Macrocyclic and Cryptand Assemblies Based on Cyclic Phosphazane ($P_2(^tBuN)_2$) Motif

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A dissertation submitted for the partial fulfilment of

BS-MS dual degree in Science

Department of Chemical Sciences

Indian Institute of Science Education and Research Mohali

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Dedicated to my parents

Certificate of Examination

This is to certify that the dissertation titled "Macrocyclic and Cryptand Assemblies Based on Cyclic Phosphazane ($P_2(^tBuN)_2$) Motif" submitted by Mr. Nitish Kumar Garg (Reg. No. MS14038) for the partial fulfilment of BS-MS dual degree programme of the institute, has been examined by the thesis committee duly appointed by the institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Date:

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Sanjay Singh at the Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Nitish Kumar Garg

Date:
Place:

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

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Acknowledgement

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Notations and Abbreviations

Å	Angstrom
AP	Atomic probe
calcd	Calculated
δ	Chemical shift in ppm
J	Coupling constant
°	Degree (angle)
°C	Degree Celsius
d	Doublet
ES	Electron spray ionization
Hz	Hertz
HRMS	High resolution mass spectrometry
IR	Infrared spectroscopy
m/z	Mass/charge
MS	Mass spectrometry
MHz	Mega hertz
Mp	Melting point
Me	Methyl group (CH_3)
m	Multiplet
NMR	Nuclear magnetic resonance
Z	No. of molecules in the unit cell
ppm	Parts per million

s	Singlet
t	Triplet
^{t}Bu	Tertiary butyl
THF	Tetrahydrofuran
V	Volume

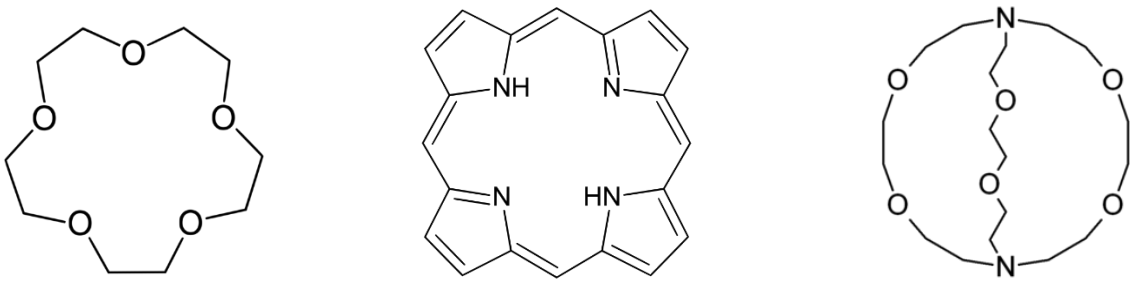
Abstract

Macrocycles have been a central subject in both synthetic and material chemistry utilizing their potential not only in host-guest chemistry but also as gas storage and modelling of biological systems. Families of organic macrocycles has far reaching impact on an extremely large area of molecular and supramolecular chemistry, spanning the fields of coordination and material chemistry. In contrast, inorganic macrocycles are far less investigated due to various factors affecting their synthesis, reactivity and purification. In spite of these challenges, it has been possible to assemble inorganic macrocycles. The high bond energy of P-N bond with relatively lower polarity, leads to the development of a new class of macromolecular chemistry. Phosph(III)azane dimers of the type $[ClP(\mu\text{-}NR)]_2$ are excellent building blocks for the formation of a range of inorganic macrocycles. The present work deals with the syntheses of inorganic-organic hybrid macrocycles using cyclodiphosph(III)azane $[ClP(\mu\text{-}N^tBu)]_2$ as a inorganic building block. Some new examples of inorganic-organic hybrid macrocycles: $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ (**2**) $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(3)** and $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{(O=)P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(4)** were synthesized by using different organic linkers and characterized by using SCXRD, HRMS and heteronuclear NMR spectroscopy. The macrocycles containing $P^{(III)}$ units were air and moisture sensitive and by oxidizing the phosphorus from +3 to +5 state, these macrocycles became air stable.

1. Introduction

1.1. Importance of macrocycles in chemistry

Macrocycles are molecular entities that display a combination of molecular recognition and complexation properties with vital implications for host–guest/supramolecular chemistry.[1] Macrocyclic chemistry has expanded remarkably since 1960s. The expansion of organic macrocycles has far reaching impact on large area of molecular and supramolecular chemistry, extended across the field of material, coordination chemistry and the biological area. Macrocycles are widely used not only in host-guest chemistry but also for gas storage and modelling of biological systems. Many synthetic macrocyclic complexes mimic some naturally occurring macrocycles such as metalloproteins, porphyrins and cobalamine.[2] The common examples include the crown ethers, calixarenes, porphyrins and cyclodextrins etc. In 1987 Nobel prize was given to Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen for their remarkable efforts in discovering and determining uses of crown ethers and cryptands. The cryptands were first prepared in 1969 and form a series of well-defined host guest complexes (cryptates) with alkali and alkaline-earth metals. These molecules are three-dimensional analogues of crown ethers but are more selective for the guest ions. Some common examples of organic macrocycles which have been extensively investigated in various studies includes crown ethers, porphyrins and cryptands (Fig 1.1).

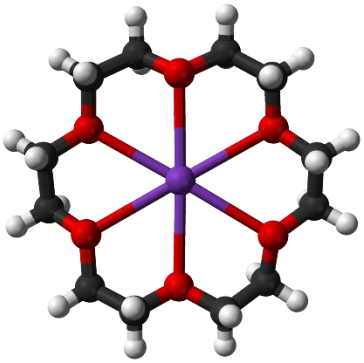


[15]-Crown-5 Porphyrin [2.2.2] cryptand

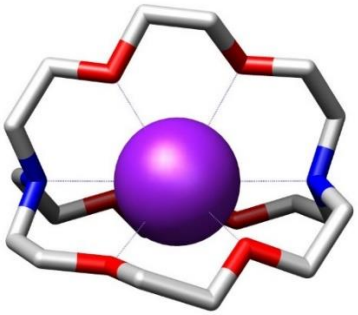
Fig 1.1. Some common organic macrocycles.

These macrocycles and cryptands having hard donor (O and N) show very good affinity for alkali metal cations. These interactions also helped in the isolation of alkali metal anions like K^-.[3] The three-dimensional cavity inside the cryptand act as a host for guest ions. Cryptands form complexes with many cations like NH_4^+, alkali metals, lanthanides and alkaline-earth metals. The most common cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$ which is generally known as [2.2.2]cryptand. Nature of

donor site plays a vital role in selectivity. The macrocycles having soft donor like sulfur will enhance complexes with ions like Ag^+ and hamper hard alkali metal ions while oxygen and nitrogen preferentially coordinate with alkali metals. Some well-known examples of macrocycles encapsulating a potassium ion includes [18]-crown-6 and [2.2.2]cryptand (Fig. 1.2.).



[18]-crown-6 coordinating a potassium cation



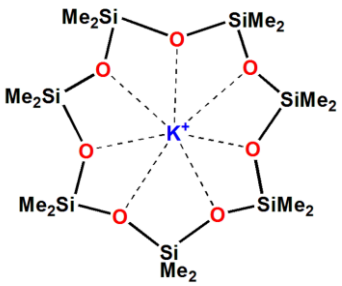
Structure of [2.2.2]cryptand encapsulating a potassium cation

Fig 1.2. Organic macrocycles encapsulating a potassium cation.

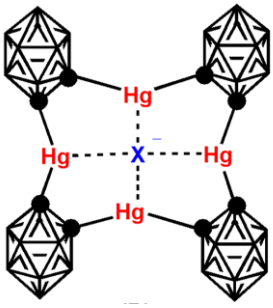
Macrocyclic complexes of transition metals are very important due to their biological activities, including antifertile, antibacterial antiviral, anticarcinogenic and antifungal. Macrocyclic metal complexes of lanthanides e.g., Gd(III) are used as MRI (magnetic resonance imaging) contrast agents.[2] Macrocycles and cryptands are classified in three classes on the basis of type of atoms present in the cyclic core: (i) organic (ii) inorganic and (iii) hybrid organic-inorganic.

Organic macrocycles are widely explored in molecular, supramolecular, coordination and materials chemistry. Inorganic macrocycles are still rare due to various factors affecting their synthesis, reactivity and purification.[4] Some of the reasons for scarcity of inorganic macrocycles are: (i) Availability of various oxidation states of inorganic elements. (ii) Greater range of available orbitals and hybridization state which leads to the diverse range of bonding connectivity. (iii) Polar nature of bonds. (iv) Formation of multi-products. (v) Moisture sensitivity. Due to all these reasons, there is an inherent problem in the selective synthesis and isolation of inorganic macromolecular systems that also leads to the lower thermodynamic stability or kinetically more labile nature. In spite of these many challenges mentioned above, it has been possible to assemble inorganic macrocycles. Organic macrocycles show affinity for cations while the inorganic macrocycles can bind with cations as well as anions. The behavior of inorganic macrocycles is dominated by anion coordination through electropositive metal centers of the macrocyclic host and in some examples cation binding is also seen

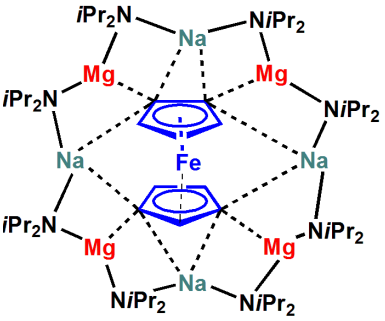
through donor atoms like oxygen, nitrogen and sulfur. Fig 1.3 below depicts some well-known examples of inorganic macrocycles with both the donor and acceptor properties.[5-7]



Potassium complex of donor type silicon macrocycle



A tetrameric Hg(II) metallacarborand coordinating a halide ion (X = Cl^-, Br^-)



"Inverse crown"- acceptor for organic, inorganic and organometallic anions

Fig 1.3. Some examples of inorganic macrocycles.

In general, to synthesize a stable macrocycle, the central challenge is that the ring closing reactions do not favor the formation of large rings. Instead, small rings or polymers tend to form. This kinetic problem can be addressed by using high dilution reaction whereby intramolecular processes are favored relative to polymerization. Another important requirement for the synthesis of macrocycle is that the substrate or building block should be pre-organized and rigid.

1.2. Cyclodiphosphazane $[ClP(\mu\text{-}N^tBu)]_2$ as a building block to form macrocycles

Cyclodiphosphazane are four membered inorganic ring systems containing alternating trivalent nitrogen and phosphorus atoms. Cyclodiphosphazane are also known as diazadiphosphetidines as it contain two phosphorous and two nitrogen atoms. They have a rigid and almost planar framework.[9] It exist in cis and trans isomeric forms with a small energy difference and in the solid state, thermodynamically preferred cis isomer has been isolated (Fig 1.4). The pre-organized cis form is beneficial in the synthesis of macrocycles. The high bond energy of P-N bond (290 kJ mol^{-1}) also favours the formation of such inorganic macrocycles. The X-ray structure of the first cyclodiphosphazane $[ClP(\mu\text{-}N^tBu)]_2$ was determined in 1971.[10] Cyclodiphosphazane has shown versatility in both coordination chemistry and supramolecular chemistry. It can act as both neutral and anionic ligands in coordination chemistry and useful scaffolds in supramolecular chemistry.[9] Scheme 1 depicts the synthesis of cyclodiphosphazane $[ClP(\mu\text{-}N^tBu)]_2$ published by Wright and co-workers in 2001.[8] The dimer $[ClP(\mu\text{-}N^tBu)]_2$ was readily

prepared by the 1:3 stoichiometric reaction of PCl_3 with $^tBuNH_2$ in THF. The additional equivalents of $^tBuNH_2$ were used to neutralize the HCl formed in the reaction mixture.

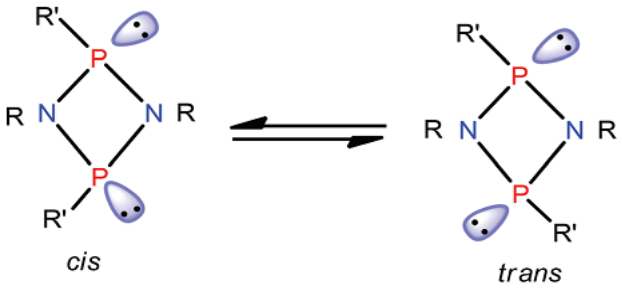
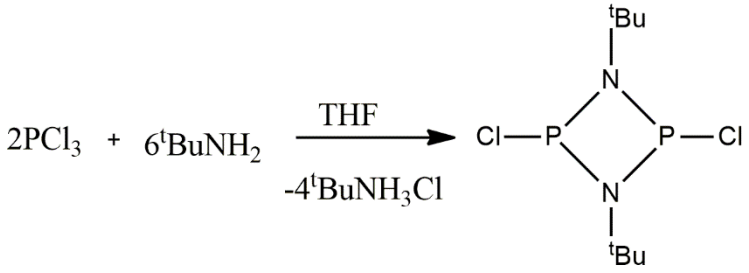
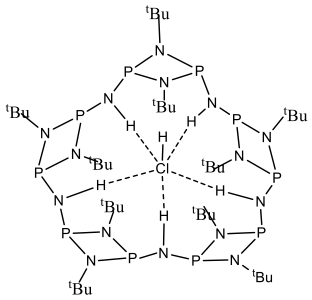


Fig 1.4. Cis and trans isomeric forms of $[ClP(\mu\text{-}N^tBu)]_2$.

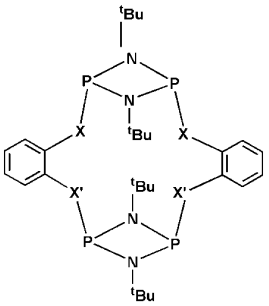


Scheme 1. Synthesis of cyclodiphosphazane $[ClP(\mu\text{-}NtBu)]_2$.

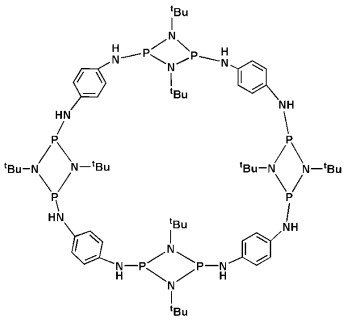
This compound fulfils the basic requirements of a building block in being reactive and highly symmetrical monomer with a rigid framework and pre-organised to form stable macrocycles. Various reports are present in which $[ClP(\mu\text{-}N^tBu)]_2$ acts as a building block. Fig 1.5 depicts some examples of inorganic and inorganic-organic hybrid macrocycles using cyclodiphosphazane as a building block. The crown like hexameric selenium bridged,[13] tetrameric oxygen bridged,[14] and hexameric sulfur bridged[15] phosphazane macrocycles are some of the well-known examples of inorganic macrocycles. The synthesis of these inorganic macrocycles faced many synthetic challenges and the approach used for nitrogen bridged macrocycles could not be applied in these cases. The extension of oxygen bridged systems to selenium macrocycle was achieved by Wurtz-type reaction of a mixture of cis- and trans-$[(Se=)ClP(\mu\text{-}N^tBu)]_2$ with Na metal, which led to the formation of hexameric macrocycle.[15] Therefore, the lack of common synthetic strategy led us to investigate other different pathways to obtain some new examples of macrocycles.



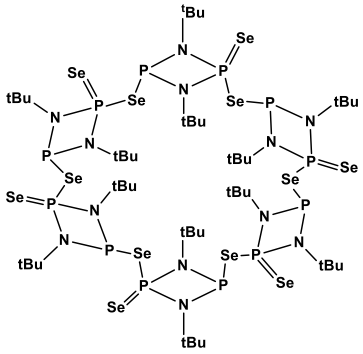
pentameric macrocycle
encapsulating a chloride ion



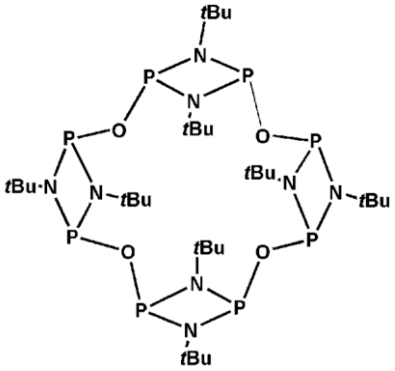
X = X’ = O, NH
X = O, X’ = NH



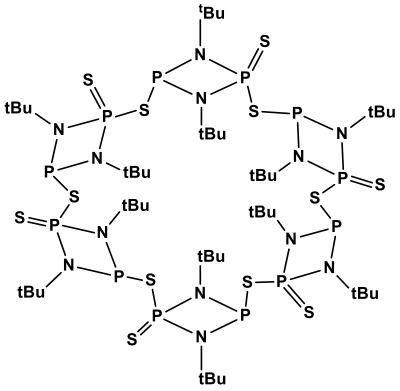
tetrameric phosphazane macrocycle
$[\{P(\mu\text{-}N^tBu\}_2\{1,4\text{-}(NH)_2\ C_6H_4\}]_4$



hexameric selenium-bridged
macrocycle



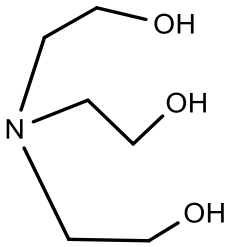
tetrameric oxygen-bridged
macrocycle



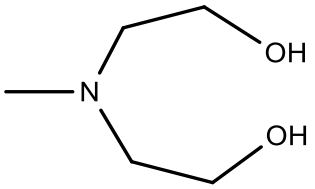
hexameric sulfur-bridged
macrocycle

Fig 1.5. Macrocycles with cyclodiphosphazane as a building block.[13-17]

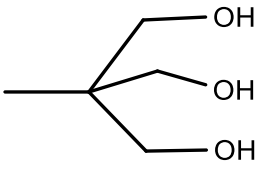
Herein, we have investigated some synthetic routes to prepare some new examples of inorganic macrocycles and cryptands containing phosphorus and nitrogen atoms by using cyclodiphosphazane $[ClP(\mu\text{-}N^tBu)]_2$ as a building block. We used some organic linkers to synthesize some new examples of macrocycles and cryptands (Fig 1.6).



triethanolamine
TEA



N-methyldiethanolamine



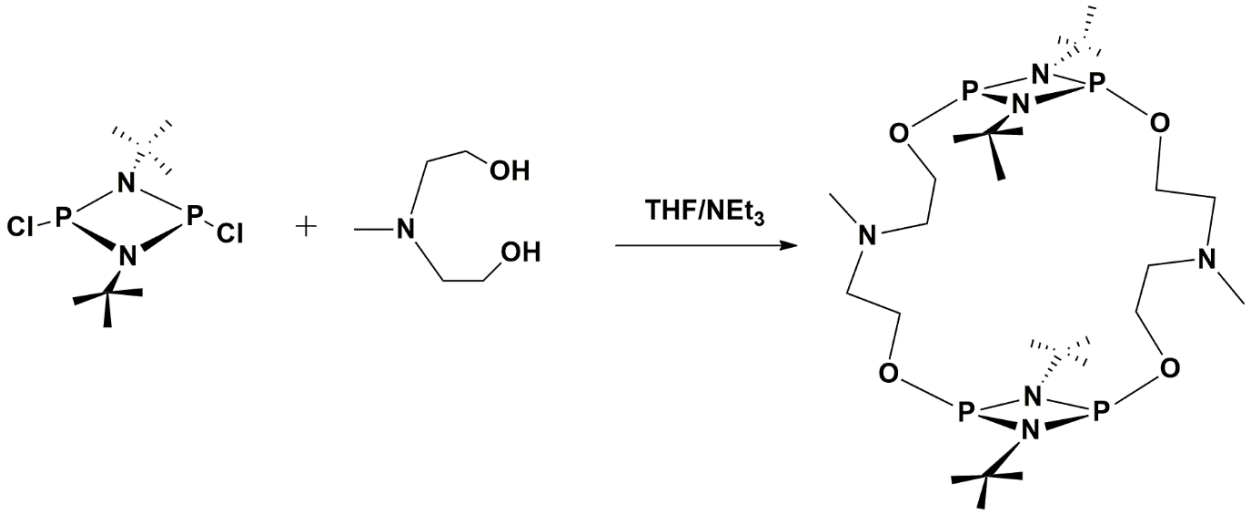
1,1,1-tris(hydroxymethyl)ethane

Fig. 1.6. Linkers used to synthesize macrocycles and cryptands.

2. Results and Discussion

2.1. Synthesis and characterization of [{P(μ-N^{t}Bu)}$_2${O(CH$_2$)$_2$N(Me)(CH$_2$)$_2$O}]$_2$ (1)

The precursor [ClP(μ-N^{t}Bu)]$_2$ has been synthesized by using the reported procedure.[8] The 1:1 reaction of N-methyldiethanolamine and [ClP(μ-N^{t}Bu)]$_2$ has been carried out at room temperature for 12 hours in the presence of triethylamine as a base to get the dimeric macrocycle [{P(μ-N^{t}Bu)}$_2${O(CH$_2$)$_2$N(Me)(CH$_2$)$_2$O}]$_2$ (**1**) in a single step (Scheme 2). Compound **1** was found to be a white solid and it is highly soluble in benzene, hexane and toluene. Compound **1** was found to be very sensitive to the open atmosphere. The melting point of **1** was found to be 127 ^{o}C. Compound **1** was characterized by using HRMS and ^{1}H, ^{13}C, ^{31}P{^{1}H} NMR spectroscopy. HRMS spectrum of **1** showed a signal at *m/z* = 643.3548 (calcd. 643.3517 [M+H]$^+$) corresponding to the dimeric macrocycle. In ^{31}P{^{1}H} NMR spectrum, the signal was found to be at δ = 134.4. Four signals in ^{1}H NMR spectrum at δ = 1.28 ppm (36H,s) for four ^{t}Bu groups, 2.38 ppm for methyl protons attached to nitrogen (6H,s) and poorly resolved triplet signals at 2.69 ppm (8H) and 3.98 ppm (8H) corresponds to methylene groups of the linker. In ^{13}C NMR spectrum, the peaks at δ = 31.2 ppm and 60.1 ppm were for ^{t}Bu groups, 44.3 ppm and 51.2 ppm correspond to methylene groups and the peak at 58.0 ppm is attributed for methyl group attached to nitrogen.

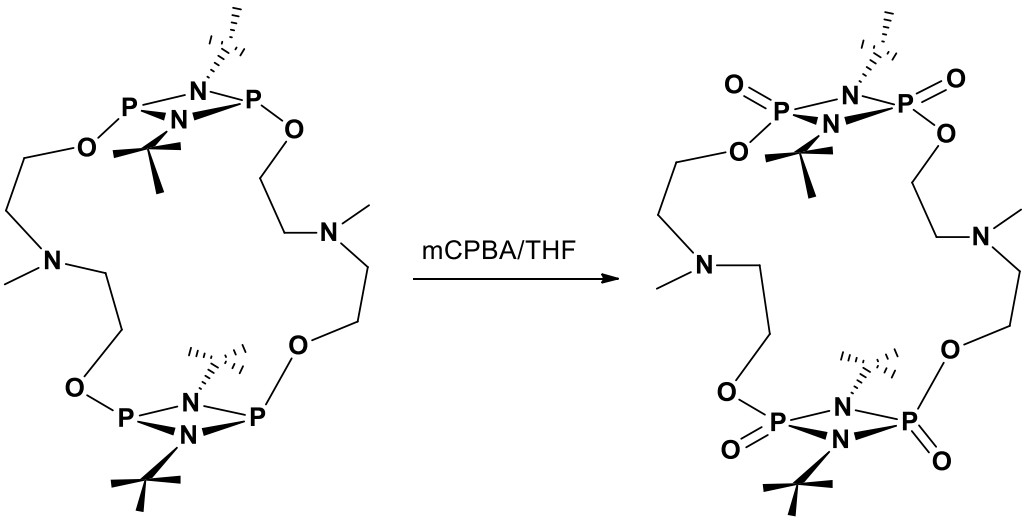


Scheme 2. Synthesis of [{P(μ-N^{t}Bu)}$_2${O(CH$_2$)$_2$N(Me)(CH$_2$)$_2$O}]$_2$ **(1)**.

2.2. Synthesis and characterization of $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ (2)

Compound **1** was sensitive to the open atmosphere, it readily decomposes in the presence of air or moisture and this can be attributed to the presence of phosphorus in +3 oxidation state. Based on a previous literature report[12], we oxidized the P^{III} centers to P^V by using mCPBA as an oxidizing agent to make the air and moisture stable compound **2**.

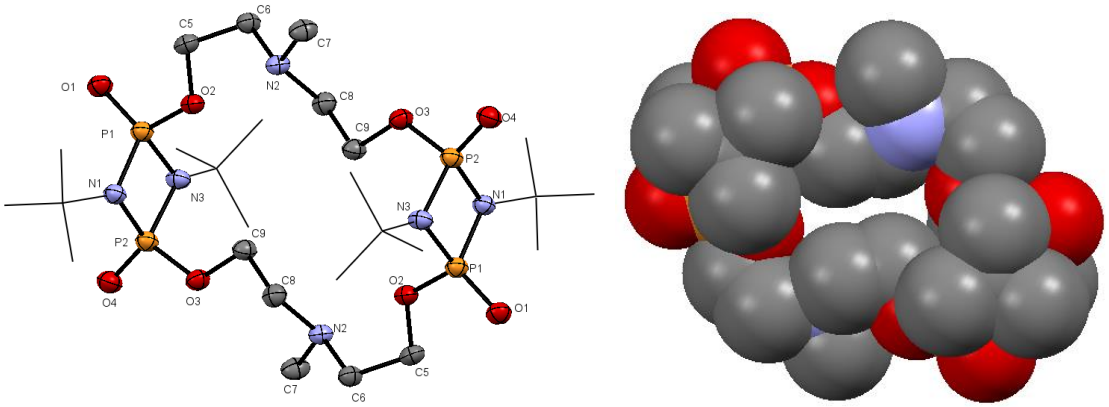
The 1:4 reaction between compound **1** and mCPBA has been carried out at room temperature for 12 hours to get the dimeric macrocycle with P(III) centers oxidized to P(V) state $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ (**2**) (Scheme 3). Compound **2** was found to be a white solid. The melting point was found to be 92-94 ^oC. The single crystals of **2** were obtained in THF at 4 ^0C. Compound **2** was characterized by using SCXRD, HRMS and ^1H, ^{13}C, $^{31}P\{^1H\}$ NMR spectroscopy. HRMS spectrum of **2** showed a signal at *m/z* = 643.3548 (calcd. 643.3517 $[M+H]^+$) corresponding to the oxidized dimer of compound **1**. In $^{31}P\{^1H\}$ NMR spectrum, the signal at δ = -4.2 ppm showed the presence of P=O bond in the molecule which is in accordance with the value reported for similar bonds in literature.[12] Four signals in ^1H NMR spectrum at δ = 1.43 ppm (36H, s) for four ^{t}Bu groups, 2.44 ppm for methyl protons attached to nitrogen (6H, s) and poorly resolved triplet signals at 2.87 ppm (8H) and 4.25 ppm (8H) for methylene group attributed to the formation of oxidized dimeric macrocycle. In ^{13}C NMR spectrum, the peaks at δ = 30.3 ppm and 66.0 ppm were for ^{t}Bu groups, the signals at δ = 43.3 ppm and 55.1 ppm correspond to methylene groups and the peak at 57.2 ppm for methyl group attached to nitrogen.



Scheme 3. Synthesis of $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(2)**

The single crystal X-ray structure of **2** showed that this molecule crystallized in triclinic crystal system with *P* -1 space group and the presence of two different phosphorus environments, as a result of the

oxygen lone pair oriented *exo*- and *endo*- to the core. The size of the macrocyclic cavity measures across the diagonal P1-P1 was found to be 8.73 Å, whereas the closest distance between two N-methyl nitrogen atoms were 6.26 Å. These distances were found to be slightly different from the unoxidized macrocycle (9.86 Å and 6.17 Å respectively). Along with compound **2**, THF (solvent used) and *m*-chlorobenzoic acid (byproduct of the reaction) also crystallized (confirmed by SCXRD and ^{1}H, ^{13}C, $^{31}P\{^{1}H\}$ NMR spectroscopy).

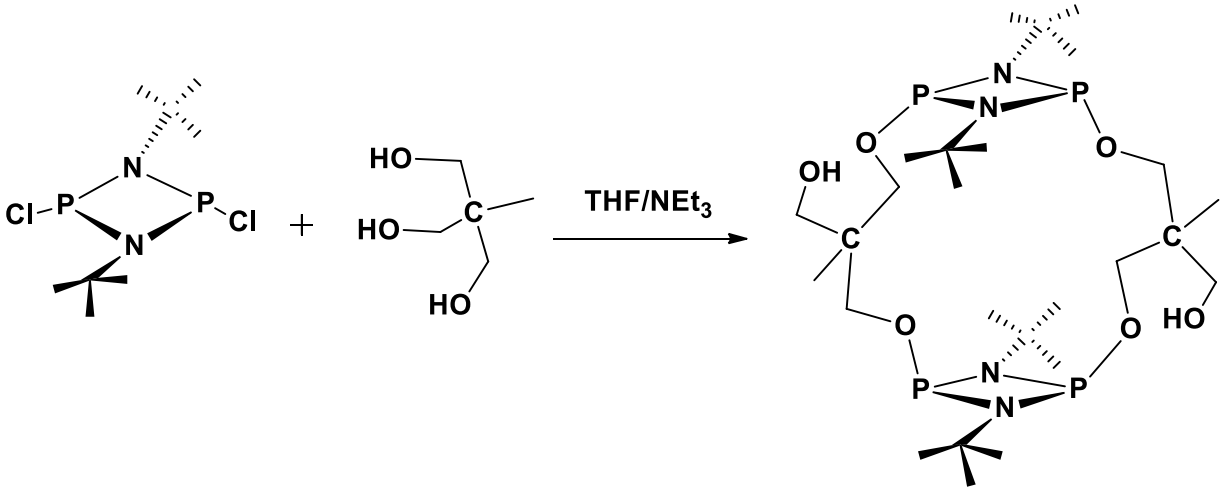


(a) **(b)**

Fig 1.7. (a) Single crystal X-ray structure of $[\{(O=)P(\mu\text{-}N^{t}Bu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ (**2**). **(b)** Space filling model showing the cavity size. All hydrogen atoms have been omitted for clarity. Ellipsoids set at 50% probability. Selected bond lengths [Å]: P(1)-N(2) 1.672(3), P(1)-N(3) 1.671(3), P(1)-O(1) 1.473(2), P(2)-O(4) 1.466(2), P(2)-O(3) 1.582(2), O(3)-C(9) 1.459(3), C(9)-C(8) 1.523(4), C(8)-N(2) 1.502(4), N(2)-C(7) 1.504(4), N(2)-C(6) 1.506(4), C(6)-C(5) 1.500(4), C(5)-O(2) 1.455(3), O(2)-P(1) 1.584(2), P(1)-O(1) 1.473(2); and bond angles [^{o}]: O(1)-P(1)-N(1) 120.60(13), P(1)-N(3)-P(2) 94.91(14), N(3)-P(2)-N(1) 84.99(13), N(1)-P(2)-O(4) 120.43(15), O(4)-P(2)-O(3) 108.55(12), P(2)-O(3)-C(9) 121.49(13), C(9)-C(8)-N(2) 114.2(2), C(7)-N(2)-C(6) 109.6(2) and C(5)-O(2)-P(1) 121.21(13).

2.3. Synthesis and characterization of [(HOCH$_2$)(Me)C(CH$_2$O-)$_2$(μ-{P$_2$(μ-N^{t}Bu)$_2$})$_2$(-OCH$_2$)$_2$C(Me)(CH$_2$OH)] (3)

Further we have used 1,1,1-tris(hydroxymethyl)ethane as a linker to synthesize the cryptand like bicyclic macrocycle. The 2:3 reaction of 1,1,1-tris(hydroxymethyl)ethane and [ClP(μ-N^{t}Bu)]$_2$ was performed at room temperature for 12 hours in the presence of triethylamine as a base in THF (Scheme 4). Instead, we isolated the monocyclic macrocycle **3**. Then 1:1 reaction of 1,1,1-tris(hydroxymethyl)ethane and [ClP(μ-N^{t}Bu)]$_2$ has been performed to optimize the reaction conditions for **3**. Compound **3** was found to be sensitive to the open atmosphere and highly soluble in hexane and toluene. Compound **3** was characterized by using HRMS and ^{1}H, ^{31}P{^{1}H} NMR spectroscopy. HRMS spectrum of **1** showed a signal at *m/z* = 645.3259 (calcd. 645.3229 [M+H]$^+$) corresponding to the dimeric macrocycle. In ^{1}H NMR spectrum, the signals at δ = 0.86 ppm for two methyl groups, 1.27 ppm for four ^{t}Bu groups, 3.5-4.2 ppm for methylene and hydroxyl groups along with minor impurities. In ^{31}P{^{1}H} NMR spectrum, the major signal found at δ = 174.0 ppm lies in the range of expected product containing P(III).

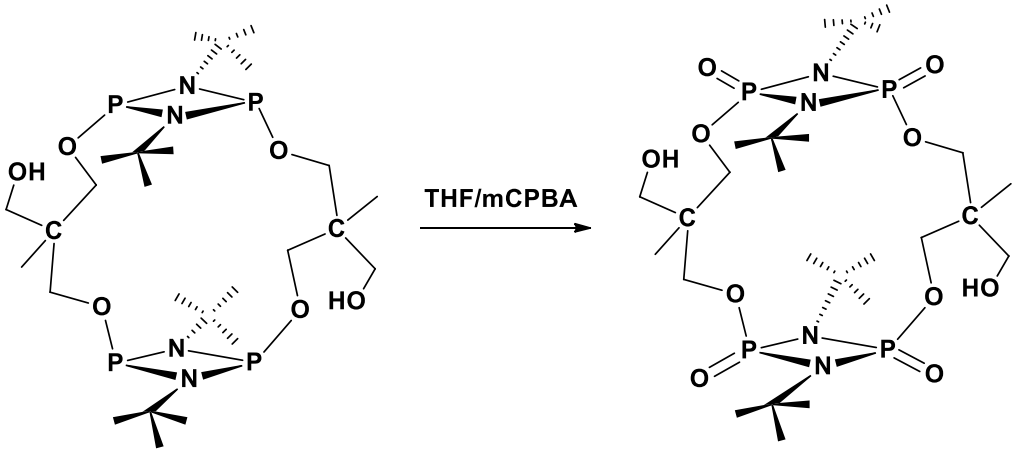


Scheme 4. Synthesis of [(HOCH$_2$)(Me)C(CH$_2$O-)$_2$(μ-{P$_2$(μ-N^{t}Bu)$_2$})$_2$(-OCH$_2$)$_2$C(Me)(CH$_2$OH)] **(3)**.

2.4. Synthesis and characterization of [(HOCH$_2$)(Me)C(CH$_2$O-)$_2$(μ-{(O=)P$_2$(μ-N^{t}Bu)$_2$})$_2$(-OCH$_2$)$_2$C(Me)(CH$_2$OH)] (4)

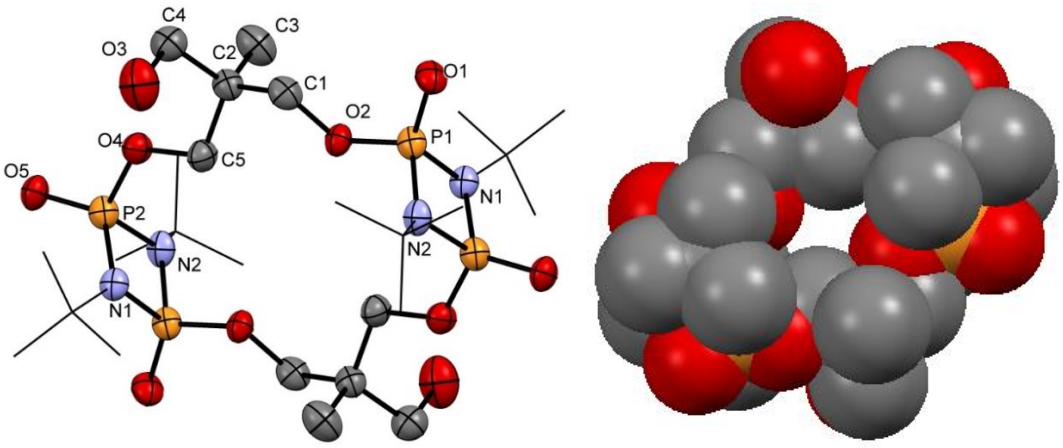
The 1:1 reaction of 1,1,1-tris(hydroxymethyl)ethane and [ClP(μ-N^{t}Bu)]$_2$ has been carried out at room temperature for 12 hours in the presence of triethylamine as a base to get the dimeric macrocycle **3.** To get the air stable macrocycle, compound **3** was oxidized by using mCPBA. The 1:4 reaction between **3** and mCPBA has been carried out at room temperature for 12 hours to get the oxidized dimeric macrocycle [(HOCH$_2$)(Me)C(CH$_2$O-)$_2$(μ-{(O=)P$_2$(μ-N^{t}Bu)$_2$})$_2$(-OCH$_2$)$_2$C(Me)(CH$_2$OH)] (**4**) (Scheme

5). Compound **4** was dissolved in minimum amount of THF to afford the colourless crystals at room temperature. Compound **4** was characterized by SCXRD, HRMS and $^{31}P\{^{1}H\}$ NMR spectroscopy. HRMS spectrum of **4** showed a signal at *m/z* = 709.3058 (calcd. 709.3025 $[M+H]^{+}$) corresponding to the oxidized macrocycle. In the in-situ $^{31}P\{^{1}H\}$ NMR spectrum, the major signal at δ = -5.4 ppm showed the presence of P=O bond in the molecule which is in accordance with the value reported for similar bonds in literature.[12] ^{1}H and ^{13}C NMR were not conclusive. It could be due the formation of multiple products in the reaction.



Scheme 5. Synthesis of $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{(O=)P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(4)**.

From single crystal X-ray structure of **4**, it was found that the molecule crystallized in triclinic crystal system having *P* -1 space group. The solid state structure of **4** showed the presence of two different phosphorus environments, as a result of the oxygen lone pair oriented *exo*- and *endo*- to the core. The size of the macrocyclic cavity measuring across the diagonal P2-P2 was found to be 6.74 Å whereas the C2-C2 separation was 6.24 Å. The size of the cavity is slightly smaller as compared to the cavity in macrocycle **2**, it could probably be due to less number of atoms in the ring skeleton. Macrocycle **2** has a 20 atom skeleton whereas macrocycle **4** has only 16 atoms in its core.



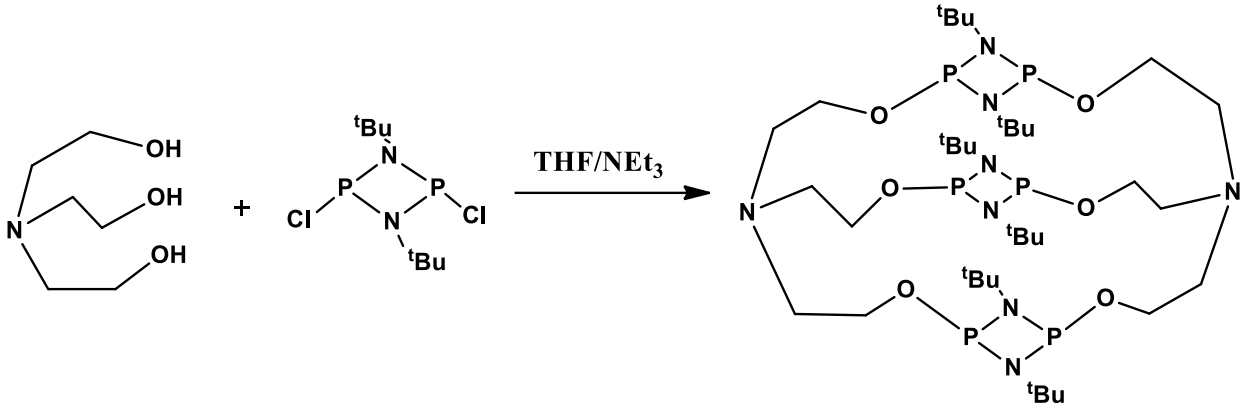
(a) **(b)**

Fig 1.8. (a) Single crystal X-ray structure of [(HOCH$_2$)(Me)C(CH$_2$O-)$_2$(μ-{(O=)P$_2$(μ-N^{t}Bu)$_2$})$_2$(--OCH$_2$)$_2$C(Me)(CH$_2$OH)] **(4)**. **(b)** Space filling model showing the cavity size. All hydrogen atoms have been omitted for clarity. Ellipsoids set at 50% probability. Selected bond lengths [Å]: P(2)-O(5) 1.463(3), N(1)-P(2) 1.666(4), N(2)-P(2) 1.672(4), P(2)-O(4) 1.579(3), O(4)-C(5) 1.464(5), C(5)-C(2) 1.507(6), C(2)-C(4) 1.541(7), C(4)-O(3) 1.460(7), C(2)-C(3) 1.534(7), C(1)-C(2) 1.542(7), C(1)-O(2) 1.453(6), O(2)-P(1) 1.576(3), P(1)-O(1) 1.469(3); and bond angles [^{o}]: O(5)-P(2)-N(1) 120.79(19), O(5)-P(2)-N(2) 119.9(2), N(2)-P(2)-O(4) 110.52(19), P(2)-O(4)-C(5) 120.8(3), O(4)-C(5)-C(2) 109.1(4), C(5)-C(2)-C(4) 110.2(4), C(2)-C(4)-O(3) 109.8(5), C(1)-C(2)-C(3) 110.1(4), C(1)-O(2)-P(1) 120.1(3), O(1)-P(1)-O(2) 113.0(2) and O(1)-P(1)-N(1) 121.62(19).

2.5. Synthesis and characterization of [N(CH$_2$CH$_2$O-)$_3$(μ-{P$_2$(μ-N^{t}Bu)$_2$})$_3$(-OCH$_2$CH$_2$)$_3$N] (5)

The 2:3 reaction between triethanolamine and [ClP(μ-N^{t}Bu)]$_2$ has been carried out at room temperature for 12 hours in the presence of triethylamine as a base, to obtain the bicyclic macrocycle **5** in a single step (Scheme 6). Compound **5** was found to be a white solid and it is soluble in hexane and toluene. Compound **5** is sensitive to the open atmosphere. Repeated efforts to obtain crystals of **5** were not successful and therefore the structure of **5** cannot be determined unambiguously. The characterization of **5** was done with HRMS and ^{1}H, ^{31}P{^{1}H} NMR spectroscopy. HRMS spectrum of **5** showed a signal at *m/z* = 905.4512 (calcd. 905.4548 [M+H]$^+$) which corresponds to the cryptand **5**. In ^{1}H NMR spectrum, peaks at δ = 1.40 ppm corresponds to singlet for 54H of six ^{t}Bu groups, poorly resolved triplet signals at 2.83 ppm (12H) and 3.91 ppm (12H) for methylene groups attributed to the formation of bicyclic macrocycle. In ^{31}P{^{1}H} NMR the major signal at δ 134.3 ppm corresponds to the cryptand **5** and the

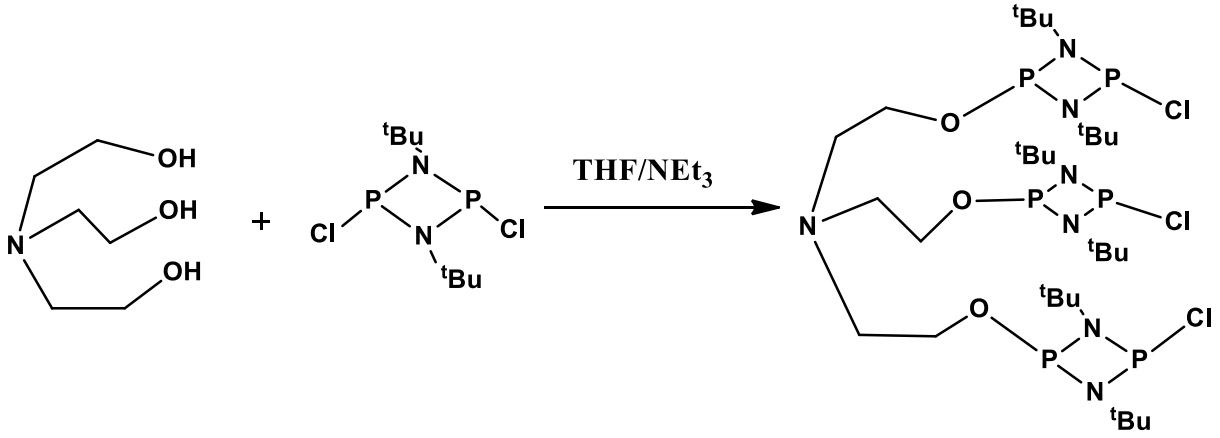
peaks at δ = 212.9, 122.8, 84.9, 13.3 and -9.5 were assigned to impurities that could have formed during the course of the reaction.



Scheme 6. Synthesis of $[N(CH_2CH_2O\text{-})_3(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_3(\text{-}OCH_2CH_2)_3N]$ **(5)**.

2.6. Synthesis and characterization of $[N(CH_2CH_2O\text{-})_3\{P(\mu\text{-}N^tBu)_2PCl\}_3]$ (6)

In order to perform a controlled synthesis of **5**, we tried to synthesize compound **6** (Scheme 7). A 1:3 reaction of triethanolamine and $[ClP(\mu\text{-}N^tBu)]_2$ was carried out at room temperature for 12 hours in the presence of triethylamine as a base to get tris(P_2N_2)-triethanolamine in a single step (Scheme 7). Compound **6** was found to be a white solid and it is soluble in hexane and toluene. Compound **6** was very sensitive to the open atmosphere. Compound **6** was characterized by using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. In $^{31}P\{^1H\}$ NMR spectrum, two doublets at δ = 138.1 ppm ($^2J_{P\text{-}P}$ = 39 Hz) and 189.4 ppm ($^2J_{P\text{-}P}$ = 37 Hz) showed the presence of two different phosphorus environments in the product. Three signals in ^1H NMR spectrum, at δ = 1.34 ppm corresponds to singlet for 54H of six ^{t}Bu groups, 2.9 (12H) and 4.01 (12H) for methylene groups attributed to the formation compound **6**.



Scheme 7: Synthesis of $[N(CH_2CH_2O\text{-})_3\{P(\mu\text{-}N^tBu)_2PCl\}_3]$ **(6)**

Table 1. Crystal data and structure refinement details of macrocycles 2 and 4.

Compound[a]	**2·(THF)$_2$(*m*-chlorobenzoic acid)$_2$**	**4·(THF)$_2$**
Chemical formula	$C_{24}H_{40}ClN_3O_7P_2$	$C_{68}H_{136}N_8O_{24}P_8$
Molar mass	579.98	1697.60
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
T [K]	99.99(10)	100.0(2)
a [Å]	14.2266(6)	10.3140(13)
b [Å]	15.0536(7)	11.1765(14)
c [Å]	15.8224(8)	19.1848(15)
α [°]	94.821(4)	90
β [°]	99.229(4)	92.428(9)
γ [°]	115.338(4)	90
V [Å3]	2978.3(3)	2209.5(4)
Z	4	1
D(calcd.) [g·cm^{-3}]	1.293	1.276
μ(Mo-$K\alpha$) [mm^{-1}]	0.280	0.230
Reflections collected	56906	26212
Independent reflections	20898	14324
Data/restraints/parameters	20898/0/681	14324/0/503
$R1$,$wR2[I>2\sigma(I)]$[a]	0.0937, 0.2392	0.1203, 0.2973
R1, wR2 (all data)[a]	0.1617, 0.3279	0.2179, 0.4031
GOF	1.048	1.001

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $wR2 = [\Sigma w(|Fo^2| - |Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$

3. Experimental Section

3.1. General procedure

All syntheses were carried out under inert atmosphere of dry nitrogen in oven dried glassware using standard Schlenk techniques or a glove box where O_2 and H_2O levels were maintained usually below 0.5 ppm. All the glassware were dried at 150 ^oC in an oven for at least 12 h and assembled hot and cooled *in vacuo* prior to use. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Sigma-Aldrich.

3.2. Single crystal X-ray structural determination

Single crystal X-ray diffraction data of **2** and **4** were collected using a RigakuXtaLAB mini diffractometer equipped with Mercury375M CCD detector. The data were collected with graphite monochromatic MoKα radiation (λ = 0.71073 Å) at 100.0(2) K using scans. During the data collection the detector distance was 50 mm (constant) and the detector was placed at 2θ = 29.85° (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite.[29] The crystal structures were solved by using either OLEX2[30] or WINGX package using SHELXS-97[31] and the structure were refined using SHELXL-97 2008. All non-hydrogen atoms were refined anisotropically. All the graphics were generated using Mercury 3.2.

3.3. Synthesis of $[\{P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ (1)

To a solution of N-methyldiethanolamine (0.24 g, 2.00 mmol) in 20 mL THF and Et_3N (2 mL, excess) at -70 ^0C was added dropwise a solution of $[ClP(\mu\text{-}N^tBu)]_2$ (0.55 g, 2.00 mmol) in THF (30 mL). The reaction mixture was brought back to room temperature and stirred for 12h. All volatiles were removed under vacuum. The compound was extracted in hexane (60 mL). The solution was then kept at -10 ^0C for few days to get the precipitate of pure compound. ^1H NMR (400MHz, $CDCl_3$): δ = 1.28 (s, 36H, ^{t}Bu), 2.38 (s, 6H, NMe), 2.69 (t, $^3J_{H\text{-}H}$ = 8Hz, 8H, NCH_2), 3.98 (broad t, 8H, OCH_2). ^{13}C NMR: (100.6 MHz, $CDCl_3$) δ = 31.2, 44.3, 51.2, 58.0, 60.1. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 134.4. HRMS (AP^+): *m/z* calculated for $C_{26}H_{58}N_6O_4P_4$: $[M+H]^+$ 643.3548; found 643.3517.

3.4. Synthesis of [{(O=)P(μ-N^{t}Bu)}$_2${O(CH$_2$)$_2$N(Me)(CH$_2$)$_2$O}]$_2$ (2)

To a solution of N-methyldiethanolamine (0.24 g, 2.00 mmol) in 20 mL THF and Et_3N (2 mL, excess) a solution of [ClP(μ-N^{t}Bu)]$_2$ (0.55 g, 2.00 mmol) in THF (30 mL) was added dropwise at -70 ^{0}C. The reaction mixture was brought back to room temperature and stirred for 12h. All volatiles were removed under vacuum and the product was extracted in hexane (60 mL). Product was redissolved in THF (30 mL). A separate solution of mCPBA (0.70 g, 4.10 mmol) in 30 mL THF was added to the above solution at -78 ^{o} C and then stirred at room temperature for 10 h. The solution was concentrated and kept for crystallization at 4 ^{o} C. ^{1}H NMR (400MHz, $CDCl_3$): δ = 1.43 (s, 36H, ^{t}Bu), 2.44 (s, 6H, NMe), 2.87 (broad t, 8H, NCH_2), 4.25 (broad t, 8H, OCH_2).(THF signals at δ = 1.8 ppm, 3.7ppm and *m*-chlorobenzoic acid signals at δ = 7.38 (t, $^3J_{H-H}$ = 8Hz, 2H), 7.53 (d, $^3J_{H-H}$ = 8Hz, 2H), 7.94 (d, $^3J_{H-H}$ = 8Hz, 2H), 8.04 (s, 2H)) ^{13}C NMR : (100.6MHz, $CDCl_3$) δ = 30.2, 43.3, 55.1, 57.1 and 66.0.(THF signals at δ = 25.6, 67.9 and m-Chlorobenzoic acid signals at δ = 128.1, 129.7, 130.0, 132.2, 133.1, 134.5, 168.7) ^{31}P{^{1}H} NMR (162.0MHz, $CDCl_3$): δ = -4.2 ppm. HRMS (ESI): *m/z* calculated for $C_{26}H_{58}N_6O_8P_4$: $[M+H]^+$ 707.3345; found 707.3318.

3.5. Synthesis of [(HOCH$_2$)(Me)C(CH$_2$O-)$_2$(μ-{P$_2$(μ-N^{t}Bu)$_2$})$_2$(-OCH$_2$)$_2$C(Me)(CH$_2$OH)] (3)

To a solution of 1,1,1-tris(hydroxymethyl)ethane (0.24 g, 2.00 mmol) in 20 mL THF and Et_3N (2 mL, excess) at -70 ^{0}C was added dropwise a solution of [ClP(μ-N^{t}Bu)]$_2$ (0.55 g, 2.00 mmol) in THF (30 mL). The reaction mixture was brought back to room temperature and stirred for 12h. All volatiles were removed under vacuum and the product was extracted in hexane (60 mL). The solvent was removed to get the desired product. ^{1}H NMR (400MHz, $CDCl_3$): δ = 0.86 ppm (s, Me), 1.27 (s, ^{t}Bu), 3.5-4.2 (CH_2, OH and some impurities). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ = 174.0 ppm. (Impurities at δ = 91.2, 140.4 and 173.4 ppm). HRMS (ESI): *m/z* calculated for $C_{26}H_{56}N_4O_6P_4$: $[M+H]^+$ 645.3259; found 645.3229.

3.6. Synthesis of [(HOCH$_2$)(Me)C(CH$_2$O-)$_2$(μ-{(O=)P$_2$(μ-N^{t}Bu)$_2$})$_2$(-OCH$_2$)$_2$C(Me)(CH$_2$OH)] (4)

To a solution of 1,1,1-tris(hydroxymethyl)ethane (0.24 g, 2.00 mmol) in 20 mL THF and Et_3N (2 mL, excess) at -70 ^{0}C was added dropwise a solution of [ClP(μ-N^{t}Bu)]$_2$ (0.55 g, 2.00 mmol) in THF (30 mL). The reaction mixture was brought back to room temperature and stirred for 12h. All

volatiles were removed under vacuum. The compound was extracted in hexane (60 mL). Product was redissolved in THF (30 mL). A solution of mCPBA (0.70g, 4.10 mmol) in 30 mL THF was added to the above solution at -78 ^{o}C and then stirred at room temperature for 10 h. The solution was concentrated and kept for crystallization at room temperature. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$): δ = -5.48 ppm. (Minor impurities at δ = -9.6, 3.6, 10.9 and 13.2 ppm). HRMS (ESI): *m/z* calculated for $C_{26}H_{56}N_4O_{10}P_4$: $[M+H]^+$ 709.3058; found 709.3025.

3.7. Synthesis of $[N(CH_2CH_2O\text{-})_3(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_3(\text{-}OCH_2CH_2)_3N]$ (5)

To a solution of triethanolamine (0.44 g, 3.00 mmol) in 20 mL THF and Et_3N (2 mL, excess), a solution of $[ClP(\mu\text{-}N^tBu)]_2$ (1.23g, 4.50 mmol) in THF (30 mL) was added dropwise at -70 ^{0}C. The reaction mixture was brought back to room temperature and stirred for 24h. All volatiles were removed under vacuum. The product was extracted in hexane (50 mL). Hexane was evaporated to get the product. ^{1}H NMR (400MHz, $CDCl_3$): δ = 1.40 (s, 54H, ^{t}Bu), 2.83 (broad t, 12H, NCH_2), 3.91 (broad t, 12H, OCH_2). $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 134.3 (Impurities at δ = 212.8, 122.8, 84.9, 13.4 and -9.6). HRMS (AP^+): *m/z* calculated for $C_{36}H_{78}N_8O_6P_6$: $[M+H]^+$ 905.4548; found 905.4512.

3.8. Synthesis of $[N(CH_2CH_2O\text{-})_3\{P(\mu\text{-}N^tBu)_2PCl\}_3]$ (6)

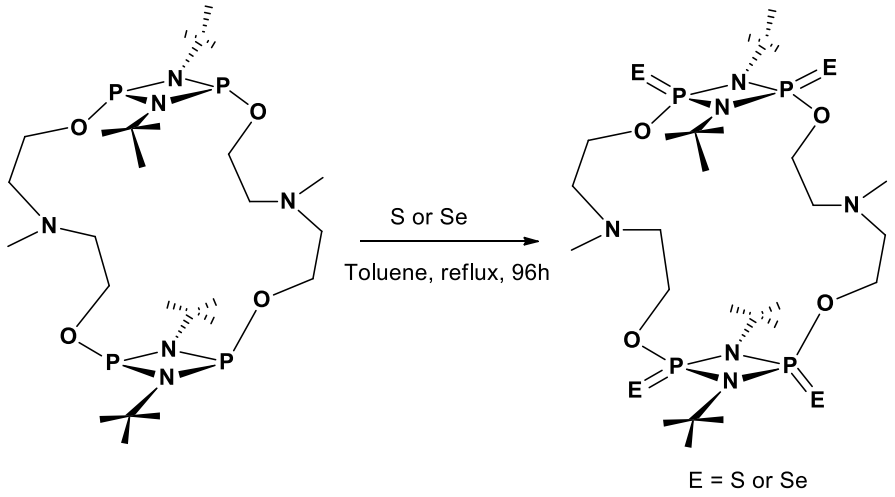
To a solution of triethanolamine (0.14 g, 1.00 mmol) in 20 mL THF and Et_3N (2 mL, excess) a solution of $[ClP(\mu\text{-}N^tBu)]_2$ (0.82 g, 3 mmol) in Toluene (30 mL) was added dropwise at -70 ^{0}C. The reaction mixture was brought back to room temperature and stirred for 24h. All volatiles were removed under vacuum. The product was extracted in hexane (50 mL). Hexane was evaporated to get the product. ^{1}H NMR (400MHz, $CDCl_3$): δ = 1.30 (s, 54H, ^{t}Bu), 2.90 (broad t, 6H, NCH_2), 4.0 (broad t, 6H, OCH_2), $^{31}P\{^{1}H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 138.1(d, $^{2}J_{P\text{-}P}$ = 38.9 Hz), 189.4(d, $^{2}J_{P\text{-}P}$ = 37.3 Hz) ppm (Impurities at δ = 207.5, 85.1 and -7.9).

4. Conclusion

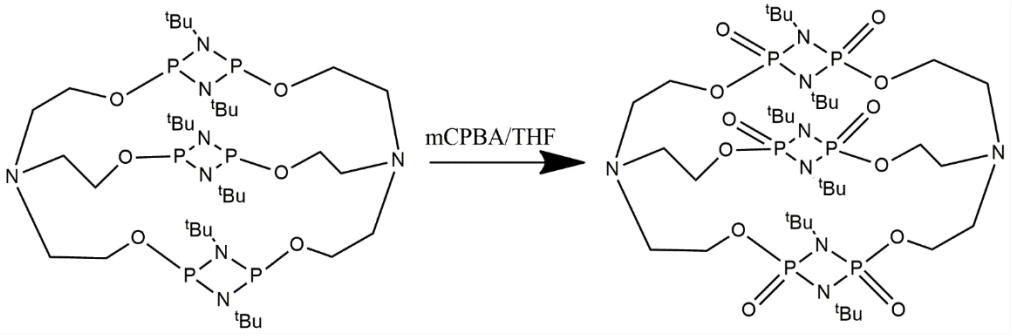
In the present work, we have synthesized some new examples of inorganic-organic hybrid macrocycles: $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(2)**, $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(3)** and $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{(O=)P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(4)** by using different organic linkers and characterized by SCXRD, HRMS and heteronuclear NMR spectroscopy. The single crystal X-ray structure of **2** and **4** showed the presence of two different phosphorus environments, as a result of the oxygen lone pairs oriented *exo*- and *endo*- to the core, while only one signal was observed in $^{31}P\{^1H\}$NMR. The macrocycles containing $P^{(III)}$ units were air and moisture sensitive and by oxidizing the phosphorus from +3 to +5 state, these macrocycles became air stable. The cavity size of these macrocycles can be used to entrap a guest ion. The formation of bicyclic macrocycle shows the feasibility of the reaction however, that needs to be investigated based on SCXRD to ascertain the composition and size of the macrocycle.

5. Future Directions

1. For the air stable macrocycles, we need to explore them in coordination chemistry, especially with respect to their host guest behavior with both cations and anions.
2. We are trying to oxidize the macrocycle **1** by using sulfur and selenium.



3. We are also trying to oxidize the cryptand by using the same synthetic strategy. However, that needs to be investigated based on SCXRD.



4. One of the challenges ahead is to develop more systematic strategy to synthesize the bicyclic macrocycle by using cyclodiphosphazane as a building block.

6. References

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Supporting Information

Heteronuclear NMR spectra (^{1}H, ^{13}C, $^{31}P\{^{1}H\}$) and HRMS spectra of compounds reported in this dissertation

Contents

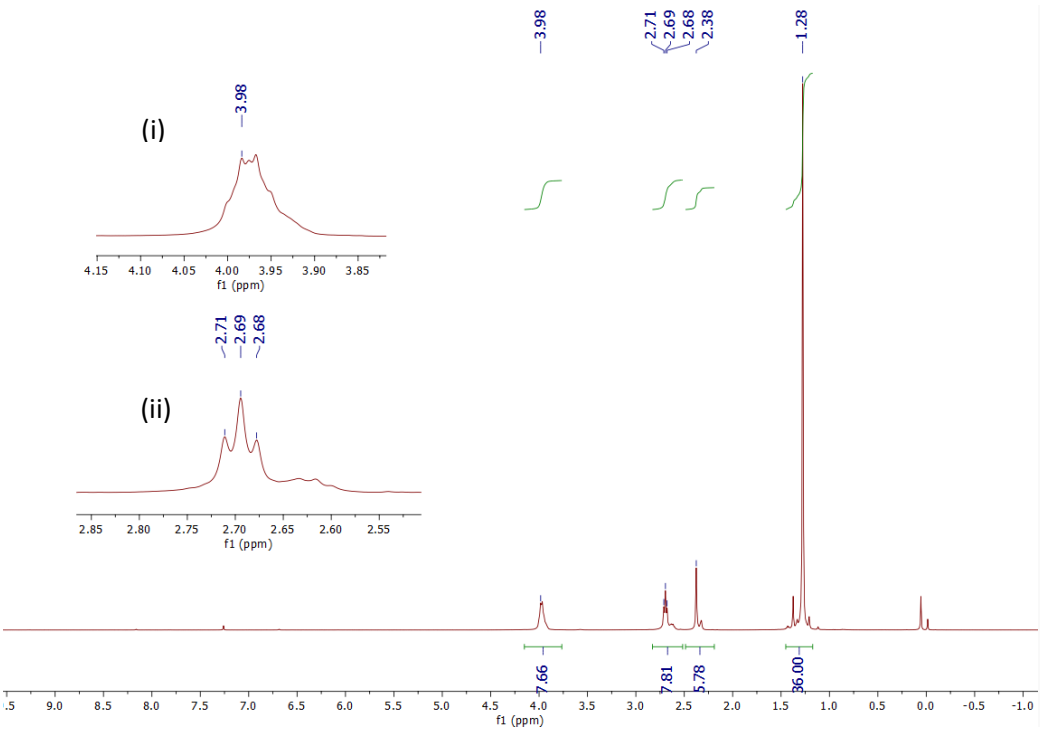

Fig S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $[\{P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(1).** Insets (i) and (ii) show the expansion of selected region.

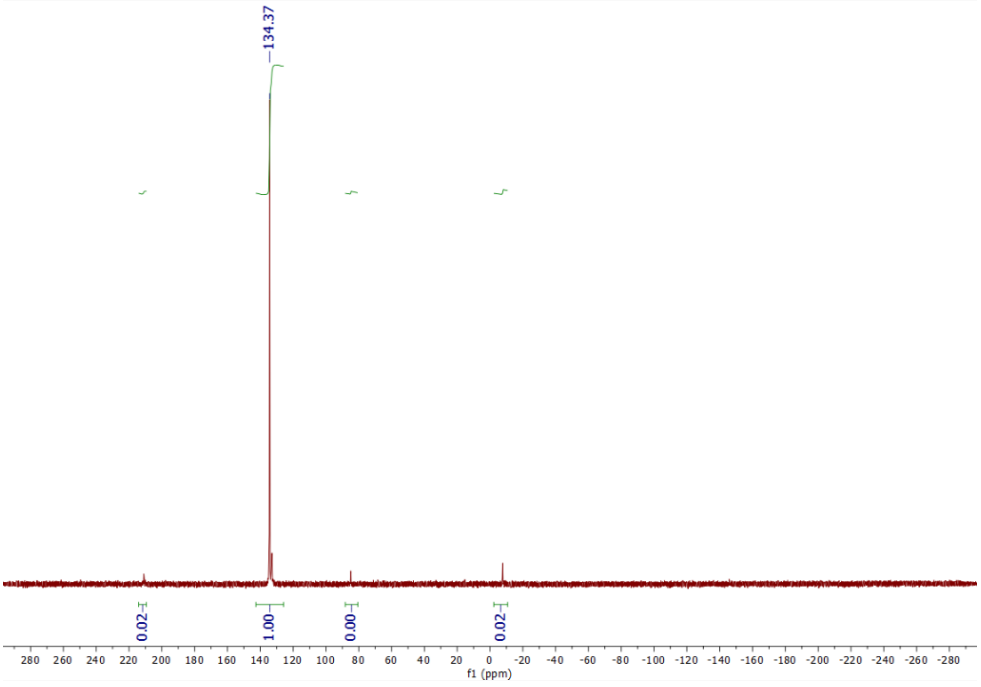

Fig S2. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of $[\{P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(1)**.

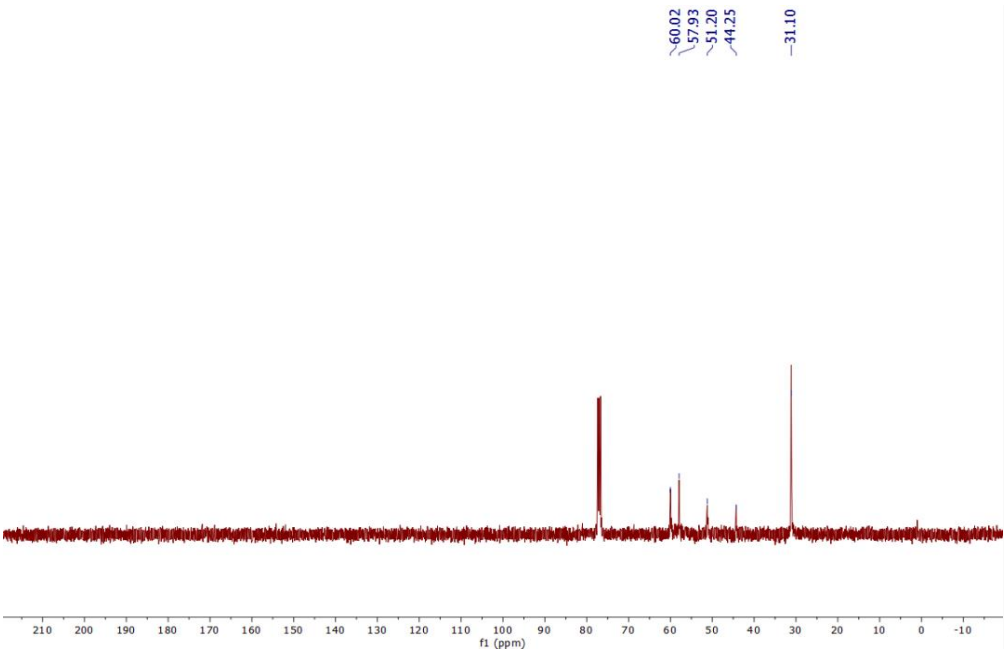

Fig S3. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of $[\{P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(1).**

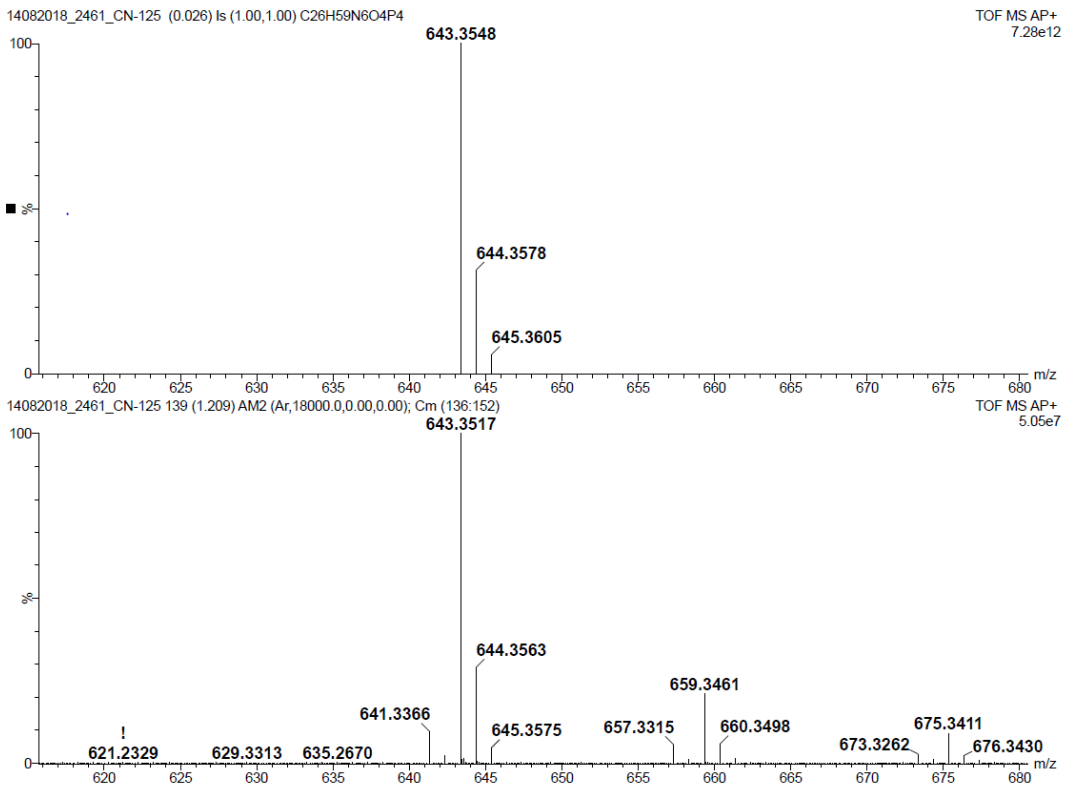

Fig S4. HRMS spectrum [calculated (top) and observed (bottom)] of $[\{P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(1).**

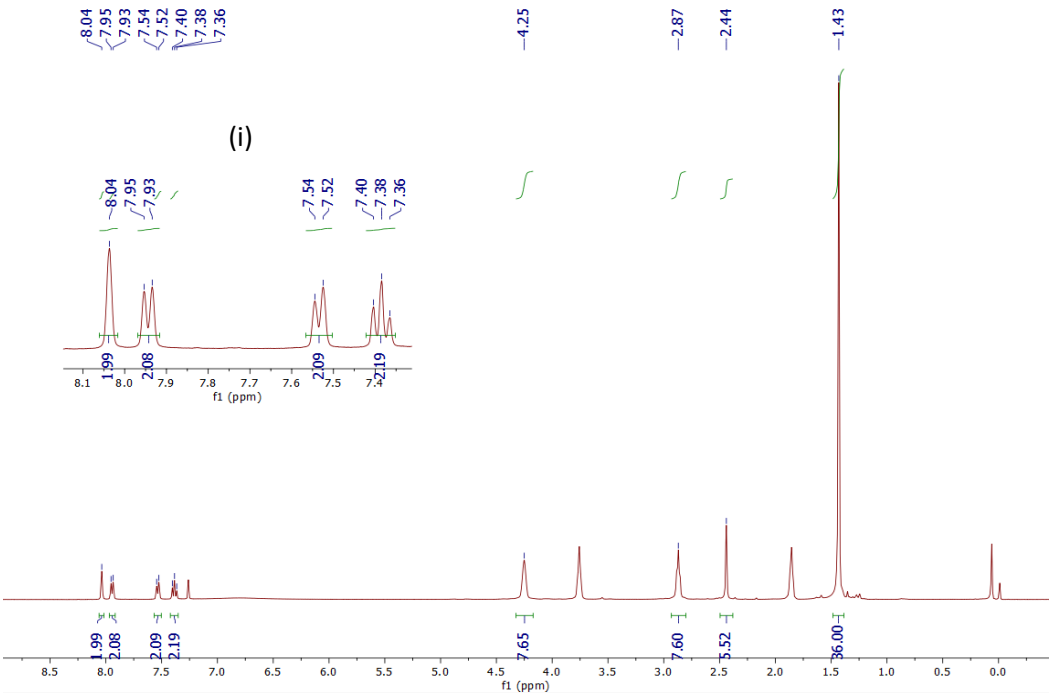

Fig S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(2).** Inset (i) shows the expansion of selected region.

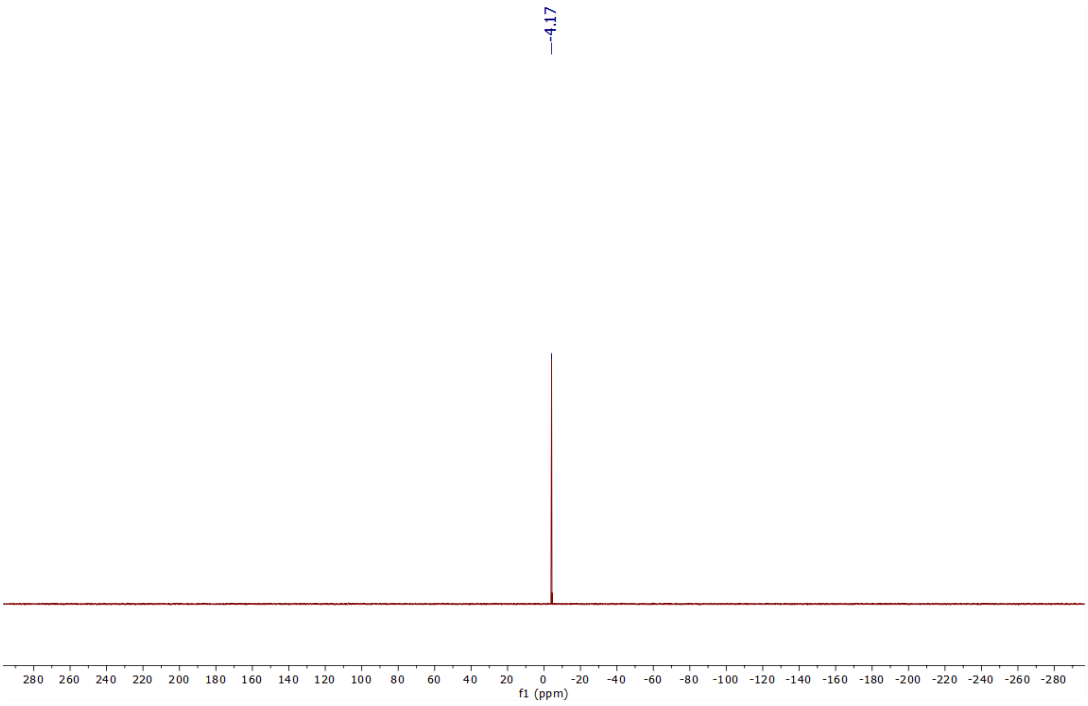

Fig S6. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(2).**

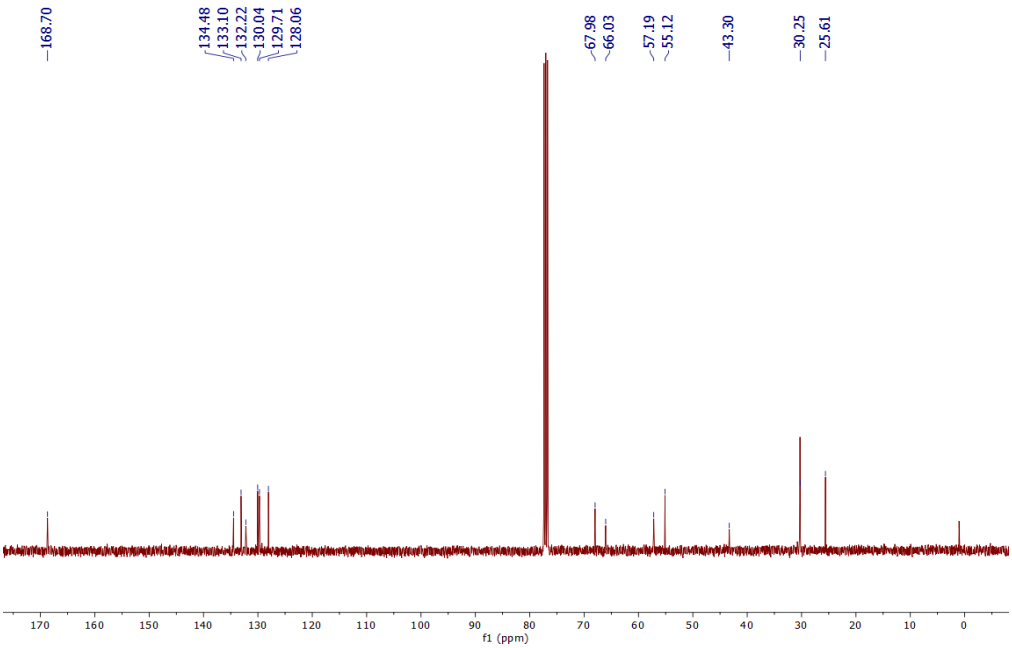

Fig S7. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(2).**

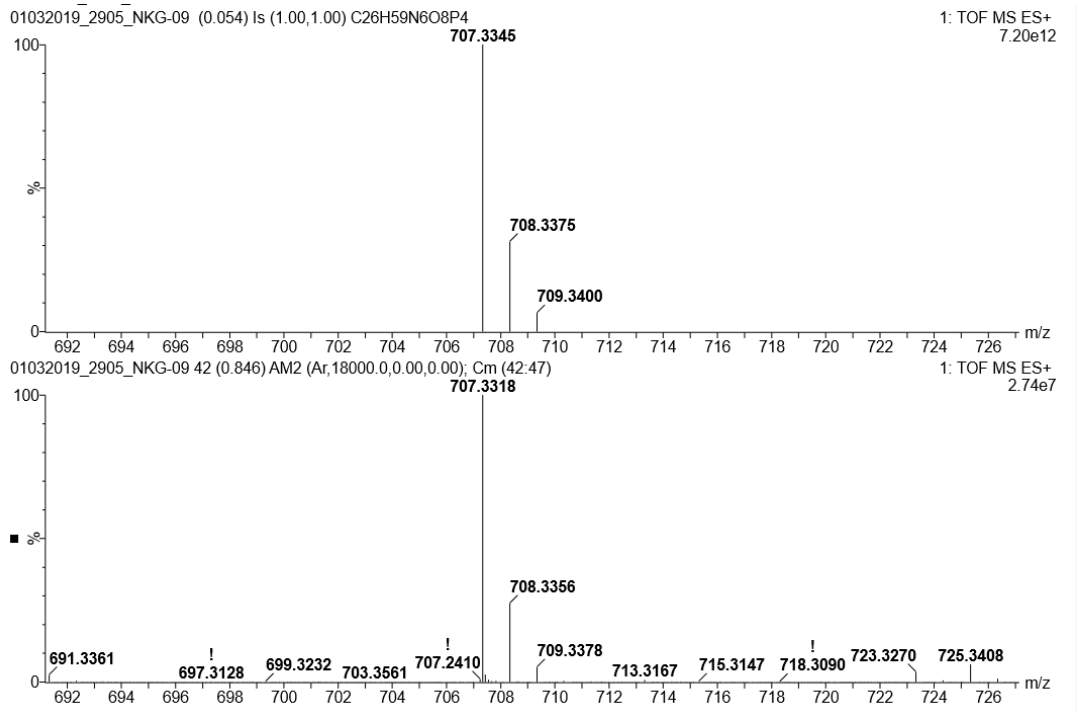

Fig S8. HRMS spectrum [calculated (top) and observed (bottom)] of $[\{(O=)P(\mu\text{-}N^tBu)\}_2\{O(CH_2)_2N(Me)(CH_2)_2O\}]_2$ **(2).**

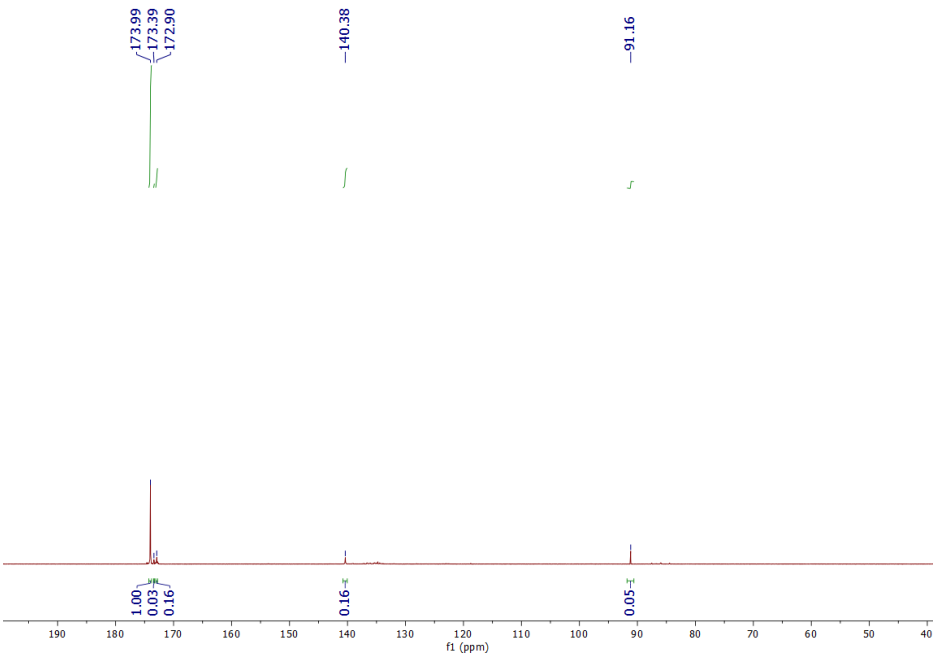

Fig S9. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(3)**

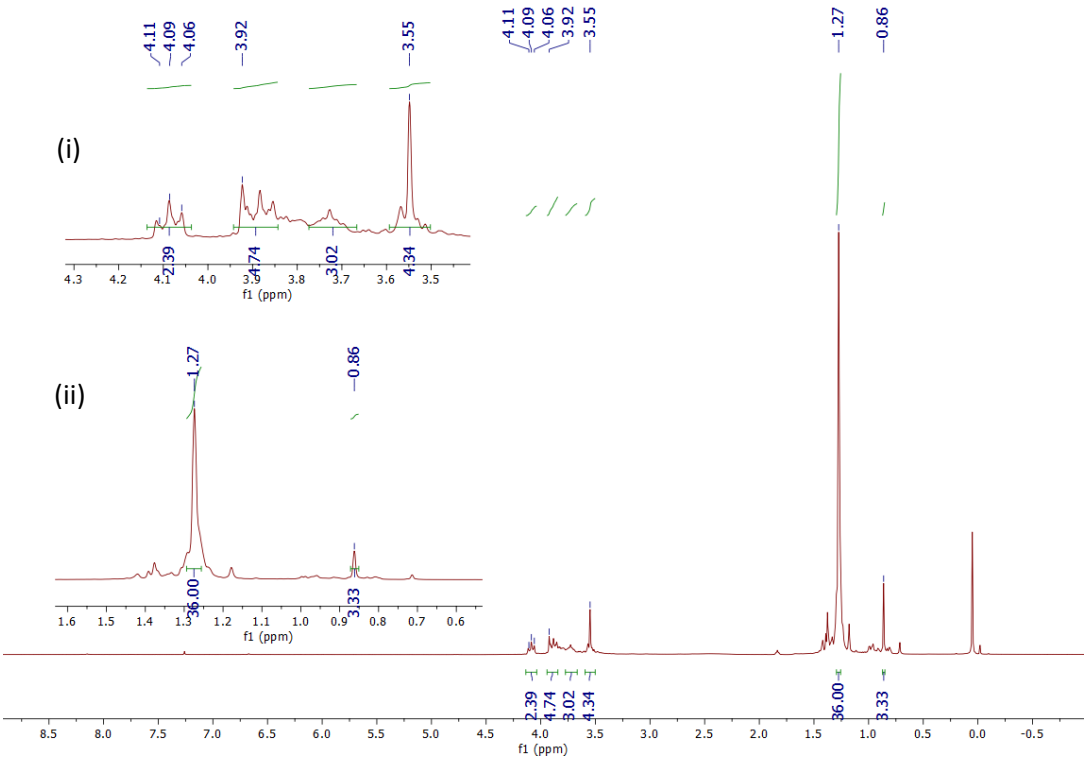

Fig S10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(3)**. Insets (i) and (ii) show the expansion of selected region.

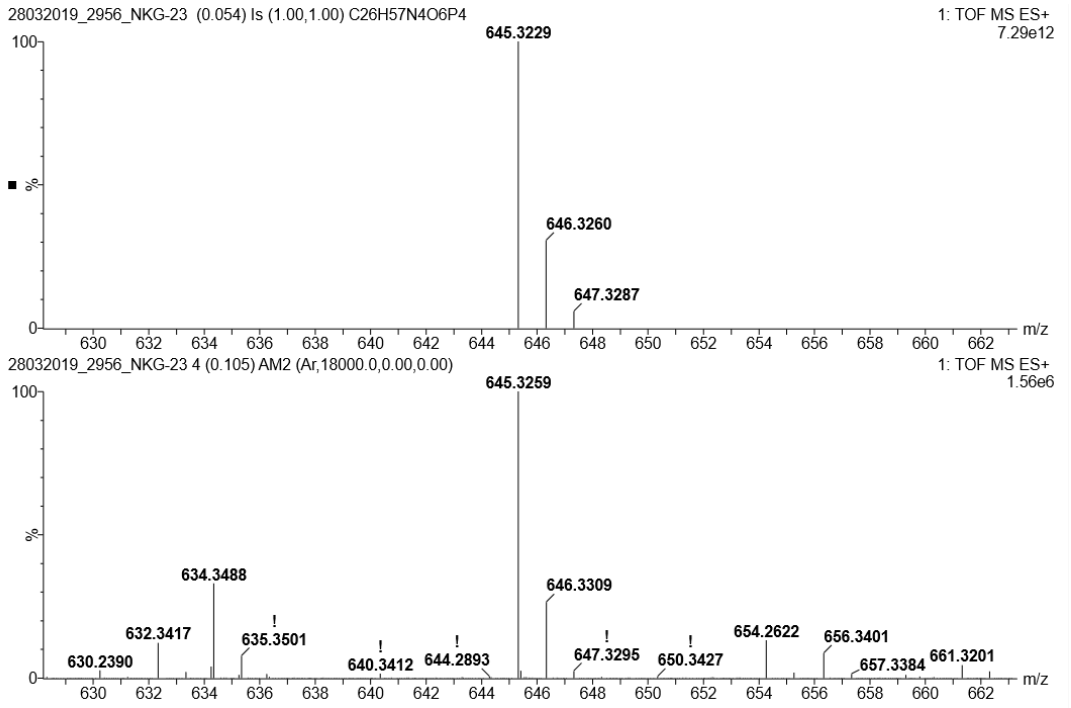

Fig S11. HRMS spectrum [calculated (top) and observed (bottom)] of $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(3)**

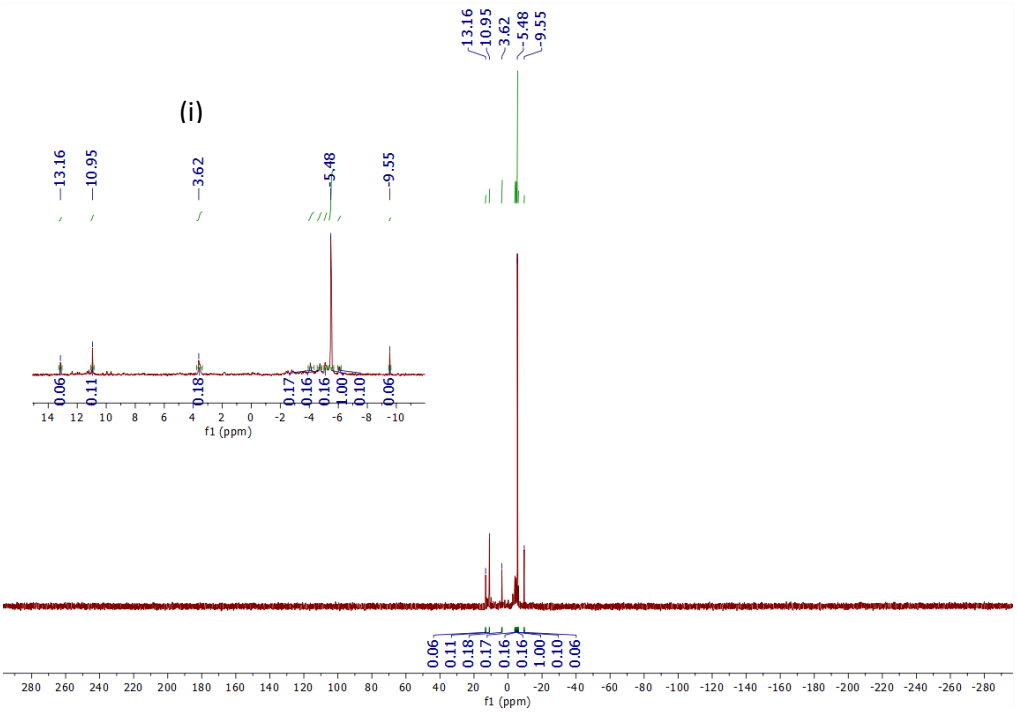

Fig S12. In-situ $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{(O{=})P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}OCH_2)_2C(Me)(CH_2OH)]$ **(4)**. Inset (i) shows the expansion of selected region.

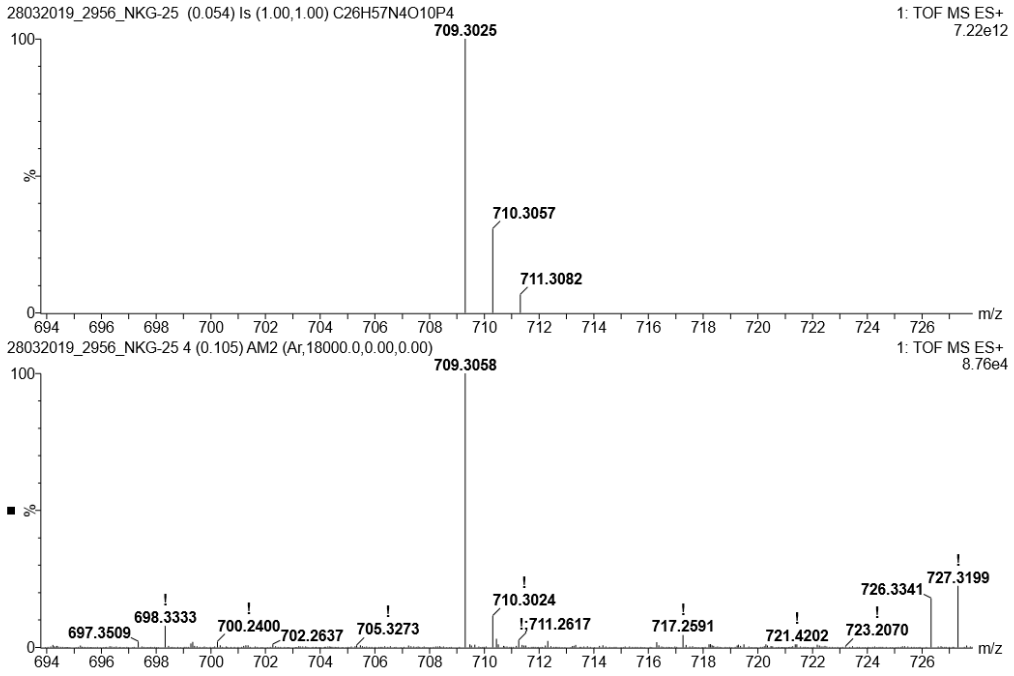

Fig S13. HRMS spectrum [calculated (top) and observed (bottom)] of $[(HOCH_2)(Me)C(CH_2O\text{-})_2(\mu\text{-}\{(O{=})P_2(\mu\text{-}N^tBu)_2\})_2(\text{-}\ OCH_2)_2C(Me)(CH_2OH)]$ **(4)**

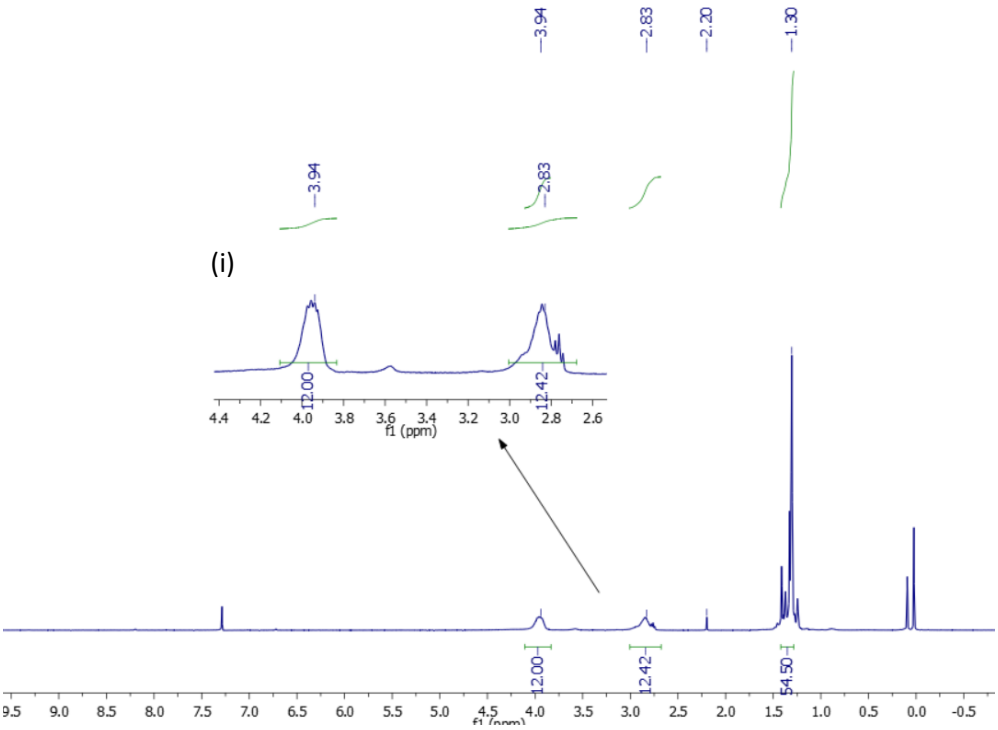

Fig S14. ^1H NMR spectrum ($CDCl_3$, 400 MHz) of $[N(CH_2CH_2O\text{-})_3(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_3(\text{-}OCH_2CH_2)_3N]$ **(5)**. Inset (i) shows the expansion of selected region.

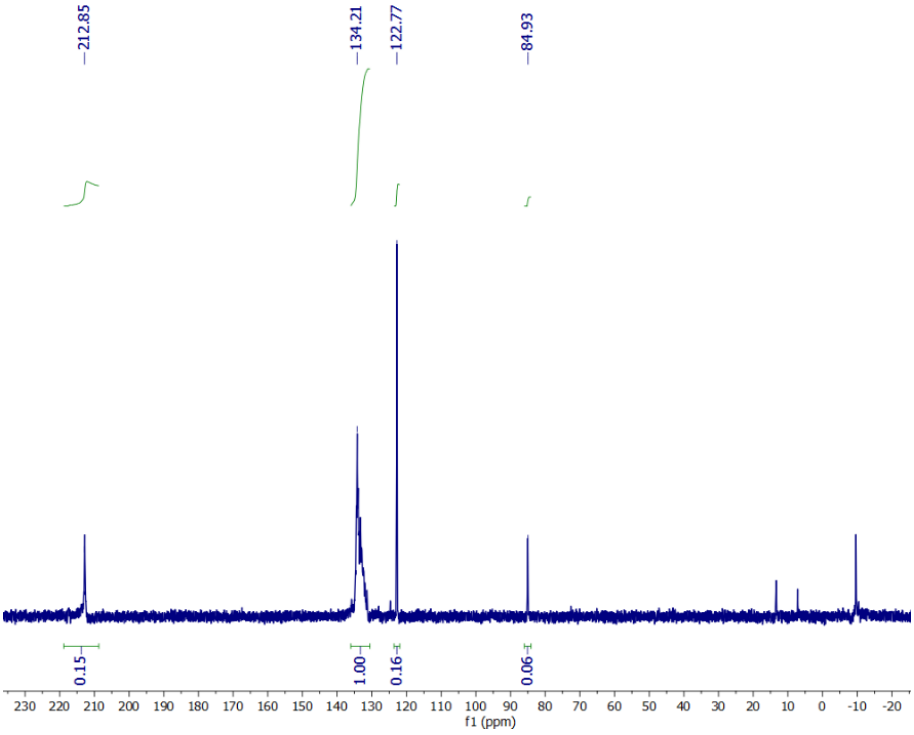

Fig S15. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 162 MHz) of $[N(CH_2CH_2O\text{-})_3(\mu\text{-}\{P_2(\mu\text{-}N^tBu)_2\})_3(\text{-}OCH_2CH_2)_3N]$ **(5)**

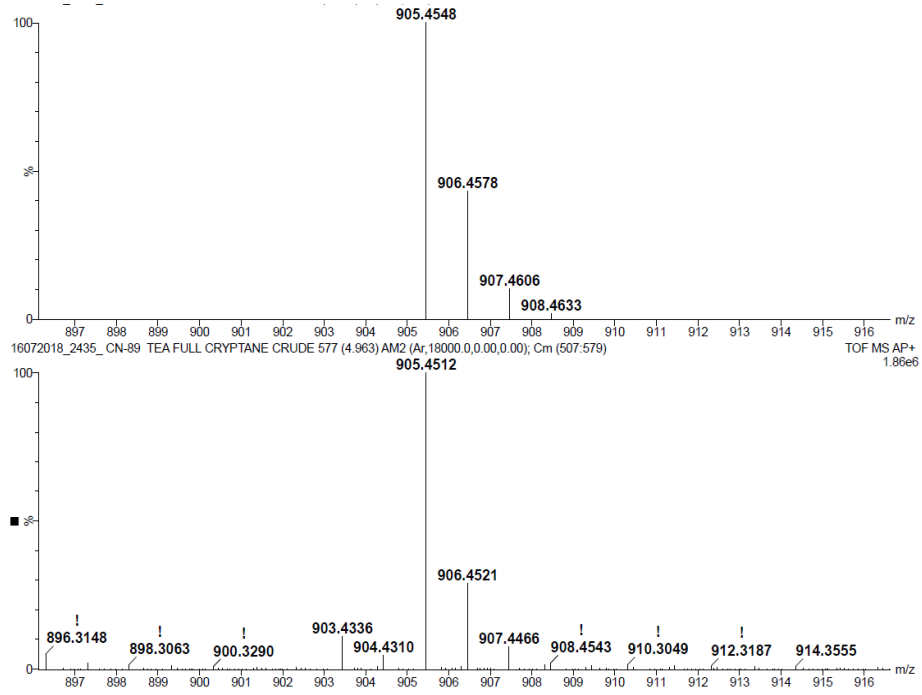

Fig S16. HRMS spectrum [calculated (top) and observed (bottom)] of $[N(CH_2CH_2O\text{-})_3(\mu\text{-}\{P_2(\mu\text{-}$ $CH_2)_3N]$ **(5)**

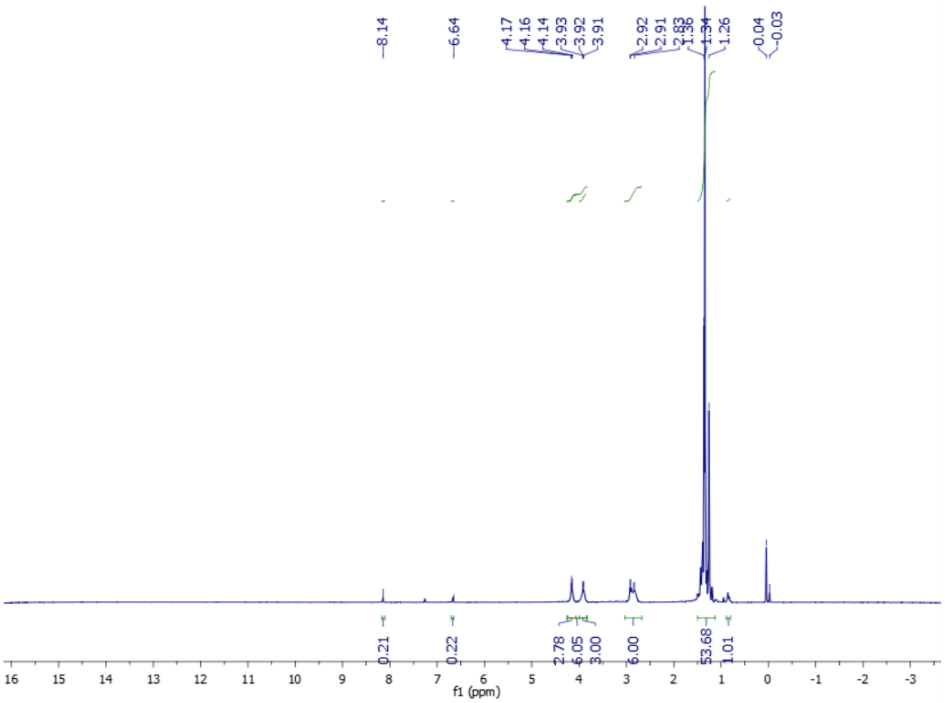

Fig S17. ^{1}H NMR spectrum for [N(CH$_2$CH$_2$O-)$_3${P(μ-N^{t}Bu)$_2$PCl}$_3$] **(6)**

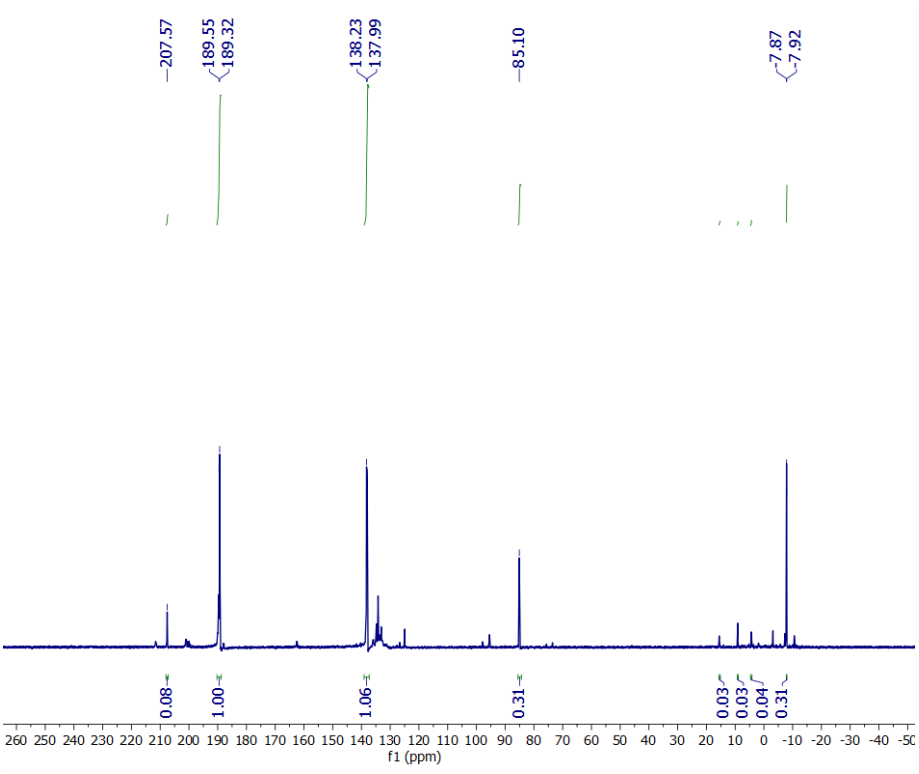

Fig S18. ^{31}P{^{1}H} NMR spectrum of [N(CH$_2$CH$_2$O-)$_3${P(μ-N^{t}Bu)$_2$PCl}$_3$] **(6)**