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FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

PhD Thesis Summary

The role of phosphavinyl(chalcogenoxo)phosphoranes in the stabilization of new *p* and *d* block metal species

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Contents

Keywords: phosphavinyl(chalcogenoxo)phosphorane, metal complexes, germylene

General introduction

This work presents a bibliographic and an experimental study regarding the synthesis and characterization of several phosphavinyl(chalcogenoxo)phosphorane derivatives as ligands in the synthesis of coordinative and organometallic compounds as well as in the stabilization of low valent E(II) species.

The PhD thesis contains two parts: part I which presents a bibliographic review and part II that contains the original contributions. The main objectives of this thesis, namely the synthesis and characterization of electron rich P=C-P and P=C-P(=X) (X= O, S, Se) type derivatives, the synthesis and characterization of coordination compounds of above mentioned derivatives towards transition metals and the synthesis and characterization of the first tetrylene species stabilized by using a P=C-P moiety are detailed in the three chapters of the original contributions.

PART I. BIBLIOGRAPHIC REVIEW

The chemistry of derivatives bearing a P=C-P or a P=C-P(=X) (X = chalcogen atom) moiety is an interesting research topic due to their potential use as building blocks in organometallic chemistry or in coordination chemistry. The stability of these type of systems was achieved by using bulky substituents with strong steric effects and/or substituents with electronic effects at the level of both phosphorus atoms. Given that the P=C-P(=X) type compounds have the phosphorus atoms in two different oxidation states, P(III) and P(V), such derivatives can act as ligands in obtaining the corresponding phosphavinyl(chalcogenoxo)phosphorane coordination derivatives with numerous *d*-block metals. Furthermore, due to their multiple coordination possibilities (lone pair of electrons from sp^2 phosphorus atom, the chalcogen atom and the P=C double bond), the phosphavinyl(chalcogenoxo)phosphorane compounds can act as building blocks in the synthesis of both organometallic and coordination compounds or in the stabilization of low valent E(II) (E = Si, Ge, Sn, Pb) species.

In the first two parts of the bibliographic review, the synthesis and characterization of derivatives bearing a P=C-P or a P=C-P(=X) (X = O, S) unit along with the synthesis and characterization of their complexes with a variety of *d*-block metals such as Au, W, Pd and Pt were described. Only one gold complex was reported so far in the scientific literature in contrast to several examples of tungsten and palladium complexes.

In the last part of the bibliographic review, a short introduction on tetrylenes is presented together with the synthesis of several E(II) species stabilized with N-heterocyclic carbenes. Moreover, the synthesis and characterization of the first germylenes and stannylenes stabilized with derivatives bearing a P=C moiety along with their reactivity study towards chalcogens and several metal fragments were described.

PART II. ORIGINAL CONTRIBUTIONS

Chapter 1. Synthesis of electron rich P=C-P and P=C-P(=X) (X = O, S, Se) type derivatives

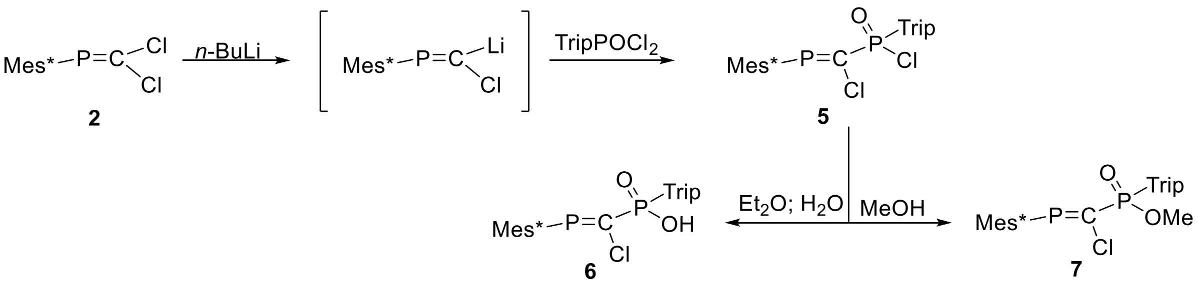
1.1.Introduction

The chemistry of derivatives containing a P=C-P or a P=C-P(=X) (X = chalcogen atom) moiety has received a great interest due to their possible applications as ligands in the synthesis of new coordination and organometallic compounds.[1] The stability of these type of compounds can be increased by using bulky substituents with strong steric effects or/and by using substituents with electronic effects.

In this chapter we present the synthesis and the physico-chemical and structural characterization of derivatives containing a P=C-P or a P=C-P(=X) (X= O, S, Se) unit which will be further used as ligands in obtaining of new coordination and organometallic compounds The experimental study was enhanced by a theoretical investigation through DFT methods focusing on the coordination preferences of these type of systems and how different substituents at the level of the phosphorus atoms influence their properties.

1.2. Synthesis of phosphavinyl(oxo)phosphorane derivatives bearing a P=C-P(=O) unit

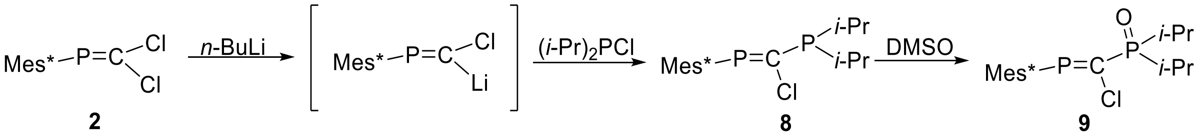
In order to obtain derivative Mes*P=C(Cl)-P(=O)(Cl)Trip **5**, one equivalent of *n*-BuLi was added to a solution of Mes*P=CCl$_2$[2,3] **2** in THF, at low temperature, leading to the formation of a organolithium intermediate Mes*P=C(Cl)Li which will further react with the corresponding 2,4,6-tri-*iso*-propylphenylphosphonic dichloride **4** (TripPOCl$_2$)[4] to form the target compound in good yield (Scheme 1).



Scheme 1. Synthesis of Mes*P=C(Cl)-P(=O)(Cl)Trip (**5**), Mes*P=C(Cl)-P(=O)(OH)Trip (**6**) and Mes*P=C(Cl)-P(=O)(OMe)Trip (**7**)

In attempts to obtain crystals for an X-Ray diffraction study, the addition of diethyl ether to compound **5** afforded, after several days, the formation of hydrolysis product **6** as white crystals. Furthermore, the reaction of phosphavinylphosphorane **5** with methanol led, within several days, to a new derivative Mes*P=C(Cl)-P(=O)(Trip)(OMe) **7** (see Scheme 1).

As presented in Scheme 2, derivative Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$ **9** was obtained in two reaction steps. Firstly, a solution of (*i*-Pr)$_2$PCl in THF was added to the lithiated derivative of the dichlorophosphaalkene **2** at low temperature. The resulting product, Mes*P=C(Cl)-P(*i*-Pr)$_2$ **8**, was obtained as a light-yellow oil and was used further without other purification.

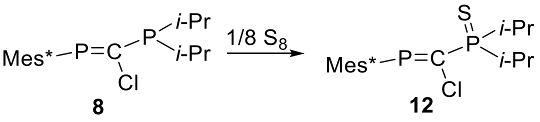


Scheme 2. Synthesis of Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$ (**9**)

Further, derivative **8** was reacted with DMSO in refluxing toluene affording separation of derivative **9** as colorless crystals in pentane, at low temperature.

1.3. Synthesis of phosphavinyl(thioxo)phosphorane derivatives bearing a P=C-P(=S) unit

Synthesis of derivative Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** undergoes by a similar method to that described for compound **9** through the oxidation of derivative **8** with a 100% excess of sulfur as presented in Scheme 3.

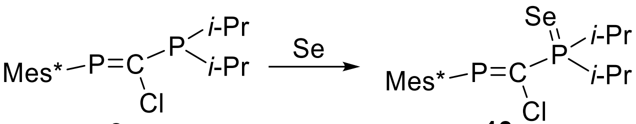


Scheme 3. Synthesis of Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ (**12**)

After purification, derivative Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** was obtained as yellow crystals from pentane at room temperature.

1.4. Synthesis of a phosphavinyl(selenoxo)phosphorane derivative bearing a P=C-P(=Se) unit

Derivative Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** was obtained in a similar manner as its sulfur analogue as presented in Scheme 4.



Scheme 4. Synthesis of Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ (**13**)

After purification, derivative **13** was obtained as yellow crystals from pentane and toluene at -20 °C.

1.5. Physico-chemical and structural characterization

1.5.1. NMR investigations

All obtained derivatives **5-9**, **12** and **13** were characterized in solution by ^{1}H, ^{13}C, ^{31}P, HSQC, HMBC, COSY nuclear magnetic resonance (NMR) spectroscopy. All NMR spectra were recorded in $CDCl_3$. The ^{31}P{^{1}H} NMR data recorded for compounds **5**, **6**, **7**, **9, 12** and **13** are presented in Table 1.

Table 1. ^{31}P{^{1}H} NMR data ($CDCl_3$) of derivatives **5**, **6**, **7**, **9**, **12** and **13**.

Compound	**δ^{31}P{^{1}H}(ppm)**		**$^{2}J_{P,P}$ (Hz)**
	P=C	**P-C**	
Mes*P=C(Cl)-P(=O)(Cl)Trip **5**	309.1	41.0	139.2
Mes*P=C(Cl)-P(=O)(OH)Trip **6**	297.2	34.1	130.3
Mes*P=C(Cl)-P(=O)(OMe)Trip **7**	301.4	32.0	117.4
Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$ **9**	321.1	56.8	58.4
Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12**	330.7	74.4	85.8
Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13**	336.1	69.8	95.4

The signals attributed for phosphorus atom involved in P=C unit of derivatives **5**, **6**, **7**, **9**, **12** and **13** are downfield shifted compared to the signal for starting material Mes*$PCCl_2$ **2** which is observed at 232.3 ppm. All ^{31}P NMR signals are in the expected range according to scientific literature for similar derivatives, with values ranges from 297 to 336 ppm for the P(III) atoms and from 32-75 ppm for the P(V)atoms.[5,6,7,8]

The other NMR investigation are detailed in the current thesis.

1.5.2. X-ray diffraction studies

The solid-state structures of derivatives **6**, **9**, **12** and **13** were unambiguously determined through single crystal X-ray diffraction analysis. Single crystals of **6** were obtained by slow evaporation from a diethyl ether solution, at room temperature.

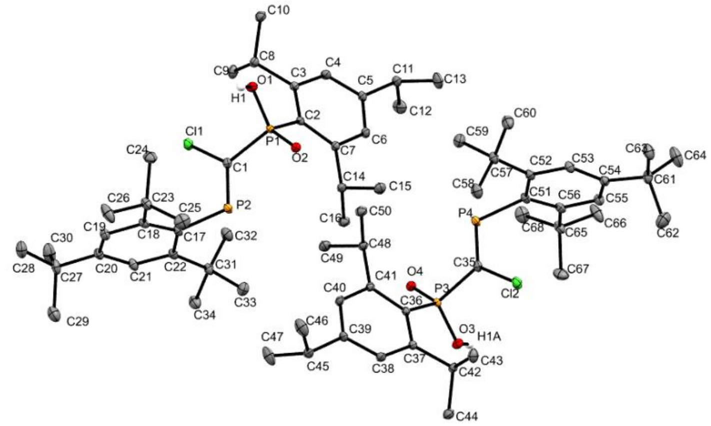


Figure 1. Molecular structure of Mes*P=C(Cl)-P(=O)(OH)Trip **6** shown with 40% probability ellipsoids; ($R_{P(V)}$) isomer (left) and ($S_{P(V)}$) isomer (right). Hydrogen atoms are omitted for clarity.

The P=C bond lengths are 1.683(1) (molecule 1) and 1.682(1) Å (molecule 2), while the Mes*(C)-P bond length has the same value for both enantiomers of 1.838(1) Å. The P=C-P angles are 117.5(1) and 118.2(1)° in the expected range for similar derivatives.[5]

Crystallization from pentane (compounds **9** and **12**) and from pentane and toluene (compound **13**), at low temperature, afforded single crystals suitable for X-ray diffraction study. Derivatives **9**, **12** and **13** crystallize in monoclinic space groups $P\,2_1/c$ and $P\,2_1/n$ with one molecule in the asymmetric unit as presented in Figure 2.

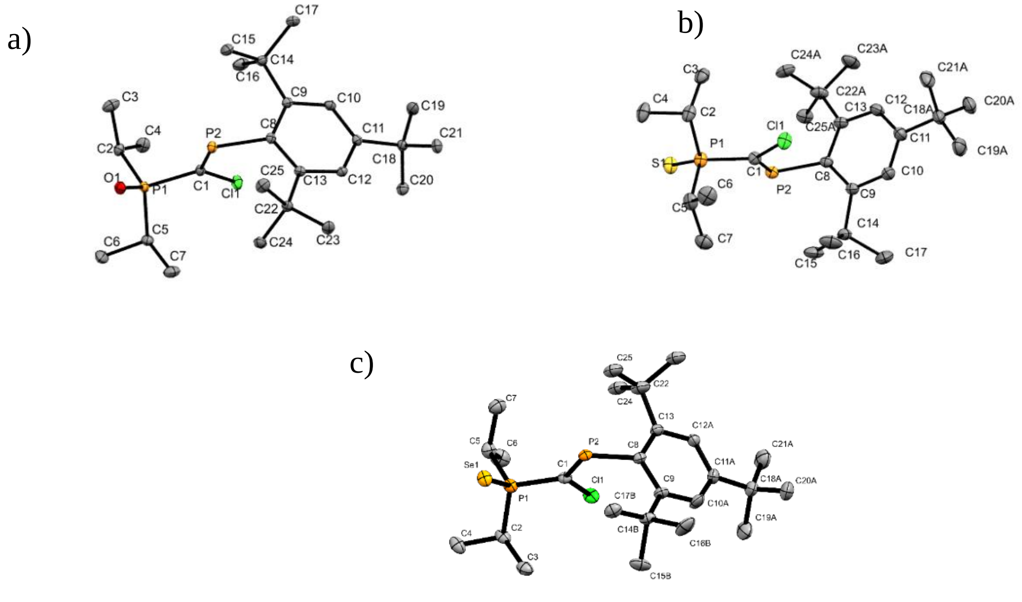


Figure 2. Molecular structures of **9** (a), **12** (b) and **13** (c) shown with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The main geometrical parameters are, as expected, very similar between compounds **9**, **12** and **13**. Thus, the P=C bond length for derivatives **9** and **12** is 1.681(1) Å while, for derivative **13** is 1.680(2) Å, having similar values to that observed in the case of compound **6** (1.683(1) Å).

1.5.3. Mass spectrometry analyses

For all newly obtained derivatives **5-7**, **9**, **12** and **13** high resolution mass spectra were recorded using electrospray ionization (ESI). The HRMS data are presented in the current thesis.

1.6. DFT study

DFT calculations were performed in order to gain more information about the structural and the electronic feature of derivatives bearing a P=C-P(=X) (X = O, S) moiety. According to these theoretical investigations, the bulkiness of R and the electronegativity of R' groups affect only in a lesser extent the P=C, C-P and P=X bond lengths where the bond distance increases with the bulkiness of R groups.

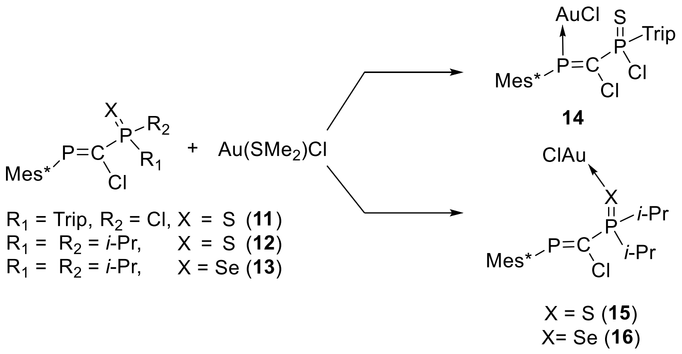
Chapter 2. A study regarding the coordination capacity of phosphavinyl(chalcogenoxo)phosphoranes (P=C-P(=X); X = O, S, Se) towards transition metals

2.1. Introduction

In this chapter a study regarding the coordination capacity of phosphavinyl(chalcogenoxo)phosphoranes derivatives towards transition metals (Au, W, Pd) is presented. This work aims to bring valuable insights about the role played by several organic groups in the stabilization of P=C-P(=X) type derivatives and their effects on the coordination capacity of these compounds to *d*-block metals. The synthesis and characterization of all newly obtained complexes is summarized in the following sections.

2.2. Coordination abilities of derivatives **5**, **11**, **12** and **13** to gold fragments

The coordination ability of Mes*P=C(Cl)-P(=S)(Cl)Trip **11**, Mes*P=C(Cl)-P(=S)(i-Pr)$_2$ **12** or Mes*P=C(Cl)-P(=Se)(i-Pr)$_2$ **13** toward gold fragments was investigated by using Au(SMe$_2$)Cl. The pathway for synthesis of new gold complexes containing a P=C-P(=S) unit is presented in Scheme 5.



Scheme 5. Synthesis of {Mes*P=C(Cl)-P(=S)(Cl)Trip}AuCl **(14)** {Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$}AuCl **(15)** and of {Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$}AuCl **(16)**

Three new gold complexes were obtained in characterized in solution through NMR spectroscopy and HRMS spectrometry. Thus, reaction between derivative **11** and one equivalent of Au(SMe$_2$)Cl lead to the formation of gold complex {Mes*P=C(Cl)-P(=S)(Cl)Trip}AuCl **14** which was highlighted in solution through multinuclear NMR spectroscopy. In the ^{31}P{^{1}H} NMR spectrum two doublets were observed: one at 251.1 ppm assigned to P(III) phosphorus atom and the other one at 70.1 ppm for P(V) atom with a coupling constant of 81.5 Hz.

In the case of gold complex **15**, the reaction undergoes in dichloromethane, at room temperature and was completed after 20 minutes. According to the ^{31}P{^{1}H} NMR spectrum, a different behavior was observed: the resonance signals attributed for the two phosphorus atoms (327.3 and 73.8 ppm for P(III) and P(V)) remains almost unshifted compared with signals for **12** (330.7 ppm for P(III) and 74.4 ppm for P(V)). However, the difference between the coupling constants (68.7 Hz for the gold complex **15** and 85.8 Hz for the compound **12**) supported by NMR and HRMS analyses suggest the formation of new gold complex, {Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$}AuCl **15**. The solid-state structures of derivatives **15** was unambiguously determined through single crystal X-ray diffraction study (Figure 3).

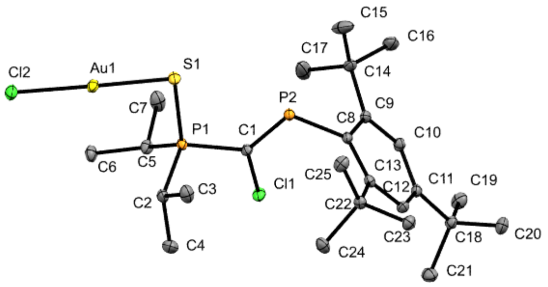


Figure 3. Molecular structure of **15** shown with 40% probability ellipsoids. Hydrogen bonds and benzene molecules are omitted for clarity.

The P=C and P=S bond lengths are is 1.686(1) Å respectively 2.024(1) Å, slightly longer in comparation to the ligand but, in case of P-C bond length, a small shortening was observed.

Even if, in solid-state, the coordination of ligand **12** to gold is achieved through the sulfur atom, in solution complex **15** is expected to exhibit fluxionality. According to DFT calculations, a very low energy difference between gold complexes formed via S→Au and P(III)→Au coordination was observed where the computed gap is less than 0.5 kcal·mol^{-1}.

The reaction between derivative Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** and one equivalent of Au(SMe$_2$)Cl was in CH$_2$Cl$_2$, leads to the formation of gold complex **16** which was completely characterized in solution by NMR and HRMS experiments and in solid state through X-ray diffraction analysis on single crystal. The ^{31}P{^{1}H} NMR spectrum of **16** displays two resonance signals one at 331.4 ppm assigned to the P(III) phosphorus atom and the other one at 64.1 ppm for P(V) atom with a coupling constant of 92.0 Hz. For both resonance signals satellites peaks were observed, where the P-Se coupling constant for the most deshieled signal is 71.6 Hz, while the other coupling constant suggest a strong P-Se coupling with a value of 664.2 Hz.

Single crystals of **16** was obtained by slow diffusion but, due to the poor stability in solution at room temperature and low solubility in different organic solvents, only poor-quality crystals cloud be obtained. Even if the complete refinement of the structure could not be possible, the X-ray data indicates that the coordination to the gold fragment is realized through the Se atom (Figure 4).

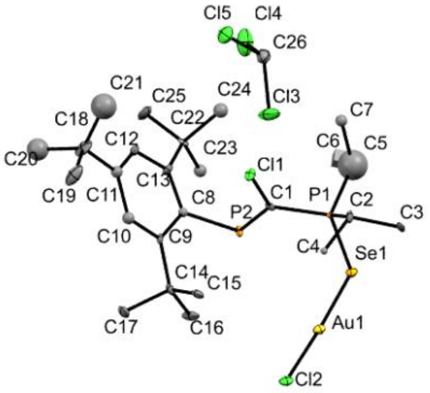
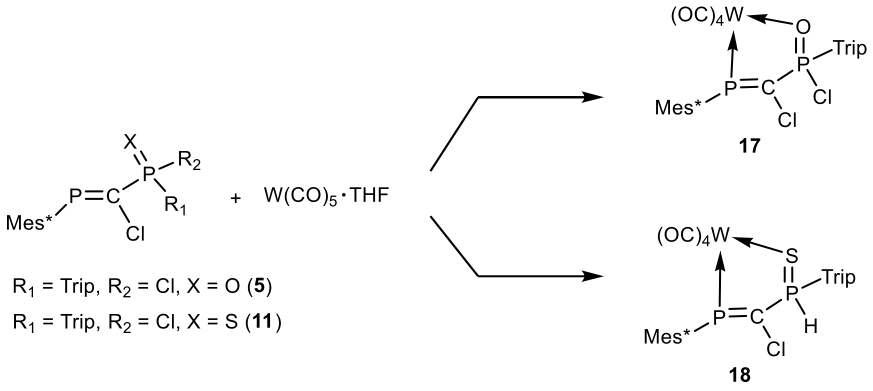


Figure 4. The asymmetric unit of **16** shown with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The coordination behavior of complex **16** was investigated by means of DFT calculations and, according to these data, the gold complex formed through Se→Au is with *ca.* 2.5 kcal·mol^{-1} more stable than the one formed through a P(III)→Au coordination.

2.3. Coordination abilities of derivatives **5** and **11** to tungsten fragments

In order to complete our study regarding the coordination ability of P=C-P(=X) (X = O, S) type derivatives to *d*-block metals and analyzing the role played by the organic groups grafted on the P(V) phosphorus atom in coordination preferences, reactions of derivative **5** and **11** with $W(CO)_5$·THF were performed as presented in Scheme 6.



Scheme 6. Synthesis of {Mes*P=C(Cl)-P(=O)(Cl)Trip}$W(CO)_4$ **(17)** and of {Mes*P=C(Cl)-P(=S)(Trip)H}$W(CO)_4$ **(18)**

The reaction between derivative Mes*P=C(Cl)-P(=O)(Cl)Trip **5** and freshly prepared $W(CO)_5$·THF lead to the formation of the corresponding chelate complex, {Mes*P=C(Cl)-P(=O)(Cl)Trip}$W(CO)_4$ **17**. Derivative **17** was obtained as dark red crystals and was completely characterized in solution by multinuclear NMR, HRMS, and in solid state by single crystal X-ray diffraction study. In the $^{31}P\{^1H\}$ NMR spectrum, two doublets were observed with a chemical shift at 332.4 ppm for the P(III) phosphorus atom and a chemical shift at 73.0 for the P(V) with a coupling constant of 104.1 Hz. Moreover, for the signal assigned to the phosphorus atom involved in the P=C double bond, satellites were also observed due to the coordination to tungsten atom.

The solid-state structure of derivative **17** was unambiguously determined through X-ray diffraction study on single crystal (Figure 5).

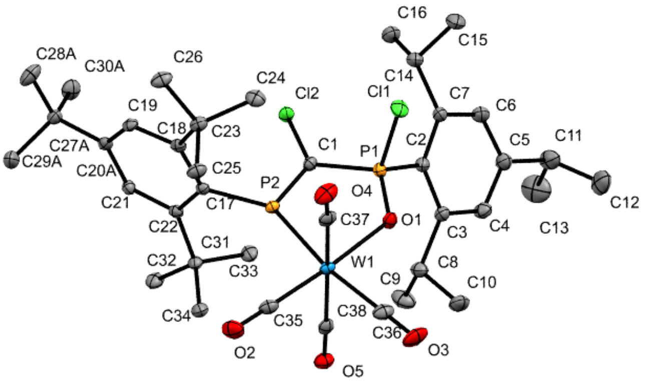


Figure 5. Molecular structure of **17** (($S_{P(V)}$) isomer) shown with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

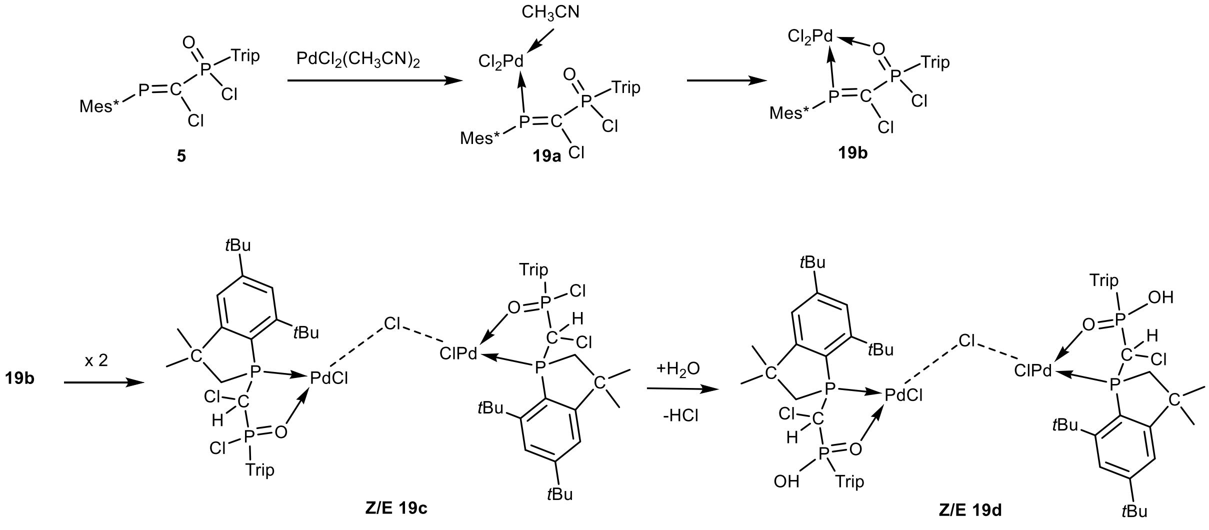
The coordination of ligand **5** to metal fragment is achieved through the oxygen and P(III) phosphorus atom resulting a chelate complex **17** with a distorted octahedral geometry around the tungsten center.

In order to obtain the corresponding chelate complex with sulfur, derivative Mes*P=C(Cl)-P(=S)(Trip) **11** was allowed to react with $W(CO)_5\cdot THF$ in a similar manner as compound **5** but, in this case, the target complex could not be obtained after several days. Therefore, a different synthetic method was used: a solution of **11** and $W(CO)_6$ in THF was irradiated for 6 hours using an immersion Hg vapor lamp. After purification and recrystallization from pentane at low temperature, the complex {Mes*P=C(Cl)-P(=S)(Trip)H}$W(CO)_4$ **18** was obtained as a brown powder. The newly obtained derivative **18** was completely characterized in solution through NMR spectroscopy. Thus, the $^{31}P\{^1H\}$ NMR spectrum displays two doublet resonance signals at 299.2 ppm signal assigned to P(III) phosphorus atom and one doublet at 10.3 ppm for P(V) with a coupling constant of 128.3 Hz.

2.4. Coordination abilities of derivatives **5**, **7**, **9**, **11**, **12** and **13** to palladium fragments

In order to understand how the substituents attached to the P(V) phosphorus atom in derivatives bearing P=C-P(=X) (X = O, S, Se) moieties can influence the coordination mode to transitional metals, the reactions between derivatives Mes*P=C(Cl)-P(=O)(Trip)Cl **5**, Mes*P=C(Cl)-P(=O)(OMe)Trip **7**, Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$ **9**, Mes*P=C(Cl)-P(=S)(Cl)Trip **11,** Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** and Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** wih palladium fragments were performed.

Firstly, derivative **5** was reacted with $PdCl_2(CH_3CN)_2$ in dichloromethane at room temperature (Scheme 7). After one hour of stirring, the $^{31}P\{^1H\}$ displays two doublets at 255.6 ppm assigned to P(III) atom and at 71.6 ppm for P(V) atom with a coupling constant of 99.4 Hz suggesting the formation of compound **19a**. The newly obtained complex was characterized in solution by NMR spectroscopy.



Scheme 7. Synthesis of palladium complexes **(19a)-(19d)**

Derivative **19a** evolves overnight into a new palladium complex **19b** which was separated due to its low solubility in pentane and completely characterized in solution. In the $^{31}P\{^1H\}$ NMR spectrum two doublets were observed: one at 219.2 ppm for P(III) phosphorus atom and the other one at 42.5 attributed for P(V) atom with a coupling constant of 79.5 Hz. In attempts to obtain single crystals suitable for an X-ray diffraction study, we found out that derivative **19b** evolved in solution after 2 days into a mixture of *Z/E* isomers of a dimeric palladium complex which contain a bridged chlorine atom **19c** as presented in Scheme 7. Derivative **19b** undergoes hydrolysis following the formation of compound **19d** which was completely characterized in solution. Thus, in the $^{31}P\{^1H\}$ NMR spectrum two resonance signals were observed one at 47.6 and the other one at 51.3 ppm with a coupling constant of 20.1 Hz.

The solid-state structure of derivative **19d** unambiguously determined through X-ray diffraction study on single crystal as presented in **Figure 6**.

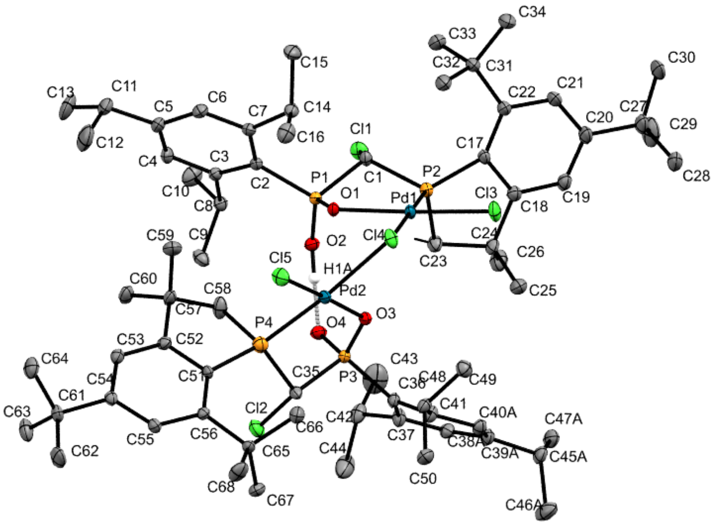
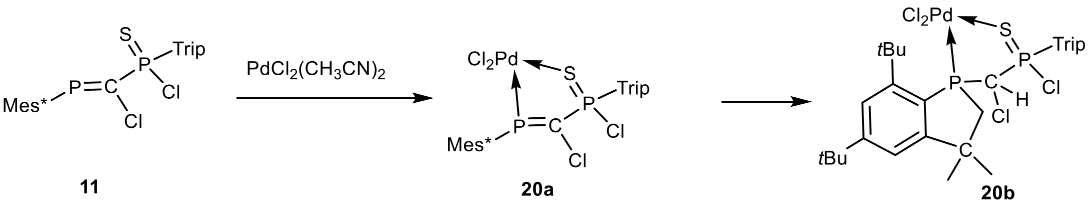


Figure 6. Molecular structure of **19d** shown with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The solid structure of **19d** contains two palladium atoms linked to each other through a bridging chlorine atom. Moreover, the presence of the five membered ring is due to the C_{sp3}–H bond activation of methyl group from *t*-Bu group of Mes* and intramolecular *trans*-addition to the P=C moiety.

Further, derivative Mes*P=C(Cl)-P(=S)(Cl)Trip **11** was allowed to react with $PdCl_2(CH_3CN)_2$ to form two palladium complexes, as presented in Scheme 8.



Scheme 8. Synthesis of palladium complexes **(20a)** and **(20b)**

After stirring the reaction mixture for 30 minutes at room temperature, intermediate **20a** was obtained and was only characterized in solution by $^{31}P\{^{1}H\}$ NMR. The recorded $^{31}P\{^{1}H\}$ NMR spectrum exhibits two resonance signals at 267.5 pm for P(III) atom and at 89.7 ppm for P(V) atom with a coupling constant of 127.2 Hz suggesting the formation of a chelate complex that contains the P=C double bond. The reaction mixture quickly evolves into a more stable derivative {CyMes*P-CH(Cl)-P(=S)(Cl)Trip}$PdCl_2$ **20b** which was completely characterized in solution by NMR and HRMS. Thus, in the $^{31}P\{^{1}H\}$ NMR spectrum two doublets resonance signals were observed: one at 102.6 ppm for cy-Mes*P phosphorus atom and one at 69.2 ppm for P(V) phosphorus atom with a coupling constant of 46.8 Hz.

Derivative **20b** was obtained as yellow crystals from recrystallisation in pentane at low temperature. The solid-state structure of palladium complex **20b** was determined through single crystal X-ray diffraction analysis as presented in **Figure 7**.

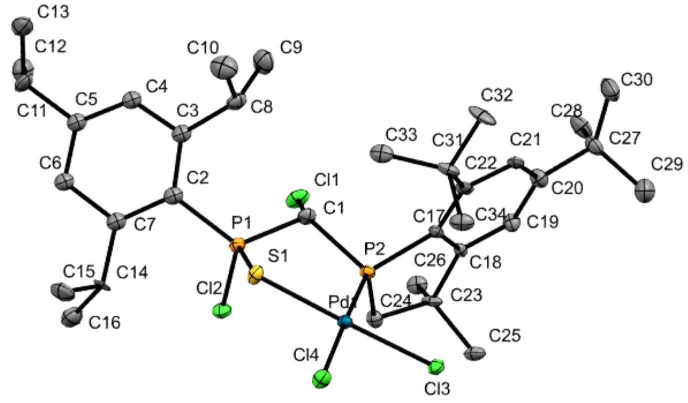
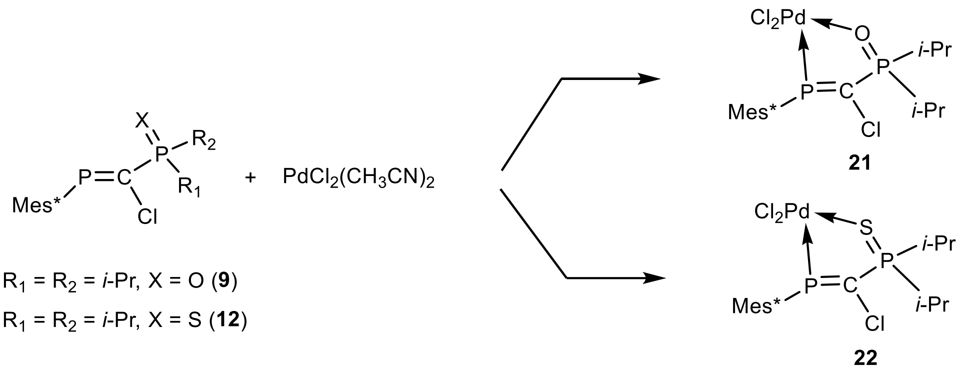


Figure 7. Molecular structure of **20b** shown with 40% probability ellipsoids. Only ($R_{\mathrm{P(V)}}$, $R_{\mathrm{P(III)}}$) isomer is shown. Hydrogen atoms are omitted for clarity.

The crystal of compound **20b** contains a racemic mixture of two (R_{P}, R_{P}) and (S_{P}, S_{P}) isomers. The (Mes*)P-C bond lengths are 1.90(1) and 1.89(1) Å in good agreement with those reported for compound **19d**.

To verify if indeed the presence of a nucleophile atom/group grafted on P(V) atom leads to the formation of the five membered cycle in case of palladium complexes, reactions of Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$ **9**, Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** and Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** with $PdCl_2(CH_3CN)_2$ (for **9** and **12**) and $PdCl_2$(COD) (for **13**) in CH_2Cl_2 were performed. When derivatives **9** and **12** were reacted with palladium fragment, the corresponding chelate complexes **21** and **22** respectively were obtained as presented in **Scheme 9**.



Scheme 9. Synthesis of {Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$}PdCl$_2$ **(21)** and of {Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$}PdCl$_2$ **(22)**

Both palladium complexes **21** and **22** were completely characterized in solution through the usual spectroscopic and spectrometric methods and, in the case of derivative **22** in solid state by single crystal X-ray diffraction. The ^{31}P{^{1}H} NMR spectrum of derivative **21** exhibits two resonance signals at 262.0 ppm for P(III) atom and at 89.1 ppm for P(V) phosphorus atom with a coupling constant of 47.9 Hz. Similar values were also observed for complex **22**: 283.6 ppm for P(III) atom and 79.2 ppm for P(V) atom ($^2J_{P,P}$ = 68.8 Hz).

Single crystals of **22** suitable for an X-ray diffraction study were obtained from dichloromethane at room temperature. The solid-state structure of **22** is presented in Figure 8.

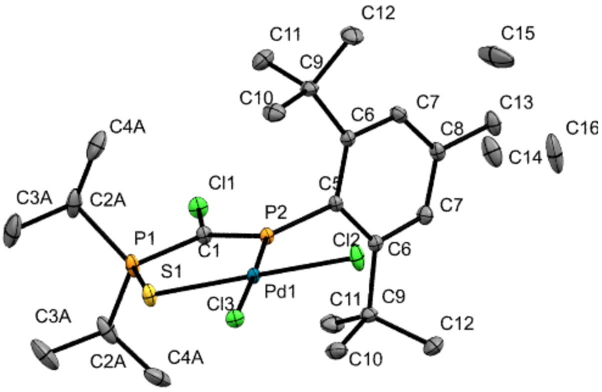
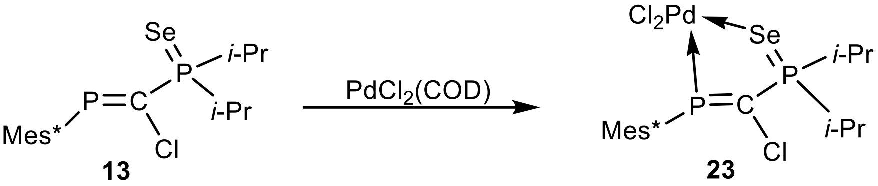
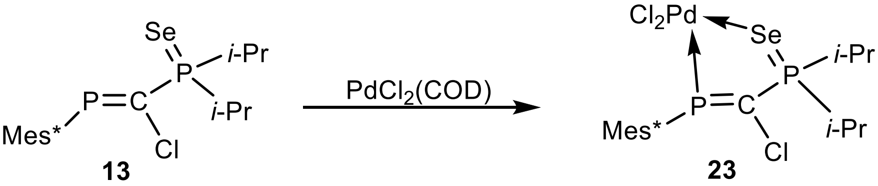


Figure 8. Molecular structure of **22** show with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The geometry around the metal center is almost ideal square planar and the other geometrical parameters are in the expected range for such derivatives.

Furthermore, derivative Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** was allowed to react with PdCl$_2$(COD) in the same manner as its sulfur or oxygen analogues to form the corresponding chelate complex **23** (Scheme **10**).





Scheme 10. Synthesis of {Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$}PdCl$_2$ (**23**)

Palladium complex **23** was obtained as orange crystals form a mixture of toluene and hexane at low temperature and was completely characterized in solution. In the ^{31}P{^{1}H} NMR spectrum two doublets resonance signals were observed: one at 284.0 ppm assigned to P(III) phosphorus atom ($^2J_{P,P}$ = 76.3 Hz) and the other one at 64.1 ppm for P(V) atom ($^2J_{P,P}$ = 76.3 Hz, $^1J_{P,Se}$= 526.2 Hz). Moreover, the ^{77}Se NMR spectrum displays a doublet of doublets at -103.2 ppm ($^1J_{P,Se}$= 526.2 Hz and $^3J_{P,Se}$ = 21.9 Hz) suggesting the formation of the new complex.

The solid-state structure of derivative **23** was unambiguously determined through X-ray diffraction study on single crystal and is displayed in Figure 9.

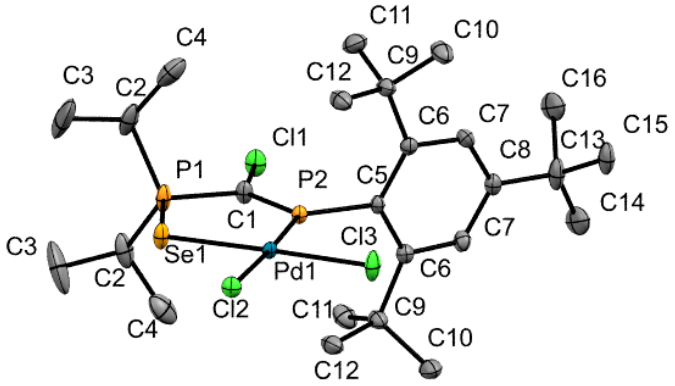


Figure 9. Molecular structure of **23** show with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

In the case of derivative **23**, the geometry around the palladium atom is almost ideal square planar as previously observed in case of palladium complex **22**. The P=C and C-P bond lengths are 1.670(3) Å and 1.796(3) Å respectively, having similar values with those reported in the case of derivative **22**.

Cahapter 3. New tetrylenes stabilized with phosphavinyl(chalcogenoxo)phosphoranes derivatives

3.1. Introduction

In this chapter, a comprehensive theoretical study by means of DFT, QTAIM and NBO calculations regarding the stabilization of E(II) species with phosphavinyl(chalcogenoxo)-phosphorane derivatives. The theoretical investigation is combined with an experimental study focusing on the behavior of P=C-P(=X) type systems towards organolithium reagents followed by the synthesis and characterization of the first tetrylene species stabilized with phosphavinyl(chalcogenoxo)phosphoranes.

3.2.Theoretical investigations of E(II) species stabilized with phosphavinyl(chalcogenoxo)phosphoranes derivatives

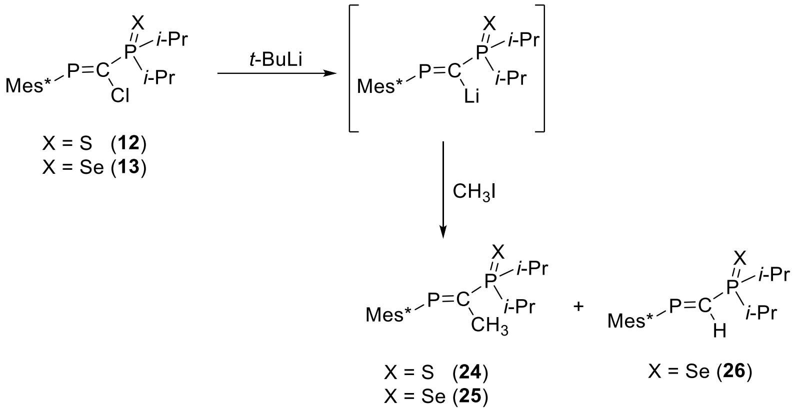
In order to evaluate the stabilization of E(II) (E = Si, Ge, Sn, Pb) species induced by the phosphavinyl(chalcogenoxo)phosphorane derivatives, Density functional theory (DFT), natural bond orbital (NBO) and quantum theory atoms in molecules (QTAIM) calculations were performed.

According to the theoretical investigations, the most stable tetrylenes that contain a ligand with a P=C-P(E) moiety, due to chelating effects, are silylenes while on the opposite side, the lower stability was found to be in the case of stannylenes and plumbylenes. Also, the bulkiness or the electronegativity of the substituents grafted on both phosphorus atoms seems to affect only to a lesser extent the stabilization of the investigated tetrylenes.

3.3. Reactivity study of phosphavinyl(chalcogenoxo)phosphorane derivatives with organolithium reagents

A reactivity study towards lithium derivatives of Mes*P=C(Cl)-P(=O)(Cl)Trip **5,** Mes*P=C(Cl)-P(=S)(Cl)Trip **11**, Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$ **9,** Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** and Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** were performed with both *n*-BuLi and *t*-BuLi reagents and the most promising results were obtained when *t*-BuLi was used. From the results obtained, we assumed that compounds **9**, **12** and **13**, bearing only one chlorine atom that can be involved in a halogen/lithium exchange reaction, to be more suitable as building blocks toward E(II) species. The best results were obtained when the lithiation of the P=C-P(=X) type derivatives was performed with *t*-BuLi, in a 1:2 molar ratio.

Derivative Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** was reacted with *t*-BuLi in toluene at -80°C. After 30 minutes, CH_3I was added dropwise to the dark red reaction mixture. After filtration of the inorganic salts, derivative **24** was obtained as a light-yellow powder from toluene (**Scheme 11**). Compound **24** was completely characterized in solution by NMR and HRMS experiments.



Scheme 11. Synthesis of Mes*P=C(CH_3)-P(=S)(*i*-Pr)$_2$ **(24)** and Mes*P=C(CH_3)-P(=Se)(*i*-Pr)$_2$ **(25)**

The $^{31}P\{^1H\}$ NMR spectrum shows characteristic signals at 316.3 ppm assigned to P(III) phosphorus atom and at 72.6 ppm for P(V) atom with a coupling constant of 85.8 Hz. Furthermore, in the ^{31}P NMR spectrum, the presence of a doublet of quartets resonance signal assigned to the P(III) atom strongly suggest the presence of the CH_3 group at the level of the central carbon atom.

The reaction of derivative **13** and CH_3I was performed in the same manner as in the case of derivative **24** (Scheme 11). In the $^{31}P\{^1H\}$ NMR spectrum two doublets resonance signals were observed: one at 307.2 ppm assigned to the P(III) phosphorus atom and the other one at 69.3 ppm for P(V) atom with a coupling constant of 74.6 Hz. In this case, in the $^{31}P\{^1H\}$ NMR spectrum, besides the corresponding signals for derivative **25**, two doublets resonance signals were also observed at 348.7 ppm (for P(III) atom) and 56.1 ppm (for P(V) atom) corresponding to the protonated derivative **26**.

Moreover, the solid-state structure of the methylated derivative **25** was determined by single crystal X-ray diffraction analysis (Figure 10).

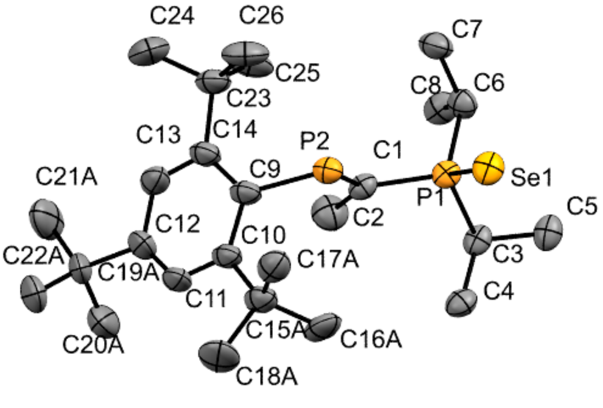
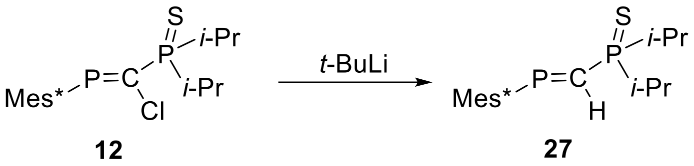


Figure 10. Molecular structure of **25** shown with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

When derivative **12** was allowed to react with *tert*-butyllithium, the corresponding protonated derivative was formed (Scheme 12). Derivative **27** was obtained as a pale-yellow solid from toluene and was completely characterized in solution by NMR spectroscopy and HRMS spectrometry.



Scheme 12. Synthesis of Mes*P=C(H)-P(=S)(*i*-Pr)$_2$ **(27)**

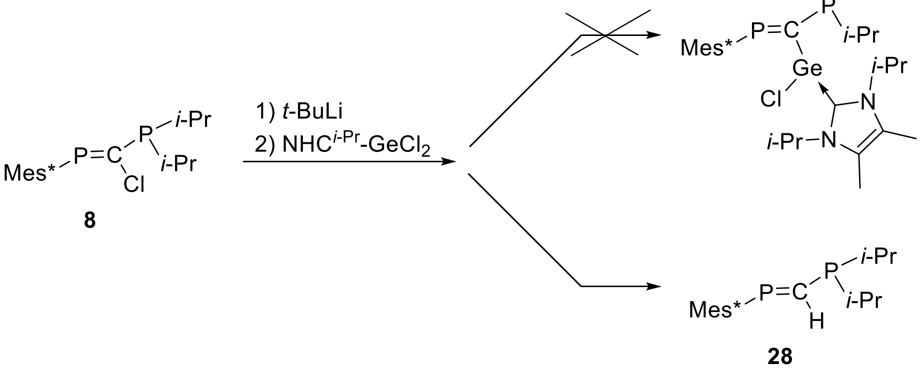
In the $^{31}P\{^1H\}$ NMR spectrum two doublet signals at a chemical shift of 354.5 ppm (for P(III) atom) and at 63.6 ppm (for P(V) atom) with a coupling constant of 73.0 Hz were observed. Moreover, the presence of a doublet of doublets resonance signal assigned to P(III) phosphorus atom, in the ^{31}P NMR spectrum, strongly suggest the formation of a C-H bond.

3.4. Novel tetrylenes stabilized with ligands bearing a P=C-P and P=C-P(=X) (X = S, Se) unit

3.4.1. Reactions of Mes*P=C(Cl)-P(*i*-Pr)$_2$ **(8)** with NHC$^{i\text{-Pr}}$-GeCl$_2$ and GeCl$_2$·dioxane

In order to evaluate the connection capacity of derivatives containing a P=C-P unit to Ge(II) species, reactions between Mes*P=C(Li)-P(*i*-Pr)$_2$ and two Ge(II) species, namely NHC$^{i\text{-Pr}}$-GeCl$_2$[9] respectively GeCl$_2$·dioxane, were performed.

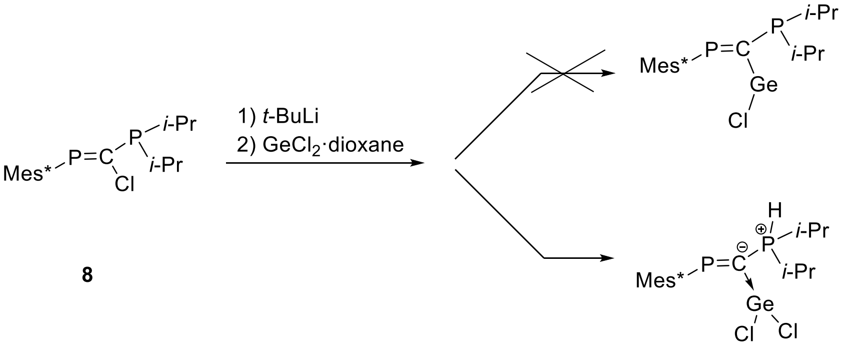
The reaction between the lithiated derivative of **8** was reacted with the NHC$^{i\text{-Pr}}$-GeCl$_2$ lead only to the formation of a protonated compound and not the desired germylene species as show in Scheme 13.



Scheme 13. Reaction of Mes*P=C(Li)-P(*i*-Pr)$_2$ with NHC$^{i\text{-Pr}}$-GeCl$_2$

In the $^{31}P\{^1H\}$ NMR spectrum two doublets were observed at a chemical shift of 306.1 ppm for the *sp*^{2} phosphorus atom and at 16.1 ppm for P(V) atom with a coupling constant of 154.8 Hz. The presence, in the ^{31}P NMR spectrum, of a doublet of doublets for the signal assigned to P(III) atom strongly suggests the formation of derivative **28**.

When the same lithiated derivative Mes*P=C(Li)-P(*i*-Pr)$_2$ of **8** was reacted with a sterically less protected germylene source ($GeCl_2$·dioxane) derivative **29** was obtained and was completely characterized in solution by multinuclear NMR spectroscopy and HRMS as well as in solid state, by X-ray diffraction analysis. In the $^{31}P\{^1H\}$ NMR spectrum, two doublets resonance signals were observed: one at 402.4 ppm in the expected range for the *P*=C atom and the second at 24.7 ppm attributed to the C-*P* atom ($^2J_{P,P}$ = 90.0 Hz). The high coupling constant ($^1J_{P,H}$ = 493.6 Hz) observed in ^{31}P NMR spectrum for the signal corresponding to the P=C-*P* atom suggests the presence of a hydrogen atom directly bonded on it. Thus, the only plausible structure for the newly obtained compound **29** is the one presented in **Scheme 14**.



Scheme 14. Reaction of Mes*P=C(Li)-P(*i*-Pr)$_2$ with $GeCl_2$·dioxane

Moreover, the proposed structure for derivative **29** was confirmed in solid-state by a single crystal X-ray diffraction study (Figure 11).

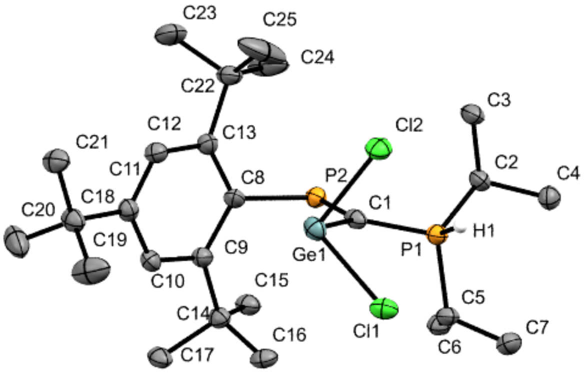
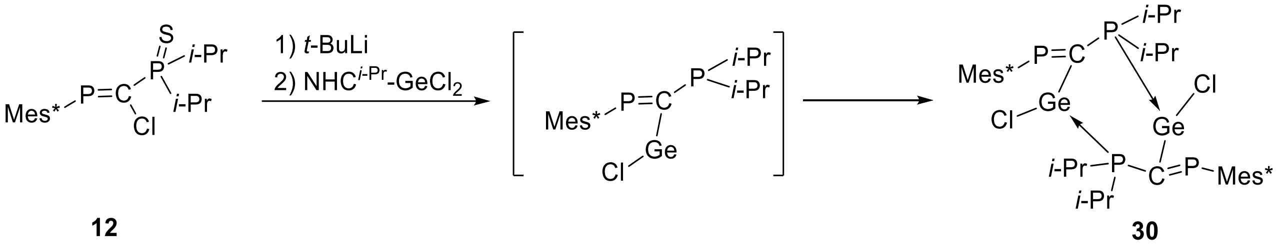


Figure 11. Molecular structure of **29** shown with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Derivative **29** crystalizes in the *Pbca* space group and the geometry around the Ge atom is distorted trigonal pyramidal with angles Cl1-Ge1-Cl2 of 93.87(5)°, Cl1-Ge1-C1 of 93.3(1)° and Cl2-Ge1-C1 of 90.2(1)°.

3.4.2. Reactions of Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **(12)** with NHC$^{i\text{-Pr}}$-GeCl$_2$ and GeCl$_2$·dioxane

Derivative Mes*P=C(Li)-P(=S)(*i*-Pr)$_2$ was allowed to reacted with NHC$^{i\text{-Pr}}$-GeCl$_2$ as presented in Scheme 15. According to ^{31}P NMR investigations, a mixture of compounds including the protonated derivative **27**, were obtained.



Scheme 15. Reaction of Mes*P=C(Li)-P(=S)(*i*-Pr)$_2$ with NHC$^{i\text{-Pr}}$-GeCl$_2$

In attempts to separate the obtained derivatives by crystallization from different solvents, single crystals of derivative **30**, suitable for an X-ray diffraction study were obtained (**Figure 12**).

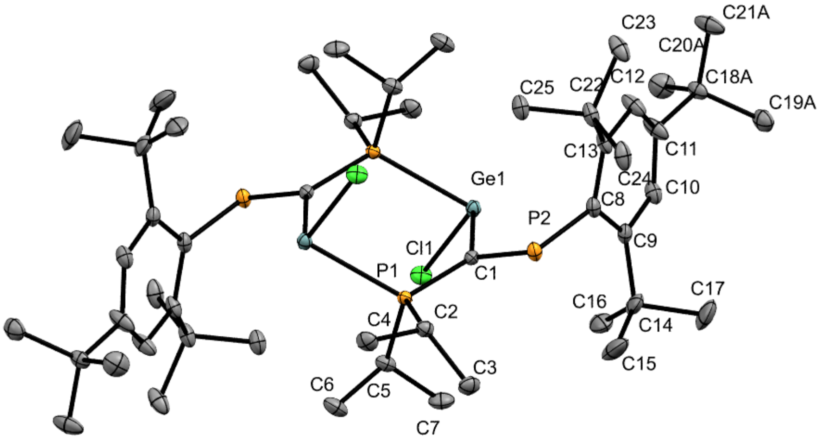
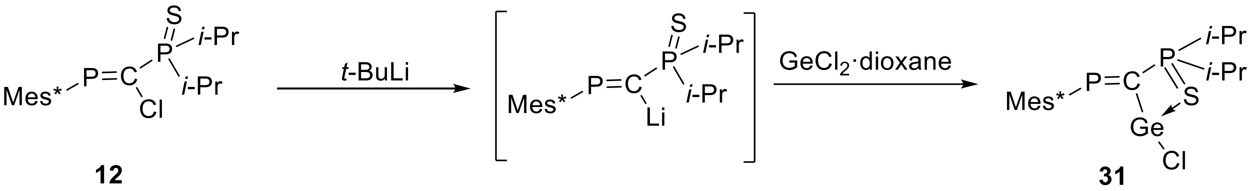


Figure 12. Molecular structure of **30** shown with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity.

As presented in ***Scheme 16***, when derivative Mes*P=C(Li)-P(=S)(*i*-Pr)$_2$ was allowed to react with GeCl$_2$·dioxane in the same conditions as previously described derivatives, a new chelate derivative **31** was obtained and was completely characterized in solution by NMR and HRMS experiments.



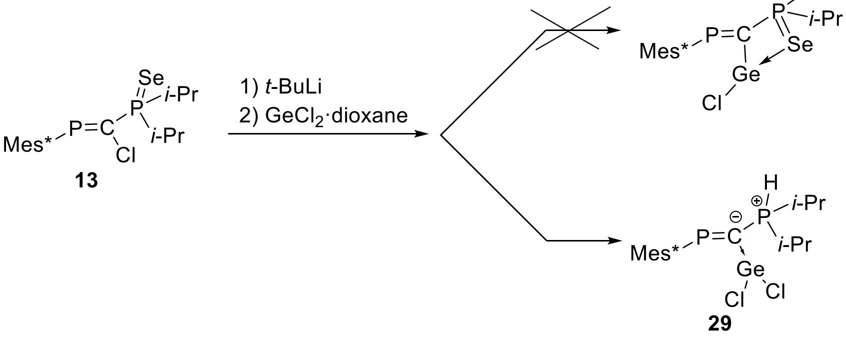
Scheme 16. Reaction of Mes*P=C(Li)-P(=S)(*i*-Pr)$_2$ with GeCl$_2$·dioxane

In the ^{31}P{^{1}H} RMN spectrum, two doublets were observed one at 379.3 ppm for P(III) atom and one at 78.4 ppm for P(V) atom with a coupling constant of 78.5 Hz, in good agreement with those reported for ligand **12**.

3.4.3. Reactions of Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **(13)** with NHC$^{i\text{-Pr}}$-GeCl$_2$, GeCl$_2$·dioxane and SnCl$_2$

The reaction between derivative Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** and NHC$^{\text{i-Pr}}$-GeCl$_2$ *via* the lithiated intermediate leads, as observed in the ^{31}P NMR spectra recorded on the crude reaction mixture, to several compounds having the P=C-P moiety that could not be separated.

When Mes*P=C(Li)-P(=Se)(*i*-Pr)$_2$ was allowed to react with GeCl$_2$·dioxane, the reaction leads to the formation of derivative **29**, as previously observed when derivative **8** was used as starting material (Scheme 17).



Scheme 17. Reaction between Mes*P=C(Li)-P(=Se)(*i*-Pr)$_2$ with GeCl$_2$·dioxane

Derivative **29** was completely characterized in solution through NMR and HRMS experiments and in solid state by single crystal X-ray diffraction. The ^{31}P{^{1}H} NMR spectrum exhibits two resonance signals at 402.3 ppm signal assigned to P(III) atom and at 24.7 ppm for phosphorus atom which is not involved in the double bond.

General conclusions

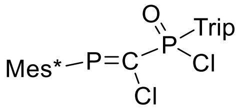
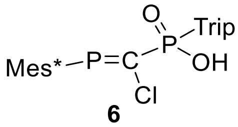
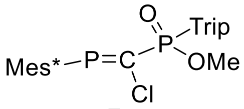
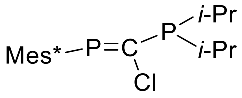
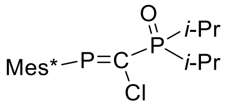
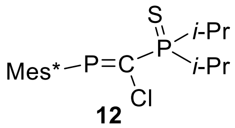
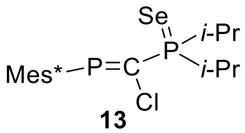
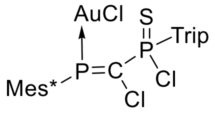
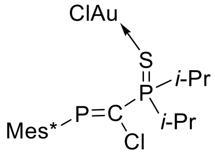
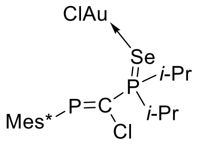
The present work, being structured in two main parts, aims to bring valuable information in the field of phosphavinyl(chalcogenoxo)phosphoranes derivatives. In the first part, a bibliographic review regarding the synthesis, physico-chemical and structural characterization of derivatives bearing a P=C-P or a P=C-P(=X) (X = S, O) unit was presented. Even if there are several examples of derivatives bearing a P=C-P(=S) unit, the number of derivatives which contain an oxygen atom is limited. Also, the coordination capacity of these derivatives towards transition metals such as Au, W, Pt and Pd was presented. In the case of gold complexes, only one example was reported so far by contrast with various examples of tungsten and palladium complexes. Additionally, a short introduction of tetrylenes together with several examples of E(II) species stabilized with N-heterocyclic carbenes and with derivatives containing a P=C unit was described. For the latter, a reactivity study towards chalcogens and several transition metals was detailed.

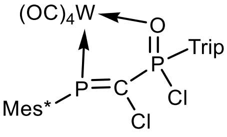
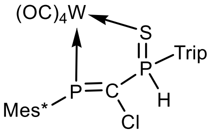
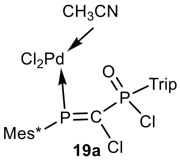
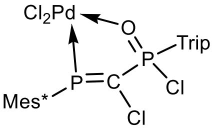
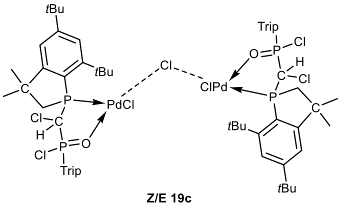
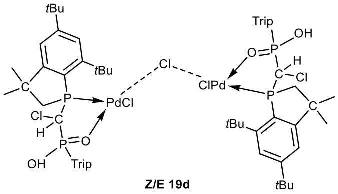
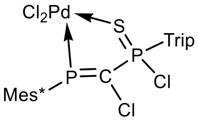
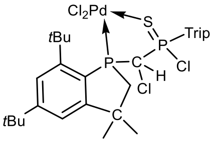
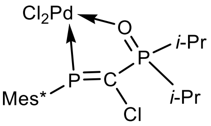
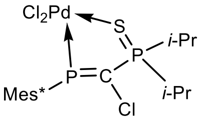
The second part of this thesis contains the original contributions being divided in three chapters. In the first chapter, the synthesis and characterization of phosphavinyl-(chalcogenoxo)phosphoranes derivatives Mes*P=C(Cl)-P(=O)(Cl)Trip **5**, Mes*P=C(Cl)-P(=O)(OH)Trip **6**, Mes*P=C(Cl)-P(=O)(OMe)Trip **7**, Mes*P=C(Cl)-P(=O)(*i*-Pr)$_2$ **9**, Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** and Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** were presented. All newly obtained derivatives found to be stable in air/moisture environment with the exception of derivative **5** which was found to be stable only under inert atmosphere. The phosphavinyl(chalcogenoxo)phosphoranes derivatives were further investigated by theoretical means. According to DFT calculations, in the case of investigated systems, the bulkiness and the electronegativity of substituents directly bonded to the phosphorus atom seems to affect only in a less extent the main bond lengths (P=C, C-P and P=X).

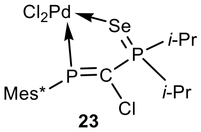
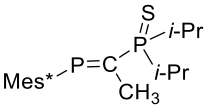
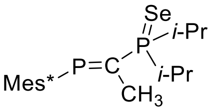
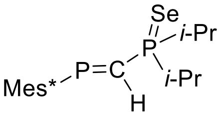
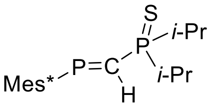
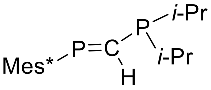
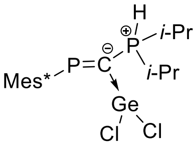
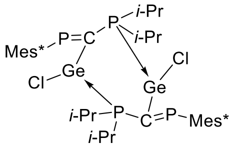
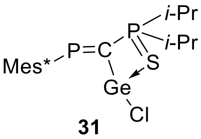
The second chapter contains an extensive study regarding the coordination capacity of phosphavinyl(chalcogenoxo)phosphoranes derivatives towards *d*-block metals *e.g* Au(I), W(0), Pd(II), Cu(II) and Zn(II). In the case of the gold fragment, three coordination compounds {Mes*P=C(Cl)-P(=S)(Cl)Trip}AuCl **14**, {Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$}AuCl **15** and {Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$}AuCl **16** were obtained. In the complex **14**, the connection of the ligand to the gold moiety was achieved through the lone pair of electrons of P(III) atom, while in case of derivatives **15** and **16** the coordination to the metal centre was made through the chalcogen atom. According to DFT calculations, the gold complex **15** is expected to exhibit fluxionality in solution even if, in solid state, only the coordination derivative obtained through the S→Au bond was observed. In the case of tungsten fragments, two new coordination compounds were obtained {Mes*P=C(Cl)-P(=O)(Cl)Trip}W(CO)$_4$ **17** and {Mes*P=C(Cl)-P(=S)(Trip)H}W(CO)$_4$ **18**. In both cases, the corresponding ligand coordinates in a bidentate mode to the metal fragment. Considering the palladium fragments, we noticed that the coordination capacity of phosphavinyl(chalcogenoxo)phosphoranes derivatives is strongly influenced by the substituents grafted on the P(V) atom. Thus, when the substituent is a chlorine atom, the formation of a five-membered heterocycle formed by a C-H bond activation was observed in the corresponding palladium complexes. By contrast, when two identical organic groups were attached to the P(V) atom, three chelate complexes were obtained. All newly obtained derivatives were characterized in solution through usual spectroscopic and spectrometric methods and, where applicable, in solid state by single crystal X-ray diffraction.

In the last chapter, a theoretical study is firstly presented with regard to the stabilization of E(II) species through rich electron ligands containing a P=C-P(=X) moiety. According to the theoretical calculations, we highlighted that the most stable E(II) species are silylenes while the lowest stability was observed in the case of stannylenes and plumbylenes. Further, a reactivity study of phosphavinyl(chalcogenoxo)phosphoranes derivatives towards organolithium reagents is detailed. In this case, the most promising results were obtained when the lithiation of the P=C-P(=X) derivatives was performed with *t*-BuLi, in a 1:2 molar ratio, in diethyl ether. Moreover, in order to obtain the first E(II) species stabilized with phosphavinyl(chalcogenoxo)phosphoranes derivatives, reactions between Mes*P=C(Cl)-P(*i*-Pr)$_2$ **8**, Mes*P=C(Cl)-P(=S)(*i*-Pr)$_2$ **12** and Mes*P=C(Cl)-P(=Se)(*i*-Pr)$_2$ **13** with *t*-BuLi followed by addition of NHC$^{i\text{-Pr}}$-GeCl$_2$, GeCl$_2$·dioxane and SnCl$_2$ were investigated. Thus, the reaction between Mes*P=C(Li)-P(*i*-Pr)$_2$ with NHC$^{i\text{-Pr}}$-GeCl$_2$ lead only to the corresponding protonated derivative, while when using GeCl$_2$·dioxane, a newly germylene Mes*P=C(→GeCl$_2$)-PH(*i*-Pr)$_2$ **29** was obtained. In the case of the reaction between Mes*P=C(Li)-P(=S)(*i*-Pr)$_2$ with NHC$^{i\text{-Pr}}$-GeCl$_2$, the ^{31}P NMR analysis highlighted the formation of a mixture of compounds that contain the P=C-P moiety. Moreover, the Mes*P=C(Li)-P(=S)(*i*-Pr)$_2$ derivative was allowed to react with GeCl$_2$·dioxane to form the corresponding chelate derivative **31**. When derivative Mes*P=C(Li)-P(=Se)(*i*-Pr)$_2$ was reacted with GeCl$_2$·dioxane, the same germylene **29** was obtained. All newly obtained derivatives were characterized in solution through NMR and HRMS experiments and, in some cases, in solid state through single crystal X-ray diffraction.

List of newly obtained derivatives

Compound	NMR analysis	HRMS analysis	X-ray diffraction analysis
Chapter I			
 **5**	✓	✓	
 **6**	✓	✓	✓
 **7**	✓	✓	
 **8**	✓		
 **9**	✓	✓	✓
 **12**	✓	✓	✓
 **13**	✓	✓	✓
Chapter II			
 **14**	✓		
 **15**	✓	✓	✓
 **16**	✓	✓	✓

Compound	NMR analysis	HRMS analysis	X-ray diffraction analysis
 **17**	✓		✓
 **18**	✓		
 **19a**	✓		
 **19b**	✓	✓	
 **Z/E 19c**		✓	
 **Z/E 19d**	✓		✓
 **20a**	✓		
 **20b**	✓	✓	✓
 **21**	✓	✓	
 **22**	✓	✓	✓

Compound	NMR analysis	HRMS analysis	X-ray diffraction analysis
 **23**	✓	✓	✓
Chapter III			
 **24**	✓	✓	
 **25**	✓		✓
 **26**	✓		
 **27**	✓	✓	
 **28**	✓		
 **29**	✓	✓	✓
 **30**	✓		✓
 **31**	✓	✓	

References

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[1] Ziółkowska, A.; Szynkiewicz, N.; Ponikiewski, Ł. Overview of the Synthesis and Catalytic Reactivity of Transition Metal Complexes Based on C=P Bond Systems. *Organometallics* **2023**, *42*, 505-537.

[2] Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. Synthesis and structure of bis(2,4,6-tri-tert-butylphenyl)diphosphene: isolation of a true phosphobenzene. *J. Am. Chem. Soc.* **1981**, *103* (15), 4587–4589.

[3] Goede, S. J.; Bickelhaupt, F. Synthesis and Reactions of *P*-Supermesityl-*C*-halophosphaalkenes. *Chem. Ber.* **1991**, *124* (12), 2677-2684.

[4] Chandrasekhar, V.; Sasikumar, P.; Boomishankar, R.; Anantharaman, G. Assembly of Lipophilic Tetranuclear (Cu_4 and Zn_4) Molecular Metallophosphonates from 2,4,6-Triisopropylphenylphosponic Acid and Pyrazole Ligands. *Inorg. Chem.* **2006**, *45* (8), 3344-3351.

[5] Nishide, K.; Liang, H.; Ito, S.; Yoshifuji, M. Preparation and properties of palladium(II) complexes of 3-oxo-1-(2,4,6-tri-t-butylphenyl)-1,3-diphosphapropenes. *J. Organomet. Chem.* **2005**, *690*, 4809-4815.

[6] Ito, S.; Liang, H.; Yoshifuji, M. Preparation, structure, and some coordination properties of 2-chloro-3,3-diphenyl-3-thioxo-1-(2,4,6-tri-t-butylphenyl)-1,3-diphosphapropene. *Chem. Commun.* **2003**, 398-399.

[7] Septelean, R.; Nemes, G.; Escudié, J.; Silaghi Dumitrescu, I.; Ranaivonjatovo, H.; Petrar, P.; Gornitzka, H.; Silaghi-Dumitrescu, L.; Saffon, N. vic-Dichlorodiphosphapropenes – Synthesis and Coordination Ability. *Eur. J. Inorg. Chem.* **2009**, 628–634.

[8] Septelean, R.; Muresan, A.; Soran, A.; Moraru, I.-T.; Nemes, G. New stable 2,3-dichloro, 1,3-diphosphapropenes; Synthesis and characterization. *Rev. Roum. Chim.* **2020**, *65* (6), 579-585.

[9] Rupar, P. A.; Staroverov, V. N.; Ragogna, P. J.; Baines, K. M. A Germanium(II)-Centered Dication. *J. Am. Chem. Soc.* **2007**, *129* (49), 15138–15139.