Variable coordination behaviour of pyrazole-containing N,P and N,P(O) ligands towards palladium(II)[†]

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Three bidentate, mixed-donor ligands based on a triphenylphosphine unit bearing a pyrazole group in the ortho-position of one phenyl ring have been synthesised; the N,P ligand [2-(3-pyrazolyl)phenyl]diphenylphosphine **pzphos** has been synthesised and transformed into new N, P(O) and N, P(S)derivatives, [2-(3-pyrazolyl)phenyl]diphenylphosphine oxide pzphos(O) and [2-(3-pyrazolyl)phenyl]diphenylphosphine sulfide pzphos(S), respectively. The coordination chemistry of pzphos and pzphos(O) towards palladium(II) has been investigated. Depending on the ligand to metal molar ratio employed in the reactions of palladium(II) with **pzphos**, either the 1 : 1 chelate [Pd(pzphos)Cl₂] **1a** or the 2 : 1 N,Pchelate [Pd(pzphos),]Cl₂ 1b was obtained. 1b contains two six-membered chelate rings in which the chlorides have been displaced from the inner coordination sphere of palladium. Exchange of the chloride anions in **1b** for perchlorate anions was achieved using $AgClO_4$ to give $[Pd(pzphos)_2][ClO_4]_2$ **1c**. Reaction of pzphos(O) under the same conditions forms the 2 : 1 adduct [Pd(pzphos(O))₂Cl₂] 2b regardless of the metal to ligand ratio or the order of addition of reactants. Unlike the N,P chelate 1b, the N, P(O) ligands in complex **2b** bind in a monodentate fashion through the N-donor atoms of the pyrazole rings. Abstraction of the chloro ligands in compound **2b** using AgClO₄ gave the 2 : 1 N, P(O)chelate $[Pd{pzphos(O)}_2][ClO_4]_2$ 2c, in which entropically unfavourable 7-membered chelate rings are formed. X-Ray diffraction has been used to confirm the solid-state structures of the pzphos(O) ligand and the complexes 1b, 1c, 2b and 2c.

Introduction

Over recent years, considerable attention has been drawn towards the coordination chemistry of hybrid ligands *i.e.* those molecules containing significantly different donor groups. Of particular interest are the metal complexes of hybrid 'hemilabile' ligands,^{1,2} containing at least one substitutionally inert donor group plus one or more substitutionally labile donor groups. These ligands, in the presence of a small molecule substrate, can allow the donor group with the lowest affinity towards the metal to dissociate to create a vacant coordination site which is then available to accommodate the new substrate. The 'anchor' effect of the stronger, permanentlybound donor group means that after the substrate has left the coordination sphere of the metal, chelation can again occur to stabilise the metal. These enticing properties of hemilabile ligands has led them to receive much interest in the field of catalysis,²⁻¹¹ as well as in small-molecule sensing, $^{\rm 12}$ functional materials, $^{\rm 3,13,14}$ and molecular activation. $^{\rm 15-21}$

Coincidentally, during the course of our research, the ligand, [2-(3-pyrazolyl)phenyl]diphenylphosphine (**pzphos**), which consists of a triphenylphosphine unit (soft donor) bearing a pyrazole group (hard donor) in the *ortho*-position of one phenyl ring, was independently published,^{22,23} albeit by a different synthetic route. Our route is shown in Scheme 1 and we are interested in this family of pyrazole-containing ligands for a number of reasons, namely; (i) the potential hemilability of the parent complex; (ii) the ease of derivatisation by chalcogenation of the phosphine moiety thus giving rise new to N, P(O), N, P(S) and N, P(Se) ligands; (iii) the scope for further functionalisation by alkylation of the N–H moiety. This last feature is particularly appealing as it may enable modifications of the steric or electronic properties of the ligand, which could be used to tune the ligand's coordination behaviour towards a metal centre.

A structurally similar ligand bearing the same triphenylphosphine unit, in this case attached to the pyrazolyl ring *via* the nitrogen atom (1-position) has recently been reported and has been shown to be active in the nickel catalysed oligomerisation of ethylene.²⁴ Furthermore, a bis(pyrazol-1-yl)methane ligand bearing diphenylphosphine groups directly attached to the pyrazole rings, rather than through a phenyl-linker, has also been described in the literature,²⁵ thus highlighting the ongoing interest in this field of chemistry. In addition, the coordination behaviour of a range of

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N,P ligands²⁶⁻²⁸ is well established in the literature and to a lesser extent, the chemistry of N, P(O) ligands.²⁹⁻³⁶ The work presented herein, describes the formation of two chalcogen derivatives of **pzphos** and the coordination chemistry of the N,P and N,P(O)ligands, pzphos and pzphos(O), towards palladium(II).

. NMe∕

pzphos(S)

Results and discussion

Ligand synthesis

The synthesis of the three ligands is outlined in Scheme 1: Ligand precursor A was synthesised using a different approach to the three-step synthesis described recently by Sun et al.22 Instead, a facile one step synthesis which involved heating a solution of potassium diphenylphosphide and 2-fluoroacetophenone in THF was used to synthesise A rapidly and in high yield.³⁷ A was then converted into the pzphos ligand in good yield in two steps. The chalcogen derivatives were synthesised by reaction of pzphos with hydrogen peroxide or sulfur to produce the respective phosphine oxide and phosphine sulfide ligands, pzphos(O) and pzphos(S). All three ligands were isolated as air-stable, white solids in good yields and were fully characterised. As shown in Table 1, the ³¹P NMR spectra of the phosphorus(v) species pzphos(O) and pzphos(S) show characteristic upfield shifted singlets at +35.8 ppm and +43.3 ppm, respectively, compared to the phosphorus(III) parent ligand, **pzphos** at -11.4 ppm.

Slow diffusion of pentane into a chloroform solution of the ligand produced single crystals suitable for X-ray analysis. The solid-state structure of pzphos(O) shows that the molecule dimerises in the solid state via intermolecular hydrogen bonding between adjacent molecules (Fig. 1). It is interesting to note that the hydrogen bond from the pyrazole N-H donor is shared equally between two acceptors on the opposing molecule: the unprotonated pyrazole nitrogen and the oxygen atom of the P(O) moiety. This dimerisation is also observed in solution as the N-H in the ¹H NMR spectrum is far downfield at 13.24 ppm, whereas the parent complex pzphos (containing no P=O group) shows the corresponding N–H peak at 10.57 ppm (Table 1). This is likely to be the result of reduced electron density around the N-H hydrogen, due to the sharing of its electron density with both

Table 1 IR, ¹	H and ${}^{31}P{H}$ NMR data for	the three	ligands							
	$^{31}P{H} MR^{a} \delta/ppm$	IWN H1	₹" δ/ppm							IR ^b ν/cm^{-1}
Ligand	Ь	HN	5-pz	4-pz	3-Ph	4-Ph	5-Ph	6-Ph	Ph-H	HN
pzphos	-11.4	10.57	7.48 (d)	6.34 (m)	7.60 (dd)	7.42 (ddd)	overlap with	7.03 (ddd)	7.26–7.37 (m)	3187
pzphos(O)	+35.8	13.24	7.32 (d)	6.25 (br s)	7.78 (ddd)	overlap with	7.30 (m)	7.14 (ddd)	7.38–7.64 (m)	3186
pzphos(S)	+43.3	12.54	7.17 (d)	6.08 (br s)	overlap at 7.57 (m)	F11-11 at /.01	7.37 (m)	7.18 (dd)	7.82 (m) & 7.37–7.44 (m)	3220
" Recorded in (CDCl ₃ solution. ^{<i>b</i>} Recorded a	s KBr disc	·							



Fig. 1 The molecular structure of **pzphos(O)** (50% probability ellipsoids). The N–H···O hydrogen bonds have N···O, H···O (Å), and N–H···O (°) of 2.91, 2.54 and 133 respectively; the N–H···N hydrogen bonds have N···N, H···N (Å), and N–H···N (°) of 2.94, 2.22 and 141 respectively.

the pyrazole nitrogen *and* the oxygen atom. A similar effect may also be observed with the sulfur derivative, **pzphos(S)**, as evidenced by the downfield position (12.54 ppm) of the corresponding N–H hydrogen in the ¹H NMR spectrum.

Coordination chemistry

Reactions of *N*,*P* **ligand, pzphos.** The reactions performed with the *N*,*P* ligand **pzphos** are outlined in Scheme 2. Addition of **pzphos** in dichloromethane to $Pd(COD)Cl_2$ in a 1 : 1 molar ratio gave a yellow precipitate that could be crystallised by slow diffusion of pentane into a chloroform solution of the complex. This complex **1a** was analysed by NMR spectroscopy and X-ray crystallography and was found to be identical to the complex independently synthesised by Sun *et al.*²² by the similar reaction of **pzphos** with $Pd(PhCN)_2Cl_2$. In this complex, a single **pzphos** ligand chelates to the palladium *via* the N and P donor groups with the remaining two coordination sites occupied by chloro ligands.

Upon increasing the ligand-to-metal ratio from 1 : 1 to 2 : 1, we found that addition of Pd(COD)Cl₂ to **pzphos** gave a different product in solution. This was evidenced by the ³¹P NMR spectrum of the reaction solution (taken after 1 h of stirring) which contained a major peak at +31.8 ppm, corresponding to the new species, and an additional smaller peak at +25.7 ppm corresponding to traces

of the 1 : 1 complex **1a**. Complex **1b** was isolated as a yellow solid by precipitation of a dichloromethane solution with hexane.

It was also possible to form **1b** by a stepwise process by first forming and isolating **1a** and then reacting this with a further equivalent of the **pzphos** ligand (shown in Scheme 2). The formation of the bis-chelate species **1b** is noteworthy as it has been previously reported that it was only possible to isolate the mono-chelate species **1a**, even when using a large excess of **pzphos** in the reaction with Pd(PhCN)₂Cl₂.²²

The ³¹P{H} NMR spectrum of **1b** showed one singlet at +31.6 ppm (*c.f.* **pzphos** ligand; $\delta = -11.4$ ppm) indicating the coordination of the **pzphos** ligands to the palladium centre in chemically equivalent environments. The N–H hydrogen of the pyrazole ring was found to be significantly shifted downfield in the ¹H NMR spectrum to 14.86 ppm compared to the free **pzphos** ligand ($\delta = 10.57$ ppm), suggesting coordination of the adjacent nitrogen atom of the pyrazole ring to the metal centre (Table 2). The bis-ligated nature of **1b** was confirmed by ESI mass spectrometry which showed a molecular ion peak at 761 m/z corresponding to [Pd(pzphos)₂]⁺ and suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a chloroform solution of **1b**.

The solid state structure of 1b shows the palladium to have a distorted square planar geometry with the two pzphos ligands chelating in a *cis* fashion resulting in a dicationic species in which two chloride anions balance the charge (Fig. 2, Table 3). The N-H hydrogen atoms are linked to the chloride anions by N- $H \cdots Cl$ hydrogen bonds (see ESI).[†] Within each ligand the linked C₆ and C₃N₂ rings are distinctly twisted with respect to each other, the torsion angles for the C-C bond between them being ca. 20 and 26° for the N(4) and N(2) ligands, respectively. The two {Pd,P,N} coordination planes are twisted with respect to each other by ca. 15°, a distortion that may in part be due to a π - π stacking interaction between pendant phenyl rings on adjacent ligands (dashed line in Fig. 2). These interactions are supported by the ambient temperature ¹H NMR spectrum which shows some significantly broadened peaks in the aromatic region. Following this observation, variable temperature spectra were recorded upon cooling the solution to 223 K (aromatic region shown in Fig. 3).

At 223 K, the spectrum consists of sharp peaks and as the temperature is increased, some of these peaks coalesce forming broad signals. It is apparent that not all of these aromatic



Scheme 2 Reactions of pzphos with palladium(II).





Fig. 2 Molecular structure of complex **1b** (30% probability ellipsoids). The π - π stacking interaction (dashed line) has centroid \cdots centroid and mean interplanar separations of *ca.* 3.57 and 3.18 Å respectively, the two rings being inclined by *ca.* 7°.

 Table 3
 Selected bond lengths (Å) and angles (°) for 1b

Pd-N(2)	2.072(4)	Pd-P(1)	2.2565(13)
Pd-N(4)	2.074(4)	Pd-P(2)	2.2541(13)
N(2)-N(1)	1.360(6)	N(4)-N(3)	1.344(6)
N(2)-Pd-P(1)	83.86(12)	N(4)-Pd-N(2)	92.77(16)
N(2)-Pd-P(2)	168.33(12)	P(1)-Pd-N(4)	169.39(12)
P(1)-Pd-P(2)	101.57(5)	N(4)-Pd-P(2)	83.63(12)

hydrogens are involved in fluxional behaviour as some resonances are temperature-independent. From the COSY ¹H NMR spectrum recorded at 223 K it has been possible to assign the peaks in these spectra; the non-fluxional hydrogens have been assigned as those attached to the pyrazolyl and phenyl rings which comprise the backbone of the ligand. The remaining hydrogens, which all display fluxional behaviour, are those which are present in the diphenylphosphine moiety of the ligand–metal complex. We ascribe this low temperature phenomenon to hindered rotation about the P–Ph bonds resulting in hydrogens occupying different spatial positions and hence unique chemical environments for periods of time comparable to the NMR timescale. These hydrogens are therefore observed as separate resonances while at higher temperatures, the energy barrier to rotation is overcome hence these peaks begin to coalescence.

Exchange of the chloride counter-anions in **1b** for perchlorate anions was achieved by addition of two equivalents of silver perchlorate, with the driving force of this reaction being the precipitation of silver chloride (Scheme 2). The ³¹P NMR of the yellow solid product **1c** shows a single peak with chemical shift +34.1 ppm (*cf.* **1b**; $\delta = +31.6$ ppm) and the N–H in the ¹H NMR spectrum is found at 13.42 ppm (Table 2). The ¹H NMR shows broad peaks corresponding to the diphenylphosphine hydrogens. These broad peaks split into sharp resonances at low temperatures as seen previously for complex **1b** (see ESI).[†]

Layering of hexane above a dichloromethane solution of **1c** yielded single crystals suitable for X-ray analysis. The solid state structure of **1c** shows the palladium to have a distorted square planar geometry with the two **pzphos** ligands chelating in a *cis*



Fig. 3 Variable temperature (283 K to 223 K) ¹H NMR spectra of complex 1b.

fashion (Fig. 4, Table 4). As seen for complex **1b**, a π - π stacking interaction between pendant phenyl rings on adjacent ligands is observed (dashed line in Fig. 4), and may be responsible for the



Fig. 4 Molecular structure of the cation in **1c** (30% probability ellipsoids). The π - π stacking interaction (dashed line) has centroid \cdots centroid and mean interplanar separations of *ca.* 3.89 and 3.25 Å respectively, the two rings being inclined by *ca.* 2°.

Table 4Selected bond lengths (Å) and angles (°) for 1c

Pd–N(1)	2.0738(17)	Pd–P(12)	2.2614(6)
Pd–N(31)	2.0763(17)	Pd–P(42)	2.2545(6)
N(1)–N(2)	1.357(3)	N(31)–N(32)	1.352(2)
N(1)-Pd-P(12)	85.68(5)	N(1)-Pd-N(31)	91.73(7)
N(1)-Pd-P(42)	170.37(5)	P(12)-Pd-N(31)	169.37(5)
P(12)-Pd-P(42)	99.39(2)	N(31)-Pd-P(42)	84.71(5)

twisting of the two {Pd,P,N} coordination planes with respect to each other (by *ca.* 14°). Within each ligand the linked C_6 and C_3N_2 rings are distinctly twisted with respect to each other, the torsion angles for the C–C bond between them being *ca.* 25 and 26° for the N(1) and N(31) ligands respectively. The N–H hydrogen atoms are linked to the perchlorate anions by N–H · · · O hydrogen bonds (see ESI).†

Reactions of N,P(O) **ligand, pzphos(O).** The N,P(O) ligand **pzphos(O)** displays different coordination behaviour since the 'soft' phosphine group is now replaced by a 'hard' phosphine oxide donor that has a lower affinity towards palladium(II). Formation of a chelate ring is now entropically disfavoured due to the increased size of the potential chelate ring, now sevenmembered as opposed to the six-membered complexes of **pzphos** described above. The reactions performed between **pzphos(O)** and Pd(COD)Cl₂ are outlined in Scheme 3.

The reactivity of **pzphos(O)** was first examined by addition of a dichloromethane solution of Pd(COD)Cl₂ to two equivalents of **pzphos(O)**. The ${}^{31}P{H}$ NMR spectrum of the reaction solution was recorded after stirring at room temperature for 1 h, with the chemical shift of the predominant species occurring at +33.0 ppm (cf. free ligand; $\delta = 35.8$ ppm). This indicated that the oxide group was not coordinated to the palladium as a significant downfield shift is expected to occur on coordination as a result of the inductive deshielding effect upon the phosphorus atom. The product **2b** was isolated by addition of hexane to the reaction solution and the ${}^{31}P{H}$ and ${}^{1}H NMR$ spectra were recorded of the resultant yellow solid (Table 2). The downfield position of the N-H in the ¹H NMR spectrum (13.51 ppm) suggests coordination of the pyrazolyl ring has occurred, in a similar fashion to the pzphos complexes described above. As such, it was hypothesised that a 2:1 ligand-to-metal complex had formed with the two ligands binding through their pyrazole nitrogens only and with the remaining



Scheme 3 Reactions of pzphos(O) with palladium(II).

coordination sites around the palladium centre being occupied by two chloro ligands. This stoichiometry was supported by FAB (+ve) mass spectral data showing a palladium isotope pattern at 869 m/z corresponding to [Pd{pzphos(O)}_2Cl_2]⁺. To confirm this structure, crystals were grown by slow diffusion of pentane into a chloroform solution of the **2b** and were subsequently analysed by X-ray crystallography.

The solid state structure of **2b** shows the palladium to have a square planar geometry with the two **pzphos** ligands bound in a monodentate fashion *via* Pd–N bonds. In contrast to the **pzphos** complex **1b**, the two ligands are coordinated in a *trans* fashion with two chloro ligands occupying the remaining two sites around the palladium (Fig. 5, Table 5). Within each ligand the linked C_6 and C_3N_2 rings are distinctly twisted with respect to each other, the torsion angle for the C–C bond between them being *ca*. 39°. This distortion may be caused by the molecule adopting a conformation that facilitates intramolecular N–H···O hydrogen bonding between the N(1)–H donor and the O(1) acceptor.



Fig. 5 Molecular structure of **2b** (30% probability ellipsoids). The intramolecular N–H···O hydrogen bonds (dashed lines) have N···O, H···O (Å), and N–H···O (°) of 2.69, 1.92 and 144 respectively.

The combination of the hard oxide donor on **pzphos(O)** and the increased size of the potential chelate ring (now seven-membered)

Table 5Selected bond lengths (Å) and angles (°) for 2b

Pd-N(2)	1.999(2)	Pd-Cl(1)	2.2995(7)
N(1)-N(2)	1.348(3)	P(1)-O(1)	1.496(2)
N(2)-Pd-Cl(1)	89.19(7)	N(2)-Pd-N(2')	180
N(2')-Pd-Cl(1)	90.81(7)	Cl(1)'-Pd-Cl(1)	180

disfavours chelation, in contrast to the behaviour of the **pzphos** ligand. Since the ligands do not chelate, the *trans* form is observed as steric interactions between the two ligands are minimised. This structure further differs from the uncoordinated **pzphos(O)** ligand and the **pzphos** complexes **1a–1c** in that the N–H hydrogen has 'swapped' the nitrogen atom to which it is bonded, and consequently, coordination to palladium now occurs through the nitrogen in the 1'-position (Fig. 6).



Fig. 6 Variable bonding modes of pzphos (left) and pzphos(O) (right).

This coordination mode in **2b** is presumed to result from the monodentate behaviour of the **pzphos(O)** ligand which permits the fluxional N–H hydrogen to reside on the nitrogen atom that produces the most energetically favourable configuration in the resultant complex, *i.e.* where steric interactions between the ligand moieties and the metal are minimised. This is achieved by coordination at the 1'-position, thus leaving the bulky triphenylphosphine oxide moiety on the 'other side' of the pyrazolyl ring, pointing away from the metal. This bonding mode has previously been observed for a palladium(II) complex of a 3-substituted pyrazole ligand.³⁸ Further stabilisation for this form is also achieved by the formation of intramolecular N–H···O hydrogen bonds.

The lack of formation of a seven-membered chelate has been observed previously with another N,P(O) ligand towards palladium(II).³⁶ Although formation of a seven-membered chelate has been observed in the palladium(II) complexes of N,N^{39} and N,P ligands,⁴⁰ it is disfavoured in the case of oxygen donors due to the lower affinity of these donor groups towards palladium. In contrast, chelation of six-membered N,P(O) ligands around palladium has been observed previously,³¹ although in one case it required an excess of palladium over ligand and heating at reflux for several hours.³⁵ In our attempts to synthesise the *mono* chelate structure **2a**, we found that even when using forcing conditions (extended reaction times, reflux, excess of palladium), the bis adduct **2b** would form preferentially with no traces of a chelated species being observed by ³¹P NMR spectroscopy.

It was, however, anticipated that by adding two equivalents of silver perchlorate to a solution of 2b, coordination of the oxide group could be encouraged by removal of the chloro ligands. This reaction was performed accordingly and after stirring the reaction solution at room temperature for 30 min, the ${}^{31}P{H}$ NMR spectrum revealed a mixture in which the predominant species occurred at 52.9 ppm, with smaller peaks present at 35.3 and 33.3 ppm. This species was subsequently isolated as a vellow powder by addition of hexane to the reaction mixture and recrystallisation from hot MeOH. The ³¹P{H} NMR spectrum showed a singlet at 53.8 ppm enabling us to tentatively ascribe this complex as the bis-chelated species 2c as its ${}^{31}P{H}$ chemical shift closely resembled that of a similarly coordinated N, P(O)species.³¹ In order to confirm the structure of 2c, X-ray analysis was performed on a single crystal grown by slow diffusion of pentane into a chloroform solution of the complex. Indeed, the solid state structure shows the palladium to have a square planar geometry with two pzphos(O) ligands chelating in a trans fashion (Fig. 7, Table 6). Each of the seven membered $C_3NP(O)Pd$ chelate rings has a distorted boat conformation. As a consequence of chelation, the linked C₆ and C₃N₂ rings within each ligand are distinctly twisted with respect to each other, the torsion angle for the C–C bond between them being $ca. 50^{\circ}$.



Fig. 7 Molecular structure of the cation in 2c (30% probability ellipsoids).

This structure reveals that the N–H hydrogen of the **pzphos(O)** ligand has reverted back to the 1-position of the pyrazole ring (Fig. 7). This makes available the nitrogen in the 2-position for coordination to the metal and thus allows formation of the sevenmembered chelate. Tautomerisation of this kind is required for chelation as when the ligand coordinates *via* the nitrogen in the 1'-position (as in **2b**), the rigidity of the ligand prevents the oxide group from approaching the palladium centre.

Table 6Selected bond lengths (Å) and angles (°) for 2c

Pd-N(2)	2.008(4)	Pd–O(1)	2.009(3)
N(1)-N(2)	1.339(7)	P(1)–O(1)	1.526(4)
N(2)-Pd-O(1)	92.89(16)	N(2')-Pd-O(1)	87.11(16)
N(2)-Pd-N(2')	180	O(1)-Pd-O(1')	180

Conclusions

Relatively simple ligand tuning has been employed to demonstrate the variable coordination behaviour of the N,P ligand **pzphos** and the related N,P(O) ligand, **pzphos(O)** towards palladium(II). This tuning effect has demonstrated the potential hemilability of these species, while **pzphos** favoured chelation in all cases, **pzphos(O)** acted as a monodentate N-donor that could be forced into a bidentate chelating mode by abstraction of the chloro ligands. To our knowledge, this is the first structurally characterised example of an N,P(O) hybrid ligand chelating at a palladium(II) centre.⁴¹ Investigations are currently underway in our laboratory into the catalytic properties of these complexes as well as the further functionalisation of the ligands *via* substitution at the pyrazolyl nitrogen. We have found the coordination chemistry of the N,P(S)ligand **pzphos(S)** to be less straightforward, and the results of these investigations will be presented in due course.

Experimental

All reagents, unless stated otherwise were purchased from commercial suppliers without further purification. Elemental analyses were performed by Stephen Boyer at the London Metropolitan University. ¹H, ¹³C{H} and ³¹P{H} NMR spectra were recorded on Bruker Av-400, DRX-400 or Av-500 spectrometers. Chemical shifts are reported in ppm using the residual proton impurities in the solvents. Pseudo-triplets which occur as a result of identical *J*value coupling to two chemically inequivalent protons are assigned as dd and are recognised by the inclusion of only one *J*-value. Mass spectra were recorded on a Micromass Autospec Q spectrometer by Mr J. Barton and Mr G. Tucker of the Department of Chemistry, Imperial College, London. Infrared absorption spectra were collected either as KBr discs or Nujol mulls using a Perkin Elmer RX FT-IR spectrometer. Ligand precursor **A** was prepared as reported previously.³⁷

Ligand syntheses

1-(2'-Diphenylphosphino)3-dimethylamino-2-propene-1-one B. Using a variation of a literature procedure,42 2'-(diphenylphosphino)acetophenone (12.35 g, 40.6 mmol) and N,Ndimethylformamide dimethylacetal (25 ml, excess) were heated at 120 °C for 12 h over which time the yellow solution turned deep brown. After cooling to room temperature, the excess N,Ndimethylformamide dimethyl acetal was removed in vacuo to leave a dark orange solid which was broken up and stirred in pentane (100 ml) and filtered to produce an orange solid which was dried in vacuo (13.48 g, 92%). Analysis was carried out on a sample recrystallised from CH₂Cl₂/hexane. ¹H NMR (+25 °C, CDCl₃, 400 MHz), $\delta = 7.64$ [dd (${}^{3}J_{HH} = 6.9$ Hz, ${}^{4}J_{HH} = 3.8$ Hz), 1H, 3-Ph], 7.38 [ddd (${}^{3}J_{HH} = 7.7$ Hz, ${}^{3}J_{HH} = 7.6$ Hz, ${}^{4}J_{HH} = 1.2$ Hz), 1H, 4-Ph], 7.27–7.35 [m, 12H, 5-Ph + *o*,*m*,*p*-Ph + CHNMe₂], 7.06 [dd (${}^{3}J_{HH} = 7.3$ Hz, ${}^{4}J_{HH} = 3.5$ Hz), 1H, 6-Ph], 5.43 [d (${}^{3}J_{HH} =$ 12.6 Hz), 1H, COCH], 2.96 [s, 3H, NCH₃], 2.71 [s, 3H, NCH₃]. ³¹P{H} NMR (+25 °C, CDCl₃, 162.05 MHz), $\delta = -10.3$. IR (KBr disc), $v/cm^{-1}1637(CO)$. MS(EI), $m/z = 359 [M]^+$. Anal. (%); Calc. (found) for C₂₃H₂₂NOP: C, 76.9 (76.8); H, 6.17 (6.03); N, 3.90 (3.83).

[2-(3-Pyrazolyl)phenyl]diphenylphosphine pzphos. Hydrazine hydrate (10 ml, excess) was added dropwise to a solution of **B** (12.00 g, 33.4 mmol) in hot ethanol (150 ml) and stirred under reflux for 3 h. Removal of the solvent gave an orange solid to which was added water (50 ml) and the solid was collected by filtration. The aqueous washings were extracted into CHCl₃ (200 ml) and the organic fraction was separated and used to dissolve the solid. Drying (MgSO₄), filtration and concentration followed by recrystallisation from CHCl₃/hexane gave a colourless solid. Yield = 9.33 g (91%). ¹H NMR (+25 °C, CDCl₃, 500 MHz), $\delta = 10.57$ [s, 1H, NH], 7.60 [dd (${}^{3}J_{HH} = 7.1$ Hz, ${}^{4}J_{HH} = 3.7$ Hz), 1H, 3-Ph], 7.48 [d (${}^{3}J_{HH} = 2.0$ Hz), 1H, 5-pz], 7.42 [ddd (${}^{3}J_{HH} =$ 7.7 Hz, ${}^{3}J_{\rm HH} = 7.6$ Hz, ${}^{4}J_{\rm HH} = 1.3$ Hz), 1H, 4-Ph], 7.33–7.37 [m, 6H, *m*,*p*-Ph], 7.26–7.31 [m, 4H, *o*-Ph], 7.03 [ddd (${}^{3}J_{HP} = 7.8$ Hz, ${}^{3}J_{\rm HH} = 4.2$ Hz, ${}^{4}J_{\rm HH} = 1.1$ Hz), 1H, 6-Ph], 6.34 [m, 1H, 4-pz]. ³¹P{H} NMR (+25 °C, CDCl₃, 162.05 MHz), $\delta = -11.4$. ¹³C{H} NMR (+25 °C, CDCl₃, 500 MHz), δ = 146.9 [s, 3-pz], 140.0 [s, 5-pz], 137.1 [d, $({}^{1}J_{CP} = 10.6 \text{ Hz})$, *i*-Ph], 136.1 [d $({}^{2}J_{CP} = 17.3 \text{ Hz})$, 2-Ph], 134.3 [s, 6-Ph], 133.9 [d, $({}^{2}J_{CP} = 19.7 \text{ Hz})$, o-Ph], 131.8 [s, 1-Ph], 130.0 [d (${}^{3}J_{CP} = 5.5$ Hz), 3-Ph], 128.9 [s, 5-Ph], 128.8 [s, 4-Ph], 128.6 [d (${}^{3}J_{CP} = 7.6$ Hz), m-Ph], 128.3 [s, p-Ph], 106.5 [s, 4-pz]. IR (KBr disc), ν/cm^{-1} 3187 cm⁻¹(NH). MS(EI), m/z =328 [M]⁺. Anal. (%): Calc. (found) for C₂₁H₁₇N₂P: C, 76.8 (77.0); H, 5.22 (5.00); N, 8.53 (8.35).

[2-(3-Pyrazolyl)phenyl]diphenylphosphine oxide pzphos(O). A solution of pzphos (0.30 g, 0.91 mmol) and H_2O_2 (27.5% in H_2O_2 135 μ L, 1.10 mmol) in CH₂Cl₂ (30 ml) was stirred for 1 h after which time H₂O (40 ml) was added and the organic layer separated, dried (MgSO₄) and concentrated to dryness to give a colourless solid. Yield = 0.20 g (63%). ¹H NMR (+25 °C, CDCl₃, 500 MHz), $\delta = 13.24$ [s, 1H, NH], 7.78 [ddd (${}^{3}J_{HH} = 7.8$ Hz, ${}^{4}J_{HH} = 4.2$ Hz, ${}^{5}J_{\rm HH} = 1.0$ Hz), 1H, 3-Ph], 7.61 [m, 5H, o-Ph + 4-Ph], 7.50 [m, 2H, *p*-Ph], 7.41 [m, 4H, *m*-Ph], 7.32 [d (${}^{3}J_{HH} = 1.8$ Hz), 1H, 5-pz], 7.30 [m, 1H, 5-Ph], 7.14 [ddd (${}^{3}J_{HP} = 14.6$ Hz, ${}^{3}J_{HH} = 7.8$ Hz, ${}^{4}J_{HH} =$ 1.1 Hz), 1H, 6-Ph], 6.25 [s, 1H, 4-pz]; ³¹P{H} NMR (+25 °C, $CDCl_3$, 162.05 MHz), $\delta = +35.8$. ¹³C{H} NMR (+25 °C, CDCl_3, 500 MHz), $\delta = 141.8$ [s, 3-pz], 139.7 [s, 5-pz], 134.9 [d (${}^{2}J_{CP} =$ 8.0 Hz), 2-Ph], 134.1 [d (${}^{2}J_{CP} = 12.1$ Hz), 6-Ph], 132.7 [s, 4-Ph], 132.2 [s, *p*-Ph], 131.7 [d (${}^{2}J_{CP} = 9.8$ Hz), *o*-Ph], 131.3 [d (${}^{3}J_{CP} =$ 9.6 Hz), 3-Ph], 130.9 [s, *i*-Ph], 130.0 [s, 1-Ph], 128.6 [d (${}^{3}J_{CP} =$ 12.4 Hz), *m*-Ph], 127.3 [d (${}^{3}J_{CP} = 12.4$ Hz), 5-Ph], 105.3 [s, 4-pz]. IR (Nujol), v/cm^{-1} 3186 cm⁻¹(NH); MS(EI), m/z = 344 [M]⁺. Anal. (%): Calc. (found) for C₂₁H₁₇N₂OP: C, 73.3 (73.1); H, 4.98 (5.01); N, 8.14 (8.02). Crystals suitable for X-ray studies were grown by slow diffusion of pentane in a chloroform solution of this complex.

[2-(3-Pyrazolyl)phenyl]diphenylphosphine sulfide pzphos(S). A solution of pzphos (0.30 g, 0.91 mmol) and S₈ (44 mg, 0.17 mmol) in CH₂Cl₂ (15 ml) was stirred for 1 h and then reduced in volume to ~5 ml and hexane added dropwise. The resultant off-white precipitate was collected by filtration, washed with hexane and dried *in vacuo*. Yield = 0.25 g (76%). ¹H NMR (+25 °C, CDCl₃, 500 MHz), δ = 12.54 [s, 1H, NH], 7.82 [dd (³J_{HH} = 13.6 Hz, ⁴J_{HH} = 7.1 Hz), 4H, *o*-Ph], 7.57 [m, 2H, 3-Ph + 4-Ph], 7.44 [m, 2H, *p*-Ph], 7.37 [m, 4H, *m*-Ph], 7.37 [m, 1H, 5-Ph], 7.18 [dd (³J_{HP} = 14.9 Hz, ³J_{HH} = 8.0 Hz), 1H, 6-Ph], 7.17 [d (³J_{HH} = 1.8 Hz), 1H, 5-pz], 6.08 [s, 1H, 4-pz]. ³¹P{H} NMR (+25 °C, CDCl₃, 500 MHz), δ = 139.7 [s, 3-43.13 C{H} NMR (+25 °C, CDCl₃, 500 MHz)] = 139.7 [s, 3-43.13 C{H}

pz], 139.3 [s, 5-pz], 133.4 [d (${}^{2}J_{CP} = 11.2$ Hz), 6-Ph], 133.2 [s, *i*-Ph], 132.6 [s, 1-Ph], 132.4 [d (${}^{3}J_{CP} = 9.8$ Hz), 3-Ph], 132.0 [d (${}^{2}J_{CP} = 10.7$ Hz), *o*-Ph], 131.9 [s, 4-Ph], 131.7 [s, *p*-Ph], 130.7 [s, 2-Ph], 128.4 [d (${}^{3}J_{CP} = 12.7$ Hz), *m*-Ph], 128.1 [d (${}^{3}J_{CP} = 12.3$ Hz), 5-Ph], 105.9 [s, 4-pz]. IR (KBr disc), *v*/cm⁻¹ 3220 cm⁻¹(NH). MS(EI), *m*/*z* = 360 [M]⁺. Anal. (%): Calc. (found) for C₂₁H₁₇N₂PS: C, 70.0 (70.1); H, 4.75 (4.83); N, 7.77 (7.66).

Complex syntheses

Synthesis of palladium perchlorate complexes. Caution! Although we did not observe any explosive behaviour with the perchlorate compounds described below, all metal perchlorates must be treated as potentially explosive species and appropriate safety measures must be taken. See for example reference.⁴³

[Pd(pzphos)Cl₂] 1a. Pzphos (0.33 g, 1.0 mmol) in CH₂Cl₂ (10 ml) was added dropwise to a stirred solution of Pd(COD)Cl₂ (0.29 g, 1.0 mmol) in CH₂Cl₂ (20 ml). The orange solution was stirred for 10 min causing a yellow solid to precipitate. This was collected by filtration, stirred with hexane (20 ml), filtered and dried *in vacuo* to give a bright yellow solid. Yield = 0.46 g (91%). ¹H NMR (+25 °C, CDCl₃, 500 MHz), $\delta = 13.14$ [s, 1H, NH] 7.90 $[ddd ({}^{3}J_{HH} = 7.9 \text{ Hz}, {}^{4}J_{HH} = 4.4 \text{ Hz}, {}^{5}J_{HH} = 1.0 \text{ Hz}), 1\text{H}, 3\text{-Ph}], 7.70$ $[dddd ({}^{3}J_{HH} = 7.9 \text{ Hz}, {}^{4}J_{HH} = 1.5 \text{ Hz}), 1\text{H}, 4\text{-Ph}], 7.65 [dd ({}^{3}J_{HH} =$ 2.8 Hz, ${}^{3}J_{HH} = 1.8$ Hz), 1H, 5-pz], 7.61 [m, 4H, o-Ph], 7.54 [m, 2H, *p*-Ph], 7.44 [m, 4H, *m*-Ph], 7.42 [m, 1H, 5-Ph], 7.05 [ddd (${}^{3}J_{HP}$ = 10.8 Hz, ${}^{3}J_{HH} = 7.9$ Hz, ${}^{4}J_{HH} = 1.2$ Hz), 1H, 6-Ph], 6.86 [m, 1H, 4-pz]. ³¹P{H} NMR (+25 °C, CDCl₃, 162.05 MHz): $\delta = +25.6$. IR (KBr disc), ν/cm^{-1} 3230 cm⁻¹(NH). MS(EI), m/z = 471 [M-Cl]⁺. Anal. (%): Calc. (found) for C₂₁H₁₇Cl₂N₂PPd: C, 49.9 (49.8); H, 3.39 (3.33); N, 5.54 (5.42). Yellow needles suitable for X-ray studies were grown by slow diffusion of pentane in a chloroform solution of the complex.

[Pd(pzphos)₂]Cl₂ 1b. Pd(COD)Cl₂ (65 mg, 0.23 mmol) in CH₂Cl₂ (15 ml) was added dropwise to a solution of pzphos (150 mg, 0.46 mmol) in CH₂Cl₂ (15 ml). After stirring overnight, the volume of the solvent was reduced to 10 ml and hexane (10 ml) was added causing a yellow solid to precipitate. This was collected by filtration and dried *in vacuo*. Yield = 150 mg (78%). ¹H NMR $(-50 \text{ °C}, \text{CDCl}_3, 400 \text{ MHz}), \delta = 14.54 \text{ [s, 1H, NH]}, 8.05 \text{ [dd]}$ $({}^{3}J_{\rm HH} = 12.8$ Hz, ${}^{4}J_{\rm HH} = 7.9$ Hz), 1H, Ph], 7.96 [dd $({}^{3}J_{\rm HH} =$ 7.5 Hz, ${}^{4}J_{\rm HH} = 3.4$ Hz), 1H, 3-Ph], 7.96 [br s, 2H, Ph], 7.76 [s, 1H, 5-pz], 7.64 [dd, $({}^{3}J_{HH} = 7.6 \text{ Hz})$, 1H, 4-Ph], 7.42 [m, 3H, Ph], 7.30 [dd (${}^{3}J_{HH} = 7.7$ Hz), 1H, 5-Ph], 7.22 [m, 1H, Ph], 7.06 [dd $({}^{3}J_{HH} = 7.4 \text{ Hz}), 1\text{H}, \text{Ph}], 6.79 \text{ [m, 2H, 6-Ph + Ph]}, 6.53 \text{ [s, 1H, 4-}$ pz], 5.94 [dd (${}^{3}J_{HH} = 9.0$ Hz), 1H, Ph]. ${}^{31}P{H}$ NMR (+25 °C, CDCl₃, 162.05 MHz), $\delta = +31.6$ (s). IR (KBr disc), ν/cm^{-1} 3290 cm⁻¹(NH). MS(ESI), $m/z = 761 [Pd(pzphos)_2]^+$. Anal. (%): Calc. (found) for C42H34Cl2N4P2Pd.2CH2Cl2: C, 52.6 (52.6); H, 3.82 (3.62); N, 5.58 (5.37). Yellow crystals suitable for X-ray studies were grown by slow diffusion of pentane in a chloroform solution of this complex.

Alternative synthesis of 1b. A solution of pzphos (32 mg, 0.10 mmol) in CH_2Cl_2 (10 ml) was added to a solution of 1a (50 mg, 0.10 mmol) in CH_2Cl_2 (10 ml) and stirred overnight. The solution was concentrated to half the volume and hexane (10 ml) added dropwise causing a yellow solid to precipitate. The solid was collected by filtration and dried *in vacuo* to give 1b as evidenced by

identical ¹H and ³¹P{H} NMR data for both compounds. Yield = 55 mg (70%).

[*Pd(pzphos)*₂][*ClO*₄]₂ *1c.* Pd(COD)Cl₂ (87 mg, 0.30 mmol) in CH₂Cl₂ (5 ml) was added dropwise to a solution of pzphos (200 mg, 0.61 mmol) in CH₂Cl₂ (20 ml). After stirring for 1 h, silver perchlorate (114 mg, 0.64 mmol) was added and the flask stirred overnight in the dark during which time AgCl precipitated. Filtration through a pad of Celite and concentration of the filtrate to dryness gave a yellow powder which was stirred with hexane (20 ml), filtered and recrystallised from hot methanol to give a yellow solid. Yield = 180 mg (61%). ¹H NMR (+ $25 \degree$ C, d⁶-acetone, 400 MHz), $\delta = 13.42$ [s, 1H, NH], 8.19 [dd (${}^{3}J_{HH} = 2.8$ Hz, ${}^{4}J_{HH} =$ 0.7 Hz), 1H, 5-pz], 8.08 [ddd (${}^{3}J_{HH} = 7.8$ Hz, ${}^{4}J_{HH} = 4.3$ Hz, ${}^{5}J_{HH} =$ 1.2 Hz), 1H, 3-Ph], 7.90 (br m, 2H, Ph), 7.85 [dd (${}^{3}J_{HH} = 7.8$ Hz), 1H, 4-Ph], 7.40–7.70 [br m, 4H, Ph], 7.59 [dd (${}^{3}J_{HH} = 8.0$ Hz), 1H, 5-Ph], 7.08–7.25 [br m, 2H, Ph], 7.05 [ddd (${}^{3}J_{HP} = 11.1$ Hz, ${}^{3}J_{\rm HH} = 7.9$ Hz, ${}^{4}J_{\rm HH} = 0.8$ Hz), 1H, 6-Ph], 6.99 [dd (${}^{3}J_{\rm HH} = 7.8$ Hz, ${}^{3}J_{\rm HH} = 1.6$ Hz), 1H, 4-pz]. ${}^{31}P{\rm H}$ NMR (+25 °C, d⁶-acetone, 162.09 MHz): $\delta = +34.1$. IR (Nujol), ν/cm^{-1} 3302 cm⁻¹(NH). $MS(FAB + ve), m/z = 761 [Pd(pzphos)_2]^+$. Anal. (%): Calc. (found) for C42H34Cl2N4O8P2Pd: C, 52.4 (52.5); H, 3.56 (3.69); N, 5.82 (5.73). Single crystals for X-ray analysis were grown in an NMR tube by layering hexane above a CH₂Cl₂ solution of the product.

Attempted synthesis of $[Pd\{pzphos(O)\}Cl_2]$ 2a. Pzphos(O) (30 mg, 0.09 mmol) in CH₂Cl₂ (10 ml) was added dropwise to a refluxing solution of Pd(COD)Cl₂ (30 mg, 0.10 mmol) in CH₂Cl₂ (20 ml). The refluxing solution was stirred for 16 h and ³¹P{H} NMR of the reaction solution recorded (+25 °C, CH₂Cl₂/CDCl₃, 162.05 MHz): $\delta = +32.8$, indicating formation of the bis adduct **2b**.

 $[Pd{pzphos(O)}_2Cl_2]$ 2b. Pd(COD)Cl₂ (21 mg, 0.07 mmol) in CH₂Cl₂ (10 ml) was added dropwise to a solution of **Pzphos(O)** (50 mg, 0.15 mmol) in CH₂Cl₂ (20 ml). After stirring for 2 h, half the solvent was evaporated under a stream of N_2 to give a yellow solution to which hexane was added dropwise (5 ml) causing a pale yellow precipitate to form. This was collected by filtration, washed with hexane (5 ml) and dried in vacuo to give a pale yellow powder. Yield = 52 mg (83%). ¹H NMR (+25 °C, CDCl₃, 400 MHz), δ = 13.51 [s, 1H, NH], 7.81 [dd (${}^{3}J_{HH} = 2.1 \text{ Hz}$), 1H, 5-pz], 7.74 [m, 4H, o-Ph], 7.61 [dd (${}^{3}J_{HH} = 7.5$ Hz), 1H, 4-Ph], 7.57 [dd (${}^{3}J_{HH} = 7.6$ Hz), 1H, 3-Ph], 7.53 [m, 2H, p-Ph], 7.47 [m, 4H, m-Ph], 7.37 [dd $({}^{3}J_{HH} =$ 7.5 Hz), 1H, 5-Ph], 7.22 [dd (${}^{3}J_{HP} = 14.2$ Hz, ${}^{3}J_{HH} = 7.5$ Hz), 1H, 6-Ph], 6.19 [dd (${}^{3}J_{HH} = 2.2$ Hz), 1H, 4-pz]. ${}^{31}P{H}$ NMR $(+25 \text{ °C}, \text{CDCl}_3, 162.05 \text{ MHz}), \delta = +32.7 \text{ (s). IR (Nujol)}, v/\text{cm}^{-1}$ $3196 \text{ cm}^{-1}(\text{NH})$. MS(FAB+ve), $m/z = 869 [\text{Pd}\{\text{pzphos}(\text{O})\}_2 \text{Cl}_2]^+$. Anal. (%): Calc. (found) for C₄₂H₃₄Cl₂N₄O₂P₂Pd: C, 58.3 (58.2); H, 3.96 (4.00); N, 6.47 (6.39). Yellow crystals suitable for X-ray studies were grown by slow diffusion of pentane in a chloroform solution of this complex.

[*Pd*{*pzphos(O)*}₂][*ClO*₄]₂ *2c.* AgClO₄ (25 mg, excess) was added to a suspension of **2b** (34 mg, 0.04 mmol) in CH₂Cl₂ (5 ml). After stirring overnight, half the solvent was evaporated under a stream of N₂ to give a yellow solution to which hexane was added dropwise (5 ml) causing a yellow precipitate to form. This was collected by filtration, washed with hexane (5 ml) and dried *in vacuo* to give **2c** as yellow powder. Yield = 24 mg (60%). ¹H NMR (+25 °C, CDCl₃, 400 MHz), δ = 12.35 [s, 1H, NH], 8.27 [dd (³J_{HH} = 7.4 Hz, ⁴J_{HH} = 4.4 Hz), 1H, 3-Ph], 8.12 [dd (³J_{HH} =

7.7 Hz), 1H, 4-Ph], 7.60–7.85 [m, 10 H, *o,m,p*-Ph], 7.35–7.50 [m, 2 H, 5,6-Ph], 7.31 [d (${}^{3}J_{\text{HH}} = 2.0$ Hz), 1H, 5-pz], 6.02 [m, 1H, 4-pz]. ${}^{31}P{H}$ NMR (+25 °C, CDCl₃, 162.05 MHz), $\delta = +53.9$ (s). IR (CH₂Cl₂ solution), *v*/cm⁻¹ 3686 cm⁻¹(NH). MS(FAB +ve), *m*/*z* = 900 [Pd{pzphos(O)}₂ClO₄]⁺. Anal. (%): Calc. (found) for C₄₂H₃₄Cl₂N₄O₁₀P₂Pd: C, 50.8 (50.7); H, 3.45 (3.43); N, 5.64 (5.58). Yellow crystals suitable for X-ray studies were grown by slow diffusion of pentane in a chloroform solution of this complex.

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