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PhD thesis

Sulfur(IV)/(VI) pincer-type ligands for the stabilization of metallylenes: synthesis, characterization and applications

Ligands soufrés (IV)/(VI) de type pince pour la stabilisation des métallylènes : synthèse, caractérisation et applications

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FOREWORD

General Information

All manipulations were performed in a dry, oxygen-free atmosphere of argon by using standard Schlenk-line and glove-box techniques. The solvents were purified using MBRAUN SBS-800 purification system.

The NMR spectra were recorded with a Bruker Avance II 300 apparatus: ¹H (300.13 MHz), ¹³C (75.48 MHz), ¹¹⁹Sn (111.92 MHz) at 298 K. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (¹H and ¹³C{1H}) or with an external reference (SnMe₄ for ¹¹⁹Sn). The NMR assignments were confirmed by COSY (¹H-¹H), HSQC (¹H-¹³C), and HMBC (¹H-¹³C) experiments.

Mass spectrometry (MS) spectra were measured with a Hewlett-Packard 5989A in the electron impact mode (70 eV). High-resolution mass spectrometry (HRMS) spectra were measured with a GCT Premier Waters in DCI mode (CH₄). Melting points were measured in a sealed capillary using the Stuart automatic melting point SMP40 apparatus. IR spectra were measured using a Varian 640-IR FT-IR spectrometer.

The X-ray data were collected at 193(2) K on a Bruker - AXS APEX II Quazar diffractometer, equipped with a 30 W air-cooled microfocus source using MoK α radiation (wavelength = 0.71073 Å). Phi- and omega- scans were used. The data were integrated with SAINT¹ and an empirical absorption correction with SADABS was applied.² The structures were solved by direct methods using SHELXS-97 and refined using a least-squares method on F^2 , ShelXL-2014/7 for compounds 9 and 10b and ShelXL-97 for 15.³ All non-H atoms were refined with anisotropic displacement parameters.

Calculations were carried out at the B3LYP/Def2-TZVP^{4,5} level of theory including Grimme's dispersion correction,⁶ and in addition at the M11-L/Def2-TZVP level of theory.^{5,7} All the calculations were performed using the Gaussian 09 package,⁸ including the Natural Bond Orbital (NBO)⁹ analysis for which the Gaussian implemented version of this programme¹⁰ was used.

Abbreviations

Ar	aryl
cod	1,5-cyclooctadiene
COSY	correlation spectroscopy
Ср	Cyclopentadienyl
dba	dibenzylideneacetone
Су	cyclohexyl
Dip	2,6-diisopropyl-phenyl
DFT	Density Functional Theory
DMSO	dimethyl sulfoxide
Et	ethyl
НМВС	Heteronuclear Multiple Bond Correlation
HMQC	Heteronuclear Multiple Quantum Coherence
<i>i</i> -Pr	isopropyl
IR	Infrared Spectroscopy
mCPBA	meta-chloroperoxybenzoic acid
Me	methyl
Mes	2,4,6-tri-methyl-phenyl
Mes*	2,4,6-tri-tert-butyl-phenyl
MS	Mass Spectrometry
NBO	Natural Bond Orbital
<i>n</i> -Bu	normal-butyl
NHC	N-heterocyclic carbenes
NMR	Nuclear Magnetic Resonance
Ph	phenyl
ppm	parts per million

rt	room temperature
<i>t</i> -Bu	<i>tert</i> -butyl
Tbt	2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
THF	tetrahydrofuran
Тір	2,4,6-tri -isopropyl-phenyl
TMS	trimethylsilyl
Tol	tolyl

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GENERAL INTRODUCTION

A few decades ago metallylenes, the heavier analogues of carbene, were merely chemical curiosities. Then, after the successful isolation of several divalent species, their chemistry began to develop, they became extensively studied. They proved to be versatile species due to their characteristic structure (lone pair of electrons, vacant p orbital in the singlet ground state) and amphoteric character. First their study was only for fundamental research, however several discoveries have shown promising possibilities for applications, thus the chemistry of metallylenes became a well-studied research field.

Studies showed that the ligand plays a key role in the stabilization and reactivity of these species, therefore the research of metallylenes presents a series of different substituents.

The present work is a study on metallylenes stabilized by sulfonyl and sulfinyl containing O,C,O-chelating pincer ligands.

Pincer ligands were first used to obtain transitional metal complexes, a field where they proved many times their efficiency, having an important part in the applications of these species in catalysis or material sciences. Lately pincer ligands are used also for stabilizing metallylenes, the literature presenting examples for germylenes, stannylenes and plumbylenes supported by different types of pincers.

The topicality of the chemistry of low valent heavier group 14 elements and the versatility of the pincer type ligands showed that there are still many aspects to explore in this field, thus the study of metallylenes with new sulfur containing pincer ligands offered a topic to research.

The present work is a study on metallylenes stabilized by sulfonyl and sulfinyl containing pincer ligands. It describes the design, synthesis and characterization of three types of pincer ligands and their use for obtaining stable metallylenes.

Chapter one is a bibliographic overview, first summing up generalities and most common examples of metallylenes and pincer ligands, then presenting a detailed literature study on the pincer-type ligand, their synthesis, most important characteristics and reactivity.

Chapter two presents the synthesis and characterization of a new *para* substituted bis-sulfonyl pincer ligand. Then it shows the synthesis, characterization and properties of a germylene and stannylene stabilized with the before mentioned pincer ligand.

The third chapter presents the synthetic routes and characterization of an asymmetric pincer-type ligand containing a sulfone group and a sulfoxide one. It also presents the synthesis and characterization of a germylene and stannylene and their reactivity.

In the fourth chapter there are presented the investigations on the bis-sulfinyl pincer ligand and its use in obtaining derivatives containing p-block elements.

This work is a study aiming to show the many potentials of these novel derivatives in their use as O,C,O chelating pincer ligands for metallylenes.

1. BIBLIOGRAPHIC REVIEW

1.1. Generalities about the metallylenes

The chemistry of divalent species of group 14 elements, known as metallylenes (heavier analogues of carbene) saw a great development in the last decades, due to their versatility. The synthetic routes, the investigation of the properties, stability and applications of these compounds are included in multiple reviews.^{1–3}

The metallylenes R_2M : (where M = Si, Ge, Sn, Pb) are divalent species, with preference for the $(ns)^2(np)^2$ configuration of the valence electrons and the singlet ground state. The singlet metallylenes have a vacant p-orbital and a lone pair of electrons with high s-character, as illustrated in Figure 1. ^{1,3}



Figure 1. Metallylenes in singlet ground state

These characteristics give the specific behavior and reactivity of the metallylenes, which will be discussed below.

For the synthesis of the divalent species of the heavier group 14 elements several synthetic routes are known, examples are depicted in Scheme 1.



Scheme 1. General synthetic routes to obtain metallylenes

The most common methods to obtain metallylenes are either through the reduction of a M(IV) species to M(II) or the substitution of a halogen atom in a M(II) halide.^{1–4} R₂M(II) derivatives can be obtained by the photolysis or thermolysis of acyclic or cyclic mono-, oligoor polymetallanes,⁴ among which the photochemical reductive elimination of a disilane R'₃Si-SiR'₃ to form a R₂M derivative is a method mostly employed in the case of silylenes and germylenes.^{3,4} Photochemical or thermal reduction of cyclic systems (metalliranes or metallirenes), containing one or more heavier group 14 elements, leads to the formation of divalent species by the elimination of olefins or alkynes. The reduction of R₂MX₂ dihalides (X = Cl, Br, I) with the use of a reducing agent also gives the target metallylenes.^{3,4} The substitution of a halogen atom of a M(II)X₂ species is also a widely used method to obtain MRX or MR₂ type derivatives. For the synthesis of stannylenes and plumbylenes this method is easily applicable because of the high stability of SnCl₂ and PbCl₂, while in the case of the germylene, the GeCl₂ precursor is used as a complex with 1,4-dioxane. This method is rarely used to obtain silylenes because the SiCl₂ is unstable in normal conditions and an NHC stabilized SiCl₂ derivative is known in the literature only since 2009.^{5–7}

The before mentioned characteristics (shown in Figure 1) are the source of the high reactivity and rapid dimerization of the metallylenes. They have two reactive sites in their

singlet ground state, as shown in Figure 1, the lone pair of electrons and the vacant p orbital, which give the ambiphilic character of these derivatives. They can behave either as an electrophile (Lewis acid) or a nucleophile (Lewis base) depending on the reagent. Among the most frequently seen reactivities of the metallylenes are reported the following: insertion, substitution, cycloaddition, reduction, oxidation and coordination reactions.^{1,3,4,8,9} Some examples of reactions for the metallylenes are presented in Scheme 2.



Scheme 2. Examples of reactions of the metallylenes

 $R_2M(II)$ type metallylenes in the presence of R'X reagents (X = halogen, OH) give insertion products, insertion reactions into C-O, C-H, Si-H, N-H, B-H, etc. lead to the formation of insertion products, and insertion into the sigma bonds of H₂ or NH₃ molecules was also showed to take place.^{3,4,10} Addition and cycloaddition reactions take place with alkenes, alkynes or other unsaturated compounds, while the formation of heavier ketone analogues is possible through oxidation reactions.^{3,4} In the case of halometallylenes RMX (R = organic group, X = halogen atom) the nucleophilic substitution of the halogen atom gives a large variation of products.^{8,9} Because of the existence of the lone pair of electrons, the formation of coordination complexes of metallylenes with transition metals is possible (Scheme 2).^{11,12} However, many studies showed, that the reactivity of the metallylenes is largely influenced by the nature of the ligand bonded to the divalent group 14 element.⁴

In order to isolate the metallylenes in their monomeric form different stabilization methods must be employed. One of the most frequently used methods is the kinetic stabilization by the use of bulky organic substituents. The ligands can sterically block the self-dimerization or oligomerization of the divalent species and also block the access to the highly reactive vacant p orbital, as illustrated on Figure 2.³ In the literature there are examples of metallylenes, where the use of bulky organic ligands such as Dis, Tip, Tbt, Mes^{*}, Dip led to the stabilization of metallylenes. ^{1,3}



Figure 2. Kinetic stabilization of metallylenes

Another method for stabilization of these species is by the thermodynamic effect of electron donating substituents linked to the central divalent atom, where electron density transfer takes place from the ligand into the empty p-orbitals of the central atom, compensating their electron deficiency as shown in Figure 3.³



M = Si, Ge, Sn, Pb

Figure 3. Thermodynamic stabilization of metallylenes

The substituents containing electron-donating heteroatoms like N, O, P, lead to the thermodynamic stabilization of these systems. Diamino-, diphosphino-, diaryloxy- and dialkoxy-substituted metallylenes of the type shown on Figure 4 were isolated and characterized.^{3,13}



Figure 4. Thermodynamically stabilized metallylenes

However, in most of the cases the stabilization of metallylenes is realized by the overall thermodynamic and kinetic stabilization effects of the substituents. There are also examples of metallylenes where the stabilization of the divalent center is realized through electron donation of a Lewis base into the vacant p orbital by intramolecular coordination of a donor group 'built-in' the ligand backbone or by intermolecular coordination of an electron donor, as shown in Figure 5.³



M = Si, Ge, Sn, Pb

Figure 5. Stabilization of metallylenes by inter- and intramolecular coordination

The most common examples for stabilization through intermolecular coordination are the metallylenes where an N-heterocyclic carbene is acting as a Lewis-base, as shown in Figure 6. In the literature there are several NHC stabilized metallylenes, starting from the dihalogeno-metallylenes³ to derivatives containing phosphaalkenyl moieties.^{14,15}



Figure 6. NHC stabilized metallylenes

Using monoanionic bidentate ligands such as amidinate or aminotroponiminate ligands an intramolecular $N \rightarrow M$ coordination contributes to the stabilization of divalent halogeno-metallylenes, as shown in Figure 7.^{3,16,17}



Figure 7. Amidinate and aminotroponiminate ligands stabilized metallylenes

Intramolecular coordination of the metallylenes can be achieved with the use of a ligand with a pendant arm, as seen in the examples presented in Figure 8.^{3,18,19}



Figure 8. Intramolecular stabilization of metallylenes with pendant arms containing ligands

Another method of stabilization is by the use of pincer-type ligands. In this case also, the intramolecular coordination plays an important role to obtain the metallylenes. This stabilization method is discussed in detail bellow.

1.2. Generalities about pincer ligands

The monoanionic, tridentate ligand platform, named "pincer ligands",²⁰ are commonly used in the field of the organometallic chemistry. They first appeared in literature in the 1970s. Their versatility was quickly noticed and since then they have been used in several areas. The importance of these ligands lies in the particular structure they exhibit and the properties induced by this. In the last few decades, the research led to the development of a considerable number of different pincer ligands, however, in this work, the focus is on the ECE'-type pincer ligands with aryl backbone.

The pincer ligands are considered a privileged ligand platform because of the possibilities to fine-tune their properties by bringing modifications to their structure (Figure 9).²¹



Figure 9. The pincer-type ligand and the possibilities to modify the structure

In all the complexes the ML_n metal or metalloid fragment is covalently bonded to the ligand through the monoanionic site, which can be a sp^2 or sp^3 hybridized C atom. Additionally, there are interactions with one or both of the neutral heteroatom donors. The majority of the pincer complexes have an aryl ring linked via a σ -bond to the metal or metalloid. The substituents on the backbone, usually in *para* position, can offer the modulation of the electronic density at the metal. The other major structural feature of the pincers is the flanking donor sites coordinated to the central atom, situated in the ortho position. The nature of the donor atoms, the length of the arm, and the substituents on the donor atoms create the environment around the metal and the ease to modify them allows a control over the properties of the complex.^{21,22}

Pincer ligands are mainly used in the chemistry of transition metals with applications in organic synthesis, catalysis, material science. The first examples of pincer ligand supported transition metal complexes were published in 1976 by Shaw²³, then a few years later by Kaska²⁴. In both cases the ligand is a PCP-type tridentate ligand with which Ni, Pd, Pt, Rh, Ir complexes were obtained (Figure 10). In the same time van Koten and Noltes reported an NCN-type pincer used in metalloid complexes containing Sn²⁵ and in transition metal complexes with Pt and Pd (Figure 10) ²⁶ The first SCS aryl pincer complex of Pd (Figure 10) was also described by Shaw.²⁷



Figure 10. First examples of pincer complexes

After this pioneering work, a great number of transition metal and metalloid complexes were published with different ligand platforms. The variation of the ligand backbone, the substituents on it, the flanking arms or the donor sites allowed access to a large number of compounds. There are several papers and books to review the pincer ligand supported complexes, the more important ones being the works of Gerard van Koten^{21,28} and David Morales-Morales²⁹. However, in the present work, the interest is on the aryl backbone supported, ECE'-type pincers.

To control the properties of the transition metal complexes, fact that is important later in the applications, the structure of the ligand can be modulated. In the case of the pincer ligands the most common modifications are at the level of the substituents on the central aromatic backbone or at the donor groups.

The effect of the substituents on the backbone was studied for different metal complexes. Beside the pincers with no substituents in *meta* and *para* position, there are examples of complexes functionalized either in *meta* or in *para* positions or both. These substituents include alkyl groups (Me, Et, t-Bu), aryl groups, halogens, NO₂, NH₂, OR, C(O)OR. Studies were conducted on the effect of the substituents on the properties of the complexes and it was shown that, depending on the functional groups, it is possible to modulate the electronic environment at the metal, to change the solubility of the compound, to adjust the chelating properties of the pincer and to influence the reactivity of the complex.^{30,31,32}

The choice of the *ortho* substituents on the central aromatic ring and the nature of the donor atoms is also an important aspect in the synthesis of pincer ligand supported complexes. The most common choices of donor atom are P, N, S, O, but there are other examples too. The phosphine group based PCP-type pincer ligands are very common, where the *ortho* substituents are generally either -CH₂-PR₂ or -O-PR₂, coordinating to the metal fragment through the P atom. Examples of such complexes are presented in Figure 11.^{21,29}



Figure 11. Pincer ligand stabilized transition metal complexes

Beside the multiple examples of transition metal complexes supported by different pincer-type ligands, tetravalent tin derivatives were also obtained. In Figure 12 examples of tetraorgano tin and diorgano-dihalogeno tin derivatives are presented where phosphonate based OCO-pincer type ligands were used.^{29,33}



Figure 12. Organotin(IV) derivatives with pincer ligands

Similarly, hypervalent silicon species were obtained with pincer-type ligands, as shown in Figure 13. ^{34–38}



Figure 13. Organosilicon species with pincer ligands

Encouraged by the results achieved using pincer-type ligands to obtain transition metal complexes or *p*-block element derivatives, metallylenes stabilized by such ligands were also studied.

1.3. Pincer ligand stabilized metallylenes

Pincer ligand stabilized divalent tin species were first mentioned in the literature in 1981.³⁹ Zuckerman and co-workers studied $SnCl[C_6H_3-2,6-(CH_2NMe_2)_2-]$, 2-CH₃OC₆H₄SnCl, 2-*i*-C₃H₇OC₆H₄SnCl, 2,4,6-(CH₃O)₃C₆H₂SnCl species by Mossbauer and IR spectroscopy and assumed the presence of divalent tin species with coordination through oxygen and nitrogen atoms, but the paper did not contain structural information.³⁹

The first completely characterized pincer ligand stabilized metallylene was synthesized by van Koten and co-workers in 1989.⁴⁰ The NCN-pincer ligand stabilized chlorostannylene was obtained starting from the corresponding lithiated ligand, as shown in Scheme 3.



Scheme 3. Synthesis of the first NCN-pincer ligand stabilized chlorostannylene

Starting from these promising results, the use of pincer ligands in the stabilization of divalent group 14 species started to grow. Although there are several examples of stannylenes supported by pincer-type ligands, only a scarce number of germylenes and plumbylenes are known up to date in the literature.

1.3.1 Germylenes

In the case of halogermylenes only NCN-pincer ligand stabilized species are presented in literature. Bibal et al. presented the first examples of divalent germanium compounds with these ligands. The chlorogermylenes were obtained by treating 2,6-bis(dialkylaminomethyl)- phenyl lithium with GeCl₂·dioxane,⁴¹ as shown in Scheme 4.



Scheme 4. Synthesis of NCN-pincer stabilized chlorogermylenes

The metallylenes were characterized by NMR spectroscopy and mass spectrometry. The NMR spectra show the signals for the central aromatic ring and reveal that in solution the amino-side chains are equivalent. The crystal and molecular structure of the germylene with the NCN-pincer ligand containing the -NEt₂ donor groups was determined by X-ray diffraction, evidencing the intramolecular N \rightarrow Ge coordination of 2.337(11) and 2.570(10) Å. The Ge-Cl bond is oriented almost orthogonal to the plane of the aryl ligand (97.2(4)°) with the bond length of 2.309(4) Å. Figure 14 shows the solid state structure of the amino-NCNpincer stabilized germylene.⁴¹



Figure 14. Solid state structure of the amino-NCN-pincer stabilized germylene⁴¹

These structural features of the compound suggest that the nitrogen atoms of the side chain interact with the vacant p orbitals of the germanium atom and the lone pair is localized in an orbital with high *s* character. Furthermore, the presence of a germanium – *ipso*-carbon back bonding is indicated by the surprisingly short Ge-C bond length (1.941(11) Å) compared to other chlorogermylenes (1.989(5)-2.402(3) Å).^{41–44} This is the result of the electronic effects of the N—Ge donation and the increased electrophilic character of the *ipso*-carbon through the withdrawing inductive effect of the *ortho* CH₂NEt₂ moieties.⁴¹

Next, the reactivity of the presented chlorogermylenes (Scheme 4)⁴¹ was also evaluated. There is the possibility to substitute the chlorine atom by other polar groups or the interaction of the germylenes with transition metals.

The first studies were realized with the goal to evidence a germyne⁴⁵. Although the pincer-germylenes were first mentioned in this paper, they were not isolated, their role was only as intermediaries to obtain the diazogermylenes, as shown in Scheme 5.⁴⁵



Scheme 5. Synthetic route to diazogermylenes

Through irradiation of the diazogermylene in the presence of a trapping agent, ArGe(OR²)₂CH₂SiMe₃ (Ar = 2,6-($R^{1}_{2}NCH_{2}$)₂C₆H₃, R^{1} = *i*-Pr, R^{2} =Me, *t*-Bu) species were formed, which were an evidence of a germyne intermediary.⁴⁵

The NCN-pincer ligand stabilized chlorogermylenes ArGeCl [Ar = 2,6-bis-((diethylamino) methyl)phenyl] proved to be good precursors to obtain functionalized germylenes ArGeNR₂ (R = SiMe₃, *i*-Pr) through nucleophilic substitution reactions.⁴⁶ The functionalized germylene ArGeN(*i*-Pr)₂ was used in reaction with 2,4,6-trimethylphenol to form an oxygermylene (Scheme 6)⁴⁶, to prove the reactivity of the covalent Ge-N bond. In reaction with W(CO)₅·THF, complexes were formed in the case of both germylenes ArGeNR₂ (R = SiMe₃, *i*-Pr), which were then used to form stable hydroxygermylenes, as presented in Scheme 6.⁴⁶



Scheme 6. Reactivity of the functionalized germylene ArGeNR₂

The crystallographic study of the hydroxygermylene-tungsten complex ArGeOH·W(CO)₅ showed shorter N→Ge interactions (2.113(3) Å) then in the germylene ArGeNR₂ (R = SiMe₃, *i*-Pr) (2.390(3) and 2.699(1) Å) due to the germanium-tungsten interaction.⁴⁶ In the case of the hydrolysis of the (bis(trimethylsilyl))aminogermylenetungsten complex ArGeN(SiMe₃)₂·W(CO)₅, beside the hydroxygermylene-tungsten complex presented in Scheme 6, a siloxygermylene-tungsten complex ArGeOSiMe₃·W(CO)₅ is also formed, explained by the hydrolysis of the silicon-nitrogen bond.⁴⁶ The imino-based NCN-pincer ligand, an *ortho*-iminophenyl NCN-pincer ligand was also employed to obtain halogermylenes. The germylene was obtained by adding GeCl₂·dioxane to the lithiated 2,6-diiminophenyl ligand, as presented in Scheme 7.⁴³



Scheme 7. Synthesis and reactivity of imino-based NCN-pincer ligand germylene

The crystal and molecular structure of the o-imino donor stabilized chlorogermylene was determined by X-ray diffraction and it showed that the nitrogen atoms of the *ortho* substituents are coordinated to the germanium atom, with a bond length of 2.247(3) Å and 2.62(1) Å, the latter considered a weak interaction. The solid state molecular structure of the ArGeCl [Ar = 2,6-diiminophenyl = 2,6-(2,6-*i*Pr₂C₆H₃NCH)₂C₆H₃] germylene is shown in Figure 15.⁴³



Figure 15. Solid state molecular structure of the imino-NCN-pincer stabilized germylene⁴³

The main interest in the study of the imino-NCN-pincer ligand was to obtain a digermylene and to evaluate its reactivity. By adding KC₈ in THF to the ArGeCl (Ar = 2,6-diiminophenyl), the expected digermylene was obtained. The synthetic route is shown in Scheme 7.⁴³ The X-ray analysis showed that the Ge-Ge bond has a single bond character with the bond length of 2.5059(5) Å and the Ge-N interactions are slightly shorter than in the starting ArGeCl germylene (1.986(3) and 2.036(3) Å). The reaction of this digermylene with KC₈ in Et₂O in the presence of tetramethylenediamine (tmeda) resulted in the cleavage of the Ge-Ge bond and the formation of a germanium-potassium complex, where the Ge is found as a germylidenide anion. The negative charge on the germanium atom is stabilized by the electron delocalization in the heterocycles. This anion could be obtained directly from the ArGeCl germylene too, with an excess of KC₈, as shown in Scheme 7.⁴³

With the purpose of isolating other functionalized germylenes, So et al. tested the reactivity of the germylene ArGeCl [Ar = $2,6-(2,6-iPr_2C_6H_3NCH)_2C_6H_3$] toward different compounds, as presented in Scheme 8.⁴⁷



Scheme 8. Reactivity of NCN-pincer based germylene

From the reaction of the ArGeCI [Ar = 2,6-(2,6-iPr₂C₆H₃NCH)₂C₆H₃] with Me₃SnOH a germylene hydroxide was obtained. It cocrystallizes with Me₃SnCl and the solid state structures show that interactions of the N atoms of the *ortho*-imino groups with the germanium atom are still present in the molecule, with a bond length of 2.493(11) and 2.325(10) Å.⁴⁷ When treating the ArGeCI [Ar = 2,6-(2,6-iPr₂C₆H₃NCH)₂C₆H₃] germylene with NaN₃, a germylene azide was formed, evidenced through NMR and IR spectroscopy , which subsequently was treated with 1-adamantylphosphaalkyne. The 1,3-dipolar cycloaddition resulted in a germanium(II) triazophosphole, as shown in Scheme 8.⁴⁷

Germylene ArGeCl [Ar = 2,6-(2,6-iPr₂C₆H₃NCH)₂C₆H₃] with excess of Ca in THF forms a germylidenediide dianion radical complex[ArGe]^{.2-}·Ca(THF)₃²⁺. The studies showed that the

reaction goes through a gemanium(I) radical [ArGe·].⁴⁴ When Mg excess is added to the ArGeCl germylene the formation of a dimer is observed.⁴⁴ The reactions are depicted in Scheme 9.



Scheme 9. Reaction of ArGeCl germylene with Ca and Mg

When the substituent on the N atom of the *ortho*-imino group in the 2,6bis(imino)phenyl ligand is changed from 2,6-diisopropylphenyl group to *tert*-butyl group, the reaction of stabilized germylene towards Li was investigated.⁴⁸ The ArGeCl germylene was obtained by the addition of n-BuLi followed by GeCl₂·dioxane to 2,6-bis-iminophenyl bromide ArBr [Ar = 2,6-(tBuNCH)₂C₆H₃]. The germylene thus formed was completely characterized, the solid state molecular structure showing Ge-N interactions of 2.2981(17) and 2.57(1) Å and Ge-Cl bond of 2.3477(5) Å, values comparable to those reported for ArGeCl where Ar = 2,6-(2,6-iPr₂C₆H₃NCH)₂C₆H₃.⁴⁸ In reaction with Li a bis-germylene was formed, as shown in Scheme 10. It was proposed that the imine moiety of the ligand is reduced to an imine radical anion which, through a C-C coupling reaction, forms the bisgermylene. By adding more Li to the bis-germylene, a lithium germylidenide is formed by C-C bond activation. The germylidenide anion can be formed directly from the ArGeCl germylene too (Scheme 10).⁴⁸



Scheme 10. Reaction of ArGeCl towards Li

A germylene with a similar structure, stabilized by a slightly modified pincer ligand than the one presented in Scheme 7 and Figure 15, was synthetized by Roesky and his team. The synthetic route and reactivity of the ArGeCl [Ar = $2,6-(2,6-iPr_2C_6H_3NCMe)_2C_6H_3$] is presented in Scheme 11.⁴⁹



Scheme 11. Synthesis and reactivity of an imino-NCN-pincer ligand based germylene

By treating the obtained chlorogermylene with $K[B(sec-Bu)_3H]$ the corresponding Ge(II) hydride was obtained and characterized.⁴⁹ The X-ray analysis reveals that the nitrogen atoms from the *ortho*-imino groups of the ligand coordinate to the germanium atom with the bond length 2.2722(15) and 2.2746(15) Å stabilizing the compound by donating electron density to the empty p orbital of the Ge atom.⁴⁹

Until now, in the literature there are no examples of germylenes stabilized by an OCO-pincer ligand beside the ones presented in this work.

1.3.2. Stannylenes

In the literature there are examples of several pincer ligand stabilized stannylenes. As mentioned before, the first NCN-pincer ligand stabilized stannylene was synthesized in 1989 by van Koten and his team,⁴⁰ as shown in Scheme 3. The 2,6-bis(dimethylaminomethyl)-phenyl pincer ligand based ArSnCl [Ar = 2,6-(Me₂NCH₂)₂C₆H₃] stannylene was completely characterized by NMR spectroscopy and X-ray diffraction. The NMR spectra present the characteristics for the pincer ligand. The solid state molecular structure (presented in Figure 16) shows that the 2,6-(CH₂NMe₂)₂C₆H₃ ligand binds in a tridentate fashion to the tin atom through the C1 atom of the aromatic ring and the coordination of the N atoms of the *ortho*-amino groups. The Sn-N interactions are of 2.525(8) and 2.602(8) Å, in the range of intramolecular tin-nitrogen distances. The Sn-Cl bond is oriented almost orthogonal to the plane of the aromatic ring (95.0(3)°) with a bond length of 2.488 Å.⁴⁰



Figure 16. Solid state molecular structure of the amino-NCN-pincer stabilized stannylene⁴⁰

Reaction of the ArSnCl [Ar = 2,6-(Me₂NCH₂)₂C₆H₃] stannylene with 4-tolyllithium gave a diaryltin(II) derivative, as shown in Scheme 12.⁴⁰ The diaryltin(II) compound undergoes oxidative addition in reaction with methyl-iodide, leading to an ionic tin(IV) iodide. A heaxacoordinate Sn(IV) compound was obtained by the oxidative addition of iodine I₂.^{40,50} The reactions are shown in Scheme 12.



Scheme 12. Reactivity of the NCN-pincer stabilized ArSnCl stannylene

Starting from the NCN-pincer stabilized chlorostannylene ArSnCl [Ar = 2,6- $(Me_2NCH_2)_2C_6H_3$] with the addition of K[sBu_3BH] an organotin(I) species was obtained, according to the reaction presented in Scheme 13. ⁵¹ The diorganodistannyne thus formed was characterized by NMR spectroscopy and X-ray analysis. The solid state molecular structure showed that the Sn-Sn bond length is 2.9712(12) Å, in the range of a single tin-tin bond. The Sn-N bond lengths vary between 2.585(9) and 2.631(9) Å, close to the values in the parent stannylene ArSnCl.⁵¹



Scheme 13. Synthesis of the ArSnSnAr

Redox-type reactions were carried out on the diorganostannyne ArSnSnAr [Ar = 2,6- $(Me_2NCH_2)_2C_6H_3$] described in Scheme 13 in the presence of chalcogens.^{52–54} S, Se and Te were used as oxidizing agents to show that the tin(I) atom forms an organotin(II) chalcogenate with an Sn-E-Sn unit (E = S, Se, Te), as depicted in Scheme 14, through a two-step oxidation and the cleavage of the Sn-Sn bond.^{52–54} In all three cases the organotin(II) chalcogenates were characterized by NMR spectroscopy and X-ray diffraction. The solid

state structures present the structural characteristics of a divalent tin species and show that the tin-chalcogene bond lengths are in the range of single bonds: 2.5944(5) and 2.6056(5) Å in the case of the Sn-Se bond,⁵² 2.4758(11) and 2.4889(11) Å in the case of the tin(II)sulfide,⁵³ 2.8974(3) and 2.7270(3) Å for the tin(II) telluride.⁵⁴ The intramolecular Sn-N distances vary between 2.520 and 2.685 Å, with no significant change from the values found in the distannyne ArSnSnAr suggesting comparable Lewis acidity of the tin atom. ^{51–54}



Scheme 14. Reaction of ArSnSnAr with chalcogens

In a large excess of selenium, an organotin(IV) selenide was formed, a triseleneoxostannonic acid anhydride is formed, with two terminal Sn-Se bonds, as shown in Scheme 14.⁵² In the case of sulfur and tellurium, the corresponding derivatives are not stable, and the formation of different derivatives with chalcogene and tin containing heterocycles was evidenced.^{53,54}

The reactivity of the NCN-pincer ligand stabilized stannylene ArSnCl $[Ar = 2,6-(Me_2NCH_2)_2C_6H_3]$ was tested toward transition metal complexes too. In reaction with Pd complexes the stannylene acts as a 2 electron-donor through the Sn atom (Scheme 15).⁵⁵



Scheme 15. Reaction of the ArSnCl stannylene toward Pd complexes

X-ray analysis showed that in the tin-palladium complex (ArSnCl)(2- $(Me_2NCH_2)C_6H_4$)PdCl the Pd(0)-Sn(II) distance of 2.4956(8) Å is relatively short compared to Pd-Sn bond length in similar derivatives.^{55–59} The Sn-N distances of 2.424(5) and 2.505(5) Å indicate the presence of intramolecular interactions.⁵⁵ In reaction with (PPh₃)₂PdCl₂ the formation of a dimeric derivative is observed, with the PdCl₂ moiety bridging two ArSnCl [Ar = 2,6-(Me₂NCH₂)₂C₆H₃] molecules, as shown in Scheme 15, with the Sn-Pd bond length of 2.5197(9) Å and the Sn-N distances of 2.422(1) and 2.499(1) Å.⁵⁵ The same complex can be obtained in the presence of Pd(PPh₃)₄. In this case it is presumed that ArSnSnAr is also formed in the reaction mixture.⁶⁰ A similar, iodide-substituted palladium complex is obtained from the ArSnCl in the presence of Pdl₂.⁵⁶

The $(ArSnCl)(2-(Me_2NCH_2)C_6H_4)PdCl$ complex can undergo Sn-Cl substitution in the presence of AgOC(O)CH₃ (AgOAc) to give a monoacetate substituted complex, presented in Scheme 16.⁶⁰ The geometric parameters of the acetate-substituted complex are similar to those of the chloro-substituted analogue. ^{55,60}



Scheme 16. Substitution reaction of the ArSnCl-Pd complex

The ArSnCl chlorostannylene $[Ar = 2,6-(Me_2NCH_2)_2C_6H_3]$ also reacts with bisacetonitrile dicarbonyl cyclopendadienyl molybdenium tetrafluoroborate to form a molybdenum complex, seen in Scheme 17.⁶⁰



Scheme 17. Formation of stannylene-Mo complex

The X-ray analysis of the Mo complex with ArSnCl stannylene shows a Sn-Mo bond length of 2.7195(9) Å, shorter than other examples, suggesting the strong donor capacity of the stannylene. The Sn atom is penta-coordinated, with the Sn-N intramolecular interactions of 2.494(6) and 2.567(7) Å.⁶⁰

Ruthenium and another palladium complex were obtained from the NCN-pincer chlorostannylene ArSnCI [Ar = 2,6-(Me₂NCH₂)₂C₆H₃].⁵⁷ In reaction with the allylpalladium(II) chloride dimer the complex [Pd(η^3 -C₃H₅)(ArSnCI)CI] is formed, as depicted in Scheme 18. The X-ray analysis shows that the stannylene is coordinated to the palladium atom with a Sn-Pd distance of 2.5556(5) Å and the N-Sn coordination distances of 2.456(4) and 2.507(4) Å are not affected by the coordination to the Pd atom.⁵⁷



Scheme 18. Formation of stannylene-palladium and -ruthenium complexes

Ruthenium complexes of the ArSnCl stannylene [Ar = 2,6-(Me₂NCH₂)₂C₆H₃] were also obtained, with $[(\eta^{6}-\text{benzene})\text{RuCl}]_{2}(\mu-\text{Cl})_{2}$ or $[(\eta^{6}-\text{ cymene})\text{RuCl}]_{2}(\mu-\text{Cl})_{2}$ and $[(CO)_{3}\text{RuCl}]_{2}(\mu-\text{Cl})_{2}$ (Scheme 18 and Scheme 19). Similarly a Rh complex was also formed with $[(CO)_{2}\text{Rh}]_{2}(\mu-\text{Cl})_{2}$ (Scheme 19).⁵⁷



Scheme 19. Synthesis of stannylene-Ru and -Rh complexes

Similarly to the stannylene ArSnCl - Pd complex $[Ar = 2,6-(Me_2NCH_2)_2C_6H_3]$, platinum complexes were obtained and characterized, the reactions are depicted in Scheme 20.⁵⁶ In both cases the tin atoms are pentacoordinated, with the Sn-Pt distances of 2.4865(4) (Cl substituted Pt) and 2.5532(5) Å (I substituted Pt) and the Sn-N interactions between

2.439(4) and 4.526(5) Å.⁵⁶ The iodine substituted platinum complex is formed by adding Nal to the chlorine substituted stannylene-platinum complex. A halogen exchange is observed on the tin and platinum atoms and the formation of the *trans* isomer, considering the halogen atoms.⁵⁶



Scheme 20. Formation of the stannylene-platinum complexes

The reactivity of the stannylene-platinum complex was tested towards Na(pyt) (pyt = pyridine-2-thionate), as presented in Scheme 21.^{61,62} The formation of a mixture of new complexes was observed. The structure of the platinum complex with the Sn-Pt bond supported through the pyridine-2-thionate was determined by X-ray diffraction, showing a six-coordinate tin(II) atom with a distorted octahedral geometry. The analysis of the geometrical parameters of the complex and an NBO analysis revealed that the tin-platinum interaction is formed through the donation from a stannylidenium (ArSn^{II})⁺ fragment to a [Pt(pyt)₂Cl]⁻ anion. ⁶¹ The same process can be observed with the iodine analogue, but with a slightly different structural arrangement.⁶²


Scheme 21. Reactivity of the pincer stannylene ArSnCl - Pt complex

A tungstenpentacarbonyl organostannylene complex $ArSn(Cl)W(CO)_5$ [Ar = 2,6-(Me₂NCH₂)₂C₆H₃] was prepared as shown in Scheme 22. ⁶³ The X-ray analysis shows, that the tin atom is five-coordinated with a distorted square-pyramidal configuration and the Sn-N distances of 2.543(3) and 2.5526(3) Å. From the reaction of the stannylene-tungsten complex with AgCB₁₁H₁₂ the formation of an organostannylidenium carboranate aqua complex is observed, according to Scheme 22. ⁶³



Scheme 22. Synthesis and reactivity of a stannylene-tungsten complex

The stannylene-tungsten complex ArSn(Cl)W(CO)₅ [Ar = 2,6-(Me₂NCH₂)₂C₆H₃] forms the corresponding tin(II) hydride in reaction with K[sBu₃BH], which can further undergo hydrolysis to give a tin(II) hydroxide, as presented in Scheme 23. The X-ray analysis of the hydroxide derivative reveals a μ -hydroxido-bridged dimer. ⁶⁴



Scheme 23. Reactivity of the stannylene-tungsten complex

In a similar manner to the stannylene-tungsten complex, a chromium complex $ArSn(CI)Cr(CO)_5$ [Ar = 2,6-(Me₂NCH₂)₂C₆H₃] was also obtained, which by treatment with NaOMe formed a tin(II) methoxide, as depicted in Scheme 24. The formation of the compounds was evidenced by NMR and IR spectroscopy.⁶⁵



Scheme 24. Synthesis and reactivity of stannylene-chromium complex

Through hydrolysis, the tin(II) methoxide gives a μ -hydroxido-bridged dimer, as presented in Scheme 25. The X-ray analysis shows that the Sn-N distances of 2.514(2) Å are similar to those in the chlorostannylene ArSnCl [Ar = 2,6-(Me₂NCH₂)₂C₆H₃]. By treatment with HOTf, a cyclization product is formed and the deamination of the Me₂N-CH₂- moiety is observed with the formation of a new C-O bond, as shown in Scheme 25.



Scheme 25. Reactivity of the stannylene-chromium complex

The imino-based pincer type ligands used to stabilize the germylenes proved to have the same effect in the case of the stabilization of the divalent tin species.

A new stannylene was prepared by adding *n*-BuLi then SnCl₂ to 2,6-bis[N-(2',6'diisopropyl phenyl)ketimino]phenyl-1-bromide, according to Scheme 26. Treatment of the stannylene ArSnCl [Ar = $\{2,6-iPr_2C_6H_3NC(CH_3)\}_2C_6H_3$] with KC₈ gave a bis-stannylene with a Sn-Sn bond, as shown in Scheme 26.⁶⁶ The solid state structure of the ArSnSnAr shows two unsymmetrically coordinated tin atoms with +1 oxidation state. One of the tin atoms is fourcoordinated; interactions with both of the N atoms of the *ortho* substituents can be observed (2.6879(17) and 2.4129(16) Å). The second tin atom is coordinated to only one of the nitrogen atoms with a distance of 2.2228(16) Å, which is considerably shorter than the other Sn-N distances. The Sn-Sn bond length is 2.8981(9) Å.⁶⁶ The bis-stannylene ArSnSnAr activates P₄, a selective cleavage of one P-P bond is observed, forming a new derivative with one P₄ tetrahedron inserted into the Sn-Sn bond, and the two tin atoms symmetrically fourcoordinated, as depicted in Scheme 26.⁶⁶



Scheme 26. Synthesis and reactivity of imino-NCN-pincer stabilized stannylene

Similarly to the diimino-NCN-pincer stabilized germylene (Scheme 11), the tin analogue ArSnCl [Ar = $\{2,6-iPr_2C_6H_3NC(CH_3)\}_2C_6H_3$] forms the corresponding hydride in the presence of K-selectride, as shown in Scheme 27.⁴⁹ The solid state structure shows that the tin atom is four-coordinated with the Sn-N interactions of 2.4538(3) and 2.4664(14) Å.⁴⁹



Scheme 27. Synthesis of the diimino-NCN-pincer stannylene hydride

Stannylenes were obtained with slightly modified 2,6-diiminophenyl ligands too, as

depicted in Scheme 28.^{18,67} Using 2,6-dimethylphenyl and *tert*-butyl as substituents on the *ortho*-imino groups of the 2,6-bis(imino)phenyl ligand, NCN-pincer stabilized chlorostannylenes of the type ArSnCl were obtained and characterized. In the case of the stannylene ArSnCl [Ar = 2,6-(CHN*t*Bu₂)₂C₆H₃] the X-ray analysis showed the Sn-N distances of 2.507(2) and 2.597(2) Å, similar to other Sn-N interaction, however the Sn-Cl bond of

2.5624(5) Å was observed to be slightly longer than in other chlorostannylenes.⁶⁷ In the presence of KC₈, in both cases, a distannyne was obtained and characterized. The solid state structures showed the Sn-Sn bond length of 2.9250(5) Å [Ar = 2,6-(CHN(2',6'-Me₂-C₆H₃)₂C₆H₃], 2.9491(4) Å [Ar = 2,6-(CHNtBu)₂C₆H₃], indicating Sn-Sn single bond, whereas the Sn-N interactions are comparable to intramolecular Sn-N coordinatons.^{18,67} The reaction of the distannyne obtained with the NCN-pincer ligand 2,6-(CHNtBu)₂C₆H₃, with excess of KC₈ led to the cleavage of the tin-tin bond and forms a potassium stannylidenide ArSnK·THF. The K atom is coordinated with a THF molecule and is η^5 -coordinated to the SnCCCN five-membered ring, where an electron delocalization is likely in order to stabilize the negative charge on the tin atom (Scheme 28).⁶⁷



Scheme 28. Synthesis and reactivity of 2,6-diiminophenyl ligand stabilized stannylenes

Beside the diamino and diimino based NCN-pincer ligand, OCO-type pincers were also employed for the stabilization of stannylenes, using alkoxy-methylene moieties or phosphonate groups in *ortho* position of the central aromatic ring.

Using an OCO-type pincer ligand, where the *ortho* substituents on the aromatic ring are O-donor ether groups, ArSnCl (Ar = $2,6-(ROCH_2)_2C_6H_3$ and R = Me and *t*-Bu) stannylenes were synthesized, as illustrated on Scheme $29.^{68,69}$ Both stannylenes were characterized by NMR spectroscopy and mass spectrometry, exhibiting the characteristics for a pincer stabilized chlorostannylene. ⁶⁹



Scheme 29. Synthesis of OCO-pincer stabilized stannylene and stannylene-tungsten complex

By adding W(CO)₅SnCl₂ to $[2,6-(ROCH_2)_2C_6H_3]Li$ (R = Me, *t*-Bu) stannylene pentacarbonyl-tungsten complexes were obtained, as presented in Scheme 29. The solid state structures show that the Sn-O interactions in the methyl-substituted complex are of 2.391(5) and 2.389(5) Å, while in the *tert*-butyl substituted one 2.464(3) and 2.513(3) Å. The Sn-Cl bond length in the methyl-substituted complex is 2.440(15) Å and in the *tert*-butyl substituted complex is 2.382(11) Å. These values, along with the data gained from the NMR spectroscopy suggest that the O—Sn coordination is influenced by the substituents on the oxygen atom in the *ortho*-substituents of the aromatic ring in the pincer ligand, stronger in the methyl substituted complex than in the *tert*-butyl substituted one. The interactions increase the stability of the complexes, so that the methyl-substituted stannylene-tungsten complex is stable at exposure to air.⁶⁹ The reaction of this complex with K[*s*-Bu₃BH] results in the formation of the corresponding stannylene-tungsten hydride. The NMR spectroscopy indicates the characteristic data for such compounds.⁶⁹

In a similar manner, a chromium complex was also obtained, as shown on Scheme 30. ⁷⁰ $Cr(CO)_5SnCl_2\cdot THF$ was added to $[2,6-(MeOCH_2)_2C_6H_3]Li$ to form a stannylenepentacarbonylchromium complex. The structure of the complex is similar to that with tungsten (Scheme 29), the Sn-O distances are of 2.393(3) and 2.409(3) Å, suggesting strong interactions. Starting from the chlorostannylene chromium complex, an organostannylidenium trifluorosulfonate aqua complex is formed in the presence of AgOTf, while with $Ag[CB_{11}H_{12}]$ the stannylidenium carbaborate was obtained.⁷⁰



Scheme 30. Synthesis and reactivity of stannylene-chromium complex

Another mono-anionic OCO-pincer ligand, 4-*t*-Bu-2,6-[P(O)(OEt)₂]₂-C₆H₂, was synthesized then employed for the stabilization of low valent tin derivatives.^{33,71,72} By adding LDA then SnCl₂, SnBr₂, or SnI₂, ArSnX [X = Cl, Br, I Ar = 4-*t*-Bu-2,6-[P(O)(OEt)₂]₂-C₆H₂] stannylenes were obtained, as shown on Scheme 31. The NMR, IR and Mössbauer spectroscopy showed characteristics for heteroleptic organostannylenes. The ¹¹⁹Sn NMR spectra exhibit triplet signals at -100 ppm for the chlorostannylene, at -68 ppm for the bromostannylene and at -22 ppm for the iodostannylene, in all three cases with a coupling constant ¹¹⁹Sn-³¹P of 116-117 Hz.^{71,72} A halogenostannylenes were also obtained with a slightly modified ligand, using isopropoxy- instead of ethoxy-groups as substituents on the phosphorus atoms at the *ortho* positions of the aromatic ring.⁷² The data acquired by NMR and Mössbauer spectroscopy are in accordance with the structural change of the halogenostannylenes stabilized by the phosphonate based OCO-pincer ligand. The X-ray analysis of the ArSnX stannylenes show that the Sn-O distances are between 2.408 and 2.478 Å, suggesting strong interactions.⁷²



Scheme 31. Synthesis of the phosphonate OCO-pincer stabilized stannylenes

Nucleophilic substitution of the halogen takes place in the presence of different compounds, as depicted in Scheme 32.⁷¹ The chlorostannylene reacts with lithium derivatives to give new divalent tin compounds. The data collected from NMR spectroscopy and X-ray analysis shows the characteristics of such compounds.^{71,72}



Scheme 32. Substitution reactions of the OCO-pincer stabilized stannylenes

Oxidative addition at ArSnX stannylenes $[X = Cl, Br, Ar = 4-t-Bu-2,6-[P(O)(OEt)_2]_2-C_6H_2]$ was achieved by adding sulfur, bromine or $Ph_3C^+PF_6^-$ giving tetravalent tin derivatives as shown in Scheme 33.⁷¹



Scheme 33. Reactivity of the OCO-pincer stannylenes

By adding SnCl₄ to the chlorostannylene ArSnCl [Ar = 4-*t*-Bu-2,6-[P(O)(OEt)₂]₂C₆H₂], a redox process takes place to form a trichlorotin derivative, as shown in Scheme 34,⁷³ where the tin atom is hexacoordinated. The ¹¹⁹Sn chemical shift at -528.8 ppm suggests the high donor capacity of the OCO-pincer ligand, with strong Sn-O interactions. The X-ray analysis shows the Sn-O interactions of 2.225(3) and 2.221(3) Å.⁷³



Scheme 34. Reactivity of the ArSnCl stannylene $[Ar = 4-t-Bu-2,6-[P(O)(OEt)_2]_2C_6H_2]$ towards SnCl₄

Tin(II) containing cations of the ArSnCl stannylene [Ar = 4-t-Bu-2,6-[P(O)(Oi-Pr)_2]_2C₆H₂] were obtained stabilized by intermolecular coordination of the Lewis bases 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (NHC^{Dip}) or 4-dimethylaminopyridine (DMAP), as shown in Scheme 35.⁷⁴ The structural features of the products exhibit some steric constraints and a high s character of the lone pair of electrons on the tin atoms. In the ¹¹⁹Sn NMR spectra the triplet signals at -169 and -170 ppm, respectively, show the similar electronic environment of the tin atoms. The tin(II)–DMAP adduct in reaction with elemental sulfur gives a dimeric derivative linked by a four-membered ring, maintaining the positive charge, as depicted in Scheme 35.⁷⁴



Scheme 35. Tin(II) cations stabilized by NHC^{Dip} and DMAP

Transition metal complexes were also obtained starting from the OCO-pincer stabilized stannylenes ArSnCl [Ar = 4-t-Bu-2,6-[P(O)(OR)₂]₂C₆H₂ R = Et, *i*-Pr], forming tungsten, chromium and iron complexes, as shown on Scheme 36.^{71,72,75} The ¹¹⁹Sn NMR spectra show high frequency shifts for the signals of the complexes compared to the ArSnCl

stannylene. The solid state structures show the Sn-O bond lengths to vary between 2.313(2) and 2.354(2) Å suggesting stronger interactions than in the starting stannylenes. 71,72,75



Scheme 36. Formation of stannylene-transition metal complexes

In the case of ArSnCl chlorostanylene where Ar = 4-t-Bu-2,6-[P(O)(O*i*-Pr)₂]₂C₆H₂, the tungsten-pentacarbonyl complex undergoes a halogen exchange in the presence of an excess of KF to form a fluorido-substituted stannylene complex. The fluoride-substituted stannylene complex reacts with Ph₂PSiMe₃ to form a diphenylphosphanido-substituted derivative, which in the presence of W(CO)₅·THF gives a trimetallic complex through coordination of the lone pair of electrons of the phosphorus atom, as presented in Scheme 37.⁷⁵



Scheme 37. Reactivity of the stannylene-tungsten complex

The chromium-pentacarbonyl stannylene complex ArSnCl(Cr(CO)₅) Ar = 4-*t*-Bu-2,6-[P(O)(O*i*-Pr)₂]₂C₆H₂] undergoes substitution reactions of the chlorine atom, according to Scheme 38. Triflate- and perchlorate- substituted stannylenes were obtained by adding AgOTf or AgClO₄ to the stannylene-chromium complex. The structural features of the substituted complexes are similar to the starting chlorine-substituted complex. Further substitution takes place with the addition of 4-dimethylaminopyridine or triphenylphosphane oxide to form donor stabilized tin(II) perchlorate salts.⁷⁶



Scheme 38. Reactivity of the stannylene-chromium complex

Other transition metal complexes of the ArSnCl stannylene [Ar = 4-*t*-Bu-2,6-[P(O)(O*i*-Pr)₂]₂C₆H₂] were obtained with platinum, palladium and ruthenium, as shown in Scheme 39.^{56,77} The NMR spectroscopic analysis and X-ray diffraction show the characteristics for Pd, Pt and Ru complexes, where the stannylenes act as ligands for the metals through coordination of their lone electron pair. The Sn-M (M = Pt, Pd, Ru) distances and the Sn-O distances are in the range of values for similar compounds.^{56,77}



Scheme 39. Formation of stannylene-palladium, -platinum and -rhutenium complexes

Stannylene complexes were obtained containing two transition metal moieties by adding HW(CO)₃Cp to the ArSnCl stannylene or to its chromium complex ArSnCl(Cr(CO)₅) [Ar = 4-t-Bu-2,6-[P(O)(O*i*-Pr)₂]₂C₆H₂], as presented in Scheme 40.⁷⁸ In the first case the ArSn{W(CO)₃Cp]₂][W(CO)₃Cp] is formed through a spontaneous auto-ionization process of the intermediary ArSn{W(CO)₃Cp}₃ species. The two complexes were shown to be isoelectronic.⁷⁸



Scheme 40. Synthesis of stannylene-metal complexes

A ferrocenyl-bridged bis-stannylene was obtained from the ArSnCl stannylene Ar = 4t-Bu-2,6-[P(O)(Oi-Pr)₂]₂C₆H₂] by adding 1,1'-dilithiumferrocenyl, as shown in Scheme 41.⁷⁹ Then, in reaction with W(CO)₆ and C₇H₈Cr(CO)₄ transition metal complexes were obtained where the bis-stannylene acts as a bis-monodentate ligand (in the case of the tungsten complex) or as a bidentate-chelating ligand (in the case of the chromium complex). These compounds were tested for their redox activity by electrochemical techniques, showing that the stannylene moieties act as electron donors, increasing the electron density on the ferrocene core, resulting an easier oxidation than in the case of the unsubstituted ferrocene.⁷⁹



Scheme 41. Formation of the ferrocenyl-bridged bis-stannylene

The reaction of ArSnCl stannylene [Ar = 4-t-Bu-2,6-[P(O)(O*i*-Pr)₂]₂C₆H₂] with KC₈ or sodium naphthalenide gives an organotin(I) derivative ArSnSnAr, as shown in Scheme 42.⁸⁰ The solid state structure reveals that the Sn-Sn bond length is of 3.0486(6) Å, suggesting a single bond. The Sn-O interactions of 2.430(2) and 2.427(2) Å are slightly longer than in the starting stannylene. The ArSnSnAr tin(I) compound disproportionates to form a diorganostannylene ArSnAr and elemental tin. The organotin(I) compound in the presence of PhI(OAc)₂ gives a tin(II) acetate, as shown in Scheme 42.⁸⁰



Scheme 42. Synthesis and reactivity of tin(I) derivative

The organotin(I) derivative ArSnSnAr [Ar = 4-*t*-Bu-2,6-[P(O)(O*i*-Pr)₂]₂C₆H₂] reacts with diaryl dichalcogenides (Ar-E-E-Ar, E = S, Se, Te, R = Ph, Py) to give divalent and tetravalent tin derivatives, as shown in Scheme 43. In the tin(II) chalcogenoarylates the tin atom is four coordinated and the Sn-O interactions have values between 2.4069(17) and 2.4971(17) Å, close to those in the ArSnCl chlorostannylene. The C(ipso)-Sn-E (E = S, Se, Te) bond angles are relatively small (85.45(6)° – 89.56(5)°) suggesting a high s character of the lone electron pair on the divalent tin atom. When adding PySSPy, a tetravalent tin derivative is formed with three –SPy groups linked to the tin atom, then after heating gives a benzoxaphosphastannole derivative through a cyclization reaction, as shown in Scheme 43.⁸¹



Scheme 43. Reactivity of the tin(I) ArSnSnAr [Ar = 4-t-Bu-2,6-[P(O)(Oi-Pr)₂]₂C₆H₂] derivative

Reaction of the ArSnCl stannylene $[Ar = 4-t-Bu-2,6-[P(O)(Oi-Pr)_2]_2C_6H_2]$ with BF₃·OEt₂ gave an adduct with an O \rightarrow BF₃ interaction, as shown in Scheme 44. The structural analysis shows very different Sn-O coordinations, with the bond lengths of 2.222(2) and 2.7477(18) Å, as a result of the O-BF₃ coordination. The ¹¹⁹Sn NMR exhibits two signals explained by an equilibrium between the ArSnCl stannylene and its adduct with BF₃.⁸²



Scheme 44. Formation of the stannylene-BF₃ adduct

1.3.3. Silylenes and plumbylenes

Up to date there are no examples of divalent silicon derivatives stabilized by pincertype ligands. In the case of plumbylenes, there are a few examples where the stabilization is realized through a pincer ligand, however these were not as much investigated as the corresponding germanium and tin species.

An ArPbBr plumbylene [Ar = 2,6-(CHN(2,6-*i*-Pr₂C₆H₃)₂C₆H₃)] was obtained, as shown in Scheme 45. The NMR spectra show characteristic signals for pincer ligand stabilized metallylenes while the X-ray analysis reveals that the 2,6-diiminophenyl group acts as a tridentate ligand to the divalent Pb atom. The Pb-N interactions are 2.637(16) and 2.691(17) Å. The reaction of the ArPbBr plumbylene with Li in excess led to the formation of a plumbylidene anion. The treatment with SnCl₂ in THF gave the ArPbPbAr 2,6-diiminophenyllead(I) dimer, as presented in Scheme 45.⁸³



Scheme 45. Synthesis and reactivity of the NCN-pincer stabilized plumbylene

Phosphonate based OCO-pincer ligands were also used to obtain ArPbCI plumbylenes [Ar = 4-t-Bu-2,6-[P(O)-OR)₂]₂C₆H₂, R = Et, *i*-Pr), as shown in Scheme 46.^{33,72,84} The NMR data reveals the characteristics of metallylenes stabilized by such ligands. The

solid state structures show that the Pb-O distances are 2.518(2) Å in the ethoxy substituted pincer ligand and 2.560(2) Å in the isopropoxy substituted analogue.^{72,84} In the case of the ethoxy substituted ligand the reactivity of the plumbylene was tested towards lithium diisopropylamide, lithium bis(trimethylsilyl)methane and sodium thiophenolate to give the corresponding organolead(II) derivatives, as shown in Scheme 46.⁸⁴



Scheme 46. Synthesis and reactivity of the OCO-pincer stabilized plumbylenes

1.4. Conclusions

The metallylenes, divalent species of group 14 elements, present a series of different reactivities owing to their particular structure with a lone pair of electrons and vacant p orbital. Several types of ligands with steric and electronic stabilization effect were used to obtain the metallylenes, however there are considerably fewer examples with pincer-type ligands. The literature presents metallylenes isolated with the use of N,C,N-chelating pincer ligands containing imino groups or amino-methylene moieties, O,C,O-chelating pincers with phosphonate groups or alkoxy-methylene moieties. There are a significant number of stannylenes obtained with such ligands, but only a few examples for germylenes and plumbylenes.

All these divalent species stabilized by the chelating effect of the pincer ligands present the characteristic reactivity of metallylenes and it was shown that the modulation of the pincer ligand induce changes on the behavior of the metallylenes. However, sulfonyl and sulfinyl based pincer ligands are less studied, there is only a sole example of stannylene with such a ligand described by our group.⁸⁵ These observations encouraged us to explore this subject in order to evaluate the effect of different sulfonyl and sulfinyl containing pincer ligands on the stabilization of metallylenes. Thus, three O,C,O-chelating ligands were designed, synthetized and studied, a bis-sulfonyl pincer ligand, containing two sulfone groups in *ortho* position of the central aromatic ring, a sulfone-sulfoxide pincer ligand, with one sulfone group and one sulfoxide group and a bis-sulfoxide type pincer ligand containing two sulfoxide groups.

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1.5. References

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ORIGINAL CONTRIBUTIONS

2. BIS-SULFONE LIGAND

2.1. Introduction

In the first chapter the advantages of the pincer-type ligands were presented in their role for the stabilization of metallylenes. Based on these data from the literature, a novel pincer ligand was envisioned, containing sulfonyl groups in the *ortho* position of the central aromatic ring, an *O*,*C*,*O*-chelating, SO₂-C-SO₂ donor system, which was not observed before. The originality of this ligand system is owed first for the presence of the sulfonyl groups as oxygen donors, then by its " E_2CE_2 " (E = O) donor character, different than the before presented ECE-type pincers (E = O, N). The efficiency of the novel *O*,*C*,*O*-chelating O₂S-C-SO₂ pincer system lies in its ability to act as an adjustable ligand in metallylenes thanks to the presence of two chelating oxygen atoms on each sulfur atom of the sulfonyl groups, as illustrated in Figure 17.



Figure 17. Adjustable character of the bis-sulfone ligand system

The pincer-type ligands containing the sulfonyl moieties could provide the intramolecular stabilization of the metallylenes by the coordination of either one of the oxygen atoms of the sulfonyl groups, leading to metallylenes with particular characteristics.

This chapter presents at first a summary on the preliminary results obtained on the bissulfone based pincer-type ligand, previously reported.^{1,2} Then the original contributions on a *para*-substituted bis-sulfone ligand will be presented, highlighting its versatility in the stabilization of metallylenes.

2.1. First bis-sulfone ligand and stannylene – preliminary results

The bis-sulfone ligand was first described in 1995, obtained through a coupling reaction (aromatic nucleophilic substitution) between 1,3-benzenedithiol and an iron cyclopentadienyl complex, followed by oxidation with mCPBA, then photolysis (Scheme 47).³



Scheme 47. Synthesis of bis-sulfone through photolysis

The same bis-sulfone was then synthetized in our group, via two other methods. One method consisting of a palladium catalysed cross coupling reaction between *para*-toluene thiol and 1,3-diiodobenzene to form the bis-thioether, followed by an oxidation reaction with mCPBA to obtain the target bis-sulfone (Scheme 48).^{1,2}



Scheme 48. Synthesis of the bis-sulfone by oxydation reaction

Another method was also developed, a one-step reaction, via a palladium catalysed cross-coupling reaction between 1,3-diiodobenzene and sodium *para*-toluene sulfinate (Scheme 49). The resulting bis-sulfone was completely characterized by the usual physico-chemical and computational methods.



Scheme 49. Synthesis of bis-sulfone by direct coupling reaction

Crystal and molecular structures were obtained for both the *cis* and *trans* rotameric conformations (Figure 18).¹ The bis-sulfone crystallizes in the *cis* rotameric conformation when single crystals were obtained in toluene and in the *trans* rotameric form when using THF.



The above described bis-sulfone was then used to obtain new metallylenes. The deprotonation of the ligand was realized by adding *n*-BuLi in toluene at -40°C. Then the carbanion was added to a suspension of $SnCl_2$ or $GeCl_2$ ·dioxane in toluene at 0 °C, to obtain the corresponding stannylene or germylene (Scheme 50).



Scheme 50. Synthesis of the metallylenes

During the synthesis of the metallylenes the formation of a secondary product is also observed, formed through the addition of an *n*-butyl moiety on the central aromatic ring, as shown on Scheme 50.

Both the germylene and the stannylene were evidenced by NMR spectroscopy, MS, IR, but only the stannylene could be separated, purified and characterized by single crystal X-ray diffraction (Figure 19).^{1,2}



Figure 19. Solid state molecular structure of the stannylene

The molecular structure shows that the bis-sulfone acts as a tridentate ligand, the oxygen atoms bind to the tin atom, with bond lengths of 2.458(7) and 2.543(7) Å

respectively, thus stabilizing the metallylene. It is to notice, that the two tolyl groups are situated on the same side of the central aromatic ring, together with the Cl atom.^{1,2}

2.2. Synthesis and characterization of the *para*-substituted bissulfone ligand

For the present work, a second generation of bis-sulfone ligand⁴ was designed, by introducing a *tert*-butyl group in the *para* position of the central aromatic ring (Figure 20). The bulky substituent offers a steric protection of the *meta* position (H3) favoring the deprotonation at the H1 thus limiting the formation of secondary products. The sulfonyl groups have *ortho* director effect, resulting reaction at the H1, but also in *meta* position and on the tolyl groups. The existence of the two sulfonyl groups activates the H1 position which becomes more acidic and by deprotonation process only the expected compound is obtained as shown in Figure 20.



Figure 20. Possible deprotonation positions of the *para*-substituted bis-sulfone

The 1,3-bis{(4-methylphenyl)sulfonyl}-5-*tert*-butylbenzene (further named bissulfone **1**) was synthetized in a similar manner to 1,3-bis{(4methylphenyl)sulfonyl}benzene¹, first by a two-step reaction, then by the direct one-step route.

For the first method, the bis-thioether **2** was synthetized by a palladium catalysed coupling reaction of 1,3-dibromo-5-*tert*-butylbenzene and *para*-toluene thiol. The bis-

thioether **2** was oxidized using *meta*-chloroperoxybenzoic acid (mCPBA) to obtain the bissulfone **1** (Scheme 51).



Scheme 51. Two-step synthetic pathway to obtain the bis-sulfone 1

The formation of a sulfone by the coupling reaction of an aryl-halide and arylsulfinates is known in the literature; studies show that Pd₂(dba)₃ with Xantphos as ligand, in toluene, and using Cs₂CO₃ as base are giving the best results.⁵ Based on these information, together with the results shown in the case of the 1,3-bis{(4methylphenyl)sulfonyl}benzene¹, a direct method was also employed to obtain the parasubstituted bis-sulfone 1, similar to the one shown in Scheme 49. Bis-sulfone 1 was obtained by a palladium-catalysed cross coupling reaction of 1,3-dibromo-5-t-butylbenzene and sodium *p*-toluenesulfinate, as presented in Scheme 52.



Scheme 52. Synthesis of the bis-sulfone ligand 1 by direct coupling reaction

The mechanisms of the coupling reaction to form a bis-aryl-sulfone is discussed in several sources in literature.^{5,6} Based on these information, the proposed mechanism schematics of the catalytic coupling reaction of 1,3-dibromo-5-*t*-butylbenzene and sodium *p*-toluenesulfinate is shown in Scheme 53. The first step is an oxidative addition of the bromo-benzene to the palladium(0) complex ($Pd_2(dba)_3$ and Xantphos) forming an

arylpalladium(II) complex. Next, the transmetalation takes place to form an arylsulfonylpalladium(II) complex as intermediate. This is followed by the reductive elimination step giving the sulfone and regenerating the Pd(0) catalyst, which then participates in the next coupling reaction.



Scheme 53. Catalytic mechanism for the formation of bis-sulfone 1

Compound **1** was filtered through silica-gel, then the solvents were evaporated. White crystals were obtained by crystallization in ethanol at room temperature with 60% yield. The NMR spectra show the characteristic signals of the tolyl and of the central aromatic cyclic moieties, as shown in Table 1. The most noteworthy being the resonance seen for the H1 at 8.23 ppm (t, ${}^{4}J_{HH}$ = 1.6 Hz) in the ¹H NMR spectrum and the corresponding signal for C1 in ¹³C NMR at 154.9 ppm. It is to note that in the ¹H NMR the H3 and H5 presents a doublet at 8.08 ppm (${}^{4}J_{HH}$ = 1.6 Hz). Following the shift of these signals is an easy method to monitor the deprotonation and metalation reactions.

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¹ H NMR (δ ppm)	8.23, t J = 1.6 Hz	7.81, d J = 8.3 Hz,	8.08, d J = 1.6 Hz	7.31, d J = 8.1 Hz	2.40	1.31
¹³ C NMR (δ ppm)	C1	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Me	<i>t</i> -Bu
	154.9	127.9	128.6	130.3	21.7	31.0
	<u><i>C</i>(</u> CH₃)₃	C2, C6	С7	C10	C4	
	35.7	137.7	143.6	144.9	155.0	

Table 1. ¹H and ¹³C NMR data (in CDCl₃) of compound 1

The crystallographic study confirms the formation of the ligand and reveals only the presence of the *trans* rotameric form. The molecular structure in solid state of **1** is shown in Figure 21 together with the most significant geometrical parameters.



Figure 21. Molecular structure of compound **1** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted and tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.438(2); S1-O2 1.441(2); S2-O3 1.440(2); S2-O4 1.441(2); O1-S1-O2 119.47(11), O3-S2-O4 119.87(13); O1-S1-C6 106.80(11), O2-S1-C6 107.62(10), O3-S2-C2 107.66(11), O4-S2-C2 107.17(12), C1-C6-S1 118.86(18), C1-C2-S2 118.94(19).

The two tolyl groups are not parallel, they are situated on opposite sides of the central benzene in an almost orthogonal position with angles of 72.03 and 81.61°. The sulfur-oxygen bond distances of 1.428(2) - 1.441(2) Å are in the range of normal S=O bonds found in literature (1.43 Å).^{7–9}

DFT calculations realised on the bis-sulfone **1** show that the energy barrier of the $cis \rightarrow trans$ rotation is low (2.69 kcal/mol), suggesting that the *trans* orientation observed in the solid state molecular structure can be related to the packing effects.

2.3. Synthesis of metallylenes with the bis-sulfone ligand

The deprotonation of the bis-sulfone ligand **1** is realized by addition of *n*-BuLi in toluene at -40 °C (Scheme 54).



Scheme 54. Lithiation reaction of bis-sulfone 1

Quenching the lithiated bis-sulfone with D₂O proves that the desired lithiated compound is formed with almost full conversion. However trace amounts of compound **5** are observed in the ¹H NMR (Scheme 55). This secondary compound **5** is probably formed through the elimination of ToISO₂Li to form an aryne. The aryne can act as a nucleophile in the presence of *n*-butyllithium, forming the addition product **5**. No deuterium atom is present in the molecule of compound **5**, because three triplet signals can be observed at chemical shifts 7.35 ppm (t, ⁴J_{HH} = 1.70 Hz), 7.54 ppm (t, ⁴J_{HH} = 1.66 Hz) and 7.76 ppm (t, ⁴J_{HH} = 1.70 Hz) for the protons on the central aromatic ring.



Scheme 55. The quenching of lithiated derivative 3 with D₂O

The metallylenes were obtained by the reaction of the carbanion **3** with the appropriate metallylene dichloride (GeCl₂·dioxane, SnCl₂ or PbCl₂), affording the corresponding chlorometallylenes, germylene **6**, stannylene **7** and plumbylene **8** (Scheme 56).



Scheme 56. Synthesis of the metallylenes 6, 7 and 8

To synthesize the corresponding silylene, usually a two-step reaction is required, first to obtain a Si(IV) precursor, then to reduce it to the corresponding Si(II) derivative (Scheme 57).



Scheme 57. Planned synthesis of silylene

Several methods were tried to obtain the chlorosilylene, using different silicon derivatives, such as SiCl₄, SiHCl₃, NHC-SiCl₂, Si(OMe)₄, ClSiMe₃, etc., but none worked, the introduction of the silicon atom was not possible with the methods used by us, thus the silylene could not be evidenced.

Compounds **6** and **7** were obtained with full conversion and isolated with 60% yield as white solids, slightly soluble in DCM, THF and toluene, and not at all in diethyl-ether or pentane. Plumbylene **8** was evidenced by ¹H NMR analysis, but showed to be very unstable, decomposes rapidly, preventing any further analysis. Germylene **6** and stannylene **7** were characterized by ¹H, ¹³C NMR analysis and ¹¹⁹Sn NMR in the case of the stannylene **7**, highresolution mass spectrometry, IR spectroscopy and single crystal X-ray diffraction. In the ¹H NMR characteristic signals for the aromatic protons can be observed, the disappearance of the triplet signal for the H1 at 8.23 ppm highlights the formation of the metallylenes. Figure 22 shows the aromatic region of the ¹H NMR spectra for the obtained metallylenes **6** (in green), **7** (in blue) and **8** (in purple) in comparison with the bis-sulfone **1** (red).



Figure 22. Aromatic region of the ¹H NMR spectra of compounds 1, 6, 7 and 8

In the ¹³C NMR spectra, upfield-shifted signals of the C1 (ipso) of the central aromatic ring to 159.9 and 169.8 ppm in **6** and **7**, respectively, were observed, compared to

154.9 ppm for the bis-sulfone **1**. These values are comparable to those reported previously in *O*,*C*,*O*-coordinated chlorogermylenes¹⁰ and stannylenes^{1,11–13}. All the specific signals for metallylenes **6**, **7** and **8** are presented in Table 2.

metallylen	$ \begin{array}{c} M & 0 \\ 0 \\ -6 \\ -8 \\ -9 \\ -9 \\ -9 \\ -9 \\ -9 \\ -9 \\ -9$	H8, H12 (o-Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu	
¹ Η NMR (δ ppm)	germylene 6	8.07, d J = 8.4 Hz,	7.75	7.38, d J = 8.5 Hz	2.43	1.21	
	stannylene 7	8.09, d J = 8.40 Hz	7.80	7.37, d J = 8.07 Hz	2.42	1.20	
	plumbylene 8	7.82, d J = 8.42 Hz	8.09	7.33, d J = 7.97 Hz	2.42	1.32	
		C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Me	<i>t</i> -Bu
¹³ C NMR (δ ppm)	6	159.9	128.7	129.2	130.6	21.9	31.0
	7	169.8	128.7	129.6	130.6	21.9	31.0
		<u>С</u> (СН ₃) ₃	C2, C6	C7	C10	C4	
	6	35.5	145.1	135.4	146.1	156.2	
	7	35.5	146.3	135.8	145.9	155.5	

Table 2. ¹H and ¹³C NMR data for germylene **6** and stannylene **7** and ¹H NMR data for plumbylene **8** (in CDCl₃)

The ¹¹⁹Sn NMR spectrum of stannylene **7** displays a sharp signal at -14.95 ppm (in CDCl₃), a value close to the one previously reported by using the bis-phenylsulfone ligand (- 25.36 ppm), suggesting comparable S=O \rightarrow Sn(II) coordination.

Single crystals of **6** and **7**, suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane in a CH_2Cl_2 (for **6**) and THF (for **7**) solution at room temperature. The metallylenes **6** and **7** are isostructural, the determined molecular structures are shown in Figure 23 together with the most important geometrical parameters.


Figure 23. Molecular structure of compounds **6** and **7** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg] for **6**: S1-O1 1.463(2), Ge1-C1 2.030(3), Ge1-Cl1 2.287(2), Ge1-O1 2.359(2), C1-Ge1-Cl1 93.78(5), C1-Ge1-O1 77.95(5), O1-Ge1-O1A 155.90(10). **7**: S1-O1 1.465(11), Sn1-C1 2.214(2), Sn1-Cl1 2.359(13), Sn1-O1 2.451(12); C1-Sn1-Cl1 95.22(3), C1-Sn1-O1 73.99(3), O1-Sn1-O1A 147.99(5).

Both metallylenes **6** and **7** crystallize in the monoclinic space group (*C*2/c), the chlorine atoms are disordered over two positions, each with 50% site occupancy. The molecular structures of **6** and **7** show that the bis-sulfonyl ligand is bonded in a tridentate fashion to the germanium or tin atom. The flanking tolyl groups are in relative *trans*-orientation considering the central aromatic ring, that is in contrast with the structure of the previously described bis-sulfonyl stannylene (Figure 19), where the tolyl groups are positioned on the same side of the central ring.¹ The group germanium and tin atoms are four coordinated and, considering the lone pair of electrons, present a distorted seesaw geometry.¹⁴ For the C1–Ge1–O1 angle a value of 77.95(5)° is observed and 73.99(3)° for the C1–Sn1–O1 because of the the formation of five-membered rings through coordination of the sulfonyl groups to the germanium or tin atom. The heterocycles are nearly coplanar with the phenyl backbone. The group 14 element, C1 and C4 lie on a two-fold axis thus the values of the Ge-O bonds (2.359(2) Å) and the Sn-O bonds (2.451(12) Å) are identical. The O→Sn donor bond length of 2.451(12) Å is close to those previously reported for the stannylene [2,6-{(p-tolyl)SO₂}₂C₆H₃]SnCl of 2.458(7) and 2.543(7) Å.¹

The binding mode using an *O*,*C*,*O*-chelating pincer type ligand to stabilize germanium divalent species is not presented in the literature up to date, the only comparison can be made with an oxygen-donor-stabilized germanium(II) compound: $[2,4-(tBu)_2-6-(CH_2OtBu)-(C_6H_2)]$ GeCl where the O \rightarrow Ge donor bond is much shorter (2.073(2) Å)¹⁵ and with the (1,8-dimethoxy-9-anthracenyl)-chlorogermylene (2.357 and 2.386 Å).¹⁶ For the case of germylene **6** no significant variations are observed between the S=O free bonds (S1–O2, 1.437(2) Å) and the S=O with the oxygen atom coordinated to the metallylene (S1–O1, 1.463(2) Å). These values are also close to those previously seen in the starting bis-sulfonyl compound **1** and are in the range of normal S=O bonds (1.43 Å) presented in the literature.^{7–9} The Ge1-Cl1 bond (2.287(2) Å) is oriented orthogonal to the plane of the aryl ligand and its value compares with the one observed in the N,C,N pincer ligand stabilized germylene (chapter 1, Figure 14) (2.309(4) Å).¹⁰ In the case of stannylene **7**, the Sn1-Cl1 bond of 2.359(13) Å is shorter than the one observed for the stannylene [2,6-{(p-tolyl)SO₂}₂C₆H₃]SnCl (2.454(3) Å) obtained in a *cis* conformation.^{1,4}

The C1-Ge1 bond length of 2.030(3) Å in germylene **6** is comparable to values found in other halogermylenes (1.941(11) - 2.402(3) Å).^{10,17} In the case of the stannylene **7** the C1-Sn1 bond length is 2.214(2) Å, similar to those previously reported in the literature (2.158(8) - 2.244(2) Å).^{11,13,18}

DFT calculations were performed to obtain further information about the structure and the specific interactions. For both metallylenes three isomers were considered: two isomers with the flanking tolyl groups in a *cis* conformation with respect to the central aromatic ring (isomers I and II, see Figure 24) and the isomer with a *trans* orientation of the flanking tolyl groups (isomer III).



Figure 24. Germylene isomers calculations

The most stable isomers in the case of the novel metallylenes **6** and **7** were calculated to be those with the tolyl groups and the chlorine atom in a *cis* orientation with respect to the central ring (isomers **6_I** and **7_I**). However, the difference in energy from the *trans* structures (**6_III** and **7_III**, identified in solid state by X-ray analysis) is only 1.67 kcal in the case of the germylene **6** (Figure 24) and 3.46 kcal in the case of the stannylene **7** (Figure 25), values at the limit of significance of the calculations.



Figure 25. Stannylene isomers calculations

NBO analyses were also performed on the *trans* isomer structures (**6_III** and **7_III**) for both the germylene **6** and the stannylene **7**. They show interactions of the lone pairs situated on oxygen atoms of the sulfonyl groups with a vacant orbital with *p* character on the germanium or tin atoms. Both lone pairs on each of the oxygen atom are involved, but the interaction is significantly stronger for one of the lone pairs, situated in an orbital oriented towards the germanium atom (Figure 26). In the case of the calculated **6_III** isomer, these interactions amount to a calculated energy of 60.2 kcal/mol. Similar charge-transfer interactions occur for the tin derivative **7_III**, summing up to about 70 kcal/mol. (Figure 26).



Figure 26. NB orbitals involved in charge transfer between LP's on one of the oxygen atoms (a,b) and a vacant orbital on the germanium atom (c) for structure **6_III** (hydrogen atoms are omitted for clarity)

Mulliken and NBO charges for the group 14 element (Ge and Sn) and the chlorine atom in model derivatives **6_III** and **7_III** were also calculated. The results are shown in Table 3 and suggest a stronger ionic character for the Sn-Cl bond than for Ge-Cl. The calculated MO bond order is also higher in the case of the tin-chlorine bond (1.33 for Sn-Cl and 1.25 for the Ge-Cl bond).

 Table 3. Calculated atomic charges for type III isomers of the bis-sulfonyl-metallylenes (6_III and 7_III)

Derivative	Atom	Mulliken charge	NBO charge
6_111	Ge	0.415	1.031
	Cl	-0.358	-0.534
7_111	Sn	0.775	1.172
	Cl	-0.486	-0.611

2.4. Reactivity of the bis-sulfone stabilized metallylenes

As presented in the literature review in Chapter 1, metallylenes can react at multiple points: the halogen atom, the vacant *p* orbitals and the lone pair of electrons (Figure 27).



M = Ge, Sn

Figure 27. Metallylene in singlet ground state

Thus, substitution reactions of the halogen atom, cycloadditions and coordination reactions are possible. To evidence the chemical properties of the newly obtained metallylenes **6** and **7**, these reactions were tested and the results are described in this chapter.

2.4.1. Substitution reactions

In order to evaluate the stability and behaviour towards different compounds of the germylene **6** and stannylene **7**, substitution of the chlorine atom with several functional groups was tested in reactions with organolithium derivatives or lithium salts: RLi (R = Me, OMe, C=C-SiMe₃, BEt₃H, BH₄ (Scheme 58)). In none of the cases the expected reaction took place, in the resulting reaction mixture the starting bis-sulfone ligand was observed.



Scheme 58. Substitution reactions of the metallylenes

The presence of the bis-sulfone **1** in the resulting reaction mixtures suggests the lability of the C-Ge and C-Sn bond.

2.4.2. Cycloaddition reactions

Oxidative additions of metallylenes are well known methods to confirm the existence of a divalent species, $^{19-21}$ the metallylenes forming adducts with chalcogens (S, Se), ketones or *ortho*-quinones etc. $^{22-31}$

First, reaction of the germylene **6** and stannylene **7** with sulfur was tested (Scheme 59). In both cases, the reactions occur with the formation of insoluble precipitates, which could not be identified by the usual methods.



Scheme 59. Reaction with sulfur

Treatment of germylene **6** and the stannylene **7** with 3,5-di-*tert*-butyl-*ortho*-quinone gave new cycloaddition products in both cases.



Scheme 60. Reaction of germylene 6 with o-quinone

The chlorogermylene **6** reacts easily with 3,5-di-*tert*-butyl-o-benzoquinone to form the corresponding cycloadduct **9**, stable under inert atmosphere (Scheme 60). The ¹H NMR spectrum shows the characteristic aromatic signals of the quinone group, the doublets at 6.68 and 6.75 ppm (⁴J_{HH} = 2.24 Hz). The downfield shift of the signal for the *meta* protons on the central aromatic ring (from 7.75 ppm in germylene **6** to 7.99 ppm in germylene cycloadduct **9**) suggests reaction at the germanium atom. The doublet signals for the *ortho* and *meta* protons of the tolyl groups for cycloadduct **9** (8.04 ppm, ³J_{H-H} = 8.37 Hz and *o*-CH Tol 7.39 ppm, d, ³J_{H-H} = 7.99 Hz) show no significant change compared to the starting germylene **6** (8.07 ppm, d, ³J_{H-H} = 8.4 Hz and 7.38 ppm, d, ³J_{H-H} = 8.5 Hz).

	H8, H12 (o-Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	H15, H17	t-Bu quinone	Ме	t-Bu	
¹ Η NMR (δ ppm)	8.04, d J = 8.37 Hz	7.99	7.39, d J = 7.99 Hz	6.68, d J = 2.24 Hz 6.75, d J = 2.24 Hz	1.26 1.45	2.45	1.21	
	C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	C15, C17	<i>t-</i> Bu quinone	Me	t-Bu
¹³ C NMR (δ	not seen	128.7	131.1	130.3	107.9 114.2	29.7 31.8	21.9	30.6
ppm)	<u>С(</u> СН ₃) ₃	C2, C6	C7	C10	C4	C14, C16	<u>C(</u> CH₃)₃ quinone	C13 C18
	35.7	146.8	136.5	145.8	158.7	134.8 141.7	34.6 34.8	143.6 147.6

Table 4. ¹H and ¹³C NMR data for compound **9** (in CDCl₃)

Light green crystals, suitable for X-Ray analysis were obtained in $CDCl_3$. The determined molecular structure in solid state is shown in Figure 28 as well as the most important geometrical parameters.



Figure 28. Molecular structure of compound **9** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen and disordered atoms and the solvent molecules are omitted, tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.439(3), Ge1-C1 1.958(4), Ge1-Cl1 2.108(1), Ge1-O3 2.568(3), Ge1-O1 2.841(3), Ge1-O5 1.789(3), Ge1-O6 1.794(3); C1-Ge1-Cl1 118.06(11), C1-Ge1-O3 77.51(12), C1-Ge1-O1 72.62(13), O1-Ge1-O3 130.40(9), C1-Ge1-Cl1 118.06(11), O5-Ge1-O6 91.75(12), C1-Ge1-O6 112.37(14), C1-Ge1-O5 109.74(14), Cl1-Ge1-O6 112.54(9), Cl1-Ge1-O5 109.74(14).

The molecular structure shows that the bis-sulfone ligand is present under the *trans* rotameric conformation, with the tolyl groups at opposite sides of the central aromatic ring. The Ge-O1 and Ge-O3 distances of 2.841(3) and 2.568(3) Å are larger than in the case of the germylene **6** (2.359(2) Å). In the literature^{32,33} Ge-O interactions between 2.51 and 3.23 Å are considered weak interactions, closer to a van der Waals interaction (sum of van der Waals radii is 3.40 Å) than a covalent bond (1.95 Å average covalent bond length).^{32–34} Considering the above mentioned interaction, in compound **9** the germanium atom is tetracoordinated. The Ge-O5 and Ge-O6 bonds with the benzoquinone with the length of 1.789(3) and 1.794(3) Å are slightly shorter than values in other o-benzoquinone – germylene cycloadducts (1.813(3) – 1.868(3) Å)^{20,21} and they are significantly shorter than the sum of the covalent radii of germanium and oxygen atoms.^{34,35}

The same reaction was realized in the case of the stannylene **7**, as shown in Scheme 61 and the resulting product was analyzed by NMR spectroscopy and mass spectrometry.



Scheme 61. Reaction of stannylene 7 with benzoquinone

In the ¹H NMR the signals for the methyl and *t*-butyl groups do not show changes compared to those for the starting stannylene **7**, however for the aromatic signals changes can be observed. In the ¹H NMR the characteristic aromatic signals of the quinone group can be observed as doublets at 6.58 and 6.62 ppm (${}^{4}J_{HH}$ = 2.30 and 2.34 Hz). A downfield shift of the meta protons of the central aromatic ring from 7.92 ppm in stannylene **7** to 7.98 and 8.07 ppm in cycloadduct **10**, a downfield shift of the signal for the meta protons of the tolyl groups of bis-sulfone ligand to 8.38 ppm shown as a doublet of doublets (${}^{3}J_{H-H}$ = 8.06 and

 ${}^{2}J_{H-H}$ =18.16 Hz) compared to 8.20 ppm (in THF-D₈, d, ${}^{3}J_{H-H}$ = 8.42 Hz) in stannylene **7** can be observed, for the protons in *ortho* position of the tolyl groups a triplet can be seen at 7.42 (${}^{3}J_{H-H}$ = 8.68 Hz), also downfield shifted from 7.40 ppm (d, ${}^{3}J_{H-H}$ = 8.62 Hz), all these confirming the formation of a tin cycloadduct. The ¹H NMR shifts and their multiplicity suggested that the tolyl groups are not equivalent as in stannylene **7**, fact that could be explained by only one oxygen atom of the two sulfonyl groups of the ligand coordinates to the tin atom. The ¹³C NMR spectrum revealed also in this case the specific signals for all the carbon atoms involved in the cycloadduct product. The signals for the ¹H and ¹³C NMR are shown in Table 5. In the mass analysis (DCI NH₃) spectrum the peak at 817.0 which corresponds to [M+1]⁺ (C₃₈H₄₅ClO₆S₂Sn M = 816.1) is an evidence for the formation of compound **10a**.

	H8, H12 (o-Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	H15, H17	t-Bu quinone	Me	t-Bu	
¹ Η NMR (δ ppm)	8.38, dd J = 8.06, 18.16 Hz	7.98 8.07	7.42, t J = 8.68 Hz	6.58, d J = 2.30 Hz 6.62, d J = 2.34 Hz	1.27 1.48	2.39	1.19	
	C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	C15, C17	t-Bu quinone	Me	<i>t-</i> Bu
¹³ C NMR (δ	134.6	129.4 130.3	131.0 131.5	130.7 130.8	108.4 112.4	30.1 32.3	21.3	30.6
ppm)	C2, C6	C7	C10	C13 C18	C14, C16	<u>С</u> (СН ₃) ₃	<u>C(</u> CH₃)₃ quinone	C4
	139.7 140.9	136.9 137.6	146.4, 147.2	146.7 <i>,</i> , 147.4	136.5	34.5 <i>,</i> 35	35.4 5.6	155.1

Table 5. ¹H and ¹³C NMR data for compound **10a** (in THF-D₈)

A few single crystals, suitable for X-ray analysis, were obtained from a sample of **10a** in $CDCl_3$ at room temperature. The solid state molecular structure presented in Figure 29 shows that the Sn-Cl bond hydrolysis took place, followed by dimerization with the formation of the Sn-O(H)-Sn bridge.



Figure 29. Molecular structure of compound **10b** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen and disordered atoms and the solvent molecules were omitted, tolyl and t-butyl groups were simplified. Selected bond distances [Å] and bond angles [°]: S1-O1 1.464(3), S1-O2 1.436(3), S2-O3 1.434(3), S2-O4 1.438(3) Sn1-C1 2.194(4), Sn1-O3 3.309(3), Sn1-O1 2.308(3), Sn1-O5 2.023(3), Sn1-O6 2.007(2), Sn1-O7 2.069(3), Sn1-O7A 2.112(3) Sn1A-O7 2.112(3), Sn1A-O7A 2.069(3); O5-Sn1-O6 82.36(10), O6-Sn1-O7 92.53(12), O6-Sn1-O7A 88.74(11), O5-Sn1-O7 104.08(12), O5-Sn1-O7A 170.90(11), O7-Sn1-O7A 74.32(13), Sn1-O7-Sn1A 105.68(13), O6-Sn1-C1 155.48(14), O5-Sn1-O1 100.76(12), O7A-Sn1-O1 152.44(11), O7-Sn1-O1 79.30(11), C1-Sn1-O1 79.30(13).

The solid state molecular structure presented in Figure 29 shows that the tin atom is hexacoordinated, the tolyl groups of the bis-sulfone are in *cis* rotameric conformation, the bis-sulfone ligand coordinates through only one oxygen atom of the bis-sulfonyl groups, this supporting the presence of two different signals for the meta protons and the protons on the tolyl groups in the NMR spectra. The Sn1-O1 bond length of 2.308(3) Å is significantly shorter than in the starting stannylene **7** (2.451(12) Å), suggesting a stronger S=O \rightarrow Sn coordination. However, the distance between Sn1 and O3 is too large (3.309(3) Å) to be considered a chemical interaction.

The solid state structure also showed the presence of a strong intramolecular interaction between the hydrogen atoms of the Sn-O(H)-Sn bridge and the oxygen atom O3 (Figure 29) of the sulfonyl groups with the distances bridging OH ...O3 of 1.96(4)Å,

interaction that contributes to the positioning of the bridge hydrogen atoms out of the plane of the Sn1-O7-Sn1A-O7A cycle, with *trans* orientation one from the other considering the heterocycle. These intramolecular interactions were additionally evidenced through DFT calculations, where the calculated distances between the H atoms (of the bridging OH groups) and the oxygen ones of the sulfonyl groups were of 1.851 Å.

The 1H NMR spectrum on the crystals of **10b** in THF-D₈ showed broad signals at chemical shifts similar to those of compound **10a**.

DFT calculations were carried out on cycloadducts **9** and **10** in order to obtain further information about their structural features and the specific interactions in the molecules. Three isomers were considered in both cases, as depicted in Figure 30. Calculations showed that isomer **I** is the most stable, however the energy differences between the isomers are very small, between 0.8 and 3.9 kcal/mol (Figure 30). The same isomer for compound **9** was identified in solid state (Figure 28), while for compound **10** in the Sn-O(H)-Sn bridged dimer isomer III was seen in the solid state molecular structure. This can be explained by the small energy differences between the isomers and the sterical hindrances in the molecule (Figure 29).



Figure 30. Energy differences obtained by DFT calculations between the isomers of cycloadducts 9 (on the left) and 10 (on the right)

For the most stable isomer 9_1 of the germanium benzoquinone adduct, the distances between the Ge atom and the O ones in the benzoquinone moiety were

calculated to be 1.807 Å and 1.805 Å. These values are shorter than typical Ge-O bonds or than their sum of covalent radii (1.86 Å)^{34,35} and can be explained by hyperconjugative interactions ($LP_0 \rightarrow \sigma^*_{Ge-R}$ with R = C, O, CI), as already seen in previous studies for similar bonding patterns.³⁶ The calculated bond lengths of the corresponding tin analogue **10_I** (2.018 Å and 2.033 Å) were also shorter than their sum of covalent radii (2.05 Å),³⁴ however, the differences were smaller than those identified for the Ge-O bonds, as a consequence of the decreasing hyperconjugative effect down in the group.³⁴

NBO analyses realized on the investigated compounds **9** and **10** revealed hyperconjugative effects involving the CI atom, the total amount of energy corresponding to these interactions seemed to decrease from germanium derivative **9** to the tin derivative **10**. The total hyperconjugation energy corresponding to the $LP_0 \rightarrow \sigma^*_{M-C}$ (M = Ge, Sn) interactions was calculated to be 17.1 kcal/mol in compound **9_I** and only 3.2 kcal/mol in compound **10_I**. For this reason, hyperconjugative effects can be assumed as further stabilization of the Ge-CI bond by comparison to its tin analogue. In cycloadducts **9_I** and **10_I**, the Mulliken and NBO charges (Table 6) for Ge or Sn and CI atoms revealed an increased ionic character for Sn-CI chemical bonding than that of the Ge-CI one. Thus, the increased ionic character of Sn-CI bond together with weaker stabilization through hyperconjugation by comparison to the Ge-CI bond, can explain the formation of dimer **10b**, which was identified in the solid state (Figure 29).

Derivative	Atom	Mulliken charge	NBO charge
9_1	Ge	0.921	2.022
	Cl	-0.272	-0.375
10 I	Sn	1.276	2.106
-	Cl	-0.318	-0.470

Table 6. Calculated Mulliken and NBO charges for derivatives 9_I and 10_I.

The large distances between the Ge atom and the O atoms of the sulfonyl groups in cycloadduct **9_I** with calculated values of 2.515 Å and 3.086 Å (2.568(3) and 2.841(3) Å observed in the solid state molecular structure) indicate a tetra-coordinate geometry for the

Ge atom. In addition, NBO analyses were carried out on the optimized structure of 9_1 showing weak donor-acceptor interactions between the lone pairs (LPs) of the O atoms in the pincer ligand and a vacant p orbital on the Ge one (Figure 31) with the calculated energy between 3.5 and 18 kcal/mol indicating the tetrahedral geometry at the Ge center.



Figure 31. NB orbitals involved in charge transfer interactions for cycloadduct **9_I**, occurring between the O's LPs and the Ge atom; **a**. vacant p orbital situated on the Ge atom; **b-d**. p orbitals on the O atoms of the sulfonyl groups. Hydrogen atoms were omitted for clarity.

In **10_I**, the computed distances between the O atoms of the sulfonyl groups and the Sn atom were of 2.406 Å and of 2.625 Å, being in agreement with previously reported values for Sn-O coordinative bonds.^{1,37–40} NBO calculations showed charge transfer interactions from the LPs situated on the O atoms into vacant *p* orbitals on the Sn, as seen on Figure 32, with the calculated amounts of energy about 25 kcal/mol and 47 kcal/mol.



Figure 32. NB orbitals involved in the strongest charge transfer interactions identified for the Sn-O coordinative bonds in derivative **10_I**; **a**. vacant acceptor orbital on Sn atom; **b**, **c**. donor *p* orbitals on the O atoms found in the coordinative bonds.

For the optimized structure of dimeric species **10b** the calculated geometrical parameters were in agreement with the obtained experimental data. The calculated Sn-O distances contained in the two Sn-O(H)-Sn bridges were equal two by two, thus, the two shorter Sn-O distances (2.078 Å) can be considered covalent, while the other two bonds (2.150 Å) rather coordinative, as a consequence of the μ -coordination of the -OH groups from the hydrolyzed species **10_III**. In addition, the molecular geometries of the hydrolyzed derivatives **10** were also optimized in order to assess the stability of dimer **10b** related to the free monomeric species. The energy of **10b** was calculated to be with around 40 kcal lower than two times the energy of the hydrolyzed derivatives **10**, highlighting the increased stability of the cycloadduct **10b** compared to the unpaired monomers.

2.4.3 Complexation reactions

The metallylenes stabilized by the intramolecular donor $E \rightarrow M$ coordination of the pincer ligands have an increased Lewis base character of the M(II) atom, which should increase their complexation ability to Lewis acids.⁴¹

In order to assess the σ -donor properties and the adjustable-ligand character of the newly obtained germylene **6** and stannylene **7**, complexation reactions were realized with transition metal carbonyls, the ones with iron being presented in Scheme 62.



Scheme 62. Syntheses of the metallylene iron complexes.

The solution of germylene **6** or stannylene **7** in THF was added to a THF solution of $Fe_2(CO)_9$ in excess, then stirred at room temperature overnight, giving dark orange mixtures.

After evaporation of the solvent and extraction with diethyl ether, the stannylene iron complex **12** was isolated as an orange powder in 69 % yield. Dark orange crystals, suitable for single crystal X-ray analysis, were obtained at – 25 °C in toluene. Compound **12** was also characterized by multinuclear NMR and IR spectroscopy and high-resolution mass spectrometry. The ¹¹⁹Sn NMR shows a down-field shift of the signal (192.48 ppm in THF-D₈) compared to that of the starting stannylene (- 33.30 ppm in THF-D₈), suggesting the formation of the expected compound. A similar observation, suggesting a decrease of the electron density on the tin atom upon complex formation, was reported for various iron-stannylene complexes.^{12,42,43} The coordination of the stannylene to the iron carbonyl was also evidenced by the ¹H and ¹³C NMR. Data for the ¹H and ¹³C NMR are shown in Table 7.

$CI Fe(CO)_4$	H8, H12 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu	
¹ H NMR (δ ppm)	8.13, d J = 8.4 Hz	8.20	7.51, d J = 8.0 Hz	2.43	1.26	
	C1 (<i>ipso</i>)	C8, C12 (<i>o</i> -Tol)	C3 <i>,</i> C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Me	t-Bu
¹³ C NMR (δ ppm)	150.6	129.9	130.7	131.4	21.4	30.6
C NIVIK (ö ppm)	<u>С(</u> СН ₃) ₃	C2, C6	С7	C10	C4	<u>c</u> o
	36.4	145.1	135.1	147.8	159.9	214.1

Table 7. ¹H and ¹³C NMR data for stannylene-iron complex **12** (in THF-D₈)

In the ¹H NMR the characteristic signals for the stannylene moiety can be observed. The most significant change is the downfield shift of the signal for the meta protons on the central aromatic ring, from 7.92 ppm for stannylene **7** (in THF-D₈) to 8.20 ppm. Furthermore, in the ¹³C NMR spectrum the signal at 214.1 ppm is a characteristic CO resonance, also proving the existence of the tin-iron complex. Additionally, the presence of three CO stretching frequencies at 2040, 1963 and 1905 cm⁻¹ are characteristic for such complexes.⁴⁴

In the case of the germylene analogue **6**, the formation of several compounds was observed. However, some colourless crystals were separated from the reaction mixture and the X-ray crystallographic study confirms the presence of the germylene iron complex **11**.

Complete analytical data for compound **11** could not be acquired because of its low stability in solution and the very small quantity of isolated product. The molecular structures of complexes **11** and **12** are shown in Figure 33 with selected bond lengths and angles.



11

12

Figure 33. Molecular structures of compounds **11** and **12** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the solvent molecules are omitted, tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg] for **11**: S1-O1 1.467(6), S2-O3 1.479(8), Ge1-Cl1 2.138(4), Ge1-O3 2.257(7), Ge1-O1 2.329(6), Ge1-Fe1 2.296(2); C1-Ge1-Cl1 105.9(3), C1-Ge1-O3 79.9(3), C1-Ge1-O1 78.6(3), O1-Ge1-O3 157.1(2). **12**: S1-O1 1.469(2), S2-O3 1.469(2), Sn1-Cl1 2.389 (6), Sn1-O3 2.354(2), Sn1-O1 2.377(2), Sn1-Fe1 2.442(1); C1-Sn1-Cl1 98.42(6), C1-Sn1-O3 76.07(7), C1-Sn1-O1 75.03(7), O1-Sn1-O3 150.32(6).

In both complexes **11** and **12**, the flanking tolyl groups are positioned on the same side of the central aromatic ring, not on opposite, as seen in the starting germylene **6** and stannylene **7** (Figure 23 and Figure 33). This could be explained by the steric hindrance of the Fe(CO)₄ fragment. Furthermore, it also shows that the coordination to the germanium or the tin atoms is possible with either one of the oxygen atoms of the bis-sulfonyl groups, emphasizing the adjustable character of the *O*,*C*,*O*-chelating E₂CE₂-type pincer metallylenes. In both complexes, the group 14 atom has a distorted trigonal bipyramidal geometry with the O1 and O3 atoms occupying the axial positions and the C1, Cl1 and Fe1 atoms occupying the equatorial ones. The O1–Sn1–O3 angle of 150.32(6)° is slightly more open than that seen in the starting chlorostannylene **7** (147.99(5)°). The Sn-O distances (2.377(2) and 2.354(2) Å) are shorter than the one found in the stannylene **7** (2.451(12) Å) indicating stronger Sn-O interaction due to the enhanced electropositive character of the tin(II) atom. The Sn-Fe bond length (2.442(1) Å) is close to those observed in a N-heterocylic stannylene iron complex (2.430(1) and 2.429(1) Å)⁴² and slightly longer than that in a bis(aryloxide) stannylene iron one (2.408(1) Å)⁴⁴. To the best of our knowledge, the stannylene iron complex **12** is the second example of a pincer ligand stabilized divalent tin derivative coordinated to the tetracarbonyl iron fragment and the first complex whose structure was determined by single crystal X-ray diffraction analysis. In the germylene complex **11**, the Ge-O distances of 2.257(7) and 2.329(6) Å are slightly shorter than those in the germylene **6** (2.359(2) Å). The Ge-Fe bond distance (2.296(2) Å) is in the range of the values obtained for stabilized germylene iron complexs.⁴⁵

NBO analysis performed on the germylene-iron and the stannylene-iron complexes **11** and **12** reveals $O \rightarrow Ge$ and $O \rightarrow Sn$ interactions involving lone pairs on the oxygen atom and a vacant orbital bearing a major contribution from a p –type orbital on the germanium or tin atom, similar, but stronger than those found for the stabilized metallylenes **6** and **7**. The energy of these interactions is around 75 kcal/mol in the case of the germanium complex, and 100 kcal/mol for the tin-iron derivative, which can explain the smaller $O \rightarrow M$ (M = Ge, Sn) distances in the iron complex when compared to the free metallylenes.



Figure 34. NB orbitals for complex 11

Figure 34 illustrates the NB orbitals computed for complex **11**, which are involved in the coordination bond formation. Similar results were obtained for the other complexes.

The reactivity of the compounds **6** and **7** towards a tungsten carbonyl complex was also evaluated (Scheme 63). The reaction of stoichiometric amounts of the metallylenes **6** or **7** and $W(CO)_5$ ·THF in THF at room temperature led to the corresponding complexes **13** and **14** in moderate yields (31 – 38%). After workup, they were isolated as yellow powder for **13** and colourless crystals for **14**, soluble in THF and chlorinated solvents. Both compounds are stable after several days of exposure to air.



Scheme 63. Syntheses of the metallylene-tungsten complexes 13 and 14

Both complexes **13** and **14** were characterized by NMR and IR spectroscopy and MS spectrometry. The 1 H and 13 C NMR data are shown in Table 8.

The ¹H NMR spectra showed typical resonances expected for the alkyl (*t*-Bu and Me) and aryl groups, with no major shift from those seen in the starting metallylenes. The significant change is at the *meta* protons of the central aromatic ring, shifting from 7.75 to 7.81 ppm in the case of the germylene **6** and from 7.80 to 7.90 ppm in the case of the stannylene **7**, as a result of the coordination to the tungsten pentacarbonyl moiety.

Table 8.	. ¹ H and ¹	¹³ C NMR dat	a for germyle:	ne-tungsten	complex 13	and stannyl	ene-tungsten
complex	x 14 (in C	DCl ₃)					

Cl Cl Cl Cl Cl Cl Cl Cl Cl Cl	$M(CO)_{5}$ M O O O O O O O O O O O O O O O O O O O	H8, H12 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu	
¹ H NMR	Germylene-W 13	8.03, d J = 8.41 Hz	7.81	7.42, d J = 7.99 Hz	2.46	1.22	
(δ ppm)	Stannylene-W 14	8.02, d J = 8.40 Hz	7.90	7.42, d J = 8.00 Hz	2.45	1.23	

		C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Me	<i>t-</i> Bu
	13	158.6	128.8	129.5	130.8	22.0	30.9
¹³ C NMR	14	not seen	128.7	129.8	130.9	22.0	31.0
(δ ppm)		<u>C</u> (CH₃)₃	C2, C6	C7	C10	C4	<u>c</u> o
	13	35.8	143.5	134.0	147.0	156.2	196.8, 200.7
	14	35.8	144.8	134.4	146.9	158.1	L91.3, 196.3, 199.6

The ¹³C NMR spectra revealed the presence of two signals at 196.8 and 200.7 ppm for **13** and 196.1 and 199.5 ppm for **14**, indicating the existance of equatorial and axial CO groups in the W(CO)₅ moiety. As expected, coordination of the stannylene results in a down-field shift of the ¹¹⁹Sn resonance (50.4 ppm in CDCl₃) in comparison with that of the starting stannylene (-14.95 ppm in CDCl₃). The IR spectra of germylene-tungsten complex **13** and stannylene-tungsten complex **14** recorded in nujol exhibits the characteristic patterns for an W(CO)₅L moiety^{46,47} with CO stretching bands in the 2069-1949 cm⁻¹ region for compound **13** and in the 2071-1900 cm⁻¹ region for derivative **14** respectively. Single crystals of complexes **13** and **14** suitable for X-ray diffraction analysis were obtained from CH₂Cl₂ solutions. The solid state molecular structures are shown in Figure 35 together with the most important geometrical parameters.

The asymmetric unit of compound **13** contains two crystallographically independent molecules with a similar structural arrangement, thus only one is discussed (Figure 35).

The germanium and tin atoms are in a distorted trigonal bipyramidal configuration with the O1 and O3 atoms in the axial and the C1, Cl1 and W1 atoms in the equatorial positions. In both cases, the metallylenes occupy the apical position of the W(CO)₅ fragment. The tin-oxygen bond lengths (2.381(3) and 2.416(3) Å) are around those reported for $\{2,6-[P(O)(OiPr)_2]_2-4-tBu-C_6H_2\}CISnW(CO)_5$ (2.313(2) and 2.346(2) Å)⁴⁸ and for [2,6-(ROCH₂)₂C₆H₃]CISnW(CO)₅ (R=Me, 2.391(5) and 2.389(5) Å; R=tBu, 2.464(3) and 2.513(3) Å).⁴⁹ The Sn-W distance (2.718(1) Å) is slightly shorter than the corresponding distances in complexes containing pincer ligand with phosphonato- groups (2.7263(11) Å)⁴⁸ or amino-, alkoxy groups (2.7630(3),⁵⁰ 2.7321(5) and 2.7655(4),⁴⁹) respectively.



13

14

Figure 35. Molecular structures of compounds **13** and **14** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the solvent molecules are omitted, tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg] for **13**: S1-O1 1.459(3), S2-O3 1.468(4), Ge1-Cl1 2.191(1), Ge1-O3 2.287(3), Ge1-O1 2.318(3), Ge1-W1 2.550(8); C1-Ge1-Cl1 105.79(13), C1-Ge1-O3 79.66(15), C1-Ge1-O1 78.82(15), O1-Ge1-O3 157.03(12). **14**: S1-O1 1.458(3), S2-O3 1.462(3), Sn1-Cl 2.162(4), Sn1-Cl1 2.358(1), Sn1-O3 2.381(3), Sn1-O1 2.416(3), Sn1-W1 2.718 (5); C1-Sn1-Cl1 97.20(12), C1-Sn1-O3 75.24(15), C1-Sn1-O1 74.55(14), O1-Sn1-O3 149.32(11).

No significant variations of the Ge-O bond lengths were observed between the two germylene-iron **11** and tungsten **13** complexes, they are shorter than those in the germylene **6**. The germanium-tungsten distance (2.550(1) Å) is in the range of values found for tungsten-germylene complexes.^{51,20,52–55} As previously observed for the metallylene iron complexes, the tolyl groups are in a *cis* position.

2.4.4. Reactivity of stannylene-iron complex

The substitution of the chlorine atom is also possible starting from the transition metal complexes of metallylenes.^{56,57}

Based on the results obtained after the reactions carried out starting from germylene **6** and stannylene **7** in order to substitute the chlorine atom, where this was not possible, a new route was also explored. Starting from the stannylene-iron complex **12**

substitution reactions with different compounds were tested, for example MeOLi, EtOLi or LiBEt₃H, as shown in Scheme 64.



Scheme 64. Expected reaction scheme of complex 12 with ROLi

In these cases the expected compound was not formed. However, from a sample of the reaction mixture in THF-D₈ of complex **12** with MeOLi some single crystals were separated and analysed by X-ray diffraction (compound **15**). In the solid state molecular structure, shown in Figure 36, the formation of a hydroxide-bridged dimer can be seen, where two OH moieties are bridging the two stannylene-iron complex moieties. The IR spectrum recorded for the crystals of complex **15** showed the specific CO stretching frequencies at 2041, 2027, 1951, 1931, 1896 cm⁻¹, characteristic for metal-carbonyl complexes.⁴⁴ No further analysis could be done on the separated crystals because of their insolubility in commonly used solvents.



Figure 36. Molecular structure of compound **15** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the solvent molecules are omitted, tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: Sn1-C1 2.202(3), Sn1A-C1A 2.186(2), Sn1-O1 2.475(2), Sn1-O3 2.814(2), Sn1A-O1A 2.658(2), Sn1A-O3A 2.614(2), Sn1-O5 2.071(2), Sn1-O5A 2.104 (2), Sn1A-O5 2.095(2), Sn1A-O5A 2.101(2), Sn1-Fe1 2.474(1), Sn1A-Fe1A 2.461(1); C1-Sn1-O5 110.88(9), C1-Sn1-O5A 94.74(9), C1A-Sn1A-O5 103.36(8), C1A-Sn1A-O5A 92.46(9), C1-Sn1-Fe1 127.27(7), C1A-Sn1A-Fe1A 134.61(7), O1-Sn1-O3 138.49(6), O1A-Sn1A-O3A 137.58(6).

This compound is probably the result of the hydrolysis of the complex, probably after contamination with moisture or oxygen in the crystallization process.

Similar hydroxide-bridged tin derivatives can be found in the literature,^{37–40,58} they are usually formed in the presence of water.

The solid state molecular structure of complex **15** shows that the tin atom is hexacoordinated, the bis-sulfone ligand binds in a tridentate fashion, with the Sn1-O1 and Sn1-O3 distances between 2.475(2) and 2.814(2) Å, suggesting medium-strong interaction. This interaction is weaker than in the case of the stannylene **7** (2.451(12) Å) and the stannylene-iron complex **12** (2.3543(17) and 2.3775(17) Å), which can be a consequence of the steric crowding around the tin atom and the hydroxide-bridge. The tin atoms and the oxygen atoms forming the bridge are almost coplanar, with a torsion angle of 3.67°, with the

angle at the Sn atoms of 69.25(7) and 69.62(7)° and wider angles at the oxygen atoms (109.68(9) and 111.22(9)°). These values are similar to values seen in other hydroxidebridged tin containing moieties (69.9(3) – 73.68(7)° for the O-Sn-O angle and 105.6(2) – 109.57(12)° for the Sn-O-Sn angle). 26,27,58,29

The molecular structure of dimeric species **15** was also characterized through DFT calculations, the geometrical parameters being in good agreement with the solid state data. The computed Mulliken charges were around 1.5 for the Sn atom, while for Fe atom these charges were calculated to be very close to 0 suggesting that the Sn-Fe bonding was formed through the coordination of LP electrons of Sn into vacant orbitals of the Fe atom.

2.5. The reactivity of bis-sulfone 1 toward phosphorus compounds

The introduction of a phosphorus atom on the bis-sulfone ligand is also an interest in our research groups. First, phosphorus containing compounds have an important role in organometallic chemistry,^{59,60} being widely used as ligands either in transition metal complexes⁶¹ or compounds containing p-block elements.^{62,63} The second reason to the following study was to further validate the pincer ligand character of the bis-sulfone **1**. In the literature there are only a few examples for phosphines stabilized by pincer ligands.^{64–67}

Initially, the reaction of the lithiated bis-sulfone **1** with chlorodiphenylphosphine was tested. In this case no reaction took place (Scheme 65).



Scheme 65. Reaction of bis-sulfone 1 towards Ph₂PCl

Next, the ability of the bis-sulfone ligand to stabilize a dichlororophosphine was evaluated. Trichlorophosphine was added at low temperature to the carbanion of the bis-sulfone **1**. The reaction occurs as shown in Scheme 66, using a slightly modified method from literature.^{64,68,69}



Scheme 66. Synthesis of bis-sulfone-PCl₂ 16

The formation of the new dichlorophosphine **16** was evidenced by NMR spectroscopy. In the ³¹P NMR spectrum the singlet signal appears at 139 ppm (C₆D₆), in the range of chemical shifts for organochlorophosphines.^{70,71} The ¹H NMR of compound **16** confirms that reaction took place at C1 by the disappearance of the triplet signal for H1 at 8.90 ppm (C₆D₆, ⁴J_{HH} = 1.64 Hz). A downfield shift of the *meta* protons on the central aromatic ring (H3 and H5) can also be observed from 8.25 ppm (C₆D₆, d, ⁴J_{HH} = 1.64 Hz) to 8.47 ppm (C₆D₆, d, ⁴J_{HH} = 1.74 Hz). In the ¹³C NMR for compound **16** the signal for the C1 atom appears at 137.3 ppm as a doublet with a coupling constant of 104.3 Hz, due to the bonding with the phosphorus atom, downfield shifted from 124.6 ppm for bis-sulfone **1**. Similarly, coupling with the phosphorus atom can be observed in the case of several other signals for the aromatic carbon atoms. The ¹H and ¹³C NMR data for dichlorophosphine **16** are presented in Table 9.

The solid state molecular structure shows that the tolyl groups are positioned on opposite sides of the central aromatic ring. The phosphorus atom is not coplanar with the central aromatic ring, it is 0.514 Å out of the plane. The C1-P1 bond length of 1.859(3) Å and P-Cl bond lengths of 2.0500(14) and 2.0565(13) Å, are close to values found in other organo-dichlorophosphines.^{68,72}

	H8, H12 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu	
¹ H NMR (δ ppm)	7.78, d J = 8.17 Hz	8.47 J = 1.74	6.67, d J = 7.97 Hz	1.78	0.86	
	C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C3 <i>,</i> C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Ме	t-Bu
¹³ C NMR (δ ppm)	137.3, d J = 104.3	128.3, d J = 4.48	133.2	130.0	21.2	30.1
e min (o ppin)	<u>С</u> (СН₃)₃	C2, C6	С7	C10	C4	
	35.3	149.0 J = 22.71	140.1, J = 1.04	144.5	157.1	

Table 9. ¹H and ¹³C NMR data for dichlorophosphine **16** (in C_6D_6)

The structure of the bis-sulfone-dichlorophosphine **16** was confirmed by single crystal X-ray diffraction, the molecular structure is presented in Figure 37.



Figure 37. Molecular structure of compound **16** the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.435(3), S1-O2 1.441(3), S2-O3 1.434(3), S2-O4 1.432(3), P1-C1 1.859(3), Cl1-P1 2.0500(14), Cl2-P1 2.0565(13), C1-P1-Cl1 104.37(11), C1-P1-Cl2 99.57(11), Cl1-P1-Cl2 102.80(6), P1-C1-C2 115.1(2), P1-C1-C6 129.1(3).

In the presence of ethanol and oxygen, the oxidation of the phosphorus atom takes place, together with the substitution of the chlorine atoms, forming compound **17**, as shown in Scheme 67.



Scheme 67. Formation of phosphorus compound 17

In the ³¹P NMR spectra of compound **17** a doublet signal could be seen at 12.60 ppm (${}^{1}J_{PH} = 615.43$ Hz), upfield shifted compared to dichlorophosphine **16** (139 ppm), characteristic to P(V) phosphorus atom and the coupling constant of 615 Hz suggesting the presence of a hydrogen atom linked to the phosphorus atom.⁷⁰ The ¹H NMR spectrum shows the signals for the methyl and *tert*-butyl group and the aromatic protons of the bissulfone ligand of the formed compound, with a slight downfield shift compared to the dichlorophosphine **16**. At 1.11 ppm a triplet and at 4.13-4.35 ppm multiplet signals can be seen for the ethoxy group linked to the phosphorus atom. The hydrogen atom linked to the phosphorus atom could not be assigned without doubt in the ¹H NMR spectrum.

15 14 0 $ -$	H8, H12 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu	H14, H15 (OEt)
¹ H NMR (δ ppm)	8.02, d J = 7.82 Hz	8.59, d J = 2.62	6.71, d J = 7.90 Hz	1.76	0.94	1.11, t, (J = 6.96 Hz) 4.13 (m) 4.35 (m)

Table 10. ¹H NMR data for compound **17** (in C_6D_6)

Single crystals suitable for X-ray analysis were obtained, the molecular structure presented in Figure 38, confirming the structure of compound **17**.



Figure 38. Molecular structure of compound **17** the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *t*-butyl groups are simplified.

The solid state molecular structure of compound **17** shows a similar geometrical arrangement to compound **16**.

After the successful synthesis and characterization of the bis-sulfone dichlorophosphine **16**, the following step was to obtain the corresponding bis-sulfone phosphaalkene.

Phosphaalkenes represent an important ligand in the chemistry of low valent p-block elements and their transition metal complexes, numerous studies proving their utility.^{53,59,60,63,73–75} The most commonly used phosphaalkene is the Mes*P=CCl₂, but there are examples with other organic groups linked to the phosphorus atom. Based on these observations, a bis-sulfone dichlorophosphaalkene was obtained starting from the bis-sulfone-dichlorophosphine **16**, following literature procedures (Scheme 68).^{76,77}



Scheme 68. Synthesis of phosphaalkene 18

The formation of the bis-sulfone phosphaalkene **18** was evidenced by NMR spectroscopy, mainly through the ³¹P NMR, where a singlet signal can be observed at 201.6 ppm, downfield shifted compared to the dichlorophosphine **16**, a characteristic behaviour for phosphaalkenes.^{59,70,76,77} The ¹H and ¹³C NMR also confirm the formation of the expected compound, data presented in Table **11**.

$\begin{array}{c} CI\\ C-CI\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\$	H8, H12 (o-Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu				
¹ H NMR (δ ppm)	7.71, d J = 8.31 Hz	8.54	7.26, d J = 8.08 Hz	2.37	1.46				
¹³ C NMR (δ ppm)	C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Me	<i>t</i> -Bu			
	146.3, d J = 3.06	128.9	131.7	129.9	21.8	31.1			
	<u>С</u> (СН₃)₃	C2, C6	C7	C10	C4	P=C			
	35.9	13 13	36.3 37.0	144.9	156.0	Not seen			

Table 11. ¹H and ¹³C NMR data for dichlorophosphaalkene **18** (in C_6D_6)

The dichlorophosphaalkene **18** is stable at air for a short time, after a few days decomposition can be observed with the formation of the bis-sulfone ligand **1**.

The coordination ability of the bis-sulfone phosphaalkene **18** was tested towards $Cl_2Pd(cod)$ complex, but it led to the formation of several compounds with signals in ³¹P NMR in the 0-50 ppm region, suggesting the oxidation of the phosphorus atom, forming P(V) derivatives.

2.6. Reaction of bis-sulfone 1 with transition metals

Pincer ligands are mainly known for their role in the chemistry of transition metal complexes,⁷⁸ thus the bis-sulfone ligand **1** was also tested to obtain such complexes with the aim to further analyze the utility of the ligand. The synthesis of a palladium and a ruthenium complex was realized with bis-sulfone **1**, according to the synthetic route shown in Scheme 69 and the formation of the new compounds was evidenced by NMR spectroscopy.



Scheme 69. Synthesis of palladium complex 19 and ruthenium complex 20

In the case of the palladium complex **19** and ruthenium complex **20**, the ¹H NMR, as depicted in Figure 39, shows the disappearance of the triplet signal for the H1 proton at 8.90 ppm (C_6D_6 , ${}^4J_{HH}$ = 1.64 Hz), indicating the formation of the new compounds.



Figure 39. ¹H NMR spectra of the aromatic region of compounds 1, 19 and 20

In the aromatic region signals for the *ortho* protons of the tolyl groups are downfield shifted from 7.82 ppm (d, ${}^{3}J_{HH} = 8.32$ Hz) in bis-sulfone **1** to 8.55 ppm (d, ${}^{3}J_{HH} = 8.28$ Hz) in the case of complex **19** and to 8.61 ppm (d, ${}^{3}J_{HH} = 8.38$ Hz) for complex **20**, while the signals for the meta protons of the central aromatic ring are upfield shifted from 8.25 ppm (d, ${}^{4}J_{HH} = 1.64$ Hz) for bis-sulfone **1** to 8.06 ppm (s) for complex **19** and 7.32 ppm (d, ${}^{4}J_{HH} = 1.37$ Hz) for complex **20**. All these data, presented in Table 12, confirm the formation of the complexes. However, the ¹H NMR spectra also suggest by the presence of signals at 2.48, 2.81 ppm and 5.44, 6.38 ppm that in the case of the palladium complex **19** a cyclooctadiene group is still linked to the metal, while in the case of the ruthenium complex **20** two triphenylphosphine groups are bonded to the Ru atom (signals at 6.87-7.03, 7.84, 7.55 ppm, integration corresponding to 30H). The ¹³C NMR data also confirm these observations.

		H8, H12 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu	CH₂ and CH (cod)	PPh3
¹ H NMR	Pd complex 19	8.55, d J = 8.28 Hz	8.06	6.75, d J = 7.96 Hz	1.73	0.86	2.48, 2.81 5.44, 6.38	-
(δ ppm)	Ru complex 20	8.61, d J = 8.38 Hz	7.32, d J = 1.37 Hz	6.71, d <i>J</i> = 8.09 Hz	1.76	0.85	-	7.84, 7.55 6.87-7.03

Table 12. ¹H NMR data for palladium complex 19 (in C_6D_6) and ruthenium complex 20 (in C_6D_6)

Single crystals of complex **19**, suitable for X-ray analysis were obtained by diffusion of pentane in CH_2Cl_2 solution and the molecular structure is shown in Figure 40.



Figure 40. Molecular structure of compound **19** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.433(2), S1-O2 1.450(3), S2-O3 1.440(2), S2-O4 1.422(3), Pd1-C1 2.004(3), Pd1-Cl1 2.3433(12), C1-Pd1-Cl1 86.04(10), Pd1-C1-C2 122.7(2), Pd1-C1-C6 122.1(2)

The solid state molecular structure confirms the formation of the complex, with a palladium atom linked to the carbon atom C1, however, contrary to the expectations, and as deduced from the ¹H NMR, not only a chlorine atom is linked to the palladium atom, but

also the cyclooctadiene group remains coordinated. The palladium atom is four coordinated, with the usual square planar geometry. The geometrical features are in agreement with values from the literature for other palladium complexes with pincer ligands.^{78,79}

2.7. Conclusions

In this chapter the synthesis, characterization and various reactions of a novel, *para*substituted bis-sulfone pincer-type ligand were presented. It was shown that the optimal geometrical features of this pincer ligand allowed the synthesis of new metallylenes, the germanium derivative being the first example of a germylene stabilized by an O,C,Ochelating pincer-type ligand presented in the literature.

The reactivity of both the germylene and the stannylene was tested toward various reagents, obtaining cycloadducts with *ortho*-benzoquinone and transition metal complexes with iron and tungsten carbonyls. It was shown that this *O,C,O*-chelating E₂CE₂ type bissulfone pincer ligand has the ability to function as an adjustable pincer ligand by its ability to coordinate to the central atom through either one of the oxygen atoms of the sulfonyl groups.

In order to obtain more information of the bis-sulfone ligand, various reactions were realized to obtain phosphorus containing derivatives and transition metal complexes. In all the cases new compounds were obtained confirming the versatility of the pincer ligand and showing further possibilities for its uses beside the stabilization of metallylenes.

2.8. Experimental Section

Synthesis of compound 2



A mixture of 157 mg of Pd₂dba (0.17 mmol, 5 mol%) and 198 mg of Xantphos (0.34 mmol, 10 mol%) in 2 ml of toluene was stirred for 5 minutes, then 1.276 g of *p*-toluenethiol (10.27 mmol, 3 eq), 1 g of 1,3-dibromo-5-*t*-butylbenzene (3.42 mmol, 1 eq) and 10.2 ml of KOH solution (50% aqueous solution) with 10 ml of distilled water in 15 ml of toluene were added. The biphasic system was heated to 90°C for 48h. After cooling to room temperature, 15 ml of CH₂Cl₂ was added and the layers were separated. The aqueous phase was washed with 15 mL of CH₂Cl₂, than all organic phases were washed with a saturated NaCl solution then dried over Na₂SO₄. After evaporating all solvents, a red oil remained. The bis-thioether **2** was separated from the mixture by column chromatography (cyclohexane) (yield = 59%)

¹H NMR (CDCl₃) δ = 1.23 (s, 9H, *t*-*Bu*), 2.35 (s, 6H, Me), 6.82 (t, 1H, ${}^{4}J_{HH}$ = 1.66 Hz, CH Ph), 7.10 (d, 4H, ${}^{3}J_{HH}$ = 7.89 Hz, *m*-CH Tol), 7.135 (d, 2H, ${}^{3}J_{HH}$ = 1.67 Hz, *m*-CH Ph), 7.245 (d, 4H, ${}^{3}J_{HH}$ = 7.58 Hz, *o*-CH Tol) ¹³C NMR (CDCl₃) δ = 21.3 (Me), 31.2 (*t*-Bu), 35.0 (*C*(CH₃)₃), 124.6, 126.9, 130.1, 130.7, 132.5, 137.8, 137.9, 152.8 **m.p.** = 75-76 °C

MS (DCI NH₃) $(C_{24}H_{26}S_2)$ $[M+1]^+ 379.1$

Elemental analysis calcd for C₂₄H₂₆S₂: C 76.14; H 6.92; found C 76.21; H 6.61;

Synthesis of compound 1



Method I: To a solution of 0.712 g of bis-thioether **2** (1.88 mmol) in 20 ml of $CHCl_3$ were added slowly 2.782 g of mCPBA (11.28 mmol, 70%). The white mixture was left stirring for
72h then 28 ml of saturated NaHCO₃ solution was added. The mixture was extracted with 3x100 ml of CH_2Cl_2 . The organic phase was washed with 14 ml of saturated NaCl solution and dried over Na₂SO₄. After evaporating all solvent, the remaining white solid was dried under vacuum then purified by column chromatography (CH_2Cl_2). Crystallization from ethanol gave white crystals suitable for X-ray study (420 mg, 50% yield).

Method II: A mixture of tris(dibenzylidenacetone)dipalladium (314 mg, 0.0342 mmol, 2 mol%) and Xantphos (495 mg, 0.8561 mmol, 5 mol%) in 20 ml of toluene was stirred for 5 minutes, then sodium *p*-toluenesulfinate (7.32 g, 41.0945 mmol, 2.4 eq), 1,3-dibromo-5-*t*-butylbenzene (5 g, 17.1227 mmol, 1 eq), Cs_2CO_3 (16.74 g, 51.3681 mmol, 3 eq) and 150 ml of toluene were successively added. The mixture was refluxed for 48 hours. After cooling to room temperature, 150 ml of H₂O were added and the aqueous phase was extracted three times with 75 ml of CH₂Cl₂, then the organic phase was washed with 75 ml of saturated NaCl solution and dried over Na₂SO₄. All solvents were evaporated under reduced pressure and the remaining solid was purified by silica gel chromatography (dichloromethane). After crystallization from ethanol white crystals were obtained (4.85g, 64% yield). (M.p. = 203-204 °C).

¹**H NMR (CDCl₃)** δ = 1.31 (s, 9H, *t-Bu*), 2.4 (s, 6H, Me), 7.31 (d, 4H, ${}^{3}J_{HH}$ = 8.1 Hz, *m*-CH Tol), 7.81 (d, 4H, ${}^{3}J_{HH}$ = 8.3 Hz, *o*-CH Tol), 8.08 (d, 2H, ${}^{4}J_{HH}$ = 1.6 Hz, *m*-CH Ph), 8.23 (t, 1H, ${}^{4}J_{HH}$ = 1.6 Hz, CH Ph).

¹³**C NMR (CDCl₃)** δ = 21.7 (Me), 31.0 (*t*-Bu), 35.7 (C*t*-Bu), 124.0 (C1), 127.9 (*C8, C12*), 128.6 (*C3, C5*), 130.3 (*C9, C11*), 137.7 (*C7*), 143.6 (C2, C6), 145.0 (*C10*), 155.0 (*C4*).

¹**H NMR (THF-D**₈) δ = 1.32 (s, 9H, *t-Bu*), 2.37 (s, 6H, Me), 7.35 (d, 4H, ${}^{3}J_{HH}$ = 8.04 Hz, *m*-CH Tol), 7.86 (d, 4H, ${}^{3}J_{HH}$ = 8.30 Hz, *o*-CH Tol), 8.13 (d, 2H, ${}^{4}J_{HH}$ = 1.60 Hz, *m*-CH Ph), 8.26 (t, 1H, ${}^{4}J_{HH}$ = 1.57 Hz, CH Ph)

¹**H NMR (C₆D₆)** δ = 0.87 (s, 9H, *t-Bu*), 1.74 (s, 6H, Me), 6.61 (d, 4H, ${}^{3}J_{HH}$ = 7.99 Hz, *m*-CH Tol), 7.82 (d, 4H, ${}^{3}J_{HH}$ = 8.31 Hz, *o*-CH Tol), 8.25 (d, 2H, ${}^{4}J_{HH}$ = 1.63 Hz, *m*-CH Ph), 8.91 (t, 1H, ${}^{4}J_{HH}$ = 1.62 Hz, CH Ph)

¹**H NMR (py-D**₅) δ = 1.17 (s, 9H, *t-Bu*), 2.15 (s, 6H, Me), 7.21 (d, 4H, ³J_{HH} = 7.73 Hz, *m*-CH Tol), 7.13 (d, 4H, ³J_{HH} = 8.24 Hz, *o*-CH Tol), 8.50 (d, 2H, ⁴J_{HH} = 1.59 Hz, *m*-CH Ph), 8.96 (t, 1H, ⁴J_{HH} = 1.59 Hz, CH Ph) IR (nujol) v_{SO} (cm⁻¹) = 1321 , 1300, 1103 MS (DCI NH₃) (C₂₄H₂₆O₄S₂) [M+18]⁺ 460 Elemental analysis calcd for C₂₄H₂₆O₄S₂ (442.13): C, 65.13; H, 5.92; found: C, 64.91; H, 5.41.

Synthesis of compound 6



To a solution of bis-sulfone **1** (1g, 0.0023 mol) in 40 mL of toluene cooled to -40°C, n-butyl lithium (1.48 mL, 0.0024 mol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a suspension of GeCl₂·dioxane (0.523 g, 0.0023 mol) in 2 mL of toluene at 0°C. The dark red reaction mixture was allowed to warm to room temperature then stirred 18 hours. After the evaporation of the volatiles, the solid was washed with CH₂Cl₂, obtaining a white powder (724 mg, yield=58%) (m.p. = 260 °C, dec). Colourless crystals suitable for X-ray analysis were obtained by slow diffusion of pentane in CH₂Cl₂ solution.

¹**H NMR (CDCl₃)** δ = 1.21 (s, 9H, *t-Bu*), 2.43 (s, 6H, Me), 7.38 (d, 4H, ${}^{3}J_{HH}$ = 8.5 Hz, *m*-CH Tol), 7.75 (s, 2H, *m*-CH Ph), 8.07 (d, 4H, ${}^{3}J_{HH}$ = 8.4 Hz, *o*-CH Tol).

¹³C NMR (CDCl₃) δ = 21.9 (Me), 31.0 (*t*-Bu), 35.5 (C *t*-Bu), 128.7 (*C8*, *C12*), 129.2 (*C3*, *C5*), 130.6 (*C9*, *C11*), 135.4 (C7), 145.1 (C2, C6), 146.1, (*C10*), 156.2 (C4), 159.9 (C1).

IR (nujol) v_{SO} (cm⁻¹) = 1280, 1270, 1114

HR-MS (DCI CH₄): (C₂₄H₂₅ClGeO₄S₂) [M]⁺ calcd: 550.0094, found: 550.0129.

Synthesis of compound 7



To a solution of bis-sulfone **1** (1g, 0.0023 mol) in 40 mL of toluene cooled to -40°C, n-butyl lithium (1.48 mL, 0.0024 mol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a suspension of SnCl₂ (0.428 g, 0.0023 mol) in 2 mL of toluene at 0°C. The dark red reaction mixture was allowed to warm to room temperature then stirred 18 hours. After the evaporation of the volatiles, the solid was washed with CH_2Cl_2 , resulting a white powder (840 mg, yield=62%) (m.p. = 260 °C, dec). Colourless crystals suitable for X-ray analysis were obtained by slow diffusion of pentane in THF solution.

¹**H NMR (CDCl₃)** δ = 1.20 (s, 9H, *t-Bu*), 2.42 (s, 6H, Me), 7.37 (d, 4H, ³*J*_{HH} = 8.07 Hz, *m*-CH Tol), 7.80 (s, 2H, *m*-CH Ph), 8.09 (d, 4H, ³*J*_{HH} = 8.40 Hz, *o*-CH Tol).

¹³C NMR (CDCl₃) δ = 21.9 (Me), 31.0 (*t*-Bu), 35.5 (C *t*-Bu), 128.7 (*C8*, *C12*), 129.6 (*C3*, *C5*), 130.6 (*C9*, *C11*), 135.8 (C7), 146.3 (C2, C6), 145.9 (*C10*), 155.5 (C4), 169.8 (C1).

¹¹⁹Sn NMR (CDCl₃) δ = -14.95, (THF-D₈) δ = -33.3.

IR (nujol) v_{SO} (cm⁻¹) = 1278, 1267, 1115

HR-MS (DCI CH₄) (C₂₄H₂₅ClSnO₄S₂) calcd: 595.9900, found: 595.9907.

Synthesis of compound 8



To a solution of bis-sulfone **1** (310 mg, 0.7 mol) in 12 mL of toluene cooled to -40°C, n-butyl lithium (0.46 mL, 0.735 mol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a suspension of $PbCl_2$ (195 mg, 0.7 mmol) in 2 mL of toluene at 0°C. The dark red reaction mixture was allowed to warm to room temperature then stirred 18 hours. After the evaporation of the volatiles, a red solid was obtained.

¹**H NMR (CDCl₃)** δ = 1.32 (s, 9H, *t-Bu*), 2.42 (s, 6H, Me), 7.33 (d, 4H, ${}^{3}J_{HH}$ = 7.97 Hz, *m*-CH Tol), 7.82 (d, 4H, ${}^{3}J_{HH}$ = 8.42 Hz, *o*-CH Tol), 8.09 (s, 2H, *m*-CH Ph).



To a solution of germylene **6** (150 mg, 0.2729 mmol) in 4 ml of THF was added dropwise a solution of 3,5-di-*tert*-butyl-*ortho*-benzoquinone (60.1 mg, 0.2729 mmol) in 1 ml of THF. The pale yellow suspension slowly became soluble, clear green-yellow solution. The reaction mixture was let stirring at room temperature overnight. Solvents were evaporated under vacuum. The green-yellow solid was washed with diethyl-ether. (80 mg, yield=57%) Crystals were obtained in CDCl₃.

¹**H NMR (CDCl₃)** δ = 1.21 (s, 9H, *t*-Bu quinone), 1.26 (s, 9H, *t*-Bu quinone), 1.45 (s, 9H, *t*-Bu), 2.45 (s, 6H, Me), 6.68 (d, 1H, ${}^{4}J_{H-H}$ = 2.24, *H* quinone), 6.75 (d, 1H, ${}^{4}J_{H-H}$ = 2.24, *H* quinone), 7.39 (d, 4H, ${}^{3}J_{H-H}$ = 7.99 Hz, *m*-CH Tol), 7.99 (s, 2H, *m*-CH Ph), 8.04 (d, 4H, ${}^{3}J_{H-H}$ = 8.37 Hz, *o*-CH Tol)

¹**H NMR (THF-D**₈) δ = 1.24 (s, 18H, *t*-Bu quinone), 1.38 (s, 9H, *t*-Bu), 2.43 (s, 6H, Me), 6.62 (d, 1H, ${}^{4}J_{H-H}$ = 2.22, H quinone), 7.46 (d, 4H, ${}^{3}J_{H-H}$ = 8.57 Hz, *m*-CH Tol), 8.10 (d, 4H, ${}^{3}J_{H-H}$ = 8.37 Hz, *o*-CH Tol), 8.17 (s, 2H, *m*-CH Ph)

¹³**C NMR (CDCl₃)** δ = 21.9 (s, Me), 29.7 (s, *t*-Bu), 30.6 (s, *t*-Bu quinone – 1.21 ppm in ¹H NMR) 31.8 (s, *t*-Bu quinone – 1.26 ppm in ¹H NMR), 34.6 and 34.8 (s, *C t*-Bu quinone), 35.7 (s, C *t*-Bu), 107.9 (s, H quinone – 6.68 ppm in ¹H NMR), 114.2 (s, H quinone – 6.75 ppm in ¹H NMR), 128.8 (*o*-*C*H Tol), 130.3 (*m*-*C*H Tol), 131.1 (*m*-*C*H Ph), 134.8 and 141.7 (C14 and C16), 136.5 (C7), 143.6 and 147.6 (C13 and C18), 145.8 (C10), 146.8 (C2, C6), 158.7 (C4);

m.p. = 268-269°C decomposition at 275 °C

MS (DCI NH₃) (C₃₈H₄₇ClGeO₆S₂) [M-1]⁺ 771.0



To a solution of stannylene **7** (125 mg, 0.2729 mmol) in 4 ml of THF a solution of 3,5-di-*tert*butyl-*ortho*-benzoquinone (60.1 mg, 0.2729 mmol) in 1 ml of THF was added dropwise. The pale yellow suspension slowly became soluble, clear green-yellow solution. The reaction mixture was let stirring at room temperature overnight. Solvents were evaporated under vacuum. The green-yellow solid was washed with diethyl-ether. (62 mg, yield=45%) Crystals of **10b** were obtained from CDCl₃.

¹**H NMR (THF-D**₈) δ = 1.19 (s, 9H, *t*-Bu quinone), 1.27 (s, 9H, *t*-Bu quinone), 1.48 (s, 9H, *t*-Bu), 2.39 (s, 6H, Me), 6.58 (d, 1H, ${}^{4}J_{H-H}$ = 2.30, H quinone), 6.62 (d, 1H, ${}^{4}J_{H-H}$ = 2.34, H quinone), 7.42 (m, 4H, ${}^{3}J_{H-H}$ = 8.68 Hz, ${}^{3}J_{H-H}$ = 10.84 Hz *m*-CH Tol), 7.98 (s, 1H, *m*-CH Ph), 8.07 (s, 1H, *m*-CH Ph), 8.38 (dd, 4H, ${}^{3}J_{H-H}$ = 8.06 Hz, ${}^{2}J_{H-H}$ = 18.16 Hz, *o*-CH Tol)

¹**H NMR (CDCl₃)** δ = 1.18-1.32 (m, 18H, *t*-Bu and *t*-Bu quinone), 1.49 (s, 9H, *t*-Bu quinone), 2.45 (s, 6H, Me), 6.76 (broad s, 1H, CH-quinone), 7.06 (broad s, 1H, CH-quinone), 7.39 (d, 4H, ${}^{3}J_{H-H}$ = 7.40 Hz, *m*-CH Tol), 7.93 (s, 2H, *m*-CH Ph), 8.11 (d, 4H, ${}^{3}J_{H-H}$ = 8.01 Hz, *o*-CH Tol);

¹**H NMR (THF-D**₈) δ = 1.19 (s, 9H, *t*-Bu), 1.27 (s, 9H, *t*-Bu quinone), 1.48 (s, 9H, *t*-Bu quinone), 2.39 (s, 6H, Me), 6.58 (d, 1H, ${}^{4}J_{H-H}$ = 2.30, *H* quinone), 6.62 (d, 1H, ${}^{4}J_{H-H}$ = 2.34, *H* quinone), 7.42 (t, 4H, *J* = 8.68 Hz, *m*-CH Tol), 7.98 (s, 1H, *m*-CH Ph), 8.07 (s, 1H, *m*-CH Ph), 8.38 (dd, 4H, *J* = 8.06 Hz, *J* = 18.16 Hz, *o*-CH Tol);

¹³C NMR (THF-D₈) δ = 21.3 (Me), 30.1 (*t*-Bu quinone – 1.48 ppm in ¹H NMR), 30.6 (*t*-Bu) 32.3 (*t*-Bu quinone – 1.27 ppm in ¹H NMR), 34.5, 35.4 and 35.6 (*C t*-Bu and *C t*-Bu quinone), 108.4 (H quinone – 6.58 ppm in ¹H NMR), 112.4 (H quinone – 6.62 ppm in ¹H NMR), 129.4 and 130.3 (*o*-CH Tol), 130.7 and 130.8 (*m*-CH Tol), 131.0 (*m*-CH Ph for 7.98 ppm in ¹H NMR),131.5 (*m*-CH Ph for 8.07 ppm in ¹H NMR), 134.6 (C1) 136.5 (C14, C16), 136.9 and 137.6 (C7), 139.7 and 140.9 (C2, C6), 146.4, 146.7, 147.2, 147.4 (C10, C13, C18), 155.1 (C4); **MS (DCI NH₃)** ($C_{38}H_{47}CISnO_6S_2$) [M+1]⁺ 817.0



A solution of germylene **2** (268 mg, 0.49 mmol) in 6.5 ml of THF was added to a solution of $Fe_2(CO)_9$ (355 mg, 0.98 mmol) in 6.5 ml of THF at -20°C. The mixture was allowed to warm slowly to room temperature then stirred overnight. Solvents were evaporated and the compound was extracted with Et_2O . Colourless crystals suitable for X-ray analysis were obtained in Et_2O at room temperature.

Synthesis of compound 12



A solution of stannylene **3** (100 mg, 0.17 mmol) in 3 ml of THF was added to a suspension of $Fe_2(CO)_9$ (122.1 mg, 0.34 mmol) in 3 ml of THF at -20°C. The mixture was allowed to warm slowly to room temperature then stirred overnight. Solvents were evaporated and the compound was extracted with Et_2O as an orange powder (88 mg, 69%). Dark orange crystals suitable for X-ray analysis were obtained in toluene at -25°C. (m.p. = 80-81 °C, dec at 100-102°C)

¹**H NMR (THF-D**₈) δ = 1.26 (s, 9H, *t-Bu*), 2.43 (s, 6H, Me), 7.51 (d, 4H, ${}^{3}J_{HH}$ = 8.0 Hz, *m*-CH Tol), 8.13 (d, 4H, ${}^{3}J_{HH}$ = 8.4 Hz, *o*-CH Tol), 8.20 (s, 2H, *m*-CH Ph).

¹³**C NMR (THF-D**₈) δ = 21.4 (Me), 30.6 (*t*-Bu), 36.4 (C *t*-Bu), 129.3 (*C8, C12*), 130.7 (*C3, C5*), 131.4 (*C9, C11*), 135.1 (C7), 145.1 (C2, C6), 147.8 (*C10*), 150.6 (C1), 159.9 (C4), 214.1 (CO).

¹¹⁹Sn NMR (THF-D₈) δ = 192.48

IR (nujol) v_{SO} (cm⁻¹) = 1297, 1109; v_{CO} (cm⁻¹) = 2040, 1963, 1905.

HR-MS (DCI CH₄): (C₂₈H₂₅ClSnO₈S₂Fe) [M]⁺ calcd: 764.9127, found: 764.9130.



To a solution of W(CO)₅·THF freshly prepared by irradiation (4 hours) of W(CO)₆ (96 mg, 0.27 mmol) in 10 ml of THF, a solution of germylene **6** (150 mg, 0.27 mmol) in 4 ml of THF was added at room temperature. The reaction mixture was stirred at room temperature for 72 hours then heated at 45°C for 3 hours. Solvents were evaporated under vacuum, the compound extracted with CH₂Cl₂. Colorless crystals were obtained in CH₂Cl₂ at -25°C. (73 mg, yield = 31%)

¹**H NMR (CDCl₃)** δ = 1.22 (s, 9H, *t-Bu*), 2.46 (s, 6H, Me), 7.42 (d, 4H, ${}^{3}J_{HH}$ = 7.99 Hz, *m*-CH Tol), 7.81 (s, 2H, *m*-CH Ph), 8.03 (d, 4H, ${}^{3}J_{HH}$ = 8.41 Hz, *o*-CH Tol),

¹³**C NMR (CDCl₃)** δ = 22.0 (Me), 30.9 (*t*-Bu), 35.8 (C *t*-Bu), 128.8 (*C8, C12*), 129.5 (*C3, C5*), 130.8 (*C9, C11*), 134.0 (C7), 143.5 (C2, C6), 147.0 (*C10*), 147.9 (C1), 158.6 (C4), 196.8 and 200.7 (CO)

m.p. = 228 °C, dec at 245°C

IR (nujol) v_{SO} (cm⁻¹) = 1287 , 1114; v_{CO} (cm⁻¹) = 2069 , 1981, 1949

Elemental analysis calcd for C₂₉H₂₅ClO₉S₂GeW (873.93): C, 39.87; H, 2.88; found C 38.97; H 2.71.

Synthesis of compound 14



To a solution of W(CO)₅·THF freshly prepared by irradiation (4 hours) of W(CO)₆ (102 mg, 0.29 mmol) in 10 ml of THF, a solution of stannylene **7** (150 mg, 0.25 mmol) in 4 ml of THF was added at room temperature. The reaction mixture was heated at 45°C for 4 hours then stirred at room temperature for 60 hours. Solvents were evaporated under vacuum, the compound was extracted with CH₂Cl₂, giving a light yellow powder (90mg, 38% yield). Colorless crystals were obtained in CH₂Cl₂ at -25°C. (m.p. = 193 °C, decomposition at 240 °C) ¹H NMR (CDCl₃) δ = 1.23 (s, 9H, *t*-Bu), 2.45 (s, 6H, Me), 7.42 (d, 4H, ³J_{HH} = 8.0 Hz, *m*-CH Tol), 7.90 (s, 2H, *m*-CH Ph), 8.02 (d, 4H, ³J_{HH} = 8.4 Hz, *o*-CH Tol).

¹³**C NMR (CDCl₃)** δ = 22.0 (Me), 31.0 (*t*-Bu), 35.8 (C *t*-Bu), 128.7 (*C8, C12*), 129.8 (*C3, C5*), 130.9 (*C9, C11*), 134.4 (C7), 144.8 (C2, C6), 146.9 (*C10*), 158.1 (C4), not seen (C1), 191.3, 196.3 and 199.6 (CO)

¹¹⁹Sn NMR (CDCl₃) δ = 50.4

m.p. = 193 °C, decomposition at 240 °C

IR (nujol) v_{SO} (cm⁻¹) = 1259, 1114; v_{CO} (cm⁻¹) = 2071, 1992, 1920, 1894,

Elemental analysis calcd for C₂₉H₂₅ClO₉S₂SnW (919.12): C, 37.87; H, 2.74; found C, 38.34; H, 2.90

Isolation of compound 15

A few crystals of compound **15** suitable for X-ray analysis were isolated in from an NMR sample of the reaction mixture of compound **12** with MeOLi in THF-D₈ kept at room temperature. Single crystal X-ray diffraction and IR analysis were realized on the crystals and are discussed in the main text.

Synthesis of compound 16



To a solution of bis-sulfone **1** (300 mg, 0.678 mmol) in 12 mL of toluene cooled to -40°C, nbutyl lithium (0.44 mL, 0.711 mmol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a solution of freshly distilled PCl₃ (0.118 mL, 1.356 mmol, 2 eq) in 2 mL of toluene at -40°C. The dark red reaction mixture slowly turned white while it was allowed to warm to room temperature then it was stirred for 18 hours. After the evaporation of the volatiles, the solid was extracted with Et_2O and the lithium salts were eliminated by centrifugation in toluene. The compound was obtained as a white powder (185 mg, yield=50%). Colourless crystals suitable for X-ray analysis were obtained in toluene solution.

¹**H NMR (C**₆**D**₆) δ = 0.85 (s, 9H, *t-Bu*), 1.76 (s, 6H, Me), 6.64 (d, 4H, ${}^{3}J_{HH}$ = 8.10 Hz, *m*-CH Tol), 7.78 (d, 4H, ${}^{3}J_{HH}$ = 8.20 Hz, *o*-CH Tol), 8.48 (d, 2H, ${}^{4}J_{HH}$ = 1.54 Hz, *m*-CH Ph).

¹³**C** NMR (C_6D_6) δ = 21.2 (Me), 30.1 (t-Bu), 35.3 (C t-Bu), 128.3 (d, J_{C-P} = 4.47 Hz, *C8*, *C12*), 130.0 (*C9*, *C11*), 132.2 (*C3*, *C5*), 137.29 (d, J_{C-P} = 104.29 Hz, *C1*), 140.1(*C7*), 144.5 (*C10*), 149.0 (d, J_{C-P} = 22.71 Hz, *C2*, *C6*) 157.1 (*C4*).

³¹P NMR ($C_6 D_6$) $\delta = 139.12$

Characterization of compound 17



To a solution of dichlorophosphine **16** in C_6D_6 were added 10 μ L of distilled EtOH.

¹**H NMR (C**₆**D**₆) δ = 0.94 (s, 9H, *t-Bu*), 1.76 (s, 6H, Me), 1.11, (t, 3H, ${}^{3}J_{HH}$ = 6.96 Hz -O-CH₂-CH₃), 4.13 and 4.35 (m, 2H, -O-CH₂-CH₃) 6.71 (d, 4H, ${}^{3}J_{HH}$ = 7.90 Hz, *m*-CH Tol), 8.02 (d, 4H, ${}^{3}J_{HH}$ = 7.82 Hz, *o*-CH Tol), 8.89 (d, 2H, ${}^{4}J_{HH}$ = 2.62 Hz, *m*-CH Ph). ³¹**P (C**₆**D**₆) δ = 12.60 (d, ${}^{1}J_{P-H}$ = 615.43 Hz)

³¹P{H} (C₆D₆) δ = 12.59



To a solution of bis-sulfone **1** (300 mg, 0.678 mmol) in 12 mL of toluene cooled to -40°C, nbutyl lithium (0.44 mL, 0.711 mmol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a solution of freshly distilled PCl₃ (0.118 mL, 1.356 mmol, 2eq) in 2 mL of toluene at -40°C. The dark red reaction mixture slowly turned white while it was allowed to warm to room temperature then it was stirred for 18 hours. All volatiles were evaporated, the white solid was solubilized in 12 mL THF and freshly distilled CHCl₃ (55 µL, 0.678 mmol) was added to this solution. The mixture was cooled down to -100°C and *n*-BuLi (0.89 mL, 1.42 mmol, 2eq, 1.6 M in hexane) was added dropwise. The red reaction mixture was allowed to warm to room temperature, and slowly became transparent. The mixture was stirred 18 hours at room temperature. After evaporating all volatiles the compound was washed with pentane and obtained as a white solid.

¹**H NMR (CDCl₃)** δ = 1.46 (s, 9H, *t-Bu*), 2.37 (s, 6H, Me), 7.26 (d, 4H, ${}^{3}J_{HH}$ = 8.08 Hz, *m*-CH Tol), 8.54 (s, 4H, *m*-CH Ph), 7.71 (d, 2H, ${}^{3}J_{HH}$ = 8.31 Hz, *o*-CH Tol).

¹³C NMR (CDCl₃) δ = 21.8 (Me), 31.1 (*t*-Bu), 35.9 (C *t*-Bu), 128.9 (*C8*, *C12*), 129.9 (*C9*, *C11*), 131.7 (*C3*, *C5*), 146.3 (d, J_{C-P} = 3.06 Hz, *C1*), 136.3 and 137.0 (*C7 and C2*, *C6*), 144.9 (*C10*), 156.0 (*C4*), *C*=P not seen.

³¹P NMR (C_6D_6) δ = 139.12



To a solution of bis-sulfone **1** (150 mg, 0.34 mmol) in 6 mL of toluene cooled to -40°C, nbutyl lithium (0.22 mL, 0.36 mmol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a suspension of $Cl_2Pd(cod)$ (97 mg, 0.34 mmol) in 2 mL of toluene at -40°C. The dark red reaction mixture was stirred for 15 minutes at this temperature then allowed to warm slowly to room temperature and stirred for 18 hours, to become a black solution. After the evaporation of the volatiles, the compound was washed with Et_2O and obtained as a dark grey powder. (135 mg, yield=58%) Colorless crystals suitable for X-ray analysis were obtained by slow diffusion of pentane in CH_2Cl_2 solution.

¹**H NMR (CDCl₃)** δ = 1.05 (s, 9H, *t-Bu*), 2.37 (s, 6H, Me), 2.95 and 3.12 (m, *CH*₂ COD) 5.54 (m, 2H, *CH* COD), 6.34 (m, 2H, *CH* COD), 7.26 (d, 4H, ${}^{3}J_{HH}$ = 7.98 Hz, *m*-CH Tol), 7.56 (s, 2H, *m*-CH Ph), 8.08 (d, 4H, ${}^{3}J_{HH}$ = 8.30 Hz, *o*-CH Tol).

¹**H NMR (C**₆**D**₆) δ = 0.86 (s, 9H, *t-Bu*), 1.73 (s, 6H, Me), 2.48 and 2.81 (m, CH₂ COD) 5.44 (m, 2H, CH COD), 6.38 (m, 2H, CH COD), 6.75 (d, 4H, ${}^{3}J_{HH}$ = 7.96 Hz, *m*-CH Tol), 8.06 (s, 2H, *m*-CH Ph), 8.55 (d, 4H, ${}^{3}J_{HH}$ = 8.28 Hz, *o*-CH Tol).

¹³C NMR (C₆D₆) δ = 21.8 (Me), 30.8 (*t*-Bu), 34.4 (C *t*-Bu), 28.2 and 31.3 (CH₂ COD), 107.4 and 122.4 (CH COD), 128.8 (*C8, C12*), 129.8 (*C3, C5*), 131.8 (*C9, C11*), 139.0, 140.4, 144.1, 147.7, 149.7.

HR-MS (DCI CH₄): (C₃₂H₃₇O₄S₂PdCl) [M-Cl]⁺ calcd: 655.1179, found: 655.1182.



To a solution of bis-sulfone **1** (150 mg, 0.34 mmol) in 6 mL of toluene cooled to -40°C, nbutyl lithium (0.22 mL, 0.36 mmol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a suspension of (PPh₃)₃RuCl₂ (325 mg, 0.34 mmol) in 1 mL of toluene at -40°C. The dark red solution was allowed to warm slowly to room temperature and stirred for 18 hours. After the evaporation of the volatiles, the compound was washed with Et₂O and pentane to obtain it as a light brown powder. (110 mg, yield=30%).

¹**H NMR (C**₆**D**₆) δ = 0.85 (s, 9H, *t-Bu*), 1.77 (s, 6H, Me), 6.71 (d, 4H, ³J_{HH} = 8.09 Hz, *m*-CH Tol), 6.87-7.03 (m, PPh₃), 7.32 (d, 2H, ⁴J_{HH} = 1.37 Hz, *m*-CH Ph), 7.55 (m, PPh₃), 7.85 (m, PPh₃), 8.61 (d, 4H, ³J_{HH} = 8.38 Hz, *o*-CH Tol).

¹³C NMR (C₆D₆) δ = 21.2 (Me), 31.1 (*t*-Bu), 34.5 (C *t*-Bu), 130.5 (*C8*, *C12*), 127.1 (d, J = 2.28 Hz, *C3*, *C5*), 129.8 (*C9*, *C11*), 144.7 (C7), 145.8 (C2, C6), 136.8, (*C10*), 148.3 (d, J = 1.87 Hz, C4), 186.7 (dd, J = 10.09 and 76.09 Hz, C1), 127.3, 127.4, 127.6, 127.8, 129.6 (PPh₃), 134.2 (d, J = 9.33 Hz, PPh₃), 135.4, 135.7 (PPh₃), 135.5 (d, J = 10.99 Hz, *o*,*m*-CH PPh₃), 136.2 (d, J = 10.82 Hz, *o*,*m*-CH PPh₃), 138.3 (d, J = 28.11 Hz, *ipso*-PPh₃)

³¹P{H} NMR (C_6D_6) δ = 25.4 (d, ² J_{P-P} = 23.45 Hz), 52.3 (d, ² J_{P-P} = 23.39 Hz)

2.9. Bibliography

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3. SULFONE-SULFOXIDE LIGAND

In the present Chapter 3, a sulfone-sulfoxide ligand is presented, containing one sulfonyl and one sulfinyl group.

In the literature there are many examples of compounds containing either sulfonyl or sulfinyl groups with various roles, ^{1–7} some examples are presented in **Figure 41**.



Figure 41. Examples of sulfone and sulfoxide based derivatives from the literature

However, there are only a small number of compounds containing both moieties^{8–11} and no examples of such compounds employed as pincer ligands. Examples of molecules containing both sulfonyl and sulfinyl groups are presented in Figure 42. It is to note, that in the case of the transition metal complexes, even if these compounds contain one sulfone and one sulfoxide group, these are of sulfenato- or sulfinato-type derivatives.^{11–13}



Figure 42. Examples of compounds containing both sulfonyl and sulfinyl groups

The effect of the sulfonyl and sulfinyl groups was tested in different situations, as seen from the examples presented in the literature, but so far the studies did not include the preparation of metallylenes or their potential pincer-type ligand behaviour.

3.1. Synthesis and characterization of the sulfone-sulfoxide ligand

For the present research, a second sulfur based pincer-type ligand was designed, containing one sulfonyl and one sulfinyl group. The asymmetry of this ligand and the effect of both the sulfonyl and the sulfinyl groups can offer new characteristics to the target metallylenes and complexes.

The 1-(p-tolylsulfinyl)-3-tosyl-5-*tert*-butyl-benzene (named sulfone-sulfoxide **23**) was obtained via two synthetic routes. In the first method, a bromo-sulfoxide was coupled with a sulfinate to introduce the two different groups in the molecule. The other method consists of the oxidation of the bis-thioether **2**.

For the first method, the bromo-thioether was synthesized by a palladium catalysed coupling reaction of p-toluenethiol and tri-tertbutyldibromobenzene (Scheme 70).



Scheme 70. Synthesis of the bromo-thioether 21

The formation of the bromo-thioether was evidenced by ¹H NMR spectroscopy, presenting three characteristic triplet signals for H1, H3 and H5 hydrogen atoms of the central aromatic ring at 7.10 (t, ${}^{4}J_{HH}$ = 1.69 Hz), 7.23 (t, ${}^{4}J_{HH}$ = 1.63 Hz) and 7.31-7.34 (m) ppm.

The bromo-thioether was oxidized to obtain the corresponding bromo-sulfoxyde. Two methods were used for the oxidation reaction, one using H_2O_2 as oxydizing agent and acetic acid as solvent, the other using mCPBA in CH_2Cl_2 .



Scheme 71. Synthesis of the bromo-sulfoxide 22

The formation of the bromo-sulfoxide was evidenced by ¹H NMR spectroscopy and X-ray diffraction.

The ¹H NMR analysis of compound **22** shows the deshielding of the characteristic triplet signals for the aromatic hydrogen atoms, compared to compound **21**, the expected effect of the sulfoxide group. The signals of the H1, H3 and H5 hydrogen atoms shift from 7.10 (t, ${}^{4}J_{HH} = 1.69$ Hz), 7.23 (t, ${}^{4}J_{HH} = 1.63$ Hz), 7.31-7.34 (m) ppm in compound **21** to 7.48 (t, ${}^{4}J_{HH} = 1.65$ Hz), 7.51-7.54 (m), 7.62 (t, ${}^{4}J_{HH} = 1.62$ Hz) ppm in compound **22**.

Single crystals suitable for X-ray analysis were obtained in CH_2Cl_2 . The solid state structure is presented in Figure 43.



Figure 43. Molecular structure of compound **22** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted and tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S2-O3 1.4921(15), C7-S1-C2 97.06(9)

A palladium catalyzed cross-coupling reaction of the bromo-sulfoxyde **22** and sodium *para*-toluene sulfinate was used to obtain the desired compound, as shown in Scheme 72.



Scheme 72. Synthesis of sulfone-sulfoxide 23

The obtained sulfone-sulfoxide **23** was purified by column chromatography and obtained as a white-beige solid. The overall yield of this method was 22%.

A second method was also used for obtaining compound **23**, through an oxidation reaction of a bis-thioether. Bis-thioether **2** was obtained by a cross-coupling reaction of 1,3-dibromo-5-tert-butylbenzene and *para*-toluene thiol, catalyzed by a palladium-xantphos complex, as presented in Scheme 73 and as mentioned before in Chapter 2, Scheme 5.



Scheme 73. Synthesis of bisthioether 2

The bis-thioether **2** was purified by column chromatography and was isolated as a white powder. Compound **2** was completely characterized by NMR spectroscopy and X-ray analysis. The ¹H NMR spectra showed characteristic signal for the H1, a triplet at δ = 6.82 (⁴J_{HH} = 1.66 Hz), while in the ¹³C NMR the signal for the C1 atom is at 126.9 ppm The ¹H and ¹³C NMR data are presented in Table 13.

bis-sulfone 1	H1	H8, H12 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu
¹ H NMR (δ ppm)	6.82, t J = 1.66 Hz	7.25, d J = 8.3 Hz,	7.14, d J = 1.6 Hz	7.10, d J = 8.1 Hz	2.35	1.23
¹³ C NMR (δ ppm)	C1	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Me	t-Bu
	126.9	130.1	124.6	132.5	21.3	31.2
	<u>С</u> (СН₃)₃	C2, C6	С7	C10	C4	
	35.0	137.8,	/137.9	130.7	152.8	

Table 13. ¹H and ¹³C NMR data (in CDCl₃) of compound 2

Suitable crystals for X-Ray diffraction were obtained in CH_2Cl_2 . The solid state structure of **2** is shown in Figure 44 together with the most significant geometrical parameters.



Figure 44. Solid state structure of bis-thioether **2** (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *t*-butyl groups are simplified. Selected bond lengths [Å] and angles [deg]: C6-S1 1.7710(15), S1-C7 1.7766(16), C2-S2 1.7734(16), S2-C13 1.7714(17), C6-S1-C7 103.76(7), C2-S2-C13 103.01(7)

The bis-thioether **2** crystallizes in the orthorhombic space group (P $2_1 2_1 2_1$), with three molecules in the unit cell. Since all three molecules present similar geometric parameters data for one molecule is presented. It is to note that the tolyl groups are placed in an almost parallel position with the C-S-C bond angle at 103°.

The bis-thioether **2** was oxidized to obtain a mixture of compounds, as shown on Scheme 74. In the literature there are several studies on oxidation of sulfides to sulfoxides or sulfones using different solvents, catalysts and oxidants on various substrates.^{14–20} However, these studies do not mention the selective formation of compounds containing one sulfonyl and one sulfinyl group.

Two methods were tested, following procedures described in the literature²¹⁻²³ but adapted to the present case, one where the oxidation is realized by adding hydrogenperoxide to the bis-thioether in anhydrous acetic acid, and a second method, where mCPBA was added to a solution of bis-thioether in CH₂Cl₂. The second method proved to be more efficient, affording only slightly higher yield, but considerably lower reaction time, 1 hour compared to 24 hours. The formation of the target compound was followed by thin layer chromatography.



Scheme 74. Synthesis of sulfone-sulfoxide 23

The mixture of the three compounds was separated through column chromatography, using as eluent either mixture of cyclohexane and ethyl acetate (8:2) or toluene and ethyl acetate (8:2). The sulfone-sulfoxide was separated with 39% yield (global yield 37%). Transparent crystals of the compound were obtained in acetone. The sulfone-sulfoxide was completely characterized by NMR spectroscopy and X-ray diffraction. The ¹H and ¹³C signals were assigned using bidimensional NMR experiments (COSY, HSQC, HMBC).

Because of the existence of two different functional groups, the sulfonyl and the sulfinyl groups, the symmetry of the bis-sulfone, like in compound **1** is no longer present. Thus, the signals of the hydrogen and carbon atoms differ, even if in some cases only slightly. Spectroscopic studies presented in literature, realized on different sulphide, sulfonyl or sulfinyl containing compounds, investigating the shielding and deshielding effect of these functional groups, show that the sulfone group has a greater deshielding effect on the adjacent aromatic or aliphatic moieties than the sulfoxide ones.^{24–26} The downfield shift of the signals in ¹H NMR is an expected phenomenon because of the polarity of the sulfone and the sulfoxide group.

Upon a detailed study of the ¹H NMR data for the H1, H3 and H5 protons of the central aromatic ring a triplet signal was observed at 7.96 ppm (t, ${}^{4}J_{HH} = 1.72$ Hz) and a doublet signal at 7.86 ppm (in CDCl₃, ${}^{4}J_{HH} = 1.73$ Hz) at first assigned to the *meta* protons H3 and H5. This doublet signal for H3 and H5 seemed to be unusual, because they are not identical due to the existence of the two different sulfonyl and sulfinyl functional groups. Indeed, if a concentrated NMR sample was used, a triplet signal could be observed at 7.95 ppm (t, ${}^{4}J_{HH} = 1.70$ Hz), at first assigned for H1, and two overlapped triplets at 7.86 and 7.87 ppm (t, ${}^{4}J_{HH} = 1.60$ Hz, 1.65 Hz) instead of the previously seen doublet signal.



Figure 45. Aromatic region of the ¹H NMR of sulfone-sulfoxide **23** and the corresponding deuterated derivative **26**

For further understanding and to explain this observation, variable temperature ¹H NMR analysis was realized in CDCl₃. In the ¹H NMR spectra of the sulfone-sulfoxide **23** at -75 °C two triplet signals can be seen at 7.83 (${}^{4}J_{HH}$ = 1.56 Hz) and 7.86 (${}^{4}J_{HH}$ = 1.64) instead of a doublet signal (or a doublet of triplets), as expected for the compound. All these suggest a dynamic behavior of the sulfone-sulfoxide **23** due to the existence of both the sulfonyl and sulfinyl groups in the molecule. This could result in easier adaptability of the ligand which can play a role in the stabilization of the target metallylenes. The ¹H NMR spectra of sulfone-sulfoxide **23** at different temperatures are presented in Figure 46.



Figure 46. ¹H NMR spectra in CDCl₃ of sulfone-sulfoxide 23 at different temperatures

In order to assign these three triplet signals for the H1, H3 and H5 protons of sulfone-sulfoxide **23**, bidimensional NMR experiments (COSY, HSQC, HMBC) were employed, fragments of the HMBC and HSQC spectra are shown in Figure 47. In the HSQC spectrum a correlation can be seen between the signals at 121 ppm in ¹³C NMR, assigned for the C1 carbon atom, and one of the signals from the doublet of triplets at 7.9 ppm. Furthermore, in the HMBC spectrum there is a correlation between the signal at 35 ppm in ¹³C NMR, assigned for the quaternary carbon atom of the *tert*-butyl group (*C*(CH₃)₃) and both signals

at 8.0 and 7.9 ppm. All these suggest that the triplet signal at 7.95 ppm is for one of the *meta* protons of the central aromatic ring (H3, H5) and the signal for the H1 proton is found at 7.87 ppm (t, ${}^{4}J_{HH}$ = 1.60 Hz). This observation was further confirmed from the ¹H NMR (Figure 45) of the deuterated compound **26** (Scheme 75), where the signal at 7.96 ppm (d, ${}^{4}J_{HH}$ = 1.77 Hz) is still there, this, together with the signal at 7.86 ppm (d, ${}^{4}J_{HH}$ = 1.78 Hz) being assigned for the H3 and H5 protons.



Figure 47. Fragment from the HSQC and HMBC bidimensional NMR experiments for compound **23** (CDCl₃)

However, in THF-D₈ the ¹H NMR spectrum of sulfone-sulfoxide **23** exhibits three triplet signals for the H1, H3 and H5 aromatic protons at 7.94 (t, 1H, J = 1.68 Hz, m-Ph), 7.98 (t, 1H, J = 1.74 Hz, m-Ph), 8.03 (t, 1H, J = 1.59 Hz, C1).

The ¹H NMR spectra exhibits the characteristic signals of the tolyl and of the central aromatic cyclic moieties, ¹H and ¹³C NMR data are presented in Table 14.

11 12 7 10 9 8 3 4 5 18 19 14 10 9 8 3 4 5 18 19 14 10 10 10 10 10 10 10 10 10 10	H1	H8, H12 (o-Tol)	H14, H18 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11, H15, H17 (<i>m</i> -Tol)	Me	t-Bu
¹ H NMR (δ ppm) in CDCl ₃	7.87, t J = 1.60 Hz	7.77, d J = 8.32 Hz	7.49, d J = 8.21 Hz	7.86, t J = 1.65 Hz, 7.95, t J = 1.70 Hz	7.24- 7.30, m	2.36 2.39	1.29
¹ Η NMR (δ ppm) in THF-D ₈	8.03, t, J = 1.59 Hz	7.58, d, J = 7.81, d, J =	= 8.19 Hz = 8.29 Hz	7.94, t, J = 1.68 Hz 7.98, t, J = 1.74 Hz	7.27, d, J = 7.92 Hz 7.33, d, J = 7.94 Hz	2.37 2.33	1.30
	C1	C8, C12 (<i>o</i> -Tol)	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11, C15, C17 (<i>m</i> -Tol)	C2	C6
	121.2	127.9	125.1	125.7 126.5	130.2 130.4	147.7	143.2
¹³ C NMR (δ ppm)	С7	C13	C10	C16	C4	Me	<i>t</i> -Bu
	141.7	138.1	144.7	142.4	154.7	21.5 21.7	31.1
	<u>C(</u> CH ₃) ₃						

Table 14. ¹H (in CDCl₃ and THF-D₈) and ¹³C NMR data (in CDCl₃) of compound 23

Single crystals of sulfone-sulfoxide **23** suitable for single crystal X-ray analysis were obtained in acetone, the solid state structure is presented in Figure 48. The X-ray analysis showed that the O atoms of the sulfonyl and sulfinyl groups present different occupancy for four atoms: O1 is present with 99% occupancy, O2 with 68%, O3 with 100% and O4 with 42%, O3 being distorted over two positions (O3 and O4). This suggests the possibility of different conformations for the sulfone-sulfoxide **23**.



Figure 48. Molecular structure of compound **23** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted and tolyl and t-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.477; S1-O2 1.306; S2-O3 1.389; O1-S1-O2 119.O3, O1-S1-C6 106.19, O2-S1-C6 106.52, O3-S2-C2 106.25, C1-C6-S1 117.97, C1-C2-S2 118.61.

The tolyl groups of the sulfone-sulfoxide **23** are situated on opposite sides of the central aromatic ring, similar to bis-sulfone **1**, with the sulfur-oxigen bond distances close to the values in the literature for S=O bonds in sulfoxides (1.43 Å).^{27,28,5}

3.2. Synthesis of metallylenes with the sulfone-sulfoxide ligand

The corresponding lithium derivative was obtained by adding toluene or THF at -80 °C to a solid mixture of the sulfone-sulfoxide and LDA, as shown in Scheme 75. LDA was previously prepared and kept as a solid in the glovebox. After quenching with D₂O, the formation of a sole product was observed by the complete disappearance of the signal for the H1 proton at 7.86 ppm (CDCl₃). From the triplet signals at 7.95 ppm and 7.86 ppm in the ¹H NMR of sulfone-sulfoxide **23**, two doublet signals remain at 7.96 ppm (d, ⁴J_{HH} = 1.77 Hz) and 7.86 ppm (d, ⁴J_{HH} = 1.78 Hz), assigned for H3 and H5 protons, as shown in Figure 45, this

suggesting that the deprotonation is quantitative and leads to the expected compound **26** (Scheme 75).



Scheme 75. Deprotonation reaction of sulfone-sulfoxide 23

To obtain the metallylene with the sulfone-sulfoxide ligand, the carbanion was added to a solution of GeCl₂·dioxane or SnCl₂ in toluene or THF and left with stirring at room temperature overnight. After evaporating all volatiles the remaining solid was extracted with dichloromethane then washed with diethyl ether and pentane to give a white powder in good yield. The stannylene and germylene are soluble in THF, toluene, dichloromethane and DMSO but not at all in diethyl ether and pentane. The process of obtaining germylene **27** and stannylene **28** is depicted in Scheme 76.



Scheme 76. Synthesis of germylene 27 and stannylene 28

The new germylene **27** and stannylene **28** were characterized by NMR spectroscopy and MS spectrometry. The ¹H NMR data of germylene **27** and stannylene **28** are presented in Table 15.

M = Ge	27, Sn 28	H8, H12 (o-Tol)	H14, H18 (o-Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11, H15, H17 (<i>m</i> -Tol)	Me	t-Bu
¹ H NMR	germylene 27	8.10, d J = 8.31 Hz	7.31-7.36,m	7.80, s	7.31-7.36,m	2.41	1.18
(δ ppm)	stannylene 28	8.13, d J = 8.38 Hz	7.31-7.37, m	7.72,s 7.72, s	7.31-7.37, m	2.41 2.39	1.16

Table 15. ¹H data (in CDCl₃) of compound 27 and 28

The clear evidence for the formation of the metallylenes **27** and **28** in NMR spectroscopy is the disappearance of the triplet signal at 7.95 ppm (in CDCl₃) for the H1 proton in the ¹H NMR spectra of the compounds, when compared with the sulfone-sulfoxide ligand **23**, as depicted in Figure 49. Furthermore, a slight downfield shift can be observed for the signals for the *o*-tolyl groups from 7.77 ppm (d, ³J_{HH} = 8.32 Hz) for sulfone-sulfoxide **23** to 8.10 ppm (d, ³J_{HH} = 8.31 Hz) for germylene **27** and 8.13 ppm (d, ³J_{HH} = 8.38 Hz) for stannylene **28**. The same behavior can be observed in THF-D₈. In the ¹³C NMR spectrum the significant downfield shift can be seen for the signal of the C1 carbon atom from 126.5 ppm in sulfone-sulfoxide **23** to 162.4 ppm in germylene **27** and 172.4 ppm in stannylene **28**. These effects can be observed in the case of the bis-sulfone **1** and the corresponding germylene **7** and stannylene **8**, as described in chapter 2.





In CDCl₃ the germylene **27** and stannylene **28** were not completely soluble, causing the signals in ¹H NMR to become broader, the NMR analysis was realized in THF-D₈ and DMSO-D₆. ¹H and ¹³C NMR data for stannylene **28** recorded in THF-D₈ is presented in Table 16. The ¹H and ¹³C NMR spectra in DMSO-D₆ are presented in the Experimental part.

The assignment of the signals in the ¹H and ¹³C NMR spectra was realized based on two dimensional COSY, HSQC and HMBC correlations. The ¹¹⁹Sn NMR spectrum for stannylene **28** exhibits a broad signal at 61.3 ppm in THF-D₈.

Sn Cl 11 10 9 8 3 4 5 18 17 16 10 10 10 10 10 10 10 10 10 10	H8, H12 (<i>o</i> -Tol)	Н14, Н (<i>о</i> -То	18)	H3 (<i>m</i> -Ph)	H5 (<i>m</i> -Ph)		H9, H11 (<i>m</i> -Tol)
	8.19, d J = 8.36 Hz	7.93, bro J = 7.58	ad d, SHz	7.79, d J = 1.42 Hz	7.62, d J = 1.42	Hz J	7.37, d = 8.08 Hz
¹ Η NMR (δ ppm)	H15, H17 (<i>m</i> -Tol)	,	Me (C10)	Me (C16)	t-I	3u	
	7.34, d J = 8.12 H	z	2.38	2.35	1.:	17	
	C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C14, C1 (<i>o</i> -Tol)	8 C3) (<i>m</i> -Ph)	C5 (<i>m</i> -Ph)	C9, C11, (<i>m</i> -Tol)	C15, C17 (<i>m</i> -Tol)
	172.4	129.8	128.6	12 12	.6.5 .7.8	131.0	131.4
¹³ C NMR (δ ppm)	C2	C6	С7	C13	C10	C16	C4
	149 151	.6 .1	138.6	139.6	144.9	145.8	155.2
	Me	t-Bu	<u><i>С</i>(</u> СН₃)	3			
	21.6 21.7	31.2	36.0				

Table 16. ¹H and ¹³C NMR data (in THF-D₈) of compound **28**

The presence of the molecular peak at 579.9988 in the mass spectrum of stannylene **28** is also a proof for the formation of the expected stannylene.

3.3. Reactivity of the sulfone-sulfoxide stabilized metallylenes

The coordination ability of the new germylene **27** and stannylene **28** was evaluated towards iron and tungsten, as shown on Scheme 77 and Scheme 78.





The reaction of germylene **27** with iron pentacarbonyl did not take place. In the ¹H NMR of the reaction mixture only the signals for the starting germylene **27** were observed. A mixture of compounds which could not be separated and identified was obtained from the reaction of germylene **27** with tungsten carbonyl complex.

Stannylene **28** reacts with diironnonacarbonyl and pentacarbonyl tungsten·THF, giving the corresponding complexes, as presented in Scheme 78.



Scheme 78. Synthesis of stannylene-iron complex 31 and stannylene-tungsten complex 32

The ¹H NMR analysis of the stannylene-iron complex **31** shows the downfield shifts for the aromatic protons, characteristic for such complexes. The ¹³C NMR shows characteristic signal for the carbon atoms in the carbonyl groups of the complex **31** at 214.7 ppm. In both spectra the ¹H and ¹³C NMR some signals are larger, probably because of a dynamic behavior of the compound. This dynamic behavior could be caused by the coordination of the oxygen atoms of the sulfonyl and sulfinyl groups. It can be noticed that, because of the non-symmetric structure of the sulfone-sulfoxide ligand, the signals for the two tolyl groups and the central aromatic ring are different in both ¹H and ¹³C NMR spectra. ¹H and ¹³C NMR data for complex **31** are presented in Table 17.

Cl Fe(CO) ₄ 11 12 52 15 13 14 17 16 17 17 17 17 17 17 17 17 17 17	H8, H12 (<i>o</i> -Tol)	H14, H18 (<i>o</i> -Tol)	H3 (<i>m</i> -Ph)	H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)
¹ H NMR (δ ppm)	8.13, d J = 8.26 Hz	7.89, broad s	8.08, d J = 1.33 Hz	7.70, broad s	7.47, d J = 8.11 Hz
	H15, H17 (<i>m</i> -Tol)	Me (C10)	Me (C16)	t-Bu	
	7.40, d J = 7.49 Hz	2.42	2.38	1.24	

Table 17. ¹H and ¹³C NMR data (in THF-D₈) of compound **31**

¹³ C NMR (δ ppm)	C1 (ipso)	C8, C12 (<i>o</i> -Tol)	C14, C18 (<i>o</i> -Tol)	C3 (<i>m</i> -Ph)	C5 (<i>m</i> -Ph)	C9, C11, (<i>m</i> -Tol)	C15, C17 (<i>m</i> -Tol)
	146.5	5.5129.3128.8128.4/128.6127.5		131.2	131.5		
	C2	C6	С7	C13	C10	C16	C4
	133.8/154.3		136.2	137.2	146.9	145.9	158.8
	Me	t-Bu	<u>С</u> (СН ₃) ₃	со			
	21.3 21.4	30.8	36.3	214.7 211.3			

The ¹¹⁹Sn NMR spectrum of complex **31** shows two signals at 224 and 242 ppm, a downfield shift compared to stannylene **28** (61 ppm), as expected for the stannylene-iron complexes and as previously seen in the case of stannylene **7** (-33.30 ppm in THF-D₈) and complex **12** (192.48 ppm in THF-D₈). A variable temperature NMR experiment from 25 to 50°C (Figure 50) reveals that the two signals are present in both spectra recorded at 25°C and 50°C.



Figure 50. ¹¹⁹Sn NMR of complex **31** at 25 °C and at 50 °C

The two signals in the ¹¹⁹Sn NMR suggests the presence of two isomers. The proposed structures of the isomers are shown in Figure 51. The appearance of the two isomers could be explained by the coordination of the oxygen atoms of the sulfonyl and sulfinyl groups to the tin atom creating a chiral tin atom.



Figure 51. Proposed isomeric structures of stannylene-iron complex 31

The mass spectrometry also confirms the formation of the stannylene-iron complex **31** by the presence of the molecular peak at 747.9157 in HR-MS DCI-CH₄.

Reaction of stannylene **28** with pentacarbonyl tungsten THF complex gives stannylene-tungsten complex **32**, as shown on Scheme 78. The formation of the new compound was evidenced by NMR spectroscopy. In the ¹H NMR spectrum the shift of the signals for the aromatic protons is characteristic for such complexes.²⁹ NMR data of complex **32** are presented in Table 18.

$\begin{array}{c} CI & W(CO)_5 \\ \hline 0 & Sn & O \\ 11 & 7 & 2 & 16 \\ 10 & 9 & 3 & 45 & 18 & 17 & 16 \\ \hline 10 & 9 & 3 & 45 & 18 & 17 & 16 \\ \hline \end{array}$	H8, H12 (<i>o</i> -Tol)	H14, H18 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	H15, H17 (<i>m</i> -Tol)
complex 32					
	8.14, d <i>J</i> = 8.34 Hz	7.86-7.98, broad s	8.01, d, J = 1.33 Hz 7.86-7.98, broad s	7.46, d J = 8.02 Hz	7.40, d J = 8.18 Hz
¹ H NMR (δ ppm)	Me (C10, C16)	<i>t</i> -Bu			
	2.42 2.38	1.22			

Table 18. ¹H and ¹³C NMR data (in THF-D₈) of compound **32**
The presence of the molecular peak at 904.9279 in HR-MS DCI-CH₄ also confirms the formation of the stannylene-tungsten complex **32**.

Reaction of the stannylene **28** with platinum or gold gave insoluble compounds. Multiple coordination sites are available in the stannylene **28**, thus several structures are possible for the complexes. In Scheme 79 the most probable structures are shown.



Scheme 79. Reaction of stannylene 28 with Pt and Au and proposed structures

In the reaction of stannylene **28** with (COD)PtCl₂ in THF an insoluble solid was formed. The solid proved to be soluble only in DMSO. The ¹H NMR spectrum shows the formation of a new compound, however the ¹³C and ¹¹⁹Sn NMR could not be recorded, not even at 60°C. This could indicate that the complexation to platinum gives a compound where the steric hindrance or the dynamics of the molecule cause difficulty in recording the NMR spectra. The ¹H NMR registered at 60°C in DMSO-D₆ shows five doublet signals in the aromatic region, two singlet signals at 2.38 and 2.43 ppm for the methyl groups of the tolyl groups and a singlet signal at 1.20 ppm for the *tert*-butyl group, corresponding to the sulfone-sulfoxide ligand of the complex. All the aromatic signals are deshilded, compared to the stannylene, which is an indication for the formation of the complex. ¹H NMR data for the stannylene-platinum complex **34** are presented in Table 19.

The ¹H NMR spectra in CDCl₃ of the stannylene gold complex **33**, indicates the formation of a new compound. Furthermore, the ¹¹⁹Sn NMR spectrum shows two signals, at -90 ppm and at 182 ppm. However, further analysis could not be realized due to the high insolubility of the compound in CDCl₃ and to the fact that in THF-D₈ in the ¹H and ¹³C NMR spectra only large signals could be seen.

Cl ₂ Cl ₂	H8, H12 (<i>o</i> -Tol)	H14, H18 (o-Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	H15, H17 (<i>m</i> -Tol)
	8.15 J = 8.25	7.84, d J = 8.08	8.07 8.11	7.56, d J = 8.10	7.47, d J = 8.14
¹ Η NMR (δ ppm)	Me (C10, C16)	<i>t</i> -Bu			
	2.38 2.43	1.20			

Table 19. ¹H NMR data (in DMSO-D₆) of compound 33

The ¹H NMR spectra of compound **33** compared to the starting stannylene **28** and the ¹¹⁹Sn NMR spectra are presented in Figure 52.



Figure 52. ¹H and ¹¹⁹Sn NMR spectra of compound 33

3.3. Conclusions

In this chapter a sulfone-sulfoxide type pincer ligand was presented. The new pincertype ligand contains one sulfonyl and one sulfinyl group in the *ortho* position of the central aromatic ring. The two different *ortho*-substituents cause the asymmetry of the molecules and lead to multiple possible structures of the metallylenes and their complexes. The formation of a germylene and stannylene was evidenced with this new sulfone-sulfoxide ligand and their reactivity was tested toward transition metal complexes. Even though the structure of the metallylenes and their transition metal complexes was not determined by single crystal X-ray diffraction, the NMR and mass analysis provided the evidence for the formation of the new derivatives. The presented results are promising, they represent the beginning of a new research area in the chemistry of pincer-ligand stabilized metallylenes.

3.4. Experimental Section





A mixture of tris(dibenzylideneacetone)dipalladium (157 mg, 0.017 mmol, 5 mol%) and Xantphos (198 mg, 0.34 mmol, 10 mol%) in 2 ml of toluene was stirred for 5 minutes, then *p*-toluenethiol (510 mg, 4.11 mmol, 1.2 eq), 1,3-dibromo-5-*t*-butylbenzene (1 g, 3.42 mmol, 1 eq) in 15 ml of toluene and a 50% aqueous solution of KOH (10.18 ml, 7.69 g, 136.98 mmol, 40 eq) were successively added. The mixture was heated at 90°C for 24 hours. After cooling to room temperature, the phases were separated, the aqueous phase was extracted three times with 15 ml of CH_2Cl_2 , then the organic phase was washed two times with 20 ml of saturated NaCl solution and dried on Na_2SO_4 . All solvents were evaporated under reduced pressure and the remaining solid was purified by silica gel chromatography (cyclohexane). The monothioether was obtained as a transparent yellowish oil (450 mg, 39% yield).

¹**H NMR** (**CDCl**₃) δ = 1.26 (s, 9H, *t-Bu*), 2.37 (s, 3H, Me), 7.10 (t, 1H, ${}^{4}J_{HH}$ = 1.69 Hz, CH-Ph), 7.17 (d, 2H, ${}^{3}J_{HH}$ = 7.9 Hz, CH-Tol), 7.23 (t, 1H, ${}^{3}J_{HH}$ = 1.63 Hz, CH-Ph), 7.31-7.34 (m, 3H, CH-Ph and CH-Tol).

Synthesis of compound 21



Method I

To a solution of bromo-thioether **21** (400 mg, 1.19 mmol) in 1.6 ml of acetic acid a 33 wt% H_2O_2 solution was added (0.11 ml) in 0.9 ml of acetic acid. After stirring at room temperature for 20 minutes 1 ml of acetic acid was added and stirred for 24h. 15 ml of saturated KOH solution was added to neutralize the mixture. After addition of 4 ml of CH₂Cl₂, the phases were separated and the aqueous phase was extracted four times with 7 ml of CH₂Cl₂. The organic phase was evaporated to obtain a white solid. The compound was separated by column chromatography (cyclohexane/ EtOAc 8/2). A white solid was obtained (220 mg, yield = 52%)

Method II

To a solution of bromo-monothioether **21** (450 mg, 1.34 mmol) in 11 ml of CH_2CI_2 a solution of *meta*-chloroperoxybenzoic acid (301.1 mg, 1.74 mmol, 77%, 1.3 eq) in 11 ml of CH_2CI_2 was added dropwise at 22°C. After stirring at this temperature for 15 min, 40 mL of saturated aqueous solution of NaHCO₃ was added and the layers were separated. The organic phase was evaporated and the white solid was purified by column chromatography to obtain a white powder (386 mg, yield = 82%).

¹**H NMR (CDCl₃)** δ = 1.30 (s, 9H, *t-Bu*), 2.38 (s, 3H, Me), 7.28 (d, 2H, *J* = 7.92 Hz, CH-Tol), 7.48 (t, 1H, ${}^{4}J_{HH}$ = 1.65 Hz, CH-Ph), 7.51-7.54 (m, 3H, CH-Ph and CH-Tol), 7.62 (t, 1H, ${}^{4}J_{HH}$ = 1.62 Hz, CH-Ph).

Synthesis of compound 2



A mixture of Pd_2dba_3 (784 mg, 0.086 mmol, 5 mol%) and Xantphos (991 mg, 1.71 mmol, 10 mol%) in 5 ml of toluene was stirred for 5 minutes, then *p*-toluenethiol (6.380 g, 51.40 mmol, 3 eq), of 1,3-dibromo-5-*t*-butylbenzene (5 g, 0.017 mmol, 1 eq), a KOH solution (50.9 ml, 50% aqueous solution) and 80 ml of toluene were added. The biphasic system was heated to 90°C for 48h. After cooling to room temperature, 75 ml of CH₂Cl₂ was added and the layers separated. The aqueous phase was washed with 75 mL CH₂Cl₂, than all organic phases were washed with a saturated NaCl solution then dried on Na₂SO₄. After evaporating all solvents, red oil remained. The bis-tioether was purified by column chromatography (cyclohexane) (6.18 g, yield = 95%)

¹**H NMR (CDCl₃)** δ = 1.23 (s, 9H, *t-Bu*), 2.35 (s, 6H, Me), 6.82 (t, 1H, ${}^{4}J_{HH}$ = 1.66 Hz, CH Ph), 7.10 (d, 4H, ${}^{3}J_{HH}$ = 7.89 Hz, *m*-CH Tol), 7.14 (d, 2H, ${}^{4}J_{HH}$ = 1.67 Hz, *m*-CH Ph), 7.24 (d, 4H, ${}^{3}J_{HH}$ = 7.58 Hz, *o*-CH Tol)

¹³C NMR (CDCl₃) δ = 21.3 (Me), 31.2 (*t*-Bu), 35.0 (*C*(CH₃)₃), 124.6, 126.9, 130.1, 130.7, 132.5, 137.8, 137.9, 152.8

m.p. = 75-76 °C

MS (DCI NH₃) $(C_{24}H_{26}S_2)$ $[M+1]^+ 379.1$

Elemental analysis calcd calculated for C₂₄H₂₆S₂: C 76.14; H 6.92; found C 76.21; H 6.61;

Synthesis of compound 23



Method I

A mixture of tris(dibenzylideneacetone)dipalladium (10 mg, 0.0114 mmol, 2 mol%) and Xantphos (16 mg, 0.0285 mmol, 5 mol%) in 1 ml of toluene was stirred for 5 minutes, then sodium *p*-toluenesulfinate (122 mg, 0.6832 mmol, 1.2 eq), bromo-monosulfoxide **22** (200 mg, 0.5693 mmol, 1 eq), Cs_2CO_3 (278 mg, 0.8540 mmol, 1.5 eq) and 4 ml of toluene were successively added. The mixture was refluxed for 22 hours. After cooling to room temperature, 10 ml of ethyl acetate and 7 ml of H₂O were added and the aqueous phase was extracted two times with 10 ml of ethyl acetate, then the organic phase was washed with 20 ml of H₂O and dried on Na₂SO₄. All solvents were evaporated under reduced pressure and the remaining solid was purified by silica gel chromatography (cyclohexane/EtOAc 8/2). A white solid was obtained (164 mg, 68% yield).

Method II

To a solution of bis-thioether **2** (200 mg, 0.5283 mmol) in 0.8 ml of acetic acid a 33 wt% H_2O_2 solution was added (0.159 ml, 3eq) in 0.5 ml of acetic acid. After stirring at room temperature for 20 minutes 0.5 ml more acetic acid was added and stirred for 22h. A KOH solution was added to the mixture dropwise until the pH became 10 (15 mL) and 4 ml of CH_2Cl_2 were added. The phases were separated, the aqueous phase was extracted four times with 10 ml of CH_2Cl_2 and the organic phase was washed two times with 20 ml of saturated NaCl solution. The organic phase was evaporated to obtain a white solid. (28% conversion, calculated from ¹H NMR spectrum)

Method III

To a solution of bis-thioether **2** (3 g, 0.0079 mol) in 50 ml of CH_2Cl_2 a solution of mCPBA (4.5g, 0.0262 mol, 3 eq) in 50 ml of CH_2Cl_2 was added dropwise at 0°C. The mixture was stirred at 0°C for one hour and at room temperature for 20 minutes then washed three times with 75 ml saturated aqueous solution of NaHCO₃ and all solvents evaporated. The sulfone-sulfoxide **23** was obtained in the mixture with the bis-sulfone and bis-sulfoxide. The compounds were separated by column chromatography (cyclohexane/ ethyl acetate – 8/2) to obtain the sulfone-sulfoxide as a white powder (1.32g, 39% yield)

¹**H NMR (CDCl₃)** δ = 1.29 (s, 9H, *t-Bu*), 2.36 (s, 3H, Me), 2.38 (s, 3H, Me), 7.24-7.30 (m, 4H, *m-Tol*), 7.49 (d, 2H, ${}^{3}J_{HH}$ = 8.21 Hz, *o-Tol H9,H11*), 7.77 (d, 2H, ${}^{3}J_{HH}$ = 8.32 Hz, *o-Tol H14,H18*), 8.86 (t, 1H, ${}^{1}J_{HH}$ = 1.65 Hz, *H3/H5*), 8.86 (t, 1H, ${}^{4}J_{HH}$ = 1.60 Hz, *H1*), 7.95 (t, 1H, ${}^{4}J_{HH}$ = 1.70 Hz, *H3/H5*).

¹³**C NMR (CDCl₃)** δ = 21.5 (Me), 21.7 (Me), 31.1 (t-Bu), 35.7 (C t-Bu), 127.9 (C8, C12), 121.2 and 125.7 (C3, C5), 130.2 and 130.4 (C9, C11, C15, C17), 141.7 (C7), 147.7 (C2), 143.2 (C6), 138.1 (C13), 144.7 (C10), 142.4 (C16), 154.7 (C4), 126.5 (C1).

¹**H NMR (THF-D**₈) δ = 1.30 (s, 9H, *t-Bu*), 2.33 (s, 3H, Me), 2.37 (s, 3H, Me), 7.27 (d, 2H, ${}^{3}J_{HH}$ = 7.92, *m-Tol*), 7.33 (d, 2H, ${}^{3}J_{HH}$ = 7.94 Hz, *m-Tol*), 7.58 (d, 2H, ${}^{3}J_{HH}$ = 8.19 Hz, *o-Tol*), 7.81 (d, 2H, ${}^{3}J_{HH}$ = 8.29 Hz, *o-Tol*), 7.94 (t, 1H, ${}^{4}J_{HH}$ = 1.68 Hz, *m-Ph*), 7.98 (t, 1H, ${}^{4}J_{HH}$ = 1.74 Hz, *m-Ph*), 8.03 (t, 1H, ${}^{4}J_{HH}$ = 1.59 Hz, *C1*).

Mp = 128 °C

Synthesis of compound 27



To a mixture of sulfone-sulfoxide **23** (600mg, 1.41 mmol) and LDA (1.55 mmol) as solids were added at -80°C 12 ml of toluene or THF. The mixture was allowed to warm up slowly to -30°C during 3 hours, until it became a clear dark red-green solution. Then it was cooled to -40°C and added to a suspension of GeCl₂·dioxane (391.4 mg, 1.6896 mmol, 1.2 eq) in 2 ml of toluene or THF. The orange mixture was allowed to warm up slowly to room temperature then stirred for 20 hours. All volatiles were evaporated; the product was extracted with CH_2Cl_2 then washed with Et_2O and pentane to obtain a light yellow powder (600 mg, 79% yield).

¹**H NMR (CDCl₃)** δ = 1.18 (s, 9H, *t-Bu*), 2.41 (s, 6H, Me), 7.31-7.36 (m, 6H, *m*-CH Tol and *o*-Tol), 7.80 (s, 2H, *m*-CH Ph), 8.10 (d, 2H, ${}^{3}J_{HH}$ = 8.31 Hz, *o*-CH Tol).

¹³C NMR (THF-D₈) δ = 21.8, 21.9 (Me), 31.0 (*t*-Bu), 35.4 (C *t*-Bu), 126.6, 125.8, 125.2, 124.9, 124.6, 121.3, 127.9 128.0, 128.7, 129.4, 130.2, 130.5, 131.1 (*C3, C5 – mPh, C8, C12 – oTol, C8, C12 – oTol, C9, C11 mTol*), 135.8, 137.2, 145.0, 145.5, 147.5 (C7 – ipsoTol, *C10 pTol,* C2, C6 – oPh), 155.3 (C4 – p Ph), 162.4 (C1).

Synthesis of compound 28



To a mixture of sulfone-sulfoxide **23** (300mg, 0.70 mmol) and LDA (0.77 mmol) as solids were added at -80°C 12 ml of toluene or THF. The mixture was allowed to warm up slowly to -30°C during 3 hours, until it became a clear dark red-green solution. Then it was cooled to - 40°C and added to a suspension of SnCl₂ (160.2 mg, 0.8448 mmol, 1.2 eq) in 2 ml of toluene or THF. The orange mixture was allowed to warm up slowly to room temperature then stirred for 20 hours. All volatiles were evaporated; the product was extracted with CH_2Cl_2 then washed with Et_2O and pentane to obtain a light yellow powder (300 mg, 73% yield).

¹**H NMR (THF-D**₈) δ = 1.16 (s, 9H, *t-Bu*), 2.34 (s, 3H, Me SO), 2.37 (s, 3H, Me SO2), 7.33 (d, 2H, ${}^{3}J_{HH}$ = 8.05 Hz, *m*-CH Tol SO), 7.37 (d, 2H, ${}^{3}J_{HH}$ = 8.23 Hz, *m*-CH Tol SO2), 7.63 (d, 1H, ${}^{4}J_{HH}$ = 1.20 Hz, *m*-CH Ph SO), 7.79 (d, 1H, ${}^{4}J_{HH}$ = 1.1 Hz, *m*-CH Ph SO2), 7.94 (large, 2H, *o*-CH Tol SO), 8.18 (d, 2H, ${}^{3}J_{HH}$ = 8.26 Hz, *o*-CH Tol SO2).

¹³**C** NMR (THF-D₈) δ = 21.6 (Me), 21.7 (Me), 31.2 (*t*-Bu), 36.0 (C *t*-Bu), 126.5 (*C3*, *C5* – *mPh SO2*), 127.8 (*C3*, *C5* – *mPh SO2*), 128.6 (large signal *C8*, *C12* – *oTol SO*), 129.8 (*C8*, *C12* – *oTol SO2*), 131.0 (*C9*, *C11 mTol SO2*) 131.4 (*C9*, *C11 mTol SO*), 138.6 (C7 – ipsoTol SO2), 139.6 (C7 – ipsoTol SO), 144.9 (*C10* – *p Tol SO*), 145.8 (*C10* – *pTol SO2*), 149.6 and 151.1 (C2, C6 – oPh), 155.2 (C4 – p Ph), 172.4 (C1).

¹¹⁹Sn NMR (THF-D₈) $\delta = 61.3$

¹**H NMR (DMSO-D**₆) δ = 1.13 (s, 9H, *t-Bu*), 2.34 (s, 3H, Me SO), 2.38 (s, 3H, Me SO2), 7.39 (d, 2H, ${}^{3}J_{HH}$ = 8.25 Hz, *m*-CH Tol SO), 7.45 (d, 2H, ${}^{3}J_{HH}$ = 8.32 Hz, *m*-CH Tol SO2), 7.78 (d, 2H, ${}^{4}J_{HH}$ = 3.58 Hz, *m*-CH Ph), 8.00 (d, 2H, ${}^{3}J_{HH}$ = 8.24 Hz, *o*-CH Tol SO), 8.13 (d, 2H, ${}^{3}J_{HH}$ = 8.31 Hz, *o*-CH Tol SO2).

¹³C NMR (DMSO-D₆) δ = 21.0 (Me), 21.1 (Me), 30.5 (*t*-Bu), 35.0 (C *t*-Bu), 126.2 (*C3*, *C5* - *mPh*), 127.5 (*C8*, *C12* – *oTol SO*), 128.3 (*C8*, *C12* – *oTol SO2*), 130.2 and 130.3 (*C9*, *C11 mTol*), 136.7 (C7 – ipsoTol SO2), 137.8 (C7 – ipsoTol SO), 143.6 (*C10* – *p Tol SO*), 145.0 (*C10* – *pTol SO2*), 146.7 (C2, C6 – oPh SO), 149.2 (C2, C6 – oPh SO2), 153.8 (C4 – p Ph), 171.6 (C1). ¹¹⁹Sn NMR (DMSO-D₆) δ = -30

HR-MS (DCI CH₄) (C₂₄H₂₅ClSnO₃S₂) calcd: 575.9951, found: 575.9988

Synthesis of compound 31



A solution of stannylene **28** (100 mg, 0.17 mmol) in 3 ml of THF was added to a suspension of $Fe_2(CO)_9$ (62.7 mg, 0.17 mmol) in 3 ml of THF at -20°C. The mixture was allowed to warm slowly to room temperature then stirred for 4 hours. Solvents were evaporated and the compound was extracted with Et₂O, as an orange powder (40 mg, 31%).

¹**H NMR (THF-D**₈) δ = 1.24 (s, 9H, *t-Bu*), 2.38 (s, 3H, Me SO), 2.42 (s, 3H, Me SO2), 7.40 (d, 2H, ${}^{3}J_{HH}$ = 7.49 Hz, *m*-CH Tol SO), 7.37 (d, 2H, ${}^{3}J_{HH}$ = 8.11 Hz, *m*-CH Tol SO2), 7.70 (broad s, 1H, m-Ph SO), 8.08 (d, 1H, ${}^{3}J_{HH}$ = 1.33 Hz, *m*-CH Ph SO), 7.89 (large, 2H, *o*-CH Tol SO), 8.13 (d, 2H, ${}^{3}J_{HH}$ = 8.26 Hz, *o*-CH Tol SO2).

¹³**C NMR (THF-D₈)** δ = 21.3 (Me), 21.4 (Me), 30.8 (*t*-Bu), 36.3 (C *t*-Bu), 128.4 and 127.5 (*C3*, *C5* – *mPh*), 128.6 and 128.8 (*C14*, *C16* – *oTol SO*), 129.3 (*C8*, *C12* – *oTol SO2*), 131.2 (*C9*, *C11 mTol SO2*) 131.5 (*C15*, *C17 mTol SO*), 136.2 (C7 – ipsoTol SO2), 137.2 (C13 – ipsoTol SO), 145.9 (*C16* – *p Tol SO*), 146.9 (*C10* – *pTol SO2*), 133.8 and 154.3 (C2, C6 – oPh), 158.8 (C4 – p Ph), 146.5 (C1), 214.7 and 211.3 (CO).

¹¹⁹Sn NMR (THF-D₈) δ = 224.5 and 241.9

HR-MS (DCI CH₄) (C₂₈H₂₅ClSnO₇S₂Fe) calcd: 747.9099, found: 747.9157

Synthesis of compound 32



To a solution of $W(CO)_5$ ·THF freshly prepared by irradiation (4 hours) of $W(CO)_6$ (61 mg, 0.17 mmol) in 10 ml of THF, a solution of stannylene **28** (100 mg, 0.17 mmol) in 4 ml of THF was added at room temperature. The reaction mixture was stirred at room temperature for 4 days. Solvents were evaporated under vacuum, the compound extracted with CH_2Cl_2 , giving a light yellow powder.

¹**H NMR (THF-D₈)** δ = 1.22 (s, 9H, *t-Bu*), 2.38 (s, 3H, Me), 2.42 (s, 3H, Me), 7.40 (d, 2H, ${}^{3}J_{HH}$ = 7.70 Hz, *m*-CH Tol), 7.46 (d, 2H, ${}^{3}J_{HH}$ = 8.02 Hz, *m*-CH Tol), 7.86 (large, 1H, *m*-CH Ph), 8.01 (d, 1H, ${}^{1}J_{HH}$ = 1.42 Hz, *m*-CH Ph), not seen (, 2H, *o*-CH Tol), 8.14 (d, 2H, ${}^{3}J_{HH}$ = 8.34 Hz, *o*-CH Tol). **HR-MS (DCI CH₄)** (C₂₉H₂₅ClSnO₈S₂W) calcd: 904.9290, found: 904.9279

Synthesis of compound 33



To a mixture of stannylene **28** (100 mg, 0.17 mmol) and ClAu(SMe₂) (50.8 mg, 0.17 mmol) were added 3 ml of THF. The mixture was stirred for 30 minutes at room temperature and the dark violet precipitate was filtered off. From the orange filtrate all volatiles were evaporated to give an orange powder. (20 mg).

¹H NMR (CDCl₃) δ = 1.20 (s, 9H, *t*-Bu), 2.44 (s, 3H, Me), 2.48 (s, 3H, Me), 7.38 (dd, 5H, J = 2.69 and 10.92 Hz), 7.45 (d, 2H, J = 8.17 Hz), 7.67 (large d, 2H, J = 5.23 Hz), 7.79 (d, 1H, J = 1.04 Hz), 7.85 (d, 2H, J = 8.33 Hz), 7.98 (large d, 1H, J = 6.24 Hz), 8.26 (d, 2H, J = 8.41 Hz). ¹¹⁹Sn NMR (THF-D₈) δ = -90.67 and 182





To a solution of stannylene **28** (100 mg, 0.17 mmol) in 2 ml THF a mixture of $Pt(COD)Cl_2$ (64.5mg, 0.17 mmol) in 4 ml of THF was added at -80 °C. The orange mixture was allowed to

warm slowly to room temperature then stirred for 4 hours. Solvents were evaporated and the compound was washed with pentane to obtain an orange powder (60 mg).

¹H NMR (DMSO-D₆) δ = 1.20 (s, 9H, *t*-*Bu*), 2.38 (s, 3H, Me), 2.43 (s, 3H, Me), 7.47 (d, 2H, ${}^{3}J_{HH}$ = 8.14 Hz, *m*-CH Tol), 7.56 (d, 2H, ${}^{3}J_{HH}$ = 8.10 Hz, *m*-CH Tol), 7.84 (d, 2H, ${}^{3}J_{HH}$ = 8.08 Hz, *o*-CH Tol), 8.07 and 8.011 (s, 2H, *m*-CH Ph), 8.15 (d, 2H, ${}^{3}J_{HH}$ = 8.25 Hz, *o*-CH Tol).

3.5. Bibliography

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4. BIS-SULFOXIDE LIGAND

4.1. Introduction

In Chapter 2 and Chapter 3 a bis-sulfone and a sulfone-sulfoxide type pincer ligand were presented and their role in the stabilization of germylenes and stannylenes was investigated. A third type of pincer ligand was designed in this series, a new bis-sulfoxide ligand. The present Chapter 4 shows the synthesis of the new pincer ligand containing two sulfinyl groups and the investigation of the role of the new ligand in the stabilization of metallylenes.

Compounds containing aryl sulfoxide (sulfinyl) moieties are well known and used as ligands in several catalytic reactions, as reagents in asymmetric synthesis.¹⁻⁶

The synthesis of the sulfoxides can be realized by different methods: the arylation of sulfenate anions (coupling reaction, nucleophilic substitution, electrophilic attack) to form a C-SO bond, ^{7–11} or by oxidation of a sulfide (thioether).^{12–21}

Derivatives containing two sulfinyl groups are also known, employed with different roles, for example known for their transition metal or lanthanide complexes, ligand in transition metal catalyzed reactions or various catalytic processes. ^{3,5,15,16,22–29} Examples of molecules of these types are presented in Figure 53.



Figure 53. Examples of molecules containing sulfoxide groups

In most of the cases the coordination to the metal center is realized through the sulfur atom of the sulfinyl group.^{3,15,23,24,27,30–34} However, coordination through the oxygen atom is also a possibility, some examples are presented in the literature,^{16,23,34–37} Some of these are illustrated in Figure 54.^{27,38–40}



Figure 54. Examples of derivatives for coordination through the oxygen atoms of the sulfinyl groups

The most common method of obtaining sulfoxides is by oxidation of thioethers.³ Various oxidizing agents can be used, for example H_2O_2 or *meta*-chloroperbenzoic acid

(mCPBA).^{1,2} It is challenging to obtain a selective oxidation, because there is the possibility of obtaining both the sulfoxide and the sulfone. Several methods were developed for selective oxidation, obtaining only a sulfoxide and not the sulfone.^{1,2}

However, when there are two thioether groups, the possibility of obtaining a mixture of several compound beside the desired one, is high.

4.2. Synthesis and characterization of the bis-sulfoxide ligand

Bis-sulfoxide **24** can be obtained through different methods that will be presented in this chapter. According to the first method using a precursor of sulfenate anion, thioether **35** was prepared by adding *para*-toluene thiol to *tert*-butyl acrylate as shown in Scheme 80, then oxidized to the corresponding sulfoxide **36** (3-(*p*-toluenesulfinyl)-propionic acid *tert*-butyl ester), using a synthetic route described in literature.^{7,8,41}



Scheme 80. Synthesis of thioether 35 and the β -sulfinylester 36

From the β -sulfinylester **36** with the addition of a base sulfenate anions can be generated and used as precursors of sulfoxides.^{7,8,41} Based on these, a palladium catalyzed coupling reaction of dibromo-*tert*-butyl benzene and β -sulfinylester **36** was used to obtain the target bis-sulfoxide **24**, as shown in Scheme 81.



Scheme 81. Synthetic path tried to obtain bis-sulfoxide 24

The use of sulfinyl based derivatives, such as β -sulfinylester **36**, is a proven method to form a carbon-sulfur bond through the generation of a sulfenate anion ArSO^{-,8-10} For the case of the palladium-catalyzed coupling reaction between dibromo-*tert*-butyl benzene and β -sulfinylester **36**, the proposed reaction mechanism, based on data from the literature,⁸⁻¹⁰ is shown in Scheme 82. In a first step the deprotonation of the β -sulfinylester takes place generating an enolate, then through a retro-Michael reaction a sulfenate is formed. Through a transmetallation reaction between the sulfenate ion and the palladium(II) complex, formed by the oxidative addition of the dibromo-*tert*-butyl benzene to the Pd(0) complex, a diaryl-sulfoxide is formed through reductive elimination (Scheme 82).



Scheme 82. Proposed reaction mechanism for the reaction between dibromo-*tert*-butyl benzene and β -sulfinylester 36

The reaction was realized according to the procedure described in Scheme 81, using two different bases (KOH and Cs_2CO_3). The ¹H NMR analysis of the reaction mixture showed the formation of multiple compounds in both cases, but they could not be identified.

Bis-sulfoxide **24** can be obtained by oxidation of the corresponding bis-thioether, as shown in Chapter 3, Scheme 74. First bis-thioether **2** was obtained by a palladium catalyzed cross coupling reaction between *para*-toluene-thiol and 3,5-dibromo-tert-butyl-benzene, as shown in Chapter 2 and Chapter 3, and Scheme 83. Oxidation with H_2O_2 in acetic acid gave bis-sulfoxide **24**, as shown on Scheme 83.



Scheme 83. Synthesis of bis-sulfoxide 24

After purifying the obtained mixture by column chromatography (cyclohexane:EtOAc), the bis-sulfoxide ligand **24** was obtained as a mixture of 50-50% of the *meso* and *dl* diastereomers, as shown Figure 55.



Figure 55. Meso and dl diastereomers of bis-sulfoxide 24

The *dl* diastereomer can be separated from the mixture in small quantity by fractional crystallization from acetone. It was characterized by NMR spectroscopy and single crystal x-ray diffraction.

In the ¹H NMR spectra a downfield shift can be observed for the H1 from 6.82 ppm in the bis-thioether **2** to 7.50 ppm (t, ⁴ J_{HH} = 1.56 Hz) in bis-sulfoxide **24**, which suggests the presence of the sulfinyl groups. After the assignment of the signals in the ¹H NMR of bissulfoxide **24**-*dI* with two dimensional NMR analysis, the signals for the *meso* isomer could also be assigned, the data are presented in Table 20. The ratio of each diastereomer was determined from the ¹H NMR, where the signals for the H3 and H5 appear as two doublet signals (${}^{4}J_{HH}$ =1.57 and 1.56 Hz), which can be distinguished very easily. In the case of the signals for the other protons, these overlap in some part.

bis-sulf	$\int_{1}^{1} \int_{2}^{2} \int_{2}^{1} \int_{2$	H1	H8, H12 (<i>o</i> -Tol)	H3, H5 (<i>m</i> -Ph)	H9, H11 (<i>m</i> -Tol)	Me	t-Bu
¹ H NMR (δ ppm)	dl	7.50, t J = 1.56 Hz	7.45, d J = 8.21 Hz,	7.74, d J = 1.57 Hz	7.23, d J = 7.92 Hz	2.36	1.29
	meso	7.58, t J = 1.55 Hz	7.48, d J = 8.23 Hz,	7.71, d J = 1.56 Hz	7.25, d J = 7.85 Hz	2.37	1.28
		C1	C8, C12 (<i>o</i> -Tol)	C3, C5 (<i>m</i> -Ph)	C9, C11 (<i>m</i> -Tol)	Me	<i>t-</i> Bu
¹³ C NMR (δ ppm)	dl meso	118.3 118.4	125.1	123.7	130.3	21.6	31.2
		<u>C</u> (CH₃)₃	C2, C6	С7	C10	C4	
	dl meso	35.7 35.8	147.3	142.0 142.1		154.5 154.6	

Table 20. ¹H and ¹³C NMR data for bis-sulfoxide 24, diastereomers *dl* and *meso* (in CDCl₃)

The signals for the meso and *dl* isomers of bis-sulfoxide **24** in the ¹³C NMR spectra are very close of each other, with a difference of 0.02-0.1 ppm (0.77 - 10.41 Hz). The data is taken from the ¹³C NMR of a 50-50% and a 95-5% mixture of the two diastereomers and the signals were assigned with the help of two dimensional NMR experiments (COSY, HSQC, HMBC). The chemical shifts for the carbon atoms of the bis-sulfoxide **24** are presented in Table 20.

Crystals of the bis-sulfoxide **24**-*dl* suitable for X-ray analysis were obtained in acetone, the molecular solid state structure is presented in Figure 56.



Figure 56. Molecular structure of compound **24**-*dl* in solid state (50 % probability level for the thermal ellipsoids). For clarity, the solvent and hydrogen atoms are omitted; tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.4992(10); S2-O2 1.4933(12); O1-S1-C2 106.42(6), O2-S2-C6 106.80(6), C1-C2-S1 118.71(10), C1-C6-S2 117.81(9).

Bis-sulfoxide **24**-*dl* crystallizes in a monoclinic space group (C 2/c), (with a molecule of acetone in the crystal lattice) and the structure shows that tolyl groups of the bis-sulfoxide are situated on the same side of the central aromatic ring. The S=O bond lengths of 1.4992(10) and 1.4933(12) Å are in the range of S=O bonds found in sulfoxides presented in the literature (1.478-1.515Å).^{42–44} We can observe O...H interactions between the O atoms of the sulfoxide groups and the H atoms of the aromatic ring (O2-H5 2.525 and O1-H1 2.603 Å) intramolecular short contacts similar to those found for sulfoxides 2.35-2.97 Å.⁴³

The crystal packing reveals a three dimensional arrangement due to the intermolecular short contacts (part of the crystal packing of **24**-*dl*, showing π - π interactions is displayed in Figure 57). The bis-sulfoxide molecules are arranged with their tolyl groups in parallel position with a neighboring molecule's tolyl group, with offset face to face π - π (H \cdots π) (parallel-displaced) interactions between 3.645 and 3.819 Å (with the distance between the H and the center of the aromatic ring of 3.285 - 3.715 Å and the interplanar distance of 3.557 Å) in the range of values shown in literature⁴⁵ for this kind of interactions.



Figure 57. Crystal packing of compound 24-d/

While trying to separate the two diastereomers of bis-sulfoxide **24** with fractional crystallization, crystals were obtained where the *meso* and *dl* isomers were present together in 95% *dl* - 5% *meso* and 78% *meso* – 22% *dl* mixture.

In the mixture of 95% *dl* - 5% *meso* of the bis-sulfoxide **24** the structure of the molecules is similar to that of the 100% *dl*, with the tolyl groups positioned on the same side of the central aromatic ring, as depicted in Figure 58.



Figure 58. Solid state structures of the *dl* and *meso* diastereomers of bis-sulfoxide **24** in the 95% *dl* - 5% *meso*

Bis-sulfoxide **24** in the mixture 95% *dl* - 5% *meso* crystalizes in a monoclinic C 2/c space group with a molecule of acetone. The *dl* stereoisomer is present with 95% occupancy in the crystal, while the *meso* isomer in 5% occupancy. The crystal packing is similar to the case where the *dl* isomer is 100%, showing a three dimensional arrangement through several intermolecular interactions. The geometrical parameters present only slight differences compared to the **24**-*dl*.

In the other case, the *meso* isomer of bis-sulfoxide **24** is present in the crystal with 78% occupancy and the *dl* with 22%. In the solid state structure, shown in Figure 59, we can observe that the tolyl groups are in relative *trans* rotameric form, they are situated on opposite sides in report to the central aromatic ring. It is to note, that in the case when the *dl* isomer is found in higher percentage, the *cis* rotameric form can be observed in the solid state structures, as shown in Figure 56 and Figure 58. This arrangement could be explained by the crystal packing.



Figure 59. Solid state structures of the *dl* and *meso* diastereomers of bis-sulfoxide 24 in the 22% *dl* - 78% *meso*

Bis-sulfoxide **24** crystallizes in triclinic P -1 space group. The S-O bond lengths are of 1.490 and 1.495 Å, furthermore S(=O)…HC interaction can be observed, of 2.443 Å (O1…H1) and 2.526 Å (O2…H5). It is to note, that in this case the crystal packing displays a two

dimensional arrangement, as depicted in Figure 60, not a three dimensional one as for the case of the **24**-*dl* diastereomer. The distance between the planes including the central aromatic ring of the molecules is 4.33 Å and 4.78Å. Between two molecules an aryl edge-face interaction can be observed (3.580 Å, C-H...centroid distance of 2.89 Å).



Figure 60. Crystal packing of 24-meso diasteromer

The separation of the *meso* and *dl* diastereomers was tried using several eluents in differet ratios (cyclohexane, ethyl acetate, dichloromethane, toluene, hexane) and chromatography columns (RediSep Rf Gold high performance silica)

An HPLC experiment was performed with an Agilent HPLC 1200 instrument on a chiral column ((R,R)-Whelk-O 1Pirkle-type Chiral Column) at 30°C using as mobile phase a mixture of hexane – 2-propanol – dichloromethane in the ratio 85:14:1, which led to a

successful separation; it was shown that in these conditions it is possible to separate the *dl* and the *meso* diastereomers of the bis-sulfoxide **24**. Furthermore, the *d*- and *l*- enantiomers could also be separated, as seen on Figure 61. However, the experiment was realized on a qualitative column, so far, it could not be done at a bigger scale.



Figure 61. Chromatogram obtained by the HPLC separation of the isomers of compound 24

4.3. Synthesis of metallylenes

A first step was the deprotonation test of the bis-sulfoxide **24**. The carbanion of the bis-sulfoxide ligand was obtained by adding LDA to a solution of bis-sulfoxide **24** (60% *dl* and 40% *meso* mixture calculated from the ¹H NMR) in THF at low temperature as depicted in Scheme 84.



Scheme 84. Deprotonation reaction of bis-sulfoxide 24

To find the optimal conditions for the deprotonation, the lithiated derivative **37** was quenched with D_2O . The ¹H NMR spectra of compound **38** showed that deprotonation is complete and almost quantitative (5% starting material left) after 30 minutes of the addition of the LDA at -80°C and the lithiated compound **37** is stable for at least 30 minutes at -40 °C. Experiments showed that deprotonation works in toluene or THF, using either freshly prepared LDA solution or in solid form, previously prepared. The efficiency of the deprotonation was followed by the disappearance of the triplet signal at 7.58 ppm for the H1 in the ¹H NMR of the bis-sulfoxide **24**.

Reaction of the lithium derivative **37** with $GeCl_2$ ·dioxane or $SnCl_2$ at low temperature, as shown in Scheme 85, gave a mixture of several compounds.



Scheme 85. Synthesis of germylene 39 and stannylene 40

The formation of the metallylenes was confirmed by ¹H NMR spectroscopy, where the disappearance (or diminution) of the triplet signal at 7.58 ppm for the H1 proton of bis-sulfoxide **24** is observed, as it can be seen on Figure 62.



Figure 62. Part of the ¹H NMR spectra of bis-sulfoxide 24 and metallylenes 39 and 40

The 1H NMR for both the germylene **39** and stannylene **40** show a downfield shift of the signals of the aromatic protons in the 7.27 – 7.85 ppm region. The formation of the stannylene **40** is confirmed by the ¹¹⁹Sn NMR by the appearance of a signal at 75 ppm. The ¹³C NMR spectrum of the stannylene shows two signals at 169.7 and 170.1 ppm (in CDCl₃), characteristic for the ipso C1 atom of a metallylene (169.8 ppm in CDCl₃ for stannylene **7** and 172.4 ppm in THF-D₈ for stannylene **28**). Furthermore, in the mass spectrum peaks for [M+CH₃OH]⁺ (C₂₄H₂₆O₂S₂SnCl+CH₃OH) at 597.0, [M-Cl] (C₂₄H₂₅O₂S₂Sn) at 529.0 and a dimeric

species $[C_{48}H_{50}O_4S_4Sn]^+$ at 939.2 can be observed, species that suggest the existence of the stannylene in the mixture. However, the mixtures could not be separated and purified, thus further analysis was not realized.

4.4. Synthesis of trimethylsilyl-bis-sulfoxide

For a better understanding of the behavior of bis-sulfoxide **24**, reaction with trimethylsilyl chloride and chlorodiphenylphosphine was carried out.

To the lithiated bis-sulfoxide **37**, obtained starting from a mixture of 80% *dl* and 20% *meso* of the bis-sulfoxide **24** a large excess of ClSiMe₃ was added, as shown on Scheme 86. According to the 1H NMR analysis of the reaction mixture, the expected compound **41** was obtained in a mixture of several compounds. This mixture was purified by column chromatography using as mobile phase a mixture of ethyl acetate and cyclohexane (10:90). One of the two diastereomers of compound **41** was separated from the mixture, the other one was recovered as a mixture of the two diastereomers.



Scheme 86. Reaction of bis-sulfoxide 24 with ClSiMe₃

Single crystals suitable for X-ray analysis were separated from a dichloromethane solution of the mixture of the two diastereomers of compound **41**. The solid state structure is presented in Figure 63.



Figure 63. Molecular structure of compound **41** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, the solvent molecules and hydrogen atoms are omitted; tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.5002(16); S2-O2 1.5002(17), C1-Si1 1.9255(18); O1-S1-C2 106.19(9), O2-S2-C6 106.77(9), C1-C2-S1 122.28(13), C1-C6-S2 121.24(13), C6-C1-Si1 119.77(13), C2-C1-Si1 126.95(13).

Compound **41** crystallizes in the triclinic space group (P-1) with two molecules in the asymmetric unit. The solid state structure shows the *meso* diastereomer of the compound, with the tolyl groups positioned on the same side of the central aromatic ring. The oxygen atoms are not in the proximity of the silicon atom, there are no interactions between these. In the crystal packing interactions can be observed between the O1 and O2 oxygen atoms of the sulfinyl groups and the hydrogen atoms of the neighboring molecules, between 2.5 and 2.8 Å, as shown in Figure 64.



Figure 64. Crystal packing of compound 41

4.5. Synthesis of diphenylphosphine-bis-sulfoxide

In order to further analyze the behavior of the bis-sulfoxide ligand **24**, the reaction with chlorodiphenylphosphine was realized, as presented in Scheme 87. The formation of the new compound was evidenced by multinuclear NMR spectroscopy. Although the ¹H and ³¹P NMR show the formation of multiple compounds, in the ¹H NMR the disappearance of the signals for H1 protons of the bis-sulfoxide **24** suggest the formation of the expected compound. In the ³¹P NMR several signals can be observed in the -22 – -8.6 ppm region, an upfield shift compared to the starting CIPPh₂ from 81.8 ppm, characteristic for triaryl phosphines.⁴⁶ The signal for the major compound **42** is found at -21.7 ppm (65 %)



Scheme 87. Synthesis of diphenylphosphine-bis-sulfoxide 42

The purification of the mixture was tried using column chromatography (mobile phase: ethyl acetate and cyclohexane, 20:80) but this did not lead to the separation of the compounds. Single crystals suitable for X-ray diffraction were obtained from acetone, however not in a sufficient amount to realize all the necessary characterizations on the pure compound. The solid state structure of compound **42** is shown on Figure 65.



Figure 65. Molecular structure of compounds **42** and **43** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, the solvent molecules and hydrogen atoms are omitted; tolyl and *t*-butyl groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.488(4); S2-O2 1.492(3), C1-P1 1.839(4), P1-O3 1.383(13); O1-S1-C2 104.6(2), O2-S2-C6 106.1(2), C1-C2-S1 121.9(4), C1-C6-S2 120.8(3), C6-C1-P1 127.1(3), C2-C1-P1 117.0(3).

Single crystal X-ray analysis showed the *meso* diastereomer. In the mixture both the –PPh₂ and -P(O)Ph₂ derivatives are present, as a result of slow oxidation of the bis-sulfoxide diphenyl phosphine. The tolyl groups are positioned on the same side of the central aromatic ring, the oxygen atoms of the sulfinyl groups are too far from the phosphorus atom, making impossible the existence of an interaction between them. This is similar to the case of compound **41**.

In the crystal packing of compound **43** interactions between the oxygen atoms and the hydrogen atoms of the neighboring molecules and the acetone can be observed, at a length between 2.3 and 2.7 Å, as shown on Figure 66.





Figure 66. Crystal packing of compound 43

4.5. Conclusion

In this chapter it was presented the synthesis and characterization of a new bissulfoxide. It was shown that it has potential applications as a pincer-type ligand for obtaining metallylenes. However, the use of the bis-sulfoxide **24** as a mixture of the two diastereomers *dl* and *meso* in the reactions leads to a mixture of isomers of the products as well. Reactions with trimethylsilyl chloride and chlorodiphenylphosphine showed that deprotonation at the H1 of the bis-sulfoxide **24** and reactions with *p* block elements are possible. The compounds could be isolated by column chromatography, as shown in the case of the trimethylsilyl derivative **41**. Even if it was shown that it is possible to separate the diastereomers and the *d* and *l* enantiomers of the bis-sulfoxide **24**, the high costs of the chiral column necessary for this makes the process more difficult. These observations suggest that if a sample containing only one of the diastereomers, or even the enantiopure bis-sulfoxide **24**, the metallylenes could be obtained and separated.

4.6. Experimental part

Synthesis of compound 35⁸



To a solution of 5 g of p-toluene thiol (40.26 mmol) in 10 mL of CH_2CI_2 were added 0.56 g of K_2CO_3 (4.03 mmol, 10 mol%) and 6.49 mL (44.28 mmol, 1.1 eq) of tert-butyl acrylate. After 72 hours of stirring at room temperature, the reaction mixture was washed twice with 15 mL of H_2O and 15 mL of brine. After separation, the organic layer was dried on Na_2SO_4 . After evaporating all volatiles a transparent oil was obtained (7.9 g, 77% yield).

¹**H NMR (CDCl₃)** δ = 1.45 (s, 9H, *t-Bu*), 2.30 (s, 3H, Me), 2.50 (t, 2H, ³J_{HH} = 7.44 Hz, CH₂), 3.07 (t, 2H, ³J_{HH} = 7.44 Hz, CH₂), 7.09 (d, 2H, ⁴J_{HH} = 7.89 Hz, CH Tol), 7.28 (d, 2H, ³J_{HH} = 8.15 Hz, CH Tol)

Spectral data in agreement with those already reported in the literature⁸

Synthesis of compound 36⁸



To 16 g of wet neutral alumina (16 g Al_2O_3 and 3.2 mL H_2O) a solution of 4 g of thioether **35** (15.85 mmol) in 30 mL of CH_2Cl_2 was added, then 9.74 g of Oxone[®] (15.85 mmol) were added. The reaction mixture was refluxed for 6 hours. After cooling down to room temperature and filtration, all volatiles were evaporated to obtain a yellow oil. Purification by column chromatography (eluent: CH_2Cl_2) afforded a light yellow solid in 67% yield (2.74 g)

¹**H NMR (CDCl₃)** δ = 1.42 (s, 9H, *t-Bu*), 2.41 (s, 3H, Me), 2.44 (m, 1H, CH₂-CH₂), 2.73 (m, 1H, CH₂-CH₂), 2.92 (m, 1H, CH₂-CH₂), 3.14 (m, 1H, CH₂-CH₂), 7.33 (d, 2H, ${}^{3}J_{HH}$ = 8.07 Hz, CH Tol), 7.50 (d, 2H, ${}^{3}J_{HH}$ = 8.09 Hz, CH Tol)

Spectral data in agreement with those already reported in the literature⁸
Synthesis of compound 24

Method I

To a solution of 5.4 g (0.014 mol) of bis-thioether **2** in 32 ml of glacial acetic acid, a solution of 2.6 ml of H_2O_2 (33wt%, 0.028 mmol, 2 eq) in 18 ml of glacial acetic acid was added dropwise. The mixture was stirred at room temperature for 48 hours, while a clear solution was obtained. A saturated solution of KOH was added to the reaction mixture until a neutral pH was obtained. Then 25 ml of CH_2Cl_2 were added and the layers were separated. The aqueous layer was extracted six times with 25 ml of CH_2Cl_2 , the organic layers were united and washed twice with 50 ml of aqueous saturated NaCl solution then dried on Na_2SO_4 . After evaporating the solvent, a white sticky solid was obtained. The bis-sulfoxide was separated from the mixture by column chromatography (cyclohexane:ethyl acetate 8/2). It was obtained as a white powder (3.4 g, 58% yield), a mixture of 50 - 50% of the *meso* and *dl* diastereomers. The *dl* isomer could be separated by fractional crystallization from acetone. Transparent crystals were obtained of the *dl* diastereomer or mixtures where the two diastereomers were present in different ratios.

Method II

To a solution of bis-thioether **2** (3 g, 7.9 mmol) in 50 ml of CH_2Cl_2 a solution of mCPBA (4.5 g, 26.2 mmol, 3 eq) in 50 ml of CH_2Cl_2 was added dropwise at 0°C. The mixture was stirred at 0°C for one hour and at room temperature for 20 minutes then washed three times with 75 ml of a aqueous saturated solution of NaHCO₃ and all solvents evaporated. The bis-sulfoxide was separated by column chromatography (cyclohexane/ ethyl acetate – 8/2) as the mixture of the *meso* and *dl* diastereomers (0.8 g, 25 % yield).

¹H NMR (CDCl₃)

dl isomer: δ = 1.29 (s, 9H, *t-Bu*), 2.36 (s, 6H, Me), 7.23 (d, 4H, ³J_{HH} = 7.92 Hz, m-CH Tol), 7.45 (d, 4H, ³J_{HH} = 8.21 Hz, *o*-CH Tol), 7.50 (t, 1H, ⁴J_{HH} = 1.56 Hz, H1 Ph), 7.74 (d, 2H, ⁴J_{HH} = 1.57 Hz, *m*-CH Ph),

meso isomer: δ = 1.28 (s, 9H, *t-Bu*), 2.37 (s, 6H, Me), 7.25 (d, 4H, ${}^{3}J_{HH}$ = 7.85 Hz, *m*-CH Tol), 7.48 (d, 4H, ${}^{3}J_{HH}$ = 8.23 Hz, *o*-CH Tol), 7.58 (t, 1H, ${}^{4}J_{HH}$ = 1.56 Hz, H1 Ph), 7.71 (d, 2H, ${}^{4}J_{HH}$ = 1.56 Hz, *m*-CH Ph).

¹³C NMR (CDCl₃)

meso isomer δ = 21.6 (Me), 31.2 (t-Bu), 35.8 (C *t*-Bu), 118.3 (C1),), 123.8 (C3, C5), 125.1 (C8, C12, 130.3 (C9, C11), 142.0 and 142.2 (C7, C10), 147.3 (C2, C6), 154.5 (C4),

dl isomer δ = 21.6 (Me), 31.2 (t-Bu), 35.7 (C *t*-Bu), 118.4 (C1), 123.7 (C3, C5), 125.2 (C8, C12), 130.3 (C9, C11), 142.0 and 142.1 (C7, C10), 147.3 (C2, C6), 154.6 (C4),

Synthesis of compound 37 and 38



Method I: To a solution of 300 mg of bis-sulfoxide **24** (0.73 mmol) in 12 ml of THF cooled to -80 °C, a freshly prepared LDA solution in THF (0.80 mmol, 10% excess) was added. The dark orange solution was stirred at this temperature for 30 minutes then warmed up to -40°C and stirred for another 30 minutes.

Method II: To a solution of 100 mg of bis-sulfoxide **24** (0.73 mmol) in 12 ml of THF (or toluene) cooled to -80 °C, a solution of LDA (prepared previously and kept as solid in the glovebox) in THF (or toluene) (0.80 mmol, 10% excess) was added. The dark orange solution was stirred at this temperature for 30 minutes then warmed up to -40°C and stirred for another 30 minutes.



To the solution of the lithiated compound **37** D_2O (1 mL) was added then stirred for 5 minutes at room temperature to obtain a light yellow solution. Solvents were evaporated and compound **38** was obtained as a white solid.

Synthesis of compound 39



The freshly prepared solution of the lithiated compound **37** was added on a solution of $GeCl_2$ ·dioxane (169.3 mg, 0.73 mmol, 1 eq) in 2 mL of THF (or toluene) at -40°C. The yellow mixture was allowed to warm slowly to room temperature then stirred for 16 hours. The white precipitate was filtered off, solvents were evaporated, the solid was washed with pentane and extracted with Et₂O. A light yellow solid was obtained as a mixture of compounds.

Synthesis of compound 40



The freshly prepared solution of the lithiated compound **37** was added on a solution of SnCl₂ (138.6 mg, 0.73 mmol, 1eq) in 2 mL of THF (or toluene) at -40°C. The yellow mixture was

stirred in the cooling bath for one hour then at room temperature for another hour. Solvents were evaporated, the solid was extracted with CH_2CI_2 . A white solid was obtained as a mixture of compounds.

¹**H NMR (CDCl₃)** δ = 1.13-1.16 (*t-Bu*), 2.35-2.37 (Me), 7.27-7.30 (CH Tol), 7.34 (CH Tol/Ph), 7.69 (d, ${}^{3}J_{HH}$ = 8.10 Hz, CH Tol/Ph), 7.83 (d, ${}^{3}J_{HH}$ = 8.10 Hz, *m*-CH Tol).

¹³**C NMR (CDCl₃)** δ = 21.6, 21.7 (Me), 31.1 (t-Bu), 35.3 (C *t*-Bu), 118.3-153.9 many signals, 169.7 and 170.1 (C1).

¹¹⁹Sn (CDCl₃) δ = 75.07

Synthesis of compound 41



To a solution of 100 mg of bis-sulfoxide 24 (0.24 mmol) in 4 ml toluene or THF cooled to -80 °C a freshly prepared LDA solution in THF (0.27 mmol, 10% excess) was added dropwise. The orange solution was stirred at this temperature for 30 minutes, then a large excess of trimethylsilyl chloride (0.5 ml) was added. After stirring at room temperature overnight, volatiles were evaporated and the product was purified by column chromatography (ethyl acetate/cyclohexane 2/8) (76 mg, 64% yield). Transparent crystals were obtained in CH_2Cl_2 .

meso diastereomer

¹**H NMR (CDCl₃)** δ = 0.54 (s, 9H, *Me*₃Si), 1.21 (s, 9H, *t-Bu*), 2.38 (s, 6H, Me), 7.19 (s, 8H, *J*_{Si-H} = 9.01 Hz, *o*- and *m*-CH Tol), 8.05 (s, 2H, *m*-CH Ph).

²⁹Si NMR (CDCl₃) δ = -2.18

dl diastereomer

¹**H NMR (CDCl₃)** δ = 0.59 (s, 9H, *Me*₃Si), 1.11 (s, 9H, *t-Bu*), 2.36 (s, 6H, Me), 7.25 (d, 4H, ${}^{3}J_{HH}$ = 8.14 Hz, *m*-CH Tol), 7.31 (d, 4H, ${}^{3}J_{HH}$ = 8.42 Hz, *o*-CH Tol), 7.90 (s, 2H, *m*-CH Ph).

²⁹Si NMR (CDCl₃) $\delta = -1.85$

Synthesis of compound 42



To a solution of 200 mg of bis-sulfoxide (0.49 mmol) in 6 ml of THF cooled to -80 °C a solution of 103.4 mg of LDA (0.54 mmol, 1.1 eq, previously prepared, 55.5% LDA in LDA*THF complex) in 2 ml of THF was added at -80°C. After stirring the mixture at this temperature for 30 minutes, 0.12 ml of chlorodiphenylphosphine (0.66 mmol, 1.35 eq) was added. The mixture was stirred at room temperature overnight and volatiles were evaporated to obtain a yellow solid as a mixture of two diastereomers. Transparent crystals were obtained in acetone.

¹**H NMR (CDCl₃)** δ = 1.29-135 (*t-Bu*), 2.32-2.38 (Me), 7.06 – 8.20 (CH Tol and CH Ph).

³¹**P** NMR (CDCl₃) δ = -21.8 (major compound), -21.8- -8.8, 31.7 (minor compounds)

4.7. References

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GENERAL CONCLUSIONS

The presented work shows the design, synthesis and characterization of new sulfurcontaining pincer type ligands and their application in the stabilization of metallylenes.

In the first chapter a bibliographic study was realized on the pincer-ligand supported metallylenes, their characteristics and reactivity. From this literature overview resulted, that up to date pincer ligands, containing sulfonyl or sulfinyl groups in *ortho* position of the central aromatic group, were not used to obtain the divalent species of group 14 elements, beside the one example of 1,3-bis{(4-methylphenyl)sulfonyl}-benzene shown in the preliminary results.

Inspired by these results and the information gathered from the literature, for the present work, a second generation of pincer ligands was designed by introducing a *tert*-butyl group in *meta* position to the sulfonyl groups. These bis-sulfone ligands represent a new class of *O*,*C*,*O*-chelating pincer type ligands in the chemistry of metallylenes, by their " E_2CE_2 " character, different from the previously reported ligands of ECE-type (E = O, N).

The second chapter presents the synthesis and characterization of the new SO₂-C-SO₂ bis-sulfone ligand and presents the synthetic paths used to obtain new germylene and stannylene. It is to note, that the germylene represents the first example of a divalent germanium derivative stabilized by an *O,C,O*-pincer-type ligand fully characterized and presented in the literature. The reactivity of the metallylenes was tested towards iron- and tungsten carbonyls to obtain transition metal complexes. It was shown, that the bis-sulfone acts as an adjustable ligand, coordination to the central atom being possible through either one of the oxygen atoms, feature owed to the "E₂CE₂" character of the pincer ligand. The ability of the bis-sulfone ligand was also tested to obtain phosphorus containing derivatives and transition metal complexes, to validate the versatility of this ligand.

Furthermore, the effect of the introduction of stereogenic information in the molecules was also investigated, by obtaining a sulfone-sulfoxide pincer ligand with one sulfonyl and one sulfinyl group in *ortho* position of the central aromatic ring and a bis-sulfoxide one with two sulfinyl groups. In chapters three and four it was shown that these ligands also lead to the formation of divalent germanium and tin derivatives and their ability to form transition metal complexes was also evidenced.

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ANNEXE

Crystallographic data of the newly obtained compounds presented in the thesis

Crystallographic data for compound 1

Assymetric unit					
Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions	C ₂₄ 442 192 0.7 Mc P20 a = b = c =				
Volume	232				
Z	4				
Density (calculated)	1.2				
Absorption coefficient	0.2				
F(000)	93				
Crystal size	0.6				
Theta range for data collection	5.1				
Index ranges	-20				
Reflections collected	380				
Independent reflections	572				
Completeness to theta = 28.28°	99.				
Absorption correction	Ser				
Max. and min. transmission	0.9				
Refinement method	Ful				
Data / restraints / parameters	57				
Goodness-of-fit on F ²	1.0				
Final R indices [I>2sigma(I)]	R1				
R indices (all data)	R1				
Largest diff. peak and hole	0.2				



Molecule

 $H_{26}O_4S_2$ 2.57 3(2) K ′1073 Å onoclinic (1)/c 15.1205(15) Å α= 90°. 12.8912(12) Å β= 113.425(4)°. 12.9721(10) Å $\gamma = 90^{\circ}$. 20.1(4) Å³ 267 Mg/m³ 256 mm⁻¹ 6 50 x 0.05 x 0.05 mm³ 4 to 28.28°.)<=h<=20, -17<=k<=17, -17<=l<=17 017 20 [R(int) = 0.0993] .2 % mi-empirical from equivalents 9873 and 0.8614 II-matrix least-squares on F² 20 / 78 / 301)43 = 0.0538, wR2 = 0.1197 = 0.1178, wR2 = 0.1418 0.276 and -0.292 e.Å⁻³



Asymmetric Unit



Molecule

Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 28.72 Max. and min. transmission **Refinement method** Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

549.62 193(2) K 0.71073 A monoclinic, C2/c a = 15.7935(12) Å $\alpha = 90^{\circ}$ b = 14.6499(9) Å $\beta = 108.535(3)^{\circ}$ c = 11.0566(7) Å $\gamma = 90^{\circ}$ 2425.5(3) A^3 4, 1.505 Mg/m^3 1.574 mm^-1 1128 0.18 x 0.04 x 0.04 mm 2.72 to 28.72 deg. -21<=h<=19, -19<=k<=19, -14<=l<=14 8934 / 3139 [R(int) = 0.0339] 99.6 % 0.7458 and 0.6871 Full-matrix least-squares on F^2 3139 / 24 / 167 1.084 R1 = 0.0423, wR2 = 0.1139 R1 = 0.0525, wR2 = 0.1206 0.752 and -1.139 e.A^-3

C24H25ClGeO4S2



Asymmetric Unit



Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 27.87 Max. and min. transmission **Refinement method** Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

 $C_{24}H_{25}CIO_4S_2Sn$ 595.72 193(2) K 0.71073 A monoclinic, C2/c a = 15.970(2) Å $\alpha = 90^{\circ}$ b = 14.9457(16) Å $\beta = 110.257(4)^{\circ}$ c = 11.0548(11) Å $\gamma = 90^{\circ}$ 2475.4(5) A^3 4, 1.599 Mg/m^3 1.337 mm^-1 1200 0.12 x 0.06 x 0.02 mm 3.07 to 27.87 deg. -20<=h<=20, -19<=k<=19, -14<=l<=14 46461 / 46461 [R(int) = 0.0000] 99.7 % 0.7456 and 0.5948 Full-matrix least-squares on F^2 46461 / 25 / 170 1.022 R1 = 0.0715, wR2 = 0.1156 R1 = 0.1393, wR2 = 0.1398 0.996 and -1.399 e.A^-3

Crystallographic data for compound 9-2CDCl₃





Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

Volume Ζ Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges **Reflections collected** Independent reflections Completeness to theta = 27.88° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F² Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

C40 H47 Cl7 Ge O6 S2 1008.64 193(2) K 0.71073 Å Monoclinic C2/c a = 29.1591(13) Å $\alpha = 90^{\circ}$. b = 19.3774(9) Å $\beta = 108.392(3)^{\circ}$. c = 17.3168(7) Å $\gamma = 90^{\circ}$. 9284.7(7) Å³ 8 1.443 Mg/m^3 1.195 mm⁻¹ 4144 0.27 x 0.17 x 0.06 mm³ 5.11 to 27.88°. -38<=h<=38, -25<=k<=25, -22<=l<=22 77651 10994 [R(int) = 0.1038] 99.2 % Semi-empirical from equivalents 0.9274 and 0.7392 Full-matrix least-squares on F² 10994 / 388 / 656 1.018 R1 = 0.0574, wR2 = 0.1386 R1 = 0.1117, wR2 = 0.1680

0.638 and -0.587 e.Å⁻³

Crystallographic data for compound 10b·6CDCl₃





Empirical formula		$C_{28}H_{25}CIFeGeO_8S_2$	
Formula weight		717.49	
Temperature		193(2) K	
Wavelength		1.54178 A	
Crystal system, space group		monoclinic, P21/n	
Unit cell dimensions		a = 12.756(4) Å	α = 90 °
		b = 10.549(3) Å	β = 93.339(8) °
		c = 22.740(6) Å	γ = 90 °
Volume		3054.7(16) A^3	
Z, Calculated density		4, 1.560 Mg/m^3	
Absorption coefficient		7.508 mm^-1	
F(000) 145	56		
Crystal size		0.10 x 0.10 x 0.02 mn	n
Theta range for data collection		11.19 to 74.50 deg.	
Limiting indices		-13<=h<=15, -13<=k<	=8, -27<=l<=28
Reflections collected / unique		16093 / 6103 [R(int) = 0.1812]	
Completeness to theta = 74.50		97.7 %	
Max. and min. transmission		0.8644 and 0.5206	
Refinement method		Full-matrix least-squa	ares on F^2
Data / restraints / parameters		6103 / 116 / 416	
Goodness-of-fit on F^2		1.013	
Final R indices [I>2sigma(I)]		R1 = 0.0883, wR2 = 0	.1841
R indices (all data)		R1 = 0.2020, wR2 = 0	.2396
Largest diff. peak and hole		0.637 and -0.749 e.A	^-3

Crystallographic data for compound 12.0.5(C7H8)



Crystallographic data for compound 13·CH₂Cl₂



R1 = 0.0378, wR2 = 0.1037

R1 = 0.0535, wR2 = 0.1088

1.916 and -1.805 e.A^-3

Empirical formula	$2(C_{29}H_{25}CIGeO_{9}S_{2}W)\cdot 0.5(CH_{2}CI_{2})\cdot 0.5(CH_{2}CI_{2})$	
Formula weight	1831.95	
Temperature	253(2) K	
Wavelength	0.71073 A	
Crystal system, space group	triclinic, P-1	
Unit cell dimensions	a = 11.013(2) Å	α= 112.774(10) °
	b = 18.273(4) Å	β = 102.463(10) °
	c = 21.087(5) Å	γ = 90.150(10) °
Volume	3802.8(14) A^3	
Z, Calculated density	4, 1.600 Mg/m^3	
Absorption coefficient	4.107 mm^-1	
F(000)	1788	
Crystal size	0.20 x 0.12 x 0.08 mr	n
Theta range for data collection	5.11 to 26.37 deg.	
Limiting indices	-13<=h<=13, -22<=k<	<=22, -26<=l<=26
Reflections collected / unique	113985 / 15419 [R(ir	nt) = 0.0602]
Completeness to theta = 26.37	99.1 %	
Max. and min. transmission	0.7454 and 0.5899	
Refinement method	Full-matrix least-squ	ares on F^2
Data / restraints / parameters	15419 / 171 / 903	
Goodness-of-fit on F^2	1.068	

Final R indices [I>2sigma(I)]

Largest diff. peak and hole

R indices (all data)

198



Crystallographic data for compound 15·2(C₄H₈O)



- Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions
- Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Observed reflections ([I>2sigma(I)] Completeness to theta = 26.37 Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

 $C_{56}H_{52}Fe_2O_{18}S_4Sn_2\cdot 2(C_4H_8O)$ 1634.55 193(2) K 0.71073 A monoclinic, P 21/n a = 14.583(2) A $\alpha = 90^{\circ}$. β= 92.991(9)°. b = 29.315(4) A $\gamma = 90$ °. c = 16.325(3) A6969.4(19) 4, 1.558 Mg/m^3 1.306 mm^-1 3312 0.10 x 0.08 x 0.06 mm 5.10 to 26.37 deg. -18<=h<=18, -36<=k<=36, -20<=l<=20 111151 / 14143 [R(int) = 0.0567] 11374 99.2 % 0.7456 and 0.7049 Full-matrix least-squares on F^2 14143 / 534 / 983 1.027 R1 = 0.0295, wR2 = 0.0600 R1 = 0.0450, wR2 = 0.0666 0.373 and -0.384 e.A^-3



Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 25.242 Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Extinction coefficient Largest diff. peak and hole

C₂₄H₂₅Cl₂O₄PS₂ 543.43 193(2) K 0.71073 A Monoclinic, C 2/c a = 29.159(2) A α= 90 deg. β = 126.9898(19) deg. b = 10.4902(8) A c = 20.9926(14) A γ = 90 deg. 5129.0(6) A^3 8, 1.407 Mg/m^3 0.507 mm^-1 2256 0.250 x 0.050 x 0.050 mm 5.232 to 26.371 deg. -36<=h<=36, -13<=k<=13, -26<=l<=26 56705 / 5202 [R(int) = 0.1945] 99.1 % Full-matrix least-squares on F^2 5202 / 0 / 303 1.004 R1 = 0.0477, wR2 = 0.0946 R1 = 0.1134, wR2 = 0.1223 n/a

0.366 and -0.462 e.A^-3





Asymmetric Unit Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 31.12 Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

Molecule $C_{32}H_{37}CIO_4PdS_2$ 691.59 193(2) K 0.71073 A monoclinic, C c a = 16.4077(10) A $\alpha = 90 \text{ deg.}$ $\beta = 108.147(3) \text{ deg.}$ b = 16.1834(9) A c = 12.3729(8) A $\gamma = 90 \text{ deg.}$ 3122.0(3) A^3 4, 1.471 Mg/m^3 0.849 mm^-1 1424 0.12 x 0.06 x 0.06 mm 1.81 to 31.12 deg. -23<=h<=23, -23<=k<=23, -17<=l<=17 34996 / 9860 [R(int) = 0.0444] 99.4 % 0.7461 and 0.6861 Full-matrix least-squares on F^2 9860 / 360 / 465 1.035 R1 = 0.0391, wR2 = 0.0837 R1 = 0.0621, wR2 = 0.0972 0.430 and -0.692 e.A^-3



Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 30.54 Max. and min. transmission **Refinement method** Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

C₁₇H₁₉BrOS 351.28 193(2) K 0.71073 A monoclinic, P 21/c a = 12.3587(5) A α = 90 deg. b = 12.4755(5) A $\beta = 107.9286(13) \text{ deg.}$ c = 11.0104(4) A $\gamma = 90 \text{ deg.}$ 1615.16(11) A^3 4, 1.445 Mg/m^3 2.668 mm^-1 720 0.38 x 0.18 x 0.14 mm 3.27 to 30.54 deg. -17<=h<=17, -17<=k<=17, -15<=l<=14 49038 / 4919 [R(int) = 0.0680] 99.6 % 0.7461 and 0.5813 Full-matrix least-squares on F^2 4919 / 0 / 185 0.916 R1 = 0.0364, wR2 = 0.1089 R1 = 0.0570, wR2 = 0.1256 0.816 and -0.966 e.A^-3



Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 31.87 Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

 $C_{24}H_{26}S_2$ 378.57 193(2) K 0.71073 A orthorhombic, P 21 21 21 a = 14.5367(7) A $\alpha = 90 \text{ deg.}$ b = 14.9341(6) A $\beta = 90 \text{ deg.}$ γ = 90 deg. c = 29.9629(13) A 6504.7(5) A^3 12, 1.160 Mg/m^3 0.250 mm^-1 2424 0.44 x 0.32 x 0.30 mm 2.72 to 31.87 deg. -21<=h<=21, -22<=k<=22, -40<=l<=44 127528 / 22291 [R(int) = 0.0342] 99.8 % 0.7463 and 0.6967 Full-matrix least-squares on F^2 22291/0/718 1.053 R1 = 0.0476, wR2 = 0.1150 R1 = 0.0655, wR2 = 0.1254 0.331 and -0.499 e.A^-3



Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient Max. and min. transmission F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 25.242 Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

 $C_{24}H_{26}O_3S_2$ 426.57 193(2) K 0.71073 A Triclinic, P-1 a = 9.035(4) A $\alpha = 100.829(17) \text{ deg.}$ b = 9.959(4) A β = 101.45(3) deg. c = 13.309(10) A $\gamma = 102.442(15) \text{ deg.}$ 1112.4(11) A^3 2, 1.274 Mg/m^3 0.261 mm^-1 0.7457 and 0.7052 452 0.18 x 0.12 x 0.04 mm 5.142 to 26.367 deg. -11<=h<=11, -12<=k<=12, -15<=l<=16 17659 / 4475 [R(int) = 0.0255] 98.3 % Full-matrix least-squares on F^2 4475 / 0 / 280 1.114 R1 = 0.0506, wR2 = 0.1160 R1 = 0.0582, wR2 = 0.1195 0.452 and -0.471 e.A^-3



- Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions
- Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 33.83 Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole
- $2(C_{24}H_{26}O_2S_2), C_3H_6O$ 879.21 193(2) K 0.71073 A monoclinic, C2/c a = 24.8465(7) A $\alpha = 90 \text{ deg.}$ $\beta = 107.4850(10) \text{ deg.}$ b = 9.9110(3) A c = 20.1353(5) A $\gamma = 90 \text{ deg.}$ 4729.3(2) A^3 4, 1.235 Mg/m^3 0.246 mm^-1 1872.0 0.28 x 0.22 x 0.20 mm 2.89 to 33.83 deg. -38<=h<=38, -15<=k<=15, -26<=l<=31 48006 / 9469 [R(int) = 0.0392] 99.4 % 0.7467 and 0.6933 Full-matrix least-squares on F^2 9469 / 60 / 304 1.016 R1 = 0.0466, wR2 = 0.1218 R1 = 0.0751, wR2 = 0.1382 0.625 and -0.605 e.A^-3

Crystallographic data for compound 41·CH₂Cl₂





Molecule

Empirical formula 2(C₂₇H₃₄O₂S₂Si), CH₂Cl₂ Formula weight 1050.43 Temperature 193(2) K Wavelength 0.71073 A Crystal system, space group triclinic, P-1 Unit cell dimensions a = 10.787(3) A $\alpha = 79.02(2) \text{ deg.}$ b = 14.787(7) A $\beta = 88.844(12) \text{ deg.}$ c = 18.645(7) A γ = 79.565(16) deg. Volume 2871(2) A^3 Z, Calculated density 2, 1.215 Mg/m^3 Absorption coefficient 0.342 mm^-1 F(000) 1116 Crystal size 0.48 x 0.12 x 0.10 mm Theta range for data collection 2.85 to 30.02 deg. -15<=h<=15, -20<=k<=20, -26<=l<=26 Limiting indices Reflections collected / unique 128302 / 16681 [R(int) = 0.0447] Completeness to theta = 30.02 99.4 % Max. and min. transmission 0.7460 and 0.7016 **Refinement method** Full-matrix least-squares on F^2 16681 / 117 / 670 Data / restraints / parameters Goodness-of-fit on F^2 1.048 Final R indices [I>2sigma(I)] R1 = 0.0519, wR2 = 0.1248 R indices (all data) R1 = 0.0799, wR2 = 0.1438 Largest diff. peak and hole 0.814 and -1.052 e.A^-3





Empirical formula Formula weight Temperature Wavelength Crystal system, space group Unit cell dimensions

Volume Z, Calculated density Absorption coefficient F(000) Crystal size Theta range for data collection Limiting indices Reflections collected / unique Completeness to theta = 26.47 Refinement method Data / restraints / parameters Goodness-of-fit on F^2 Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole $C_{36}H_{35}O_2PS_2, C_3H_6O$ 656.81 193(2) K 0.71073 A monoclinic, P 21/n a = 15.0226(12) A $\alpha = 90$ deg. b = 9.7451(8) A $\beta = 106.964(4) deg.$ $c = 24.670(2) A \gamma = 90 deg.$ 3454.4(5) A^3 4, 1.263 Mg/m^3 0.238 mm^-1 1392 0.1 x 0.04 x 0.02 mm 1.43 to 26.47 deg. -18<=h<=18, -12<=k<=12, -30<=l<=29 38408 / 7076 [R(int) = 0.0716] 99.1 % Full-matrix least-squares on F^2 7076 / 63 / 446 1.121 R1 = 0.0817, wR2 = 0.2530 R1 = 0.1331, wR2 = 0.3063 0.880 and -0.934 e.A^-3

Coordination Chemistry

Bis-Sulfonyl O,C,O-Chelated Metallylenes (Ge, Sn) as Adjustable Ligands for Iron and Tungsten Complexes

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Dedicated to Dr. Annie Castel on the occasion of her retirement

Abstract: The synthesis and characterization of an E_2CE_2 bissulfonyl aryl pincer ligand and its efficiency for the stabilization of compounds containing low-valent Group 14 elements (Ge and Sn) are reported. Complexation reaction of these metallylenes with iron or tungsten complexes resulted in the modulation of the oxygen atoms of the sulfonyl groups implicated in the stabilization of the Group 14 elements, demonstrating the original adjustable character of the bis-sulfonyl O_2 S-C-SO₂ aryl pincer.

Introduction

The ability of pincer ligands to form coordinate bonds with transition metals has been extensively investigated,^[1] although their chemistry with Group 14 elements is less developed. Van Koten and co-workers synthesized the first tin(II)-based NCN pincer, and this led to a surge of interest due to the ability of these ligands to stabilize reactive species with low-valent Group 14 atoms.^[2] However, the main *ortho* substituents were limited to amino, alkoxy-methylene moieties (A^3 and B^4), imino or phosphonate groups (C^5 and D^6 ; Figure 1).

Recently, we have shown the efficiency of a novel O_2S -C-S O_2 pincer system (**E**) to stabilize a tin(II) species (Figure 1).^[7] In addition to the originality of the stabilization of the stannylene by sulfonyl groups, this ligand differs from previous ECE pincers by its E_2CE_2 character due to the presence of two chelating oxygen atoms on each sulfur atom. This characteristic led us to consider the potential use of such metallylenes as adjustable ligands of transition metals by modulation of the oxygen

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 available on the WWW under http://dx.doi.org/10.1002/chem.201504507. It contains experimental procedures, physicochemical data, and X-ray data for compounds 1–7.



Figure 1. Examples of pincer complexes of chlorometallylenes.

atoms of the sulfonyl group implicated in the stabilization of the Group 14 element.

To validate our hypothesis, we envisioned a new O_2S -C-S O_2 pincer ligand that was able to stabilize not only a stannylene, but also the corresponding germylene congener. Knowing that the modification of the aryl backbone could affect the electron density at the metal,^[8] we considered the substitution of the *para* position with an electron-donating group, such as *tert*-butyl. Herein, we report how the substitution at the central phenyl group of the bis-sulfonyl pincer ligand gave a new family of metallylenes (Ge and Sn). These Group 14 low-valent species were fully characterized, and their coordination properties were tested with iron and tungsten carbonyl complexes.

Results and Discussion

The *para*-substituted ligand **1** was synthesized in a similar manner to 1,3-bis[(4-methylphenyl)sulfonyl]benzene using

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Scheme 1. Synthesis of the bis-sulfone ligand 1.

a palladium-catalyzed cross-coupling reaction between 1,3-dibromo-5-*tert*-butylbenzene and sodium *p*-toluenesulfinate (Scheme 1).^[7]

After purification by silica-gel column, compound 1 was isolated as white crystals by crystallization in ethanol at room temperature in 60% yield. The NMR spectra showed the characteristic signals of the tolyl and of the central aromatic cyclic moieties, the most noteworthy being the C(1)H resonance at $\delta = 8.23$ (t, ${}^{4}J_{HH} = 1.6$ Hz) in the ¹H NMR spectrum. The crystallographic study confirms the formation of the ligand and reveals only the presence of the *trans* rotameric form (Figure 2).



Figure 2. Molecular structure of compound 1 in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, and tolyl and *tert*-butyl groups are simplified. Selected bond lengths [Å] and angles [°]: S1-O1 1.438(2), S1-O2 1.441(2), S2-O3 1.440(2), S2-O4 1.441(2); O1-S1-O2 119.47(11), O3-S2-O4 119.87(13), O1-S1-C6 106.80(11), O2-S1-C6 107.62(10), O3-S2-C2 107.66(11), O4-S2-C2 107.17(12), C1-C6-S1 118.86(18), C1-C2-S2 118.94(19).

The sulfur atoms are roughly co-planar with the benzene ring (0.010 and 0.032 Å out of the plane). The two tolyl groups are not parallel and lie on opposite sides of the central benzene in an almost orthogonal position with angles of 72.03 and 81.61°. The S–O bond length (1.428(2)–1.441(2) Å) is in the range of normal S=O bonds (1.43 Å).^[9] DFT calculations showed that the energy barrier of the *cis*→*trans* rotation is low (2.69 kcal mol⁻¹), which suggests that the *trans* orientation can be related to the packing effects.

The deprotonation of the bis-sulfone ligand 1 with *n*BuLi in toluene at -40 °C, followed by substitution reaction with the appropriate metallylene dichloride (GeCl₂·dioxane or SnCl₂), gave the corresponding chlorometallylenes **2** and **3** in 60% yield (Scheme 2).



Scheme 2. Synthesis of the new metallylenes.

After workup, compounds 2 and 3 were isolated as white solids slightly soluble in dichloromethane, THF, and toluene, but not in diethylether or pentane. They were characterized by ¹H, ¹³C, and ¹¹⁹Sn NMR analysis, as well as high-resolution mass spectrometry. In the ¹³C NMR spectra, upfield-shifted signals of the central carbon ($\delta = 159.9$ and 169.8 ppm in **2** and **3**, respectively) were observed, comparable to those reported previously in ECE-coordinated chlorogermylenes^[3h] and stannylenes. $^{\scriptscriptstyle [2,6a,b,7]}$ The $^{\scriptscriptstyle 119}\text{Sn}$ NMR spectrum displays a sharp signal at $\delta = -14.95$ ppm (in CDCl₃), close to that obtained previously by using the bis-phenylsulfone ligand (-25.36 ppm), suggesting comparable S=O \rightarrow Sn^{II} coordination. Single crystals of 2 and 3, suitable for X-ray diffraction analysis, were obtained by slow diffusion of pentane in a CH₂Cl₂ (for 2) and THF (for 3) solution at room temperature. The metallylenes 2 and 3 are isostructural, and their structures are shown in Figure 3.

Both compounds 2 and 3 crystallize in a monoclinic space group (C2/c), with the chlorine atom disordered over two positions, each with 50% site occupancy. The molecular structures of 2 and 3 reveal that the bis-sulfonyl ligand is bonded in a tridentate fashion to the germanium and tin, respectively. The flanking tolyl groups are in relative trans orientation. This is in contrast with the structure of the previously described stannylene E, in which the flanking tolyl groups are situated on the same side of the central ring (Figure 1).^[7] The Group 14 elements (Ge and Sn) are four coordinated and, considering the lone pair of electrons, exhibit a distorted seesaw geometry.^[5d] A value of 77.95(5)° is observed for the C1-Ge1-O1 angle and 73.99(3)° for the C1-Sn1-O1 due to the formation of five-membered rings by coordination of the sulfonyl groups to the germanium or tin atoms. The heterocycles are nearly co-planar with the phenyl backbone, with the sulfur atom lying 0.016 and 0.049 Å for 2 and 3, respectively, and the oxygen 0.141 and 0.045 Å out of the plane defined by the other atoms. The Group 14 element, C1, and C4 lie on a twofold axis; therefore, the values of the Ge-O (2.359(2) Å) and the Sn-O bonds (2.451(12) Å) are identical. The O \rightarrow Sn donor bond length is close to those reported for the stannylene SnCl[2,6-{(p-tolyl)-SO₂}₂C₆H₃] (2.458(7) and 2.543(7) Å).^[7]

Because the binding mode using an O-C-O pincer-type ligand to stabilize germanium divalent species is unknown to

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Figure 3. Molecular structure of compounds **2** and **3** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *tert*-butyl groups are simplified. Selected bond lengths [Å] and angles [°] for **2**: S1–O1 1.463(2), Ge1–C1 2.030(3), Ge1–Cl1 2.287(2), Ge1–O1 2.359(2); C1-Ge1-Cl1 93.78(5), C1-Ge1-O1 77.95(5), O1-Ge1-O1 A 155.90(10). For compound **3**: S1–O1 1.465(11), Sn1–C1 2.214(2), Sn1–Cl1 2.359(13), Sn1–O1 2.451(12); C1-Sn1-Cl1 95.22(3), C1-Sn1-O1 73.99(3), O1-Sn1-O1 A 147.99(5).

date, the sole comparison can be made with an oxygen-donorstabilized germanium(II) compound GeCl[2,4-(tBu)₂-6- $(CH_2OtBu)-(C_6H_2)]$, in which the O \rightarrow Ge donor bond is much shorter (2.073(2) Å)^[10] and with the (1,8-dimethoxy-9-anthracenyl)-chlorogermylene (2.357 and 2.386 Å).^[11] No significant variations were observed between the S=O with the oxygen atom coordinated to the metallylene (S1-O1 1.463(2) Å) and the S=O free bonds (S1-O2 1.437(2) Å). These values are also close to those previously present in the starting bis-sulfonyl compound 1 and are in the range of normal S=O bonds (1.43 Å).^[9] The Ge1-Cl1 bond (2.287(2) Å), oriented orthogonal to the plane of the aryl ligand, compares well with that observed in the germylene stabilized by a N,C,N pincer ligand (A, Figure 1; 2.309(4) Å).^[3h] In the case of 3, the Sn1–Cl1 bond (2.359(13) Å) is shorter than that observed for the stannylene CHEMISTRY A European Journal Full Paper

SnCl[2,6-{(p-tolyl)SO₂}₂C₆H₃] (2.454(3) Å) obtained in a *cis* conformation.

DFT calculations were performed to gain further insight into the structure and the specific interactions. Three isomers were considered for both metallylenes: two isomers, in which the flanking tolyl groups adopt a cis conformation with respect to the central aromatic ring (isomers I and II, see the Supporting Information) and the isomer with a trans orientation of the flanking tolyl groups (isomer III). The most stable isomers in the case of the new metallylenes are calculated to be the isomers with both the tolyl groups and the chlorine atom in a cis orientation with respect to the central ring (isomers 2_I and 3_I), but the difference in energy from the trans structures (2_III and 3_III, identified in solid state) is only 1.67 kcal in the case of the germylene 2 and 3.46 kcal in the case of the tin analogue 3, values at the limit of significance of the calculations. Natural bond orbital (NBO) analyses performed on the trans isomer structures for both the germylene and the stannylene compounds showed interactions between lone pairs situated on oxygen atoms and a vacant orbital with p character on the Group 14 element. In the case of the calculated 2_III isomer, these interactions amount to a calculated energy of 60.2 kcal mol⁻¹. Similar charge-transfer interactions (summing up to about 70 kcal mol⁻¹) also occur for the tin derivative. Mulliken and NBO charges for the Group 14 element and the chlorine atom in model derivatives 2_III and 3_III were calculated (see the Supporting Information, Table 5.1) and suggest a stronger ionic character for the Sn--Cl bond than for Ge--Cl. The calculated MO bond order is also higher in the case of the tin-chlorine bond (1.33 for Sn-Cl and 1.25 for the Ge-Cl bond).

In the pincer-stabilized metallylenes, the Lewis-base character of the M^{II} atom is increased as a result of the intramolecular donor $E \rightarrow M$ coordination that should facilitate their complexation with Lewis acids.^[1b] To assess the σ -donor properties and the adjustable-ligand character of the newly obtained germylene **2** and stannylene **3**, we performed complexation reactions with carbonyl transition metals (Scheme 3).

The reactions of compounds **2** and **3** with an excess of $[Fe_2(CO)_9]$ were performed overnight in THF at room temperature, giving dark orange solutions. After evaporation of the solvent and extraction with diethylether, the stannylene iron complex **5** was isolated as an orange powder in a good yield



Scheme 3. Syntheses of the metallylene iron and tungsten complexes.



(69%). Crystallization in toluene at -25 °C gave dark orange crystals suitable for X-ray single-crystal analysis. Compound **5** was also characterized by multinuclear NMR and IR spectros-copies and high-resolution mass spectrometry. The downfield shift of the ¹¹⁹Sn signal (δ =192.48 ppm in [D₈]THF) compared to that of the starting stannylene (-33.30 ppm in [D₈]THF) is to be noted.

A similar observation, suggesting a decrease of the electron density on the tin atom upon complex formation, was reported for various iron-stannylene complexes.[6a, 12, 13] Additionally, the coordination of the stannylene was proved by the presence of a CO resonance at $\delta = 214.1$ ppm in the ¹³C NMR spectrum and the presence of three CO stretching frequencies at 2040, 1963, and 1905 cm⁻¹, characteristic for such complexes.^[14] The formation of several compounds was observed when starting from the germylene analogue 2; however, some colorless crystals were separated from the reaction mixture, and the X-ray crystallographic study confirms the presence of the germylene iron complex 4. Because of its low stability in solution and the very small quantity of isolated product, complete analytical data for 4 could not be acquired. The molecular structures of complexes 4 and 5 are depicted in Figure 4 with selected bond lengths and angles.

Interestingly, in both complexes 4 and 5, the flanking tolyl groups are positioned on the same side of the central aromatic ring, not on opposite, as in the starting germylene 2 and stannylene 3 (Figures 3 and 4). This could be explained by the steric hindrance of the [Fe(CO)₄] fragment. It also shows that the coordination to the Ge or the Sn atoms is possible with either one of the oxygen atoms of the bis-sulfonyl groups, highlighting the adjustable character of the E₂CE₂-type pincer metallylenes. In both complexes, Group 14 atom exhibits a distorted trigonal bipyramidal geometry with the O1 and O3 atoms occupying the axial positions, and the C1, Cl1, and Fe1 atoms occupying the equatorial ones. The O1-Sn1-O3 angle (150.32(6)°) is marginally more open than that seen in the starting chlorostannylene (147.99(5)°). The Sn–O distances (2.377(2) and 2.354(2) Å) are shorter than that found in the stannylene 3 (2.451(12) Å) suggesting stronger Sn-O interaction due to the enhanced electropositive character of the tin(II) atom. The Sn-Fe bond length (2.442(1) Å) is close to those observed in a N-heterocyclic stannylene iron complex (2.430(1) and 2.429(1) Å),^[12] but slightly longer than that in a bis(aryloxide) stannylene iron one (2.408(1) Å).[14] To the best of our knowledge, complex 5 is the second example of a pincerligand-stabilized stannylene coordinated to the tetracarbonyl iron fragment and the first complex the structure of which was determined by single-crystal X-ray diffraction analysis. In the germylene complex analogue 4, the Ge–O distances (2.257(7) and 2.329(6) Å) are different and also slightly shorter than those in the germylene 2 (2.359(2) Å). The Ge–Fe bond length (2.296(2) Å) is in the range of the values obtained for stabilized germylene-iron complexes.[15]

NBO analysis performed on the germylene–iron and the stannylene–iron complexes revealed $O \rightarrow Ge/Sn$ interactions involving lone pairs on the Group 16 element and a vacant orbital bearing a major contribution from a p-type orbital on the



Figure 4. Molecular structures of compounds **4** and **5** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the co-crystallized solvent molecules are omitted, tolyl and *tert*-butyl groups are simplified. Selected bond lengths [Å] and angles [°] for **4**: S1–O1 1.467(6), S2–O3 1.479(8), Ge1–Cl1 2.138(4), Ge1–O3 2.257(7), Ge1–O1 2.329(6), Ge1–Fe1 2.296(2); C1-Ge1-Cl1 105.9(3), C1-Ge1-O3 79.9(3), C1-Ge1-O1 78.6(3), O1-Ge1-O3 157.1(2). For compound **5**: S1–O1 1.469(2), S2–O3 1.469(2), Sn1–Cl1 2.389(6), Sn1–O3 2.354(2), Sn1–O1 2.377(2), Sn1–Fe1 2.442(1); C1-Sn1-Cl1 98.42(6), C1-Sn1-O3 76.07(7), C1-Sn1-O1 75.03(7), O1-Sn1-O3 150.32(6).

germanium/tin atom, similar, but stronger than those found for the stabilized metallylenes. The energy of these interactions sums up to almost 75 kcal mol⁻¹ in the case of the germanium complex, and 100 kcal mol⁻¹ for the tin–iron derivative, which can account for the smaller $O \rightarrow M$ distances in the iron complex compared to the free metallylenes.

The reactivity of the compounds 2 and 3 towards a carbonyl tungsten complex was also addressed (Scheme 3). The reaction of stoichiometric amounts of the metallylenes 2 or 3 and $[W(CO)_5$ -THF] in THF at room temperature led to the corresponding complexes 6 and 7 in moderate yields (31–38%).

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After workup, they were isolated as yellow powder for **6** and colorless crystals for **7**, which were soluble in THF and chlorinated solvents. Both compounds are stable after several days of exposure to air.

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The ¹H spectra showed typical resonances expected for the alkyl (tBu) and aryl groups. The ¹³C NMR spectra revealed the presence of two signals ($\delta = 196.8$ and 200.7 ppm for **6** and $\delta =$ 196.1 and 199.5 ppm for **7**), indicating the presence of equatorial and axial CO groups in the [W(CO)₅] moiety. As was expected, coordination of the stannylene results in a downfield shift of the ¹¹⁹Sn resonance (δ = 50.4 ppm in CDCl₃) in comparison with that of the starting stannylene ($\delta = -14.95$ ppm in CDCl₃). The IR spectra of 6 and 7 recorded in Nujol exhibited the characteristic patterns for an $[W(CO)_5L]\xspace$ moiety $^{[16]}\xspace$ with CO stretching bands in the $\tilde{v} = 2069 - 1949 \text{ cm}^{-1}$ region for the germylene-tungsten complex **6** and in the $\tilde{v} = 2071 - 1900 \text{ cm}^{-1}$ region for the stannylene-tungsten complex 7, respectively. Single crystals of complexes 6 and 7 suitable for X-ray diffraction analysis were obtained from CH₂Cl₂ solutions. The asymmetric unit of compound 6 contains two crystallographically independent molecules with a similar structural arrangement, and as a consequence, only one is discussed (Figure 5).

The germanium and tin atoms are in the same distorted trigonal bipyramidal configuration with the O1 and O3 atoms in the axial and the C1, Cl1, and W1 atoms in the equatorial positions. In both cases, the metallylenes occupy the apical position of the [W(CO)₅] fragment. The Sn–O bond lengths (2.381(3) and 2.416(3) Å) are between those reported for $[SnW(CO)_5Cl{2,6-[P(O)(OiPr)_2]_2-4-tBu-C_6H_2}]$ (2.313(2))and 2.346(2) Å)^[6f] and for [SnW(CO)₅Cl[{2,6-(ROCH₂)₂C₆H₃}] (R = Me, 2.391(5) and 2.389(5) Å; R = tBu, 2.464(3) and 2.513(3) Å).^[4a] The Sn-W distance (2.718(1) Å) is slightly shorter than the corresponding distances in related complexes containing pincer ligand with phosphonato groups (2.7263(11) Å)^[6f] or amino, alkoxy groups (2.7630(3),^[17] 2.7321(5), and 2.7655(4) Å,^[4a] respectively). No noticeable variations of the Ge-O bond lengths were observed between the two germylene-iron 4 and tungsten 6 complexes, but they are shorter than those in the germylene 2. The germanium-tungsten distance (2.550(1) Å) is in the classic range for tungsten-germylene complexes.^[3g, 18] As was previously observed for the metallylene iron complexes, the tolyl groups lie in a cis position.

Conclusion

We have shown that the modification of the central ring of a bis-sulfonyl ligand gives access to the first germylene stabilized by an O,C,O aryl pincer ligand, and to the corresponding stannylene. These new metallylenes have been used as twoelectron carbene-like ligands for stabilization of iron or tungsten complexes. The initial *trans* form of the metallylenes, observed in solid state by X-ray diffraction, is modified during the complexation reaction with transition metals to the corresponding *cis* form by modification of the oxygen atom of the sulfonyl group implicated in the stabilization of the metallylene. The reactivity of these new adjustable E₂CE₂ pincer li-



Figure 5. Molecular structures of compounds **6** and **7** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the co-crystallized solvent molecules are omitted, tolyl and *tert*-butyl groups are simplified. Selected bond lengths [Å] and angles [°] for **6**: S1–O1 1.459(3), S2–O3 1.468(4), Ge1–Cl1 2.191(1), Ge1–O3 2.287(3), Ge1–O1 2.318(3), Ge1–W1 2.550(8); C1-Ge1-Cl1 105.79(13), C1-Ge1-O3 79.66(15), C1-Ge1-O1 78.82(15), O1-Ge1-O3 157.03(12). For compound **7**: S1–O1 1.458(3), S2–O3 1.462(3), Sn1–Cl 2.162(4), Sn1–Cl1 2.358(1), Sn1–O3 2.381(3), Sn1–O1 2.416(3), Sn1–W1 2.718 (5); C1-Sn1-Cl1 97.20(12), C1-Sn1-O3 75.24(15), C1-Sn1-O1 74.55(14), O1-Sn1-O3 149.32(11).

gands and their corresponding complexes is currently under investigation.

Experimental Section

CCDC 1427613 (1), 1427614 (2), 1427615 (3) 1427616 (4), 1427617 (5), 1427618 (6), and 1427619 (7) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: DFT calculations • germylene • pincer systems • stannylene • sulfonyl ligand

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Reactivity of bis-Sulfonyl O,C,O-Chelated-Metallylenes in Cycloaddition with ortho-Quinone: An Experimental and Computational Study

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Dedicated to the 50th anniversary of the Laboratoire Hétérochimie Fondamentale et Appliquée LHFA

Abstract: The reactivity of a germylene and a stannylene containing O,C,O-coordinating pincer-type ligand $[2,6-(RO_2S)_2-4-t-BuC_6H_2]^-$ (R = tolyl) was investigated towards ortho-benzoquinone. The effect of the bis-sulfonyl O₂S-C-SO₂ type pincer ligand and the benzoquinone group on the stability of the resulting cycloadducts was studied through experimental and computational techniques. The structures of the obtained products were determined in solution and in solid state by multinuclear NMR and IR spectroscopy, MS spectrometry, and single crystal X-ray diffraction. DFT calculations carried-out at the B3LYP-D3/Def2-TZVP and M11-L/Def2-TZVP levels of theory were performed in order to bring further clarification concerning the nature of the chemical bonding and the coordination geometry of these species. In addition, the stability of the metallylenes towards hydrolysis and dimerization was assessed.

extensively investigated, whereas their behavior towards lowvalent group 14 species is not overly developed until now. The first pincer ligand stabilized metallylene was synthesized by van Koten and co-workers, an NCN-pincer ligand based tin(II) species³ which was fully characterized. Since then, several other examples of pincer ligand stabilized metallylenes with amino-⁴, alkoxy-methylene⁵ moieties, imino-⁶ or phosphonate⁷ groups as *ortho* substituents were presented in literature (Figure 1).^{8,9}



Introduction

The chemistry of divalent species of group 14 elements, heavier analogues of carbenes known as metallylenes, saw a great development in the last decades, due to their versatile chemistry.¹ In order to stabilize the reactive species containing low-valent group 14 atoms and due to the ease with which the electronic and geometric properties of pincer framework can be modified, the pincer ligands began to be increasingly more exploited. The most common ECE-coordinating pincer-type ligands contain a neutral or monoanionic aryl backbone (pyridyl or phenyl group) linked to two-electron donor atoms (E = N, P, O, S) through different types of spacers.² The ability of pincer ligands to stabilize coordinative compounds has been

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Supporting information for this article is given via a link at the end of the document. It contains experimental procedures, physicochemical data, data obtained from the DFT calculations and X-ray data for compounds 3 , 5 , 6 .

Figure 1. Examples of pincer-chelated chloro-metallylenes.

The efficiency of a novel bis-sulfone pincer system of the type O₂S-C-SO₂ stabilizing tin(II) species was recently highlighted.⁸ The originality of the newly reported bis-sulfone pincer ligand lies not only in the stabilization of the stannylene through the sulfonyl groups, but also by its E₂CE₂ character induced by the presence of two chelating oxygen atoms linked on each sulfur atom leading to the potential formation of different isomeric systems. The first O₂S-C-SO₂ pincer ligand allowed the stabilization of a new stannylene derivative (Figure 1).⁸ Recently, we have described the stabilization effect of a modified bissulfonyl pincer ligand obtained by substitution of the central phenyl group of the bis-sulfone previously mentioned in the para position with the electron-donating *tert*-butyl group.⁹ The efficiency of the new para-substituted bis-sulfonyl pincer ligand was emphasized not only for the stabilization of low-valent group 14 elements (M = Ge, Sn) but also for their iron and tungsten complexes obtained by ligand-exchange reactions between a carbonyl group and the O₂S-C-SO₂ para-substituted pincer ligand. To note, that in the case of the obtained complexes, the flanking tolyl groups are positioned on the same side of the central aromatic ring, not on opposite, as in the starting germylene and stannylene. This could be explained by the steric hindrance of the M(CO)_n fragment. It also shows that the coordination to the Ge or Sn atoms is possible through either of the oxygen atoms of the bis-sulfonyl groups, highlighting the adjustable character of E₂CE₂ like pincer metallylenes.⁹ To assess the effect induced by the para-substituted bis-sulfonyl pincer ligand on the metallylenes, we have performed a series of investigations regarding the reactivity of these species.
Halogenated metallylenes, species usually stabilized in singlet state, can undergo reactions at multiple points: vacant *p* orbitals, electron lone pairs or halogen atoms.¹ Thus, besides the coordination reactions previously reported, of the germylene and stannylene to a transition metal,⁹ the stabilization of these heavier analogues of carbenes by cycloaddition reactions is also possible. On the other hand, oxidative additions represent experimental methods used to confirm the divalent character of these species¹⁰ thus, metallylenes form adducts with chalcogens (S, Se), ketones or *ortho*-guinones.^{1,11}

Herein, we report the synthesis, structural characterization and a computational study performed on the newly obtained benzoquinone adducts of the previously mentioned bis-sulfonyl O,C,O-chelated-metallylenes, in order to emphasize the impact of the quinones and the *para*-substituted *bis*-sulfonyl pincer ligand on the stability of these group 14 species.

Results and Discussion

The bis-sulfonyl O,C,O-chelated-germylene **1** and stannylene **2**, previously reported by our group⁹, reaction with 3,5-di-*tert*-butyl-ortho-quinone is a good method to certify the specific divalent character of these species¹² and also to evaluate the stability of the discussed derivatives.

Treatment of metallylene **1** and **2** with *ortho*-quinone led to new cycloaddition products **3** and **4** (Scheme 1).



Scheme 1. Reaction of germylene 1 and stannylene 2 with ortho-quinone.

The chlorogermylene **1** reacts with 3,5-di-tert-butyl-obenzoquinone to form easily the corresponding cycloadduct 3 (Scheme 1), stable under inert atmosphere even for a long period of time. NMR analysis performed on compound 3 in solution revealed the characteristic signals in ¹H NMR spectrum of the quinone group (doublets at 6.68 and 6.75 ppm (${}^{4}J_{H-H}$ = 2.24 Hz). The downfield shift of the signal for the meta protons on the central aromatic ring of the bis-sulfone pincer system, from 7.75 ppm in germylene 1 to 7.99 ppm in germylene cycloadduct 3 suggested that the reaction occurred at the germanium atom. The signals for the ortho and meta protons of the tolyl groups (8.04 ppm, d, ${}^{3}J_{H-H}$ = 8.37 Hz and o-CH Tol 7.39 ppm, d, ${}^{3}J_{H-H}$ = 7.99 Hz) show no significant change compared to germylene **1** (8.07 ppm, d, ${}^{3}J_{H-H}$ = 8.4 Hz and 7.38 ppm, d, ${}^{3}J_{H-H}$ = 8.5 Hz). The ¹³C NMR spectrum showed the specific signals for all the carbon atoms involved in product 3, as presented in the experimental part. Light green crystals for the germanium cycloadduct **3**, suitable for X-ray analysis, were obtained by crystallization in chloroform. The determined structure in solid state is shown in Figure 2, as well as selected geometric parameters.

According to the solid state structure, the bis-sulfone ligand is present under the *trans* rotameric conformation. The Ge-O1 and Ge-O3 distances of 2.841(3) and 2.568(3) Å between the germanium atom and the oxygen atoms of the sulfonyl groups are considerably larger than those identified for germylene 1 (2.359(2) Å), while the Ge-O5 (1.789(3) Å) and Ge-O6 (1.794(3) Å) bonds with the benzoquinone are slightly shorter than typical Ge-O distances identified in other *o*-benzoquinone-germylene cycloadducts (1.813(3) – 1.868(3) Å)¹⁰ and they are significantly shorter than the sum of the covalent radii of Ge and O (1.86 Å).¹³



Figure 2. Molecular structure of compound 3 in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen and disordered atoms and the co-crystallized solvent were omitted, tolyl and *t*-butyl groups were simplified. Selected bond distances [Å] and bond angles [°]: S1-O1 1.439(3), Ge1-C1 1.958(4), Ge1-C1 1.2.108(1), Ge1-O3 2.568(3), Ge1-O1 2.841(3), Ge1-O5 1.789(3), Ge1-O6 1.794(3); C1-Ge1-C1 118.06(11), C1-Ge1-O3 77.51(12), C1-Ge1-O1 72.62(13), O1-Ge1-O3 130.40(9), C1-Ge1-C1 118.06(11), O5-Ge1-O6 91.75(12), C1-Ge1-O5 1102.77(14), C1-Ge1-O5 109.74(14), C11-Ge1-O6 112.54(9), C11-Ge1-O5 109.74(14).

The literature data 14 suggest that a Ge-O type connection ranging between 2.51 and 3.23 Å can be considered rather as a weak interaction, being closer to a van der Waals interaction (sum of van der Waals radii is 3.40 Å) 15 than to a covalent bond (1.95 Å). 13

In the case of stannylene **2**, the same reaction with 3,5-di-*tert*butyl-*ortho*-quinone was performed and the resulted product **4** was characterized in solution and in solid state. The analysis of NMR spectra, recorded on the freshly obtained solution of **4**, and the purified compound (washed with diethyl-ether), indicated the formation of the desired tin cycloadduct. The specific signals revealed in ¹H NMR spectrum for the quinone group, doublets situated at 6.58 and 6.62 ppm (⁴*J*_{H-H} = 2.30 and 2.34 Hz), the

downfield shift of the meta protons of the central aromatic ring from 7.92 ppm in stannylene 2 to 7.98 and 8.07 ppm in cycloadduct 4, the downfield shift of the signal for the meta protons of the tolyl groups of bis-sulfone ligand to 8.38 ppm shown as a doublet of doublets $({}^{3}J_{H-H} = 8.06 \text{ and } {}^{2}J_{H-H} = 18.16 \text{ Hz})$ compared to 8.20 ppm (in THF-d₈, d, ${}^{3}J_{HH}$ = 8.42 Hz) in stannylene 2, and for the protons in ortho position of the tolyl groups a triplet can be seen at 7.42 (${}^{3}J_{H-H}$ = 8.68 Hz), also downfield shifted from 7.40 ppm (d, ${}^{3}J_{H-H}$ = 8.62 Hz), all confirmed the formation of a tin cycloadduct. The ¹H NMR shifts and their multiplicity also suggested that the tolyl groups are not equivalent as in stannylene 2, which can be explained by the fact that only one oxygen atom of the two sulfonyl groups of the ligand coordinates to the tin atom. The ¹³C NMR spectrum revealed also in this case the specific signals for all the carbon atoms involved in the cycloadduct product, as presented in the experimental part.

The mass analysis (DCl NH₃) spectrum exhibits a peak at 817.0 which corresponds to $[M+1]^{+}$ of compound **4** (C₃₈H₄₅ClO₆S₂Sn M = 816.1), evidencing its formation.

In order to obtain suitable single crystals for determining the structure in solid state, the THF was removed and chloroform was added to a sample of product **4**; then a few single crystals were isolated at room temperature, after several weeks. The solid state structure presented in Figure 3 shows that compound **5** was formed, probably by the Sn-Cl bond hydrolysis followed by dimerization with the formation of the Sn-O(H)-Sn bridge (Figure 3).

The X-ray diffraction analysis revealed that in compound **5** the tolyl groups of the bis-sulfone are in *cis* rotameric conformation, probably due to the steric hindrance in the molecule. The tin atom (in +4 oxidation state) is hexacoordinated, the bis-sulfone ligand coordinating through only one oxygen atom of the bis-sulfonyl groups; this coordination pattern explaining the appearance of different signals for the *meta* protons of the central aromatic ring (two singlet signals at 7.97 and 8.07 ppm). The Sn1-O1 bond length of 2.308(3) Å is significantly shorter than the one measured in the starting stannylene **2** (2.451(12) Å), suggesting a stronger S=O \rightarrow Sn coordination, while the distance encountered between Sn1 and O3 is 3.309(3) Å.

Furthermore, the solid state structure showed the presence of a strong intramolecular interaction between the hydrogen atoms of the Sn-O(H)-Sn bridge and the oxygen atom O3 (Figure 3) of the sulfonyl groups (distances $-OH_{bridge}...O3$ is 1.96(4)Å), interaction that contributes to the positioning of the bridge hydrogen atoms out of the plane of the Sn1-O7-Sn1A-O7A cycle, oriented in trans position one from the other considering the heterocycle. These interactions were additionally evidenced through DFT calculations, the calculated distances between the H atoms (of the bridging -OH groups) and the oxygen ones of the sulfonyl groups were of 1.851 Å.

In order to correlate the structural features of the tin cycloadduct **5** identified in the solid state with the ones in solution, ¹H NMR experiment was realized in THF-D8. The ¹H NMR spectrum on the crystals showed broad signals at chemical shifts similar to those on the crude mixture (or the pure compound **4**).



Figure 3. Molecular structure of compound **5** in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen and disordered atoms and the co-crystallized solvent were omitted, tolyl and *t*-butyl groups were simplified. Selected bond distances [Å] and bond angles [°]: S1-O1 1.464(3), S1-O2 1.436(3), S2-O3 1.434(3), S2-O4 1.438(3) Sn1-C1 2.194(4), Sn1-O3 3.309(3), Sn1-O1 2.308(3), Sn1-O5 2.023(3), Sn1-O6 2.007(2), Sn1-O7 2.069(3), Sn1-O7 A 2.112(3) Sn1A-O7 2.112(3), Sn1A-O7A 2.069(3); O5-Sn1-O6 82.36(10), O6-Sn1-O7 92.53(12), O6-Sn1-O7A 88.74(11), O5-Sn1-O7 104.08(12), O5-Sn1-O7A 170.90(11), O7-Sn1-O7A 74.32(13), Sn1-O7-Sn1A 105.68(13), O6-Sn1-C1 155.48(14), O5-Sn1-O1 90.76(12), O7A-Sn1-C1 111.98(14), O7-Sn1-C1 98.15(12), O6-Sn1-O1 78.92(10), O5-Sn1-O1 100.70(11), O7A-Sn1-O1 152.44(11), O7-Sn1-O1 79.30(11), C1-Sn1-O1 79.30(13).

Figure 4. Molecular structure of compound 6 in the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen and disordered atoms and the co-crystallized solvent molecules were omitted, tolyl and *t*-butyl groups were simplified. Selected bond distances [Å] and bond angles [°]: Sn1-C1 2.202(3), Sn1A-C1A 2.186(2), Sn1-O1 2.475(2), Sn1-O3 2.814(2), Sn1A-O1A 2.658(2), Sn1A-O3A 2.614(2), Sn1-O5 2.071(2), Sn1-O5A 2.104 (2), Sn1A-O5 2.095(2), Sn1A-O5A 2.101(2), Sn1-Fe1 2.474(1), Sn1A-Fe1A 2.461(1); C1-Sn1-O5A 92.46(9), C1-Sn1-O5A 94.74(9), C1A-Sn1A-O5 103.36(8), C1A-Sn1A-O5A 92.46(9), C1-Sn1-Fe1 127.27(7), C1A-Sn1A-Fe1A 134.61(7), O1-Sn1-O3 138.49(6), O1A-Sn1A-O3A 137.58(6).

The formation of the Sn-O(H)-Sn bridge was also highlighted in the case of the stannylene-iron complex **6**, synthesized and characterized by our group.⁹ The single crystals separated from a THF-d₈ solution and analyzed by X-ray diffraction showed the formation of a hydroxide-bridged dimer, where two OH groups were bridged between two stannylene-iron complex moieties (Figure 4). The IR spectrum recorded for the crystals of complex **6** showed the specific CO stretching frequencies at 2041, 2027, 1951, 1931, 1896 cm⁻¹, characteristic for metal-carbonyl complexes. ¹⁶ No further analysis could be done on the separated crystals due to their insolubility in commonly used solvents.

The X-ray diffraction analysis revealed that tin atom (in +2 oxidation state) is hexacoordinated, the bis-sulfone ligand is binding in a tridentate fashion; the Sn1-O1 and Sn1-O3 distances ranging between 2.475(2) and 2.814(2) Å, indicating medium-strong interactions. The tin atoms and the oxygen ones forming the bridge are almost coplanar, with a torsion angle of 3.67°, with the O5-Sn-O5A angle at the Sn atoms of 69.25(7) and 69.62(7)° and wider angles at the oxygen atoms O5-Sn-O5A (109.68(9) and 111.22(9)°). These values are at the lower and upper limit of similar, hydroxide-bridged tin containing moieties (69.9(3) – 73.68(7)° for the O-Sn-O angle and 105.6(2) – 109.57(12)° for the Sn-O-Sn angle)¹⁷.

In the case of compound **6** the solid state structure indicated that the O-H bonds of the Sn-O(H)-Sn bridge are positioned in the same plane as the Sn1-O5-Sn1A-O5A heterocycle, not out of the plane as in the case of compound **5**. No intramolecular interactions between H5 (Figure 4) and the oxygen atoms of the sulfonyl groups can be observed, the distances of 2.235 - 4.160 Å being larger than typical O-H secondary interactions. Similar results were delivered by the DFT calculations, the computed distances between H5 and the oxygen of the sulfonyl groups ranging within 2.371-2.550 Å.

Similar hydroxide-bridged tin derivatives were previously reported in the literature^{17, 18} being usually formed in the presence of water.

DFT analysis

In order to assess the structural behavior of the bis-sulfonyl O,C,O-chelated-cycloadducts **3** and **4** and also for a better understanding of the electronic effects occurring within them, DFT calculations were performed, using the B3LYP hybrid functional ¹⁹ along with Grimme's D3 dispersion correction ²⁰ (B3LYP-D3 in the text) and Def2-TZVP basis set²¹.

Three isomers were considered for each of the cycloadducts: one conformation placing the flanking tolyl groups in *trans* with respect to the central ring (Isomer I), two other isomers having the tolyl moieties in *cis*, whilst the quinone groups being oriented in *cis* (Isomer II) or *trans* (Isomer III) with respect to them (Figure 5).

The most stable molecular structures of cycloadducts **3** and **4** were calculated to be those of Isomer I in both cases (Figure 5). However, for both compounds **3** and **4** the energy differences between the investigated isomers were very small: around 1.3 kcal/mol between **3_I** and **3_III** and 3.9 kcal/mol between **3_I** and **3_III** and 2.4

kcal/mol between **4_I** and **4_II** (Table S1), these values stressing the adjustable rotameric conformational behavior of the pincer ligands.



Figure 5. Molecular geometries corresponding to the investigated isomers of germanium cycloadducts (compounds 3_I, 3_II and 3_III); similar structures were obtained for the corresponding tin derivative's isomers (4_I, 4_II, 4_III). Hydrogen atoms were omitted for simplicity.

For isomer **3_I** (the most stable germanium benzoquinone adduct according to the calculations and also the one identified in the solid state) short distances between the Ge atom and the O ones contained in the quinone unit were identified, with calculated values of 1.807 Å and 1.805 Å (Table S2) and which are shorter than typical Ge-O bonds or than their sum of covalent radii (1.86 Å).¹³ These short lengths can be explained in terms of hyperconjugative interactions (LP_O $\rightarrow \sigma_{Ge-R}$ with R = C O, CI), as already pointed out in previous studies²² carried out for similar bonding patterns. The calculated lengths of the corresponding Sn-O bonds in **4_I** (2.018 Å respectively 2.033 Å, see Table S2) were as well shorter than their sum of covalent radii (2.05 Å); however, the differences were smaller than those identified for the Ge-O bonds, as a consequence of the decreasing hyperconjugative effect down in the group.²²

NBO analysis carried out on the investigated compounds revealed, in addition, occurrence of hyperconjugative effects involving the CI atom. Yet, the total amount of energy corresponding to these interactions seemed to decrease significantly from germanium derivative **3** to the tin derivative **4**; for instance, the total hyperconjugation energy corresponding to the LP_O $\rightarrow \sigma^*_{M-C}$ (M = Ge, Sn) interactions was calculated to be 17.1 kcal/mol in compound **3_1** and only 3.2 kcal/mol in compound **4_1**. Thus, hyperconjugative effects can be accounted as further stabilization of the Ge-CI bond by comparison to its tin analogue.

In cycloadducts **3_I** and **4_I**, the Mulliken and NBO charges (Table 1) for Ge/Sn and CI atoms revealed an increased ionic character for Sn-CI chemical bonding than that of the Ge-CI one. Thus, the increased ionic character of Sn-CI bond together with poorer stabilization through hyperconjugation by comparison to the Ge-CI bond, can stand as an explanation for the formation of dimer **5**, which was identified in the solid state.

Table 1. Calculated Mulliken and NBO charges for derivatives 3_I and 4_I.

Isomer	Atom	Mulliken Charge	NBO charge
3_1	Ge	0.921	2.022
	CI	-0.272	-0.375
4_I	Sn	1.276	2.106
	CI	-0.318	-0.470

Regarding the coordination geometry of cycloadduct **3_I**, large distances between the Ge and the O atoms from the pincer ligand (with calculated values of 2.515 Å and 3.086 Å respectively) indicate rather a tetra-coordinate geometry for the Ge atom. In addition, NBO analyses carried out on the optimized structure of **3_I** showed weak interactions between the lone pairs (LPs) of the O atoms in the pincer ligand and a vacant *p* orbital on the Ge one (Figure S2); the calculated amount of energy for these donor-acceptor interactions was about 18 kcal/mol for the short Ge-O contact (the one with calculated distance of 2.515 Å) and insignificant for the other one (around 3.5 kcal/mol), pointing out the tetrahedral geometry at the Ge center.

In 4_I, the computed distances between the O atoms of the sulfonyl groups and the Sn atom were of 2.406 Å and of 2.625 Å, being in agreement with previously reported lengths^{8,18} for Sn-O coordinative bonds. Moreover, NBO calculations revealed charge transfer interactions from the LPs situated on the O atoms into vacant p orbitals on the Sn (Figure S3). The calculated amounts of energy for each contact were about 47 kcal/mol for the shorter Sn-O coordinative bond and 25 kcal/mol for the larger one. On the other hand, isomer 4_III may play a more important role in the formation of dimer 5 than compound **4_I**. However, as previously pointed out,⁹ pincer ligands exhibit adjustable rotameric conformational behavior and in addition the calculated energy difference between the two isomers was very small (see Table S1). Moreover, the length of the Sn-O bonds and NBO analysis performed on the equilibrium geometry of this isomer suggested similar bonding patterns as those identified for stannylene 4_I.

In the optimized structure of dimeric species **5** (presented in Figure S4), the calculated geometrical parameters were in agreement with the obtained experimental data (selected parameters are presented in Table S3). The calculated Sn-O distances contained in the two Sn-O(H)-Sn bridges were equal two by two, with the equal bonds being displaced on opposite positions in the four-membered ring formed. Thus, the two shorter Sn-O distances (2.078 Å) can be considered covalent, while the other two bonds (2.150 Å) are rather coordinative in nature, as a consequence of the μ -coordination of the -OH groups from the hydrolyzed species **4_III**.

In addition, the molecular geometries of the hydrolyzed derivatives 4 (further noted as 4_I_OH, 4_II_OH and 4_III_OH) were also optimized (see Figure S5), in order to assess the stability of dimer 5 related to the free monomeric species. The energy of 5 was calculated to be with around 40 kcal lower than two times the energy of the hydrolyzed derivatives 4 (Table S4), highlighting the increased stability of the cycloadduct 5 compared to the unpaired monomers.

The molecular structure of dimeric species **6** (Figure S6) was also characterized through DFT calculations. Selected geometrical parameters are presented in Table S5 in the Supporting Information, being in good agreement with the solid state data. The computed Mulliken charges were around 1.5 for the Sn atom (1.490 and 1.492 respectively) while for Fe, these charges were calculated to be very close to 0 (-0.054 and -0.057) suggesting that the Sn-Fe bonding was formed through the coordination of LP electrons of Sn into vacant orbitals of the Fe atom.

Conclusions

The reaction of the bis-sulfonyl O,C,O-chelated germylene and stannylene with ortho-quinone gave the corresponding cycloadducts, that were characterized by the usual physico-chemical methods (multinuclear NMR and IR spectroscopy, MS spectrometry, single crystal X-ray diffraction).

In the case of cycloadduct **3**, a tetracoordinated Ge atom is present in the molecule and no Ge-O interactions were observed with the bis-sulfonyl ligand. For the tin analogue the formation of a Sn-O(H)-Sn bridged dimer was observed, where the Sn atom is hexacoordinated (compound **5**). The intramolecular interactions between the H atoms of the bridging –OH groups and the oxygen atoms of the sulfonyl groups led to a *trans* orientation of the H atoms with respect to the 4-memberded heterocycle formed.

DFT calculations emphasized the increased stability towards hydrolysis of **3**, related to its heavier analogue **4**. Thus, the more pronounced ionic character of the Sn-Cl bond compared to the Ge-Cl one and in addition the enhanced stabilization of the Ge-Cl bond through hyperconjugative effects can stand as an explanation of the different behaviour of the two species. Moreover, NBO analysis shed light on the nature of chemical bondings formed within the investigated compounds.

Experimental Section

All manipulations were performed in a dry, oxygen-free atmosphere of argon by using Schlenk-line and glove-box techniques; the solvents were purified using MBRAUN SBS-800 purification system. The NMR spectra were recorded with a Bruker Avance II 300 apparatus: ¹H (300.13 MHz), ¹³C (75.48 MHz), ¹¹⁹Sn (111.92 MHz) at 298 K. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (¹H and ¹³C{¹H}) or with an external reference (SnMe₄ for ¹¹⁹Sn). The NMR assignments were confirmed by COSY (¹H), HSQC (¹H-¹³C), and HMBC (¹H-¹³C) experiments. Mass spectrometry (MS) spectra were measured with a Hewlett-Packard 5989A in the electron impact mode (70 eV). High-resolution mass spectrometry (HRMS) spectra were measured with a GCT Premier Waters in DCI mode (CH₄). Melting point was measured in a sealed capillary using the Stuart automatic melting point SMP40 apparatus. IR spectra were measured using a Varian 640-IR FT-IR spectrometer.

The X-ray data were collected at 193(2) K on a Bruker - AXS APEX II Quazar diffractometer, equipped with a 30 W air-cooled microfocus sourceusing MoK α radiation (wavelength = 0.71073 Å). Phi- and omega-

scans were used. The data were integrated with SAINT²³ and an empirical absorption correction with SADABS was applied ²⁴. The structures were solved by direct methods using SHELXS-97 and refined using a least-squares method on F^2 (ShelXL-2014/7 for **3** and **5** and ShleXL-97 for **6**) ²⁵. All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined as riding models except for H on the Sn-O(H)-Sn bridge for compounds **5** and **6** (located by difference Fourier map and freely refined without any restraint) CCDC 1557820 (**3**), CCDC 1557821 (**5**) and CCDC 1557822 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data request/cif</u>.

Computational Details

Calculations were performed within the DFT framework using the B3LYP hybrid functional¹⁹ in conjunction with Grimme's D3 dispersion correction²⁰ and the valence triple- ς Def2-TZVP basis set²¹ and Stuttgart effective core potentials for the Sn atom. In addition, calculations were also carried out at the M11-L/Def2-TZVP level of theory, better agreement with the experimental data being however identified for the former functional. The results delivered by the M11-L functional²⁶ are available exclusively in the Supporting Information. All the calculations were performed using the Gaussian 09 package²⁷ and included geometry optimizations and frequency analysis. The integration grid used was of 99 radial shells and 950 angular points for each shell (99,950) while the optimization criteria were set to tight. NBO²⁸ *single-point* calculations were performed on the optimized structures using the Gaussian implemented version of the NBO Program.²⁹

Synthesis of compound 3

To a solution of germylene 1^9 (150 mg, 0.2729 mmol) in 4 ml THF a solution of 3,5-di-tert-butyl-ortho-benzoquinone (60.1 mg, 0.2729 mmol) in 1 ml THF was added dropwise giving a pale yellow suspension that slowly turned into a green-yellow clear solution. After stirring the reaction mixture overnight, the solvent was removed under vacuum giving a solid green-yellow residue. The latter was carefully washed with diethyl ether in order to remove unreacted starting material giving 80 mg (57% yield) of compound **3** from which NMR spectra were recorded. Single crystals of **3** suitable for X-ray diffraction analysis were obtained from CDCl₃.

¹H NMR (CDCl₃) δ = 1.21 (s, 9H, *t*-Bu), 1.26 (s, 9H, *t*-Bu quinone), 1.45 (s, 9H, *t*-Bu quinone), 2.45 (s, 6H, Me), 6.68 (d, 1H, ${}^{4}J_{H-H}$ = 2.24, H quinone), 6.75 (d, 1H, ${}^{4}J_{H-H}$ = 2.24, *H* quinone), 7.39 (d, 4H, ${}^{3}J_{H-H}$ = 7.99 Hz, *m*-CH Tol), 7.99 (s, 2H, *m*-CH Ph), 8.04 (d, 4H, ³J_{H-H} = 8.37 Hz, o-CH Tol) ¹H NMR (THF-D₈) δ = 1.24 (s, 18H, *t*-Bu quinone), 1.38 (s, 9H, *t*-Bu), 2.43 (s, 6H, Me), 6.62 (d, 1H, ${}^{4}J_{H-H}$ = 2.22, H quinone), 6.65 (d, 1H, ${}^{4}J_{H-H}$ = 2.22, H quinone), 7.46 (d, 4H, ³J_{H-H} = 8.57 Hz, *m*-CH Tol), 8.10 (d, 4H, ³J_{H-H} = 8.37 Hz, o-CH Tol), 8.17 (s, 2H, *m*-CH Ph); ¹³C NMR (CDCl₃) δ = 21.9 (Me), 29.7 (s,*t*-Bu quinone – 1.45 ppm in ¹H NMR), 30.6 (*t*-Bu), 31.8 (t-Bu quinone - 1.26 ppm in ¹H NMR), 34.6 and 34.8 (C t-Bu quinone), 35.7 (C t-Bu), 107.9 (H quinone - 6.68 ppm in ¹H NMR), 114.2 (H quinone - 6.75 ppm in ¹H NMR), 128.8 (o-CH Tol), 130.3 (m-CH Tol), 131.1 (m-CH Ph), 134.8 and 141.7 (C14 and C16), 136.5 (C7), 143.6 and 147.6 (C13 and C18), 145.8 (C10), 146.8 (C2, C6), 158.7 (C4); m.p. = 268-269°C decomposition at 275 °C; MS (DCI NH₃) (C₃₈H₄₇ClGeO₆S₂) [M+1]⁺ 771.0

Synthesis of compound 4

To a solution of stannylene $\mathbf{2}^9$ (125 mg, 0.2729 mmol) in 4 ml THF a solution of 3,5-di-tert-butyl-ortho-benzoquinone (60.1 mg, 0.2729 mmol)

in 1 ml THF was added dropwise giving a pale yellow suspension that slowly turned into a green-yellow clear solution. After stirring the reaction mixture overnight, the solvent was removed under vacuum giving a solid green-yellow residue. The latter was carefully washed with diethyl ether in order to remove unreacted starting material giving 62 mg (45% yield) of compound **4** from which NMR spectra were recorded. Single crystals of **5** suitable for X-ray diffraction analysis were obtained from CDCl₃.

¹H NMR (CDCl₃) δ = 1.18-1.32 (m, 18H, *t*-Bu and *t*-Bu quinone), 1.49 (s, 9H, t-Bu quinone), 2.45 (s, 6H, Me), 6.76 (broad s, 1H, CH-quinone), 7.06 (broad s, 1H, CH-quinone), 7.39 (d, 4H, ³J_{H-H} = 7.40 Hz, *m*-CH Tol), 7.93 (s, 2H, *m*-CH Ph), 8.11 (d, 4H, ³J_{H-H} = 8.01 Hz, *o*-CH Tol); ¹H NMR (THF-D₈) δ = 1.19 (s, 9H, *t*-Bu), 1.27 (s, 9H, *t*-Bu quinone), 1.48 (s, 9H, *t*-Bu quinone), 2.39 (s, 6H, Me), 6.58 (d, 1H, ${}^{4}J_{H-H}$ = 2.30, H quinone), 6.62 (d, 1H, ${}^{4}J_{H-H}$ = 2.34, H quinone), 7.42 (t, 4H, J = 8.68 Hz, m-CH Tol), 7.98 (s, 1H, *m*-CH Ph), 8.07 (s, 1H, *m*-CH Ph), 8.38 (dd, 4H, J = 8.06 Hz, J = 18.16 Hz, *o*-CH Tol); ¹³C NMR (THF-D₈) δ = 21.3 (Me), 30.1 (*t*-Bu quinone - 1.48 ppm in ¹H NMR), 30.6 (*t*-Bu) 32.3 (*t*-Bu quinone - 1.27 ppm in ¹H NMR), 34.5, 35.4 and 35.6 (C t-Bu and C t-Bu quinone), 108.4 (H quinone - 6.58 ppm in ¹H NMR), 112.4 (H quinone - 6.62 ppm in ¹H NMR), 129.4 and 130.3 (o-CH Tol), 130.7 and 130.8 (m-CH Tol), 131.0 (m-CH Ph for 7.98 ppm in ¹H NMR),131.5 (m-CH Ph for 8.07 ppm in ¹H NMR), 134.6 (C1) 136.5 (C14, C16), 136.9 and 137.6 (C7), 139.7 and 140.9 (C2, C6), 146.4, 146.7, 147.2, 147.4 (C10, C13, C18), 155.1 (C4); MS (DCI NH₃) ($C_{38}H_{47}CISnO_6S_2$) [M+1]⁺ 817.0. IR (nujol) $u_{SO}(cm^{-1}) =$ 1280, 1252, 1132, 1082.

Isolation of compound 5

A few crystals of compound **5**, suitable for X-ray analysis, were isolated from a sample of **4** in CDCl₃. kept for several weeks at room temperature. Single crystal X-ray diffraction and ¹H NMR are presented in the Results and Discussions part of the main text.

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Ce travail de thèse présente la synthèse, la caractérisation et la réactivité de métallylènes stabilisés par différents ligands pinces fonctionnalisés par des substituants soufrés à différents états d'oxydation.

Les métallylènes, analogues lourds des carbènes, présentent dans leur état fondamental singulet une paire d'électrons et une orbitale p vacante. Ces caractéristiques donnent à ces espèces un comportement et une réactivité particulière. La littérature décrit de nombreux exemples de métallylène stabilisés par différents types de ligands, parmi lesquels les ligands de type pince gagnent actuellement en importance. Dans la chimie des complexes de métaux de transition, il a déjà été démontré que les ligands de type pince constituent un type de plateforme efficace grâce aux possibilités de modulation des propriétés des complexes liées à la modulation du squelette du ligand. Au cours des dernières décennies, ces ligands se sont révélés efficaces pour la stabilisation de métallylènes stables. Cependant, un seul exemple de métallylène stabilisé par un ligand de type pince contenant du soufre a été reporté dans la littérature. Au cours de cette étude, des ligands pinces O,C,O chélatants contenant des groupement sulfonyles et sulfinyles ont été conçus, synthétisés et complètement caractérise par les méthodes physico-chimiques et computationnelle et leurs effets sur la stabilisation des métallylènes ont été étudiés. Dans un premier temps, un ligand pince de type bis-sulfone a été obtenu et étudié pour la synthèse de nouveaux métallylènes. A partir de ce ligand, un germylène et un stannylène ont été caractérisés, le germylène étant le premier exemple dans la littérature d'une espèce de germanium divalente stabilisée par un ligand pince de donneur d'oxygène. La réactivité des métallylènes a été testée pour obtenir des produits de cycloaddition avec l'orthobenzoquinone et des complexes des métaux de transition (fer et tungstène). Il a été démontré que la bis-sulfone se comporte comme un ligand ajustable de type pince O,C,O-chélatant, la coordination pouvant être possible par l'un ou l'autre des atomes d'oxygène des groupements sulfonyles. De même, un ligand sulfone-sulfoxyde et un ligand bissulfoxyde, contenant respectivement un groupe sulfonyle et un groupe sulfinyle ou deux groupes sulfinyles, ont été synthétisés. Dans les deux cas, les ligands ont été testés pour la stabilisation de métallylènes. A partir du ligand bis-sulfoxyde, un mélange a été obtenu en raison de l'existence des diastéréomères méso et dl, en rapport avec le caractère stéréogène de l'atome de soufre tandis qu'à partir du ligand sulfonesulfoxyde, un nouveau stannylène a été caractérisé et sa réactivité a été testée pour la stabilisation de complexes de métaux de transition.

Pour les trois types des ligands pince O,C,O-chélatants à base de soufre, une méthode de synthèse efficace a été développée. Ces nouveaux ligands ont été entièrement caractérisés par les méthodes physicochimiques courantes et ont été utilisés pour la stabilisation de métallylènes. Ainsi un germylène et des stannylènes stables ont été isolés et caractérisés, démontrant l'efficacité de cette nouvelle classe de ligands de type pince.