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New 1,3-phosphagermafluorenyl compounds.
Synthesis and reactivity.

PhD Thesis Summary

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Public defense: 8 July 2022, Cluj-Napoca

Table of Contents

Part I

Part II

Chapter I

Chapter II

REACTIVITY STUDY OF NEW GERMAPHOSPHAALKENYL DERIVATIVES: SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION 105

Chapter III

NEW GERMAPHOSPHAALKENYL DERIVATIVES: REACTIVITY TOWARDS TRANSITION METALS 188

Keywords: germaphosphaalkenyl compounds; germaphosphapropenes; germafluorenyl; coordination compounds; metal complexes; solid-state structure

Part I – BIBLIOGRAPHIC REVIEW: UNSATURATED HETEROALKENYL DERIVATIVES

Introduction

The chemistry of P=C–Ge and P=C=Ge type derivatives represents an exciting topic in the field of doubly bonded heterocompounds. From the fundamental point of view this chemistry provides new scientific information on systems containing *p* block heavy elements trapped in cumulative double bonds. Additionally, from the applicative point of view, different coordination possibilities can be explored, leading to the formation of new coordination compounds. Moreover, these unsaturated species can be used as catalysts in the field of green chemistry. Obtaining novel green catalysts represents a new concept in the scientific community in order to develop new sustainable technologies.

When it comes to P=C–Ge and P=C=Ge type derivatives, only a scarce number of stable compounds were successfully obtained and isolated. The scientific literature is not very rich in such references. Not many P=C=Ge heteroallenes were prepared and characterized. Few literature data were reported about the stabilization of such systems, even fewer about their applications.

The investigations performed in this field concluded that it is possible to obtain heteroallenic species by using proper substituents around unsaturations, thus preventing further dimerization or decomposition of the target highly reactive product. To this respect, the subject remains a continuous preoccupation for the scientific world, because this type of unsaturated systems are likely to have special electronic and structural properties.

Their isolation in monomeric form was possible by use of suitable bulky protective groups connected to the phosphorus and germanium atoms, thus involving mainly steric stabilization. Besides the steric effect, the electronic properties could also contribute to stabilize such systems through electron delocalization near the reactive centers. Thus, additional research can be performed herein in order to better understand the behaviour of this type of unsaturated compounds to find the most suitable way for their stabilization.

In this context, the major objective of this study consists in evaluating the electronic effects of the organic groups which could provide additional stabilization for the P=C–Ge and P=C=Ge moieties. In this respect, the main purpose is to investigate the influence of introducing the germanium element into a fluorenyl cycle.

I.1. Unsaturated germaalkenyl derivatives

I.1.1. Synthesis of germaallenic compounds containing Ge=C=C moiety

I.1.2. Reactivity of germaallenic compounds containing Ge=C=C moiety

I.1.3. Physico-chemical properties of Ge=C=C type compounds

I.2. Unsaturated germaphosphaalkenyl derivatives

I.2.1. Synthesis of P=C–Ge type compounds

I.2.2. Physico-chemical properties of P=C–Ge type compounds

I.2.3. Reactivity study of germaphosphaalkenyls containing a P=C–Ge moiety

I.2.4. Reactivity of Mes*P=C=GeTip(tBu) phosphagermaallene

I.2.5. Physico-chemical properties of germaphosphaalkenyl derivatives

I.3. Coordination ability of heterophosphaalkenyl derivatives

I.4. Conclusions

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Part II – ORIGINAL CONTRIBUTIONS

CHAPTER I

NEW GERMAPHOSPHAALKENYL DERIVATIVES: SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION

I.1. Introduction

We investigated the influence of electronic and structural properties of the fluorenyl system and explored the way in which this substituent could provide additional stabilization effects for the target P=C–Ge systems. We report herein, the synthesis, characterization, structure and reactivity study of new germaphosphaalkenyl compounds containing P=C–Ge moiety where the germanium atom is inserted into a fluorenyl ring.

I.2. Synthesis of new germaphosphaalkenyl derivatives

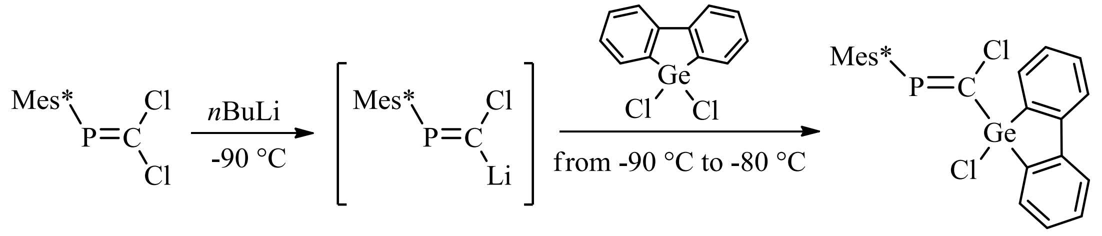
As a first step in obtaining the target germaphosphaalkenyl compounds, the synthesis of the corresponding key precursors was performed. Large scale production of Mes*P=CCl_2 **8** was achieved by a well known synthetic method. The germanium containing precursor, 9,9-dichloro-9-germafluorene **57** was also obtained by a method previously described in the literature.

I.2.1. Synthesis of phosphaalkenyl precursor, *P*-supermesityl-*C*-dichlorophosphaalkene

I.2.2. Synthesis of germafluorene precursor, 9,9-dichloro-9-germafluorene

I.2.3. Synthesis of novel Mes*P=C(Cl)–Ge(Cl)Fl and [Mes*P=C(Cl)]$_2$–GeFl

In order to obtain the first 3,1-germaphosphapropene **58**, 9,9-dichloro-9-germafluorene was reacted with one equivalent of lithiated dichlorophosphaalkene, as it is shown in the following scheme.



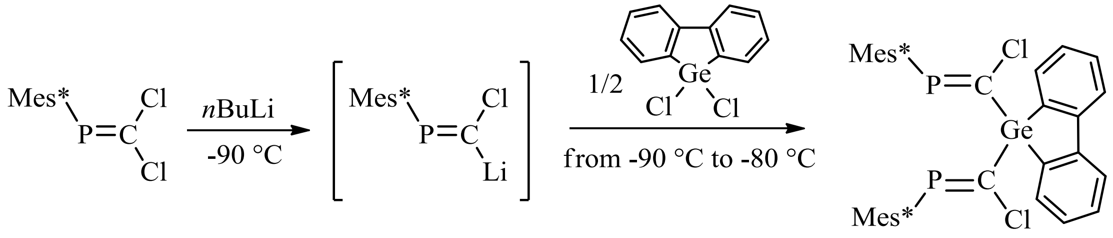
8 **58**

Scheme 33. Synthesis of Mes*P=C(Cl)–Ge(Cl)Fl **58**.

Addition of *n*BuLi to a solution of Mes*P=CCl$_2$ in THF at −90 °C yielded the lithiated derivative Mes*P=CCl(Li) as a dark red solution. Its reaction with 9,9-dichloro-9-germafluorene was performed at −90 °C. The reaction led to the formation of a new product with a characteristic chemical shift of 297.9 ppm in ^{31}P NMR spectrum.

The 3,1-germaphosphapropene **58** was unambiguously characterized in solution by NMR spectroscopy and mass spectrometry, and its solid state structure was determined by single crystal X-ray diffraction.

When using two equivalents of the lithiated Mes*P=CCl(Li) the expected germadiphosphapropene **59** was obtained in good yield, 58% (Scheme 34).



8 **59**

Scheme 34. Synthesis of [Mes*P=C(Cl)]$_2$–GeFl **59**.

The formation of **59** involves an intermolecular elimination of lithium chloride leading to the disubstituted product. The characteristic chemical shift at 290.1 ppm in ^{31}P NMR spectra was attributed to the equivalent phosphorus atoms from derivative **59**. The new 9,9-bis(phosphaalkenylchloro)-9-germafluorene **59** was completely characterized in solution and in solid state.

I.3. Physico-chemical properties of the new germaphosphaalkenyl derivatives: 9-chloro-9-phosphaalkenylchloro-9-germafluorene and 9,9-bis(phosphaalkenylchloro)-9-germafluorene

I.3.1. NMR spectroscopy and mass spectrometry investigations

The new derivatives 9-chloro-9-phosphaalkenylchloro-9-germafluorene **58** and 9,9-bis(phosphaalkenylchloro)-9-germafluorene **59** were characterized in solution by NMR spectroscopy methods such as ^{1}H, ^{13}C, ^{31}P, COSY, HSQC, and HMBC. The ^{31}P NMR spectra of **58** and **59** show characteristic signals at 297.9 ppm and 290.1 ppm, respectively, downfield shifted compared to the starting dichlorophosphaalkene, **8** (232.3 ppm).[2]

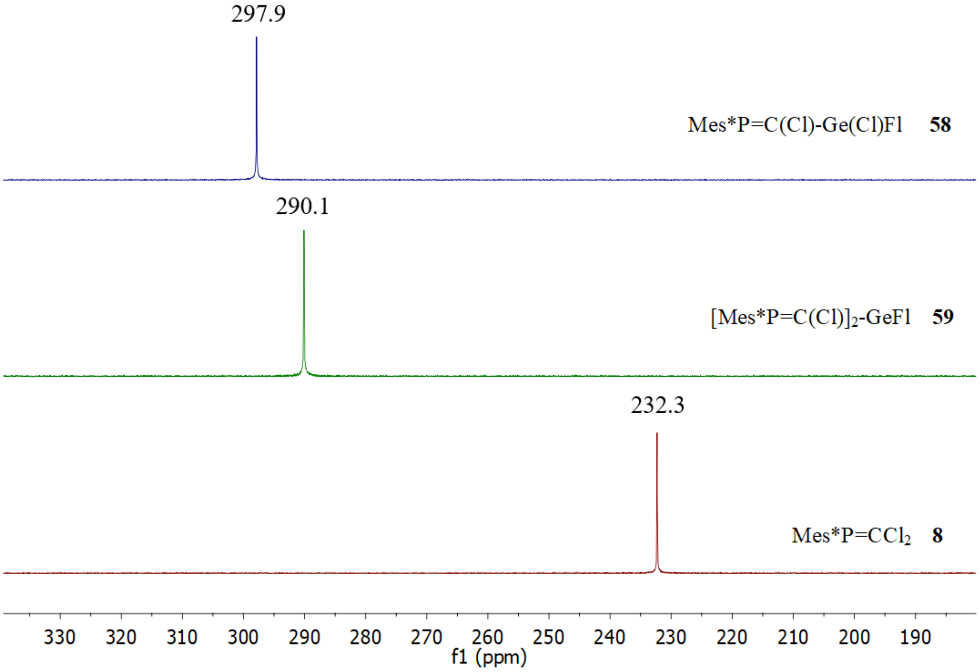


Figure 7. Characteristic ^{31}P NMR signals for the new germaphosphapropenes **58** and **59** in comparison with the starting phosphaalkene **8**.

The ^{1}H NMR spectra of compounds **58**, **59**, and **57** (Figure 8) show specific signals of the fluorenyl cycle consisting of two doublets and two triplets situated in the aromatic region between 7.3 ppm and 8.0 ppm. In all cases, the $^{3}J_{HH}$ coupling constant is in the range of 7–8 Hz. Besides this, in some cases $^{4}J_{HH}$ couplings were also observed with much lower values (between between 0.5 Hz and 1.2 Hz).

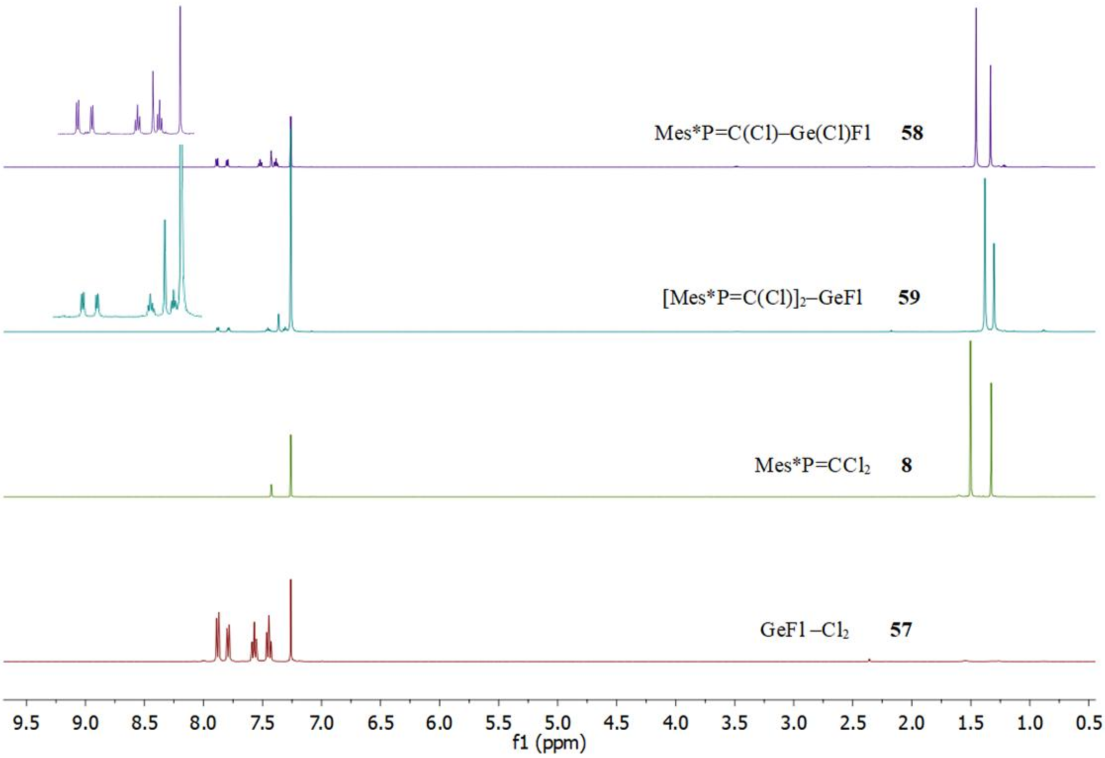


Figure 8. ^{1}H NMR spectra for germaphosphapropenes **58** and **59** and for the starting phosphaalkene **8** and germafluorene **57**.

Representative for the 9-chloro-9-phosphaalkenylchloro-9-germafluorene **58** in ^{13}C NMR spectrum is the resonance signal situated at 162.3 ppm which appears as a doublet with $^1J_{P=C}$ = 84.2 Hz.

For 9,9-bis(phosphaalkenylchloro)-9-germafluorene **59** a characteristic doublet of doublets was observed, explained by the presence of two identical phosphorus atoms in the structure of this derivative. The central carbon atom couples with both phosphorus atoms giving rise to a doublet of doublets at 165.2 ppm with $^1J_{P=C}$ = 79.2 Hz and $^3J_{PC}$ = 7.5 Hz.

Both derivatives **58** and **59** were characterized by high resolution mass spectrometry (HRMS). The molecular peaks were highlighted and evidenced with good accuracy, demonstrating the formation of the target products.

In this respect, for compound **58** with molecular formula $C_{31}H_{38}Cl_2GeP$, the calculated mass [M+1] was 585.1294, while the value for the found mass was 585.1324. Similarly, for **59** having the formula $C_{50}H_{67}Cl_2GeP_2$, 873.3301 was the calculated [M+1] value and 873.3259 was determined by the used HRMS method.

I.3.2. Molecular structure analysis in solid state for Mes*P=C(Cl)–Ge(Cl)Fl and [Mes*P=C(Cl)]$_2$–GeFl

The solid state structure of 9-chloro-9-phosphaalkenylchloro-9-germafluorene **58** was determined by single crystal X-ray diffraction and is presented in Figure 11.

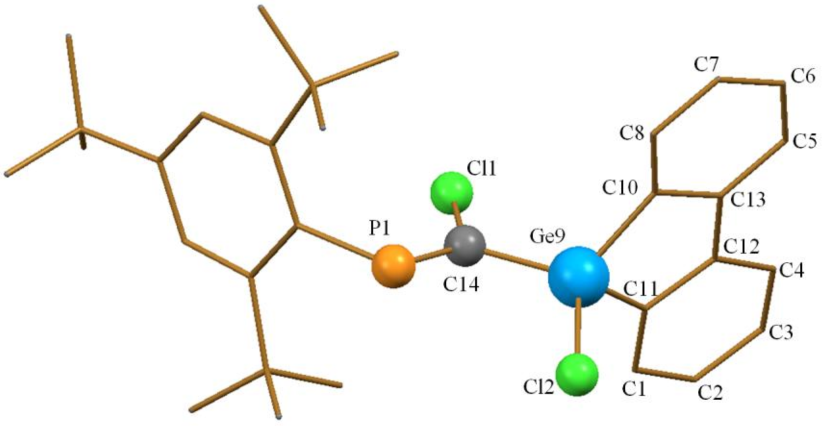


Figure 11. Molecular structure of Mes*P=C(Cl)–Ge(Cl)Fl **58**. Hydrogen atoms are omitted for clarity.

The solid state structure shows only one molecule in the asymmetric unit. The supermesityl group (Mes*) and the 9-germafluorenyl moiety are in *trans* position towards the phosphorus-carbon double bond. The germanium center exhibits a distorted tetrahedral geometry. The torsion angles C*ipso*–P1–C14–Ge9 (−179.5(2)°) and Cl1–C14–Ge9–Cl2 (−161.1(1)°) prove the formation of the *trans* isomer (*E*). The P1–C14 bond lenght of 1.846(3) Å is comparable with other reported values,[8] while the C14–Ge9 bond distance (1.937(3) Å) is slighly shorter than those found for similar compounds.[8,24–26]

The great stability towards air and moisture allowed the easy manipulation and solid state structure determination of the novel diphosphagermapropene **59**, by means of X-ray diffraction. The molecular structure of this compound is presented in Figure 12. Only one molecule exists in the asymmetric unit cell of **59**, just like in the case of **58**. The germafluorenyl heterocycle and the two Mes* groups are in *trans* position relative to the corresponding P=C bonds.

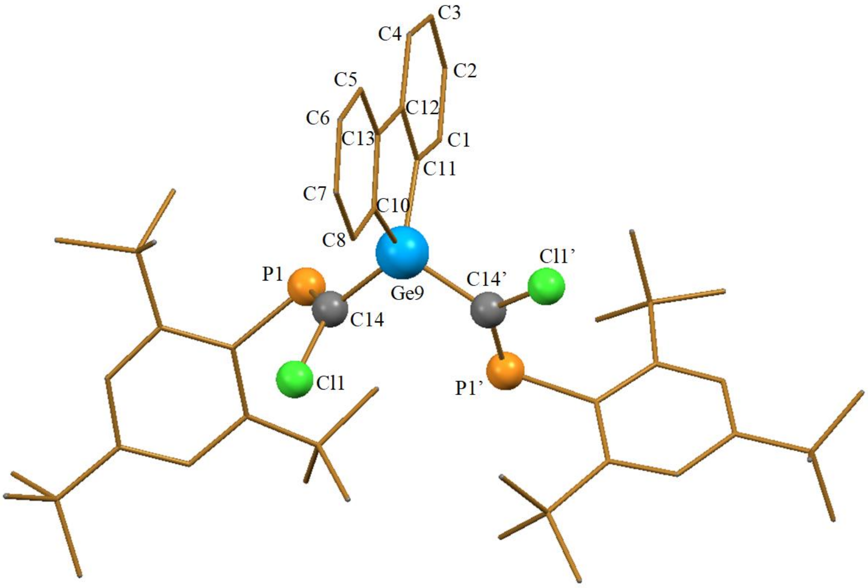


Figure 12. Molecular structure of $[Mes^{*}P{=}C(Cl)]_2$–GeFl **59**. Hydrogen atoms are omitted for clarity.

In both compunds **58** and **59**, the geometry around the heavy germanium atom is distorted tetrahedral. Due to the geometry established by the 9-germafluorene ring, the most distorted angle si the one defined by C10–Ge9–C11: 90.9(1)° for Mes*P=C(Cl)–Ge(Cl)Fl and 90.3(2)° in the case of $[Mes^{*}P{=}C(Cl)]_2$–GeFl.

Additionally, in order to better understand the influence of including the Ge atom into the fluorenyl ring, several structural features were investigated using DFT calculations. Because the secondary electronic effects could also play significant roles in the investigated species, NBO and NICS analyses were performed. The calculated geometrical parameters using DFT methods are in good agreement with those reported through experimental methods.

Both derivatives (**58** and **59**) present great solubility in frequently used organic solvents and proved high stability in air/moisture environment.

The reactivity study of these newly obtained compounds will be presented next.

I.4. Conclusions

I.5. Experimental part

Appendix I

References

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CHAPTER II

REACTIVITY STUDY OF NEW GERMAPHOSPHAALKENYL DERIVATIVES: SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION

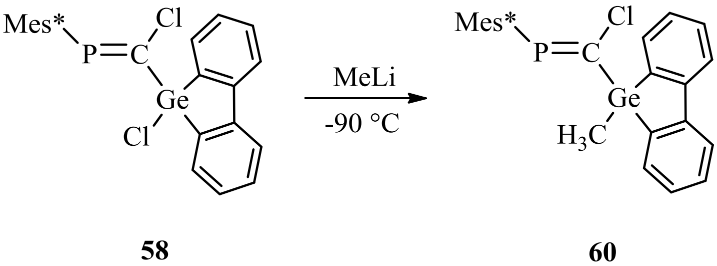
II.1. Introduction

The new stable and fully characterized derivatives obtained in our laboratory,[3] namely the monosubstituted 9-chloro-9-phosphaalkenylchloro-9-germafluorene, **58**, and disubstituted 9,9-bis(phosphaalkenylchloro)-9-germafluorene, **59**, were further investigated in terms of chemical reactivity.[17] We report herein a reactivity study of the novel germaaphosphalkenyl derivatives, together with the synthesis, characterization and structural investigations of the obtained products.

II.2. Reaction of 9-chloro-9-phosphaalkenylchloro-9-germafluorene with organolithium reagents

II.2.1. Reaction of 9-chloro-9-phosphaalkenylchloro-9-germafluorene with MeLi

As a first step, the reaction of the novel and stable monosubstituted derivative Mes*P=C(Cl)–Ge(Cl)Fl **58** with MeLi was tested (Scheme 35). Fortunately, the sole formation of a new compound was observed by means of ^{31}P NMR spectroscopy investigations (δ: 283.0 ppm).



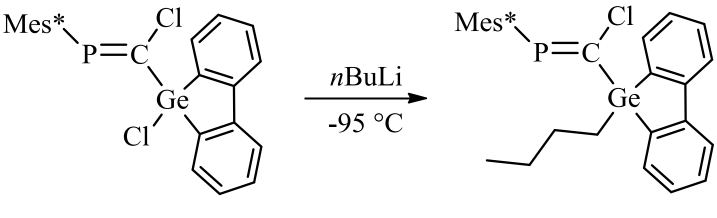
58 **60**

Scheme 35. Synthesis of Mes*P=C(Cl)–Ge(CH_3)Fl **60**.

The formation of **60** involves an intermolecular elimination of lithium chloride followed by the formation of a new germaniun-carbon bond (Ge–CH_3), leading to the alkylated product. The 9-methyl-9-phosphaalkenylchloro-9-germafluorene **60** was unambiguously characterized in solution by NMR studies, high resolution mass spectrometry and its solid state molecular structure was also confirmed by X-ray diffraction techniques performed on the isolated monocrystals.

II.2.2. Reaction of 9-chloro-9-phosphaalkenylchloro-9-germafluorene with *n*BuLi

Reaction of *n*BuLi with Mes*P=C(Cl)–Ge(Cl)Fl was conducted following a similar synthetic method as in the previous case (reaction with MeLi). *n*BuLi was added dropwise to a cooled THF solution of **58** (Scheme 36).



58 **61**

Scheme 36. Synthesis of Mes*P=C(Cl)–Ge($CH_2CH_2CH_2CH_3$)Fl **61**.

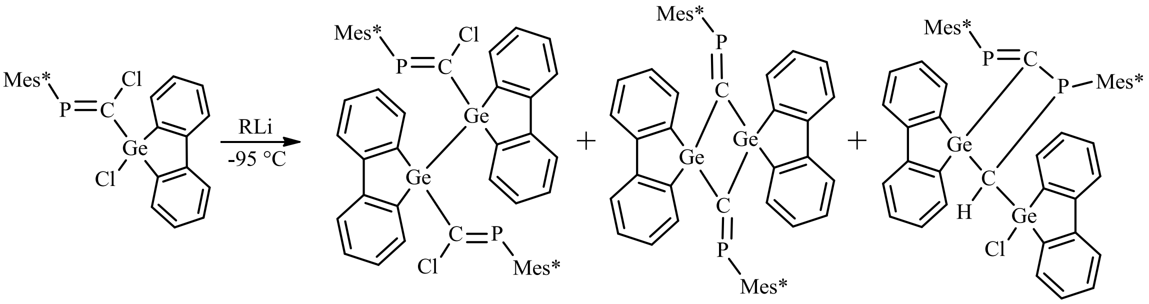
The new derivative **61** was completely characterized in solution and in solid state, all data revealing that the reaction underwent with the alkylation of the Ge–Cl unit.

The ^{31}P NMR signal for the new product appears at 282.8 ppm and it is similar with the chemical shifts previously reported for germaphosphapropenes bearing two organic stabilizing groups.[18–23]

II.2.3. Reaction of 9-chloro-9-phosphaalkenylchloro-9-germafluorene with *t*BuLi and *s*BuLi

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with bulkier lithium reagents was also performed. In this regard, the chemical behaviour in the presence of *t*BuLi and *s*BuLi was investigated. The alkyllithium was slowly added to a solution of Mes*P=C(Cl)–Ge(Cl)Fl **58**. The same pattern was observed in both circumstances, either using *t*BuLi or *s*BuLi. No major differences were disclosed in terms of conversion rates.

The reaction in the presence of a bulkier lithium reagent (*t*BuLi and *s*BuLi) occured with formation of dimeric compounds (Scheme 37).



58 **62** **63** **64**

Scheme 37. Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with RLi (R = *t*Bu and *s*Bu).

The first successfully separated product was derivative **62**, [Mes*P=C(Cl)–GeFl]$_2$ as a white powder from a cooled concentrated pentane solution. Despite the low conversion rate of around 22%, the purification of derivative **62** was possible due to its low solubility in pentane. Characterization in solution by multinuclear NMR spectroscopy and high resolution mass spectrometry (HRMS) were accomplished. The characteristic chemical shift in ^{31}P NMR appears as a singlet at 290.4 ppm showing the formation of only one isomer.

Suitable single crystals of **62** were obtained either from a diethyl ether or a diethyl ether/chloroform solution at room temperature, by slow evaporation of the solvent, hence the solid state molecular structure determination was possible. The minor product [Mes*P=C(Cl)–GeFl]$_2$ **62** is air and moisture stable, probably due to its dimer type structure determined through solid state X-ray diffraction.

In addition to the linear dimer [Mes*P=C(Cl)–GeFl]$_2$ **62**, a new cyclic dimer **63** was nextly separated from the reaction mixture. According to the NMR investigations conducted on the crude reaction mixture, derivative **63** was formed with around 36% estimated conversion.

Two singlet signals were detected in ^{31}P and ^{31}P{H} NMR spectra situated at 384.5 and 386.4 ppm, respectively. The major compound is the one giving resonance signal at 384.5 ppm being associated with the *trans* isomer. Formation of two isomers (*cis* and *trans*) was also proved by the recorded ^{1}H and ^{13}C NMR spectra.

The newly obtained 2,4-diphosphinylidene-1,3-digermafluorenylcyclobutane, [Mes*P=C–GeFl]$_2$ **63**, is a four-member symmetric compound with two exocyclic P=C units. The *cis* and *trans* isomers relative to the P=C···C=P axis were initially detected in the crude reaction mixture. Attempts to isolate both isomers were not successful. After one week, even at low temperatures, full conversion into one isomer was observed.

The more stable derivative gives a resonance signal at 384.5 ppm in ^{31}P NMR spectra, corresponding to the *trans* isomer. The formation of this isomer was later demonstrated by solid state characterization.

For derivative **64** two dublets were observed in ^{31}P NMR spectrum situated at δ 149.7 ppm and δ −27.7 ppm, both having a coupling constant of 58.7 Hz. The chemical shifts and corresponding coupling values suggest the formation of a cyclic derivative in which only one phosphorus atom is involved in the formation of the heterocycle, as presented in Scheme 37. The first dublet signal (δ: 149.7 ppm) is in a specific range for a phosphorus atom involved in a P=C type unit, while the second dublet signal (δ: −27.7 ppm) is more likely to be assigned to a P(III) type element included in a cycle. The coupling constant of 58.7 Hz can be attributed to a $^{2}J_{PP}$ interaction.

Taking all these into account, the proposed structure for compound **64** is a germaphosphacyclobutane that contains an asymmetric heterocycle of C–Ge–C–P type, shown in Scheme 37.

Even if this germaphosphacyclobutane **64** was obtained as a major product, its complete characterization was proved to be difficult because of its high instability. In solution, derivative **64** decomposes into several compounds that could not be separated and characterized up to date. However, the purification, isolation and further structural investigations are currently in progress.

II.3. Physico-chemical properties of the newly obtained compounds by reaction of 9-chloro-9-phosphaalkenylchloro-9-germafluorene with organolithium reagents

II.3.1. NMR spectroscopy and mass spectrometry investigations

The new derivatives 9-methyl-9-phosphaalkenylchloro-9-germafluorene **60** and 9-butyl-9-phosphaalkenylchloro-9-germafluorene **61** were characterized in solution by mono- and multinuclear NMR spectroscopy methods, such as ^{1}H, ^{13}C, ^{31}P, $^{31}P\{H\}$, COSY, HSQC, and HMBC. $CDCl_3$ was used as deuterated solvent.

In ^{31}P and $^{31}P\{H\}$ NMR spectra, derivatives **60** and **61** show almost the same characteristic resonance signals situated at 283.0 ppm and 282.8 ppm, respectively, slightly upfield shifted compared to the signal given by the starting germaphosphaalkenyl compound, **58** (297.9 ppm).

Reactions with MeLi and *n*BuLi took place stereoselectively, considering that only one isomer was observed in each case (Figure 16). This is due to the fact that chlorine/lithium exchange takes place at the least hindered side of the P=C–Ge moiety.

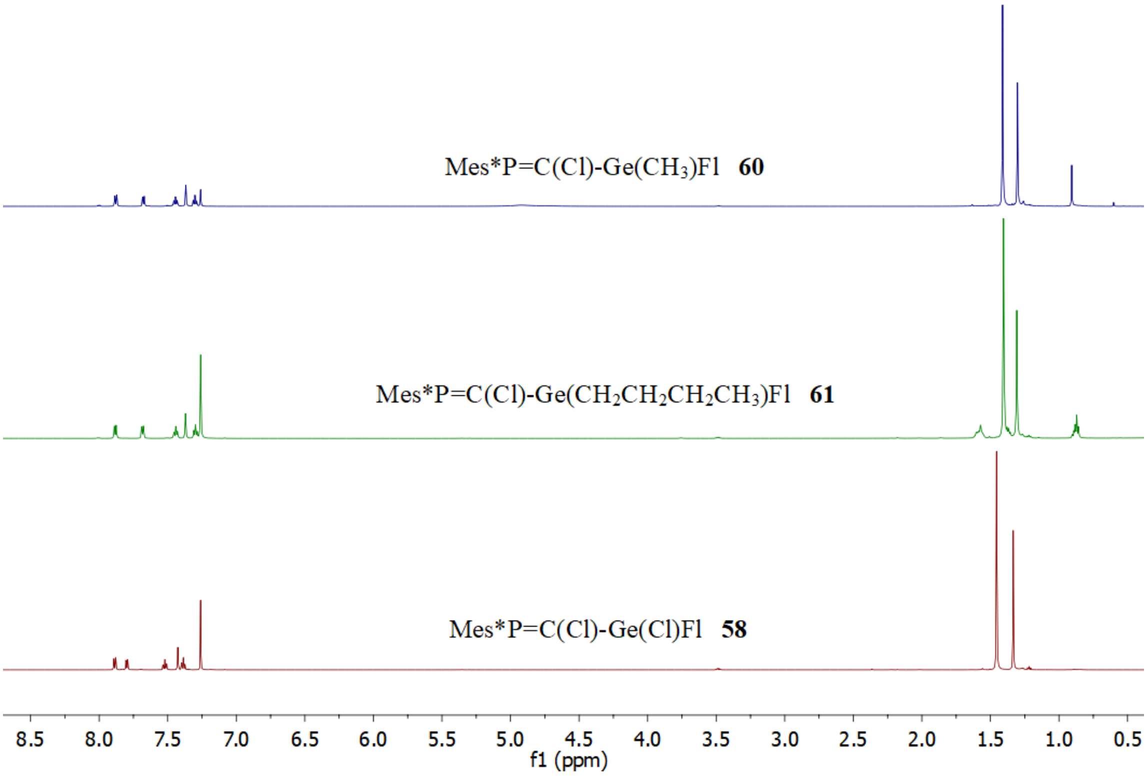


Figure 16. Characteristic ^{1}H NMR signals (600.13 MHz, CDCl$_3$) for the new alkylated germaphosphapropenes **60** and **61**
in comparison with the starting germaphosphapropene **58**.

In the ^{1}H NMR spectrum for compounds **60**, **61**, and **58** (Figure 16), the specific signals for the fluorenyl cycle can be easily recognized. Two doublets and two triplets situated in the aromatic region between 7.30 ppm and 7.90 ppm are illustrated. The $^3J_{HH}$ coupling constant is in the range of 7–8 Hz. The two new alkylated products show almost identical pattern in terms of chemical shifts in the aromatic region.

The signal at a chemical shift of 0.91 ppm was attributed to the protons from the methyl group linked to the germanium atom, Ge–CH$_3$, form 9-methyl-9-phosphaalkenylchloro-9-germafluorene **60**.

Three specific signals were observed for the protons of the butyl group of compound 9-butyl-9-phosphaalkenylchloro-9-germafluorene **61**: 0.88 ppm (m, 3H, Ge–CH$_2$CH$_2$CH$_2$**CH$_3$**), 1.37 ppm (m, 2H, Ge–CH$_2$CH$_2$**CH$_2$**CH$_3$) and 1.58 ppm (m, 4H, Ge–**CH$_2$CH$_2$**CH$_2$CH$_3$).

According to the ^{13}C NMR investigations in the case of **60** and **61**, the signal attributed to the doubly bonded carbon atom from the P=C unit (δ: 170.4 ppm for **60** and 170.0 ppm for **61**, $^{1}J_{P=C}$ = 85.5 Hz) is slightly downfield shifted (for both derivatives) in comparison with the one given by Mes*P=C(Cl)–Ge(Cl)Fl **58** (δ: 162.3 ppm, $^{1}J_{P=C}$ = 84.2 Hz).

The methyl group from 9-methyl-9-phosphaalkenylchloro-9-germafluorene **60** gives a resonance signal in ^{13}C NMR at −3.2 ppm with a coupling constant of $^{3}J_{PC}$ = 8.1 Hz. As expected, the $^{3}J_{PC}$ coupling is slightly larger (8.1 Hz) than the $^{3}J_{PC}$ coupling between the phosphorus atom and the quaternary carbon atoms (C10 and C11) from the fluorenylic unit (6.4 Hz).

The four characteristic signals for the butyl group in compound **61** were observed at chemical shifts of 13.8 ppm (Ge–$CH_2CH_2CH_2$**CH_3**), 15.1 ppm (d, $^{3}J_{PC}$ = 6.5 Hz, Ge–**CH_2**$CH_2CH_2CH_3$), 26.2 ppm (Ge–CH_2CH_2**CH_2**CH_3) and 27.4 ppm (Ge–CH_2**CH_2**CH_2CH_3) in ^{13}C NMR spectrum.

The carbon atom situated in *ipso* position of Mes* gives a doublet type resonance signal in ^{13}C NMR spectrum due to the influence of phosphorus: 135.4 ppm ($^{1}J_{P=C}$ = 60.6 Hz) for the methylated derivative and 135.9 ppm ($^{1}J_{P=C}$ = 64.0 Hz) for the butylated derivative.

The structures of derivatives **62** and **63** were also fully elucidated.

Only one isomer was obtained for the first successfully separated product **62**, [Mes*P=C(Cl)–GeFl]$_2$, as it can be seen in the recorded NMR spectra as well (Figure 19).

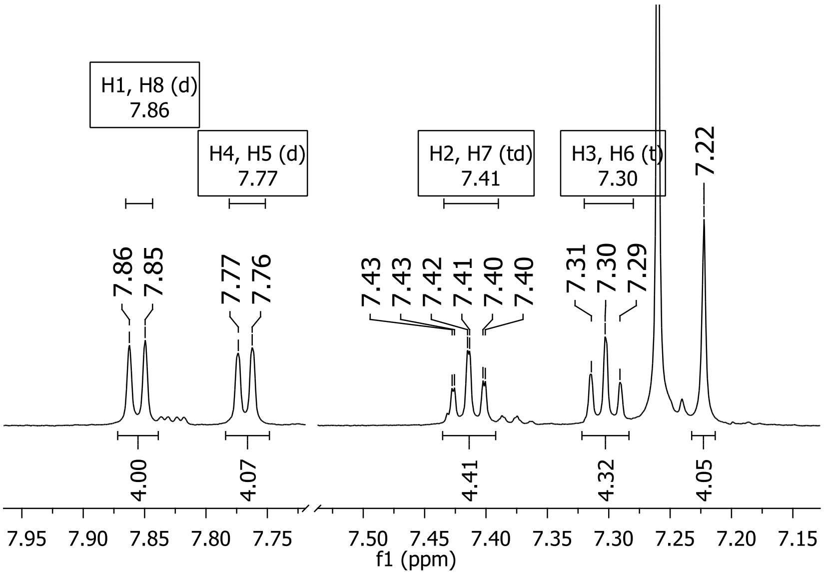


Figure 19. Fragment of the characteristic ^{1}H NMR spectra (600.13 MHz, $CDCl_3$) for the novel [Mes*P=C(Cl)–GeFl]$_2$ **62**.

Despite the dimeric type structure, derivative **62** shows the same NMR pattern as the previously presented compounds (**58**, **60**, **61**), fact which can be explained by the symmetrical and linear structure of the dimer.

In ^{13}C NMR spectrum, representative for the new bis-9-phosphaalkenylchloro-9-germafluorene **62**, is the chemical shift attributed to the carbon atom from the P=C unit: 166.9 ppm (d, $^{1}J_{P=C}$ = 82.7 Hz).

A new cyclic dimer **63** was nextly separated from the reaction mixture. Two singlet signals were detected in ^{31}P and ^{31}P{H} NMR spectra situated at 386.4 and 384.5 ppm, respectively (Figure 20). These chemical shifts were associated with *cis* and *trans* isomers relative to the P=C···C=P axis.

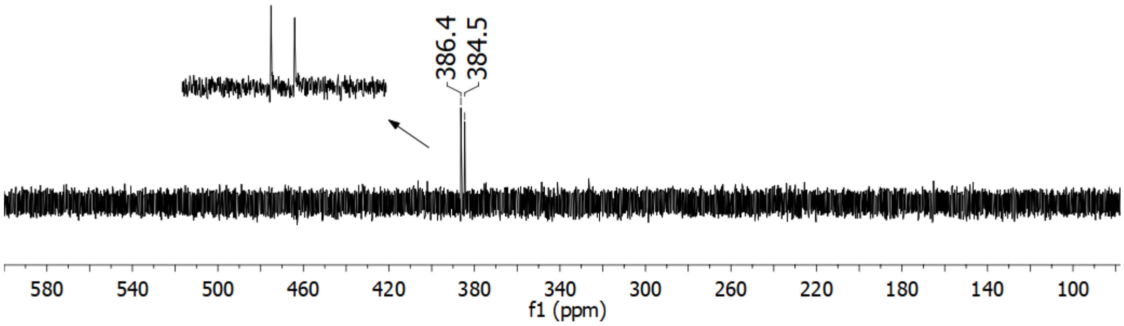


Figure 20. ^{31}P NMR spectrum for [Mes*P=C–GeFl]$_2$ **63** (*cis* and *trans* isomers).

Attempts to isolate both isomers failed. After one week only the *trans* isomer is observed in solution, suggesting the transformation into the more stable configuration. Geometrical isomerization in solution was also reported by Petrar et al. for similar compounds.[22] Likewise, the DFT calculations performed for the case of **63** indicate the slightly higher stability of the *trans* isomer. The more stable derivative gives a resonance signal at 384.5 ppm in ^{31}P NMR spectra, corresponding to the *trans* isomer.

The newly obtained *trans* 2,4-diphosphinylidene-1,3-digermafluorenylcyclobutane, [Mes*P=C–GeFl]$_2$ **63**, is a four-member symmetric compound with two exocyclic P=C units.

In the ^{13}C NMR spectrum of 1,3-digermafluorenylcyclobutane **63** the signal attributed to the equivalent carbon atoms from the two exocyclic P=C units was observed as a doublet (d, $^{1}J_{P=C}$ = 36.6 Hz) at a chemical shift of 174.7 ppm. The coupling constant ($^{1}J_{P=C}$ = 36.6 Hz) has a considerably lower value compared with the one given by the precursor ($^{1}J_{P=C}$ = 84.2 Hz).

Formation of a heterocyclic asymmetric compound was also observed by addition of *t*BuLi or *s*BuLi to the starting Mes*P=C(Cl)–Ge(Cl)Fl **58**. This germaphosphacyclobutane **64**, was obtained with an estimated conversion of around 41% which was calculated through integration of the specific signals in the ^{31}P NMR spectrum recorded for the crude reaction mixture. The main particularity of derivative **64** is the presence of two dublet signals identified in ^{31}P NMR spectrum with chemical shifts of 149.7 ppm and −27.7 ppm, both having a coupling constant of 58.7 Hz (Figure 21).

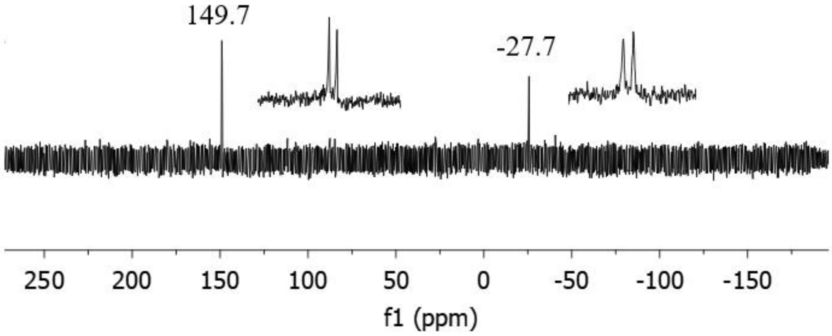


Figure 21. ^{31}P NMR spectrum for germaphosphacyclobutane **64**.

The resonance signal from 149.7 ppm (d, $^{2}J_{PP}$ = 58.7 Hz) is in the range reported for P=C moiety containing compounds, so at least one double bond was retained in the molecular structure of the new product. The second dublet (−27.7 ppm, $^{2}J_{PP}$ = 58.7 Hz) is more likely to be attributed to a P(III) type element included in a cycle and without retaining the unsaturated character for the carbon–phosphorus bond.[25]

Slow decomposition of derivative **64** was noticed in all common organic solvents leading to the formation of several unidentified side products. Even if the analyzed samples could not be purified, the recorded ^{1}H and ^{13}C NMR spectra allowed extracting additional information for the structure prediction of **64**.

The proposed structure most likely contains an exocyclic P=C bond and an intracyclic phosphorus atom, corresponding to a germaphosphacyclobutane with a four member C–Ge–C–P type asymmetric heterocycle.

High resolution mass spectrometry analyses were also performed. For derivative **60**, namely the 9-methyl-9-phosphaalkenylchloro-9-germafluorene, with molecular formula $C_{32}H_{41}ClGeP$, the calculated mass was [M+1] 565.1841, while the found mass value was 565.1826.

Similarly, for 9-butyl-9-phosphaalkenylchloro-9-germafluorene **61** having the molecular formula $C_{35}H_{47}ClGeP$, the calculated [M+1] mass was 607.2310, while almost the same value was determined by the used HRMS method (found: 607.2311).

The bis-9-phosphaalkenylchloro-9-germafluorene, $[Mes^*P{=}C(Cl){-}GeFl]_2$ **62** was also analyzed by APCI HRMS method. For the molecular formula of $C_{62}H_{75}Cl_2Ge_2P_2$, the calculated [M+1] mass was 1097.3239, while 1097.3148 was found via the used mass spectrometry method.

II.3.2. Solid state molecular structure analysis

II.3.2.1. Solid state molecular structure of 9-methyl-9-phosphaalkenylchloro-9-germafluorene

The solid state structure of 9-methyl-9-phosphaalkenylchloro-9-germafluorene **60** is presented in Figure 27. Derivative **60** crystallizes in the monoclinic system, the asymmetric unit consisting of only one molecule.

The P=C bond lenght of 1.669(1) Å for the methylated germaphosphapropene is somewhat longer than the one reported for the precursor (1.649(3) Å).[3] The same tendency is observed for the =C–Ge bond distance for **60** (1.953(1) Å) in comparison with the one given by **58** (1.937(3) Å). The germanium–carbon cyclic bonds from the fluorenylic system are slightly longer for **60** ($Ge{-}C_{Fl\ ring}$ = 1.937(1) and 1.936(1) Å) than those reported for **58** ($Ge{-}C_{Fl\ ring}$ = 1.919(4) and 1.914(3) Å). Noticeably, the Ge–Cl bond length in Mes*P=C(Cl)–Ge(Cl)Fl is 2.179(1) Å and the $Ge{-}CH_3$ distance is 1.938(1) Å for $Mes^*P{=}C(Cl){-}Ge(CH_3)Fl$.

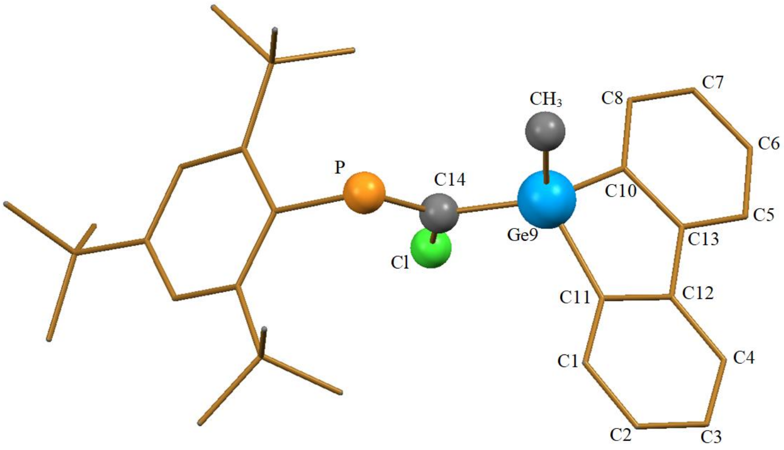


Figure 27. Molecular structure of $Mes^*P{=}C(Cl){-}Ge(CH_3)Fl$ **60**. Hydrogen atoms are omitted for clarity.

II.3.2.2. Solid state molecular structure of 9-butyl-9-phosphaalkenylchloro-9-germafluorene

The molecular structure of Mes*P=C(Cl)–Ge($CH_2CH_2CH_2CH_3$)Fl **61** is shown in Figure 29.

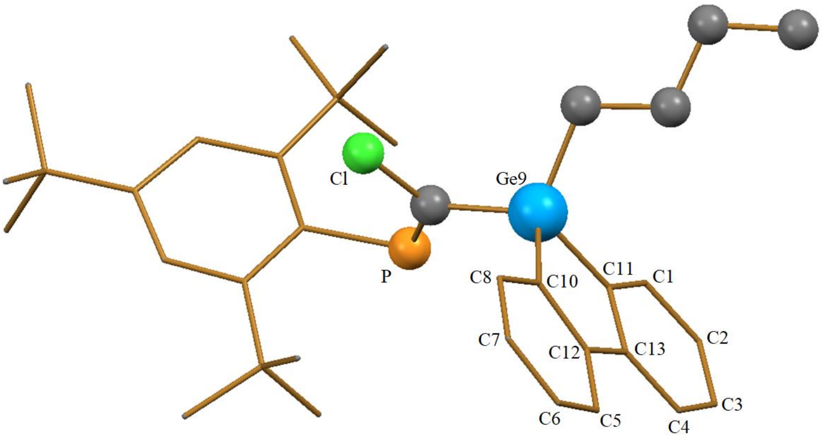


Figure 29. Molecular structure of Mes*P=C(Cl)–Ge($CH_2CH_2CH_2CH_3$)Fl **61**. Hydrogen atoms are omitted for clarity.

Only one molecule exists in the asymmetric unit of **61**, just like in the case of the methylated germaphosphapropene **60**.

The P=C bond lenght is almost similar for butyl- and methyl-germaphosphapropene (1.670(3) Å for **61** and 1.669(1) Å for **60**) while the P=C–Ge angle is also comparable for the two derivatives (120.07(19)° for **61**, 118.60(6)° for **60**). Similar bond lenghts were obtained for =C–Ge and =C–Cl. The Ge–R lenght is 1.947(4) Å for **61** and 1.938(1) Å for **60**, where R = $CH_2CH_2CH_2CH_3$ and CH_3, respectively.

The intracyclic $C_{Fl\ ring}$–Ge–$C_{Fl\ ring}$ angle for Mes*P=C(Cl)–Ge($CH_2CH_2CH_2CH_3$)Fl **61** is 88.6(8)°, while for Mes*P=C(Cl)–Ge(CH_3)Fl **60** is 89.85(5)°.

II.3.2.3. Solid state molecular structure of bis-9-phosphaalkenylchloro-9-germafluorene

Another derivative which was characterized by means of single crystal X-ray diffraction is the bis-9-phosphaalkenylchloro-9-germafluorene **62**, which was obtained as a minor product by reacting Mes*P=C(Cl)–Ge(Cl)Fl **58** with *t*BuLi (or *s*BuLi).

Single crystals of **62** were obtained from Et_2O. When a mixture of Et_2O and chloroform was used, a different way of crystallization occured in which case the asymmetric unit contains a molecule of bis-9-phosphaalkenylchloro-9-germafluorene and a molecule of chloroform, leading to **62·CHCl$_3$**. Compound **62** crystallizes in triclinic, whereas **62·CHCl$_3$** crystallizes in monoclinic system, respectively. The molecular structures of **62** and **62·CHCl$_3$** are shown in Figure 30 and Figure 31, respectively.

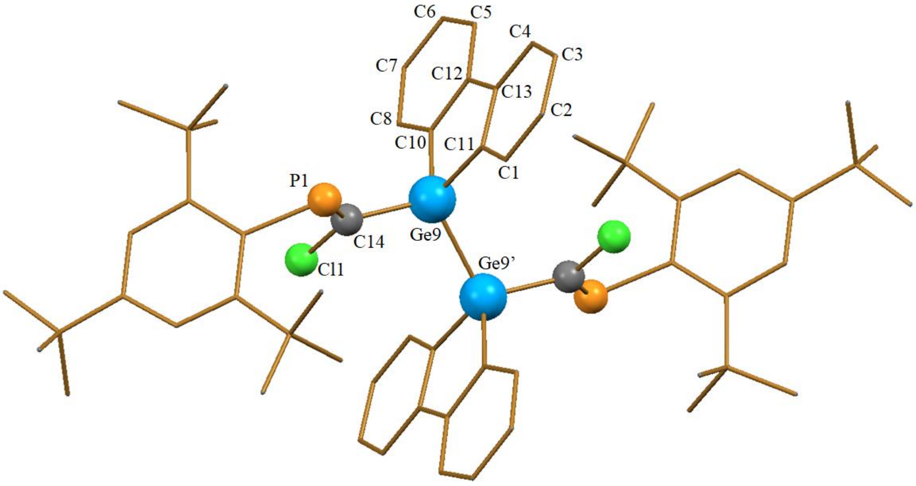


Figure 30. Molecular structure of bis-9-phosphaalkenylchloro-9-germafluorene, [Mes*P=C(Cl)–GeFl]$_2$ **62**. Hydrogen atoms are omitted for clarity.

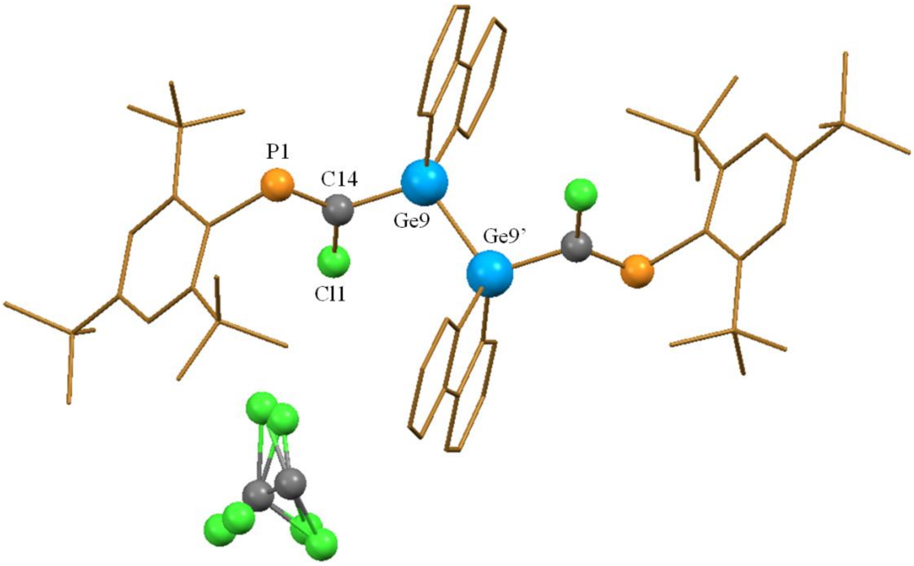


Figure 31. Molecular structure of bis-9-phosphaalkenylchloro-9-germafluorene with one molecule of chloroform, **62·CHCl$_3$**. Hydrogen atoms are omitted for clarity.

The asymmetric unit of **62** consists of a half molecule, the other half being related to the first one by an inversion center. In this respect, all substituents on the germanium center are in *trans* arrangement relative to the Ge–Ge bond.

II.3.2.4. Solid state molecular structure of 2,4-diphosphinylidene-1,3-digermafluorenylcyclobutane

A novel symmetrical cyclobutane type compound with two exocyclic P=C bonds, namely 2,4-diphosphinylidene-1,3-digermafluorenylcyclobutane, [Mes*P=C–GeFl]$_2$ **63**, was also obtained as a product from the reaction of **58** with *t*BuLi or *s*BuLi. Two geometrical isomers were initially detected in solution but attempts to isolate both of them, unfortunately, were not successful. Only the *trans* isomer was separated and fully characterized in solution and in solid state as well.

Single colourless crystals of **63** were obtained from a mixture of Et_2O and pentane allowing its molecular structure determination by solid state X-ray diffraction. Its solid state molecular structure is presented in Figure 34. The *trans* digermacyclobutane **63** crystallizes in monoclinic system with two molecules per unit cell. The Mes* substituents are in *trans* position relative to the P=C···C=P axis.

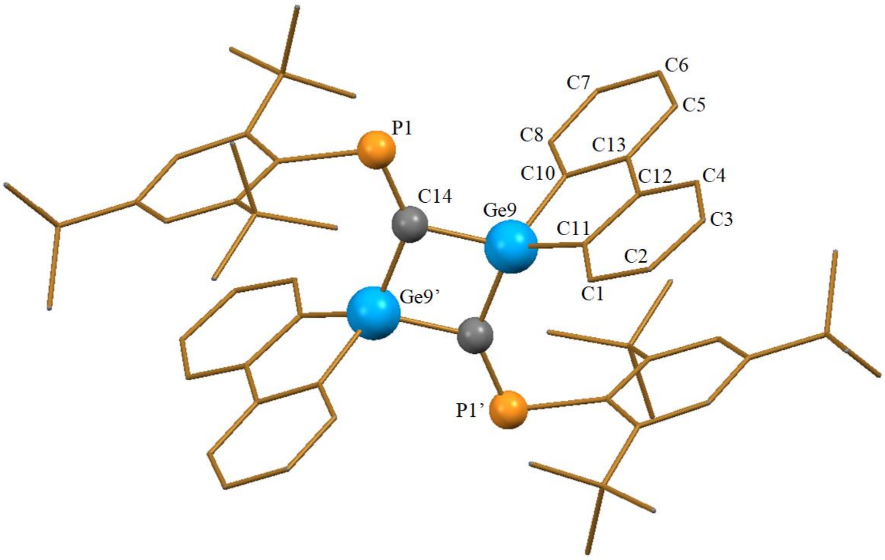


Figure 34. Molecular structure of 2,4-diphosphinylidene-1,3-digermafluorenylcyclobutane, [Mes*P=C–GeFl]$_2$ **63**. Hydrogen atoms are omitted for clarity.

The exocyclic P=C bond length in **63** is 1.657(3) Å and the two =C–Ge bonds are almost equal (1.964(3) Å and 1.962(3) Å). The P=C–Ge angles are slightly different (138.17(18)° and 128.04(17)°, respectively). For the four member planar heterocycle (with the dihedral angle of 0.00(13)°) the intracyclic Ge–C–Ge angle has 93.50(13)° and the =C–Ge–C= angle has 86.50(13)°. The dihedral angles for C_{ipso}–P=C–Ge are: 1.9(3)° and −170.2(2)°, respectively.

By the performed reactivity investigations, different types of products were obtained and characterized. Depending on the type of lithium reagent used (MeLi, *n*BuLi, *t*BuLi or *s*BuLi), the reaction takes place with alkylation at the germanium atom or with formation of dimeric species.

II.4. Reactivity of 9-chloro-9-phosphaalkenylchloro-9-germafluorene

II.4.1. Reaction of Mes*P=C(Cl)–Ge(Cl)Fl with lithium

Since the chemical behaviour of Mes*P=C(Cl)–Ge(Cl)Fl **58** towards organolithium reagents was elucidated, the next step was the investigation of its reactivity with Li.

The recorded ^{31}P and ^{31}P{H} NMR spectra revealed two characteristic singlet type resonance signals situated at 291.5 ppm (95%) and 293.8 ppm (5%) suggesting the formation of two isomers. The P=C unsaturation is retained in the structure of the new product according to the revealed chemical shifts.

Characteristic for the germafluorenyl system are the two doublet and triplet types of signals displayed in ^{1}H NMR spectrum. In this case, two specific signals are observed at chemical shifts of 7.50 ppm (d, J = 7.7 Hz) and 7.05 ppm (t, J = 7.2 Hz), respectively. Certainly, the multiplet resonance signal (7.25–7.29 ppm) can be attributed to the other two types of protons overlapped with the resonance signal given by chloroform (Figure 37).

The singlet signal with chemical shift of 7.39 ppm can most probably be attributed to the protons situated in *meta* position of Mes*. The chemical shifts corresponding to the *t*Bu *ortho* and *para* protons of Mes* are in the expected region (1.45 ppm for *o*-*t*Bu and 1.32 ppm for *p*-*t*Bu) (Figure 37).

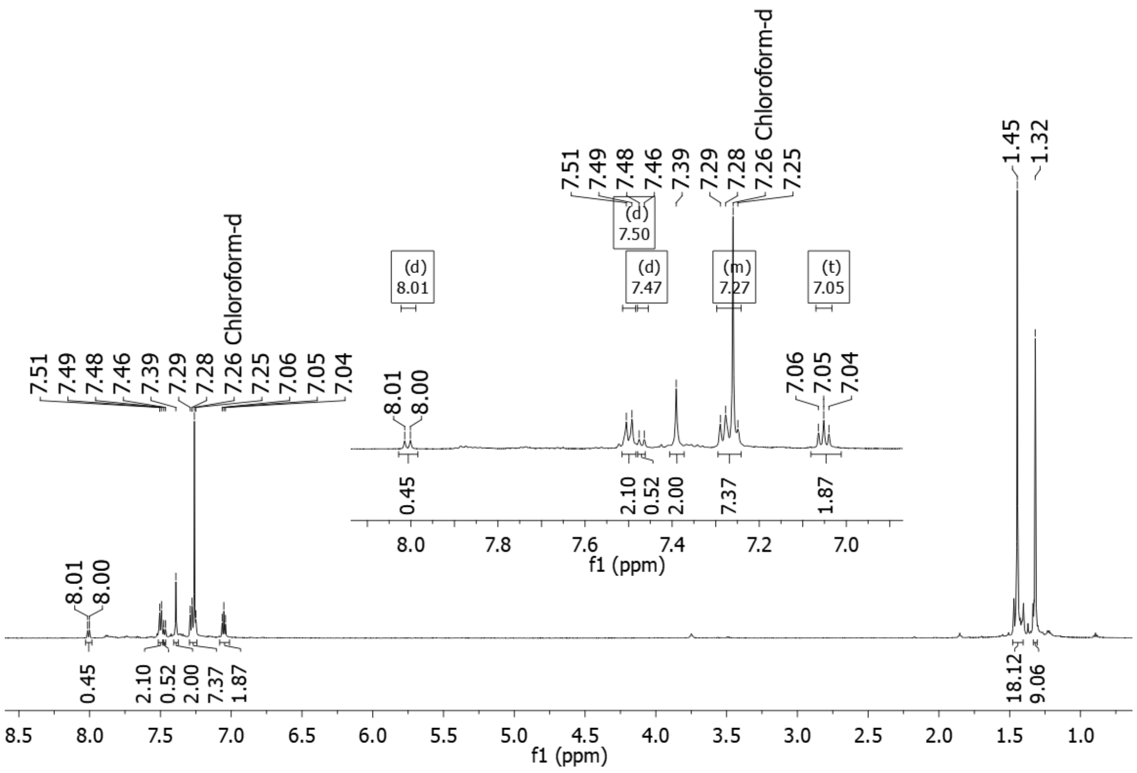


Figure 37. ^{1}H NMR spectrum (CDCl$_3$, 600.13 Hz) for reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with Li.

In the ^{1}H NMR spectrum, a doublet is observed at chemical shift of 8.01 ppm with a coupling constant of 7.9 Hz, and it is in 1:1 ratio with respect to the doublet with chemical shift of 7.47 ppm with a coupling constant of 7.1 Hz. The coupling can be attributed to a $^{3}J_{HH}$ interaction.

The ^{13}C NMR spectrum shows the same pattern as the one corresponding to the starting derivative Mes*P=C(Cl)–Ge(Cl)Fl **58**. A doublet is observed at chemical shift of 32.9 ppm ($^{4}J_{PC}$ = 4.4 Hz). The doublet signal (d, $^{1}J_{P=C}$ = 86.6 Hz) with chemical shift of 166.2 ppm can be attributed to the carbon atom involved in the P=C bond. For derivative **58** a doublet was reported with chemical shift of 162.3 ppm (d, $^{1}J_{P=C}$ = 84.2 Hz).[3]

Attempts to further purify the product were proved to be unsuccessful. Slow decomposition was observed in solution after less than 1 week, leading to multiple phosphorus atom containing side products.

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with Li was performed in toluene as well, but the reaction went with formation of several unidentified products.

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with Li in THF led to the formation of a new product. The suggested structure corresponds to a new derivative where the P=C unsaturation is retained. A dimer type structure containing a unit comparable with the configuration of the precursor is possible. However, additional experimental or theoretical investigations are necessary for the more accurate molecular structure prediction.

II.4.2. Reaction of Mes*P=C(Cl)–Ge(Cl)Fl with sodium hydride

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with NaH was tested in THF and toluene. The use of THF led to better conversions and experimental results.

Addition of 1 eq of NaH to a THF solution of Mes*P=C(Cl)–Ge(Cl)Fl **58** resulted with the formation of a new product which was analyzed through NMR spectroscopy. A singlet was displayed in the ^{31}P NMR spectrum with chemical shift of 291.6 ppm. The ratio between the newly formed compound and the starting material was 1:1. Addition of 2 eq of NaH resulted with 80% conversion into the same new product which was further analyzed by means of multinuclear NMR spectroscopy.

In ^{1}H NMR spectra (Figure 39), two singlet signals are observed in the aliphatic region with chemical shifts of 1.31 ppm and 1.43 ppm, respectively. A triplet and a doublet with chemical shifts of 7.04 ppm (t, *J* = 7.5 Hz) and 7.49 ppm (d, *J* = 7.8 Hz) can be attributed to the protons from the germafluorenyl unit.

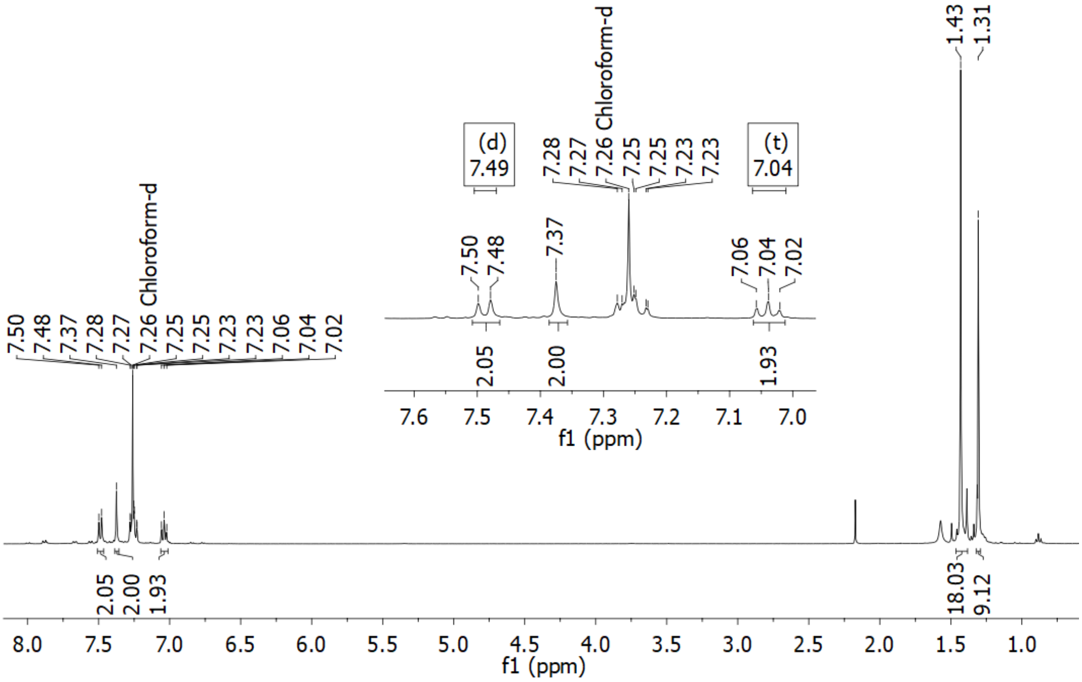


Figure 39. ^{1}H NMR spectrum ($CDCl_3$, 400.13 Hz) for reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with NaH.

In the ^{13}C NMR spectrum, two doublets with chemical shifts of 32.9 ppm (d, J = 68 Hz) and 166.2 ppm (d, J = 85.1 Hz) are observed. The coupling constant of J = 68 Hz can be attributed to a $^{4}J_{PC}$ interaction, while the coupling constant of J = 85.1 Hz to a P=C coupling (Figure 40).

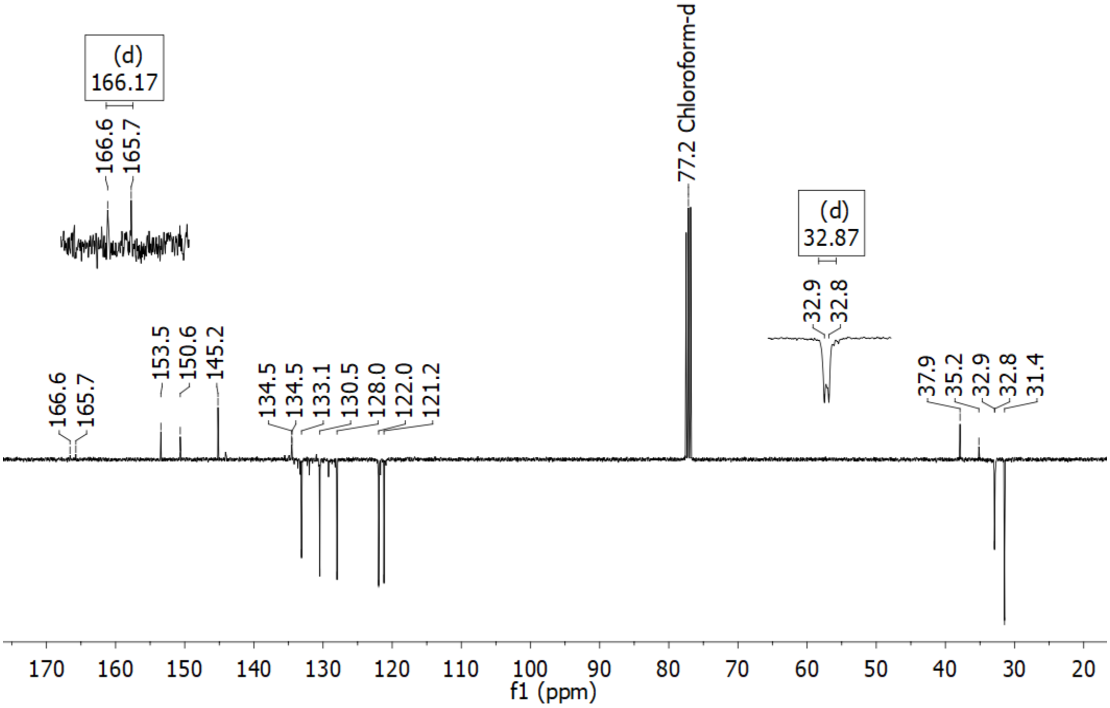


Figure 40. ^{13}C NMR spectrum (CDCl$_3$, 100.61 Hz) for reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with NaH.

As it was presented in the previous sections, different germaphosphaalkenyl compounds such as alkylated, linear dimers or cyclic symmetrical dimers, present resonance signals in ^{31}P NMR spectra with chemical shifts of 280–300 ppm for the phosphorus atom included in the P=C unit. Therefore, it is difficult to predict the exact structure of the new product resulted from reaction of **58** with Li and NaH. Anyhow, the molecular structure should be somewhat similar with that of the precursor **58**.

II.4.3. Reaction of Mes*P=C(Cl)–Ge(Cl)Fl with silver oxide

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with Ag_2O was investigated. Besides several side products, a major derivative was formed with 75% estimated conversion, giving a resonance signal at a chemical shift of 291.5 ppm in ^{31}P NMR spectrum.

According to investigations conducted in solution, the same product was obtained through reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with Li, NaH and Ag_2O. A comparison between the recorded ^{31}P and ^{1}H NMR spectra is presented in the following figures.

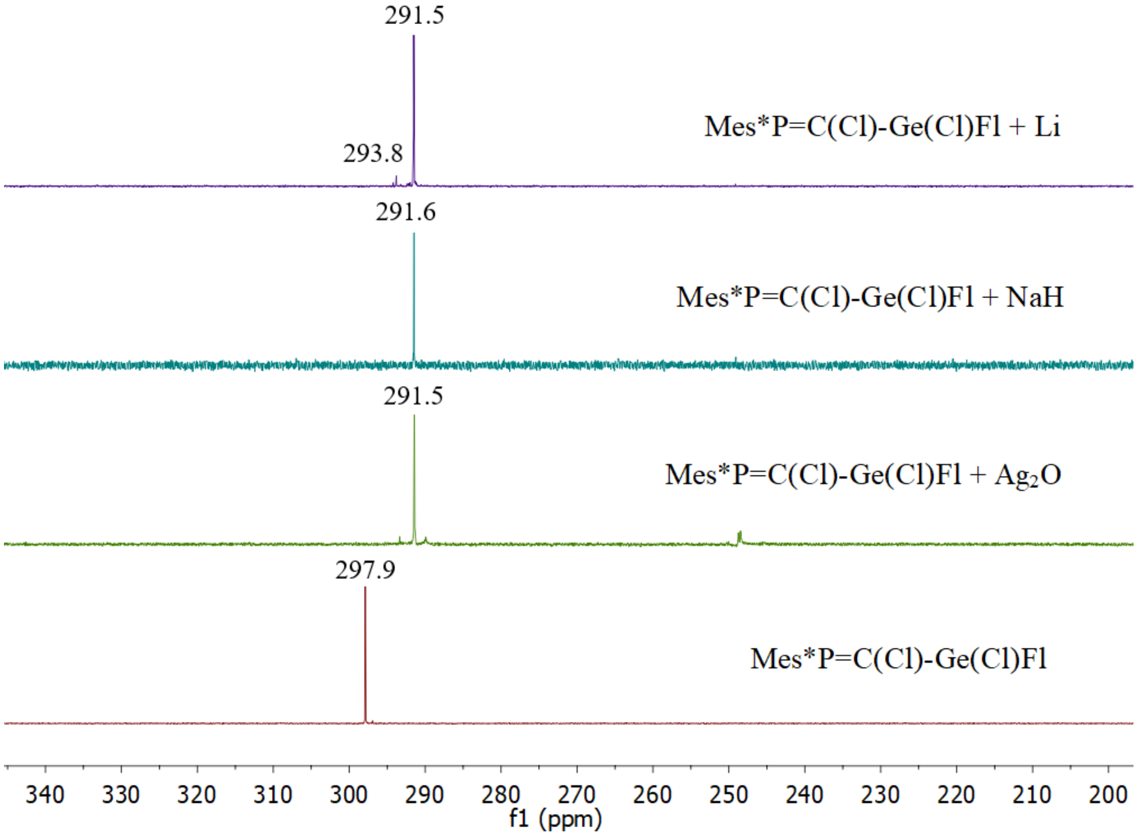


Figure 41. ^{31}P NMR spectra for Mes*P=C(Cl)–Ge(Cl)Fl **58** and for the unidentified product obtained via reaction of **58** with lithium, sodium hydride and silver oxide.

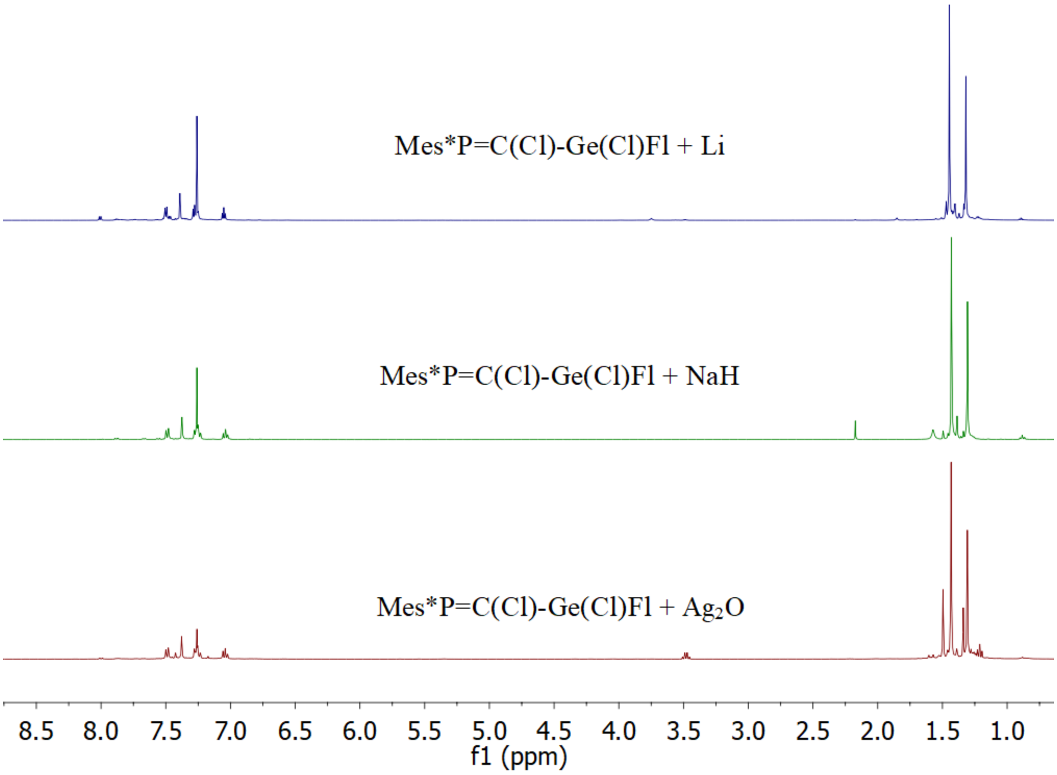


Figure 44. ^{1}H NMR spectra for Mes*P=C(Cl)–Ge(Cl)Fl **58** and for the unidentified product obtained via reaction of **58** with lithium, sodium hydride and silver oxide.

Conclusively, the structure of the newly obtained product is similar with that of the starting material, but the formation of a symmetrical dimer is also possible, with restraint of the P=C moiety.

Additionally, reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with magnesium was also investigated. Besides the 15% unreacted precursor, five singlet signals were observed in ^{31}P NMR spectrum with chemical shifts between 289 and 318 ppm.

Similarly, reaction of **58** with KC_8 led to the formation of multiple products with chemical shifts situated between 280 and 340 ppm in ^{31}P NMR spectrum.

Further investigations for the reactivity of Mes*P=C(Cl)–Ge(Cl)Fl **58** are currently in progress.

II.5. Conclusions

II.6. Experimental part

Appendix II

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CHAPTER III
NEW GERMAPHOSPHAALKENYL DERIVATIVES: REACTIVITY TOWARDS TRANSITION METALS

III.1. Introduction

The use of germafluorenyl fragment with electronic properties along with the secondary electronic interactions which can occur within the target compounds, represent a novel approach. Having these in mind, two novel derivatives were obtained and reported by our team,[11] the 9-chloro-9-phosphaalkenylchloro-9-germafluorene **58** and 9,9-bis(phosphaalkenylchloro)-9-germafluorene **59**, where the influence of the extended electronic-conjugated system of the germafluorenyl unit was investigated.

In order to assess the additional electronic and steric effects induced by transition metal containing fragments, we report herein a reactivity study of the novel germaaphosphalkenyl derivatives with *d* block elements, such as: Au, Pd, W or Fe. The coordination capacity is particularly discussed, together with the synthetic pathways, characterization and structural investigations of the obtained complexes.

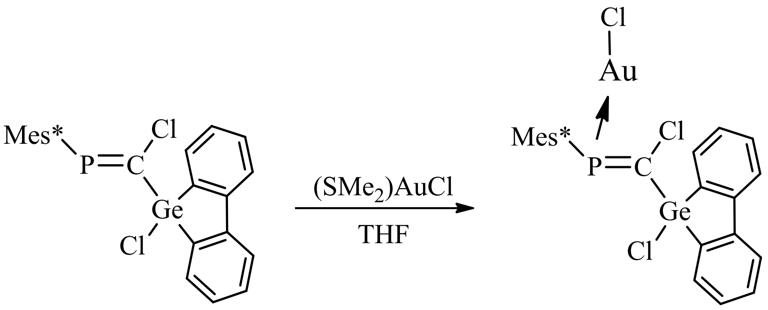
III.2. Reaction of 9-chloro-9-phosphaalkenylchloro-9-germafluorene and 9,9-bis(phosphaalkenylchloro)-9-germafluorene with transition metals

III.2.1. Reaction of Mes*P=C(Cl)–Ge(Cl)Fl and [Mes*P=C(Cl)]$_2$–GeFl with Me$_2$SAuCl

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** and [Mes*P=C(Cl)]$_2$–GeFl **59** with Me$_2$SAuCl led to successful synthesis of the corresponding gold(I) complexes: (9-chloro-9-phosphaalkenylchloro-9-germafluorene)gold(I) chloride **65** (presented in Scheme 38) and [bis(9-chloro-9-phosphaalkenylchloro)-9-germafluorene]gold(I) chloride **66** (presented in Scheme 39).

Both novel gold complexes **65** and **66** were obtained in almost quantitative yield.

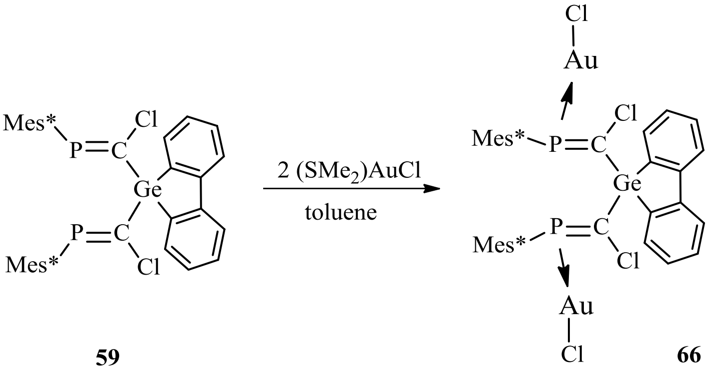
While Mes*P=C(Cl)–Ge(Cl)Fl **58** gives a specific signal at 297.9 ppm,[14] the corresponding gold complex **65** displays an upfield shifted singlet signal at 239.7 ppm. A second resonance signal is also observed in ^{31}P NMR spectrum at a chemical shift of 244.5 ppm which, most probably, corresponds to the *E* isomer of derivative **65**.



58 **65**

Scheme 38. Synthesis of (9-chloro-9-phosphaalkenylchloro-9-germafluorene)gold(I) chloride **65**.

For derivative **66** an upfield shifted resonance signal is displayed in the ^{31}P NMR spectrum of **66** (δ: 238.4 ppm) in comparison with the chemical shift given by **59** (δ: 290.1 ppm). The new product has a symmetrical structure. One gold fragment is linked to each phosphorus atom giving rise to a bimetallic coordination compound.



59 **66**

Scheme 39. Synthesis of bis[(9-chloro-9-phosphaalkenylchloro)-9-germafluorene]gold(I) chloride **66**.

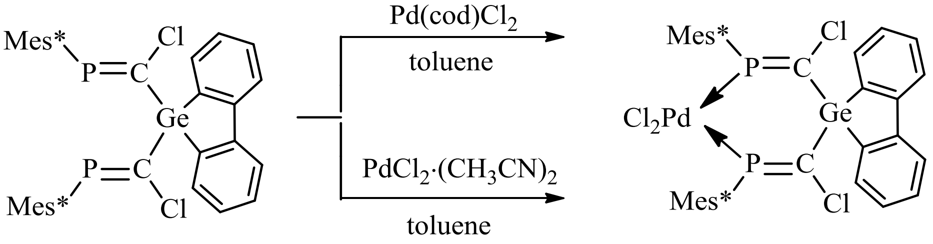
The new compounds are stable under inert atmosphere, both in solid state and in solutions at room temperature for an indefinite time.

III.2.2. Reaction of Mes*P=C(Cl)–Ge(Cl)Fl and [Mes*P=C(Cl)]$_2$–GeFl with palladium fragments

The capacity of Mes*P=C(Cl)–Ge(Cl)Fl **58** and [Mes*P=C(Cl)]$_2$–GeFl **59** to coordinate to a Pd containing fragment was tested.

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with Pd(cod)Cl$_2$ in toluene did not take place. An alternative way of synthesis consisted in the use of PdCl$_2$·(CH$_3$CN)$_2$. Unfortunately, none of the above mentioned Pd reagents reacted with Mes*P=C(Cl)–Ge(Cl)Fl **58**. For both circumstances, the ^{31}P NMR spectra indicate the formation of several phosphorus containing compounds exhibiting resonance signals in the range of 200–250 ppm, specific for phosphorus atoms included in P=C units. Giving the formation of multiple products, our attempts to isolate these species were unsuccesful so far.

By contrast, reaction of [Mes*P=C(Cl)]$_2$–GeFl **59** with Pd(cod)Cl$_2$ and PdCl$_2$·(CH$_3$CN)$_2$ efficiently occured in both cases (Scheme 40).



59 **67**

Scheme 40. Synthesis of [bis(9-chloro-9-phosphaalkenylchloro)-9-germafluorene]palladium(II) dichloride **67**.

The structure of the novel complex **67** is expected to evidence the coordination of each phosphorus atom to the same palladium center in a bidentate fashion leading to a six-membered chelate.

No major differences were observed in the conversion rates while using Pd(cod)Cl$_2$ or PdCl$_2$·(CH$_3$CN)$_2$. Both palladium catalysts showed identical efficiency for obtaining the targeted complex.

The [bis(9-chloro-9-phosphaalkenylchloro)-9-germafluorene]palladium(II) dichloride **67** was fully characterized in solution and in solide state.

III.2.3. Coordination behaviour of Mes*P=C(Cl)–Ge(Cl)Fl in reaction with tungsten and iron fragments

In order to investigate the coordination ability of Mes*P=C(Cl)–Ge(Cl)Fl **58**, reactions with $W(CO)_5THF$ and $Fe(CO)_5$ were conducted.

For the reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with $W(CO)_5THF$, the formation of a new derivative with 25% conversion (δ: 318.2 ppm in ^{31}P NMR spectrum) was observed, so 75% from the ligand remained unreacted (Figure 45, green). Then the mixture was refluxed for one additional hour. Surprinsigly, almost the same ratio of unreacted starting material was evidenced by ^{31}P NMR spectroscopy (70% unreacted Mes*P=C(Cl)–Ge(Cl)Fl **58**). The recorded ^{31}P NMR spectra displays formation of other phosphorus containing compounds as well, giving resonance signals at chemical shifts of −88.4 ppm, 274.4 ppm, 315.8 ppm and 339.7 ppm, respectively, which could not be isolated (Figure 45, red).

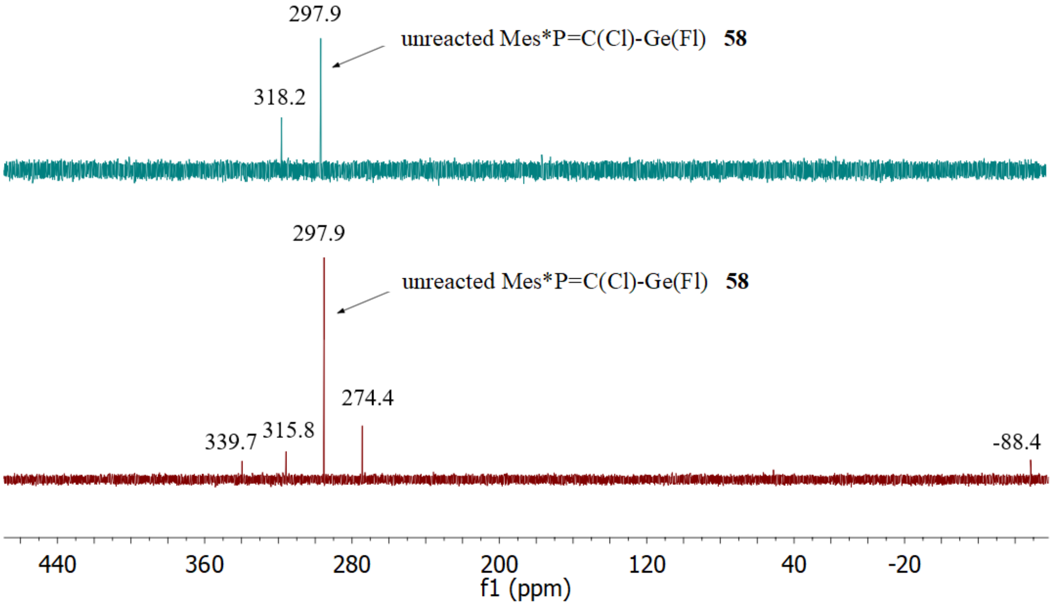


Figure 45. ^{31}P NMR spectra recorded for reaction mixture resulted by adding $W(CO)_5THF$ to a solution of Mes*P=C(Cl)–Ge(Cl)Fl **58**: after 1 h under reflux (up—green); after 2 h under reflux (down—red).

Reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with $Fe(CO)_5$ in THF led to the formation of three major compounds in 1:1:1 ratio with chemical shifts of 293.1 ppm, 293.8 ppm and 299.8 ppm, respectively, as shown in the ^{31}P NMR spectrum in Figure 46. Attempts to separate these derivatives were unsuccessful. A large quantity of precipitate was also observed, which was not soluble in common organic solvents.

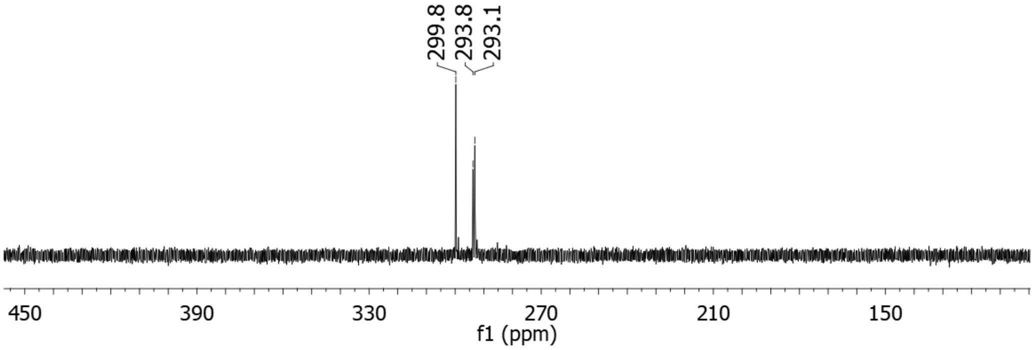


Figure 46. ^{31}P NMR spectrum recorded for reaction mixture resulted by adding $Fe(CO)_5$ to a solution of Mes*P=C(Cl)–Ge(Cl)Fl **58**.

In a parallel experiment, reaction of Mes*P=C(Cl)–Ge(Cl)Fl **58** with $Fe_2(CO)_9$ was investigated. Three derivatives were obtained and evidenced in the ^{31}P NMR spectrum recorded for the crude reaction mixture. The same 1:1:1 ratio was observed (Figure 47).

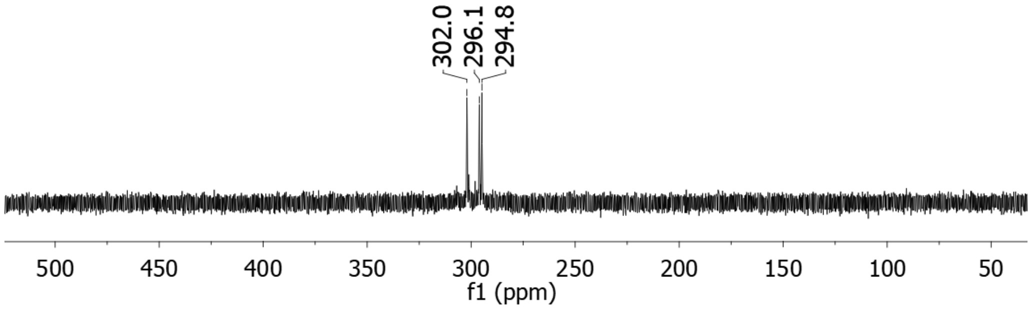


Figure 47. ^{31}P NMR spectrum recorded for reaction mixture resulted by adding $Fe_2(CO)_9$ to a solution of Mes*P=C(Cl)–Ge(Cl)Fl **58**.

Additional experimental investigations are necessary to discover the optimal conditions for obtaining the targeted metal complexes.

III.3. Physico-chemical properties of new transition metal complexes

III.3.1. NMR spectroscopy and mass spectrometry investigations

The mono- (**65**) and diphosphaalkenyl (**66**) germafluorene complexes of gold(I) were fully characterized in solution by means of NMR spectroscopy methods.

In the ^{31}P NMR spectrum of **65** two characteristic signals are displayed at chemical shifts of 239.7 ppm and 244.5 ppm, respectively, upfield shifted compared to the specific resonance signal of the ligand **58** (δ 297.9 ppm) (Figure 48).

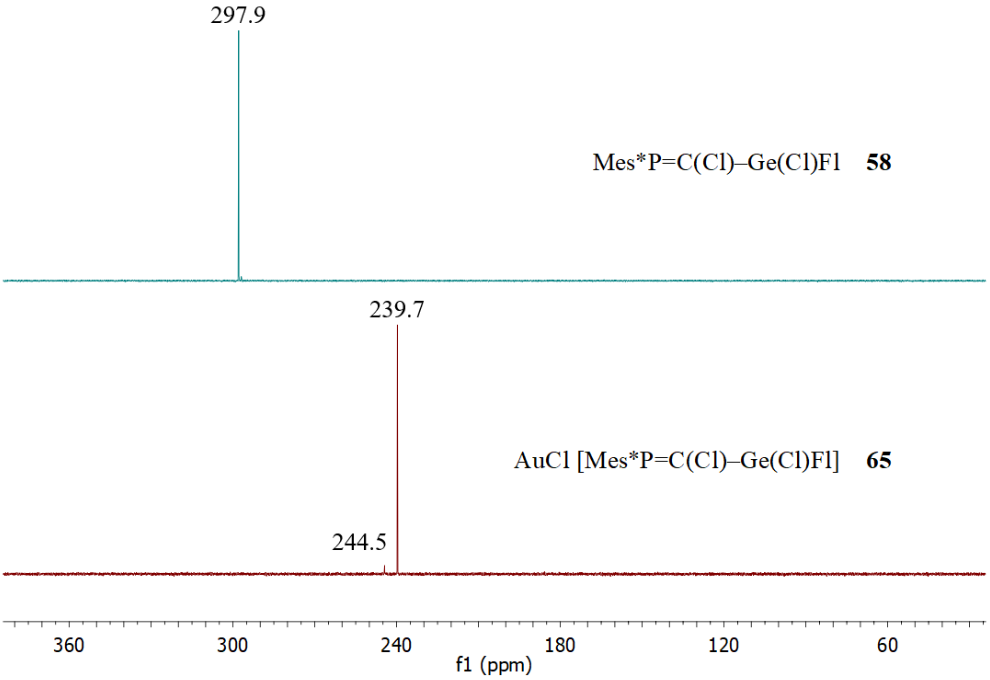


Figure 48. ^{31}P NMR spectra for recorded for Mes*P=C(Cl)–Ge(Cl)Fl **58** and its gold complex AuCl·[Mes*P=C(Cl)–Ge(Cl)Fl] **65**.

The recorded ^{1}H and ^{13}C NMR spectra for AuCl·[Mes*P=C(Cl)–Ge(Cl)Fl] **65** revealed the formation of two isomers for this gold complex (**65a** and **65b**) with slight differences in their geometry.

The ^{1}H NMR spectrum for complex **65** (Figure 49) displays the specific resonance signals for the protons of the germafluorenyl cycle in the aromatic region between 7.4 ppm and 8.0 ppm. The specific doublet in ^{1}H NMR spectrum at a chemical shift of 7.55 ppm with $^{4}J_{HH}$ = 4.0 Hz is attributed to the equivalent protons in *meta* position of Mes*.

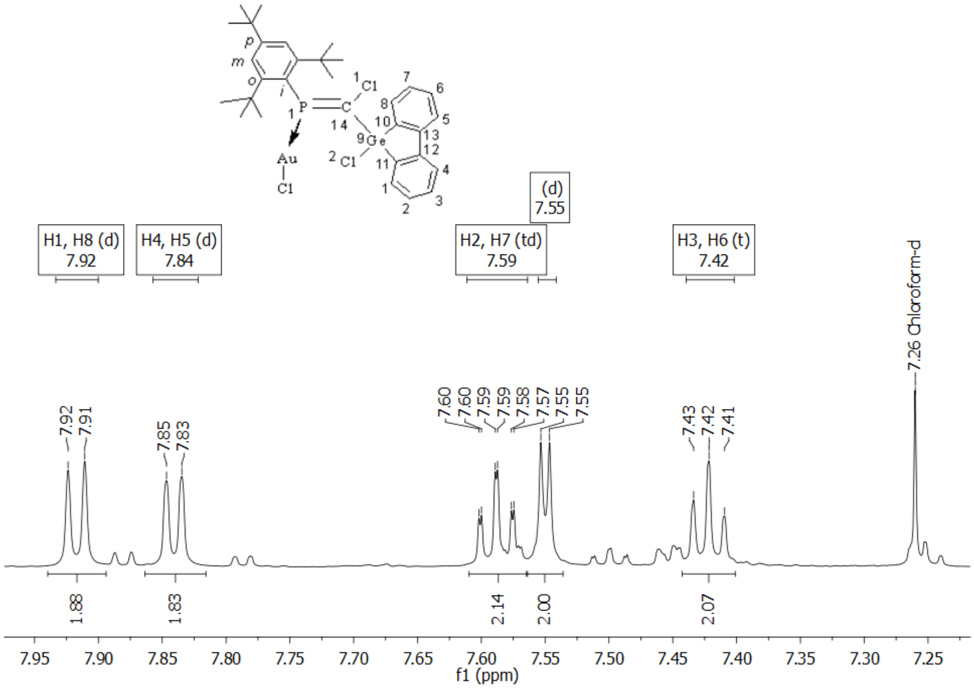


Figure 49. Fragment of the characteristic ^{1}H NMR spectrum (600.13 MHz, CDCl$_3$) recorded for the novel gold complex, AuCl·[Mes*P=C(Cl)–Ge(Cl)Fl] **65a**.

In the ^{13}C NMR spectrum, the carbon atom from the P=C unit displays a specific resonance signal at a chemical shift of 162.2 ppm in ^{13}C NMR with a considerably weaker coupling constant (d, $^{1}J_{P=C}$ = 23.0 Hz). In the case of 9-chloro-9-phosphaalkenylchloro-9-germafluorene **58**, the coupling constant is 84.2 Hz (P=C).[11]

In a similar manner, reaction of 9,9-bis(phosphaalkenylchloro)-9-germafluorene **59** with (SMe$_2$)AuCl led to the formation of a symmetrical new gold complex, **66**. The ^{31}P NMR spectra displays a resonance signal at a chemical shift of 238.4 ppm attributed to the phosphorus atoms of **66**, while the singlet signal at a chemical shift of 290.1 ppm is characteristic for the ligand (**59**) (Figure 50).

The novel complex **66** was characterized only in solution by multinuclear NMR spectroscopy experiments. Suitable single crystals for X-ray diffraction structural determination were not yet obtained.

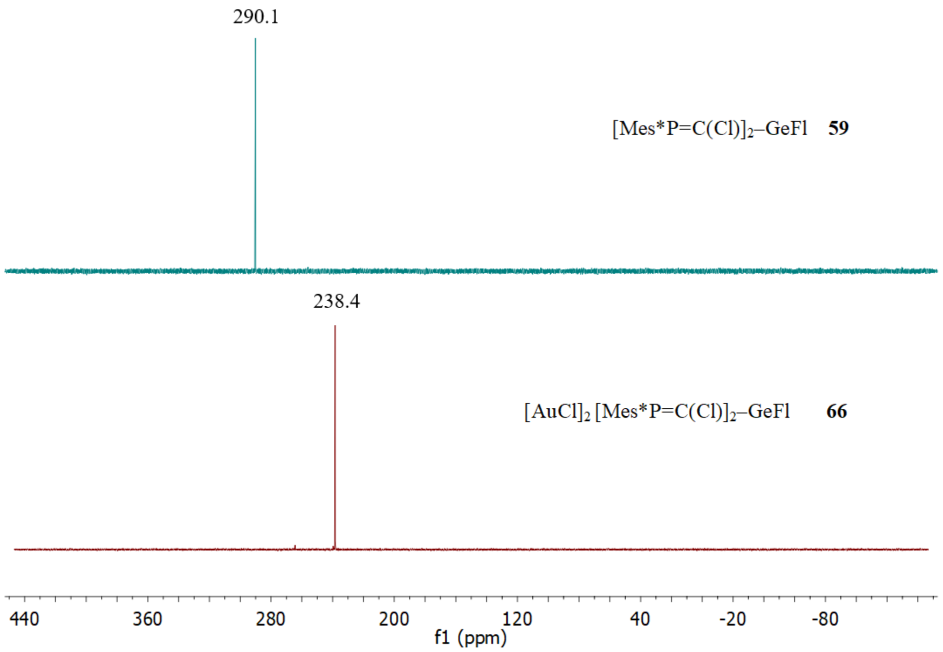


Figure 50. ^{31}P NMR spectra for recorded for [Mes*P=C(Cl)]$_2$–GeFl **59** and its gold complex [AuCl]$_2$·[Mes*P=C(Cl)]$_2$–GeFl **66**.

Another newly obtained transition metal complex was the palladium dichloride coordination compound, **67**. This Pd complex was fully characterized both in solution and in solid state. The singlet resonance signal at a chemical shift of 236.3 ppm in ^{31}P NMR spectrum is attributed to the phosphorus atoms from complex **67** (Figure 51).

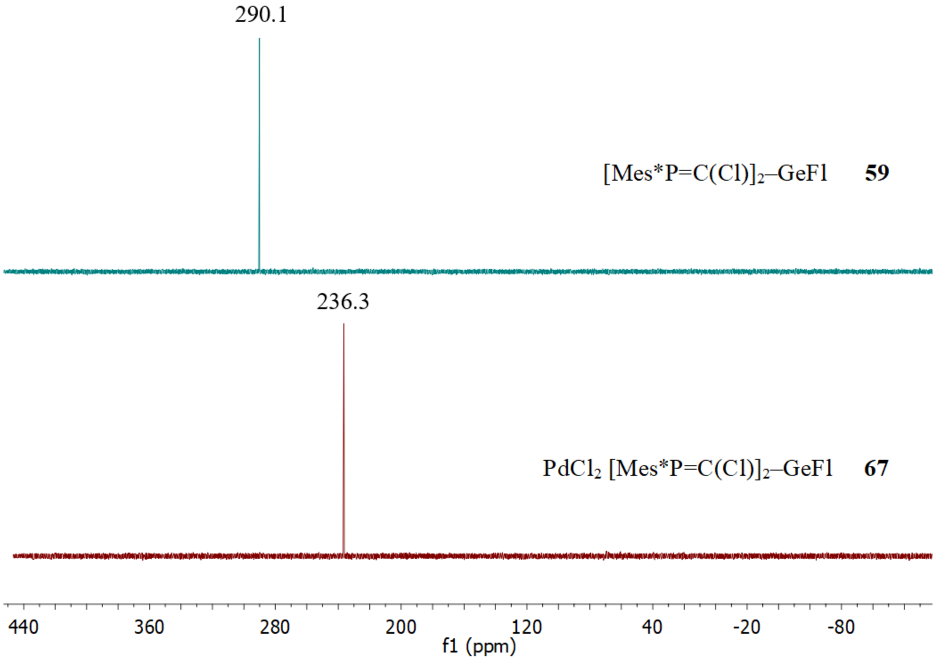


Figure 51. ^{31}P NMR spectra for recorded for [Mes*P=C(Cl)]$_2$–GeFl **59** and its palladium complex PdCl$_2$·[Mes*P=C(Cl)]$_2$–GeFl **67**.

Furthermore, high resolution mass spectrometry (HRMS-APCI) analysis was conducted for the (9-chloro-9-phosphaalkenylchloro-9-germafluorene)gold(I) chloride **65**. The molecular peak was accurately evidenced, highlighting the formation of the gold complex. For derivative **65** the calculated mass was [M+CH_3CN−Cl] 822.1146, while the found mass value was 822.11458.

III.3.2. Molecular structure analysis in solid state for novel metal complexes

III.3.2.1. Solid state molecular structure of the novel gold(I) chloride complex: (9-chloro-9-phosphaalkenylchloro-9-germafluorene)gold(I) chloride

Single crystals of (9-chloro-9-phosphaalkenylchloro-9-germafluorene)gold(I) chloride **65** were obtained from a mixture of hexane and CH_2Cl_2, at room temperature by slow evaporation of the solvents. The solid-state molecular structure determined through X-ray diffraction is presented in Figure 53.

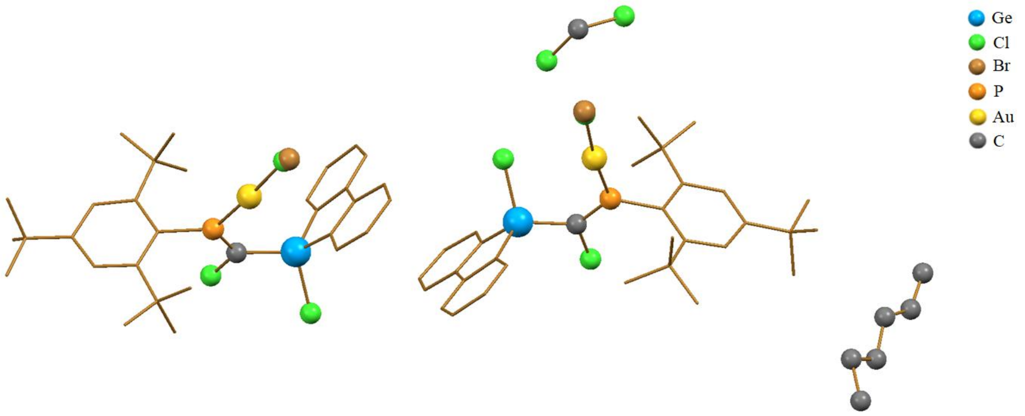


Figure 53. Molecular structure of the asymmetric unit of AuCl·[Mes*P=C(Cl)–Ge(Cl)Fl] **65** consisting of two isomers, crystallized as a solvate with one molecule of *n*-hexane and one molecule of dichloromethane. Hydrogen atoms are omitted for clarity.

The asymmetric unit consists of two isomers, **65a** (Figure 54) and **65b** (Figure 55). Both isomers contains the corresponding ligand coordinated to gold(I) chloride. Interestingly, a chlorine-bromine substitutional disorder was also identified.

The P=C bond lenghts of 1.659(3) Å and 1.658(3) Å in **65a** and **65b** are comparable with other reported values.[28] The P–C*ipso* bond distances (1.813(3) Å and 1.808(3) Å) are slighly shorter than the one characteristic for the free ligand (1.846(3) Å).

The same tendency is observed for =C–Ge bonds as well. Characteristic for the two gold complex isomers **65a** and **65b** are the P–Au bonds (2.213(1) Å and 2.208(1) Å) and Au–Cl bonds (2.246(4) Å and 2.255(8) Å).

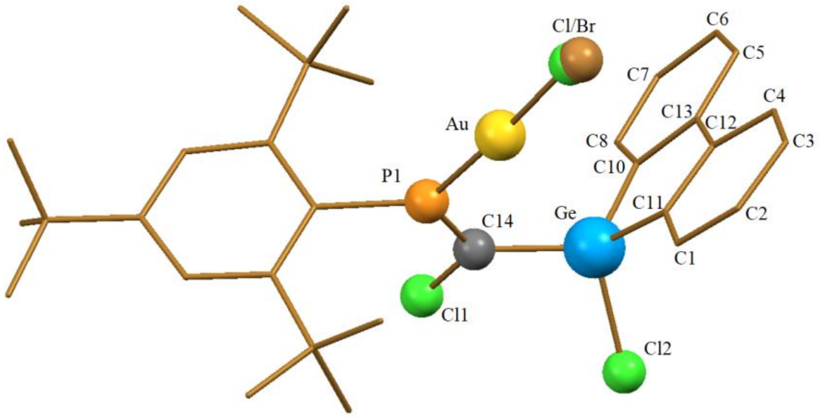


Figure 54. Molecular structure of isomer **65a**, AuCl·[Mes*P=C(Cl)–Ge(Cl)Fl]. Hydrogen atoms are omitted for clarity.

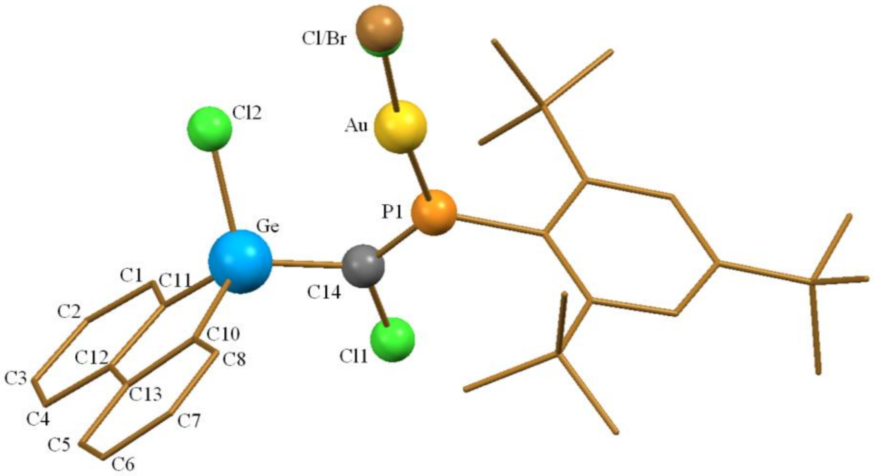


Figure 55. Molecular structure of isomer **65b**, AuCl·[Mes*P=C(Cl)–Ge(Cl)Fl]. Hydrogen atoms are omitted for clarity.

The main difference between the two isomers **65a** and **65b** is the Cl–Ge–C–Cl dihedral angle within the ligand. In isomer **65a** the ligand has a synclinal or gauche conformation [Cl2–Ge9–C14–Cl1 −45.70(15)°], while in the case of isomer **65b** an anticlinal conformation is observed [Cl2–Ge9–C14–Cl1 −145.04(12)°]. The C=P–Au angle is 120.17(10)° and 124.29(10)° for the two isomers, while the Au–P=C–Cl angle is −175.06(12)° for **65a** and −174.32(11)° for **65b**.

III.3.2.2. Solid state molecular structure of the novel palladium(II) dichloride complex: [bis(9-chloro-9-phosphaalkenylchloro)-9-germafluorene]palladium(II) dichloride

The Pd complex was obtained by reacting [Mes*P=C(Cl)]$_2$–GeFl **59** with either Pd(cod)Cl$_2$ or PdCl$_2$·(CH$_3$CN)$_2$.

[Bis(9-chloro-9-phosphaalkenylchloro)-9-germafluorene]palladium(II) dichloride **67**, crystallizes in monoclinic system, space group P21/n as a solvate with CH$_2$Cl$_2$. The asymmetric unit consists of one molecule in which the phosphaalkenyl germanium ligands coordinates to the palladium centre in a symmetric bidentate fashion, leading to the formation of a six-membered chelate (Figure 57).

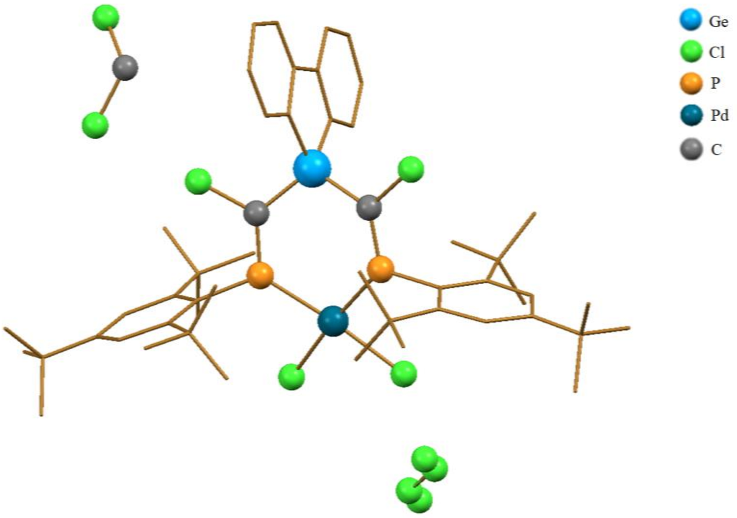


Figure 57. Molecular structure of the asymmetric unit of PdCl$_2$·[Mes*P=C(Cl)]$_2$–GeFl **67** crystallized as a sesqui solvate with CH$_2$Cl$_2$. Hydrogen atoms are omitted for clarity.

As it shown in the above figure (Figure 57) the coordination geometry around palladium is square planar, with the phosphorus atoms in a *cis* arrangement.

Notable differences can be observed by comparing the free ligand **59** with its Pd complex **67**. For instance, the C*ipso*–P=C angles in **59** are 105.8(3)° and 104.5(3)°, while in **67** the angles are 110.58(12)° and 109.51(12)°, respectively. The same tendency is observed for the P=C–Ge angles as well.

The characteristic coordinative P–Pd bonds are 2.253(1) Å and 2.254(1) Å, while the Pd–Cl bonds values are 2.309(1) Å and 2.307(1) Å, respectively (Figure 58). The P=C bond lenghts in the disubstituted [Mes*P=C(Cl)]$_2$–GeFl **59** (1.661(6) Å and 1.672(5) Å) are similar with the ones in the corresponding Pd complex **67** (1.661(3) Å and 1.660(3) Å).

The P–C*ipso* bond is slightly shorter in the chelate (1.812(3) Å and 1.813(3) Å) than in its free ligand (1.822(7) Å and 1.842(5) Å).[28]

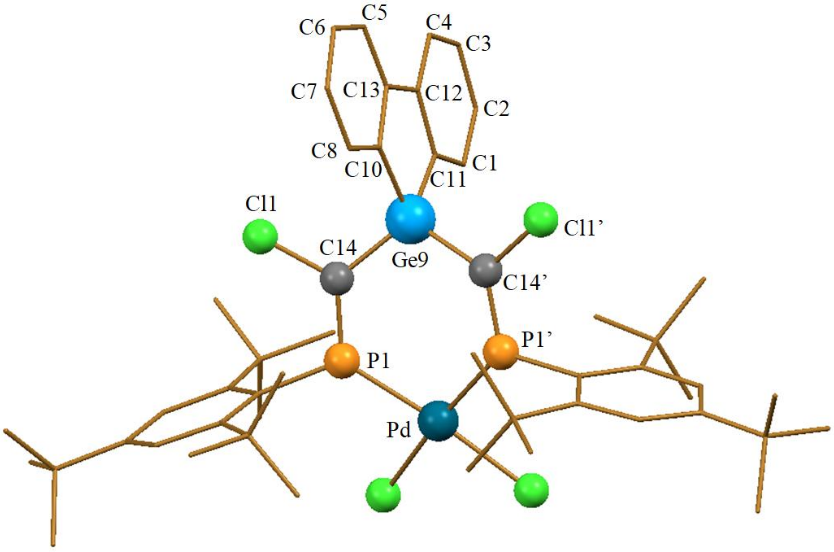


Figure 58. Molecular structure of PdCl$_2$·[Mes*P=C(Cl)]$_2$–GeFl **67**. Hydrogen atoms are omitted for clarity.

III.4. DFT calculations for the new transition metal complexes

The molecular geometries of the two new gold and palladium complexes (**65** and **67**) have also been investigated by DFT calculations. According to the obtained results, the computed geometrical parameters calculated in the gas phase are in agreement with the ones measured in solid state.

For instance, the calculated bond lengths in **65** (Figure 60) for Ge–Cl (2.158 Å), =C–Ge (1.965 Å), P=C (1.663 Å), P–Au (2.226 Å), Au–Cl (2.268 Å) and angles P–Au–Cl (177.0°), are similar with the ones determined by means of X-ray diffraction.

Secondary electronic effects were also computed by NBO analysis highlighting the hyperconjugations which occur in the molecular structure of gold complex, leading to considerable shortening of the Ge–Cl bond distance (2.158(1) Å measured, 2.158 Å computed, compared with the expected value of 2.22 Å by summing the covalent radii of Ge and Cl atoms). These observations are in agreement with previously reported theoretical findings for similar derivatives.[33–37]

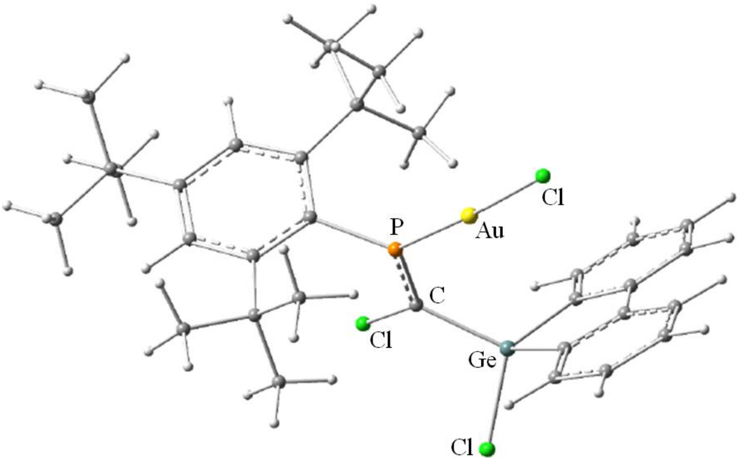


Figure 60. DFT optimized structure of complex AuCl·[Mes*P=C(Cl)–Ge(Cl)Fl] **65**.

DFT analyses performed on derivative **67**, the bidentate palladium complex, revealed the same structural features. The optimized molecular geometry of this species is presented in Figure 61.

Among the selected geometrical parameters (bond distance and angles) the most representative ones are: =C–Ge (1.947 Å), P=C (1.660 Å), P–Pd (2.269 Å), Pd–Cl (2.310 Å), P=C–Ge (126.8°), P–Pd–P (100.0°), P–Pd–Cl (85.3°), Cl–Pd–Cl (89.3°). All these computed values are in good agreement with those obtained experimentally.

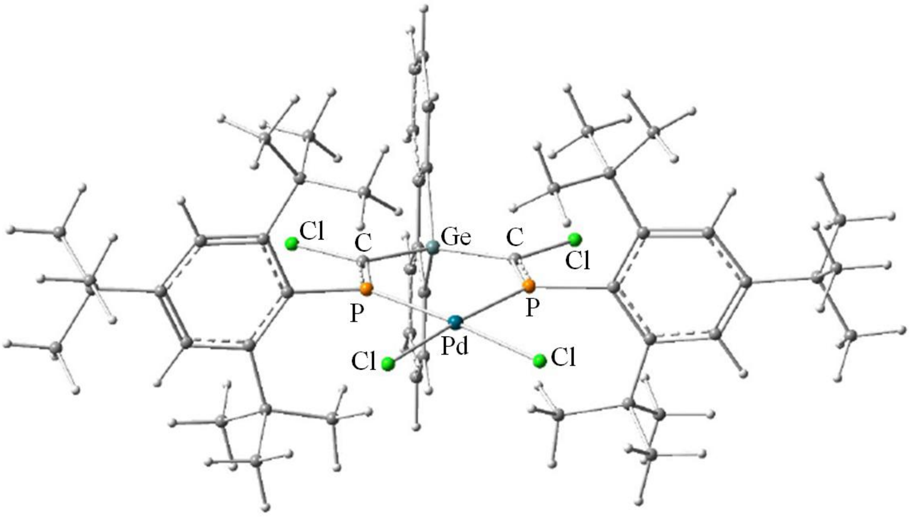


Figure 61. DFT optimized structure of complex $PdCl_2$·[Mes*P=C(Cl)]$_2$–GeFl **67**.

Additional supramolecular interactions were also investigated through DFT techniques to evaluate the impact of secondary electronic effects on the stability of phosphaalkenyl germanium derivatives.

III.5. Conclusions

III.6. Experimental part

Appendix III

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IV. GENERAL CONCLUSIONS

This study contains a complete work about the chemistry of germaphosphaalkenyl derivatives containing the P=C–Ge moiety in their structure.

A comprehensive bibliographic review is presented firstly, aiming to summarize the most relevant discoveries reported up to date. The first chapter contains information regarding the synthetic methods used to obtain the target compounds. Multiple physico-chemical characteristics are outlined. Additionally, the rich chemical reactivity is also highlighted. Such unsaturated systems are known to be highly reactive, thus novel approaches are necessary to find the suitable stabilizing conditions.

In order to bring supplementary contribution to the chemistry of such systems, new P=C–Ge type derivatives were successfully obtained in which the germanium atom is included into a fluorenyl group. Additional stabilization is expected to occur by use of this cyclic system, due to a possible extended conjugation.

The first chapter from the original contributions section provides information regarding the synthesis, complete physico-chemical properties and structural studies of the monosubstituted 9-chloro-9-phosphaalkenylchloro-9-germafluorene **58**, and the disubstituted 9,9-bis(phosphaalkenylchloro)-9-germafluorene **59**, both containing the germanium atom included into a fluorenyl ring.

In the next chapter, the reactivity of the above mentioned novel compounds was tested. Reaction with organolithium reagents (MeLi, *n*BuLi, *s*BuLi, *t*BuLi) led to either alkylated or dimeric species. Five new compounds were obtained and described, and four of them were fully chracterized both in solution and in solid state (by mass spectrometry, NMR spectroscopy and single crystal X-ray diffraction).

Next, the reactivity of 9-chloro-9-phosphaalkenylchloro-9-germafluorene **58** with Li, NaH and Ag_2O was also highlighted. Presumably, the same product was obtained in all three experiments. The newly obtained derivative was characterized only in solution by multinuclear NMR spectroscopy. Further investigations are currently in progress to elucidate the solid state molecular structure of this compound.

The last chapter presents information about the coordination ability of the two new germaphosphaalkenes, Mes*P=C(Cl)–Ge(Cl)Fl **58** and $[Mes^*P{=}C(Cl)]_2$–GeFl **59**. One palladium(II) and two gold(I) complexes were obtained and fully characterized. The solid state molecular structures revealed monodentate or bidentate coordination modes.

The coordination capacity towards tungsten and iron fragments was also investigated. Unfortunately, the reaction went with formation of several products which could not be isolated and identified.

Density functional theory (DFT) calculations coupled with natural bond orbital (NBO) techniques were also performed in order to gain useful information about all newly obtained compounds. The use of proper computational methods gave access to useful data which are in good agreement with those reported through experimental methods.

Conclusively, the novel P=C–Ge type species present a very rich reactivity and their chemical behaviour can be influenced by steric and electronic effects. The inclusion of germanium atom into a fluorenyl cycle led to additional stabilization. However, further modulation of the protecting substituents could still be discussed and additional investigations could be performed to better understand the fascinating chemistry of such systems.

Appendix

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List of abbreviations

List of publications, conference poster and oral presentations