Sulfur and Selenium Containing New Bis(phosphorylamino)pyridine Ligands and their Aluminum Complexes

Akhilrag K

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
April 2016

Dedicated to my family and friends

for their love and affection

CERTIFICATE OF EXAMINATION

This is to certify that the dissertation titled ***‘‘Sulfur and Selenium Containing New Bis(phosphorylamino)pyridine Ligands and their Aluminum Complexes’’*** submitted by **Mr. Akhilrag K** (Reg. No. MS11028) 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.

Dr. Angshuman Roy Choudhury	Dr. Ujjal K. Gautam	Dr. Sanjay Singh
		(Supervisor)

Date:

DECLARATION

The work presented in this thesis titled ***‘‘Sulfur and Selenium Containing New Bis(phosphorylamino)pyridine Ligands and their Aluminum Complexes’’*** has been done under the supervision of **Dr. Sanjay Singh** in the Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER), Mohali.

This work has not been submitted to any other institute or university for fulfilment of any degree or scholarship. This thesis is a record of work done by me and all other sources have been listed in the bibliography.

Akhilrag K

MS11028

Place:

Date:

In my capacity as a supervisor the above mentioned statements by the candidate are true to the best of my knowledge.

Dr. Sanjay Singh

Associate Professor
Department of Chemical Sciences
Indian Institute of Science Education and Research Mohali

Place:

Date:

Acknowledgement

I would like to express my sincere thanks to my guide Dr. Sanjay Singh for his inspiration and immense help in planning and executing this project work in time. The assurance and liveliness with which he supervised the work requires no elaboration. It has been my proud privilege to work under such a masterful, preeminent and illustrious advisor. I’m glad to express thankfulness to him for exposing me into a novel field of research, and without his constant guidance and support finishing this project work would have been impossible.

I am very thankful to Mr. Kuldeep Jaiswal for constant guidance in learning the experimental techniques and valuable help and suggestions in understanding some reactions. Also I would like to thank Dr. Billa Prashanth for his involvement in single crystal diffraction studies of my samples. I am taking this opportunity to thank all other lab members who maintained a cheerful research atmosphere in the lab.

I am much thankful to my thesis committee members Prof. Ramesh Kapoor, Dr. A. R. Choudhury and Dr. Ujjal K. Gautam for their tremendous inputs and support during the entire work. I acknowledge the timely and constant support from the X-ray facilities (Departmental and the central facility), NMR central facility and Informatics centre of IISER Mohali.

I am thankful to all my teachers and friends for their support during entire course of my MS project.

I also want to express my affection and love to my family members for their constant support and valuable suggestions.

List of Charts and Figures

Chart 1. Known examples of iminophosphorane based pincer ligands.

Chart 2. Some pyridine based pincer ligands containing chalcogen group.

Chart 3. Known examples of aluminum complexes containing sulfur and selenium donor atoms in ancillary ligands.

Figure 1. Single crystal X-ray structure of **LH**$_2$.

Figure 2. Single crystal X-ray structure of complex **[L′AlMe]**$_2$ (**1**).

Figure 3. Single crystal X-ray structure of **L′H**$_2$.

Figure 4. Single crystal X-ray structure of complex **[L′AlMe]**$_2$ (**2**).

List of Schemes

Scheme 1: Synthesis of $\mathbf{LH_2}$, $[2,6\text{-}(Ph_2P(S)\text{-}NH)_2C_5H_3N]$.

Scheme 2: Synthesis of $\mathbf{[LAlMe]_2}$, $[\{2,6\text{-}(Ph_2P(S)\text{-}N)_2C_5H_3N\}AlMe]_2$ **(1)**.

Scheme 3: Synthesis of $\mathbf{L'H_2}$, $[2,6\text{-}(Ph_2P(Se)\text{-}NH)_2C_5H_3N]$.

Scheme 4: Synthesis of $\mathbf{[L'AlMe]_2}$, $[\{2,6\text{-}(Ph_2P(Se)\text{-}N)_2C_5H_3N\}AlMe]_2$ **(2)**.

Scheme 5: Synthesis of $\mathbf{[LAlH]_2}$, $[\{2,6\text{-}(Ph_2P(S)\text{-}N)_2C_5H_3N\}AlH]_2$ **(3)**.

List of Tables

Table 1. Crystal data and structure refinement details for **LH_2**, [2,6-($Ph_2P(S)$-NH)$_2C_5H_3N$].

Table 2. Crystal data and structure refinement details for **[LAlMe]$_2$**, [{2,6-($Ph_2P(S)$-N)$_2C_5H_3N$}AlMe]$_2$ (**1**).

Table 3. Crystal data and structure refinement details for **$L'H_2$**, [2,6-($Ph_2P(Se)$-NH)$_2C_5H_3N$].

Table 4. Crystal data and structure refinement details for **[L′AlMe]$_2$**, [{2,6-($Ph_2P(Se)$-N)$_2C_5H_3N$}AlMe]$_2$ (**2**).

Abbreviations

δ	chemical shift
λ	wavelength
$\tilde{\nu}$	wave number
Ar	aryl
C	celsius
calcd.	calculated
d	doublet
dd	doublet of doublet
decomp.	decomposition
EI	electron impact ionization
Et	ethyl
eqv.	equivalents
g	grams
MHz	mega Hertz
hr	hours
IR	infrared
J	coupling constant
L	ligand
M	metal
m	multiplet
m/z	mass/charge
Mp	melting point
M^+	molecular ion
Me	methyl
min.	minutes
MS	mass spectrometry, mass spectra
NMR	nuclear magnetic resonance
ppm	parts per million
R, R', R"	organic substituents
s	singlet
t	triplet

THF	tetrahydrofuran
DCM	dicloromethane
V	volume
Z	number of molecules in the unit cell
Å	angstrom
°	degree
mmol	millimole
mL	milliliter

Contents

List of Charts and Figures i

List of Schemes ii

List of Tables iii

Abbreviations iv

Abstract viii

1. Introduction 1

2. Results and Discussion 5

2.1. Reaction of [2,6-(Ph_2P-NH)$_2C_5H_3N$] and sulfur: Synthesis of 2,6-bis(diphenylthiophosphorylamino)pyridine, [2,6-(Ph_2P(S)-NH)$_2C_5H_3N$] (**LH_2**) **5**

2.2. Reaction of **LH_2** and $AlMe_3$: Synthesis of [{2,6-(Ph_2P(S)-N)$_2C_5H_3N$}AlMe]$_2$, **[LAlMe]$_2$** (**1**) **7**

2.3. Reaction of [2,6-(Ph_2P-NH)$_2C_5H_3N$] and selenium: Synthesis of 2,6-bis(diphenylselenophosphorylamino)pyridine, [2,6-(Ph_2P(Se)-NH)$_2C_5H_3N$] (**$L'H_2$**) **9**

2.4. Reaction of **$L'H_2$** and $AlMe_3$: Synthesis of [{2,6-(Ph_2P(Se)-N)$_2C_5H_3N$}AlMe]$_2$, **[L'AlMe]$_2$** (**2**) **11**

2.5. Reaction of **LH_2** and AlH_3: Synthesis of [{2,6-(Ph_2P(S)-N)$_2C_5H_3N$}AlH]$_2$, **[LAlH]$_2$** (**3**) **13**

3. Experimental Section 15

3.1. General procedure **15**

3.2. Physical measurements **15**

3.3. Synthesis of **LH_2**, [2,6-(Ph_2P(S)-NH)$_2C_5H_3N$] **16**

3.4. Synthesis of **[LAlMe]$_2$**, [{2,6-(Ph_2P(S)-N)$_2C_5H_3N$}AlMe]$_2$ (**1**) **16**

3.5. Synthesis of **$L'H_2$**, [2,6-(Ph_2P(Se)-NH)$_2C_5H_3N$] **17**

3.6. Synthesis of **[L′AlMe]$_2$**, [{2,6-($Ph_2P(Se)$-N)$_2C_5H_3N$}AlMe]$_2$ (**2**) **17**

3.7. Synthesis of **[LAlH]$_2$**, [{2,6-($Ph_2P(S)$-N)$_2C_5H_3N$}AlH]$_2$ (**3**) **18**

4. Crystal Data and Refinement Details **19**

5. Summary **23**

6. Future Directions **24**

7. References **25**

Supporting Information **27**

Heteronuclear NMR spectra (^{1}H, ^{13}C, ^{31}P), HRMS spectra and IR-spectra of new compounds reported in this dissertation.

Abstract

In the field of organometallic chemistry understanding the properties of different metallic centers and controlling their chemical properties *via* appropriate co-ordinating ligand has been considered an important aspect. To stabilise different metallic centers, a number of multidentate ligands have been developed and have been extensively used in past four decades. In numerous instances, metal complexes of pincer ligands have shown remarkable stability compared to complexes with monodentate or chelating ligands. Additionally, various studies revealed that complexes of pincer type ligand can be used in homogenous catalysis. Keeping these facts in mind the present work aims to develop pincer type ligands based N/S or N/Se co-ordinating sites. These chalcogen donors (S or Se) were assembled on a pyridine based moiety, [2,6-$(Ph_2P\text{-}NH)_2C_5H_3N$] by the oxidation of P(III) centers to P(V). These attempts led to the formation of two novel pincer type ligand namely, 2,6-bis(diphenylthiophosphorylamino)pyridine, [2,6-$(Ph_2P(S)\text{-}NH)_2C_5H_3N$] (**$LH_2$**) and 2,6-bis(diphenylselenophosphorylamino)pyridine, [2,6-$(Ph_2P(Se)\text{-}NH)_2C_5H_3N$] (**$L'H_2$**). Aluminum complexes (**$[LAlMe]_2$**, **$[L'AlMe]_2$**) of these ligands have been synthesized and structurally characterized and have been found to form dimers in the solid state.

1. Introduction

In the field of organometallic chemistry understanding the properties of different metallic centres and controlling these properties *via* coordination with appropriate ligand unit is considered to be the ultimate goal. Multidentate ligands have been used in the past four decades for the stabilization of metallic centres. First reports on stabilization of metal centres *via* tetradentate monoanionic ligands came in the late 1970s.[1] Phosphinoamine ligands are also used extensively in this field to understand the chemistry exhibited by the metal complexes.[2] Similar kind of ‘pincer’3 ligands were reported further onwards and among that tridentate PNP type pincer ligands were used quite well for understanding the properties of different metal groups. Further attempts to prepare pincer PNP systems led to similar pyridine based ligands in which $–NR'PR_2$ (R' = H, alkyl, R = alkyl or aryl) moieties were present at the *ortho* positions.[4] Chart 1 shows some known examples of PNP based pincer ligands reported in the literature.

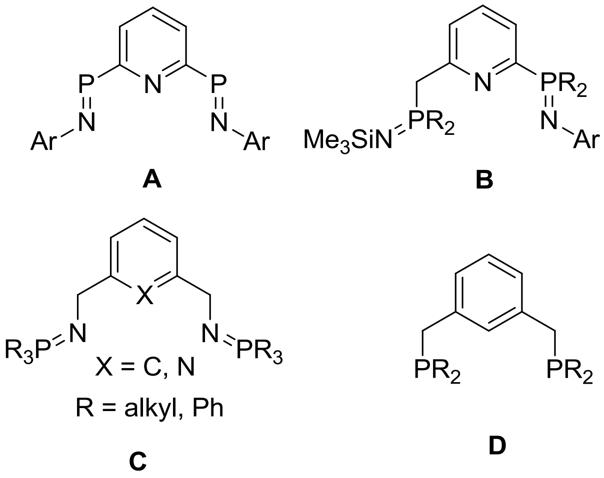
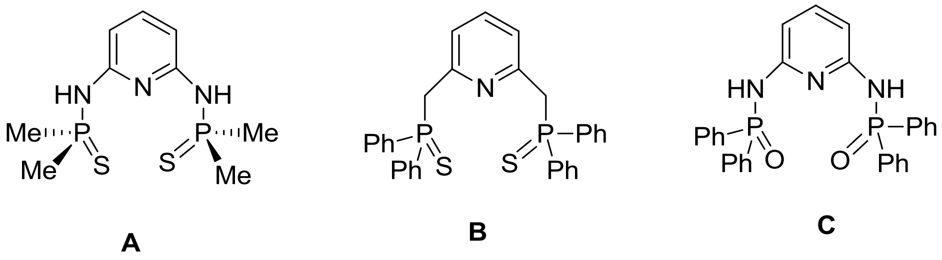


Chart 1: Known examples of iminophosphorane based pincer ligands.

Bochmann and co-workers used metal complexes (Co(II)) of the ligand **A** (Chart 1), namely *bis*(imino-phosphoranyl)pyridine for polymerization reaction studies of ethylene molecule [5] and Wang and co-workers have explored the coordination behaviour of ligand **B** (Chart 1) with metal (Al(III)) and used it as a catalyst for Ɛ-caprolactone polymerization.[6] Studies on metal complex of **C** (X = C) (Chart 1) showed that the coordination of metal with nitrogen is shielded by the exocyclic phosphorus substituents,[7] whereas ligand **C** (X = N) (Chart 1) showed that diphenylphosphine group can act as a protecting group and iminophosphorane acting as an electron donor.[8] Ligand **D** (Chart 1) got more attention due to monoanionic pincer type behaviour associated with two phosphine and one central arylic carbon.[9-10]

We have reacted pincer type PN(pyridine) ligand system namely, [2,6-$(Ph_2P\text{-}NH)_2C_5H_3N$] to prepare metal complexes. The methodology for preparation of this ligand was first introduced by *Haupt et al* in 1987.[11] This is a moiety in which the central pyridine ring contains –NHP(Ph_2) substituents at *ortho*-positions. Recently, this system has been widely used to understand the chemistry of transition metal complexes.[12] When [2,6-$(Ph_2P\text{-}NH)_2C_5H_3N$] was treated with sulfur the ligand 2,6-bis(diphenylthiophosphorylamino)pyridine, [(2,6-$Ph_2P(S)\text{-}NH)_2C_5H_3N$] (**$LH_2$**) was formed, involving oxidation of P(III) centre to P(V). Similarly, Selenium analogue 2,6-bis(diphenylselenophosphorylamino)pyridine, [(2,6-$Ph_2P(Se)\text{-}NH)_2C_5H_3N$] (**$L'H_2$**) was also prepared in an identical approach. Introduction of heavier chalcogens in the ligand framework was to bring more bonding sites to the appending metal ion and this can lead to increased stability of the metal complexes. There have been reports on the design of similar kind of ligands and some of them are mentioned in Chart 2.



A **B** **C**

Chart 2: Some pyridine based pincer ligands containing chalcogen group.

In 1999, Batsanov and co-workers reported the synthesis of 2,6-bis(dimethylthiophosphorylamino)pyridine[13] (**A**) and in 2003 there has been a report on the synthesis of 2,6-bis[(diphenylphosphino)methyl]pyridine P,P′-disulfide[14] (**B**). Very recently in 2010, Lemport and his coworkers reported the synthesis of a similar kind of ligand (**C**) in which phosphorous contains oxygen atoms instead of sulfur.[15] But none of them were able to get the solid state structure of these ligands and as such there are no further studies conducted on similar kind of systems.

There have been reports on synthesis of transition metal complexes based on PN(pyridine) system,[4b,5,12,16] but co-ordination chemistry of main group elements with these type of ligands remains unexplored. Our main focus is to explore the coordination chemistry of above ligands with aluminum. Different ligands with N-donor sites have been used to study the stabilization chemistry of aluminum metal complexes. This complexation behaviour can be explained based on highly delocalised charge on the ligand backbone along with presence of highly Lewis acidic character and hardness of nitrogen donor atoms. Introduction of soft donor atoms such as sulfur and selenium and coordination with aluminum can alter its acidic character, which can lead to the modification of chemical properties of the entire system.[17] Indeed, reports on complexation of aluminum with ligands containing sulfur and selenium as donor atoms are limited in number. Some of the known examples of aluminum complexes containing sulfur and selenium donor atoms in ancillary ligands are given in the Chart 3.

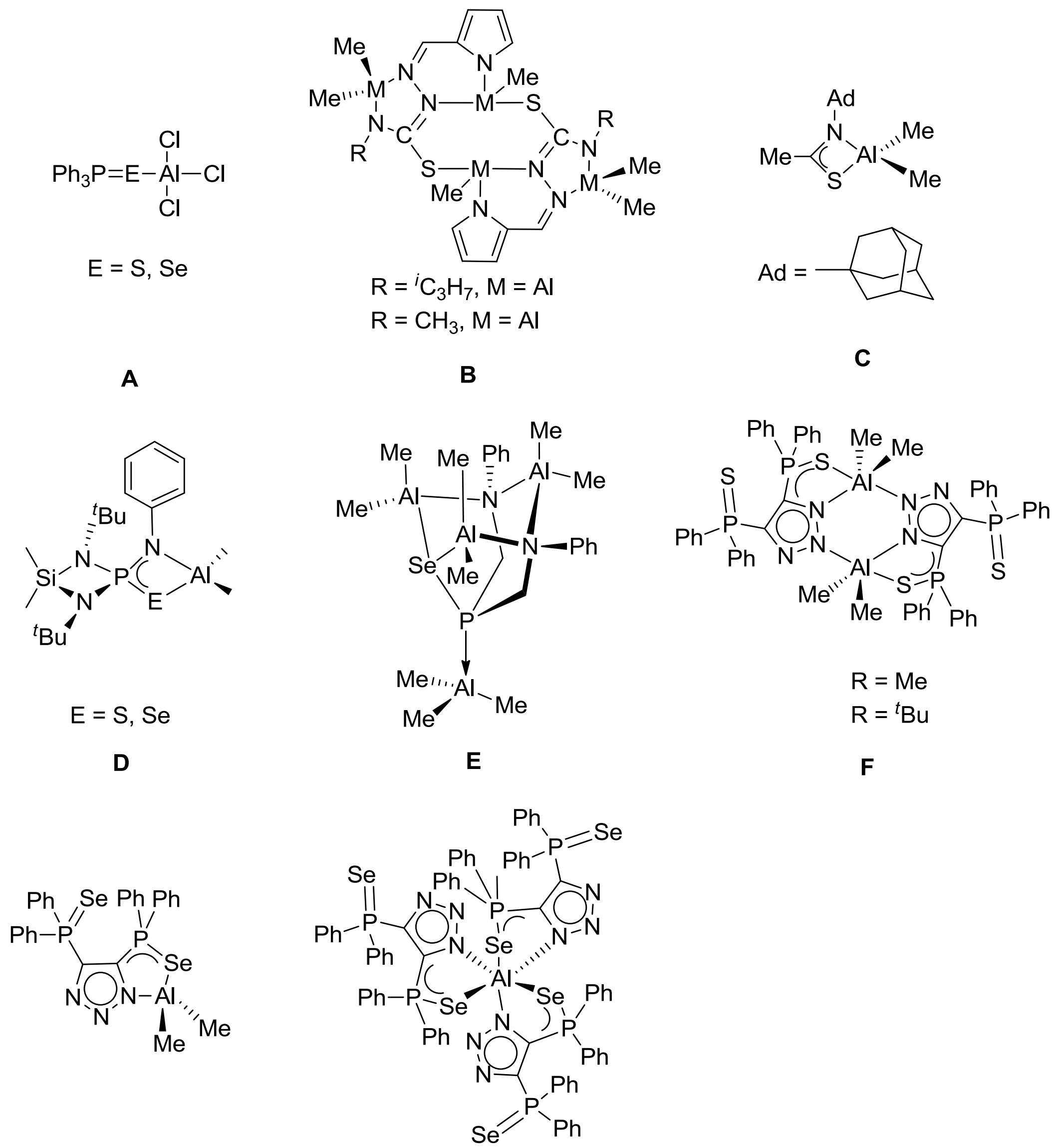


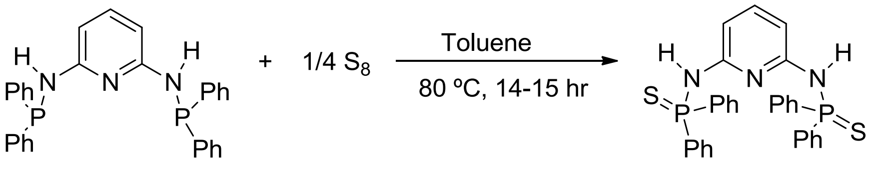
Chart 3: Known examples of aluminum complexes containing sulfur and selenium donor atoms in ancillary ligands.

Before 1990's it was generally considered as co-ordination properties of phosphine chalcogenides are independent of the chalcogen group present in it. In 1990, a thorough re-examination done by Neil Buford and co-workers using $Ph_3PE{\cdot}AlCl_3$ (**A**) systems revealed that the nature of co-ordination is governed by both the chalcogen and the acid. Compared to phosphine oxides the sulphides and selenides are restricted to the possible angle of co-ordination while forming complexes with metals.[18] In 1997, Youngjin and co-workers reported the synthesis of an extremely air-sensitive complex (**B**) where two chiral aluminum centers are present with same configuration and also it is bridged with thiolato sulfur atom.[17a] In 1998, Coles and his coworkers reported the synthesis and structural analysis of thioamidate based aluminum compound, $\{MeC(NAd)S\}AlMe_2$ (**C**), which showed planar metallacycle structure with sterically open aluminum and sulfur centers.[17b] Hangenson and co-workers synthesized the complex **D**, where solid structure studies on sulfur based aluminum complex revealed that aluminum metallic center is co-ordinated with N-P-S moiety of ligand and two methyl group in a tetrahedral manner.[17d] But they were unable to get the solid state structure of selenium analogue of this aluminum complex. In 2006, Han and co-workers reported the structural characterisation of aluminum complex $Me_3Al{\cdot}P(CH_2NPh)_2Se(AlMe_2)_3$ (**E**) which contain P-Se-Al bond. Nitrogen donor group present in the ancillary ligand also take part in the stabilisation of one of the aluminum center.[19] Preparation of aluminum complexes of triazole based chalcogen ligands (**F**, **G & H**) were reported by Jocelyn and co-workers in 2009. Complex **F** crystallizes in a dimer kind of arrangement, where aluminum centers are bridged between the sulfur containing triazole based ancillary ligands. Aluminum metal centers are co-ordinated with nitrogen of one of the ligand, as well as to sulfur and nitrogen of the second ligand. And also they reported the synthesis of **G** by treating 4,5-$(P(Se)\text{-}Ph_2)_2$tzH (tz = 1,2,3-triazole) with trimethylaluminum at room temperature, but they were unable to get the crystal structure of complex **G**. Further treatment of **G** with Al^iBu_3 gave rise to a tris-chelate product **H**, where aluminum center shows octahedral co-ordination geometry.[20] Our aim is to explore the main group chemistry using these two novel ligands namely, 2,6-bis(diphenylthiophosphorylamino)pyridine and 2,6-bis(diphenylselenophosphorylamino)pyridine on treatment with $AlMe_3$ they lead to the formation of aluminum complexes **[LAlMe]₂, (1)** and **[L′AlMe]₂, (2)**, respectively.

2. Results and Discussion

2.1. Reaction of [2,6-(Ph_2P-NH)$_2C_5H_3N$] and sulfur: Synthesis of 2,6-bis(diphenylthiophosphorylamino)pyridine, [2,6-(Ph_2P(S)-NH)$_2C_5H_3N$] (**LH_2**)

Reaction of [(2,6-Ph_2P-NH)$_2C_5H_3N$] with two equivalents of sulfur at 80 ºC in toluene resulted in the formation of the desired ligand, **LH_2** (Scheme 1) as a white powder. Single crystals of the ligand **LH_2** were grown at 4 ºC in toluene. The ligand was characterized using NMR spectroscopy, ESI-MS spectrometry and X-ray crystallographic techniques. ^{1}H NMR spectrum for **LH_2** showed almost similar chemical shifts with its precursor. The N-*H* protons were observed as a broad peak at 6.11 ppm. The *para*-hydrogen could be seen as a triplet at 7.09 ppm, whereas a doublet due to remaining two *meta*-hydrogens on the pyridine ring was observed at 6.41 ppm (Figure S1). ^{31}C NMR spectrum showed seven peaks corresponding to seven types of carbon for the ligand **LH_2** (Figure S3). The ^{31}P{^{1}H} NMR spectrum shows a peak at 51.44 ppm (Figure S2) that is downfield shifted than the starting material (25.71 ppm). The formation of ligand **LH_2** could also be confirmed by the presence of HRMS signal at 542.1077 (calcd: 542.1043 $[M+H]^+$) (Figure S4). Moreover, structure determination of ligand was done using X-ray crystallography that confirmed the formulation predicted based on NMR (Figure 1).



[2,6-(Ph_2P-NH)$_2C_5H_3N$]

LH_2

Scheme 1: Synthesis of **LH_2**, [2,6-(Ph_2P(S)-NH)$_2C_5H_3N$]

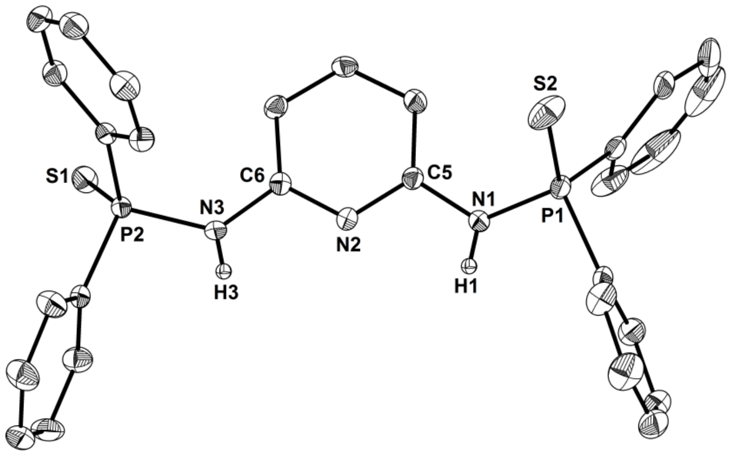
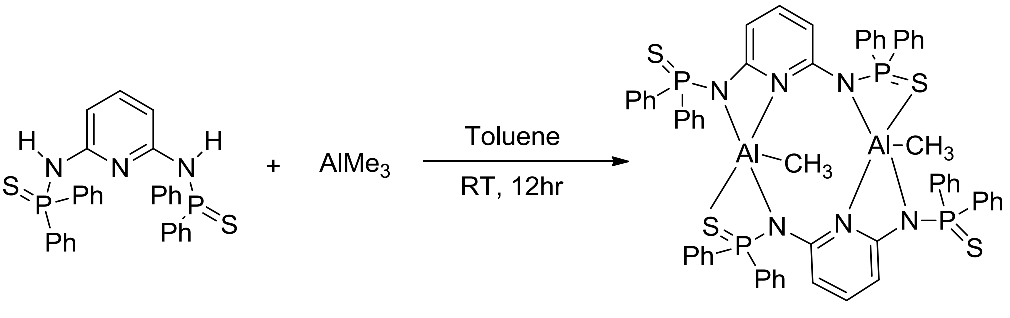


Figure 1. Single crystal X-ray structure of **LH_2**. Hydrogen atoms except on the nitrogen atoms are omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: N(2)-C(6) 1.339(2), N(2)-C(5) 1.342(1), C(5)-N(1) 1.406(2), N(1)-H(1) 0.860(1), N(1)-P(1) 1.687(1), P(1)-S(2) 1.948(3), C(6)-N(3) 1.401(1), N(3)-H(3) 0.860(1), N(3)-P(2) 1.688(3), P(2)-S(1) 1.945(3); C(6)-N(2)-C(5) 118.19(4), C(6)-N(3)-P(2) 128.66(4), C(6)-N(3)-H(3) 115.68(5), P(2)-N(3)-H(3) 115.66(4), N(3)-P(2)-S(1) 116.29(3), C(5)-N(1)-P(1) 126.82(3), C(5)-N(1)-H(1) 116.59(4), P(1)-N(1)-H(1) 116.59(4), N(1)-P(1)-S(2) 116.10(3).

X-ray diffraction studies showed that the ligand **LH_2** crystallizes in the monoclinic crystal system with $P2_1/c$ space group (Figure 1) (Table 1). From the structure it was observed that both the sulfur atoms were coordinated to phosphorous atoms *via* double bond (P(1)-S(2) 1.948(3), P(2)-S(1) 1.945(3) Å). By considering a reference plane containing pyridine ring and two nitrogen atoms, one sulfur atom (S(2)) is above the plane and other will be below the plane (S(1)) with a deviation of 1.342(2) Å and 2.543(4) Å respectively. And Both P(1) and P(2) are lying below the plane with a deviation 0.140(4) Å and 0.757(3) Å respectively. Two planes can be considered in which phosphorous atom is in common and also it passes through two phenyl rings. Dihedral angle between planes where P(1) is the common atom is 64.14(4)° and for P(2) as a common atom it is 62.14°. This angle exhibits how much twisted these phenyl rings each other, which are present on the same phosphorous atom.

2.2. Reaction of LH_2 and $AlMe_3$: Synthesis of $[\{2,6\text{-}(Ph_2P(S)\text{-}N)_2C_5H_3N\}AlMe]_2$, $[LAlMe]_2$ (1)

Equimolar reaction of $\mathbf{LH_2}$ with trimethylaluminum at room temperature in toluene leads to the formation of complex $\mathbf{[LAlMe]_2}$ (**1**) (Scheme 2) which was soluble in toluene. Complete evaporation of solvent in *vacuum* produced product **1** as a white powder. Changing the reaction conditions, varying the molar ratios $AlMe_3$ & LH_2 and temperature resulted in the formation of the same product. The obtained product was characterized thoroughly using multinuclear NMR spectroscopy, EI-MS spectrometry and X-ray crystallographic techniques. The ^1H NMR spectrum showed the Al-*Me* peak at -0.50 ppm with an integration value equal to three hydrogen atoms. As an indication of co-ordination of nitrogen donor with aluminum center, the N*H* signals disappeared in the ^1H NMR spectrum of the complex **1.** Remaining peak values were according to that of ligand backbone except the *meta*- hydrogens of pyridine ring observed as two doublets at 5.56 and 6.60 ppm, respectively (Figure S6). In ^{13}C NMR spectrum the methyl carbon attached to the aluminum metal resonated at -2.8 ppm (Figure S8). $^{31}P\{^1H\}$ NMR spectrum indicated the presence of two type of phosphorous with chemical shift values 49.28 and 57.06 ppm respectively (Figure S7), which could be fortified from the two different type of phosphorus atoms attributed in single crystal structure (Figure 2). The formation complex **1** could also be confirmed by the presence of HRMS signal at 580.0397 (calcd: 580.0397 $[M/2\text{-}H]^+$) (Figure S10).



$\mathbf{LH_2}$ $\mathbf{[LAlMe]_2}$ **(1)**

Scheme 2: Synthesis of $\mathbf{[LAlMe]_2}$, $[\{2,6\text{-}(Ph_2P(S)\text{-}N)_2C_5H_3N\}AlMe]_2$ **(1)**

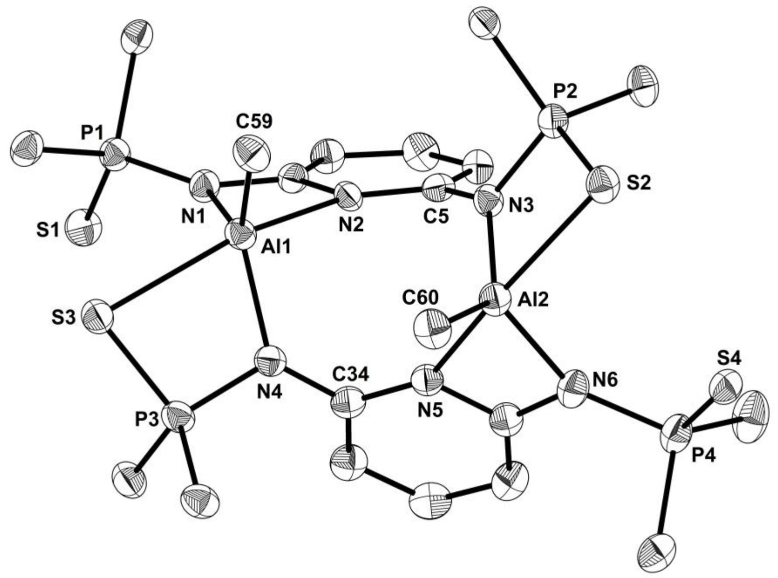


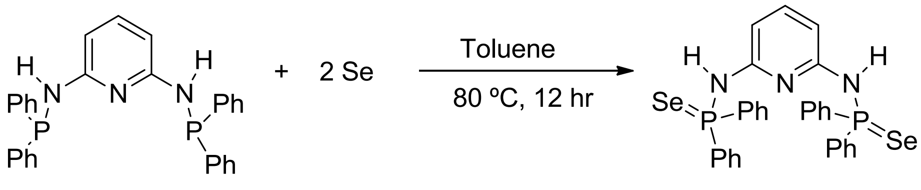
Figure 2. Single crystal X-ray structure of complex **[LAlMe]$_2$** (**1**). Phenyl rings on the phosphorous atoms and hydrogen atoms are omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: Al(1)-N(1) 1.952(6), Al(1)-N(2) 2.041(2), Al(1)-S(3) 2.555(8), Al(1)-N(4) 1.943(4), Al(1)-C(59) 1.959(6), Al(2)-N(5) 2.056(6), Al(2)-N(6) 1.954(5), Al(2)-N(3) 1.905(4), Al(2)-S(2) 2.537(3), P(1)-S(1) 1.956(4), P(2)-S(2) 1.986(5), P(3)-S(3) 1.988(3), P(4)-S(4) 1.953(5), N(1)-P(1) 1.666(5), N(3)-P(2) 1.647(5), N(4)-P(3) 1.644(6), N(6)-P(4) 1.663(5), C(5)-N(2) 1.344(6), C(5)-N(3) 1.421(6), C(34)-N(5) 1.355(6), C(34)-N(4) 1.411(7); N(2)-Al(1)-N(1) 67.23(1), N(4)-Al(1)-N(2) 91.20(1), N(1)-Al(1)-S(3) 101.94(1), N(2)-Al(1)-C(59) 101.37(2), N(4)-Al(1)-C(6) 131.31(2), N(1)-Al(1)-C(6) 120.57(2), S(3)-Al(1)-C(6) 97.39(1), N(5)-Al(2)-N(6) 66.96(1), N(5)-Al(2)-N(3) 90.17(1), S(2)-Al(2)-C(60) 96.09(1), N(5)-Al(2)-C(60) 101.21(2), N(6)-Al(2)-C(60) 119.97(2), N(3)-Al(2)-C(60) 133.94(2), N(6)-Al(2)-S(2) 104.94(1), S(3)-P(3)-N(4) 101.09(1), N(3)-P(2)-S(2) 100.95(1).

Single crystals of complex **1** were grown from concentrated solution in toluene. X-ray diffraction study showed that complex **1** crystallized in triclinic crystal system with $P\bar{1}$ space group (Figure 2) (Table 2). In complex **1** each of the aluminum center was bridged between arms of two ligands, where each aluminum center was five coordinated and adopt a distorted trigonal bipyramidal structure (*tbp*). In this structure, with respect to aluminum centre pyridine nitrogen and sulfur atoms were at axial positions and remaining three atoms were at the same plane of the distorted *tbp* structure. The bond distances of aluminum center with the atoms in the same plane were almost similar. This dimer like structure contains an eight membered macrocyclic ring in it. Metric parameters of complex **1** showed comparably good agreement with the similar reported molecule ($[Al(C_4H_9)]_2[(C_6H_5)_2P(S)CP(C_6H_5)_2(S)_2][Al(C_4H_9)_2]_2$).[21] In comparison with ($[Al(C_4H_9)]_2[(C_6H_5)_2P(S)CP(C_6H_5)_2(S)_2][Al(C_4H_9)_2]_2$), aluminum-sulfur bond lengths of complex **1** (Al(1)-S(3) 2.555(8), Al(2)-S(2) 2.537(3) Å) were slightly longer than expected, due to its axial positions in *tbp* coordinated structure. Phosphorous–sulfur bond distances (P(3)-S(3) 1.988(3), P(2)-S(2) 1.986(5) Å) in complex **1** were slightly shorter than that of ($[Al(C_4H_9)]_2[(C_6H_5)_2P(S)CP(C_6H_5)_2(S)_2][Al(C_4H_9)_2]_2$) (2.014(3) Å). In comparison with ligand (**LH_2**), elongation in bond length values between phosphorous and sulfur (P(2)-S(1) 1.945(3), P(1)-S(2) 1.948(3) A°) were observed in complex **1** (P(3)-S(3) 1.988(3), P(2)-S(2) 1.986(5) Å), which can be presumably due to the coordination of sulfur to the aluminum. On the other hand, sulfur atoms bonded only to phosphorous and not interacting with aluminum showed almost similar values in **1** (P(1)-S(1) 1.956(4), P(4)-S(4) 1.953(5) Å) as that of the ligand (**LH_2**) P=S bonds (P(1)-S(2) 1.948(3), P(2)-S(1) 1.948(3) Å). Bond length between aluminum and nitrogen atoms which are in the same plane of *tbp* structure (Al(1)-N(1) 1.952(6), Al(1)-N(4) 1.943(4), Al(2)-N(3) 1.905(3), Al(2)-N(6) 1.954(5) Å) were comparable with the value of reported molecule $[\{MeC(NAd)S\}AlMe_2]$ (Ad - Adamantyle)[17b] (1.953 Å). Aluminum–carbon bond in the $[\{MeC(NAd)S\}AlMe_2]$ (Ad - Adamantyle) (1.960(3) Å) showed almost similar length with that of complex **1** (1.965(7) Å).

2.3. Reaction of $[2,6\text{-}(Ph_2P\text{-}NH)_2C_5H_3N]$ and selenium: Synthesis of 2,6-bis(diphenylselenophosphorylamino)pyridine, $[2,6\text{-}(Ph_2P(Se)\text{-}NH)_2C_5H_3N]$ ($L'H_2$)

A mixture of $[(2,6\text{-}Ph_2P\text{-}NH)_2C_5H_3N]$ and two equivalent of selenium was taken in 50 mL of toluene and refluxed for 12 hours (Scheme 3) and complete selenium was consumed. Complete evaporation of the solvent under *vaccum* from the obtained transparent solution afforded product, **$L'H_2$** ($[2,6\text{-}(Ph_2P(Se)\text{-}NH)_2C_5H_3N]$) as a semi-white powder. Obtained product was characterized thoroughly using multinuclear NMR spectroscopy, EI-MS spectrometry and X-ray crystallographic techniques. The ^1H NMR couldn't distinguish between the starting material $[2,6(\text{-}Ph_2P\text{-}NH)_2C_5H_3N]$ and the product **$L'H_2$** due to almost similar chemical shift, whereas a downfield single peak at 47.58 ppm in the $^{31}P\{^1H\}$ NMR (Figure S13) of the product than starting material (25.71 ppm) were observed. Also the satellites at 49.99 and 45.16 ppm due to P-Se coupling ($^1J_{P\text{-}}$

$_{\mathrm{Se}}$= 785 Hz) attributed a clear indication of selenium bonded phosphorous atoms. Mass (ESI) data is also in agreement with the formation **L′H$_2$** (calcd (found) *m/z* = 637.99938 (637.9868) $[M+H]^+$) (Figure S15). Single crystals of the ligand, **L′H$_2$** were obtained from mixture of toluene and THF (90 % toluene and 10 % THF) at room temperature (Figure 3).



[(2,6-Ph$_2$P-NH)$_2$C$_5$H$_3$N]

L′H$_2$

Scheme 3: Synthesis of **L′H$_2$,** [2,6-(Ph$_2$P(Se)-NH)$_2$C$_5$H$_3$N]

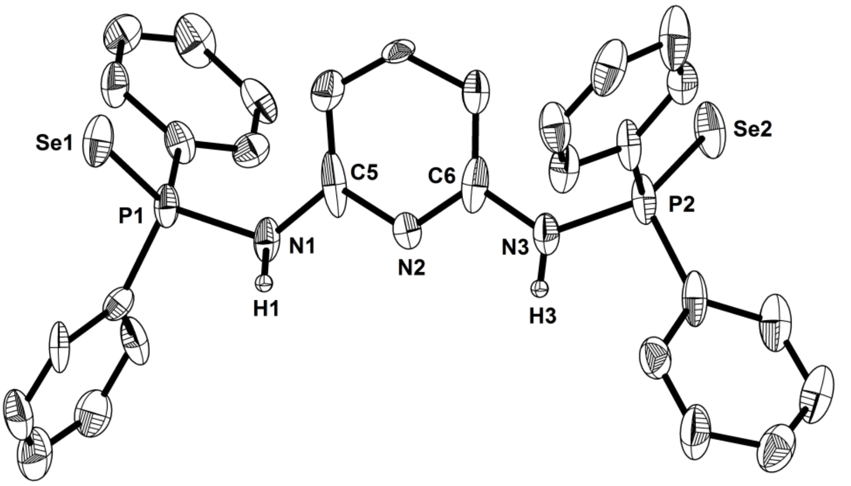
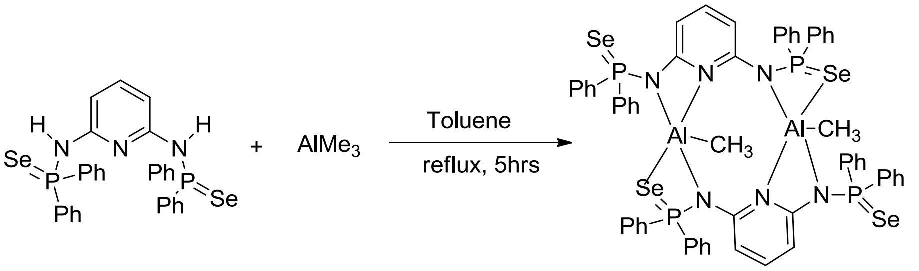


Figure 3. Single crystal X-ray structure of **L′H$_2$**. Hydrogen atoms except on nitrogen atoms are omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: N(2)-C(6) 1.386(2), N(2)-C(5) 1.334(1), C(5)-N(1) 1.383(2), N(1)-H(1) 0.862(1), N(1)-P(1) 1.669(2), P(1)-Se(2) 2.090(3), C(6)-N(3) 1.435(1), N(3)-H(3) 0.860(1), N(3)-P(2) 1.689(2), P(2)-Se(1) 2.101(4); C(6)-N(2)-C(5) 115.26(4), C(6)-N(3)-P(2) 127.07(4), C(6)-N(3)-H(3) 116.47(5), P(2)-N(3)-H(3) 116.46(4), N(3)-P(2)-Se(1) 116.43(2), C(5)-N(1)-P(1) 123.41(5), C(5)-N(1)-H(1) 109.25(4), P(1)-N(1)-H(1) 109.15(4), N(1)-P(1)-S(2) 118.38(3).

X-ray diffraction studies show that the ligand, **L′H$_2$** crystallizes in the monoclinic crystal system with *C2/c* space group (Figure 3) (Table 3). Structure of **L′H$_2$** is similar to that of **LH$_2$.** From the structure it was observed that both the selenium atoms were coordinated to phosphorous atoms *via* double bond (P(1)-Se(2) 2.090(3), P(2)-Se(1) 2.101(4) Å). And this P=Se bond length is comparable with reported molecule $Se=P(CH_2NHPh)_3$ (2.1026(12) Å).[19] By considering a plane containing pyridine ring and two nitrogen atoms, one selenium (Se(2)) will be above the plane and other (Se(1)) will be below the plane with a deviation 1.870(1) and 1.711(2) Å respectively. As comparing with the structure of **LH_2** both phosphorous atoms have less deviation from the plane, in other words both atoms are lying almost on the plane. As similar to **LH_2** phosphorous atom in **$L'H_2$** is also in distorted tetrahedral geometry, and it is coordinated with one nitrogen atom, one selenium atom and two phenyl rings. Dihedral angle between planes passing through phosphorous atoms and phenyl rings is measured. And it is observed that dihedral angle between planes where P(1) is the common atom is 79.60(5)° and P(2) is the common atom is 73.53(3)°. This angle is an indication of amount of twisting between phenyl rings on the same phosphorous atom.

2.4. Reaction of $L'H_2$ and $AlMe_3$: Synthesis of $[\{2,6\text{-}(Ph_2P(Se)\text{-}N)_2C_5H_3N\}AlMe]_2$, $[L'AlMe]_2$ (2)

Equimolar reaction of **$L'H_2$** with trimethylaluminum in toluene at refluxing conditions resulted into the formation of complex **$[L'AlMe]_2$** (**2**) (Scheme 4) which was partially soluble in toluene. After filtration and drying the product was obtained as a white powder. The product was characterized thoroughly using multinuclear NMR spectroscopy, EI-MS spectrometry and X-ray crystallographic techniques. ^{1}H NMR spectrum of **2** showed the Al-*Me* proton peak at -0.49 ppm with an integration value equal to three hydrogen atoms (Figure S17). As an indication of co-ordination of nitrogen donor with aluminum center, the N*H* signal disappeared from the proton NMR spectra of complex **2.** Remaining peak values were consistent with that of ligand backbone except the *meta*- hydrogens of pyridine ring that were observed as two doublets at 5.72 and 6.93 ppm respectively. $^{31}P\{^1H\}$ NMR spectrum of **2** indicated the presence of two type of phosphorous with chemical shift values 50.22 and 45.28 ppm (Figure S18) in equal integrity, which could be fortified from the two different type of phosphorus atoms attributed in single crystal structure (Figure 4). The formation complex **2** could also be confirmed by the presence of HRMS signal at 675.9713 (calcd: 675.9675 $[M/2\text{-}H]^-$) (Figure S21).



$L'H_2$

$[L'AlMe]_2$ (**2**)

Scheme 4: Synthesis of [**L′AlMe**]$_2$, $[\{2,6\text{-}(Ph_2P(Se)\text{-}N)_2C_5H_3N\}AlMe]_2$ (**2**)

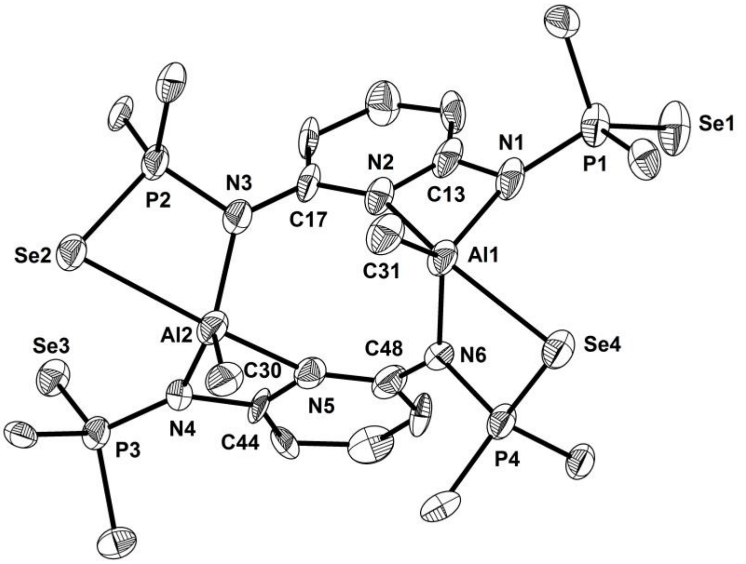


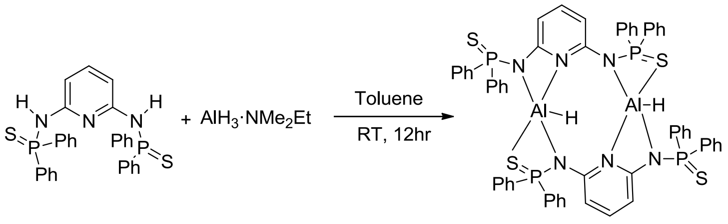
Figure 4: Single crystal X-ray structure of [**L′AlMe**]$_2$ (**2**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids have been drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: Al(2)-N(4) 1.952(6), Al(2)-N(5) 2.054(2), Al(2)-Se(2) 2.646(5), Al(2)-N(3) 1.944(4), Al(2)-C(30) 1.985(4), Al(1)-N(2) 2.037(6), Al(1)-N(6) 1.921(5), Al(1)-N(1) 1.933(4), Al(1)-Se(4) 2.689(3),Al(1)-C(31) 1.950(4), P(1)-Se(1) 2.128(4), P(2)-Se(2) 2.128(5), P(3)-Se(3) 2.106(3), P(4)-Se(4) 2.122(5), N(1)-P(1) 1.652(5), N(3)-P(2) 1.642(4), N(4)-P(3) 1.661(5), N(6)-P(4) 1.655(3), C(17)-N(2) 1.366(5), C(17)-N(3) 1.419(6), C(44)-N(5) 1.349(2), C(44)-N(4) 1.393(7); N(2)-Al(1)-N(1) 67.23(1), N(4)-Al(1)-N(2) 91.20(1), N(1)-Al(1)-S(3) 101.94(1), N(6)-Al(1)-C(31) 104.84(2), N(6)-Al(1)-N(2) 91.96(2), N(2)-Al(1)-N(1) 68.05(2), Se(4)-Al(1)-N(6) 78.02(1), N(5)-Al(2)-C(30) 37.58(1), N(5)-Al(2)-N(3) 91.58(1), Se(2)-Al(2)-N(3) 77.26(3),N(4)-Al(2)-N(5) 67.26(3),N(1)-P(1)-Se(1) 117.58(4), N(4)-P(3)-Se(3) 118.24(4), N(6)-P(4)-Se(4) 102.32(3), N(3)-P(2)-Se(2) 101.32(2).

Single crystals of complex **2** were grown from concentrated solution of DCM. X-ray diffraction study showed that complex **2** crystallized in triclinic crystal system with $P\bar{1}$ space group (Figure 2). The solid state structure of complex **2** is almost identical with that of complex **1**. As seen in the case of complex **1**, two five co-ordinated aluminum centers with a distorted trigonal bipyramidal structure (*tbp*) bridging between two ligand moeities are present in **2** as well. This dimer like structure contained an eight membered macrocyclic ring. Two types of selenium atoms are present in the molecule, one is co-ordinating with aluminum center and the other Se is not interacting with Al. Where selenium is co-ordinated with aluminum center, phosphorous-selenium bond exhibit a slight elongation (2.128 Å) as compared to P=Se bond in ancillary ligand, **L′H$_2$** (2.090Å). There are not many reports available on aluminum complexes where a Se donor is coordinated with chelated Al centre. To the best of our knowledge, compound **2** is the first example of a structurally characterized pentacordinated aluminum complex containing Al-Se bond. The compound [Al{κ^2-N,Se-[4,5-(P(Se)Ph$_2$)$_2$tz]}$_3$] (tz = 1,2,3-triazole)[20] (**H** in Chart 3) contaning a hexacoordinated aluminum center, which is co-ordinated with selenium present in the chelating ligand. Metric parameters of complex **2** showed comparably good agreement with the above mentioned molecule. In comparison with [Al{κ^2-N,Se-[4,5-(P(Se)Ph$_2$)$_2$tz]}$_3$] (tz = 1,2,3-triazole) (Al(1)-Se(1) 2.557(1), A(1)-Se(3) 2.559(1), Al(1)-Se(5) 2.539(1)), aluminum-selenium bond lengths of complex **2** (Al(2)-Se(2) 2.646(5), Al(1)-Se(4) 2.689(3) Å) were slightly longer. Phosphorous–selenium bond distances where selenium atom is in coordination with aluminum (P(4)-Se(4) 2.122(5), P(2)-Se(2) 2.128(5) Å) in complex **2** were comparable with that of [Al{κ^2-N,Se-[4,5-(P(Se)Ph$_2$)$_2$tz]}$_3$] (tz = 1,2,3-triazole) (P(1)-Se(1) 2.150(1), P(3)-Se(3) 2.161(1), P(5)-Se(5) 2.157(1)).

2.5. Reaction of LH$_2$ and AlH$_3$: Synthesis of [{2,6-(Ph$_2$P(S)-N)$_2$C$_5$H$_3$N}AlH]$_2$, [LAlH]$_2$ (3)

Equimolar reaction of **LH$_2$** with AlH$_3$·NMe$_2$Et complex solution at room temperature in toluene gave rise to the formation of complex **3** (Scheme 5) which was insoluble in toluene. After filtration and drying, product **3** was obtained as a white powder. Changing the reaction conditions such as molar ratios reactant, temperature resulted the formation of same product. The obtained product was characterized thoroughly using multinuclear NMR spectroscopy, EI-MS spectrometry. ^{1}H NMR spectra showed a broad peak at 4.96

ppm which is attributed to Al-*H* proton with an integration value equal to one hydrogen atom. As an indication of co-ordination of nitrogen donor with aluminum center, the N*H* protons disappeared from the proton NMR spectra of complex **5** (Figure S23)**.** Remaining peak values that were similar to that of ligand backbone except the *meta*- hydrogens of pyridine ring observed as two doublets at 5.54 and 6.46 ppm. The ^{31}P{^{1}H} NMR indicated the presence of two type of phosphorous with equal integrity with chemical shift values 49.68 and 56.94 ppm (Figure S24). IR spectrum shows characteristic Al-H stretch at 1857 cm^{-1} (Figure S28). All this spectroscopic data confirming the fact that alane is also reacting in the same way as AlMe$_3$ and leading to a structurally similar product. Mass (ESI) data is also in agreement with the formation of product **3** (calcd (found) *m/z* = 1135.1483 (1135.2489) $[M+H]^+$) (Figure S27).



LH$_2$

[LAlH]$_2$ (3)

Scheme 5: Synthesis of [**LAlH]$_{\mathbf{2}}$,** [{2,6-(Ph$_2$P(S)-N)$_2$C$_5$H$_3$N}AlH]$_2$ (**3**)

3. Experimental Section

3.1. General procedures

All manipulations were performed under nitrogen/argon atmosphere using Schlenk line or glove box techniques. All chemicals were purchased from Sigma-Aldrich and used without further purification. All glassware was dried at 150 °C in an oven for at least 20 hour prior to use. Toluene, THF and DCM were purified with the M-Braun solvent drying system prior to use. The starting material [2,6-$(Ph_2P\text{-}NH)_2C_5H_3N$] was prepared by following the reported procedure.[11]

3.2. Physical Measurements

The ^1H, $^{31}P\{^1H\}$, ^{13}C, spectra were recorded with a Bruker 400 MHz spectrometer with TMS as external reference; chemical shift values are reported in ppm. Heteronuclear NMR spectra were recorded ^1H decoupled. Deuterated NMR solvent $CDCl_3$ was dried over 4 Å molecular sieves. IR spectra of the compounds were recorded in the range 4000–400 cm^{-1} using a Perkin Elmer Lambda 35-spectrophotometer as nujol mull between KBr plates and KBr pellet preparation. The absorptions of various functional groups are assigned and other absorptions (moderate to very strong) are only listed. Melting points were measured in sealed capillaries on a Büchi B–540 melting point instrument. High-resolution mass spectrometry was performed with a Waters SYNAPT G2-S.

Single crystal X-ray diffraction data of **LH_2, $L'H_2$** and complex **1** were collected on a Bruker *AXS KAPPA APEX-II* CCD diffractometer (Monochromatic MoKα radiation) equipped with Oxford cryosystem 700 plus at 100 K (using 50KV and 30mA power). Data collection and unit cell refinement for the data sets were done using the Bruker APPEX-II suite, data reduction and integration were performed using SAINTV 7.685A (Bruker AXS, 2009) and absorption corrections and scaling were done using SADABSV2008/1 (Bruker AXS, 2009).[22] The crystal structures were solved by using OLEX2 package using SHELXS-97[23] and the structures were refined using SHELXL-97 2008.47.[24] Single crystal X-ray diffraction data of complex **2** were collected using a Rigaku XtaLAB 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 (using 50 KV, 12mA power). During the data collection the detector distance was 49.85 mm (constant) and the detector was placed at $2\theta = 29.85°$

(fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite.[25] The space group determination was done using Olex2.[22] The structures were solved by direct method and refined by full-matrix least-squares procedures using the SHELXL-97[24] software package using Olex2 suite. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at geometrically calculated positions and were refined using riding model. Diamond version 2.1d was used to generate graphics for the X-ray structures. The crystal data for all compounds along with the final residuals and other pertaining details are tabulated in Tables **1**–**4**. Single crystal data and refinement results are listed in the following tables.

3.3. Synthesis of LH$_2$, [2,6-(Ph$_2$P(S)-NH)$_2$C$_5$H$_3$N]

A mixture of [2,6-(Ph$_2$P-NH)$_2$C$_5$H$_3$N] (4.77 g, 10 mmol) and sulfur (0.64 g, 20 mmol) was taken (in 1:2 ratio) in 250 mL toluene. The resulting suspension was stirred at 80 ºC for overnight. The final solution was concentrated under *vacuum* after filtration and kept it for crystallization. Colorless crystals of compound **LH$_2$** were grown at -4 ºC. Yield: 3.9 g, 61.4%. Mp: 172-175ºC. **IR** (KBr, $\tilde{\nu}$ cm^{-1}) 3368 (N-H), 3051, 1599 (C-C), 1581 (C-N), 1438 (C-Ph), 1436, 1370, 1337, 1309, 1266, 1182, 1103, 1021, 998, 828, 783, 727, 692, 642, 614, 519, 483. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 6.11 (broad, 2H, N-*H*), 6.41 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, pyridine-m-*H*), 7.09 (t, 1H, $^3J_{H-H}$ = 8.0 Hz, pyridine-p-*H*), 7.44-7.56 (m, 13H, Ar), 7.95-8.00 (m, 7H, Ar). **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 105.2, 128.8, 131.6, 132.4, 132.8, 139.4, 152.2. **^{31}P{^{1}H} NMR** (162 MHz, CDCl$_3$): δ = 51.44. **MS (ESI):** calcd (found) m/z = 542.1043 (542.1077) [M+H]$^+$.

3.4. Synthesis of [LAlMe]$_2$, [{2,6-(Ph$_2$P(S)-N)$_2$C$_5$H$_3$N}AlMe]$_2$ (1)

A mixture of **LH$_2$** (0.541 g, 1 mmol) and AlMe$_3$ (1 mL, 2 mmol) was taken (in 1:2 equivalents) in 50 mL toluene. The resulting suspension was stirred at room temperature for about 12 hours. The final solution was concentrated under *vacuum* after filtration and kept it for crystallization at room temperature. Colorless crystals of compound **1** were grown at room temperature. Yield: .30 g 55%. Mp: 355-358 ºC. **IR** (KBr, $\tilde{\nu}$ cm^{-1}) 3358, 3053, 1598 (C-C), 1452 (C-Ph), 1408, 1311, 1263, 1183, 1105, 1025, 883, 817, 785, 721, 692, 641, 613, 538, 518, 485. **^{1}H NMR** (400 MHz, CDCl$_3$): δ = -0.50 (s, 3H, Al*Me*), 5.61 (d, 1H, $^3J_{H-H}$ = 8.4 Hz, pyridine-m-*H*), 6.60 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, pyridine-m-*H*), 6.9 (t, 1H, $^3J_{H-H}$ = 8.0 Hz, pyridine-p-*H*) 7.3-8.02 (m, 20H, Ar). **^{13}C NMR** (100 MHz, CDCl$_3$):

δ = -2.8, 107.2, 128.3, 128.7, 131.6, 132.3, 137.9, 142.1. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ = 49.28, 57.06. **^{27}Al NMR** (104 MHz, $CDCl_3$): δ = 70.73. **MS (ESI):** calcd (found) m/z = 580.0781 (580.0397) $[M/2-H]^-$.

3.5. Synthesis of L′H$_2$, [2,6-(Ph$_2$P(Se)-NH)$_2$C$_5$H$_3$N]

A mixture of [(2,6-Ph_2P-NH)$_2$$C_5H_3N$] (4.78 g, 10 mmol) and selenium (1.7 g, 2 mmol) were taken (in 1:2 equivalents) in 50 mL toluene. This reaction stirred at 80 ºC for 12 hours . The solution filtered. Filtrate concentrated and kept it for crystallization at room temperature. Yield: 3.3 g 51%. Mp: 175-181 ºC. **IR** (KBr, $\tilde{\nu}$ cm^{-1}) 3365 (N-H), 3049, 2284, 1599 (C-N), 1579, 1494, 1478, 1454 (C-Ph), 1435, 1398, 1368, 1335, 1309, 1264, 1183, 1171, 1097, 1020, 997, 826, 782, 738, 702, 690, 610, 557, 514, 476, 437. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.21 (broad, 2H, N-H), 6.62 (d, 2H, $^3J_{H\text{-}H}$ = 8.0 Hz, pyridine-m-*H*), 7.13 (t, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, pyridine-p-*H*), 7.43-7.65 (m, 6H, Ar), 7.9-8.0 (m, 14H, Ar). **^{13}C NMR** (100 MHz, $CDCl_3$) : δ = 105.3, 128.8, 131.8, 132.5 , 132.3, 139.2, 152.2. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$) : δ = 47.58 (with satellites at 45.15 & 50.00 ppm, $^1J_{P\text{-}Se}$= 785 Hz). **MS (ESI):** calcd (found) *m/z* = 637.9938 (637.9868) $[M+H]^+$.

3.6. Synthesis of [L′AlMe]$_2$, [{2,6-(Ph$_2$P(Se)-N)$_2$C$_5$H$_3$N}AlMe]$_2$ (2)

A mixture of **L′H$_2$** (0.635 g, 1 mmol) and $AlMe_3$ (0.5 mL, 1 mmol) was taken in 50 mL toluene. The resulting suspension was stirred at room temperature for about 4 hours. Then the suspension was refluxed for 5 hours. The product obtained was filtered and dried. Colorless crystals of compound **2** were grown at room temperature by dissolving it in DCM. Yield: 0.42 g 66%. Mp: 364-369 ºC. **IR** (KBr, $\tilde{\nu}$ cm^{-1}) 3359, 3052, 1599 (C-C), 1581, 1479 (C-Ph), 1455, 1436, 1391, 1345, 1309, 1268, 1229, 1183, 1159, 1099, 1026, 998, 823, 783, 739, 702, 691, 618, 556, 515, 428. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = -0.50 (s, 3H, Al*Me*), 5.66 (d, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, pyridine-m-*H*), 6.60 (d, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, pyridine-m-*H*), 6.90 (t, 2H, $^3J_{H\text{-}H}$ = 8.0 Hz, pyridine-p-*H*) 7.19-8.03 (m, 20H, Ar). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 152.02, 139.3, 132,9 132.2, 131.8, 128.8, 104.9, 1.094. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ = 50.22, 45.38. **^{27}Al NMR** (104 MHz, $CDCl_3$): δ = 67.34. **MS (ESI):** calcd (found) *m/z* = 675.9675 (675.9713) $[M/2-H]^+$.

3.7. Synthesis of [LAlH]$_2$, [{2,6-(Ph$_2$P(S)-N)$_2$C$_5$H$_3$N}AlH]$_2$ (3)

A mixture of **LH$_2$** (0.541 g, 1 mmol) and $AlH_3 \cdot NMe_2Et$ (2 mL, 1 mmol) were taken in 50 mL toluene. The resulting suspension was stirred at room temperature for about 12 hours. The final suspension was filtered and product **3** obtained as a white powder. Yield: .39 g 72%. Mp: 330-335 ºC (Decomp). **IR** (Nujol, $\tilde{\nu}$ cm^{-1}) 2921, 2854, 1857 (Al-H), 1585, 1565, 1455, 1410, 1377, 1333, 1266, 1183, 1109, 964, 883, 857, 818, 725, 698, 659, 546, 514, 475. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.96 (broad, 1H, Al*H*), 5.54 (d, 1H, $^3J_{H\text{-}H}$ = 7.2 Hz, pyridine-m-*H*), 6.46 (d, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz, pyridine-m-*H*), 6.87 (t, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, pyridine-p-*H*) 7.17-8.05 (m, 20H, Ar). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 107.2, 128.3, 129.1, 131.6, 132.2, 137.9, 142.1. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ = 49.68, 56.94. **^{27}Al NMR** (104 MHz, $CDCl_3$): δ = 69.72. **MS (ESI):** calcd (found) *m/z* = 1135.1483 (1135.2489) [M+H]$^+$.

.

4. Crystal Data and Refinement Details

Table 1. Crystal data and structure refinement details for LH_2, [2,6-($Ph_2P(S)$-$NH)_2C_5H_3N$]

Emperical formula	$C_{29}H_{25}N_3P_2S_2$	
Formula weight	541.58	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1/c$	
Unit cell dimensions	a = 12.706(6) Å	α = 90°
	b = 11.181(6) Å	β = 92.572(6)°
	c = 18.610(9) Å	γ = 90°
Volume	2641(2) $Å^3$	
Z	4	
Density (calculated)	1.362 Mg/mm^3	
Absorption coefficient	0.347 mm^{-1}	
F(000)	1128	
Crystal size	0.19 x 0.21 x 0.19 mm^3	
θ range for data collection	1.604 to 25.349°.	
Index ranges	$-15 \leq h \leq 15$, $-13 \leq k \leq 13$, $-22 \leq l \leq 22$	
Reflections collected	47721	
Independent reflections	4839 [R(int) = 0.0444]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4839 / 0 / 333	
Goodness-of-fit on F^2	1.023	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0278, wR2 = 0.0751	
R indices (all data)	R1 = 0.0305, wR2 = 0.0774	
Largest diff. peak and hole	0.369 and -0.259 e.$Å^{-3}$	
Diffractometer & detector	Bruker *AXS KAPPA APEX-II* CCD diffractometer	
Detector distance & tube power	50mm & (50KV, 30mA)	

Table 2. Crystal data and structure refinement details for [LAlMe]$_2$, [{2,6-(Ph$_2$P(S)-N)$_2$C$_5$H$_3$N}AlMe]$_2$ (1)

Emperical formula	C_{60} $H_{52}Al_2$ N_6 P_4 S_4	
Formula weight	1163.21	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 14.617(4) Å	α = 105.412(4)°
	b = 16.232(5) Å	β = 110.064(3)°
	c = 16.297(5) Å	γ = 94.397(4)°
Volume	3440.6(18) Å^3	
Z	2	
Density (calculated)	1.301 Mg/mm^3	
Absorption coefficient	0.304 mm^{-1}	
F(000)	1408	
Crystal size	0.19 x 0.18 x 0.21 mm^3	
θ range for data collection	1.599 to 25.349°.	
Index ranges	$-17 \leq h \leq 17$, $-19 \leq k \leq 19$, $-19 \leq l \leq 19$	
Reflections collected	43670	
Independent reflections	12613 [R(int) = 0.0686]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12613 / 0 / 815	
Goodness-of-fit on F^2	1.028	
Final R indices [I > 2 σ(I)]	R1 = 0.0632, wR2 = 0.1593	
R indices (all data)	R1 = 0.1014, wR2 = 0.1821	
Largest diff. peak and hole	1.772 and -0.656 e.Å^{-3}	
Diffractometer & detector	Bruker *AXS KAPPA APEX-II* CCD diffractometer	
Detector distance & tube power	50mm & (50KV, 30mA)	

Table 3. Crystal data and structure refinement details for L′H_2, [2,6-(Ph_2P(Se)-NH)$_2C_5H_3N$]

Empirical formula	$C_{29}H_{25}$ N_3P_2 Se_2	
Formula weight	635.45	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/*c*	
Unit cell dimensions	a = 23.176(7) Å	α = 90°
	b = 15.774(7) Å	β = 91.997(10)°
	c = 19.748(7) Å	γ = 90°
Volume	7215(5) Å^3	
Z	8	
Density (calculated)	1.354 Mg/mm^3	
Absorption coefficient	2.169 mm^{-1}	
F(000)	2944	
Crystal size	0.22 x 0.21 x 0.19 mm^3	
θ range for data collection	1.562 to 25.367°.	
Index ranges	$-27 \leq h \leq 27$, $-18 \leq k \leq 18$, $-23 \leq l \leq 23$	
Reflections collected	21581	
Independent reflections	6563 [R(int) = 0.1554]	
Completeness to theta = 25.242°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6563 / 0 / 398	
Goodness-of-fit on F^2	1.154	
Final R indices [I>2 σ(I)]	R1 = 0.1200, wR2 = 0.2963	
R indices (all data)	R1 = 0.2162, wR2 = 0.3868	
Largest diff. peak and hole	2.003 and -3.398 e.Å^{-3}	
Diffractometer & detector	Bruker *AXS KAPPA APEX-II* CCD diffractometer	
Detector distance & tube power	50mm & (50KV, 30mA)	

Table 4. Crystal data and structure refinement details for [L′AlMe]$_2$, [{2,6-(Ph$_2$P(Se)-N)$_2$C$_5$H$_3$N}AlMe]$_2$ (2)

Empirical formula	$C_{30}H_{26}N_3P_2Se_2Al$	
Formula weight	675.39	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 15.325(2) Å	α = 79.87(5)°
	b = 15.8160(3) Å	β = 68.43(4)°
	c = 15.8718(2) Å	γ = 61.74(3)°
Volume	3151.3(13) Å^3	
Z	4	
Density (calculated)	1.603 Mg/mm^3	
Absorption coefficient	2.673 mm^{-1}	
F(000)	1520	
Crystal size	0.20 x 0.18 x 0.08 mm^3	
θ range for data collection	3.036 to 25.027°.	
Index ranges	$-18\leq h\leq 18$, $-18\leq k\leq 18$, $-18\leq l\leq 18$	
Reflections collected	27332	
Independent reflections	11045 [R(int) = 0.1277]	
Completeness to theta = 25.027°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11045 / 0 / 741	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2 σ(I)]	R1 = 0.1035, wR2 = 0.2660	
R indices (all data)	R1 = 0.1607, wR2 = 0.3291	
Largest diff. peak and hole	2.540 and -1.062 e.Å^{-3}	
Diffractometer & detector	Rigaku XtaLAB mini diffractometer & Mercury375M CCD detector	
Detector distance & tube power	49.85mm & (50KV, 12mA)	

5. Summary

The present thesis covers the synthesis of novel pyridine based pincer type ligands containing N/S or N/Se co-ordinating sites. By assembling chalcogen donors sulfur and selenium on a pyridine based moiety, [2,6-$(Ph_2P\text{-}NH)_2C_5H_3N$] by the oxidation of P(III) centers to P(V), leads to the formation of two ligands namely, 2,6-bis(diphenylthiophosphorylamino)pyridine, [2,6-$(Ph_2P(S)\text{-}NH)_2C_5H_3N$] (**L$H_2$**) and 2,6-bis(diphenylselenophosphorylamino)pyridine, [2,6-$(Ph_2P(Se)\text{-}NH)_2C_5H_3N$] (**L′$H_2$**) respectively. Aluminum complexes of these ligands have been synthesized by treating it with trimethylaluminum and solid state study and other spectroscopic studies implying that both ligands are forming a dimer in solid state, which contains a eight-membered macrocyclic ring in it.

6. Future directions

The extension of the current work should focus on:

1. Investigation of coordination chemistry of sulfur and selenium donor ligands with other main group metals.
2. Generation of aluminum cationic complexes from complexes **1** and **2** and to study their catalytic activity.

7. References

(1) Moulton , C. J.; Shaw, B. L.; *J. Chem. Soc. Dalton Trans.*, **1976**, 1020-1024.

(2) a) Knorr , M.; Strohmann, C.; *Eur. J. Inorg. Chem.* **1998**, 495-499. (b) Wingerter, S.; Pfeiffer, M.; Murso, A.; Lustig, C.; Stey, T.; Chandrasekhar, V.; Stalke, D. *J. Am. Chem. Soc.* **2001**, *123,* 1381-1386.

(3) van Koten,; G. Pure Appl. Chem. **1989**, *61*, 1681-1685.

(4) a) Ansell, J.; Wills, M. *Chem. Soc. Rev.* **2002**, *31*, 259-265. (b) Oztopcu, O.; Holzhacker, C.; Puchberger, M.; Weil, M.; Mereiter, K.; Veiros, L. F.; Kirchner, K. J. Organomet. Chem. **2013**, *32*, 3042-3052.

(5) Al-Benna, S.; Sarsfield, M. J.; Pett, M. T.; Ormsby, D. L.; Maddox, P. J.; Bres, P.; Bochmann, M. *J. Chem. Soc. Dalton Trans.*, **2000**, 4247-4257.

(6) Chai, Z. Y.; Zhang, C.; Wang, Z. X. *Organometallics* **2008**, *27*, 1626-1633.

(7) Sgro, M. J.; Stephan, D. W. *Dalton Trans.*, **2011**, *40*, 2419-2421.

(8) Cheisson, T.; Auffrant, A. *Dalton Trans.*, **2014**, *43*, 13399-13409

(9) van der Vlugt, J. I.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *28*, 8832-8846.

(10) Srimani, D.; David, B. Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2013**, *52,* 4012-4015.

(11) Schirmer, W.; Flörke, U.; Haupt, H.-J. *Z. Anorg. Allg. Chem.* **1987**, *545*, 83-97.

(12) Alzamly, A.; Gambarotta, S.; Korobkov, I. *J.Organomet.Chem.* **2013**, 7107-7115.

(13) Bastanov, A. S.; Churakov, A. V.; Easson, M. A. M.; Govenlock, L. J.; Howard, J. A. K.; Moloney, J. M.; Parker, D. *J. Chem. Soc., Dalton Trans.*, **1999**, 323-329.

(14) Gan, X.; Duesler, E. N.; Parveen, S.; Paine, R. T. *Dalton Trans.*, **2003**, 4704-4708.

(15) Lemport, S. P.; Ostapchuk, P. N.; Bobrikova, A. A.; Petrovskii, P. V.; Kagramanov, N. D.; Bodrin, G. V.; Nifant'ev, E. E. *Mendeleev Commun*., **2010**, *20*, 223-235.

(16) a) Pan, Z.; Gamer, M. T.; Roesky, P. W. Z. *Anorg. Allg. Chem.* **2006**, *632*, 744-748. b) Glatz, M.; Holzhacker, C.; Bichler, B.; Mastalir, M.; Stoger, B.; Mereiter, K.; Weil, M.; Veiros, L. F.; Zanetti, N. C. M.; Kirchner, K. *Eur. J. Inorg. Chem.* **2015**, 5053-5065.

(17) a) Kang, Y.; Yang, N.; Kang, S. O.; Ko, J. *J. Oraganometallics,* **1997**, *16,* 5522-5527. (b) Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1998**, *17,* 4042-4048. (c) McMahon, C. N.; Francis, J. A.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.*, **1999**, 67-72. (d) Haagenson, D. C.; Moser, D. F.; Stahl, L. *Inorg. Chem.* **2002**, *41*, 1245-1253. (e) Briand, G. G.; Chivers, T.; Krahn, M.; Parvez, M. *Inorg. Chem.* **2002**, *41*, 6808-6815. (f) Guo, J.; Lee, J.S.; Foo, M. C.; Lau, K. C.; Xi,

H. W.; Lim, K. H.; So, C. W. *Organometallics* **2010**, *29*, 939-944. (g) Leung, W. P.; Wan, C. L.; Mak. T. C. W. *Organometallics* **2010**, *29*, 1662-1628. (h) Yang, Y. F.; Foo, C.; Ganguly, R.; Li, Y.; So, C. W. *Organometallics* 2012, *31*, 6538-6546.

(18) Burford, N.; Royan, B. W.; Spence, R. E. V. H. *J. Chem. Soc., Dalton Trans.* **1990**, 2111-2117.

(19) Han, H.; Johnson, S. A. *Organometallics* **2006**, *25*, 5594-5602.

(20) Garica, J. A.; Jancik, V.; Barroso, J.; Bonilla, S. H.; Olivares, R. C.; Toscano, R. A.; Cabrera, M. M. *Inorg. Chem*. **2009**, *48*, 5874-5883.

(21) Robinson, G. H.; Self, M. F.; Pennington, W. T.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 2424-2426.

(22) Dolomanov, O. V.: Bourhis, L. J.; Howard, J. A. K.; Puschmann, H. J. *Appl.Cryst.* **2009**,*42*, 339.

(23) G. M. Sheldrick, SHELXL-97, Program for crystal Structure Refinement, Universität Göttingen, Göttingen, FRG, 1997.

(24) "SHELXS-97, Program for Structure Solution": G. M. Sheldrick, Acta *Crystallogr., Sect.* A, **2008**, *64*, 112.

(25) CrystalClear 2.0, Rigaku Corporation, Tokyo, Japan.

Supporting information

Heteronuclear NMR spectra (^{1}H, ^{13}C, ^{31}P), HRMS spectra and IR-spectra of new compounds reported in this dissertation.

Contents

(1) Fig. **S1-S3** Heteronuclear NMR Spectra of **LH$_2$.**

(2) Fig. **S4** Mass spectrum Of **LH$_2$.**

(3) Fig. **S5** IR spectrum of **LH$_2$**.

(4) Fig. **S6-S9** Heteronuclear NMR Spectra of complex **1.**

(5) Fig. **S10** Mass spectra of complex **1.**

(6) Fig. **S11** IR spectra of complex **1.**

(7) Fig. **S12-S14** Heteronuclear NMR Spectra of **L′H$_2$.**

(8) Fig. **S15** Mass spectra of **L′H$_2$.**

(9) Fig. **S16** IR spectra of **L′H$_2$.**

(10) Fig.**S17-S20** Heteronuclear NMR Spectra of complex **2.**

(11) Fig.**S21** Mass spectra of complex **2.**

(12) Fig.**S22** IR spectra of complex **2.**

(13) Fig. **S23-S26** Heteronuclear NMR Spectra of complex **3.**

(14) Fig. **S27** Mass spectra of complex **3.**

(15) Fig. **S28** IR spectra of complex **3.**

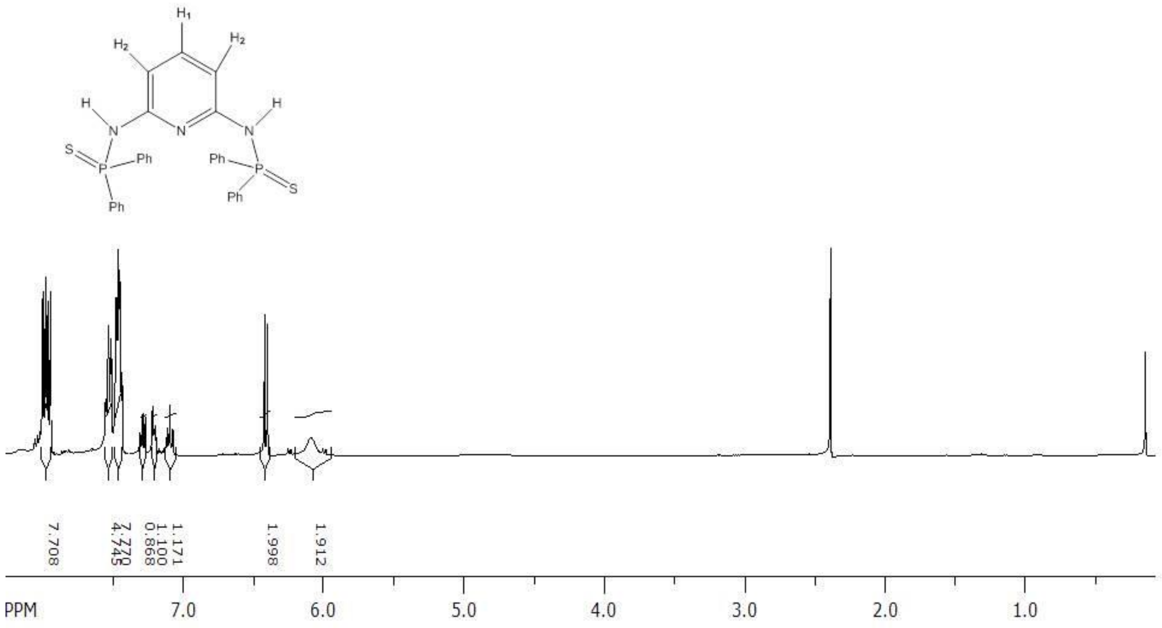


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(S)$-$NH_2)_2$] (**LH_2**).

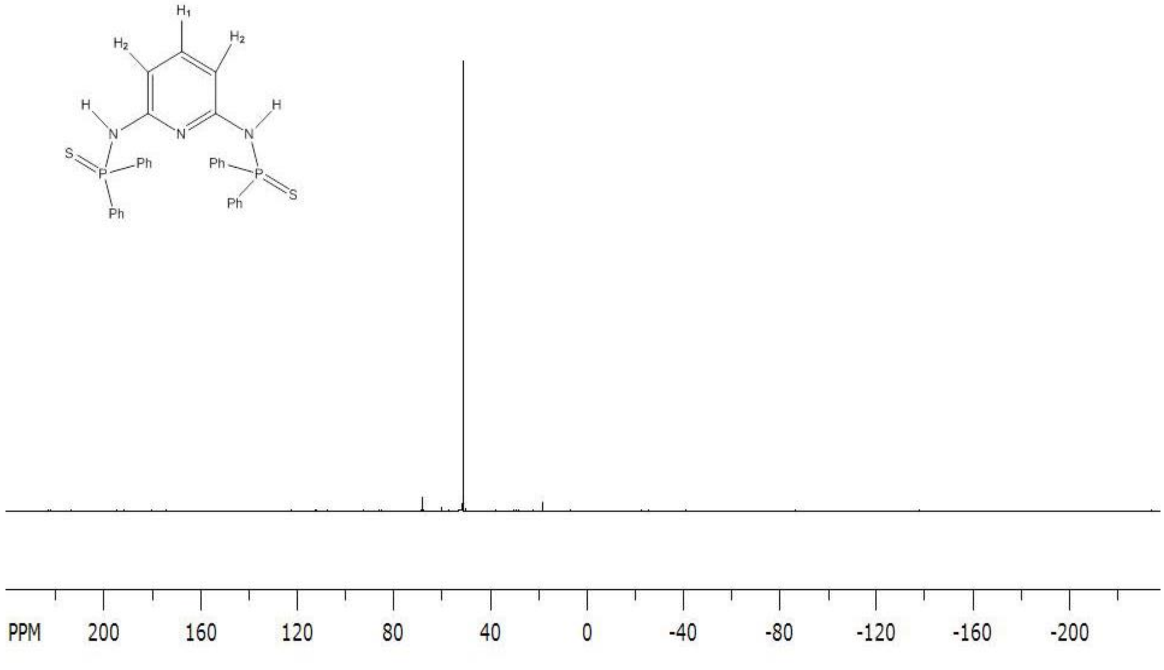


Fig. S2 ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(S)$-$NH_2)_2$] (**LH_2**).

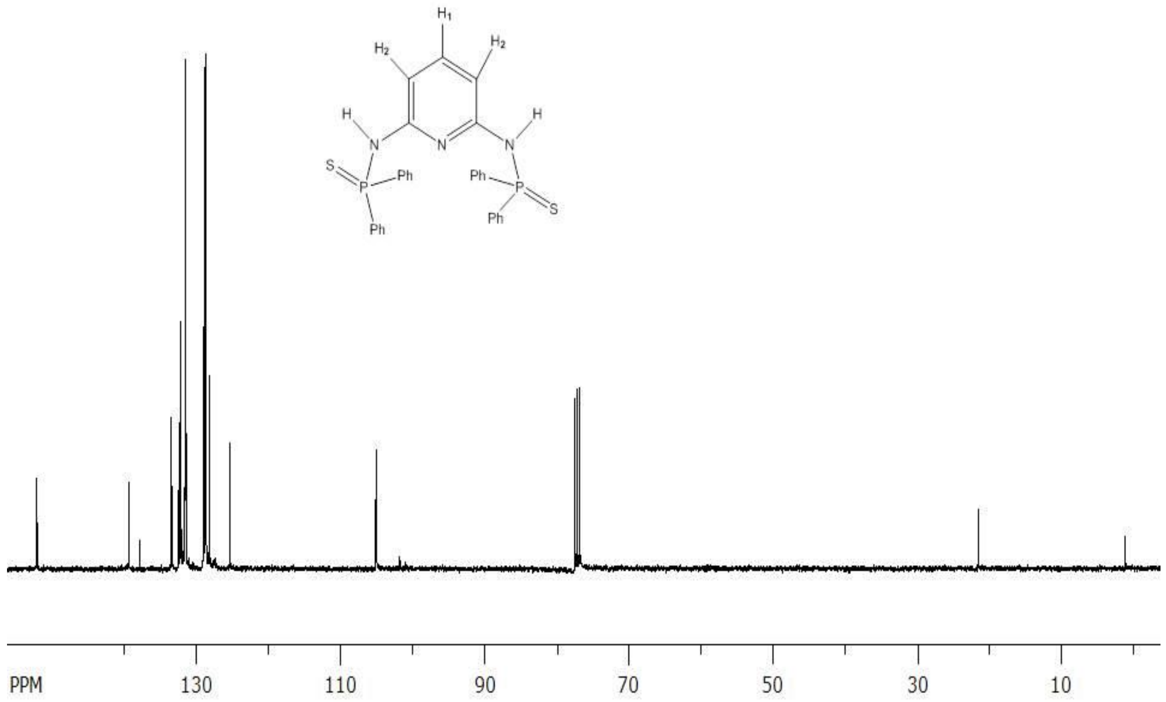


Fig. S3 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(S)-NH_2)_2$] (**LH_2**).

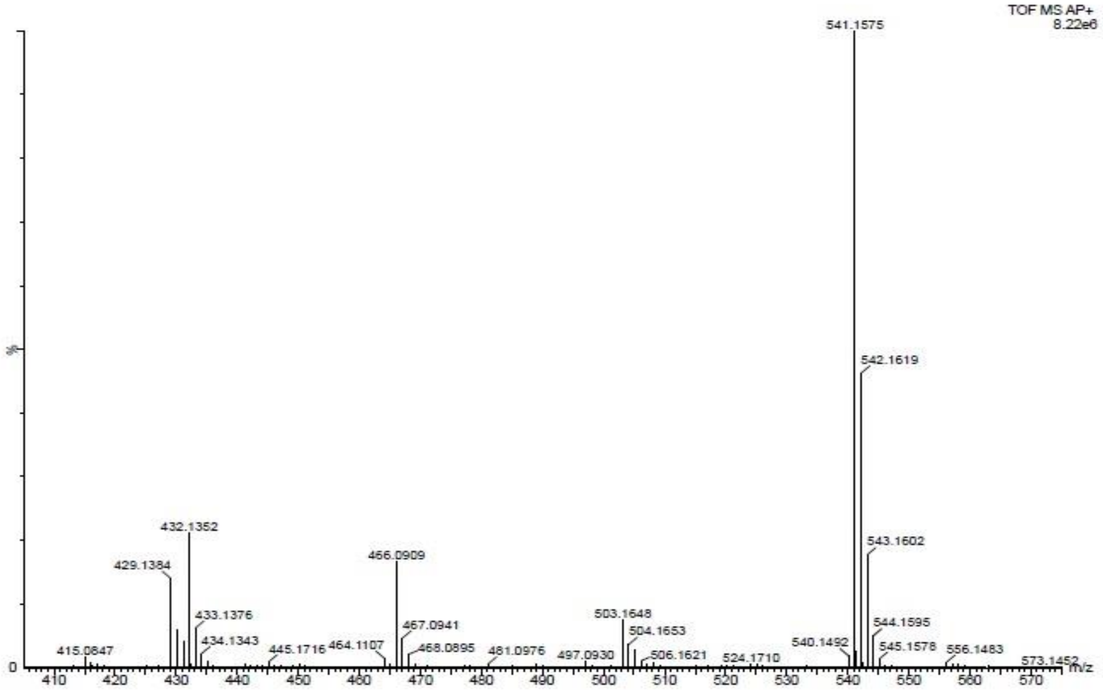


Fig.S4 Mass spectrum of [2,6-($Ph_2P(S)-NH_2)_2$] (**LH_2**).

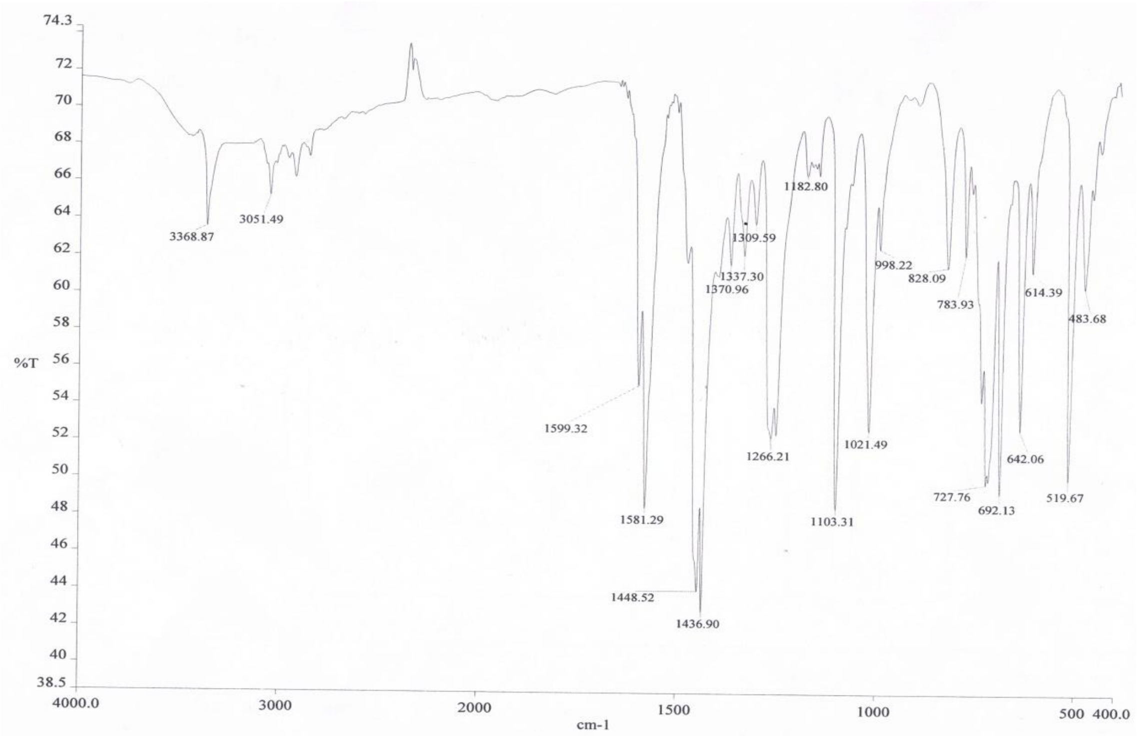


Fig. S5 IR spectrum of [2,6-($Ph_2P(S)$-NH_2)$_2$] (**LH_2**).

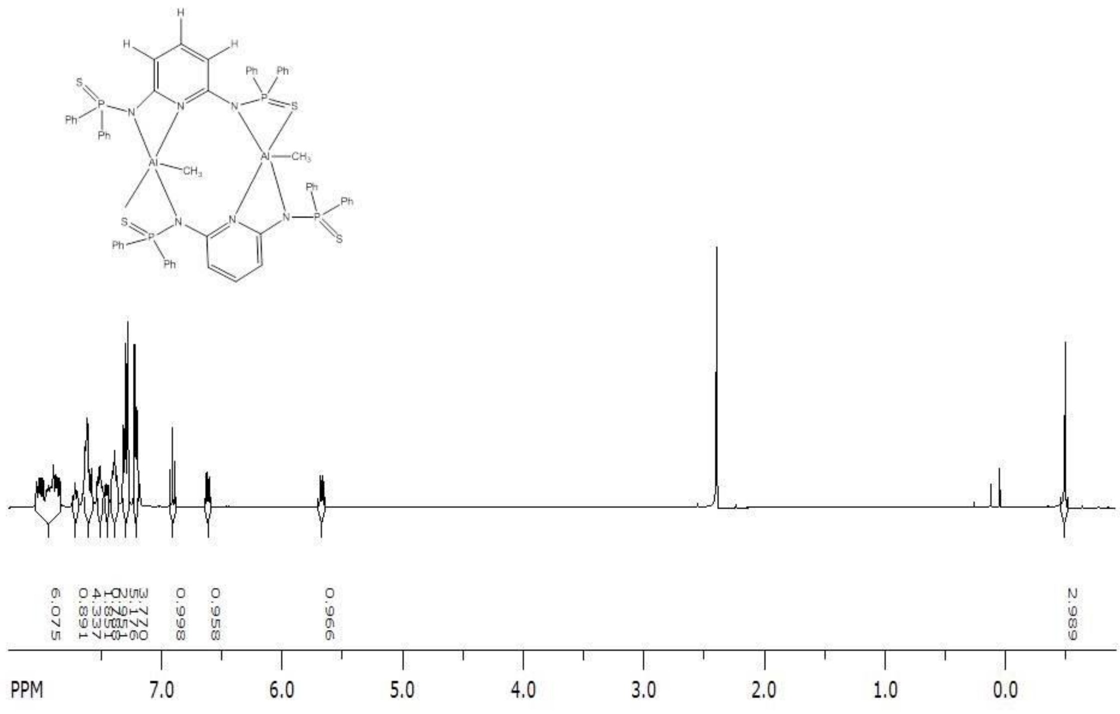


Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(S)$-N)$_2$AlMe]$_2$, **(LAlMe)$_2$** (**1**).

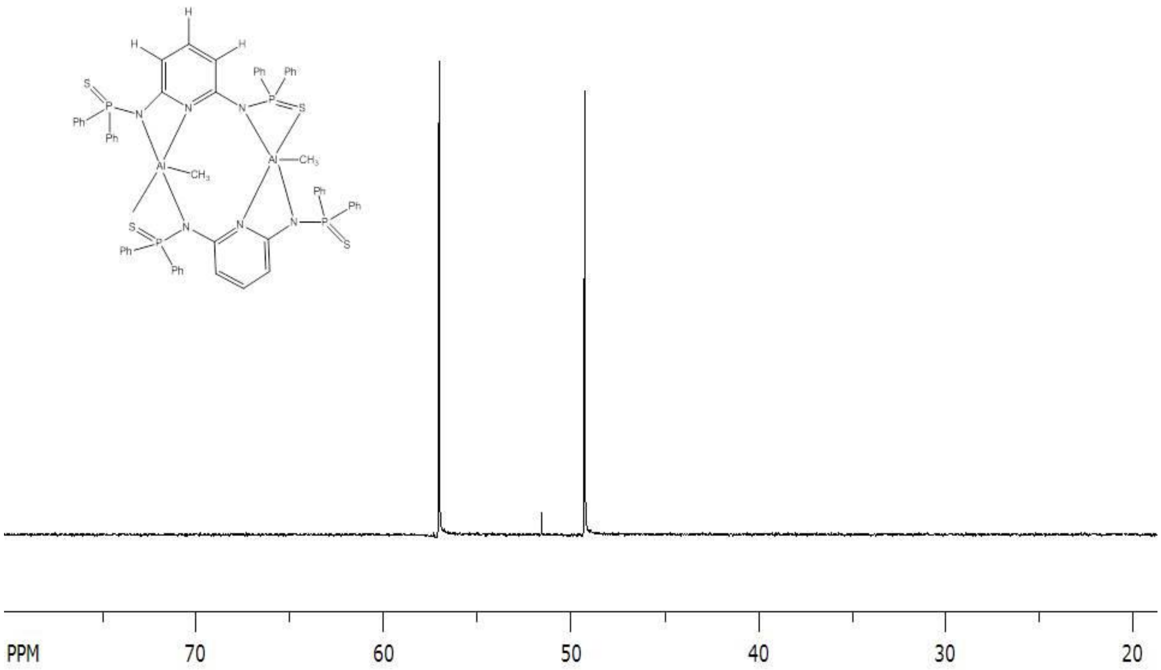


Fig. S7 $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(S)$-N)$_2$AlMe]$_2$, **(LAlMe)$_2$** (**1**).

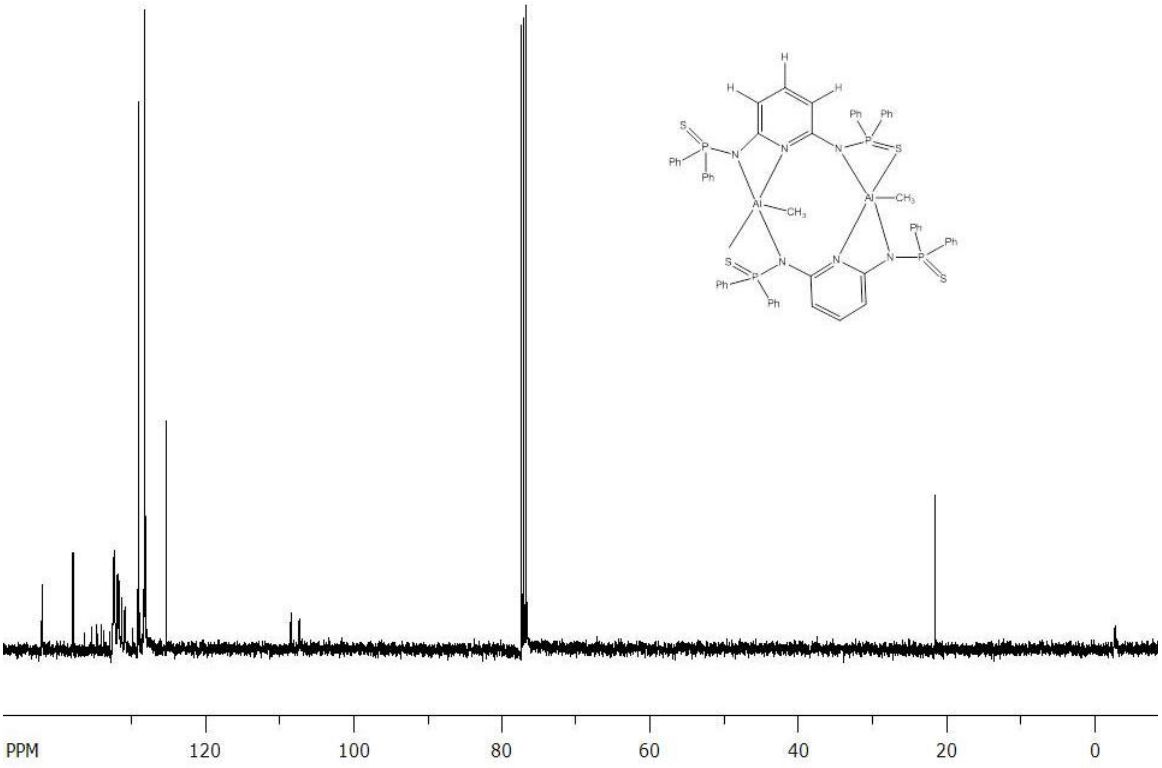


Fig. S8 ^{13}C NMR (100 MHz, $CDCl_3$)spectrum of [2,6-($Ph_2P(S)$-N)$_2$AlMe]$_2$, **(LAlMe)$_2$** (**1**).

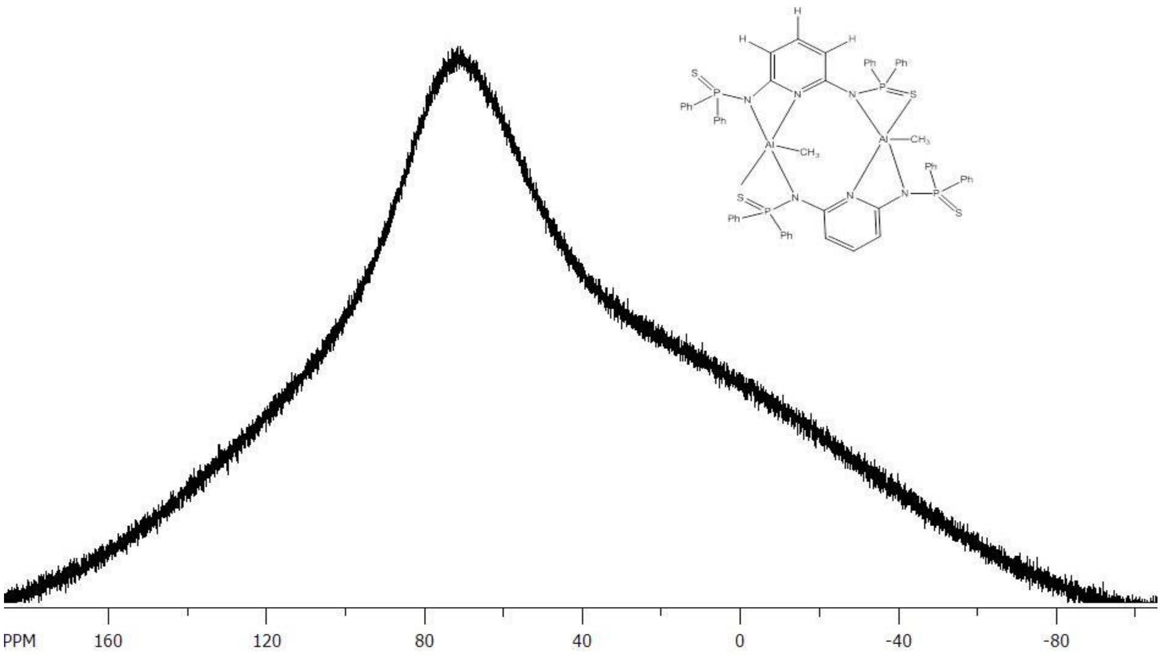


Fig.S9 ^{27}Al NMR (104MHz, CDCl$_3$) spectrum of [2,6-(Ph$_2$P(S)-N)$_2$AlMe]$_2$, **(LAlMe)$_2$** (**1**).

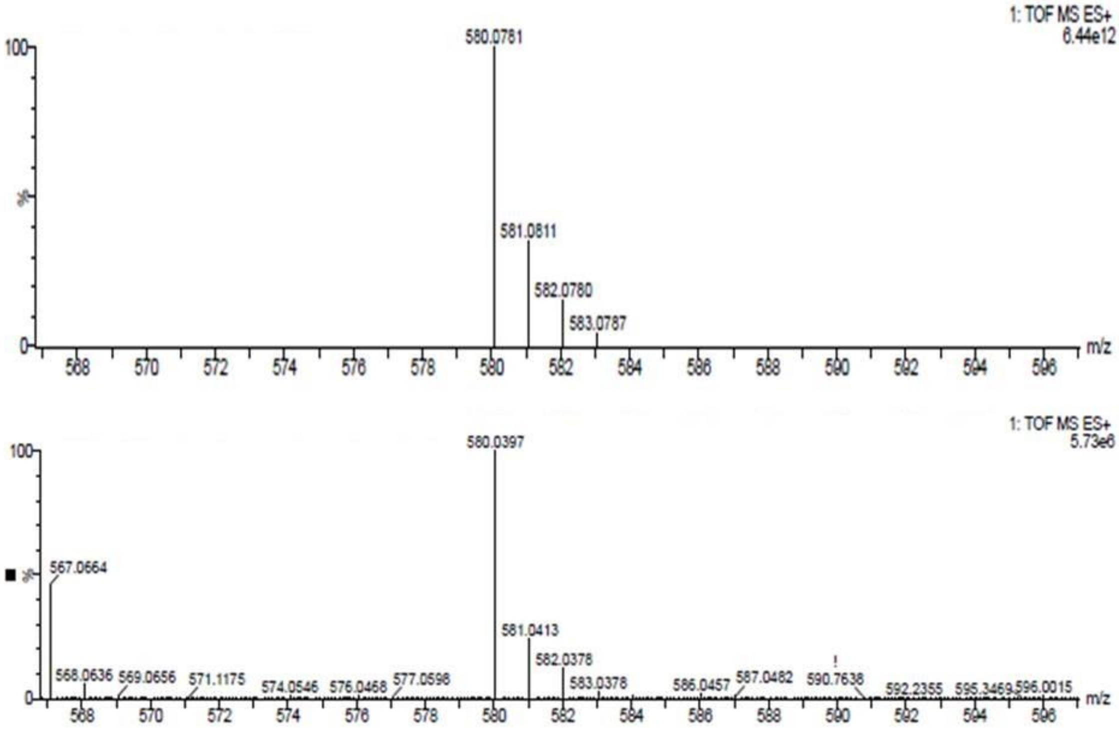


Fig.S10 Mass spectrum of [2,6-(Ph$_2$P(S)-N)$_2$AlMe]$_2$, **(LAlMe)$_2$** (**1**).

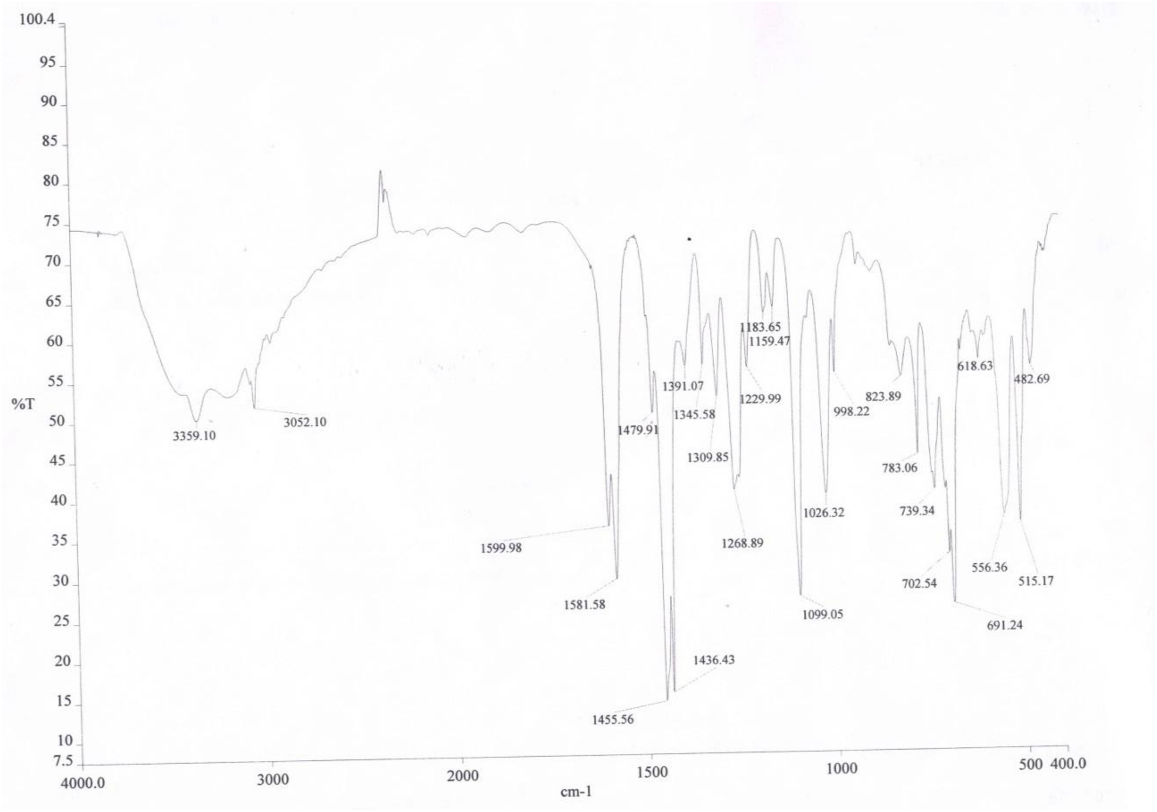


Fig.S11 IR spectrum of [2,6-($Ph_2P(S)$-N)$_2$AlMe]$_2$, **(LAlMe)$_2$** (**1**).

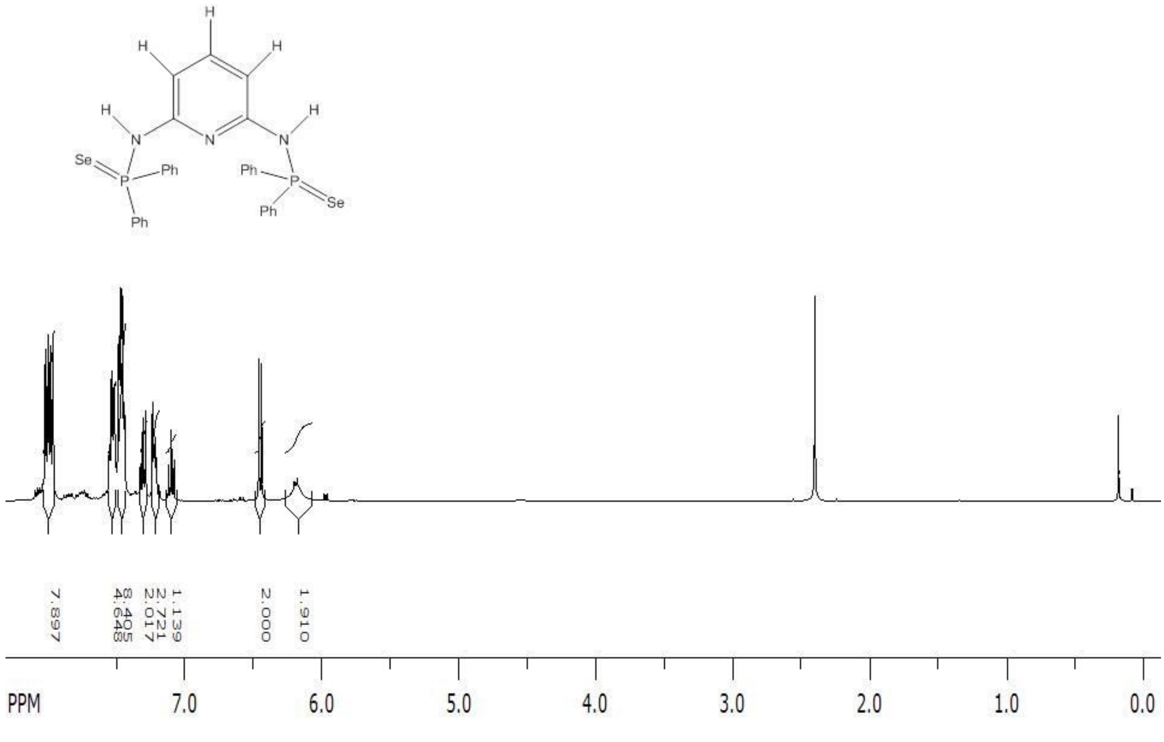


Fig.S12 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(Se)$-NH_2)$_2$] (**L′H$_2$**).

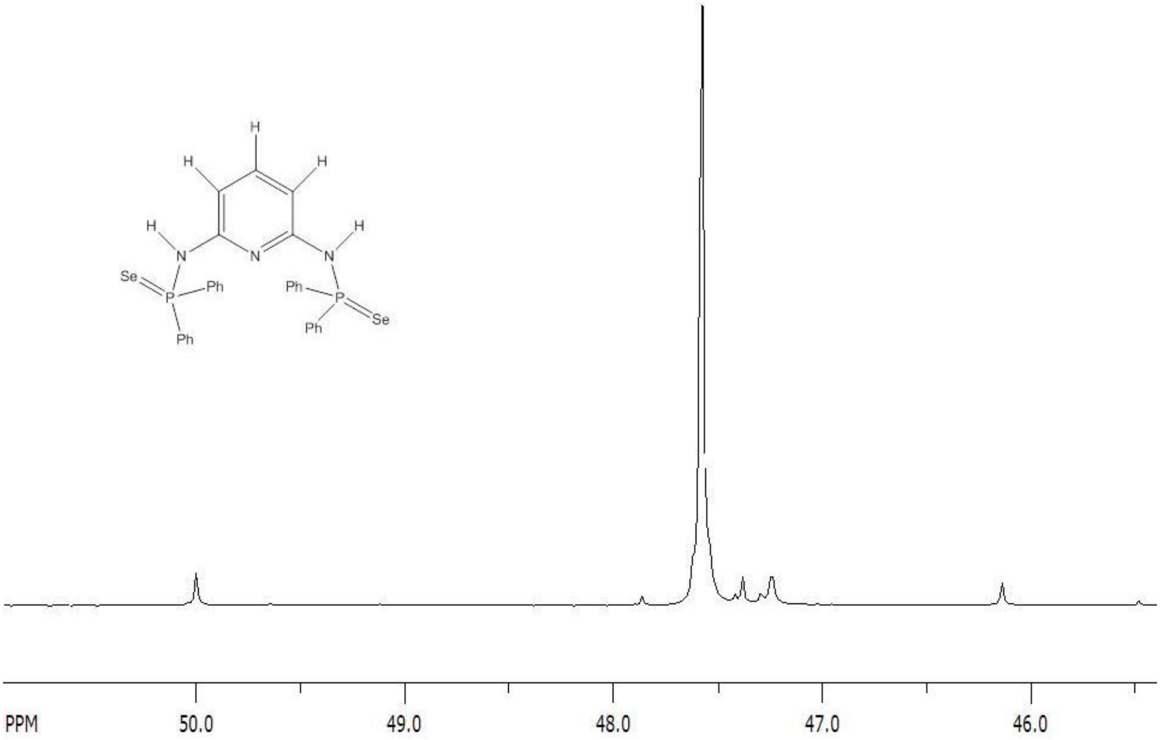


Fig.S13 $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(Se)-NH_2)_2$] (**L′H₂**).

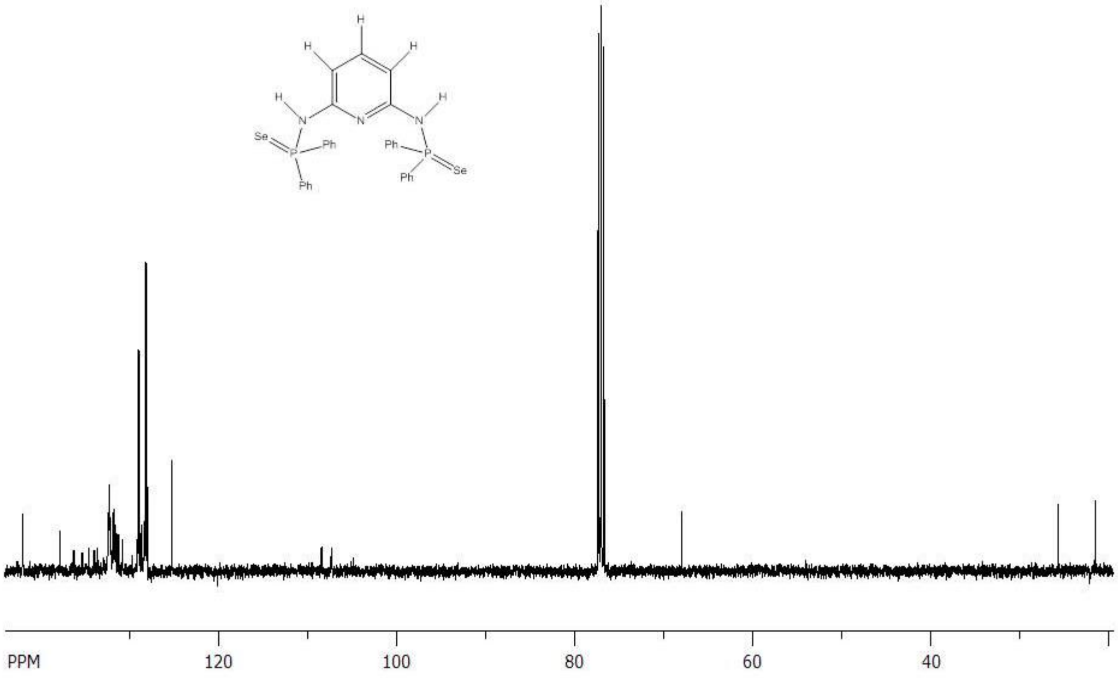


Fig.S14 ^{13}C NMR (100 MHz, C_6D_6)spectrum of [2,6-($Ph_2P(Se)-NH_2)_2$] (**L′H₂**).

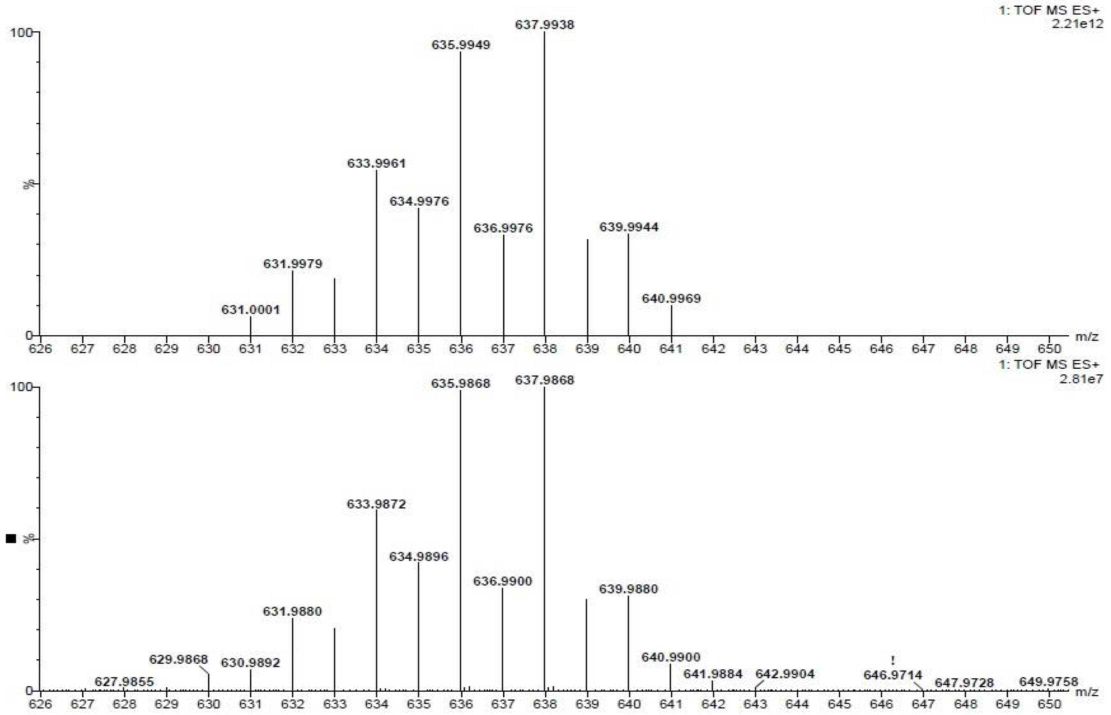


Fig.S15 Mass spectrum of [2,6-($Ph_2P(Se)$-NH_2)$_2$] (**L′H₂**).

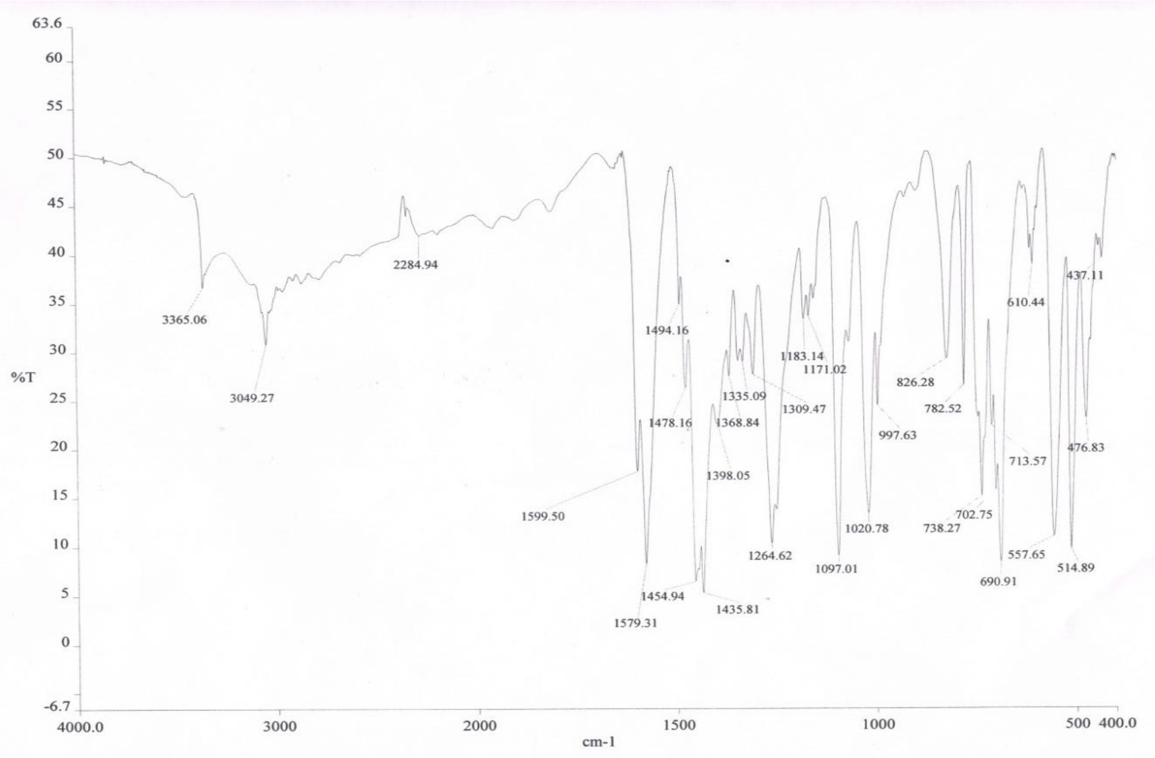


Fig.S16 IR spectrum of [2,6-($Ph_2P(Se)$-NH_2)$_2$] (**L′H₂**).

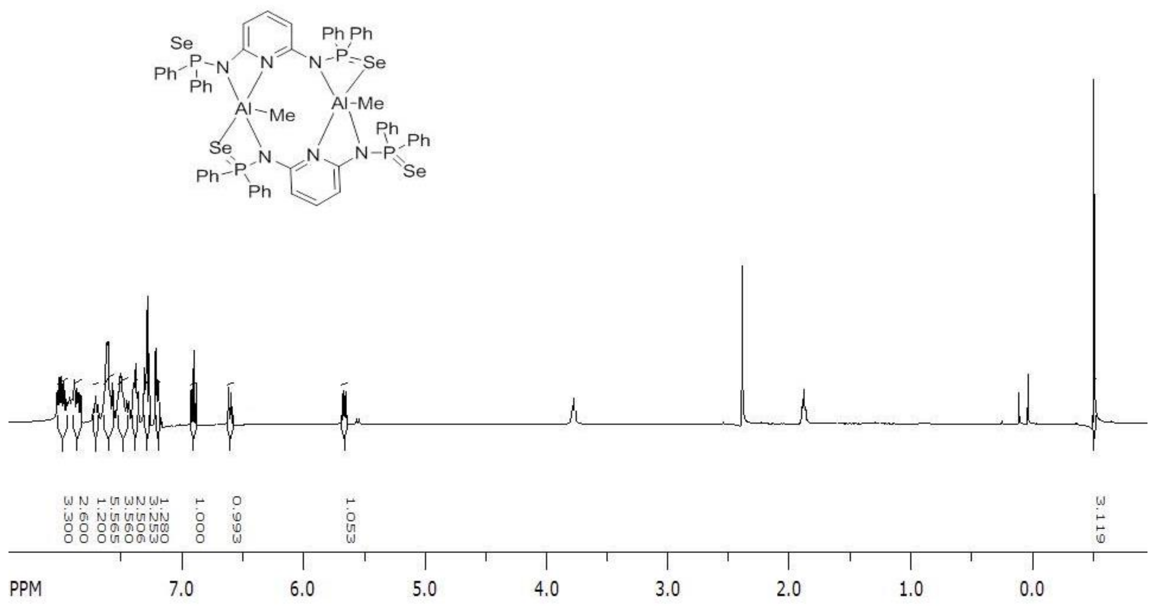


Fig.S17 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(Se)$-N)$_2$AlMe]$_2$, **(L′AlMe)$_2$** (**2**)

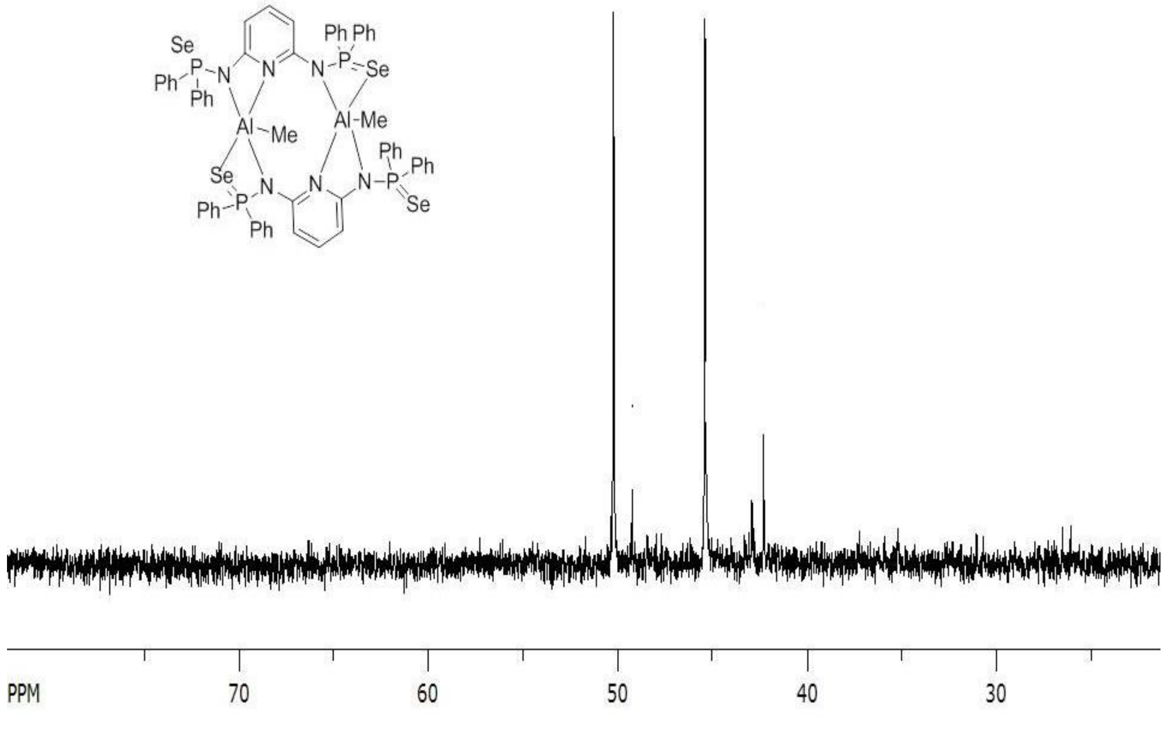


Fig.S18 ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) spectrum of [2,6-($Ph_2P(Se)$-N)$_2$AlMe]$_2$, **(L′AlMe)$_2$ (2).**

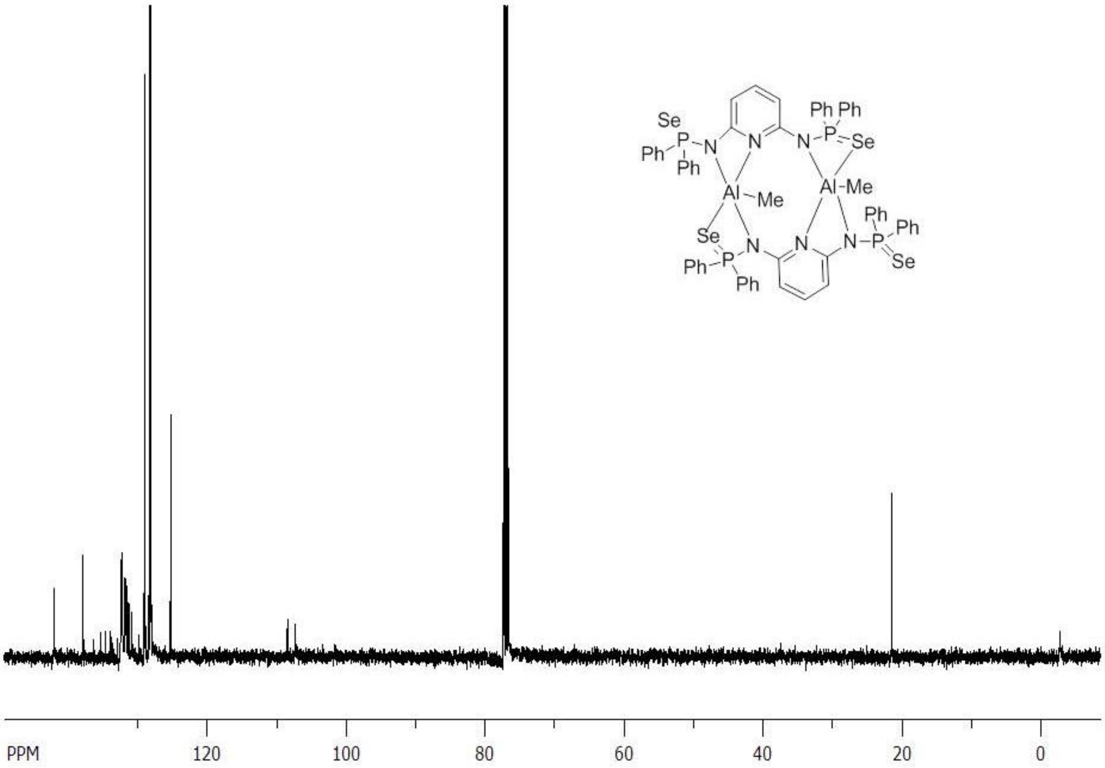


Fig.S19 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of [2,6-(Ph$_2$P(Se)-N)$_2$AlMe]$_2$, **(L′AlMe)$_2$ (2).**

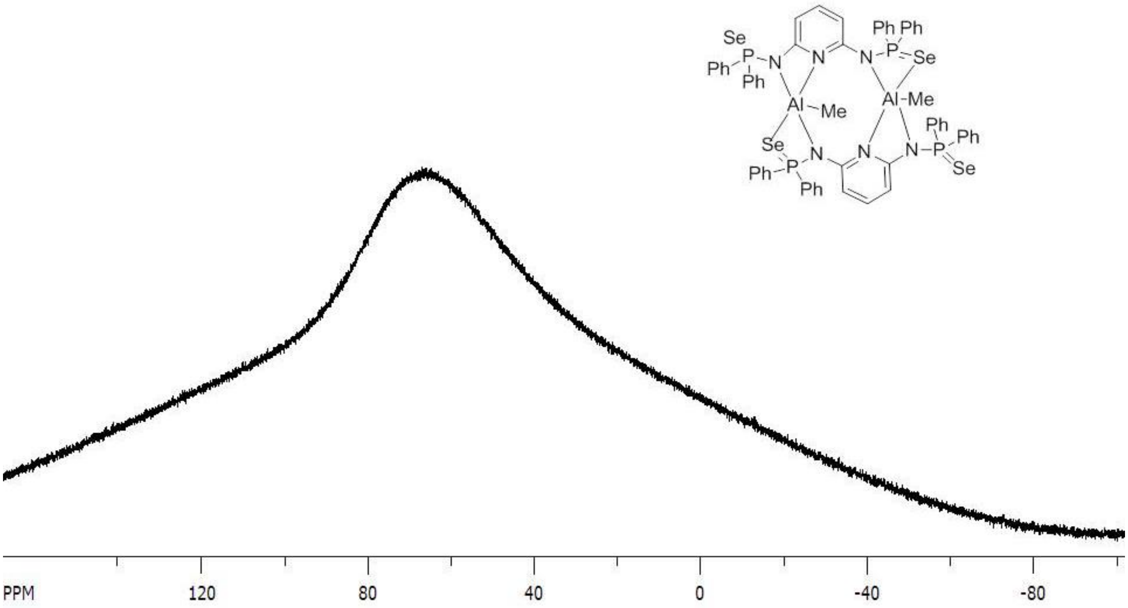


Fig.S20 ^{27}Al NMR (104MHz, CDCl$_3$) spectrum of [2,6-(Ph$_2$P(Se)-N)$_2$AlMe]$_2$, **(L′AlMe)$_2$ (2).**

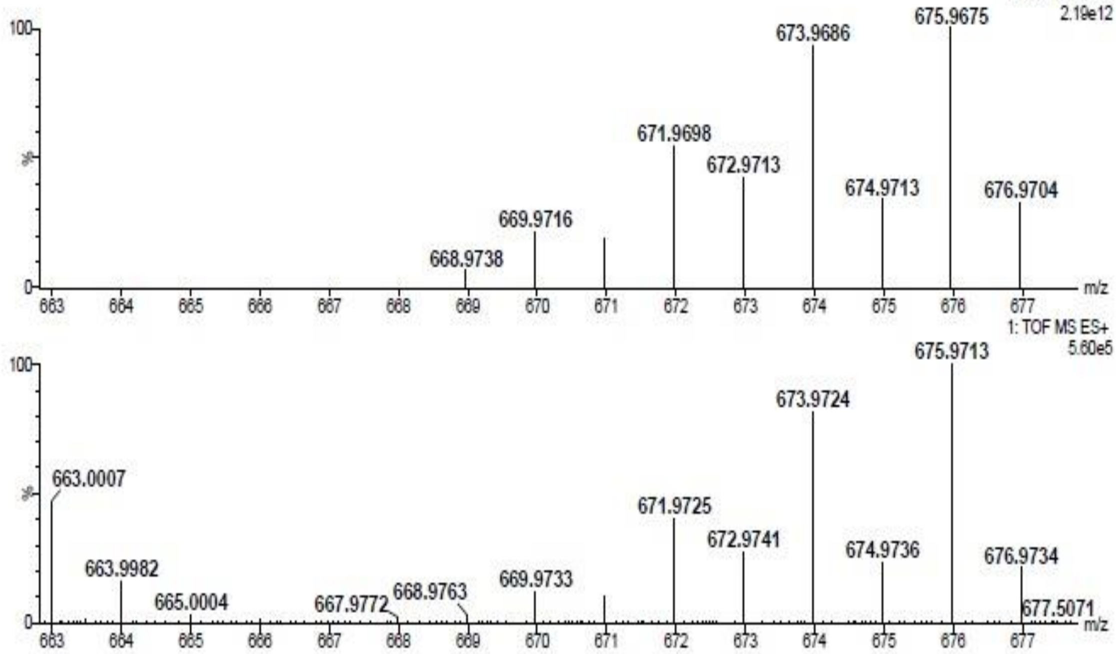


Fig.S21 Mass spectrum of [2,6-$(Ph_2P(Se)\text{-}N)_2AlMe]_2$, **(L′AlMe)₂** (**2**).

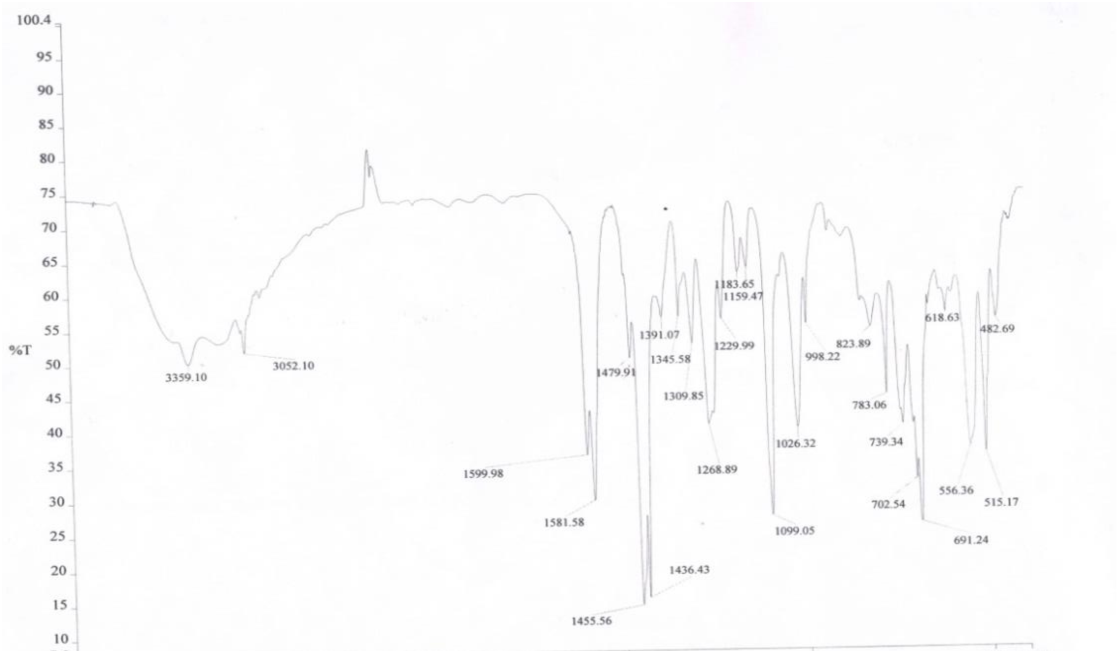


Fig.S22 IR spectrum of [2,6-$(Ph_2P(Se)\text{-}N)_2AlMe]_2$, **(L′AlMe)₂** (**2**).

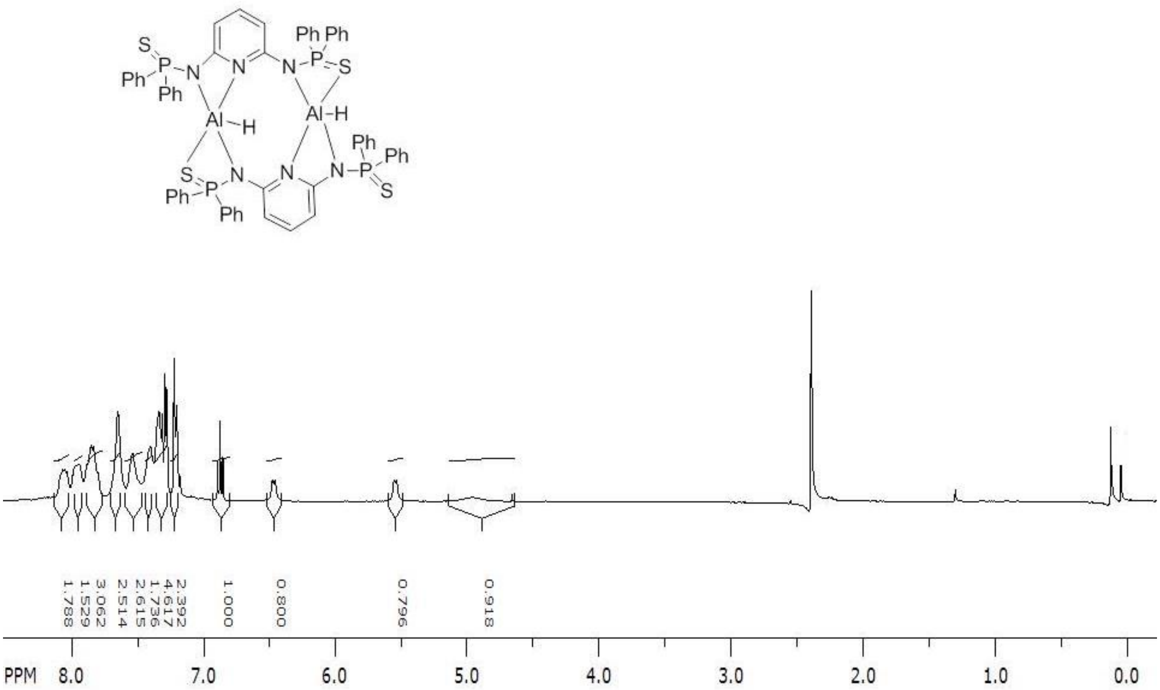


Fig.S23 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of [2,6-(Ph$_2$P(S)-N)$_2$AlH]$_2$, **(LAlH)$_2$** (**3**)

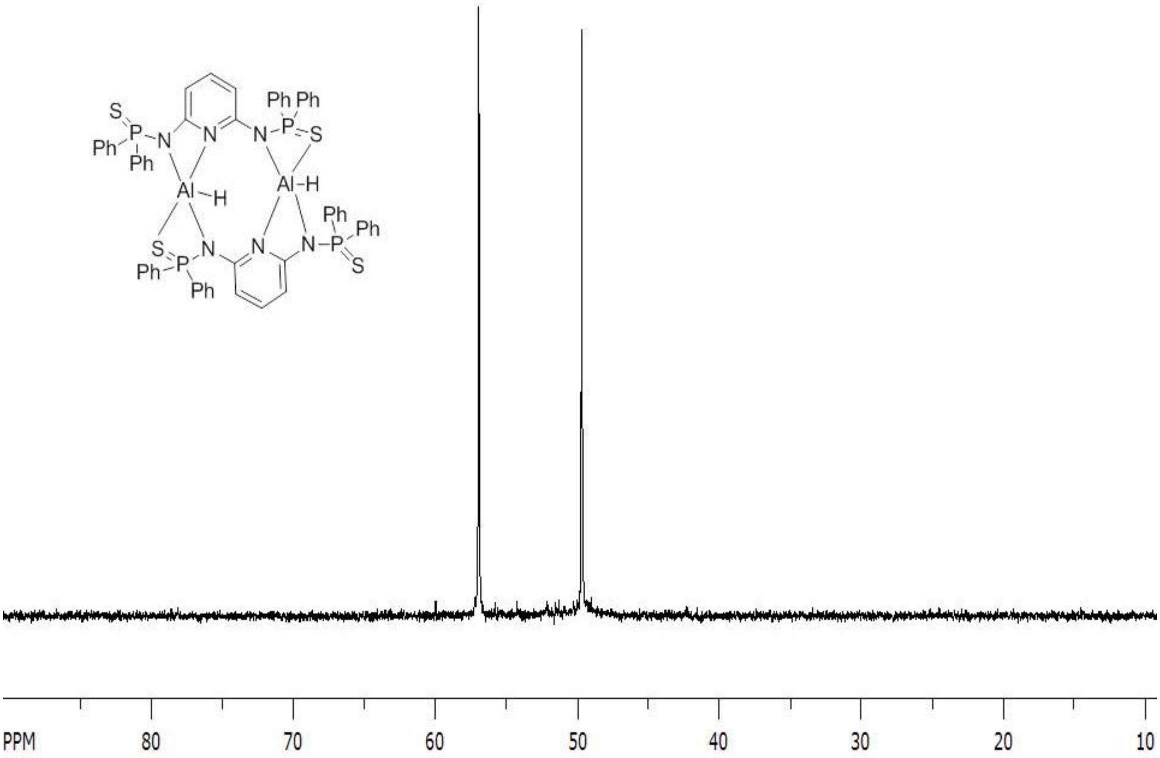


Fig.S24 ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) spectrum of [2,6-(Ph$_2$P(S)-N)$_2$AlH]$_2$, **(LAlH)$_2$** (**3**)

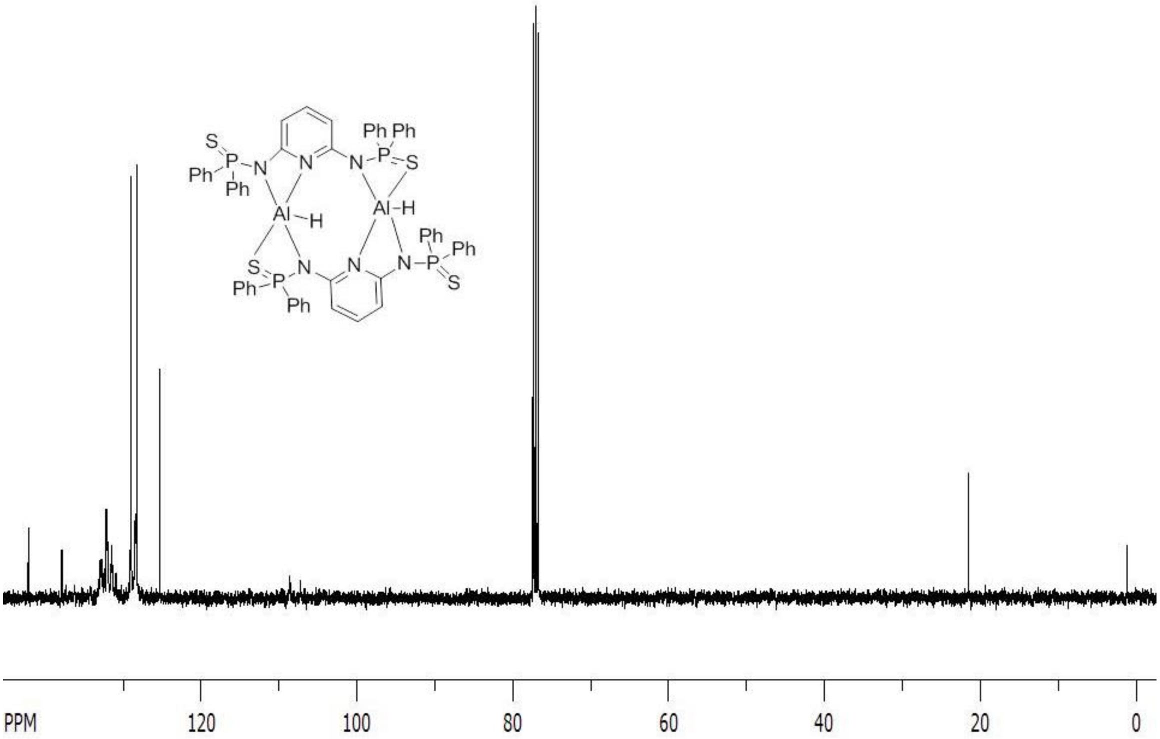


Fig.S25 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of $[2,6\text{-}(Ph_2P(S)\text{-}N)_2AlH]_2$, **$(LAlH)_2$** (**3**)

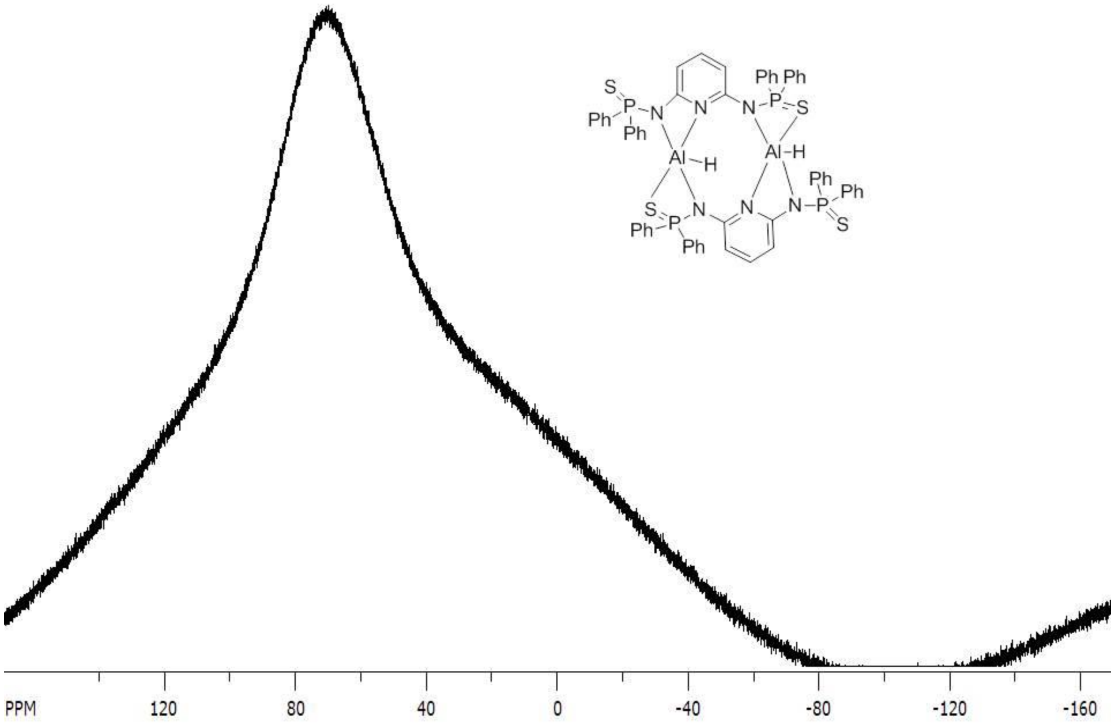


Fig.S26 ^{27}Al NMR (104 MHz, $CDCl_3$) spectrum of $[2,6\text{-}(Ph_2P(S)\text{-}N)_2AlH]_2$, **$(LAlH)_2$** (**3**)

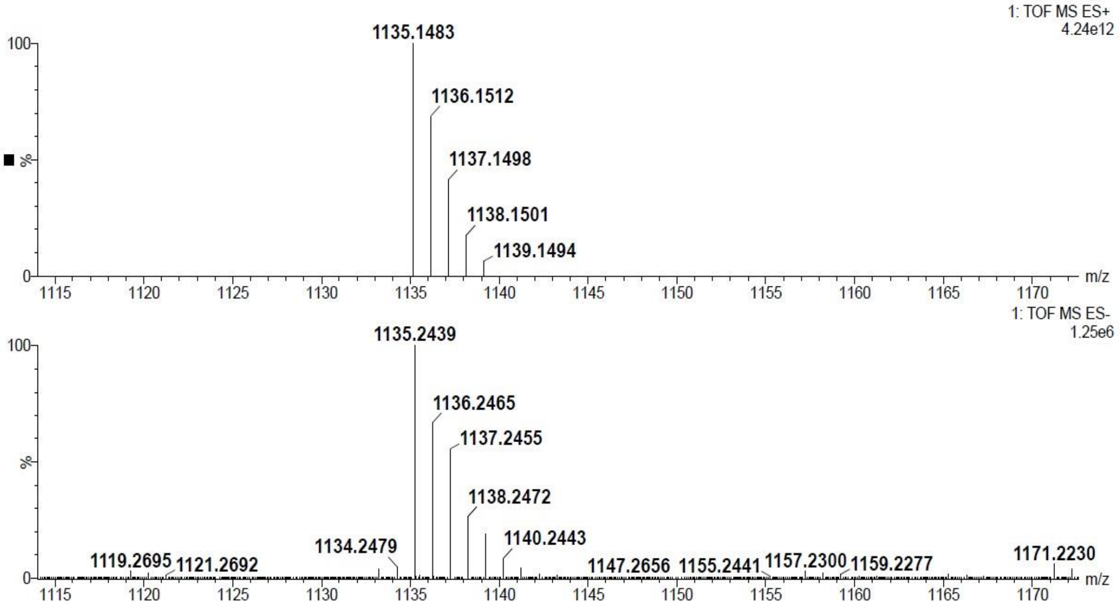


Fig.S27 Mass spectrum of [2,6-($Ph_2P(S)$-N)$_2$AlH]$_2$, **(LAlH)$_2$** (**3**)

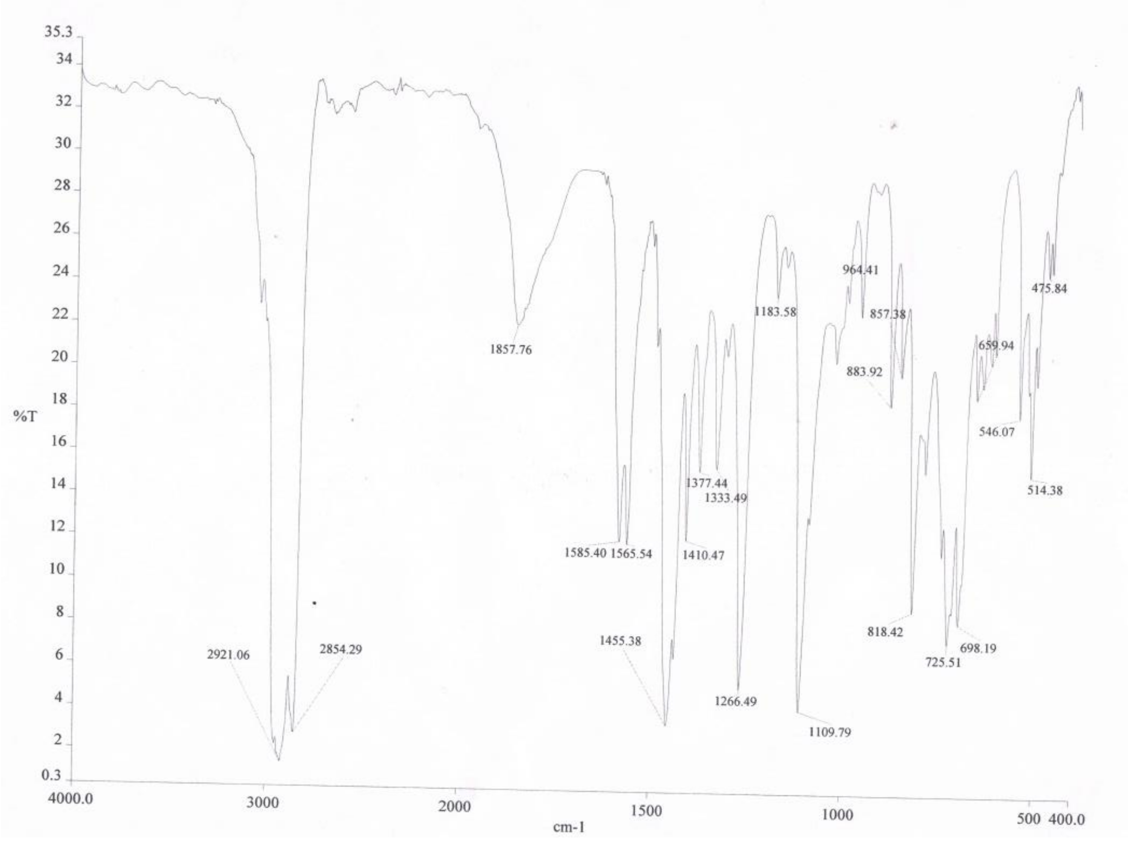


Fig.S28 IR spectrum of [2,6-($Ph_2P(S)$-N)$_2$AlH]$_2$, **(LAlH)$_2$** (**3**)