuCl(η-C_5H_5)(1,2-dpppn)] 12. To [RuCl(η-C_5H_5)(PPh_3)$_2$] (0.22 g, 0.302 mmol) in benzene (50 cm^3) was added 2,3-dpppn (0.124 g, 0.300 mmol). The mixture was refluxed for 5 h, the volume was then reduced to *ca.* 3 cm^3 *in vacuo*, and hexane (50 cm^3) was added. The mixture was set aside for 24 h at −20 °C, yielding an orange precipitate. This was filtered off, washed with hexane and dried *in vacuo*. Yield 0.11 g, 59% (Found: C, 62.66; H, 4.75. $C_{32}H_{29}ClP_2Ru$ requires C, 62.80; H, 4.78%). Mass spectrometry (FAB, Xe^+): *m*/*z* 612 (M^+) and 577 ($[M - Cl]^+$). $^{31}P-\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 73.3 (d, P_X, J_{AX} 35.2 Hz) and 87.1 (d, P_A). Selected ^1H NMR ($CDCl_3$, 200 MHz) δ 2.22 [3H, ddd, $^3J(P_AH_\alpha)$ 6.6, $^4J(P_XH_\alpha)$ 1.5, $^4J(H_\alpha H_\gamma)$ 1.4 Hz] and 4.45 (5 H, s, C_5H_5).

Crystallography

***trans*-[Pt(1,2-dpppn)$_2$][BF_4]$_2$ 10.** $C_{54}H_{48}B_2F_8P_4Pt$, $M = 1189.6$, monoclinic, space group $P2_1/n$, $a = 11.205(5)$, $b = 16.314(5)$, $c = 13.524(4)$ Å, $\beta = 96.44(3)°$, $U = 2457(1)$ Å^3, $T = 153$ K, $Z = 2$, μ(Mo-Kα) 3.08 mm^{-1}, 4718 reflections recorded, 4482 unique ($R_{int} = 0.045$), 2825 with $I > 3\sigma(I)$ used in refinement. The final $wR(F^2)$ was 0.076, $R1 = 0.055$.

[RuCl(η^5-C_5H_5)(1,2-dpppn)] 12. $C_{32}H_{29}ClP_2Ru$, $M = 612.1$, monoclinic, space group $P2_1/n$, $a = 14.866(8)$, $b = 11.297(6)$, $c = 17.389(7)$ Å, $\beta = 110.58(3)°$, $U = 2734(2)$ Å^3, $T = 296$ K, $Z = 4$, μ(Mo-Kα) 0.79 mm^{-1}, 5297 reflections measured, 5092 unique ($R_{int} = 0.030$), 3770 with $I > 3\sigma(I)$ used in refinement. The final $wR(F^2)$ was 0.038, $R1 = 0.030$.

CCDC reference number 186/951.

See http://www.rsc.org/suppdata/dt/1998/1787/ for crystallographic files in .cif format.

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