

Université  
de Toulouse

# ABSTRACT THESIS



*Lucian-Cristian Pop*

**Title : N,N'- and N,O-chelated pnictogenium cations (P, As, Sb) and germynes:  
syntheses, structural studies and reactivity**

**Pnictogénium cations (P, As, Sb) et germylènes à ligands N,N' et  
N,O-chélatants: synthèse, étude structurale et réactivité**

---

## JURY

*Mr. I. Mangalagiu, Professor at «Al.I.Cuza» University, Iași*

*Mr. J. Moreau, Professor at «Université de Montpellier», Montpellier*

*Mr. M. Drăbanu, Professor at «Babeș-Bolyai» University, Cluj-Napoca*

*Mr. P. L. Fabre, Professor at «Université de Toulouse III», Toulouse*

*Ms. L. Silaghi-Dumitrescu, Professor at «Babeș-Bolyai» University, Cluj-Napoca,  
Thesis director*

*Ms. A. Castel, Researcher at C.N.R.S., Toulouse, Thesis director*

---

**Scientific Advisers : Ms. L. Silaghi-Dumitrescu, Ms. A. Castel**

"Nothing in life is to be feared. It is only to be understood."  
"Be less curious about people and more curious about ideas."

**Marie Skłodowska Curie** - Polish - French physicist and chemist

"Science knows no country, because knowledge belongs to humanity, and is the torch which illuminates the world."

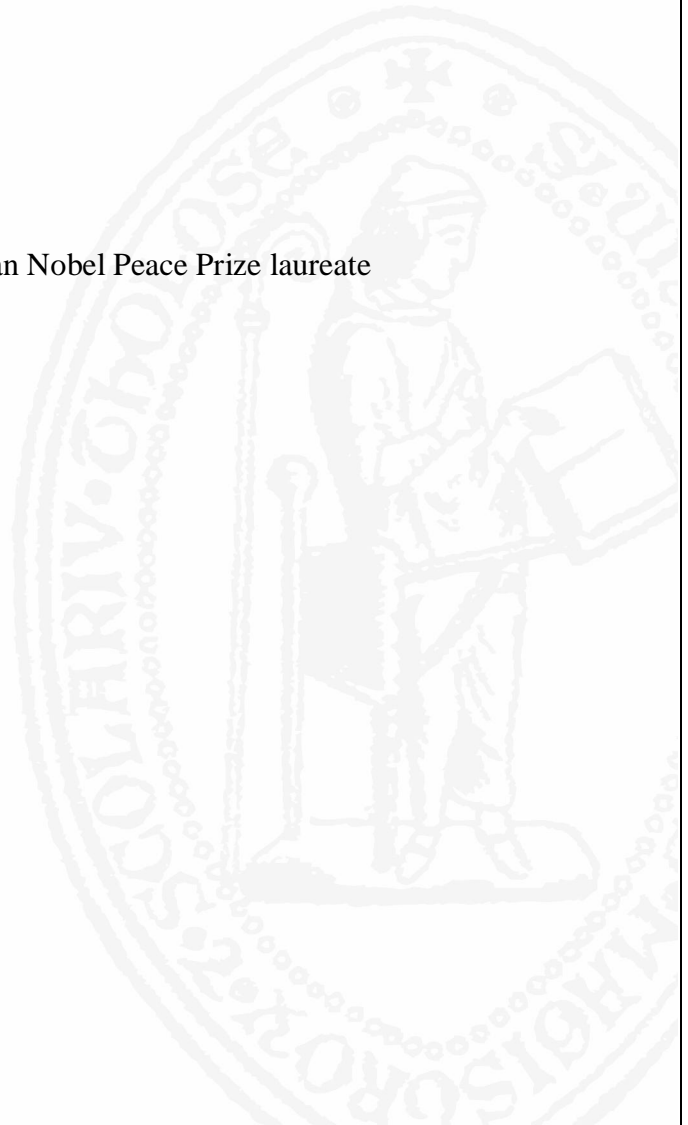
**Louis Pasteur** - French chemist and microbiologist

"The difficulty lies, not in the new ideas, but in escaping the old ones, which ramify, for those brought up as most of us have been, into every corner of our minds."

**John Maynard Keynes** - British economist

"Peace is our gift to each other."

**Elie Wiesel** – Romanian-born Jewish-American Nobel Peace Prize laureate



## Table of contents

General introduction	5
General Data and Instrumentation	9
Abbreviations and symbols	10

### CHAPTER I

#### *Pnictogenium cations: synthesis and spectroscopic studies*

Resume	12
Introduction	15
1.1 Synthesis of complexes of P, As and Sb	20
1.1.1 Synthesis of ligand precursors	20
1.1.2 Synthesis of tropolone complexes of P and As	21
1.1.3 Synthesis of aminotroponimate and aminotroponate complexes of P, As and Sb	23
1.2 Spectroscopic characterisation of aminotroponimate and aminotroponate complexes of P, As and Sb	27
1.2.1 NMR properties	28
1.2.1.1 <sup>1</sup> H NMR	28
1.2.1.2 <sup>13</sup> C NMR	32
1.2.2 Mass spectrometry study	35
1.2.3 X-Ray structural determination	35
1.3 Computational studies	39
Conclusions and perspectives	44
Experimental section	45
X-ray structures	56
Details on Computations	59
References	60

### CHAPTER II

#### *Pnictogenium cations: reactivity*

Resume	64
Introduction	67

2.1 Halide ion exchange	67
2.2 Oxidative reactions with dimethylsulfoxide, sulfur and selenium	73
2.3 Cycloaddition reaction with <i>o</i> -quinone	84
2.4 Complexation with transition metals	87
Conclusions and perspectives	94
Experimental Section	95
X-ray Structural Determination	111
References	116

### *CHAPTER III*

#### **Bridged bis(pnictogenium cations) and bis-germylenes: syntheses, spectroscopic studies and reactivity**

Resume	118
Introduction	121
3.1 Bridged bis(pnictogenium cations) (P, As, Sb)	122
3.1.1 Synthesis of ligand precursors	122
3.1.2 Synthesis of the dilithiated ligands salt	123
3.1.3 Synthesis of the bis-cations of P, As and Sb	128
3.2 Bis-germylenes	133
3.2.1 Synthesis of monogermlyenes and bis-germylenes	135
3.2.2 Computational studies	137
3.2.3 Chemical reactivity of germlyenes	142
3.2.3.1 Oxidative reactions with sulfur and selenium	142
3.2.3.2 Cycloaddition reaction with <i>o</i> -quinone	148
3.2.3.3 Complexation with transition metals	149
Conclusions and perspectives	154
Experimental Section	155
X-ray Structural Determination	185
References	188
General Conclusions	192
Compound Number Summary	196

# CHAPTER I Pnictogenium cations: synthesis and spectroscopic studies

## Introduction

Pnictogenium cations  $[R_2E_{15}]^+$  ( $E_{15} = N, P, As, Sb, Bi$ ) have attracted steady interest since the discovery of the first stable phosphonium some 40 years ago<sup>[1]</sup> both for fundamental purposes and for applications in the design of novel catalysts<sup>[2-3]</sup>.

Phosphenium cations ( $[R_2P:]^+$ ) are the isolobal and isovalent analogues of singlet carbenes<sup>[4]</sup>. Carbenes are compounds with a neutral divalent carbon atom and only six electrons in its valence shell<sup>[5],[6]</sup> having the general formula  $R_2C:$ . In terms of the electronic theory of bonding, which says that bonds between atoms are formed by a sharing of electrons, a carbene is a compound in which only two of the four valence, or bonding electrons of a carbon atom are actually engaged in bonding with other atoms. Phosphenium cations as carbenes have a formally  $sp^2$ -hybridized central element and a lone pair of electrons in a  $\sigma$ -type orbital, as well as an unhybridized, empty  $np$   $\pi$ -type orbital (Chart 1). Because of this electronic structure, such species are expected to be both amphiphilic and amphoteric<sup>[4]</sup>.

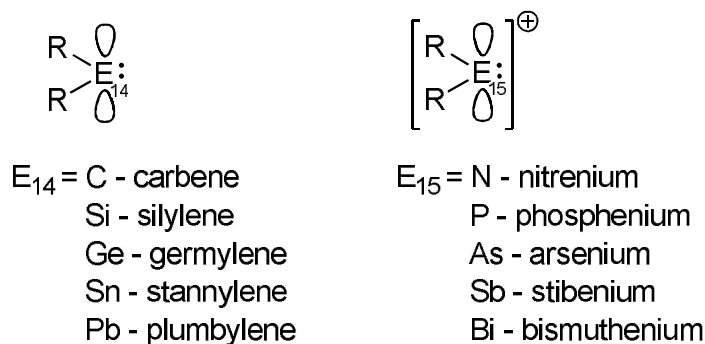


Chart 1

In another view, phosphenium ions can be also considered to constitute one member of an isoelectronic series that extends from silicenium<sup>[7]</sup> to chloronium<sup>[8]</sup> ions (Chart 2).

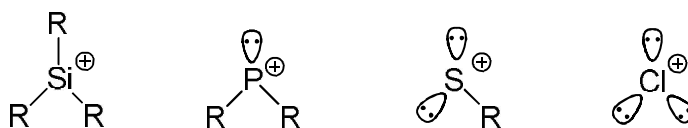


Chart 2

The birth certificate was signed in 1964 when the first stable phosphonium cations (**I**, **II**) were synthesized by Dimroth and Hoffmann<sup>[1]</sup> (Chart 3).

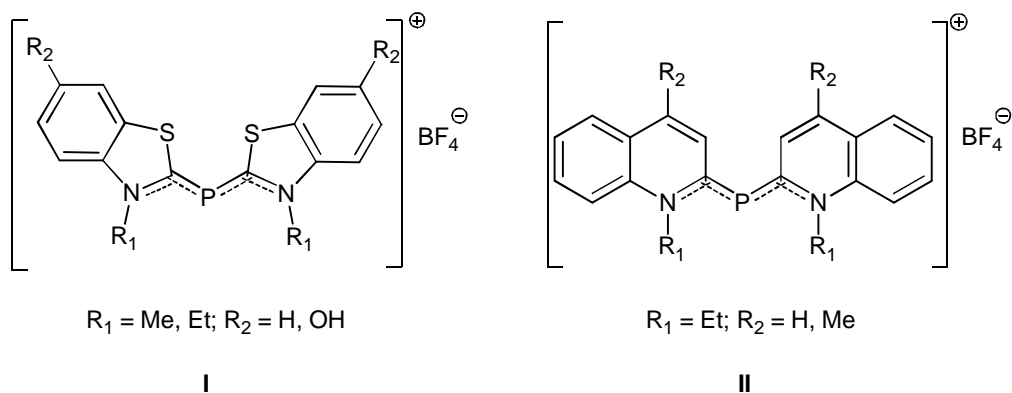


Chart 3

In 1972 the first stable cyclic phosphonium cations were reported independently by Fleming et al.<sup>[9]</sup> **III** and by Maryanoff and Hutchins<sup>[10]</sup> **IV**. From 1972 and onwards, the chemistry of these species has grown strongly; the first three X-Ray structural determinations (**V** - **VII**) date from 1978 (Cowley et al.<sup>[11]</sup>, Schmidpeter et al.<sup>[12]</sup>) and 1979 (Pohl et al.<sup>[12-13]</sup>) for the following species (Chart 4).

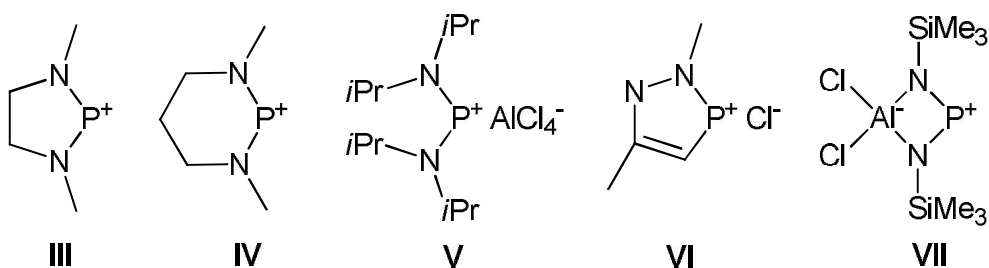


Chart 4

In 1985, Cowley and Kemp<sup>[14]</sup> emphasized the increasing interest in the study of this species isoelectronic with carbene. The presence of a vacant orbital and a lone pair confers to these amphoteric derivatives a great diversity in reactivity in organic chemistry and in coordination chemistry.

Their stability depends on charge delocalization by using heteroatom bonding or/and by incorporation of the pnictogen atom into a conjugated  $\pi$ -system. Generally, the used substituents present electron rich centers that allow  $\pi$ -donation upon the cationic phosphorus center  $[\text{V}^{\text{I11}}, \text{Me}_2\text{N}(\text{Cl})\text{P}^+]^{\text{I15-16}}$ . A large variety of cyclic structures has been reported<sup>[14, 17-19]</sup> represented by **IX** – **XIV**<sup>[3]</sup> (Chart 5), among them the cyclic five membered one seems to dominate.

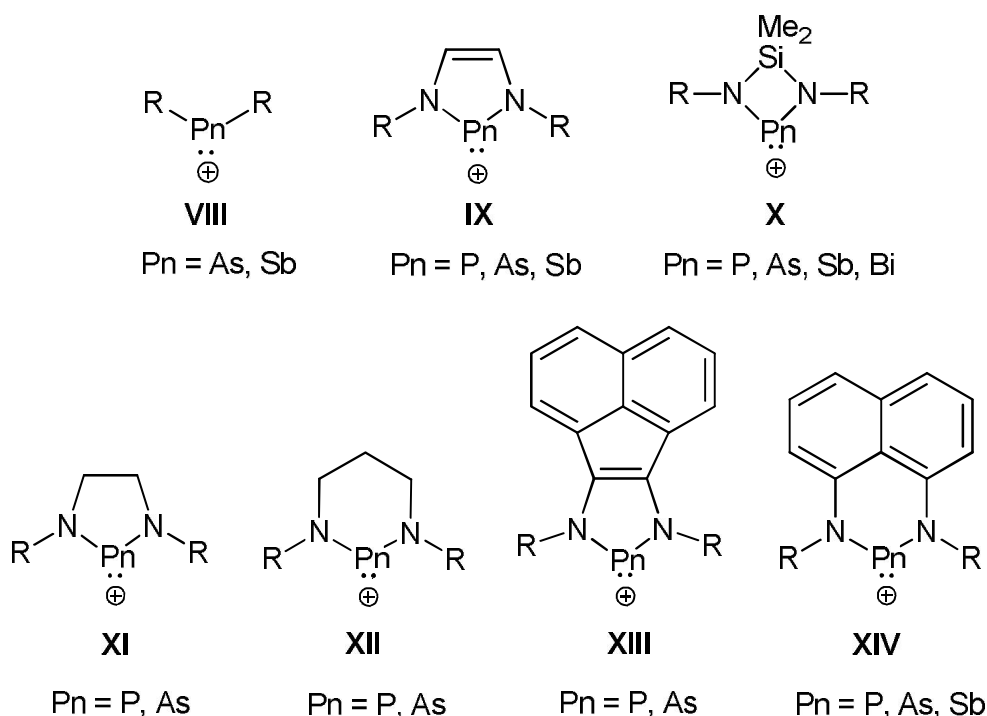
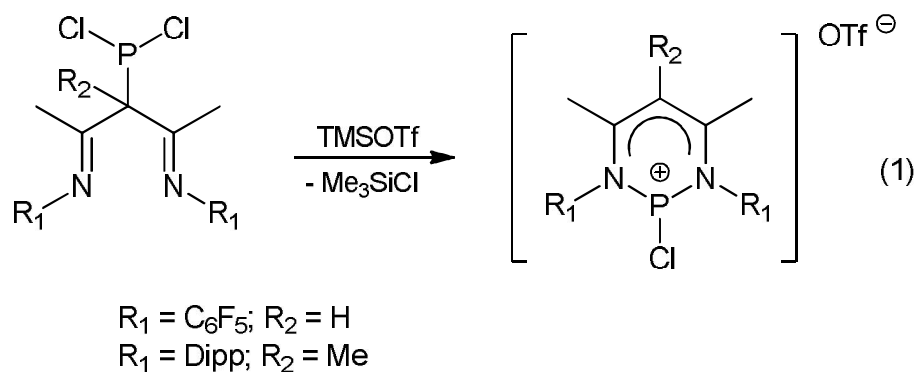


Chart 5

More recently, some tricoordinated species having aminoiminoligands with a covalent  $\text{E}_{15}\text{-N}$  bond and a coordinative  $\text{E}_{15}\text{-N}$  bond have been reported. Examples of such ligands include  $\beta$ -diketiminates<sup>[20]</sup> and amidinates<sup>[21]</sup>. However, the use of a  $\beta$ -diketiminato ligand suffers from a lack of generality since the preparation of a  $\text{N,N}'$ -chelated phosphonium cation supported by a  $\beta$ -diketiminato ligand hinges on the use of: i) an electronegative substituent (e.g.  $\text{C}_6\text{F}_5$ ) at the nitrogen atoms and/or ii) of an alkyl substituent at the  $\gamma$ -carbon of the  $\beta$ -diketiminato to circumvent phosphorus substitution at this site (Equation 1). Moreover, computational studies suggest that a  $\beta$ -diketiminato ligand was unsuitable for stabilization of pnictogenium cations<sup>[22]</sup>.



In spite of the fact that the major part of work has been dedicated to phosphonium ions, cations with other group - 15 elements were also prepared. Today, stable cations centered at dicoordinate arsenic and antimony are known as well, even if examples of low valent antimony complexes are not so common than their phosphorus counterparts.

Examples of genuine cations **VIII**<sup>[23-24]</sup> became known<sup>[25]</sup> only over the last decades. Their stability relies commonly on mesomeric interaction with  $\pi$ -donor substituents<sup>[14],[19, 23-24]</sup> and practically all stable cations known carry one or two amino ( $NR'_2$ ) or thiolato ( $SR'$ ) groups. As previously described in the case of phosphoniums, this mesomeric stabilization can be enhanced by incorporating the dicoordinate species into an unsaturated ring (**IX**<sup>[18, 26-28]</sup>, Chart 5).

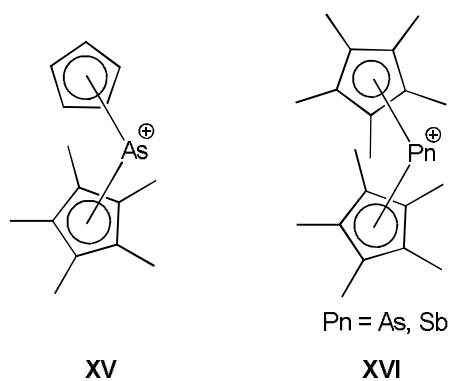
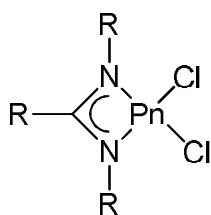


Chart 6

Low coordinate cationic arsenic centres have also been observed in the particular  $Cp^*AsCp$  and  $Cp^*_2Pn$ , **XV** and **XVI**<sup>[29]</sup>, which involve a bent sandwich  $\pi$ -complex coordination (Chart 6). Isolation of the first structurally characterized example was only made possible by incorporating the dicoordinate As unit into a diamidonaphthenic framework (**XIII**, Chart 5)<sup>[31]</sup>.

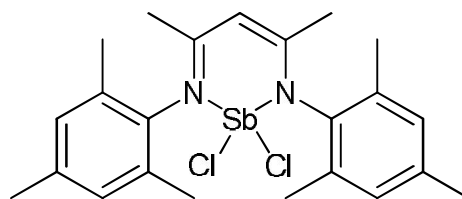


Just a few compounds with amino-imino ligands were reported and in all cases only the formation of antimony and bismuth dichloro species was observed (**XVII**, **XVIII**, Chart 7)<sup>[30-31]</sup>.



Pn = Sb, Bi

**XVII**

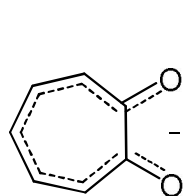


**XVIII**

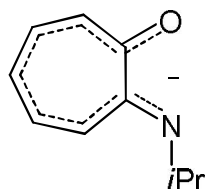
Chart 7

All attempts to chloride ion abstraction failed leading to the ligand salt.

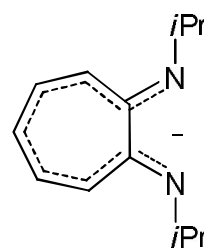
As a part of our ongoing studies of strategies to stabilize low-coordinate phosphorus atom,<sup>[32] [33]</sup> we identified the monoanionic ligands: tropolonate (from the neutral 2-hydroxy-2,4,6-cycloheptatrien-1-one), aminotroponate (from the neutral 2-(isopropylamino)cyclohepta-2,4,6-trien-1-one) and aminotroponimate (from the neutral N-isopropyl-7-(isopropylimino)cyclohepta-1,3,5-trien-1-amine) where the hydroxy and carbonyl groups are successively replaced par amino or/and imino groups (Chart 8) as highly promising candidates for stabilizing phosphonium ions. These ligands are particularly useful as they can be prepared in high yields, crystallize easily and have the ability to stabilize low oxidation state compounds.



Tropolonate



Aminotroponate



Aminotroponimate

Chart 8

Tropolone is formally an  $\alpha$ -diketone, non-benzenoid aromatic compound in the form of a seven-membered ring. The tropolonato anion is a bidentate ligand, which forms a five-

membered chelate ring upon complexation to a metal ion. The functional groups of tropolone (carbonyl and hydroxyl) make it possible to coordinate a number of different d-block and f-block metal ions (in oxidation states from +I to +VI). Having all these properties, tropolone and its derivatives have been studied in various fields such as medicine, material science and agriculture<sup>[34-37]</sup>.

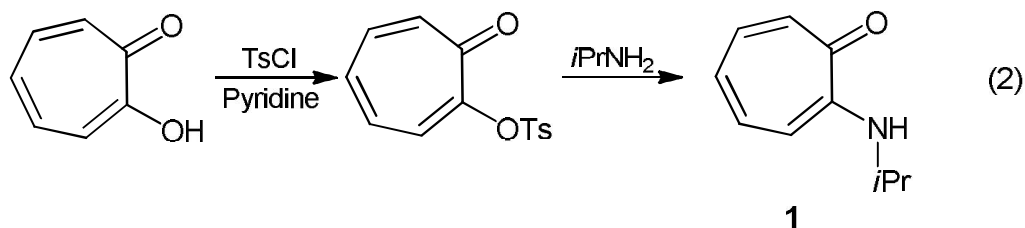
Aminotroponimines ([ATI]<sup>-</sup>) are a well known class of ligands which have found extensive use in coordination chemistry leading to a large number of transition-metal and main-group complexes<sup>[38-39]</sup>. On one hand, this ligand displays heteroatom bonding and a highly conjugated 10  $\pi$ -electron system that should allow charge delocalization when incorporating the pnictogenium atom in the  $\pi$ -electron backbone. On the other hand, and in marked contrast to the  $\beta$ -diketiminato scaffold, [ATI]<sup>-</sup> is expected to form stable five-membered chelate rings and its anticipated fused ring structure should disfavor side reactions analogous to those observed in the  $\beta$ -diketiminato system. Only a few aminotroponate complexes of main-group<sup>[40]</sup> and transition-metals<sup>[41-45]</sup> are known. However, in both cases the coordination chemistry of these ligands by electron-rich elements from Groups 15 to 17 remains totally unexplored.

## 1.1 Synthesis of complexes of P, As and Sb

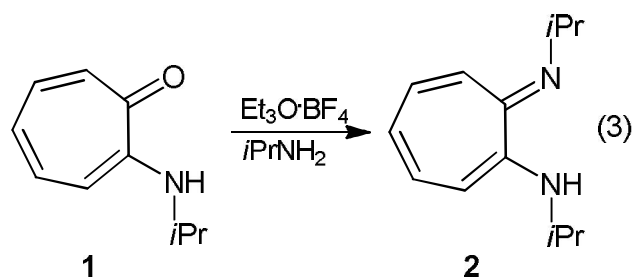
Besides the tropolone which was purchased from Aldrich and used as received, we prepared the ligand precursors, the aminotropone and aminotroponimine.

### 1.1.1 Synthesis of ligand precursors

The 2-(isopropylamino)tropolone [(iPr)ATI]H, **1**, was synthesized by a direct nucleophilic displacement of the tosyl group from the 2-(tosyloxy)tropolone using an excess of isopropylamine and was isolated in 97 % yield (Equation 2).



Starting from 2-(isopropylamino)tropolone, an ethylation reaction with Et<sub>3</sub>O·BF<sub>4</sub> followed by the treatment with excess of isopropylamine gave [(iPr)<sub>2</sub>ATI]H **2** as a bright yellow solid (Equation 3).



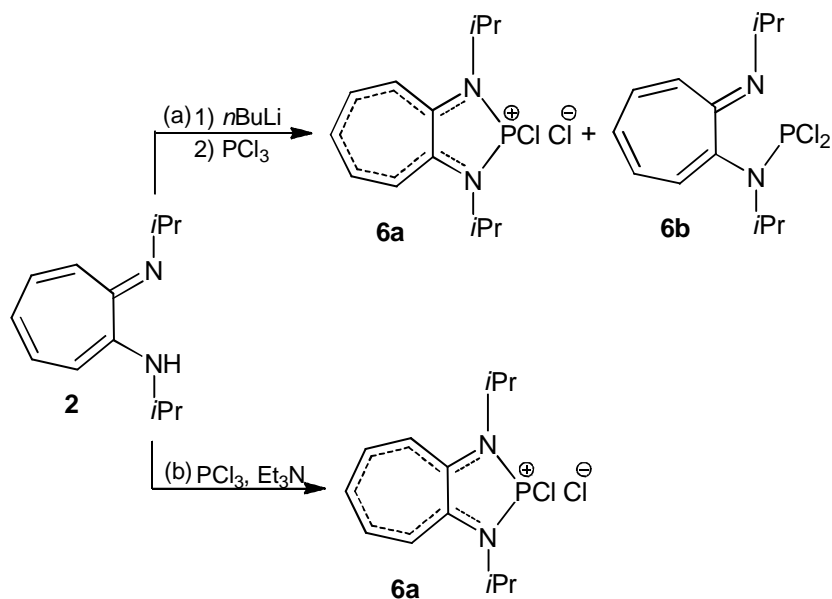
All these compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, the results being in accordance with the literature data<sup>[46]</sup>.

### 1.1.2 Synthesis of tropolone complexes of P and As

The chemical reactions starting from tropolone proved to be much more complex regardless of the path followed: dehydrochloride coupling reaction or action of lithiated derivatives. Indeed, the absence of bulky groups such as amino (N-*i*Pr) can promote the grafting of several tropolone entities on phosphorus.

### 1.1.3 Synthesis of aminotroponimate and aminotroponate complexes of P, As and Sb

We then extended these reactions to aminotroponimate and aminotroponate ligands<sup>[47]</sup> (Scheme 1).



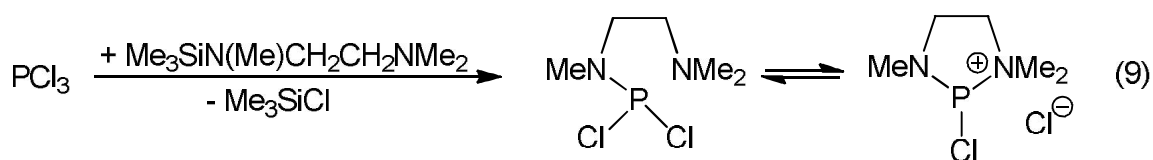
Scheme 1

Firstly, the addition of one equivalent of *n*BuLi to a diethyl ether solution of *N*-isopropyl-2-(isopropylamino)troponimine (*i*Pr<sub>2</sub>ATI)H **2** at 0 °C afforded the transient lithiated compound which in turn reacted with PCl<sub>3</sub> (Scheme 1 (a)). The <sup>31</sup>P NMR analysis of the reaction mixture indicated two products which displayed resonances at 134.47 ppm and 160.95 ppm. Secondly, in sharp contrast, the reaction of PCl<sub>3</sub> with a mixture of triethylamine and (*i*Pr<sub>2</sub>ATI)H in toluene at room temperature for 3 h yielded selectively the compound which exhibited a signal at 134.47 ppm (Scheme 1 (b)).

Single crystals suitable for X-ray crystallographic analysis were grown from a dichloromethane solution at -30 °C. The molecular representation (Figure 5) shows unambiguously the formation of the N,N'-chelated chlorophosphenium cation **6a**. If we consider the compound **6a** as a phosphonium, the chemical shift observed is among the most shielded. Indeed, in the case of phosphoniums, the range of values is fairly wide ranging from 77 - 500 ppm<sup>[48]</sup> and depends heavily on the nature of the ligand and its ability to spread the positive charge. For example, in the case of aminophospheniums Me<sub>2</sub>NP<sup>+</sup>Y (Y = *t*Bu) the positive charge is mainly localized on the phosphorus, with a chemical shift of 513.2 ppm<sup>[49]</sup>. When Y = C≡N, a shielded signal is observed at 77 ppm<sup>[48]</sup> which can be attributed to a delocalization of the charge on the nitrile group.

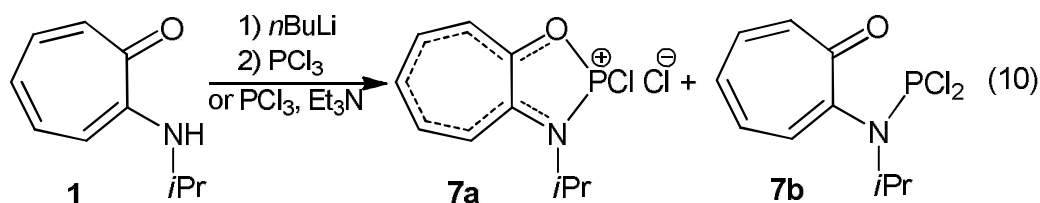
The values generally observed for N-heterocyclic phosphonium cations are in the range of 200 to 260 ppm<sup>[12]</sup>. In our case, the <sup>31</sup>P chemical shift of 134.47 ppm is lower, presumably because of the delocalization of the positive charge on the ligand backbone.

Concerning the second product **6b**, the <sup>31</sup>P NMR resonance (δ 160.95) is in the typical region for aminodichlorophosphines<sup>[50]</sup>. The simultaneous formation of both dissociated and non-dissociated forms has been already reported but not clearly evidenced with N,N',N'-trimethylethylenediamine<sup>[51-53]</sup> as substituent (Equation 9).



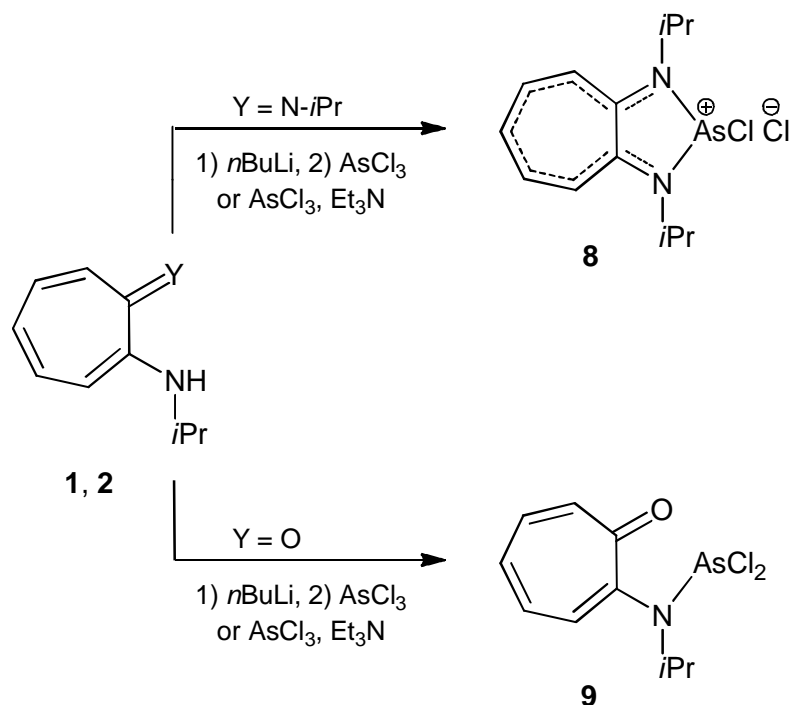
An equilibrium between covalent and ionic compounds has been suggested with displacement to covalent species upon heating<sup>[52]</sup>. In our case, the cationic form **6a** seems to be more stable than **6b** probably due to the presence of a conjugated backbone.

Next, we tested the coordinating properties of 2-(isopropylamino)tropone ((*i*PrAT)H **1** toward the phosphorous atom. Regardless of the procedure used (Equation 10), a mixture of two compounds **7a** and **7b** ( $^{31}\text{P}$  NMR:  $\delta$  155.70 ppm and 171.01 ppm respectively) was always obtained with ratios varying from 1:1 to 2:1.



Yellow crystals were isolated by slow crystallization from dichloromethane in the case of the dehydrohalide coupling reaction, and structurally identified as the cationic form **7a**. However, it was more unstable than the N,N'-chelated analogue **6a**, particularly in solution with formation of ligand **1**. Moreover, compared to **6a**, the  $^{31}\text{P}$  chemical shift ( $\delta$  155.70 ppm) is slightly shifted to low field, probably due to less effective charge dispersion, although a similar downfield shift of the ring protons was observed in the  $^1\text{H}$  NMR spectrum. Compound **7b** has a signal at 171.01 ppm in the expected region for such a dichlorophosphine<sup>[50]</sup>.

With  $\text{AsCl}_3$ , the resulting products strongly depend on the nature of the ligand. While, with the aminotroponimate ligand, only the dissociated form **8** was obtained independently of the experimental conditions used, with the aminotroponate ligand the dichloroarsine **9** was formed exclusively (Scheme 2) as shown by X-ray structure analysis (Figure 7).

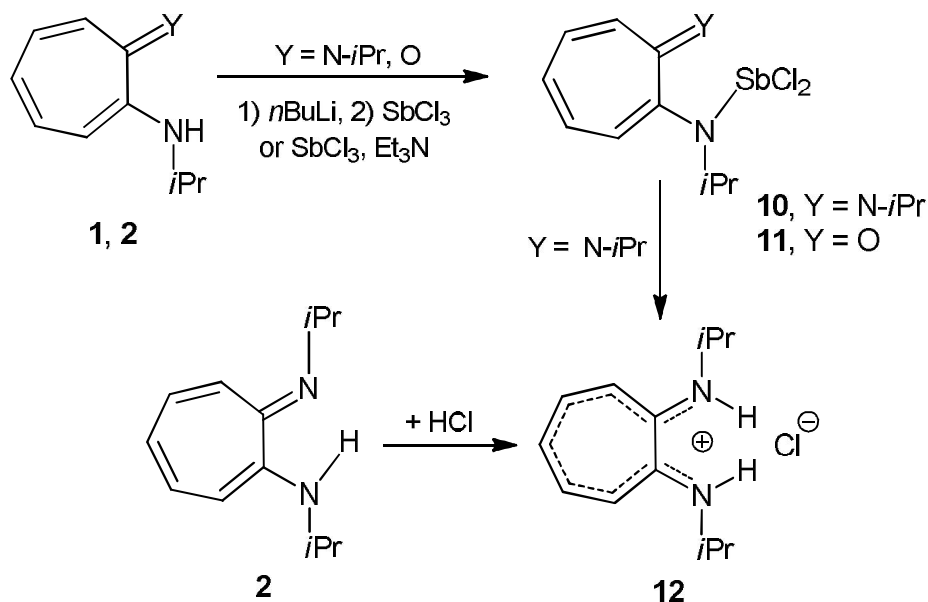


Scheme 2

All products supported by aminotroponate and aminotropoiminate were isolated as yellow air-sensitive solids in 48-60 yields. It should be noted that, in all cases, higher yields have been obtained using the dehydrohalide coupling route and that the N,O-chelated products (**7** and **9**) were generally more unstable than the N,N'-chelated analogues (**6** and **8**), particularly in solution with formation of aminotroponone. They were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and in some cases by single-crystal X-ray diffraction studies.

In the case of SbCl<sub>3</sub>, regardless of the path (nucleophilic substitution reaction using the monolithiated ligand or a base induced dehydrohalide coupling reaction) the <sup>1</sup>H NMR spectrum shows the formation of the same product having deshielded signals belonging to the aromatic system. This suggests the major presence of ionic species but without structural confirmation it was difficult to specify the correct molecular structure.

Moreover, compound **10** quickly decomposes in solution giving the aminotroponimate chlorhydrate salt **12** (Scheme 3), which can be obtained easily by adding HCl to an Et<sub>2</sub>O solution of **2**. Recently, this phenomenon was observed in the case of MesnacnacSbCl<sub>2</sub> which decomposes towards the ligand salt, [MesnacnacH<sub>2</sub>]<sup>+</sup>, a protonated species at both nitrogen atoms<sup>[30]</sup>.



Scheme 3

Attempts to prepare the desired bismuthenium cations supported by these ligands were unsuccessful.

## 1.2 Spectroscopic characterization of aminotroponiminate and aminotroponate complexes of P, As and Sb

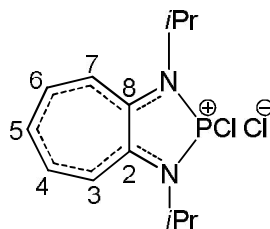
The ideal method to characterize and determine the structure of these compounds is NMR spectroscopy due to the fact that all of them are diamagnetic and there are several nuclei which can be thoroughly analyzed by this means. These include the classical  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR all of which have a nuclear spin number  $+ \frac{1}{2}$ . Since  $^{13}C$  NMR detects only the  $^{13}C$  isotope of carbon, whose natural abundance is only 1.1 %, because the main carbon isotope,  $^{12}C$ , is not detectable by NMR since it has zero spin, the sensitivity of Carbon-13 NMR is extremely low; thus, highly concentrated samples and long measurement time are required<sup>[54]</sup>.

Mass spectrometry was employed for elucidating the chemical structures of the new sensitized compounds. The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measurement of their mass-to-charge ratios<sup>[55]</sup>.

Elemental analysis and X-ray diffraction studies were also carried out for some of these compounds.

## 1.2.1 NMR Properties

Atom labeling used in the NMR assignments of **1**, **2**, **6a**, **6b**, **7a**, **7b**, **8**, **9**, **10**, **11** and **12** is given below (e.g. **6a**):



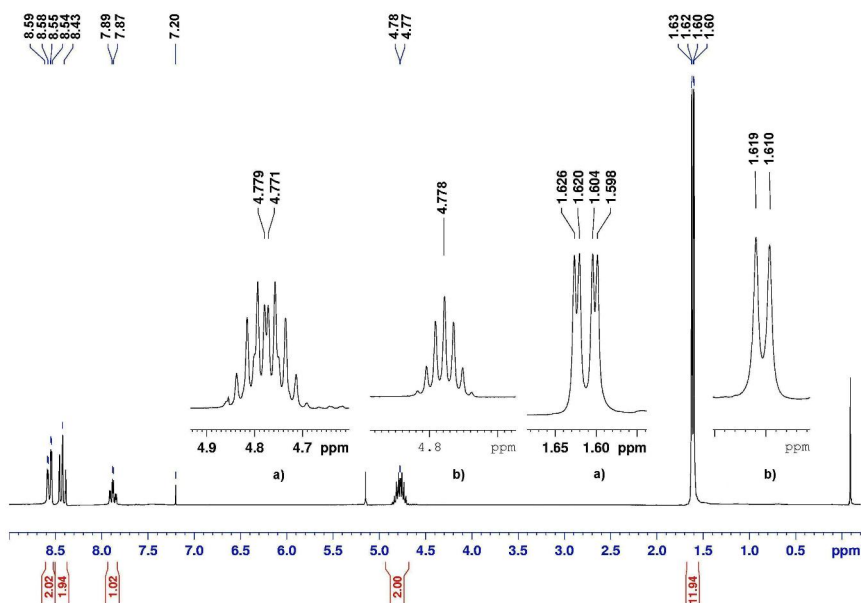
**Figure 1:** Numbering of atoms in compound **6a**

### 1.2.1.1 $^1\text{H}$ NMR

Depending on the local chemical environment, different protons in a molecule resonate at slightly different frequencies. Methyl and methine groups present characteristic signals as well as the aromatic protons in position 3-7 which range from 6.00 to 8.65 ppm.

As expected,  $^1\text{H}$  NMR shows the presence of equivalent  $\text{CH}_3$  groups in **12** which are deshielded in relation to starting ligand.

Because nuclei themselves are little magnets they influence each other, changing the energy and hence frequency of nearby nuclei as they resonate, a phenomenon known as spin-spin coupling. It is to note the long-range spin-spin coupling constants between P and H observed for **6a** ( $^6J_{\text{HP}} = 3.4$  Hz,  $\text{H}_5$ ) and **7b** ( $^5J_{\text{HP}} = 1.0$  Hz,  $\text{H}_4$ ).



**Figure 2:**  $^1\text{H}$  NMR spectrum for compound **6a**. a) signals of  $\text{CH}_3$  and CH non decoupled of P; b) signals of  $\text{CH}_3$  and CH decoupled of P



### 1.2.1.2 $^{13}\text{C}$ NMR

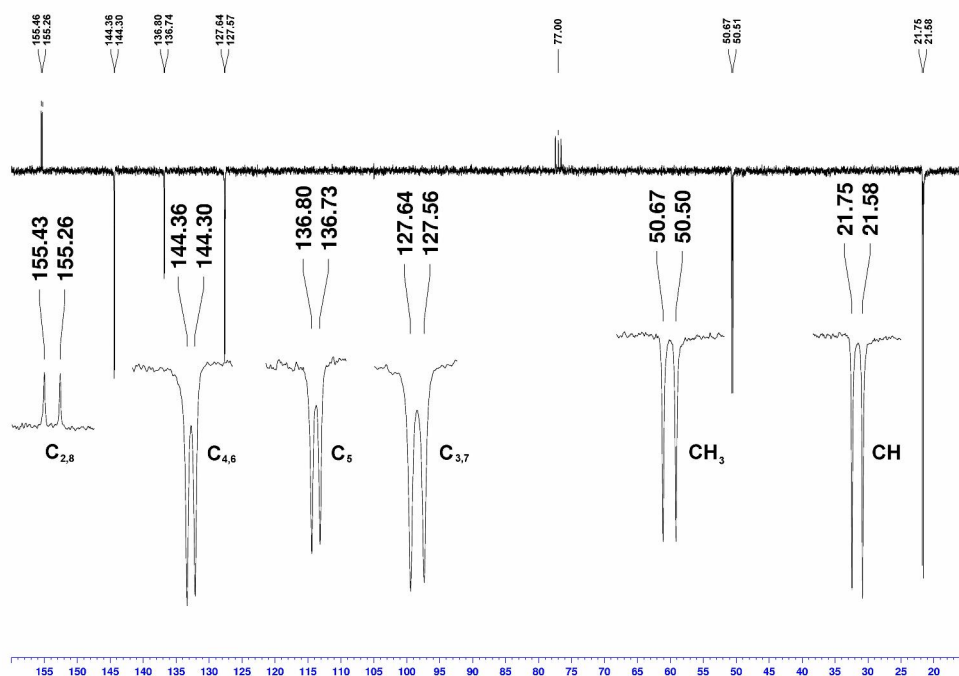
The Carbon-13 NMR spectrum can be divided into two groups. First, the signals between 21.18 and 51.20 ppm belong to an alkyl group. Secondly, those which ranged from 108.65 to 176.52 ppm belong to the aromatic carbon atoms.

For **6b** we also observe two signals for  $\text{CH}_3$ ,  $\text{CH}$  and  $\text{C}_{2,8}$  due to the asymmetry of the molecule.

As previously observed in the  $^1\text{H}$  NMR spectra, the resonances for the ring carbons are significantly shifted downfield compared to those of the ligands.

Quaternary carbons ( $\text{C}_{2,8}$ ) have weaker and narrower signals than those of carbons attached to protons and present the highest chemical shifts. For phosphonium cations, the coupling constant P-C is decreasing from 12.7 to 5.0 Hz ( $\text{C}_{2,8}$  to  $\text{C}_5$ ) in the case of **6a** and from 15.5 to 2.0 Hz ( $\text{C}_2$  to  $\text{C}_5$ ) for compound **7a**.

If we compare the neutral ligand **2** and the salt **12**, sensibly different signals can be seen in Carbon-13 NMR for the two compounds due to the similarity of these two molecules.



**Figure 3:**  $^{13}\text{C}$  NMR spectrum for compound **6a** (for atom numbering see Figure 1 section 2.1)

### 1.2.2 Mass spectrometry study

The existence of the molecular peak depends on the dissociated or non dissociated character of the molecule. In the case of **6b** and **10** (non dissociated species) we observed in the mass spectrum the presence of the  $[M^+]$  peak at 304 and 396 amu respectively and  $[M-Cl]$  peak at 269 and 361 amu while for the dissociated species **8**, and partial dissociated species **9** and **11** the presence of the  $[M^+ - Cl]$  peak at 313 amu, 272 amu and 320 amu, respectively was only observed. In the particular case of **6a** a protonated fragment,  $[M-Cl+H]$ , at 270 amu can be seen.

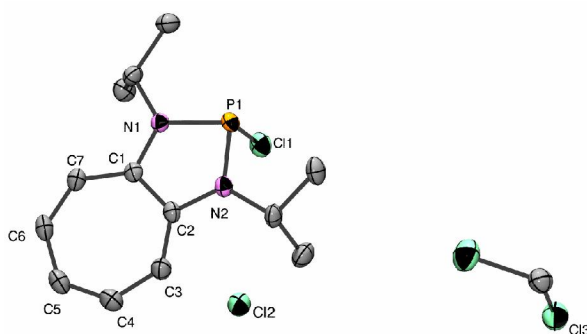
### 1.2.3 X-ray analyses

X-ray structure determinations were carried out for **6a**, **7a**, **8** and **9**. Their molecular structures (including selected bond lengths and bond angles) are shown in Figures 5-7.

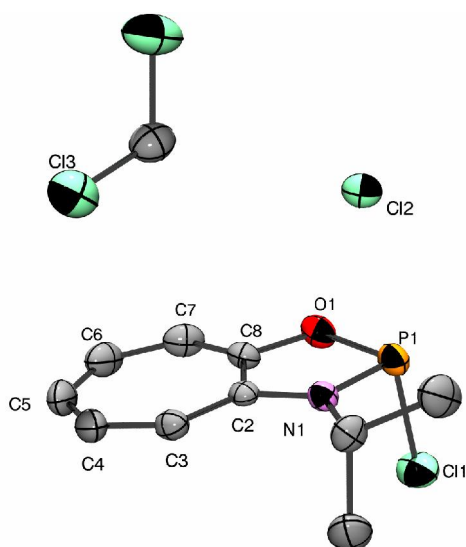
All compounds show the same general features in the solid state: they consist of separated ion-pairs with chlorine as anion. The cationic parts are formed by PCl and AsCl units, which are stabilized by the chelating ligand systems.

In the asymmetric compound **7a**, the P-O bond [1.646(2) Å] is between a typical P-O single bond (1.71 Å) and a P=O double bond (1.40 Å),<sup>[56]</sup> which confirms the very strong covalent bond character of this formally donor bond. Consequently, the CO bond (1.365 Å) is about 10 pm longer than in the neutral corresponding tropone (1.245 Å),<sup>[57]</sup> and other comparable tropones, like 2-amino-5-methoxycarbonyltropone (1.255 Å),<sup>[58]</sup> 2-(4-fluoroanilino)tropone (1.251 Å, mean value)<sup>[59]</sup> or 2-(2,6-di-isopropylanilino)tropone (1.252 Å)<sup>[43]</sup>.

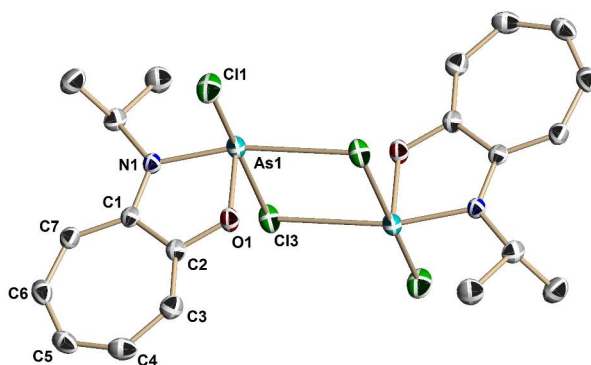
Interestingly, compound **9**, which is closely related to **7a**, adopts a very different structure. The asymmetric unit contains two molecules of **9** which are very similar with little difference in the bond distances (Figure 7). The <sup>1</sup>H NMR data are in good agreement with the solid-state structure and the observation of down-field shifted ring protons.



**Figure 5:** Molecular structure of compound **6a** (50 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.



**Figure 6:** Molecular structure of compound **7a** (50 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.



**Figure 7:** Molecular structure of compound **9** (50 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.

### 1.3 Computational studies

In order to gain more insight about the electronic state of these cations, Density Functional Theory (DFT) calculations were done on phosphonium cations **6a**, **7a**, **8** and **9** using the Amsterdam Density Functional package, ADF 2005<sup>[60]</sup>. The input parameters for the geometry optimization were generated from the X-ray crystallographic data of **6a**, **7a**, **8** and **9**. For **6a** and **7a**, the HOMO are localized into the bicyclic systems and the heteroatoms (N, O,

Cl), whereas the LUMO are more localized on the seven-membered cycle and less on the heterocycle. The phosphorous lone-pair resides in HOMO-1 orbitals that are at 0.79 and 0.76 eV below their corresponding HOMO while in **8** and **9** the arsenic lone-pair resides in HOMO-4 orbitals that are at 2.04 and 2.05 eV below their corresponding HOMO.

The NICS (Nucleus-Independent Chemical Shifts) values<sup>[61-62]</sup> are influenced by the sigma bonds so the NICS(1) values are considered as better indicators of  $\pi$ -electron delocalization. These data show that the electron delocalization in the seven-membered ring is similar in all compounds; however, the five-membered ring exhibits some differences, displaying somewhat lower NICS(1) values for **7a** and **9** than for **6a** and **8** respectively. Thus, the  $\pi$ -electrons in the five-membered ring are less delocalized, in accordance with the bond lengths in this ring and the chemical shifts in the <sup>31</sup>P NMR. The out-of-plane component of the NICS(1) value, NICS(1)<sub>zz</sub>, might be considered as another indicator of the electron delocalization<sup>[63]</sup>.

These computational studies and the X-ray structural data indicate an extensive delocalization of the positive charge over the seven-membered ring cycle suggesting that these species could be formally better described as chlorophosphines bearing a cationic substituent.

## Conclusions and perspectives

An easy and direct route to the first phosphenium and arsenium cations supported by N,N' or N,O-chelation derived from a tropolone scaffold was achieved. The presence of a  $\pi$ -unsaturated backbone in the aminotroponimate and aminotroponate ligands not only prevents the competitive  $\gamma$ -carbon substitution previously observed for diketiminate ligand but also allows a complete positive charge delocalization on the seven-membered cycles. This result was confirmed by the X-ray structural data and DFT calculations.

## Chapter II Pnictogenium cations: reactivity

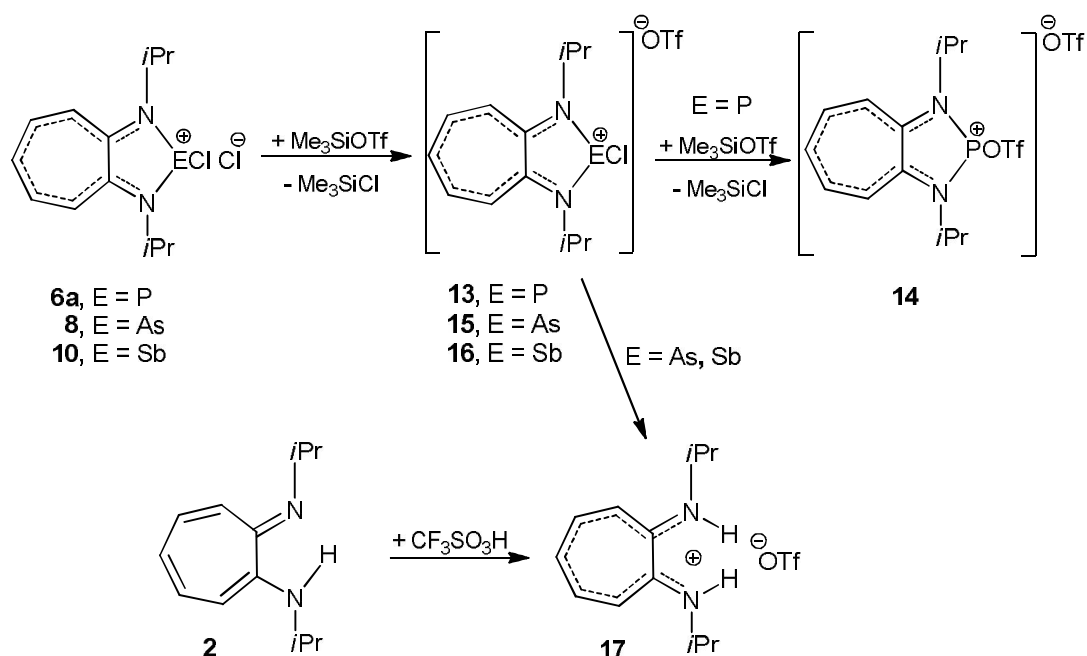
### Introduction

The main goal of this chapter is to perform some characteristic reactions such as halide ion exchange, oxidative addition, cycloaddition, and complexation with transition metals in an attempt to learn more about their structures.

### 2.1 Halide ion exchange

Firstly we investigated substitution reactions of chloride anion by trimethylsilyl triflate.

Treatment of phosphonium cation **6a** with stoichiometric amount of  $\text{Me}_3\text{SiOTf}$  in dichloromethane at room temperature resulted in  $\text{Me}_3\text{SiCl}$  elimination and formation of two new compounds **13** (35 %) and **14** (65 %) which display  $^{31}\text{P}$  chemical signals at 136.16 and 111.05 ppm (Scheme 1).



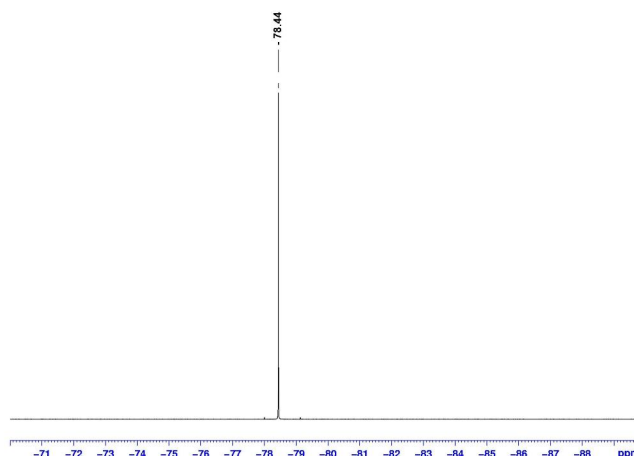
Scheme 1

Starting from **8** or **10**, only one product **15** or **16** was obtained (Scheme 1); **15** was structurally identified as a cationic species.

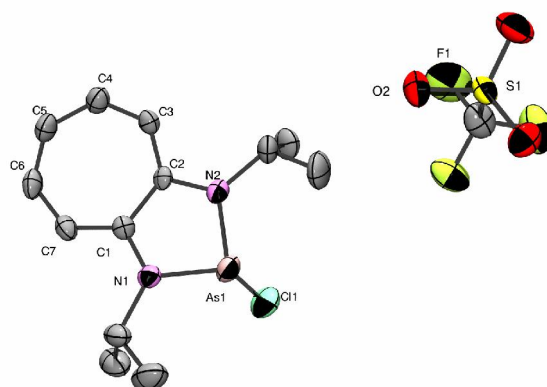
If compared with the parent pnictogenium compounds, the  $^1\text{H}$  NMR data show almost similar deshielding of the ring protons confirming the formation of cationic species and delocalization of the positive charge on the ligand. Within the group 15 series, a slightly deshielding effect can be seen for the aromatic protons of **13** (except for  $\text{H}_5$ ) and **14** while for **15** and **16** the inverse phenomenon of shielding was found.

$^{19}\text{F}$  Fluorine is a sensitive nucleus which yields sharp signals, has a spin of  $\frac{1}{2}$  and a relative abundance of 100 %, making measurements very fast (comparable with  $^1\text{H}$  NMR).

All these derivatives display in  $^{19}\text{F}$  NMR resonances between -78.44 ppm and -77.17 ppm which correspond to values expected for these triflate compounds<sup>[64]</sup>. We present the  $^{19}\text{F}$  NMR spectrum for **15** in figure 1.



**Figure 1:**  $^{19}\text{F}$  NMR spectrum of **15**

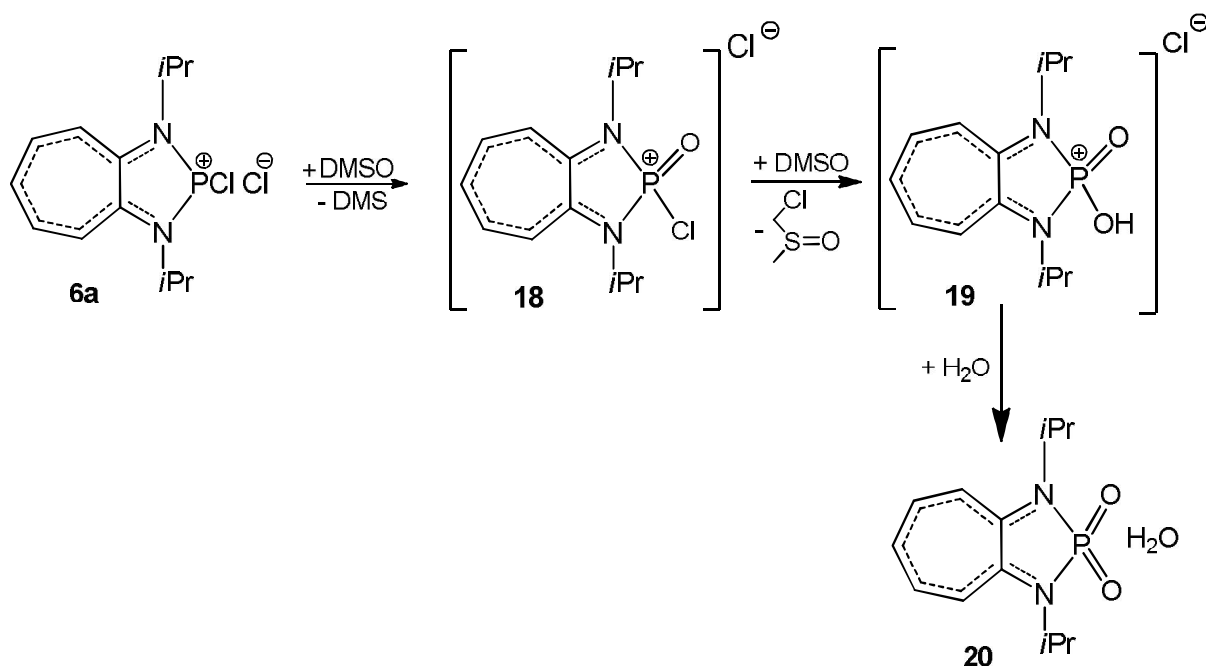


**Figure 3:** Molecular structure of **15** (50 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.

The molecular representation (Figure 3) shows the formation of well-separated N,N'-chelated arsenium cation and triflate anion.

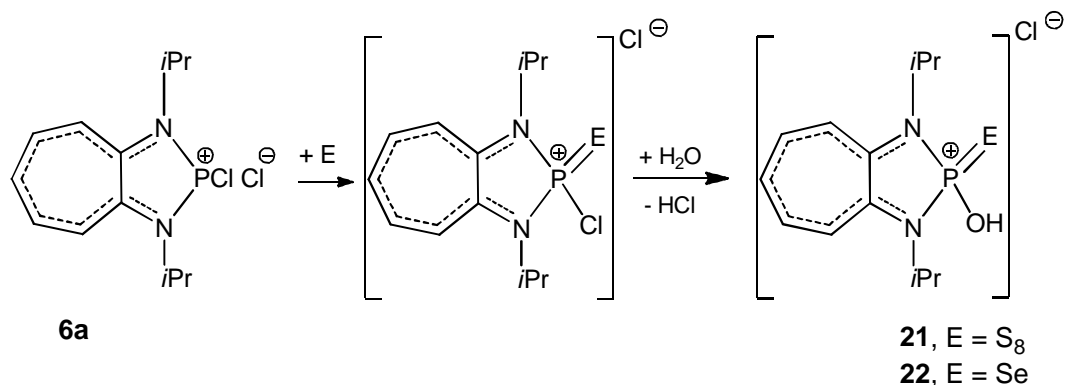
## 2.2 Oxidative reactions with dimethylsulfoxide, sulfur and selenium

We first tried a reaction with DMSO. The addition of a stoichiometric amount of DMSO at room temperature leads to the formation of oxidation product **18** after removal of dimethyl sulfide. As has already been described in the literature for chlorophosphines<sup>[65]</sup> a side reaction of hydroxylation was observed in the presence of an excess of DMSO (Scheme 2).



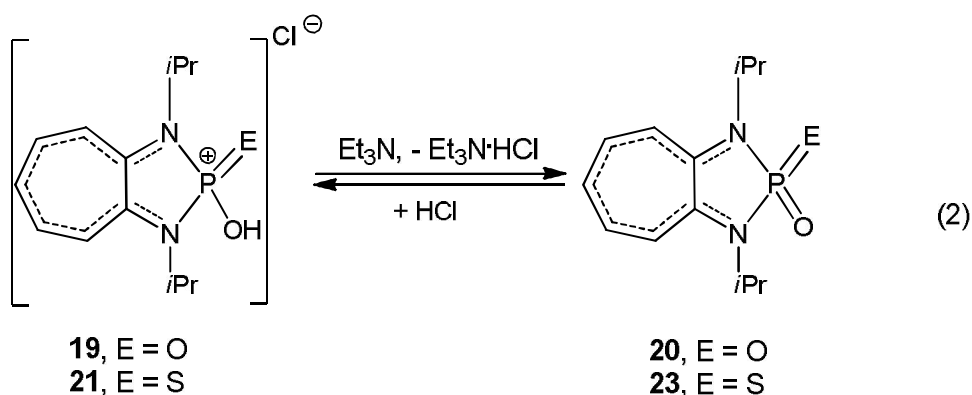
Scheme 2

The oxidation reaction with sulfur seems more difficult and was observed only at dichloromethane reflux for 14 hours. The dichlorothiophosphoryl intermediate compound could not be characterized in this case and evolved very rapidly towards hydroxythiophosphonium cation **21** whose structure was determined by X-ray diffraction (Scheme 3).



Scheme 3

Starting from hydroxyoxo- and hydroxythio-phosphonium **19** and **20**, the elimination of HCl was performed in the presence of a base such as Et<sub>3</sub>N leading to the corresponding di-oxo- and thiooxophosphorane **20** and **23**.



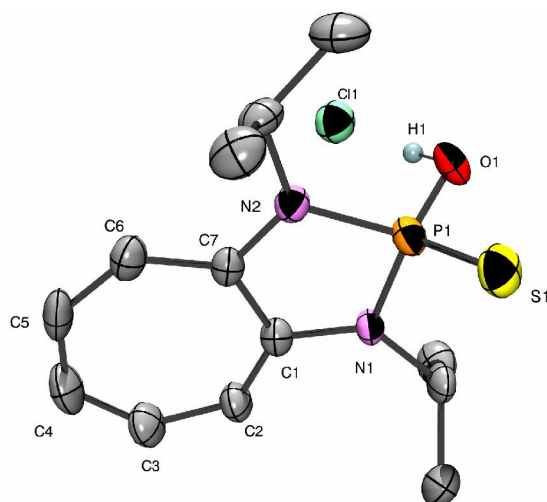
It must be underlined that compounds **20** and **23** are respectively the first examples of aminometaphosphonate and of its sulfur equivalent stabilized by intramolecular complexation.

All the compounds have been perfectly characterized spectroscopically.

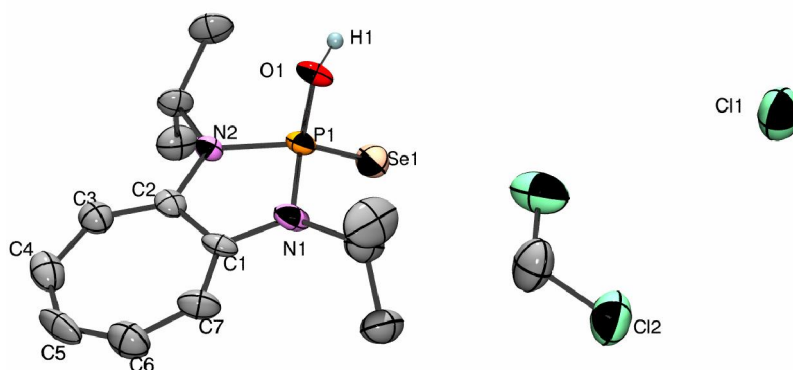
The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}NMR spectra of compounds **18** - **23** show the expected set of signals for the (*i*Pr<sub>2</sub>ATI) ligand. The <sup>1</sup>H NMR spectra of all these compounds display three well-separated signals which correspond to H<sub>5</sub>, H<sub>4,6</sub> and H<sub>3,7</sub>, except **20** for which we cannot distinguish the signals for the aromatic system. The methyl groups of the isopropyl substituents of **18**, **21**, **22** and **23** appear as two sets of doublets in the <sup>1</sup>H NMR spectrum suggesting different environments for the methyl groups.



A slow crystallization at low temperature in dichloromethane allowed the isolation of crystals of compounds **21** and **22** (Figures 6 and 7).

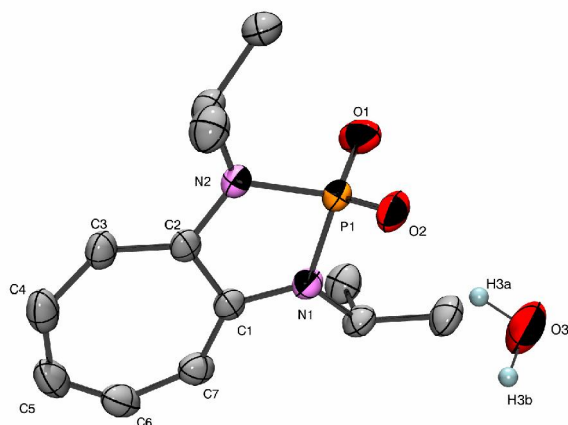


**Figure 6:** Molecular structure of **21** (50 % probability level for the thermal ellipsoids). All H (except H1) atoms have been omitted for clarity.

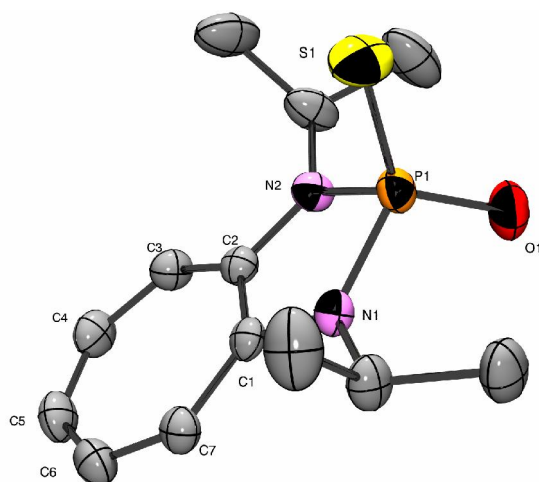


**Figure 7:** Molecular structure of **22** (50 % probability level for the thermal ellipsoids). All H (except H1) atoms have been omitted for clarity.

The study of their structures by X-ray diffraction shows that there is no interaction between the cationic phosphorus species and the chloride anion. The phosphorus atom is four-coordinate with small N-P-N angles.



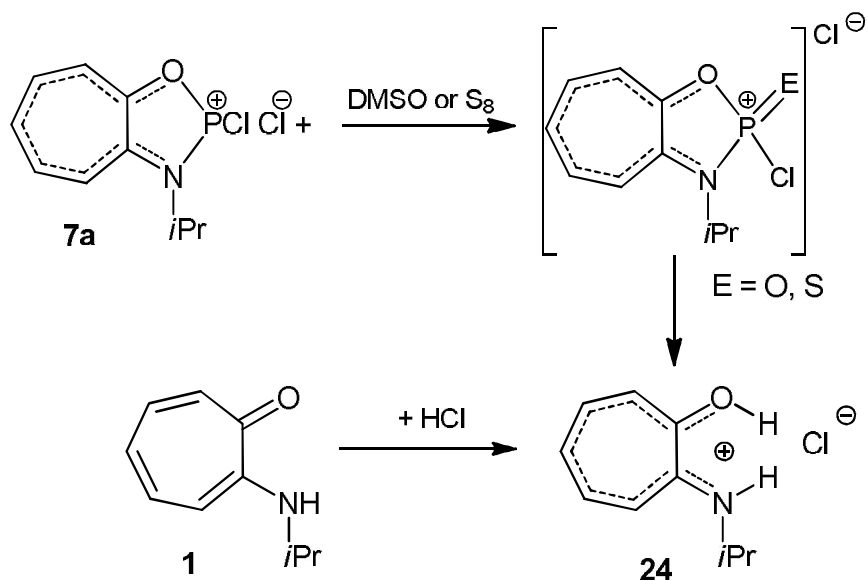
**Figure 8:** Molecular structure of **20** (50 % probability level for the thermal ellipsoids). All H (except H from H<sub>2</sub>O) atoms have been omitted for clarity.



**Figure 9:** Molecular structure of **23** (50 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.

All these oxidative reactions with chlorophophenium cation supported by aminotroponate ligand **7a** appeared to be more difficult because of its lower stability in solution and thermally.

The oxidation of **7a** with DMSO occurs very rapidly giving a new product which displays a <sup>31</sup>P NMR signal at 4 ppm in the typical region of the phosphorus oxides (Scheme 4).

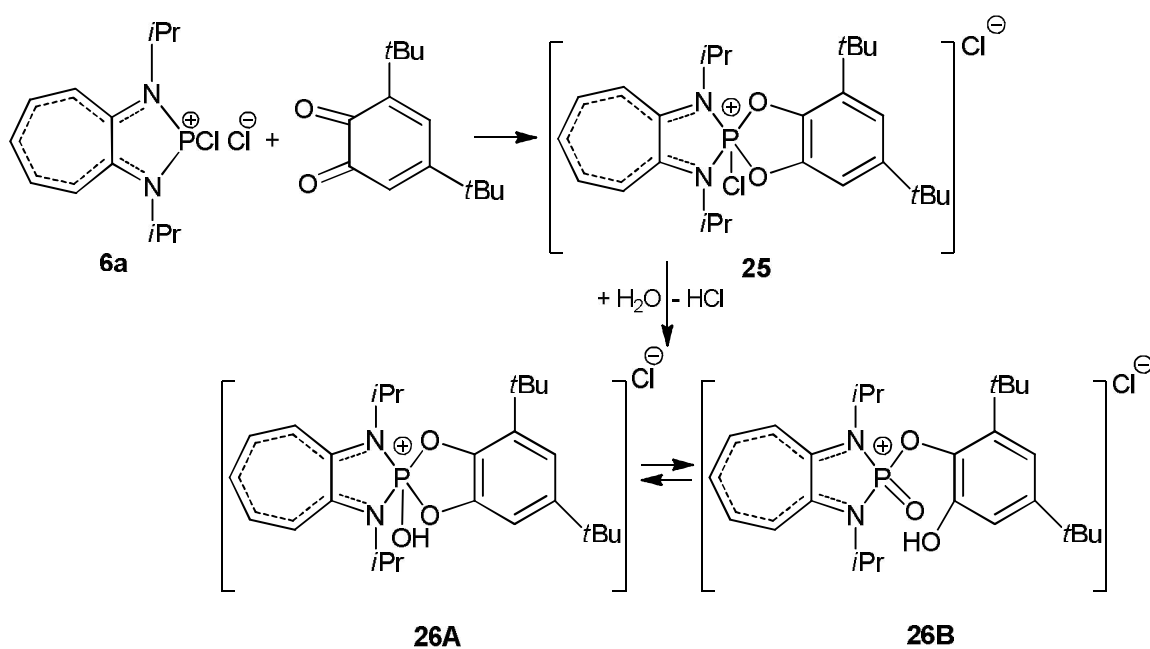


Scheme 4

### 2.3 Cycloaddition reaction with *o*-quinone

One of the characteristic reactions of phosphoniums is the cycloaddition reaction with dienes in which they behave as dienophiles<sup>[48]</sup>.

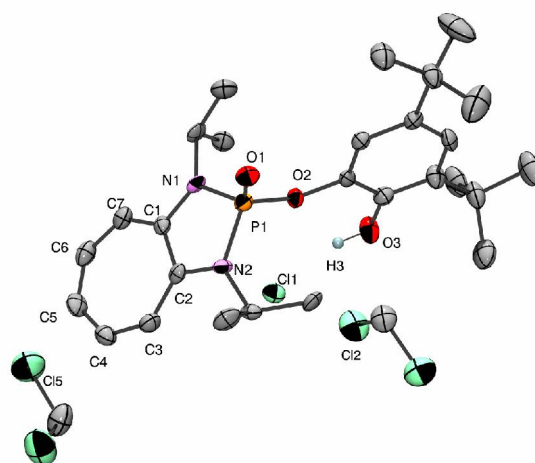
Immediate reaction was observed with 3,5-di-*tert*-butyl-1,2-benzoquinone at room temperature.



Scheme 5

Compound **25** is very sensitive to hydrolysis in solution and rapidly gives the corresponding hydroxy compound **26A**. It has been shown in literature<sup>[66]</sup> that such hydroxyphosphoranes were in equilibrium with their phosphate ester form **26B** and that this balance would be shifted to the B form in the presence of acid.

The <sup>1</sup>H NMR spectrum for the two phosphorus cycloadducts shows all the protons are more deshielded for **25** if compared with **26B**.

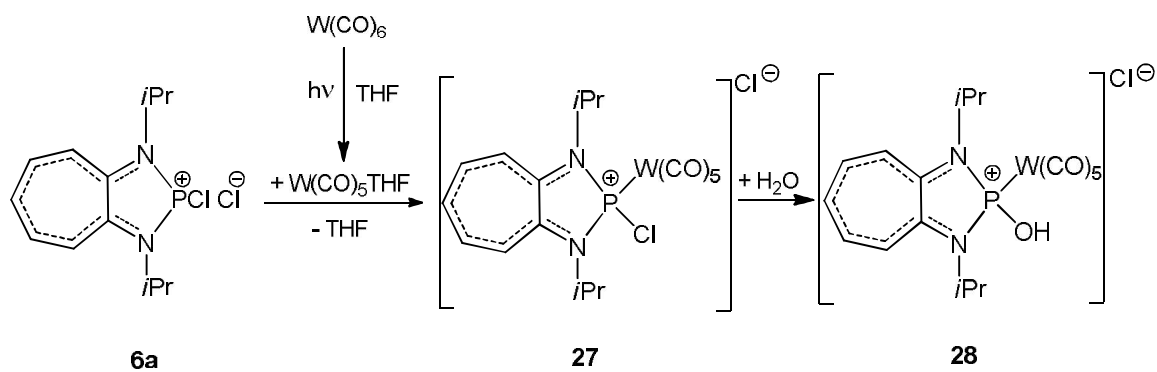


**Figure 10:** Molecular structure of **26B** (50 % probability level for the thermal ellipsoids). All H (except H3) atoms have been omitted for clarity.

## 2.4 Complexation with transition metals

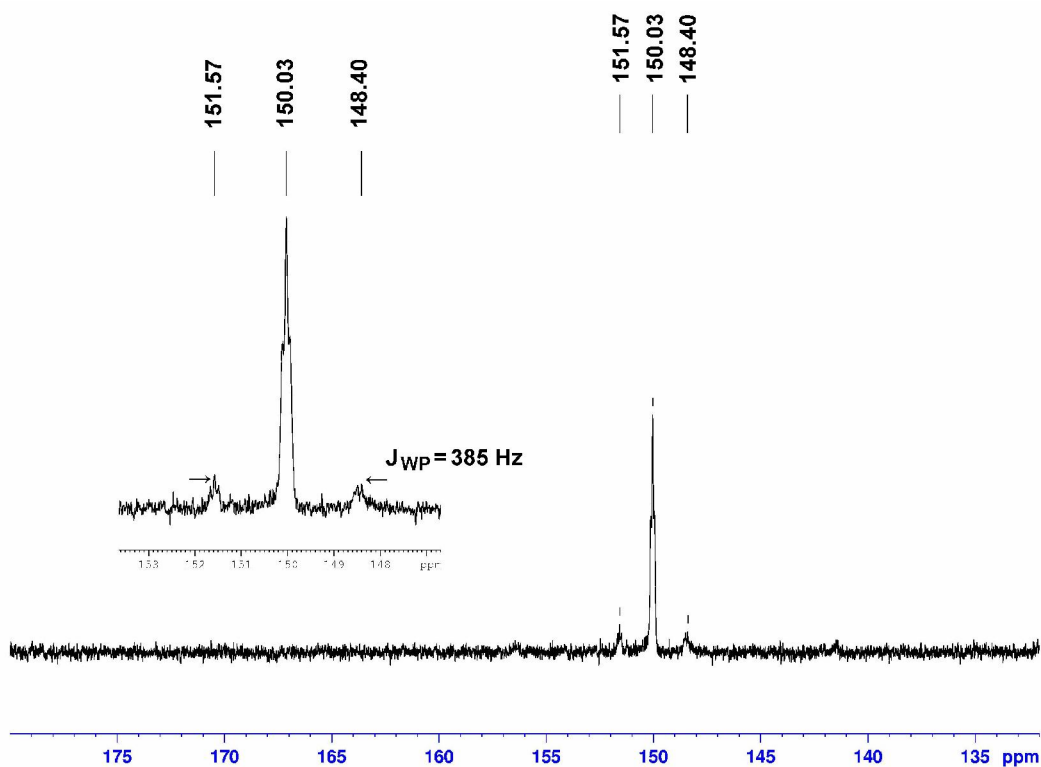
Thanks to a high-lying phosphorus lone-pair orbital (HOMO-1), the phosphonium cation **6a**, can behave as valuable ligand for metal-transition complexation. To evaluate its ability, we tried a test with a tungsten complex.

The reaction was performed using stoichiometric amount of cation **6a** and complex  $W(CO)_5THF$  in THF at room temperature (Scheme 6) and led to a mixture of complex **27** and its hydroxyl analog **28** which were perfectly characterized by NMR analyses. A slow crystallization in deuterated chloroform solution at room temperature gave brown crystals identified to complex **28** by X-ray analysis.

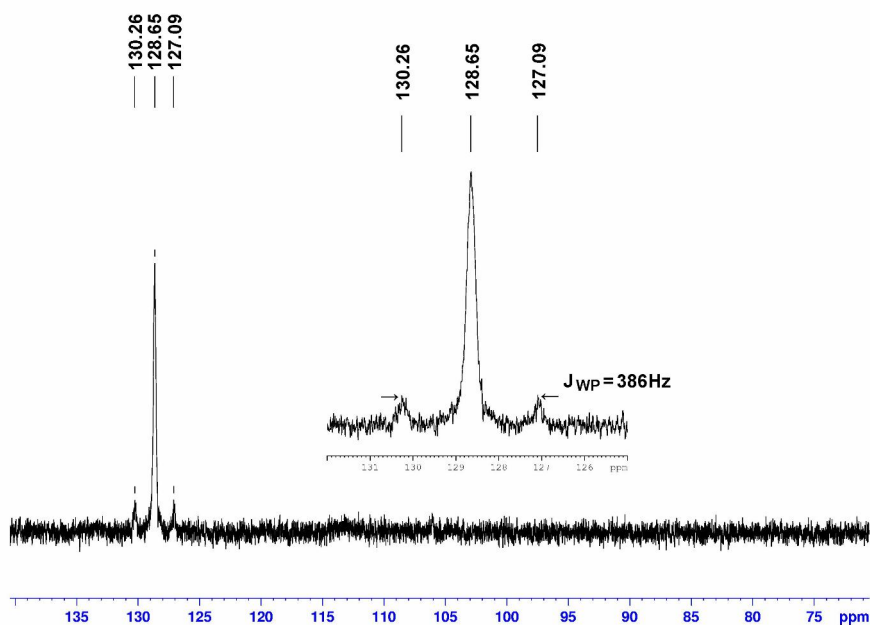


Scheme 6

The  $^{31}\text{P}$  NMR spectra show two resonances at 150.03 and 128.65 ppm accompanied by satellites of tungsten with coupling constants  $J_{\text{WP}} = 385$  and 386 Hz for **27** (75 %) and **28** (25 %) respectively (Figure 11 and 12).



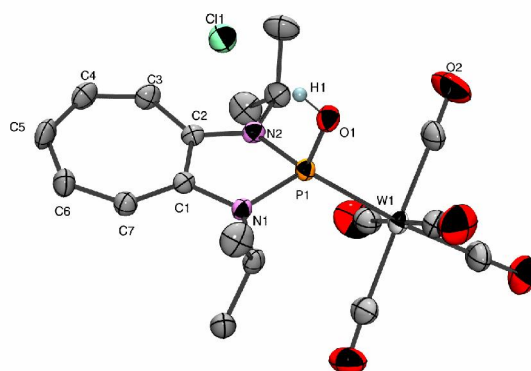
**Figure 11:**  $^{31}\text{P}$  NMR spectrum for compound **27**



**Figure 12:**  $^{31}\text{P}$  NMR spectrum for compound **28**

Due to the great resemblance of these two transition metal complexes, both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show nearly identical signal, but shielded for aromatic system compared with **6a**.

The molecular representation (Figure 14) shows unambiguously the formation of the N,N'-chelated tungstenphosphenium cation **28**.

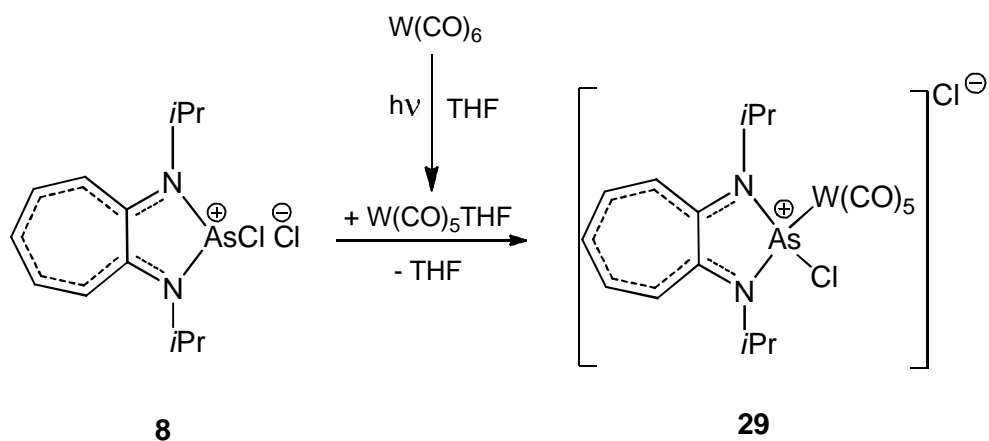


**Figure 14:** Molecular structure of **28** (50 % probability level for the thermal ellipsoids). All H (except H1) atoms have been omitted for clarity.

The phosphorus atom is tetracoordinate with a nearly identical N-P-N angle.

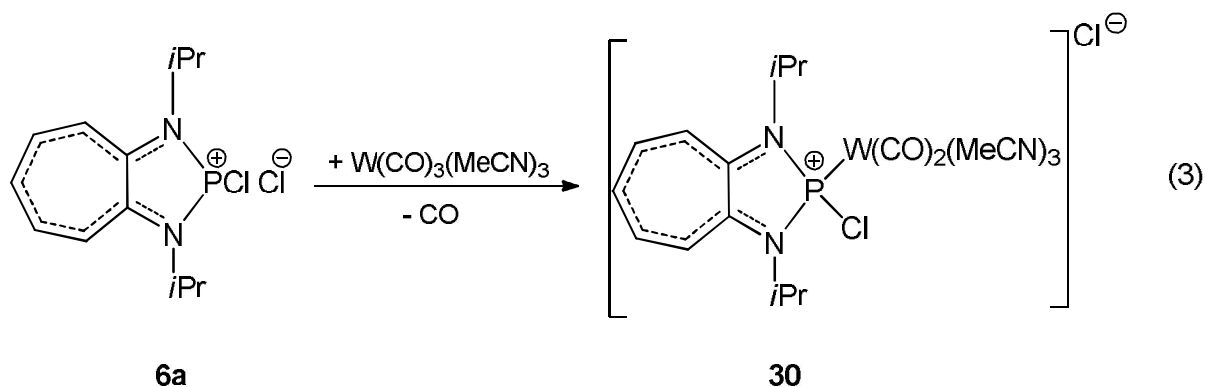
The N-heterobicyclic unit is nearly planar and almost perpendicular to the  $\text{W}(\text{CO})_5$  system.

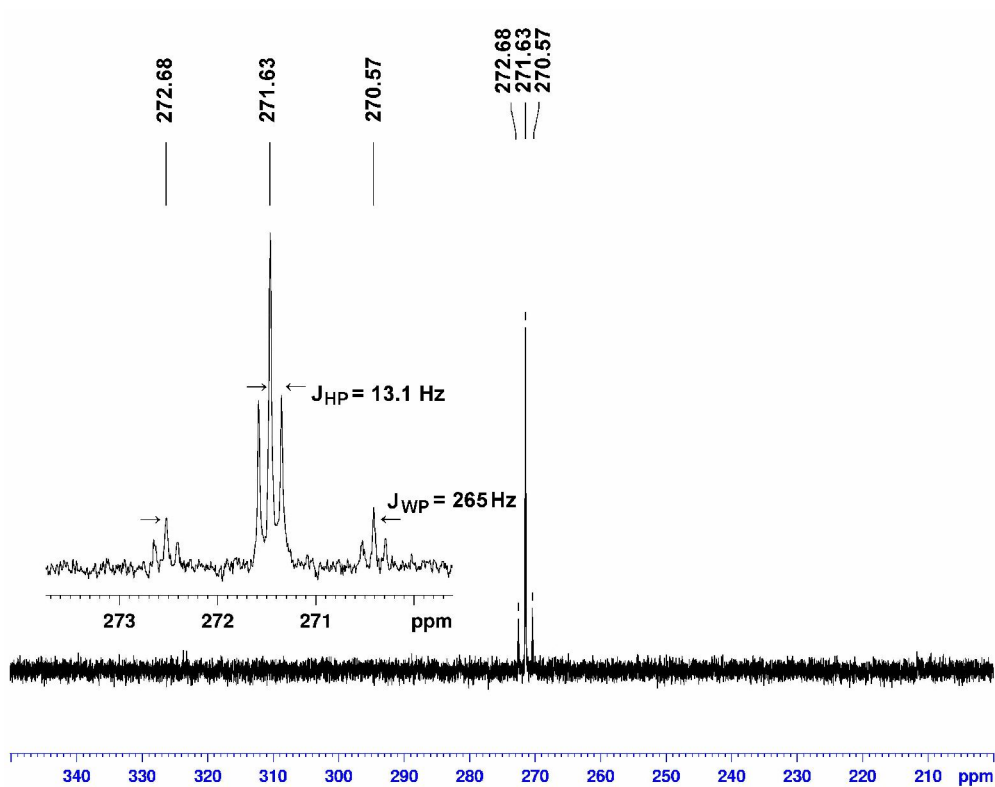
We extended the reactions with the tungsten complex to the arsenium analogue **8**. The reaction with  $W(CO)_5THF$ , gives a yellow compound tentatively identified as **29** by  $^1H$  NMR (Scheme 7).



Scheme 7

We also tried direct substitution of a carbonyl group by the phosphonium cation **6a** in  $W(CO)_3(MeCN)_3$  (Equation 3). We observed in  $^{31}P$  NMR spectrum the appearance of a new signal at 271.63 ppm (Figure 15) comparable to that observed in the case of a phosphonium with a cyclopentadienyl ligand<sup>[67]</sup>.





**Figure 15:**  $^{31}\text{P}$  NMR spectrum for compound **30**; the coupling constant between  $^1\text{H}$  and  $^{183}\text{W}$  can be observed

## Conclusions and perspectives

The study of pnictogenium cations reactivity has been further developed.

Several oxidative reactions were carried out using dimethylsulfoxide, sulfur or selenium. In all cases, the phosphonium cation has been, not only more reactive, but also gave stable and unexpected products. In particular, it allowed the syntheses and the structural characterization of the first examples of an aminometaphosphonate and of its sulfur equivalent stabilized by intramolecular complexation.

The cycloaddition reaction with *o*-quinone confirms their dienophilic nature with formation of phosphate ester derivatives.

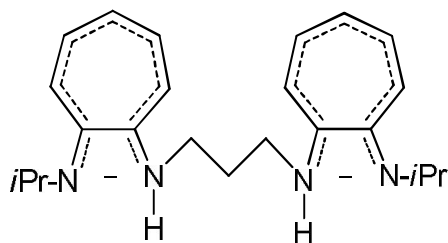
Another interesting feature is their ability to act as ligand in the sphere of coordination of transition-metal complexes. A novel cationic tungsten complex which is isolobal to transition metal carbene complexes could be synthesized and structurally characterized.



## Chapter III Bridged bis(pnictogenium cations) and bis-germylenes: syntheses, spectroscopic studies and reactivity

### Introduction

Aminotroponimines are a well known class of ligands which have found extensive use in coordination chemistry as formal substitutes for cyclopentadienyl groups<sup>[38, 46, 68-72]</sup>. In the first chapter, we have also demonstrated the high potential of this ligand in the stabilization of pnictogenium cations. Recently Roesky<sup>[73]</sup> has synthesized bridged aminotroponimines (**I**, Chart 1) and tested them as "alternatives" for *ansa*-metallocenes in the lanthanide series<sup>[57, 74-76]</sup>.



**I**

Chart 1

This new bridged bis(amino-imino) ligand exhibits two different coordination modes:

- tetradentate chelation of one metal center,
- complexation of two metals in the bridged structure.

It was demonstrated that the coordination mode depended mainly on the size of the ion radius of the metal atoms or chemical element used.

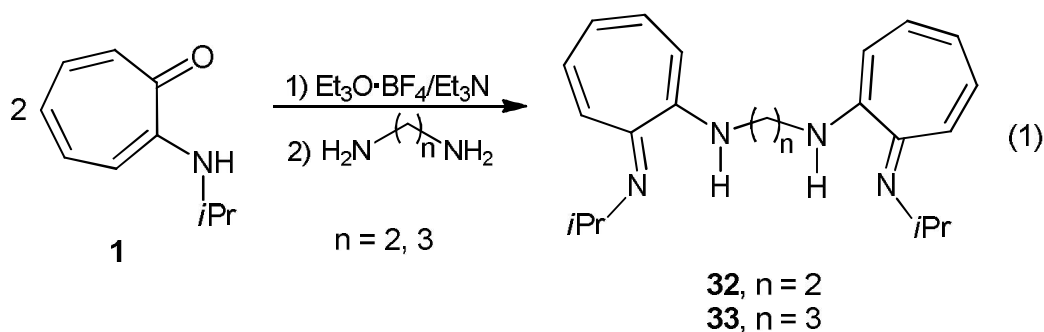
Up to date, the coordination chemistry of this bridged di-aminotroponiminate ligand remains totally unexplored for group 14 and 15 elements.

In this chapter, we describe the synthesis, characterization of novel bisphosphenium, arsenium and stibonium cations incorporating this ligand and the bridged di-aminotroponate group where the imino function was replaced by a carbonyl group. An extension to bis-germylenes will be also developed.

### 3.1 Bridged bis(pnictogenium cations) (P, As, Sb)

#### 3.1.1 Synthesis of ligand precursors

In order to study the influence of the bridge length on the stability of new compounds we decided to prepare ligands with different bridge sizes. The direct synthesis of the bridged chelating ligands, a system in which two aminotroponimine moieties are linked together (1,2-di(2-(N-isopropylamino)troponimine)ethane (**32**) or 1,3-di(2-(N-isopropylamino)troponimine)propane ( $H_2[(iPr)TP]$ ) (**33**)) was performed starting from 2-(N-isopropylamino)-tropone **1** (Equation 1)<sup>[46]</sup>. Treatment of **1** with  $Et_3O \cdot BF_4$ ,  $Et_3N$ , and 1,2-diaminoethane or 1,3-diaminopropane leads to the desired product **32** or **33** as yellow solids.

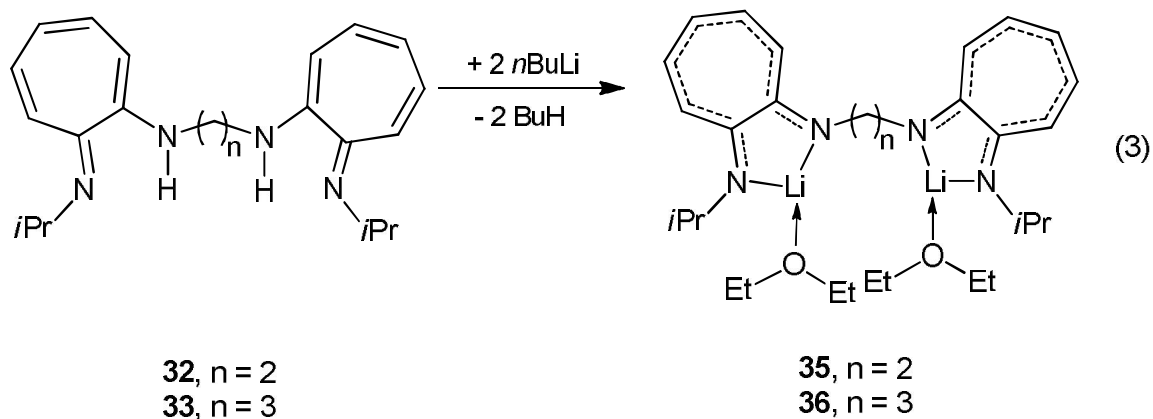


Both ligands were characterized by  $^1H$  and  $^{13}C$  NMR spectroscopy.

These ligands **32** - **34** are very soluble in almost all organic solvents, including saturated hydrocarbons such as n-pentane or hexanes.

#### 3.1.2 Synthesis of the dilithiated ligands salt

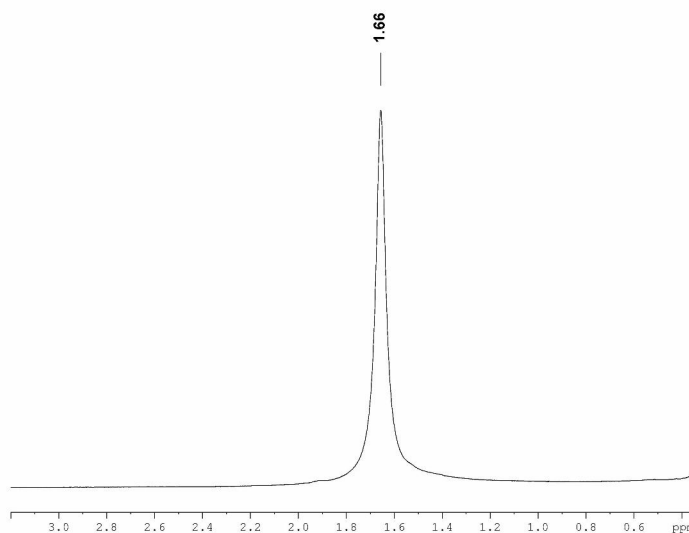
Deprotonation of 1,2-di(2-(N-isopropylamino)troponimine)ethane **32** and 1,3-di(2-(N-isopropylamino)troponimine)propane **33**, with  $nBuLi$  in hexanes affords the dilithium salts **35** and **36** as orange, air-sensitive crystalline solids which were characterized by  $^7Li$ ,  $^1H$  and  $^{13}C$  NMR spectroscopy (Equation 3).



The  $^1\text{H}$  NMR spectra of both lithiated salts, **35** and **36**, show shielded signals for the *CH* groups of the 7-membered ring compared to the starting ligands.

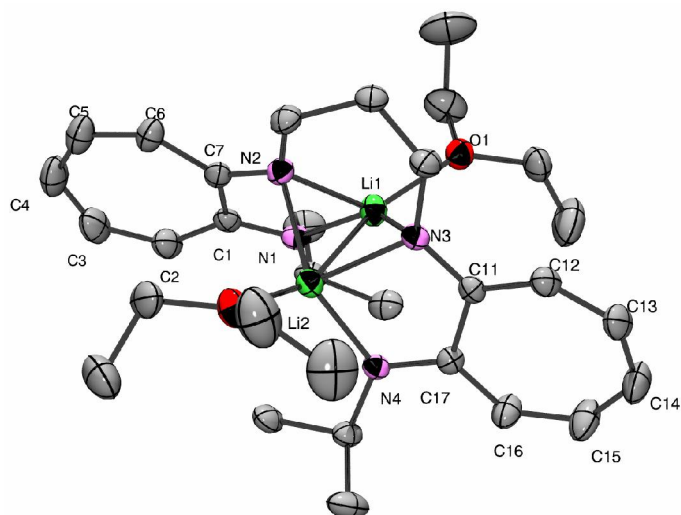
$^7\text{Li}$  nucleus has an isotopic abundance of 92.41 %, a spin of  $\frac{1}{2}$ , is highly sensitive and yields broad signals in NMR due to its high quadrupolar moment. The chemical shift range is usually rather small from -16 to 11 ppm<sup>[54, 77]</sup>.

For **35** and **36** the observed lithium resonances are broad with signals at 1.64 and 1.66 ppm (Figure 1) not far from the value obtained for  $[(\text{Me}_3\text{Si})_2\text{NLi}]$  (1.10 ppm)<sup>[77]</sup>.



**Figure 1:**  $^7\text{Li}$  NMR spectrum for **36** in THF, a broad signal can be seen

The solid-state structure of **36** was established by single crystal X-ray diffraction.

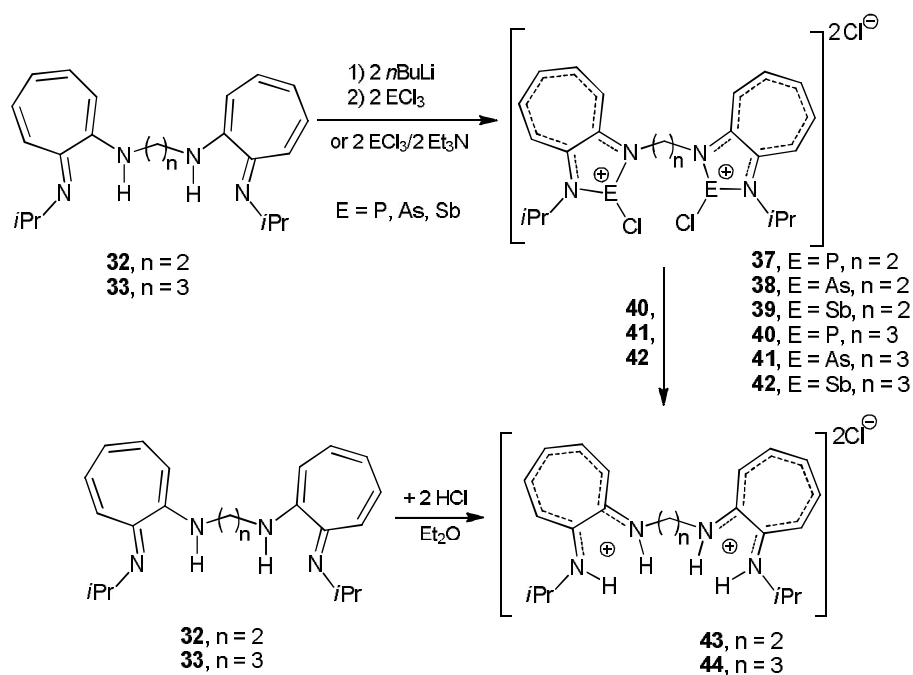


**Figure 2:** Molecular structure of compound **36** (30 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.

The salts of these new ligands are then used for the preparation of the phosphorus, arsenic and antimony compounds.

### 3.1.3 Synthesis of the bis-cations of P, As and Sb

The reactions of bridged diaminotroponimines  $H_2\{(iPrATI)_2(CH_2)_n\}$  with  $EtCl_3/Et_3N$  in toluene or  $nBuLi/EtCl_3$  in  $Et_2O$  led to bridged di-pnictogenium products of composition  $[\{(iPrATI)_2(CH_2)_n\}(ECl_2)_2]$  [ $n = 2, E = P$  (**37**), As (**38**), Sb (**39**)] and  $n = 3, P$  (**40**), As (**41**), Sb (**42**)] (Scheme 1).



Scheme 1

Compounds **37** – **42** were obtained as yellow crystalline solids very slightly soluble in organic solvents with an appreciable sensitivity towards air and moisture. They cannot be separated from the salts (Et<sub>3</sub>N·HCl or LiCl) and isolated in a pure state. Moreover, as in the case of antimony aminotroponiminato derivative **10**, a slow decomposition in solution was observed both for **40**, **41** and **42** leading to the corresponding salt **44**.

In order to determine the unknown products which are present in the reaction mixture of **37**, **38** and **39** we also synthesized the corresponding ligand salt **43**, but, surprisingly, the signals that correspond for the salt ligand does not match with the signals found for the impurities.

However, all the compounds could be perfectly characterized by standard spectroscopic techniques.

The use of these ligands was then extended to the stabilization of low coordinated group 14 species.

### 3.2 Bis-germylenes

Germlyenes are heavier analogues of carbenes<sup>[78-82]</sup>, where the germanium atom exists in a formal divalent oxidation state<sup>[83-85]</sup>. The germlyenes are expected to be of great importance in fundamental and applied chemistry as a result of their differences and similarities to carbenes.

The dichlorogermylene complex Cl<sub>2</sub>Ge·1,4-dioxane<sup>[86-87]</sup> is known to be stable and isolable compared to the very transient CCl<sub>2</sub>.

In contrast to the carbon atom, the heavier germanium atom has a low ability to form hybrid orbitals. The germanium atom therefore prefers the 4s<sup>2</sup>4p<sup>2</sup> valence electron configurations in its divalent species<sup>[88-89]</sup>. Since two electrons remain as a lone pair in the 4s orbital, the ground state of H<sub>2</sub>Ge: is a singlet, unlike the case of H<sub>2</sub>C:, where the ground state is a triplet. Substituted germlyenes generally have a singlet ground state with a vacant p-orbital and a lone pair of valence orbitals. This extremely high reactivity must be due to their vacant p-orbitals, since 6 valence electrons are less than the 8 electrons of the “octet rule”. Their lone pair is expected to be inert due to its high s-character. In order to stabilize germlyenes enough to be isolated, either some thermodynamic and/or kinetic stabilization of the reactive vacant p-orbital is required. A range of “isolable” germlyenes has been synthesized through the thermodynamic stabilization of coordinating Cp\* ligands, the

inclusion of heteroatoms such as N, O, and P, and/or the introduction of kinetic stabilization using bulky substituents<sup>[90]</sup>.

Knowledge about bis-germylenes is limited to some cyclic (the first synthesis and characterization of such a compound, the trimeric species (GeNAr), where Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, was described in 1990)<sup>[91]</sup> or acyclic (stabilized using a bulky ligand such as -N(SiMe<sub>3</sub>)<sub>2</sub>)<sup>[92]</sup> derivatives.

In this context, our group reported the preparation of *p*-phenylene and *p*-biphenylene-bridged germanocenes where the germanium(II) atoms are linked to the cyclopentadienyl ring (V, Chart 4)<sup>[93]</sup>.

More recently, the preparation and coordination chemistry of bis-germylenes containing two benzannulated NHGe (N-heterocyclic germylene) units that can coordinate to transition metals in a chelating fashion (VI, Chart 4) were described by Zabula et al.<sup>[94-96]</sup>. These studies only involved N-heterocyclic germylenes featuring two normal covalent bonds.

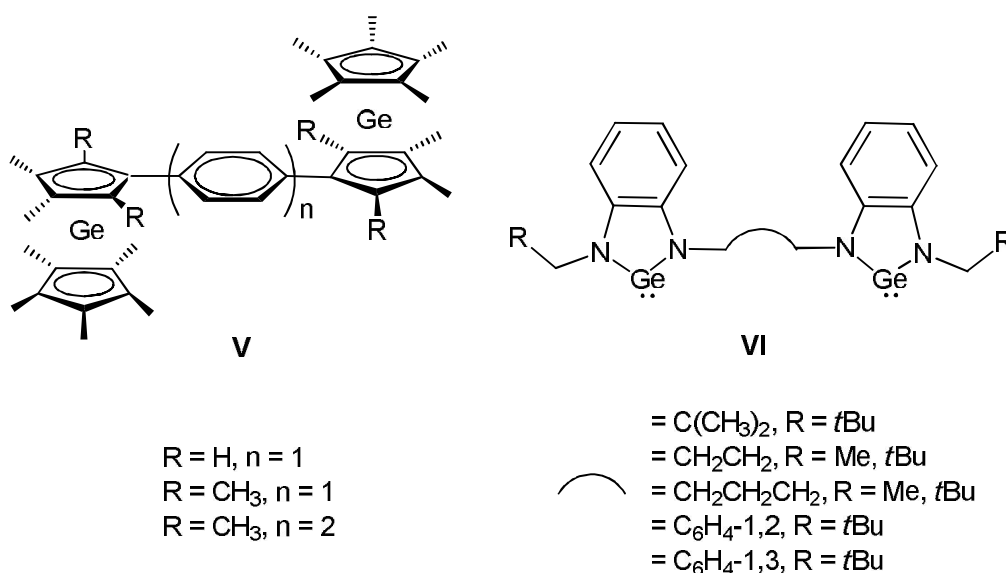
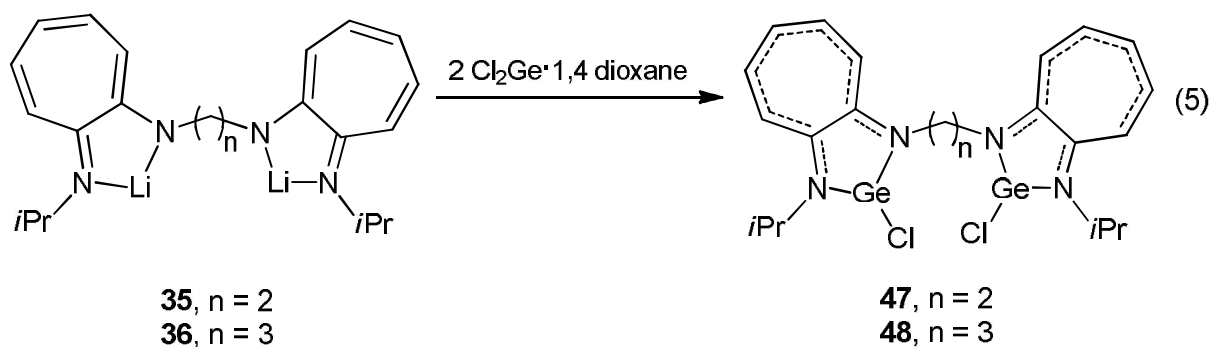


Chart 4

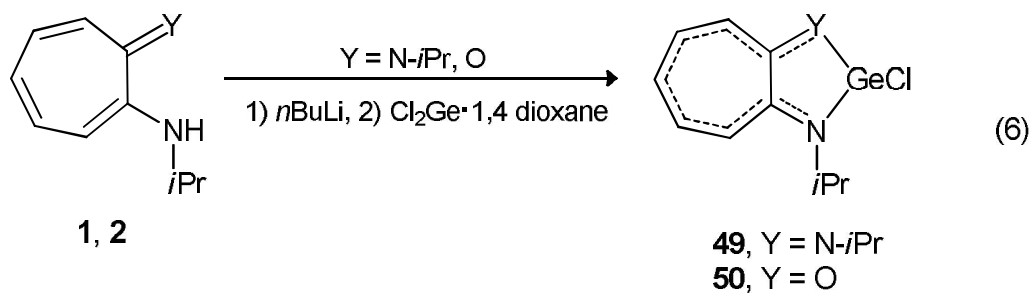
### 3.2.1 Synthesis of monogermynes and bis-germylenes

Bis-germylenes **47** and **48** were prepared by reaction of the di-lithiated derivatives **32** and **33** with Cl<sub>2</sub>Ge·1,4-dioxane in diethylether at -78°C (Equation 5). The orange-yellow products were isolated in good yields and fully characterized.



Besides the NMR investigations, both **47** and **48** were characterized by EI or CI mass spectrometry. However for compound **48** we were able to determine the high resolution mass spectrometric weight. The measured mass agrees to 4.49 ppm with the calculated exact mass.

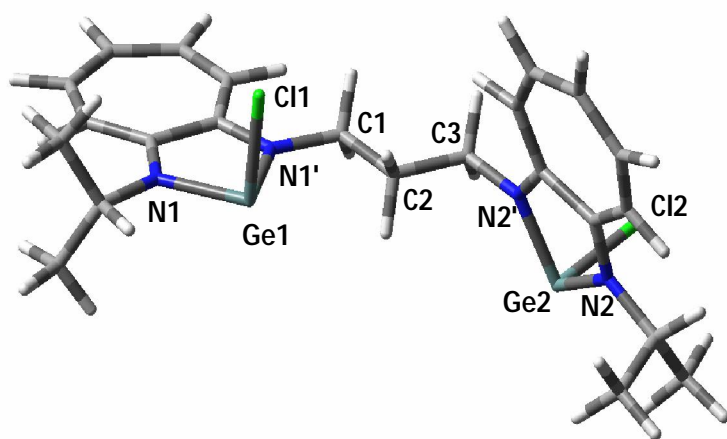
Concerning the aminotroponate units, their chelating properties remain totally unexplored in the germanium series not only for bis-germylenes but for monogermylene as well. In a first step, we prepared the chlorogermylene **50** by treatment of  $\text{Cl}_2\text{Ge} \cdot 1,4\text{-dioxane}$  with the lithium salt of the aminotroponone **1** using the experimental procedures described for the germylene containing aminotroponimate ligand **49** (1:1 molar ratio in diethyl ether at low temperature)<sup>[97]</sup> (Equation 6). These yellow products were isolated in good yields.



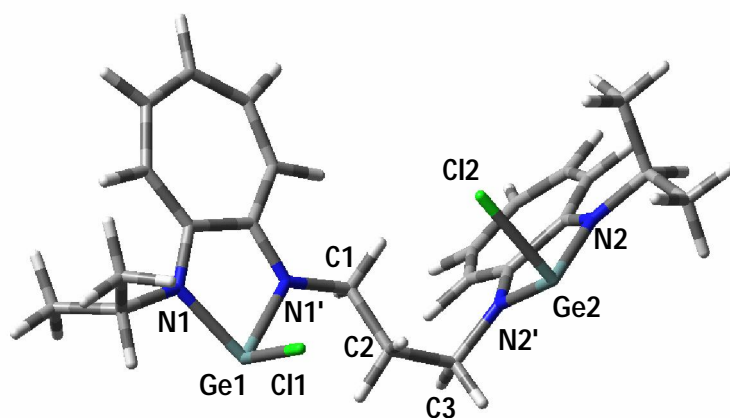
Depending on the deuterated solvent used, the analysis of  $^1\text{H}$  NMR spectrum of **50** shows a single doublet for the methyl of isopropyl groups like in the case of **49** when  $\text{CD}_3\text{Cl}$  is employed or two different large signals when  $\text{C}_6\text{D}_6$  is utilized. In the  $^{13}\text{C}$  NMR spectra, the identification of the carbon atoms of the seven-membered chelated ring were made according to the literature<sup>[46, 98]</sup>.

### 3.2.2 Computational studies

In order to get further insight about the molecular structure and the electronic state of the bis-germylene **48**, DFT(B3LYP) calculations were performed using the program Gaussian<sup>[99]</sup> with 6-31G(d,p) basis set. The structures, total and relative energies are depicted in Figures 3 and 4. The nature of the stationary points after optimization was checked by calculations of the harmonic vibration frequencies. Two minima were found on the surface energy potential one with the two germanium atoms directed toward the same direction, named pseudo-*Cis* and another one with the germanium atoms in opposite position, named pseudo-*Trans*.



**Figure 3:** Compound **48**, pseudo-*Trans* conformer



**Figure 4:** Compound **48**, pseudo-*Cis* conformer



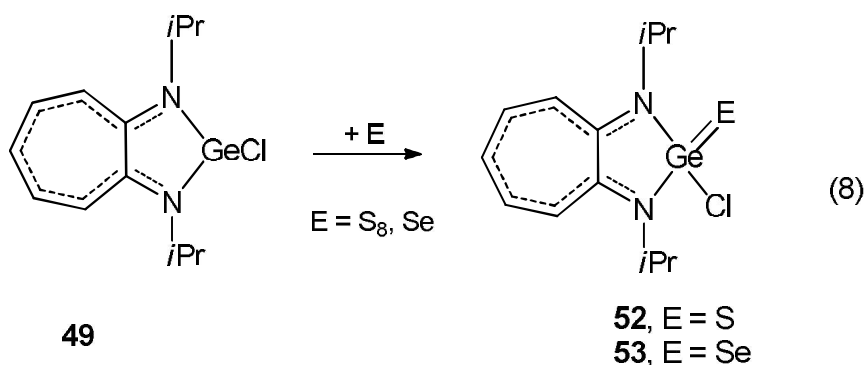
### 3.2.3 Chemical reactivity of germylenes

#### 3.2.3.1 Oxidative reactions with sulfur and selenium

In recent years, the chemistry of double bonded species between group 14 and 16 heavier elements  $M=E$  ( $M = \text{Si, Ge, Sn}$ ;  $E = \text{S, Se, Te}$ ) analogues of ketone, has attracted steady interest<sup>[100]</sup>. Examples such as  $\text{Si}=E$  ( $E = \text{S}$ )<sup>[101-102]</sup>,  $\text{Ge}=E$  ( $E = \text{S, Se, Te}$ )<sup>[103-109]</sup> and  $\text{Sn}=E$  ( $E = \text{S, Se, Te}$ )<sup>[110-115]</sup> have been synthesized and structurally characterized. In contrast, compounds involving double bonded elements bearing chlorines have been much less investigated. Only, few examples with  $\beta$ -diketiminates as ligands were reported<sup>[116]</sup>. The oxidation reaction of germylenes by chalcogens seems to constitute an efficient route to such species.

Firstly, we tried these reactions with monogermylenes **49** and **50**.

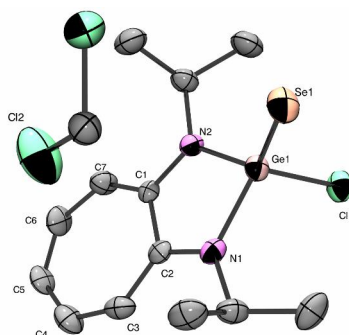
Treatment of chlorogermylene **49** with elemental sulfur and selenium in chloroform at 60 °C for 2 h and 4.5 h afforded the germanethioacid chloride **52** and germaneselenoacid chloride **53** as yellow solids (Equation 8). All these chalcogen derivatives were obtained in good yield. In contrast, with the phosphorus analogs **21** and **22**, these germathione and germaneselenone were not very air and moisture sensitive and hydrolysis of the Ge-Cl bond was never observed.



The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **52** and **53** show similar patterns and display the expected sets of signals.

In the  $^{77}\text{Se}$  NMR spectrum of compound **53** the resonance was observed at -44.91 ppm and seems to indicate that the bonding in solution can be described as intermediates between  $\text{Ge}^+-\text{Se}^-$  and  $\text{Ge}=\text{Se}$  resonance structure<sup>[116]</sup>.

Single crystal of **53** has been subjected to X-ray diffraction analysis and the corresponding molecular structure is shown in Figure 9.



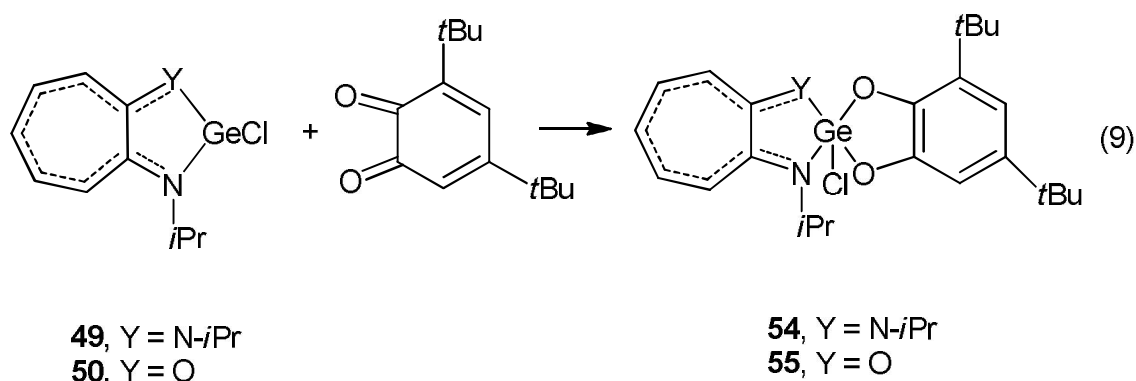
**Figure 9:** Molecular structure of compound **53** (50 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.

These data confirm that compound **53** is monomer in the solid state.

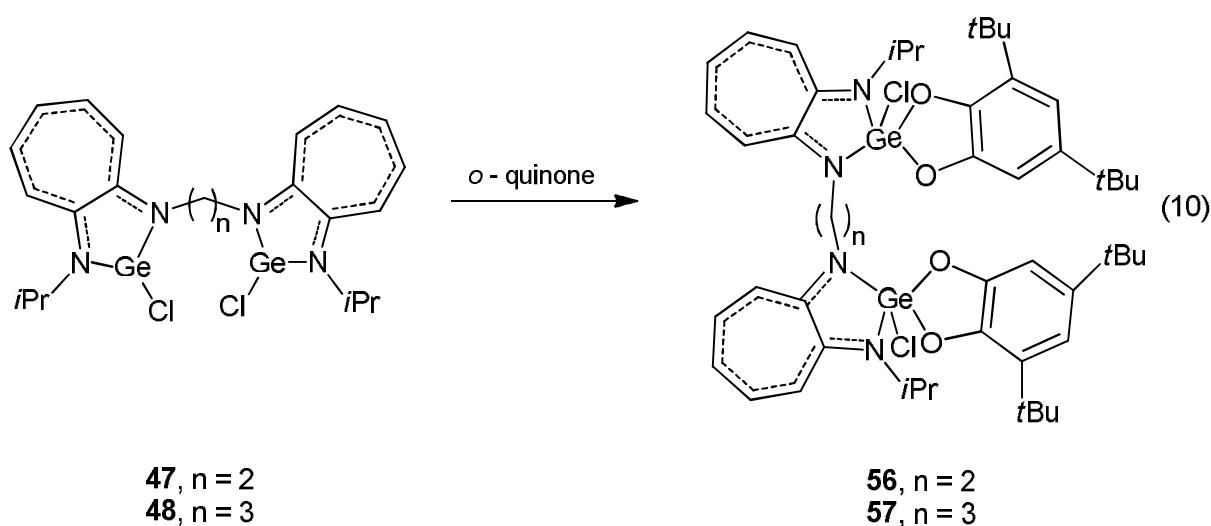
### 3.2.3.2 Cycloaddition reaction with *o*-quinone

One of the characteristic reactions for germylenes is the oxidative cycloaddition reaction with an *ortho* quinone.

The addition of 3,5-di-*tert*-butyl-*ortho*-quinone in THF solution at room temperature on germylenes **49** and **50** causes a slow discoloration of the quinone solution. The corresponding cycloadducts **54** and **55** could then be easily isolated after evaporation of the solvent and characterized (Equation 9).



Similarly, treatment of bis-germylenes **47** and **48** with *o*-benzoquinone at room temperature in THF led to the cyclic products **56** and **57**. The discoloration process of the quinone solution is ended in 1.5 h. After evaporation of the THF, the corresponding cycloadducts were isolated as yellow powders (Equation 10).



Cycloladducts **54** - **57** were fully characterized by multinuclear NMR spectroscopy and mass spectrometry.

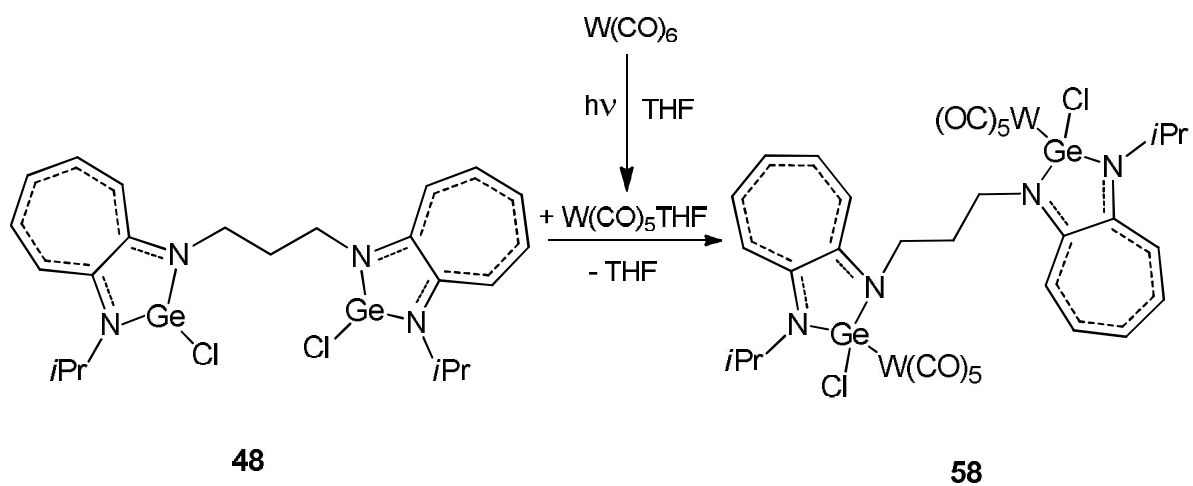
### 3.2.3.3 Complexation with transition metals

The lone pair on germanium could also allow the coordination on a transition metal<sup>[48]</sup>.

During the past few years, the chemistry of stable homoleptic (where the transition metal has only one type of ligand)<sup>[117]</sup> and heteroleptic (where the transition metal has more than one type of ligand)<sup>[117]</sup> divalent compounds of germanium<sup>[118]</sup> and of their transition metal complexes<sup>[119-120]</sup> has been the focus of considerable attention.

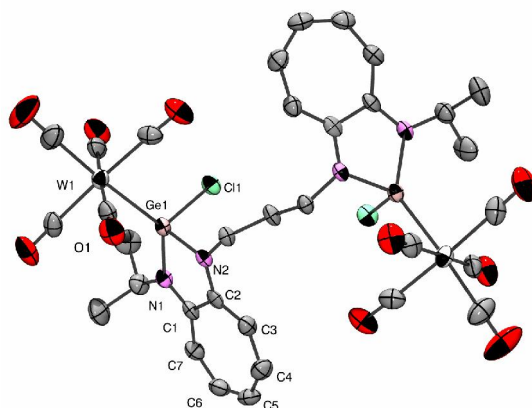
Like cationic transition metal phosphonium complexes, the analogous  $M_{14}(II)$ -transition metal complexes are of potential interest for many applications (e.g., as catalysts for cationic or ring-opening polymerizations) because of the possibility that the increased electrophilicity that results from the positive charge may enhance substrate coordination and activation<sup>[121]</sup>.

The reaction of the divalent species **48** with the pentacarbonyltungsten·THF intermediate in tetrahydrofuran gave the expected germylene tungsten complex in very good yield. The compound was fully characterized. X-ray quality crystal was grown from  $CH_2Cl_2$  at room temperature (Scheme 2).



Scheme 2

This new complex with tungsten crystallizes as monomer with no interaction in the solid state; the structure of **58** is depicted in Figure 10.



**Figure 10:** Molecular structure of compound **58** (50 % probability level for the thermal ellipsoids). All H atoms have been omitted for clarity.

The germylene units adopt an *anti* arrangement toward each other and the alkyl bridge exhibits an all *trans* conformation.

## Conclusions and perspectives

In this last chapter, we have prepared the first bridged bis-pnictogenium (P, As and Sb) cations supported by aminotroponimate (N,N') and aminotroponate (N,O) ligands using direct two-step synthetic pathways: a nucleophilic substitution reaction by an aminolithiated derivative or a base-induced dehydrohalogenation coupling reaction. The  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses confirmed the formation of cationic species with high delocalization of the positive charge on the  $\pi$ -conjugated backbone.

An extension to the corresponding bis-germylenes was also described. Theoretical calculations using DFT(B3LYP) have been carried out showing that the conformation, named pseudo-*Trans* with the germanium atoms in opposite position, was slightly more stable than the pseudo-*Cis* conformation with the two germanium atoms directed toward the same direction.

Some tests of reactivity such as oxidative reaction with chalcogens (sulfur and selenium) and cycloaddition reaction with *o*-quinone were also performed in comparison with the corresponding monogermynes. In both cases, these species retain their divalent character.

The  $\sigma$ -donor character of these bis-germylenes was highlighted by their easy complexation with transition metal complexes. For the first time, a stable trans-disubstituted germanium(II)-tungsten carbonyl complex was prepared and structurally characterized.

## Abstract

This thesis entitled “N,N'- and N,O-chelated pnictogenium cations (P, As, Sb) and germylenes: syntheses, structural studies and reactivity” is structured in three chapters dealing with:

- the syntheses of new pnictogenium cations (P, As, Sb) supported by aminotroponate and aminotroponimate ligands
- the study of pnictogenium cations reactivity
- the syntheses of new bridged bis-pnictogenium cations (P, As, Sb), syntheses and reactivity of new germylenes and bridged bis-germylenes

In the first chapter an easy and direct route to the first phosphonium and arsenium cations supported by N,N' or N,O-chelation derived from a tropolone scaffold was presented. These new compounds were fully characterized by various spectroscopic methods, X-ray analyses and DFT calculations. The expected Lewis amphotericism which is illustrated on the one hand, by the high-lying phosphorus lone-pair orbital (HOMO-1), and on the other hand, by the delocalized positive charge opens up new perspectives for the involvement of these ambiphilic species as valuable ligands for new catalysts.

The second chapter concerns the reactivity of these new pnictogenium cations. A variety of reactions including oxidation (with dimethylsulfoxide, sulfur or selenium), cycloaddition and halide ion extraction were studied. The first example of an aminometaphosphonate (and its sulfur equivalent) stabilized by intramolecular complexation was reported. For the first time, a hydroxyphosphonium cation stabilized by complexation with pentacarbonyltungsten was prepared and its structure elucidated by X-ray single-crystal diffraction study.

The last chapter refers to the synthesis and characterization of bridged bis(pnictogenium) cations with an extension to divalent germanium compounds. Among the most noteworthy result is the stable bis-germylene pentacarbonyl tungsten complex.

**Key words:** phosphonium, arsenium, germylene, O,O' ligand N,O ligand N,N' ligand, chelates

## Selected references

- [1] K. Dimroth, P. Hoffman, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 384.
- [2] N. J. Hardman, M. B. Abrams, M. A. Pribisko, T. M. Gilbert, R. L. Martin, G. J. Kubas, R. T. Baker, *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 1955.
- [3] H. A. Spinney, I. Korobkov, G. A. DiLabio, G. P. A. Yap, D. S. Richeson, *Organometallics* **2007**, *26*, 4972.
- [4] B. D. Ellis, P. J. Ragogna, C. L. B. Macdonald, *Inorg. Chem.* **2004**, *43*, 7857.
- [5] A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913.
- [6] H. M. Tuononen, R. Roesler, J. L. Dutton, P. J. Ragogna, *Inorg. Chem.* **2007**, *46*, 10693.
- [7] J. B. Lambert, W. J. Schulz, *J. Am. Chem. Soc.* **1983**, *105*, 1671.
- [8] G. A. Olah, *Halonium Ions*, Wiley: New York **1975**.
- [9] S. Fleming, M. K. Lupton, K. Jekot, *Inorg. Chem.* **1972**, *11*, 2534.
- [10] B. E. Maryanoff, R. O. Hutchins, *J. Org. Chem.* **1972**, *37*, 3475.
- [11] A. H. Cowley, M. C. Cushner, J. S. Szobota, *J. Am. Chem. Soc.* **1978**, *100*, 7784.
- [12] P. Friedrich, G. Huttner, J. Luber, A. Schmidpeter, *Chem. Ber.* **1978**, *111*, 1558.
- [13] S. Pohl, *Chem. Ber.* **1979**, *112*, 3159.
- [14] A. H. Cowley, R. A. Kemp, *Chem. Rev.* **1985**, *85*, 367.
- [15] M. G. Thomas, C. W. Schultz, R. W. Parry, *Inorg. Chem.* **1977**, *16*, 994.
- [16] R. W. Kopp, A. C. Bond, R. W. Parry, *Inorg. Chem.* **1976**, *15*, 3042.
- [17] G. Reeske, C. R. Hoberg, N. J. Hill, A. H. Cowley, *J. Am. Chem. Soc.* **2006**, *128*, 2800.
- [18] C. J. Carmalt, V. Lomeli, B. G. McBurnett, A. H. Cowley, *Chem. Commun.* **1997**, 2095.
- [19] D. Gudat, *Coord. Chem. Rev.* **1997**, *163*, 71.
- [20] D. Vidovic, Z. Lu, G. Reeske, J. A. Moore, A. H. Cowley, *Chem. Commun.* **2006**, 3501.
- [21] S. P. Green, C. Jones, G. Jin, A. Stasch, *Inorg. Chem.* **2007**, *46*, 8.
- [22] B. D. Ellis, C. L. B. Macdonald, *Inorg. Chim. Acta* **2007**, *360*, 329.
- [23] N. Burford, T. M. Parks, B. W. Royan, J. F. Richardson, P. S. White, *Can. J. Chem.* **1992**, *71*, 703.
- [24] N. Burford, C. L. B. Macdonald, T. M. Parks, G. Wu, B. Borecka, W. Kiviatkowski, T. S. Cameron, *Can. J. Chem.* **1996**, *74*, 2209.
- [25] D. Gudat, T. Gans-Eichler, M. Nieger, *Heteroatom Chem.* **2005**, *16*, 327.
- [26] M. K. Denk, S. Gupta, A. J. Lough, *Eur. J. Inorg. Chem.* **1999**, 41.
- [27] I. A. Litvinov, V. A. Naumov, T. V. Gryaznova, A. N. Pudovik, A. M. Kibadin, *Dolk. Akad. Nauk. SSSR* **1990**, *312*, 623.
- [28] D. Gudat, H. Haghverdi, H. Hupfer, M. Nieger, *Chem. -Eur. J.* **2000**, *6*, 3414.
- [29] P. Jutzi, T. Wippermann, C. Kruger, H. Kraus, *Angew. Chem. Int. Edit.* **1983**, *22*, 250.
- [30] L. A. Lesikar, A. F. Richards, *J. of Organometallic Chem.* **2006**, *691*, 4250.
- [31] B. Lyhs, S. Schultz, U. Westphal, D. Blaser, R. Boese, M. Bolte, *Eur. J. Inorg. Chem.* **2009**, 2247.
- [32] R. Menye-Biyogo, F. Delpech, A. Castel, V. Pimienta, H. Gornitzka, P. Rivière, *Organometallics* **2007**, *26*, 5091.
- [33] R. Menye-Biyogo, F. Delpech, A. Castel, P. Rivière, H. Gornitzka, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 5610.
- [34] J. Zhang, P. D. Badger, S. J. Geib, S. Petoud, *Inorg. Chem.* **2007**, *46*, 6473.
- [35] K. Lyczko, W. Starosta, I. Persson, *Inorg. Chem.* **2007**, *46*, 4402.
- [36] Y. Jianlin, Y. Yaxian, G. Renao, *Spect. Acta Part A* **2006**, *64*, 1072.
- [37] A. T. Balaban, I. Haiduc, H. Hopfl, N. Farfan, R. Santillan, *Main Group Metal Chemistry* **1996**, *19(6)*, 385.
- [38] P. W. Roesky, *Chem. Soc. Rev.* **2000**, *29*, 335.
- [39] H. V. R. Dias, Z. Wang, W. Jin, *Coord. Chem. Rev.* **1998**, *176*, 67.
- [40] D. Pappalardo, M. Mazzeo, P. Montefusco, C. Tedesco, C. Pellecchia, *Eur. J. Inorg. Chem.* **2004**, 1292.

- [41] N. Meyer, K. Löhnwitz, A. Zulys, P. W. Roesky, M. Dochnahl, S. Blechert, *Organometallics* **2006**, *25*, 3730.
- [42] S. Dehnen, M. R. Bürgstein, P. W. Roesky, *J. Chem. Soc., Dalton Trans.* **1998**, 2425.
- [43] F. A. Hicks, M. Brookhart, *Organometallics* **2001**, *20*, 3217.
- [44] S. Datta, P. W. Roesky, S. Blechert, *Organometallics* **2007**, *26*, 4392.
- [45] N. Meyer, R. Rüttinger, P. W. Roesky, *Eur. J. Inorg. Chem.* **2008**, 1830.
- [46] H. V. R. Dias, W. Jin, R. E. Ratcliff, *Inorg. Chem.* **1995**, *34*, 6100.
- [47] L.-C. Pop, N. Katir, A. Castel, L. Silaghi-Dumitrescu, F. Delpech, I. Silaghi-Dumitrescu, H. Gornitzka, D. MacLeod-Carey, N. Saffon, *J. Organomet. Chem.* **2009**, *694*, 1562.
- [48] M. Sanchez, M. R. Mazières, L. Lamandé, R. Wolf, *Multiple Bonds and Low Coordination Chemistry in Phosphorous Chemistry*, (Eds: M. Regitz, O. Scherer), Georg Thieme Verlag, Stuttgart **1990**, 129.
- [49] A. H. Cowley, M. Lattman, J. C. Wilburn, *Inorg. Chem.* **1981**, *20*, 2916.
- [50] R. B. King, N. D. Sadani, *Synth. React. Inorg. Met.-Org. Chem.* **1985**, 149.
- [51] N. Burford, P. J. Ragogna, *J. Chem. Soc., Dalton Trans.* **2002**, 4307.
- [52] W. Becker, D. Schomburg, P. G. Jones, R. Schmutzler, *Phosphorus Sulfur Silicon* **1990**, *49/50*, 109.
- [53] T. Kaukorat, I. Neda, R. Schmutzler, *Coord. Chem. Rev.* **1994**, *137*, 53.
- [54] D. M. Grant, R. K. Harris, *Encyclopedia of Nuclear Magnetic Resonance*, John Wiley & Sons **1996**.
- [55] O. D. Sparkman, *Mass spectrometry desk reference*. Pittsburgh: Global View Pub. **2000**.
- [56] L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, N. Y., **1960**.
- [57] P. W. Roesky, M. R. Bürgstein, *Inorg. Chem.* **1999**, *38*, 5629.
- [58] K. Kubo, T. Matsumoto, M. Hashimoto, A. Mori, *Acta Cryst.* **2006**, *E62*, o3584.
- [59] G. Steyl, *Acta Cryst.* **2007**, *E63*, o4353.
- [60] S. ADF2006.01, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com/>. Methods and results are presented in Supporting Information.
- [61] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.
- [62] P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669.
- [63] C. Corminboeuf, T. Heine, G. Seifert, P. v. R. Schleyer, J. Weber, *Phys. Chem. Chem. Phys.* **2004**, *6*, 273.
- [64] C. H. Dungan, J. R. V. Wazer, *Compilation of reported F(19) NMR chemical shifts, 1951 to mid-1967*, **1970** Wiley-Interscience, New York.
- [65] E. H. Amonoo-Neize, S. K. Ray, R. A. Shaw, B. C. Smith, *J. Chem. Soc.* **1965**, 6250.
- [66] F. Ramirez, M. Nowakowski, J. F. Marecek, *J. Am. Chem. Soc.* **1977**, *99*, 4515.
- [67] D. Gudat, M. Nieger, E. Niecke, *J. Chem. Soc. Dalton. Trans.* **1989**, 693.
- [68] H. V. R. Dias, W. Jin, Z. Wang, *Coord. Chem. Rev.* **1998**, *176*, 67.
- [69] M. R. Bürgstein, H. Berberich, P. W. Roesky, *Organometallics* **1998**, *17*, 1452.
- [70] P. W. Roesky, *Eur. J. Inorg. Chem.* **1998**, 593.
- [71] P. W. Roesky, *Chem. Ber.* **1997**, *130*, 859.
- [72] H. V. R. Dias, W. Jin, Z. Wang, *Inorg. Chem.* **1996**, *35*, 6074.
- [73] P. W. Roesky, *Inorg. Chem.* **1998**, *37*, 4507.
- [74] P. W. Roesky, *J. Organomet. Chem.* **2000**, *603*, 161.
- [75] M. R. Bürgstein, W. Roesky, *Organometallics* **2003**, *22*, 1372.
- [76] N. Meyer, A. Zulys, P. W. Roesky, *Organometallics* **2006**, *25*, 4179.
- [77] I. Fernandez, E. M. Viviente, F. Breher, P. S. Pregosin, *Chem. Eur. J.* **2005**, *11*, 1495.
- [78] P. Jutzi, A. Becker, H. G. Stammer, B. Neumann, *Organometallics* **1991**, *10*, 1647.
- [79] W. Petz, *Chem. Rev.* **1986**, *86*, 1019.
- [80] M. F. Lappert, R. S. Rowe, *Coord. Chem. Rev.* **1990**, *100*, 267.
- [81] J. Barrau, J. Escudié, J. Satgé, *Chem. Rev.* **1990**, *90*, 283.



- [82] G. L. Wegner, R. J. F. Berger, A. Schier, H. Schmidbaur, *Organometallics* **2001**, *20*, 418.
- [83] M. Weidenbruch, *Eur. J. Inorg. Chem.* **1999**, 373.
- [84] J. Barrau, G. Rima, *Coord. Chem. Rev.* **1998**, *178-180*, 593.
- [85] W. P. Neumann, *Chem. Rev.* **1991**, *91*, 311.
- [86] P. T. Matsunaga, J. Kouvetakis, T. L. Groy, *Inorg. Chem.* **1995**, *34*, 5103.
- [87] T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert, A. J. Thorne, *J. Chem. Soc., Dalton Trans.* **1986**, 1551.
- [88] T. Sasamori, N. Tokitoh, R. B. King, *Encyclopedia of Inorganic Chemistry II*, Ed. John Wiley & Sons: Chichester, U.K. **2005**.
- [89] T. Fueno, *The Transition State: A Theoretical Approach*, Ed. Gordon and Breach Science Publishers: Langhorne, PA **1999**.
- [90] Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479.
- [91] R. A. Bartlett, P. P. Power, *J. Am. Chem. Soc.* **1990**, *112*, 3660.
- [92] S. Kobayashi, S. Cao, *Chem. Lett.* **1994**, *25*, 941.
- [93] J. Rouzaud, A. Castel, P. Rivière, H. Gornitzka, J. M. Manriquez, *Organometallics* **2000**, *19*, 4678.
- [94] A. V. Zabula, F. E. Hahn, T. Pape, A. Hepp, *Organometallics* **2007**, *26*, 1972.
- [95] F. E. Hahn, A. V. Zabula, T. Pape, F. Hupka, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1341.
- [96] F. E. Hahn, A. V. Zabula, T. Pape, A. Hepp, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2397.
- [97] H. V. R. Dias, Z. Wang, *J. Am. Chem. Soc.* **1997**, *119*, 4650.
- [98] T. Nozoe, K. Imafuku, B.-Z. Yin, M. Honda, Y. Hara, T. Anoloh, H. Yamamoto, *Bull. Chem. Soc. Jpn* **1988**, *61*, 2531.
- [99] *Gaussian 98, Revision A.11.3; Gaussian, Inc.: Pittsburgh, PA 2002*.
- [100] Y. Ding, Q. Ma, I. Uson, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, *J. Am. Chem. Soc.* **2002**, *124*, 8542.
- [101] P. Arya, J. Boyer, F. Carre, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot, C. Priou, *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016.
- [102] H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11578.
- [103] M. Veith, S. Becker, V. Huch, *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237.
- [104] M. C. Kuchta, G. Parkin, *J. Chem. Soc., Chem. Commun.* **1994**, 1351.
- [105] T. Matsumoto, N. Tokitoh, R. Okazaki, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316.
- [106] N. Tokitoh, T. Matsumoto, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 2337.
- [107] S. R. Foley, C. Bensimon, D. S. Richeson, *J. Am. Chem. Soc.* **1997**, *119*, 10359.
- [108] G. Ossig, A. Meller, C. Bronneke, O. Muller, M. Schafer, R. Herbst-Irmer, *Organometallics* **1997**, *16*, 2116.
- [109] T. Matsumoto, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1999**, *121*, 8811.
- [110] R. Guillard, C. Ratti, J.-M. Barbe, D. Dubois, K. M. Kadish, *Inorg. Chem. Ber.* **1991**, *30*, 1537.
- [111] Y. Matsushashi, N. Tokitoh, R. Okazaki, *Organometallics* **1993**, *12*, 2573.
- [112] M. C. Kuchta, G. Parkin, *J. Am. Chem. Soc.* **1994**, *116*, 8372.
- [113] Y. Zhou, D. S. Richeson, *J. Am. Chem. Soc.* **1996**, *118*, 10850.
- [114] W.-P. Leung, W.-H. Kwok, L. T. C. Law, Z.-Y. Zhou, T. C. W. Mak, *J. Chem. Soc., Chem. Commun.* **1996**, 505.
- [115] M. Saito, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 11124.
- [116] W. P. Leung, K. H. Chong, Y. S. Wu, C. W. So, H. S. Chan, T. C. W. Mak, *Eur. J. Inorg. Chem.* **2006**, 808.
- [117] A. D. McNaught, A. Wilkinson, *IUPAC. Compendium of Chemical Terminology, 2nd ed. Blackwell Scientific Publications, Oxford* **1997**.
- [118] O. Kuhl, *Coord. Chem. Rev.* **2004**, *248*, 411.
- [119] C. Bibal, S. Mazière, H. Gornitzka, C. Couret, *Organometallics* **2002**, *21*, 2940.
- [120] I. Saur, G. Rima, K. Miqueu, H. Gornitzka, J. Barrau, *J. Organomet. Chem.* **2003**, *672*, 77.
- [121] I. Saur, S. G. Alonso, J. Barrau, *Appl. Organometal. Chem.* **2005**, *19*, 414.

