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**Cyclodiphosphazane based pincer ligand, [2,6- $\mu$ -(*t*BuN)P(*t*BuHN)PO]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>I]: Ni<sup>II</sup>, Pd<sup>II</sup>, Pt<sup>II</sup> and Cu<sup>I</sup> complexes and catalytic studies**

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**Abstract.** Synthesis and late-transition metal complexes of pincer capable cyclodiphosphazane, 2,6- $\mu$ -(*t*BuN)P(*t*BuHN)PO]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>I (**1**) is described. The condensation of 2-iodoresorcinol with *cis*-{CIP( $\mu$ -N<sup>*t*</sup>Bu)<sub>2</sub>PN(H)<sup>*t*</sup>Bu} produced a difunctional derivative **1** in good yield. The treatment of Ni(COD)<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> or Pt(PPh<sub>3</sub>)<sub>4</sub> with **1** afforded pincer complexes [2,6- $\mu$ -(*t*BuN)P(*t*BuHN)PO]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MI] (**2** M = Ni; **3** M = Pd and **4** M = Pt). The reaction of complex **3** with copper halides resulted in the formation of heterobimetallic complexes bridged by rhombic {Cu( $\mu$ -X)}<sub>2</sub> units, [{{Cu( $\mu$ -X)}<sub>2</sub>{ $\mu$ -(*t*BuN)P(*t*BuHN)PO]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>PdI]} (**5** X = I and **6** X = Br). The crystal structures of **1** – **3**, **5** and **6** were established by single X-ray diffraction studies. The palladium complex **3** was tested for catalytic P-arylation of diphenylphosphine oxide (Ph<sub>2</sub>P(O)H) under microwave irradiation. Moderate to good catalytic activity was observed with aryl bromides.

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## Introduction

The family of pincer ligands attracted much attention in recent years<sup>1</sup> mainly because of their applications in homogenous catalysis,<sup>2-5</sup> sensors,<sup>6</sup> and supramolecular chemistry.<sup>7-9</sup> The pincer skeleton generally consists of two mutually *trans* chelating neutral donor groups and a central aromatic backbone. The neutral donors are typically phosphines (PR<sub>2</sub>),<sup>7, 8, 10</sup> arsines,<sup>11</sup> amines (NR<sub>2</sub>),<sup>8, 12-15</sup> thioethers (SR),<sup>13, 16-20</sup> selenoethers (SeR)<sup>21</sup> and N-heterocyclic carbenes (NHCs)<sup>22-24</sup> or a pair of donor groups among these functionalities.<sup>18, 25, 26</sup> The pincer complexes of phosphorus donor ligands have been studied extensively.<sup>27-35</sup> The steric and electronic properties of pincer ligands can be controlled by carefully modifying the substituents on donor groups and aromatic backbone.<sup>34, 36</sup> However, modification of stereochemical parameters often require tedious multistep synthesis. In this context, pincer complexes bearing bis(phosphinite) POCOP backbone are of special interest due to their relatively easy synthetic access.<sup>37</sup>

Functionalized pincer complexes with multiple coordination sites are used to construct heterobimetallic complexes with mono- or polynuclear pincer fragments. Incorporation of second metal center to a pincer framework can enhance their catalytic activity by synergic interactions.  $\eta^6$ -Coordination of the organometallic fragments such as [Ru( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)]<sup>+</sup>, to the central arene ring of pincer complex to afford heterobimetallic products have been reported by Gebbink and co-workers and others.<sup>38-42</sup> Spectroscopic and electrochemical data have shown that the electrophilic organometallic fragments act as powerful electron-withdrawing groups. van Koten and coworkers recently reported the synthesis of heterobimetallic and trimetallic complexes using a ditopic pincer terpyridine hybrid ligand.<sup>43</sup> Peripherally metallated porphyrin pincer hybrids are successfully utilized as catalysts in Michael addition reaction,<sup>44</sup> Heck reaction<sup>45</sup> and allylation reactions.<sup>46</sup> Although they provide robust platform

for multi-pincer assemblies, the role of porphyrin backbone in catalytic cycle is not clearly understood.

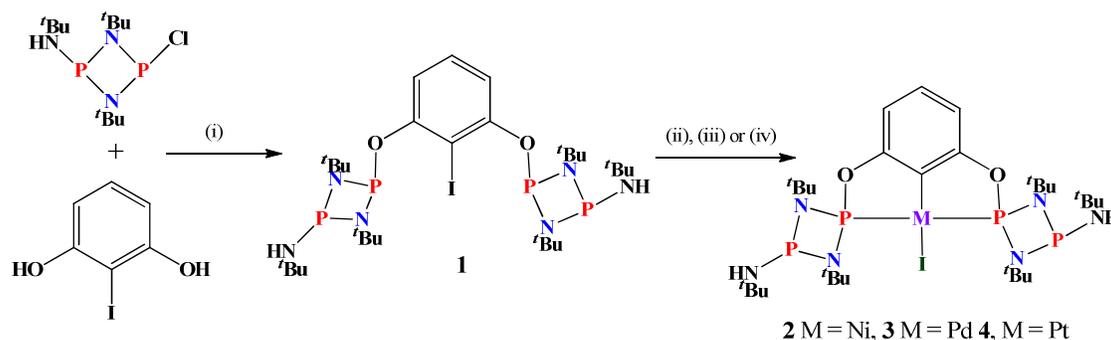
The oxidative addition of low valent metal precursors to prefunctionalized ligands has been used as an alternate method when direct cyclometalation is unsuccessful.<sup>2, 3, 47</sup> The method becomes more important when acid-labile, thermally unstable or sterically bulky substituents are present in the pincer ligand, since direct cyclometalation by C–H activation normally requires high temperature and longer reaction time and formally releases acid (HX).<sup>9, 27</sup>

In our quest for new type of phosphorus based ligand systems for catalytic and biological applications, we have synthesized several functionalized phosphorus based ligands including various cyclodiphosphazane derivatives and studied their complexation behavior, catalytic applications and antitumor properties.<sup>48, 49</sup> Slight modifications of the phosphorus substituents of cyclodiphosphazanes have brought significant changes in their coordination behavior resulting in the formation of several mononuclear complexes to metallo-macrocycles and coordination polymers.<sup>50, 51</sup> We, herein report the synthesis of pincer complexes based on acyclic dimer of cyclodiphosphazane. The preliminary investigations on the catalytic activity of palladium complex in P-arylation of diphenylphosphine oxide (Ph<sub>2</sub>P(O)H) is also reported.

## Results and discussion

**Ligand synthesis and oxidative addition reactions.** An iodo-substituted acyclic dimer of cyclodiphosphazane, 2,6- $\{\mu\text{-}(t\text{BuN})\text{P}(t\text{BuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{I}$  (**1**) having a rigid aromatic scaffold was synthesized by the reaction of *cis*- $\{\text{ClP}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{H})^t\text{Bu}\}$  with 2-iodoresorcinol. The compound **1** is a white crystalline solid moderately stable towards air and moisture. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** exhibits two doublets centered at 112.7 and 144.1 ppm, for amino-P and aryloxo-P atoms, respectively, with a <sup>2</sup>J<sub>PP</sub> coupling of 12 Hz. The reaction of

2,6- $\{\mu\text{-}(\text{tBuN})\text{P}(\text{tBuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{I}$  (**1**) with  $\text{Ni}(\text{COD})_2$ ,  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$  or  $\text{Pt}(\text{PPh}_3)_4$  in THF under refluxing conditions resulted in the formation of corresponding pincer complexes,  $[2,6\text{-}\{\mu\text{-}(\text{tBuN})\text{P}(\text{tBuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{MI}]$  (**2** M = Ni; **3** M = Pd and **4** M = Pt) as shown in Scheme 1. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2**, **3** and **4** follow similar pattern. For example, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of platinum complex **4** consists of two signals at 121.6 and 99.2 ppm for coordinated and uncoordinated phosphorus centers, respectively, with former showing a  $^1J_{\text{PtP}}$  coupling of 3925 Hz. No  $^2J_{\text{PP}}$  coupling was observed in any of the metal complexes.<sup>52</sup> From the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectral data it is clear that the aryloxo-P atoms are coordinating to the metal centers. The EI mass spectra of complexes **2** and **3** showed  $[\text{M}+\text{H}]$  ion peaks at  $m/z$  845.10 and 892.71, respectively. The structures of **1** – **3** have been confirmed by single crystal X-ray diffraction studies.

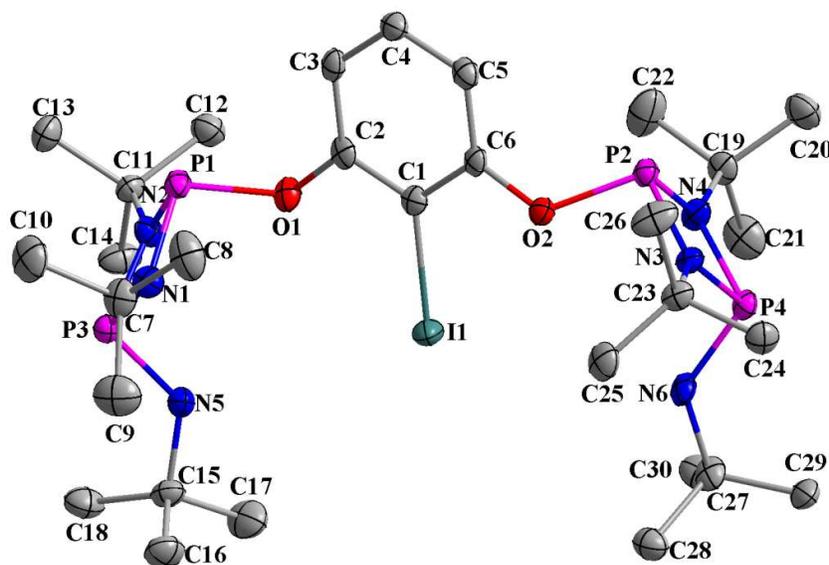


Scheme 1. Synthesis and complexation reactions of ligand **1**. Reagents and conditions: (i)  $\text{Et}_3\text{N}$ ,  $\text{Et}_2\text{O}$ ,  $0\text{ }^\circ\text{C}$ ; (ii)  $\text{Ni}(\text{COD})_2$ , THF,  $\Delta$ , 6h; (iii)  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ , THF,  $\Delta$ , 6h; (iv)  $\text{Pt}(\text{PPh}_3)_4$ , THF,  $\Delta$ , 6h.

**Molecular structures of 2,6- $\{\mu\text{-}(\text{tBuN})\text{P}(\text{tBuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{I}$  (**1**), and  $[2,6\text{-}\{\mu\text{-}(\text{tBuN})\text{P}(\text{tBuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{MI}]$  (**2** M = Ni and **3** M = Pd).** The perspective views of molecular structures **1** – **3** along with the atom labeling schemes are shown in Figures 1 – 3. The selected bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ] are listed in Table 1, while the crystallographic data and the details of the structure determination are given in Table 2.

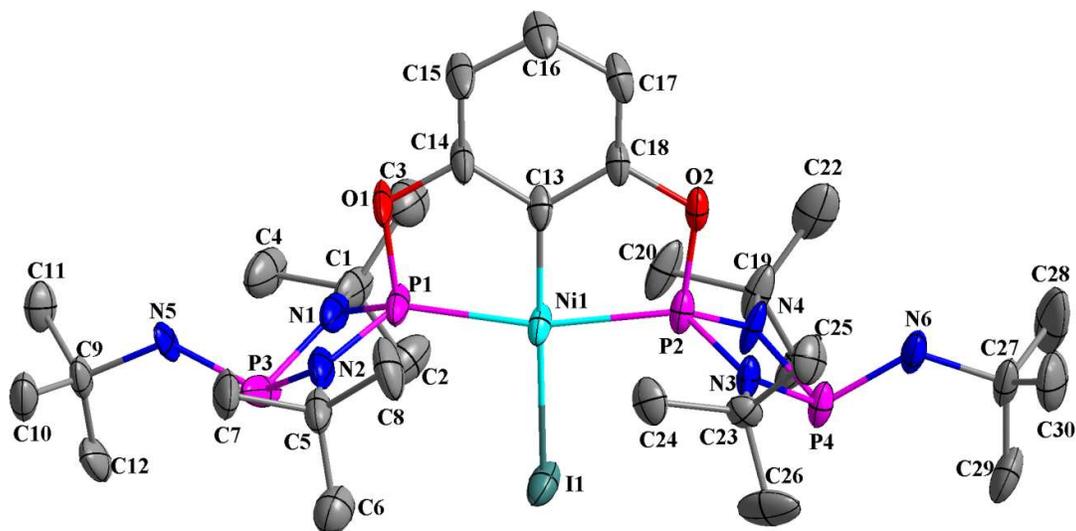
The crystals suitable for single crystal X-ray diffraction study were obtained from toluene solution of **1** at  $-20\text{ }^\circ\text{C}$ . The average P–O bond distance [ $1.700\text{ \AA}$ ] in **1** is longer than the

same in analogous compounds, 1,3- $\{\mu\text{-}(t\text{BuN})\text{P}(t\text{BuHN})\text{PO}\}_2\text{C}_6\text{H}_4$  [1.6705(13) Å],<sup>53</sup>  $\{\text{CH}_2\text{OP}(\mu\text{-}N^t\text{Bu})_2\text{PN}(\text{H})^t\text{Bu}\}_2$  [1.6383(14) Å],<sup>54</sup>  $\text{Et}_2\text{C}(\text{CH}_2\text{OP}(\mu\text{-}N^t\text{Bu})_2\text{PN}(\text{H})^t\text{Bu})_2$  [1.629(2) Å],<sup>55</sup> and  $\{t\text{Bu}(\text{H})\text{NP}(\mu\text{-}N^t\text{Bu})_2\text{POC}_6\text{H}_4\text{PPh}_2\text{-}o\}$  [1.6881(11) Å].<sup>52</sup> The average endocyclic P–N bond distance of phosphorus bearing an aryloxo substituent is 1.684 Å, whereas the average P–N bond distance, where phosphorus is bound to exocyclic nitrogen is 1.743 Å. Generally, the longer P–N bonds are associated with phosphorus atom having an exocyclic nitrogen substituent, whereas phosphorus bearing oxo-, alkoxo-, aryloxo-, or halo-substituents show shorter P–N bond distances.<sup>56, 57</sup> The exocyclic P3–N5 [1.666(3) Å] and P4–N6 [1.659(3) Å] bond distances are shorter than the average endocyclic P–N [1.715(3) Å] bond distances. The P<sub>2</sub>N<sub>2</sub> rings in **1** are slightly puckered with a folding along N···N axis, as indicated by the dihedral angle between the corresponding N–P–N planes (P1N1P3N2 = 6.13° and P2N3P4N4 = 1.24°).

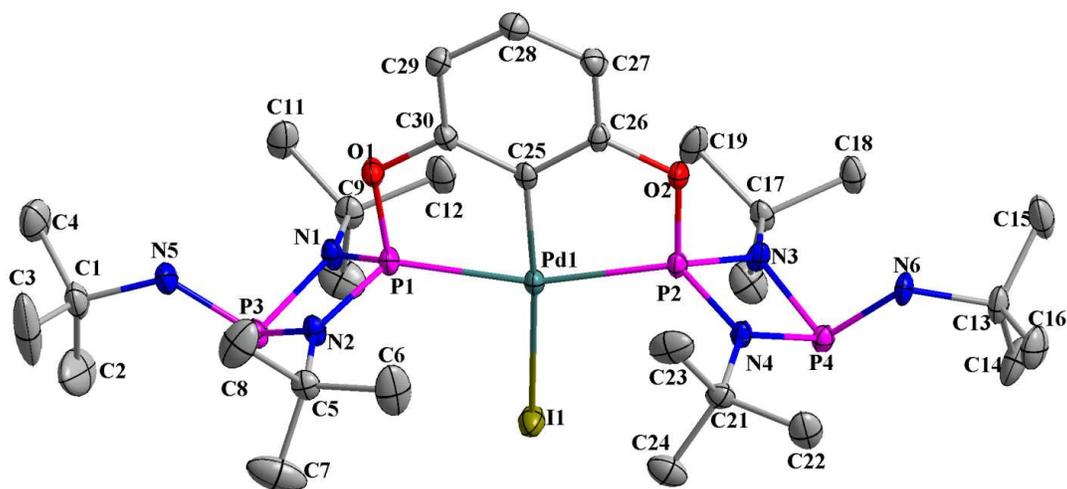


**Figure 1.** The molecular structure of 2,6- $\{\mu\text{-}(t\text{BuN})\text{P}(t\text{BuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{I}$  (**1**). All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Symmetry operation  $i = -x, -y, z+1/2$ .

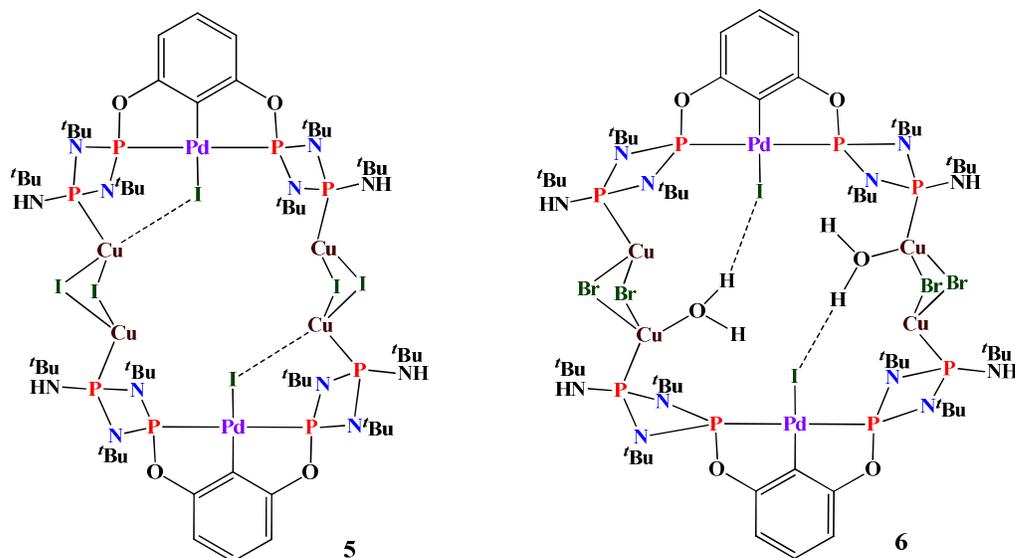
The crystal structures of **2** and **3** confirm the oxidative addition of C—I bond to metal centre along with the coordination of two aryloxo-phosphorus atoms. The geometry around the metal center in both the complexes **2** and **3** is distorted square planar. A slight distortion primarily arises from the relatively small P–M–P angles in **2** [166.28(6)°] and **3** [162.20(4)°]. The average P–O bond distances in **2** [1.652 Å] and **3** [1.648 Å] are shorter than the same in ligand **1** [1.700 Å]. The Ni1–P1 and Ni1–P2 bond distances are 2.1668(13) Å and 2.1621(11) Å, respectively. The Ni–P bond distances are similar to those observed in [NiCl{2,6-C<sub>6</sub>H<sub>3</sub>(OPPh<sub>2</sub>)<sub>2</sub>}] [2.157 Å] and [NiI{2,6-C<sub>6</sub>H<sub>3</sub>(OPPh<sub>2</sub>)<sub>2</sub>}] [2.158 Å].<sup>58-60</sup> The P1–O1 and P2–O2 bond distances in **3** are essentially the same [1.648(3) Å] and are slightly shorter than those of free ligand **1** [P1–O1 = 1.694(3) Å and P2–O2 = 1.708(3) Å]. The Pd1–C25 (1.980(3) Å) and Pd1–I1 (2.6608 Å) bond distances in **3** are similar to those reported for analogous pincer complexes of the type [PdI{2,6-C<sub>6</sub>H<sub>3</sub>(OPR<sub>2</sub>)<sub>2</sub>}] (Pd–C, 1.98 to 2.02 Å and Pd–I, 2.40 to 2.66 Å).<sup>47</sup> The Pd1–P1 and Pd1–P2 bond distances are 2.2758(9) Å and 2.2910(9) Å, respectively. The M–P bond distances in nickel complex **2** are slightly shorter than the same in palladium complex **3** which is expected due to the larger atomic radius of palladium. The C–M–I bonds are almost linear in both **2** (176.92°) and **3** (174.79(9)°). The metallocycles and the benzene rings are coplanar; two P<sub>2</sub>N<sub>2</sub> rings are pointed outwards from metal centre in both the complexes.



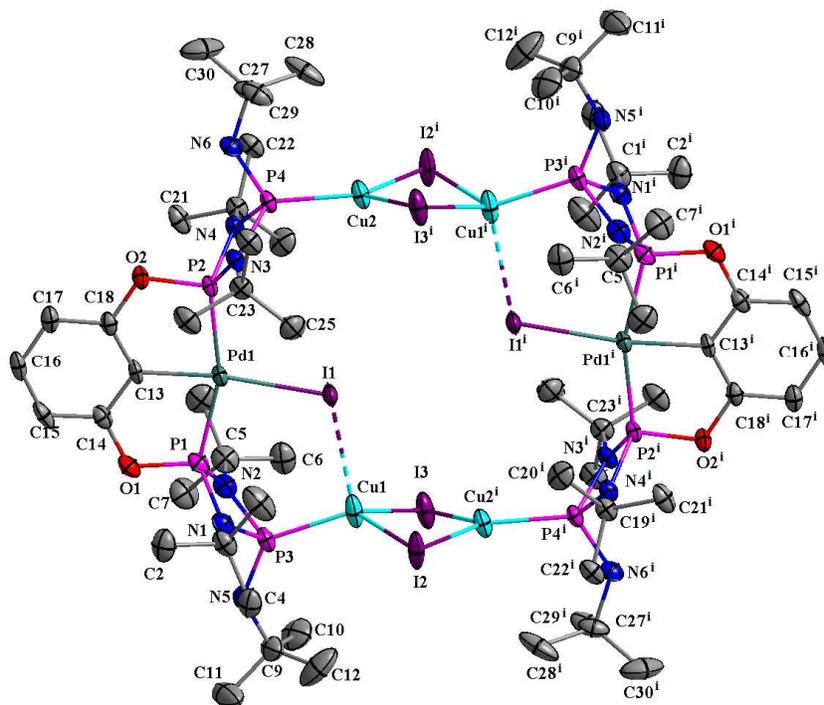
**Figure 2.** Molecular structure of  $[2,6-\{\mu-(t\text{BuN})\text{P}(t\text{BuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{NiI}]$  (**2**). All hydrogen atoms and lattice solvents are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Symmetry operation  $i = -x+1/2, y+1/2, -z+1/2$ .



**Figure 4.** The molecular structure of  $[2,6-\{\mu-(t\text{BuN})\text{P}(t\text{BuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{PdI}]$  (**3**). All hydrogen atoms and lattice solvents are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Symmetry operation  $i = -x, y+1/2, -z+1/2$ .



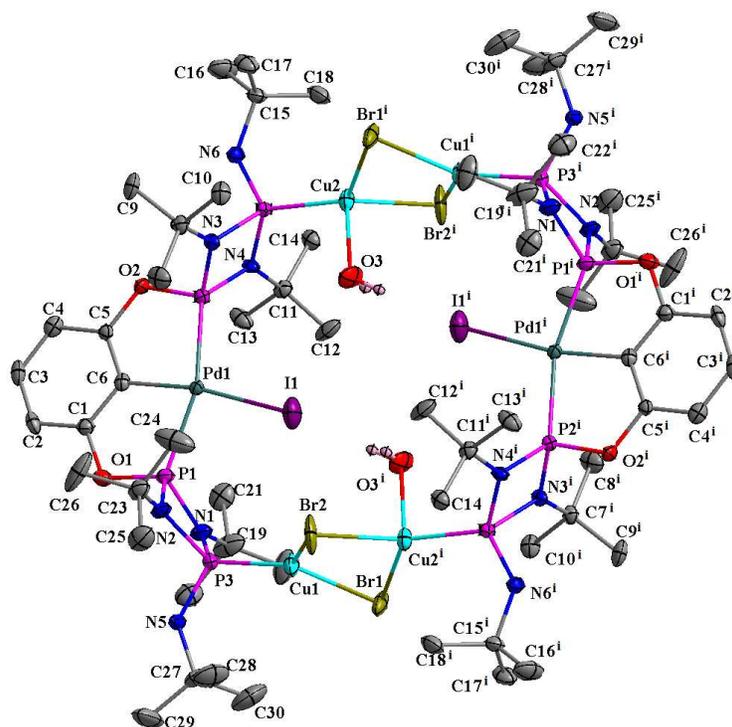
**Synthesis of multi-metallic copper(I)-palladium(II) complexes.** The multi-metallic complexes **5** and **6** were obtained by reacting the metallo-ligand 2,6- $\mu$ -(tBuN)P(tBuHN)PO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>PdI (**3**) with two equiv of CuI or CuBr. The dimeric complexes bridged by rhombic {Cu( $\mu$ -X)}<sub>2</sub> units were precipitated out from the reaction mixture as insoluble off white solids. However, partial solubility of compound **5** in DMSO allowed spectral characterization. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **5** showed two resonances; a sharp singlet at 122 ppm was assigned to palladium bound phosphorus centers, whereas the broad resonance at 75.0 ppm was due to the phosphorus centers coordinated to copper atoms. The molecular structures of **5** and **6** were established by single crystal X-ray analysis.



**Figure 5.** The molecular structure of  $[\{\{\text{Cu}(\mu\text{-I})\}_2\}2,6\text{-}\{\mu\text{-}(\text{t-BuN})\text{P}(\text{t-BuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{PdI}]$  (**5**). All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Symmetry operation  $i = -x+1/2, y+1/2, -z+1/2$ .

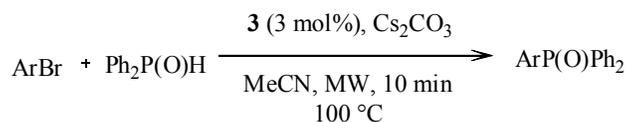
**Molecular structures of complexes 5 and 6.** The X-ray quality crystals of complexes **5** and **6** were obtained by slow diffusion of copper halide solution in acetonitrile into a dichloromethane solution of **3** at room temperature. The pincer units in **5** and **6** are bridged by rhombic  $\{\text{Cu}(\mu\text{-X})\}_2$  units to form pincer dimers. The rhombic  $\{\text{Cu}(\mu\text{-X})\}_2$  units present in **5** and **6** consists of both tricoordinated and tetracoordinated copper centers (Figures 5 and 6). The tricoordinated copper centers adopt trigonal planar geometry, whereas the tetracoordinated copper centers assume distorted tetrahedral geometry. The  $\text{Cu1-I1}_{\text{Pd}}$  bond distance in **5** is 2.9302(12) Å. The average Cu-I bond distance [2.557 Å] for tricoordinated copper centers is less than the same in the tetracoordinated centers [2.654 Å]. The increase in the bond lengths are due to the increase in coordination number from three to four. Similar trend is also observed in complex **6**. The tricoordinated copper centers in **5** and **6** adopt planer

geometry ( $\Sigma\angle\text{Cu} = 359.9^\circ$ ). In **6**, one of the copper atoms of  $\{\text{Cu}(\mu\text{-Br})\}_2$  units is coordinated by a water molecule. The water molecule shows weak interactions with palladium bound iodine atom with a H—I distance of 2.239 Å and O—H—I bond angle of  $171.8^\circ$ . The average Cu—P bond distance in **5** (2.209 Å) is marginally greater than the same in **6** (2.196 Å). The Pd1—I1 [2.6724(9) Å] and Pd1—C [1.993(5) Å] bonds in **5** are slightly elongated compared to that of **3** [Pd1—I1 (2.6608(4) Å and Pd1—C 1.980(3) Å] due to the interaction of palladium bound iodine with copper center. Similar elongations of bond lengths are not observed in **6**. The four-membered  $\{\text{Cu}_2(\mu\text{-X})_2\}$  and  $\text{P}_2\text{N}_2$  rings are slightly puckered as indicated by their torsion angles.



**Figure 6.** The molecular structure of  $[\{\{\text{Cu}(\mu\text{-Br})\}_2(\text{OH}_2)\}_2, 6\text{-}\{\mu\text{-}(\text{tBuN})\text{P}(\text{tBuHN})\text{PO}\}_2\text{C}_6\text{H}_3\text{PdI}]$  (**6**). All hydrogen atoms and lattice solvents are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Symmetry operation  $i = -x+1/2, y+1/2, -z+1/2$ .

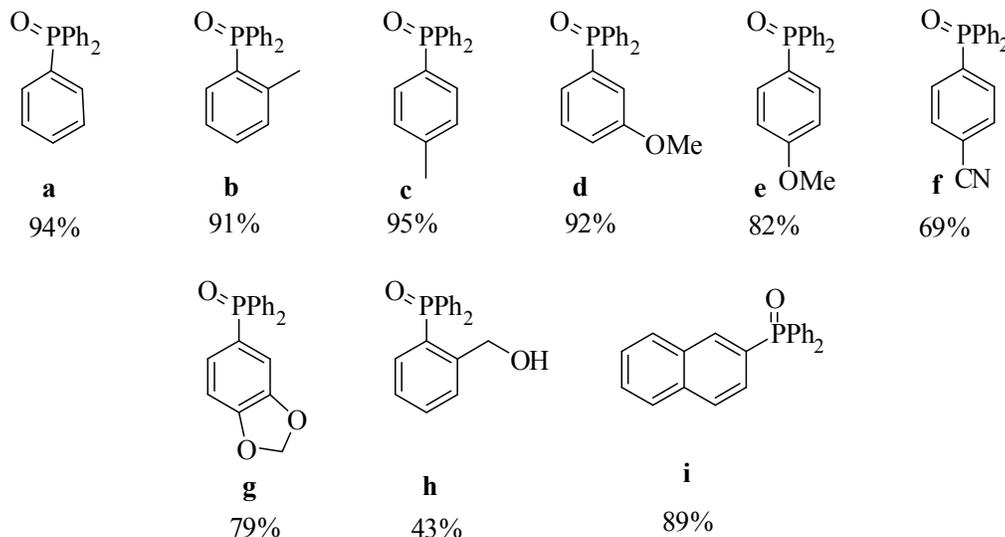
**Catalytic P-arylation reactions.** The aryl phosphine oxides are of importance due to their applications in polymer chemistry,<sup>61</sup> and photoelectric materials.<sup>62</sup> Also, many of them are used as ligands or ligand precursors in organo- and transition metal catalysis.<sup>63</sup> Synthesis of arylphosphine oxides generally involves Li or Mg reagents; however, they lack functional groups tolerance. Metal catalyzed C–P bond forming reactions offer a versatile alternative method.<sup>61, 64</sup> Several Palladium,<sup>65, 66</sup> nickel<sup>67</sup> and copper<sup>68</sup> based catalytic systems have been employed for the preparation of aryl phosphonates and phosphine oxides by P-arylation of H-phosphine oxides. Recently, palladacycles were effectively utilized in C–P bond forming reactions.<sup>65, 69</sup> In order to evaluate the catalytic efficiency of palladium pincer complex **3**, P-arylation reactions were performed under microwave irradiation conditions.



**Scheme 2.** P-arylation reactions

Initially, the coupling of bromobenzene with diphenylphosphine oxide was performed to test the catalytic ability of palladium complex **3** under microwave irradiation. An excellent yield of triphenylphosphine oxide was obtained when Cs<sub>2</sub>CO<sub>3</sub> was used as a base in acetonitrile at 100 °C. The coupling reaction was strongly influenced by the base. Replacing Cs<sub>2</sub>CO<sub>3</sub> with K<sub>2</sub>CO<sub>3</sub> or K<sub>3</sub>PO<sub>4</sub> gave only moderate conversions. Several aryl halides were tested for P-arylation reaction and moderate to good yields of arylphosphine oxides are obtained (Scheme 2). For example, bromobenzene or bromotoluenes underwent P-arylation reaction with good yield in acetonitrile (Chart 1, entries **a** – **c**). Both the electron donating and electron withdrawing substituents showed good conversions (Chart 1, entries **d** – **i**). In

contrast, the coupling reaction of 2-bromopyridine or 4-chloroacetophenone with diphenylphosphine oxide was not successful and resulted in negligible conversions.



**Chart 1.** Substrate scope in P-arylation reaction

## Conclusions

The present study has shown that the cyclodiphosphazane based ligand **1** can serve as an attractive template for the synthesis of mono- and multi-metallic complexes. The oxidative addition of low-valent metal precursors to **1** produced pincer complexes in good yield. The uncoordinated phosphorus centers in palladium complex were utilized to make mixed copper-palladium complexes. Interestingly, in the complex **6**, two of the copper centers are coordinated by water molecules. The palladium bound iodine atoms show bonding interactions with copper atoms which can be exploited in catalytic reactions as this interaction can polarize the Pd–I bond. These features not seen in conventional pincer ligands may come handy in tuning the catalytic activity of such complexes for various organic transformations. The catalytic activity of palladium complex **3** was tested for P-arylation reaction of diphenylphosphine oxide. Good yields were observed with aryl bromide

substrates. Current investigations are directed towards the study of cooperative effect of two metal centers in Cu--Pd heterometallic complexes for various catalytic transformations.

### Experimental section

**General procedures.** All manipulations were performed using standard vacuum line and Schlenk techniques under nitrogen atmosphere unless otherwise stated. All the solvents were purified by conventional procedures and distilled prior to use.<sup>70</sup> The compounds 2-iodoresorcinol,<sup>71</sup> *cis*-{ClP( $\mu$ -N<sup>t</sup>Bu)<sub>2</sub>PN(H)<sup>t</sup>Bu},<sup>72</sup> Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>,<sup>73</sup> Pt(PPh<sub>3</sub>)<sub>4</sub><sup>74</sup> and CuBr<sup>75</sup> were prepared according to the published procedures. CuI and Ni(COD)<sub>2</sub> were purchased from Aldrich chemicals and used as such without further purification. Other chemicals were obtained from commercial sources and purified prior to use.

**Instrumentation.** The NMR spectra were recorded at the following frequencies: 400 MHz (<sup>1</sup>H), 100 MHz (<sup>13</sup>C), 162 or 202 MHz (<sup>31</sup>P) using either Varian VXR 400, Bruker AV 400 or AV 500 spectrometers. <sup>13</sup>C and <sup>31</sup>P NMR spectra were acquired using broad band decoupling. The spectra were recorded in CDCl<sub>3</sub> (or DMSO-*d*<sub>6</sub>) solutions with CDCl<sub>3</sub> (or DMSO-*d*<sub>6</sub>) as internal lock; chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported in ppm downfield from TMS, used as internal standard. The chemical shifts of <sup>31</sup>P NMR spectra are referred to 85% H<sub>3</sub>PO<sub>4</sub> (in D<sub>2</sub>O) as external standard. The signals are quoted as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). The microanalyses were performed using a Carlo Erba Model 1112 elemental analyzer. The mass spectra were recorded using Waters Q-ToF micro (YA-105). The melting points were observed in capillary tubes and are uncorrected.

**Synthesis of 2,6- $\{\mu$ -(<sup>t</sup>BuN)P(<sup>t</sup>BuHN)PO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>I (1).** To a mixture of 2-iodoresorcinol (0.7 g, 2.97 mmol) and triethylamine (1.1 g, 1.5 mL, 11.6 mmol) in diethyl ether (25 mL) was added dropwise a solution of *cis*-{ClP( $\mu$ -N<sup>t</sup>Bu)<sub>2</sub>PN(H)<sup>t</sup>Bu} (1.85 g, 5.94 mmol) in diethyl ether (30 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. Triethyl amine hydrochloride formed was filtered through a frit layered with

activated Celite. The solvent was evaporated under reduced pressure to obtain **1** as white solid. Analytically pure product of **1** was obtained by recrystallizing the crude product in toluene. Yield: 73% (1.7 g). Mp: 126–130 °C. Anal. Calcd. for C<sub>30</sub>H<sub>59</sub>IN<sub>6</sub>O<sub>2</sub>P<sub>4</sub>: C, 45.81; H, 7.56; N, 10.68. Found: C, 45.48; H, 7.43; N, 10.74. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.12–7.05 (m, 3H, Ar), 3.41 (d, <sup>2</sup>J<sub>PH</sub> = 8.0 Hz, 2H, NH), 1.37–1.30 (m, br, 54H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 156.3, 128.3, 112.5, 112.3, 51.7, 51.6, 32.8, 31.4. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ 144.1 (d, <sup>2</sup>J<sub>PP</sub> = 12 Hz), 112.7 (d). MS (EI): *m/z* 661.1 [M–I]<sup>+</sup>.

**Synthesis of [2,6- $\{\mu\text{-}^t\text{BuN}\}\text{P}^t\text{(BuHN)PO}\}_2\text{C}_6\text{H}_3\text{NiI}$ ] (**2**).** A mixture of **1** (0.04 g, 0.051 mmol) and Ni(COD)<sub>2</sub> (0.014 g, 0.051 mmol) in THF (20 mL) was refluxed for 6 h. The reaction mixture was allowed cool to room temperature. The solution was filtered and the solvent was removed under vacuum to obtain a yellow solid. The yellow solid was washed twice with hot petroleum ether to obtain yellow crystalline material of **2**. Analytically pure **2** was obtained by recrystallizing the crude product in a 1:1 mixture of dichloromethane-petroleum ether. Yield: 72% (0.031 g). Mp: >254 °C (dec). Anal. Calcd. for C<sub>30</sub>H<sub>59</sub>IN<sub>6</sub>O<sub>2</sub>P<sub>4</sub>Ni·CH<sub>2</sub>Cl<sub>2</sub>: C, 40.02; H, 6.61; N, 9.03. Found: C, 39.79; H, 7.32; N, 8.75. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.07 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, Ar, 1H), 6.47 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, Ar, 2H), 3.29 (d, <sup>3</sup>J<sub>PH</sub> = 6.8 Hz, NH, 2H), 1.46 (s, <sup>t</sup>Bu, 36H), 1.36 (s, <sup>t</sup>Bu, 18H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 160.3, 135.5, 128.9, 105.1, 52.5, 32.2. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>): δ 133.6 (s), 101.7 (s). MS (EI): *m/z* 845.1 [M+H]<sup>+</sup>.

**Synthesis of [2,6- $\{\mu\text{-}^t\text{BuN}\}\text{P}^t\text{(BuHN)PO}\}_2\text{C}_6\text{H}_3\text{PdI}$ ] (**3**).** This compound was prepared analogously to **2** by refluxing a mixture of Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (0.078 g, 0.075 mmol) and **1** (0.12 g, 0.153 mmol) in THF (20 mL). Yield: 71% (0.11 g). Mp: 265–268 °C. Anal. Calcd. for C<sub>30</sub>H<sub>59</sub>IN<sub>6</sub>O<sub>2</sub>P<sub>4</sub>Pd: C, 40.35; H, 6.66; N, 9.41. Found: C, 40.77; H, 6.60; N, 9.05. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.10 (tt, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, <sup>5</sup>J<sub>PH</sub> = 1.6 Hz, 1H, Ar), 7.00 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H, Ar), 3.31 (d, <sup>2</sup>J<sub>PH</sub> = 7.2 Hz, 2H, NH), 1.42 (s, <sup>t</sup>Bu, 36H), 1.36 (d, <sup>4</sup>J<sub>PH</sub> = 1.3 Hz, <sup>t</sup>Bu,

18H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.1, 129.1, 128.7, 106.0, 52.7, 33.0, 32.2.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  126.7 (s), 100.8 (s). MS (EI):  $m/z$  892.7  $[\text{M}]^+$ .

**Synthesis of [2,6- $\mu$ -( $t$ -BuN)P( $t$ -BuHN)PO] $_2$ C $_6$ H $_3$ PtI] (4).** This compound was prepared analogously to **2** by refluxing a mixture of  $\text{Pt}(\text{PPh}_3)_4$  (0.064 g, 0.051 mmol) and **1** (0.04 g, 0.051 mmol) in THF (20 mL). Yield: 79% (0.039 g). Mp:  $>270$  °C. Anal. Calcd. for  $\text{C}_{30}\text{H}_{59}\text{I}_6\text{N}_6\text{O}_2\text{P}_4\text{Pt}$ : C, 36.70; H, 6.06; N, 8.56. Found: C, 36.36; H, 5.89; N, 8.85.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30–7.08 (m, Ar, 3H), 3.29 (d,  $^3J_{\text{PH}} = 7$  Hz, NH, 2H), 1.36 (s,  $t$ Bu, 36H), 1.30 (s,  $t$ Bu, 18H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.2, 133.6, 128.5, 105.4, 52.5, 32.8.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  121.6 (s,  $^1J_{\text{PtP}} = 3925$  Hz), 99.2 (s).

**Synthesis of [Cu( $\mu$ -I)] $_2$ [2,6- $\mu$ -( $t$ -BuN)P( $t$ -BuHN)PO] $_2$ C $_6$ H $_3$ PdI] (5).** An acetonitrile (5 mL) solution of CuI (0.0145 g, 0.0761 mmol) was added dropwise over a well stirred solution of **3** (0.034 g, 0.0387 mmol) in dichloromethane (5 mL) and stirring was continued for another 4 h at room temperature. The solvent was evaporated, and the residue was washed with petroleum ether (5 mL) and dried under reduced pressure to form the analytically pure product **5** as off white solid. Yield: 93% (0.045 g). Mp:  $>270$ °C. Anal. Calcd. for  $\text{C}_{60}\text{H}_{118}\text{I}_6\text{N}_{12}\text{O}_4\text{P}_8\text{Cu}_4\text{Pd}_2$ : C, 28.28; H, 4.67; N, 6.60. Found: C, 28.20; H, 4.40; N, 6.85.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.16 (t,  $^3J_{\text{HH}} = 7.8$  Hz, Ar, 2H), 6.65 (d,  $^3J_{\text{HH}} = 7.8$  Hz, Ar, 4H), 5.50 (br, s, NH, 4H), 1.41 (s,  $t$ Bu, 72H), 1.40 (s,  $t$ Bu, 36H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  122.0 (s), 75.0 (br, s).

**Synthesis of [Cu( $\mu$ -Br)] $_2$ [2,6- $\mu$ -( $t$ -BuN)P( $t$ -BuHN)PO] $_2$ C $_6$ H $_3$ PdI] (6).** This compound was prepared analogously to **5** by adding a solution of CuBr (0.0081 g, 0.0562 mmol) in acetonitrile (5 mL) to the solution of **3** (0.0251 g, 0.0281 mmol) in dichloromethane (5 mL). Yield: 90% (0.029 g). Mp:  $>270$ °C. Anal. Calcd. for  $\text{C}_{60}\text{H}_{118}\text{N}_{12}\text{O}_4\text{P}_8\text{I}_2\text{Br}_4\text{Cu}_4\text{Pd}_2$ : C, 30.54; H, 5.04; N, 7.12. Found: C, 30.55; H, 5.01; N, 7.31.

**General procedure for the catalytic P-arylation reactions.** The reactions were performed in a sealed tube containing a mixture of aryl halide (1.0 equiv), diphenylphosphine oxide (1.0 equiv), Cs<sub>2</sub>CO<sub>3</sub> (1.2 equiv), catalyst **3** (3 mol%) and acetonitrile (4 mL). An initial microwave power of 150 W was applied to reach 100 °C temperature. After specified reaction time, the reaction mixture was filtered through Celite and diluted with H<sub>2</sub>O (5 mL) and Et<sub>2</sub>O (5 mL) followed by extraction with diethylether (2 × 5 mL). The combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude products were purified by silica gel column chromatography using ethyl acetate as the eluent. Yields were calculated versus diphenylphosphine oxide.

**X-Ray crystallography.** Crystal of each of the compounds **1 – 3**, **5** and **6** suitable for X-ray crystal analysis were mounted on a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected using 606 scans in  $\omega$  (0.3° per scan) at  $\varphi = 0, 120$  and  $240^\circ$  using the SMART<sup>76</sup> software package, or the APEX2<sup>77</sup> program suite. The raw data were reduced to F<sup>2</sup> values using the SAINT+ software. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS<sup>78</sup>). The structures **2** and **5** were solved by heavy atom method, while remaining structures were solved by direct method and refined by full-matrix least-squares procedures using the SHELXTL program package.<sup>78</sup> Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS). Hydrogen atoms attached to carbon were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Those attached to nitrogen were placed in locations derived from a difference map and also included as riding contributions as for the others. The

isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for phenyl hydrogen and 1.5 times for  $C(CH_3)_3$ . In the final refinement, the hydrogen atoms were riding with the carbon atom to which they were bonded. The details of X-ray structural determinations are given in Table 2. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1023326 (compound **1**), 1023322 (compound **2**), 1023323 (compound **3**), 1023324 (compound **5**) and 1023325 (compound **6**).

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### Supporting Information

X-ray crystallographic files in CIF format for the structure determinations of **1 – 3, 5** and **6** and copies of  $^{31}P\{^1H\}$  NMR spectra of the compounds.

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**Table 1.** Selected bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ] for **1** – **3**, **5** and **6**

	bond lengths [ $\text{\AA}$ ]						bond angles [ $^\circ$ ]				
	<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>	<b>6</b>		<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>	<b>6</b>
P1–O1	1.694(3)	1.650(4)	1.648(3)	1.647(3)	1.642(5)	N1–P1–N2	82.87(14)	84.4(2)	84.97(14)	84.6(2)	84.2(3)
P2–O2	1.708(3)	1.653(4)	1.648(3)	1.657(3)	1.652(5)	N1–P3–N2	79.67(14)	79.4(2)	79.39(14)	80.34(19)	80.6(3)
P1–N1	1.686(3)	1.664(4)	1.658(3)	1.670(4)	1.662(6)	N1–P3–N5	105.23(14)	103.8(3)	103.85(16)	107.5(2)	106.6(3)
P3–N2	1.740(3)	1.744(4)	1.758(3)	1.650(4)	1.725(7)	P1–N1–P3	98.36(15)	97.4(2)	97.83(15)	95.4(2)	96.5(3)
P3–N5	1.666(3)	1.604(7)	1.655(3)	1.650(4)	1.639(6)	P1–M–P2		166.28(6)	162.20(4)	161.35(5)	162.01(6)
C–I	2.091(3)					I1–M–C		176.92(12)	174.79(9)	171.31(11)	170.64(18)
P1–M		2.1668(13)	2.2758(9)	2.2570(13)	2.2607(16)	M–P1–O1		104.53(13)	103.97(9)	105.57(12)	104.88(18)
P2–M		2.1621(12)	2.2910(9)	2.2901(12)	2.2826(15)	P1–M–C		83.21(12)	81.12(9)	80.44(11)	80.68(19)
M–I1		2.5027(7)	2.6608(4)	2.6724(9)	2.6123(10)	P1–M1–I1		98.31(4)	93.90(3)	91.17(4)	90.43(5)
M–C		1.868(4)	1.980(3)	1.993(5)	1.989(7)	P2–M1–I1		95.37(4)	103.88(3)	107.40(3)	107.52(5)
Cu1–P3				2.2223(16)	2.218(2)	M–I1–Cu1				112.49(2)	
Cu2–P4				2.1958(14)	2.1738(18)	P3–Cu1–I1				98.63(4)	
Cu1–I1				2.9303(12)		P3–Cu1–X				122.49(5)	127.03(9)
Cu1–X2				2.6426(12)	2.461(7)	P4–Cu2–X				126.98(4)	125.55(7)
Cu2–X2				2.5595(10)	2.549(7)	X–Cu1–X				103.42(3)	105.6(2)
Cu2–O3					2.212(12)	X–Cu2–X				109.15(3)	101.10(18)

**Table 2.** Crystallographic Information for Compounds **1** – **3**, **5** and **6**.

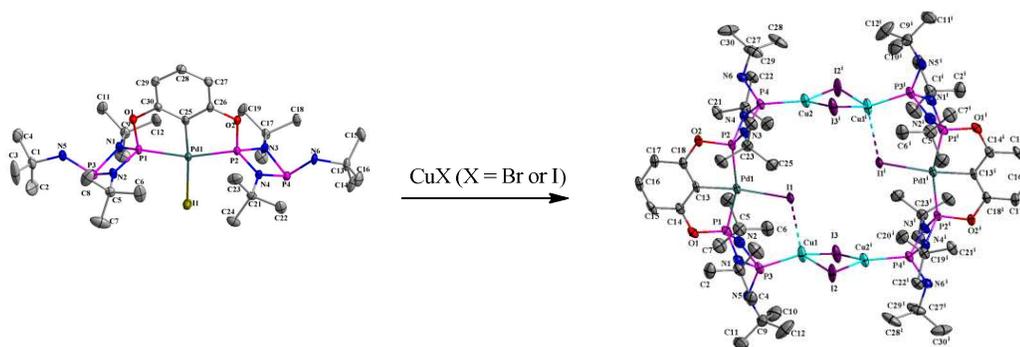
	<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>	<b>6</b>
Formula	C <sub>30</sub> H <sub>59</sub> IN <sub>6</sub> O <sub>2</sub> P <sub>4</sub>	C <sub>30</sub> H <sub>59</sub> IN <sub>6</sub> NiO <sub>2</sub> P <sub>4</sub> · 2CHCl <sub>3</sub>	C <sub>30</sub> H <sub>59</sub> IN <sub>6</sub> O <sub>2</sub> P <sub>4</sub> Pd· 2CHCl <sub>3</sub>	C <sub>60</sub> H <sub>118</sub> Cu <sub>4</sub> I <sub>6</sub> N <sub>12</sub> O <sub>4</sub> P <sub>8</sub> Pd <sub>2</sub>	C <sub>60</sub> H <sub>120</sub> Br <sub>4</sub> Cu <sub>4</sub> I <sub>2</sub> N <sub>12</sub> O <sub>5</sub> P <sub>8</sub> Pd <sub>2</sub> · CH <sub>2</sub> Cl <sub>2</sub>
Formula Weight	786.61	1084.06	1131.75	2547.78	2462.77
Crystal System	Orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>Pca</i> 2 <sub>1</sub> (No. 29)	P12 <sub>1</sub> /n1 (No. 14)	P12 <sub>1</sub> /c1 (No. 14)	P12 <sub>1</sub> /n 1 (No. 14)	P12 <sub>1</sub> /n 1 (No. 14)
a [Å]	28.754(3)	16.6214(16)	15.3398(15)	15.390(4)	15.4735(8)
b [Å]	8.4632(8)	15.2055(15)	16.6898(17)	19.203(5)	19.4221(10)
c [Å]	16.4274(15)	19.0941(19)	18.9655(19)	18.045(5)	17.5182(9)
α [°]	90	90	90	90	90
β [°]	90	91.530(1)	94.375(2)	111.990(4)	113.460(1)
γ [°]	90	90	90	90	90
V [Å <sup>3</sup> ]	3997.6(7)	4824.1(8)	4841.4(8)	4945(2)	4829.5(4)
Z	4	4	4	2	2
ρ <sub>calc</sub> [gcm <sup>-3</sup> ]	1.307	1.493	1.553	1.711	1.694
μ (Mo-K <sub>α</sub> ) [mm <sup>-1</sup> ]	0.994	1.542	1.519	3.245	3.757
F(000)	1640	2216	2288	2480	2440
T (K)	100	100	100	100	100
2θ range [°]	2.4-29.0	1.8-27.9	2.0-28.3	1.8-28.2	1.8-27.9
Total no. of reflns	10480	102296	106851	84469	82607
No. of indep reflns	9838	19001	19796	10524	9073
R <sub>int</sub>	0.0413	0.095	0.052	0.054	0.068
R	0.0382	0.0563	0.0459	0.0434	0.0627
wR	0.0929	0.1020	0.1020	0.1037	0.1949
S	1.131	1.06	1.17	1.03	1.05

Where  $w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 1.2733P]$ , where  $P = (F_o^2 + 2F_c^2)/3$

Synopsis and graphics for the contents page

**Cyclodiphosphazane based pincer ligand, 2,6- $\mu$ -  
(<sup>t</sup>BuN)P(<sup>t</sup>BuHN)PO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>: Ni<sup>II</sup>, Pd<sup>II</sup>, Pt<sup>II</sup> and Cu<sup>I</sup> complexes, and catalytic  
studies**

Guddekoppa S. Ananthnag<sup>a</sup>, Joel T. Mague<sup>b</sup> and Maravanji S. Balakrishna<sup>\*,a</sup>



Pincer complexes derived from difunctional cyclodiphosphazanes and their multimetallic macrocycles and catalytic studies have been described.

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