

Platinum Group Metal Chemistry of Functionalised Phosphines

PROPERTIES AND APPLICATIONS OF THEIR COORDINATION COMPLEXES

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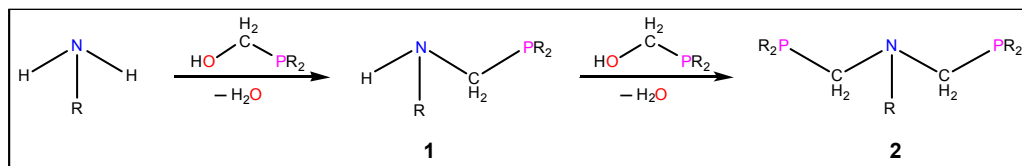
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Tertiary phosphines are a large class of fascinating ligands commonly used in platinum group metal (pgm) coordination chemistry. They play an important role in areas ranging from homogeneous catalysis to selective metal extraction chemistry and to therapeutic applications. In this article, pgm-containing complexes of new functionalised mono-, di- and polytertiary phosphines, derived from straightforward condensation reactions, are reviewed. These phosphines have been used as building blocks in supramolecular chemistry and for constructing novel hexanuclear pgm complexes, as ligands for bridging homo- and heterobimetallic late transition metals, and in the field of precious metal-based catalysis.

Tertiary phosphines arguably remain the lynchpin of much of our understanding about coordination chemistry, catalysis and other applications using metal complexes. Their extreme flexibility originates from the ease with which their steric and electronic properties, bite angle, solubility and chirality can be regulated in a precise and controlled way. Trivalent phosphorus ligands have frequently been used in coordination and organometallic chemistry as a means of stabilising the metal centre, typically a pgm. Tertiary phosphines can dictate the coordination number of a metal centre. For example, low-coordinate linear or trigonal planar geometries can be stabilised by bulky ligands such as tricyclohexylphosphine (PCy₃) and tri(*tert*-butyl)phosphine (P(^tBu)₃). Furthermore the electronic properties, and hence reactivity, of the metal centre can be influenced by substituents bound to the phosphorus donor atom. In our research group at Loughborough University, we have been interested in phosphorus

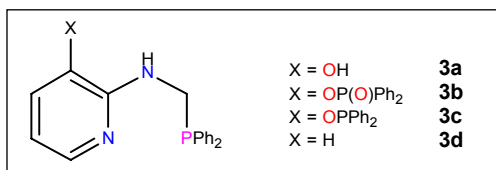
ligands for over a decade. In this article, some of our recent achievements are reviewed, along with contributions from others, in this stimulating field of pgm chemistry.

The preparative strategy for ligands 1 and 2, illustrated in Scheme I, relies on an established variant of the classic Mannich condensation reaction (1). In our work, many ligands of both types have been synthesised in high yields by a single step procedure, using a phosphorus-based Mannich condensation (PBMC) reaction. Adaptation of this simple methodology to non-symmetric ditertiary phosphines will also be discussed. Our initial contribution to this field stemmed from reports (2, 3) that diphenyl-2-pyridylphosphine (Ph₂P(2-C₅H₄N)) could be used, in conjunction with simple palladium(II) salts and a strong acid, typically *p*-toluenesulfonic acid (*p*-MeC₆H₄SO₃H), as an efficient homogeneous alkyne carbonylation catalyst system. Drent *et al.* (2) proposed that the 2-pyridyl (2-C₅H₄N) group is



Scheme I Synthetic approaches to new aminophosphine ligands 1 and 2

necessary for two reasons. Firstly, it facilitates the carbonylation of alkynes by accessing different coordination capabilities of $\text{Ph}_2\text{P}(2\text{-C}_5\text{H}_4\text{N})$, using the phosphorus and/or nitrogen donor atoms. Secondly, it acts as a 'proton messenger' through an intermediate Pd(II) species bearing a pendant pyridinium group. We have prepared new functionalised pyridylphosphines and investigated their ligating properties to pgms (4). As will be shown, hydrogen bonding, invariably using the secondary amine group, was a key aspect. Its action was characterised through crystallographic solid-state studies. Using the PBMC approach illustrated in Scheme I, the first ligand synthesised was 3a. Phosphine 3a and its derivatives 3b and 3c exhibited a plethora of coordination modes (monodentate, chelating, bridging) when complexed to an array of pgms such as ruthenium(II), rhodium(III), iridium(III) and platinum(II).



Recently, phosphine 3d was shown to bridge two dichloropalladium(II) ($\text{Cl}_2\text{Pd(II)}$) metal centres in a head-to-tail fashion (Figure 1), affording the 12-membered metallocycle 4 (5, 6). One feature we routinely observed when closely related pyridylphosphines were studied by single-crystal X-ray diffraction (XRD) was the presence of

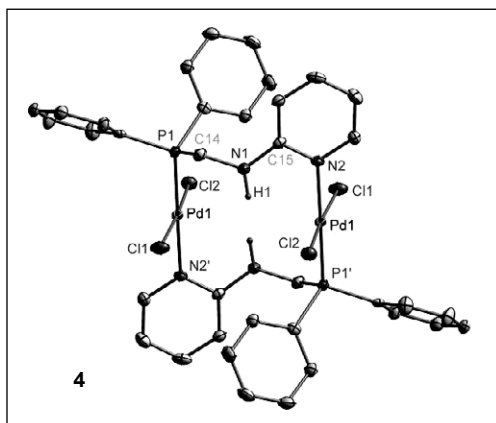


Fig. 1 Single crystal X-ray structure of palladium(II) phosphine complex 4

intermolecular H-bonded dimer pairs involving the secondary amine ($-\text{NH}$) group (7). These early findings prompted us to probe in more detail these secondary interactions with other pgm complexes of functionalised tertiary and ditertiary phosphines. In particular, the ability of carboxylic acids to associate through H-bonding led us to design and synthesise new ligands for supramolecular chemistry and crystal engineering.

Crystal Engineering

Given the versatility of tertiary phosphines, we were intrigued to find that their use in supramolecular chemistry is often reserved to that of spectator or ancillary ligand (8). Our efforts to study the solid-state packing behaviour of an isomeric series of metal complexes containing phosphorus-based ligands were thwarted by a lack of suitable examples in the literature. With this in mind, and identifying commercially available isomeric amines with hydroxyl/carboxylic acid groups as attractive reagents, a range of highly functionalised ditertiary phosphines were synthesised using a PBMC route (Scheme I). These were isolated in good to high yields and complexed to afford an isomeric series of seven square-planar dichloropalladium(II) compounds. Crystallographic studies showed that these complexes H-bond in a manner highly dependent on the disposition of the functional groups on the *N*-arene ring. Some of the isomers are shown in Figure 2. Solid-state structures are formed, composed of 20-membered dimer pairs, 5a, 1D-polymeric chains, 5b, or ladders, 5c, containing 38-membered rings (9).

More strikingly, changing the labile Pd(II) source from $\text{PdCl}_2(\text{cod})$ to $\text{Pd}(\text{CH}_3\text{Cl})(\text{cod})$ (cod = cycloocta-1,5-diene) afforded the novel self-assembled hexameric Pd compound 6 in high yield (10). In this example, the ligand bridges two Pd(II) metal centres *via* an unusual P_2O -tridentate coordination mode to give a large 48-membered metallocycle possessing a unique hexagonal arrangement. Other hexameric analogues, of nanometre dimensions, have also been reported (10). Self-assembly, using a range of H-bonding interactions, have also been studied in linear gold(I) complexes (11) and half-sandwich

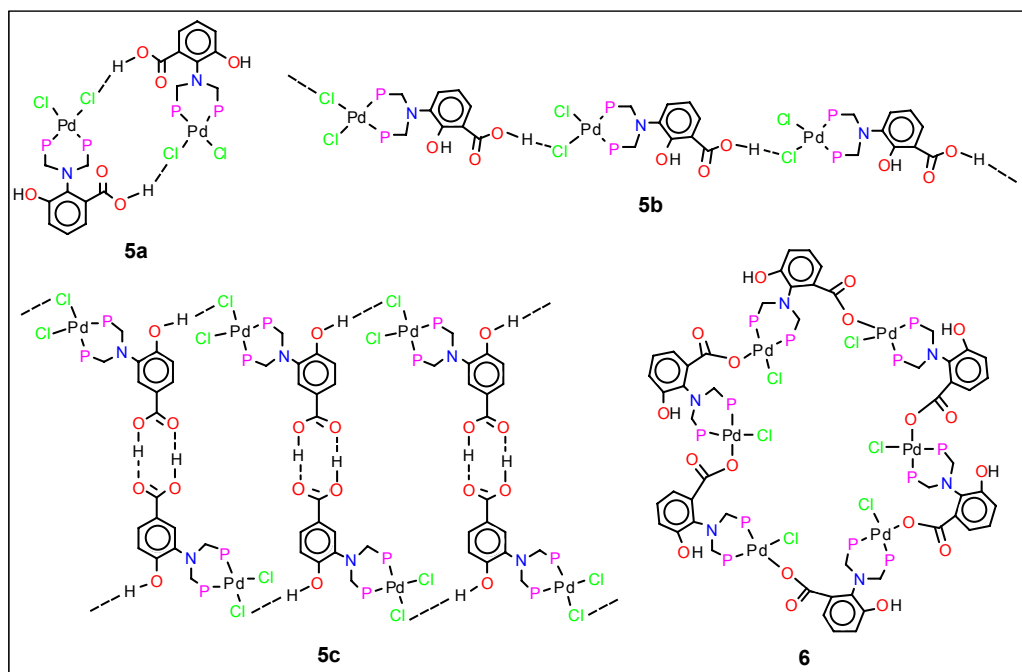


Fig. 2 Structural motifs of different square-planar palladium(II) phosphine complexes **5a–5c** and **6**. Phenyl groups on phosphorus (pink) are omitted for clarity and dashed lines indicate hydrogen-bonding contacts

organometallic Ru(II) complexes (**12**) using our isomeric phosphine ligands. This area of pgm tertiary phosphine chemistry, coupled with controlled H-bonding capabilities, coincides with new interest in supramolecular-based pgm catalysts (**13**).

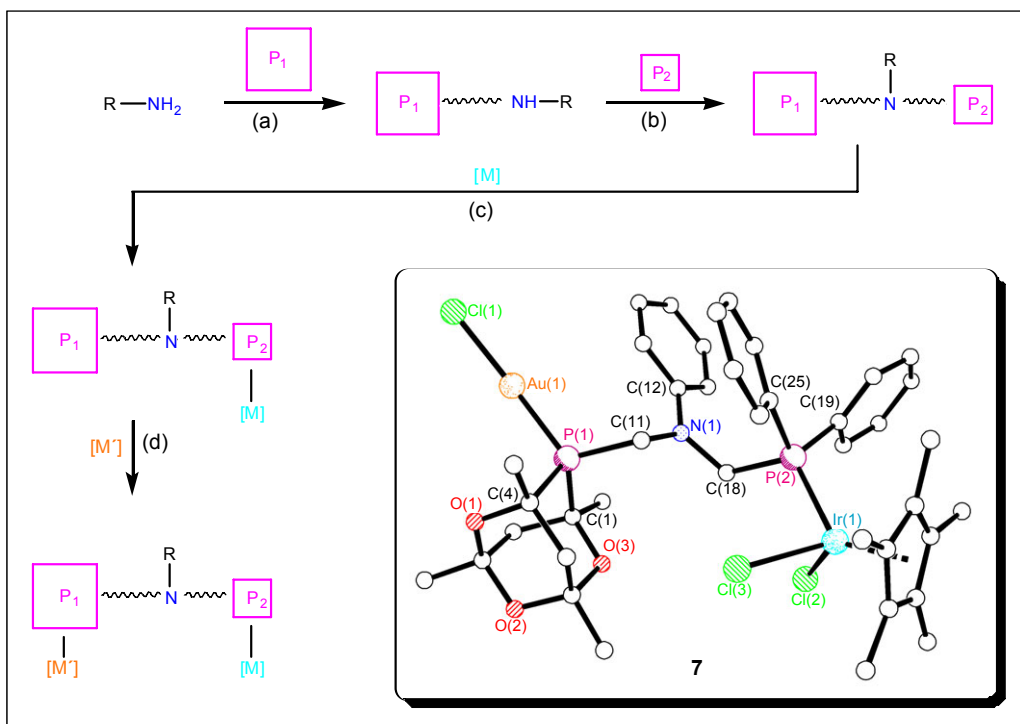
Mixed Metal Complexes

Symmetric diphosphines are normally known to use both phosphorus donor sites for coordination, thereby forming a classic chelate ring. We were interested in investigating whether, by manipulating the ligand structure, it would be possible to sequentially coordinate a metal centre at one P-donor site, then add a second metal centre to the remaining noncoordinated position (**14**). To accomplish this, our PBMC approach was modified such that two sterically dissimilar P-based groups (P_1 and P_2) could be introduced in two consecutive steps (Scheme II, Steps (a) and (b)). By choosing suitable pgm precursors, for example dichloro(*p*-cymene)ruthenium(II) dimer $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$, or a dichloropentamethylcyclopentadienyl metal dimer $[\text{MCl}_2(\text{Cp}^*)]_2$ ($\text{M} = \text{Rh}, \text{Ir}$), novel

organometallic ‘piano-stool’ complexes were obtained (Scheme II, Step (c)). These ‘metalloligands’ were used to prepare heterobimetallic complexes (Scheme II, Step (d)) with distinct metal combinations such as Ru(II)/Au(I) or Ir(III)/Au(I), **7**. A recent extension to this work, using a new nonsymmetric ligand incorporating $-\text{PPh}_2$ and $-\text{PAd}$ groups (PAd = phosphaadamantane), allowed us to prepare Ru_2Pd and Ru_2Pt trinuclear complexes, in which the square-planar PdCl_2 or PtCl_2 metal centres have two bulky phosphaadamantane cages *trans* to each other (**15**).

Supported P–C–N–C–P Catalysts

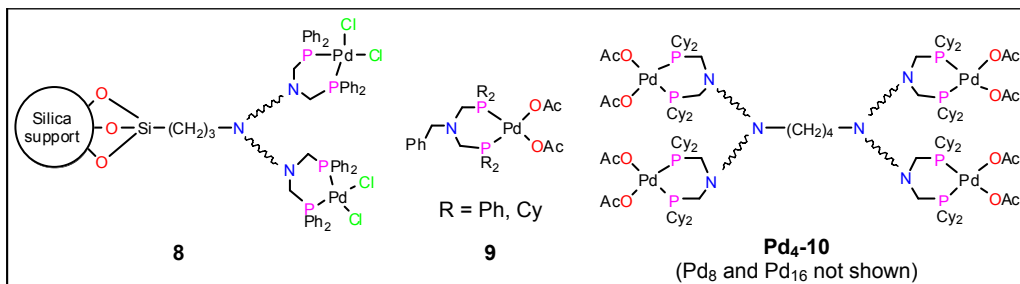
Complexes of the pgms are extremely valuable as catalysts for many homogeneous catalysed reactions in the chemical and pharmaceutical industries. While homogeneous catalysis offers many rewards over heterogeneous catalysis, its major handicap is the requirement to separate the catalyst from (by)products and unused reactants. This has important industrial implications, affecting the economic viability of a process. Modification of the skeletal P–C–N–C–P frame-



Scheme II Cartoon illustration showing the synthesis of mixed metal dinuclear phosphine complexes (P_1 and P_2 are P-based groups). The insert shows an X-ray structure of the heterobimetallic phosphine complex 7

work of ligand 2, shown in Scheme I, has enabled phosphines to be studied in homogeneous catalysis, and allowed the development of new methods for the separation of the pgm catalyst. The variety of these ligands will be illustrated later in this article, and hinges on the tunability of the R group on the central N atom, rather than on the P donor atoms as discussed previously. This facilitates attachment to different solid supports. The following examples serve to illustrate some recently published approaches, and highlight the importance of using chelating diphosphines to aid

catalyst stability. Lu and Alper (16) showed how the recovery and recycling of catalysts could be realised using dendrimers peripherally decorated with catalytically active Pd(II) metal centres, supported on silica gel. The preparation of dendrimer complexes on silica, such as 8, involved first synthesising the diphosphine by reaction of the appropriate primary amine with (hydroxymethyl)diphenylphosphine ($\text{Ph}_2\text{PCH}_2\text{OH}$), then complexing using the labile Pd(II) complex $\text{PdCl}_2(\text{PhCN})_2$. These Pd-based dendrimers were used for the intramolecular cyclocarbonylation of



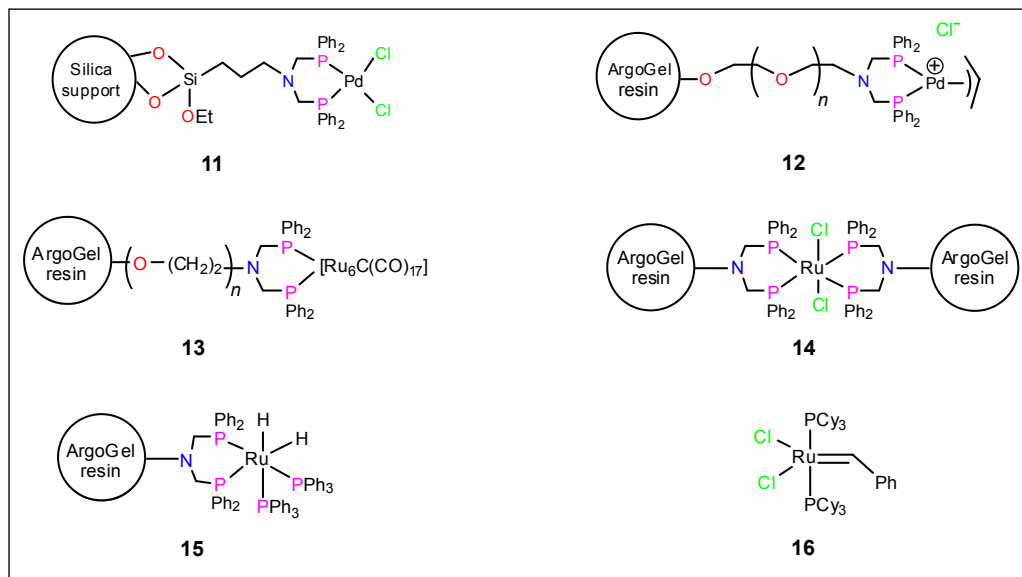
iodinated aryl amines and various 12- to 18-membered ring macrocycles were generated. Dendrimer complexes such as **8** attached to silica gel permitted simple filtration and reuse (up to eight times) without any significant diminution in catalytic activity.

On a similar theme, the monomeric complex **9** and metallodendrimer **Pd₄-10**, along with two higher generations related to **Pd₄-10**, were found to be efficient catalysts for Suzuki coupling reactions of chloro- and bromoarenes (17). Recovery and reuse was possible with the dendrimer-based Pd catalysts, while recovery of the single metal site complex **9** was hampered by rapid decomposition, affording a catalytically inactive black precipitate.

Two independent research groups (18, 19) have prepared the silica-supported P–C–N–C–P diphosphine catalyst **11** using the PBMC ligand synthesis strategy shown in Scheme I. Long and coworkers (18) loaded the supported catalyst **11** into standard teflon tubing and performed carbonylative cross-coupling reactions with different aryl halides and benzylamine. The microtube reactor permitted catalyst reuse for a number of cycles. ¹¹CO radiolabelled amides could also be synthesised by this method. Uozumi and Nakai (20) prepared a supported diphosphine from ArgoGel™-NH₂ (from Argonaut Technologies Inc, now owned by Biotage AB) and

Ph₂PCH₂OH, and characterised the product by gel-phase ³¹P magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopic studies. Reacting the diphosphine with the allylpalladium dimer [PdCl(η³-C₃H₅)₂] in toluene at 25°C for 15 min gave complex **12**. In aqueous potassium carbonate, complex **12** was an effective catalyst for the Suzuki-Miyaura coupling of aryl halides and aryl- or vinylboronic acids and could be reused up to three times. Employing the same tactic for attachment to solid supports, treatment of the commercially available ArgoGel™ amine resin with diphenylphosphine/paraformaldehyde (Ph₂PH/(CH₂O)_n), followed by addition of [Ru₆C(CO)₁₇], gave compound **13** as dark red beads (21). No catalytic data was reported for **13**; however, phosphine-free [Ru₆C(CO)₁₇] variants were shown to be promising hydrogenation catalysts for cyclohexene.

Related phosphine-modified ArgoGel™ amine-based compounds, in this instance containing the pentaruthenium cluster [Ru₅C(CO)₁₅], were shown to act as gas sensors for hydrogen sulfide (H₂S), carbon monoxide (CO) and sulfur dioxide (SO₂) (22). Changes were monitored by Fourier transform infrared (FTIR) spectroscopy and by colour changes of the beads prior to and after gas addition. Furthermore the ArgoGel™-NH₂ resin was used to prepare sup-



ported octahedral Ru(II) diphosphine complexes 14 and 15 as brown and yellow beads respectively (23). Both compounds were shown to hydrogenate supercritical carbon dioxide in the presence of dimethylamine (HN(CH₃)₂) to give dimethylformamide (DMF, HCON(CH₃)₂). The catalysts could be reused up to four times, after decantation and drying under vacuum, with some loss in catalytic activity. Polymer-based phosphine resins have recently been shown to act as scavengers for removal of Grubbs' catalyst, 16, from reaction mixtures, and could be separated by simple filtration delivering > 95% Ru-free reaction products (24).

Conclusions and Future Work

The PBMC approach continues to be an attractive, yet simple, preparative method for accessing new trivalent phosphorus(III) ligands. Phosphines offer important insights into how structural ligand modifications can be made, allowing different ligating modes to be adopted at pgm centres. Furthermore, careful incorporation of highly polar functional groups can lead to diverse solid-state

structures. The ease of using the PBMC approach to target late transition metal-based catalysts, with recyclable properties, offers practical alternatives in the field of homogeneous catalysis.

Unpublished recent work from our group has taken us back to some earlier studies reviewed in *Platinum Metals Review* (25). We are using tetrakis(hydroxymethyl)phosphonium chloride (THPC), itself a precursor used to prepare tris(hydroxymethyl)phosphine (THP), as a starting reagent for the preparation of neutral and cationic phosphorus-containing ligands. The pgm coordination chemistry of these new ligands has provided us with some interesting results that will be published shortly (26).

Acknowledgements

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Martin Smith was born in Royston, Hertfordshire, U.K., and grew up in the neighbouring village of Melbourn. He was awarded a B.Sc. in Chemistry at the University of Warwick, U.K., and completed his Ph.D. at Bristol University in the group of Professor Paul Pringle. After postdoctoral positions and a Royal Society Fellowship with Professors Tony Deeming (University College London), Brian James (University of British Columbia, Canada) and Derek Woollins (Loughborough University) he took up a Lectureship at Loughborough University in 1997. He was promoted to Senior Lecturer in 2008. His research interests are focused on pgm phosphine complexes and their applications in catalysis.