

# Chloro bridged Palladium (II) hexamers supported by tris imido phosphate tri-anions and studies of their catalytic evaluations

A thesis

Submitted in partial fulfillment of the requirements

Of

B.S M.S Dual Degree Programme

By

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# Certificate

This is to certify that this dissertation entitled “*Chloro Bridged Palladium (II) Hexamers Supported by Tris Imido Phosphate Tri Anions and Studies of their Catalytic Evaluations*” towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by “**Arun Dixith Reddy Shada** at IISER Pune” under the supervision of “**Dr R Boomi Shankar**, Assistant Professor, Chemistry” during the academic year 2013-2014

**Date:** 2<sup>nd</sup> April 2014, Pune

**Place:** Pune

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## DECLARATION

I hereby declare that the matter embodied in the report entitled “*Chloro Bridged Palladium (II) Hexamers Supported by Tris Imido Phosphate Tri Anions and Studies of their Catalytic Evaluations*” are the results of the investigations carried out by me at the Department of Chemistry, IISER PUNE, under the supervision of **Dr. R Boomi Shankar** and the same has not been submitted elsewhere for any other degree.

**Date:** 2<sup>nd</sup> April 2014, Pune

**Mr. Arun Dixith Reddy Shada**

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## *Acknowledgements*

*I express my reflective gratitude to my research supervisor Dr. R. Boomi Shankar for his precious suggestion, incisive guidance and decisive insights during the entire course of B.S -M.S Research. I am also thankful to him for giving me freedom to pursue my own ideas and for standing by my side in each step I have taken. I find myself privileged to have worked under his kind guidance. My everlasting gratitude goes towards him.*

*I thank Director, Prof. K. N. Ganesh, for giving outstanding research facilities, financial support that I have been privileged with, during my research here at Indian Institute of Science of Education and Research (IISER) Pune, India. I would like to acknowledge my sincere gratitude to my Thesis Advisory Committee (TAC) member Dr. M. Jeganmohan for his intellectual support, encouragement and valuable suggestions. My honest regards to all the faculty of the Department of Chemistry for their motivation and encouragement.*

*My sincerest thankfulness goes towards my senior Dr. Arvind Gupta for his help throughout my research and guiding me in all possible ways and giving moral confidence during tough times. I would like to extend my gratitude towards my lab mates Anant, Ashok, Mahesh, Vijaykanth, Raja Shekar and Indra for their cooperation in finishing my thesis successfully. It would not have been possible for me to come to this successful ending of my project without their support.*

*I acknowledge the help from Archana for X-ray instrumental support, Swati M. Dixit for recording MALDI-TOF/TOF and CHN analysis and Neeraj for PXRD. Ravi Kiran, Kishore and Chenna Reddy for their suggestions in organic chemistry. Gopal and Kiran for Crystal structure solutions, 104 lab members and all my beloved ones.*

*The thesis remains incomplete without mentioning the motivation blessings and love of my family members for their understanding, encouragement, patience, unending support and blessings in my every endeavor without which my M.S. could not be completed. They are the main soul and inspiration for each and every step that I achieve in my life.*

*Finally I pray to almighty God whose blessings made me able to complete the research work and submit this thesis for B.S-M.S degree.*

*ARUN REDDY*

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## List of Abbreviations Used

A	Appendix
Ac	Acyl
Anal.	Analysis
Ar	Aryl
Bu.	Butyl
Calcd.	Calculated
Cy	Cyclohexyl
DCM	Dichloromethane
DMF	N, N-Dimethyl formamide
DMSO	Dimethyl Sulfoxide
ESI	Electron Spray Ionization
Et	Ethyl
EtOH	Ethanol
EPR	Electron Paramagnetic Resonance
Mg	Milligram
$\mu$ L	Microliter
$\mu$ M	Micro molar
Min	Minutes
N	Normal
HRMS	High resolution mass spectrometer
Hrs	Hours
IR	Infrared Spectroscopy
Mmol	milli moles
Me	Methyl
MeOH	Methanol
MALDI-TOF	Matrix-Assisted Laser Desorption /Ionization – Time of Flight
MP (mp)	Melting point
MOF	Metal Organic Framework
NMR	Nuclear Magnetic Resonance
ORTEP	Oak Ridge Thermal Ellipsoid Program
RT	Room Temperature
Ph	Phenyl
Py	Pyridyl
THF	Tetrahydrofuran
TOF	Time of Flight
TMS	Tetramethylsilane
Pr	Propyl
Ppm	parts per million
UV	Ultraviolet

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## Abstract

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Employing  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ , a facile deprotonation route to access the highly basic tris(alkylimido)phosphate trianions,  $[(\text{NR})_3\text{PO}]^{3-}$  ( $\text{R} = {}^n\text{Pr}, {}^n\text{Bu}, {}^i\text{Pr}, {}^o\text{Hex}$ ), analogous to the orthophosphate ( $\text{PO}_4^{3-}$ ) ion in polar and in protic solvents has been achieved. Octahedral and prismatic  $\text{Pd}_6$ -clusters of these imido-trianions having the formula  $\{\text{Pd}_3[(\text{NR})_3\text{PO}](\text{Cl})_3\}_n$  ( $n = 1$  or  $2$ ) or as mixed-bridged clusters of the type  $\{\text{Pd}_3[(\text{NR})_3\text{PO}](\text{OAc})_2(\text{Cl})\}_2$  ( $n = 1$  or  $2$ ) were isolated exclusively in all these reactions in which the trianionic species acts as the tripodal chelating ligand to the trinuclear  $\text{Pd}_3$ -unit. Reactivity studies aiming at the  $\text{Pd}(\text{II})$  centers in these clusters with nucleophilic reagents such as primary amines ( $\text{R}''\text{NH}_2$ ) have led to a new trimeric cluster of formula  $\{\text{Pd}_3[(\text{NR})_3\text{PO}](\text{Cl})_3(\text{R}''\text{NH}_2)_3\}$  in which the tripodal coordination of the  $\text{Pd}-\text{N}_{\text{imido}}$  moieties remained unaffected. Similarly, reaction of  $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}](\text{Cl})_3\}_2$  with 1,1'-ferrocenedicarboxylic acid (FDC-H) replaces the four chloro bridges with two FDC bridges  $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}](\text{FDC})(\text{Cl})\}_2$ . These reactions showed that the trinuclear  $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}]\}^{3+}$  motif is stable in solution and can be linked with suitable carboxylate linkers to yield the elusive high-nuclearity neutral cage molecules for  $\text{Pd}(\text{II})$  ions and also exemplifying the robustness of the  $\text{Pd}_3$ -unit in all these clusters. We have also shown the catalytic activity of these  $\text{Pd}(\text{II})$  complexes in Mizoroki- Heck type coupling reactions in presence of  $\text{Cu}(\text{OAc})_2$  and Suzuki coupling reactions in presence of  $\text{Na}_2\text{CO}_3$ . We have also reported the Suzuki coupling reactions of aryl halides to biaryls in aqueous phase as well.

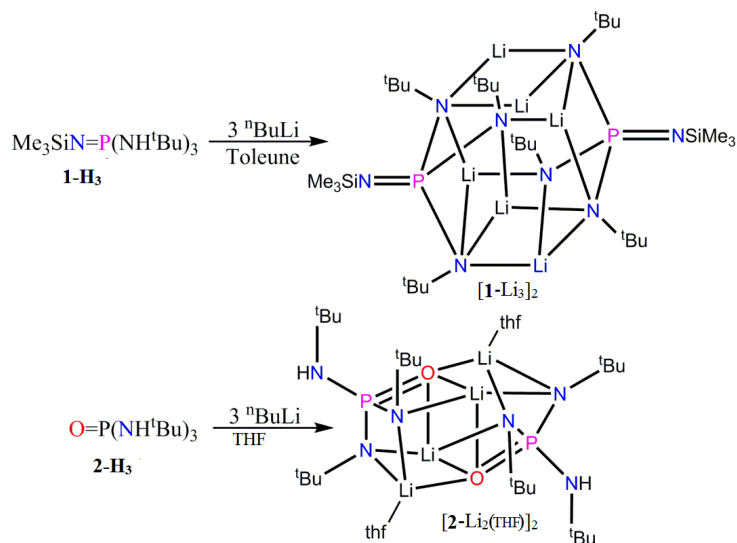


## 1. Introduction:

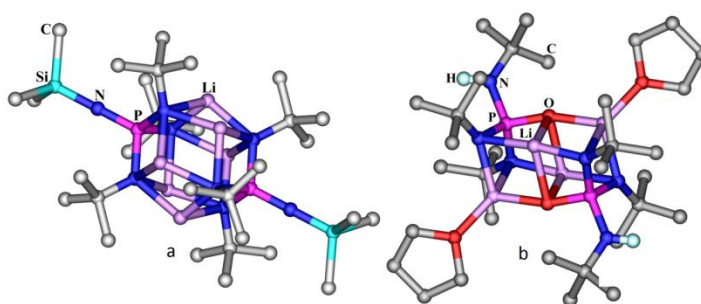
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Hetero atom ligands containing a phosphorus–nitrogen bond have been known for over three decades. Phosphorus groups have been shown to form bonds with nitrogenous groups with relative ease, and compounds containing phosphorous–nitrogen (P–N) bonds are chemically stable. These facts make the investigation of P–N bonds containing ligands an interesting project. Aryl-nitrogen, aryl-oxygen, and aryl-acetylene bonds are prevalent in many compounds that are of biological, pharmaceutical, and materials interest. Over the years in recognition of their widespread importance, many synthetic methods have emerged for the formation of these bonds.

Especially, Phosphorous oxo-anions containing imido analogues are of great research interest in main group chemistry. The compounds that contain P–N<sub>amino/imino</sub> bonds make them more stable and hence accounts for the formation of various ligands used in synthesis of metal complexes that have applications in catalytic systems for oligomerization and polymerization, ring opening polymerization of lactic acids, organic bond activation, hydroamination, and transfer hydrogenation etc.<sup>1</sup> The study of Tris(amido) P(V) ligands in deprotonation chemistry resulting in coordination complexes with interesting cage and cluster structures is of great interest (Scheme 1.1). First attempts in this area was done by Chivers and co-workers, they have shown the full deprotonation of the imido tris(amido) phosphate ligand P(NSiMe<sub>3</sub>)[N(H)<sup>t</sup>Bu]<sub>3</sub>, **1-H<sub>3</sub>**, with <sup>n</sup>BuLi to generate the first example of a heteroleptic tetra-imido phosphate trianion, analogous to [PO<sub>4</sub>]<sup>3-</sup> ion, which formed a hexameric complex of formula [**1-Li<sub>3</sub>**]<sub>2</sub> (Figure 1.1a).<sup>2</sup> However, the analogous tris(amido) ligand **2-H<sub>3</sub>** achieved only double deprotonation and resulted in the formation of the imido anion analogous to [HPO<sub>3</sub>]<sup>2-</sup> ion, owing to the coordination of the phosphoryl oxygen atom (Figure 1.1b). The structure of [**2-Li<sub>2</sub>(THF)**]<sub>2</sub> is a Centrosymmetric dimer consisting of four Li<sup>+</sup> cations linked by two dianionic ligand moieties of **2**.

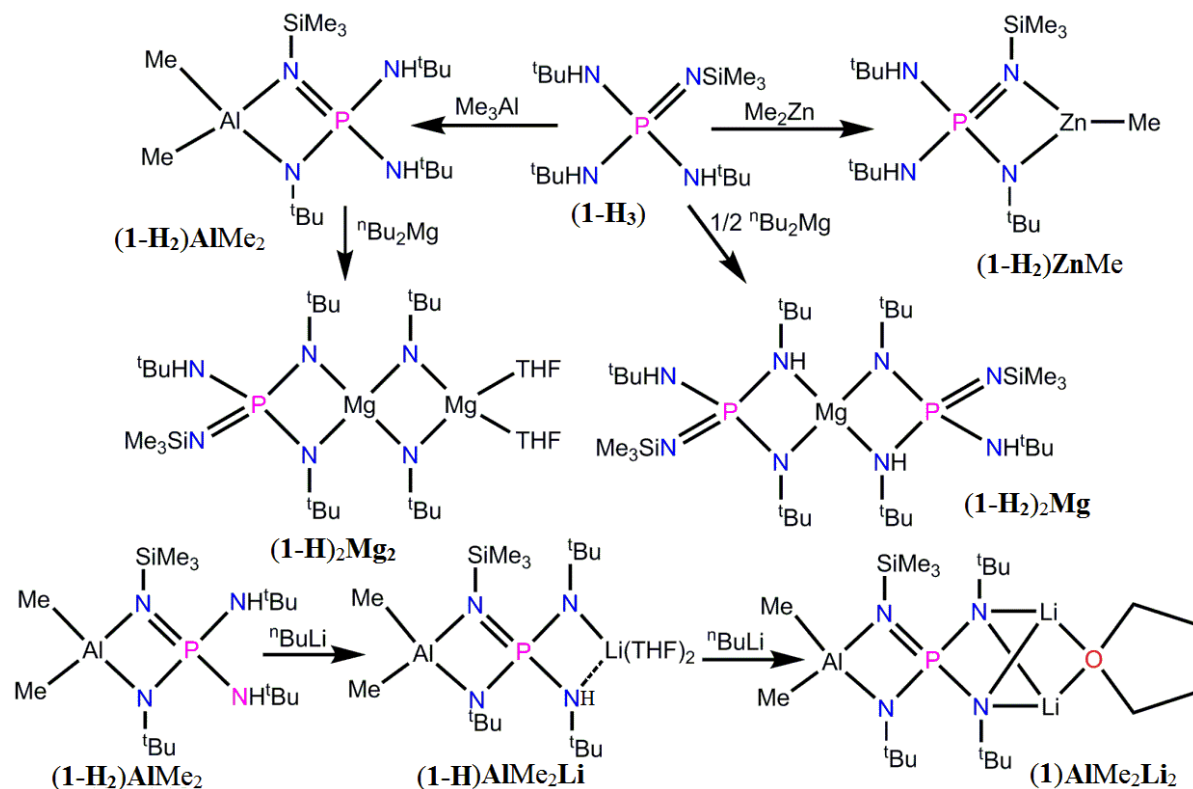


**Scheme 1.1:** Synthesis of bis- and tri-imido phosphate anions.

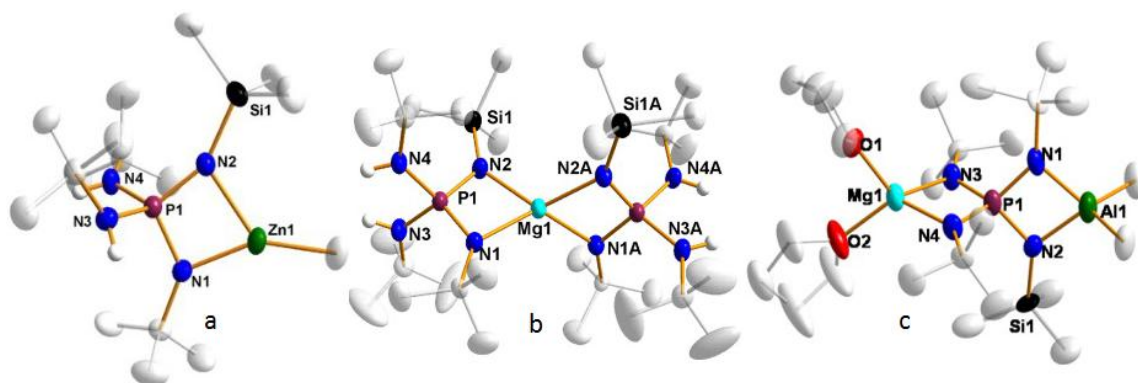


**Figure 1.1:** Crystal structure of (a) Tetrakisimido-phosphate and (b) face-sharing double-cubane complex.

The heteroleptic precursor **1-H<sub>3</sub>** was further tested for deprotonation with various other organometallic reagents such as  $^n\text{Bu}_2\text{Mg}$ ,  $\text{Me}_2\text{Zn}$ ,  $\text{Et}_2\text{Zn}$  and  $\text{Me}_3\text{Al}$ . To their surprise, these reagents were unable to achieve complete de-protonation, in all these instances only a mono-deprotonation was observed during the initial reactions.<sup>3</sup> However, the Al complex **1-H<sub>2</sub>AlMe<sub>2</sub>** was able to undergo further deprotonation in presence of  $^n\text{BuLi}$  or  $^n\text{Bu}_2\text{Mg}$  (Scheme 1.2). Deprotonation was performed using 1 or 2 equivalents of  $n\text{-BuLi}$ , yielding a mono and di-lithiated bimetallic complexes where the coordination sphere of Li was completed by THF. Similarly, reaction of **1-H<sub>2</sub>AlMe<sub>2</sub>** with  $^n\text{Bu}_2\text{Mg}$  resulted in complete deprotonation in which the coordination sphere of Mg was completed by THF. However, attempted metalation of **1-H<sub>2</sub>AlMe<sub>2</sub>** with  $^n\text{BuLi}$  or  $^n\text{Bu}_2\text{Mg}$  resulted in nucleophilic displacement of methylzinc fragment by Li or Mg (Scheme 1.2).



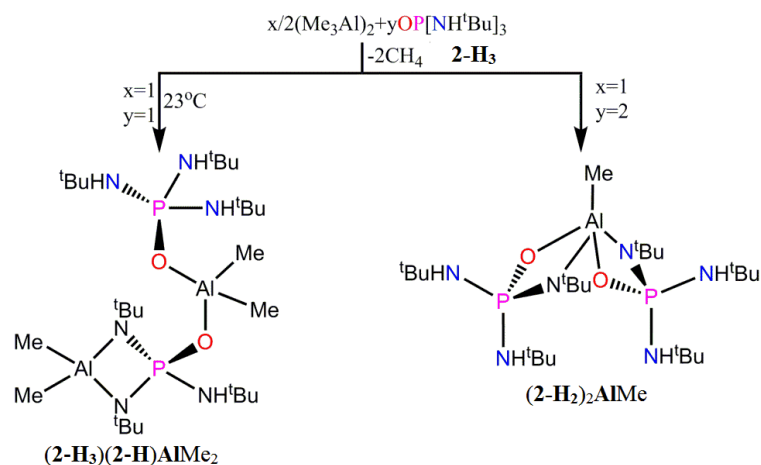
**Scheme 1.2:** Schematic representation for the synthesis of iminophosphate complexes.



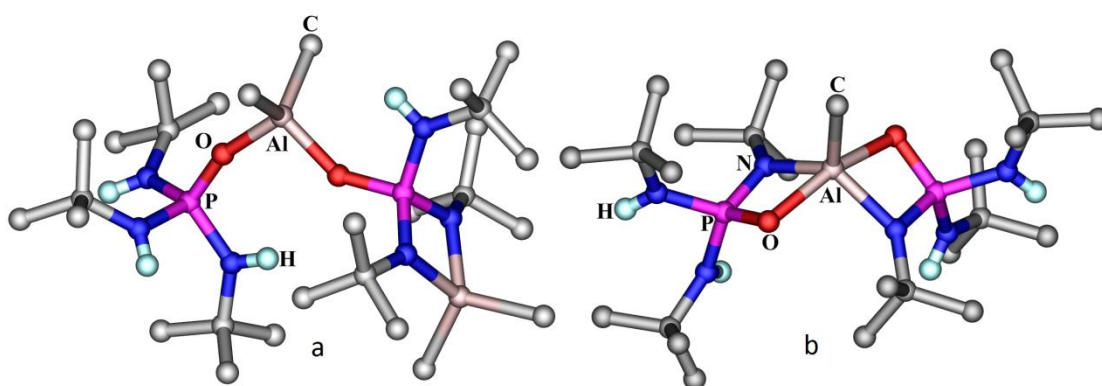
**Figure 1.2:** Crystal structures of monomeric Zn and Mg complexes<sup>4,5</sup>.

Chivers et al. have also studied the deprotonation in the phosphoramidate **2-H<sub>3</sub>** using organo aluminium reagents. Depending on the stoichiometry and reaction condition they have reported two types of complexes in these reactions. A 1:1 molar ratio of **2-H<sub>3</sub>** and Me<sub>3</sub>Al at room temperature gave a mixture of products in which the compound **(2-H<sub>3</sub>)(2-H)AlMe<sub>2</sub>** was obtained as a major product and **(2-H<sub>2</sub>)<sub>2</sub>AlMe** as a minor product, as traced by <sup>1</sup>H and <sup>31</sup>P NMR. But when the reaction was performed

with 2:1 molar ratio of reagents in refluxing n-hexane,  $(2\text{-H}_2)_2\text{AlMe}$  was obtained exclusively. (Scheme 1.3)<sup>6</sup> The complex  $(2\text{-H}_3)(2\text{-H})\text{AlMe}_2$  consists of two  $\text{Al}^{3+}$  centers and two ligand motifs, out of which one ligand is doubly deprotonated with one residual amino arm and other with no deprotonation and is found to be coordinated to one of the  $\text{Al}^{3+}$  center via its phosphoryl oxygen atom. Both the  $\text{Al}^{3+}$  ions are tetra-coordinated having two residual methyl groups on each of them. The remaining two contacts on each of these two  $\text{Al}^{3+}$  ions were respectively provided by two  $\text{N}_{\text{imido}}$  sites from one of the ligand moieties and two phosphoryl oxygens from two different ligands. On the other hand the  $\text{Al}^{3+}$  ion in the mononuclear complex  $(2\text{-H}_2)_2\text{AlMe}$  exhibits a distorted trigonal bipyramidal coordination having two chelating O,  $\text{N}_{\text{imido}}$  ligand contacts and one residual methyl group. (Figure 1.3)



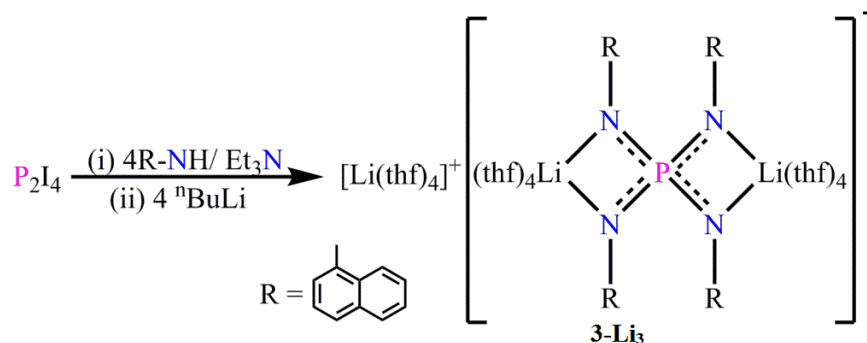
**Scheme 1.3:** Schematic representation for the synthesis of iminophosphate Al-complex.



**Figure 1.3:** Crystal structure of  $(2\text{-H}_3)(2\text{-H})\text{AlMe}_2$  and  $(2\text{-H}_2)_2\text{AlMe}$ .

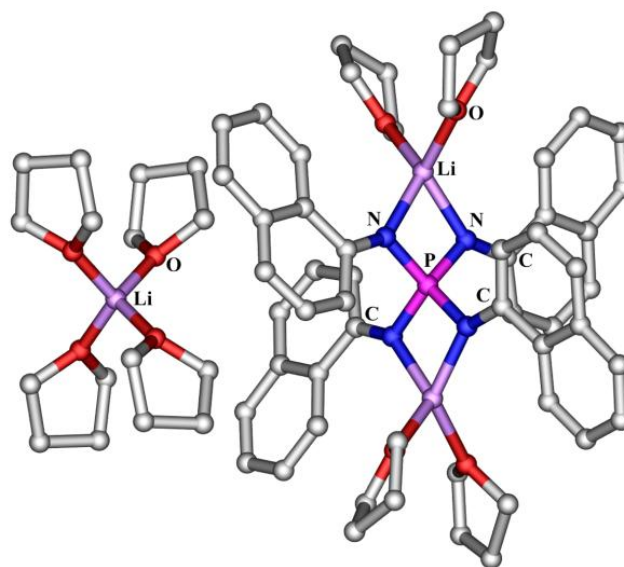
The first example of the homoleptic tetra-imidophosphate trianion was reported by Wright and co-workers in an unprecedented reaction.<sup>7</sup> They have

reported the reaction of diphosphorus tetraiodide with  $\alpha$ -naphthylamine and subsequent addition of butyllithium which resulted in lithium complex.<sup>8</sup> X-ray structure determination revealed a solvent separated ion pair **3-Li<sub>3</sub>** (Figure 1.4).



**Scheme 1.4:** Synthesis of Tetrakis(imido)phosphate anion.

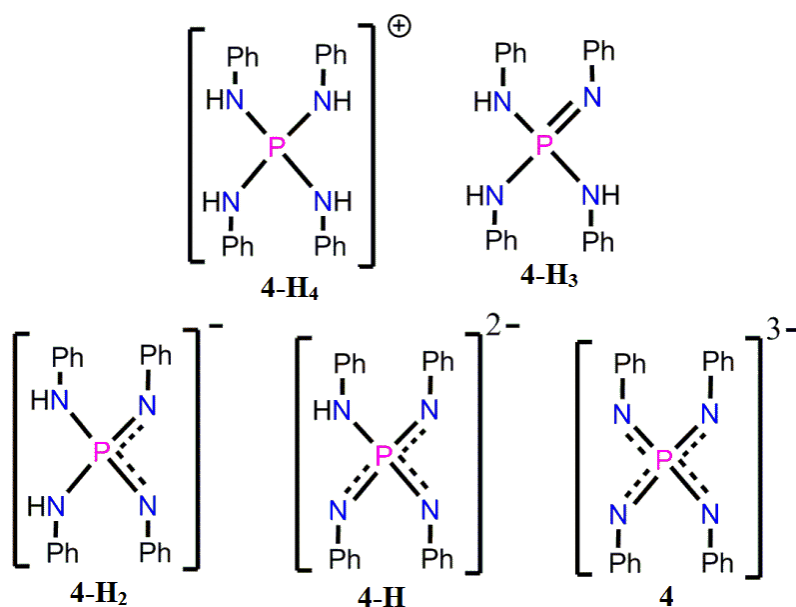
The complex anion consists of the trianionic ligand accommodating two lithium ions in two bidentate chelating sites. The cationic complex contains a lithium ion surrounded by four THF molecules.



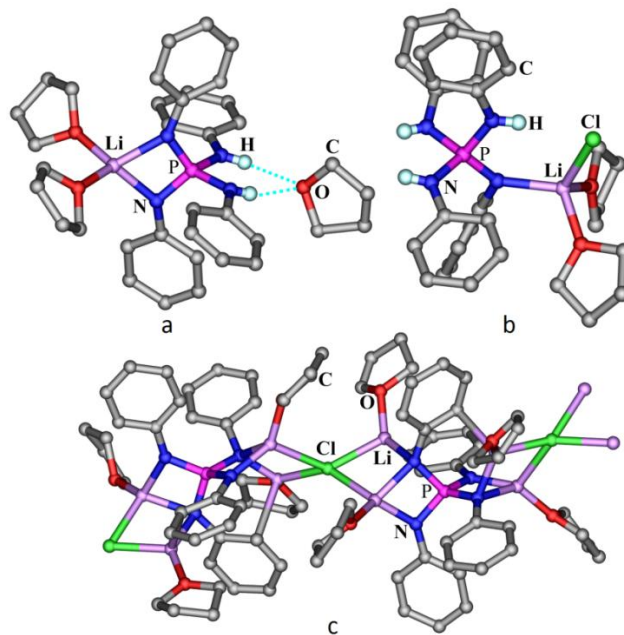
**Figure 1.4:** Crystal structures of Li complex of tetrakisimido phosphate (**3-Li<sub>3</sub>**).

Subsequently, Steiner and coworkers have shown step-wise deprotonation of tetraanilino phosphonium cation,  $[\text{P}(\text{NHPH})_4]^+$  (**4-H<sub>4</sub>**), by  $^n\text{BuLi}$  in THF.<sup>9,10</sup> Thus, the deprotonation reaction of  $[\text{P}(\text{NHPH})_4]\text{Cl}$  generates the neutral phosphine imine  $[\text{P}(\text{NHPH})_3(\text{NPh})]$  (**4-H<sub>3</sub>**), monoanionic  $[\text{P}(\text{NHPH})_2(\text{NPh})_2]^-$  (**4-H<sub>2</sub>**), dianionic  $[\text{P}(\text{NHPH})(\text{NPh})_3]^{2-}$  (**4-H**) and trianionic  $[\text{P}(\text{NPh})_4]^{3-}$  (**4**) species upon treatment with 1, 2, 3 and excess equivalence of  $^n\text{BuLi}$  respectively (Figure 1.5 & 1.6). The

formations of these imido species were monitored by  $^{31}\text{P}$ -NMR and their solid state structures have also been obtained. Since the oxo ( $=\text{O}$ ) and imino ( $=\text{NR}$ ) groups as well as hydroxyl ( $-\text{OH}$ ) and amido ( $-\text{NHR}$ ) groups are isoelectronic, we can see these neutral, monoanionic, dianionic and trianionic species as analogues of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), dihydrogenphosphate ( $\text{H}_2\text{PO}_4^-$ ), monohydrogen phosphate ( $\text{HPO}_4^{2-}$ ) and orthophosphate ( $\text{PO}_4^{3-}$ ) ions, respectively. Here though the oxo phosphate analogues form highly networked solid state structures, their N analogues have a tendency to form structures with lower dimensionality because of the presence of organic substitution at the N atom. All these properties suggest that similar platforms with functionalized ligand periphery can be synthesized which can be utilized as building blocks for materials with unique connectivity patterns.



**Figure 1.5:** Tetraanilino phosphonium cation and its neutral, mono-, di- and tri-anionic forms.



**Figure 1.6:** Crystal structures of (a)  $13\text{Li}(\text{THF})_{3.5}$ , (b)  $13\text{LiCl}(\text{THF})_2$ ,  
(c)  $3\text{Li}_2\text{Cl}(\text{THF})_6$

All the previously mentioned procedures uses highly basic organometallic reagents along with Phosphonium salts like  $[(\text{NHPh})_4\text{P}]\text{Cl}$  or phosphoramides like  $[(\text{RNH})_3\text{P}=\text{E}]$  ( $\text{E}=\text{NSiMe}_3, \text{O}, \text{S}$  or  $\text{Se}$ ) for P(V)imido anions synthesis. But the presence of residual metal-alkyl, aryl, silylamide bonds in these reactions renders these complexes as highly reactive and limits their utility to anhydrous aprotic and non-polar solvents. Thus our group was interested in deriving a simple strategy for the deprotonation of the N-H bonds in these amido P(V) ligands under ambient conditions. Previous literature survey reports that the use of Lewis acid transition metal ions such as  $\text{Cu}^{+2}$  ions in these deprotonation reactions leads to the cleavage of P-N bonds rather than the required N-H bonds deprotonation.<sup>11</sup> In this effort, our group has devised new strategies for obtaining these imido P(V) anions in protic and polar medium which involves the use of a less-acidic softer transition metal ion in combination with a stronger conjugate base as a leaving group. Thus by employing Ag(I) ion the deprotonation chemistry of a series of amino P(V) compounds viz., a phosphonium salt 1,  $[\text{P}(\text{NH}^2\text{py})_4]\text{Cl}$ , a phosphine imine 2,  $[\text{P}(\text{N}^2\text{py})(\text{NH}^2\text{py})_3]$  and a phosphoramidate 3,  $[\text{PO}(\text{NH}^2\text{py})_3]$  featuring 2-pyridyl ( $^2\text{py}$ ) substituents were developed. These results showed that depending upon relative reactivities of the Ag(I) salts, it was possible to achieve single or multiple deprotonation resulting in the formation of mono- and di-anionic imido phosphate anions. However, complete

deprotonation of all the amido groups in these ligands could not be achieved using these Ag(I) salts. Hence, we started looking at using other such reactive soft metal ions for these reactions.

Palladium and its compounds are widely used in catalysis and organic synthesis, and the organometallic chemistry of palladium involving Pd-C bonds has been focused primarily on the divalent oxidation state in presence of phosphine and nitrogen based donor ligands. Various Pd-based cyclo-metallated and intramolecular coordination system have shown to have applications in organic synthesis<sup>12</sup>. Palladium catalyzed carbon-carbon bond formation is one of the most useful protocols in organic synthesis and medicinal chemistry. The basic advantage of Palladium salt is its usage in coupling reactions that simplifying the lengthy organic reactions to single step; this is of peer interest to organic chemists in recent time.

Spurred by the utility of palladium and its compounds for various bond activation reactions, our group was interested in using the palladium salts in deprotonation reactions of tris(alkylamido) phosphate ligands, [(RNH)<sub>3</sub>P=O]. Thus it has been recently shown that the fully deprotonated tris(imido)phosphate trianions of the type [(RN)<sub>3</sub>PO]<sup>3-</sup> can be obtained from [(NHR)<sub>3</sub>PO] and Pd(OAc)<sub>2</sub> in polar solvents such as CH<sub>3</sub>OH, CH<sub>3</sub>CN, (CH<sub>3</sub>)<sub>2</sub>SO etc. This shows that Pd(OAc)<sub>2</sub> provides a facile deprotonation route to access the highly basic tris(alkylimido) phosphate trianions, [(RN)<sub>3</sub>PO]<sup>3-</sup>, in polar and in protic solvents. These highly basic anions were isolated as their corresponding tri- and prismatic hexa-nuclear Pd(II) clusters of the type {Pd<sub>3</sub>[(NR)<sub>3</sub>PO](OAc)<sub>3</sub>}<sub>n</sub> (n = 1 or 2) or as mixed-bridged clusters of the type {Pd<sub>3</sub>[(N<sup>i</sup>Pr)<sub>3</sub>PO](OAc)<sub>2</sub>(OR')<sub>2</sub>} (R' = Me or H) depending upon the R and R' groups and the reaction solvents.<sup>13</sup> In order to check the role of bridging ligands in formation of these and other kinds of clusters we set out to explore the utility of various Pd(II) salts such as Pd(OAc)<sub>2</sub> and PdCl<sub>2</sub> in reactions with the amido phosphate ligands. Herein, we have described the general utility of these deprotonation reactions and role of bridging ligands in controlling the nature of the hexameric imido Pd(II) cluster assemblies. During these studies, we have achieved the fully deprotonated species [(RN)<sub>3</sub>PO]<sup>3-</sup> as their corresponding chloro-bridged hexameric clusters {Pd<sub>3</sub>[(NR)<sub>3</sub>PO](Cl)<sub>3</sub>}<sub>2</sub> (**C**<sup>1</sup>, R = <sup>n</sup>Pr; **C**<sup>2</sup>, R = <sup>n</sup>Bu) and mixed chloro-



acetate bridged hexameric clusters  $\{Pd_3[(NR)_3PO](OAc)_2(Cl)\}_2$  (**C**<sup>7</sup>, R = <sup>i</sup>Pr; **C**<sup>8</sup>, R = <sup>o</sup>Hex). The chloro-bridged hexameric cluster  $\{Pd_3[(NR)_3PO](Cl)_3\}_2$  (R = <sup>i</sup>Pr) was subjected to further reaction with nucleophilic reagents such as primary amines (R''NH<sub>2</sub>). These reactions lead to a trimeric species of formula  $\{Pd_3[(NR)_3PO](Cl)_3(R''NH_2)_3\}$ , (R = <sup>i</sup>Pr) obtained via the symmetrical cleavage of the hexamer. This suggests that the three Pd-N<sub>imido</sub> moieties attached to the Pd<sub>3</sub>-subunit exhibits a remarkable stability and remains unaffected during the cleavage reaction. We then tried to replace the chloro bridges by reacting the clusters with various spacers like ferrocene dicarboxylic acid, isonicotinic acid, sulphur powder and triphenyl phosphine with an intention to obtain larger assemblies for these hexanuclear clusters. Thus, have successfully replaced four bridging chloride ions with two 1, 1 Ferrocene dicarboxylate ions (FDC) from **C**<sup>1</sup>. Then we went on to explore the preliminary catalytic activity of these chloro-bridged hexameric clusters **C**<sup>2</sup>, **C**<sup>4</sup>, **C**<sup>5</sup> and **C**<sup>6</sup> in various coupling reactions such as Mizoroki-Heck (M-H) type coupling reaction of phenyl boronic acid with alkenes, Suzuki cross coupling reactions with phenyl boronic acid. These reactions showed that the chloro-bridged Pd(II) clusters are excellent catalysts for most of the studied reactions.

## 2. Experimental section:

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### 2.1 General Remarks

All manipulations involving phosphorus halides were performed under dry nitrogen atmosphere in standard Schlenk-glassware. Solvents were dried over potassium (hexane) and sodium (toluene). The primary amines were purchased from Merck or from Aldrich and used as received. The halide precursor  $\text{POCl}_3$  was purchased locally (SPECTROCHEM, India) and was distilled prior to use. The ligands  $\text{L}^1\text{-H}_3$  and  $\text{L}^2\text{-H}_3$  were synthesized using literature methods.<sup>14</sup> NMR spectra were recorded on a Jeol 400 MHz spectrometer ( $^1\text{H}$  NMR: 400.13 MHz,  $^{13}\text{C}\{^1\text{H}\}$ NMR: 100.62 MHz,  $^{31}\text{P}\{^1\text{H}\}$  NMR: 161.97 MHz) or on a Bruker 500 MHz ( $^1\text{H}$  NMR: 500.00 MHz,  $^{13}\text{C}\{^1\text{H}\}$ NMR: 125.725 MHz,  $^{31}\text{P}\{^1\text{H}\}$  NMR: 202.404 MHz) spectrometer at room temperature using  $\text{SiMe}_4$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) as standards. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were obtained on an Applied Bio system MALDI-TOF/TOF spectrometer. Fourier transform infrared (FT-IR) spectra were taken on a Perkin-Elmer spectrophotometer with samples prepared as KBr pellets. Melting points were obtained using an Electro thermal melting point apparatus and were uncorrected.

### 2.2 Synthesis:

**$\text{L}^1\text{-H}_3$ :**  $\text{POCl}_3$  (5 ml, 8.23 g 0.0536 mol) was added drop wise to an excess of n-propyl amine (23.12 ml, 16.69 g, 0.282 mol) in toluene (250 mL) at 0 °C. The resulting mixture was slowly brought to room-temperature and stirred for 4 h. The precipitated n-propylammonium chloride was removed by filtration. The filtrate was reduced to 80 mL and hexane (50 mL) was added to it and left at -15 °C for 2 days to yield colorless crystals. Yield 95% (11.5 g, based on P). M.P. 120-124°C.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.57.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.85 (m, 2H), 1.50 (dd,  $J = 14.4, 7.3$  Hz, 2H), 0.91 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  77.16, 43.41, 25.72, 11.88. FT-IR data in KBr pellet ( $\text{cm}^{-1}$ ): 3490, 3185, 1640, 1460, 1420, 1389, 1175, 1111, 938, 887, 792, 540; ESI(+): 222.16  $[\text{M}+\text{H}]^+$ . Anal. Calcd. for  $\text{C}_9\text{H}_{24}\text{N}_3\text{OP}$ : C, 48.85; H, 10.93; N, 18.99. Found: C, 49.04; H, 10.85; N, 18.64.

**$\text{L}^2\text{-H}_3$ :**  $\text{POCl}_3$  (5 ml, 8.23 g 0.0536 mol) was added drop wise to an excess of n-butyl amine (28.61 ml, 21.1 g, 0.288 mol) in toluene (250 mL) at 0 °C. The resulting

mixture was refluxed for 4 h at room temperature a white precipitate formed. The n-butylammonium chloride was removed by filtration and washed with toluene. The volume of the filtrate was reduced to 80 mL and hexane (50 mL) was added, and after 2 days at  $-15\text{ }^{\circ}\text{C}$  a dense white impure semisolid was formed. The impure solid was used as it is for further reaction. Crude yield 94% (13 g, based on P)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.88 (tt,  $J = 14.1, 6.9\text{ Hz}$ , 2H), 1.45 (m, 2H), 1.33 (dq,  $J = 14.0, 7.1\text{ Hz}$ , 2H), 0.91 (dd,  $J = 9.5, 5.0\text{ Hz}$ , 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  77.16, 40.88, 34.11, 19.79, 13.52.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.63. FT-IR data in KBr pellet ( $\text{cm}^{-1}$ ): 3430, 3173, 1654, 1613, 1465, 1374, 1200, 1105, 1065, 1010, 933, 827, 769, 578. ESI(+): 264.36  $[\text{M}+\text{H}]^+$ , Anal. Calcd. for  $\text{C}_{12}\text{H}_{30}\text{N}_3\text{OP}$ : C, 54.73; H, 11.48; N, 15.96. Found: C, 54.45; H, 11.98; N, 15.66.

**C<sup>1</sup>:** To a solution of  $[\text{OP}(\text{NH}^n\text{Pr})_3]$ , **L<sup>1</sup>-H<sub>3</sub>**, (20 mg, 0.08 mmol) in methanol and bis(benzonitrile)palladium(II) chloride  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (39 mg, 0.24 mmol) in acetonitrile was added. The resulting mixture was stirred for 1 h and kept for crystallization. Orange block like crystals were obtained after 3 weeks. Yield 90% (52 mg, based on P). M.P.  $200\text{-}204\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  2.35 (dd,  $J = 7.7, 6.8\text{ Hz}$ , 2H), 1.63 (dd,  $J = 14.9, 7.4\text{ Hz}$ , 2H), 0.84 (t,  $J = 7.4\text{ Hz}$ , 3H);  $^{13}\text{C}$  NMR (101 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  45.52, 39.52, 23.47, 10.92;  $^{31}\text{P}$  NMR (162 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  16.22. FT-IR data in KBr pellet ( $\text{cm}^{-1}$ ): 3454, 1728, 1561, 1413, 1275, 1175, 1041, 976, 752, 634; ESI(+): 1281.58  $(\text{M}+\text{Na})^+$ , 698  $(\text{M}-\text{C}_4\text{H}_9)^+$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{42}\text{Cl}_6\text{N}_6\text{O}_2\text{P}_2\text{Pd}_6$ : C, 16.79; H, 3.29; N, 6.53. Found: C, 16.50; H, 3.20; N, 6.38.

**C<sup>2</sup>:** To a solution of  $[\text{OP}(\text{NH}^n\text{Bu})_3]$ , **L<sup>2</sup>-H<sub>3</sub>**, (20mg, 0.06 mmol) in methanol and bis(benzonitrile)palladium(II) chloride  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  (51 mg, 0.18 mmol) in acetonitrile was added. The resulting mixture was stirred for 1 h and kept for crystallization. Dark red crystals were obtained after 4 weeks. Yield 90% (69 mg, based on P). M.P.  $190\text{-}192\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  2.67 (d,  $J = 5.6\text{ Hz}$ , 2H), 1.35 (dd,  $J = 14.6, 7.5\text{ Hz}$ , 2H), 1.26 (dd,  $J = 14.9, 7.2\text{ Hz}$ , 2H), 0.85 (t,  $J = 7.2\text{ Hz}$ , 3H);  $^{13}\text{C}$  NMR (101 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  77.79, 77.16, 72.11, 57.97, 51.80;  $^{31}\text{P}$  NMR (162 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  76.90. FT-IR data in KBr pellet ( $\text{cm}^{-1}$ ): 3322, 1659, 1431, 1404, 1213, 1016, 637; ESI(+): 1366.6124  $(\text{M}+\text{H})^+$ , 836  $(\text{M}/2)^+$ . Anal. Calcd. for  $\text{C}_{24}\text{H}_{54}\text{Cl}_6\text{N}_6\text{O}_2\text{P}_2\text{Pd}_6$ : C, 21.01; H, 3.97; N, 6.13. Found: C, 23.87; H, 4.04; N, 5.88.

**C<sup>7</sup>:** *Method A:* To a solution of [OP(NH<sup>i</sup>Pr)<sub>3</sub>], (20 mg, 0.06 mmol) in methanol, palladium acetate Pd(OAc)<sub>2</sub> (27 mg, 0.12 mmol) in methanol was added and stirred for 30 minutes then bis(benzonitrile)palladium(II) chloride Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (17 mg, 0.18 mmol) in acetonitrile was added. The resulting mixture was stirred for 1 h and kept for crystallization. Dark red crystals were obtained after 4 weeks. *Method B:* To a solution of [OP(NH<sup>i</sup>Pr)<sub>3</sub>]<sup>+</sup>(<sup>i</sup>PrNH<sub>3</sub><sup>+</sup> Cl<sup>-</sup>), (20 mg, 0.06 mmol) in methanol, palladium acetate Pd(OAc)<sub>2</sub> (41 mg, 0.18 mmol) in methanol was added and stirred for 30 minutes. The resulting mixture was stirred for 1 h and kept for crystallization. Yield 90% (69 mg, based on P). M.P. 189-192°C; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>-d) δ 76.39; FT-IR data in KBr pellet (cm<sup>-1</sup>) 3322, 1659, 1431, 1404, 1213, 1016, 637; ESI(+): 1378.6124 (M+H)<sup>+</sup>, 689 (M/2)<sup>+</sup>. Anal. Calcd. for C<sub>26</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>10</sub>P<sub>2</sub>Pd<sub>6</sub>: C, 22.59; H, 3.94; N, 6.08. Found: C, 22.87; H, 4.04; N, 5.88.

**C<sup>8</sup>:** *Method A:* To a solution of [OP(NH<sup>c</sup>Hex)<sub>3</sub>], (35 mg, 0.06 mmol) in methanol, palladium acetate Pd(OAc)<sub>2</sub> (27 mg, 0.12 mmol) in methanol was added and stirred for 30 minutes then bis(benzonitrile)palladium(II) chloride Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (17 mg, 0.18 mmol) in acetonitrile was added. The resulting mixture was stirred for 1 h and kept for crystallization. *Method B:* To a solution of [OP(NH<sup>c</sup>Hex)<sub>3</sub>], (35 mg, 0.06 mmol) in methanol, palladium acetate Pd(OAc)<sub>2</sub> (41 mg, 0.18 mmol) in methanol was added and stirred for 30 minutes. The resulting mixture was stirred for 1 h and kept for crystallization. Dark red crystals were obtained after 4 weeks. Yield 85% (69 mg, based on P). M.P. 195-197°C; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>-d) δ 75.08; FT-IR data in KBr pellet (cm<sup>-1</sup>) 3332, 1649, 1421, 1408, 1216, 1065, 636; ESI(+): 1678.6124 (M+H)<sup>+</sup>, 839 (M/2)<sup>+</sup>. Anal. Calcd. for C<sub>44</sub>H<sub>78</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>10</sub>P<sub>2</sub>Pd<sub>6</sub>: C, 32.57; H, 4.85; N, 5.18. Found: C, 32.87; H, 4.64; N, 5.08.

**C<sup>9</sup>:** To a solution of **C<sup>3</sup>** (30 mg, 0.04 mmol) in methanol, isopropylamine (12.0 mg, 14 μL, 0.12 mmol) was added. The resulting mixture was stirred for 30 minutes and kept for crystallization. Pale yellow colored solid was obtained upon slow evaporation. Yield 80% (72 mg, based on P). M.P. 143-145 °C; <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD): δ 1.28 (m, 12H, CH<sub>2</sub>), 1.33 (s, 27H, CH<sub>3</sub>), 1.65 (m, 3H, CH), 1.88 (m, 6H, CH<sub>2</sub>), 2.08 (br, 6H, NH<sub>2</sub>), 2.63 (s, 9H, CH<sub>3</sub>COO), 2.74 (m, 12H, CH<sub>2</sub>); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD): δ 25.08, 25.79, 27.66, 32.50, 38.02, 40.86, 52.86, 179.35; <sup>31</sup>P-NMR (161 MHz, CD<sub>3</sub>OD): δ 72.01; FT-IR data in KBr pellet (cm<sup>-1</sup>): 3477, 1718,

1619, 1568, 1408, 1283, 1145, 1032, 968, 748, 625; MALDI-TOF/TOF: 840 (M+Na)<sup>+</sup>. Anal. Calcd. for C<sub>18</sub>H<sub>8</sub>N<sub>6</sub>OPPd<sub>3</sub>: C, 26.33; H, 5.98; N, 10.23. Found: C, 26.03; H, 5.83; N, 10.22.

**C<sup>10</sup>**: To a solution of **C<sup>1</sup>** (20 mg, 0.013 mmol) in methanol, 1, 1' Ferrocene dicarboxylic acid (Cp)<sub>2</sub>Fe(COOH)<sub>2</sub> (7.21 mg, 0.026 mmol) in methanol was added. The mixture was stirred for 1 h, filtered and kept for crystallization. Dark orange-colored crystals were obtained in 10 days. Yield: 60% (13 mg). M.P: 205-208°C. <sup>31</sup>P NMR (162 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 76.93; FT-IR data in KBr pellet (cm<sup>-1</sup>): 543, 679, 745, 9587, 1011, 1131, 1188, 1256, 1315, 1374, 1405, 1432, 1480, 1580, 1648 and 3389. MALDI-TOF/TOF: 1811 (M+K)<sup>+</sup> Anal. Calcd. for C<sub>42</sub>H<sub>58</sub>N<sub>6</sub>O<sub>10</sub>Cl<sub>2</sub>P<sub>2</sub>Pd<sub>6</sub>: C, 29.85; H, 3.46; N, 4.66. Found: C, 30.12; H, 3.68; N, 4.23.

**4.2a**: Prepared from reaction of phenyl boronic acid (1.2 equiv) with n-butyl acrylate (**4.1a**) in presence of the trinuclear complex (3 mol %) and Cu(OAc)<sub>2</sub> (2 equiv) in DMF at 100 °C for 4 h (scheme 4.1). Pale yellow semisolid was purified from silica gel chromatography with eluent (3% ethyl acetate in hexanes). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.69 (d, J = 16.0 Hz, 1 H), 7.54 – 7.52 (m, 2 H), 7.40 – 7.37 (m, 3 H), 6.45 (d, J = 16.0 Hz, 1 H), 4.22 (t, J = 4.0 Hz, 2 H), 1.74 – 1.66 (m, 2 H), 1.50 – 1.40 (m, 2 H), 0.97 (t, J = 8.0 Hz, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 167.2, 144.64, 134.5, 130.2, 128.9, 128.1, 118.3, 64.5, 30.8, 19.2, 13.84. HRMS (ESI): calc. for [(C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>)Na] (M+Na)<sup>+</sup> 227.1048, measured 227.1047.

**4.2b**: Prepared from reaction of phenyl boronic acid (1.2 equiv) with methyl acrylate (**4.1b**) in presence of the trinuclear complex (3 mol %) and Cu(OAc)<sub>2</sub> (2 equiv) in DMF at 100 °C for 4 h (scheme 4.1). Pale yellow liquid was purified from silica gel chromatography with eluent (3% ethyl acetate in hexanes). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.71 (d, J = 16.0 Hz, 1 H), 7.55 – 7.53 (m, 2 H), 7.41 – 7.39 (m, 3 H), 6.46 (d, J = 16.0 Hz, 1 H), 3.82 (s, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 167.5, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.9. HRMS (ESI): calc. for [(C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>)Na] (M+Na)<sup>+</sup> 185.0578, measured 185.0579.

**4.2c**: Prepared from reaction of phenyl boronic acid (1.2 equiv) with methyl acrylate (**4.1c**) in presence of the trinuclear complex (3 mol %) and Cu(OAc)<sub>2</sub> (2 equiv) in DMF at 100 °C for 4 h (scheme 4.1). Pale yellow liquid was purified from silica gel

chromatography with eluent (3% ethyl acetate in hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.68 (d,  $J = 16.0$  Hz, 1 H), 7.55 – 7.52 (m, 2 H), 7.49 – 7.38 (m, 3 H), 6.44 (d,  $J = 16.0$  Hz, 1 H), 4.93 – 4.87 (s, 1 H), 1.95 – 1.91 (m, 2 H), 1.80 – 1.76 (m, 2 H), 1.60 – 1.54 (m, 1 H), 1.52 – 1.46 (m, 2 H), 1.44 – 1.40 (m, 1 H), 1.34 – 1.26 (m, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  166.5, 144.3, 134.8, 130.2, 128.9, 128.1, 118.3, 72.8, 31.8, 25.5, 23.9. HRMS (ESI): calc. for  $[(\text{C}_{15}\text{H}_{18}\text{O}_2)\text{Na}] (\text{M}+\text{Na})^+$  253.1204, measured 253.1203.

**4.2d:** Prepared from reaction of phenyl boronic acid (1.2 equiv) with methyl acrylate (**4.1d**) in presence of the trinuclear complex (3 mol %) and  $\text{Cu}(\text{OAc})_2$  (2 equiv) in DMF at 100 °C for 4 h (scheme 4.1). Pale yellow liquid was purified from silica gel chromatography with eluent (3% ethyl acetate in hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.59 (d,  $J = 8.0$  Hz, 4 H), 7.43 (t,  $J = 8.0$  Hz, 4 H), 7.33 (t,  $J = 8.0$  Hz, 2 H) 7.19 (s, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  137.4, 128.2, 127.7, 126.8. HRMS (ESI): calc. for  $[(\text{C}_{14}\text{H}_{12})\text{H}] (\text{M}+\text{H})^+$  181.1017, measured 181.1018.

**4.4a:** Prepared from the treatment of phenyl boronic acid (2 equiv) with 4-bromotoluene (**4.3a**) in presence of the trinuclear complex (0.5 mol %) in DMF at 100 °C for 16 h (Scheme 4.2). White solid was purified from silica gel chromatography with eluent (1% ethyl acetate in hexanes);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.56 (m, 2H), 7.51 (d,  $J = 8.1$  Hz, 2H), 7.44 (t,  $J = 7.7$  Hz, 2H), 7.34 (dd,  $J = 10.3, 4.4$  Hz, 1H), 7.28 – 7.23 (m, 2H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.64, 137.36, 129.81, 129.05, 127.31, 77.16, 21.44. HRMS (ESI): calc. for  $[\text{C}_{13}\text{H}_{12}] (\text{M}+\text{H})^+$  169.0939, measured 169.1235

**4.4b:** Prepared from the treatment of phenyl boronic acid (2 equiv) with 4-iodoanisole (**4.3b**) in presence of the trinuclear complex (0.5 mol %) in DMF at 100 °C for 16 h (Scheme 4.2). White solid was purified from silica gel chromatography with eluent (1% ethyl acetate in hexanes);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 1.4$  Hz, 1H), 7.54 (d,  $J = 2.0$  Hz, 2H), 7.53 (d,  $J = 2.2$  Hz, 1H), 7.42 (t,  $J = 7.6$  Hz, 2H), 7.31 (d,  $J = 7.4$  Hz, 1H), 7.04 – 6.91 (m, 2H), 3.86 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.12, 140.81, 133.77, 128.86, 128.21, 126.88, 114.32, 77.16, 55.81. HRMS (ESI): calc. for  $[\text{C}_{13}\text{H}_{12}\text{O}] (\text{M}+\text{H})^+$  185.0888, measured 185.0608.

**4.4c:** Prepared from the treatment of phenyl boronic acid (2 equiv) with 4-iodoacetophenone (**4.3c**) in presence of the trinuclear complex (0.5 mol %) in DMF at 100 °C for 16 h (Scheme 4.2). White solid was purified from silica gel chromatography with eluent (1% ethyl acetate in hexanes); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d) δ 8.06 – 8.02 (m, 2H), 7.73 – 7.66 (m, 2H), 7.66 – 7.60 (m, 2H), 7.52 – 7.44 (m, 2H), 7.44 – 7.36 (m, 1H), 2.65 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>-d) δ 198.49, 146.19, 140.67, 136.44, 129.21, 128.99, 127.84, 77.16, 27.40. HRMS (ESI): calc. for [C<sub>14</sub>H<sub>12</sub>O] (M+H)<sup>+</sup>196.0888, measured 197.0288

**4.4d:** Prepared from the treatment of phenyl boronic acid (2 equiv) with 4-iodonitrobenzene (**4.3d**) in presence of the trinuclear complex (0.5 mol %) in DMF at 100 °C for 16 h (Scheme 4.2). Brownish white solid was purified from silica gel chromatography with eluent (1% ethyl acetate in hexanes); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 – 8.27 (m, 2H), 7.76 – 7.72 (m, 2H), 7.63 (dd, J = 8.2, 1.4 Hz, 2H), 7.54 – 7.44 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>-d) δ 147.72, 147.14, 138.85, 129.25, 129.01, 127.90, 127.48, 124.94, 124.21. HRMS (ESI): calc. for [C<sub>12</sub>H<sub>9</sub>NO<sub>2</sub>] (M+H)<sup>+</sup> 200.0888, measured 200.0288.

## 2.3 Crystallography

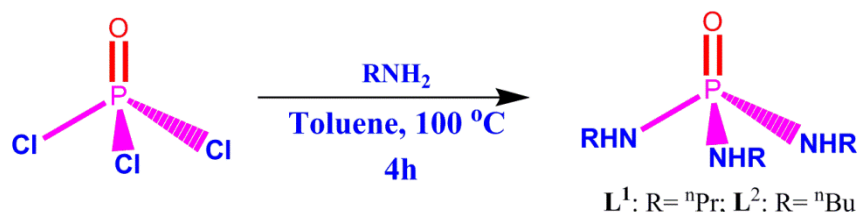
Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for **C**<sup>1</sup>, **C**<sup>2</sup>, **C**<sup>7</sup>, **C**<sup>8</sup>, **C**<sup>9</sup> and **C**<sup>10</sup>. Structures were refined by full-matrix least-squares against F<sup>2</sup> using all data (SHELX97).<sup>15</sup> Crystallographic data for all these compounds are listed in (Appendix 5). All non-hydrogen atoms were refined anisotropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. One of the three iso-propyl groups in the asymmetric unit of **C**<sup>3</sup> was disordered. Atom positions of the disordered C-atoms were isotropically refined over two positions using similar distances and similar U-restraints refined over two positions with SAME/SADI commands in the SHELX. The encapsulated solvents in structure **C**<sup>1</sup> were disordered and refined over two positions with SAME/SADI commands in the SHELX. For all the solvent encapsulated structures the solvated atoms in the packing cavities were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.



### 3. Result and Discussion:

#### 3.1 Synthesis:

The phosphoric triamide ligands, [(NHR)<sub>3</sub>PO] (**L**<sup>1</sup>, R = <sup>n</sup>Pr; **L**<sup>2</sup>, R = <sup>n</sup>Bu), were prepared by a slightly modified literature procedure (Scheme 3.1).<sup>16</sup> These ligands were found to be impure containing the amine hydrochloride by-products as indicated by NMR and crystallography. The reactivity of these ligands were further tested with Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> in an appropriate polar solvent at room temperature with the view of obtaining various chloro-bridged imido-Pd(II) clusters (Scheme 3.2). Crystals of {Pd<sub>3</sub>[(N<sup>n</sup>Pr)<sub>3</sub>PO](Cl)<sub>3</sub>}<sub>2</sub> (**C**<sub>1</sub>) and {Pd<sub>3</sub>[(N<sup>n</sup>Bu)<sub>3</sub>PO](Cl)<sub>3</sub>}<sub>2</sub> (**C**<sub>2</sub>) were obtained from the respective reaction of **L**<sup>1</sup> and **L**<sup>2</sup> with Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> in MeOH/MeCN within 15 days. Interestingly, it was found that the reaction of [(NHR)<sub>3</sub>PO] (R = <sup>i</sup>Pr, <sup>c</sup>Hex) with a 2:1 mixture of Pd(OAc)<sub>2</sub> and Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> respectively in MeOH/MeCN (scheme 3.2) gave a mixed chloro and acetate bridged clusters. Crystals of {Pd<sub>3</sub>[(N<sup>i</sup>Pr)<sub>3</sub>PO](Cl)(OAc)<sub>2</sub>}<sub>2</sub> (**C**<sup>7</sup>) and {Pd<sub>3</sub>[(N<sup>c</sup>Hex)<sub>3</sub>PO](Cl)(OAc)<sub>2</sub>}<sub>2</sub> (**C**<sup>8</sup>) were obtained in two weeks. A much simpler procedure for obtaining these mixed-bridged clusters involves the direct use of these impure ligands with Pd(OAc)<sub>2</sub>.

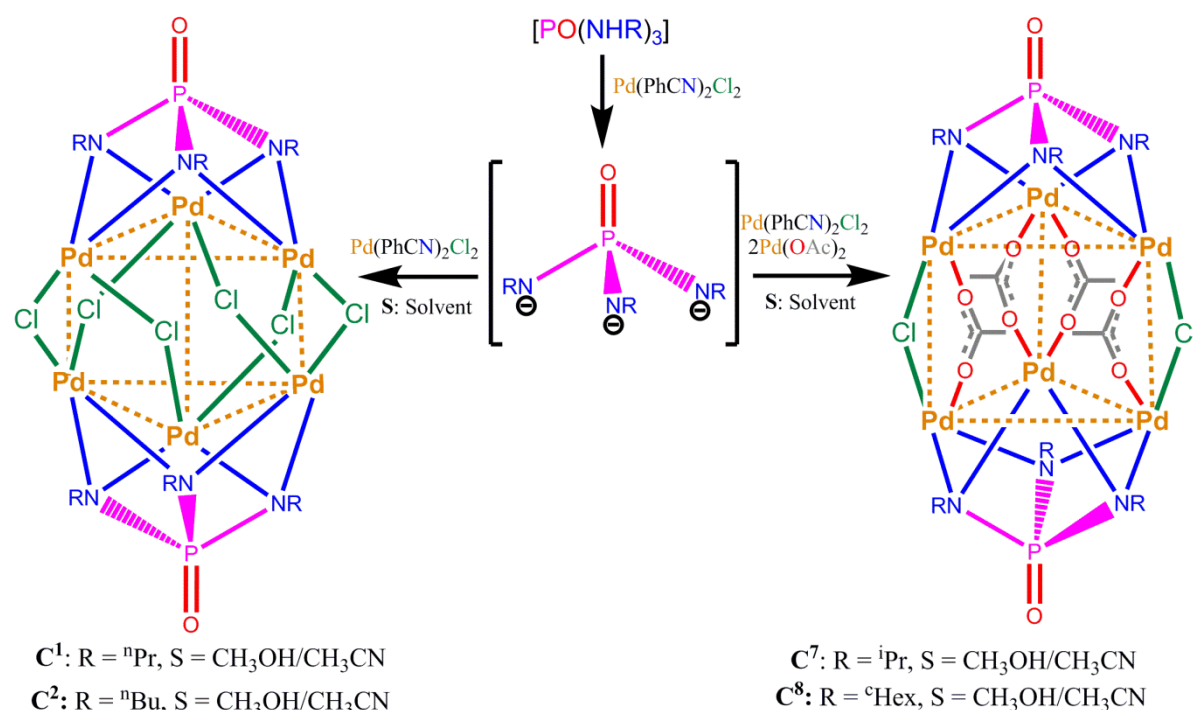


**Scheme 3.1:** Synthetic routes to access phosphoric triamide ligands.

The chloro bridged hexameric clusters **C**<sup>1</sup> and **C**<sup>2</sup> contain two triangular Pd<sub>3</sub>-motifs, in which the Pd(II) atoms are bound to three chelating N<sub>imido</sub> moieties, arranged in a staggered conformation. Related hexameric clusters {Pd<sub>3</sub>[(NR)<sub>3</sub>PO](Cl)<sub>3</sub>}<sub>2</sub> (**C**<sup>3</sup>, R = <sup>i</sup>Pr; **C**<sup>4</sup>, R = <sup>c</sup>Hex; **C**<sup>5</sup>, R = <sup>t</sup>Bu) having other substituents on the imido N-atoms were also synthesized in our group (unpublished results). Interestingly, we have observed two different conformations for these six chloro-bridged hexameric clusters **C**<sup>1</sup>-**C**<sup>6</sup>. While the clusters **C**<sup>1</sup>-**C**<sup>5</sup> contain an staggered arrangement of the two Pd<sub>3</sub>-subunits, an eclipsed conformation was observed in case of **C**<sup>6</sup> owing to the bulkiness of the <sup>t</sup>butyl arms at N<sub>imido</sub> sites (**C**<sup>6</sup>, R = <sup>t</sup>Bu).

However, in the case of mixed chloro-acetate bridged clusters we observed only the prismatic arrangement of the two triangular Pd<sub>3</sub> moieties having an eclipsed conformation. This mixed bridge arrangement is due to the presence of amine chloride salt in the impure ligand which acts as a chloride source. The two acetate bridges were always labile as reported earlier in case of all acetate bridges clusters so this chloride ions present along with impure ligand replaces the two acetate bridges and form the mixed chloro and acetate bridged clusters.

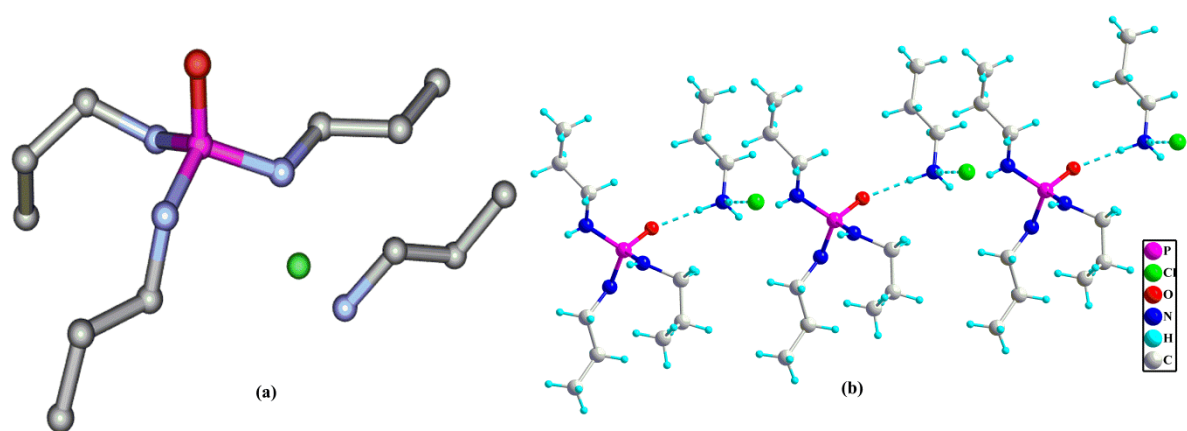
The <sup>31</sup>P-NMR of these compounds gave a single peak around the region between δ 76.0-77.5 ppm consistent with the signal for the imido-trianions. Further, the ESI(+) or MALDI-TOF mass spectra of these compounds gave an isotopic distribution of peaks centered at the values corresponding to their [M]<sup>+</sup> or [M+Na]<sup>+</sup> ions along with other prominent fragment ion peaks (Supporting information).



**Scheme 3.2:** Synthetic routes to access the all chloro bridged and mixed bridged hexanuclear Pd(II) clusters of the tris(alkylimido) phosphate trianions

### 3.2 Crystal Structures

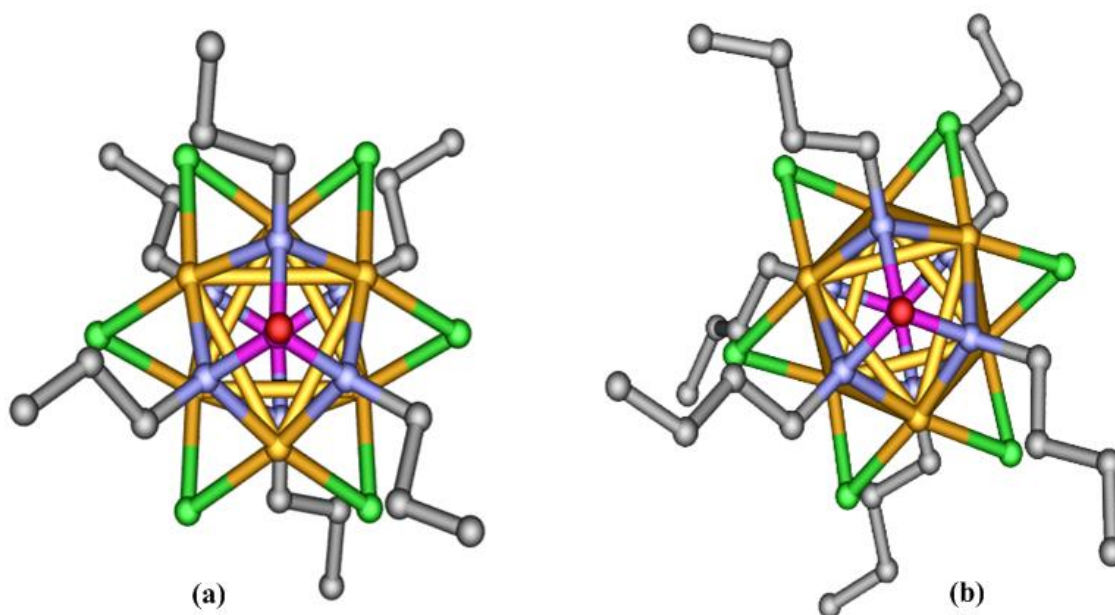
The ligand **L**<sup>1</sup> was crystallized as the amine hydrochloride adduct as **L**<sup>1</sup>·<sup>n</sup>PrNH<sub>3</sub>·Cl in monoclinic space group P2(1)/c with its asymmetric unit consisting of one ligand moiety and one <sup>n</sup>propyl ammonium chloride moiety (Figure 3.1). The molecular structure of this ligand shows that it exhibits a 2D-hydrogen bonded structure in which the [<sup>n</sup>PrNH<sub>3</sub>]<sup>+</sup> cation interacts with both the chloride ion as well as the phosphoryl oxygen. From this structure it is evident that the ligands **L**<sup>1</sup> and **L**<sup>2</sup> could not be purified due to this strong inter-molecular N-H...O and N-H...Cl interactions and is the reason for the formation of the chloro-bridges in the reactions of these ligands with Pd(OAc)<sub>2</sub>.



**Figure 3.1:** Crystal Structure of (a) **L**<sup>1</sup>, (b) Depiction of hydrogen bonding.

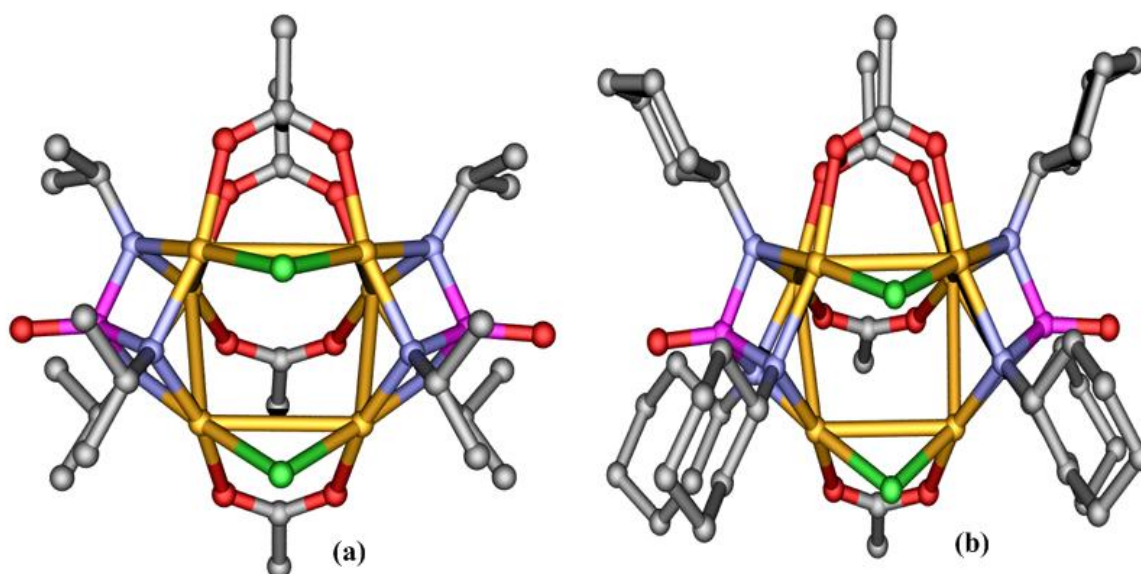
Compound **C**<sup>1</sup> was crystallized in the triclinic space group P-1 with one benzonitrile solvate molecule. The molecular core consists of hexanuclear palladium cluster and two triply deprotonated trianionic ligand moieties (**L**<sup>1</sup>) which are counter balanced by six chloride ions (Figure 3.2a). The cluster core consists of two triangular Pd<sub>3</sub> units arranged in staggered conformation and are held together with six μ<sup>2</sup>-bridging chloride ions resulting a hexa nuclear palladium cluster. The triangular Pd<sub>3</sub> units are blocked by ligand N<sub>imido</sub> moieties (**L**<sup>1</sup>) from one side of its Pd<sub>3</sub>-plane. Each palladium atom is tetra coordinated with two imido-nitrogens and two μ<sup>2</sup>-bridged chloride ions. Each trianionic ligand is hexadentate and coordinated with the triangular Pd<sub>3</sub> unit at almost similar bond distances ranging from 2.04(2) to

2.06(3) Å. Similarly, Compound **C**<sup>2</sup> (Figure 3.2b) was crystallized in triclinic space group P-1 and exhibit similar structural features.



**Figure 3.2:** Crystal Structure of (a) **C**<sup>1</sup>, (b) **C**<sup>2</sup>

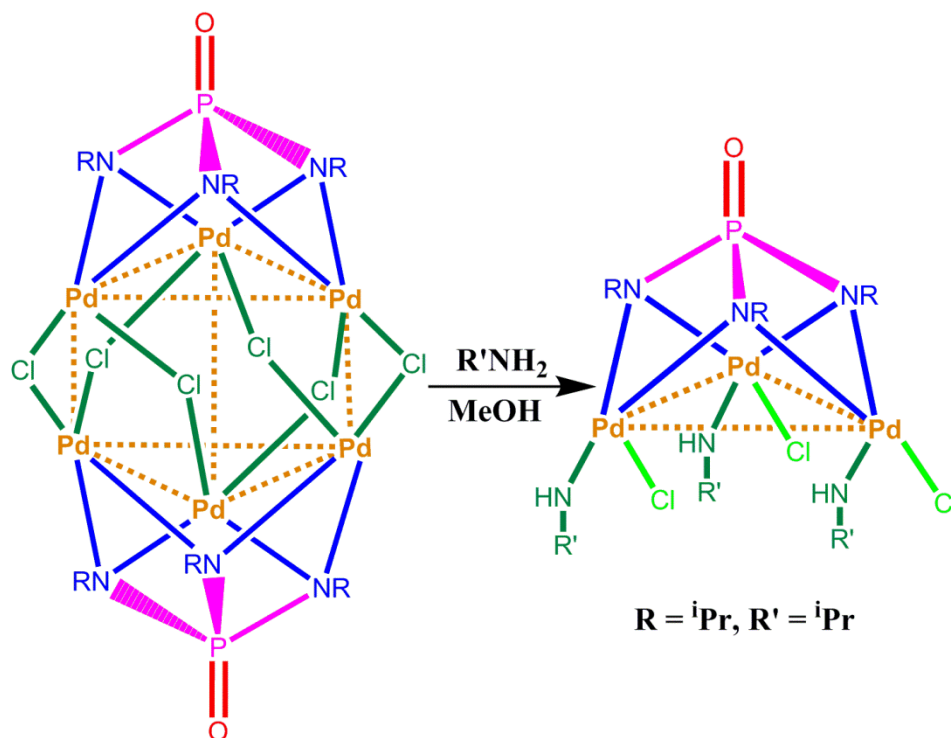
The molecule **C**<sup>7</sup> is crystallized in monoclinic space group Pnma with one half of molecule in asymmetric unit. Molecular core consists of Pd<sub>6</sub> cluster unit sandwiched between two fully deprotonated ligand molecules, four acetate bridges and two chlorine bridges (Figure 3.3a) The two trinuclear Pd<sub>3</sub> units are arranged in prismatic arrangement and are connected with four acetate bridges and two chloride bridges. Each palladium atom has square pyramidal geometry and out of three Pd one is coordinated with two bridging carboxylate units and two deprotonated ligand nitrogens. Whereas, remaining two Pd atoms are coordinated with one carboxylate oxygen, two nitrogens of ligand and one bridging chloride ion. Each imido-nitrogen is bonded to two Pd(II) centers at almost equal distances ranging from 2.052(3) to 2.061(3) Å indicating the trianionic charge is equally delocalized on the three N-sites. Similarly, compound **C**<sup>8</sup> (figure 3.3b) was crystallized in orthorhombic space group Cmc21 and exhibit an almost equivalent structural characteristics.



**Figure 3.3:** Crystal Structure of (a) **C<sup>7</sup>**, (b) **C<sup>8</sup>**.

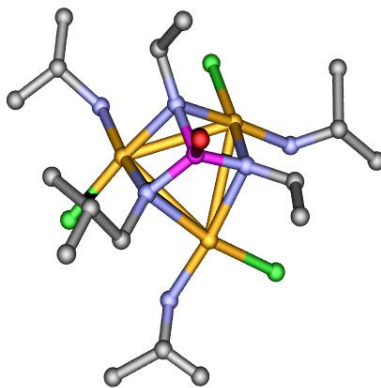
### 3.3 Reactivity Studies of tri- and hexa nuclear Pd(II) complexes

In order to test the robustness of the tripodally chelated (Pd–N<sub>imido</sub>)<sub>3</sub> moieties in **C<sup>1</sup>**, **C<sup>2</sup>** and other chloro based cluster we studied the reactivity of these complexes in the presence of a primary amine which acts as a nucleophilic reagent to the Pd(II) ions. Thus, the reaction of **C<sup>3</sup>** with stoichiometric equivalents of isopropyl amine in MeOH proceeds spontaneously as observed by a visual color change in solution (from orange to yellow) from which yellow-colored crystals of **C<sup>9</sup>** was obtained (Scheme 3.3). Single-crystal X-ray analysis of the crystals of **C<sup>9</sup>** indicates the presence of a new trinuclear species of the formula {Pd<sub>3</sub>[(NR)<sub>3</sub>PO](Cl)<sub>3</sub>(RNH<sub>2</sub>)<sub>3</sub>} (**C<sup>9</sup>**, R= <sup>i</sup>Pr). The new trinuclear assembly (**C<sup>9</sup>**) was obtained via a nucleophilic attack on the Pd(II) ions by the amino groups from a symmetrical cleavage of the hexa nuclear cluster. This type of amine-triggered cleavage of a dinuclear Pd(II) species to a mononuclear complex is attributed to the rigid tripodal chelation of the imido-phosphate which provides the necessary stability to the Pd<sub>3</sub> units.



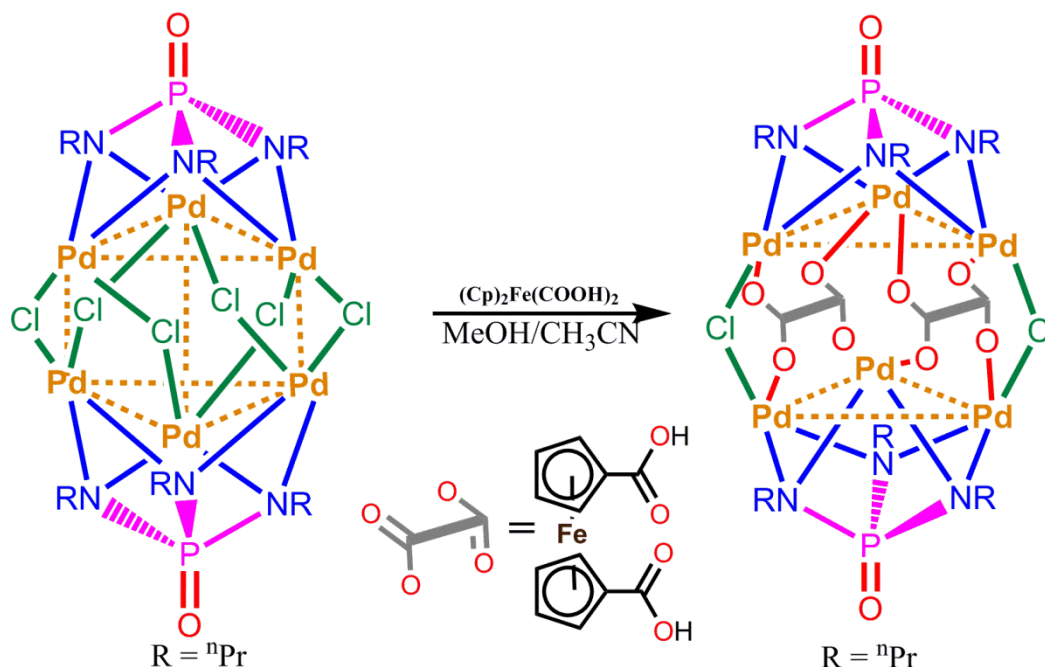
**Scheme 3.3:** Synthetic routes to access hexanuclear Pd(II) clusters of the tris(alkylimido) phosphate trianions

The molecular structure of **C<sup>9</sup>** was solved in orthorhombic space group Pca21. The molecular core consists of a Pd<sub>3</sub> triangle, a fully deprotonated ligand, three isopropyl amine and three chloride ions (Figure 3.4). Each Pd(II) atom is in coordinated with two ligand nitrogens, one free <sup>iso</sup>propyl amine and a chloride ion resulting square pyramidal geometry. Each of the ligand's imido nitrogen is coordinated with two palladium atoms making the ligand a hexadentate chelating ligand.



**Figure 3.4:** Crystal Structure of **C<sup>9</sup>**

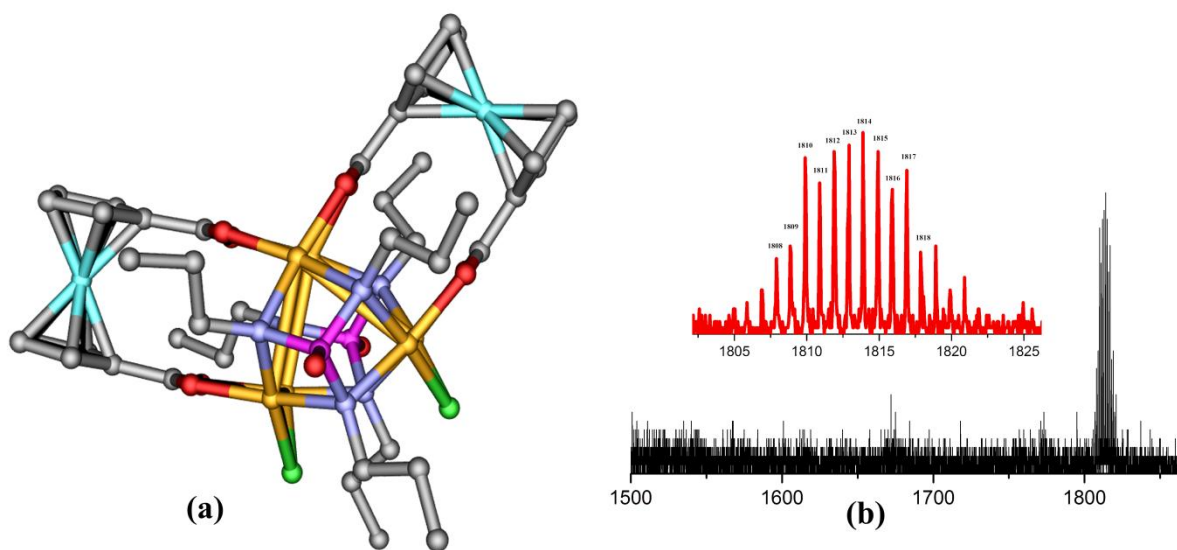
These reactions showed that the trinuclear  $\{Pd_3[(NR)_3PO]\}^{3+}$  motif is stable in solution and can be linked with suitable carboxylate linkers which might increase the space between the two hexa-nuclear  $Pd_3$ - units which might result in an elusive high-nuclearity neutral cage molecules for Pd(II) ions. So we reacted these cages  $\{Pd_3[(NR)_3PO](OAc)_2(Cl)\}_2$  (**C<sup>1</sup>**, R= <sup>n</sup>Pr) with 1,1'-ferrocenedicarboxylic acid (FDC-H) (Scheme 3.4) which resulted in replacement of four chloro bridges with two FDC bridges  $\{Pd_3[(NR)_3PO](FDC)(Cl)\}_2$  (**C<sup>10</sup>**) (R= <sup>n</sup>Pr). The MALDI-TOF mass spectrum of **C<sup>10</sup>** gave an isotopic distribution around 1810 corresponding to the  $[M+K]^+$  ion conforming the formation of the complex (figure 3.5(b)). However, no clean reactions were observed for **C<sup>3</sup>** with other linkers such as isonicotinic acid, sulphur powder and triphenyl phosphine. The solid compounds obtained in these reactions were dissolved in THF and kept for crystallization. The crystals obtained in these reactions were found to be the Pd(II) complexes of the corresponding linker ligands as the imido ligands were found to be expelled in these reactions.



**Scheme 3.4:** Synthesis of ferrocene based Pd(II) clusters of the tris(alkylimido) phosphate trianions.

The molecular structure of **C<sup>10</sup>** was solved in monoclinic space group C2/c. The asymmetric unit has three palladium atoms, one ligand moiety, one ferrocene dicarboxylate and a chloride ion. (Figure 3.5(a)) The molecular core consist of a  $Pd_6$

unit connected with two fully deprotonated ligands, two ferrocene dicarboxylate and two bridging chloride ions. Pd<sub>6</sub> unit consist of two triangularly arranged Pd<sub>3</sub> units in prismatic arrangement which is arranged in an eclipsed manner. Each palladium atom has square pyramidal geometry and out of the three Pd atoms one is coordinated with two carboxylate oxygens and two deprotonated ligand nitrogens. Whereas, remaining two Pd atoms are coordinated with one carboxylate oxygen, two ligand nitrogens and one bridging chloride ion. Each ferrocene dicarboxylate is coordinated to the Pd(II) atom of two different triangular Pd<sub>3</sub> units.



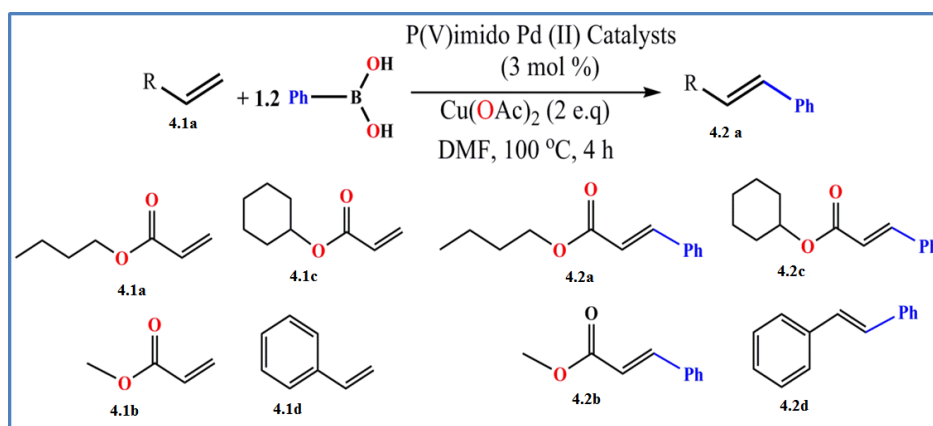
**Figure 3.5:** (a) Crystal Structure of C<sup>10</sup>, (b) MALDI data



## 4. Applications in Catalytic Reactions:

Inspired by their rigid Pd-N<sub>imido</sub> tripodal motifs, we were curious to see whether the Pd(II) atoms in these clusters are still active for catalytic reactions. As these imido-motifs are strongly bound to the Pd(II) atoms, we thought a catalytic reaction that utilizes the Pd(II) ions as an active catalyst would be more suitable to examine. Hence we employed these complexes in various coupling reactions like the Mizoroki-Heck type reactions in which the Pd(II) species catalyzes the coupling reaction of phenyl boronic acid with alkenes,<sup>17</sup> The treatment of phenyl boronic acid (1.2 equiv) with n-butyl acrylate (**4.1a**) in presence of the trinuclear complex **C**<sup>2</sup> (3 mol %) and Cu(OAc)<sub>2</sub> (2 equiv) in DMF at 100 °C for 4 h leads to the corresponding phenylated trans-alkene derivative (**4.2a**) in 90% isolated yield (Scheme 4.1).

The reaction was also tested with the hexameric complexes **C**<sup>4</sup>, **C**<sup>5</sup> and **C**<sup>6</sup> under same conditions which gave the alkene product **4.2a** in 90%, 95% and 92% yields, respectively. Similarly, we have tried the coupling reaction with few more alkenes such as methyl acrylate (**4.1b**), c-hexyl acrylate (**4.1c**) and styrene (**4.1d**) in presence of all these three cluster motifs. Noticeably, **C**<sup>5</sup> acts as a better catalyst for all these substrates yielding the coupled products **4.2b-d** in 98%, 92% and 98% yields, respectively (Table 1). As observed before,<sup>17</sup> the catalytic reaction presumably proceeds via the trans-metalation of the phenyl boronic acid with Pd(II) complexes followed by insertion of the alkene substrate that subsequently undergoes β-hydride elimination in presence of Cu(OAc)<sub>2</sub>, which acts both as an acetate source as well as an oxidant in the catalytic cycle.



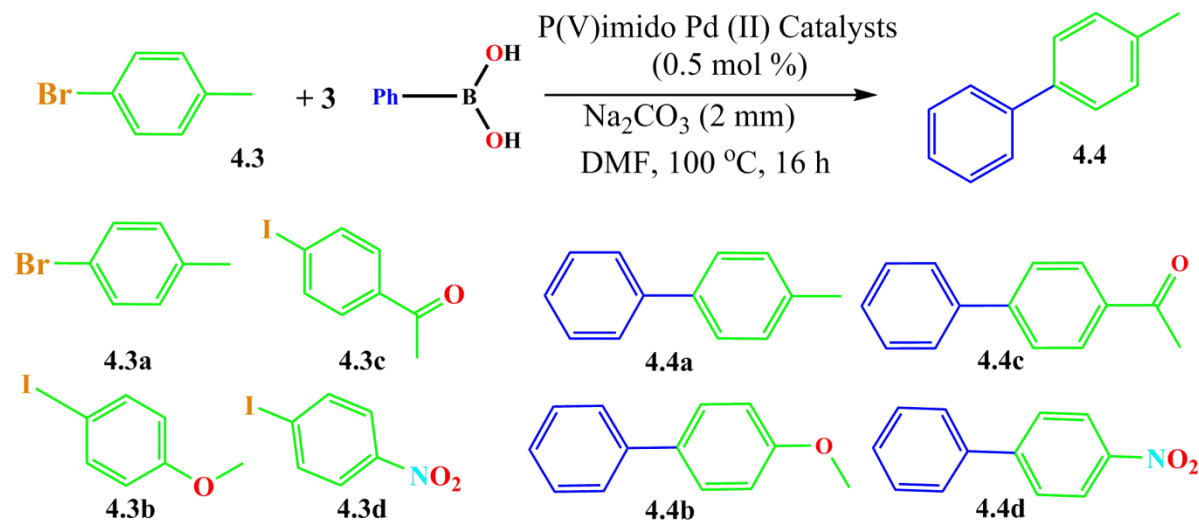
**Scheme 4.1:** M-H type reaction of PhB(OH)<sub>2</sub> with various alkenes.

Starting Material	Coupled Product	% Yield of the Product			
		<b>C<sup>2</sup></b>	<b>C<sup>4</sup></b>	<b>C<sup>5</sup></b>	<b>C<sup>6</sup></b>
4.1a	4.2a	94	90	95	92
4.1b	4.2b	92	91	98	92
4.1c	4.2c	90	90	92	90
4.1d	4.2d	94	94	98	95

**Table 4.1:** M-H Type Reaction of PhB(OH)<sub>2</sub> with Alkenes.

Furthermore, we employed our chloro-bridged clusters in the Suzuki type reactions in which the Pd(II) species catalyzes the coupling reaction of 4-bromotoluene with phenylboronic acid as a model reaction to study the effectiveness of our clusters on this reaction.<sup>18</sup> The treatment of phenyl boronic acid (2 equiv) with 4-bromotoluene (**4.3a**) in presence of the trinuclear complex **C<sup>5</sup>** (0.5 mol %) in DMF at 100 °C for 16 h leads to the corresponding bi-aryl derivative **4.4a** in 75% isolated yield.

The reaction was also tested with the hexameric complexes **C<sup>2</sup>**, **C<sup>4</sup>** and **C<sup>6</sup>** under same conditions which gave the bi-aryl product **4.4a** in 55%, 50% and 70% yields, respectively. Similarly, we have tried the coupling reaction with few more aryl-halides such as 4-iodoanisole (**4.3b**), 4-Iodoacetophenone (**4.3c**) and 4-Iodonitrobenzene (**4.3d**) in presence of all these four cluster motifs. Noticeably, again **C<sup>5</sup>** acts as a better catalyst for all these substrates yielding the coupled products **4.4b-d** in 68%, 75% and 65% yields, respectively (Table 2). As observed before,<sup>18</sup> the catalytic reaction presumably proceeds via the trans-metalation of the phenyl boronic acid with Pd(II) complexes followed by insertion of the aryl substrate that subsequently undergoes reductive elimination.

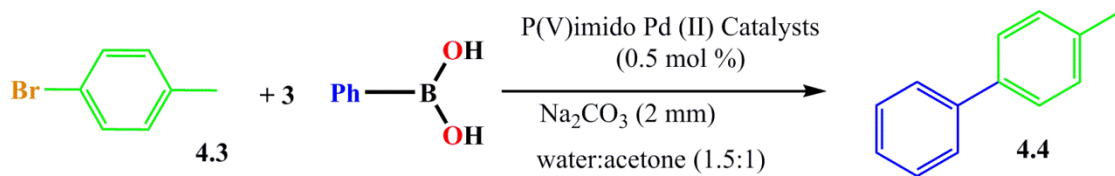


**Scheme 4.2:** Suzuki reaction of  $\text{PhB}(\text{OH})_2$  with various aryl halides.

Starting Material	Coupled Product	% Yield of the Product			
		$\text{C}^2$	$\text{C}^4$	$\text{C}^5$	$\text{C}^6$
4.3a	4.4a	55	50	75	70
4.3b	4.4b	58	60	68	65
4.3c	4.4c	65	60	75	70
4.3d	4.4d	58	62	65	60

**Table 4.2:** Suzuki Reaction of  $\text{PhB}(\text{OH})_2$  with Aryl halides.

We have extended the scope of usefulness of our catalysts by performing Suzuki reaction in water considering its safety, cost and significance to environmentally benign processes. The efficiency of the catalytic system was evaluated by the coupling of 4-bromotoluene and 1.5 eq of phenylboronic acid in a 1.5:1 mixture of water and acetone (Scheme 6). 30% yield of desired product was obtained in the presence of  $\text{C}^5$  (0.5 mol %) for 4 h.<sup>18</sup> Doubling the loading of phenylboronic acid increased the yield to 40%. Increasing the duration of reaction to 6h or more did not result any further increase in the product and with the decrease in reaction time from 4h resulted poor yield. This reaction was carried out with other complexes  $\text{C}^2$ ,  $\text{C}^4$  and  $\text{C}^6$  and the yields are reported in Table 3. Similar studies aiming at the reactivity and the catalytic studies for the mixed chloro and acetate-bridged hexameric clusters are currently under study. Also, efforts to prepare the chiral Pd(II) complexes from the corresponding chiral amido-phosphate ligands as precursors for use in asymmetric catalysis is currently under study.



**Scheme 4.3:** Suzuki reaction of  $\text{PhB(OH)}_2$  with 4-bromotoluene in presence of water/acetone.

Coupled product	Time	% Yield of the Product			
		C <sup>2</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>
	1h	12	5	10	10
	2h	25	20	32	25
	4h	35	30	40	30
	6h	36	32	42	30

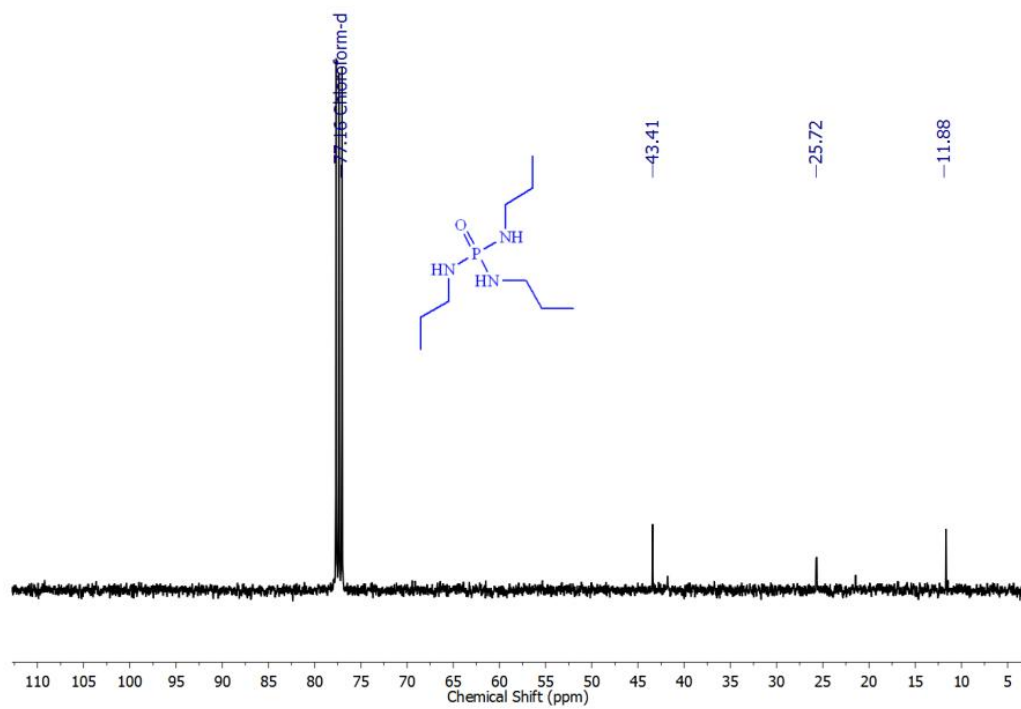
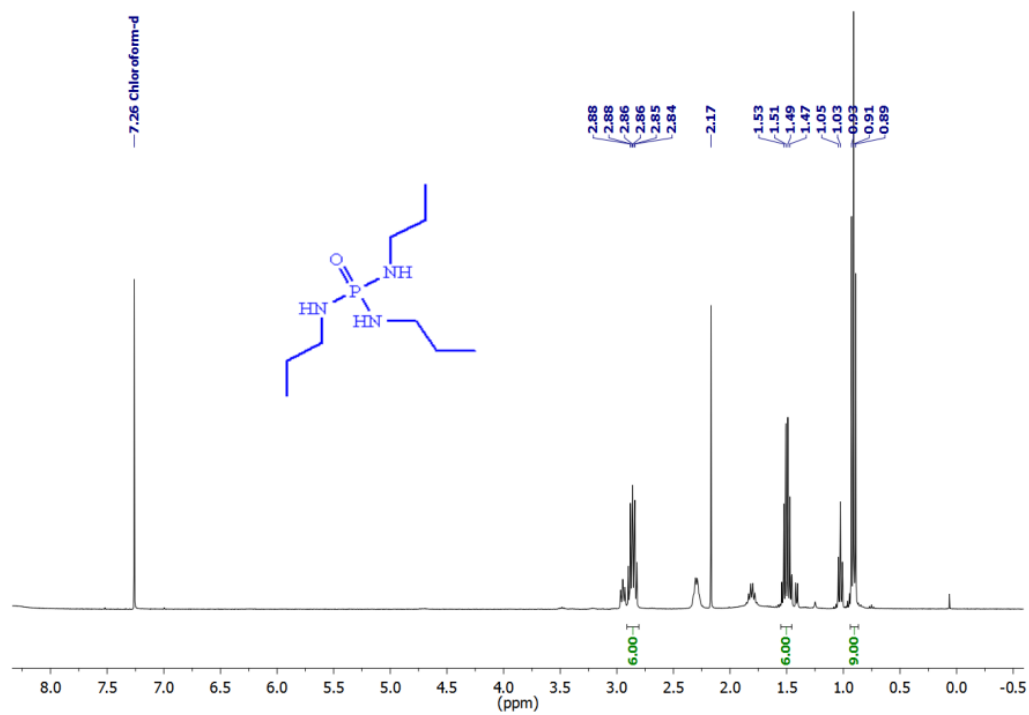
**Table 4.3:** Suzuki Reaction of  $\text{PhB(OH)}_2$  with 4-bromotoluene in presence of water/acetone.

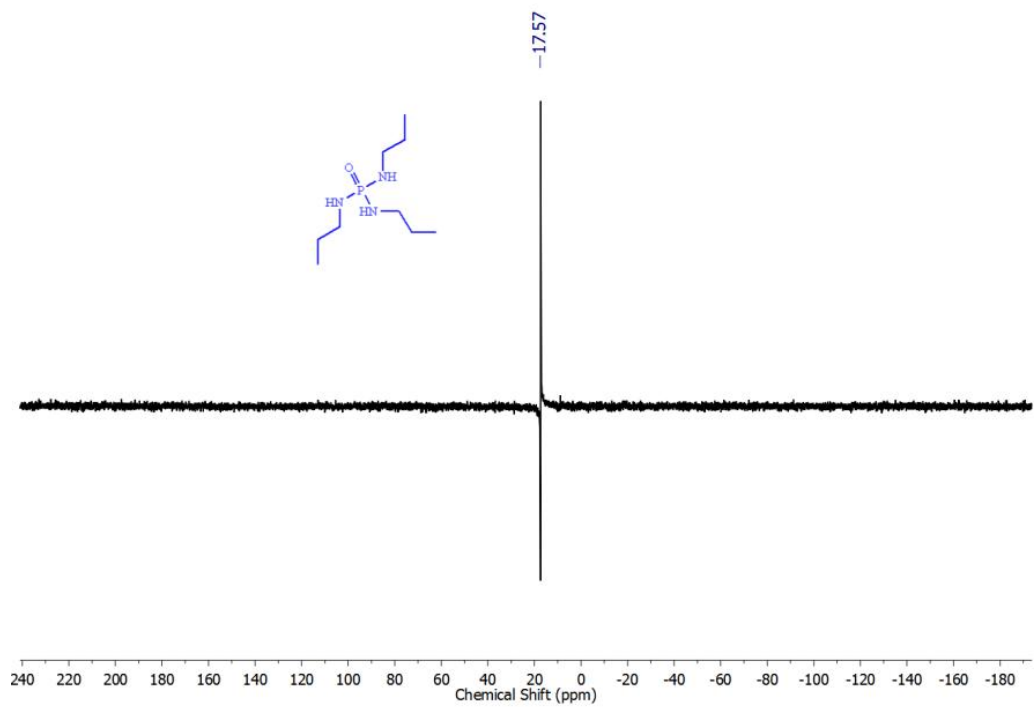
## 5. Conclusions:

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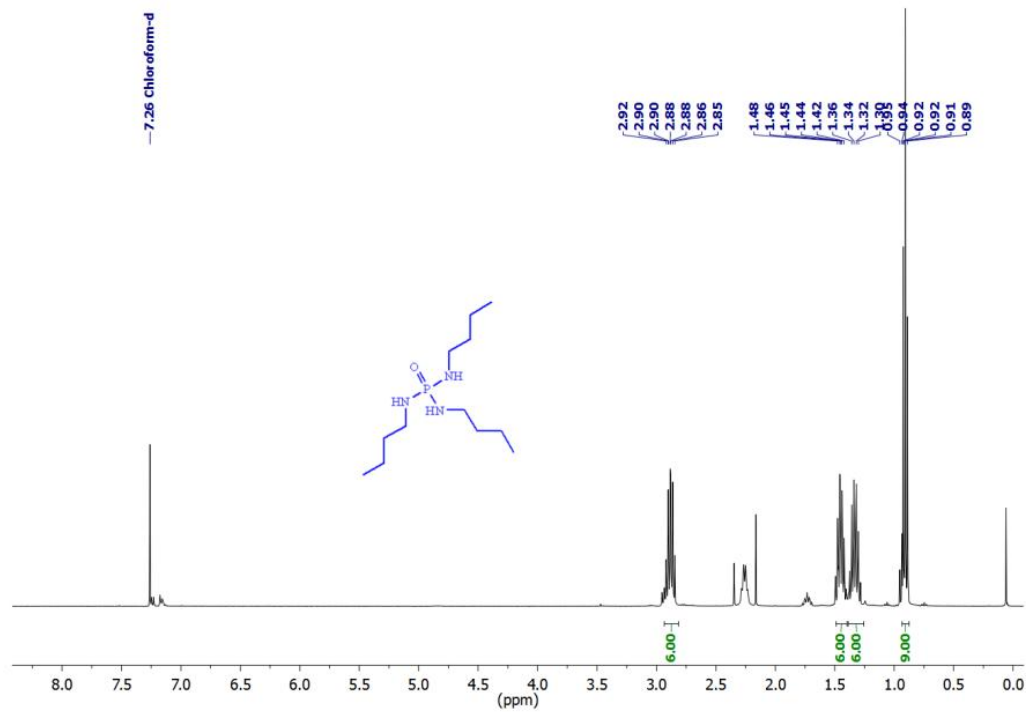
In conclusion we have shown that  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  and  $\text{Pd}(\text{OAc})_2$  provides a facile deprotonation route to access the highly basic tris(alkylimido) phosphate trianions,  $[(\text{RN})_3\text{PO}]^{3-}$ , in polar and in protic solvents. Chloro-bridged hexameric Pd(II) clusters and mixed chloro and acetate bridged hexameric Pd(II) clusters of these trianions were isolated exclusively in all these reactions in which the trianionic species acts as a tripodal chelating ligand to the trinuclear  $\text{Pd}_3$ -unit. We observed an octahedral cluster assembly for the substituents  $^n\text{Pr}$  and  $^n\text{Bu}$  on the imido-P(V) backbone whereas in case of the mixed chloro and acetate-bridged hexameric clusters, a prismatic arrangement of the  $\text{Pd}_6$ -assembly was observed with substituents such as  $^o\text{Hex}$  and  $^i\text{Pr}$  on the imido-P(V) backbone. Reactivity studies on the hexameric clusters featuring the chloro groups with primary amines have led to a symmetric cleavage of the prismatic assemblies in which the tripodally chelated  $(\text{Pd}-\text{N}_{\text{imido}})_3$  moieties remained unaffected. We have successfully replaced four chloro bridges in the an octahedral complex with di carboxylic bridges in the reaction of 1,1'-ferrocenedicarboxylic acid (FDC). The robustness of the  $\text{Pd}_3$ -unit in all these clusters is expected to offer a stable platform for catalytic reactions in which the trianionic ligand would act as a perfect spectator ligand and the substrate will approach the Pd(II) ions from the side that is trans to the Pd-Nimido sites. Also, the crystalline nature of these imido- $\text{Pd}_3$  motifs is an added advantage as it can assist in isolating various organic-intermediate species and thus would provide useful inputs on understanding reaction mechanisms. We have also demonstrated the catalytic activity of these complexes in M-H type coupling reactions and Suzuki coupling reactions which proves that these clusters are worthy candidates for catalytic applications.

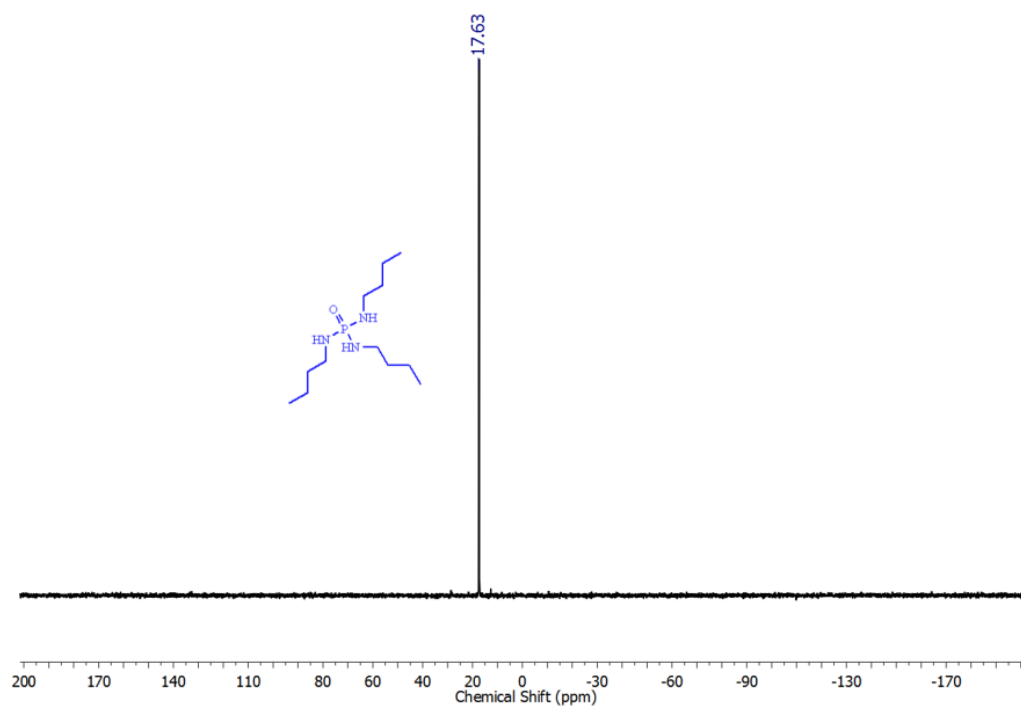
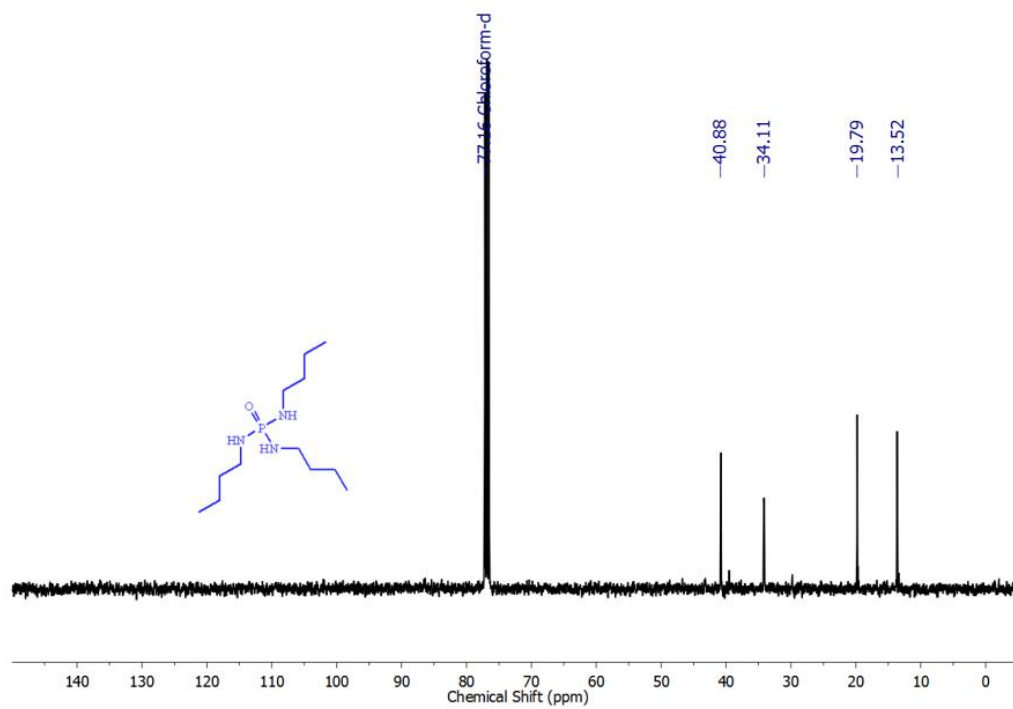
## 6. Supplementary Information





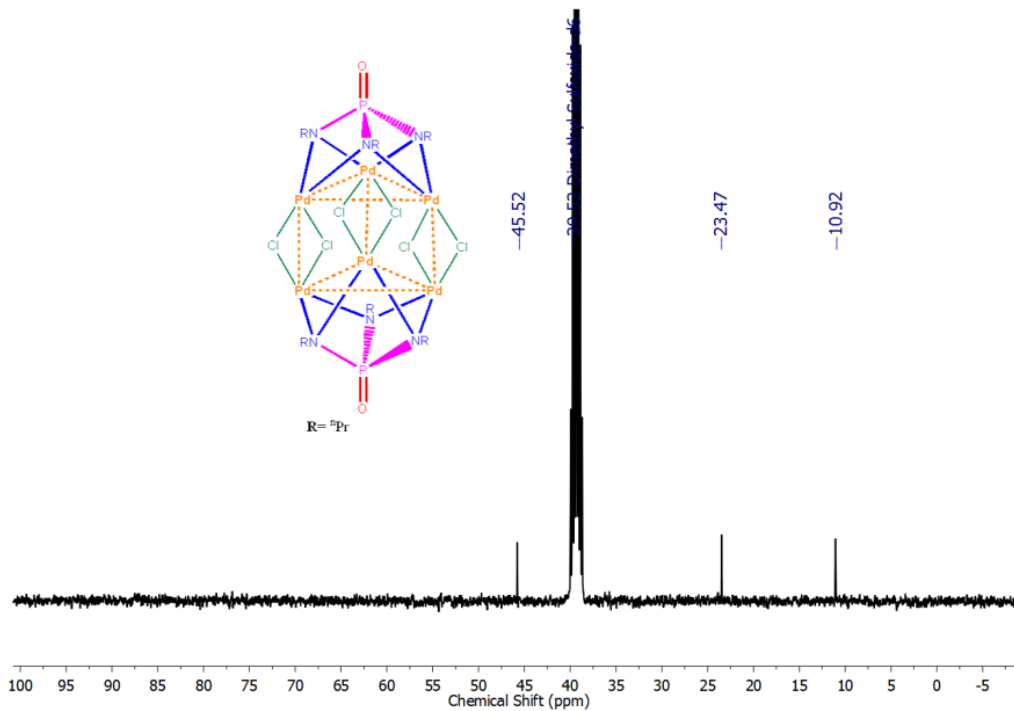
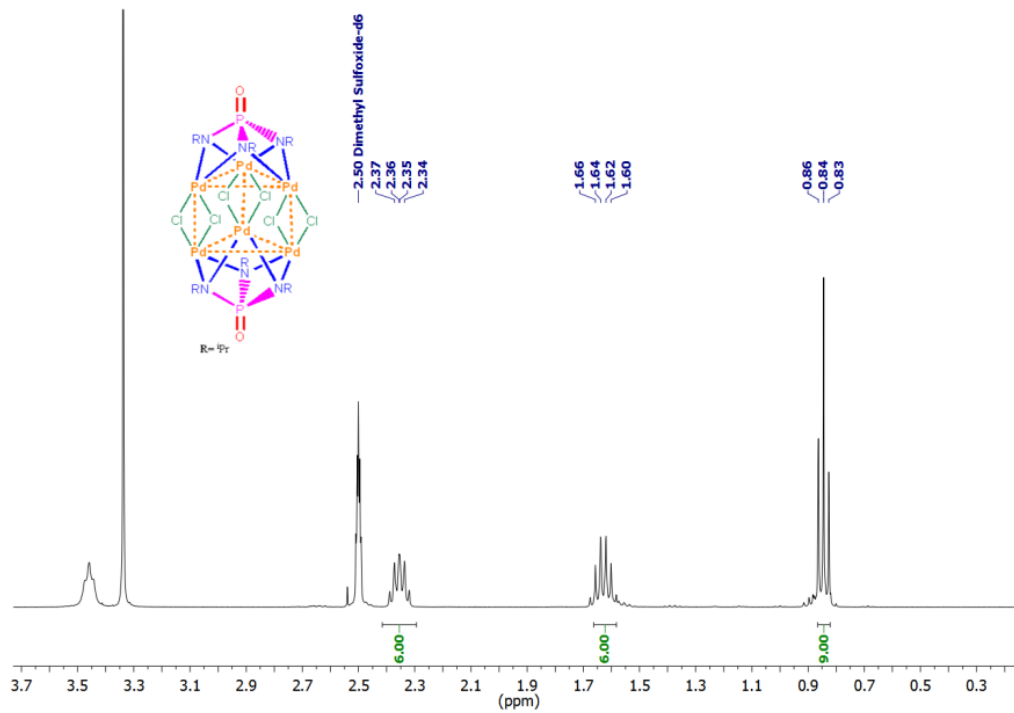
### <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR Spectra of Compound L<sup>1</sup>-H<sub>3</sub>.

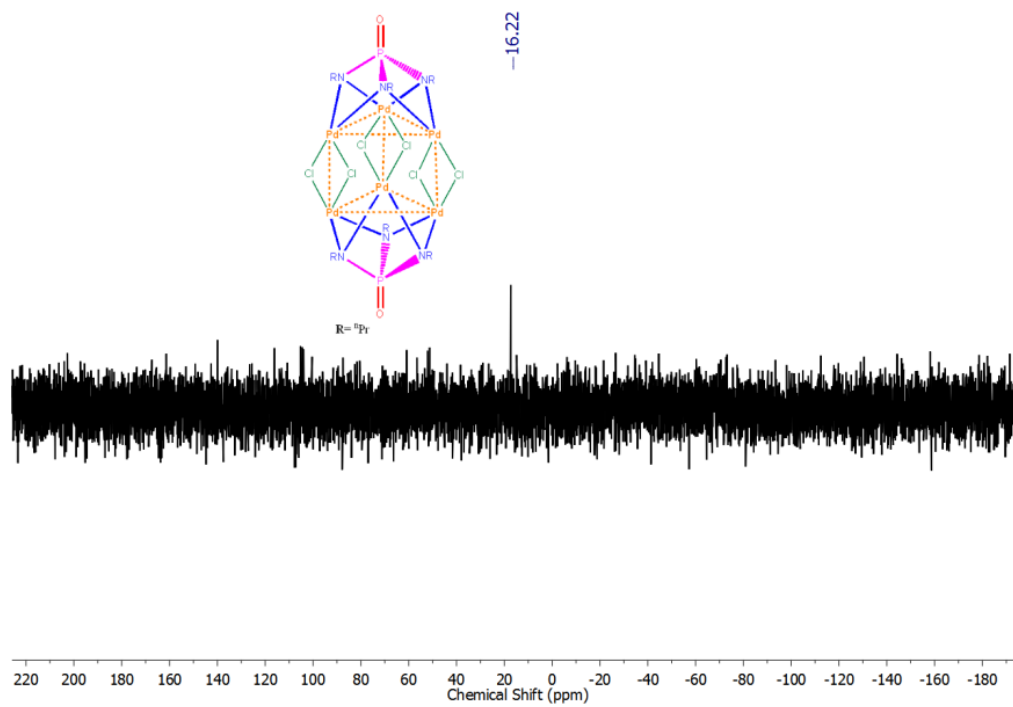




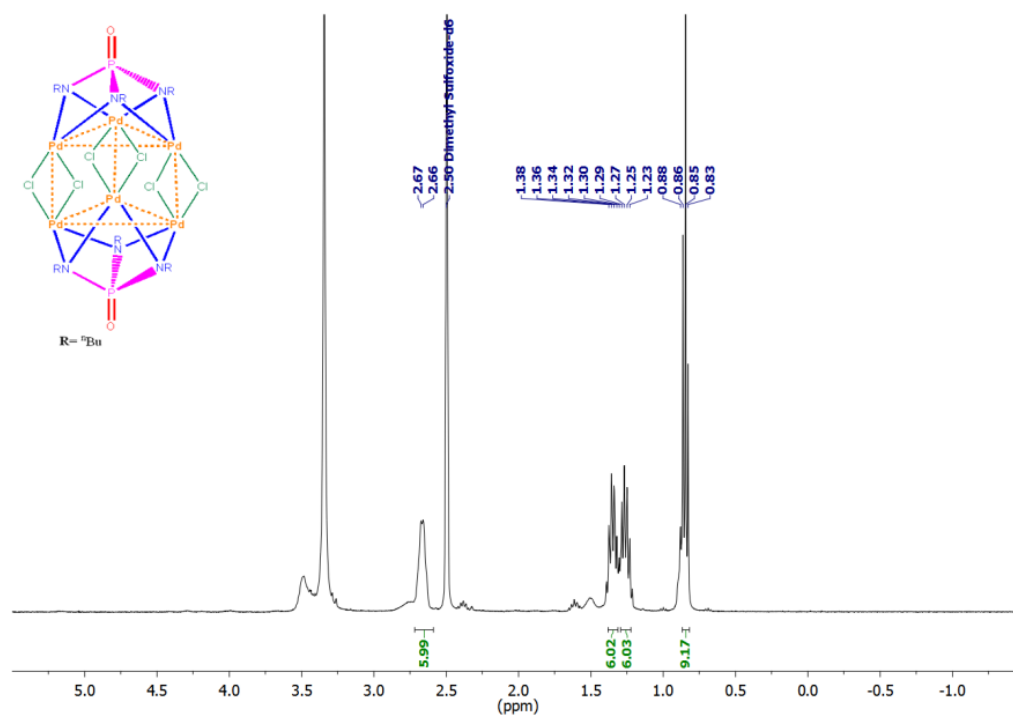
**<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR Spectra of Compound L<sup>2</sup>-H<sub>3</sub>.**

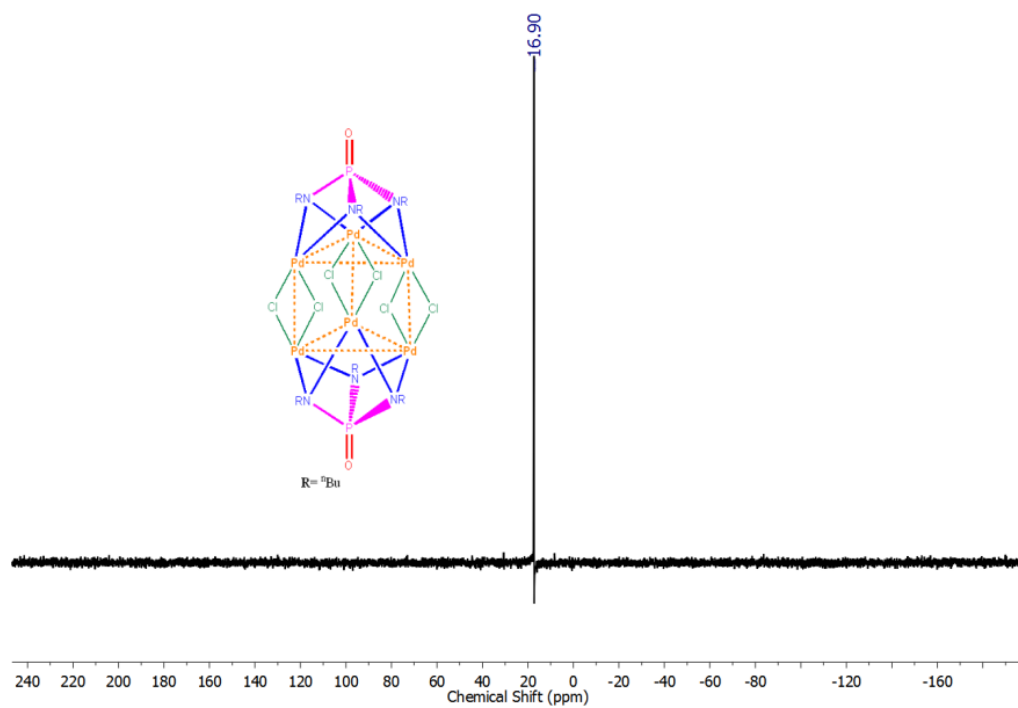
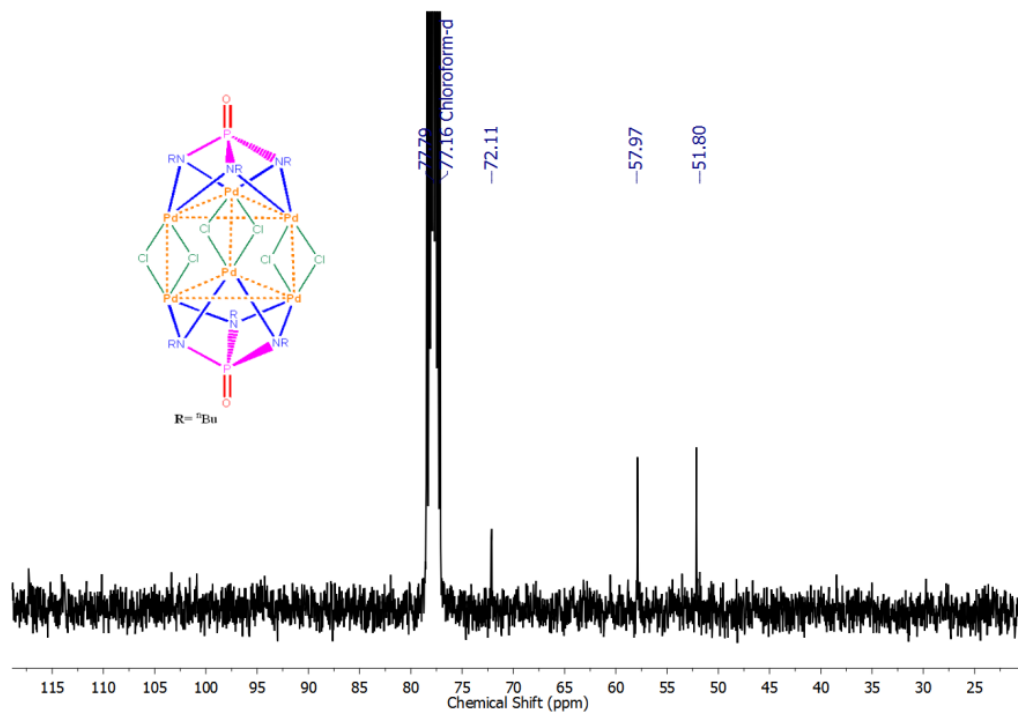




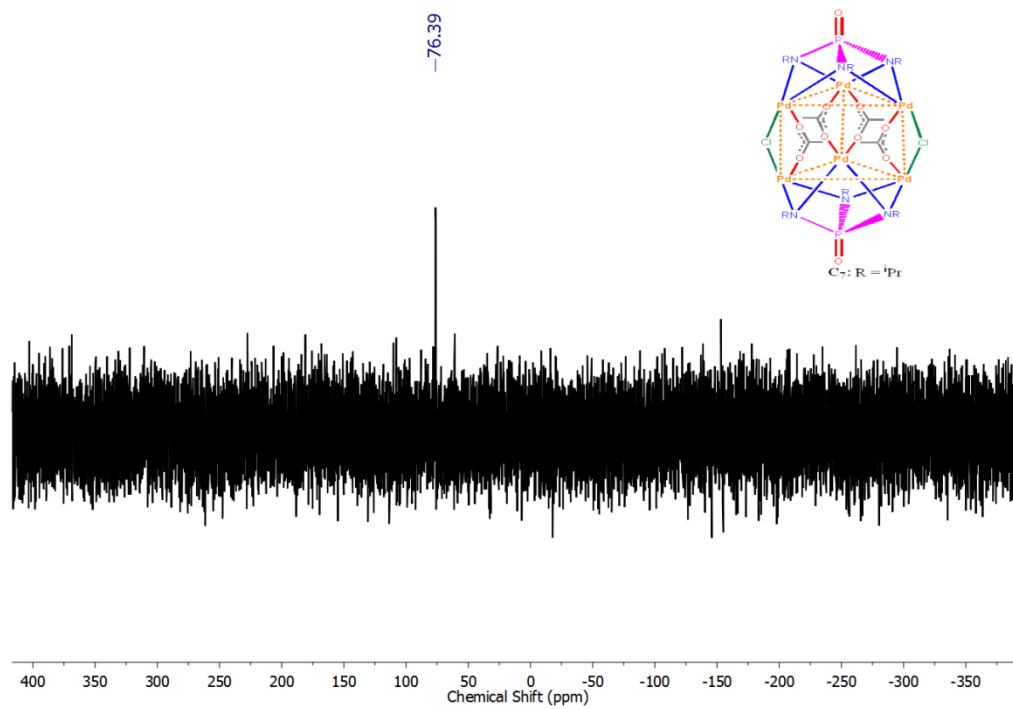


### $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR Spectra of Compound C<sup>1</sup>.

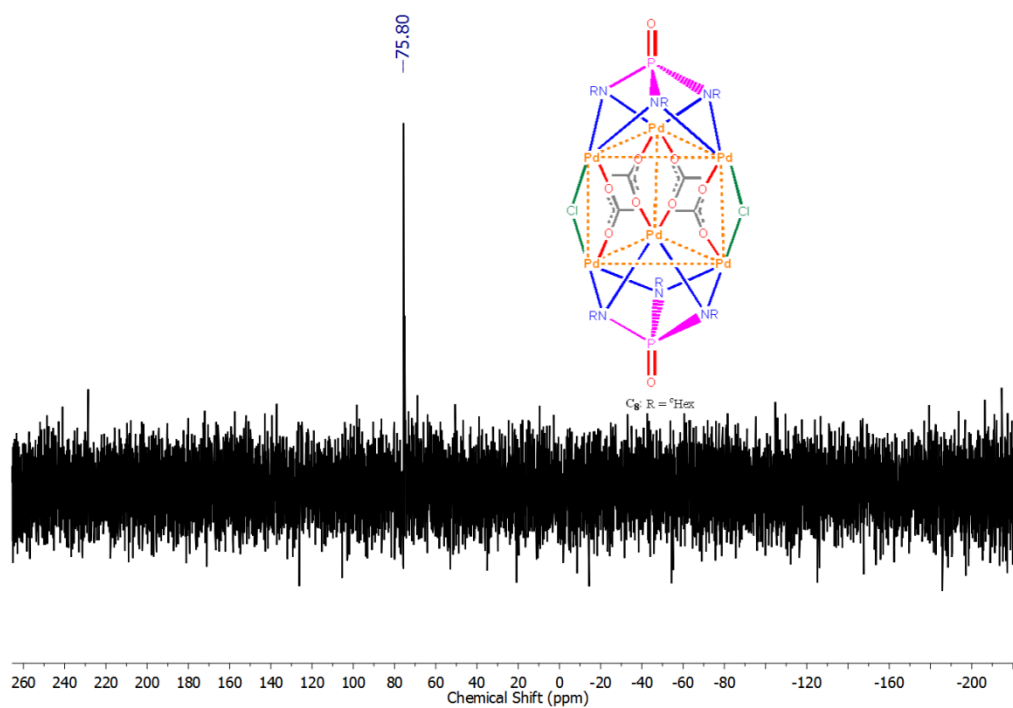




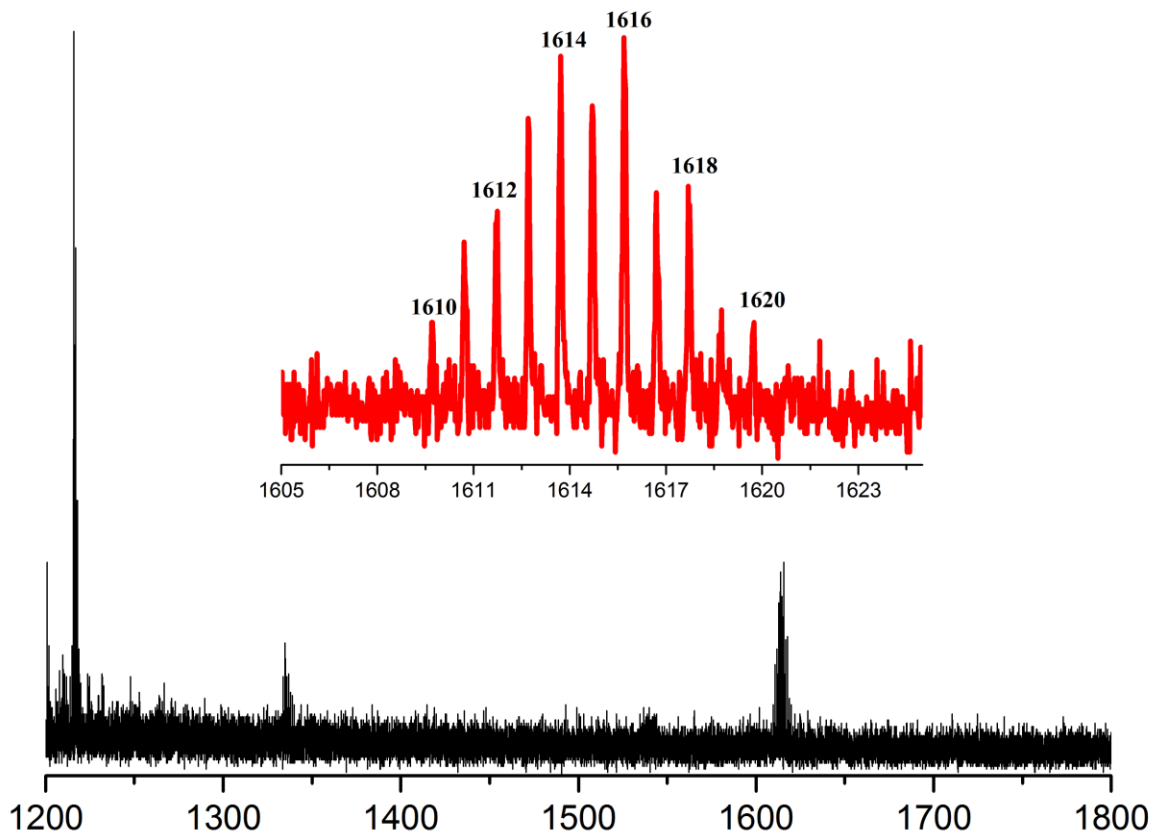
**<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR Spectra of Compound C<sup>2</sup>.**



**<sup>31</sup>P NMR Spectra of Compound C<sup>7</sup>.**



**<sup>31</sup>P NMR Spectra of Compound C<sup>8</sup>.**



**MALDI-TOF for C<sup>8</sup>.**

**Table 4: Crystallographic Data**

Compound	L <sup>1</sup> -H <sub>3</sub>	C <sup>1</sup>	C <sup>2</sup>
Chemical formula	C <sub>12</sub> H <sub>33</sub> ClN <sub>4</sub> OP	C <sub>18</sub> H <sub>42</sub> C <sub>6</sub> N <sub>6</sub> O <sub>2</sub> P <sub>2</sub> Pd <sub>6</sub>	C <sub>24</sub> H <sub>54</sub> Cl <sub>6</sub> N <sub>6</sub> O <sub>2</sub> P <sub>2</sub> Pd <sub>6</sub>
Formula weight	315.20	1281.51	1365.61
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 21/c	P -1	P -1
a (Å); α (°)	11.3521(11); 90	8.4714(11); 86.563(3)	12.7362(18); 79.164(3)
b (Å); β (°)	18.4661(17); 102.89(18)	9.1437(12); 76.432(3)	12.8603(17); 74.208(3)
c (Å); γ (°)	9.4572 (9); 90	12.8302(17); 87.216(2)	13.7745(19); 71.452(3)
V (Å <sup>3</sup> ); Z	1932.5(3); 8	963.7(2); 2	2045.5(5); 2
ρ (calc.) mg m <sup>-3</sup>	1.372	2.219	2.067
μ(Mo K <sub>α</sub> ) mm <sup>-1</sup>	0.513	3.265	2.700
2θ <sub>max</sub> (°)	50	50	50
R(int)	0.0192	0.0456	0.0713
Completeness to θ	100 %	99.5 %	99.9 %
Data / param.	3941 / 190	4783/ 185	10153 / 421
GOF	1.048	2.881	0.837
R1 [F>4σ(F)]	0.0469	0.0521	0.0427
wR2 (all data)	0.1377	0.1447	0.1474
max. peak/hole (e.Å <sup>-3</sup> )	1.333 / -0.362	4.097 / -2.430	2.481 / -1.788

Compound	C <sup>7</sup>	C <sup>8</sup>	C <sup>10</sup>
Chemical formula	C <sub>26</sub> H <sub>54</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub> Pd <sub>6</sub>	C <sub>44</sub> H <sub>76</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub> Pd <sub>6</sub>	C <sub>42</sub> H <sub>62</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub> Pd <sub>6</sub>
Formula weight	1377.69	1617.88	1789.6288
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	P n m a	C mc21	C 2/c
a (Å); α (°)	25.582(2); 90	25.582(2); 90	22.614(3); 90
b (Å); β (°)	17.4982(15); 90	17.4982(15); 90	9.9960(12); 111.429(3)
c (Å); γ (°)	9.7489(8); 90	9.7489(8); 90	24.764(3); 90
V (Å <sup>3</sup> ); Z	4364.0(6); 8	4364.0(6); 6	5210.7(12); 4
ρ (calc.) mg m <sup>-3</sup>	2.103	2.103	2.152
μ(Mo K <sub>α</sub> ) mm <sup>-1</sup>	2.668	2.668	2.785
2θ <sub>max</sub> (°)	50	50	52
R(int)	0.0656	0.0656	0.0995
Completeness to θ	100 %	100 %	100 %
Data / param.	5609 / 288	5609 / 259	5346 / 320
GOF	1.152	1.073	1.019
R1 [F>4σ(F)]	0.0522	0.0498	0.0506
wR2 (all data)	0.1638	0.1237	0.1327
max. peak/hole (e.Å <sup>-3</sup> )	2.392 / -2.391	2.505/ -1.896	1.413 / -1.176

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