A new potentially hexadentate \( \text{N}_2\text{P}_2\text{N}_2 \) ligand has been prepared and its coordination chemistry to the late transition metal ions Pd(II) and Pt(II) investigated. The ligand bonds in a chelating fashion via the diphosphine backbone to PdCl\(_2\) and PtCl\(_2\) while the appended pyridyl groups remain non-bonding. Abstraction of the chloride ions from the platinum complex results in fluxional exchange of the pyridyl groups in solution at room temperature on the NMR timescale. X-ray crystallographic analysis of this platinum complex revealed a tetracoordinate complex with two bound and two free pyridyl arms.

Ligands that contain a combination of phosphorus and nitrogen donor atoms have been widely studied for their diverse coordination chemistry and catalytic applications. Bidentate N,P ligands in particular have received considerable attention with regards to catalytic applications because of the interplay of electronic and steric effects of the N and P donors at the metal centre. The nitrogen donor can enhance oxidative addition by virtue of being a strong sigma donor while the phosphorous donor may stabilise the metal ion in a low oxidation state and provide steric protection. Additionally, depending on the metal centre, either the N or P donors can behave in a hemilabile fashion and provide vacant coordination sites for substrate molecules. Multidentate ligands containing a mixture of N or P donor atoms such as the tetradentate \( \text{P}_2\text{N}_2 \) Trost’s ligands, based on a dianmine backbone and peripheral phosphine ligands, and other related tetradentate N,P ligand systems are now also relatively common. In contrast, however, multidentate N,P ligand systems comprising of a diphosphine backbone and two or more peripheral nitrogen donor atom are comparatively rare. Examples of such ligand systems include the \( \text{N}_2\text{P}_2 \) ligands that contain chiral phosphorus atoms substituted with alkylamine, oxazoline or pyridyl groups. Ligands with up to six mixed N,P donors are rarer still and include the \( \text{N}_2\text{P}_2\text{N}_2 \) tetrapyridyl substituted diphosphines and the potentially hexadentate \( \text{N},\text{N}-\text{dimethylanilinyl} \) substituted diphosphines. Such multidentate P,N ligand systems are of considerable interest for the preparation of heteromultimetallic complexes, metal sequestering and for catalysis owing to the controlled geometry of the chelating diphosphine backbone and potentially hemilabile behaviour of the appended N atoms. Herein we report the synthesis of a new and potentially hexadentate \( \text{N}_2\text{P}_2\text{N}_2 \) ligand system based on an ortho-phenyl diphosphine backbone with four peripheral pyridyl arms and investigate its coordination chemistry to Pd(II) and Pt(II).

The \( \text{N}_2\text{P}_2\text{N}_2(\text{phen}) \) ligand (1) was obtained in quantitative yield as viscous colourless liquid by reaction of 1,2-bis[bis(hydroxymethyl)phosphino]benzene\(^{28}\) with 4 equivalents of 2-methylaminopyridine in methanol (scheme 1). The \( ^{31}\text{P} \{^1\text{H}\} \) NMR spectrum displayed a single resonance at -38.5 ppm. The palladium(II) and platinum(II) dichloride complexes \( [\text{PdCl}_2(\text{N}_2\text{P}_2\text{N}_2(\text{phen}))] \) (2) and \( [\text{PtCl}_2(\text{N}_2\text{P}_2\text{N}_2(\text{phen}))] \) (3) were readily prepared by reaction of equimolar amounts ligand 1 with the Pd and Pt dichloride cyclooctadiene complexes in CH\(_2\)Cl\(_2\) at room temperature (scheme 1). The \( ^{31}\text{P} \{^1\text{H}\} \) NMR spectrum of 2 showed a single downfield shifted resonance at 65.9 ppm while complex 3 displayed well defined singlet at 40.2 ppm with distinctive \(^{195}\text{Pt} \) satellites and a coupling constant \((J_{\text{Pt-P}} = 3433\text{Hz})\) characteristic of the expected cis-chelating diphosphine structure.\(^{28}\) \(^{1}\text{H} \) NMR spectra for complexes 2 and 3 are, as expected, similar to the aromatic regions of the free and show that the peripheral pyridyl groups remain uncoordinated. As is the case with the free ligand, the methylene protons of the pyridyl arms of complexes 2 and 3 are in two chemically distinct environments which results two separate resonances and geminal coupling of these protons to each other as well as two bond coupling to phosphorus. Interestingly, one the methylene protons of complex 3 displays distinctive three bond coupling to \(^{195}\text{Pt} \) \((J_{\text{Pt-P-P}} = 58\text{Hz})\).
In an attempt to coordinate one or more of the surrounding pyridyl arms, complex 3 was reacted with two equivalents of AgClO₄ in dichloromethane to abstract the chloride ions. The coordination of two pyridyl arms would be expected to give a four coordinate complex with two free pyridyl arms and result in the phosphorus atoms becoming chiral and thus forming a mixture of achiral meso RS/RR and chiral rac RR/SS diastereoisomers which would significantly complicate NMR spectra. The room temperature ³¹P{¹H} and ¹H NMR spectra of this new complex [Pt(N₂P₂N₂(phen)₂)](ClO₄)₂ (4) were, however, surprisingly uncomplicated considering the mixture of diastereoisomers that may be expected. The ³¹P{¹H}NMR spectrum showed a single resonance at 36.1 ppm with ¹⁹⁵Pt satellites (Andrej J. 3224 Hz) suggesting that the phosphorus atoms are in the same magnetic environment while the ¹H NMR spectrum displayed only four signals accounting for the four pyridyl protons, thus showing the equivalence of all four pyridyl groups. The ¹H NMR spectrum of 4 is however characteristically different in the pyridyl region to that of complex 3. Downfield chemical shifts of approximately 0.5 ppm were observed for the pyridyl para and meta protons of complex 4 compared to 3, which may be expected upon pyridyl coordination, however there is no significant chemical shift in the ortho proton resonance. Additionally, there is an upfield chemical shift of 0.5 ppm for one of the methylene protons of 4. The NMR data therefore suggests that the four pyridyl arms are undergoing a fluxional exchange process at the Pt(II) centre and thus a time average of the coordinated and uncoordinated pyridyl groups is observed on the NMR timescale. The pyridyl exchange process is likely to proceed via a five-coordinate Pt complex followed by dissociation of the neighbouring coordinated arm on the same P atom and rearrangement to the favoured four coordinate square planar complex (figure 3). Low temperature ¹H NMR spectra showed significant line broadening on cooling to lower
temperatures with no resolution of possible diasterisomers at the low temperature limit (183K) in CD$_2$Cl$_2$. The corresponding low temperature $^3$P($^1$H) NMR spectra showed the appearance of two broadened signals with $^{195}$Pt satellites at the low temperature limits of the spectrometer which can be explained by the magnetic inequivalence of the possible R and S phosphorus centres (fig. 4).

Fig. 4 Proposed fluxional pyridyl arm exchange process of complex 4. The two achiral meso RS/SR isomers are identical due to a plane of symmetry running through 4.

Crystals of complex 4 suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution and show a tetradentate square planar complex formed by the coordination of two pyridyl arms (figure 5). Coordination of these pyridyl groups results in the formation of two flexible six-membered chelate rings around the Pt centre with respective N-Pt-P bite angles of N(34)-Pt-P(2) 86.84$^\circ$ and N(14)-Pt-P(1) 85.58$^\circ$, while P-Pt bond distances are shortened to Pt-P(1) 2.1879(7), Pt-P(2) 2.1880(8) compared to the dichloride complex 3. In this configuration the two P atoms are now chiral and thus magnetically inequivalent; although the complex is achiral due to the plane of symmetry through the centre of the complex. It is this conformation which may be observed in the low temperature $^3$P($^1$H) NMR spectrum where two distinct resonances are observed. Interestingly no evidence of the possible RR and SS enantiomers was observed which tentatively suggests that these isomers are energetically less favourable than the meso RS/SR diastereoisomer.

In summary, we have developed a new multidentate ligand system that has been demonstrated to form diphosphine chelate complexes with Pd(II) and Pt(II) centres. Removal of the chloride ions from complex 3 resulted in the formation of a tetradentate complex with two bound pyridyl arms in the solid state. In solution this complex was found to undergo a fluxional process whereby the pyridyl arms are labile and rapidly exchange with each other at the metal centre. We are currently expanding the scope of this ligand system by varying the the chelating diphosphine backbone and peripheral nitrogen donors in addition to investigating further transition metal coordination chemistry.

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Notes and references