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ARTICLE

Multidentate 2-pyridyl-phosphine ligands – towards ligand tuning and chirality

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In the current work a range of multidentate pyridyl-phosphine ligands are synthesised with tuneable electronic and steric character, through the incorporation of a variety of alcohols into (amino)pyridyl-phosphine frameworks. The stoichiometric reactions of compounds of the type $(R_2N)_xP(2\text{-py})_{3-x}$ (2-py = 2-pyridyl) with alkyl as well as aryl alcohols result in the formation of (alkoxy)pyridyl-phosphines $(RO)_xP(2\text{-py})_{3-x}$ (R = Me, 2-Bu, Ph). This synthetic procedure also allows the introduction of enantiomerically pure alcohols, like (*R*)-(-)-2-BuOH and (*S*)-(+)-2-BuOH, and as such provides a very convenient two-step route to chiral multidentate pyridyl-phosphine ligand sets. Using the bis-amino-phosphine $(Et_2N)_2P(2\text{-py})$, the stepwise introduction of alcohols enables the synthesis of racemic alkoxy-amino-phosphines $(R_2N)(RO)P(2\text{-py})$, as well as alkoxy-phosphines $(RO)_2P(2\text{-py})$ and therefore offers easy access to a library of different pyridyl-phosphine ligands. Coordination studies of the (amino)pyridyl-phosphines and (alkoxy)pyridyl-phosphines with copper(I) reveal that ligands with two N donor atoms form dimeric arrangements, while $(PhO)_2P(2\text{-py})$, in-corporating only one N donor atom, shows completely different coordination behaviour.

Introduction

Tripodal ligands are facially-coordinating, chelate ligands which possess C_3-symmetry, and which have been applied extensively in coordination, organometallic and bioinorganic chemistry.[1] In particular, the rigid character of these ligands provides a high degree of stereochemical control in single-site catalysis, due to a reduced number of competing asymmetric environments in intermediate octahedral transition metal species.[2] In this context, a large number of studies have focused on the applications of tris-azolyl borates (Fig. 1a) and (to a lesser extent) closely related tris-pyridyl derivatives (Fig. 1b) in catalysis.[3–5]

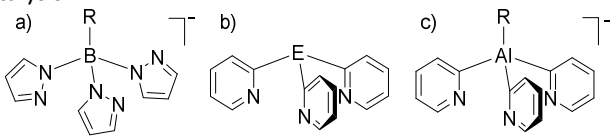

Figure 1. (a) Family of tris-azolyl borates $[HB(pz)_3]^-$, (b) neutral tripodal tris-pyridyl ligands $[E(2\text{-py})_3]$ [E = CX (X = H, OR, NH_2), N, P, P=O, As] and (c) the aluminium tris-pyridyl counterparts $[RAl(2\text{-py})_3]^-$.

As far as tris-2-pyridyl ligands are concerned, until recently studies have almost exclusively focused on ligands containing non-metal bridgeheads $[E(2\text{-py})_3]$ [2-py = 2-pyridyl, E = CX (X = H, OR, NH_2), N, P, P = O, As]. More recently, isoelectronic tripodal counterparts containing Group 13 and 14 metallic or semi-metallic bridgeheads, like aluminium, have been explored (Fig. 1c).[6–11] However, the high air-sensitivity and reactivity of the metal-bridged pyridyl compounds limit their applications as ligands in catalysis and other more robust systems, like 2-pyridyl-phosphines, have been the centre of interest.[12–17]

Although the reactivity[18–20] and coordination chemistry[4,21–26] of 2-pyridyl-phosphines have been studied in the last three decades, mixed-ligand pyridyl-phosphines and chiral examples have been largely overlooked. The introduction of chirality into pyridyl-phosphines (*via* chirality at the P atom[20] or the introduction of a chiral substituent) is a logical extension of this area which can be seen as related to similar developments of other stereogenic phosphorus ligands which have dominated the area of asymmetric catalysis, like BINAP,[27] DuPhos[28–30] and DIPAMP.[31,32] To date, only a few mixed-ligand examples of 2-pyridyl-phosphines have been reported in the literature, which are mainly based on phenyl analogues, such as diphenyl(2-pyridyl)phosphine, $Ph_2P(2\text{-py})$, and phenyl-bis(2-pyridyl)phosphine, $PhP(2\text{-py})_2$.[33–43] Other derivatives like $(Me_2N)_2P(2\text{-py})$,[44] $EtPhP(2\text{-py})$,[45] $CyP(2\text{-py})_2$,[46] lithiated phosphanylamine $[Li\{(2\text{-py})_2PNSiMe_3\}]_2$[47] or (2-picolyl)phosphane derivatives, like Ph_2PPic (Pic = 2-picolyl, CH_2-2-py)[48–51]and $Ph_2P(NSiMe_3)Pic$,[52,53] have been investigated but represent rare examples in this field.

Encouraged by the potential for new developments in this area, our focus in the current paper is to (i) explore synthetic routes to new multidentate pyridyl-phosphine ligands, (ii) to investigate the synthetic route(s) which may allow chiral examples to be obtained and (iii) to examine the coordination behaviour of the new ligands. For this purpose we have employed mono- and bis-amino-phosphines of the types

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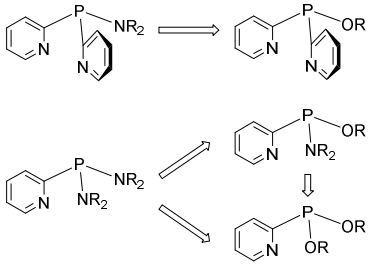
$(R_2N)_xP(2\text{-py})_{3-x}$ (where R = organic substituent, and x = 1 or 2) as the primary precursors which are readily functionalised by reactions with alcohols, yielding new (alkoxy)pyridyl-phosphines $(RO)_xP(2\text{-py})_{3-x}$ (Scheme 1).



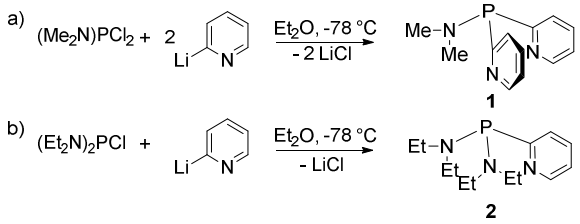
Scheme 1. (Amino)pyridyl-phosphines and their post-functionalisation.

Results and Discussion

Synthesis of (amino)pyridyl-phosphines

Amino-phosphines $(R_2N)P(2\text{-py})_2$ and bis-amino-phosphines $(R_2N)_2P(2\text{-py})$ are potentially interesting precursors to other ligand frameworks, since the greater polarity of the P-N bond,[53,54] in contrast to the P-C bond, should facilitate selective reaction with organic acids. Previously, amino-phosphine precursors have been employed in the synthesis of alkoxy-amino-phosphine ligands.[55–58] However, only two examples of bis-amino-pyridyl compounds of the type $(R_2N)_2P(2\text{-py})$ have been reported in the literature, $(Me_2N)_2P(2\text{-py})$[44] and $(Et_2N)_2P(6\text{-O}t\text{Bu-2-py})$.[59] Also some di-2-picolylphenylphosphane related amino derivatives have been described, *e. g.* $[Ph_2P(CH_2py)(NH_2)][N_3]$.[60]

In the current work, the (amino)pyridyl-phosphines $(Me_2N)P(2\text{-py})_2$ (**1**) and $(Et_2N)_2P(2\text{-py})$ (**2**) were obtained from the reactions of the corresponding phosphorus chlorides $(Me_2N)PCl_2$[61] and $(Et_2N)_2PCl$[61] (respectively) with *in situ* generated 2-pyridylithium at -78 °C in a 1 : 2 or 1 : 1 molar ratio (Scheme 2).§



Scheme 2. Synthesis of (a) the amino-phosphine **1** and (b) the bis-amino-phosphine **2**.

The reaction of $(Me_2N)PCl_2$ and Li(2-py) produced a mixture of compound **1** and other unidentified P-containing products (in addition to LiCl).§§ Pure samples of $[\{(Me_2N)P(2\text{-py})_2\}(LiCl)_3\cdot 2THF]_2$ ($[\mathbf{1}(LiCl)_3\cdot 2THF]_2$) could be obtained by crystallisation. Single-crystal X-ray analysis of $[\mathbf{1}(LiCl)_3\cdot 2THF]_2$ shows that the two $(Me_2N)P(2\text{-py})_2$ ligands in the molecular structure chelate two separate Li^+ cations using their two pyridyl nitrogen atoms (Fig. 2a), with the NMe_2 groups of each ligand remaining uncoordinated. A dimeric structure is formed which contains a central hexameric $(LiCl)_6$ core (Fig. 2b), in which two $(LiCl)_2$ ring units are bridged by two $(Me_2N)P(2\text{-py})_2$ chelated Li^+ and two Cl^- ions. To the best of our knowledge, the $(LiCl)_6$ core arrangement in $[\mathbf{1}(LiCl)_3\cdot 2THF]_2$ is unprecedented among previously reported Li-salt complexes.

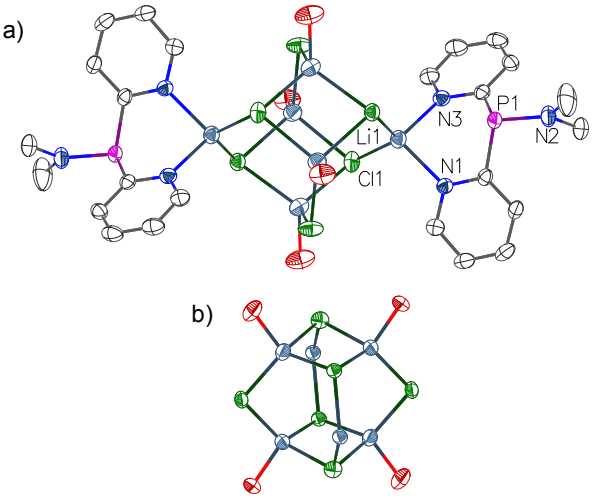
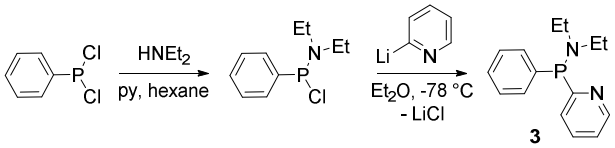


Figure 2. Structure of (a) $[\{(Me_2N)P(2\text{-py})_2\}(LiCl)_3\cdot 2THF]_2$ ($[\mathbf{1}(LiCl)_3\cdot 2THF]_2$) and (b) the $(LiCl)_6$ core. Hydrogen atoms and carbon atoms of the THF moieties are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): P(1)–C_{py}(11) 1.847(3), P(1)–C_{py}(31) 1.849(3), P(1)–N(2) 1.666(3), N_{py}(1)–Li(1) 2.044(5), N_{py}(3)–Li(1) 2.040(6), C_{py}(11)–P(1)–C_{py}(31) 100.1(2), C_{py}(11)–P(1)–N(2) 104.6(2), C_{py}(31)–P(1)–N(2) 104.2(2), P(1)–C_{py}(11/21)–N_{py}(1/3) 115.5(2), N_{py}(1)–Li(1)–N_{py}(3) 91.5(2). Blue = N, purple = P, grey = C, green = Cl, teal = Li, red = O.

Interestingly, the Me_2N group of the $(Me_2N)P(2\text{-py})_2$ ligand in $[\mathbf{1}(LiCl)_3\cdot 2THF]_2$ is almost planar (sum of RNR angles is 360°) and DFT calculations on the isolated ligand **1** (without the LiCl core) show that the HOMO involves significant electron donation from the N lone-pair electrons of the Me_2N group into one of the P-C(2-py)σ* orbitals (see ESI, Fig. S1a). This is similar to the situation found in the tungsten(0) complex $[\{(Me_2N)_2P(2\text{-py})\}][W(CO)_4]$, in which one of the Me_2N groups is again almost planar.[44]

The reaction of $(Et_2N)_2PCl$ and Li(2-py) gives the (amino)pyridyl-phosphine $(Et_2N)_2P(2\text{-py})$ (**2**), which was obtained as a pale yellow oil. Looking at the HOMO obtained from a DFT calculation of **2** (Fig. S1b), a completely different picture emerges compared to **1**. In this case the electron density is mainly located on the P-atom, which may explain the completely different coordination behaviour of the two ligands, discussed later.

As part of these studies we also prepared the related ligand $Ph(Et_2N)P(2\text{-py})$ (**3**), containing three different organic substituents, from the reaction of Li(2-py) with $Ph(Et_2N)PCl$[62] (Scheme 3). Since **3** has three different substituents, the P is stereogenic, although it is obtained as a racemic mixture.

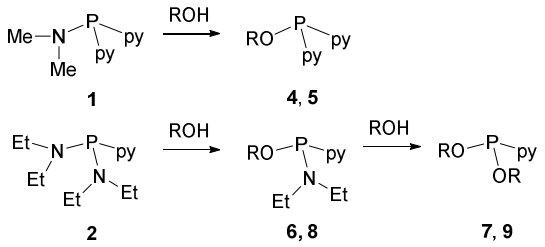


Scheme 3. Synthesis of the tri-substituted pyridyl-phosphine **3**.

Synthesis of (alkoxy)pyridyl-phosphines

The reaction of the (amino)pyridyl-phosphines $[\mathbf{1}(LiCl)_3{\cdot}2THF]_2$ and **2** with a variety of alcohols has proved to be a straightforward strategy to the desired (alkoxy)-2-pyridyl-phosphines (Scheme 4). This synthetic method not only gives access to a rarely studied ligand class[59,63,64] of multidentate (alkoxy)pyridyl-phosphines, but also allows the stepwise introduction of two different OR groups (in the case of **2**).

Previously, access to these alkoxy species has been limited due to the synthetic challenges involved in the synthesis of the key precursors $Cl_xP(2\text{-py})_{3-x}$.[§§§]



Scheme 4. Synthesis of (alkoxy)pyridyl-phosphines (R = Me, 2-Bu, Ph, py = 2-pyridyl).

The Me_2N-group in the amino(pyridyl)-phosphine $[\mathbf{1}(LiCl)_3{\cdot}2THF]_2$ can easily be replaced by a variety of alcohols. The reaction of MeOH with crude **1** gives the dimeric LiCl complex $[\{(MeO)P(2\text{-py})_2\}LiCl]_2$ ($[\mathbf{4}{\cdot}LiCl]_2$) after crystallisation (Fig. 3).

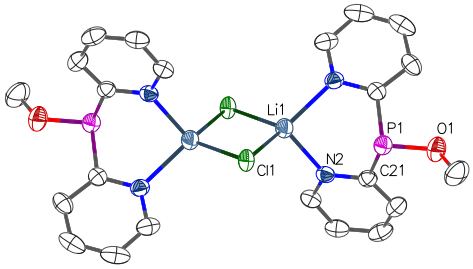


Figure 3. Structure of $[\{(MeO)P(2\text{-py})_2\}LiCl]_2$ ($[\mathbf{4}{\cdot}LiCl]_2$). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): $P(1)–C_{py}(11)$ 1.842(2), $P(1)–C_{py}(21)$ 1.843(2), P(1)–O(1) 1.629(2), $N_{py}(1)–Li(1)$ 2.105(4), $N_{py}(2)–Li(1)$ 2.052(5), $C_{py}(11)–P(1)–C_{py}(21)$ 96.3(1), $C_{py}(11)–P(1)–O(1)$ 99.3(1), $C_{py}(21)–P(1)–O(1)$ 100.8(1), $P(1)–C_{py}(11)–N_{py}(1)$ 112.9(2), $P(1)–C_{py}(21)–N_{py}(2)$ 113.7(2), $N_{py}(1)–Li(1)–N_{py}(2)$ 92.0(2). Blue = N, purple = P, grey = C, green = Cl, teal = Li, red = O.

This method was readily extended to the more sterically demanding 2-butanol. The reaction of crude **1** with racemic 2-butanol results in the formation of $(2\text{-BuO})P(2\text{-py})_2$ (**5**). The solid-state structure of **5** (Fig. 4) also consists of a dimeric lithium chloride complex $[\mathbf{5}{\cdot}LiCl]_2$, with a similar molecular structure to $[\mathbf{4}{\cdot}LiCl]_2$. This strategy allows the facile introduction of chirality, using the commercially-available (*S*)- and (*R*)-enantiomers of 2-butanol. *In situ* ^{31}P NMR spectroscopic studies using the chiral alcohols in place of the racemic 2-butanol indicate ca. 90 % conversion to the corresponding chiral phosphines (**5-*S*** and **5-*R***) under the same conditions.

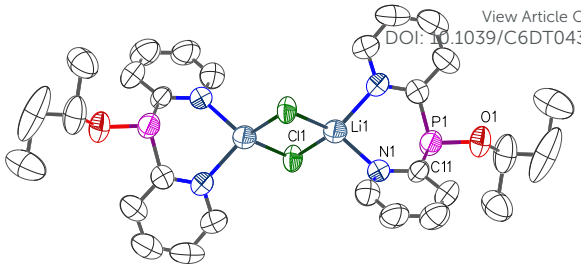


Figure 4. Structure of $[\{(2\text{-BuO})P(2\text{-py})_2\}LiCl]_2$ ($[\mathbf{5}{\cdot}LiCl]_2$). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): $P(1)–C_{py}(11)$ 1.843(6), $P(1)–C_{py}(21)$ 1.838(6), P(1)–O(1) 1.618(5), $N_{py}(1)–Li(1)$ 2.06(1), $N_{py}(2)–Li(1)$ 2.09(1), $C_{py}(11)–P(1)–C_{py}(21)$ 97.8(3), $C_{py}(11)–P(1)–O(1)$ 99.5(3), $C_{py}(21)–P(1)–O(1)$ 100.9(3), $P(1)–C_{py}(11)–N_{py}(1)$ 113.9(4), $P(1)–C_{py}(21)–N_{py}(2)$ 115.81(4), $N_{py}(1)–Li(1)–N_{py}(2)$ 92.6(4). Blue = N, purple = P, grey = C, green = Cl, teal = Li, red = O.

A comparison of the phosphine ligands in the structures of $[\mathbf{1}(LiCl)_3{\cdot}2THF]_2$, $[\mathbf{4}{\cdot}LiCl]_2$ and $[\mathbf{5}{\cdot}LiCl]_2$ shows that they are more pyramidal for the alkoxy-substituted ligands, with the sum of bond angles about the P-atoms being 309 ° in $[\mathbf{1}(LiCl)_3{\cdot}2THF]_2$, 296 ° in $[\mathbf{4}{\cdot}LiCl]_2$ and 298 ° in $[\mathbf{5}{\cdot}LiCl]_2$ (despite the increase in the steric congestion in $[\mathbf{5}{\cdot}LiCl]_2$ compared to $[\mathbf{1}(LiCl)_3{\cdot}2THF]_2$). This trend can be interpreted in terms of VSEPR theory, since there is less bonding-pair/bonding-pair repulsion in the (alkoxy)pyridyl-phosphines.

The reaction of $(Et_2N)_2P(2\text{-py})$ (**2**) with different alcohols allows the stepwise introduction of alkoxy groups, depending on the nucleophilicity of the alcohol used. In the case of more nucleophilic MeOH the isolation of the mono-substituted product $(Et_2N)(MeO)P(2\text{-py})$ (**6**) did not prove to be possible at room temperature, since the di-substituted product $(MeO)_2P(2\text{-py})$ (**7**) is formed simultaneously even in the 1 : 1 stoichiometric reaction of **2**. *In situ* ^{31}P NMR spectroscopic studies revealed that after the formation of ca. 30 % of **6** the formation of di-substituted **7** starts to occur. Di-substituted $(MeO)_2P(2\text{-py})$ (**7**) is obtained from the reaction of **2** in MeOH as the solvent. In contrast, an *in situ* ^{31}P NMR spectroscopic study of the reaction of PhOH with **2** in toluene at reflux shows that the 1 : 1 reaction produces mono-substituted $(Et_2N)(PhO)P(2\text{-py})$ (**8**) and that the addition of a second equivalent gives the di-substituted product $(PhO)_2P(2\text{-py})$ (**9**) (see ESI, Fig. S35). The new ligands **8** and **9** can be obtained easily from the preparative scale reactions as pale yellow oils.

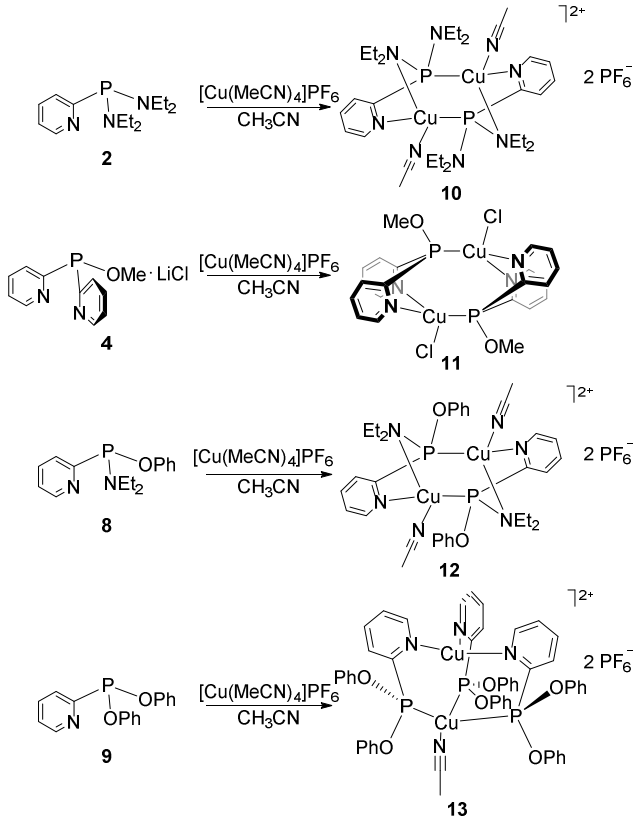
Copper(I) complexes of (amino)pyridyl-phosphines and (alkoxy)pyridyl-phosphines

The coordination chemistry of the synthesised phosphines was studied with Cu^I. In the past, copper(I) pyridyl-phosphine complexes have been of interest in catalysis[65,66] and because of their interesting photo-optical properties.[67–71]

Attempts to employ the mono-substituted ligand $(Me_2N)P(2\text{-py})_2$ ($[\mathbf{1}(LiCl)_3{\cdot}2THF]_2$) with Cu^I and other transition metal precursors using various reaction conditions were unsuccessful. However, the reaction of $(Et_2N)_2P(2\text{-py})$ (**2**) with $[Cu(MeCN)_4]PF_6$ in MeCN results in the formation of $[(MeCN)Cu\{(Et_2N)_2P(2\text{-py})\}]_2(PF_6)_2$ (**10**, Scheme 5). Similarly to

previously reported diamagnetic iron(II) and copper(I) complexes of P(2-py)$_3$ and P(6-Me-2-py)$_3$, the P-resonance of the $(Et_2N)_2P$(2-py) ligand in **10** is shifted upfield in the $^{31}P\{^1H\}$ NMR spectrum with respect to the uncoordinated ligand **2**.[17]

The different coordination behaviour of **1** compared to **2** is analogous to di-2-picolylphenylphosphane ligands, which have been investigated by electron density studies.[72]



Scheme 5. Synthesis of the Cu^I pyridyl-phosphine complexes (**10** - **13**).

The solid-state structure of **10** (Figure 5), determined by single-crystal X-ray crystallography, is that of a centrosymmetric dimer. In **10** one of the NEt_2 groups of each of the ligands **2** does not coordinate Cu^I, with each Cu^I ion being chelated by the N-atoms of the remaining NEt_2 group and the 2-py group of each ligand. The dimeric structure comes about by the formation of inter-monomer Cu-P bonds to the bridgehead P-atom of **2**.

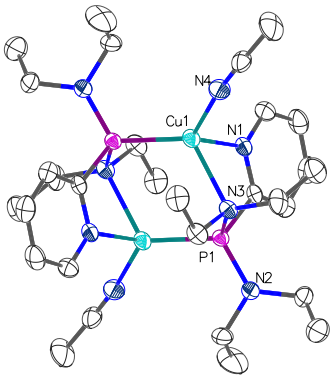


Figure 5 Dimeric structure of $[(MeCN)Cu\{(Et_2N)_2P(2\text{-py})\}]_2(PF_6)_2$ (**10**). Hydrogen atoms as well as the PF_6^- counterions are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): P(1)–C_{py}(11) 1.833(3), P(1)–N(2) 1.658(3), P(1)–N(3) 1.740(2), P(1)–Cu(1) 2.9234(8), P(1)–Cu(1′) 2.2137(8), N_{py}(1)–Cu(1) 2.072(2), N(3)–Cu(1) 2.334(3), P(1)–C_{py}(11)–N_{py}(1) 113.2(2), P(1)–Cu(1′)–N_{py}(1′) 118.74(4), P(1)–Cu(1′)–N(3′) 118.77(6). Blue = N, purple = P, grey = C, turquoise = Cu.

The reaction of the (alkoxy)pyridyl-phosphine [**4**·LiCl]$_2$ with $[Cu(MeCN)_4]PF_6$ in THF resulted in the formation of a few crystals of $[ClCu\{(MeO)P(2\text{-py})_2\}]_2$·MeOH (**11**·MeOH, Scheme 5).[§§§] The transition metal complex, which is the first example of a metal complex of an alkoxy-(bis-pyridyl) ligand, is very similar to **10** and again consists of a centrosymmetric dimer, in which each Cu^I atom is chelated by the two pyridyl-N atoms of one of the two ligands **4** and by the P-bridgehead atom of the other ligand (Fig. 6). The MeO groups of the ligands **4** are not coordinated to Cu^I, as might be expected on the basis of hard-soft concepts.

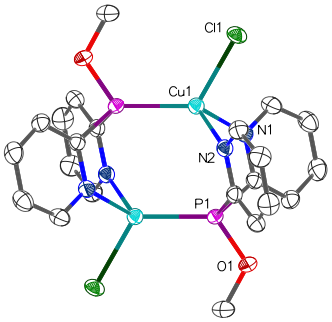


Figure 6. Structure of $[ClCu\{(MeO)_2P(2\text{-py})\}]_2$·MeOH (**11**·MeOH). Hydrogen atoms and the MeOH molecule are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): P(1)–C_{py}(11) 1.833(3), P(1)–C_{py}(21) 1.839(2), P(1)–O(1) 1.616(2), P(1)–Cu(1) 3.2108(7), P(1)–Cu(1′) 2.1641(8), N_{py}(1)–Cu(1) 2.078(2), N_{py}(2)–Cu(1) 2.072(3), P(1)–C_{py}(11)–N_{py}(1) 115.2(2), P(1)–C_{py}(21)–N_{py}(2) 115.7(2), P(1)–Cu(1′)–N_{py}(1′) 118.78(7), P(1)–Cu(1′)–N_{py}(2′) 119.76(7). Blue = N, purple = P, grey = C, green = Cl, red = O, turquoise = Cu.

The reaction of $(Et_2N)(PhO)P$(2-py) (**8**) with $[Cu(MeCN)_4]PF_6$ in MeCN yielded crystals of $[(MeCN)Cu\{(Et_2N)(PhO)P(2\text{-py})\}]_2(PF_6)_2$ (**12**, Fig. 7). Again as observed for **10**, the $^{31}P\{^1H\}$ singlet for **12** is broadened and shifted upfield relative to the free ligand. In the dimeric structure, the Cu^I atoms are chelated by the N-atoms of the Et_2N and 2-py groups of one of the ligands **8** as well as the P-bridgehead of the second ligand molecule. The PhO-groups of both ligand molecules remain uncoordinated. The structure is therefore very similar to that seen for **10** and **11**·MeOH.

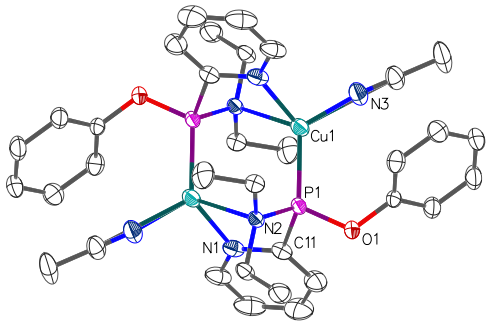


Figure 7. Dimeric structure of $[(MeCN)Cu\{(Et_2N)(PhO)P(2\text{-py})\}]_2(PF_6)_2$ (**12**). Hydrogen atoms as well as the PF_6^- counterions are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): P(1)–C_{py}(11) 1.824(2), P(1)–N(2) 1.676(2), P(1)–O(1) 1.636(1), P(1)–Cu(1) 2.9613(6), P(1)–Cu(1′) 2.1974(6), N_{py}(1)–Cu(1) 2.055(2), N(2)–Cu(1) 2.543(2), P(1)–C_{py}(11)–N_{py}(1) 112.9(1),

P(1)–Cu(1′)–N_{py}(1′) 119.60(5), P(1)–Cu(1′)–N(2′) 112.82(4). Blue = N, purple = P, grey = C, red = O, turquoise = Cu.

Ligands **2**, [**4**·LiCl]$_2$ and **8**, which contain at least two nitrogen atoms, produce similar structural arrangements with Cu^{I}. Interestingly, however, when only one nitrogen atom is present for coordination to the soft Cu^{I} centre, as in $(PhO)_2P(2\text{-py})$ (**9**), a completely different type of complex is formed. The reaction of **9** with $[Cu(MeCN)_4]PF_6$ in MeCN under reflux conditions gives $[(MeCN)Cu_2\{(PhO)_2P(2\text{-py})\}_3](PF_6)_2\cdot 3THF$ (**13**·3THF, Scheme 5, Fig. 8).

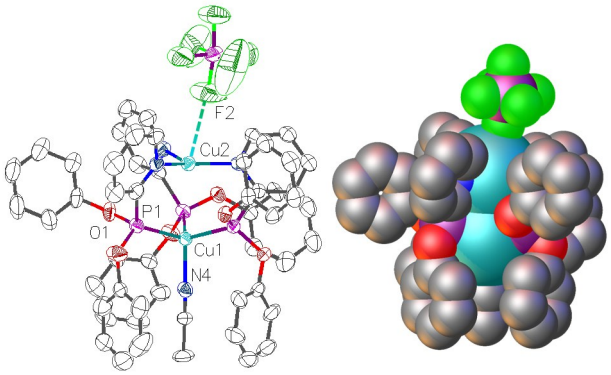
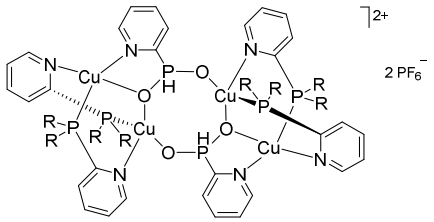


Figure 8. Structure of $[(MeCN)Cu_2\{(PhO)_2P(2\text{-py})\}_3](PF_6)_2\cdot 3THF$ (**13**·3THF) (left) and the space filling diagram (right). Hydrogen atoms, one PF_6^- counterion as well as the THF molecules are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): P–C_{py} 1.816(3)-1.827(3), P–O 1.601(3)-1.614(2), P–Cu(1) 2.2594(9)-2.2924(8), P–Cu(2) 3.062(1)-3.180(1), N_{py}–Cu(2) 1.983(2)-2.034(3), Cu(2)–F(2) 2.90(1), P–C_{py}–N_{py} 111.2(2)-114.3(3). Blue = N, purple = P, grey = C, green = F, red = O, turquoise = Cu.

In the binuclear complex $[(MeCN)Cu_2\{(PhO)_2P(2\text{-py})\}_3](PF_6)_2\cdot 3THF$ (**13**·3THF) one of the Cu^{I} centers [Cu(2)] is coordinated by three pyridyl-N atoms of three separate ligands **9**, as well being loosely coordinated by the F-atom of a PF_6^- anion (Cu•••F 2.90(1) Å) (the other of which, balancing the +2 charge, is not coordinated). Similar Cu•••F interactions have been seen in two-dimensional Cu^{II} coordination polymers of the type $\{[Cu(PF_6)(4,4'\text{-bpy})_2(MeOH)]\cdot PF_6\cdot 3MeOH\}_n$, in which Cu•••F distances of 2.306(3)-2.614(3) Å have been observed.[73] The remaining Cu^{I} center in **13**·3THF is bonded to the three P-atoms of the three ligands **9** and to a MeCN molecule, resulting in a pseudo-tetrahedral geometry. The bridging of the two Cu^{I} centers in **13**·3THF results in a short Cu•••Cu distance of 2.9431(7) Å. Similar Cu•••Cu distances were observed in dinuclear Cu^{I} complexes of $Ph_2P(2\text{-pypz})$ [(2-diphenylphosphino-6-pyrazol-1-yl)pyridine][74] and $Ph_2P(2\text{-py})$[68] but cannot be considered as significant metallophilic interactions. As seen before in the structures of **11** and **12**, the PhO groups of **9** are not bonded to Cu^{I}. Again this is due to the hardness of the O atoms relative to the soft N- and P-ligand set. Once more the $^{31}P\{^1H\}$ NMR shift of **13**·3THF is shifted upfield and the signal is broadened in comparison with the free ligand **9**.

When the reaction of **9** with $[Cu(MeCN)_4]PF_6$ in MeCN was carried out at room temperature (instead of at reflux), in addition to the broad signal at δ = 120.1 ppm (in CD_3CN) for **13** a sharp singlet at δ = 21.6 ppm was repeatedly observed in the $^{31}P\{^1H\}$ NMR spectrum. This signal splits into a doublet ($^1J_{PH}$ = 597.2 Hz) in the ^{31}P spectrum, suggesting the formation of a P-H containing species. Further confirmation of this comes from X-ray crystallography of crystals of this new species. This shows that the new complex is $[\{OP(O)(H)(2\text{-py})\}Cu_2\{(PhO)_2P(2\text{-py})\}_2](PF_6)_2\cdot 2THF$ (**14**·2THF), which contains $(PhO)_2P(2\text{-py})$ (**9**) and $[OP(O)(H)(2\text{-py})]^-$ ligands, the later ligand apparently resulting from hydrolysis of **9** by adventitious water. The formation of the $[OP(O)(H)(2\text{-py})]^-$ ligand accounts for the observation of a P-H resonance in the $^{31}P\{^1H\}$ NMR spectrum. The complicated centrosymmetric structural arrangement of **14**·2THF contains a central $Cu_2P_2O_4$ ring unit. The four Cu^{I} ions have pseudo-tetrahedral geometries, and are coordinated by the $[OP(O)(H)(2\text{-py})]^-$ ligands (using the two O- and the pyridyl-N atoms) and by the ligand **9** (using one of the pyridyl-N and the bridgehead P-atom) (Fig. 9). Compound **14**·2THF is not thermally stable. *In situ* ^{31}P NMR spectroscopic studies of a solution of crystals of **14**·2THF dissolved in MeCN shows that the $[OP(O)(H)(2\text{-py})]^-$ ligand completely decomposes after reflux (72 h), leaving only the resonance for $(PhO)_2P(2\text{-py})$ (**9**). This observation explains why **13**·3THF is formed exclusively in the reaction at reflux, in the absence of the hydrolysis product **14**·2THF.

a)



14

b)

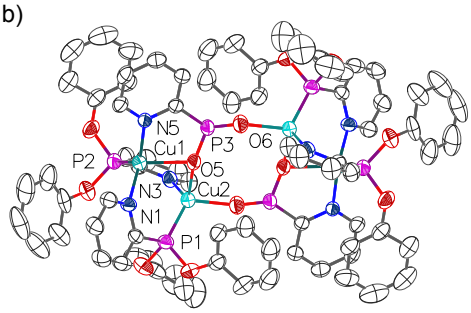


Figure 9. (a) Schematic structure (R = OPh) and (b) solid-state structure of $[\{OP(O)(H)(2\text{-py})\}Cu_2\{(PhO)_2P(2\text{-py})\}_2](PF_6)_2\cdot 2THF$ (**14**·2THF) Hydrogen atoms, PF_6^- counterions as well as THF molecules are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): P–C_{py} 1.815(6)-1.824(6), P–OPh 1.614(4)-1.631(4), P(3)–O 1.474(4)-1.490(4), P(1′)–Cu(2) 2.128(2), P(2′)–Cu(1) 2.148(2), N(1)–Cu(1)–N(3) 111.2(2), O(5)–Cu(2′)–O(6′) 100.5(2). Blue = N, purple = P, grey = C, red = O, turquoise = Cu.

Conclusions

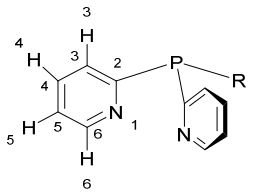
In the current work we have shown that the 2-pyridyl-phosphine ligand set can be extensively elaborated upon using a simple set of synthetic approaches. The alkoxy-phosphines $(RO)_xP(2\text{-py})_{3-x}$ are easily derived from amino-phosphines $(R_2N)_xP(2\text{-py})_{3-x}$ by direct reactions with alcohols. In addition, step-wise reaction of alcohols with the amino-phosphines can be used to obtain multidentate alkoxy-amino phosphines

(R_2N)(RO)P(2-py) (containing three different substituents). We have also investigated the coordination chemistry of a range of these new ligand systems for the first time, showing that both the pyridyl-N and bridgehead-P atoms can be involved in coordination to the soft Cu^{I} centres. Ligands of this type containing two or more N-donor atoms show completely different coordination behaviour to those in which only one N-donor is present.

The synthetic approach that we have developed for easy modification of the 2-pyridyl-phosphine ligand framework provides the potential means for the introduction of chirality, by creating stereogenic P-bridgeheads or through the introduction of chiral alkoxide groups. Transition metal complexes of this type could find versatile applications in asymmetric catalytic reactions.

Experimental Section

All experiments were carried out on a Schlenk-line under N_2 atmosphere or in an N_2-filled glove box (Saffron type α). Toluene, diethyl ether *n*-hexane and THF were dried under nitrogen over sodium or sodium/benzophenone, respectively, whereas acetonitrile, methanol and dichloromethane were dried over calcium hydride. 2-Bromopyridine and phosphorus trichloride were purified by distillation prior to use. All other reagents were used as purchased from the supplier. $(Me_2N)PCl_2$[59] and $(Et_2N)_2PCl$[61] and $Ph(Et_2N)PCl$[62] were prepared according to literature procedures. ^{1}H, $^{13}C\{^{1}H\}$, $^{7}Li\{^{1}H\}$, $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra were recorded on a Bruker Avance 400 QNP or Bruker Avance 500 MHz cryo spectrometer. ^{1}H, $^{13}C\{^{1}H\}$, $^{7}Li\{^{1}H\}$, $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra at 298 K were measured at 400.14 MHz, 100.63 MHz, 161.98 MHz and 155.51 MHz, respectively, unless noted otherwise. δ and *J* values are given in ppm and Hz, respectively. All spectra were recorded in $CDCl_3$, CD_3CN, d_8-THF, CD_3COCD_3 or d_8-toluene with $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P, 85% in D_2O) as external standards. Unambiguous assignments of NMR resonances were made on the basis of 2D NMR experiments (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments). Scheme 6 depicts the labelling scheme for NMR assignments used in the experimental section. Elemental analyses were obtained using a Perkin Elmer 240 Elemental Analyser.



Scheme 6. Atom labelling scheme used in the NMR studies for the pyridyl-phosphine compounds.

Synthesis of $(Me_2N)P(2\text{-py})_2$ ($[1(LiCl)_3{\cdot}2THF]_2$). 2-Bromopyridine (1.53 mL, 2.53 g, 16 mmol) in 20 mL of diethyl ether was added dropwise over a period of 30 min to a solution of *n*BuLi (10.00 mL, 16 mmol, 1.6 M in *n*-hexane) at -78 °C. The resulting dark orange solution was stirred for 3 h at -78 °C. To this dark red mixture, $(Me_2N)PCl_2$ (0.92 mL, 1.17 g, 8 mmol) in 15 mL of diethyl ether was added. After the addition, the suspension was allowed to warm to room temperature overnight. The formed pale orange solution, containing a brown precipitate, was filtered and the solid dried *in vacuo*. The solid consists of a mixture of **1** and other P-containing products (86 % product, 14 % side products according to $^{31}P\{^{1}H\}$ NMR) as well as LiCl (m(total) = 1.70 g). Layering of a saturated THF solution with *n*-hexane resulted in the crystallisation of $[\{(Me_2N)P(2\text{-py})_2\}(LiCl)_3{\cdot}2THF]_2$. ^{1}H NMR (d_8-THF), δ = 8.71 - 8.67 (2H, m, H6), 7.72 - 7.65 (4H, m, H3,4), 7,22 - 7.16 (2H, m, H5), 3.69 - 3.63 (8H, m, THF, OCH_2), 2.82 (6H, d, J_{PH} = 9.0, CH_3), 1.85 - 1.78 (8H, m, THF, CH_2). $^{31}P\{^{1}H\}$ NMR (d_8-THF), δ = 60.1 (s). $^{13}C\{^{1}H\}$ NMR (d_8-THF), δ = 165.7 (d, J_{CP} = 1.9, C2), 150.3 (d, J_{CP} = 10.4, C6), 135.5 (d, J_{CP} = 2.1, C3/4), 126.5 (d, J_{CP} = 17.7, C3/4), 122.3 (s, C5), 68.0 (s, THF, OCH_2), 43.0 (d, J_{CP} = 14.5, CH_3), 26.2 (s, THF, CH_2). $^{7}Li\{^{1}H\}$ NMR (d_8-THF), δ = 0.35 (s). Elemental analysis, calcd. for $[\{(Me_2N)P(2\text{-py})_2\}(LiCl)_3{\cdot}2THF]_2$, C 47.9, H 6.0, N 8.4; found C 46.8, H 6.1, N 7.9.

Synthesis of $(Et_2N)_2P(2\text{-py})$ (2). 2-Bromopyridine (1.9 mL, 20 mmol) in 25 mL of diethyl ether was added dropwise over a period of 30 min to a solution of *n*BuLi (12.5 mL, 20 mmol, 1.6 M in *n*-hexane) at -78 °C. The resulting dark orange solution was stirred for 2 h at -78 °C. $(Et_2N)_2PCl$ (4.20 mL, 20 mmol) was added dropwise, resulting in a dark brown mixture. After stirring overnight (over which time the reaction reached RT), a dark-green solution with a precipitate was formed. This solution was then filtered to remove the solid. The solvent was removed *in vacuo* and distillation of the resulting dark brown oil under reduced pressure (b. p. 82 °C, 0.1 mbar) gave a yellow oil. Yield: 2.87 g, 11.30 mmol, 57 %. ^{1}H NMR ($CDCl_3$), δ = 8.70 - 8.68 (1H, m, H6), 7.61 - 7.56 (1H, m, H4), 7.56 - 7.51 (1H, m, H3), 7.06 - 7.02 (1H, m, H5), 3.16 - 3.07 (8H, m, CH_2), 1.14 (12H, t, J_{HH} = 7.1, CH_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$), δ = 93.9 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$), δ = 165.9 (d, J_{CP} = 16.3, C2), 150.1 (d, J_{CP} = 7.6, C6), 135.0 (s, C4), 126.5 (d, J_{CP} = 22.3, C3), 121.1 (s, C5), 43.5 (d, J_{CP} = 16.3, CH_2), 14.5 (d, J_{CP} = 2.3, CH_3). Elemental analysis, calcd. for $(Et_2N)_2P(2\text{-py})$, C 61.6, H 9.6, N 16.6; found C 61.7, H 9.8, N 16.1. HR-MS (ESI, +, DCM): m/z: 254.1772, calcd. 254.1781 (3.4 ppm error), [M+].

Synthesis of $(Et_2N)PhP(2\text{-py})$ (3). 2-Bromopyridine (1.90 mL, 20 mmol) in 25 mL of diethyl ether was added dropwise over a period of 40 min to an *n*BuLi solution (12.5 mL, 20 mmol, 1.6 M in *n*-hexane) at -78 °C. The dark red mixture was stirred for 3 h and then $(Et_2N)PhPCl$ in 5 mL of diethyl ether was added dropwise. The resulting dark brown mixture was warmed up to room temperature overnight, resulting in an orange solution with a pale brown precipitate. After the mixture was filtered over Celite, the solvent was removed affording a crimson oil (m = 2.84 g). The dark red oil was distilled under reduced pressure to afford **3** as yellow oil. Yield: 1.05 g, 4.1 mmol, 20 %. ^{1}H NMR (500.20 MHz, $CDCl_3$), δ = 8.71 (1H, d, J_{HH} = 4.7, H6), 7.67 - 7.62 (1H, m, H4), 7.54 - 7.51 (1H, m, H3), 7.45 - 7.41 (2H, m, Ph-H-ortho), 7.37 - 7.29 (3H, m, Ph-H-meta, para), 7.18 - 7.14 (1H, m, H5), 3.21 - 3.08 (4H, m, CH_2), 0.99 (6H, t, J_{HH} = 7.1, CH_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$), δ = 59.7 (s). $^{13}C\{^{1}H\}$ NMR (125.78 MHz, $CDCl_3$), δ = 165.8 (d, J_{CP} = 16.3, C2), 149.9 (d, J_{CP} = 11.0, C6), 139.3 (d, J_{CP}

=13.8, Ph-Cq), 135.2 (d, J_{CP} = 2.2, C4), 132.3 (d, J_{CP} = 20.1, Ph-ortho), 128.3 (s, Ph-meta, para), 128.0 (d, J_{CP} = 6.2, Ph-meta, para), 126.4 (d, J_{CP} = 18.1, C3), 121.7 (s, C5), 44.6 (d, J_{CP} = 15.4, CH_2), 14.4 (d, J_{CP} = 3.0, CH_3). Elemental analysis, calcd for (Et_2N)PhP(2-py), C 69.8, H 7.4, N 10.9; found C 70.3, H 7.5, N 10.9. MS (ESI, +, MeCN): m/z: 259.1362, calcd. 254.1359 (1.18 ppm error), [M+].

Synthesis of (MeO)P(2-py)$_2$ ([4·LiCl]$_2$). The crude precipitate of (Me_2N)P(2-py)$_2$·LiCl + LiCl (1.00 g, 3.18 mmol) was stirred in MeOH (40 mL) overnight resulting in a clear orange solution. After the solvent was removed *in vacuo* the product was obtained as brown oil, which could be crystallised as [{(MeO)P(2-py)$_2$}LiCl]$_2$ from a concentrated THF solution at -14 °C. Crystalline yield: 0.22 g, 0.84 mmol, 27 %. ^{1}H NMR ($CDCl_3$), δ = 8.78 (2H, d, J_{HH} = 4.8 , H6), 7.68 - 7.64 (4H, m, H3,4), 7.23 - 7.18 (2H, m, H5), 3.89 (3H, d, J_{PH} = 13.5, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$), δ = 99.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$), δ = 164.3 (d, J_{CP} = 8.3, C2), 150.6 (d, J_{CP} = 10.4, C6), 136.1 (d, J_{CP} = 4.1, C4), 125.0 (d, J_{CP} = 21.1, C3), 123.4 (s, C5), 58.2 (d, J_{CP} = 21.2, CH_3). ^{7}Li{^{1}H} NMR ($CDCl_3$), δ = 2.33 (s). Elemental analysis, calcd. for [{(MeO)P(2-py)$_2$}LiCl]$_2$, C 43.6, H 3.7, N 9.3; found C 44.7, H 3.9, N 9.9.

Synthesis of (2-BuO)P(2-py)$_2$ ([5·LiCl]$_2$). The crude compound (Me_2N)P(2-py)$_2$·LiCl + LiCl (1,36 g, 4.30 mmol) and 2 eq of racemic 2-butanol (0.79 mL, 8.7 mol) were heated overnight at 90 °C in 15 mL of toluene. The mixture was filtered over Celite and the solvent was removed, resulting in 0.79 g of a brown oil with a purity of 80 % according to ^{31}P{^{1}H} NMR spectroscopy. Colourless single-crystals of [{(2-BuO)P(2-py)$_2$}LiCl]$_2$ could be obtained from layering a saturated THF solution with *n*-hexane. Crystalline yield: 0.070 g, 0.23 mmol, 5 %. ^{1}H NMR ($CDCl_3$), δ = 8.83 (2H, d, J_{HH} = 5, H6), 7.76 - 7.67 (4H, m, H3,4), 7.25 - 7.20 (2H, m, H5), 4.24 - 4.14 (1H, m, OCH), 1.93 - 1.81 (1H, m, CH_2), 1.78 - 1.65 (1H, m, CH_2), 1.41 (3H, d, J_{HH} = 6.4, $OCHCH_3$), 0.98 (3H, t, J_{HH} = 7.5, CH_2CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$), δ = 88.1 (s). ^{13}C{^{1}H} NMR ($CDCl_3$), δ = 164.9 (d (br), J_{CP} = 35.8, C2), 150.8 (d, J_{CP} = 10.1, C6), 136.5 (d, J_{CP} = 4.0, C3/4), 124.9 - 124.5 (m, C3/4), 123.4 (d, J_{CP} = 2.5, C5), 80.9 (d, J_{CP} = 20.8 , OCH), 31.1 (d, J_{CP} = 5.6, CH_2), 21.8 (d, J_{CP} = 5.6, $OCHCH_3$), 10.1 (s, CH_2CH_3). ^{7}Li{^{1}H} NMR ($CDCl_3$), δ = 2.51 (s). Elemental analysis, calcd. for [{(2-BuO)P(2-py)$_2$}LiCl]$_2$, C 55.6, H 5.7, N 9.3; found C 55.8, H 5.8, N 9.0.

Synthesis of (*S*)-(2-BuO)P(2-py)$_2$ ([5-*S*·LiCl]$_2$). Crystals of [{(Me_2N)P(2-py)$_2$}(LiCl)$_3$·2THF]$_2$ (0.017g, 0.034 mmol) were reacted with (*S*)-(+)-2-Butanol (6.3 µL, 0.068 mmol) in 0.6 mL of d_8-toluene in a Young's NMR tube. The mixture was heated overnight at 85 °C. The phosphine **5-*S*** was obtained in 91 % yield according to ^{31}P{^{1}H} NMR spectroscopy. ^{1}H NMR (d_8-tol), δ = 8.66 - 8.57 (2H, m, H6), 7.69 - 7.63 (2H, m, H3), 7.10 - 7.04 (2H, m, H4), 6.63 - 6.56 (2H, m, H5), 4.11 - 4.01 (1H, m, OCH), 1.79 - 1.69 (1H, m, CH_2), 1.59 - 1.52 (1H, m, CH_2), 1.28 (3H, d, J_{HH} = 6.3, $OCHCH_3$), 0.88 (3H, t, J_{HH} = 3.7, CH_2CH_3). ^{31}P{^{1}H} NMR (d_8-tol), δ = 93.1 (s).

Synthesis of (*R*)-(2-BuO)P(2-py)$_2$ ([5-*R*·LiCl]$_2$). Crystals of [{(Me_2N)P(2-py)$_2$}(LiCl)$_3$·2THF]$_2$ (0.015g, 0.030 mmol) were reacted with (*R*)-(-)-2-Butanol (5.5 µL, 0.060 mmol) in 0.6 ml of d_8-toluene in a Young's NMR tube. The mixture was heated overnight at 85 °C. The phosphine **5-*R*** was obtained in 94 % yield according to ^{31}P{^{1}H} NMR spectroscopy. ^{1}H NMR (d_8-tol), δ = 8.66 - 8.61 (2H, m, H6), 7.69 - 7.63 (2H, m, H3), 7.10 - 7.04 (2H, m, H4), 6.63 - 6.56 (2H, m, H5), 4.11 - 4.01 (1H, m, OCH), 1.82 - 1.68 (1H, m, CH_2), 1.58 - 1.50 (1H, m, CH_2), 1.28 (3H, d, J_{HH} = 6.3, $OCHCH_3$), 0.88 (3H, t, J_{HH} = 7.4, CH_2CH_3). ^{31}P{^{1}H} NMR (d_8-tol), δ = 92.8 (s).

Synthesis of (MeO)$_2$P(2-py) (7). A mixture of **2** (0.666 g, 2.63 mmol) and 30 mL MeOH was heated overnight at 50 °C. The mixture was dried under vacuum resulting in a clear pale yellow oil. Yield: 0.35 g, 2.05 mmol, 73 %. ^{1}H NMR ($CDCl_3$), δ = 8.81 - 8.78 (1H, m, H6), 7.77 - 7.69 (2H, m, H3,4), 7.28 - 7.23 (1H, m, H5), 3.65 (6H, d, J_{PH} = 10.6, Me). ^{31}P{^{1}H} NMR ($CDCl_3$), δ = 150.1 (s). ^{13}C{^{1}H} NMR ($CDCl_3$), δ = 163.7 (d, J_{CP} = 6.0, C2), 150.3 (d, J_{CP} = 11.4, C6), 135.6 (s, C4), 125.1 (d, J_{CP} = 15.9, C3), 123.9 (s, C5), 53.8 (d, J_{CP} = 9.2, CH_3). Elemental analysis, calcd. for ($MeO)_2$P(2-py), C 49.1, H 5.9, N 8.2; found C 49.6, H 6.0, N 8.4. HR-MS (ESI, +, MeCN): m/z: 172.0518, calcd. 172.0522 (-2.52 ppm error), [M+].

Synthesis of (Et_2N)(PhO)P(2-py) (8). **2** (0.860 g, 3.40 mmol) and PhOH (0.319 g, 3.40 mmol) were brought to reflux in toluene (20 mL) overnight. After the solvent was removed *in vacuo* the product was obtained as yellow oil. Yield: 0.81 g, 2.93 mmol, 86 %. ^{1}H NMR ($CDCl_3$), δ = 8.81 - 8.79 (1H, m, H6), 7.96 - 7.92 (1H, m, H3), 7.76 (1H, tt, J_{HH} = 7.6, 2.0, H4), 7.36 - 7.30 (2H, m, Ph-H-meta), 7.28 - 7.25 (1H, m, H5), 7.17 - 7.13 (m, 2H, Ph-H-ortho), 7.09 - 7.04 (1H, m, Ph-H-para), 3.22 - 3.05 (4H, m, CH_2), 1.00 (6H, t, J_{HH} = 7.3, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$), δ = 120.2 (s). ^{13}C{^{1}H} NMR ($CDCl_3$), δ = 164.7 (d, J_{CP} = 11.6, C2), 156.7 (d, J_{CP} = 8.3, Ph-Cq), 150.2 (d, J_{CP} = 13.2, C6), 135.9 (s, C4), 129.6 (s, Ph-meta), 126.1 (d, J_{CP} = 14.7, C3), 123.2 (s, C5), 122.4 (d, J_{CP} = 1.6, Ph-H-para), 119.9 (d, J_{CP} = 9.4, Ph-ortho), 43.2 (s, CH_2), 15.0 (d, J_{CP} = 3.8, CH_3). Elemental analysis, calcd. for (Et_2N)(PhO)P(2-py), C 65.7, H 7.0, N 10.2; found C 65.3, H 7.2, N 10.1. HR-MS (ESI, +, MeCN): m/z: 275.1310, calcd. 275.1308 (0.95 ppm error), [M+].

Synthesis of (PhO)$_2$P(2-py) (9). A mixture of **2** (0.837 g, 3.30 mmol) and two equivalents of PhOH (0.622 g, 6.61 mmol) were brought to reflux for 41 h in toluene (18 mL). After the solvent was removed *in vacuo* the resulting pale yellow oil was purified by vacuum distillation and then heated at 100 °C (to remove the excess PhOH) for 2 h to afford **9** in 96 % purity (according to ^{31}P{^{1}H} NMR spectroscopy). Yield: 0.43 g, 1.46 mmol, 44 %. ^{1}H NMR (CD_3CN), δ = 8.88 (1H, d, J_{HH} = 4.7, H6), 7.98 - 7.94 (1H, m, H3), 7.86 (1H, tt, J_{HH} = 7.7, 16, H4), 7.47 - 7.42 (1H, m, H5), 7.37 - 7.31 (4H, m, Ph-H-meta), 7.17 - 7.12 (4H, m, Ph-H-ortho, para). ^{31}P{^{1}H} NMR (CD_3CN), δ = 142.8 (s). ^{13}C{^{1}H} NMR (CD_3CN), δ = 162.5 (d, J_{CP} = 5.0, C2), 155.0 (d, J_{CP} = 4.2, Ph-Cq), 150.1 (d, J_{CP} = 15.8, C6), 136.3 (s, C4), 129.7 (s, Ph-meta), 125.0 (s, C5), 124.6 (d, J_{CP} = 12.9, C3), 124.0 (d, J_{CP} = 1.1, Ph-ortho/para), 120.1 (d, J_{CP} = 7.6, Ph-ortho/para). Elemental analysis, calcd. for ($PhO)_2$P(2-py), C 69.2, H 4.8, N 4.7; found C 69.6, H 5.0, N 4.5. HR-MS (ESI, +, MeCN): m/z: 296.0842, calcd. 296.0835 (2.25 ppm error), [M+].

Synthesis of [(MeCN)Cu{($Et_2N)_2$P(2-py)}]$_2$($PF_6)_2$ (10). 2 (0.01g, 0.4 mmol) and [Cu(MeCN)$_4$]PF_6 (0.15g, 0.4 mmol) were reacted in MeCN (20 mL). The bright yellow mixture was stirred overnight and the solvent was removed completely under vacuum. Colourless crystals could be grown from layering a

saturated DCM solution with *n*-hexane. Crystalline yield: 74 mg, 0.074 mmol, 19 %. ^{1}H NMR (CD_3COCD_3), δ 8.75 (1H, s (br), py-H), 8.10 - 7.31 (3H, m, py-H), 3.25 - 2.88 (8H, m, CH_2), 1.99 (3H, s, MeCN), 1.13 (12H, t, J_{HH} = 6.7, CH_3). ^{31}P{^{1}H} NMR (CD_3COCD_3), δ = 84.0 (s, br), -144.6 (sep, J_{PF} = 707.1, PF_6). ^{13}C{^{1}H} NMR spectrum could not be obtained due to extensive line broadening. Elemental analysis, calcd. for $[(MeCN)Cu\{(Et_2N)_2P(2\text{-}py)\}]_2(PF_6)_2$, C 35.8, H 5.4, N 11.1; found C 35.1, H 5.3, N 10.6.

Synthesis of $[ClCu\{(MeO)P(2\text{-}py)_2\}]_2$·MeOH (11·MeOH). 0.091 g $[\{(MeO)P(2\text{-}py)_2\}LiCl]_2$ ([**4**·LiCl]$_2$) (0.35 mmol) and $[Cu(MeCN)_4]PF_6$ (0.13 g, 0.35 mmol) were brought to reflux in 15 mL THF. After the solvent was removed MeOH was added and the mixture was filtered over Celite. A few colourless crystals of **11**·MeOH could be grown from a saturated MeOH solution at -14 °C.

Synthesis of $[(MeCN)Cu\{(Et_2N)(PhO)P(2\text{-}py)\}]_2(PF_6)_2$ (12). 8 (0.248 g, 0.9 mmol) and $[Cu(MeCN)_4]PF_6$ (0.337g, 0.9 mmol) in MeCN (15 mL) were brought to reflux for 2 h. The yellow solution was filtered over Celite and the solvent was removed under reduced pressure, resulting in a yellow oil. Colourless crystals could be obtained from a saturated DCM solution at -14 °C after two days. Crystalline yield: 0.05 g, 0.048 mmol, 5 %. ^{1}H NMR (CD_3CN), δ = 8.77 - 8.73 (1H, m, H6), 8.01 - 7.94 (1H, m, H3), 7.94 - 7.86 (1H, m, H4), 7.47 - 7.42 (1H, m, H5), 7.42 - 7.36 (2H, m, Ph-H), 7.20 - 7.13 (3H, m, Ph-H), 3.22 - 3.07 (4H, m, CH_2), 1.96 (MeCN solvent residual signal partially overlaps with the signal of the coordinated MeCN molecules), 0.98 (6H, t, J_{HH} = 7.1, CH_3). ^{31}P{^{1}H} NMR (CD_3CN), δ = 107.8 (s, br), -144.6 (sep, J_{PF} = 705.9, PF_6). ^{13}C{^{1}H} NMR (CD_3CN), δ = 160.3 (d, J_{CP} = 76.5, C2), 155.4 (s, Ph-Cq), 151.3 (d, J_{CP} = 17.3, C6), 137.5 (s, C4), 130.5 (s, Ph), 126.6 (d, J_{CP} = 18, C3), 125.5 (s, C5), 124.9 (s, Ph), 121.9 (d, J_{CP} = 6.2, Ph), 118.2 (s, MeCN), 42.8 (d, J_{CP} = 11.0, CH_2), 14.7 (s, CH_3), 0.76 (s, MeCN). Elemental analysis, calcd. for $[(MeCN)Cu\{(Et_2N)(PhO)P(2\text{-}py)\}]_2(PF_6)_2$, C 39.0, H 4.3, N 8.0; found C 38.8, H 4.3, N 8.0.

Synthesis of $[(MeCN)Cu_2\{(PhO)_2P(2\text{-}py)\}_3](PF_6)_2$·3THF (13·3THF). $(PhO)_2P(2\text{-}py)$ (0.103 g, 0.035 mmol) and $[Cu(MeCN)_4]PF_6$ (0.087 g, 0.023 mmol) in MeCN (10 mL) were brought to reflux overnight. The solvent was removed under reduced pressure, resulting in an orange oil, which was washed with *n*-hexane. Yield: 0.10g, 0.074 mmol, 64 %. A few colourless crystals could be grown from layering a saturated THF solution with diethyl ether. ^{1}H NMR (CD_3CN), δ = 8.73 (3H, s (br), H6), 7.95 - 7.84 (6H, m, H3,4), 7.50 (3H, s (br), H5), 7.39 - 7.30 (12H, Ph-H), 7.24 - 7.10 (18H, Ph-H), 1.99 (MeCN solvent residual signal partially overlaps with the signal of the coordinated MeCN molecules). ^{31}P{^{1}H} NMR (CD_3CN), δ = 120.7 (s, br), -144.6 (sep, J_{PF} = 705.6, PF_6). ^{13}C{^{1}H} NMR (CD_3CN), δ = 154.04 (s, Ph-Cq), 151.4 (d, J_{CP} = 18.9, C6), 137.9 (s, C3/4), 130.8 (s, Ph), 127.2 (s (br),C5), 127.1 (s (br), C3/4), 126.2 (s, Ph), 121.9 (d, J_{CP} = 5.2, Ph), 117.3 (MeCN), 1.32 (MeCN). Correct elemental analysis could not be obtained due to the presence of free PhOH as a contaminant.

Synthesis of $[\{OP(O)(H)(2\text{-}py)\}Cu_2\{(PhO)_2P(2\text{-}py)\}_2]_2(PF_6)_2$ ·2THF (14·2THF). The reaction of 0.12 g of $(PhO)_2P(2\text{-}py)$ (**9**) (0.41 mmol) and $[Cu(MeCN)_4]PF_6$ (0.103 g, 0.28 mmol) in 12 mL MeCN was stirred overnight at room temperature, resulting in a pale yellow solution. After the solvent was removed colourless crystals of **14**·2THF could be grown from a saturated THF solution at -14 °C. Crystalline yield: 0.048 g, 4 %. In the following NMR assignment the ligand **9** will be referred to as L1 whereas $[OP(O)(H)(2\text{-}py)]^-$ will be denoted as L2. ^{1}H NMR (CD_3CN), δ = 8.84 (1H, d, J_{HH}= 4.7, py-H, L2), 8.81 (2H, d, J_{HH}= 4.2, py-H, L1), 8.02 - 7.89 (6H, m, py-H, L1, L2), 7.77 (1H, d, J_{PH}= 597.2, PH, L2), 7.65 - 7.60 (1H, m, py-H, L2), 7.56 - 7.51 (2H, m, L1), 7.43 - 7.35 (8H, m, Ph-H, L1), 7.26 -7.17 (12H, m, Ph-H, L1). ^{31}P{^{1}H} NMR (CD_3CN), δ = 119.8 (s, br, L1), 21.6 (s, L2), -144.6 (sep, J_{PF} = 706.5, PF_6). ^{31}P NMR (CD_3CN), δ = 119.8 (s, br, L1), 21.6 (d, J_{PH}= 597.2, PH, L2), -144.6 (sep, J_{PF} = 706.5, PF_6). ^{13}C{^{1}H} NMR spectrum could not be obtained due to extensive line broadening. Elemental analysis, calcd. for $[\{OP(O)(H)(2\text{-}py)\}Cu_2\{(PhO)_2P(2\text{-}py)\}_2]_2(PF_6)_2$, C 46.6, H 3.3, N 4.2; found C 46.5, H 3.7, N 4.1.

Computational Details

Geometry optimisation of the ligand sets **1** and **2** were carried out using the Gaussian-Program package.[75] The optimised structures were obtained employing the B3LYP functional[76–78] in conjunction with a 6-31g** basis set.[79,80] Frequency calculations of the optimised structures were carried out in order to proof the absence of imaginary frequencies. Molecular orbitals were visualised using the program VMD - Visual Molecular Dynamics.[81]

Single-crystal X-ray crystallography

Single-crystal X-ray diffraction was carried out at 180(2) K on a Bruker D8-QUEST PHOTON-100 diffractometer using an Incoatec IμS Cu microsource (λ = 1.5418 Å). Data collection and processing were carried out using the APEX2/APEX3 packages. Structures were solved using SHELXT[82] and refined using SHELXL-2014.[83] Details of the refinements are provided in the ESI (Table S1 and S2). CCDC 1505955-1505962.

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Notes and references

§ Primary amino substituents (RNH) were not employed because the reactions of primary amines (RNH_2) with PCl_3 normally produce P-N ring compounds.[84]

§§ Since the bulk purity of **1** could be improved, $(Me_2N)_2PCl$, instead of the more easily assessable ethyl congener $(Et_2N)_2PCl$ was selected as precursor.

§§§ It is not possible to synthesise $Cl_xP(2\text{-}py)_{3-x}$ by variation of the stoichiometry in the reaction of PCl_3 with Li(2-py) because

only the tri-substituted compound $P(2\text{-py})_3$ is obtained.[12] Only very recently has a two-step route to $Cl_2P(2\text{-py})$ been introduced, involving the reaction of a 2-pyridyl organo-zinc intermediate with PCl_3.[85] In the current work we have found that the reaction of $(RO)_xPCl_{3-x}$ and Li(2-py) only resulted in the formation of an intractable mixture of products.

§§§§ Unfortunately, **11**·MeOH could not be isolated in significant yield, despite repeated attempts.

1 C. Moberg, *Angew. Chem., Int. Ed.*, 1998, **37**, 248.
2 J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic, 1978.
3 N. Kitajimaj and W. B. Tolman, *Coordination Chemistry with Sterically Hindered Hydrotris(pyrazoly)borate Ligands: Organometallic and Bioinorganic Perspectives*, 1995, Vol. 43.
4 L. F. Szczepura, L. M. Witham and K. J. Takeuchi, *Coord. Chem. Rev.*, 1998, **174**, 5.
5 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943.
6 I. Schrader, K. Zeckert and S. Zahn, *Angew. Chem., Int. Ed.*, 2014, **53**, 13698.
7 K. Zeckert, S. Zahn and B. Kirchner, *Chem. Commun.*, 2010, **46**, 2638.
8 F. Reichart, M. Kischel and K. Zeckert, *Chem. - A Eur. J.*, 2009, **15**, 10018.
9 R. García-Rodríguez and D. S. Wright, *Chem. - A Eur. J.*, 2015, **21**, 14949.
10 R. García-Rodríguez, H. R. Simmonds and D. S. Wright, *Organometallics*, 2014, **33**, 7113.
11 R. García-Rodríguez and D. S. Wright, *Dalton Trans.*, 2014, **43**, 14529.
12 G. Kurtev, K. Ribola, D. Jones, R. A. Cole-Hamilton, D. J. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 55.
13 B. A. Trofimov, N. K. Gusarova, A. V. Artem'ev, S. F. Malysheva, N. A. Belogorlova, A. O. Korocheva, O. N. Kazheva, G. G. Alexandrov and O. A. Dyachenko, *Mendeleev Commun.*, 2012, **22**, 187.
14 B. A. Trofimov, A. V. Artem'ev, S. F. Malysheva, N. K. Gusarova, N. A. Belogorlova, A. O. Korocheva, Y. V. Gatilov and V. I. Mamatyuk, *Tetrahedron Lett.*, 2012, **53**, 2424.
15 F. R. Keene, M. R. Snow and E. R. T. Tiekink, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, **44**, 757.
16 F. R. Keene, M. R. Snow, P. J. Stephenson and E. R. T. Tiekink, *Inorg. Chem.*, 1988, **27**, 2040.
17 S. Hanf, R. García-Rodríguez, A. D. Bond, E. Hey-Hawkins and D. S. Wright, *Dalton Trans.*, 2016, **45**, 276.
18 A. Steiner and D. Stalke, *Organometallics*, 1995, **14**, 2422.
19 A. Steiner and D. Stalke, *J. Chem. Soc., Chem Commun.*, 1993, **6**, 444.
20 A. Steiner and D. Stalke, *Angew. Chem., Int. Ed.*, 1995, **34**, 1752.
21 A. G. Walden and A. J. M. Miller, *Chem. Sci.*, 2015, **6**, 2405.
22 A. N. Kharat, B. T. Jahromi and A. Bakhoda, *Transition Met. Chem.*, 2011, **37**, 63.
23 A. Bakhoda, N. Safari, V. Amani, H. R. Khavasi and M. Gheidi, *Polyhedron*, 2011, **30**, 2950.
24 A. Bakhoda, H. R. Khavasi and N. Safari, *Cryst. Growth Des.*, 2011, **11**, 933.
25 W. Huber, R. Linder, J. Niesel, U. Schatzschneider, B. Spingler and P. C. Kunz, *Eur. J. Inorg. Chem.*, 2012, 3140.
26 A. M. Kluwer, I. Ahmad and J. N. H. Reek, *Tetrahedron Lett.*, 2007, **48**, 2999.
27 R. Noyori, *Chem. Soc. Rev.*, 1989, **18**, 187.
28 M. J. Burk, *J. Am. Chem. Soc.*, 1991, **113**, 8518.
29 M. J. Burk, *Acc. Chem. Res.*, 2000, **33**, 363.
30 M. J. Burk, J. E. Feaster and R. L. Harlow, *Organometallics*, 1990, **9**, 2653.
31 W. S. Knowles, *Angew. Chem., Int. Ed.*, 2002, **41**, 1998.
32 B. D. Vineyard, W. S. Knowles, G. L. Bachman and D. J. Weinkauff, *J. Am. Chem. Soc.*, 1977, **99**, 5946.
33 G. R. Newkome, *Chem. Rev.*, 1993, **93**, 2067.
34 A. N. Kharat, A. Bakhoda, T. Hajiashrafi and A. Abbasi, P*hosphorus, Sulfur Silicon Relat. Elem.*, 2010, **185**, 2341.
35 W. Tang and X. Zhang, *Chem. Rev.*, 2003, **103**, 3029.
36 M. D. Le Page, B. O. Patrick, S. J. Rettig and B. R. James, *Inorg. Chim. Acta*, 2015, **431**, 276.
37 T. Zhang, C. Ji, K. Wang, D. Fortin and P. D. Harvey, *Inorg. Chem.*, 2010, **49**, 11069.
38 J. A. Casares, P. Espinet, J. M. Martín-Álvarez and V. Santos, *Inorg. Chem.*, 2006, **45**, 6628.
39 A. N. Kharat, B. Tamaddoni Jahromi, A. Bakhoda and A. Abbasi, *J. Coord. Chem.*, 2010, **63**, 3783.
40 A. Nemati Kharat, A. Bakhoda, S. Foroutannejad and C. Foroutannejad, *Z. Anorg. Allg. Chem.*, 2011, **637**, 2260.
41 M. J. Calhorda, C. Ceamanos, O. Crespo, M. C. Gimeno, A. Laguna, C. Larraz, P. D. Vaz and M. D. Villacampa, *Inorg. Chem.*, 2010, **49**, 8255.
42 X. K. Wan, Z. W. Lin and Q. M. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 14750.
43 H. Tinnermann, C. Wille and M. Alcarazo, *Angew. Chem., Int. Ed.*, 2014, **53**, 8732.
44 K. Nishide, S. Ito and M. Yoshifuji, *J. Organomet. Chem.*, 2003, **682**, 79.
45 S. Kuang, Z. Zhang, K. Chinnakali, H. Fun and T. C. W. Mak, *Inorg. Chim. Acta*, 1999, **293**, 106.
46 M. Driess, F. Franke and K. Merz, *Eur. J. Inorg. Chem.*, 2001, 2661.
47 S. Wingerter, M. Pfeiffer, A. Murso, C. Lustig, T. Stey, V. Chandrasekhar and D. Stalke, *J. Am. Chem. Soc.*, 2001, **123**, 1381.
48 A. Murso, M. Straka, M. Kaupp, R. Bertermann and D. Stalke, *Organometallics*, 2005, **24**, 3576.
49 I. Objartel, H. Ott and D. Stalke, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2373.
50 I. Objartel, N. A. Pott, M. John and D. Stalke, *Organometallics*, 2010, **29**, 5670.
51 A. Murso and D. Stalke, *Dalton Trans.*, 2004, 2563.
52 A. Murso and D. Stalke, *Eur. J. Inorg. Chem.*, 2004, 4272.
53 N. Kocher, D. Leusser, A. Murso and D. Stalke, *Chem. - A Eur. J.*, 2004, **10**, 3622.
54 A. Steiner, S. Zacchini and P. I. Richards, *Coord. Chem. Rev.*, 2002, **227**, 193.
55 V. A. Imukhametov, M. N. Garifzyanova, G. G. Azancheev, N. M. Al'fonsov, *Russ. J. Gen. Chem.*, 1999, **69**, 1965.
56 S. D. Stamatov and S. A. Ivanov, *Phosphorus, Sulfur Silicon*

Relat. Elem., 1989, **45**, 73.
57 K. Skopek and J. A. Gladysz, *J. Organomet. Chem.*, 2008, **693**, 857.
58 E. E. Nifantiev, A. I. Zavalishina and E. I. Smirnova, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1981, **10**, 261.
59 M. N. Birkholz, N. V. Dubrovina, H. Jiao, D. Michalik, J. Holz, R. Paciello, B. Breit and A. Börner, *Chem. - A Eur. J.*, 2007, **13**, 5896.
60 A. Murso and D. Stalke, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1025.
61 P. Wucher, J. B. Schwaderer and S. Mecking, *ACS Catal.*, 2014, **4**, 2672.
62 M. Oliana, F. King, P. N. Horton, M. B. Hursthouse and K. K. Hii, *J. Org. Chem.*, 2006, **71**, 2472.
63 J. Wieland and B. Breit, *Nat. Chem.*, 2010, **2**, 832.
64 B. Breit and W. Seiche, *J. Am. Chem. Soc.*, 2006, **78**, 249.
65 J. G. Woollard-Shore, J. P. Holland, M. W. Jones and J. R. Dilworth, *Dalton Trans.*, 2010, **39**, 1576.
66 G. Chelucci, G. Orru and G. A. Pinna, *Tetrahedron*, 2003, **59**, 9471.
67 E. I. Musina, A. V Shamsieva, I. D. Strelnik, T. P. Gerasimova, D. B. Krivolapov, I. E. Kolesnikov, E. V Grachova, S. P. Tunik, C. Bannwarth, S. Grimme, S. A. Katsyuba, A. A. Karasik and O. G. Sinyashin, *Dalton Trans.*, 2016, **45**, 2250.
68 D. M. Zink, M. Bächle, T. Baumann, M. Nieger, M. Kühn, C. Wang., W. Klopper, U. Monkowius, T. Hofbeck, H. Yersin and S. Bräse, *Inorg. Chem.*, 2013, **52**, 2292.
69 D. Volz, D. M. Zink, T. Bocksrocker, J. Friedrichs, M. Nieger, T. Baumann, U. Lemmer and S. Bräse, *Chem. Mater.*, 2013, **25**, 3414.
70 V. J. Catalano, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and D. Pascual, *DaltonTrans.*, 2014, **43**, 16486.
71 J.-J. Cid, J. Mohanraj, M. Mohankumar, M. Holler, G. Accorsi, L. Brelot, I. Nierengarten, O. Moudam, A. Kaeser, B. Delavaux-Nicot, N. Armaroli and J.-F. Nierengarten, *Chem. Commun.*, 2013, **49**, 859.
72 I. Objartel, D. Leusser, F. Engelhardt, R. Herbst-Irmer and D. Stalke, *Z. Anorg. Allg. Chem.*, 2013, **639**, 2005.
73 S. I. Noro, Y. Hijikata, M. Inukai, T. Fukushima, S. Horike, M. Higuchi, S. Kitagawa, T. Akutagawa and T. Nakamura, *Inorg. Chem.*, 2013, **52**, 280.
74 S. M. Kuang, Z.-Z. Zhang, Q.-G. Wang and T. C. W. Mak, *J. Organomet. Chem.*, 1998, **558**, 131.
75 Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
76 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
77 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B Condens. Matter*, 1988, **37**, 785.
78 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
79 G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *J. Chem. Phys.*, 1988, **89**, 2193.
80 G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.*, 1991, **94**, 6081.
81 A. Humphrey, W.Dalke and K. Schulten, *J. Molec. Graph.*, 1996, **14**, 33.
82 G. M. Sheldrick, Acta Crystallogr., *Sect. A: Found. Crystallogr.*, 2015, **71**, 3.
83 G. M. Sheldrick, , *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3.
84 E. J. Amigues, C. Hardacre, G. Keane and M. E. Migaud, *Green Chem.*, 2008, **10**, 660.
85 X. Chen, H. Zhu, T. Wang, C. Li, L. Yan, M. Jiang and J. Liu, *J. Mol. Catal. A.: Chem.*, 2016, **414**, 37.

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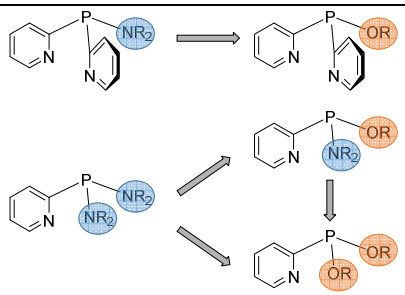
Multidentate 2-pyridyl-phosphine ligands – towards ligand tuning and chirality S. Hanf, R. García-Rodríguez, S. Feldmann, A. D. Bond, E. Hey-Hawkins and D. S. Wright		The incorporation of a variety of alcohols into (amino)pyridyl-phosphine frameworks provides access to a library of multidentate (alkoxy)pyridyl-phosphines. Their coordination chemistry with Cu^{I} is explored.