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PhD thesis summary

N-heterocyclic carbene stabilized phosphaalkenyl Ge(II) and Sn(II) compounds: synthesis, reactivity and DFT calculations

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KEYWORDS:

metallylenes, N-heterocyclic carbenes, germylene, stannylene, complexation, DFT calculation

GENERAL INTRODUCTION

The chemistry of metallylenes (R_2Si:, R_2Ge:, R_2Sn: and R_2Pb:) has received considerable attention due to their carbene-like properties. Such compounds are very reactive and tend to polymerize. They can be stabilized kinetically by incorporating bulky ligands, and/or thermodynamically by using electron-donating substituents at the metal 14 centre. Recently, the intermolecular coordination has aroused a great interest particularly with the use of N-heterocyclic carbenes (NHC) as stabilizing co-ligand. Transient metallylenes could be isolated using this last strategy. However, among the large number of stable monomeric germanium(II) compounds reported to date, there are surprisingly few examples of stable alkenyl group 14 divalent species; the last ones have generally been obtained by hydrometallation reactions. No tin analogue is known up to date. In our group, we highlighted the great interest of the phosphaalkenyl moieties for access not only to novel derivatives but also for their ability to give various types of complexation reactions. As a part of ongoing studies on low coordinate group 14 species, we envisaged now to develop a new class of germylenes and stannylenes using both the phosphaalkenyl –P=C< unit as ligands and the stabilizing coordination properties of the N-heterocyclic carbenes.

The first part of this work is devoted to previous literature on metallylenes (silylenes, germylenes, stannylenes and plumbylenes) stabilized by N-heterocyclic carbenes. Their syntheses, physico-chemical and structural properties and their reactivity will be descried in this chapter.

The second chapter describes the syntheses of the first mono- and disubstituted phosphaalkenylgermylenes and -stannylenes. For that, the nucleophilic substitution of dichlorometallylenes will be considered. Detailed physico-chemical data (multinuclear NMR, mass spectrometry) and X-ray structural studies of all species are presented.

In the third chapter, we present various tests of reactivity such as oxidation reactions with chalcogen atoms (S, Se) and we will try to evaluate the role of the N-heterocyclic carbene in the stabilization of doubly bonded compounds. These phosphaalkenylmetallylenes are also particularly interesting due to their multiple possibility of coordination (lone pair on phosphorus, divalent centre and phosphorus–carbon double bond). Several coordination reactions to various transition metals will be performed.

The fourth chapter focuses on theoretical studies of bis(phosphaalkenyl)germanium(II) and -tin(II) derivatives. Using DFT models could be explained the effect of the substituents in β and γ positions, the high reactivity of the double bonded M=E species, the formation ability of M_2E_2 (M = Ge, Sn; E = S, Se) and the coordination ability of the model germylenes to pentacarbonyltungsten complex. The structure of free- and N-heterocyclic carbene-stabilized germylenes and stannylenes (already obtained experimentally) together with the bicoordinated tungsten(diphosphaalkenyl)germylene will be theoretically investigated, in order to validate the method and bases sets comparing the calculated data with the experimentally obtained geometrical parameters.

CHAPTER 1

Bibliographic review: N-heterocyclic carbene stabilized metallylenes

Since the first N-heterocyclic carbene, the 1,3-di-1-adamantyl-imidazol-2-ylidene (NHC^{Ad}), was synthesized by Arduengo and coworkers in 1991,[1] these species are well investigated due to their remarkable stability from the strong $N \rightarrow C_{carbene}$ π donation.[2] Due to this effect a largely filled p(π) orbital at the carbene carbon atom occurred which allows a higher stability to the N-heterocyclic carbene. The carbene derived benzimidazole[3] and acyclic representatives[4] were also investigated, but the Arduengo type imidazole-based carbenes are much more stable and more promising than the named representatives.[5]

Carbenes are more stable in triplet state with sp^2 hybridization of the carbenic carbon atom, while metallylenes (silylenes, germylenes and stannylenes) are isovalent with singlet carbenes and they are more stable in the singlet state (*Figure 1*).[6-10] The frontier molecular orbitals of divalent main atoms consist of a lone pair of electrons and an empty p-orbital. Therefore, they can in principle act both as Lewis acids and Lewis bases, depending on the substituents. As a result of their amphoteric properties, the metallylenes are highly reactive, short-lived and difficult to characterize unless stabilization by steric bulk or electronic groups.[8,11-13]

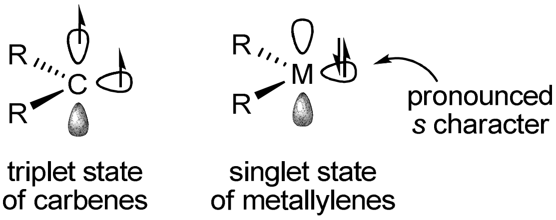


Figure 1: The metallylenes are more stable in the singlet state

N-heterocyclic carbenes (NHC) are widely used as Lewis bases in stabilization of different maingroup compounds.[14-19] Their coordination to the highly reactive divalent silicon(II), germanium(II), tin(II) or lead(II) derivatives also allows the isolation and characterization of transient metallylenes. When the metallylenes accept the electron pair coming from the Lewis-base N-heterocyclic carbene they act as π-acceptor remaining only the possibility to donate electrons to another acceptor. This σ-donor character is well represented in their reactions with various transition metal fragments.[20-22]

In this chapter we report the main results regarding the use of NHC as stabilizing co-ligand of metallylenes (syntheses, characterization and reactivities).

CHAPTER 2

N-heterocyclic carbene stabilized phosphaalkenyl Ge(II) and Sn(II) compounds: synthesis and physicochemical properties

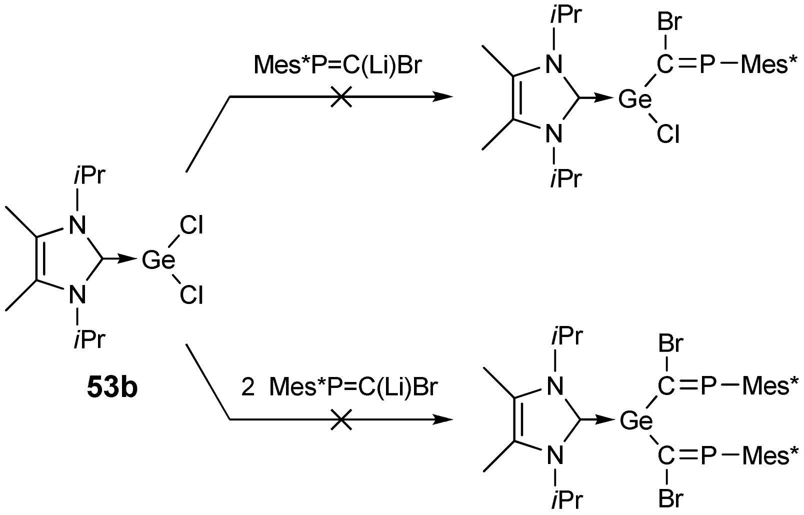
The chemistry of the heavier group 14 element carbene analogues has received wide interest because of their special properties and reactivity.[1-4] Among the stabilization strategies of germylenes or stannylenes, the intermolecular coordination has aroused a great interest in the last decades particularly with the use of N-heterocyclic carbenes (NHC) as stabilizing co-ligand as we have demonstrated in the *Chapter 1*. However among the large number of stable monomeric stable germanium(II) and tin(II) derivatives reported to date,[1,3,4] there are surprisingly few examples of stable alkenyl group 14 divalent species.[4-6]

In our group, we highlighted the great interest of phosphaalkenyl units (–C(Y)=PAr) not only for access to novel compounds but also for their ability to give various types of complexation.[7,8] This prompted us to extend these studies to the group 14 elements.

In this chapter, we describe the synthesis, the physicochemical properties and the structural studies of the chloro(phosphaalkenyl)stannylene NHC^{iPr}–Sn(Cl)[C($SiMe_3$)=PMes*], the first example of mixed substituted NHC-stannylene derivative, and the disubstituted bis(phosphaalkenyl)germylene NHC^{iPr}–Ge[C(Cl)=PMes*$]_2$, and -stannylene NHC^{iPr}–Sn[C(Cl)=PMes*$]_2$ both stabilized by complexation with an N-heterocyclic carbene unit.

Syntheses of phosphaalkenyl germylene and stannylene

In order to obtain the first monosubstituted N-heterocyclic carbene stabilized phosphaalkenyl-germylene of type NHC$^{i\mathrm{Pr}}$–Ge(Cl)[C(Br)=PMes*], NHC$^{i\mathrm{Pr}}$–$GeCl_2$ **53b** was reacted with one equivalent of lithiated dibromophosphaalkene **110** (*Scheme 1*). Dropwise addition of a solution of *n*-BuLi to a solution of Mes*P=CBr_2 in THF at -100 °C yielded the lithiated derivative Mes*P=C(Li)Br as orange solution. After adding NHC$^{i\mathrm{Pr}}$–$GeCl_2$ at low temperature, the color of the mixture changed to yellow and the ^{31}P NMR spectral signal at 278 ppm showed the presence of a new product. The solution was evaporated and filtered with toluene, but the yellow filtrate solution obtained was very unstable and decomposed to several unidentifiable products in very short time. All attempts to isolate and to characterize this compound failed.



Scheme 1: Possible synthetic routes of mono- NHC^{iPr}–Ge(Cl)[C(Br)=PMes]and di(phosphaalkenyl)germylene NHC^{iPr}–Ge$[C(Br)=PMes^*]_2$*

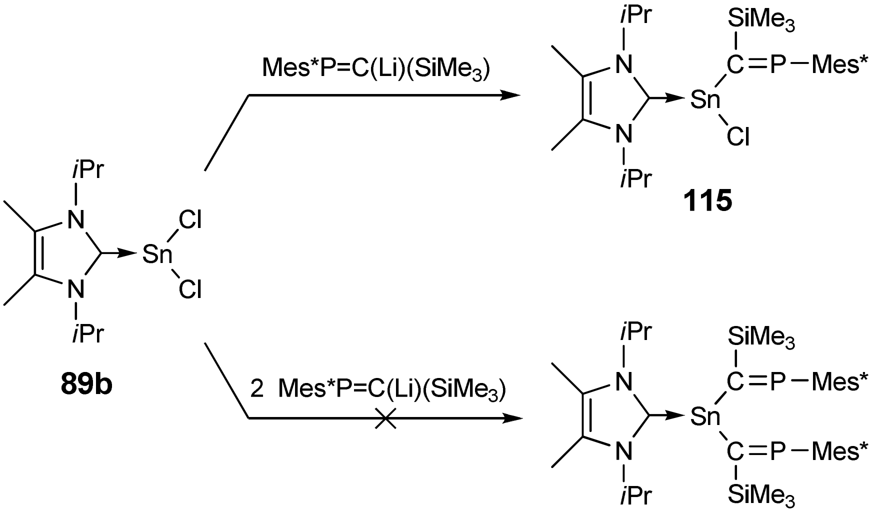
Another possible way was using a more bulky group on the carbon atom. For this reason $SiMe_3$ group was chosen as substituent and the used reagent was the lithiated derivative of Mes*P=C(Cl)$SiMe_3$ **111**.

The reaction between Mes*P=C(Li)$SiMe_3$ and NHC$^{i\mathrm{Pr}}$–$GeCl_2$ only led to the formation of the two isomers of Mes*P=C(H)$SiMe_3$ in low yield, that are the hydrolyzed products of the lithiated compound identified by ^{31}P NMR studies.

After none of these methods was successful in the synthesis of the mono- and di(phosphaalkenyl)germylene derivatives, our intentions have been focused to obtain and to characterize the stannylene analogs.

Addition of NHC^{iPr}–SnCl$_2$ in 1:1 equivalent ratio to a solution of Mes*P=C(Li)SiMe$_3$, obtained by adding *t*-BuLi to Mes*P=C(Cl)SiMe$_3$ **111** in THF at low temperature, afforded the apparition of a new product confirmed by the presence of a low fielded signal at 344.9 ppm in ^{31}P NMR spectra (*Scheme 2*). In the reaction mixture a large quantity of chloro-phosphaalkene has remained together with the *E/Z* isomers of the hydrolyzed form of Mes*P=C(H)SiMe$_3$.

Compound **115** was isolated after several treatments of the mixture with toluene and pentane as yellow powder in moderated yield. It was extremely air- and moister sensitive.



Scheme 2: Synthesis of mono-(phosphaalkenyl)stannylene
NHC^{iPr}–Sn(Cl)[C(SiMe$_3$)=PMes]* ***115***

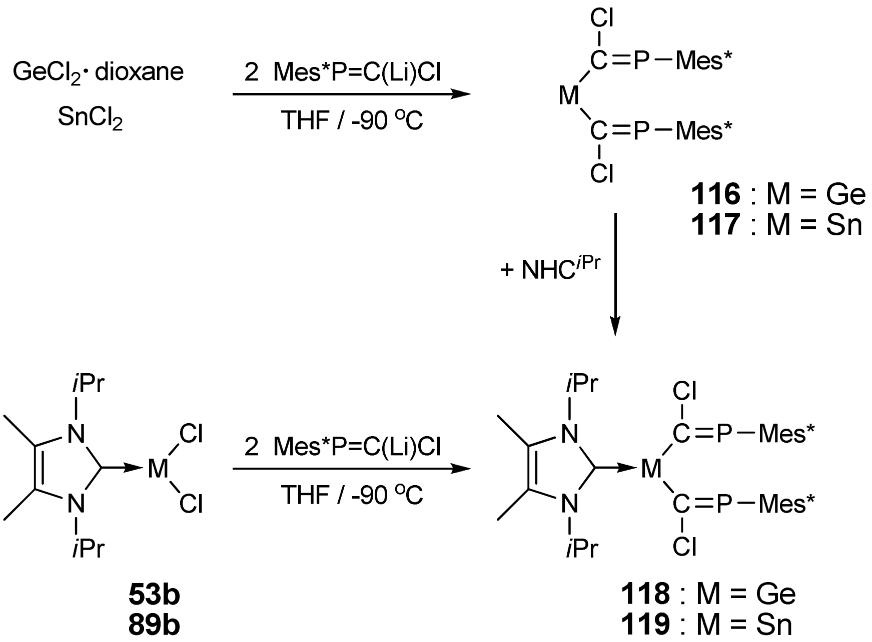
The stannylene **115** was unambiguously characterized in solution by NMR studies and its structure was confirmed by X-ray diffraction analysis of the isolated crystalline product.

Encouraged by the successful synthesis of mono-(phosphaalkenyl)stannylene, the synthesis of disubstituted stannylene NHC^{iPr}–Sn[C(SiMe$_3$)=PMes*]$_2$ was also tried using two equivalents of the lithiated reagent Mes*P=C(Li)SiMe$_3$ (*Scheme 2*). Unfortunately, in this case only the decomposition products were observed.

To obtain and to characterize the first di(phosphaalkenyl)germylene further possible synthetic routes were investigated using dichlorophosphaalkene Mes*P=CCl$_2$ **109** as starting compound.

Firstly, the reaction of Cl$_2$Ge·dioxane with two equivalents of Mes*P=C(Li)Cl was performed in THF at low temperature. The ^{31}P NMR spectrum of the mixture revealed the presence of a large signal at 297.0 ppm (in THF) which vanished after three hours at room temperature. This signal was attributed to the transient di(phosphaalkenyl)germylene Ge[C(Cl)=PMes*]$_2$ **116** which could not be isolated (*Scheme 3*).

In the second step, NHC stabilized dichlorogermylene was used as starting derivative. The synthesis was realized in THF by addition of NHC^{iPr}–GeCl$_2$ **53b** to a solution of Mes*P=C(Li)Cl at -90 °C. The germylene **118** was isolated as brown powder in good yield (84%).



Scheme 3: Synthesis of disubstituted M[C(Cl)=PMes]$_2$ and NHC^{iPr}–M[C(Cl)=PMes*]$_2$ (M = Ge, Sn)*

The di(phosphaalkenyl)germylene NHC^{iPr}–Ge[C(Cl)=PMes*]$_2$ **118** was fully characterized in solution and also in solid state.

To a solution of **116** in THF in an NMR tube, **1b** was added using glove box techniques. After some minutes at room temperature, the ^{31}P NMR spectrum indicates the disappearance of the broad signal at 297.0 ppm and the presence of the sole signal of the di(phosphaalkenyl)germylene **118** at 263.8 ppm (in THF) (*Scheme 3*). This confirmed the transient formation of the free di(phosphaalkenyl)germylene Ge[C(Cl)=PMes*]$_2$ **116**.

The same observation was noticed for the stannylene analog (*Scheme 3*).

In all cases, it was not possible to prepare the mono phosphaalkenyl-substituted germanium(II)- or tin(II) compound.

Physicochemical properties

The chloro-stannylene **115** is extremely air- and moisture sensitive; a slow decomposition was observed also in C_6D_6. For this reason its characterization in solution was carried out in deuterated toluene. Both of the stable metallylenes **118** and **119** are air- and moisture-sensitive, but they are stable up to 60 °C in THF and in toluene. In CH_2Cl_2 and $CHCl_3$ a rapid decomposition was observed.

Their structures were established by NMR spectroscopy in solution and by X-ray diffraction studies on the single crystals.

The new metallylenes NHC^{iPr}–Sn(Cl)[C($SiMe_3$)=PMes*]$_2$ **115** and NHC^{iPr}–M[C(Cl)=PMes*]$_2$ (M = Ge **118**, Sn **119**) were fully characterized by ^{1}H, ^{13}C, ^{29}Si, ^{31}P, ^{119}Sn NMR spectroscopies in solution.

In ^{31}P NMR spectra **118** and **119** show signals at 265.7 ppm and 277.4 ppm ($^2J_{P-^{117/119}Sn}$ = 349.1 and 364.1 Hz) respectively (in C_6D_6) (*Table 1*). This sole signal indicates the formation of only one isomer, probably the *E*/*E* form for steric reasons. The intermediate lithium compound Mes*P=C(Li)Cl was exclusively formed as the *Z* isomer. These chemical shifts in ^{31}P NMR are in the range of well known metallaphosphaalkenes.[10-13]

*Table 1: ^{31}P NMR data (in C_6D_6) of **109**, **111**, **115-119***

Compounds	**Value**
109	232.9
111	287.2
115	344.9 $^2J_{P-Sn}$ = 298.9 Hz
116*	297.0 (broad)
118	265.7
117*	264.0 (broad)
119	277.4 $^2J_{P-^{117/119}Sn}$ = 349.1, 364.1 Hz

* *in THF*

The chemical shift in ^{31}P NMR of the germylene **118** and the stannylene **119** (*Figure 2*) are low shifted in comparison with the value of 232.9 ppm reported for the starting dichloro-phosphaalkene Mes*P=CCl_2 **109**.[14]

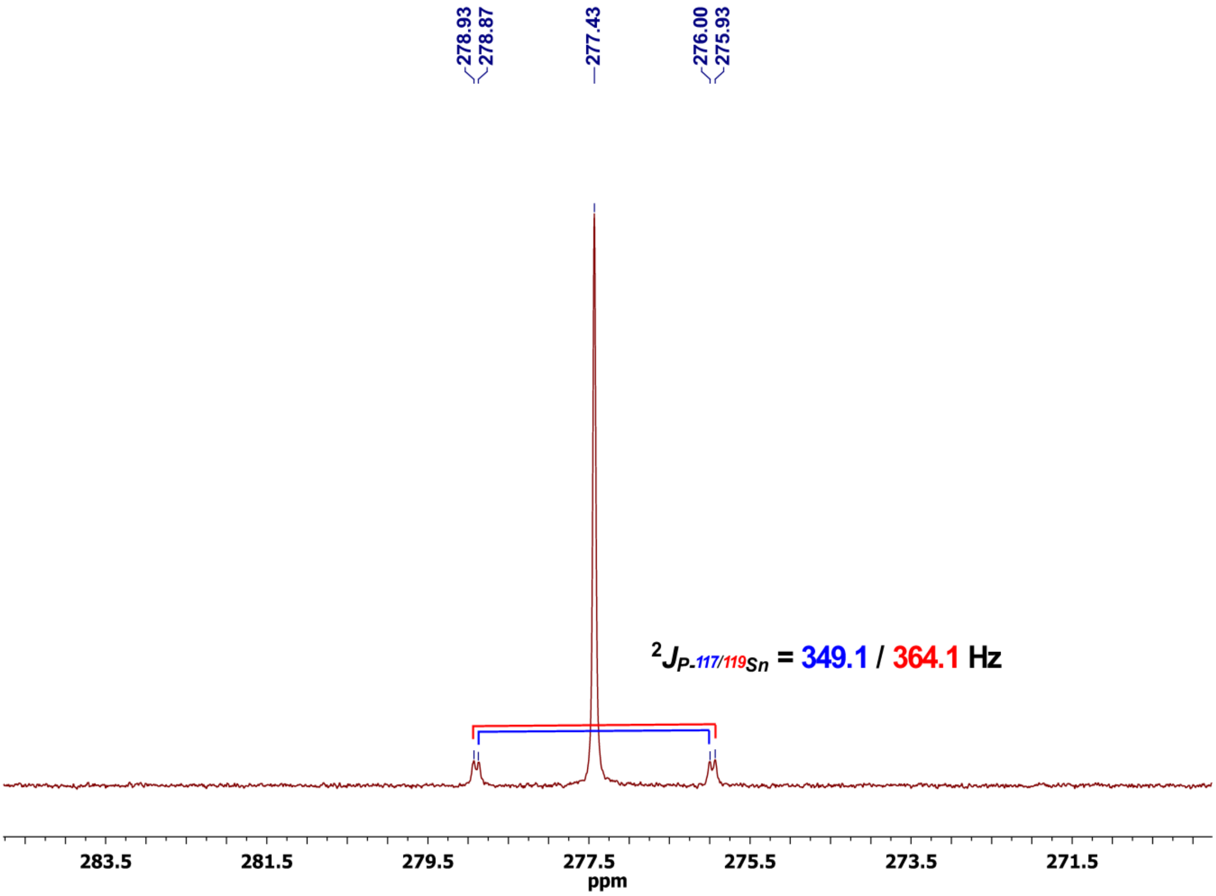


Figure 2: ^{31}P NMR spectrum (in C_6D_6) of compound ***119***

The assignments of ^{1}H signals together with those in ^{13}C NMR spectra were obtained from 2D heteronuclear experiments (HSQC and HMBC). $^{1}H\{^{31}P\}$ NMR studies were also necessary to determine the $J_{H\text{-}P}$ coupling constants in the case of C_6H_2 fragments.

According to the ^{13}C NMR studies in the case of **115**, **118** and **119**, the carbenic carbon atoms of the carbene **1b** are upfield shifted that is in agreement with the coordination of the carbenes.[17] The stannylene NHC^{iPr}–Sn[(Cl)C=PMes*$]_2$ **119** shows a signal in the ^{119}Sn NMR spectrum at -130.8 ppm having a $^{2}J_{Sn\text{-}P}$ = 360.0 Hz coupling constant. The chlorostannylene **115** appears as a doublet at 52.2 ppm ($^{2}J_{P\text{-}Sn}$ = 304.9 Hz) (*Figure 3*).

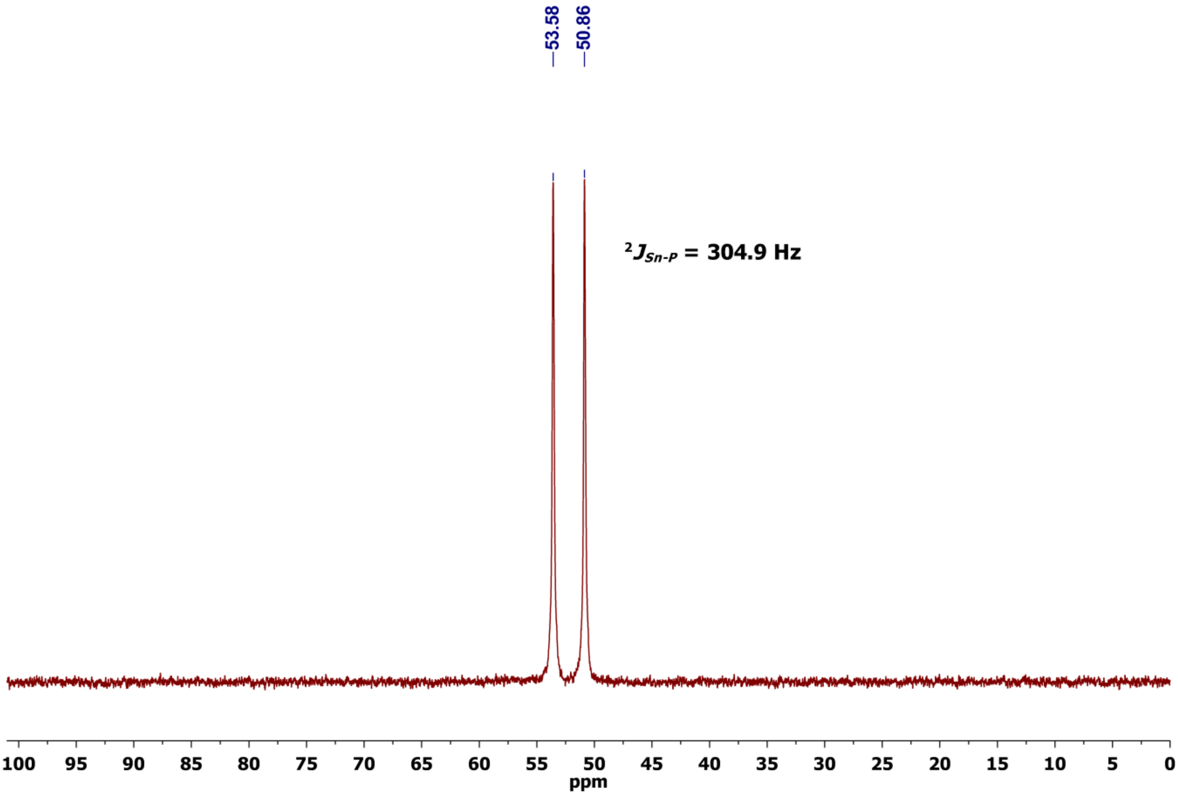


*Figure 3: ^{119}Sn NMR spectrum (in toluene-d_8) of compound **115***

The chemical shift of **119** is higher field shifted by comparison with the starting compound of NHC$^{i\text{Pr}}$–SnCl$_2$ **89b** (-59.4 ppm). This behavior was observed for the NHC$^{i\text{Pr}}$–SnR$_2$ structures reported recently having different substituents; when R = Si(SiMe$_3$)$_3$ the signal in ^{119}Sn NMR was observed at -196.8 ppm and when R = Sn(SiMe$_3$)$_3$ the main Sn atom showed a signal at -138.3 ppm.[18]

The solid structures of the new metallylenes **115**, **118** and **119** were unambiguously determined by X-ray diffraction analyses (Figure 4 and Figure 5). In all cases the main center exhibits a distorted pyramidal geometry with the sums of the angles of 302.19°, 294.91° and 295.59° respectively.

The C$_{\text{carbene}}$–Sn bond lengths in phosphaalkenyl(chloro)stannylene **115** (2.289(7) Å, *Figure 4*) and in diphosphaalkenylstannylene **119** (2.316(2) Å, *Figure 5*) suggest a similar strength as for the donor/acceptor interaction in the starting NHC$^{i\text{Pr}}$–SnCl$_2$ **89b** (2.290(5) Å),[15] but weaker than the one in the recently reported coordinative derivative NHC$^{\text{Dip}}$–SnH$_2$–W(CO)$_5$ **98** (2.230(6) Å).[19]

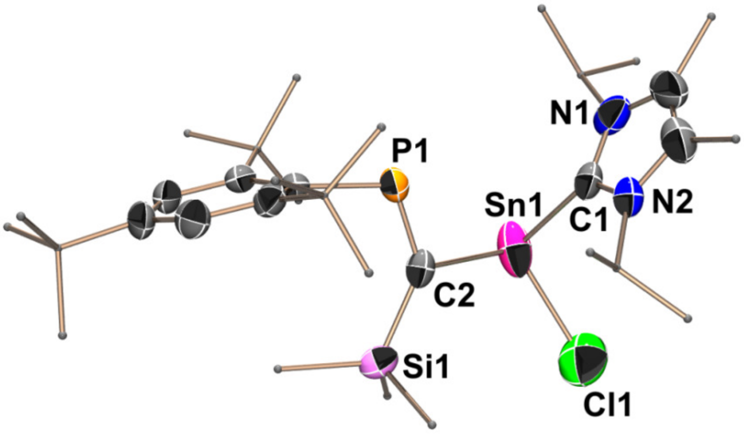


*Figure 4: Molecular structure of compound **115** in the solid state (50 % probability level for the thermal ellipsoids). The asymmetric unit contains two independent molecules; only one is shown here. For clarity, hydrogen atoms are omitted and methyl/isopropyl/t-Bu groups are simplified.*

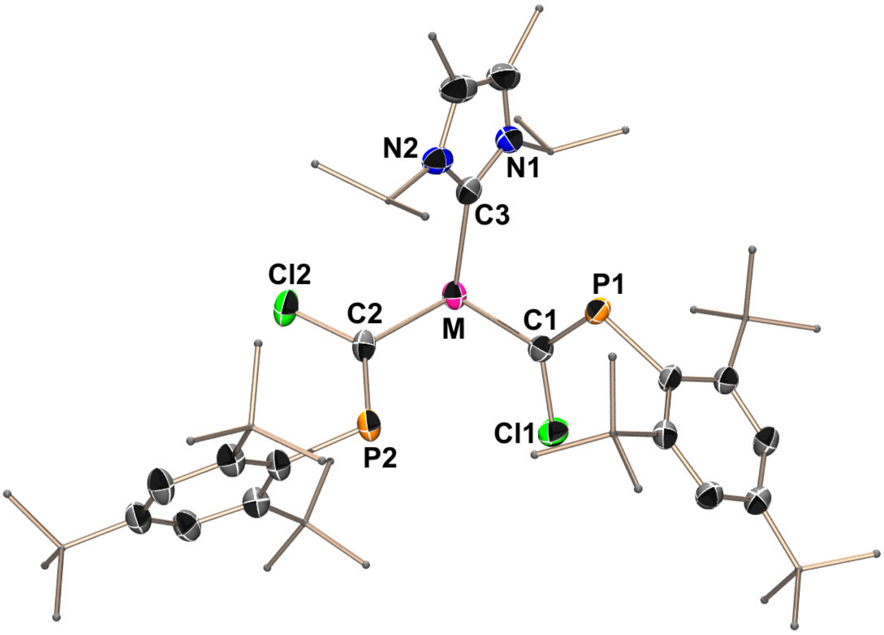


*Figure 5: Molecular structure of compound **118** (M = Ge) and **119** (M = Sn) in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted and methyl/isopropyl/t-Bu groups are simplified.*

The Ge–CP bond lengths of **118** (2.011 Å and 2.014 Å) and bond angle C2–Ge–C3 (100.39°) are among the shortest described in literature (bonds length range: 2.012-2.067 Å and angles range: 102.79-114.4°).[22-24]

In all cases the P=C bonds lengths (1.65-1.67 Å) are not showing large variety, taking values in the expected range for this fragment.[25]

CHAPTER 3

N-heterocyclic carbene stabilized phosphaalkenyl Ge(II) and Sn(II) compounds: reactivity

In the previous chapter (*Chapter 2*) we have described the syntheses of the new compounds NHC^{iPr}–Sn(Cl)[C($SiMe_3$)=PMes*], NHC^{iPr}–Ge[C(Cl)=PMes*$]_2$, NHC^{iPr}–Sn[C(Cl)=PMes*$]_2$, the first representatives of a new class of metallylenes using the phosphaalkenyl –P=C< units as ligands and stabilized by the coordination of N-heterocyclic carbene NHC^{iPr}. The physicochemical and structural studies showed the presence of tricoordinated group 14 elements with the lone pair occupying an orbital with high s character. It would be interesting to verify whether these germanium and tin compounds retain their specific character of divalent species. Therefore, some characteristic reactions such as oxidation by elemental chalcogens which constitutes an usual and clean route to double bonded species M=E (M = Si, Ge, Sn; E = S, Se, Te) will be performed.[1,2] Moreover, although numerous germanium and tin compounds with double bond to chalcogens have been isolated using kinetic and/or thermodynamic stabilization,[3-8] the examples of M=E stabilized by NHC are rare. To the best of our knowledge, only few derivatives of the type NHC–SiR_2=E (E = O, S, Se, Te) and NHC–GeR_2=O, stable at room temperature, were described.[9-11]

The –P=C–M^{II} moiety is also particularly interesting since due to the multiple possibilities of reaction or coordination (lone pair on phosphorus, divalent main atom center and P=C double bonds). It can potentially present an unexpected and rich reactivity. While numerous NHC–silylene transition metal complexes (W, V, Co, Fe, Rh, Ni, Cr, Mo) were reported,[12-17] complexes obtained by the coordination of the NHC-germylenes and -stannylenes to transition metals are rare; only few complexes of this type exist to date: NHC^{Dip}–$MH_2W(CO)_5$ and NHC^{Dip}–$MCl_2W(CO)_5$ (M = Ge, Sn).[18,19] It would be interesting to test both the coordinating ability of the phosphaalkenyl ligand and the effect of the NHC co-ligand in these reactions.

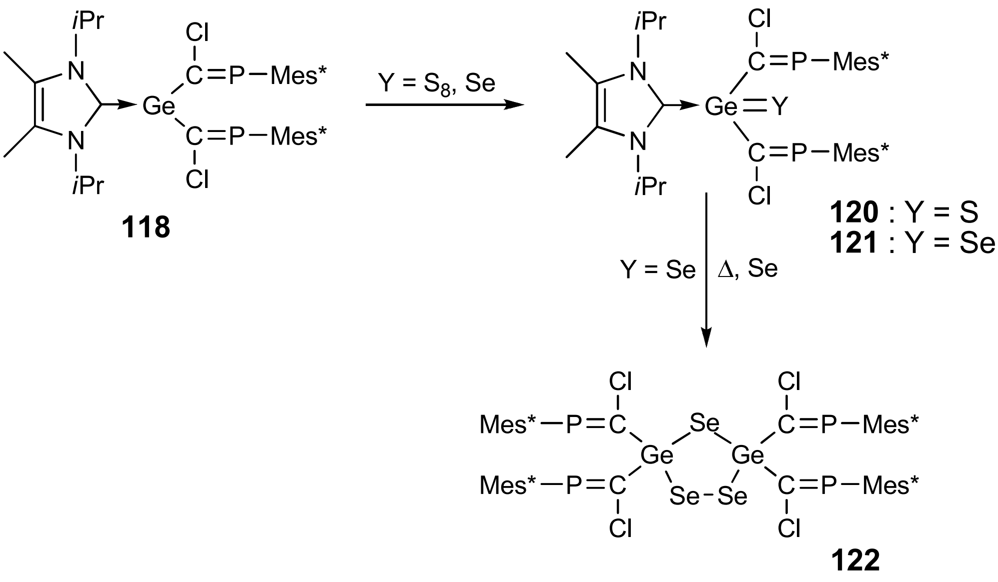
In this chapter we present the reactivity of these new metallylenes with elemental chalcogens and their coordination reactions to various transitionmetals (tungsten, molybdenum, platinum and gold).

Oxidative reactions

Oxidation reactions were performed on germylene **118** and stannylene **119** with elemental sulfur and selenium.

In the case of the germylene NHC^{iPr}–Ge[C(Cl)=PMes*]$_2$ **118**, rapid reactions took place with both sulfur and selenium (*Scheme 4*). The ^{31}P NMR spectra show the presence of a sole signal at 289.9 ppm for **120** and 291.3 ppm for **121**, slightly downfield shifted in comparison with that of the parent compound **118** (265.7 ppm). These data indicate the presence of a P=C moiety and confirm that no oxidative addition reaction occurs at the phosphorus atom.

The transient germathione **120** was only characterized by ^{1}H and ^{31}P NMR studies. Its slowly decomposes leading to several unidentifiable products and none of them could be separated from the mixture.



*Scheme 4: Reaction of germylene **118** with elemental sulfur and selenium*

By contrast, the germaselenone **121**, obtained in good yield (96%) by treating the germylene **118** with elemental selenium at room temperature, was stable enough to be fully characterized in solution by NMR spectroscopy (*Table* 2). The ^{77}Se NMR spectrum displays a singlet at -173.7 ppm (*Table 4*) that is in the range of the values observed for germaselenones stabilized by intramolecular complexation (-28.7 to -348 ppm).[8,22]

A slow crystallization at low temperature in toluene allowed the isolation of orange crystals suitable for an X-ray diffraction study and the molecular structure of compound **121** is shown in *Figure 6*. The germanium atom is four-coordinated in a tetrahedral environment. The Ge–Se distance of 2.2426(7) Å is in good agreement with the values reported for Ge=Se bonds (2.199(1) and 2.223(9) Å).[8,22]

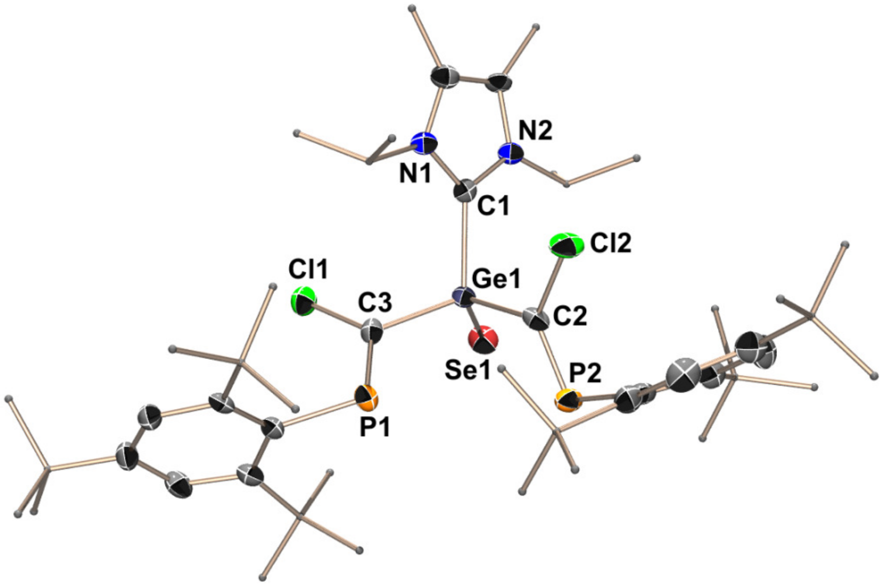


*Figure 6: Molecular structure of compound **121** in the solid state (50 % probability level for the thermal ellipsoids). The asymmetric unit contains two independent molecules; only one is shown. For clarity, hydrogen atoms and crystallization solvent (toluene) are omitted and methyl/isopropyl/t-Bu groups are simplified.*

Heating the reaction mixture of **121** at 80 °C for 2.5 hours with an excess of selenium, an unusual thermal cyclization reaction takes place, to give a Ge_2Se_3 inorganic ring derivative **122**. This triselenadigermolane is probably formed by an initial head-to-tail dimerization followed by selenium insertion.

Compound **122** was isolated as an air stable powder in good yield (59%), and was fully characterized. ^{1}H and ^{13}C NMR indicate the absence of the NHC^{iPr} groups; the ^{31}P NMR shows nearly the same chemical shift (δ = 295.8 ppm) as in **121** (*Table* 2). In the ^{77}Se spectrum two signals were observed at -160.4 ppm and -500.0 ppm (*Figure 7*).

Compound **122** was characterized also by X-ray diffraction analyses (*Figure 8*). It contains a non-planar Ge_2Se_3 inorganic ring. So far, only two similar heterocycles (tetradentate $[Ge_2Se_7]^{-4}$ anions) have been reported.[23,24]

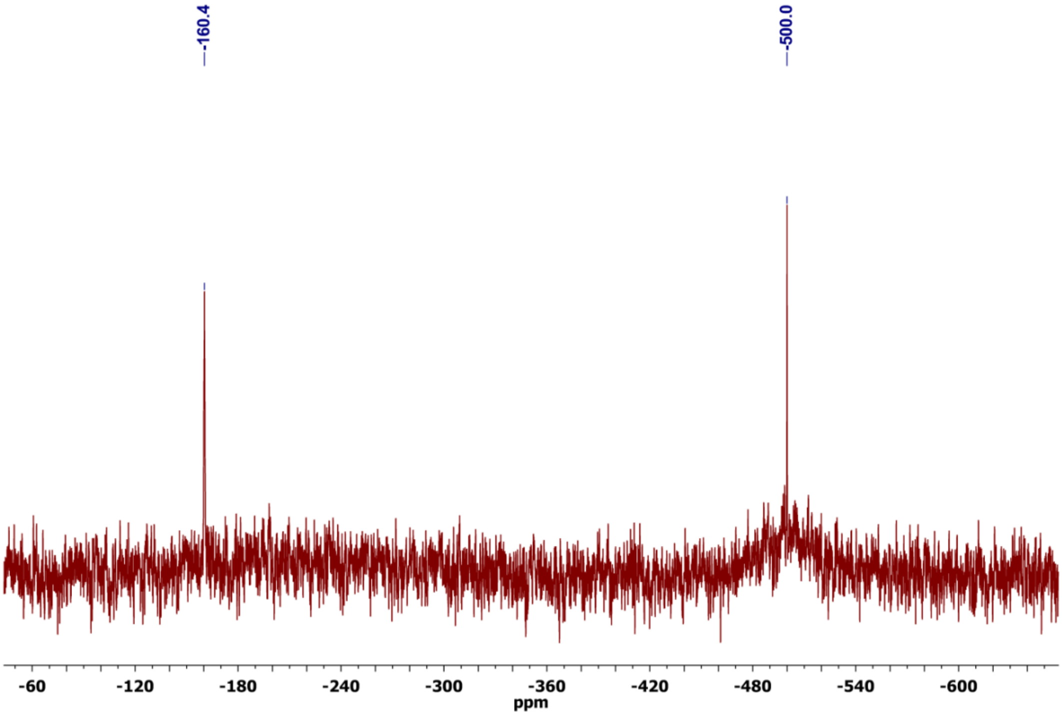


Figure 7: ^{77}Se NMR spectrum (in C_6D_6) of triselenadigermolane **122**

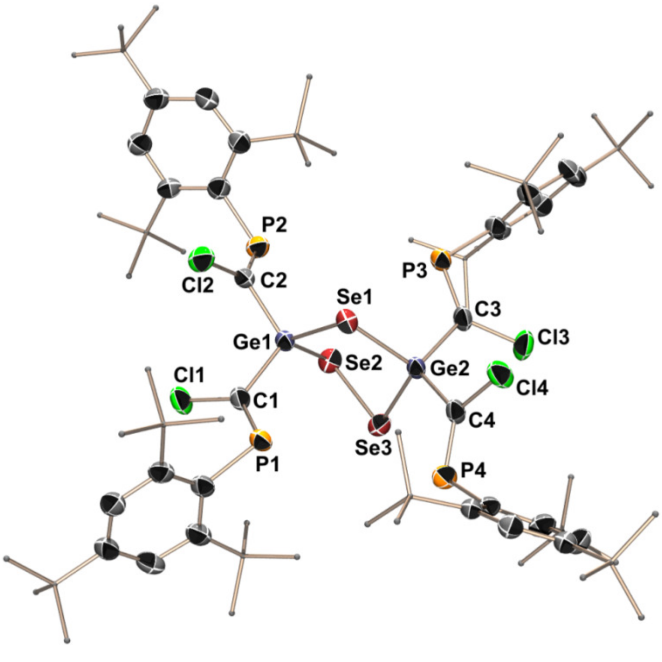


Figure 8: Molecular structure of compound ***122*** *in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and crystallization solvent (pentane) are omitted and t-Bu groups are simplified.*

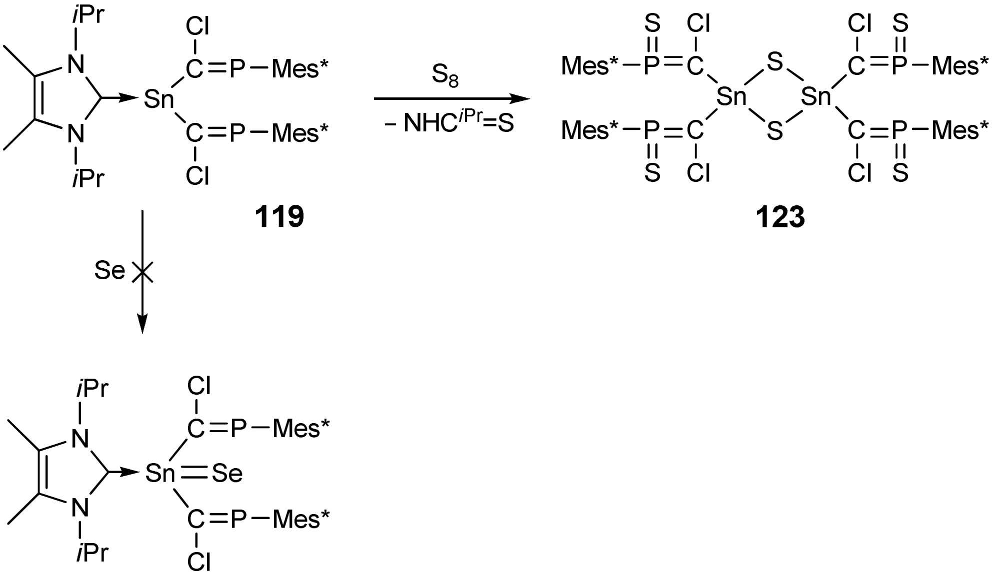
As observed for cyclic tetraselenagermolanes,[25] the five-membered ring in compound **122** displays a distorted half-chair conformation in which the two germanium and the two selenium atoms (Se1 and Se2) almost lie in the same plane with the third selenium (Se3) at 1.365 Å out of the mean plane.

By heating the reaction mixture of **122** with a large excess of selenium, the formation of compound with a P=Se unit has not been observed.

Table 2: ^{31}P NMR data (in C_6D_6) of compounds ***118-123***

Compounds	Value
118	265.7
120	289.9
121	291.3
122	295.8
119	277.4 $^2J_{P\text{-}^{117/119}Sn}$ = 349.1, 364.1 Hz
123	189.2 $^2J_{P\text{-}^{117/119}Sn}$ = 258.8, 270.7 Hz

A different behavior was observed when starting from the stannylene analogue. Addition of an excess of sulfur to the compound **119** led to a new product after some minutes at room temperature (*Scheme 5*). The ^{31}P NMR spectrum (*Table 2*) displayed a sole signal at 189.2 ppm ($^2J_{P\text{-}^{117/119}Sn}$ = 258.8/270.7 Hz) showing that the four phosphorus atoms are magnetically equivalent. This low field chemical shift is characteristic of a $\lambda^5\sigma^3$ phosphorus atom; similar chemical shifts have been reported for derivatives with a Mes*P(=S)=CGe moiety.[26]



Scheme 5: Oxidation reactions of stannylene ***119***

In addition, a triplet of triplet at -95.3 ppm with two coupling constants ($^2J_{Sn\text{-}P}$ = 270.7 Hz and $^4J_{Sn\text{-}P}$ = 7.5 Hz) was observed in the ^{119}Sn NMR spectrum (*Figure 9*) in agreement with the formation of such metalloheterocycles (*Table 3*).

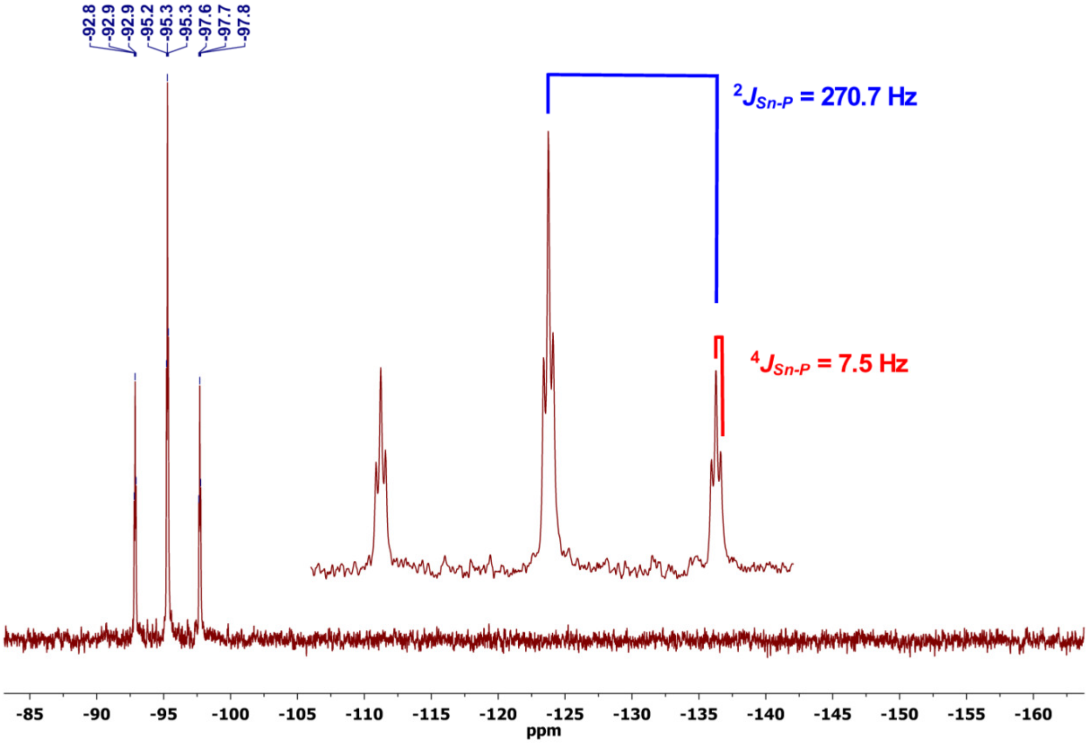


Figure 9: ^{119}Sn NMR spectrum (in C_6D_6) of dithiadistannetanne ***123***

The chemical shift of **123** in ^{119}Sn spectrum is considerably upfield shifted by comparing with the stannylene **119** (δ = -130.8 ppm) (*Table 3*). This effect is the effect of the oxidation of the central tin atom.

*Table 3: ^{119}Sn NMR data (in C_6D_6) of compounds **119** and **123***

Compounds	Value
119	-130.8, t; $^2J_{Sn\text{-}P}$ = 360.0 Hz
123	-95.3, tt; $^2J_{Sn\text{-}P}$ = 270.7 Hz, $^4J_{Sn\text{-}P}$ = 7.5 Hz

The X-ray studies confirmed the exclusive formation of the dimer (*Figure 10*). Compound **123** has a dinuclear, four-membered ring structure with bridging sulfur atoms in which the tin atom exhibits a distorted tetrahedral geometry. The four-membered ring is planar by symmetry. This heterocycle was probably formed by dimerization of the transient stannathione S=Sn[C(Cl)=PMes*]$_2$ and sulfur oxidative addition to the phosphorus atoms.

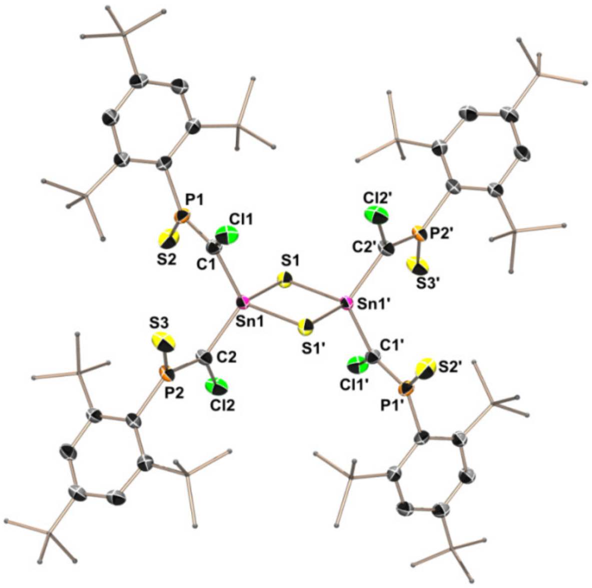
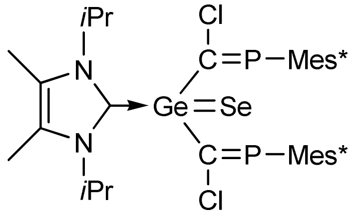
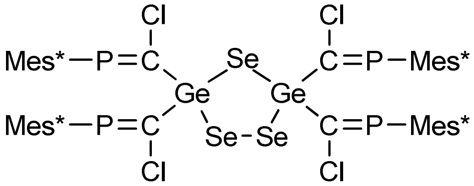


*Figure 10: Molecular structure of compound **123** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and crystallization solvent (toluene) are omitted and t-Bu groups are simplified.*

The dithiadistannetanne **123** is thermally stable; when heating the reaction mixture with an excess of sulfur, the formation of five-membered rings has never been observed although is known from the literature the formation of cyclic products with SnS_4 or $SnSe_4$ inorganic rings in the case of various diarylstannylene using S_8 or Se in excess.[31]

Table 4: ^{77}*Se NMR data (in* C_6D_6*) of compounds* ***121*** *and* ***122***

Compounds		**Value**
121		-173.7
122		-160.4 and -500.0

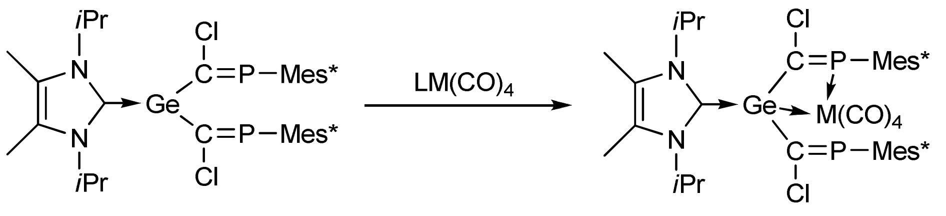
By contrast, no reaction occurs at room temperature between **119** and selenium; heating the reaction mixture at 40 °C involved a slow decomposition of the stannylene (*Scheme 5*).

Complexation reactions

One of the great interest of germylene **118** is to have multiple coordination sites, the divalent metal center, the C=P double bonds and the phosphorus atoms, potentially leading to mono-, bi- or tridentate derivatives.

In order to investigate its coordination ability to transition-metals, reactions with $(cod)W(CO)_4$ (cod = 1,5-cyclooctadiene) and $(nbd)Mo(CO)_4$ (nbd = 2,5-norbornadiene) were examined (*Scheme 6*). Displacement of the ligands (cod or nbd) occurred easily in THF at 60 °C.

The complexes **124** and **125** were isolated in good yields (73% and 67%, respectively) as brown or yellow powders. They are soluble in common organic solvents, especially in chlorinated solvents where they are perfectly stable in contrast with the non-coordinated germylene **118**.



118

124 : M = W, L = 1,5-cyclooctadiene
125 : M = Mo, L = 2,5-norbornadiene

*Scheme 6: Reacting germylene **118** with (cod)W(CO)$_4$ and (nbd)Mo(CO)$_4$*

The ^{31}P NMR spectrum of tungsten(diphosphaalkenyl)germylene **124** (*Figure 11*) showed two resonances, one at 267.2 ppm with additional satellites due to the coupling with tungsten ($^{1}J_{P\text{-}W}$ = 214.7 Hz) and the second one at 281.9 ppm suggesting that the two phosphaalkenyl fragments are not equivalent with only one phosphorus atom directly bonded to tungsten.

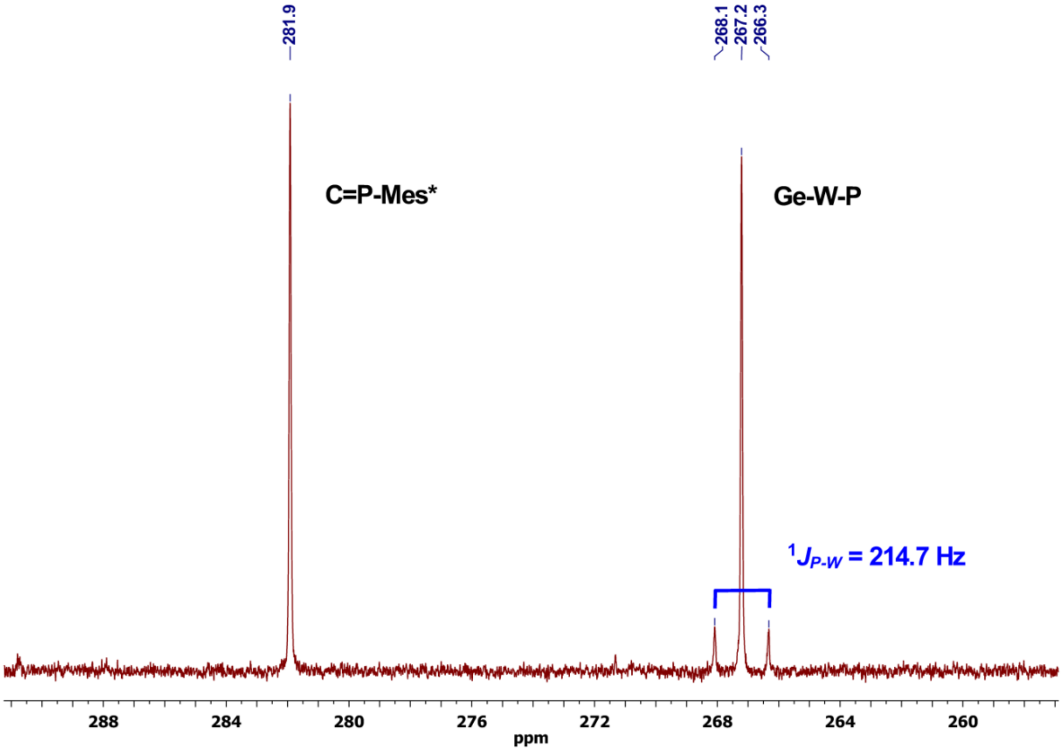


*Figure 11: ^{31}P NMR spectrum (in C$_6$D$_6$) of tungsten(diphosphaalkenyl)germylene **124***

The NMR spectra of the molybdenum(diphosphaalkenyl)germylene **125** differ only in respect with chemical shifts (^{31}P NMR, δ (C$_6$D$_6$): = 280.2 (PMo), 296.2 (P)) (*Table 5*).

The ^1H and ^{13}C NMR spectra of **124** and **125** show the same complexity with the non-equivalence not only of the isopropyl groups, but also of the carbons of the Mes* moiety. In addition in the ^{13}C NMR spectrum, four doublets (coupling with the phosphorus atom) were observed for CO groups.

For both of the compounds, the IR spectra exhibit four CO stretching vibrations of similar intensity (*Figure 12*) characteristic of a $LW(CO)_4$ moiety.[26,35]

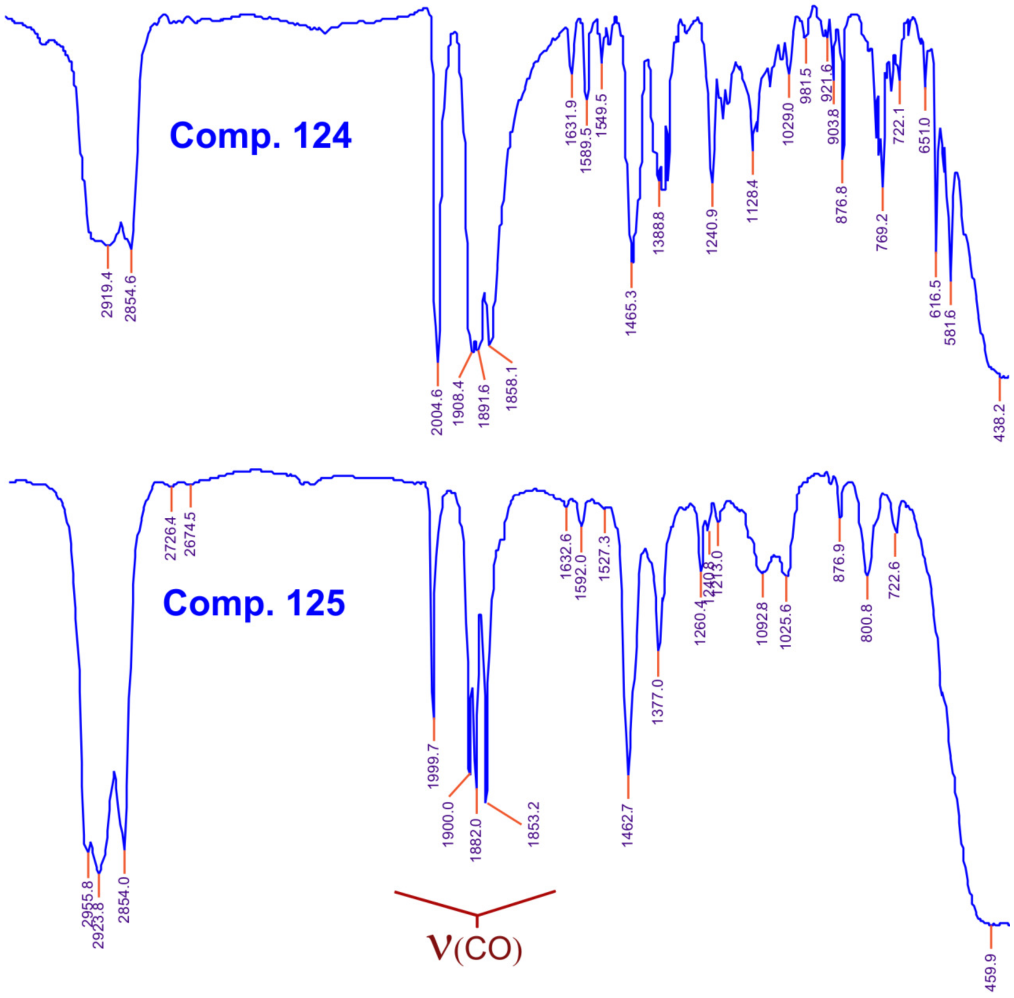


*Figure 12: IR spectra of tungsten- **124** and molybdenum(diphosphaalkenyl)germylene **125***

Suitable crystals for X-ray crystallography study of **124** were obtained from CH_2Cl_2 at -24 °C. The data confirms the coordination of only one phosphorus atom, the second C(Cl)=PMes* ligand remaining "pendent" (*Figure 13*). The tungsten centre is octahedrally coordinated.

The germanium atom adopts a distorted tetrahedral geometry. The Ge–W bond length (2.6508(4) Å) is one of the longest to be reported in germylene complexes,[37-42] and is close to the value of a germanium–tungsten single bond 2.681(3) Å.[43,44]

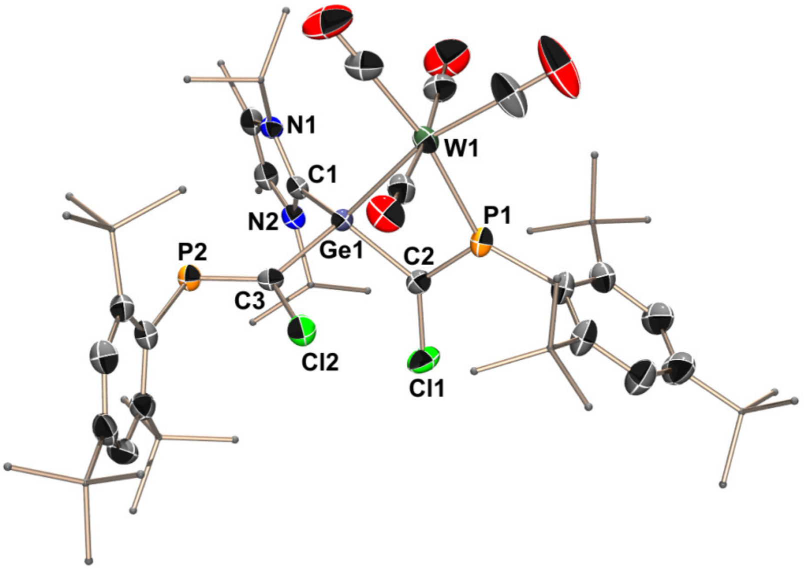
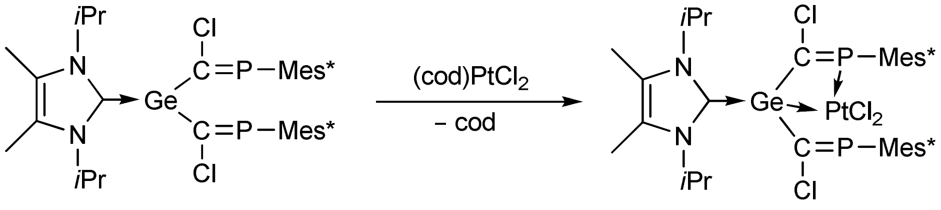


*Figure 13: Molecular structure of compound **124** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and crystallization solvent (dichloromethane) are omitted and methyl/isopropyl/t-Bu groups are simplified.*

Compound **118** also reacts rapidly with (cod)PtCl$_2$ obtained from hydrated chloroplatinic acid[45] to give the platinum(diphosphaalkenyl)germylene **126** derivative, which has low solubility in pentane, toluene and benzene, but is soluble in chloroform, dichloromethane and THF (*Scheme 7*). Surprisingly, this complex is perfectly air- and moisture-stable.



118 **126**

*Scheme 7: Synthesis of platinum(diphosphaalkenyl)germylene **126***

Up to date, there is only one example of platinum germylene complex: $(Et_3P)_2PtGe[N(SiMe_3)_3]_2$[46] and compound **126** is the first example of N-heterocyclic carbene stabilized germylene-platinum derivative. The ^{31}P NMR spectrum of **126** shows two signals with the satellites of platinum (δ ($CDCl_3$) = 216.0 ppm, $^{1}J_{P\text{-}Pt}$ = 4587.4 Hz, P-Pt and 294.4 ppm, $^{3}J_{P\text{-}Pt}$ = 60.7 Hz) (*Figure 14*).

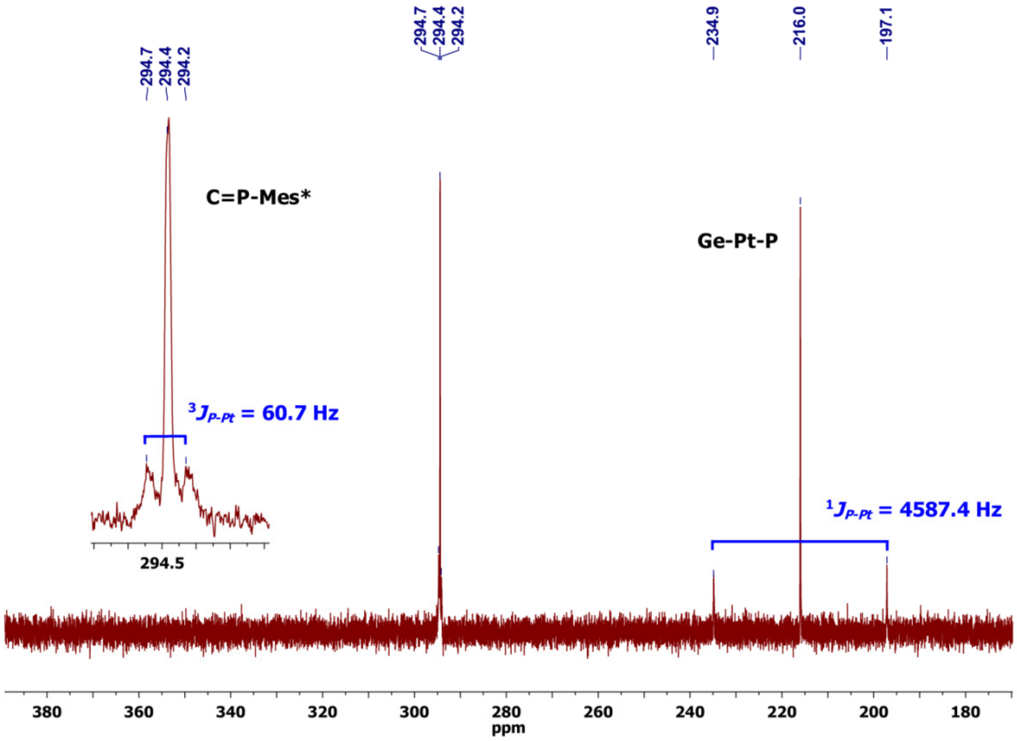


Figure 14: ^{31}P NMR spectrum (in $CDCl_3$) of platinum(diphosphaalkenyl)germylene ***126***

Suitable crystals for an X-ray diffraction study were obtained from diethylether at 4 °C (*Figure 15*). The Pt center exhibits a slightly distorted square planar geometry with Cl3-Pt1-Ge1 bond angle of 168.79(3)° and Cl4-Pt1-P1 of 170.41(4)°.

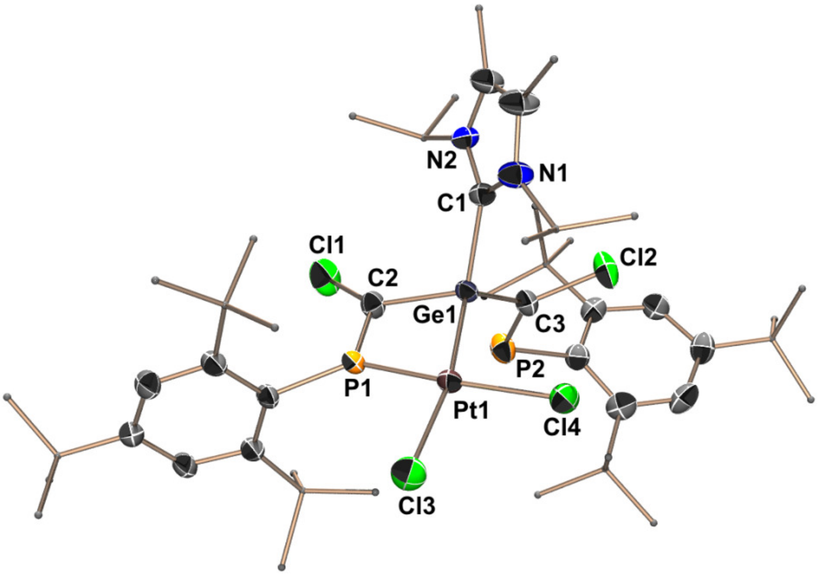
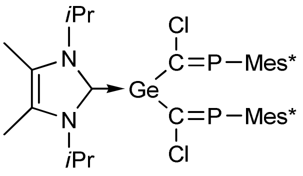
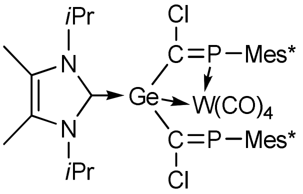
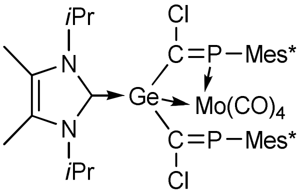
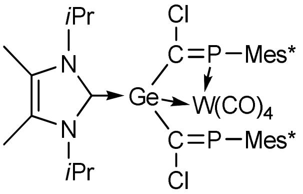
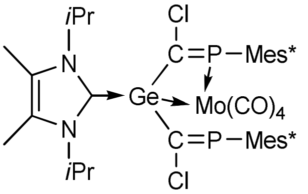
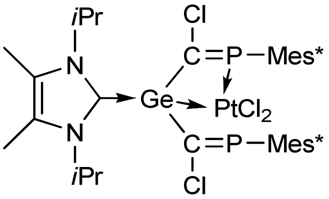
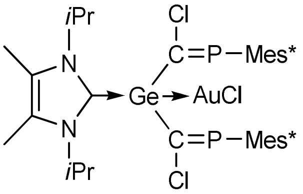
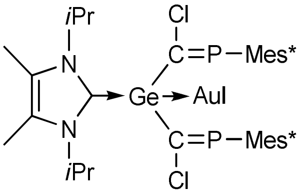


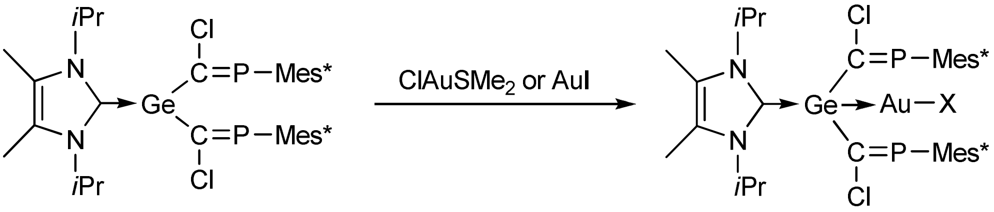
Figure 15: Molecular structure of compound ***126*** *in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and co-crystallized solvent (Et_2O) are omitted and methyl/isopropyl/t-Bu groups are simplified.*

*Table 5: ^{31}P NMR data (in C_6D_6 or in CD_2Cl_2) of compounds **118** and **124-128***

Compounds		**Value**
118		265.7
124		267.2 P-W $^{1}J_{P\text{-}W}$ = 214.7 Hz 281.9
125		280.2 P-Mo 296.2
124*		264.7 P-W $^{1}J_{P\text{-}W}$ = 210.8 Hz 280.4
125*		278.7 P-Mo 293.3
126*		214.5 P-Pt $^{1}J_{P\text{-}Pt}$ = 4612.1 Hz 294.5 $^{3}J_{P\text{-}Pt}$ = 62.8 Hz
127		293.0
128		292.6

** in CD_2Cl_2*

Compound **118** also gives an immediate and very clean reaction with one equivalent of $ClAuSMe_2$ or AuI leading quantitatively to the gold complexes **127** and **128** (*Scheme 8*). The chloro- and iodo-gold(diphosphaalkenyl)germylene were isolated in very good yield as brown or orange powders, soluble in all common solvents.



118

127 : X = Cl
128 : X = I

Scheme 8: Synthesis of gold-containing NHC-germylene adducts

These complexes are very stable towards oxidation and hydrolysis. The ^{31}P and ^{1}H NMR spectra are consistent with the presence of a symmetrical species in each case (*Table 5*).

Suitable crystals for an X-ray diffraction study were grown from dichloromethane (for **127**) and from benzene (for **128**) at room temperature (*Figure 16*). These complexes are isomorphous and their structures show the sole formation of Ge(II)–Au(I) adducts.

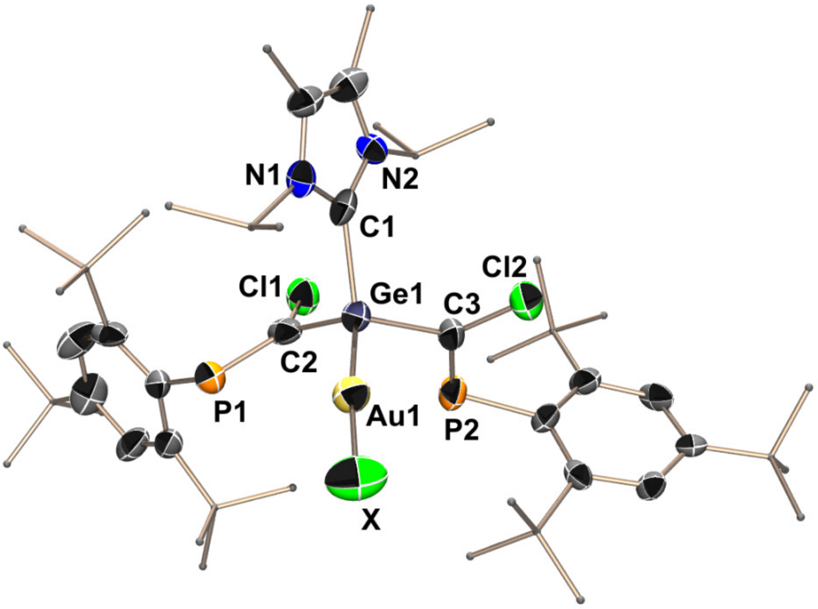


*Figure 16: Molecular structure of compounds **127** (X = Cl) and **128** (X = I) in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and crystallization solvent (dichloromethane in the case of **127** and benzene in case of **128**) are omitted and methyl/isopropyl/t-Bu groups are simplified.*

The gold atom presents an almost linear coordination with bond angles Ge1-Au1-Cl3 of 177.07(3)° in **127** and Ge1-Au1-I1 of 176.75(2)° in **128**. The Ge–Au distances of 2.3449(3) Å in **127** and 2.3641(6) Å in **128**, are similar to those previously reported for Ge(II)–Au distances 2.346(2) Å.[48]

CHAPTER 4

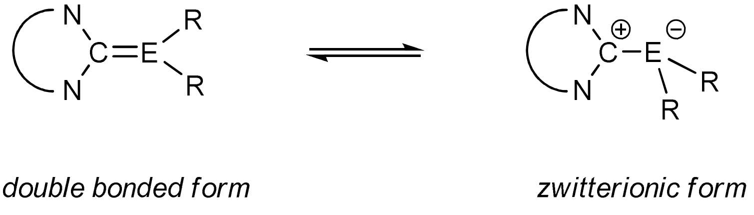
Theoretical investigation of phosphaalkenyl Ge(II) and Sn(II) systems: singlet-triplet gaps, dimerization ability and coordination preferences to transition metal fragments

Because of difficulties arising in their experimental stabilization and characterization, computational chemistry brings useful information about the structure and properties of metallylenes. Special attention was dedicated to the evaluation of singlet-triplet separation in metallylenes.[3-5]

Referring to the theoretical investigation of the N-heterocyclic carbene stabilized metallylenes, several main questions arise like: establishing the donor–acceptor character of the E–$C_{carbene}$ bond, demonstrating the presence of a pronounced zwitterionic form in contrast to the E=C double bonded form, calculating the singlet-triplet gaps or investigating the influence of the substituents in α position with respect to the metallic atom.

The donor–acceptor character of the E–$C_{carbene}$ bond was reported by several authors, in the case of dihalogenosilylene, chloro(aryl)silylenes, germylene and stannylene.[7-10] Using various methods and basis sets, theoretical calculations suggest a strongly polarized and an almost completely filled natural E–$C_{carbene}$ bond orbital in these Lewis base–Lewis acid complexes.

The zwitterionic form with a strongly polarized carbene–metallylenes bond was demonstrated experimentally by the geometrical data of the plumbylene NHC^{iPr}–$PbTip_2$,[12] but also by DFT calculations. For the parent compound $H_2Pb{=}CH_2$, a planar geometry was reported with the Pb=C bond length of 2.045 Å,[13] while the $C_{carbene}$–Pb bond length in NHC^{iPr}–$PbTip_2$ was significantly longer (2.54 Å).[12] These data suggest that the zwitterionic form is more adapt to describing the structure, than an E=C double bond (*Scheme 9*).



Scheme 9: Possible electronic structures for NHC–metallylenes (E = Pb)

Several combined experimental and theoretical DFT studies by Baines and co-workers conclude that N-heterocyclic carbenes are excellent electron donors for divalent germanium compounds.[14-16]

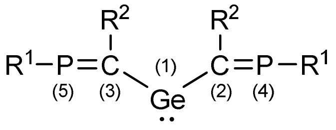
It has already been proposed that the presence of a π bond in an α position to the germanium(II) atom should allow an electron delocalization between the Ge atom and the multiple bond.[17,18] According to computational data of N-heterocyclic carbene stabilized germylenes, the substituents on germanium atom strongly affect the formation energy of the NHC–germylene complex, but there is no correlation with the $C_{carbene}$–Ge bond length.[15]

Part of this chapter describes a theoretical study on bis(phosphaalkenyl)germanium(II) compounds $Ge(CR^2=PR^1)_2$ (R^1 = H, Me, Ph, Mes; R^2 = H, Me, Ph, F, Cl, $SiMe_3$), in which the presence of the phosphaalkenyl substituents could induce various electronic and steric stabilization effects. The same effect was investigated in the case of bis(phosphaalkenyl)stannylene(II) compounds $Sn(CR^2=PH)_2$ (R^2 = H, Me, Ph, F, Cl, $SiMe_3$). The structure of N-heterocyclic carbene-stabilized germylenes and stannylenes (already obtained experimentally) was theoretically investigated.

The high reactivity of the double bonded M=E species to form M_2E_2 (M = Ge, Sn; E = S, Se) cyclic dimers will also be treated in the level of theory, and this study takes also into account the effect of several substituents at the phosphaalkene unit $–CR^2=PR^1$. The coordination ability of the model germylenes towards a pentacarbonyltungsten complex will also be described, as well as the modeling of the experimentally obtained dicoordinated tungsten(diphosphaalkenyl)germylene.

Theoretical investigation of free- and NHC carbene stabilized metallylenes

A theoretical investigation of bis(phosphaalkenyl)germanium(II) species of the type $Ge(CR^2{=}PR^1)_2$ (R^1 = H, Me, Ph, Mes; R^2 = H, Me, Ph, F, Cl, $SiMe_3$) was performed in this work. The optimized structures of the singlet and triplet states of the germylenes were calculated in order to evaluate the singlet-triplet gaps. The effect of different groups in β and γ positions relative to the germanium atom was also evaluated (*Figure 17*).



R^1 = H, Me, Ph, Mes
R^2 = H, Me, Ph, Cl, F, $SiMe_3$

Figure 17: The theoretically investigated model germylenes $Ge(CR^2{=}PR^1)_2$

The R^1 and R^2 substituents were chosen to cover a large range of electronic or steric effects. The energy differences between the singlet and triplet states for the investigated structures are presented in *Table 6* together with the geometrical data for the singlet structures.

All calculations were performed on the *E,E* isomers with respect to the P=C double bonds using BP86/6-311+G(d,p), taking into account their higher stability and the fact that they are more likely to form than structures containing a *Z,Z* orientation.

Table 6: Calculated energy differences between the singlet and triplet states of $Ge(CR^2{=}PR^1)_2$ and geometrical data for the singlet structures

R^1	R^2	$E_t – E_s$ gap (kcal/mol)	Bond length (Å)		Angle (°)	Bond order			
			C–Ge	P–C	C-Ge-C	Ge(1)-C(2)	Ge(1)-C(3)	C(2)-P(4)	C(3)-P(5)
H	H	20.99	2.01	1.69	95.8	0.83	0.83	1.86	1.86
	Me	25.49	2.00	1.71	100.7	0.82	0.82	1.72	1.72
	Ph	24.71	2.00	1.71	99.9	0.79	0.78	1.63	1.67
	Cl	26.17	2.01	1.71	100.0	0.77	0.77	1.73	1.73
	F	27.97	2.01	1.72	94.9	0.83	0.83	1.73	1.73
	$SiMe_3$	18.32	1.99	1.70	98.0	0.74	0.74	1.80	1.80

Me	**H**	24.66	2.00	1.69	95.5	0.84	0.84	1.80	1.80
	Me	26.09	1.99	1.71	101.8	0.83	0.83	1.67	1.67
	Ph	26.24	2.01	1.71	101.1	0.79	0.78	1.62	1.66
	Cl	30.63	2.00	1.71	97.1	0.78	0.78	1.64	1.64
	F	30.96	2.01	1.71	100.1	0.87	0.87	1.72	1.72
	$SiMe_3$	19.61	2.02	1.70	102.8	0.79	0.70	1.72	1.79
Ph	**H**	24.02	2.00	1.69	95.5	0.84	0.84	1.74	1.74
	Me	26.28	2.00	1.71	101.7	0.82	0.82	1.65	1.65
	Ph	23.47	2.03	1.71	100.2	0.74	0.74	1.68	1.68
	Cl	28.64	2.01	1.71	97.8	0.77	0.77	1.61	1.61
	F	30.98	2.01	1.72	100.0	0.88	0.88	1.67	1.67
	$SiMe_3$	22.06	2.01	1.71	103.5	0.78	0.74	1.70	1.71
Mes	**H**	22.94	2.00	1.70	95.6	0.84	0.84	1.78	1.78
	Me	25.09	2.00	1.71	101.6	0.82	0.82	1.66	1.66
	Ph	24.59	2.01	1.72	98.1	0.81	0.78	1.68	1.63
	Cl	27.93	2.00	1.71	97.7	0.77	0.77	1.63	1.63
	F	28.16	2.01	1.72	99.6	0.86	0.86	1.70	1.70
	$SiMe_3$	22.29	2.00	1.71	104.2	0.79	0.79	1.69	1.69

The estimated BP86/6-311+G(d,p) energy gaps between the singlet and triplet states of the model germylenes vary between 18 and 31 kcal/mol, depending on the nature of both R^1 and R^2. These values are in agreement with the results previously reported in the literature for the heavier metallylenes, in which the singlet state analogues were calculated to be more stable (energy gaps of 16.7–19.6 kcal/mol for SiH_2, 21.9–26.8 kcal/mol for GeH_2 and, about 25 kcal/mol for SnH_2, depending on the method employed).[3-5]

The singlet-triplet gap is influenced by the electronic properties of groups bonded in β position to the germanium atom. The smallest energy gaps were obtained when the most electropositive group, namely the $SiMe_3$, was bonded to the phosphorus atom. The presence of an electronegative atom, like Cl or F, leads to higher differences between the singlet and triplet state, while substituents such as H, Me and Ph give moderate energy gaps (*Table 6*).

The calculated P=C double bond length varies between 1.69–1.72 Å, at the upper limit of the range.[22,23]

The HOMO and LUMO for the $Ge(CH=PH)_2$ model derivative are shown in *Figure 18*. It can be noticed that the HOMO is localized on the C=P system (*Figure 18*-a), while the LUMO as anticipated, has a pronounced antibonding character (*Figure 18*-b).

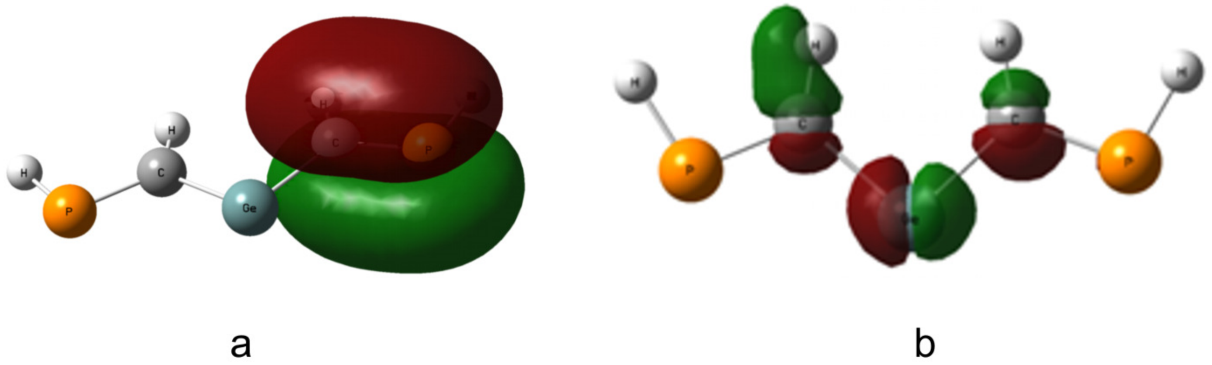


Figure 18: HOMO (a) and LUMO (b) for the singlet state of $Ge(CH=PH)_2$

A similar conclusion was posted by analyzing the HOMO and LUMO model of $Ge[C(Cl)=PMes]_2$ (*Figure 19*), which is really close to the synthetically obtained germylene $Ge[C(Cl)=PMes^*]_2$ **116**.

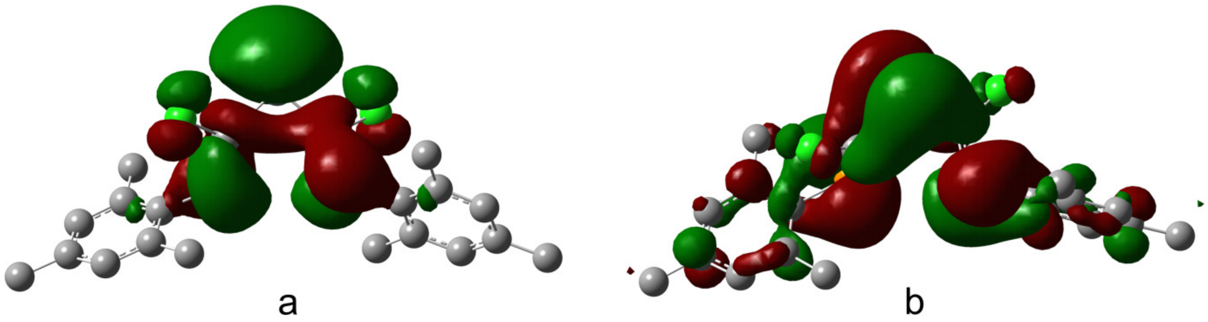
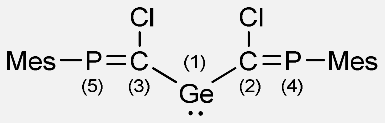
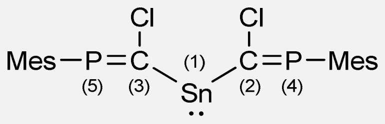


Figure 19: HOMO (a) and LUMO (b) for the singlet state of $Ge[C(Cl)=PMes]_2$

For modeling the tin(II) derivatives the bis(phosphaalkenyl)stannylene $Sn(CR^2=PH)_2$ (R^2 = H, Me, Ph, F, Cl, $SiMe_3$) was chosen. In all cases the higher stability of the singlet state was reported (the values of ΔE are between 23.64–29.91 kcal/mol) having almost the same energy gaps as in the case of $Ge(CR^2{=}PH)_2$.

When R^1 = Mes and R^2 = Cl the investigated system differs only by the presence of a Mes group instead of Mes* from the experimentally obtained structures of type $M[C(Cl){=}PMes^*]_2$ (M = Ge **116**, Sn **117**). For both of the model metallylenes, the singlet states were found to be more stable (*Table 7*).

Table 7: Data for singlet and triplet state of the system M[C(Cl)=PMes]₂ (M = Ge, Sn) system

		ΔE	**Bond length (Å)**		**Angle (°)**
		kcal/mol	**C–M**	**P–C**	**C(2)-M(1)-C(3)**
	***Singlet***	0.00	2.00	1.71	97.7
	Triplet	27.93	1.95	1.73	119.4
	***Singlet***	0.00	2.22	1.71	96.0
	Triplet	29.47	2.17	1.72	117.1

On the base of their X-ray structures, theoretical calculations were performed by modeling the two experimentally obtained germylene NHC^{iPr}–$Ge[C(Cl){=}PMes^*]_2$ **118** and stannylene NHC^{iPr}–$Sn[C(Cl){=}PMes^*]_2$ **119** (*Table* 8 and *Table 9*), to explain their very different reactivity.

The model structures were investigated using the same method and basis sets BP86/6-311+G(d,p) as in the previous case, and the LANL2TZ basis set for the Sn atom. To reduce the complexity of the systems, simplified compounds were examined, with Mes groups as substituents on the phosphorus atoms. Standard density functionals such as BP86 and B3LYP have proved to be excellent methods for predicting bond lengths and bond dissociation energies of carbenes and carbene-metal complexes.[25]

Table 8: Comparison between the solid state structure and the calculated local minimum of NHC^{iPr}–Ge[C(Cl)=PMes]$_2$* ***118***

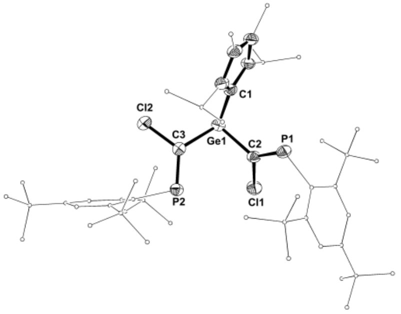
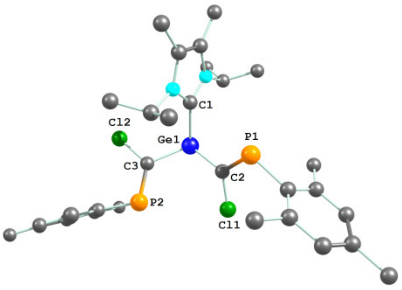
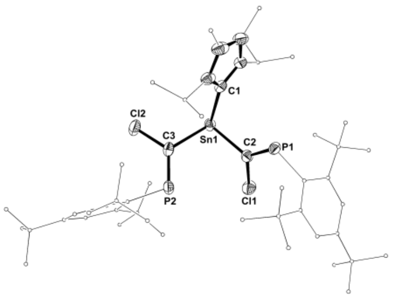
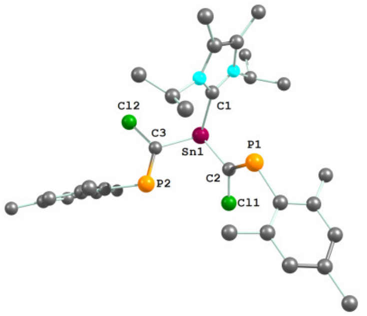
		X-ray structure of 118 ***(with Mes*)***	**Optimized structure** ***(with Mes)***
		 	
Energy [a.u.]		---	-4996.924
Bond lengths [Å]	Ge1–C1	2.09	2.11
	Ge1–C2	2.01	2.03
	Ge1–C3	2.01	2.03
	P1–C2	1.68	1.71
	P2–C3	1.68	1.71
	Cl1–C2	1.76	1.78
	Cl2–C3	1.77	1.80
Angles [°]	C1-Ge1-C2	96.0	97.0
	C1-Ge1-C3	105.8	100.4
	C2-Ge1-C3	100.4	104.6
	P1-C2-Ge1	125.8	124.1
	P2-C3-Ge1	122.8	124.8
Mulliken atomic charges	Ge1	---	0.92
	C1	---	-2.17
	C2	---	-0.74
	C3	---	-0.11
	P1	---	-1.42
	P2	---	-1.25

Table 9: Comparison between the solid state structure and the calculated local minimum of NHC^{iPr}*–Sn[C(Cl)=PMes*]*$_2$ ***119***

		X-ray structure of 119 *(with Mes*)*	Optimized structure *(with Mes)*
			
Energy [a.u.]		---	-2923.088
Bond lengths [Å]	Sn1–C1	2.32	2.37
	Sn1–C2	2.23	2.26
	Sn1–C3	2.24	2.25
	P1–C2	1.67	1.70
	P2–C3	1.67	1.70
	Cl1–C2	1.76	1.78
	Cl2–C3	1.77	1.80
Angles [°]	C1-Sn1-C2	93.5	93.2
	C1-Sn1-C3	103.2	98.6
	C2-Sn1-C3	98.2	97.9
	P1-C2-Sn1	125.7	126.0
	P2-C3-Sn1	122.7	122.8
Mulliken atomic charges	Sn1	---	0.97
	C1	---	-0.92
	C2	---	-0.94
	C3	---	-0.81
	P1	---	-1.09
	P2	---	-0.84

The geometrical data of model and experimentally obtained metallylenes are showing very good correlation.

The values of the P=C double bonds in the optimized geometries are in each case slightly longer than in the monocrystals (with around 0.03 Å, which corresponds to a 1.7 % of difference). These variations are less significant and they probably indicate the largest steric hindrance of the bulkier Mes* group in the case of **118** and **119**.

Only the basis of ^{31}P NMR spectra, which show one signal at 265.7 ppm for **118** and at 277.4 ppm for **119**, respectively, the sterical conformation of the metallylenes cannot be forecasted. According to the solid state structure, the conformation was proved to be *E*,*E* with respect to the P=C double bonds. The higher stability of the *E*,*E* isomers, indicated experimentally, is also predicted by theoretical calculations by the smaller energy of the *E,E* form when compare with the *Z*,*Z* isomer.

Dimerization of double bonded species M=E

To increase our understanding of the experimental results, theoretical calculations were performed in order to explain the differences in reactivity between the germanium(II) and the tin(II) derivatives with elemental chalcogens. The geometry of model compounds $M(=E)[C(Cl)=PMes]_2$ (M = Ge, Sn; E = S, Se) was optimized at the BP86 level, using the 6-311+G(d,p) basis set for period 1-3 elements and LANL2TZ for the tin atom. The head-to-tail four-membered rings resulting from a dimerisation at the level of the M=E bond have also been investigated.

The calculated values for bond lengths and angles are in fair agreement with the experimental data. The formation of the 4-atom-containing cycle through a head-to-tail dimerization is favored in all cases, as it can be seen from the negative values of the ΔE, calculated by the formula below

$$\Delta E = E_{dimer} - 2\cdot E_{monomer}$$

However, in the case of the tin derivatives, the stabilization afforded by the formation of the inorganic Sn_2S_2 ring is more pronounced than for the germanium analogues, in both the sulfur and the selenium derivatives (*Figure 20*).

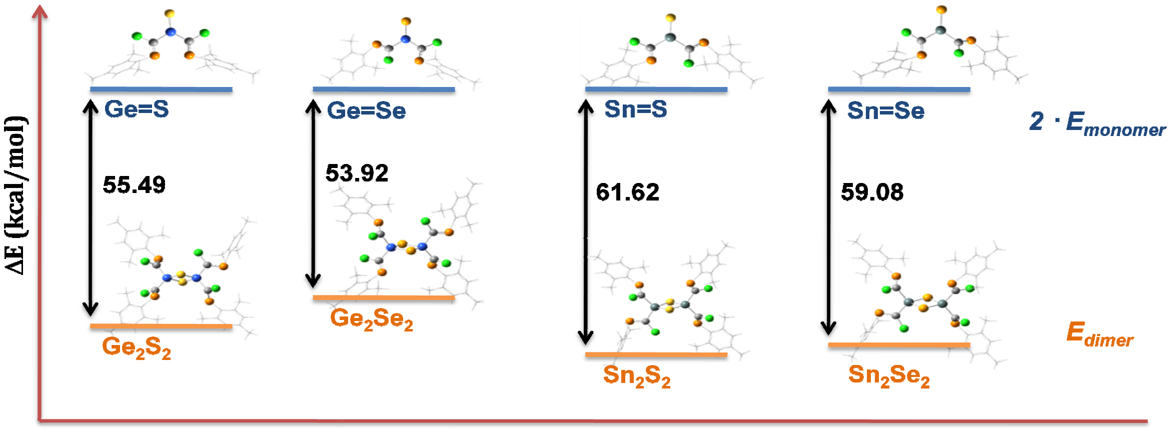
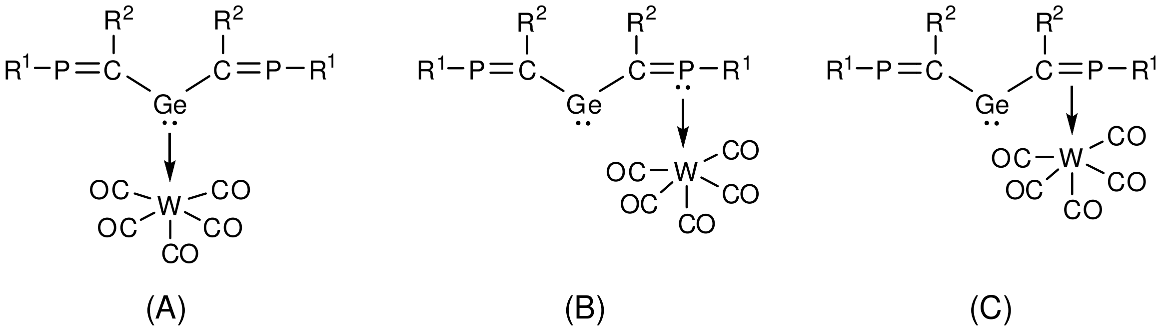


Figure 20: Optimized geometries of double bonded M=E and dimeric M_2E_2 (M = Ge, Sn; E = S, Se) derivatives

Complexation of metallylenes to transition metal fragments

Another way to stabilize germylenes is through coordination to transition metals. Three coordination possibilities are presented: through the Ge (**A**) or the P atom (**B**) or through the P=C double bond (**C**) (*Scheme 10*). All calculations were performed for the singlet state germylenes, in the *E,E* configuration, starting from their optimized geometries (*Table 10*).



Scheme 10: Coordination possibilities of $Ge(CR^2{=}PR^1)_2$ (R^1 = H, Me, Ph, Mes; R^2 = H, Me, Ph, Cl, F, $SiMe_3$) germylenes to $W(CO)_5$ fragment

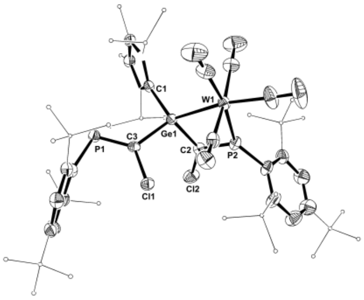
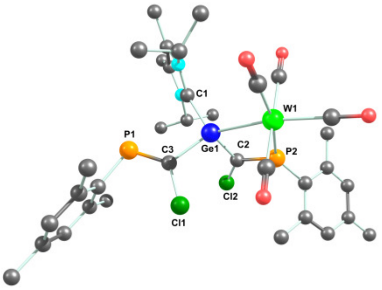
The calculations performed, using BP86/6-311+G(d,p) and LANL2TZ for the W atom, showed that the preferred coordination is in each case through the germanium atom, rather than the phosphorus or the π-bond. The energy differences between the three possible forms vary between 1.18 and 26.01 kcal/mol, the more stable structure being in each case the one containing the Ge→$W(CO)_5$ moiety (*Table 10*).

Table 10: Calculated energy differences between type ***A****,* ***B*** *and* ***C*** *structures using BP86/6-311+G(d,p) and LANL2TZ for the tungsten atom*

R^1	**R^2**	**Isomer**	**ΔE**	**C-Ge-C bond**	**Bond lengths [Å]**		**Distances [Å] of W atom from**			
			(kcal/ mol)	**angle [°]**	**C–Ge**	**P=C**	**Ge**	**C**	**P**	**Midpoint P=C bond**
H	**H**	**W···Ge**	0.00	101.7	1.96	1.69	2.55	-	-	-
		W···P	8.58	96.9	1.99	1.69	-	-	2.46	-
		W···P=C	6.97	98.6	1.99	1.76	-	2.44	2.70	2.41
	Me	**W···Ge**	0.00	107.0	1.99	1.70	2.56	-	-	-
		W···P	8.97	94.6	2.04	1.69	-	-	2.49	-
		W···P=C	9.32	104.6	2.02	1.77	-	2.51	2.69	2.44
	Ph	**W···Ge**	0.00	105.8	2.00	1.70	2.55	-	-	-
		W···P	6.24	96.6	2.04	1.70	-	-	2.49	-
		W···P=C	10.33	105.3	2.02	1.78	-	2.57	2.68	2.47
	Cl	**W···Ge**	0.00	104.4	1.99	1.70	2.54	-	-	-
		W···P	8.39	96.7	2.04	1.69	-	-	2.49	-
		W···P=C	7.87	103.9	2.01	1.78	-	2.50	2.69	2.44
	F	**W···Ge**	0.00	103.5	1.98	1.71	2.53	-	-	-
		W···P	9.28	99.1	2.01	1.72	-	-	2.47	-
		W···P=C	6.21	96.6	2.01	1.77	-	2.57	2.70	2.49
	$SiMe_3$	**W···Ge**	0.00	104.2	1.98	1.71	2.57	-	-	-
		W···P	7.55	101.0	2.03	1.69	-	-	2.50	-
		W···P=C	10.04	108.0	2.02	1.76	-	2.45	2.69	2.42
Me	**H**	**W···Ge**	0.00	105.2	1.95	1.69	2.56	-	-	-
		W···P	8.55	97.5	1.99	1.69	-	-	2.48	-
		W···P=C	11.10	104.9	1.99	1.75	-	2.42	2.74	2.43
	Me	**W···Ge**	0.00	103.0	1.98	1.70	2.56	-	-	-
		W···P	8.57	101.8	2.02	1.69	-	-	2.53	-
		W···P=C	11.53	110.5	2.03	1.75	-	2.48	2.71	2.44
	Ph	**W···Ge**	0.00	104.7	1.99	1.71	2.57	-	-	-
		W···P	6.55	99.8	2.04	1.69	-	-	2.51	-
		W···P=C	13.59	106.8	2.03	1.78	-	2.55	2.71	2.47
	Cl	**W···Ge**	0.00	104.3	1.98	1.71	2.55	-	-	-
		W···P	8.35	100.9	2.01	1.71	-	-	2.49	-
		W···P=C	11.23	104.7	2.01	1.78	-	2.53	2.71	2.46
	F	**W···Ge**	0.00	103.6	1.97	1.71	2.54	-	-	-
		W···P	7.41	99.0	2.01	1.72	-	-	2.48	-
		W···P=C	9.23	99.7	2.01	1.77	-	2.57	2.72	2.50
	$SiMe_3$	**W···Ge**	0.00	105.0	1.99	1.70	2.58	-	-	-

		W···P	5.96	102.5	2.04	1.68	-	-	2.52	-
		W···P=C	1.18	98.4	2.09	1.74	-	2.54	2.66	2.45
Ph	**H**	**W···Ge**	0.00	101.6	1.95	1.69	2.57	-	-	-
		W···P	10.08	97.7	1.99	1.69	-	-	2.50	-
		W···P=C	10.62	98.8	2.00	1.74	-	2.45	2.76	2.46
	Me	**W···Ge**	0.00	102.7	1.99	1.70	2.56	-	-	-
		W···P	8.79	102.4	2.02	1.70	-	-	2.51	-
		W···P=C	12.19	105.9	2.03	1.77	-	2.52	2.73	2.47
	Ph	**W···Ge**	0.00	104.9	1.99	1.71	2.57	-	-	-
		W···P	7.79	99.9	2.04	1.68	-	-	2.52	-
		W···P=C	21.70	97.8	2.11	1.77	-	2.62	2.70	2.51
	Cl	**W···Ge**	0.00	105.1	1.98	1.71	2.55	-	-	-
		W···P	8.86	97.2	2.03	1.69	-	-	2.51	-
		W···P=C	12.57	104.4	2.02	1.78	-	2.51	2.74	2.47
	F	**W···Ge**	0.00	105.1	1.97	1.71	2.55	-	-	-
		W···P	8.90	99.0	2.01	1.73	-	-	2.50	-
		W···P=C	10.50	103.2	2.02	1.76	-	2.50	2.76	2.48
	SiMe$_3$	**W···Ge**	0.00	104.9	2.00	1.70	2.58	-	-	-
		W···P	7.41	104.5	2.04	1.69	-	-	2.52	-
		W···P=C	2.75	99.0	2.08	1.75	-	2.55	2.67	2.46
Mes	**H**	**W···Ge**	0.00	101.7	1.95	1.70	2.56	-	-	-
		W···P	9.06	94.6	2.00	1.69	-	-	2.49	-
		W···P=C	13.54	102.5	2.01	1.74	-	2.41	2.80	2.46
	Me	**W···Ge**	0.00	105.9	1.99	1.71	2.58	-	-	-
		W···P	8.60	102.6	2.02	1.70	-	-	2.52	-
		W···P=C	23.48	95.7	2.13	1.74	-	2.56	2.56	2.45
	Ph	**W···Ge**	0.00	106.3	1.99	1.71	2.58	-	-	-
		W···P	7.16	102.4	2.04	1.69	-	-	2.53	-
		W···P=C	23.57	105.9	2.07	1.76	-	2.50	2.83	2.52
	Cl	**W···Ge**	0.00	104.7	1.98	1.71	2.55	-	-	-
		W···P	10.17	100.3	2.02	1.71	-	-	2.51	-
		W···P=C	25.13	98.9	2.05	1.76	-	2.40	2.75	2.44
	F	**W···Ge**	0.00	104.8	1.98	1.71	2.56	-	-	-
		W···P	8.91	99.1	2.01	1.72	-	-	2.50	-
		W···P=C	18.41	96.6	2.03	1.76	-	2.48	2.89	2.54
	SiMe$_3$	**W···Ge**	0.00	106.6	1.99	1.70	2.59	-	-	-
		W···P	5.98	102.7	2.02	1.69	-	-	2.53	-
		W···P=C	26.01	111.8	2.05	1.77	-	2.43	2.76	2.45

Table 11: Comparison between the solid state structure of tungsten(diphosphaalkenyl)germylene ***124*** *and the calculated structure of the model*

		Compound 124 *RX data*	**DFT model of comp. 124** *(with Mes groups)*
			
Energies	E (a.u.)	---	-5518.4645347
Bond lengths [Å]	Ge1–C1	2.04	2.08
	Ge1–C2	2.01	2.04
	Ge1–C3	1.97	2.01
	P1–C3	1.67	1.70
	P2–C2	1.67	1.70
	P1–Mes	1.85	1.86
	P2–Mes	1.85	1.84
	W1–Ge1	2.65	2.70
	W1–P1	2.49	2.49
	W1–P2	---	---
Angles [°]	C1–Ge1–C2	112.5	111.9
	C1–Ge1–C3	100.6	98.8
	Ge1–C2–P2	99.6	98.2
	Ge1–C3–P1	125.8	123.6
	Mes–P2–C2	112.6	114.2
	Mes–P1–C3	102.8	105.8
	Ge1–W1–P2	66.4	66.1
	P1–W1–P2	---	---
Mulliken atomic charges	Ge1	---	1.28
	C1	---	-3.33
	C2	---	0.37
	C3	---	-0.45
	P1	---	-1.38
	P2	---	-2.35
	W	---	1.60
Dipol. mom.		---	1.55

The C-Ge-C bond angles in the coordinated germylenes are wider than for the non-coordinated ones, while the Ge–C bond length is shorter. As expected, NBO analysis indicates the back donation from the W to the Ge atom.

A model of tungsten(diphosphaalkenyl)germylene **124** was theoretical investigated in singlet state employing the RBP86 functional and using the 6-311+G(dp) basis set for the main group elements and LANL2TZ for the tungsten atom. The agreement with the experimental data is fair (*Table 11*).

The calculated atomic charge of the $C_{carbene}$ atom is -3.33, which can explain the considerable upfield shifted signal in ^{13}C NMR of **124** (157.11 ppm) when compared with the $C_{C=P}$ carbon atoms (182.09 ppm and 187.87 ppm).

GENERAL CONCLUSION

This thesis consists of a complete work on the topic of NHC carbene stabilized metallylenes: starting from a bibliographic review followed by the synthesis, physicochemical properties, reactivity and theoretical calculation of a new chemical class, so called N-heterocyclic carbene stabilized phosphaalkenyl-germylenes and -stannylenes.

The first part presents the synthesis and reactivity of the N-heterocyclic carbene stabilized silylenes, -germylenes, -stannylenes and -plumbylenes reported to date. The number of the reported NHC–metallylenes was growing fast in the last decade. These species are unstable, very reactive, and could only be obtained and investigated under oxygen-free atmosphere.

In the next chapter, the synthesis and the physicochemical properties of N-heterocyclic carbene stabilized phosphaalkenyl-metallylenes are presented. Five new metallylenes were described in this chapter: the free- and N-heterocyclic carbene stabilized phosphaalkenyl-germylenes and -stannylenes and a mono chloro-substituted analogue of stannylene. Three of these compounds were isolated and fully characterized in solution by NMR spectroscopy and also in solid state by X-ray diffraction studies. In general they are stable under argon atmosphere at room temperature in non-chlorinated solvents.

Then, the reactivity of these first N-heterocyclic carbene stabilized bis(phosphaalkenyl)-metallylenes are presented in a separate chapter. In general, two types of reactions were investigated: oxidation reactions by elemental chalcogens which afford double bonded or cyclisation products and coordination reactions with various transition-metals like W, Mo, Pt or Au which give some unexpected coordinating preferences. In this chapter nine products are described, most of them fully characterized also by X-ray diffraction analyses. The oxidation and complexation products are more stable than their starting compounds, several example are stable also in water. This behavior should allow them to be widely used in the future because of their stability, chirality or possible biological effects.

Finally, the last chapter of the thesis is a part of the theoretical calculation on the model phosphaalkenyl-disubstituted metallylenic systems. Several questions are answered by DFT calculation raised during the experimental work, like: stabilization effect of the different substituents, singlet-triplet energy gaps, exclusively formation of only one isomers or dimerisation ability of the double bonded compounds. The correlation between the solid state structure and the calculated local minimum of the model structures are really good, which means that the methods and basis sets used during the theoretical investigation could adequately describe the model metallylenic systems.

BIBLIOGRAPHY[1]

CHAPTER 1

1. Arduengo, A. J.; Harlow, R. L.; Kline, M., *J. Am. Chem. Soc.* **1991,** *113*, 361-363.
2. Nemcsok, D.; Wichmann, K.; Frenking, G., *Organometallics* **2004,** *23*, 3640-3646.
3. Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D., *Chem. Eur. J.* **1999,** *5*, 1931-1935.
4. Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G., *Angew. Chem. Int. Ed. Engl.* **1996,** *35*, 1121-1122.
5. Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Herdtweck, E., *J. Organomet. Chem.* **2003,** *684*, 235-248.
6. Neumann, W. P., *Chem. Rev.* **1991,** *91*, 311-334.
7. Barrau, J.; Rima, G., *Coord. Chem. Rev.* **1998,** *178-180*, 593-622.
8. Mizuhata, Y.; Sasamori, T.; Tokitoh, N., *Chem. Rev.* **2009,** *109*, 3479-3511.
9. Lollmahomed, F.; Huck, L. A.; Harrington, C. A.; Chitnis, S. S.; Leigh, W. J., *Organometallics* **2009,** *28*, 1484-1494.
10. Rupar, P. A.; Staroverov, V. N.; Baines, K. M., *Science* **2008,** *322*, 1360-1363.
11. Nagendran, S.; Roesky, H. W., *Organometallics* **2008,** *27*, 457-492.
12. Mandal, S. K.; Roesky, H. W., *Chem. Commun.* **2010**, 6016-6041.
13. Asay, M.; Jones, C.; Driess, M., *Chem. Rev.* **2011,** *111*, 354-396.
14. Kirmse, W., *Eur. J. Org. Chem.* **2005**, 237-260.
15. Diez-Conzalez, S.; Nolan, S. P., *Annu. Rep. Prog. Chem., Sect. B.* **2005,** *101*, 171-191.
16. Kuhn, N.; Al-Sheikh, A., *Coord. Chem. Rev.* **2005,** *249*, 829-857.
17. Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S., *J. Chem. Soc., Chem. Commun.* **1995**, 1157-1158.
18. Stabenow, F.; Saak, W.; Weidenbruch, M., *Chem. Commun.* **1999**, 1131-1132.
19. Wang, Y.; Robinson, G. H., *Inorg. Chem.* **2011,** *50*, 12326-12337.
20. Ghadwal, R. S.; Azhakar, R.; Pröpper, K.; Holstein, J. J.; Dittrich, B.; Roesky, H. W., *Inorg. Chem.* **2011,** *50*, 8502-8508.
21. Thimer, K. C.; Al-Rafia, I. S. M.; Ferguson, M. J.; McDonald, R.; Rivard, E., *Chem. Commun.* **2009**, 7119-7121.
22. Al-Rafia, I. S. M.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E., *J. Am. Chem. Soc.* **2011,** *133*, 777-779.
23. Kuhn, N.; Kratz, T., *Synthesis* **1993**, 561-562.
24. Kuhn, N.; Kratz, T.; Bläser, D.; Boese, R., *Chem. Ber.* **1995,** *128*, 245-250.
25. Jafarpour, L.; Stevens, E. D.; Nolan, S. P., *J. Organomet. Chem.* **2000,** *606*, 49-54.
26. Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M., *J. Am. Chem. Soc.* **1992,** *114*, 5530-5534.

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[1] Original bibliography of the thesis

27. Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M., *Tetrahedron* **1999,** *55*, 14523-14534.
28. Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D., *Angew. Chem. Int. Ed.* **2009,** *48*, 5683-5686.
29. Filippou, A. C.; Chernov, O.; Schnakenburg, G., *Chem. Eur. J.* **2011,** *17*, 13574-13583.
30. Filippou, A. C.; Chernov, O.; Blom, B.; Stumpf, K. W.; Schnakenburg, G., *Chem. Eur. J.* **2010,** *16*, 2866-2872.
31. Cui, H.; Cui, C., *Dalton Trans.* **2011,** *40*, 11937-11940.
32. Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F.; Schleyer, P. R.; Robinson, G. H., *Science* **2008,** *321*, 1069-1071.
33. Filippou, A. C.; Chernov, O.; Schnakenburg, G., *Angew. Chem. Int. Ed.* **2009,** *48*, 5687-5690.
34. Tanaka, H.; Ichinohe, M.; Sekiguchi, A., *J. Am. Chem. Soc.* **2012,** *134*, 5540-5543.
35. Boesveld, W. M.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; von Ragué Schleyer, P., *Chem. Commun.* **1999**, 755-756.
36. Azhakar, R.; Tavčar, G.; Roesky, H. W.; Hey, J.; Stalke, D., *Eur. J. Inorg. Chem.* **2011**, 475-477.
37. Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Stalke, D., *Chem. Eur. J.* **2010,** *16*, 85-88.
38. Al-Rafia, I. S. M.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E., *Chem. Commun.* **2012,** *48*, 1308-1310.
39. Al-Rafia, I. S. M.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E., *Angew. Chem. Int. Ed.* **2011,** *50*, 8354-8357.
40. Li, J.; Merkel, S.; Henn, J.; Meindl, K.; Döring, A.; Roesky, H. W.; Ghadwal, R. S.; Stalke, D., *Inorg. Chem.* **2010,** *49*, 775-777.
41. Tavčar, G.; Sen, S. S.; Azhakar, R.; Thorn, A.; Roesky, H. W., *Inorg. Chem.* **2010,** *49*, 10199-10202.
42. Filippou, A. C.; Chernov, O.; Stumpf, K. W.; Schnakenburg, G., *Angew. Chem. Int. Ed.* **2010,** *49*, 3296-3300.
43. Jana, A.; Tavčar, G.; Roesky, H. W.; Schulzke, C., *Dalton Trans.* **2010,** *39*, 6217-6220.
44. Karsch, H. H.; Schlüter, P. A.; Bienlein, F.; Herker, M.; Witt, E.; Sladek, A.; Heckel, M., *Z. Anorg. Allg. Chem.* **1998,** *624*, 295-309.
45. Ghadwal, R. S.; Sen, S. S.; Roesky, H. W.; Granitzka, M.; Kratzert, D.; Merkel, S.; Stalke, D., *Angew. Chem. Int. Ed.* **2010,** *49*, 3952-3955.
46. Ghadwal, R. S.; Roesky, H. W.; Schulzke, C.; Granitzka, M., *Organometallics* **2010,** *29*, 6329-6333.
47. Ghadwal, R. S.; Roesky, H. W.; Granitzka, M.; Stalke, D., *J. Am. Chem. Soc.* **2010,** *132*, 10018-10020.
48. Tanaka, H.; Inoue, S.; Ichinohe, M.; Driess, M.; Sekiguchi, A., *Organometallics* **2011,** *30*, 3475-3478.
49. Arguengo, A. J.; Dias, R. H. V.; Calabrese, J. C.; Davidson, F., *Inorg. Chem.* **1993,** *32*, 1541-1542.
50. Rupar, P. A.; Staroverov, V. N.; Ragogna, P. J.; Baines, K. M., *J. Am. Chem. Soc.* **2007,** *129*, 15138-15139.

51. Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G., *Angew. Chem. Int. Ed.* **2009,** *48*, 9701-9704.
52. Ruddy, A. J.; Rupar, P. A.; Bladek, K. J.; Allan, C. J.; Avery, J. C.; Baines, K. M., *Organometallics* **2010,** *29*, 1362-1367.
53. Rupar, P. A.; Staroverov, V. N.; Baines, K. M., *Organometallics* **2010,** *29*, 4871-4881.
54. Rupar, P. A.; Jennings, M. C.; Ragogna, P. J.; Baines, K. M., *Organometallics* **2007,** *26*, 4109-4111.
55. Bantreil, X.; Nolan, S. P., *Nat. Protoc.* **2011,** *6* (1), 69-77.
56. Rupar, P. A.; Jennings, M. C.; Baines, K. M., *Organometallics* **2008,** *27*, 5043-5051.
57. Onyszchuk, M.; Castel, A.; Rivière, P.; Satgé, J., *J. Organomet. Chem.* **1986,** *317*, C35-C37.
58. Katir, N.; Matioszek, D.; Ladeira, S.; Escudié, J.; Castel, A., *Angew. Chem. Int. Ed.* **2011,** *50*, 5352-5355.
59. Rivière, P.; Castel, A.; Satgé, J.; Guyot, D., *J. Organomet. Chem.* **1986,** *315*, 157-164.
60. Satgé, J.; Massol, M.; Rivière, P., *J. Organomet. Chem.* **1973,** *56*, 1-39.
61. Inoue, S.; Driess, M., *Angew. Chem. Int. Ed.* **2011,** *50*, 5614-5615.
62. Baines, K. M.; Stibbs, W. G., *Coord. Chem. Rev.* **1995,** *145*, 157-200.
63. Ward, M. J.; Rupar, P. A.; Murphy, M. W.; Yiu, Y.-M.; Baines, K. K.; Sham, T. K., *Chem. Commun.* **2010,** *46*, 7016-7018.
64. Richards, A. F.; Brynda, M.; Power, P. P., *Chem. Commun.* **2004**, 1592-1593.
65. Castel, A.; Rivière, P.; Satgé, J.; Ko, Y.-H., *J. Organomet. Chem.* **1988,** *342*, C1-C4.
66. Bantu, B.; Pawar, G. M.; Decker, U.; Wurst, K.; Schmidt, A. M.; Buchmeiser, M. R., *Chem. Eur. J.* **2009,** *15*, 3103-3109.
67. Masamune, S.; Sita, L. R., *J. Am. Chem. Soc.* **1985,** *107*, 6390-6391.
68. Weidenbruch, M.; Schäfer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H., *Chem. Ber.* **1992,** *125*, 561-566.
69. Hahn, F. E.; Wittenbecher, L.; Kühn, M.; Lügger, T.; Fröhlich, R., *J. Organomet. Chem.* **2001,** *617-618*, 629-634.
70. Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M., *Angew. Chem. Int. Ed.* **1999,** *38*, 187-189.

CHAPTER 2

1. Nagendran, S.; Roesky, H. W., *Organometallics* **2008,** *27*, 457-492.
2. Mizuhata, Y.; Sasamori, T.; Tokitoh, N., *Chem. Rev.* **2009,** *109*, 3479-3511.
3. Asay, M.; Jones, C.; Driess, M., *Chem. Rev.* **2011,** *111*, 354-396.
4. Mandal, S. K.; Roesky, H. W., *Chem. Commun.* **2010**, 6016-6041.
5. Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D., *J. Am Chem. Soc.* **2009,** *131*, 1288-1293.
6. Jana, A.; Roesky, H. W.; Schulzke, C., *Dalton Trans.* **2010,** *39*, 132-138.

7. Petrar, P. M.; Nemes, G.; Silaghi-Dumitrescu, I.; Ranaivonjatovo, H.; Gornitzka, H.; Escudié, J., *Chem. Commun.* **2007**, 4149-4151.
8. Septelean, R.; Nemeş, G.; Escudié, J.; Silaghi-Dumitrescu, I.; Ranaivonjatovo, H.; Petrar, P. M.; Gornitzka, H.; Silaghi-Dumitrescu, L.; Saffon, N., *Eur. J. Inorg. Chem.* **2009**, 628-634.
9. Ditto, S. R.; Card, R. J.; Davis, P. D.; Neckers, D. C., *J. Org. Chem.* **1979,** *44*, 894-896.
10. Pearson, D. E.; Frazer, M. G.; Frazer, V. S.; Washburn, L. C., *Synthesis* **1976**, 621-623.
11. Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T., *J. Am. Chem. Soc.* **1981,** *103*, 4587-4589.
12. Goede, S. J.; Bickelhaupt, F., *Chem. Ber.* **1991,** *124*, 2677-2684.
13. van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F., *Organometallics* **1996,** *15*, 174-180.
14. Yoshifuji, M.; Sasaki, S.; Inamoto, N., *Tetrahedron Lett.* **1989,** *30*, 839-842.
15. Niecke, E.; Nieger, M.; Schmidt, O.; Gudat, D.; Schoeller, W. W., *J. Am. Chem. Soc.* **1999,** *121*, 519-527.
16. Yoshifuji, M.; Ito, S., *Top. Curr. Chem.* **2003,** *223*, 67-89.
17. Kuhn, N.; Kratz, T., *Synthesis* **1993**, 561-562.
18. Mironov, V. F.; Gar, T. K., *Zh. Obshch. Khim.* **1975,** *45*, 103-108.
19. Rupar, P. A.; Staroverov, V. N.; Ragogna, P. J.; Baines, K. M., *J. Am. Chem. Soc.* **2007,** *129*, 15138-15139.
20. Kuhn, N.; Kratz, T.; Blaser, D.; Boese, R., *Chem. Ber.* **1995,** *128*, 245-250.
21. Lochschmidt, S.; Schmidpeter, A., *Phosphorus Sulfur Silicon Relat. Elem.* **1986,** *29*, 73-109.
22. Appel, R.; Knoll, F., *Adv. Inorg. Chem.* **1989,** *33*, 259-361.
23. Markovski, L. N.; Romanenko, V. D., *Tetrahedron* **1989,** *45*, 6019-6090.
24. Weber, L., *Angew. Chem. Int. Ed. Engl.* **1996,** *35*, 271-288.
25. Rupar, P. A.; Jennings, M. C.; Baines, K. M., *Organometallics* **2008,** *27*, 5043-5051.
26. Rupar, P. A.; Jennings, M. C.; Ragogna, P. J.; Baines, K. M., *Organometallics* **2007,** *26*, 4109-4111.
27. Katir, N.; Matioszek, D.; Ladeira, S.; Escudié, J.; Castel, A., *Angew. Chem. Int. Ed.* **2011,** *50*, 5352-5355.
28. Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E., *J. Am. Chem. Soc.* **2011,** *133*, 777-779.
29. Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S., *J. Chem. Soc., Chem. Commun.* **1995**, 1157-1158.
30. Jutzi, P.; Becker, A.; Stammler, H. G.; Neumann, B., *Organometallics* **1991,** *10*, 1647-1648.
31. Simons, R. S.; Pu, L. H.; Olmstead, M. M.; Power, P. P., *Organometallics* **1997,** *16*, 1920-1925.
32. Wegner, G. L.; Berger, R. J. F.; Schier, A.; Schmidbaur, H., *Organometallics* **2001,** *20*, 418-423.
33. Șeptelean, R.; Ranaivonjatovo, H.; Nemeş, G.; Escudié, J.; Silaghi-Dumitrescu, I.; Gornitzka, H.; Silaghi-Dumitrescu, L.; Massou, S., *Eur. J. Inorg. Chem.* **2006**, 4237-4241.

CHAPTER 3

1. Power, P. P., *Chem. Rev.* **1999,** *99*, 3463-3504.
2. Tokitoh, N.; Okazaki, R., *Adv. Organomet. Chem.* **2001,** *47*, 121-166.
3. Matsumoto, T.; Tokitoh, N.; Okazaki, R., *J. Am. Chem. Soc.* **1999,** *121*, 8811-8824.
4. Leung, W.-P.; Kwok, W.-H.; Zhou, Z.-Y.; Mak, T. C. W., *Organometallics* **2000,** *19*, 296-303.
5. Ding, Y.; Ma, Q.; Uson, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G., *J. Am. Chem. Soc.* **2002,** *124*, 8542-8543.
6. Ding, Y.; Ma, Q.; Roesky, H. W.; Uson, I.; Noltemeyer, M.; Schmidt, H.-G., *Dalton Trans.* **2003**, 1094-1098.
7. Foley, S. R.; Yap, G. P. A.; Richeson, D. S., *J. Chem. Soc., Dalton Trans.* **2000**, 1663-1668.
8. Leung, W.-P.; Chong, K.-H.; Wu, Y.-S.; So, C.-W.; Chan, H.-S.; Mak, T. C. W., *Eur. J. Inorg. Chem.* **2006**, 808-812.
9. Xiong, Y.; Yao, S.; Driess, M., *J. Am. Chem. Soc.* **2009,** *131*, 7562-7563.
10. Yao, S.; Xiong, Y.; Driess, M., *Chem. Commun.* **2009**, 6466-6468.
11. Yao, S.; Xiong, Y.; Driess, M., *Chem. Eur. J.* **2010,** *16*, 1281-1288.
12. Al-Rafia, I. S. M.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E., *Chem. Commun.* **2012,** *48*, 1308-1310.
13. Ghadwal, R. S.; Azhakar, R.; Pröpper, K.; Holstein, J. J.; Dittrich, B.; Roesky, H. W., *Inorg. Chem.* **2011,** *50*, 8502-8508.
14. Li, J.; Merkel, S.; Henn, J.; Meindl, K.; Döring, A.; Roesky, H. W.; Ghadwal, R. S.; Stalke, D., *Inorg. Chem.* **2010,** *49*, 775-777.
15. Tavčar, G.; Sen, S. S.; Azhakar, R.; Thorn, A.; Roesky, H. W., *Inorg. Chem.* **2010,** *49*, 10199-10202.
16. Filippou, A. C.; Chernov, O.; Stumpf, K. W.; Schnakenburg, G., *Angew. Chem. Int. Ed.* **2010,** *49*, 3296-3300.
17. Filippou, A. C.; Chernov, O.; Schnakenburg, G., *Chem. Eur. J.* **2011,** *17*, 13574-13583.
18. Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E., *J. Am. Chem. Soc.* **2011,** *133*, 777-779.
19. Inoue, S.; Driess, M., *Angew. Chem. Int. Ed.* **2011,** *50*, 5614-5615.
20. Barrau, J.; Balaji, V.; Mich, J., *Organometallics* **1989,** *8*, 2034-2036.
21. Sen, S. S.; Ghadwal, R. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D., *Organometallics* **2011,** *30*, 1030-1033.
22. Ding, Y.; Ma, Q.; Roesky, H. W.; Herbst-Irmer, R.; Uson, I.; Noltemeyer, M.; Schmidt, H.-G., *Organometallics* **2002,** *21*, 5216-5250.
23. van Almsick, T.; Loose, A.; Sheldrick, W. S., *Z. Anorg. Allg. Chem.* **2005,** *631*, 21-23.
24. Kromm, A.; Sheldrick, W. S., *Z. Anorg. Allg. Chem.* **2008,** *634*, 1005-1010.

25. Tokitoh, N.; Matsumoto, T.; Okazaki, R., *Tetrahedron Lett.* **1992,** *33*, 2531-2534.
26. Şeptelean, R.; Nemeş, G.; Escudié, J.; Silaghi-Dumitrescu, I.; Ranaivonjatovo, H.; Petrar, P. M.; Gornitzka, H.; Silaghi-Dumitrescu, L.; Saffon, N., *Eur. J. Inorg. Chem.* **2009**, 628-634.
27. Matsuhashi, Y.; Tokitoh, N.; Okazaki, R., *Organometallics* **1993,** *12*, 2573-2583.
28. Hitchcock, P. B.; Jang, E.; Lappert, M. F., *J. Chem. Soc., Dalton Trans.* **1995**, 3179-3187.
29. Tokitoh, N.; Saito, M.; Okazaki, R., *J. Am. Chem. Soc.* **1993,** *115*, 2065-2066.
30. Saito, M.; Tokitoh, N.; Okazaki, R., *Organometallics* **1996,** *15*, 4531-4536.
31. Saito, M.; Tokitoh, N.; Okazaki, R., *J. Am. Chem. Soc.* **2004,** *126*, 15572-15582.
32. Appel, R.; Casser, C., *Tetrahedron Lett.* **1984,** *25*, 4109-4112.
33. van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F., *Organometallics* **1996,** *15*, 174-180.
34. Bouška, M.; Dostál, L.; Padělková, Z.; Lyčka, A.; Herres-Pawlis, S.; Jurkschat, K.; Jambor, R., *Angew. Chem. Int. Ed.* **2012,** *51*, 3478-3482.
35. Hutchinson, B.; Nakamoto, K., *Inorg. Chim. Acta.* **1969,** *3*, 591-595.
36. Filippou, A. C.; Weidemann, N.; Philippopoulos , A. I.; Schnakenburg, G., *Angew. Chem. Int. Ed.* **2006,** *45*, 5987-5991.
37. Matioszek, D.; Katir, N.; Saffon, N.; Castel, A., *Organometallics* **2010,** *29*, 3039-3046.
38. Aysin, R.; Koroteev, P.; Korlyukov, A.; Zabula, A.; Bukalov, S.; Leites, L.; Egorov, M.; Nefedov, O., *Russ. Chem. Bull.* **2010,** *59*, 348-360.
39. Petz, W., *Chem. Rev.* **1986,** *86*, 1019-1047.
40. Tokitoh, N.; Manmaru, K.; Okazaki, R., *Organometallics* **1994,** *13*, 167-171.
41. Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O.; Lang, H.; Zsolnai, L., *J. Organomet. Chem.* **1985,** *282*, 331-348.
42. Jutzi, P.; Hampel, B.; Hursthouse, M. B.; Howes, A. J., *J. Organomet. Chem.* **1986,** *299*, 19-27.
43. Pu, L.; Twamley, B.; Haubrich, S. T.; Olmstead, M. M.; Mork, B. V.; Simons, R. S.; Power, P. P., *J. Am. Chem. Soc.* **2000,** *122*, 650-656.
44. Filippou, A. C.; Portius, P.; Winter, J. G.; Kociok-Köhn, G., *J. Organomet. Chem.* **2001,** *628*, 11-24.
45. Drew, D.; Doyle, J. R.; Shaver, A. G., *Inorg. Synth.* **1990,** *28*, 346-351.
46. Litz, K. E.; Henderson, K.; Gourley, R. W.; Holl, M. M. B., *Organometallics* **1995,** *14*, 5008-5010.
47. Yamashita, H.; Kobayashi, T.; Tanaka, M., *Organometallics* **1992,** *11*, 2330-2333.
48. Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W., *Organometallics* **2006,** *25*, 2851-2858.
49. Anandhi, U.; Sharp, P. R., *Inorg. Chim. Acta.* **2006,** *359*, 3521-3526.
50. Tiekink, E. R. T.; Kang, J.-G., *Coord. Chem. Rev.* **2009,** *253*, 1627-1648.

CHAPTER 4

1. Neumann, W. P., *Chem. Rev.* **1991,** *91*, 311-334.
2. Mizuhata, Y.; Sasamori, T.; Tokitoh, N., *Chem. Rev.* **2009,** *109*, 3479-3511.
3. Barthelat, J.-C.; Saint Roch, B.; Trinquier, G.; Satgé, J., *J. Am. Chem. Soc.* **1980,** *102*, 4080-4085.
4. Balasubramanian, K., *J. Chem. Phys.* **1988,** *89*, 5731-5738.
5. Kassaee, M. Z.; Buazar, F.; Soleimani-Amiri, S., *J. Mol. Struct. THEOCHEM* **2008,** *866*, 52-57.
6. Ehlert, T. C.; Margrave, J. L., *J. Chem. Phys.* **1964,** *41*, 1066-1072.
7. Boesveld, W. M.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; von Ragué Schleyer, P., *Chem. Commun.* **1999**, 755-756.
8. Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D., *Angew. Chem. Int. Ed.* **2009,** *48*, 5683-5686.
9. Filippou, A. C.; Chernov, O.; Schnakenburg, G., *Angew. Chem. Int. Ed.* **2009,** *48*, 5687-5690.
10. Filippou, A. C.; Chernov, O.; Blom, B.; Stumpf, K. W.; Schnakenburg, G., *Chem. Eur. J.* **2010,** *16*, 2866-2872.
11. Frison, G.; Sevin, A., *J. Chem. Soc., Perkin Trans. 2.* **2002**, 1692-1697.
12. Stabenow, F.; Saak, W.; Weidenbruch, M., *Chem. Commun.* **1999**, 1131-1132.
13. Jacobsen, H.; Ziegler, T., *J. Am. Chem. Soc.* **1994,** *116*, 3667-3679.
14. Rupar, P. A.; Jennings, M. C.; Baines, K. M., *Organometallics* **2008,** *27*, 5043-5051.
15. Ruddy, A. J.; Rupar, P. A.; Bladek, K. J.; Allan, C. J.; Avery, J. C.; Baines, K. M., *Organometallics* **2010,** *29*, 1362-1367.
16. Rupar, P. A.; Staroverov, V. N.; Baines, K. M., *Organometallics* **2010,** *29*, 4871-4881.
17. Kenney, J. W.; Simons, J.; Purvis, G. D.; Bartlett, R. J., *J. Am. Chem. Soc.* **1978,** *100*, 6930-6936.
18. Kassaee, M. Z.; Buazar, F.; Soleimani-Amiri, S.; Momeni, M. R., *J. Mol. Struct. THEOCHEM* **2009,** *899*, 46-53.
19. Bauschlicher, C. W.; Schaefer, H. F.; Bagus, P. S., *J. Am. Chem. Soc.* **1977,** *99*, 7106-7110.
20. Wegner, G. L.; Berger, R. J. F.; Schier, A.; Schmidbaur, H., *Organometallics* **2001,** *20*, 418-423.
21. Jutzi, P.; Becker, A.; Stammler, H. G.; Neumann, B., *Organometallics* **1991,** *10*, 1647-1648.
22. Fischer, R. C.; Power, P. P., *Chem. Rev.* **2010,** *110*, 3877-3923.
23. Lide, D. R., *CRC Handbook of Chemistry and Physics*. CRC Press: Boca Raton, Florida, 2009-2010.
24. Bundhun, A.; Ramasami, P.; Schaefer, H. F., *J. Phys. Chem. A.* **2009,** *133*, 8080-8090.
25. Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L., *Coord. Chem. Rev.* **2009,** *253*, 687-703.
26. Burns, W. A.; Leopold, K. R., *J. Am. Chem. Soc.* **1993,** *115*, 11622-11623.
27. Jonas, V.; Frenking, G.; Reetz, M. T., *J. Am. Chem. Soc.* **1994,** *116*, 8741-8753.

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