

Metallylene-sulfur compounds: synthesis, characterization and applications in coordination and catalysis

Nicolas Lentz

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Nicolas LENTZ

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Metallylene-Sulfur Compounds: Synthesis, Characterization and Applications in Coordination and Catalysis

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> Thèse dirigée par David MADEC

> > Jury

M. Jean-Philippe GODDARD, Rapporteur Mme Emmanuelle SCHULZ, Rapporteur M. Eric MANOURY, Examinateur M. David MADEC, Directeur de thèse

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Résumé de thèse

Cette thèse est consacrée à l'étude de plusieurs ligands originaux appartenant à la famille des métallylènes, i-e germylènes et stannylènes, avec des fonctions symétriques ou asymétriques. Ces fonctions présentent un atome de soufre commun à toutes les molécules. Les fonctions soufrées ont été incorporées de manières diverses et ont permis d'obtenir différentes propriétés en chimie de coordination ainsi qu'en catalyse.

Le premier chapitre débute dans un premier temps par une introduction sur les rappels historiques du développement de la synthèse des métallylènes. La nature et les propriétés des différents éléments du groupe 14 à bas état d'oxydation sont discutés et démontrent les différences et similarités entre tous les membres de cette famille (Schéma 1).



Schéma 1: Les carbènes et les dérivés lourds à l'état libre

Dans un second temps, la synthèse de dérivés du germanium (II) y est traitée selon les différentes voies de synthèse. Enfin, la stabilité des germylènes est abordée en discutant des méthodes développées dans la littérature pour stabiliser ces espèces électro-déficientes avec les différents substituants développés ces dernières décennies. L'utilisation des germylènes en chimie de coordination et particulièrement en catalyse est finalement abordée et démontre un engouement de plusieurs groupes et une importante multiplication des publications sur l'application des germylènes en catalyse, notamment ces dernières années. La dernière partie de l'introduction bibliographique est centrée sur la famille des sulfoxydes. Un rappel sur leurs propriétés, réactivités et effets électroniques est abordé ainsi que leurs applications en

coordination et en catalyse. Un état de l'art sur les complexes présentant un ligand du groupe 14 et une fonction sulfoxyde est présenté ainsi que leur proportion à être décrits comme des ligands hémilabiles (Schéma 2).



 $H = ligand mauvais \sigma$ -donneur

Schéma 2: Hémilabilité d'un ligand bidente par addition de CO

Le deuxième chapitre se concentre sur la synthèse et la chimie de coordination de ligands germylène- α -sulfoxyde avec des complexes des groupes 6 et 8. L'approche synthétique des composés germylène- α - sulfoxyde a été envisagée par réaction de substitution nucléophile d'un atome de chlore lié au germanium avec un carbanion sulfinylé. Le synthon germylène de départ sélectionné est l'amidinatochlorogermylène AmGeCl publié par notre groupe en 2015 et obtenu par condensation d'un lithien sur un carbodiimide puis transmétallation par le GeCl₂•dioxane. L'atome de chlore du composé AmGeCl est facilement substituable par différents nucléophiles afin d'obtenir des architectures complexes qui ont données lieu à plusieurs publications dans la littérature. Cette stratégie a notamment été utilisée pour la synthèse de ligands de type pince publiée par le groupe de Driess en 2012. La déprotonation en α du sulfoxyde est facilement réalisable avec une base faiblement nucléophile comme le LDA (Schéma 3).



Schéma 3: Synthèse de 1a

Cependant, l'addition du carbanion sulfinylé sur le composé AmGeCl n'a pas permis d'obtenir le composé **1a** et uniquement un mélange de produits a été identifié en RMN du ¹H. En effet, la formation de di-*iso*-propylamine durant la déprotonation laisse place à des réactions secondaires avec le germylène de départ ou le composé désiré. Afin de les éviter, la di-*iso*propylamine a été éliminée par évaporation, ce qui a permis d'obtenir **1a** avec un bon rendement de 72%. Le produit **1a** a pu être identifié de façon indubitable par RMN du ¹H avec les signaux caractéristiques des hydrogènes en α du sulfoxyde. Ils apparaissent en effet sous forme d'un signal A-B correspondant à un groupement CH₂ en α d'un centre asymétrique. La RMN du ¹³C montre aussi un signal caractéristique pour le carbone qui joue le rôle de pont entre le germanium et le sulfoxyde. En effet, ce carbone est secondaire dans le produit **1a** alors qu'il est primaire dans le sulfoxyde de départ.

La réaction a ensuite été étendue à des sulfoxydes et des germylènes possédant différents types de groupements (Schéma 4).



Schéma 4: Différent germylene-sulfoxyde synthétisé 1b-f

1b-f ont été obtenus selon la même méthode de synthèse que **1a**. Cette large gamme de ligands permet d'étudier l'influence de l'encombrement stérique sur le germylène, grâce aux groupements *iso*-propyle (**1a-b**) ou cyclohexyle (**1c-d**), mais aussi sur le sulfoxyde, grâce aux groupements aryle (**1a-b-e**) ou alkyle (**1f**).

Finalement, la réaction a été étendue aux autres états d'oxydations du soufre, le S(II) et le S(VI) (Schéma 5).



Schéma 5: Synthèse du ligand S(II) 1g et du ligand S(VI) 1h

1g-h ont été obtenus selon la même méthode de synthèse que **1a** à l'exception de la base employée. Cette fois-ci, le potentiel nucléophile de la base n'est plus un problème et le *n*-BuLi est utilisé en lieu et place du LDA, et donc d'introduire directement le nucléophile lithié en solution avec le germylène. La synthèse de ces dérivés a permis de comparer la stabilité et l'influence de la fonction sulfoxyde sur le ligand germylène mais aussi de pouvoir les comparer en vue d'applications en chimie de coordination et en catalyse. Il est important de noter que **1h** a pu être aussi cristallisé et analysé en diffraction des rayons X grâce à ses propriétés physiques uniques, comparées aux ligands thioéther et sulfoxyde qui se présentent sous forme d'huiles à température ambiante.

L'étude de la chimie de coordination de ces différents ligands a ensuite été envisagée à à partir de la propriété de cette famille de germylènes à pouvoir coordiner un métal à travers un groupement fortement σ -donneur, le germylène, et un groupement faiblement σ -donneur, le sulfoxyde. Dans un premier temps, le tungstène a été choisi comme métal de transition. En effet, il a déjà été démontré dans notre laboratoire en 2012 par Annie Castel *et al.* qu'un complexe germylène bidente de tungstène peut être obtenu à partir du précurseur W(cod)(CO)₄. La réaction de **1b** avec le même précurseur de tungstène a permis l'obtention du complexe **3b** (Schéma 6).



Schéma 6: Formation du complexe bis-germylene tungstène 3b

Le complexe bis-germylène **3b** a été caractérisé au travers de plusieurs méthodes d'analyses comme la RMN du ¹³C, la spectroscopie IR et la diffraction des rayons X. La réaction a été étendue à l'analogue du molybdène et $Mo(nbd)(CO)_4$ a été choisi comme précurseur (Schéma 7). Ainsi, la même réactivité a pu être observée et le complexe bis-germylène molybdène **4b** a été obtenu et caractérisé à travers les mêmes analyses que **3b**.



Schéma 7: Formation du complexe bis-germylene molybdène 4b

L'obtention de complexes bis-germylene tungstène et molybdène en chimie de coordination nous a amené à sélectionner de nouveaux métaux de transition. Dans un premier temps, le ruthénium est apparu comme une excellente alternative. En effet, plusieurs exemples de germylènes coordinés au ruthénium sont décrits dans la littérature et cette observation est aussi valable pour la fonction sulfoxyde. C'est pourquoi Ru(PPh₃)₃Cl₂ a été sélectionné comme précurseur. La réaction avec **1a** a permis d'obtenir le complexe bidente **5a** avec un rendement raisonnable de 56% (Schéma 8).



Schéma 8: Formation du complexe bidente germylene ruthénium 5a

Le complexe **5a** a été entièrement caractérisé par plusieurs méthodes d'analyses comme la RMN, la spectroscopie IR et la diffraction des RX, démontrant ainsi une coordination bidente du germanium et de l'oxygène du sulfoxyde au ruthénium. Ce complexe est parfaitement stable à température ambiante dans des conditions inertes et nous a amenés à sélectionner un autre précurseur de ruthénium, (RuCl₂(*p*-cymène))₂, pour obtenir une série de complexes monodentes. Dans un premier temps, la réaction a été effectuée avec **1b** pour obtenir **6b** avec un bon rendement de 80% (Schéma 9).



Schéma 9: Formation du complexe monodente germylene ruthénium 6b

Le complexe **6b** a été entièrement caractérisé par plusieurs méthodes d'analyses comme la RMN, la spectroscopie IR et la diffraction des RX. La réaction de coordination a ensuite été étendue à tous les ligands (Schéma 10). A nouveau, tous les complexes de ruthénium obtenus ont été entièrement caractérisés et sont stables à température ambiante sous atmosphère inerte.



Schéma 10: Formation des complexes monodente germylene ruthénium 6b-d-f-g-h

Enfin, la chimie de coordination a aussi été étudiée avec des métaux tels que le fer, le cuivre et l'or mais aucun complexe n'a pu être caractérisé.

Le troisième chapitre est consacré à la synthèse de nouveaux ligands germylènesulfoxyde avec une nouvelle architecture. Le nouveau design a été rationnalisé grâce aux résultats obtenus à travers la chimie de coordination de la première génération de ligands et de complexes, comme par exemple, l'obtention de bis-germylene pour la coordination du groupe 6 ou l'absence de coordination du soufre du sulfoxyde pour tous les métaux. Ces observations nous ont motivés à augmenter la distance entre les deux groupements afin de savoir si le groupement espaçant le germylene et le sulfoxyde peut avoir une influence sur la chimie de coordination. La formation de ligands germylene- β -sulfoxyde a donc été entreprise. Cependant, la déprotonation en β d'un alkylsulfoxyde n'étant pas facilement accessible, il a été décidé de substituer la position en α avec un groupement ¹Bu afin de permettre une réaction d'*ortho*lithiation. Le ligand 7 a été obtenu en utilisant la même procédure synthétique que la première génération, c'est-à-dire une substitution nucléophile (Schéma 11).



Schéma 11: Synthèse du ligand germylene-β-sulfoxyde 7a

La structure du produit **7a** a pu être déterminée indubitablement par RMN du ¹H et ¹³C avec des signaux caractéristiques. L'hydrogène en *ortho* du germanium apparaît sous forme d'un singulet ainsi que le carbone relié au germanium qui apparaît comme un carbone quaternaire alors qu'il est tertiaire dans le produit de départ.

Enfin, la chimie de coordination de ce ligand a été étudiée avec le même précurseur de tungstène utilisé précédemment (Schéma 12).



Schéma 12: Formation du complexe germylene tungstène 8

Le complexe **8** a été isolé comme un complexe bidente de tungstène avec le soufre du sulfoxyde et le germanium coordinés au centre métallique. La structure a pu être déterminée par RMN du ¹³C, en IR et en diffraction des rayons X. Finalement, la réaction a été étendue au molybdène avec le même précurseur utilisé précédemment (Schéma 13).



Schéma 13: Formation du complexe germylene molybdène 9

Le changement du groupement espaçant le germylene et le sulfoxyde a définitivement impacté la coordination du sulfoxyde afin d'obtenir des complexes bidentes avec les métaux de transition du groupe 6 contrairement à des complexes bis-monodentes avec la première génération.

La coordination a ensuite été étudiée avec le ruthénium. Le précurseur Ru(PPh₃)₃Cl₂ a été sélectionné comme précédemment (Schéma 14).



Schéma 14: Formation du complexe bidente germylene ruthénium 10a

De façon surprenante, un complexe à 16 électrons a été obtenu et le complexe de ruthénium **10a** a été caractérisé par RMN du ³¹P avec un singulet à 38 ppm mais aussi indubitablement caractérisé par spectrométrie de masse. Cependant, la diffraction aux rayons

X de ce complexe n'a pas permis de caractériser le complexe **10a** car un nouveau complexe de bis-ruthénium **10b** a été obtenu systématiquement au cours des cristallisations réalisées (Schéma 15).



Schéma 15: Formation du complexe 10b lors de la cristallisation

Le complexe **10b** montre des déplacements chimiques différents en RMN du ³¹P avec un singulet à 29 ppm et deux doublets à 44 et 52 ppm. La particularité de ce nouveau complexe est d'avoir deux atomes de chlore et la fonction sulfoxyde qui joue le rôle de pont entre les deux atomes de ruthénium. Il s'agit du premier exemple où un atome de soufre et un atome d'oxygène d'un même sulfoxyde coordinent deux centres métalliques différents avec une fonction sulfoxyde asymétrique.

Finalement, la chimie de coordination de 7 a été étudiée avec le groupe 10. Ni $(cod)_2$ a été utilisé comme précurseur métallique pour conduire à la formation du complexe **11a** (Schéma 16).



Schéma 16: Formation du complexe de nickel 11a

Le complexe de nickel **11a** a pu être caractérisé par RMN du ¹H et par diffraction des rayons X. Cependant la faible stabilité du complexe, qui se dégrade totalement en quelques heures, n'a pas permis son utilisation en catalyse. C'est pourquoi du monoxyde de carbone a été additionné pour stabiliser le complexe et obtenir le complexe de nickel tricarbonyle **11b** (Schéma 17), qui a été entièrement caractérisé par RMN et diffraction des rayons X.



Schéma 17: Formation du complexe de nickel 11b par addition de CO

L'hémilabilité du ligand est indubitablement démontrée de part cette réaction et l'échange du ligand sulfoxyde par un ligand carbonyle sans décoordination du germylène. La σ -donation du germylène a aussi pu être évaluée par le paramètre électronique de Tolman et comparer à d'autres ligands comme par exemple les NHC ou les phosphines.

Le quatrième chapitre est consacré à la synthèse de nouveaux ligands germylènesulfonimidamide avec une nouvelle architecture basée sur l'équivalent d'un amidinate avec un

S(VI). La synthèse des différents sulfonimidamides a été réalisée avec plusieurs groupements *i*-Pr ou mésityle, permettant d'obtenir un soufre symétrique ou asymétrique de façon racémique (Schéma 18).



Schéma 18: Formation des sulfonimidamides 12a et 12b

Les sulfonimidamides **12a** et **12b** ont été entièrement caractérisés par RMN et diffraction des rayons X. Ces ligands ont ensuite permis d'obtenir les germylènes homoleptiques correspondants par protonolyse avec le réactif Ge(HMDS)₂ (Schéma 19). L'élimination de l'amine formée après une nuit de réaction permet d'obtenir les germylènes **13a** et **13b** avec de bons rendements selon une méthode efficace.



Schéma 19: Formation par protonolyse des germylènes 13a et 13b

Les germylènes **13a** et **13b** ont pu être entièrement caractérisés par RMN et diffraction des rayons X et comparés au ligand de départ. Cette réaction a ensuite été étendue aux dérivés lourds des germylènes, les stannylènes. En suivant le même protocole expérimental, les

stannylènes homoleptiques correspondants ont pu être obtenus par protonolyse avec Sn(HMDS)₂ et ont été entièrement caractérisés (Schéma 20).



Schéma 20: Formation par protonolyse des stannylènes 14a et 14b

Finalement, des calculs DFT ont été réalisés pour déterminer la stabilisation électronique du ligand en fonction du métallylène et l'influence apportée par les différents substituants présents sur l'azote sur cette stabilisation.

Finalement, le cinquième et dernier chapitre est consacré à l'application des différents complexes et métallylènes en catalyse. Les différents complexes de ruthénium de première génération et le complexe à 16 électrons de deuxième génération ont été testés en catalyse et leur activité a été comparée. La catalyse sélectionnée est la réaction de transfert d'hydrogène qui consiste en la réduction d'un composé carbonylé en son alcool correspondant en milieu protique (Schéma 21).



Schéma 21: Réaction de transfert d'hydrogène

Dans un premier temps, les complexes *p*-cymène **6b-d-f-g-h** ont été utilisés pour la réduction de l'acétophénone dans l'*iso*-propanol avec une base (KOH) et 2 mol% de catalyseur (Schéma 22).



Schéma 22: Réduction de l'acétophénone en son alcool correspondant

La conversion de l'alcool a été vérifiée après deux heures de réaction par RMN du ¹H avec un étalon interne, le 1,2,4,5-tétramethylbenzène (Tableau 1).

Catalyseur	6b	6d	6 f	6g	6h
Conversion (%)	76	57	43	29	23

Tableau 1: Réduction de l'acétophénone en son alcool correspondant par 6b-d-f-g-h

Après 2 heures de réactions à 80 °C, l'alcool correspondant a été obtenu avec un rendement de 76% en utilisant le complexe de ruthénium **6b** comme catalyseur. L'augmentation de l'encombrement stérique avec un groupe cyclohexyle sur l'amidinate entraîne une baisse de l'activité et la conversion avec **6d** est de 57%. **6f** montre l'importance du groupement aryle car une chute de la conversion à 43% est observée, cette baisse peut être expliquée par l'instabilité du complexe et la formation d'*iso*-butène et d'un acide sulfinique lors du chauffage. Finalement l'influence du groupe sulfoxyde est notable car les dérivés thioéther et sulfone présentent des activités bien moindres de 29 et 23% respectivement pour **6g** et **6h**. Finalement, le complexe **5a** a été utilisé pour la réaction de transfert d'hydrogène avec le même substrat et dans les mêmes conditions en faisant varier la température et le temps de réaction.

Catalyseur (5a)					
Temps (h)	2	4	2	28	72
Température (°C)	80	50	25	25	25
Conversion (%)	97	97	26	87	97

Tableau 2: Réduction de l'acétophénone en son alcool correspondant par 5a

Après 2 heures de réactions à 80 °C, l'alcool a pu être entièrement converti en utilisant le complexe de ruthénium **5a**. Cette même observation a pu être réalisée à 50 °C après 4 heures. La conversion complète peut aussi être atteinte à 25 °C après 72 heures. Nous observons que la cinétique est assez lente car après 2 heures à 25 °C, l'alcool est déjà converti à hauteur de 26%. C'est pourquoi la version énantiopure a été synthétisé et testée en catalyse. Cependant, les résultats obtenus ont montré une induction asymétrique modeste au travers d'un excès énantiomérique de 21%.

Dans un dernier temps, le complexe **5a** a été utilisé pour réduire différentes cétones et aldéhyde (Tableau 3).

Entry	Carbonyle	Alcool	t (H)	Conversion (%)
1	● ●	OH	72	97
2	Br	Br	72	97
3		O H	72	97
4	F F F F	F ₃ C	72	97
5		OH	72	97
6	● ●	OH	4	97



L'extension à plusieurs cétones *para*-substituées a permis d'obtenir les alcools correspondants chimio-sélectivement. En effet, **5a** peut réduire une cétone en présence d'un groupement bromé, méthoxylé ou trifluorométhane sélectivement en 72 heures à 25 °C. La réduction dans les mêmes conditions a aussi permis de réduire la benzophénone et finalement le benzaldéhyde en 4 heures. Un essai avec une cétone plus encombrée, l'adamantyl-méthyl-cétone, a montré aucune réactivité et cela même après 96 heures de réaction.

Finalement, les stannylènes **16a** et **16b** ont été utilisés en catalyse de polymérisation de la ε -caprolactone. Les tests ont été réalisés dans le toluène à 100 °C (Schéma 23).



Schéma 23: Catalyse de polymérisation de la ε-caprolactone

Dans un premier temps, **16a** a été utilisé et a montré une conversion de 29% après une heure de réaction avec un bon PDI de 1.09. En laissant la réaction se dérouler, la conversion monte jusqu'à 77% après 7 heures. Enfin, **16b** montre une activité supérieure avec une conversion de 89% après une 1 heure. Cependant, cette activité est associée à une réaction de trans-estérification des chaînes polymériques avec un PDI moyen de 1.66.

En conclusion, la formation de ligands α et β sulfoxide-germylène a été réalisée avec une variation du groupement espaçant les deux entités. Les variations ont aussi permis d'obtenir des ligands germylènes avec des encombrements stériques différents et variés, mais aussi avec des degrés d'oxydation de l'atome de soufre différents (thioéther et sulfone). Cette variabilité a permis d'étudier la stabilité, l'influence de l'état d'oxydation du soufre et de l'encombrement stérique sur le germylène.

Ces ligands ont ensuite été utilisés en chimie de coordination pour obtenir des complexes avec des métaux de transition des groupes 6, 8 et 10. Ces complexes ont montré différentes propriétés de coordination avec la formation de systèmes monodentes, bismonodentes et bidentes. Les complexes de ruthénium ont aussi été appliqués en catalyse pour la réaction de transfert d'hydrogène afin de réduire l'acétophénone. Les résultats obtenus ont permis une réduction à température ambiante. Une extension à plusieurs cétones substituées ainsi qu'à la benzophénone et au benzaldéhyde dans les mêmes conditions a été réalisée. La catalyse énantiosélective a été testée et les résultats obtenus ont montré une induction asymétrique modeste.

Enfin, la synthèse de nouveaux germylènes et stannylènes avec un équivalent d'amidinate soufré, un sulfonimidamide, a été réalisée avec succès. La caractéristique de cette fonction est de pouvoir modifier simplement les groupes sur les azotes mais aussi d'avoir la possibilité d'insérer un soufre asymétrique. Les différents stannylènes ont été utilisés en catalyse de polymérisation de la ε-caprolactone. L'activité et les résultats obtenus sont encourageants pour appliquer ces catalyseurs en polymérisation de lactides.

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General Procedures

General Procedures

General handling conditions

All the manipulations have been carried out under inert Argon atmosphere, using the standard Schlenk techniques. The solvents used have been purified by a purificator MBraun SPS-800 over filtrating columns filled with molecular sieves of 0.4 nm, and have been stocked under Argon atmosphere. The solids have been manipulated in glove-box under Argon atmosphere. The addition of carbonyl monoxide was done by removing the atmosphere of a pressure tube and addition of the gas at 1.5 bars.

Equipment

Nucleus Magnetic Resonance (NMR).

¹H, ¹³C, ³¹P and ¹¹⁹Sn were recorded with the following spectrometers: Bruker Avance 300, 400 and 500 MHz. The complete characterization of the products has been done using 1D experiments, as well as 2D analysis, such as COSY (¹H -¹H), HSQC (¹H -¹³C), and NOESY. The chemical shift has been counted positively verse the low field, and expressed in part per million (ppm). The coupling constant are expressed in Hz. The abbreviations to describe the signals are: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), sept (septuplet), m (multiplet), Ar (aromatic), Ar/q (quaternary aromatic), J^{AB} (coupling constant between A and B) and br (broad signal).

Melting point.

Melting points were measured with a capillary Electrothermal Stuart SMP40 apparatus. samples have been prepared in the glove-box before the analysis.

Infrared (IR).

IR spectra were measured on a Varian 640-IR FT-IR spectrometer. The samples have been prepared in nujol or in a dichloromethane solution under Argon atmosphere.

X-ray diffraction analysis.

Single-crystal X-ray data were collected at low temperature (193(2)K) on a Bruker-AXS APEX II Quazar diffractometer equipped with a 30W air-cooled microfocus source or on a Bruker-AXS PHOTON100 D8 VENTURE diffractometer, using MoK radiation (λ = 0.71037 Å). The structures were solved by the direct method (SHELXS-97) or by direct intrinsic phasing method (SHELXT) and refined by full-matrix least-squares method on F2. All non-H atoms were refined with anisotropic displacement parameters.

Mass spectroscopy.

The mass spectroscopy analysis was done using two technics, direct chemical ionization (DCI-CH4) methods, and recorded on a GCT Premier Waters mass spectrometer or on a Maldi micro MX microMass in an anthracene matrix (ratio product/matrix: 1/100).

Theoretical calculations.

The theoretical calculations have been carried out by Dr Jean-Marc Sotiropoulos (directeur de recherche in IPREM laboratory at the University of Pau, France).

HPLC analysis.

Determination of ee was performed on a HPLC with a chiralcel OD column at a flow rate of 1 mL/min with a mobile phase of Heptane/*i*-PrOH (96/4). The two enantiomers were detected with an UV detector at 210 nm with a retention time of 12.4 min and 14.7min.

SEC analysis.

The number-average and weight-average molar masses (Mn and Mw, respectively) and molar mass distributions (Đ) of the polymer samples were determined by size exclusion chromatography (SEC) at 35 °C with a Waters 712 WISP high-speed liquid chromatograph equipped with a R410 refractometer detector. Tetrahydrofuran (THF) was used as the eluent, and the flow rate was set up at 1.0 mL/min. A SHODEX precolumn (polystyrene AT806M/S Mw = 50000000 g/mol) and two STYRAGEL columns (HR1, 100–5000 g/mol, and HR 4E, 50–100000 g/mol) were used. Calibrations were performed using polystyrene standards (400–100000 g/mol).

Abbreviations

Abbreviations

Abbreviations

Å = Ångström ACN = AcetonitrileAmGeCl = Amidinatochlorogermylene Cat = Catalyst cod = Cyclooctadiene coe = Cyclooctene Cy = Cyclohexyl DCM = Dichloromethane DFT = Density Functional Theory DIC = Di-*iso*-propylcarbodiimide Dipp = 2,6-Di-*iso*-propylphenyl DMS = Dimethylsulfur DMSO = Dimethylsulfoxide ee = Enantiomeric excess eq = Equivalent $Ge(HMDS)_2 = bis(Hexamethyldisilamide)germylene$ h = hourH-HMDS = Hexamethyldisilazane HMDS = Hexamethyldisilamide HPLC = High Performance Liquid Chromatography H-transfer = Hydrogen transfer i-Pr = iso-propyl IR = Infra-redL.B. = Lewis baseLDA = Lithium di-*iso*-propylamine MALDI-TOF = Matrix Assisted Laser Desorption Ionisation - Time of Flight Me = Methylmes = Mesityl nbd = Norbornadiene n BuLi = *n*-Butyl Lithium NHC = N-Heterocyclic Carbene NHGe = N-Heterocyclic Germylene NMR = Nucleus Magnetic Resonance oct = octoate = ethylhexanoate

Abbreviations

PDI = Polydispersity index

PES = Potential-electronic surface

ppm = Parts per million

REP = Ring expansion polymerization

ROP = Ring opening polymerization

R.T. = Room Temperature

SEC = Size exclusion chromatography

 t Bu = *tert*-Butyl

 $T(^{\circ}C) =$ temperature in Celsius

t(h) = time in hour

TEP = Tolman Electronic Parameter

THF = Tetrahydrofuran

Tiip = tri-*iso*-propylbenzene

T.M. = Transition Metal

TMEDA = Tetramethylethylenediamine

TMS = Trimethylsilyl

Tol = Toluene

UV = UltraViolet

Chapter I:

General Introduction

Chapter I:

General Introduction

Abstract

Germylenes, heavier analogues of carbenes, have attracted considerable interest the last decades since the breakthrough of NHC. Although the derivatives of the group 14 family should present similarities, some differences are also expected. Still multiples questions are unsolved concerning germylenes and specially their properties as ligands and their possible influence in a catalytic cycle.

In order to obtain a satisfactory answer, many groups have published their results based on the effect of stabilizing substituents on the electronic and steric properties of germylenes. The results showed that the stabilizing substituents have a major effect on the reactivity and so the further applications.

Nevertheless, several groups achieved to obtain stable germylene complexes and applied successfully these complexes as active pre-catalysts. The results obtained from the catalysis and the theoretical studies performed led to envisage germylenes as a novel class of ligands that should be able to present new activity, selectivity or stability properties in catalysis.

I. Historical aspects

I.1. General aspects of metallylenes

Catalysis is one of the most important and useful tools of modern chemistry to form polymers, drugs or small molecules to sustain human needs with lower cost in time and energy.

The design of new ligands for transition metals have been widely investigated to obtain novel electronic and steric properties and therefore novel catalytic activity. Therefore, these past decades, several Nobel prizes were attributed to chemists on this field like R. F. Heck, E. I. Negishi¹ and A. Suzuki² in 2010 for the cross-coupling reactions or Y. Chauvin,³ E. H. Grubbs⁴ and R. R. Schrock⁵ in 2005 for metathesis. Both of these catalyses took a renewed interest with the introduction of novel σ -donors ligands like N-Heterocyclic carbenes (NHC).⁶

Metallylenes, group 14 neutral elements at the +II oxidation state (Scheme 1), are one of the hottest topics explored by chemists these past decades since the isolation of the first stable carbene by Baceiredo *et al.* in 1988 and due to their numerous applications nowadays as organoreagents, organocatalysts and ligands.^{7–9}



Scheme 1: Carbenes and heavier analogues in ground state

These divalent species are defined as electron deficient with only 6 electrons on their valence shell. They possess two non-bonding orbitals defined as p_{π} and σ and two different metallylenes can be distinguished depending on the electron distribution between these orbitals p_{π} and σ (Scheme 2): triplet, with unpaired electrons in separate orbitals ($n\sigma 1n\pi 1$) and singlet, with both electrons paired ($n\sigma 2n\pi 0$).¹⁰ The difference between a triplet and a singlet will fundamentally depend on the energy level of the σ orbital.



Scheme 2: Degenerate energy levels of triplet and singlet state

The ground state of metallylenes depends on the energy gap between p_{π} and σ orbitals (Table 1).^{8,11,12} The comparison of dihydrometallylenes showed that only dihydrocarbene is more stable in triplet state compared to all the heavier analogues that are stable in singlet state. The gap increases in favor of singlet state with the size of the group 14 elements. The difference remains the same even with the cyclic derivative (C₄H₄M:)

H ₂ M:	H ₂ C:	H ₂ Si:	H ₂ Ge:	H ₂ Sn:	H ₂ Pb:
ΔE_{S-T} (Kcal/mol)	-9	16.7	21.8	24.8	34.8
C ₄ H ₄ M:	C ₄ H ₄ C:	C ₄ H ₄ Si:	C ₄ H ₄ Ge:	C ₄ H ₄ Sn:	C ₄ H ₄ Pb:
ΔE_{S-T} (Kcal/mol)	-9.6	14.8	22.8	26.2	27.3

Table 1: Energy gap between singlet and triplet states

This observation can be explained by the size of the ns and np orbitals. The difference changes dramatically with the heavier analogues, np orbitals become larger than ns orbitals as the quantic number increases. The effect on metallylene ground state is to favor the σ orbital and so the singlet state and to induce difficulties to the hybridation.^{13–15} Another effect observed by the size of the orbitals is the lone pair presenting a larger s character while the empty orbital presents a higher electrophilic character.

I.2. Synthetic route to germanium (II) species

The general procedure to obtain germylenes proceeds via reduction of the most stable Ge(IV) form to obtain the Ge(II) derivative. The synthetic pathway is essentially based on elimination or reduction reaction of the corresponding dihalogeno precursors (Scheme 3).^{16,17}

 $R_{2}GeX_{2} \xrightarrow{n \text{ Red}} R > Ge: + Red_{n}X_{2}$ $R_{2}GeY_{1}Y_{2} \xrightarrow{\text{Elimination}} R > Ge: + Y_{1}Y_{2}$ Scheme 3: Synthetic pathways to Ge(II)

The main starting material used for germylenes synthesis is GeCl₂•dioxane which is obtained from the reduction of GeCl₄ with a reducing agent. This reaction, described by Mironov in 1975, is still used nowadays by trapping the *in situ* formed GeCl₂ with dioxane. Another way to obtain functionalized germylenes was described by Herrmann in 1992 by reduction of Ge(IV) dichloride in Ge(II) derivative in a good 75% yield by using two equivalents of lithium as reducing agent (Scheme 4).¹⁸ Latter, Okazaki *et al.* used the same procedure with lithium naphthalenide to obtain a diarylgermylene from the corresponding dibromodiarylgermane.¹⁹



Scheme 4: Formation of Ge(II) by metallic reduction

Synthesis of germylenes via cyclo-elimination reaction was reported by Neumann *et al.* in 1980 (Scheme 5).^{20,21} Dimethylgermylene was formed at 70 °C by releasing the pyrene derivative. However, dimethylgermylene was highly reactive and trapped in situ with several reagents like dimethylbutadiene, (*Z*)-stilbene or dimethyltindichloride.



Scheme 5: Synthesis of Ge(II) by cyclo-elimination reaction and reactivity towards alkenes and tin derivatives

Retro cyclo-addition was also studied by the group of Okazaki in 1995 (Scheme 6).^{22,23} The novel germanium (IV) bearing a germacyclopropane group performed the retro cycloaddition and released the germylene with formation of phenylacetylene. Finally, Ge–C bond cleavage was proposed by the group of Müller in 2016.²⁴ The addition of NHC to 7silanorbornadienes led to the formation of silylenes stabilized by NHC and calculation study with the germanium derivative suggests that this reaction could be applied to the formation of the corresponding germylenes. However, there are still no reports of this reaction with germanium to date.



Scheme 6: Synthesis of Ge(II) by elimination reaction

Finally, a synthetic route to generate germanium (II) species via photolysis was studied by the group of Masamune in 1985 (Scheme 7).²⁵ The intermediate germylene was obtained under irradiation of a disilagermane. However, the diarylgermylene was highly reactive and gave a dimer characterized after quenching with methanol. Nevertheless, formation of the diarylgermylene intermediate was determined by rapid addition of methanol to give the addition product.



Scheme 7: Synthesis of Ge(II) via photolysis reaction

I.3. Functionalization and stabilization of germylenes

Most of the research including germanium (II) is based on functionalization of germylenes to promote them as organoreagents, organocatalysts, ligands or even transient intermediates. That is why GeCl₂•dioxane is the most commonly used precursor. Indeed, it can be easily functionalized by nucleophilic substitution of both chlorine atoms with different groups.

However, due to the difference of nucleophilicity and electrophilicity of the germylene center compared to carbene, two different ways of stabilization were developed and employed in the literature: kinetic stabilization and thermodynamic stabilization. Indeed, the lack of stabilization of germylene can be characterized by high reactivity with other molecules or by dimerization reaction. As an example, Lappert *et al.* have reported in 1976 the synthesis of the first dialkylgermylene (Scheme 8).²⁶ It appears that the germylene has a monomeric form in solution and a dimeric form in solid state, the Ge=Ge double bond of the dimeric specie being shown by Raman spectroscopy. However, dimerization reaction can be avoided by increasing the steric hindrance of only one substituent on the moiety as reported by Jutzi in 1991.²⁷ The publication showed that replacement of one hydrogen atom by a trimethylsilyl substituent can avoid the dimerization reaction in the solid state as observed on the X-ray structure.



Scheme 8: Effect of steric hindrance on di-alkylgermylenes

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The first way to stabilize a germylene center is kinetic stabilization, which implies bulky substituents around the germylene center to avoid any electrophilic or nucleophilic attack by using steric hindrance. Several examples are reported in the literature with different substituents (Scheme 9), going from dialkylgermylenes as seen with Lappert and Jutzi,^{26,27} cyclic germylenes published by Kira in 1999,²⁸ mono-arylgermylenes published by Power in 1997²⁹ to di-arylgermylenes published by Matsuo in 2012.³⁰ X-ray structures of all germylenes showed a V-shaped geometry with a Ge–C σ -bond length of 2.00 to 2.07Å.



Scheme 9: Kinetic stabilization of some selected germylenes

Steric hindrance has another impact on the germylenes reactivity. Matsuo *et al.* demonstrated the importance of the substituent bulkiness, in 2012, with the synthesis of $(\text{Eind})_2\text{Ge}$: that possess two bulky Eind groups (Scheme 9). The non-common steric hindrance around the germylene allowed an oxidation reaction and the synthesis of the first example of a stable germanone, heavier analogue of ketone, without stabilization by an intra or inter molecular Lewis base.³⁰

The second way to stabilize a germylene center is the thermodynamic stabilization. Two different categories will be discussed and developed due to its wide utilization in germylenes chemistry. The first method of stabilization consists in the π -donating of an α -heteroatom in the p empty orbital of the metallylene. Indeed, the strategy employed independently by Öfele and Wanzlick,^{31,32} in 1968 to synthetize the first NHC-complex of mercury and chromium, was then used by Arduengo *et al.* to form the first stable and "bottelable" carbene.³³ The method has been transferred to the heavier analogue by Hermann *et al.* who reported the synthesis of the NHGe in 1992 (Scheme 10).^{18,34} NHGe was obtained independently by nucleophilic substitution of GeCl₂•dioxane with a dilithium diamide salt and by reduction of the corresponding NHGe^{IV}Cl₂ with two equivalents of Li⁰ in 75 % and 80 % yields respectively. X-ray structure showed a planar 5-membered ring with a Ge–N σ -bond distance of 1.83 Å.



Scheme 10: Different pathways for the synthesis of NHGe

Nevertheless, the first thermodynamically stabilized germylene was published by Lappert *et al.* in 1974.³⁵ Chlorine atoms of GeCl₂•dioxane were easily substituted by HMDS lithium salt in diethyl ether to afford (HMDS)₂Ge: as a stable oil in 67% yield. This precursor was then used to obtain several substituted germylenes by protonolysis. The first example was also introduced by Lappert and Atwood in 1980 for the synthesis of the first bis-alkoxide germylene in 66% yield (Scheme 11).³⁶ X-ray structure showed a V-shaped geometry with a Ge–O σ -bond length of 1.81 Å. Since, the method was applied in many reactions, as example, in the use of sensitive ligands in basic conditions or for the easiness of removing H-HMDS as by-product under reduced pressure.^{37,38}



Scheme 11: Formation of alkoxy-germylene by protonolysis

Interestingly, different NHGe were reported before the group of Herrmann with a similar strategy consisting to substitute the chlorine atoms of GeCl₂•dioxane with the corresponding lithium amide salt. The different NHGe reported are the 4-member ring published by Veith in 1982 with a 91% yield ^{39,40} the 5-membered ring published by Meller in 1985 with yields of 27% (R = CH₃) and 67% (R = C₆H₅) respectively ⁴¹ and the benzimidazole ring published by Meller in 1989 with 87% yield (Scheme 12).⁴² The lack of X-ray structures, for the first two compounds, surely influenced the fact that they were unnoticed or less cited by other groups. However, X-ray structure of the third one was confirmed as a monomeric planar compound in solid state with no dimerization reaction, Ge–N σ -bond presents a distance of 1.86 Å close to the one report by Herrmann two years later.¹⁸ Recently, Cabeza *et al.* have

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published a derivative in 67% yield with phosphine arm to obtain a pincer ligand.^{43,44} It is important to note that Hahn *et al.* have reported numerous bidentate and pincer ligands with a NHGe topology.^{45–47}



Finally, the second method of thermodynamic stabilization is based on the donation ability of at least one Lewis base. The lone pair of the Lewis base is overlapping with the germylene empty orbital intramolecularly or intermolecularly (Scheme 13). Many properties can be easily modulated through this method by modification of the steric hindrance, the atom bonded to the metallylene, the nature of the Lewis base or the number of Lewis bases used.



Scheme 13: Different methods of thermodynamic stabilization using an intra or an intermolecular Lewis base

The first germylene stabilized by a nitrogen Lewis base was published by Veith in 1989 (Scheme 14).⁴⁸ The polycyclic lithium silylamide salt was reacted with GeCl₂•dioxane to form the corresponding germylene in 82% yield. The X-ray structure of the germylene was not reported. Nevertheless, its formation was proved via its oxidation with molecular oxygen and sulfur, leading to the germanone dimer and the first stabilized germanethione with 68% and 98% yields respectively. X-ray structure of germanethione showed a trigonal-planar geometry with an additional Ge–N dative bond, two nitrogen are σ -bonded with a length of 1.88 Å close

to the one reported by Meller above,⁴² and one nitrogen is dative bonded with a larger distance of 2.05 Å.



Scheme 14: Example of donation of a Lewis base

In 1997, Lappert *et al.*, Leung *et al.* and Meller *et al.* have reported the same year the first diaryl and dialkyl germylenes stabilized with a Lewis base following the same experimental procedure, i-e nucleophilic substitution of GeCl₂•dioxane with the corresponding aryl or alkyl lithium salts (Scheme 15).^{49–51} The homoleptic diarylgermylene synthesized by Lappert was obtained in 65% yield. ¹H NMR spectrum showed only one singlet for the -2,6-NMe₂ substituents at room temperature, while two separate signals at 178 K were observed. This result indicates a fast exchange, at room temperature, between the -2,6-NMe₂ substituents for the stabilization of the germylene. This exchange is slowed down with the temperature and gets closer to the X-ray structure with only one nitrogen donating to the germanium center. The homoleptic dialkylgermylene, synthesized by Meller and Leung independently, was obtained in 53% or 67% yield. X-ray structure showed a square-pyramidal geometry with Ge–C σ -bond length of 2.13 and 2.14 Å, and Ge–N dative bond distance of 2.27 and 2.31 Å respectively. The difference in Ge–N dative bond distance compare to the structure obtained by Veith can be explained by variation of nitrogen donation to the germanium center.



Scheme 15: Lewis base stabilization of some selected germylene

Then several heteroleptic germylenes were reported with only one substituent bearing the Lewis base (Scheme 16). Jutzi *et al.* reported in 1998 the synthesis of the arylchlorogermylene with only one nitrogen as Lewis base in 72% yield.⁵² Later in 2002, Couret *et al.* published an arylchlorogermylene with two nitrogen as Lewis base in a good 90% yield.⁵³

Both germylenes were characterized by X-ray crystallography and the structures showed a Ge-C σ -bond distance in allowance with the previous reported germylenes by Lappert, Meller and Leung (2.02 and 1.94 Å). However, Ge–N dative bond distances are totally different in both complexes. In the case of Jutzi, the distance is 2.09 Å, closing to the one reported by Veith with also one nitrogen as Lewis base.⁴⁸ In the case of Couret, the distances are 2.34 and 2.57 Å, one nitrogen has a common dative bond when the other one presents a larger distance. In 2001, Jutzi et al. published a heteroleptic and a homoleptic germylene stabilized by an ether substituent in 45% and 62% yield. Both germylene were characterized by X-ray crystallography and the structures showed an usual Ge–C σ -bond distance (2.00 and 2.06 Å). Moreover, only one oxygen stabilizes the germanium center with a Ge–O distance of 2.07 (heteroleptic) and 2.19 Å (homoleptic). The influence of the steric hindrance on the oxygen atom was investigated by replacing the *t*-Bu group by *i*-Pr or Me. Unfortunately, the corresponding germylenes were not stable and the product of insertion into O-Me bond was isolated. In order to force the stabilization with two oxygens, Yamamoto et al. published in 2005 a strained germylene in 72% yield. X-ray structure showed a Ge–O distance of 2.36 and 2.39 Å. More recently, our group reported the stabilization of germanium center with sulfone substituent in 60% yield.⁵⁴ X-ray structure showed a distorted seesaw geometry with usual Ge-C distance of 2.03 Å and Ge–O dative bond distance of 2.36 Å.



Scheme 16: Lewis base stabilization of some selected germylenes

The utilization of intermolecular Lewis base to stabilize germylenes was introduced by Jones *et al.* in 2006 (Scheme 17).⁵⁵ They have reported the reaction of anionic gallium(I) Nheterocyclic carbene analogue with Lappert dialkylgermylene dimer, which results in stabilization of the monomeric species in 56% yield. X-ray structure of the compound showed a Ga–Ge distance of 2.54 Å and typical Ge–C distance of 2.08 and 2.09 Å. Germylene is interacting with potassium, chelated by TMEDA, with a typical bond of 3.44 Å as reported by the authors.



Scheme 17: Intermolecular Lewis base stabilization

The same reactivity towards Lappert's germylene dimer was reported with different NHGa in 2007.⁵⁶ The same year, Baines *et al.* applied the utilization of NHC as intermolecular Lewis base in the stabilization of dialkylgermylene dimer and dichlorogermylene (Scheme 18).^{57,58} X-ray structures obtained from these compounds showed pyramidal geometry with a Ge–C_{NHC} length of 2.08 and 2.11 Å, in the range of Ge–C σ -bond which is particularly short for a dative bond.



Scheme 18: Intermolecular Lewis base stabilization of some selected germylenes

Stabilization with an intermolecular Lewis base is now well known and has been applied by using a large diversity of stabilizing compounds involving nitrogen, phosphorus, arsenic, oxygen, sulfur and selenium atoms.⁵⁹

Chapter I: General Introduction

Finally, germylenes can be stabilized by a combination of a π -donating heteroatom and a Lewis base. Thus, Hahn *et al.* have reported in 2017 the stabilization of a chlorogermylene with an intramolecular amino-NHC (Scheme 19).⁶⁰ Germylene was obtained by protonolysis of Ge(HMDS)₂ with the amino-NHC starting material in 86% yield. X-ray structure displayed usual bond distance for Ge–C of 2.06 Å and Ge–N of 1.89 Å.



Scheme 19: Thermodynamic stabilization by a α -heteroatom and a Lewis base

Recently, Nagendran *et al.* have reported a novel stable germanium (II) stabilized by a *N*-oxide function without oxidation of the germylene (Scheme 20).⁶¹ Germylene was obtained by metathesis in an excellent 96% yield. X-ray structure exhibits an usual Ge–S and Ge–O bond length of 2.44 Å and 2.03 Å. However, the monomeric form suggests that the *N*-oxide ligand acts as a strong electron donor and provides sufficient electronic stabilization to avoid dimerization while the compound doesn't show steric protection.



Scheme 20: N-oxide stabilization without direct oxidation of germylene

Concerning the stabilization of germylene by oxygen-atoms, keto-enolato germylenes are well known since decades. Indeed, Stobart *et al.* have reported in 1976 the synthesis of several homoleptic and heteroleptic keto-enolato germylenes (Scheme 21).⁶² X-ray structures of these germylenes have been described by the same group in 1979.⁶³ Heteroleptic keto-enolato germylene showed a pyramidal geometry with Ge–O bond distance of 1.93 and 1.91 Å, which is shorter than the usual Ge–O dative bond.

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Scheme 21: Different keto-enolato based germylenes

The stability of the germylenes is enhanced by electronic delocalization that gave enough electron to avoid dimerization of the germanium center without using bulky substituent.

Karsh *et al.* published in 1988 a homoleptic germylene phosphorus 4π delocalized system (Scheme 22).^{64 31}P NMR spectroscopy reveals that both phosphorus are equivalent at room temperature. However, different signals can be observed at -100 °C, which reveal a fast exchange between both phosphorus at higher temperature. The observation was explained by X-ray analysis. The structure obtained showed a pseudo trigonal bipyramidal geometry with two phosphorus σ -bonded (2.55 Å) in axial position while the two-remaining phosphorus are datively bonded (2.93 Å) in equatorial position.



Scheme 22: Phosphorus 4π delocalized stabilization of germylenes

Other 4π delocalized based germylenes were developed and reported later in the literature (Scheme 23). The first amidinatogermylene was published by Richeson *et al.* in 1997.⁶⁵ Mazières *et al.* in 2010 synthesized a novel 2,4-diaza-3-phosphagermatidines in a low 18% yield.⁶⁶ Interestingly, X-ray structure showed a Ge–N distance similar for both nitrogen (1.98 Å), with also same P–N distance (1.60 Å). Latter in 2016, Singh *et al.* have reported an iminophosphonamide based germylene with different substituents on the nitrogen atoms.⁶⁷ In 2015, Stalke *et al.* have published a sulfur(VI)phosphanyl germylene in 68 % yield.⁶⁸ Finally, Nakata *et al.* have reported another sulfurgermylene in 2017 with 59% yield.⁶⁹ Again, nitrogen are at equal distance to the germanium center in each compounds.



Scheme 23: 4π delocalized stabilization of some selected germylenes

Amidinate based germylenes have been widely explored after the report of Richeson.⁷⁰ It can be rationalized by their easiness of their preparation and the possibility to functionalize three different positions (Scheme 24). It is important to note that nitrogen atoms are located at the same distance to germanium in the heteroleptic compound.



Scheme 24: Synthesis of amidinatogermylenes and further functionalizations

The substituent on the nitrogen (R_2) can be modulated to offer a large variety of steric hindrances going from the small group, *i*-Pr,⁷¹ to the bulky group, Diip.⁷² However, the steric hindrance has shown no notable influence on the stabilization or the reactivity of germylenes. Indeed, the reactivity towards potassium is the same for both *t*-Bu or Diip group (Scheme 25). The reaction leads to the formation of the dimer of germanium (I) which is stable and possesses a Ge–Ge single bond with a lone pair on each germanium.^{72,73}



Scheme 25: Reactivity of AmGeCl toward metallic reductant

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On the other hand, the substituent on the central carbon of the amidinate group (R_1) has an influence on the electronic properties of the metallylene. In comparison, Jones reported in 2008 the formation of the guanidinatechlorogermylene with a di-cyclohexylamine group at R_2 position (Scheme 26).⁷⁴ The amine group enhanced in electron the amidinate ring which increased the donation to the germylene. The consequence was an elongation of the Ge–Cl bond (2.24 Å) compared to the one reported also by Jones in 2006 with a *t*-Bu group at R_1 position (2.17 Å).⁷²



Scheme 26: Effect of the substituent on the central carbon of the amidinate group on the stabilization of germylene

Finally, the last position to functionalize is on the germanium. The strategy is a conventional nucleophilic substitution of chlorine as seen above. Alvarez *et al.* have published in 2014 the use of *t*-BuLi as a nucleophile and obtained the corresponding germylene in 85% yield (Scheme 27).⁷⁵



Scheme 27: Nucleophilic substitution on germylene

Karsh *et al.* have reported in 1998 a homoleptic amidinatogermylene in 81% yield.⁷⁶ X-ray structure showed a bi-pyramidal geometry with a donor and a bonded nitrogen, Ge–N length are respectively 2.30 and 1.98 Å. However, ¹H NMR spectrum exhibits only a single set of signals corresponding to the amidinate moieties at room temperature, which indicates a rapid exchange equilibrium between both nitrogen atoms. Moreover, the nucleophilic substitution

allows to different groups, such as Jones and Driess, to integrate various chemical functions and even to form bidentate or pincer ligands (Scheme 28).^{74,77,78} Thus, the amidinato system has been extensively studied and used in metallylene chemistry.^{72,74,75,79,80}



Scheme 28: Some selected amidinate based germylenes

Transposition to 6π delocalized systems, as seen before with Stobbart, are numerous in the literature.^{62,81} However, β -dicetiminates and pyridyl-1-azaallyl appear to be the most used ligands in germylene chemistry. Leung *et al.* have reported in 2005 the synthesis of the heteroleptic germylene pyridyl-1-azaallyl in 62% yield (Scheme 29).⁸² X-ray structure showed a pyramidal geometry with regular distance of Ge–N σ -bond (1.92 Å) and a short dative bonded length (2.02 Å). Later, Leung *et al.* have reported the nucleophilic substitution of the chlorine by nucleophiles in order to obtain several substituted germylenes.⁸³



Scheme 29: 6π delocalized stabilization of germylenes

According to the same approach, several β -dicetiminates derivatives were reported the same year, in 2001, by three different groups, Roesky, Barrau and Dias (Scheme 30).^{84–86} All these germylenes are structurally comparable that can be isolated in good yields (60-90%) and characterized by X-ray crystallography. Interestingly, nitrogen atoms are at equal distance to the germanium center which reveals a delocalization of electron even at the solid state with a Ge–N distance of 1.96 and 1.98 Å. The distance is slightly longer than a normal σ -bond and

gets closer to the distance of two dative bonds. Again, the chlorine atom was substituted by several nucleophiles to obtain numerous novel heteroleptic germylenes.^{81,87,88}



Scheme 30: Others 6π delocalized germylenes

Finally, the last family of germylenes stabilized by delocalization is a 10π delocalized system, aminotroponiminate. Dias *et al.* have published the first example in 1997 with an excellent yield of 92% (Scheme 31).⁸⁹ X-ray structure showed a usual Ge–N bond distance of 1.94 Å for both nitrogen in allowance with the literature for a delocalized compound. Later, several germylenes could be obtained thanks to nucleophilic substitution.^{90,91}



Scheme 31: 10π delocalized stabilization of some selected germylenes

Recently, Castel *et al.* have reported, in 2015, the synthesis of new substituted aminotroponiminate for the synthesis of germanium nanoparticles (Scheme 32).⁹² They showed and studied the formation of Ge/GeO₂ core/shell NPs.



Scheme 32: 10π delocalized germylene applied to the formation of nanoparticles
I.4. Germylenes in coordination chemistry and applications in catalysis

Stable germylenes can be applied in many reactions as reagents, catalysts or ligands. Interestingly, the method used to stabilize the germylenes plays a preponderant role in any reactions. Indeed, the kinetic stabilization offers steric hindrance to the center, which includes small electronic modification of the germylene. The empty orbital remains very reactive and the lone pair has a high s character. For the thermodynamic stabilization, the electronic is modified, that means the lone pair can be more σ -donor and the empty orbital is deactivated. However, the reactivity of germylenes is well explored compared to their ability to act like σ -donor ligands. In comparison, carbenes or silylenes are well known in coordination chemistry and their catalytic processes are well defined. The difference is mainly due to the difficulty of obtaining sufficiently robust germylenes complexes to envision their use in a catalytic cycle.

Germylenes usually have the same type of coordination as Fischer carbene due to the singlet state of the free ligand (Scheme 33). However, Sekiguchi *et al.* have recently published in 2015 an example of Schrock type complex by coordination of germylenes with group IV metal. Hf=Ge double bond was confirmed by many analysis like DFT calculations, X-ray crystallography and UV measurement.^{93,94}



Scheme 33: Coordination of Fischer and Schrock carbenes

Frenking *et al.* reported in 1998 a theoretical study on the σ -donor properties of carbenes, silylenes and germylenes with group 11 transition metals, Cu, Ag and Au.⁹⁵ The study compared the bond dissociation energy between the metal and the group 14 element. The result of the calculations confirmed the general trend that metal-ligand bond strengths is stronger with carbene than silylene than germylene. Another general trend was observed for the metal-ligand bond is stronger with gold than copper than silver. However, Szilvási *et al.* have published

another theoretical study in 2017 on the σ -donor and π -acceptor properties of a large panel of germylenes and they compared them with PPh₃, PCy₃ and basic NHCs.⁹⁶ The results confirmed that germylenes are basically less σ -donor than NHCs, but better than phosphines in general. Nevertheless, the calculations also showed that germylenes are better π -acceptors than most of NHCs and phosphines. That is why germylenes can be considered for performing different catalytic steps difficult to develop with other ligands.

The method used to stabilize germylenes is fundamental to apply them in coordination chemistry. As seen before, germylenes can be stabilized by kinetic or thermodynamic stabilization. Kinetic stabilization is barely used for the coordination chemistry because the empty orbital remains very reactive. Nevertheless, several examples of kinetic germylenes complexes are available in the literature with carbonyl ligands without any application in catalysis. Lappert *et al.* have reported in 1974 the first application of dialkylgermylenes in coordination chemistry of several metals like iron, tungsten, chromium and platinum (Scheme 34).⁹⁷ However, only chromium complex was crystalized. Okazaki *et al.* have published in 1994 the first example of diarylgermylenes complexed to a transition metal.⁹⁸ The pentacarbonyl chromium and tungsten complexes were obtained in low 5.5% and 6.3% yields respectively. X-ray structure of tungsten complex exhibits a distance for Ge–W bond of 2.59 Å in allowance with tungsten-germylene complex reported latter with a thermodynamic stabilization.



Scheme 34: Kinetic stabilization of some selected germylene complexes

Latter, Don Tilley *et al.* have reported a novel efficient method to obtain group VIII complexes. The synthetic pathway is to incorporate a Ge(IV) species with the transition metal to permit an α -H migration and an elimination of toluene (Scheme 35).



Scheme 35: Hydrogen substituted ruthenium-germylene complex

It was first published in 2009 with the synthesis of the germylene ruthenium hydride complex in 67% yield (Scheme 36).¹⁰² X-ray structure exhibits an extremely short Ru–Ge bond length of 2.28 Å compared to the cationic one reported three years after (2.33 Å).¹⁰³ Tobita *et al.* expanded the reaction to iron complex in 2017 with a yield of 67%.¹⁰⁴ Again, X-ray structure showed an extremely short Fe–Ge bond length of 2.19 Å.



Scheme 36: Hydrido-germylene complexes of group VIII

On the other hand, thermodynamic stabilization appears easier due to a large amount of transition metals examples with well-defined germylene ligands. Indeed, the electrons brought to the metallylene center increase the σ -donation of the lone pair and decrease the reactivity of the empty orbital. Lewis base and π -donating of an α heteroatom are the twodifferent ways to stabilize the germanium center as previously discussed (Scheme 37).



Scheme 37: Geometry of thermodynamic germylene complexes

The main difference between these two kinds of stabilization is in close relationship of the geometry of the complexes that directly influences the stability. Concerning the geometry, when germylene is coordinated to a transition metal, π -donating stabilization induces a planar geometry, sp² type, whereas Lewis base induces a tri-coordinated center geometry. It is important to note that the hybridization of heavy atoms is very difficult due to the poor

overlapping between the molecular orbitals.¹³ That is why π -donating complexes are unfavoured with the planar geometry, sp² type. Nevertheless, examples can be found in literature.¹⁸ One of them was reported in 2002, by Holl *et al.*, when a germylene reported by Lappert is coordinated to palladium (Scheme 38).¹⁰⁵ The lability of germanium ligand was tested with 1,2-diphenylethanedione helding to the decoordination and the cycloaddition products which was fully isolated.



Scheme 38: Decoordination of germylene and trapping with 1,2-diphenylethanedione

Another example was reported in 1992 by Herrmann *et al.*, where *t*-Bu-NHGe coordinates a nickel carbonyl complex (Scheme 39). Unfortunately, they have only reported the coordination chemistry of the satured NHGe ring, the unsatured NHGe nickel complex appears to be unstable. IR spectra of the bis-germylene nickel (CO)₂ reveal two carbonyl bands at 2003 and 1945 cm⁻¹ which is particularly close to the Ni(CO)₂(PPh₃)₂ derivative with bands at 2000 and 1941 cm⁻¹. The observation showed that NHGe have a σ -donation close to PPh₃.



Scheme 39: Coordination of NHGe with Nickel carbonyl

Nevertheless, Hahn *et al.* developed an interesting synthesis of a multi-dentate ligand to overcome the problem with chelation stability. They have published in 2007 the synthesis of several benzannulated NHGe units with different linker substituents in yields from 50 to 86% (Scheme 40).⁴⁶ Two molybdenum complexes were also obtained by addition of Mo(nbd)CO₄ to the free germylene. X-ray structure exhibits an octahedral molybdenum coordinated by two

germanium atoms, and the Ge–Mo bond length of 2.53 Å is in the range of the analogues complexes previously reported in the literature.



Scheme 40: Bidentate molybdenum complex

Hahn *et al.* reported afterwards a pincer ligand,⁴⁵ a bi-dentate ligand with asymmetric arms¹⁰⁶ and finally a macrocyclic bis-germylene.¹⁰⁷ Recently, Cabeza *et al.* used the same approach to synthetize a pincer benzannulated NHGe with phosphine arms.⁴³ Unfortunately, the coordination chemistry with palladium and rhodium led to the formation of germanium (IV) derivative by insertion into the metal-chlorine bond (Scheme 41).



Scheme 41: Formation of germyl complexes

Subsequently, Cabeza *et al.* have investigated the coordination chemistry with nickel, platinum and iridium, they obtained the same oxidative insertion into M–Cl bond. Surprisingly, ruthenium was obtained as the only complex with a chlorine atom where germylene acted as a ligand (Scheme 42).^{44,108}



Scheme 42: Coordination or oxidative addition of pincer germylene-phosphine ligands

Nowadays, Lewis base stabilization has appeared as an evidence and is mainly used to obtain germylene complexes stable enough to be applied in catalysis. The complexes exhibit a wild diversity of architecture or coordination to transition metal with new properties. On this path, amidinate based germylenes are surely the most used ligands for coordination chemistry due to their easiness to prepare as shown previously.¹⁰⁹ Driess *et al.* reported in 2014 an iron pincer germylene complex with carbonyl ligands in 39% yield (Scheme 43).⁷⁸ The complex was obtained by ligand metathesis of PMe₃ with CO_{gas}. IR spectrum exhibits two bands for the carbonyl groups at 1855 and 1805 cm⁻¹, which showed that germylene have a σ -donation close, but still inferior than silylene (1830 and 1778 cm⁻¹). However, the results exhibited better donation than NHC (1928 and 1865 cm⁻¹) or phosphine (1950 and 1894 cm⁻¹) derivative.^{110,111} Lewis base stabilization have a remarkable influence on the coordination ability of germanium (II) by boosting σ -donation compare to NHGe which was equivalent to phosphine as seen with Herrmann *et al.*¹⁸



Scheme 43: Formation of iron-carbonyl complex for IR comparison

The first complex was published by Jones *et al.* in 2008 (Scheme 44).⁷⁴ The tungsten complex was obtained in 56% yield. X-ray structure exhibits a usual Ge–W bond length of 2.56 Å. Since then more than a hundred of complexes based on amidinate metallylenes are reported to date. As examples, Castel *et al.* have reported a bis-germylene tungsten and molybdenum

complexes in 2010, Cabeza *et al.* have reported a germylene manganese complex in 2014 and Madec *et al.* have reported a germylene iron complex in 2015.^{71,112,113}



Scheme 44: Selected examples of amidinategermylene complexes

An interesting observation was reported by Cabeza *et al.* in 2015 (Scheme 45).⁷⁵ They evidenced the need to tuned the chloroamidinatogermylene published by Roesky,⁷³ in 2008, to have access to coordination chemistry of group 11 transition metals. Indeed, the synthesis of AmGe-*t*-Bu derivative by nucleophilic substitution of AmGeCl with *t*-BuLi can be applied in coordination chemistry of copper, silver and gold complexes in good yields going from 61% to 95%.



Scheme 45: Importance of substituted amidinategermylene for synthesis of group 11 complexes

Starting from the same AmGe-*t*-Bu precursor, Cabeza *et al.* have published the coordination with iridium and ruthenium in 2015 (Scheme 46).¹¹⁴ Complexes were obtained in excellent yield of 98%. X-ray structure showed, for ruthenium, a Ge–Ru bond length of 2.43 Å which relies in the longest distance reported. Besides, Ge–Ir bond length is also the longest reported to date with 2.42 Å.



Scheme 46: Coordination of substituted amidinatogermylenes with group 8 and 9 complexes

Ruthenium and iridium were applied in hydrogen transfer catalysis (Scheme 47). The goal was to reduce a ketone into the corresponding alcohol in protic media.¹¹⁵ Both of the complexes are active and can reduce cyclohexanone with 55% of conversion after 24h at 50 °C for ruthenium complex, whereas iridium can fully convert the ketone into alcohol after 1.5h at the same temperature. Surprisingly, the catalysis does not need any base as additive to form the active catalyst. Indeed, the proposed catalytic cycle needs the addition of external base to generate a hydride, which is the catalytically active species. However, Manzano *et al.* described in 2009 that the presence of a free Lewis base can act as a base to generate the active species.¹¹⁶



Scheme 47: Application of group 8 and 9 complexes to hydrogen transfer catalysis

Driess *et al.* published in 2012 a germylene iridium complex (Scheme 48). C–H insertion of iridium was immediate to afford the pincer hydride iridium (III) complex.⁷⁷



Scheme 48: Germylene pincer complex of iridium

This complex was applied in catalytic C–H borylation of benzene using HBPin with one equivalent of cyclooctene (coe) as additive (Scheme 49). Addition of coe enhanced significantly the catalytic activity of the system: without coe, after 24h at 100 °C, a conversion of 46% was observed whereas it increased to 80% with one equivalent of coe. Silylene derivative followed the same behavior with 53% of conversion without coe and 90% with one equivalent. These results were explained by the authors by the fact that coe acts as an H_2 acceptor which has a beneficial effect on the catalytic cycle. Finally, the catalytic activity was compared with phosphines. Dialkylphosphine (P-*t*-Bu₂) and diaminophosphine (P(NCH₂)₂) analogues were prepared through the same synthetic pathway and showed unambiguously a drop-in activity with conversion of 64% and 21% respectively.



Scheme 49: Application of germylene iridium pincer complex to C-H borylation of benzene

The same year in 2012, Driess *et al.* have reported a bis-germylene presenting a novel ferrocene linker used to obtain a bidentate cobalt complex in 61% yield (Scheme 50).¹¹⁷ X-ray structure exhibits a Ge–Co bond length of 2.20 Å, the shortest distance known to date.



Scheme 50: Germylene pincer complex of cobalt

Cobalt bidentate complex was applied in [2+2+2] cycloaddition reactions for trimerization of phenylacetylene. Surprisingly, no reaction was found while the silylenes derivative can fully convert the starting material. The authors assumed a stronger coordination

of the Ge(II) donor centers to Co, which hampers the creation of an active site for the substrate coordination.

Latter, Driess *et al.* published in 2012 two synthesis to obtain a germylene nickel complex (Scheme 51).¹¹⁸ The first synthetic approach involves a C–Br oxidative addition on nickel (0) (57% yield) when the second consists of a C–H activation with nickel (II) precursor (88% yield).



Scheme 51: Germylene pincer complex of nickel

The complex was used in Sonogashira-Hagihara cross-coupling reaction of iodo-1octene with phenylacetylene (Scheme 52). After 24h of heating at 100 °C, the conversion was up to 53% which was the better result obtained compared to silylene (39 %) and phosphorus (40 %) analogues.



Scheme 52: Application of germylene nickel pincer complex to Sonogashira-Hagihara crosscoupling reaction

The last example of active germylene in catalysis was reported recently by Nagendran *et al.* in 2018 (Scheme 53).¹¹⁹ The catalyst is a bis-germylene platinum complex obtained in a quantitative yield from aminotroponiminate-germylene and PtCl₂(cod). It was characterized by X-ray crystallography and showed a square planar geometry around the platinum center.



Scheme 53: Bis-germylene complex of platinum

The platinum complex was applied in cyanosilylation of aldehydes and ketones successfully (Scheme 54). Benzaldehyde was fully reduced in presence of TMSCN at 50 °C after 6h. The method was expanded to a large variety of substituted arylaldehydes and alkylketones. Nevertheless, the catalyst showed no reactivity with arylketone like acetophenone and its substituted derivatives.



 $\begin{array}{l} \mathsf{R} = \mathsf{alkyl/aryl}, \, \mathsf{R'} = \mathsf{H} \; (\mathsf{aldehydes}) \\ \mathsf{R} = \mathsf{R'} = \mathsf{alkyl} \; (\mathsf{ketones}) \end{array}$

Scheme 54: Application of bis-germylene platinum complex to catalytic cyanosilylation of aldehydes and ketones

I.5. Sulfoxides in coordination chemistry, generalities and applications as hemilabile ligands

A large variety of substituents has been used over the years to stabilize germylenes which such properties that finally allowed to obtain stable functionalized germylenes for applications in catalysis. The reports of Driess, Cabeza and Nagendran published over the past years have shown that germylenes can find interesting application in catalysis with novel properties and activities.^{77,114,118,119} Interestingly, the morphologies of these complexes are limited to mono-dentate, bis-monodentate, bi-dentate and pincer ligands. However, to the best of our knowledge, there is no-report concerning hemilabile bi-dentate ligands with a strong σ donor moiety and a weaker one involving germylenes. Hemilabile concept was introduced by Jeffrey *et al.* in 1979 with the synthesis of a bis-phosphorus ether ruthenium complex (Scheme 54).¹²⁰ X-ray structure showed selective formation of only one isomer, trans phosphorusoxygen complex. Finally, hemilability of the compound was proven by selective substitution of ether ligand with carbon monoxide which showed ether has a weaker σ -donor ligand to ruthenium in comparison of phosphine.



Jeffrey, 1979

Scheme 54: Selected example of one of the first hemilabile complex

Since hemilabile complexes have found many applications in catalysis due to their ability to decoordinate partially a transition metal through the weak σ -donor moiety and allow coordination of another substrate. As examples, they were applied in ring-opening metathesis polymerization published by Linder in 1998,¹²¹ in transfer hydrogenation reported by Gao in 1999,¹²² in hydrogenation published by Kadyrov in 1998¹²³ and in various others catalysis.^{124,125}

In order to synthesize a first example of hemilabile germylene ligand, we selected sulfoxide as a valuable weak σ -donor moiety. Indeed, sulfoxide presents two major advantages, a large possibility of coordination through sulfur or oxygen atoms and the presence of a stereogenic center when the sulfur atom is substituted by two different groups (Scheme 56). ^{126–128}



Scheme 56: Sulfoxide and their coordination ability

Before discussing about sulfoxide complexes, it is important to note some structural characteristics of the sulfoxide ligand. Many discussions in the literature about molecular orbital calculations and X-ray spectroscopy have shown that sulfoxide is polarized, with a positive charge localized on the sulfur atom and a negative charge localized on the oxygen atom. These observations are in accordance with the relatively short S–O bond distance that indicate a resonance structure of three forms (Scheme 57).¹²⁶



Scheme 57: Canonical forms of sulfoxide

Coordination of sulfoxide can be imagined ahead of the reaction. Indeed, they follow the HSAB theory with a preference of oxygen for hard transition metal contrary to sulfur that prefers soft center. Calhorda *et al.* showed in 2015 that 3d transition metals prefer oxygen centers when 5d transition metals prefer sulfur, finally 4d transition metals can accept both coordination.¹²⁹ It is important to note that other effects can slightly change these observations. Peters *et al.* have reported an excellent example, in 2012, with the synthesis of two pincer sulfoxide nickel complexes bearing two phosphine arms where the sulfur atom was coordinated to Ni(0) and Ni(II) instead of oxygen (Scheme 58). The explanation advanced was the favorable and more stable 5-membered ring formed that drives a coordination with sulfur.¹³⁰



Scheme 58: Formation of pincer sulfoxide nickel complexes bearing a coordination with sulfur

Another factor can also influence the sulfoxide coordination and explain why a hard transition metal can prefer a soft sulfur atom and vice versa. In the first place, study on the nature of sulfoxide bonding with transition metal were observed from DMSO complexes to hard metals via oxygen atom and to soft metals via the sulfur atom.¹³¹ However, hardness or softness of a transition metal can be affected by the nature of the coordinated ligands.¹²⁷ Bidentate mixed ligands with a sulfoxide and another ligand can influence the coordination of sulfoxides. The electronic properties of the other ligands will have different effects on the soft and hard ability of the transition metal center: strong π -electron acceptors withdraw electron density from the transition metal center and increase metal to become harder and may be accompanied by a change in coordination of the sulfoxide from a sulfur to oxygen atom to optimize orbital overlap. Moreover, O-bonding can also be induced by the steric hindrance of the ligand around the metal center as shown by Calligaris *et al.* in 1996.¹²⁷ Finally, sulfoxide ligands coordination is the results of different electronic and steric factors.

It is relevant to note that X-ray crystallography revealed a S–O bond distance of sulfoxide modified upon coordination, passing from \sim 1.49 Å to 1.47 Å in S–bonded complexes and 1.53 Å in oxygen-bonded complexes.¹²⁷

Another important physical property of sulfoxide is their characteristics by IR spectroscopy. Indeed, IR stretching band of sulfoxide are found at approximatively 1000 to 1050 cm⁻¹, whereas sulfoxide coordinating a transition metal is totally different. The band is between 1050 and 1200 cm⁻¹ when sulfur is coordinated and the band is below 1000 cm⁻¹ when oxygen is coordinated.^{132,133} The analysis of an IR spectrum can provide useful data to determine if the sulfoxide is free or if it is coordinated by sulfur or oxygen atoms.

Sulfur and nitrogen centers are isoelectronic, it is nevertheless appropriate to demonstrate that racemization of enantiopure sulfur operate only under specific conditions compared to nitrogen. Khan *et al.* have published in 1964 a study to show that thermal racemization of sulfoxide appears only at high temperature, approximatively 200 °C.¹³⁴ The others condition to racemize a enantiopure sulfoxide are concentrate acidic media,¹³⁵ irradiation,^{136,137} and finally electron transfer (Scheme 59).¹³⁸



Scheme 59: Experimental conditions to racemize chiral sulfoxide

Nowadays, numerous examples of sulfoxide ligands are reported with different application in catalysis.¹³⁹ The first example of enantioselective catalysis with ruthenium and chiral sulfoxide ligands was published by James *et al.* in 1976, with a poor enantioselectivity obtained of 12 % *ee* in catalytic hydrogenation of olefinic carboxylic acids under H₂ (Scheme 60).¹⁴⁰



Scheme 60: First example of enantioselective catalysis using chiral sulfoxide ligand

Since then a large variety of examples were developed, reported and applied in enantioselective catalysis (Scheme 61).¹³⁹ For example, Dorta *et al.* have reported in 2008 the 1,4–addition of arylboronic acids to cyclic α,β –unsaturated ketones and esters with a bissulfoxide rhodium complex in 99% yield with 98% *ee.*¹⁴¹ Later, Liao *et al.* have published, in 2012, the asymmetric addition of arylboronic acids to NH isatins with Rh(I) sulfoxide complex in a good yield of 95% and a 92% *ee.*¹⁴² Finally, Xiao *et al.* have reported, in 2014, the asymmetric Tsuji–Trost reaction in presence of an amine-sulfoxide-phosphine ligand with yields superior to 86% and ee superior to 97%.¹⁴³



Scheme 61: Selected examples of chiral sulfoxide ligands applied in catalysis

In parallel, several groups have reported the synthesis of others hemilabile ligands with a sulfoxide function and presenting a NHC as the strong σ -donor moiety (Scheme 62). The first example was reported by Huynh *et al.* in 2009.^{144,145} The novel sulfoxide ligand present two benzimidazole arms. However, the corresponding palladium complex obtained showed no coordination of the sulfoxide moiety. Later, Cardenas *et al.* have published in 2013 the synthesis of an imidazolium-sulfoxide ligand in a good 76 % yield.¹⁴⁶ The same behavior was observed with the palladium complexes, sulfoxide has a weak interaction with the transition metal without showing any coordination. Finally, Chen *et al.* have reported in 2014 another imidazolium-sulfoxide ligand.¹⁴⁷ Coordination of oxygen and sulfur was obtained by chlorine removal of the bis-NHC dichloropalladium complex with AgPF₆, which was confirmed by X-ray analysis.



Scheme 62: Sulfoxide-NHC complexes reported

The formation of sulfoxide bidentate hemilabile complex was essentially achieved with phosphine and some examples are now available with stronger σ -donor ligand. All these results led us to the possibility of synthesizing a bidentate ligand presenting a chiral center as a useful demonstration and tool for group 14 heavier analogues in order to obtain an active catalyst, which can present asymmetric induction.

II. Conclusion

Germylenes, heavier analogues of carbenes, have attracted considerable interest the last decades since the breakthrough of NHC. Their kinetic and thermodynamic stabilization was first studied with the development of new substituents to afford novel steric and electronic properties. Thus, a large variety of ligands has been described for the synthesis of heteroleptic or homoleptic germylenes through the development of aryl, alkyl, nitrogen, oxygen, sulfur, phosphorus or even 4π , 6π , 10π delocalized substituents.

The synthesis of stable germylene complexes successfully applied in catalytic reactions was a breakthrough achieve in recent years. Interestingly, the architecture of these complexes was monodentate, bis-monodentate or pincer with any stereogenic information. That is why the lack of information about asymmetric bidentate hemilabile complexes pushed us to investigate the formation, characterization and properties of a germylene combined with a sulfoxide moiety.

First, the formation of germylene- α -sulfoxide ligands was investigated and their properties in coordination chemistry studied with several transition metals. The design of the ligands was then rationalized to prepare germylene- β -sulfoxide.

Then, the formation of a novel family of metallylenes with sulfonimidamide substituents was envisioned in order to incorporate an asymmetric sulfur (VI) directly on the skeleton of the group 14 stabilizing group.

Finally, the catalytic activity of several complexes was tested in hydrogen transfer reaction. The scope of the catalysis was investigated as well as the influence of the stereogenic center on the substrates. Polymerization was also investigated with the novel stannylene sulfonimidamide.

III. Notes and references

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Chapter II:

Germylene -α- Sulfoxide Ligands: Synthesis, Characterization and Coordination of a Novel Hemilabile Metallylene Ligand

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Abstract

Hemilabile amidinate germylene – sulfur (II, IV, VI) ligands have been synthesized in two steps in good yield from the readily available GeCl₂•dioxane and commercially available sulfoxides.

These ligands were easily converted into tungsten, molybdenum, ruthenium phosphine and ruthenium *p*-cymene complexes. NMR spectroscopy, X-ray diffraction and IR studies reveal that different types of coordination are possible with the amidinate germylenes - α - sulfur (II, IV, VI), thus confirming the hemilabile character of these ligands. Formation of monodentate, bi-dentate and bis-germylene complexes were observed through the utilization of different transition metals or metal precursors.

Chapter II: Germylene -α- Sulfoxide Ligands: Synthesis, Characterization and Coordination of a Novel Hemilabile Metallylene Ligand

I. Introduction

Stabilization of germylenes is now well known.¹ Nevertheless, germylenes are mainly studied in coordination chemistry with carbonyl complexes, confining their use in catalysis. The last chapter demonstrates that the lack of stability of germylenes is one of the reason of their scarcity in catalytic reactions and that thermodynamic stabilization appears as an evident choice for the stabilization of germylenes,

Therefore, amidinate groups have been widely explored to stabilize metallylenes thanks to their easiness of preparation and the possibility of functionalization on three different positions (Scheme 1).²



Scheme 1: Synthetic pathway of amidinatogermylenes

Amidinate group is an impressive versatile tool to stabilize germylenes with a unique opportunity to modulate it on various positions, to change the electronic and/or the steric hindrance properties. That is why amidinate groups are extensively studied and used in metallylene chemistry, numerous amidinatogermylenes being reported to date (Scheme 2).^{3–7}



Scheme 2: Examples of amidinatogermylenes
Nevertheless, coordination chemistry of germylenes is in the early beginning in comparison to carbenes, and again the scarce examples reported in catalysis are generally based on the amidinate skeleton (Scheme 3).⁸⁻¹¹



Scheme 3: Germylene complexes applied in catalysis

Our research project consists in the development of new bi-dentate hemilabile mixed metallylene-sulfoxide ligands for their application in coordination chemistry and catalysis.¹² The following part will discuss about the design, the synthesis and the properties of the ligands (Figure 1). Synthesis of germylenes combined with a sulfoxide group is challenging and attractive for multiple reasons: (i) formation of a new type of tetrylenes, (ii) possible effect of sulfoxide as intramolecular Lewis base and (iii) elaboration of bi-dentate ligands for coordination chemistry.



Figure 1: Combination of germylene stabilized with intramolecular Lewis base and sulfoxide

Then, application of the bi-dentate ligands to form complexes will be discussed latter in the chapter. Several complexes with different properties and a hemilabile character is expected with the germylene and the sulfoxide toward transition metals (Figure 2).



Figure 2: Different possibilities of coordination of hemilabile germylene-sulfoxide ligand to a transition metal

II. Results and discussion

II.1. Investigation in the formation of a germylene-sulfoxide

In early exploration of the subject, the first question was: is it possible to stabilize a germylene center with a sulfoxide function, intra or inter molecularly? The question is particularly relevant to the reactivity of sulfoxide, known as oxidant for several reactions like Swern oxidation, oxidation of alkynes to α -dicarbonyl and oxidation of thiols to disulfides.^{13–15} Certainly, the most known reaction using sulfoxide as oxidant is Swern oxidation that permits to obtained ketones from the corresponding alcohols with equimolar amounts of sulfoxide and oxalyl chloride (Scheme 4).



Scheme 4: Swern oxidation reaction

In 1987, Satgé *et al.* reported the use of DMSO as an oxidant to obtain a germanonechromium complex.¹⁶ Even though DMS was identified as resulting of the reduction of DMSO and confirmed that sulfoxide oxidized the germylene center, the germanone-chromium complex has not been isolated and only the products of further reactions were obtained. To elucidate the question of our model, reaction of $GeCl_2$ •dioxane with one equivalent of sulfinyl carbanion was carried out (Scheme 5).



Scheme 5: Reaction of sulfinyl anion with GeCl₂•dioxane

The only product identified at the end of the reaction was the protonated sulfoxide. This result can be explained according to two hypotheses: the first one was the protonation of the nucleophile due to the absence of reaction with GeCl₂•dioxane and protonation of the

carbanion by the solvent. The other possibility was the reaction with GeCl₂•dioxane occurred with formation of an unstable product that caught proton during its degradation. As a mean to go further, we tried the same reaction with 0.5 equivalent of GeCl₂•dioxane to obtain the homoleptic germylene (Scheme 6). However, the same result was observed and the protonated sulfoxide was recovered at the end of the reaction. Variation of temperature and order of addition were also investigated to obtain the product, but the same results were observed.



Scheme 6: Reaction of two equivalents of sulfinyl carbanion with GeCl₂•dioxane

Therefore, the pre-stabilization of the germylene appears necessary to perform any nucleophilic substitution with sulfinyl carbanion because alkylarylsulfoxide seems not able to stabilize enough the germylene center. The role of the pre-stabilization is also to allow the sulfoxide to coordinate transition metal without destabilization of the metallylene.

II.2. Synthesis of amidinatochlorogermylene (II) precursor

Amidinatochlorogermylenes are excellent precursors that combine both stabilization of metallylene and a good leaving group for nucleophilic substitution.¹⁷ Indeed, chlorine atom is easily accessible and has been already substituted by several strong nucleophiles.^{5,18,19}

The amidinatochlorogermylene selected is one recently reported by our laboratory.¹⁸ It shows a modest steric hindrance and a simple skeleton that should allow a convenient nucleophilic substitution and an easy structural analysis of the future ligands.

The precursor was formed in a one-pot reaction from the di-isopropylcarbodiimide (DIC) (Scheme 7). The first step is a nucleophilic addition of *t*-BuLi on the DIC, followed by transmetalation with GeCl_2 •dioxane to obtain the amidinatochlorogermylene as a pale yellow solid in a good 97% yield.

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Scheme 7: Synthesis of AmGeCl

II.3. Synthesis of amidinatogermylene (II) -α- sulfur (II, IV, VI)

The mixed germylene-sulfoxide ligand was obtained through a synthetic pathway that included a conventional nucleophilic substitution of halide. The sulfinyl carbanion was formed by deprotonation with a non-nucleophilic base to prevent any nucleophilic substitution of alkyl on the sulfur atom.²⁰ Also, the deprotonation was selectively done in α position and the regioselectivity was explained by electrostatic effect.^{21,22} Racemic methylphenylsulfoxide was used first to determine the reaction conditions.

Sulfinyl carbanion was formed by addition of LDA on the sulfoxide at -80 °C. After 1h at -80 °C and 1h at room temperature, the mixture was added to the amidinatochlorogermylene at -80 °C (Scheme 8).



Scheme 8: Synthetic pathway of 1a

¹H NMR analysis showed the formation of a complex mixture with total consumption of the starting material and none signal corresponding to **1a**. This result can be rationalized by the concomitant formation of di-*iso*-propylamine during the deprotonation that reacts with **1a**

or the amidinatochlorogermylene. Indeed, Power *et al.* reported in 2009 that germylene in presence of ammonia led to the insertion product.²³

Di-*iso*-propylamine has been removed to determine its influence. Evaporation under reduced pressure of the preformed sulfinyl carbanion was selected as the easier method to eliminate the amine. Besides, the stability of the carbanion after elimination of the amine was ascertained by a trap step with iodomethane (Scheme 9). ¹H NMR analysis of the obtained product shown clean formation of methylated product, proving the viability of the method without decomposition of the carbanion during the process.



Scheme 9: Methylation of dry sulfinyl anion

From this result, the reaction of condensation with amidinatochlorogermylene was performed in the same conditions (Scheme 14). After extraction with pentane, NMR spectroscopy analysis undoubtedly shown the formation of a clean product assimilated to **1a**. Removal of di-*iso*-propylamine was the key step to avoid the formation of side products in the synthesis.

The ¹H NMR spectrum exhibits an AB system at 2.74 ppm for the Ge-CH₂-SO, in THF-d₈, which is a characteristic signal for a -CH₂- in α position of a chiral center (Figure 3). The signal (2.74 ppm) is in the same range of the starting material (2.68 ppm), it may be explained by the close electronegativity between germanium and hydrogen. The chiral center has also a noticeable influence on the amidinate *iso*-propyl groups, even if the -N-CH-(CH₃)₂ (4.31 ppm) shows no difference compared to the starting material (4.31 ppm), the major difference observed concerns the -N-CH-(CH₃)₂. Indeed, the starting material showed two doublets, due to planar symmetry, contrary to four doublets in the product. The four signals for CH₃- groups appear as the result of the loss of symmetry in the molecule brought by the sulfoxide moiety (Figure 3).

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Figure 3: ¹H NMR spectrum of **1a** in THF-d₈

In addition, ¹³C NMR has also evidenced a solid proof on the formation of **1a** (Figure 4). A secondary carbon (61.5 ppm) was identified as the -CH₂- between the sulfoxide group and the germylene moiety, the corresponding carbon being primary in the starting sulfoxide, which undoubtedly shows the formation of 1a. Again, the chiral center has a noticeable influence on the amidinate iso-propyl groups, each carbon was found non-equivalent due to a loss of symmetry in the product. The tertiary carbons (-N-CH-(CH₃)₂) appear as two peaks with almost the same chemical shift (47.7 and 47.6 ppm) and the primary carbons (-N-CH-(CH₃)₂) appear as three peaks with two carbon overlapping (26.9, 24.5 and 24.5 ppm).



Figure 4: ¹³C NMR spectrum of **1a** in THF-d₈

1a appears as an oil at room temperature that degrades upon time at room temperature. Study of stability was realized at room temperature on a dry sample and a sample in a solution of THF-d₈ with a 10-hour stirring. Same results were obtained and showed no particular effect of the solvent on the stability of **1a** (Figure 5). The mechanism of degradation was not studied as well as the resulting products. However, it was determined that the compound **1a** was stable at -24 °C and no degradation was observed at this temperature after a week. This observation led to try low temperature crystallization without any success.

Mass spectroscopy analysis have been performed to validate the formation of **1a** with another analytical method. However, only peaks corresponding to amidinatogermylene and methylphenylsulfoxide fragments were observed by electronic impact and MALDI-TOF analysis.



Figure 5: ¹H NMR of **1a** after 10 hours in THF-d₈

1b, analogue of **1a** from methyl-*p*-tolylsulfoxide (Scheme 9), was also synthesized through the same synthetic pathway. The formation of **1b** was also confirmed by ¹H and ¹³C NMR analysis. **1b** was synthetized in order to envision an asymmetric version of our ligand. Indeed, enantiopure methyl-*p*-tolylsulfoxide was readily accessible from usual chemical company, or could be obtained easily from (-)-menthyl-*p*-toluenesulfinate.^{24,25}

Although unstable at room temperature, **1a** and **1b** have been characterized by ¹H and ¹³C NMR spectroscopy analysis. These results lead us to envisage the modulation of the two moieties to expand the synthetic strategy to a large variety of substituents.

The goal was to determine the limit of the synthetic pathway to obtain a mixed germylene-sulfoxide ligand. As well as the impact of the design on the thermal stability was studied to determine the role of the steric hindrance on the ligand.

First, steric hindrance was increased successively on both moieties. To increase bulkiness on the amidinatogermylene moiety, N-*i*-Pr group was replaced by a larger substituent. Cyclohexyl (Cy) group was chosen as an available and versatile group that can protect and remain the germylene center accessible for nucleophilic substitution (Scheme 10). Moreover, Cy-AmGeCl have been synthetized through similar procedure described for *i*-Pr-AmGeCl derivative.³ Tipp (tri-*i*-propylphenyl) and *t*-Bu were chosen as larger substituents to increase steric hindrance and change nature of the sulfoxide moiety (Scheme 10).



Scheme 10: Different germylene-sulfoxide ligands with various substituents

Starting with the corresponding sulfoxides and amidinatochlorogermylenes, **1c** - **1f** were obtained through the same synthetic pathway used for **1a** and **1b** (Scheme 10). ¹H and ¹³C NMR have exhibited similar observations (AB system, secondary carbon, loss of symmetry...) than **1a** and **1b**. The compounds were obtained as oils with the same rate of degradation at room temperature and same stability at -24 °C. Although, steric hindrance was increased on both

moieties, the bulkiness was not large enough to have any effect on the thermal stability of mixed germylene-sulfoxide system. However, the synthetic pathway allowed a simple method for the modification of the skeleton to obtain a large variety of ligands.

Finally, the influence of sulfoxide moiety on the germylene was also investigated. Sulfur (II) (thioether) and sulfur (VI) (sulfone) were chosen to replace the sulfoxide as readily available derivatives of lowest and highest oxidation state of sulfur. Moreover, thioether and sulfone can be seen as "extreme interacting form of sulfoxide" by the only possibility of interaction with sulfur, in the case of thioether, or with oxygen in the case of sulfone.

The synthetic pathway remains unchanged (Scheme 11). Indeed, *n*-BuLi can be used with thioether or sulfone to obtain the corresponding carbanion. It is important to note, in the case of thioether, that α -lithiation is preferred to *ortho*-lithiation.²⁶



Scheme 11: Synthesis of thioether (1g) and sulfone (1h) derivative

1g and 1h were obtained in the same conditions and were characterized in ¹H and ¹³C NMR analysis. The loss of asymmetric center had a predictable impact on the NMR which was to keep the same symmetry in the molecule and so the same multiplicity of peaks. The chemical shift corresponding to $-CH_2$ - spacer of 1g and 1h appeared as a singlet in the similar area as the starting materials. This observation was unsurprising because germanium and hydrogen have a close electronegativity. Still, integration of this singlet in ¹H NMR undoubtedly proved the formation of a $-CH_2$ - spacer. In addition, a secondary carbon was observed for the spacer and confirmed the formation of 1g and 1h.

The properties of these two news ligands were particularly different to the previous germylene-sulfoxide ligands and each other. Indeed, **1g** was obtained as a very sensitive oil at room temperature which appears to degrade faster than all the sulfoxides, and with a slowly degradation at -24 °C where **1a-1f** were stable at this temperature. In contrary, **1h** was isolated as a stable solid at room temperature and was characterized by X-ray crystallography. Crystals have been obtained from a saturated solution of pentane (Figure 6).



Figure 6: Molecular structure of 1h (hydrogens are omitted for clarity)

The X-ray structure of **1h** exhibits a similar distance between nitrogen and germanium atoms (1.981(3) and 1.993(3) Å) compared to the starting material AmGeCl (1.98 Å). Moreover, even if sulfones are known as poor ligands in coordination chemistry,²⁷ some examples have already been published by our group for the stabilization of metallylenes with sulfones.^{28,29} However, the oxygen-germanium distance (3.48 Å) is too far in solid state to demonstrate any stabilization interaction, the formation of a four-members ring being too strained to observe an interaction between an oxygen atom of the sulfone and the germanium. Finally, the distance germanium-carbon (2.066(3) Å) is considered as long for a Ge–C bond (1.90-2.10 Å) but not unusual.³⁰

II.4. Investigation with heavier analogue

Heavier analogue, i-e stannylene, was next studied to determine if the mixed sulfoxidestannylene could be synthetized in the same synthetic pathway as **1a-1h**. However, the corresponding AmSnCl, heavier analogue of AmGeCl, has not been reported yet in the literature.

AmSnCl was obtained through a similar procedure as AmGeCl (Scheme 12). The nucleophile, formed by addition of *t*-BuLi on DIC, was added on two equivalents of $SnCl_2$ to obtain **2b** with a reasonable yield (78 %). The excess of $SnCl_2$ was found necessary to obtain clean heteroleptic stannylene, when less amount conducted to form a product identified as the homoleptic stannylene.



Scheme 12: Synthesis of AmSnCl

2b was characterized by multinuclear NMR spectroscopy and mass spectroscopy. The ¹H and ¹³C NMR did not exhibit unusual signal or chemical shift and shown a derivative with a C₂ symmetry similar to AmGeCl. ¹¹⁹Sn NMR exhibited only one signal (55 ppm) which was in accordance with previous analogues of AmSnCl (30-69 ppm).^{31,32} However, crystallization in a saturated solution of pentane gave the product of oxidation **2d** (Figure 7). The formation of **2d** could be seen as the reaction of four molecules of **2b** with a molecule of oxygen. Two tin (II) atoms were oxidized to tin (IV) and the amidinates group of the two-remaining tin (II) have migrated to tin (IV) with the formation of the central 1,3-Sn₂O₂ ring.



Figure 7: Molecular structure of oxidation product 2d (hydrogens are omitted for clarity)

The product of oxidation was determined as the reaction of **2b** with serendipitous oxygen, similar reaction being reported by Ruzicka in 2012.³² The structure exhibits two different tin atoms with two different oxidation states (+II and +IV). Moreover, the crystals were insoluble in usual solvents as reported by Ruzicka, which characterized a similar structure by solid state NMR.

The condensation reaction of the sulfinyl carbanion with AmSnCl was tested (Scheme 13).



Scheme 13: Synthetic pathway of **2c**

¹H NMR analysis showed the formation of a complex mixture with total consumption of the starting AmSnCl and recovering of starting sulfoxide.

II.5. Coordination chemistry of amidinatogermylene (II) -α- sulfur (II, IV, VI) ligands

The first target in coordination chemistry was formation of a carbonyl complex to get information concerning the donation properties of the germylene and the sulfoxide to a transition metal. In the literature, several bi-dentate germylene carbonyl complexes have already been explored with tungsten, ruthenium and cobalt.^{33,34}

Castel *et al.*, in 2012, reported in our laboratory the formation of phosphaalkenyl germylene that reacts with $W(cod)(CO)_4$ to give the corresponding bi-dentate complex. Starting with an equimolar amount of tungsten precursor, a solution of **1b** in THF was added at room temperature and stirred overnight (Scheme 14).



Scheme 14: Bis-germylene tungsten complex

Surprisingly, the reaction led to the formation of a bis-germylene tungsten complex, **3b**. Castel *et al.* reported, in 2010, the formation of a bis-germylene tungsten complex starting with the same tungsten precursor and amidinatochlorogermylene.³⁵ Structure of bis-germylene tungsten complex **3b** was determined through multiple analysis. First in ¹H NMR, half an equivalent of tungsten precursor was remaining in solution with total consumption of **1b** (coordinated cod, **HC=CH** at 3.8 ppm in C₆D₆). Besides, ¹³C NMR and IR spectroscopy confirmed a free sulfoxide function. In ¹³C NMR, carbon monoxide ligands of **3b** have one unique signal at 208 ppm, which show their electronic and magnetic equivalence. In IR spectroscopy, peak at 1021 cm⁻¹ was characteristic of a non-coordinated sulfoxide close to **1b** at 1015 cm⁻¹. Finally, X-ray structure of **3b** was obtained from crystals grown in a THF solution at 6 °C (Figure 8).



Figure 8: Molecular structure of **3b** (hydrogens are omitted for clarity)

The structure of **3b** shows a usual distance between the germylene and the tungsten of 2.5195(2) Å (2.50-2.65 Å).^{5,33,35,36} Unsurprisingly, Ge1–N1 and Ge1–N2 bond lengths of 1.9506(18) and 1.9609(17) Å are equal and shorter than in the free AmGeCl (1.98 Å), which can explain by the coordination of the germylene lone pair to the transition metal. Ge1–C4 bond distance was also in the range of carbon-germanium single bonds with a length of 2.002(2) Å. S1–O1 shows also usual bond length of 1.481(6) Å. The other bonds length and angles were also in the normal range of a germylene-tungsten complex.

1b was used as a racemic ligand, and the formation of one or two diastereomers was investigated. Even if $3b_{R,S}$ was formed and determined by X-ray analysis, the other diastereomer could have not crystallized due to differences of physical properties. ¹H NMR of **3b** was studied at low temperature (-80 °C) in order to obtain different signals of both diastereomer without any success. Enantiopure $3b_{R,R}$ was synthetized from enantiopure $1b_R$ and ¹H and ¹³C NMR analysis shown the exact same chemical shifts in that those obtained from crystals of $3b_{R,S}$. We suppose that any diastereomeric differentiation can be observed by ¹H and ¹³C NMR spectroscopy, probably due to the wide distance separating the two sulfinyl stereogenic centers.

In order to modulate the coordination properties of the ligand and to synthesize a bidentate complex, the conditions of reaction were changed. Three parameters: (i) temperature, (ii) dilution and (iii) equivalent of W(cod)(CO)₄, were tested to study their influence on the reaction. Temperature (i) was cooled at -80 °C and dilution (ii) was increased by a factor 10. However, the results showed in both case any influence on the formation of the product. The third reaction (iii) was carried out with 10 equivalents of W(cod)(CO)₄ and led to formation of a new product. ¹³C NMR exhibited four news signals for the carbon monoxide and let hope the formation of a bi-dentate complex (Figure 9). Nevertheless, the product could not be isolated because of the excess of W(cod)(CO)₄ but this observation showed that coordination with sulfoxide, strained 4-member ring with sulfur and /or weak coordination with oxygen, was unfavorable compare to the coordination of a second germylene.

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Figure 9: ¹³C NMR (190-220 ppm) of **3b** and reaction with 10 equivalents of tungsten in C₆D₆

The coordination was also tested with **1g** and **1h** with the same metallic precursor, and, unsurprisingly, these ligands gave analog results with the formation of the corresponding bisgermylene tungsten complexes (Scheme 15).



Scheme 15: Formation of 3g and 3h

3g and **3h** were crystalized in a THF solution at 6 °C (Figure 10). The X-ray structure shows a usual distance between the germylene and the tungsten of 2.5163(6) and 2.5206(2) Å (2.50-2.65 Å). The other bonds length and angles are also in usual range with Ge1–N1 and Ge1–N2 being shorter than AmGeCl or **1h** due to a better donation of nitrogen atom to the germylene center.



Figure 10: Molecular structure of **3g** and **3h** (hydrogens are omitted for clarity)

Coordination chemistry has been extended to determine if the same reactivity would be observed with Mo(nbd)(CO)₄, lighter analogue precursor of W(cod)(CO)₄. Starting with the same precursor **1b** and half an equivalent of molybdenum precursor, **4b** was obtained after stirring overnight the mixture at room temperature in THF (Scheme 16).



Scheme 16: Bis-germylene molybdenum complex

X-ray structure of **4b** was obtained from crystals grown in a saturated THF solution at 6 °C (Figure 11). The structure shows an usual distance between the germylene and the molybdenum of 2.561(4) Å (2.50 Å).^{35,37–39} As seen before, **1b** was used as a racemic ligand and the formation of one or two diastereomers was investigated in NMR without any success.



Figure 11: Molecular structure of 4b (hydrogens are omitted for clarity)

The formation of bis-germylene group VI transition metal complexes was a milestone to choose another metal precursor. Indeed, tungsten (0) and molybdenum (0) were certainly a good choice for a coordination with sulfur, nevertheless, this coordination seems to be unfavourable with oxygen due to the size of the 4-member ring. That is why ruthenium was preferred in the continuity of the study for its ability to be coordinated either by sulfur or oxygen.⁴⁰ Equimolar amount of Ru(PPh₃)₃Cl₂ and **1b** was stirred overnight in a solution of THF at room temperature (Scheme 17).



Scheme 17: Germylene ruthenium phosphine complex

³¹P NMR showed a clean formation of **5b** with two broaden signals at 55 and 24 ppm with a signal corresponding to free PPh₃ at -5 ppm. However, purification of **5b** to remove free PPh₃ was not possible with usual solvent like pentane, which was unusual since PPh₃ is soluble in pentane contrary to **5b**. Presence of free PPh₃ in a ruthenium complex was reported in the literature by the group of Grushin in 2014 with an X-Ray structure of (Ru(PPh₃)₃Cl₂.PPh₃)

where one PPh₃ was found in the lattice without hydrogen bond, π -stacking or coordination to the metal center.⁴¹ Nevertheless, bi-dentate germylene sulfoxide ruthenium complex was formed unambiguously with an oxygen coordination of the sulfoxide, which was characterized in IR analysis with a strong band at 945 cm⁻¹. **5a**, phenyl derivative of **5b** and less soluble in usual solvent, was obtained in a moderate yield of 56 % after washing with diethyl ether to remove free PPh₃. ³¹P NMR showed a same chemical shift and broaden signals at 55 and 24 ppm as **5b**. Suitable crystals of **5b** were obtained from a saturated solution of THF at -24 °C (Figure 12).



Figure 12: Molecular structure of **5a** (hydrogens are omitted for clarity)

X-ray structure shows a distorted octahedral complex. The interatomic Ru–Ge distance (2.4429(6) Å) is in the range of the values obtained for previously cited germylene-ruthenium complexes (2.28-2.50 Å).^{10,42–45} Surprisingly, Ge1–N1 and Ge1–N2 have a bond length of 1.951(4) and 1.979(4) Å, close to free AmGeCl, which can be explained by a less donating germylene due to the strong donation of phosphine in *trans* position. It is important to note that S1-01 bond length of 1.530(3) Å respects the usual increase due to a coordination through oxygen.⁴⁶ Phosphines also have a usual distance of P1–Ru1 of 2.2661(12) Å and P1–Ru2 of 2.3832(12) Å. The two chlorine atoms occupying the axial positions but also the two PPh₃ ligands in *cis* position present a large deviation to the ideal octahedral angle [C11–Ru1–Cl2, 165.53(4)°, P1–Ru1–P2, 99.56(4)° and P1–Ru1–Ge1, 102.77(3)°] which is probably due to the steric hindrance generated of the bulky phosphine ligands. Unsurprisingly, oxygen was coordinated to ruthenium over sulfur, due to a favorable and more stable 5-member ring, also confirmed by IR analysis with a strong band at 934 cm⁻¹. The structure was especially close to (Ru(PPh₃)₃Cl₂). PPh₃ described by Grushin with similar angles [P1–Ru1–P2 of 99.6°, P1–Ru1–

P3 of 103.5° and Cl1–Ru1–Cl2 of 159.9°], and similar phosphine distances [P1–Ru1 of 2.23 Å, P2–Ru1 of 2.37 Å, P3–Ru1 of 2.44 Å]. The ruthenium-oxygen distance, 2.185(3) Å, is in the range of literature complexes bearing a phosphine in *trans* position (2.15-2.24 Å).^{47–49}

Finally, exchange of ligand of **5b** was envisaged. One equivalent of Dppp (diphenylphosphinopropane) was added at room temperature and the reaction was stirred one hour at room temperature in THF (Scheme 18).



Scheme 18: germylene ruthenium diphosphine complex 5c

 31 P NMR showed a clean formation of **5c** with two doublet signals at 47 and 26 ppm with a notable coupling constant of 47.1 Hz shoving two different phosphorus coupling with each other. However, the reaction needed 1.2 equivalent of DPPP to consume all the starting material due to the formation of a side product identified as RuCl₂Dppp₂ which could not be eliminated at the end of the reaction.

Suitable crystals were obtained from a saturated solution of THF at -24 °C (Figure 13). X-ray structure shows a distorted octahedral complex with an interatomic Ru–Ge distance comparable to **5a** of 2.4413(3) Å (2.28-2.50 Å).^{10,42–45} Phosphine and ruthenium also have an usual distance of P1–Ru1 of 2.2440(6) Å and P1–Ru2 of 2.3119(6) Å.⁴¹

Chapter II: Germylene - α - Sulfoxide Ligands: Synthesis, Characterization and Coordination of a

Novel Hemilabile Metallylene Ligand



Figure 13: Molecular structure of 5c (hydrogens are omitted for clarity)

The formation of a mono-dentate complex was also investigated with numerous transition metals. In the first exploration, $(\text{RuCl}_2(p\text{-cymene}))_2$ was selected. Indeed, Alvarez *et al.* published a ruthenium amidinatogermylene complex starting with the same precursor in 2016.¹⁰ **1b** in a solution of THF was added to half an equivalent of $(\text{RuCl}_2(p\text{-cymene}))_2$ at room temperature and the reaction was stirred overnight (Scheme 19).



Scheme 19: mono-dentate germylene ruthenium **6b** complex

6b was obtained with a good 80% yield after washing with diethyl ether. Suitable crystals for X-ray crystallography were obtained from a saturated solution of THF at -24 °C (Figure 14). The X-ray structure shows usual interatomic Ru–Ge distance of 2.4056(5) Å (2.28-2.49 Å).^{10,42–44} It is important to note that Ge1–N1 and Ge1-N2 had bond lengths of 1.942(3) and 1.956(2) Å which are slightly shorter than AmGeCl (1.98 Å) or **5b** (1.95 and 1.98 Å), which can be explained by a stronger donating germylene due to a poor donating ligand in *trans* position compare to phosphine in **5b**. The loss of symmetry due to the presence of the stereogenic sulfoxide was exhibited in ¹H NMR and ¹³C NMR analysis for the *p*-cymene group, where 4 doublets with 6 different carbons (2 quaternary and 4 tertiary) were assigned to each

aromatic hydrogen and carbon atoms respectively. The $-CH_2$ - linker between germylene and sulfoxide was the only one to show a specific shift in NMR. Indeed, in ¹H NMR an A-B system appeared clearly in C₆D₆ at 3.56 and 3.72 ppm compared to a singlet at 2.93 ppm for the starting material in the solvent. In ¹³C NMR, the signal was upfield at 50.6 ppm compared to 61.7 ppm.



Figure 14: Molecular structure of **6b** (hydrogens are omitted for clarity)

Formation of a bi-dentate complex by chlorine abstraction was also investigated from **6b** in usual conditions described in the literature (Scheme 20).⁵⁰



Scheme 20: reaction of 6b with chlorine abstractor

6b was rapidly consumed after addition of $AgPF_6$ in dichloromethane at room temperature and a new product assimilated to **6b'** was identified and characterized in ¹H and ¹³C NMR (Figure 15). **6b'** appears as two diastereoisomers in the form of two A-B systems with a 77/23 ratio calculated in ¹H NMR. Moreover **6b'** exhibits different chemical shifts for the *p*-cymene group and the methylene bridge due to the chlorine abstraction and possible coordination of the sulfoxide. However, **6b'** has not been fully characterized because of its

instability, its degradation leading to the formation of amidinatohexafluorophosphate salt characterized by X-Ray diffraction as by-product.



Finally, the reaction was tested with several chlorine abstractors such as $AgBF_4$, $SbPF_6$ and $ThPF_6$. The nature of the chlorine abstractor and the counter anion had no effect on the stability of **6b'**. Every crystals obtained were colorless and corresponded always to the degradation products.

Coordination with $[RuCl_2(p-cymene)]_2$ was extended to **1a-1c-1d-1f-1g** and **1h**. In each case, ruthenium complex was obtained in good yield and suitable crystals for X-ray diffraction crystallography were obtained from saturated solutions of THF at -24 °C (Figure 16). Similar observations, as seen for **6b**, were realized by ¹H and ¹³C NMR analysis with all the germylene ruthenium complexes. As expected for **6g** and **6h**, corresponding to the thioether and sulfone analogues, two doublets by ¹H NMR and four different aromatic carbons by ¹³C NMR (2 quaternary and 2 tertiary) were observed for the *p*-cymene group due to the loss of the asymmetric center.



Figure 16: Molecular structures of **6a-6c-6d-6f-6g** and **6h** (hydrogens are omitted for clarity)

The second transition metal used to form a mono-dentate complex was $Fe_2(CO)_9$. Coordination chemistry with this precursor was already known in our group and was carried out with **1b** in THF at room temperature (Scheme 21).¹⁸



Scheme 21: reaction of 1b with Fe₂(CO)₉

The reaction was complete after 16h and an orange-brown solid was obtained, ¹H and ¹³C NMR analysis exhibit the formation of a clean new product assimilated to **7b** (Figure 17). Formation of **7b** was also confirmed by mass-spectroscopy (m/z = 578.046). However, suitable crystals for X-ray diffraction were not obtained.

Finally, the study of Cabeza group, in 2015, pointing the importance to substitute an amidinatochlorogermylene to have access to coordination of group 11 transition metal led us to test CuCl and AuCl.SMe₂ with **1b** in THF (Scheme 22).¹⁹



Scheme 22: reaction of 1b with CuCl and [AuCl.SMe₂] in THF-d₈

The reaction was monitored by ¹H NMR and showed a total consumption of **1b** after 30 min in both cases. The new clean products were assimilated to **8b** and **9b** (Figure 17). However, these new complexes appeared very unstable, **8b** being totally degraded in a mixture of green products after 2 hours at room temperature or at -24 °C, **9b** leading to the formation of a gold mirror and a complex mixture of products in solution.



III. Conclusion

In conclusion, amidinatosulfoxide germylenes **1a-b** were synthetized and characterized undoubtedly by ¹H and ¹³C NMR analysis. The study of the modification of steric hindrance on both moieties by the preparation of **1c-f** shows any effect on the thermal stability of these new mixed ligands. However, the synthetic appears as a simple method for the modification of the skeleton to obtain a large variety of ligands and to obtain different oxidation states on the sulfur atom by the preparation of thioether and sulfone analogues **1g** and **1h**.

Tungsten (0) derivatives 2b, 2g, 2h were prepared and surprisingly showed the formation of bis-germylene complexes 3b, 3g, 3h. Coordination of tungsten with sulfur atom would formed an unfavorable strained 4-member ring for 3b and 3g, or a week coordination with oxygen for 3b and 3h, which can explain the coordination of the tungsten by a second germylene.

Ruthenium complex 5a was obtained as a bidentate hemilabile complex with germanium and oxygen atoms coordinated to the ruthenium center through a 5-member ring. X-ray structure showed a highly distorted octahedral structure with the coordination of oxygen that seems to be a result of an important steric hindrance around the metallic center, generated by PPh₃ and germanium ligand, and shows the hemilability of the ligand.

Mono-dentate coordination with $(\text{RuCl}_2(p\text{-cymene}))_2$ for the preparation of **5a-d**, **f-h** was studied. The versatility of the synthetic pathway demonstrates that the skeleton can be easily modified to obtain a large variety of steric hindrance and sulfur (II, IV, VI) derivatives with a good yield of 72-84 %.

IV. Experimental section



Amidinate(dicyclohexyl t-butyl) chloro germylene : *t*-BuLi (2 mL, 3.4 mmol, 1.7 M in pentane, 1 eq) was added to a solution of CyN=C=NCy (701 mg, 3.4 mmol, 1 eq) in diethyl ether (10 mL) at -78 °C. The solution was raised to room temperature and stirred for 4 h. Then, GeCl₂•dioxane (0.788 g, 3.4 mmol, 1 eq) was added to the solution at 0 °C, the mixture was stirred for 15 h at room temperature. Finally, the solvent was removed under

reduced pressure and extracted with pentane (3x5 mL), to give, after removing all solvents, a white solid (1.111 g) in 88 % yield. M.p. : 74 °C; ¹H NMR (300.18 MHz, THF- d_8 , 25 °C): δ 0.85-1.95 (m, 20H, CH(CH_3)_2); 1.39 (s, 9H, C(CH_3)_3); 3.83 (m, 2H, N-CH(CH_2)_2). ¹³C{¹H} NMR (75.48 MHz, THF- d_8 , 25 °C): δ 26.0 (CH₂); 26.1 (CH₂); 26.2 (CH₂); 29.0 (C(CH₃)_3); 35.7 (CH₂); 37.9 (CH₂); 40.8 (C(CH₃)_3); 56.1 (N-CH(CH₂)_2); 177.9 (N-C-N). MS (EI : 70 eV) *m/z* (%): 373.1 ([M + 1, 20 %]⁺).

Formula	C17 H31 Ge N2 Cl	dcalc (g/cm ³)	1.300
Mol wt	371.50	$\mu (mm^{-1})$	1.751
Temp. (K)	193(2)	F(000)	784
Cryst syst	Monoclinic	cryst size (mm)	0.10 x 0.10 x 0.02
Space group	P21/c	θ range (deg.)	2.07 to 26.44°
a (Å)	9.9516(6)	index range h k l	-12<=h<=12, -13<=k<=21, -14<=l<=14
b (Å)	16.9688(9)	no of reflns collected /	9937
c (Å)	11.3866(6)	unique	3884 [R(int) = 0.0464]
α (deg.)	90	Completeness to θmax(%)	99.2 %
β (deg.)	99.127(3)	data/restraints/params	3884 / 27 / 213
γ (deg.)	90	goodness-of-fit	1.115
V (Å3)	1898.47(18)	$R1, wR2 (I > 2\sigma(I))$	0.0569, 0.1705
Z	4	R1, wR2 (all data)	0.1104, 0.2340



Amidinate (di-*iso*-propyl-*t*-butyl) methylphenylsulfoxide germylene (1a): LDA (53.4 mg, 0.5 mmol, 1.04 eq) in diethyl ether (2 mL) was added dropwise to a solution of methylphenylsulfoxide (70 mg, 0.5 mmol, 1.04 eq) in diethyl ether (2 mL) at -78 °C. The solution was stirred during 1 hour at the

same temperature (-78 °C). Then, the solution was allowed to warm up at room temperature and stirred an additional period of 45 min. Finally, the solvent was removed under reduced pressure in order to obtain a white solid. The resulting solid was dissolved in diethyl ether (2 mL) and added dropwise to a solution of chlorogermylene (138.7 mg, 0.48 mmol, 1 eq) in diethyl ether (2.5 mL) at -78 °C. The mixture was stirred during 2.5 hours at -78 °C. Then, the solution was filtered at the same temperature (-78 °C). Finally, the solvent was removed under reduced pressure to afford an oil (102 mg) in 72% yield. ¹H NMR (300.18 MHz, THF-*d*₈, 25 °C): δ 1.11 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.18 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.16 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.18 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.38 (s, 9H, C(CH₃)₃); 2.69 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 2.76 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 4.31 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 7.36-7.47 (m, 3H, CH_{Ar}); 7.65-7.70 (m, 2H, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, THF-*d*₈, 25 °C): δ 24.3 (CH(CH₃)₂); 24.5 (CH(CH₃)₂); 61.5 (GeCH₂SO); 124.4 (*C*_{Ar}); 129.9 (*C*_{Ar}); 151.5 (*C*_{Ar/q}); 171.9 (N–*C*–N).



Amidinate (di-*iso*-propyl-*t*-butyl) methyl-*p*-tolylsulfoxide germylene (1b): LDA (77 mg, 0.72 mmol, 1.1 eq) in diethyl ether (2.5 mL) was added dropwise to a solution of methyl-*p*tolylsulfoxide (110 mg, 0.72 mmol, 1.1 eq) in diethyl ether (2.5 mL) at -78 °C. The solution was stirred during 1 hour at the

same temperature (-78 °C). Then, the solution was allowed to warm up at room temperature and stirred an additional period of 45 min. Finally, the solvent was removed under reduced pressure in order to obtain a white solid. The resulting solid was dissolved in diethyl ether (5 mL) and added dropwise to a solution of chlorogermylene (189 mg, 0.65 mmol, 1 eq) in diethyl ether (5 mL) at -78 °C. The mixture was stirred during 2.5 hours at -78 °C. Then, the solution was filtered at the same temperature (-78 °C) and concentrated until it remains 1 mL of solution. The product was extracted with pentane (2x5 mL) and the solvents were removed in order to afford an oil (220 mg) in 82% yield. The compound is stable and storable at -24 °C in an inert

atmosphere of argon. ¹H NMR (300.18 MHz, THF- d_8 , 25 °C): δ 1.11 (d, ³J_{HH} = 6.3 Hz, 3H, CH(C H_3)₂); 1.15 (d, ³J_{HH} = 6.3 Hz, 6H, CH(C H_3)₂); 1.16 (d, ³J_{HH} = 6.3 Hz, 3H, CH(C H_3)₂); 1.38 (s, 9H, C(C H_3)₃); 2.36 (s, 3H, *p*-C H_3); 2.69 (d, 1H, ²J_{HH} = 13.8 Hz, GeC H_2 SO); 2.76 (d, 1H, ²J_{HH} = 13.8 Hz, GeC H_2 SO); 4.31 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 7.26 (d, 2H, ³J_{HH} = 8.2 Hz, C H_{Ar}); 7.54 (m, 2H, ³J_{HH} = 8.2 Hz, C H_{Ar}). ¹³C{¹H} NMR (75.48 MHz, THF- d_8 , 25 °C): δ 21.1 (p-CH₃); 24.3 (CH(CH₃)₂); 24.5 (CH(CH₃)₂); 26.9 (CH(CH₃)₂); 27.0 (CH(CH₃)₂); 29.4 (C(CH₃)₃); 40.7 (C(CH₃)₃); 47.6 (CH(CH₃)₂); 47.7 (CH(CH₃)₂); 61.9 (GeCH₂SO); 124.3 (C_{Ar}); 129.8 (C_{Ar}); 139.8 (C_{Ar/q}); 148.6 (C_{Ar/q}); 171.8 (N-C-N). IR (Nujol, cm⁻¹) : 1493 (med) (C=C_{arene}), 1017 (med) (SO).



Amidinate(dicyclohexyl-t-butyl)germylenemethylphenylsulfoxide (1c): LDA (49 mg, 0.46 mmol, 1.1 eq) indiethyl ether (2 mL) was added dropwise to a solution ofmethylphenylsulfoxide (65 mg, 0.46 mmol, 1.1 eq) in diethyl ether(2 mL) at -78 °C. The solution was stirred during 1 hour at thesame temperature (-78 °C). Then, the solution was allowed to

warm up at room temperature and stirred an additional period of 45 min. Finally, the solvent was removed under reduced pressure in order to obtain a white solid. The resulting solid was dissolved in diethyl ether (2 mL) and added dropwise to a solution of chlorogermylene (156 mg, 0.42 mmol, 1 eq) in diethyl ether (2.5 mL) at -78 °C. The mixture was stirred during 2.5 hours at -78 °C. Then, the solution was filtered at the same temperature (-78 °C). Finally, the solvent was removed under reduced pressure to afford an oil (132 mg) in 66% yield. ¹H NMR (300.18 MHz, THF-*d*₈, 25 °C): δ 1.07-1.33 (m, 10H, CH(*CH*₃)₂); 1.36 (s, 9H, C(*CH*₃)₃); 1.53-1.93 (m, 10H, CH(*CH*₃)₂); 2.73 (s, 2H, Ge-*CH*₂-SO); 3.80 (m, 2H, N-*CH*(CH₂)₂); 7.34-7.52 (m, 3H, C-*H*_{ar}); 7.66-7.70 (m, 2H, C-*H*_{ar}). ¹³C{¹H} NMR (75.48 MHz, THF-*d*₈, 25 °C): δ 25.3 (*C*H₂); 25.5 (*C*H₂); 25.7 (*C*H₂); 28.7 (*C*(*C*H₃)₃); 34.5 (*C*H₂); 34.7 (*C*H₂); 40.7 (*C*(*C*H₃)₃); 55.2 (*C*H(CH₂)₂); 60.8 (Ge*C*H₂SO); 123.7 (C_{Ar}); 128.5 (C_{Ar}); 129.2 (C_{Ar}); 150.7 (C_{Ar/q}); 171.1 (N–C–N).



Amidinate (dicyclohexyl-t-butyl) germylene methyl-*p***-tolylsulfoxide (1d):** LDA (49 mg, 0.46 mmol, 1.1 eq) in diethyl ether (2 mL) was added dropwise to a solution of methyl-*p***-**tolylsulfoxide (65 mg, 0.46 mmol, 1.1 eq) in diethyl ether (2 mL) at -78 °C. The solution was stirred during 1 hour at the same temperature (-78 °C). Then, the solution was allowed to

warm up at room temperature and stirred an additional period of 45 min. Finally, the solvent was removed under reduced pressure in order to obtain a white solid. The resulting solid was dissolved in diethyl ether (2 mL) and added dropwise to a solution of chlorogermylene (156 mg, 0.42 mmol, 1 eq) in diethyl ether (2.5 mL) at -78 °C. The mixture was stirred during 2.5 hours at -78 °C. Then, the solution was filtered at the same temperature (-78 °C). Finally, the solvent was removed under reduced pressure to afford an oil (132 mg) in 66% yield. ¹H NMR (300.18 MHz, THF-*D*₈, 25 °C): δ 1.20-1.82 (m, 20H, CH(CH₃)₂); 1.37 (s, 9H, C(CH₃)₃); 2.36 (s, 3H, *p*-CH₃); 2.70 (s, 2H, Ge-CH₂-SO); 3.80 (m, 2H, N-CH(CH₂)₂); 7.26 (d, 2H, ³J_{HH} = 8.2 Hz, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, THF-*D*₈, 25 °C): δ 20.5 (*p*-CH₃); 25.2 (CH₂); 25.3 (CH₂); 25.5 (CH₂); 25.5 (CH₂); 25.6 (CH₂); 25.7 (CH₂); 28.7 (C(CH₃)₃); 34.7 (CH₂); 34.5 (CH₂); 37.6 (CH₂); 37.7 (CH₂); 40.1 (C(CH₃)₃); 55.2 (CH(CH₂)₂); 55.3 (CH(CH₂)₂); 61.0 (GeCH₂SO); 123.7 (C_{Ar}); 129.1 (C_{Ar}); 139.1 (C_{Ar/q}); 147.7 (C_{Ar/q}); 170.9 (N–C–N). IR (Nujol, cm⁻¹) : 1464 (med) (C=C_{arene}), 1027 (med) (SO).



Amidinate (di-*iso*-propyle-*t*-butyl) germylene methyl-*t*butylsulfoxide (1f): LDA (77 mg, 0.72 mmol, 1.1 eq) in diethyl ether (2.5 mL) was added dropwise to a solution of methyl-*t*butylsulfoxide (110 mg, 0.72 mmol, 1.1 eq) in diethyl ether (2.5 mL)

at -78 °C. The solution was stirred during 1 hour at the same temperature (-78 °C). Then, the solution was allowed to warm up at room temperature and stirred an additional period of 45 min. Finally, the solvent was removed under reduced pressure in order to obtain a white solid. The resulting solid was dissolved in diethyl ether (5 mL) and added dropwise to a solution of chlorogermylene (189 mg, 0.65 mmol, 1 eq) in diethyl ether (5 mL) at -78 °C. The mixture was stirred during 2.5 hours at -78 °C. Then, the solution was filtered at the same temperature (-78 °C) and concentrated until it remains 1 mL of solution. Pentane (5 mL) was then added to the solution and the solution was finally filtered. The solvents were removed under reduced pressure to afford an oil (220 mg) in 82% yield. **1f** is stable and storable at -24 °C in an inert atmosphere of argon. ¹H NMR (300.18 MHz, THF-*d*₈, 25 °C): δ 1.14 (s, 9H, C(C*H*₃)₃); 1.11 (d,

 ${}^{3}J_{HH} = 6.3 \text{ Hz}, 3H, CH(CH_{3})_{2}); 1.15 (d, {}^{3}J_{HH} = 6.3 \text{ Hz}, 6H, CH(CH_{3})_{2}); 1.16 (d, {}^{3}J_{HH} = 6.3 \text{ Hz}, 3H, CH(CH_{3})_{2}); 1.39 (s, 9H, C(CH_{3})_{3}); 2.09 (d, 2H, {}^{2}J_{HH} = 11.8 \text{ Hz}, GeCH_{2}SO); 2.45 (d, 2H, {}^{2}J_{HH} = 11.8 \text{ Hz}, GeCH_{2}SO); 2.45 (d, 2H, {}^{2}J_{HH} = 11.8 \text{ Hz}, GeCH_{2}SO); 4.32 (sept., {}^{3}J_{HH} = 6.3 \text{ Hz}, 2H, CH(CH_{3})_{2}).$



Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylthioether (1g): n-BuLi (540 µL, 0.87 mmol, 1.3 eq, C =1.6 M in hexane) was added dropwise to a solution of thioanisole (108mg, 0.87 mmol, 1.3 eq) in THF (2 mL) at 0 °C. The solution was stirred

during 2 hour at the same temperature (0 °C). Then, the solution was cooled at -78 °C and added dropwise to a solution of chlorogermylene (194 mg, 0.67 mmol, 1 eq) in THF (2.5 mL) at -78 °C. The mixture was stirred during 1.5 hours at -78 °C. Then, the solution was evaporated by vacuum and the mixture was extracted with pentane (8 mL). Finally, the filtrate was evaporated under reduced pressure to afford an oil (180 mg) in 71% yield. ¹H NMR (300.18 MHz, THF*d*₈, 25 °C): δ 1.13 (d, ³J_{HH} = 6.3 Hz, 6H, CH(C*H*₃)₂); 1.20 (d, ³J_{HH} = 6.3 Hz, 6H, CH(C*H*₃)₂); 1.42 (s, 9H, C(C*H*₃)₃); 2.35 (s, 2H, GeC*H*₂SPh); 4.32 (sept., ³J_{HH} = 6.3 Hz, 2H, C*H*(CH₃)₂); 7.10-7.25 (m, 5H, C*H*_{Ar}). ¹³C {¹H} NMR (75.48 MHz, THF-*d*₈, 25 °C): δ 23.8 (CH(*C*H₃)₂); 27.4 (CH(*C*H₃)₂); 29.4 (C(*C*H₃)₃); 31.9 (Ge*C*H₂SPh); 40.8 (*C*(CH₃)₃); 47.5 (*C*H(CH₃)₂); 123.9 (C_{Ar}); 126.2 (C_{Ar}); 128.7 (C_{Ar}); 144.4 (C_{Ar/q}); 171.7 (N–C–N).



Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfone (1h): n-BuLi (510 µL, 0.82 mmol, 1.1 eq, C =1.6 M in hexane) was added dropwise to a solution ofmethylphenylsulfone (129 mg, 0.82 mmol, 1.1 eq) in THF (5 mL) at -

40 °C. The solution was stirred during 1 hour at the same temperature (-40 °C). The resulting mixture was added dropwise to a solution of chlorogermylene (218 mg, 0.75 mmol, 1 eq) in THF (2 mL) at -78 °C. The mixture was stirred during 1 hours at -78 °C. The solvent was evaporated under reduced pressure and the resulting solid was extracted with toluene (2x3 mL) at room temperature. Finally, the solvent was removed under reduced pressure to afford a pale white solid (268 mg) in 87% yield. Suitable crystals for X-ray cristallography were obtained from a saturated solution of pentane. M.p. : 112 °C. ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.99 (s, 9H, C(CH_3)_3); 1.05 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH_3)_2); 1.10 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH_3)_2); 3.18 (s, 2H, GeCH_2SO_2); 3.94 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH_3)_2); 7.01-7.07 (m, 3H, CH_{Ar}); 8.04-8.09 (m, 2H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 24.1

(CH(CH₃)₂); 26.8 (CH(CH₃)₂); 29.0 (C(CH₃)₃); 40.0 (C(CH₃)₃); 47.4 (CH(CH₃)₂); 61.4 (GeCH₂SO); 127.1 (C_{Ar}); 129.0 (C_{Ar}); 131.8 (C_{Ar}); 146.1 (C_{Ar/q}); 172.7 (N–C–N). MS (EI: 70 eV) m/z (%): 413.2 ([M + 1, 8 %]⁺). IR (Nujol, cm⁻¹): 1493 (med) (C=C_{arene}), 1305 (med) (SO), 1140 (med) (SO).

Formula	C18 H30 Ge N2 O2 S	dcalc (g/cm ³)	1.338
Mol wt	411.09	μ (mm ⁻¹)	1.616
Temp. (K)	193(2)	F(000)	864
Cryst syst	Triclinic	cryst size (mm)	0.080 x 0.050 x 0.040
Space group	P-1	θ range (deg.)	5.123 to 26.372°
a (Å)	11.4843(9)	index range h k l	-14<=h<=14, - 14<=k<=14, 0<=l<=19
b (Å)	11.9768(10)	no of reflns collected /	12373
c (Å)	15.7912(14)	unique	8243 [R(int) = 0.0828]
α (deg.)	78.646(4)	Completeness to θ max(%)	99.0 %
β (deg.)	85.022(4)	data/restraints/params	8243 / 0 / 448
γ (deg.)	73.454(3)	goodness-of-fit	1.029
V (Å3)	2040.2(3)	R1, wR2 (I > $2\sigma(I)$)	0.0458, 0.0870
Z	4	R1, wR2 (all data)	0.0899, 0.1011



Amidinate (di-*iso*-propyle-*t*-butyl) chloro stannylene (2a): *t*-BuLi (0.8 mL, 1.28 mmol, 1.6 M in diethyl ether, 1 eq) was added to a solution of *i*-PrN=C=N-*i*-Pr (0.2 mL, 1.28 mmol, 1 eq) in diethyl ether (5 mL) at -78 °C. The solution was raised to room temperature and stirred for 4 h. Then, the solution was added dropwise to $SnCl_2$ (349 mg, 2.56 mmol, 2 eq) in diethyl

ether (5 mL) at -78 °C, the mixture was stirred for 2 h at the same temperature (-78 °C) and 2 h at room temperature. Finally, the solvent was removed under reduced pressure and extracted with pentane (2x3 mL). The filtrate was concentrated under reduced pressure to give a white solid (342 mg) in 79 % yield. M.p. : 67 °C; ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.87 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.01 (s, 9H, C(CH₃)₃); 1.18 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 4.16 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂). ¹³C{¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 26.4 (CH(CH₃)₂); 29.4 (C(CH₃)₃); 42.4 (C(CH₃)₃); 46.9 (CH(CH₃)₂); 179.7 (N–C–N). ¹¹⁹Sn NMR (167.88 Hz, C_6D_6 , 25 °C): δ = 55.5 ppm.

Chapter II: Germylene - α - Sulfoxide Ligands: Synthesis, Characterization and Coordination of a

CI
Sn
CIL ₂ Sn — O [´] O — SnL ₂ CI
.Sn
CI
L = Amidinate di- <i>iso</i> -propyl-t-butyl

Crystals data of 2d obtained during crystallization of 2b with serendipitous addition of O_2 .

L = Amulate ul-150-plop	L = Amidinate di- <i>iso</i> -propyi- <i>i</i> -butyi				
Formula	C44H92Cl4N8O2Sn4	dcalc (g/cm ³)	1.607		
Mol wt	1381.90	μ (mm ⁻¹)	1.956		
Temp. (K)	193(2)	<i>F</i> (000)	1392		
Cryst syst	Monoclinic	cryst size (mm)	0.28 x 0.16 x 0.08		
Space group	P2 ₁ /n	θ range (deg.)	1.71 to 33.14		
a (Å)	9.9149(4)	index range h k l	-15<=h<=15, - 25<=k<=28, - 24<=1<=24		
b (Å)	18.13126(8)	no of reflns collected /	49041		
c (Å)	16.2508(7)	unique	10869 [R(int) = 0.0298]		
α (deg.)	90	Completeness to θ max(%)	99.9		
β (deg.)	104.495 (2)	data/restraints/params	10869 / 198 / 373		
γ (deg.)	90	goodness-of-fit	1.202		
V (Å3)	2856.7(2)	R1, wR2 (I > $2\sigma(I)$)	0.0380, 0.1098		
Ζ	2	R1, wR2 (all data)	0.0594, 0.1522		



Amidinate(di-*iso*-propyle-*t*-butyl) germylene methyl-*p*tolylsulfoxide tungsten tetracarbonyl complex (3b): Amidinate (di-*iso*-propyle-*t*-butyl) germylene methyl-*p*tolylsulfoxyde 1b (135 mg, 0.330 mmol, 1 eq) was dissolved in tetrahydrofran (5 mL). The solution was then added to tetracarbonyl(1,5-cyclooctadiene)tungsten(0) (101 mg, 0.165 mmol, 0.5 eq) in THF (2 mL). The mixture

was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the solid was washed with pentane (2x3 mL) to obtain a pale yellow solid (143 mg) in 78% yield. Crystallization from THF at 6 °C gave pale yellow crystals suitable for X-ray study. M.p. : 117 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 1.29 (s, 18H, C(CH₃)₃); 1.45 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.48 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.57 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂); 1.99 (s, 6H, *p*-CH₃); 2.94 (d, 2H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.35 (d, 2H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 4.34 (sept., ³J_{HH} = 6.3 Hz, 2H,

 $CH(CH_{3})_{2}; 4.43 \text{ (sept., }^{3}J_{HH} = 6.3 \text{ Hz}, 2H, CH(CH_{3})_{2}; 6.88 \text{ (d}, 4H, }^{3}J_{HH} = 8.2 \text{ Hz}, CH_{Ar}; 7.51 \text{ (d}, 4H, }^{3}J_{HH} = 8.2 \text{ Hz}, CH_{Ar}; 1^{3}C\{^{1}H\} \text{ NMR (75.48 MHz, C_{6}D_{6}, 25 °C)}; \delta 21.1 ($ *p* $-CH_{3}); 23.2 (CH(CH_{3})_{2}); 23.3 (CH(CH_{3})_{2}); 26.0 (CH(CH_{3})_{2}); 26.2 (CH(CH_{3})_{2}); 29.3 (C(CH_{3})_{3}); 39.8 (C(CH_{3})_{3}); 47.8 (CH(CH_{3})_{2}); 47.9 (CH(CH_{3})_{2}); 59.6 (GeCH_{2}SO); 123.7 (C_{Ar}); 129.9 (C_{Ar}); 139.7 (C_{Ar/q}); 148.2 (C_{Ar/q}); 175.2 (N-C-N); 208.0 (CO). MS (Maldi-TOF)$ *m/z* $(%): 1002 ([M - (CO)_{4}]^{+}). IR (Nujol, cm^{-1}): 2035 (s) (CO), 1996 (s) (CO), 1938 (s) (CO), 1021 (med) (SO).$

Formula	C42H64Ge2N4O6S2W, 2(C4H8O)	dcalc (g/cm ³)	1.475
Mol wt	1258.36	μ (mm ⁻¹)	3.203
Temp. (K)	193(2)	<i>F</i> (000)	642
Cryst syst	Triclinic	cryst size (mm)	0.16 x 0.12 x 0.04
Space group	P-1	θ range (deg.)	3.25 to 31.91
a (Å)	9.9512(4)	index range h k l	-14<=h<=14, - 17<=k<=17, - 19<=l<=19
b (Å)	11.6654(5)	no of reflns collected /	36625
c (Å)	13.3526(6)	unique	9692 [R(int) = 0.0346]
α (deg.)	79.8470 (10)	Completeness to θ max(%)	99.5
β (deg.)	77.244(2)	data/restraints/params	9692 / 37 / 332
γ (deg.)	70.587(2)	goodness-of-fit	1.114
V (Å3)	1416.88(11)	R1, wR2 ($I > 2\sigma(I)$)	0.0301, 0.0544
Ζ	1	R1, wR2 (all data)	0.0396, 0.0576



Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylthioether tungsten tetracarbonyl complex(3g):Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylthioether 1g (100 mg, 0.26 mmol, 1 eq) wasdissolved in tetrahydrofran (5 mL) and tetracarbonyl(1,5-cyclooctadiene)tungsten(0)(53 mg, 0.13 mmol, 0.5 eq) wasadded to the solution. The mixture was stirred during 15

hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the solid was washed with pentane (2x3 mL) to obtain a pale yellow solid (85 mg) in 64 % yield. Crystallization from toluene at 6 °C gave pale yellow crystals suitable for X-ray study. M.p. : 106 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 1.20 (s, 18H,

C(CH₃)₃); 1.33 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂); 1.49 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂); 3.23 (s, 4H, GeCH₂SPh); 4.19 (sept., ³J_{HH} = 6.3 Hz, 4H, CH(CH₃)₂); 6.90 (m, 2H, CH_{Ar}); 7.04 (m, 4H, CH_{Ar}); 7.35 (m, 4H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 22.3 (CH(CH₃)₂); 25.9 (CH(CH₃)₂); 29.5 (C(CH₃)₃); 32.6 (GeCH₂SPh); 39.7 (C(CH₃)₃); 47.7 (CH(CH₃)₂); 124.6 (C_{Ar}); 126.9 (C_{Ar}); 129.0 (C_{Ar}); 142.0 (C_{Ar/q}); 173.6 (N–C–N); 208.3 (CO). MS (Maldi-TOF) *m/z* (%): 1026 ([M - CO]⁺). IR (Nujol, cm⁻¹): 2036 (s) (CO), 1947 (s) (CO), 1899 (br) (CO).

Formula	C40H60Ge2N4O4S2W	dcalc (g/cm ³)	1.497
Mol wt	1054.10	μ (mm ⁻¹)	3.861
Temp. (K)	193(2)	<i>F</i> (000)	1060
Cryst syst	Monoclinic	cryst size (mm)	0.120 x 0.120 x 0.020
Space group	P21/c	θ range (deg.)	3.787 to 25.025
a (Å)	13.4478(7)	index range h k l	-16<=h<=16, - 12<=k<=12, - 21<=l<=21
b (Å)	10.3462(6)	no of reflns collected /	31137
c (Å)	17.9379(6)	unique	4019 [R(int) = 0.0570]
α (deg.)	90	Completeness to θ max(%)	97.4
β (deg.)	110.487(3)	data/restraints/params	4019 / 0 /248
γ (deg.)	90	goodness-of-fit	1.137
V (Å3)	2337.9(2)	R1, wR2 ($I > 2\sigma(I)$)	0.0375, 0.0927
Z	2	R1, wR2 (all data)	0.0544, 0.1006



Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfonetungstentetracarbonylcomplex(3h):Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfone1h(100 mg, 0.24 mmol, 1 eq)wasdissolved in tetrahydrofran (5 mL).The solution was thenadded to tetracarbonyl(1,5-cyclooctadiene)tungsten(0)(98mg, 0.12 mmol, 0.5 eq) in THF (2 mL).The mixture was

stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the solid was washed with pentane (2x3 mL) to obtain a pale yellow solid (115 mg) in 86% yield. Crystallization from THF at 6 °C gave pale yellow crystals suitable

for X-ray study. M.p. : 124 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 1.29 (s, 18H, C(CH₃)₃); 1.49 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂); 1.64 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂); 3.55 (s, 4H, GeCH₂SO); 4.44 (sept., ³J_{HH} = 6.3 Hz, 4H, CH(CH₃)₂); 6.91 (m, 6H, CH_{Ar}); 7.80 (m, 4H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 21.9 (CH(CH₃)₂); 26.4 (CH(CH₃)₂); 29.3 (C(CH₃)₃); 39.7 (C(CH₃)₃); 48.1 (CH(CH₃)₂); 58.3 (GeCH₂SO); 126.8 (C_{Ar}); 129.1 (C_{Ar}); 131.8 (C_{Ar}); 146.3 (C_{Ar/q}); 176.7 (N–C–N); 207.3 (CO). IR (Nujol, cm⁻¹): 2035 (s) (CO), 1999 (s) (CO), 1877 (br) (CO), 1376 (med) (SO₂), 1107 (med) (SO₂). MS (Maldi-TOF) *m/z* (%): 1090 ([M - CO]⁺).

Formula	C40H60Ge2N4O8S2W, 2(C4H8O)	dcalc (g/cm ³)	1.492
Mol wt	1262.31	μ (mm ⁻¹)	3.233
Temp. (K)	193(2)	<i>F</i> (000)	1284
Cryst syst	Monoclinic	cryst size (mm)	0.18 x 0.06 x 0.04
Space group	P2 ₁ /c	θ range (deg.)	3.17 to 29.13
a (Å)	14.4295(4)	index range h k l	-17<=h<=19, - 13<=k<=13, - 27<=l<=27
b (Å)	9.8795(3)	no of reflns collected /	103290
c (Å)	19.7788(6)	unique	7550 [R(int) = 0.0388
α (deg.)	90	Completeness to θ max(%)	99.9
β (deg.)	94.6630(10)	data/restraints/params	7550 / 65 / 340
γ (deg.)	90	goodness-of-fit	1.113
V (Å3)	2810.26(15)	R1, wR2 ($I > 2\sigma(I)$)	0.0229, 0.0443
Ζ	2	R1, wR2 (all data)	0.0315, 0.0475



Amidinate (di-*iso*-propyle-*t*-butyl) germylene methyl-*p*tolylsulfoxide molybdenum tetracarbonyl complex (4b): Amidinate (di-*iso*-propyle-*t*-butyl) germylene methyl-*p*tolylsulfoxyde 1b (150 mg, 0.367 mmol, 1 eq) was dissolved in tetrahydrofran (5 mL). The solution was then added to (bicyclo[2.2.1]hepta-2,5-

diene)tetracarbonylmolybdenum(0) (55 mg, 0.184 mmol,

0.5 eq) in THF (2 mL) at room temperature. The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the solid
was washed with pentane (2x3 mL) to obtain a pale yellow solid (159 mg) in 84% yield. Crystallization from THF at 6 °C gave yellow crystals suitable for X-ray study. M.p. : 103 °C; ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 1.28 (s, 18H, C(CH₃)₃); 1.46 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂); 1.56 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.58 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.99 (s, 6H, *p*-CH₃); 2.90 (d, 2H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.35 (d, 2H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 4.27 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 4.37 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 6.88 (d, 4H, ³J_{HH} = 8.2 Hz, CH_{Ar}); 7.53 (d, 4H, ³J_{HH} = 8.2 Hz, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 21.1 (*p*-CH₃); 23.2 (CH(CH₃)₂); 23.4 (CH(CH₃)₂); 26.2 (CH(CH₃)₂); 59.8 (GeCH₂SO); 123.7 (C_{Ar}); 129.9 (C_{Ar}); 139.7 (C_{Ar/q}); 148.4 (C_{Ar/q}); 174.8 (N–*C*–N); 216.5 (*CO*). IR (Nujol, cm⁻¹): 2021 (s) (CO), 1999 (s) (CO), 1905 (s) (CO), 1015 (med) (SO). MS (Maldi-TOF) *m/z* (%): 1026 ([M⁺).

Formula	C42H64Ge2MoN4O6S2, 2(C4H8O)	dcalc (g/cm ³)	1.362
Mol wt	1170.42	$\mu (mm^{-1})$	1.387
Temp. (K)	193(2)	<i>F</i> (000)	610
Cryst syst	Triclinic	cryst size (mm)	0.220 x 0.180 x 0.080
Space group	P-1	θ range (deg.)	3.144 to 25.684
a (Å)	9.9669(5)	index range h k l	-11<=h<=12, - 14<=k<=14, - 16<=l<=16
b (Å)	11.7085(8)	no of reflns collected /	21442
c (Å)	13.3702(10)	unique	5306 [R(int) = 0.0717]
α (deg.)	79.929(3)	Completeness to θmax(%)	98.6
β (deg.)	77.221(2)	data/restraints/params	5306 / 37 / 332
γ (deg.)	70.656(2)	goodness-of-fit	1.123
V (Å3)	3136.1(2)	R1, wR2 (I > $2\sigma(I)$)	0.0658, 0.0867
Ζ	1	R1, wR2 (all data)	0.0947, 0.0939

Chapter II: Germylene - α - Sulfoxide Ligands: Synthesis, Characterization and Coordination of a

Novel Hemilabile Metallylene Ligand



Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfoxideRuthenium complex (5a):A solution ofamidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfoxyde1a(151 mg, 0.38 mmol, 1eq) withtris(triphenylphosphine)ruthenium(II)dichloride(364mg, 0.38mmol, 1eq)in tetrahydrofran (5 mL)was stirred during 15 hour at

room temperature. Then, the mixture was filtered and the solvent was removed under reduced pressure in order to obtain a red solid. Finally, the resulting solid was washed with diethyl ether (3x5 mL) to afford a red solid (240 mg) in 58% yield. M.p. : 145 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆): δ 0.78 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 0.88 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 0.94 (s, 9H, C(CH₃)₃); 1.09 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.35 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 2.86 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.61 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.69 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 6.90 (m, 3H, CH_{Ar(sulfoxide)}); 7.09 (m, 19H, CH_{Ar(phosphine)}); 7.45 (m, 2H, CH_{Ar(sulfoxide)}); 7.93 (m, 11H, CH_{Ar(phosphine)}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆): δ 24.0 (CH(CH₃)₂); 24.8 (CH(CH₃)₂); 25.0 (CH(CH₃)₂); 25.5 (CH(CH₃)₂); 25.8 (C_{Ar(sulfoxide)}); 127.0 (³J_{PC} = 9.0 Hz, C_{Ar(phosphine)}); 128.7 (C_{Ar(phosphine)}); 128.9 (C_{Ar(sulfoxide)}); 127.0 (³J_{PC} = 19.6 Hz, C_{Ar(phosphine)}); 138.0 (¹J_{PC} = 12.2 Hz, C_{Ar(q(phosphine)}); 144.2 (C_{Ar/q(sulfoxide)}); 175.5 (N–C–N). ³¹P NMR (121.49 MHz, C₆D₆): δ 24.5 (br, Ru-PPh₃); 55.5 (br, Ru-PPh₃). MS (Maldi-TOF) *m/z* (%): 830 (M – PPh₃), 795 (M – (PPh₃ + Cl)), 760 (M – (PPh₃ + Cl + Cl)). IR (Nujol, cm⁻¹): 934 (med) (SO).

Formula	C54H60Cl2GeN2OP2RuS	dcalc (g/cm ³)	1.417
Mol wt	1091.62	μ (mm ⁻¹)	1.130
Temp. (K)	193(2)	<i>F</i> (000)	2248
Cryst syst	Monoclinic	cryst size (mm)	0.04 x 0.04 x 0.02
Space group	P2 ₁ /c	θ range (deg.)	3.45 to 25.35
a (Å)	12.5612(6)	index range h k l	-15<=h<=14, - 29<=k<=29, - 20<=l<=19
b (Å)	24.1634(10)	no of reflns collected /	58061
c (Å)	16.9752(9)	unique	9335 [R(int) = 0.1056]
α (deg.)	90	Completeness to θmax(%)	99.6

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β (deg.)	96.627(2)	data/restraints/params	9335 / 0 / 584
γ (deg.)	90	goodness-of-fit	1.032
V (Å3)	5117.9(4)	R1, wR2 (I > $2\sigma(I)$)	0.0446, 0.0996
Ζ	4	R1, wR2 (all data)	0.0866, 0.1195





Amidinate (di-iso-propyle-t-butyl) germylene methyl-ptolylsulfoxide Ruthenium complex (5c): A solution of amidinate (di-iso-propyle-t-butyl) germylene methyl-p-tolylsulfoxyde 1b (151 0.38 mg, mmol, leq) with tris(triphenylphosphine)ruthenium(II) dichloride (364mg, 0.38 mmol, 1eq) in tetrahydrofran (5 mL) was stirred during 15 hour at

room temperature. Then, DPPP (158 mg, O.45 mmol, 1.2 eq) was added to the mixture and stirred 4 hour and the solvent was evaporated under vacuum. Finally, the red solid was washed with pentane (3x5 mL) in order to obtain a pale red solid. ${}^{31}P{}^{1}H{}$ NMR (121.49 MHz, C₆D₆): δ 26.1 (d, ³J_{PP} = 47.3 Hz, Ru-*PP*h₂); 47.5 (d, ³J_{PP} = 47.3 Hz, Ru-*PP*h₂).

Formula	C46H58Cl2GeN2OP2 RuS, 1.5(C4H10O)	dcalc (g/cm ³)	1.375
Mol wt	1104.68	μ (mm ⁻¹)	1.086
Temp. (K)	193(2)	F(000)	1150
Cryst syst	Triclinic	cryst size (mm)	0.180 x 0.080 x 0.080
Space group	P-1	θ range (deg.)	5.100 to 30.508
a (Å)	9.6109(7)	index range h k l	-13<=h<=13, - 19<=k<=19, - 30<=l<=30
b (Å)	13.8981(11)	no of reflns collected /	100922
c (Å)	21.5911(16)	unique	16207 [R(int) = 0.0637]
α (deg.)	101.572(3)	Completeness to θ max(%)	99.1
β (deg.)	95.184(3)	data/restraints/params	16207 / 87 / 632
γ (deg.)	106.959(3)	goodness-of-fit	1.024
V (Å3)	2668.2(4)	$R1, wR2 (I > 2\sigma(I))$	0.0355, 0.0762
Ζ	2	R1, wR2 (all data)	0.0555, 0.0845

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Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfoxideRuthenium complex (6a):Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfoxide1a(170 mg, 0.43 mmol, 1 eq)was dissolved in tetrahydrofran (5 mL)and dichloro(p-cymene)ruthenium dimer (132 mg, 0.215 mmol,

0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then, filtered and the solvent removed under reduced pressure. Finally, the red solid was washed with Et₂O (2x3 mL) in order to obtain a pale red solid (247 mg) in 82% yield. M.p. : 164 °C (decomposition); ¹H NMR (300.18 MHz, CD_2Cl_2 , 25 °C): δ 1.29-1.37 (m, 9H, CH(CH₃)₂); 1.38-1.44 (d, ³J_{HH} = 6.3 Hz, 9H, CH(CH₃)₂); 1.59 (s, 9H, C(CH₃)₃); 2.21 (s, 3H, *p*-CH₃); 2.86 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 2.85 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.12 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 4.42 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 5.08 (m, 2H, CH_{Ar}); 5.41 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} = 1.3 Hz, CH_{Ar}); 5.53 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} = 1.3 Hz, CH_{Ar}); 7.39-7.45 (m, 3H, CH_{Ar}); 7.51-7.55 (m, 2H, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, *C*₆*D*₆, 25 °C): δ 1.8.6 (p-CH₃); 22.9 (CH(CH₃)₂); 23.2 (CH(CH₃)₃); 31.2 (CH(CH₃)₂); 39.5 (C(CH₃)₃); 50.6 (GeCH₂SO); 56.2 (CH(CH₃)₂); 56.5 (CH(CH₃)₂); 81.7 (C_{Ar}); 82.7 (C_{Ar}); 87.9 (C_{Ar}); 93.8 (C_{Art/q}); 106.7 (C_{Art/q}); 123.7 (C_{Ar}); 129.2 (C_{Ar}); 129.6 (C_{Ar}); 150.3 (C_{Art/q}); 176.8 (N–C–N).

Formula	C28H44Cl2GeN2ORuS	dcalc (g/cm ³)	1.493
Mol wt	701.29	μ (mm ⁻¹)	1.708
Temp. (K)	193(2)	<i>F</i> (000)	1440
Cryst syst	Monoclinic	cryst size (mm)	0.48 x 0.34 x 0.28
Space group	P21/n	θ range (deg.)	2.99 to 31.00
a (Å)	9.1389(14)	index range h k l	-13<=h<=13, - 29<=k<=29, - 24<=l<=24
b (Å)	20.527(3)	no of reflns collected /	117282
c (Å)	16.685(3)	unique	9912 [R(int) = 0.0353]
α (deg.)	90	Completeness to θmax(%)	99.6
β (deg.)	94.363(7)	data/restraints/params	99.12 / 511 / 501
γ (deg.)	90	goodness-of-fit	1.145

V (Å3)	3120.9(8)	R1, wR2 (I > $2\sigma(I)$)	0.0465, 0.0963
Ζ	4	R1, wR2 (all data)	0.0524, 0.1004



Amidinate(di-*iso*-**propyle-***t*-**butyl) germylene methyl**-*p*-**tolylsulfoxide Ruthenium complex (6b):** Amidinate (di-*iso*-propyle-*t*-butyl) germylene methyl-*p*-tolylsulfoxide **1b** (135 mg, 0.330 mmol, 1 eq) was dissolved in tetrahydrofran (5 mL) and dichloro(*p*-cymene)ruthenium dimer (101 mg, 0.165

mmol, 0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the red solid was washed with Et₂O (2x3 mL) in order to obtain a pale red solid (189 mg) in 80% vield. Suitable crystals for x-ray crystallography were obtained from a saturated solution of THF at -24 °C. M.p. : 169 °C (decomposition); ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.23 (d, ³J_{HH} = 6.8 Hz, 3H, CH(C H_{3})₂); 1.24 (d, ³J_{HH} = 6.8 Hz, 3H, CH(C H_{3})₂); 1.27 (d, ³J_{HH} = 6.8 Hz, 3H, CH(CH₃)₂); 1.33 (s, 9H, C(CH₃)₃); 1.35 (d, ${}^{3}J_{HH} = 6.8$ Hz, 3H, CH(CH₃)₂); 1.55 (d, ${}^{3}J_{HH} = 6.3$ Hz, 3H, CH(CH₃)₂); 1.57 (d, ${}^{3}J_{HH} = 6.3$ Hz, 3H, CH(CH₃)₂); 1.93 (s, 3H, *p*-CH₃); 1.95 (s, 3H, p-CH₃); 2.96 (sept., ${}^{3}J_{HH} = 6.3$ Hz, 1H, CH(CH₃)₂); 3.54 (d, 1H, ${}^{2}J_{HH} = 13.8$ Hz, GeCH₂SO); 3.72 (d, 1H, ${}^{2}J_{HH} = 13.8$ Hz, GeCH₂SO); 4.14 (sept., ${}^{3}J_{HH} = 6.3$ Hz, 1H, CH(CH₃)₂); 4.28 (sept., ${}^{3}J_{HH} = 6.3 \text{ Hz}, 1\text{H}, CH(CH_{3})_{2}); 4.78 \text{ (dd, 1H, } {}^{3}J_{HH} = 5.8 \text{ Hz}, {}^{4}J_{HH} = 1.3 \text{ Hz}, CH_{Ar}); 4.82 \text{ (dd, 1H, } 10.2 \text{ Hz}); 4.82 \text{ (dd, 1H, } 10.2 \text{ Hz$ ${}^{3}J_{HH} = 5.8 \text{ Hz}, {}^{4}J_{HH} = 1.3 \text{ Hz}, CH_{Ar}$; 5.25 (dd, 1H, ${}^{3}J_{HH} = 5.8 \text{ Hz}, {}^{4}J_{HH} = 1.3 \text{ Hz}, CH_{Ar}$); 5.33 (dd, 1H, ${}^{3}J_{HH} = 5.8 \text{ Hz}$, ${}^{4}J_{HH} = 1.3 \text{ Hz}$, CH_{Ar}); 6.77 (d, 2H, ${}^{3}J_{HH} = 8.2 \text{ Hz}$, CH_{Ar}); 7.45 (d, 2H, ${}^{3}J_{HH} = 8.2 \text{ Hz}, CH_{Ar}$. ${}^{13}C{}^{1}H{}$ NMR (75.48 MHz, C₆D₆, 25 °C): δ 18.8 (*p*-*C*H₃); 21.1 (*p*-*C*H₃); 22.8 (CH(CH₃)₂); 23.2 (CH(CH₃)₂); 24.4 (CH(CH₃)₂); 25.0 (CH(CH₃)₂); 25.9 (CH(CH₃)₂); 26.7 (CH(*C*H₃)₂); 29.0 (C(*C*H₃)₃); 31.2 (*C*H(CH₃)₂); 39.4(*C*(CH₃)₃); 48.0 (*C*H(CH₃)₂); 48.1 (*C*H(CH₃)₂); 50.6 (Ge*C*H₂SO); 80.8 (*C*_{Ar}); 81.5 (*C*_{Ar}); 86.8 (*C*_{Ar}); 88.1 (*C*_{Ar}); 94.0 (*C*_{Ar/q}); 108.2 $(C_{Ar/q})$; 123.6 (C_{Ar}) ; 129.9 (C_{Ar}) ; 139.6 $(C_{Ar/q})$; 147.4 $(C_{Ar/q})$; 176.9 (N-C-N). MS m/z (anthracene matrix) : 681 ($[M - Cl]^+$), 547 ([M - Cl - p-Cymene]⁺). HRMS (ESI) m/z (%): 717.1054 ($[M + 1]^+$) calcd for C₂₉H₄₆GeCl₂N₂ORuS ($[M + 1]^+$) 717.1046. IR (Nujol, cm⁻¹): 1462 (med) (C=C_{arene}), 1017 (med) (SO).

Formula	C29H46Cl2GeN2ORuS	dcalc (g/cm ³)	1.515
Mol wt	715.30	$\mu (mm^{-1})$	1.702
Temp. (K)	193(2)	<i>F</i> (000)	1472

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Cryst syst	Monoclinic	cryst size (mm)	0.040 x 0.040 x 0.020
Space group	P21/n	θ range (deg.)	5.104 to 28.282
a (Å)	15.0511(6)	index range h k l	-20<=h<=20, - 18<=k<=18, - 19<=l<=20
b (Å)	14.1158(6)	no of reflns collected /	75426
c (Å)	15.4835(6)	unique	7729 [R(int) = 0.0799]
α (deg.)	90	Completeness to θ max(%)	99.1
β (deg.)	107.5740(16)	data/restraints/params	7729 / 542 / 500
γ (deg.)	90	goodness-of-fit	1.017
V (Å3)	3136.1(2)	R1, wR2 (I > $2\sigma(I)$)	0.0364, 0.0624
Ζ	4	R1, wR2 (all data)	0.0748, 0.0728



Amidinate (dicyclohexyl-t-butyl) germylene methylphenylsulfoxide Ruthenium dichloro *p*-cymene **complex** (6c): Amidinate(dicyclohexyl-*t*-butyl) germylene methylphenylsulfoxide 1c (65 mg, 0.139 mmol, 1 eq) was tetrahydrofran (5 mL) dissolved in and dichloro(*p*-

cymene)ruthenium dimer (42 mg, 0.139 mmol, 0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the red solid was washed with Et₂O (2x2 mL) in order to obtain a pale red solid (84 mg) in 78% yield. M.p. : 173 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 1.08-1.21 (m, 4H, 4H, (CH₂)_{cy}); 1.24 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.27 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.40 (s, 9H, C(CH₃)₃); 1.43-1.94 (m, 12H, (CH₂)_{cy}); 1.97 (s, 3H, *p*-CH₃); 2.01-2.22 (m, 2H, (CH₂)_{cy}); 2.36 (m, 1H, (CH₂)_{cy}); 2.67 (m, 1H, (CH₂)_{cy}); 2.94 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 3.60 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.76 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.87 (m, 1H, CH(CH₂)₂); 3.97 (m, 1H, CH(CH₂)₂); 4.87 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} = 1.3 Hz, CH_{Ar}); 5.38 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} = 1.3 Hz, CH_{Ar}); 5.38 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} = 1.3 Hz, CH_{Ar}); 6.86-6.96 (m, 2H, CH_{Ar}); 7.52-7.55 (m, 2H, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 18.6 (*p*-CH₃); 22.9 (CH(CH₃)₂); 23.2 (CH(CH₃)₂); 25.3 (CH₂); 25.7 (CH₂); 25.9 (CH₂); 26.0 (CH₂); 26.2 (CH₂); 26.3 (CH₂); 29.1 (C(CH₃)₃); 31.2 (CH(CH₃)₂); 34.3 (CH₂); 34.8 (CH₂); 36.2 (CH₂); 37.4 (CH₂); 39.5 (C(C(H₃)₃); 50.7 (GeCH₂SO); 56.2 (CH(CH₂)₂); 56.5 (CH(CH₂)₂); 81.7

(C_{Ar/q}); 82.7 (C_{Ar/q}); 86.1 (C_{Ar/q}); 87.9 (C_{Ar}); 93.8 (C_{Ar/q}); 106.7 (C_{Ar/q}); 123.7 (C_{Ar}); 129.2 (C_{Ar}); 129.6 (C_{Ar}); 150.3 (C_{Ar/q}); 176.8 (N–C–N).

Formula	C34H52Cl2GeN2ORuS	dcalc (g/cm ³)	1.471
Mol wt	781.39	μ (mm ⁻¹)	1.519
Temp. (K)	193(2)	<i>F</i> (000)	1616
Cryst syst	Orthorhombic	cryst size (mm)	0.500 x 0.160 x 0.050
Space group	Pca2 ₁	θ range (deg.)	2.925 to 30.559
a (Å)	18.0845(6)	index range h k l	-25<=h<=23, - 13<=k<=13, - 29<=l<=29
b (Å)	9.3573(3)	no of reflns collected /	10.5479
c (Å)	20.8554(7)	unique	10806 [R(int) = 0.0560]
α (deg.)	90	Completeness to θ max(%)	99.8
β (deg.)	90	data/restraints/params	10806 / 1 / 386
γ (deg.)	90	goodness-of-fit	1.074
V (Å3)	3529.3(2)	R1, wR2 (I > $2\sigma(I)$)	0.0325, 0.0597
Ζ	4	R1, wR2 (all data)	0.0446, 0.0652



Amidinate (dicyclohexyl-*t*-butyl) germylene methyl-*p*tolylsulfoxide Ruthenium dichloro *p*-cymene complex (6d): Amidinate(dicyclohexyl-*t*-butyl) germylene methyl-*p*tolylsulfoxyde 1d (110 mg, 0.22 mmol, 1 eq) was dissolved in tetrahydrofran (5 mL) and dichloro(*p*-cymene)ruthenium

dimer (69 mg, 0.11 mmol, 0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then, filtered and the solvent removed under reduced pressure. Finally, the red solid was washed with Et₂O (2x2 mL) in order to obtain a pale red solid (138 mg) in 79% yield. M.p.: 175°C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 1.08-1.21 (m, 4H, 4H, (CH₂)_{cy}); 1.24 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.27 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.40 (s, 9H, C(CH₃)₃); 1.43-1.94 (m, 12H, (CH₂)_{cy}); 1.97 (s, 3H, *p*-CH₃); 2.01-2.22 (m, 2H, (CH₂)_{cy}); 2.36 (m, 1H, (CH₂)_{cy}); 2.67 (m, 1H, (CH₂)_{cy}); 2.94 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 3.60 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.76 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.87 (m, 1H, CH(CH₂)₂); 3.97 (m, 1H, CH(CH₂)₂); 4.87 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} = 1.3 Hz, CH_{Ar}); 4.94 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} = 1.3 Hz, CH_{Ar}); 5.31 (dd, 1H, ³J_{HH} = 5.8 Hz, ⁴J_{HH} =

1.3 Hz, CH_{Ar}); 5.38 (dd, 1H, ${}^{3}J_{HH} = 5.8$ Hz, ${}^{4}J_{HH} = 1.3$ Hz, CH_{Ar}); 6.86-6.96 (m, 2H, CH_{Ar}); 7.52-7.55 (m, 2H, CH_{Ar}). ${}^{13}C\{{}^{1}H\}$ NMR (75.48 MHz, $C_{6}D_{6}$, 25 °C): δ 18.6 (*p*-CH₃); 22.9 (CH(CH_{3})₂); 23.2 (CH(CH_{3})₂); 25.3 (CH_{2}); 25.7 (CH_{2}); 25.9 (CH_{2}); 26.0 (CH_{2}); 26.2 (CH_{2}); 26.3 (CH_{2}); 29.1 ($C(CH_{3})_{3}$); 31.2 ($CH(CH_{3})_{2}$); 34.3 (CH_{2}); 34.8 (CH_{2}); 36.2 (CH_{2}); 37.4 (CH_{2}); 39.5 ($C(CH_{3})_{3}$); 50.7 (Ge CH_{2} SO); 56.2 ($CH(CH_{2})_{2}$); 56.5 ($CH(CH_{2})_{2}$); 81.7 ($C_{Ar/q}$); 82.7 ($C_{Ar/q}$); 86.1 ($C_{Ar/q}$); 87.9 (C_{Ar}); 93.8 ($C_{Ar/q}$); 106.7 ($C_{Ar/q}$); 123.7 (C_{Ar}); 129.2 (C_{Ar}); 129.6 (C_{Ar}); 150.3 ($C_{Ar/q}$); 176.8 (N–C–N). HRMS (ESI) *m/z* (%): 797.1659 ([M + 1]⁺) calcd for $C_{35}H_{54}GeCl_2N_2ORuS$ ([M + 1]⁺) 797.1674.

Formula	C35H54Cl2GeN2ORuS	dcalc (g/cm ³)	1.460
Mol wt	795.44	μ (mm ⁻¹)	1.483
Temp. (K)	193(2)	<i>F</i> (000)	1648
Cryst syst	Monoclinic	cryst size (mm)	0.08 x 0.08 x 0.02
Space group	P2 ₁ /n	θ range (deg.)	3.49 to 27.48
a (Å)	9.5361(14)	index range h k l	-12<=h<=12, - 20<=k<=20, - 32<=l<=32
b (Å)	15.417(2)	no of reflns collected /	58979
c (Å)	24.820(5)	unique	8267 [R(int) = 0.0507]
α (deg.)	90	Completeness to θ max(%)	99.8
β (deg.)	97.325(7)	data/restraints/params	8267 / 72 / 422
γ (deg.)	90	goodness-of-fit	1.145
V (Å3)	3619.2(10)	R1, wR2 ($I > 2\sigma(I)$)	0.0326, 0.0887
Ζ	4	R1, wR2 (all data)	0.0470, 0.0965



Amidinate(di-iso-propyle-t-butyl)germylenemethyl-t-butylsulfoxideRutheniumdichlorop-cymenecomplexAmidinate(di-iso-propyl-t-butyl)germylenemethyl-t-butylsulfoxideIf(110mg, 0.29mmol, 1eq)wasdissolved intetrahydrofran(5mL)and

mg, 0.145 mmol, 0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the red solid was washed with Et_2O (2x3 mL) in order to obtain a pale red solid (132 mg) in 67% yield. Crystallization from THF at – 25 °C gave red crystals suitable for X-ray diffraction. M.p.

: 84 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 0.95 (s, 9H, SO-C(CH₃)₃); 1.23 – 1.31 (m, 12H, CH(CH₃)₂); 1.28 (s, 9H, C(CH₃)₃); 1.49 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.56 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.94 (s, 3H, *p*-CH₃); 2.98 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 3.24 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 3.32 (d, 1H, ²J_{HH} = 13.8 Hz, GeCH₂SO); 4.09 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 4.20 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 4.73 (d, 1H, ³J_{HH} = 5.8 Hz, CH_{Ar}); 4.75 (d, 1H, ³J_{HH} = 5.8 Hz, CH_{Ar}); 5.25 (d, 1H, ³J_{HH} = 5.8 Hz, CH_{Ar}); 5.31 (d, 1H, ³J_{HH} = 5.8 Hz, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 18.8 (*p*-CH₃); 22.6 (SOC(CH₃)₃); 22.8 (CH(CH₃)₂); 23.1 (CH(CH₃)₂); 24.3 (CH(CH₃)₂); 24.9 (CH(CH₃)₂); 26.0 (CH(CH₃)₂); 26.6 (CH(CH₃)₂); 28.9 (C(CH₃)₃); 31.2 (CH(CH₃)₂); 36.8 (SO-C(CH₃)₃); 39.3 (C(CH₃)₃); 47.9 (CH(CH₃)₂); 48.0 (CH(CH₃)₂); 54.3 (GeCH₂SO); 80.6 (C_{Ar/q}); 81.4 (C_{Ar/q}); 87.2 (C_{Ar/q}); 88.2 (C_{Ar}); 93.9 (C_{Ar/q}); 108.3 (C_{Ar/q}); 176.7 (N-C-N). IR (Nujol, cm⁻¹): 1017 (med). HRMS (ESI) *m/z* (%): 683.1205 ([M + 1]⁺) calcd for C₂₆H₄₈GeCl₂N₂ORuS ([M + 1]⁺) 683.1201.

Formula	C26H48Cl2GeN2ORuS	dcalc (g/cm ³)	1.478
Mol wt	681.30	μ (mm ⁻¹)	1.739
Temp. (K)	193(2)	<i>F</i> (000)	704
Cryst syst	Monoclinic	cryst size (mm)	0.200 x 0.180 x 0.140
Space group	P21	θ range (deg.)	4.104 to 34.337
a (Å)	10.3057(5)	index range h k l	-16<=h<=16, - 18<=k<=18, - 18<=l<=20
b (Å)	11.3503(6)	no of reflns collected /	44633
c (Å)	13.1474(6)	unique	12768 [R(int) = 0.0234]
α (deg.)	90	Completeness to θ max(%)	99.5
β (deg.)	95.520(2)	data/restraints/params	12768 / 81 / 350
γ (deg.)	90	goodness-of-fit	1.037
V (Å3)	1530.76(13)	R1, wR2 ($I > 2\sigma(I)$)	0.0186, 0.0470
Ζ	2	R1, wR2 (all data)	0.0207, 0.0480



Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylthioetherRuthenium dichloro p-cymene complex(6g):Amidinate(di-iso-propyl-t-butyl)germylenemethylphenylthioether1g (85 mg, 0.22 mmol, 1 eq) was dissolved in

tetrahydrofran (5 mL) and dichloro(*p*-cymene)ruthenium dimer (68 mg, 0.11 mmol, 0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the red solid was washed with Et₂O (2x3 mL) to obtain a red solid (104 mg) in 69% yield. Suitable crystals for x-ray crystallography were obtained from a saturated solution of THF at -24 °C. M.p.: 158 °C (decomposition); ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.20 (s, 9H, C(CH₃)₃); 1.21 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.28 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.33 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.93 (s, 3H, *p*-CH₃); 3.02 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 3.65 (s, 2H, GeCH₂SPh); 3.96 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 4.68 (d, ³J_{HH} = 5.7 Hz, 2H, CH_{Ar}); 5.27 (d, ³J_{HH} = 5.7 Hz, 2H, CH_{Ar}); 6.80-6.85 (m, 1H, CH_{Ar}); 6.92-6.97 (m, 2H, CH_{Ar}); 7.24-7.27 (m, 2H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 18.9 (p-CH₃); 31.2 (CH(CH₃)₂); 39.2 (C(CH₃)₃); 48.0 (CH(CH₃)₂); 80.4 (C_{Ar}); 87.9 (C_{Ar}); 94.2 (C_{Ar/q}); 108.7 (C_{Ar/q}); 124.5 (C_{Ar}); 126.8 (C_{Ar}); 129.0 (C_{Ar}); 141.2 (C_{Ar/q}); 175.2 (N-C-N). MS (Maldi-TOF) *m/z* (anthracene matrix) : 651 ([M - CH]⁺), 515 ([M - Cl – *p*-Cymene]⁺).

Formula	C28H44Cl2GeN2RuS	dcalc (g/cm ³)	1.514
Mol wt	685.29	μ (mm ⁻¹)	1.769
Temp. (K)	193(2)	<i>F</i> (000)	1408
Cryst syst	Monoclinic	cryst size (mm)	0.140 x 0.060 x 0.010
Space group	P2 ₁ /n	θ range (deg.)	4.200 to 34.750
a (Å)	11.3474(6)	index range h k l	-17<=h<=18, - 23<=k<=22, - 29<=l<=29
b (Å)	14.4680(7)	no of reflns collected /	43298
c (Å)	18.5286(10)	unique	12937 [R(int) = 0.0456]
α (deg.)	90	Completeness to θ max(%)	99.5
β (deg.)	98.650(3)	data/restraints/params	12937 / 78 / 353
γ (deg.)	90	goodness-of-fit	1.014
V (Å3)	3007.3(3)	$R1, wR2 (I > 2\sigma(I))$	0.0360, 0.0714
Ζ	4	R1, wR2 (all data)	0.0675, 0.0812

Novel Hemilabile Metallylene Ligand



Amidinate(di-iso-propyle-t-butyl)germylenemethylphenylsulfoneRuthenium dichloro p-cymene complex(6h):Amidinate(di-iso-propyl-t-butyl)germylenemethylphenylsulfone1h (200 mg, 0.486 mmol, 1 eq) was dissolvedin tetrahydrofran (5 mL) and dichloro(p-cymene)ruthenium dimer

(149 mg, 0.243 mmol, 0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure. Finally, the red solid was washed with Et₂O (2x3 mL) in order to obtain a pale red solid (293 mg) in 84% yield. Suitable crystals for X-ray crystallography were obtained from a saturated solution of THF at -24 °C. M.p.: 178 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 1.23 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.29 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.32 (s, 9H, C(CH₃)₃); 1.67 (d, ${}^{3}J_{HH} = 6.3$ Hz, 6H, CH(CH₃)₂); 1.91 (s, 3H, *p*-CH₃); 2.95 (sept., ${}^{3}J_{HH} =$ 6.3 Hz, 1H, CH(CH₃)₂); 4.15 (s, 2H, GeCH₂SO₂); 4.22 (sept., ${}^{3}J_{HH} = 6.3$ Hz, 2H, CH(CH₃)₂); 4.75 (d, 2H, ${}^{3}J_{HH} = 5.8$ Hz, C H_{Ar}); 5.24 (d, 2H, ${}^{3}J_{HH} = 5.8$ Hz, C H_{Ar}); 6.73-6.84 (m, 3H, C H_{Ar}); 7.68-7.77 (m, 2H, C H_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 18.6 (p-CH₃); 22.9 (CH(*C*H₃)₂); 23.6 (CH(*C*H₃)₂); 26.5 (CH(*C*H₃)₂); 28.9 (C(*C*H₃)₃); 31.1 (*C*H(CH₃)₂); 39.3(*C*(CH₃)₃); 48.3 (*C*H(CH₃)₂); 48.7 (Ge*C*H₂SO); 81.7 (*C*_{Ar}); 87.2 (*C*_{Ar}); 94.0 (*C*_{Ar/a}); 108.4 $(C_{Ar/a})$; 126.5 (C_{Ar}) ; 129.0 (C_{Ar}) ; 131.9 (C_{Ar}) ; 145.7 $(C_{Ar/a})$; 177.9 (N-C-N). MS m/z (anthracene matrix) : 683 ($[M - Cl]^+$), 549 ([M - Cl - p-Cymene]⁺). HRMS (ESI) m/z (%): 719.0850 ($[M + 1]^+$) calcd for C₂₈H₄₄Cl₂GeN₂O₂RuS ($[M - Cl]^+$) 719.0838. IR (Nujol, cm⁻¹): 1305 (med) (SO), 1140 (med) (SO).

Formula	C28H44Cl2GeN2O2RuS	dcalc (g/cm ³)	1.472
Mol wt	717.29	μ (mm ⁻¹)	1.652
Temp. (K)	193(2)	<i>F</i> (000)	2944
Cryst syst	Monoclinic	cryst size (mm)	0.16 x 0.15 x 0.07
Space group	P21/n	θ range (deg.)	2.94 to 25.68
a (Å)	18.7846(10)	index range h k l	-22<=h<=22, - 21<=k<=21, - 25<=l<=25
b (Å)	17.6499(8)	no of reflns collected /	249295
c (Å)	20.9404(11)	unique	12278 [R(int) = 0.0753]
α (deg.)	90	Completeness to θmax(%)	99.8

Chapter II: Germylene - α - Sulfoxide Ligands: Synthesis, Characterization and Coordination of a N

β (deg.)	111.232(2)	data/restraints/params	12278 / 452 / 825
γ (deg.)	90	goodness-of-fit	1.060
V (Å3)	6471.4(6)	R1, wR2 (I > $2\sigma(I)$)	0.0314, 0.0654
Ζ	8	R1, wR2 (all data)	0.0475, 0.0738

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Chapter III:

Hemilabile Germylene -β- Sulfoxide Ligand: Synthesis, Characterization and Coordination Properties toward Group VI, VIII and X Transition Metals

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Abstract

A hemilabile amidinate germylene $-\beta$ - sulfoxide ligand has been synthesized in two steps in good yield from the readily available GeCl₂•dioxane and aryl-*tert*-butylsulfoxide.

The germylene $-\beta$ - sulfoxide ligand was easily converted into tungsten, molybdenum, ruthenium phosphine and nickel complexes. NMR spectroscopy, X-ray diffraction and IR studies revealed that different types of coordination are possible with the amidinate germylene $-\beta$ - sulfoxide, thus confirming the hemilabile character of this ligand. The new architecture especially shows different coordination properties, compared to germylene $-\alpha$ - sulfoxide, toward group VI transition metals and ruthenium.

I. Introduction

The previous chapter showed that germylene $-\alpha$ - sulfoxide can act as a hemilabile ligand of ruthenium (II) complex via coordination by oxygen and germylene atoms (Scheme 1). On the other hand, bis-germylene complexes were obtained with group VI transition metals (molybdenum and tungsten). The formation of bis-monodentate complexes instead of a bidentate one can be explained by favorable interaction of group VI transition metals at the (0) oxidation state with soft center like sulfur. However, coordination with sulfur of germylene $-\alpha$ sulfoxide would imply the formation of an unfavorable strained 4-member ring that would be a transient intermediate to react further with another equivalent of ligand to form a more stable bis-germylene complex.



Scheme 1: Carbene and heavier analogues in ground state

The design of a 2^{nd} generation of germylene-sulfoxide ligand was considered by increasing the distance between both moieties.

The modification of the distance between the two entities could provide a variety of coordination to transition metals with germylene and sulfur or oxygen atoms of the sulfoxide group (Figure 1).¹

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Figure 1: Different possibilities of coordination of hemilabile germylene sulfoxide ligand to a transition metal

The importance of the linker between two different moieties was observed over the years with the increasing amount of publications on sulfoxide ligands. Relevant examples can be mentioned with the reports of Alcock *et al.* and Liao *et al.* in 1988 and 2011 respectively (Scheme 2).^{2,3} In the first case, oxygen and phosphorus were coordinated to rhodium through a 5-member ring. The coordination by sulfur atom appears unfavorable due to the formation of a strained 4-member ring. Nevertheless, it was confirmed latter, by Liao *et al.*, that increasing the distance between phosphorus and sulfoxide allowed to form a more favorable 5-member ring with sulfur in comparison of a 6-member ring with oxygen.



Scheme 2: Phosphinosulfoxide-rhodium complexes

Thereby, synthesis of a 2^{nd} generation of hemilabile bi-dentate ligands will be described in this chapter. Several complexes of transition metals with different properties of coordination will be characterized and compared to the 1^{st} generation of ligands.

II. Results and discussion

II.1. Synthesis of amidinatogermylene $-\beta$ - sulfoxide

Synthetic pathway to obtain the 2nd generation of ligands remains the same as previously described, exploiting the nucleophilic substitution of the chlorine atom of AmGeCl precursor. The choice of the sulfoxide moiety for this second generation was focused on the aryl-*tert*-butylsulfoxide. Indeed *ortho*-deprotonation of the aromatic ring will take place since sulfoxide acts as an *ortho*-directing group when α -position is saturated (Scheme 3).^{4,5}



Scheme 3: ortho- versus α-deprotonation of alkyl-arylsulfoxides

tert-Butyl-*p*-tolyl-sulfoxide has been obtained in two steps from the corresponding thiocresol. The first reaction consists of the formation of the corresponding thioether in acidic conditions followed by an oxidation of thioether into sulfoxide according to the report of Grela in 2009 (Scheme 4).^{6,7}



Scheme 4: Synthesis of tert-butyl-p-tolyl-sulfoxide

Finally, the first β -sulfoxide amidinatogermylene has been synthetized according to the method used for the 1st generation. *tert*-butyl-*p*-tolyl-sulfoxide was deprotonated with ⁿBuLi at -80 °C for 1h and then was added to AmGeCl at the same temperature. After 2h, the solvent was removed under reduced pressure at room temperature and extraction afforded **7a** in a good 82%yield (Scheme 5).

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Scheme 5: Synthesis of 2nd generation ligand 7a

7a was unambiguously characterized by NMR spectroscopy. ¹H NMR spectrum exhibits a characteristic singlet in the aromatic part at 7.65 ppm corresponding to the hydrogen in *ortho*-position of germylene. Moreover, the chiral center of the sulfoxide has also a noticeable impact on the amidinato *iso*-propyl groups, both -N-C*H*-(CH₃)₂ showing different chemical shifts at 3.97 and 4.10 ppm due to the loss of symmetry. However, the major difference observed concerns the -N-CH-(C*H*₃)₂ substituents. Indeed, the starting material shows two doublets, due to planar symmetry, contrary to four doublets in the product at 0.66, 0.92, 1.09 and 1.23 ppm. The four doublets of the methyl groups are again a consequence of the loss of symmetry in the molecule brought by the stereogenic sulfoxide moiety, as already observed in the 1st generation (Figure 2).



Figure 2: ¹H NMR spectrum of **7a**

¹³C NMR spectrum has also evidenced a solid proof on the formation of **7a**. Aromatic carbon bonded to germanium appears as a quaternary carbon at 138.8 ppm. The chiral center has again a noticeable influence on the amidinate *iso*-propyl groups, each carbon being non-equivalent. The tertiary carbons (-N-*C*H-(CH₃)₂) appear as two peaks with close chemical shifts (47.3 and 47.4 ppm) and the primary carbons (-N-CH-(*C*H₃)₂) appear as four different signals (24.2, 24.4, 27.5 and 27.7 ppm).

It was not possible to obtain crystals of 7a, due to its degradation at room temperature in solid state or in solution. The mechanism of degradation has not been studied as well as the resulting by-products. However, it has been determined 7a was stable at -24 °C and no degradation was observed at this temperature after a week. This observation led to try crystallization at low temperature without any success.

Mass spectroscopy analysis have been performed to validate the formation of **7a** with another analytical method. However, amidinatogermylene and *tert*-butyl-*p*-tolyl-sulfoxide fragment were the only peaks to appear in electronic impact and MALDI-TOF analysis.

Finally, the synthesis was extended to the corresponding sulfone, exploiting the *ortho*directing effect of the sulfone group. *tert*-Butyl-*p*-tolyl-sulfone was obtained in two steps from the corresponding thiocresol as previously described, via the oxidation of thioether into sulfone according to the report of Paolini in 1995 and Grela in 2009 (Scheme 6).^{8,9}



Scheme 6: Formation of *tert*-butyl-*p*-tolyl-sulfone

tert-Butyl-*p*-tolyl-sulfone was deprotonated with ^{*n*}BuLi at -80 °C for 1h and then was added to AmGeCl at the same temperature. After 2h, the solvent was removed under reduced pressure at room temperature and extraction afforded **7b** in a good 82% yield (Scheme 7).

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Scheme 7: Synthesis of 2^{nd} generation germylene - β - sulfone ligand **7b**

¹H NMR of **7b** showed the same characteristic signal as **7a** with a singlet for aromatic hydrogen in *ortho*-position of germylene at 8.08 ppm. ¹³C NMR spectrum has also evidenced a solid proof on the formation of **7b**. Indeed, all the aromatic carbons had different chemical shifts, which demonstrated the loss of symmetry induced by the germylene group in *ortho*-position compared to the starting material that showed only four signals for the aromatic carbons due to the planar symmetry.

II.2. Coordination properties of amidinatogermylene -β- sulfoxide ligand

First, coordination chemistry was studied with tungsten (0), tested in the previous chapter and **7a**. Indeed, 1^{st} generation ligand gave a bis-germylene complex in place of a bidentate one. The hypothesis was a weak or impossible coordination of sulfur through the strained 4-member ring led to the coordination of a second germylene to the tungsten. Starting with an equimolar amount of [W(cod)(CO)₄] precursor, a solution of **7a** in THF was added at room temperature and stirred overnight (Scheme 8).



Scheme 8: Synthesis of tungsten complex 8

Complex **8** was obtained with a good 89% yield. Interestingly, formation of a bidentate complex was observed with sulfur and germanium atoms coordinated to tungsten center. Coordination was determined by IR spectroscopy with a band at 1067 cm⁻¹ characteristic of a sulfur bonded to the transition metal.^{10,11} Another indication was observed in ¹³C NMR spectrum with four signals at 202.1, 206.7, 208.3 and 210.2 ppm corresponding to the carbonyls ligands of the tungsten having different chemical shifts due to the loss of symmetry brought by the bidentate coordination and the asymmetric sulfoxide center. ¹H and ¹³C NMR spectra exhibit no others special chemical shifts. Finally, X-ray structure of **2** was obtained from crystals from a THF solution at 6 °C (Figure 3).



Figure 3: Molecular structure of 8 (hydrogens are omitted for clarity)

The structure of **8** shows an octahedral geometry with an usual bond distance between the germylene and the tungsten of 2.5661(5) Å (2.50-2.65 Å), which is slightly longer than the distance observed for the 1st generation bis-germylene complex (2.52 Å).^{12–15} Unsurprisingly, Ge1–N1 and Ge1–N2 bond lengths of 1.951(3) and 1.952(3) Å are equal and shorter than the

free AmGeCl (1.98 Å) due to the coordination of the germylene lone pair to the transition metal. The other bond lengths and angles are in the normal range of a germylene-tungsten complex. It is important to note, to the best of our knowledge, that complex **8** is the first crystallized example of a tungsten complex coordinated by a sulfur atom of a sulfoxide function.

Then, coordination has been extended to determine if the same reactivity would be observed with molybdenum (0), lighter analogue of tungsten (0). Starting with the same ligand **7a** and an equimolar amount of $Mo(nbd)(CO)_4$, **9** was obtained after stirring overnight the mixture at room temperature in THF (Scheme 9).



Scheme 9: Synthesis of molybdenum complex 9

Again, a bidentate complex was obtained with sulfur and germanium atoms coordinated to molybdenum center. Coordination was confirmed by IR spectroscopy (1089 cm⁻¹) and ¹³C NMR analysis (209.3, 214.0, 216.9 and 220.8 ppm). X-ray structure of **9** was obtained from crystals grown in a saturated solution of THF at 6 °C (Figure 4). The structure shows an octahedral geometry with a germylene-molybdenum distance slightly longer of 2.5758(6) Å, but still in the range of complexes previously reported (2.50-2.54 Å).^{13,16-18} Ge1–N1 and Ge1–N2 bond lengths of 1.955(2) and 1.969(2) Å are equal and shorter than in the free AmGeCl (1.98 Å) due to coordination of the germylene lone pair to the transition metal. Again, to the best of our knowledge, this structure is the first crystallized example of a molybdenum complex coordinated by a sulfur atom of a sulfoxide function.

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Figure 4: Molecular structure of 9 (hydrogens are omitted for clarity)

The formation of bidentate germylene group VI complexes confirmed that modulation of the design of the ligand by increasing the distance between each moiety allowed coordination of the metal by the sulfur of the sulfoxide.

Then ruthenium(II) was investigated in the continuity of our study for its ability to be coordinated either by sulfur or oxygen atom, as previously observed in the previous chapter with bidentate coordination by oxygen and germanium.¹⁹ An equimolar amount of $Ru(PPh_3)_3Cl_2$ and **7a** were stirred overnight in a solution of THF at room temperature (Scheme 10).



Scheme 10: synthesis of germylene $-\beta$ - sulfoxide ruthenium complex **10a**

³¹P NMR of the crude product showed a clean formation of **10a** as a 16-electron complex with one singlet signal at 38 ppm and a singlet for two equivalents of free PPh₃ at -5 ppm. Moreover, coordination with sulfur was determined by IR spectroscopy with a characteristic band at 1095 cm⁻¹. However, even if **10a** was unambiguously characterized by

mass spectroscopy (809.1114 ($[M - Cl - i-Pr]^+$)), crystallization afforded systematically bisruthenium complex **10b** (Scheme 11). μ –SO bridged binuclear transition metal complexes were already observed in the literature with ruthenium and rhodium.^{20–24} Nevertheless, it is important to note that all the complexes characterized were obtained with DMSO and **10b** is therefore the first example of μ –SO bridged ruthenium complex with an asymmetric sulfoxide. It is also the first example characterized with two additional chlorine atoms participating at the bridge.



Scheme 11: germylene bis-ruthenium phosphine complex 10b

X-ray structure exhibits two distorted octahedral ruthenium atoms with chlorine and sulfoxide bridges (Figure 5). Germanium-ruthenium bond distance of 2.3669(5) Å is in the range of already reported complexes (2.28-2.50 Å).^{25–29} Phosphine and ruthenium have usual distance of 2.2737(11), 2.3072(12) and 2.3673(11) Å. The chlorine atoms in axial position have very particular angles, Cl1–Ru1-Cl2 of 170.43(4)° and Cl4–Ru1–Cl2 of 159.53(4)° explained by the bridge between the two ruthenium atoms. Ge1–Ru1–S1 and Ge1–Ru1–P1 angles of the 5-member ring are 84.33(3)° and 96.51(3)° respectively. The ruthenium-oxygen distance, 2.197(3) Å, is in the range of reported complexes bearing a phosphine in trans position (2.15-2.24 Å),^{30–32} but the distance is slightly longer than in the μ –SO bridge of complexes already reported (2.06-2.16 Å).^{20–23} Finally, ruthenium-sulfur bond length of 2.3374(10) Å is in the top range of bridge μ –SO complexes already described (2.19-2.34 Å).^{20–23} This result can be explained by a high donation of the phosphine located in trans-position that can weaken the bond and increase the length between ruthenium and sulfur. Nevertheless, it is to the best of our knowledge the first example of a trans-phosphine-sulfoxide complex fully characterized.



Figure 5: Molecular structure of **10b** (hydrogens are omitted for clarity)

Interestingly, when crystals of **10b** were analyzed by ³¹P NMR in CD₂Cl₂, we observed the presence of three isomers in a 68 / 18 / 14 ratio. Chemical shifts for the three isomers were observed at 28.7, 39.9 and 29.5 respectively for singlet phosphorus in *trans* position of sulfur atom. The two-other phosphorus located on the second ruthenium appeared as six doublets for the three isomers. Analysis at variable temperature was carried out to determine if temperature could have an influence on the ratio of the three isomers. However, any change of the ration was observed by varying the temperature on the range of +35 to -70 °C (Figure 6).



Two hypothesis could explain the formation of three molecules. The first hypothesis was positions isomers resulting of the interconversion of phosphine with non-bridging chlorine (Figure 7). The second hypothesis was decoordination of a bridging atom and coordination of a solvent molecule or formation of an empty site (Figure 7).



Figure 7: Possible formation of three molecules in solution

The second hypothesis, relying on decoordination, should depend on the solvent. Indeed, the ratio between the three isomers should change with a coordinating solvent compare to a non-coordinating solvent. However, ³¹P NMR of **10b** in CD₂Cl₂ and fluorobenzene shows the exact same ratio between the three isomers which prove that the solvent is not coordinating (Figure 8). Still, an empty site formed by decoordination is possible.



Figure 8: ³¹P of **10b** in CD₂Cl₂ and fluorobenzene

Finally, calculations were performed to obtain informations on the structure of the three isomers observed in solutions (The B3LYP/6-31g(d,p) basis set and SDD for Ru was used). **10b** was optimized by replacing the aryl linker with an alkene and by replacing the substituents on the amidinate by methyl groups (Figure 9).



Figure 9: Optimized molecule of **10b** used for calculations
The result on the potential-energy surface (PES) showed that decoordination, with formation of an empty site, of the sulfoxide or a bridging chloride is not occurring. This result may indicate that the three molecules are position isomers. However, the size of the molecule did not allow to obtain results to conclude yet on the structure of the three isomers with calculations.

Finally, coordination chemistry was studied with group 10 transition metal. $Ni(cod)_2$ was used as precursor in presence of an equimolar amount of **7a** in toluene at room temperature (Scheme 12).



Scheme 12: synthesis of germylene nickel(cod) complex 11a

Nickel complex **11a** was obtained after 20 min as a very unstable yellow solid. ¹H NMR spectrum showed a fast and complete formation of **11a** after 5 min and characteristic signal of coordinated cod was observed with four alkene protons observed at 5.41, 5.09, 4.85, 4.54 ppm. **11a** degraded quickly at room temperature and the product(s) formed during degradation has not been characterized but we suppose the formation of Ni(II) species because of the rapid apparition of broaden signals. It is also important to note the concomitant formation of free cod during the degradation process (Figure 10). This instability should be explained by oxidative insertion of nickel into sulfur carbon bond to form a novel Ni(II) complex as reported by Radius *et al.* in 2007.³³

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Figure 10: **11a** ¹H NMR spectrum in cod area of some crystals in young tube and monitored after 1 hour in solution at room temperature

Nevertheless, crystals of **11a** were obtained and characterized by X-ray crystallography (Figure 11).



Figure 11: Molecular structure of **11a** (hydrogens are omitted for clarity)

X-ray structure of **11a** exhibits a distorted tetrahedral geometry with an usual Ge1– Ni1 bond length of 2.2625(3) Å in the range of already reported for germylene-nickel complexes (2.09 - 2.30 Å).^{18,34–38} The Ni1–S1 bond distance, 2.1591(4) Å, is slightly longer in comparison of the results already published by Peters in 2012 (2.10-2.13 Å).³⁹ Ge1–Ni1– S1angle is 90.025(14)° which lie in 5-member ring angles. It is important to note that Ge1–N1 and Ge1–N2 bond lengths of 1.9893(14) and 1.9913(13) Å are in the same range than the free AmGeCl (1.98 Å). Indeed, Ge-N bond length usually decreases due to the higher donation of nitrogen to germanium when the latest is coordinated to a transition metal. In our case, this

result can be explained by the electron rich nickel (0) center that should perform π -back donation to the germylene center.

Finally, we have evaluated the reactivity of **11a** in a pressure of carbon monoxide to give **11b** as a stable nickel complex at room temperature in toluene (Scheme 13).



Scheme 13: synthesis of germylene nickel tricarbonyl complex 11b

The very fast ligand exchange at room temperature led to the formation of the tricarbonyl nickel complex, demonstrating the hemilabile character of the ligand by replacing the weak σ -donor by another ligand. The structure of **11b** has been determined by ¹³C NMR analysis, with only one signal for the carbonyl ligands at 199 ppm, and by IR spectroscopy with a band at 1027 cm⁻¹, confirming no coordination of sulfoxide to the nickel and finally by X-ray diffraction analysis of crystals obtained from a saturated solution of toluene at -24 °C (Figure 12).



Figure 12: Molecular structure of **11b** (hydrogens are omitted for clarity)

X-ray structure of **11b** exhibits a nickel center with a tetrahedral geometry with a slightly longer Ge–-Ni1 bond length of 2.3202(4) Å, but still in the range of already reported germylene-nickel complexes (2.09 - 2.30 Å).^{18,34–38} Ge1-N1 and Ge1–N2 bond lengths of 1.9598(18) and 1.971(2) Å are equal and shorter than in the free AmGeCl (1.98 Å), which can be explained by a better donation of the germanium to the nickel and a smaller π –back donation than for **5a**.

The specific structure of **11b** as $LNi(CO)_3$ allows a TEP (Tolman Electronic Parameter) comparison with other well-known ligands as phosphines or NHCs. The goal of TEP comparison consists in the correlation of the value of IR band stretching frequency of the carbon monoxyde ligands with the electron density of the transition metal (Figure 13).⁴⁰ In the case of an electron rich ligand , the metal–carbon bond is shorter and strengthen due to π -backbonding of the metal to the ligands that will decrease carbonyl band shift due to weaken carbon–oxygen triple bond. In the other case of an electron poor ligand, the π -backbonding is lower and will increase carbonyl band shift due to stronger carbon–oxygen triple bond.



Figure 13: Carbonyl complex to determine TEP

IR spectroscopy of **11b** shows in dichloromethane a carbonyl band at 2058 cm⁻¹, which prove a better σ -donor strength than most of the phosphines like P(OMe)₃ (2080 cm⁻¹), PMe₃ (2066 cm⁻¹) or PCy₃ (2060 cm⁻¹),⁴¹ but the result showed poorest σ -donor strength than NHCs like IMes (2052 cm⁻¹), *i*-Pr (2051 cm⁻¹) or Me (2058 cm⁻¹), or silylene (2046 cm⁻¹) (Figure 14).^{42,43} TEP comparison of tricarbonyl nickel complexes shows that **11b** stand between the σ -donation strength of trialkylphosphines and common NHCs. However, the complex can be assigned as a better σ -donor than the germylene nickel complex published by Hoge *et al.* in 2016 with a band at 2067 cm⁻¹,⁴⁴ and also better that the germylene with alkoxy bridge reported by Du Mont *et al.* in 1984 (2070 cm⁻¹) or the one reported by Denk *et al.* in 2011 (2071 cm⁻¹).^{38,45}



Figure 14: TEP comparison of several Ni(CO)₃ complexes

III. Conclusion

A 2^{nd} generation of germylene-sulfoxide ligand has been obtained by metal metathesis of AmGeCl chlorine atom with *ortho*-lithiated aromatic sulfoxide in a good 82% yield. This novel β -sulfoxide germylene ligand presents a stability comparable to that of the 1st generation. Its design presents a larger distance between sulfoxide and germylene moieties, allowing to modulate its coordination properties.

Thereby, germylene - β - sulfoxide ligand reacts with W(cod)(CO)₄ or Mo(nbd)(CO)₄ precursors to form the corresponding complexes in a good yield of 89 %. Bidentate coordination has been observed with germanium and sulfur atoms coordinated to the metal center. The characterization of bidentate germylene complexes confirmed that the formation of bis-germylene complexes obtained during the use of 1st generation α -sulfoxide germylene ligands is due to a less stable coordination of sulfur through a strained 4-member ring.

Coordination was also investigated with $Ru(PPh_3)_3Cl_2$ to give a novel 16 electron complex. Surprisingly, an unprecedented bis-ruthenium complex with sulfoxide and chlorine bridges has been obtained by crystallization. ³¹P NMR analysis show the formation of three isomers in solution whereas only one is observed in X-ray diffraction analysis.

Group 10 transition metal was also investigated with Ni(cod)₂ precursor. The corresponding complex is highly unstable. Nevertheless, its structure has been determined by X-ray diffraction analysis to show a bidentate complex with germanium and sulfur atoms coordinated to nickel (0). Reaction with carbon monoxide affords a stable tricarbonyl nickel (0) complex, confirming the hemilabile character of this ligand by exchange of the sulfoxide for a stronger σ -donating ligand. Finally, TEP comparison of carbonyl bands by IR spectroscopy shows that the σ -donor strength of germylene ligand is between the σ -donor strength of phosphines and NHCs.

IV. Experimental section



Amidinate (diisopropyle-*t*-butyl) *t*-butyl-*p*-tolylsulfoxide germylene (7a): *n*-BuLi (0.72 mmol, 0.48 mL, C = 1.6 mol/L in hexane, 1.1 eq) was added dropwise to a solution of *t*-butyl-*p*tolylsulfoxide (141.1 mg, 0.72 mmol, 1.1 eq) in toluene (3 mL) at -78 °C. The solution was stirred during 1 hour at the same temperature (-78 °C). Then the mixture was added dropwise to a solution of AmGeCl (189 mg, 0.65 mmol, 1 eq) in toluene (3 mL) at -78 °C. The mixture

was stirred during 2 hours at -78 °C and then warmed up to room temperature slowly. The solvent was evaporated under reduced pressure, the crude was then extracted with toluene (2x 2mL) and concentrated in order to afford a yellow oil (241 mg) in 82% yield. The compound is stable and storable at -24 °C in an inert atmosphere of argon. ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 0.66 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 0.92 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.09 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.14 (s, 9H, C(CH₃)₃); 1.23 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.29 (s, 9H, C(CH₃)₃); 2.20 (s, 3H, *p*-CH₃); 3,97 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 4.10 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 7.04 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}); 7.64 (s, 1H, CH_{Ar}); 7.97 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 21.5 (*p*-CH₃); 23.8 (O=SC(CH₃)₃); 24.2 (CH(CH₃)₂); 24.4 (CH(CH₃)₂); 27.5 (CH(CH₃)₂); 27.7 (CH(CH₃)₂); 29.3 (C(CH₃)₃); 40.2 (C(CH₃)₃); 138.8 (C_{Ar/q}); 145.8 (C_{Ar/q}); 159.5 (C_{Ar/q}); 171.9 (N–C–N).



Amidinate (diisopropyle-*t*-butyl) *t*-butyl-*p*-tolylsulfone germylene (7b): *n*-BuLi (0.60 mmol, 0.38 mL, C = 1.6 mol/L in hexane, 1.1 eq) was added dropwise to a solution of *t*-butyl-*p*tolylsulfone (127 mg, 0.60 mmol, 1.1 eq) in toluene (3 mL) at -78 °C. The solution was stirred during 1 hour at the same temperature

(-78 °C). Then the solution was added dropwise to a solution of AmGeCl (189 mg, 0.55 mmol, 1 eq) in toluene (2 mL) at -78 °C. The mixture was stirred during 1 hour at -78 °C and 1 hour at room temperature. The solvent was evaporated under reduced pressure, the crude was then extracted with toluene (2x 2mL) and concentrated in order to afford a light yellow solid (211 mg) in 82% yield. ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 0.93 (d, ³J_{HH} = 6.3 Hz, 6H,

CH(CH₃)₂); 1.11 (s, 9H, C(CH₃)₃); 1.34 (d, ³J_{HH} = 6.3 Hz, 6H, CH(CH₃)₂); 1.36 (s, 9H, C(CH₃)₃); 2.18 (s, 3H, *p*-CH₃); 4.10 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 6.93 (d, 1H, ³J_{HH} = 8.0 Hz, CH_{Ar}); 7.93 (d, 1H, ³J_{HH} = 8.0 Hz, CH_{Ar}); 8.08 (s, 1H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 21.6 (p-CH₃); 23.6 (CH(CH₃)₂); 24.0 (CH(CH₃)₂); 27.4 (CH(CH₃)₂); 27.6 (CH(CH₃)₂); 29.3 (C(CH₃)₃); 29.4 (S(O)₂C(CH₃)₃); 40.1 (C(CH₃)₃); 47.8 (CH(CH₃)₂); 58.9 (S-C(CH₃)₃); 127.9 (C_{Ar}); 131.4 (C_{Ar}); 134.8 (C_{Ar}); 139.0 (C_{Ar/q}); 141.9 (C_{Ar/q}); 164.7 (C_{Ar/q}); 172.2 (N-C-N).



Amidinate (diisopropyle-*t*-butyl) germylene *t*-butyl-*p*tolylsulfoxide tungsten tetracarbonyl complex (8): Amidinate (diisopropyle *t*-butyl) *t*-butyl-*p*-tolylsulfoxide germylene (7a) (140 mg, 0.31 mmol, 1 eq) was dissolved in THF (3 mL) and added to tetracarbonyl(1,5-cyclooctadiene) tungsten (0) (125 mg, 0.31 mmol, 1 eq) in THF (1 mL). The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under

reduced pressure. Finally, the solid was washed with pentane (2 x 3 mL) to obtain a pale yellow solid (206 mg) in 89% yield. Crystallization from a solution of THF at 6 °C gave pale yellow crystals suitable for X-ray diffraction analysis. M.p. : 117 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 0.54 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 0.81 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.06 (s, 9H, C(CH₃)₃); 1.20 (s, 9H, C(CH₃)₃); 1.23 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.29 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 2.13 (s, 3H, *p*-CH₃); 3.98 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 4.08 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 6.87 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}); 7.34 (s, 1H, CH_{Ar}); 8.17 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 20.9 (p-CH₃); 22.9 (CH(CH₃)₂); 24.0 (O=SC(CH₃)₃); 24.8 (CH(CH₃)₂); 25.6 (CH(CH₃)₂); 65.8 (O=S-C(CH₃)₃); 125.7 (C_{Ar}); 130.0 (C_{Ar}); 130.1 (C_{Ar}); 140.9 (C_{Ar/q}); 149.4 (C_{Ar/q}); 153.4 (C_{Ar/q}); 177.9 (N-C-N); 202.1 (CO); 206.7 (CO); 208.3 (CO); 210.2 (CO). IR (Nujol, cm⁻¹) : 2012 (s) (CO), 1901 (br) (CO), 1067 (s) (SO). MS m/z (%): 704.1 ([M – (CO+CH₃)]⁺). HRMS *m/z* (%): 747.1320 ([M + 1]⁺) calcd for C₂₆H₃₈GeN₂O₅WS ([M + 1]⁺) 747.1311.

Formula	C28H44Cl2GeN2O2RuS	dcalc (g/cm ³)	1.472
Mol wt	717.29	μ (mm ⁻¹)	1.652
Temp. (K)	193(2)	<i>F</i> (000)	2944

Cryst syst	Monoclinic	cryst size (mm)	0.16 x 0.15 x 0.07
Space group	P2 ₁ /n	θ range (deg.)	2.94 to 25.68
a (Å)	18.7846(10)	index range h k l	-22<=h<=22, - 21<=k<=21, - 25<=l<=25
b (Å)	17.6499(8)	no of reflns collected /	249295
c (Å)	20.9404(11)	unique	12278 [R(int) = 0.0753]
α (deg.)	90	Completeness to θmax(%)	99.8
β (deg.)	111.232(2)	data/restraints/params	12278 / 452 / 825
γ (deg.)	90	goodness-of-fit	1.060
V (Å3)	6471.4(6)	R1, wR2 ($I > 2\sigma(I)$)	0.0314, 0.0654
Ζ	8	R1, wR2 (all data)	0.0475, 0.0738

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Amidinate (diisopropyle-t-butyl) germylene t-butyl-p-tolyl sulfoxide molybdenum tetracarbonyl complex (9): Amidinate (diisopropyle t-butyl) t-butyl-p-tolylsulfoxide germylene (7a) (100 mg, 0.22 mmol, 1 eq) was dissolved in THF (3 mL) and added to tetracarbonyl(bicyclo[2.2.1]hepta-2,5-diene) molybdenum (0) (66 mg, 0.22 mmol, 1 eq) in THF (1 mL). The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed

under reduced pressure. Finally, the solid was washed with pentane (2 x 3 mL) to obtain a pale yellow solid (113 mg) in 78% yield. Crystallization from a solution of THF at 6 °C gave pale yellow crystals suitable for X-ray diffraction analysis. M.p. : 98 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 0.54 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 0.80 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.05 (s, 9H, C(CH₃)₃); 1.20 (s, 9H, C(CH₃)₃); 1.22 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.29 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 2.11 (s, 3H, *p*-CH₃); 3.91 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 6.90 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}); 7.32 (s, 1H, CH_{Ar}); 8.14 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 21.0 (p-CH₃); 23.0 (CH(CH₃)₂); 23.9 (O=SC(CH₃)₃); 24.8 (CH(CH₃)₂); 25.8 (CH(CH₃)₂); 25.9 (CH(CH₃)₂); 29.2 (C(CH₃)₃); 39.8 (C(CH₃)₃); 47.4 (CH(CH₃)₂); 48.2 (CH(CH₃)₂); 64.1 (O=S-C(CH₃)₃); 126.1 (C_{Ar}); 129.8 (C_{Ar}); 130.2 (C_{Ar}); 140.4 (C_{Ar/q}); 148.6 (C_{Ar/q}); 152.2 (C_{Ar/q}); 177.3 (N-C-N); 209.3 (CO); 213.9 (CO); 216.9 (CO); 220.8 (CO). IR (CH₂Cl₂, cm⁻¹) : 2005 (s) (CO), 1882 (br) (CO), 1089 (s) (SO). MS *m/z* (%): 659.24 ([M⁺).

Formula	C28H44Cl2GeN2O2BuS	deale (g/cm^3)	1 472
Tormula	C201144C12OCN2O2Ru5	deale (g/elli)	1.7/2
Mol wt	717.29	$\mu (mm^{-1})$	1.652
Temp. (K)	193(2)	<i>F</i> (000)	2944
Cryst syst	Monoclinic	cryst size (mm)	0.16 x 0.15 x 0.07
Space group	P2 ₁ /n	θ range (deg.)	2.94 to 25.68
a (Å)	18.7846(10)	index range h k l	-22<=h<=22, - 21<=k<=21, - 25<=l<=25
b (Å)	17.6499(8)	no of reflns collected /	249295
c (Å)	20.9404(11)	unique	12278 [R(int) = 0.0753]
α (deg.)	90	Completeness to θmax(%)	99.8
β (deg.)	111.232(2)	data/restraints/params	12278 / 452 / 825
γ (deg.)	90	goodness-of-fit	1.060
V (Å3)	6471.4(6)	R1, wR2 ($I > 2\sigma(I)$)	0.0314, 0.0654
Ζ	8	R1, wR2 (all data)	0.0475, 0.0738

Chapter III: Hemilabile Germylene -β- Sulfoxide Ligand: Synthesis, Characterization and Coordination Properties toward Group 6, 8 and 10 Transition Metals



Amidinate (diisopropyle-*t*-butyl) germylene *t*-butyl-*p*-tolyl sulfoxide ruthenium phosphine complex (10a): Amidinate (diisopropyle *t*-butyl) *t*-butyl-*p*-tolylsulfoxide germylene (7a) (100 mg, 0.22 mmol, 1 eq) was dissolved in THF (3 mL) and added to tris(triphenylphosphine) ruthenium dichloride (211 mg, 0.22 mmol, 1 eq). The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced pressure.

Finally, the crude was dissolved in THF (2 mL) and pentane (8 mL) was added slowly to precipite **10a**. After filtration and evaporation, a red solid (135 mg) in 69% yield was obtained with 15% of the starting PPh₃ remaining. ³¹P{¹H} NMR (121.49 MHz, C₆D₆): δ 38.0 (s, Ru-*P*Ph₃). HRMS *m/z* (%): 850.1379 ([M + ACN - Cl - *i*-Pr]⁺) calcd for C₃₉H₄₉ClGeN₃OPRuS ([M + ACN - Cl - *i*-Pr]⁺) 850.1368, 809.1114 ([M - Cl - *i*-Pr]⁺), 809.1114 ([M - Cl - *i*-Pr]⁺) calcd for C₃₇H₄₇ClGeN₂OPRuS ([M + ACN - Cl - *i*-Pr]⁺) 809.1102.



Amidinate (diisopropyle-t-butyl) germylene t-butyl-ptolylsulfoxide bis-Ruthenium phosphine complex (**10b): 10a** (135 mg, 0.15 mmol, 1 eq) was dissolved in THF (3 mL) in a vial and pentane was added in another vial. After two days of slow diffusion of pentane into THF, the crystals were filtered and washed with THF (2x 1mL) to obtain a pink solid (42 mg). M.p. : 144 °C

(decomposition); Isomer A : ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 0.24 (d, ³J_{HH} = 6.6 Hz, 3H, CH(C H_{3})₂); 0.45 (d, ³J_{HH} = 6.6 Hz, 3H, CH(C H_{3})₂); 0.51 (d, ³J_{HH} = 6.3 Hz, 3H, CH(C H_{3})₂); 0.81 (d, ³J_{HH}) $= 6.3 \text{ Hz}, 3\text{H}, CH(CH_3)_2$; 1.52 (s, 9H, C(CH₃)₃); 1.59 (s, 9H, C(CH₃)₃); 2.42 (s, 3H, p-CH₃); 3.91 (sept., ${}^{3}J_{HH} = 6.3 \text{ Hz}, 1\text{H}, CH(CH_{3})_{2}; 4.07 \text{ (sept., } {}^{3}J_{HH} = 6.3 \text{ Hz}, 1\text{H}, CH(CH_{3})_{2}; 6.18 \text{ (d, } 1\text{H}, {}^{3}J_{HH} = 8.2 \text{ Hz},$ CH_{Ar} ; 6.72-7.43 (m, 45H, CH_{Ar}); 7.91-7.94 (m, 2H, CH_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): δ 21.5 (p-CH₃); 24.4 (CH(CH₃)₂); 24.8 (CH(CH₃)₂); 25.6 (CH(CH₃)₂); 26.1 (O=SC(CH₃)₃); 27.6 (CH(*C*H₃)₂); 30.4 (C(*C*H₃)₃); 40.0 (*C*(CH₃)₃); 46.3 (*C*H(CH₃)₂); 48.1 (*C*H(CH₃)₂); 71.8 (O=S-*C*(CH₃)₃); 178.3 (N–*C*–N). ³¹P{¹H} NMR (200 MHz, C₆D₆): δ 28.7 (s, Ru-*P*Ph₃), 44.8 (d, ²J_{PP} = 42.0 Hz, Ru-PPh₃), 53.6 (d, ${}^{2}J_{PP} = 42.0 \text{ Hz}$, Ru-PPh₃). Isomer B : ${}^{1}H$ NMR (500 MHz, CDCl₃, 25 °C): δ -0.24 (d, ${}^{3}J_{HH} = 6.6$ Hz, 3H, CH(C H_{3})₂); 0.06 (d, ${}^{3}J_{HH} = 6.6$ Hz, 3H, CH(C H_{3})₂); 0.23 (d, ${}^{3}J_{HH} = 6.3$ Hz, 3H, $CH(CH_3)_2$; 0.69 (d, ${}^{3}J_{HH} = 6.3$ Hz, 3H, $CH(CH_3)_2$); 1.56 (s, 9H, $C(CH_3)_3$); 1.63 (s, 9H, $C(CH_3)_3$); 2.45 (s, 3H, *p*-C*H*₃); 3.77 (sept., ${}^{3}J_{HH} = 6.3$ Hz, 1H, C*H*(CH₃)₂); 3.96 (sept., ${}^{3}J_{HH} = 6.3$ Hz, 1H, C*H*(CH₃)₂); 6.72-7.43 (m, 50H, C H_{Ar}). ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C): δ 21.5 (p-CH₃); 23.5 (CH(CH₃)₂); 23.8 (CH(CH₃)₂); 25.0 (CH(CH₃)₂); 26.1 (O=SC(CH₃)₃); 26.7 (CH(CH₃)₂); 30.3 (C(CH₃)₃); 39.9 $(C(CH_3)_3); 47.0 (CH(CH_3)_2); 48.6 (CH(CH_3)_2); 71.9 (O=S-C(CH_3)_3); 178.0 (N-C-N).$ ³¹P{¹H} NMR (200 MHz, C_6D_6): δ 39.9 (s, Ru-*P*Ph₃), 41.6 (d, ²J_{PP} = 37.3 Hz, Ru-*P*Ph₃), 44.1 (d, ²J_{PP} = 37.3 Hz, Ru-PPh₃). Isomer C : ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 0.00 (d, ³J_{HH} = 6.6 Hz, 3H, CH(CH₃)₂); 0.16 $(d, {}^{3}J_{HH} = 6.6 \text{ Hz}, 3H, CH(CH_{3})_{2}); 0.39 (d, {}^{3}J_{HH} = 6.3 \text{ Hz}, 3H, CH(CH_{3})_{2}); 0.98 (d, {}^{3}J_{HH} = 6.3 \text{ Hz}, 3H, CH(CH_{3})_{2}$ CH(CH₃)₂); 1.52 (s, 9H, C(CH₃)₃); 1.59 (s, 9H, C(CH₃)₃); 2.46 (s, 3H, p-CH₃); 3.79 (sept., ${}^{3}J_{HH} = 6.3$ Hz, 1H, $CH(CH_3)_2$; 4.04 (sept., ${}^{3}J_{HH} = 6.3$ Hz, 1H, $CH(CH_3)_2$); 6.72-7.43 (m, 49H, CH_{Ar}); 8.44 (d, 1H, ${}^{3}J_{HH} = 8.2 \text{ Hz}, CH_{Ar}$). ${}^{13}C{}^{1}H} \text{ NMR (125 MHz, CDCl_3, 25 °C): } \delta 21.7 (p-CH_3); 23.2 (CH(CH_3)_2); 24.3$ (CH(CH₃)₂); 24.5 (CH(CH₃)₂; 26.1 (O=SC(CH₃)₃); 27.7 (CH(CH₃)₂); 30.2 (C(CH₃)₃); 40.1 (C(CH₃)₃); 46.5 (*C*H(CH₃)₂); 48.6 (*C*H(CH₃)₂); 69.7 (O=S-*C*(CH₃)₃); 178.4 (N-*C*-N). ³¹P{¹H} NMR (200 MHz, C_6D_6): δ 29.5 (s, Ru-*PPh*₃), 47.6 (d, ²J_{PP} = 40.9 Hz, Ru-*PPh*₃), 48.3 (d, ²J_{PP} = 40.9 Hz, Ru-*PPh*₃). IR (Nujol, cm⁻¹): 1162 (s) (SO). HRMS m/z (%): 1547.1821 ([M - Cl]⁺) calcd for $C_{76}H_{84}Cl_{3}GeN_{2}OP_{3}Ru_{2}S([M-Cl]^{+})$ 1547.1829.

Formula C28H44Cl2GeN2O2RuS	dcalc (g/cm^3)	1.472
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Mol wt	717.29	μ (mm ⁻¹)	1.652
Temp. (K)	193(2)	<i>F</i> (000)	2944
Cryst syst	Monoclinic	cryst size (mm)	0.16 x 0.15 x 0.07
Space group	P2 ₁ /n	θ range (deg.)	2.94 to 25.68
a (Å)	18.7846(10)	index range h k l	-22<=h<=22, - 21<=k<=21, - 25<=l<=25
b (Å)	17.6499(8)	no of reflns collected /	249295
c (Å)	20.9404(11)	unique	12278 [R(int) = 0.0753]
α (deg.)	90	Completeness to θmax(%)	99.8
β (deg.)	111.232(2)	data/restraints/params	12278 / 452 / 825
γ (deg.)	90	goodness-of-fit	1.060
V (Å3)	6471.4(6)	R1, wR2 (I $\geq 2\sigma(I)$)	0.0314, 0.0654
Ζ	8	R1, wR2 (all data)	0.0475, 0.0738

Chapter III: Hemilabile Germylene -β- Sulfoxide Ligand: Synthesis, Characterization and Coordination Properties toward Group 6, 8 and 10 Transition Metals



Amidinate (diisopropyle-*t*-butyl) *t*-butyl-*p*-tolylsulfoxide germylene nickel cyclooctadiene complex (11a): Amidinate (diisopropyle *t*-butyl) *t*-butyl-*p*-tolylsulfoxide germylene (7a) (140 mg, 0.31 mmol, 1 eq) and bis(1,5-cyclooctadiene) nickel (0) (125 mg, 0.31 mmol, 0.5 eq) were dissolved in toluene (3 mL). The mixture was stirred during 15 minutes at room temperature, the solvent was then removed under reduced pressure. Finally, the solid

was washed with pentane (2x3 mL) to obtain a yellow solid (206 mg) in 89% yield. Crystallization from a solution of toluene at -24 °C gave pale yellow crystals suitable for X-ray diffraction analysis. ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 0.51 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 0.85 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.10 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.15 (s, 9H, C(CH₃)₃); 1.28 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.41 (s, 9H, C(CH₃)₃); 1.98 (m, 1H, CH₂-HC=CH); 2.18 (s, 3H, *p*-CH₃); 2.34 (m, 2H, CH₂-HC=CH); 2.65 (m, 4H, CH₂-HC=CH); 3.22 (m, 1H, CH₂-HC=CH); 3.98 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 4.54 (m, 1H, CH₂-HC=CH); 4.85 (m, 1H, CH₂-HC=CH); 5.09 (m, 1H, CH₂-HC=CH); 5.41 (m, 1H, CH₂-HC=CH); 6.99 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}); 7.35 (s, 1H, CH_{Ar}); 8.30 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}).

Formula	C28H44Cl2GeN2O2RuS	dcalc (g/cm ³)	1.472
Mol wt	717.29	μ (mm ⁻¹)	1.652
Temp. (K)	193(2)	<i>F</i> (000)	2944
Cryst syst	Monoclinic	cryst size (mm)	0.16 x 0.15 x 0.07
Space group	P21/n	θ range (deg.)	2.94 to 25.68
a (Å)	18.7846(10)	index range h k l	-22<=h<=22, - 21<=k<=21, - 25<=l<=25
b (Å)	17.6499(8)	no of reflns collected /	249295
c (Å)	20.9404(11)	unique	12278 [R(int) = 0.0753]
α (deg.)	90	Completeness to θmax(%)	99.8
β (deg.)	111.232(2)	data/restraints/params	12278 / 452 / 825
γ (deg.)	90	goodness-of-fit	1.060
V (Å3)	6471.4(6)	R1, wR2 ($I > 2\sigma(I)$)	0.0314, 0.0654
Ζ	8	R1, wR2 (all data)	0.0475, 0.0738

Chapter III: Hemilabile Germylene -β- Sulfoxide Ligand: Synthesis, Characterization and Coordination Properties toward Group 6, 8 and 10 Transition Metals



Amidinate (diisopropyle-*t*-butyl) *t*-butyl-*p*-tolylsulfoxide germylene nickel tricarbonyl complex (11b): Amidinate (diisopropyle *t*-butyl) *t*-butyl-*p*-tolylsulfoxide germylene nickel (1,5cyclooctadiene) (11a) (80 mg, 0.13 mmol, 1 eq) in pressure tube was dissolved in C_6D_6 (0.5 mL) and $CO_{(gas)}$ atmosphere was added at room temperature (1.5 bar). The orange solution turn quickly bright yellow. Finally, the solvent was removed under reduced pressure and the solid

was washed with pentane (3x4 mL) to obtain a yellow solid (75 mg) in 93% yield. Crystallization from toluene at -24 °C gave pale yellow crystals suitable for X-ray diffraction analysis. M.p. : 132 °C (decomposition); ¹H NMR (300.18 MHz, C₆D₆, 25 °C): δ 0.62 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 0.94 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.06 (s, 9H, C(CH₃)₃); 1.16 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.26 (s, 9H, C(CH₃)₃); 1.33 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 2.12 (s, 3H, *p*-CH₃); 3.88 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 4.03 (m, 1H, CH₂-HC=CH); 6.98 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}); 7.63 (s, 1H, CH_{Ar}); 7.92 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, C₆D₆, 25 °C): δ 21.4 (p-CH₃); 23.5 (O=SC(CH₃)₃); 23.8 (CH(CH₃)₂); 24.4 (CH(CH₃)₂); 26.3 (CH(CH₃)₂); 26.5 (CH(CH₃)₂); 29.1 (C(CH₃)₃); 39.6

 $(C(CH_3)_3)$; 48.0 $(CH(CH_3)_2)$; 48.2 $(CH(CH_3)_2)$; 56.8 $(O=S-C(CH_3)_3)$; 126.6 (C_{Ar}) ; 130.0 (C_{Ar}) ; 133.0 (C_{Ar}) ; 139.6 $(C_{Ar/q})$; 145.7 $(C_{Ar/q})$; 151.2 $(C_{Ar/q})$; 173.6 (N-C-N); 199.0 (CO). IR (cm^{-1}) : 2059 (CO), 1982 (CO), 1027 (SO). HRMS m/z (%): 567.1246 $([M + 1 - CO]^+)$ calcd for $C_{24}H_{38}GeN_2O_4NiS ([M + 1]^+)$ 567.1241.

Formula	C28H44Cl2GeN2O2RuS	dcalc (g/cm ³)	1.472
Mol wt	717.29	μ (mm ⁻¹)	1.652
Temp. (K)	193(2)	<i>F</i> (000)	2944
Cryst syst	Monoclinic	cryst size (mm)	0.16 x 0.15 x 0.07
Space group	P2 ₁ /n	θ range (deg.)	2.94 to 25.68
a (Å)	18.7846(10)	index range h k l	-22<=h<=22, - 21<=k<=21, - 25<=l<=25
b (Å)	17.6499(8)	no of reflns collected /	249295
c (Å)	20.9404(11)	unique	12278 [R(int) = 0.0753]
α (deg.)	90	Completeness to θmax(%)	99.8
β (deg.)	111.232(2)	data/restraints/params	12278 / 452 / 825
γ (deg.)	90	goodness-of-fit	1.060
V (Å3)	6471.4(6)	R1, wR2 ($I > 2\sigma(I)$)	0.0314, 0.0654
Ζ	8	R1, wR2 (all data)	0.0475, 0.0738

V. Notes and references

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Chapter IV:

Design, Synthesis and Characterization of New Germylenes and Stannylenes Stabilized by Sulfonimidamides

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Abstract

Sulfonimidamide were synthesized with different substituents. This new design allowed to obtain similar or different groups on the nitrogen atom, with the formation of symmetric and asymmetric center on the sulfur atom. The design also allowed to incorporate a weak Lewis base in vision to form a hemilabile ligand.

Then, formation of homoleptic germylenes were obtained by protonolysis reaction. The reaction was finally extended to the formation of stannylenes. All the metallylenes were fully characterized by NMR spectroscopy and X-ray diffraction analysis.

Electronic properties of these new metallylenes were investigated by DFT calculations.

I. Introduction

The synthesis of new metallylenes was extensively studied the past decades and allowed to develop a large panel of electronic and steric properties¹⁻³ in order to obtain novel properties.^{4,5} Nevertheless, insertion of chirality in the design of the stabilizing substituents was only studied over few publications compared to the overall study of carbene analogues (Figure 1). Hahn *et al.* have reported in 2010 the first germylene with chiral N,N'-substituents,⁶ followed the next year by the publication of Mochida *et al.* with a bis(oxazoline) ligand and finally Baceiredo *et al.* with a P,N-stabilized germylene in 2011.^{7–9}



On the other hand, stannylenes presents the same feature as germylene and were published in the same report as germylene with one exception (Figure 2).^{6,10} Glorius *et al.* published in 2012 a [2.2]-paracyclophane derived N-heterocyclic stannylene demonstrating an interesting example of planar chirality.¹¹



Figure 2: Example of stannylene with chiral substituent

Nevertheless, no applications of asymmetric germylenes and stannylenes were reported yet. This observation led us to consider the synthesis of a new tetrylene family with a chiral center directly included into the design of the stabilizing substituent. On this path, sulfonimidamide group was selected as a valuable alternative of amidinate group (Figure 3).¹²

Sulfonimidamides have a S(VI) atom in central position with two double bonds with oxygen and nitrogen, and two single bonds with carbon and nitrogen. Delocalization of electrons was determined with identical substituents on the nitrogen atoms by Johnson *et al.* in 1979.¹³ The report showed that tautomerism undergoes through a fast proton transfer between the imine and amine atoms. It is also mentioned that the proton transfer rate depends on the substituents of both nitrogen (aryl, alkyl, dissymmetric...). It is important to note that the tetrahedral sulfur atom can exhibit a configurationally stable chiral center when substituents on the nitrogen atoms were different,^{14,15} which lead Reek *et al.* to report in 2012 the synthesis of a sulfonimidamide based ligand employed successfully in iridium asymmetric catalysis.¹⁶



Figure 3: Sulfonimidamide properties

The utilization of sulfonimidamide was also interestingly employed with bis[bis(trimethylsilyl)amido]zinc to obtained a novel homoleptic tetracoordinated zinc published in 2006 by Guzyr *et al.*¹⁷ The four nitrogen atoms are located at a distance from 2.00 to 2.03 Å of the zinc center, which indicates a 4π delocalized system between both nitrogen comparable to the amidinate substituent (Scheme 1).



Scheme 1: Stabilization of Zn(II) with sulfonimidamide

In 2015, Stalke *et al.* have published a novel triimido sulfur (VI) phosphanyl ligand for the stabilization of germylenes and stannylenes (Scheme 2).¹⁸ The heteroleptic group 14 compounds were obtained by nucleophilic substitution of the corresponding dihalogenometallylene and characterized by X-ray crystallography. Nitrogen were located, in

both case, at the same distance of the metallylene, which indicates a 4π delocalized system comparable and in accordance with the results reported by Guzyr *et al*. The authors have designed the ligand to introduce a free phosphine arm that could be used for a potential bidentate coordination with the metallylene lone pair. However, no report about coordination nor application has been published yet to the best of our knowledge even if the perspectives implied an active interest.



Scheme 2: Triimidosulfur (VI) phosphanyl metallylenes

In this chapter, synthesis of sulfonimidamides will be discussed first with the challenge of the design and the choice of the substituents. In the second part, application of sulfonimidamides for stabilization of heavier analogues of carbenes will be discussed as well as the specific properties observed.

II. Results and discussion

II.1. Synthesis and characterization of sulfonimidamides

Since the first description of sulfonimidamides by Levchenko in 1960, numerous methods were developed to synthesize these S(VI) derivatives and the most common synthetic pathways use a nucleophilic substitution of a sulfonimidoyl chloride prepared by oxidative imidation of sulfinyl chlorides, oxidative chlorination of sulfonamides or deoxychlorination of secondary sulfonamides.^{19–23} However, most of the synthesis are difficult to perform, with the use of highly reactive and toxic reagents. That is the reason we relied on the method reported by Chen in 2015 to obtain symmetric and racemic asymmetric sulfonimidamides in two steps from sulfonyl chloride derivatives (Scheme 3).²⁴ The first step consists in a simple nucleophilic substitution of chlorine atom with a primary amine in presence of triethylamine. Then, the sulfamide reacts with a chlorinating agent to form a sulfonimidoyl chloride, which is substituted by the addition of a second amine.



Scheme 3: Synthetic pathway to obtain Sulfonimidamide

The efficiency of the strategy allowed us to obtain sulfonimidamides **12a-c**, in moderate yield of 38% up to 53% (Scheme 4). **12a** was synthetized as an equivalent of AmGeCl, used previously, with a symmetric sulfur and *i*-Pr substituent on each nitrogen. Asymmetric S(VI) was introduced with **12b** that exhibits two different substituents on nitrogen, *i*-Pr and Mes. Finally, **12c** is obtained as an ammonium chloride salt certainly formed by intra or intermolecular deprotonation. The aim of **12c** is to include a weak σ -donor ligand arm in order to use it for hemilabile coordination after formation of the corresponding metallylene. Unfortunately, the lack of time did not allow us to use **12c** to form the corresponding metallylene nor to study its application in coordination chemistry.



Scheme 4: Synthesis of 12a-c

12a-c were fully characterized by NMR, mass spectroscopy and X-ray diffraction. ¹NMR spectra of **12a** and **12b** were similar with slight differences. N-*H* proton was found with a chemical shift of 5.10 ppm and aromatic protons were assigned as two multiplets at 8.08 and 7.03 ppm respectively. Slight differences were found in the chemical shift of the *i*-Pr group, C-*H* has a chemical shift of 3.62 ppm in **12a** when it was found shielded in **12b** with a chemical shift of 3.41 ppm. The same observation was observed for CH_3 with a chemical shift of 1.12 and 1.07 in **12a** and an upfield of 0.84 and 0.59 ppm in **12b**. On the other hand, **12c** was not compared due to the use of another deuterated solvent, essentially for solubility reason. Again, ¹H NMR spectrum of **12c** exhibits a very particular signal for the -N- CH_2 - CH_2 -N- group that appear as particularly complex multiplets. The multiplicity observed can be explained by the loss of symmetry due to the chiral S(VI) atom that makes each hydrogen different.

Crystals of **12a** were obtained by slow evaporation of ethyl acetate and X-ray structure exhibits an unsurprising sulfur-nitrogen bond distance different for each nitrogen (Figure 4). The difference in the distance can be easily explained by the multiplicity of sulfur-nitrogen bond, one is a single bond of 1.628(2) Å and the other one is a double bond of 1.501(2) Å. **12b** shows the same behavior with sulfur nitrogen bond length of 1.5343(10) and 1.6032(10) Å. It is important to note that the nitrogen bearing a mesityl group forms a double bond rather than the nitrogen with an alkyl substituent. The observation can be rationalized by the presence of an aromatic group that promotes a sp2 configuration and a better delocalization of the nitrogen free doublet. In both case, the structure was obtained in a dimeric form with H-bond between tertiary and secondary amine function of two molecules. Finally, **12c** was obtained by slow evaporation of dichloromethane and exhibits also H-bond between chloride and hydrogen bound to the nitrogen. The structure also follows the same rule with sulfur-nitrogen bond

distance of 1.6188(9) and 1.5154(9) Å, the single bond being located on the nitrogen with an alkyl substituent.



Figure 4: Molecular structures of 12a (left) and 12b (right) (hydrogens are omitted for clarity)

II.2. Synthesis and characterization of germylenes and stannylenes stabilized by sulfonimidamides

The next step was to study the stabilization of metallylenes by sulfonimidamides. First, nucleophilic substitution was investigated by deprotonation of sulfonimidamide **12a** with ^{*n*}BuLi (Scheme 5). However, only protonated sulfonimidamide was recovered at the end of the reaction even by using a 2:1 ratio to form the homoleptic metallylene. In order to investigate the formation of the lithiated sulfonimidamide and if the base had an influence, **12a** was subsequently deprotonated with ^{*n*}BuLi and quenched with TMSC1 in the exact same experimental conditions. The product was obtained in quantitative yield, which means that lithiated sulfonimidamide was not a strong enough nucleophile to perform the nucleophilic substitution.



Scheme 5: Formation of lithiated sulfonimidamide and reactivity with dichlorometallylenes

Nevertheless, protonolysis was considered as a valuable alternative to obtain the product due to the large variety of examples published to date and the simplicity of the method.^{11,25–28} **12a** was added to half an equivalent of $M(HMDS)_2$ where M stand for Ge and Sn (Scheme 6).



Scheme 6: Reactivity of 12a with M(HMDS)₂ (M = Ge or Sn) to obtain 13a and 14a

Homoleptic metallylenes **13a** and **14a** were obtained cleanly after a night at room temperature. **13a** and **14a** were unambiguously characterized by X-ray crystallography of crystals obtained from a saturated solution of pentane at -25 °C (Figure 5). **13a** shows a nitrogen-germanium bond distance of 2.008(12) and 2.3241(12) Å, which demonstrates that two nitrogen are σ -bonded and the two-remaining nitrogen are acting as a Lewis base. It is important to note that the σ -bond is in the usual range for a Ge-N bond length reported to date for a 4π delocalized system (1.95 -2.07 Å).^{18,29-34} S-N bond lengths are also in agreement with one single bond and one double bond with a distance of 1.5757(12) and 1.5445(13) Å corresponding to a S-N bond with a better π character than the second one. Comparison with **12a** shows than the double bond is longer ($\Delta = +0.05$ Å) and the single bond is shorter ($\Delta = -0.05$ Å), it can be explained by the delocalization of electrons between both nitrogen. **14a** shows the same observations with a nitrogen-tin σ -bond of 2.180(4) and 2.233(4) Å and a dative bond of 2.392(5) and 2.427(5) Å. S-N bond lengths are also in the same range as **13a** with single bonds of 1.580(5) and 1.573(5) Å and double bonds of 1.529(5) and 1.568(5) Å.



Figure 5: Molecular structures of 13a (left) and 14a (right) (hydrogens are omitted for clarity)

Fast exchange between dative and single bond was confirmed between each nitrogen in ¹H NMR spectrum of **13a** and **14a** with *i*-Pr group. Only one set of signals were characterized with one septet and two doublets as a result of high symmetry and equivalence of the four *i*-Pr groups at the NMR time scale.

Formation of the heteroleptic sulfonimidamide metallylene was also investigated with an equimolar amount of both reactant (Scheme 7). After 1h, reaction between **12a** and $Ge(HMDS)_2$ was monitored by ¹H NMR. Interestingly, a transient species was observed with a new peak corresponding to a HMDS group and sulfonimidamide *i*-Pr exhibiting a chemical shift totally different than **12a** or **13a**. Nevertheless, the reaction continued and formation of **13a** with $Ge(HMDS)_2$ was finally obtained after several hours at room temperature.



Scheme 7: Reactivity of 12a with an equimolar amount of $M(HMDS)_2$ (M = Ge or Sn)

Same reaction was carried out with $Sn(HMDS)_2$ and 12a. Surprisingly, no transient species was observed in these conditions and selective and fast formation of 14a was observed.

Then, protonolysis reaction was extended from **12b** to form the corresponding germylene and stannylene (Scheme 8). Unsurprisingly, the same reactivity was observed with the formation of homoleptic metallylenes **13b** and **14b**.



Scheme 8: Reactivity of 12b with M(HMDS)₂ (M = Ge or Sn) to obtain 13b and 14b

¹H NMR of **13b** shows the formation of two diastereomers in a 82:18 ratio resulting from the combination of two sulfonimidamides with an asymmetric sulfur. Other important characteristic signals are observed in ¹H NMR for both methyl in *ortho*-position and both hydrogen in *meta*-position of the mesityl substituent which appear as broad signals. Variable temperature shows that increasing temperature to +70 °C could provide better defined signals (Figure 6). We suppose a steric interaction between mesityl and the close *i*-Pr group of the second sulfonimidamide.



Figure 6: ¹H NMR variable temperature of **13b** from 25 °C to 70 °C

Surprisingly, ¹H NMR of **14b** shows the formation of only one set of signals. However, the diastereoselectivity of the reaction was not investigated. It is also important to note that methyl in *ortho*-position and hydrogen in *meta*-position appear as sharp signals, which can be explained by the heavier atom that increased the distance between both sulfonimidamides.

13b and **14b** were also characterized by X-ray crystallography (Figure 7). **13b** shows a nitrogen-germanium bond distance of 2.0269(13) - 2.0318(13) Å and 2.2257(15) - 2.2633(14) Å, which demonstrates that two nitrogen are σ-bonded and the two-remaining nitrogen were acting as a Lewis base. It is important to note that the σ-bond is in the usual range for a Ge-N bond length reported to date for a 4π delocalized system (1.95 - 2.07 Å).^{18,29–34} S-N bond lengths are also in agreement with one single bond and one dative bond with a distance of 1.5506(15) - 1.5523(15) Å and 1.5851(13) - 1.5844(13) Å in allowance with **13a**. Comparison with **12b** shows than the double bond is exchanged between the nitrogen. Indeed, S=N double bond is located on the nitrogen with a mesityl group in **12b** when S=N double bond is located on the nitrogen with a *i*-Pr group in **13b**. The same observations are observed on the structure of **14b**. Nitrogen-tin bond distances are in the usual range of 2.229(2) and 2.342(2) Å, also S-N bond lengths of 1.5554(2) and 1.576(2) Å are in agreement with **13b**. Finally, the same double bond exchange is observed between both nitrogen as previously observed with **13b**.



Figure 7: Molecular structures of 13b (left) and 14b (right) (hydrogens are omitted for clarity)

Calculations were performed on the potential-energy surface of **13b** and **14b** to support the experimental results starting with the X-ray structures (The B3LYP/6-31g(d,p) basis set and

SDD for tin was used). Mesityl group was rotated, for **13b** and **14b**, on C_{Ar} -N to calculate the potential-energy surface (Figure 8). As a first approximation (full rotation with a step by step of 20° and optimized structures), the rotation that requires more energy is with the germylene with a value of 26 kcal/mol while stannylene shows a value of 23 kcal/mol. The difference does not appear important but the result give a trend in the way of the observations observed in ¹H NMR. It is important now to refine the calculations with the consideration of the solvent and with a smaller step of 1° for the rotation.



Figure 8: Optimized structures of 13b and 14b for PES calculations

Finally, DFT calculations were performed to explore the electronic properties and the stabilization effect of the substituents on the metallylenes (Figure 9). The HOMO is located on each on the metallylene with the first unoccupied orbital located on the LUMO+4. The comparison of **13a** and **14a** indicates that tin is much more electronically stabilized than germanium. Comparison of **13a** and **13b** that exhibit different substituents on the nitrogen atoms shows a small effect on the molecular orbitals of the germylene when the stannylene with **14a** and **14b** remains in the same range. In each case, strong stabilizing interactions are found with $nN \rightarrow \sigma^*SO$ of 8 to 20 kcal/mol and $nN \rightarrow \sigma^*CC$ of mesityl or *i*-Pr of ~7 to 8 kcal/mol.


⁽right)

III. Conclusion

Sulfonimidamides have been synthesized in moderate 38-53% yields. The synthetic pathway allows to integrate various subsituents on the nitrogen atoms with a combination of *i*-Pr and mesityl groups. This design also allows the formation of symmetric and asymmetric center on the central sulfur atom.

Homoleptic germylenes and stannylenes have been obtained by protonolysis reaction with Ge(HMDS)₂ or Sn(HMDS)₂. These new metallylenes have been characterized by NMR spectroscopy and X-ray diffraction analysis. X-ray structures show different bond lengths for germanium-nitrogen or tin-nitrogen interatomic distances. However, fast exchange is observed by ¹H NMR spectroscopy at room temperature. These results lead to classify these new metallylenes as 4π delocalized stabilized systems.

Finally, DFT calculations have been performed to understand the electronic properties brought by the sulfonimidamide on the metallylene and how the design can influence its stabilization. Calculations indicate that tin is much more electronically stabilized than germanium. Comparison of the structures with mesityl substituent show a small effect on the molecular orbitals of the germylene when the stannylene remains in the same range. Surprisingly, strong stabilizing interactions were found with $nN \rightarrow \sigma^*SO$ and $nN \rightarrow \sigma^*CC$.

IV. Experimental section



N,*N'*-di-*iso*-propylbenzenesulfonimidamide (12a): Hexachloroethane (264 mg, 1.11 mmol, 1.1 eq) was added to a solution of triphenylphosphine (293 mg, 1.11 mmol, 1.1 eq) in CHCl₃ (10 mL) at room temperature. The solution was heated at reflux for 6 h. Then, the mixture was allowed to return at room

temperature and trimethylamine (210 µL, 1.52 mmol, 1.5 eq) was added, the mixture was stirred for 30 min at room temperature. N-*iso*-propylbenzenesulfonamide (200 mg, 1.01 mmol, 1 eq) was dissolved in CHCl₃ and added on the mixture. Finally, after stirring the mixture for 30 min at room temperature *iso*-propylamine (260 uL, 3.03 mmol, 3 eq) was added and the solution stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (Eluent: Petroleum Ether / Ethyl Acetate : 4 / 6, Rf = 0.78) to give a white solid (129 mg) in 53 % yield. Crystals were obtained by slow evaporation in ethyl acetate. M.p. : 66 °C; ¹H NMR (300.18 MHz, *C*₆*D*₆, 25 °C): δ 1.07 (d, ³J_{HH} = 6.5 Hz, 6H, CH(CH₃)₂); 1.12 (d, ³J_{HH} = 6.5 Hz, 6H, CH(CH₃)₂); 3.62 (sept., ³J_{HH} = 6.5 Hz, 2H, N-C*H*(CH₂)₂), 5.09 (s, 1H, N*H*), 6.98-7.08 (m, 3H, C*H*_{Ar}), 8.09-8.13 (m, 2H, C*H*_{Ar}). ¹³C{¹H} NMR (75.48 MHz, *C*₆*D*₆, 25 °C): δ 25.4 (CH(*C*H₃)₂); 25.5 (CH(*C*H₃)₂); 45.5 (*C*H(CH₃)₂); 128.0 (*C*_{Ar}); 128.6 (*C*_{Ar}); 131.3 (*C*_{Ar}); 143.3 (*C*_{Ar/q}). HRMS *m/z* (%): 241.1380 ([M + 1]⁺) calcd for C₁₂H₂₀N₂OS ([M + 1]⁺) 241.1375.

Formula	C12H20N2OS	dcalc (g/cm^3)	1.174
Mol wt	240.36	μ (mm ⁻¹)	0.222
Temp. (K)	193(2)	<i>F</i> (000)	520
Cryst syst	Triclinic	cryst size (mm)	0.140 x 0.100 x 0.040
Space group	P-1	θ range (deg.)	3.017 to 24.763
a (Å)	10.5404(7)	index range h k l	-12<=h<=12, - 12<=k<=12, - 14<=l<=14
b (Å)	10.5595(7)	no of reflns collected /	34528
c (Å)	12.5470(9)	unique	4527 [R(int) = 0.0616]
α (deg.)	76.985(2)	Completeness to θmax(%)	96.8
β (deg.)	88.549(2)	data/restraints/params	4527 / 164 / 361
γ (deg.)	89.718(2)	goodness-of-fit	1.028

Chapter IV: Design, Synthesis and Characterization of New Germylenes and Stannylenes Stabilized by Sulfonimidamides

V (Å3)	1360.18(16)	R1, wR2 (I > $2\sigma(I)$)	0.0433, 0.0961
Ζ	4	R1, wR2 (all data)	0.0714, 0.1095



N-iso-propyl-*N*'-mesitylbenzenesulfonimidamide (12b): Hexachloroethane (264 mg, 1.11 mmol, 1.1 eq) was added to a solution of triphenylphosphine (293 mg, 1.11 mmol, 1.1 eq) in CHCl₃ (10 mL) at room temperature. The solution was heated at reflux for 6 h. Then, the mixture was allowed to return

at room temperature and trimethylamine (210 µL, 1.52 mmol, 1.5 eq) was added, the mixture was stirred for 30 min at room temperature. N-*iso*-propylbenzenesulfonamide (200 mg, 1.01 mmol, 1 eq) was dissolved in CHCl₃ and added on the mixture. Finally, after stirring the mixture for 30 min at room temperature 2,4,6-Trimethylaniline (426 µL, 410 mg, 3.03 mmol, 3 eq) was added and the solution stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (Eluent: Petroleum Ether / Ethyl Acetate : 4 / 6, Rf = 0.80) to give a white solid (157 mg) in 49 % yield. Crystals were obtained by slow evaporation in ethyl acetate. M.p. : 93 °C; ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.61 (d, ³J_{HH} = 6.5 Hz, 3H, CH(CH₃)₂); 0.84 (d, ³J_{HH} = 6.5 Hz, 3H, CH(CH₃)₂); 2.15 (s, 3H, CH₃); 2.53 (s, 6H, CH₃); 3.41 (sept., ³J_{HH} = 6.5 Hz, 1H, N-CH(CH₂)₂), 5.11 (s, 1H, NH), 6.84 (s, 2H, CH_{Ar}), 6.98-7.02 (m, 3H, CH_{Ar}), 8.04-8.07 (m, 2H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 20.6 (CH₃); 20.9 (CH₃); 23.0 (CH(CH₃)₂); 24.1 (CH(CH₃)₂); 46.0 (CH(CH₃)₂); 128.0 (C_{Ar}); 128.6 (C_{Ar}); 131.3 (C_{Ar}); 143.3 (C_{Ar/q}). HRMS *m/z* (%): 317.1697 ([M + 1]⁺) calcd for C₁₈H₂₅N₂OS ([M + 1]⁺) 317.1688.

Formula	C18H24N2OS	dcalc (g/cm ³)	1.202
Mol wt	316.45	μ (mm ⁻¹)	0.189
Temp. (K)	193(2)	<i>F</i> (000)	680
Cryst syst	Triclinic	cryst size (mm)	0.480 x 0.460 x 0.120
Space group	P-1	θ range (deg.)	3.072 to 30.511
a (Å)	11.989(3)	index range h k l	-17<=h<=17, - 17<=k<=17, - 19<=l<=19
b (Å)	12.149(3)	no of reflns collected /	81609
c (Å)	13.386(3)	unique	10619 [R(int) = 0.0259]
α (deg.)	64.437(9)	Completeness to θmax(%)	99.6

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β (deg.)	88.604(8)	data/restraints/params	10619 / 0 / 415
γ (deg.)	83.874(13)	goodness-of-fit	1.042
V (Å3)	1748.5(8)	R1, wR2 (I > $2\sigma(I)$)	0.0375, 0.0989
Ζ	4	R1, wR2 (all data)	0.0370, 0.1061

by Sulfonimidamides



Dimethylammonium ethyl *iso*-propyl sulfonimidamide chloride salt (12c): Hexachloroethane (264 mg, 1.11 mmol, 1.1 eq) was added to a solution of triphenylphosphine (293 mg, 1.11 mmol, 1.1 eq) in CHCl₃ (10 mL) room temperature. The solution was heated at reflux

for 6 h. Then, the mixture was allowed to return at room temperature and trimethylamine (210 μ L, 1.52 mmol, 1.5 eq) was added, the mixture was stirred for 30 min at room temperature. N-*iso*-propylbenzenesulfonamide (200 mg, 1.01 mmol, 1 eq) was dissolved in CHCl₃ and added to the mixture. Finally, after stirring the mixture for 30 min at room temperature N,N-dimethylethylenediamine (330 uL, 3.03 mmol, 3 eq) was added and the solution stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude was purified by flash column chromatography (Eluent: DCM / MeOH : 9 / 1, Rf = 0.57) to give a white solid (129 mg) in 38 % yield. Crystals were obtained by slow evaporation in ethyl acetate. ¹H NMR (300.18 MHz, *CDCl*₃, 25 °C): δ 0.90 (d, ³J_{HH} = 6.5 Hz, 3H, CH(*CH*₃)₂); 1.20 (d, ³J_{HH} = 6.5 Hz, 3H, CH(*CH*₃)₂); 2.84 (s, 6H, N-(*CH*₃)₂), 3.01-3.29 (m, 3H, N-*CH*₂*CH*₂-N), 3.36 (sept., ³J_{HH} = 6.5 Hz, 1H, N-*CH*(CH₂)₂); 3.70-3.79 (m, 1H, N-*CH*₂*CH*₂-N), 7.45-7.49 (m, 3H, *CH*_{Ar}), 8.14-8.17 (m, 2H, *CH*_{Ar}). ¹³C{¹H} NMR (75.48 MHz, *CDCl*₃, 25 °C): δ 22.9 (*C*H(CH₃)₂); 24.6 (*C*H(CH₃)₂); 38.3 (*C*H(CH₃)₂); 44.4 (N-(*C*H₃)₂); 46.6 (N-(*C*H₃)₂); 60.3 (N-*C*H₂); 127.5 (*C*_{Ar}); 128.8 (*C*_{Ar}); 132.0 (*C*_{Ar}); 141.6 (*C*_{Ar/q}). HRMS *m/z* (%): 270.1646 ([M - Cl]⁺) calcd for C₁₃H₂₄N₃OS ([M - Cl]⁺) 270.1640.

Formula	C13H24CIN3OS	dcalc (g/cm ³)	1.241
Mol wt	305.86	μ (mm ⁻¹)	0.358
Temp. (K)	193(2)	<i>F</i> (000)	328
Cryst syst	Triclinic	cryst size (mm)	0.540 x 0.340 x 0.060
Space group	P-1	θ range (deg.)	2.986 to 33.198
a (Å)	7.5259(3)	index range h k l	-11<=h<=10, - 13<=k<=13, - 19<=l<=17
b (Å)	8.8203(4)	no of reflns collected /	22190

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c (Å)	12.6561(5)	unique	5730 [R(int) = 0.0195]
α (deg.)	94.4110(10)	Completeness to θmax(%)	99.2
β (deg.)	93.5030(10)	data/restraints/params	5730 / 78 / 211
γ (deg.)	101.3740(10)	goodness-of-fit	1.046
V (Å3)	818.68(6)	R1, wR2 (I > $2\sigma(I)$)	0.0332, 0.0806
Ζ	2	R1, wR2 (all data)	0.0414, 0.0853

by Sulfonimidamides



Bis (*N*,*N*'-di-*iso*-propylbenzenesulfonimidamide) germylene (13a): KHMDS (85.8 mg, 0.43 mmol, 2 eq) was added to GeCl₂•dioxane (49.7 mg, 0.215 mmol, 1 eq) in Et₂O at room temperature. The mixture was stirred for 2 hours and

N,N'-di-*iso*-propylbenzenesulfonimidamide (**12a**) (154 mg, 0.43 mmol, 2 eq) in Et₂O was added at the same temperature. After 16h, the solvent was removed under reduced pressure and the resulting solid was extract with pentane. The solvent was removed under reduced pressure to give a white solid in 90 % yield (107 mg). Crystallization from pentane at -25 °C gave colourless crystals suitable for X-ray study. M.p. : 105 °C (decomposition); ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.33 (d, ³J_{HH} = 6.6 Hz, 12H, CH(CH₃)₂); 1.40 (d, ³J_{HH} = 6.6 Hz, 12H, CH(CH₃)₂); 3.64 (sept., ³J_{HH} = 6.6 Hz, 4H, N-CH(CH₂)₂), 6.96-7.08 (m, 6H, CH_{Ar}), 7.89-7.91 (m, 4H, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 24.6 (CH(CH₃)₂); 25.4 (CH(CH₃)₂); 47.4 (CH(CH₃)₂); 128.9 (C_{Ar}); 129.1 (C_{Ar}); 131.4 (C_{Ar}); 141.9 (C_{Ar/q}). MS *m/z* (%): 552 (M⁺).

Formula	C24H38GeN4O2S2	dcalc (g/cm ³)	1.137
Mol wt	551.31	μ (mm ⁻¹)	1.104
Temp. (K)	193(2)	F(000)	1160
Cryst syst	Tetragonal	cryst size (mm)	0.300 x 0.200 x 0.160
Space group	I4 ₁	θ range (deg.)	2.936 to 31.886
a (Å)	21.9417(7)	index range h k l	-21<=h<=32, -32<=k<=32, -9<=l<=9
b (Å)	21.9417(7)	no of reflns collected /	38402
c (Å)	6.6868(2)	unique	5530 [R(int) = 0.0265]
α (deg.)	90	Completeness to θmax(%)	99.2

β (deg.)	90	data/restraints/params	5530 / 1 / 154
γ (deg.)	90	goodness-of-fit	1.023
V (Å3)	3219.3(2)	R1, wR2 (I > $2\sigma(I)$)	0.0198, 0.0483
Ζ	4	R1, wR2 (all data)	0.0236, 0.0503

by Sulfonimidamides



Bis (N-iso-propyl-*N*'-mesitylbenzenesulfonimidamide) germylene (13b): KHMDS (43 mg, 0.215 mmol, 2 eq) was added to GeCl₂•dioxane (25 mg, 0.108 mmol, 1 eq) in Et₂O at room temperature. The mixture was stirred for 2 hours and *N*-

iso-propyl-N'-mesitylbenzenesulfonimidamide (12b) (68 mg, 0.215 mmol, 2 eq) in Et₂O was added at the same temperature. After 16h, the solvent was removed under reduced pressure and the resulting solid was extract with pentane. The solvent was removed under reduced pressure to give a white solid in 92 % yield (70 mg). Crystallization from benzene at room temperature gave colourless crystals suitable for X-ray study. M.p. : 108 °C (decomposition); *Isomer A*: ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.72 (d, ${}^{3}J_{HH} = 6.5$ Hz, 6H, CH(CH₃)₂); 0.91 (d, ${}^{3}J_{HH} = 6.5$ Hz, 6H, CH(CH₃)₂); 2.06 (s, 6H, CH₃); 3.23 (sept., ³J_{HH} = 6.5 Hz, 4H, N-CH(CH₂)₂), 6.87-6.95 (m, 6H, C**H**_{Ar}), 7.70-7.73 (m, 4H, C**H**_{Ar}). ¹H NMR (300.18 MHz, C₆D₆, 70 °C): δ 0.73 (d, ³J_{HH} = 6.5 Hz, 6H, CH(C H_3)₂); 0.93 (d, ³J_{HH} = 6.5 Hz, 6H, CH(C H_3)₂); 2.06 (s, 6H, C H_3); 2.56 (s, 12H, CH₃); 3.25 (sept., ${}^{3}J_{HH} = 6.5$ Hz, 4H, N-CH(CH₂)₂), 6.77 (s, 4H, CH_{Ar}), 6.93-7.01 (m, 6H, CH_{Ar} , 7.70-7.73 (m, 4H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 20.9 (CH_3); 23.9 (CH(*C*H₃)₂); 25.2 (CH(*C*H₃)₂); 46.9 (*C*H(CH₃)₂); 128.9 (*C*_{Ar}); 131.6 (*C*_{Ar}); 134.0 (*C*_{Ar}); 135.9 $(C_{Ar/q})$; 140.1 $(C_{Ar/q})$. Isomer B: ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.16 (d, ³J_{HH} = 6.5 Hz, 6H, CH(CH₃)₂); 1.35 (d, ${}^{3}J_{HH} = 6.5$ Hz, 6H, CH(CH₃)₂); 2.02 (s, 6H, CH₃); 3.59 (sept., ${}^{3}J_{HH} =$ 6.5 Hz, 4H, N-CH(CH₂)₂), 6.87-6.95 (m, 6H, CH_{Ar}), 7.70-7.73 (m, 4H, CH_{Ar}). ¹H NMR (300.18 MHz, $C_6 D_6$, 70 °C): δ 1.18 (d, ${}^{3}J_{HH} = 6.5$ Hz, 6H, CH(CH₃)₂); 1.32 (d, ${}^{3}J_{HH} = 6.5$ Hz, 6H, $CH(CH_3)_2$; 2.03 (s, 6H, CH₃); 2.34 (s, 12H, CH₃); 3.62 (sept., ${}^{3}J_{HH} = 6.5$ Hz, 4H, N-CH(CH₂)₂), 6.67 (s, 4H, C**H**_{Ar}), 6.93-7.01 (m, 6H, C**H**_{Ar}), 7.70-7.73 (m, 4H, C**H**_{Ar}). MS *m/z* (%): 704 (M⁺).

Formula	C36H46GeN4O2S2,C6H6	dcalc (g/cm ³)	1.257
Mol wt	781.61	μ (mm ⁻¹)	0.882
Temp. (K)	193(2)	<i>F</i> (000)	1648
Cryst syst	Monoclinic	cryst size (mm)	0.160 x 0.140 x 0.080
Space group	P21/C	θ range (deg.)	3.526 to 29.574

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a (Å)	15.4414(5)	index range h k l	-21<=h<=21, -10<=k<=11, -46<=l<=39
b (Å)	7.9913(3)	no of reflns collected /	75752
c (Å)	33.5748(10)	unique	11552 [R(int) = 0.0337]
α (deg.)	90	Completeness to θmax(%)	99.8
β (deg.)	94.717(2)	data/restraints/params	11552 / 0 / 470
γ (deg.)	90	goodness-of-fit	1.121
V (Å3)	4119.0(2)	R1, wR2 ($I > 2\sigma(I)$)	0.0368, 0.1002
Ζ	4	R1, wR2 (all data)	0.0463, 0.1054



Bis (N,N'-di-iso-propylbenzenesulfonimidamide) stannylene (14a): *N,N'-di-iso-propylbenzenesulfonimidamide* (12a) (60 mg, 0.25 mmol, 2 eq) was dissolved in C_6D_6 (0.4 mL) and added to Sn(HMDS)₂ (55 mg, 0.125 mmol, 1 eq) at room temperature.

The mixture was stirred 20 min at room temperature and the solvent was removed under reduced pressure. The solid was extracted with pentane (3x3 mL) to give a white solid in 96 % yield (72 mg). Crystallization from benzene at room temperature gave colourless crystals suitable for X-ray study. M.p. : 117 °C (decomposition); ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 1.26 (d, ³J_{HH} = 6.6 Hz, 12H, CH(CH₃)₂); 1.46 (d, ³J_{HH} = 6.6 Hz, 12H, CH(CH₃)₂); 3.61 (sept., ³J_{HH} = 6.6 Hz, 4H, N-CH(CH₂)₂), 6.96-7.10 (m, 6H, CH_{Ar}), 7.90-7.93 (m, 4H, CH_{Ar}). ¹³C{¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 25.1 (CH(CH₃)₂); 25.9 (CH(CH₃)₂); 47.0 (CH(CH₃)₂); 129.0 (C_{Ar}); 129.1 (C_{Ar}); 131.2 (C_{Ar}); 142.4 ($C_{Ar/q}$). MS *m/z* (%): 598 (M⁺).

Formula	C24H38SnN4O2S2	dcalc (g/cm ³)	1.386
Mol wt	597.41	μ (mm ⁻¹)	1.065
Temp. (K)	193(2)	<i>F</i> (000)	1232
Cryst syst	Monoclinic	cryst size (mm)	0.380 x 0.200 x 0.040
Space group	P21/c	θ range (deg.)	2.817 to 27.102
a (Å)	8.2616(17)	index range h k l	-10<=h<=10, -55<=k<=55, -10<=l<=10
b (Å)	43.384(9)	no of reflns collected /	57645
c (Å)	8.3588(18)	unique	6312 [R(int) = 0.0305]

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α (deg.)	90	Completeness to θmax(%)	99.5
β (deg.)	107.188(6)	data/restraints/params	6312 / 0 / 8306
γ (deg.)	90	goodness-of-fit	1.457
V (Å3)	2862.2(10)	R1, wR2 (I > $2\sigma(I)$)	0.0619, 0.1329
Ζ	4	R1, wR2 (all data)	0.0627, 0.1332

by Sulfonimidamides



Bis(N-iso-propyl-N'-mesitylbenzenesulfonimidamide)stannylene(14b):N-iso-propyl-N'-

mesitylbenzenesulfonimidamide (**12b**) (60 mg, 0.19 mmol, 2 eq) was dissolved in C_6D_6 (0.4 mL) and added to $Sn(HMDS)_2$

(42 mg, 0.09 mmol, 1 eq) at room temperature. The mixture was stirred 20 min at room temperature and the solvent was removed under reduced pressure to give a white solid in 97 % yield (69 mg). Crystallization from benzene at room temperature gave colourless crystals suitable for X-ray study. M.p. : 118 °C (decomposition); ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.80 (d, ³J_{HH} = 6.5 Hz, 6H, CH(CH₃)₂); 0.85 (d, ³J_{HH} = 6.5 Hz, 6H, CH(CH₃)₂); 1.80 (s, 6H, CH₃); 2.08 (s, 6H, CH₃); 3.26 (sept., ³J_{HH} = 6.5 Hz, 4H, N-CH(CH₂)₂), 3.40 (s, 6H, CH₃); 6.62 (s, 2H, CH_{Ar}), 6.95 (s, 2H, CH_{Ar}), 6.92-6.98 (m, 6H, CH_{Ar}), 7.67-7.71 (m, 4H, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 19.3 (CH(CH₃)₂); 20.5 (CH₃); 22.1 (CH(CH₃)₂); 24.1 (CH₃); 24.9 (CH₃); 46.4 (CH(CH₃)₂); 128.5 (C_{Ar}); 128.7 (C_{Ar}); 130.3 (C_{Ar}); 130.9 (C_{Ar}); 134.0 (C_{Ar/q}); 135.0 (C_{Ar/q}); 136.7 (C_{Ar/q}); 141.0 (C_{Ar/q}); 141.5 (C_{Ar/q}). MS *m/z* (%): 750 (M⁺).

Formula	C36H46GeN4O2S2, C6H6	dcalc (g/cm ³)	1.312
Mol wt	827.71	μ (mm ⁻¹)	0.747
Temp. (K)	193(2)	<i>F</i> (000)	1720
Cryst syst	Monoclinic	cryst size (mm)	0.200 x 0.080 x 0.060
Space group	P21/c	θ range (deg.)	3.511 to 26.196
a (Å)	15.5421(8)	index range h k l	-19<=h<=19, -9<=k<=9, -42<=l<=42
b (Å)	8.0005(4)	no of reflns collected /	93362
c (Å)	33.9053(16)	unique	8352 [R(int) = 0.0739]
α (deg.)	90	Completeness to θmax(%)	99.6

β (deg.)	96.144(2)	data/restraints/params	8352 / 0 / 470
γ (deg.)	90	goodness-of-fit	1.042
V (Å3)	4191.7(4)	R1, wR2 (I > $2\sigma(I)$)	0.0348, 0.0746
Ζ	4	R1, wR2 (all data)	0.0559, 0.0835

by Sulfonimidamides

V. Notes and references

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Chapter V:

Applications in Hydrogen Transfer and Polymerization Catalysis

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Abstract

Ruthenium complexes synthesized in previous chapter II were used in hydrogen transfer reaction for the reduction of acetophenone into the corresponding alcohol in *i*-PrOH as a solvent and a reactant. Comparison of the different ligands was investigated to determine the influence of various parameters, such as the steric hindrance on sulfoxide or on the amidinate group, or the oxidation state of the sulfur atom.

Finally, hydrogen transfer reaction was investigated with asymmetric ruthenium complexes. The best conditions of catalysis were also applied to reduce various ketones and aldehyde at room temperature.

A second catalysis will be considered by using sulfonimidamide metallylenes described in chapter IV. These new metallylenes were applied in polymerization of ε -caprolactone.

I. Introduction

The transition metal chemistry of germylenes has experienced an important interest the last decade that led to the application of germylenes in different catalytic processes. Nevertheless, these applications remain sporadic compared to the use of lighter analogues such as silylenes or carbenes. However, the proof of the catalytic activity of germylene-complexes was an important milestone to their development and their activity, which allowed them to leave the field of theoretical tools.^{1,2}

Applications of germylenes-complexes can be overviewed in four different publications reported during the past decade.^{3–6} The different complexes were applied in C-H borylation of benzene, Sonogashira-Hagihara cross-coupling, hydrogen transfer reaction and cyanosilylation of aldehydes and ketones. Our interest on hydrogen transfer reaction was immediate due the large application of ruthenium complexes in this field and the possibility to generate chiral alcohol during the reaction. An excellent review on hydrogen transfer reaction was published by Wang and Astruc in 2015.⁷

Thus, Cabeza *et al.* have reported the coordination of iridium and ruthenium complexes by amidinato-*tert*-butyl germylenes in 2015 (Scheme 1).⁵



Scheme 1: Germylene-iridium I and –ruthenium II complexes applied in hydrogen transfer reaction

Iridium (I) and ruthenium (II) complexes were applied in hydrogen transfer reaction of cyclohexanone with *iso*-propyl alcohol. Both complexes were active and reduced cyclohexanone with 55% of conversion after 24h at 50 °C for ruthenium complex, whereas iridium complex fully converted the ketone into the alcohol after 1.5h at the same temperature. Surprisingly, the catalysis does not require any base as additive to form the active catalyst.

Typically, active catalysts without any addition of an external base present a free Lewis base substituent on the ligand which acts as the external base.⁸ Moreover, only one substrate, the cyclohexanone, was used for the catalysis. The reaction was unfortunately not extended to other carbonyl substrates to determine the scope and the activity of the catalyst. Addition of chloride abstractor by using AgOTf resulted in a total deactivation of the iridium (I) and ruthenium (II) catalysts (Table 1).

Entry	Catalyst (2 mol%)	AgOTf (X eq)	Reaction time	Conversion (%)
1	II	/	90 min	19
2	II	/	24 h	55
3	Ι	/	90 min	>99
4	II	3 eq	90 min	0
5	Ι	3 eq	90 min	0

Table 1: Hydrogen transfer reaction and effect of chloride abstraction

On the other hand, application of sulfoxides in asymmetric hydrogen transfer reaction was limited to the best of our knowledge to two publications (Scheme 2). The first one was published by van Leeuwen *et al.* in 2000 by using an iridium complex.⁹ The ee from 4-methylacetophenone was up to 80%. The second publication was reported by Deng *et al.* in 2012 with, again, an iridium catalysis and ee up to 65%.¹⁰



Scheme 2: Sulfoxide used in iridium-catalyzed hydrogen transfer of acetophenone

Finally, metallylenes can also be applied as organocatalysts. On this path, biodegradable polymers such as polylactide (PLA), $poly(\varepsilon$ -caprolactone) (PCL), and poly(trimethylenecarbonate) (PTMC) are of great interest due to their applications as biodegradable and biocompatible polymers. Their formations can be catalyzed with tin (II) which is a well-known catalyst to start living polymerization of several monomers like ε -caprolactone or lactide. The early work of Kricheldorf *et al.* in 1995 studied the influence and

the mechanism of $Sn(oct)_2$ in polymerization of L-lactide.¹¹ Then, several stannylenes were developed and used successfully in polymerization (Scheme 3).^{12–14}



Scheme 3: Stannylenes applied in polymerization (*ɛ*-caprolactone and lactide)

The germylene- α -sulfoxide ruthenium complexes described in chapter II will be investigated as catalyst in hydrogen transfer catalysis of acetophenone. Then, the influence of the design of the catalyst and the catalysis parameters will be studied. Finally, the new metallylenes described in chapter IV will be investigated as catalysts of polymerization of ε -caprolactone and the influence of the sulfonimidamide design on the catalysis will also be studied.

II. Results and discussion

II.1. Application of ruthenium complexes in hydrogen transfer reaction

Hydrogen transfer reaction was first investigated starting from acetophenone in *i*-PrOH by using *p*-cymene ruthenium complex **6b** as catalyst in presence of an external base (Scheme 4). It is important to note that **6b** appears perfectly stable in dry and degassed *i*-PrOH for a week at room temperature.



Scheme 4: Germylene-complexes tested in hydrogen transfer reaction

The conversion, determined by ¹H NMR analysis by using tetramethylbenzene as internal standard, was up to 76% after 2h at 80 °C. The effect of the base on the catalytic reaction was next investigated (Table 2).

Entry ^a	Catalyst (2 mol%)	base (20 mol%)	T (°C)	Reaction time (h)	Conversion (%) ^b
1	6b	КОН	80	2	76
2	"	NaOH		دد	70
3	"	K ₂ CO ₃	دد	"	51
4	66	Cs ₂ CO ₃		"	27
5	"	t-BuOK	دد	دد	32

^a The reactions were carried out in dry and degassed isopropyl alcohol (2 mL) under argon in presence of acetophenone (0.9 mmol)

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard.

Table 2: Influence of the base in hydrogen transfer reaction with complex 6b

A slight effect of the counter-cation can be observed by using sodium hydroxide (70%) in place of potassium hydroxide (76%) (Table 2, entry 1 and 2). Replacement of KOH or NaOH by potassium or cesium carbonate lead to decrease the conversion (Table 2, entries 3 and 4). A similar result has been observed during the use of *t*-BuOK (Table 2, entry 5). The nature of the base can influence the stability of the complex or the formation of the ruthenium-hydride active species.

We next studied the influence of the quantity of base (Table 3). Surprisingly, the catalyst was still active in hydrogen transfer reaction without any addition of base with the full reduction of acetophenone after a long reaction time of 18 hours (Table 3, entries 1 and 2). This result was already observed by the group of Cabeza in 2016.⁵ Moreover, modification of the quantity of base showed that 20 mol% was the ideal amount of KOH for a reaction time of 2h, the addition of a larger or a lower quantity resulting in a negative impact on the catalysis (Table 3, entries 3-5).

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Entry ^a	Catalyst (2 mol%)	KOH (X mol%)	T (°C)	Reaction time (h)	Conversion (%) ^b
1	6b	-	80	2	24
2	"	-		18	>97
3	66	10	"	2	65
4	"	20	"	2	76
5	"	40		2	64

^a The reactions were carried out in dry and degassed isopropyl alcohol (2 mL) under argon in presence of acetophenone (0.9 mmol)

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard.

Table 3: Influence of the quantity of base in hydrogen transfer reaction with complex 6b

The next parameter studied was the quantity of *i*-PrOH, i-e the concentration of the reaction (Table 4). Increasing the volume of *i*-PrOH to 3 mL induces a slight decrease of the catalytic activity (59 %), that can be explained by a dilution of the catalytic system (Table 4, entries 1 and 2). On the opposite, decreasing the volume of *i*-PrOH to 1 mL gives rise to a slight enhance of activity (88 %) after 2h, leading to a full conversion (>97 %) after 2.5 hours (Table 4, entries 3 and 4). Finally, the use of 0.5 mL of *i*-PrOH induces a slight drop of activity (73 %) that can be explained by the poor solubility of the base in these conditions, or the decrease of *i*-PrOH as reactant.

Entry ^a	Catalyst (2 mol%)	Volume <i>i</i> -PrOH (mL)	T (°C)	Reaction time (h)	Conversion (%) ^b
1	6b	2	80	2	76
2	66	3	"	2	59
3	66	1	"	2	88
4	66	1	"	2.5	>97
5	66	0.5	دد	2	73

^a The reactions were carried out in dry and degassed isopropyl alcohol (X mL) under argon in presence of acetophenone (0.9 mmol)

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard.

Table 4: Influence of the concentration in hydrogen transfer reaction with complex **6b**

Then, catalyst **6b** was compared to all the other *p*-cymene ruthenium-based complexes in order to study the influence (i) of the steric hindrance of the amidinate group, (ii) of the

substituent of the sulfoxide, (iii) of the oxidation state of the sulfur atom, (iv) of the substituent of the germylene (Scheme 5).



Scheme 5: Germylene-ruthenium complexes 6b-d-f-g-h-i

The different ruthenium complexes (2 mol%) were used in the same conditions with *i*-PrOH (2 mL) and KOH (20 mol%) at 80 °C. The conversion was monitored after 2 hours of reaction time (Table 5). Modification of the steric hindrance on the amidinate group shows an influence on the activity of the catalyst which decreases by replacing *i*-Pr (76 %) group on complex **6b** by a bulkier cyclohexyl (57 %) group on complex **6d** (Table 5, entries 1 and 2). The activity also decreases after replacing the aryl substituent on the sulfoxide (76 %) by an alkyl group (43 %) for the complex 6f (Table 5, entries 1 and 3). This result can be explained by the poor stability of complex 6f at 80°C. Indeed, a t-Bu group bonded to a sulfoxide function can undergo, by heating, the elimination of *iso*-butene and the concomitant formation of the corresponding sulfinic acid, which is known as an unstable group.¹⁵ The influence of the oxidation state of the sulfur atom can be observed comparing the corresponding thioether and sulfone complexes, 6g and 6h, that both induce an impressive drop of the catalytic activity with 29% and 23% of conversion respectively after 2 hours (Table 5, entries 4 and 5). Complex 6i has been synthesized in order to study the influence of the alkyl aryl sulfur (II/IV/VI) groups on the germanium center during the catalysis. The result shows again a decrease of the catalytic activity (39%) in comparison with complex **6b**, but this result cannot be attributed formally to complex 6i (Table 5, entry 6). Indeed, the substitution of the chlorine atom by the base during

the catalytic process might undergo as well, that will influence the steric and electronic

properties of the	active catalyst.		

Entry ^a	Catalyst (2 mol%)	T (°C)	Reaction time (h)	Conversion (%) ^b
1	6b	80	2	76
2	6d	.د	دد	57
3	6f	دد	دد	43
4	6g	دد	دد	29
5	6h		.د	23
6	6i		دد	39

^a The reactions were carried out in dry and degassed isopropyl alcohol (2 mL) under argon in presence of acetophenone (0.9 mmol) ^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard.

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard. Table 5: Catalytic activity of different ruthenium complexes **6b-d-f-g-h-i** in hydrogen transfer

reaction

Finally, complex **5a** was used in hydrogen transfer reaction in order to study the influence of the coordination of the ruthenium center by the sulfoxide group and by the triphenylphosphine (Scheme 6).



Scheme 6: Germylene-ruthenium complexes 5a, 5a.PPh₃ and 5b.PPh₃

5a was used in the same conditions in *i*-PrOH (2 mL) at 80 °C. The conversion was monitored after 2 hours of reaction time (Table 6). A full conversion is obtained after 2 hours with 20 mol% of KOH (Table 6, entry 4). Surprisingly, the catalyst is totally inactive in absence of external base (Table 6, entry 3).

Entry ^a	Catalyst (2 mol%)	KOH (X mol%)	T (°C)	Reaction time (h)	Conversion (%) ^b
1	6b	-	80	2	24
2	"	20	"	"	76
3	5a	-	"	"	<3
4	"	20	"	"	>97

^a The reactions were carried out in dry and degassed isopropyl alcohol (2 mL) under argon in presence of acetophenone (0.9 mmol)

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard. Table 6: Catalytic activity of complex **5a** in hydrogen transfer reaction

The effect of the temperature was next investigated with complexes **6b**, **5a**, **5a**, **PPh**₃ and **5b**.**PPh**₃ in presence of the same amount of base KOH (20 mol%) (Table 7). At 50 °C, during the use of complex **6b**, a 61 % maximum conversion is obtained after 17 hours (Table 7, entry 1) while a fully conversion is obtained after 4 hours with complexes **5a**, **5a**.**PPh**₃ and **5b**.**PPh**₃ (Table 7, entries 3, 5 and 6). The comparison of **5a** and **5a**.**PPh**₃ allows to determine if the presence of residual PPh₃ might have an influence on the catalytic activity for a potential application of **5b**.**PPh**₃ in asymmetric catalysis, **5b**.**PPh**₃ cannot be obtained pure without residual PPh₃. After 2 hours, the conversion is similar, 68 % compared to 74 % (Table 7, entries 2 and 4). However, the conversion is complete after 4 hours with the three different catalysts (Table 7, entries 3, 5 and 6). Finally, we observe that **5b**.**PPh**₃ is active at 25 °C with a conversion of 26 % after 2 hours and a full conversion after three days (Table 7, entries 7-10). Finally, the positive effect of the ligand can be validated by comparing the use of Ru(PPh₃)₃Cl₂ in the same conditions (Table 7, entry 11), a conversion of only 69% being obtained.

Entry ^a	Catalyst (2 mol%)	V (mL)	T (°C)	Reaction time (h)	Conversion (%) ^b
1	6b	1	50	17	61
2	5a	2	دد	2	68
3	5a		دد	4	>97
4	5a.PPh ₃		دد	2	74
5	5a.PPh ₃		"	4	>97
6	5b.PPh ₃	.د	"	4	>97
7	5b.PPh ₃	.د	25	2	26
8	5b.PPh ₃	.د	"	6	50
9	5b.PPh ₃	.د	"	28	87
10	5b.PPh ₃	دد	"	72	>97
11	Ru(PPh ₃) ₃ Cl ₂	۰۵	"	72	69

^a The reactions were carried out in dry and degassed isopropyl alcohol (X mL) under argon in presence of acetophenone (0.9 mmol)

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard.

Table 7: Catalytic activity of complexes 5a, 5a.PPh₃ and 5b.PPh₃ in hydrogen transfer

reaction

Enantiopure complexes **6b**, **6d** and **5b.PPh**₃, synthetized by using (R)-(+)-methyl-p-tolyl sulfoxide as precursor, have been tested in asymmetric hydrogen transfer of acetophenone (Table 8). The ee have been determined by HPLC analysis using a chiral OD column with an UV detector. At 50 °C, 7-8 % poor ee are obtained (Table 8, entries 1, 2 and 3). However, a moderate 21 % ee is obtained by decreasing the temperature at 25°C (Table 8, entry 4).

Entry ^a	Catalyst (2 mol%)	V (mL)	T (°C)	t (h)	Conversion (%) ^b	ee ^c
1	6b	1	50	17	61	7
2	6d	1	50	17	57	8
3	5b.PPh ₃	2	50	4	>97	7
4	5b.PPh ₃	2	25	72	>97	21

^a The reactions were carried out in dry and degassed isopropyl alcohol (X mL) under argon in presence of acetophenone (0.9 mmol)

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard.

^c ee were determined by HPLC with a chiracel OD column

Table 8: Catalytic activity of complexes 6b, 6d and 5b.PPh₃ in asymmetric hydrogen transfer

reaction

Finally, **5b.PPh₃** was used at room temperature in presence of 20 mol% of KOH to reduce several carbonyl compounds (Table 9). First, some *para*- substituted acetophenones have been used and reduced successfully after 3 days with different substituents such as bromo, methoxy or trifluoromethane groups (Table 9, entries 2-4). Interestingly, benzophenone was reduced in the same conditions and proved that steric hindrance can be increased on both sides of the ketone (Table 9, entry 5). However, steric hindrance on the substrate can also have a dramatic influence, adamantyl-methyl ketone being unchanged even after 4 days at room temperature (Table 9, entry 7). Finally, benzaldehyde has been also reduced successfully after 4 hours (Table 9, entry 6).

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Entry ^a	Carbonyl	Product	t (H)	Conversion (%) ^b
1		OH	72	>97
2	Br	Br	72	>97
3		⊖ O	72	>97
4	F F F F	F ₃ C	72	>97
5		OH	72	>97
6		OH OH	4	>97
7		/	96	n.r.

^a The reactions were carried out in dry and degassed isopropyl alcohol (2 mL) under argon in presence of carbonyl compound (0.9 mmol)

^b Determined by ¹H NMR analysis by using tetramethylbenzene (0.45 mmol) as internal standard.

Table 9: Applications of hydrogen transfer reaction to different carbonyl compounds

 $5b.PPh_3$ was successfully employed in hydrogen transfer catalysis for the reduction of several ketones and aldehyde. The enantioselective catalysis showed a moderate ee of 21% that proved the influence of the enantioselective ligand on the active catalyst species.

II.2. Catalytic activity of sulfonimidamide metallylenes in polymerization catalysis

Polycaprolactone is a polymer of great interest because of the numerous applications as biodegradable and biocompatible polymer. The polymer can be formed by catalysis with tin (II) which is a well-known catalyst to start living polymerization. Thereby, the sulfonimidamide metallylenes described in the chapter IV were envisaged in polymerization catalysis (Scheme 7).



Scheme 7: Sulfonimidamide metallylenes used in polymerization catalysis

Polymerization of ε -caprolactone was envisaged by using **14a** as catalyst in toluene at 100 °C (Scheme 8). The reaction was monitored by ¹H NMR analysis.



Scheme 8: Polymerization catalysis using 14a

After 1 hour at 100 °C, the polymerization took place with a conversion of 29 % and an interesting PDI of 1.09 (Table 10, entry 1). The conversion can reach 77 % after 7 hours with a higher PDI of 1.40, showing thus a larger polydispersity of the polymer that can be explained by trans-esterification reactions. Moreover, a deactivation of the catalyst has been observed after 7h, not allowing a full conversion (Table 10, entry 2). The results are promising and show a better activity of **14a** than other tin (II) derivatives in the absence of initiator such as primary alcohols or amines.¹²

Entry ^a	Catalyst (0.5 mol%)	t (H)	Conversion (%) ^b	PDI
1	14a	1	29	1.09
2	14a	7	77	1.40

^a The reactions were carried out in dry and degassed toluene (3 mL) under argon in presence of ε -caprolactone (8.7 mmol)

^b Determined by ¹H NMR analysis by comparing the integration of the signal of the polymer with the monomer.

Table 10: Catalytic activity of complex 14a in polymerization of *ɛ*-caprolactone

Then, the investigations of the activity of **14b**, was considered due to the steric and electronic differences of the tin (II) center (Table 11). In the same conditions as previously described, a conversion of 89% after 1 hour was obtained (Table 11, entry 1). However, moderate PDI of 1.66 showed again a larger polydispersity of the polymer due to the formation of a gel that blocked the stirring bar and increase the trans-esterification of the polymer. This problem was solved by lowering the temperature to 80 °C, which decreased significantly the activity of the catalyst without stopping the reaction. After 1h, the conversion of 11% was obtained with a better PDI of 1.18 (Table 11, entry 2). A longer reaction time afforded a conversion of 48% with a moderate PDI of 1.36 (Table 11, entry 3).

Entry ^a	Catalyst (0.5 mol%)	t (H)	T (° C)	Conversion (%) ^b	PDI
1	14b	1	100	89	1.66
2	14b	1	80	11	1.18
3	14b	6	80	48	1.36

^a The reactions were carried out in dry and degassed toluene (3 mL) under argon in presence of ε -caprolactone (8.7 mmol)

^b Determined by ¹H NMR analysis by comparing the integration of the signal of the polymer with the monomer.

Table 11: Catalytic activity of complex 14b in polymerization of ε -caprolactone

Finally, germylenes **13a** and **13b** were used in the same conditions (Table 12). However, these two catalysts appeared totally inactive in catalysis. The insertion and formation of a Ge(IV) species might be too stable to allow a catalysis with germanium.

Entry ^a	Catalyst (0.5 mol%)	t (H)	Conversion (%) ^b	PDI
1	13a	10	>5	n.d.
2	13b	10	>5	n.d.

^a The reactions were carried out in dry and degassed toluene (3 mL) under argon in presence of ε -caprolactone (8.7 mmol) ^b Determined by ¹H NMR analysis by comparing the integration of the signal of the

polymer with the monomer.

The structure of the polymer was also investigated to determine if the mechanism was a ROP or a REP to give a linear or a cyclic polycaprolactones.¹⁶ Linear polycaprolactone and ROP mechanism was determined due to end group signal found in ¹H NMR corresponding to a sulfonimidamide and a $-CH_2$ -OH end group (Figure 1). $-CH_2$ -OH end group was observed as a triplet at 3.63 ppm, moreover, aromatic signals of the sulfonimidamide group were also found in the pure polymer.



Figure 1: Polymerization catalysis using 14a

Table 12: Activity of complex **13a** and **13b** in polymerization of ε-caprolactone

III. Conclusion

Ruthenium complexes **6b-i** have been described as active catalysts in hydrogen transfer reaction of acetophenone in *iso*-propanol. Optimization of the reaction conditions during the use of **6b** as catalyst has shown the importance of the base on the catalytic activity.

Comparison of the different ligands has demonstrated the influence of the steric hindrance on the ligand. Finally, the corresponding thioether and sulfone derivatives induced a significant decrease of the activity compared to **6b**. This latter result demonstrates clearly that the sulfoxide moiety has an important impact on the catalysis by a greater activity or by a better stability. Finally, **5a** and **5b** appeared much more active than all the other ruthenium complexes allowing to reduce acetophenone at room temperature.

Hydrogen transfer reaction was finally investigated with enantiopure ruthenium complexes **6b**, **6d** and **5b**. The enantiomeric excess of the reaction at 50 °C was low. However, a moderate 21% ee was obtained at room temperature with **5b**. The same complex has also allowed the reduction of various ketones and aldehyde at room temperature.

In a second part, sulfonimidamide stannylenes **14a** and **14b** were successfully applied in polymerization of ε -caprolactone. **14a** has shown a catalytic activity with moderate to good PDI (1.09 to 1.40) for a benchmark reaction, comparable to already reported and known tin (II) catalysts. Surprisingly, **14b** appeared much more active, with high potential for polymerization catalysis. Moreover, **14b** exhibits a stereogenic center to consider its use in stereoselective polymerization.

IV. Experimental section



Amidinate (di-*iso*-propyle-*t*-butyl) chloro germylene ruthenium complex (6i): amidinatochlorogermylene (100 mg, 0.34 mmol, 1 eq) was dissolved in tetrahydrofuran (5 mL) and dichloro(*p*-cymene)ruthenium dimer (104 mg, 0.17 mmol, 0.5 eq) was added to the solution. The mixture was stirred during 15 hours at room temperature, then filtered and the solvent removed under reduced

pressure. Finally, the red solid was washed with Et₂O (2x3 mL) in order to obtain a pale red solid (175 mg) in 86% yield. Crystallization from THF at 6 °C gave red crystals suitable for X-ray study. M.p. : 173 °C (decomposition); ¹H NMR (300.18 MHz, C_6D_6 , 25 °C): δ 0.97 (s, 9H, C(CH₃)₃); 1.17 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.41 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.45 (d, ³J_{HH} = 6.3 Hz, 3H, CH(CH₃)₂); 1.95 (s, 3H, *p*-CH₃); 3.02 (sept., ³J_{HH} = 6.3 Hz, 1H, CH(CH₃)₂); 3.92 (sept., ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂); 5.06 (d, 2H, ³J_{HH} = 8.2 Hz, CH_{Ar}); 5.31 (d, 2H, ³J_{HH} = 8.2 Hz, CH_{Ar}). ¹³C {¹H} NMR (75.48 MHz, C_6D_6 , 25 °C): δ 18.2 (*p*-CH₃); 22.6 (CH(CH₃)₂); 24.3 (CH(CH₃)₂); 25.1 (CH(CH₃)₂); 28.7 (C(CH₃)₃); 30.9 (CH(CH₃)₂); 38.9 (C(CH₃)₃); 48.7 (CH(CH₃)₂); 85.3 (C_{Ar}); 85.7 (C_{Ar}); 98.3 (C_{Ar/q}); 105.1 (C_{Ar/q}); 179.5 (N–C–N).

Formula	C21H37GeN2Ru	dcalc (g/cm ³)	1.573
Mol wt	597.56	μ (mm ⁻¹)	2.117
Temp. (K)	193(2)	F(000)	1216
Cryst syst	monoclinic	cryst size (mm)	0.16 x 0.14 x 0.10
Space group	P21/n	θ range (deg.)	3.21 to 31.50
a (Å)	15.6231(6)	index range h k l	-22<=h<=22, -13<=k<=13, -25<=l<=25
b (Å)	9.2709(4)	no of reflns collected /	50694
c (Å)	17.4244(7)	unique	8387 [R(int) = 0.0334]
α (deg.)	90	Completeness to θmax(%)	99.9
β (deg.)	90.0200	data/restraints/params	8387 / 0 / 263
γ (deg.)	90	goodness-of-fit	1.082
V (Å3)	2523.75(18)	R1, wR2 ($I > 2\sigma(I)$)	0.0306, 0.0609
Ζ	4	R1, wR2 (all data)	0.0421, 0.0649
General procedure for catalytic transfer hydrogenation reaction of acetophenone with isopropyl alcohol:

In a schlenk tube, catalyst (0.018 mmol) and tetramethylbenzene (0.45 mmol, 60.3 mg) was dissolved in *i*-PrOH (X mL, see desired volume in table) and stirred for 10 min. Then, acetophenone (0.9 mmol, 105 μ L) was added and the mixture stirred at the indicated temperature for the desired time. Aliquots (0.2 mL) were dissolved in CDCl₃ (0.4 mL) and conversions were determined by ¹H NMR analysis. Determination of *ee* was performed on a HPLC with a chiralcel OD column at a flow rate of 1 mL/min with a mobile phase of heptane/*i*-PrOH (96/4). The two enantiomers were detected with an UV detector at 210 nm with a retention time of 12.4 min and 14.7min.

General procedure for catalytic polymerization of ε-caprolactone:

In a schlenk tube, catalyst (0.04 mmol) was dissolved in toluene (3 mL) and stirred for 10 min. Then, ε -caprolactone (1 g, 8.73 mmol) was added and the mixture stirred at the indicated temperature for the desired time. Aliquots (0.2 mL) were dissolved in CDCl₃ (0.4 mL) with a small amount of benzoic acid and conversions were determined by ¹H NMR analysis. Polymer was treated at the end of reaction by addition of benzoic acid. The mixture was then evaporated and the solid was then dissolved in DCM. The solution was cooled with liquid nitrogen and methanol was added drop to drop to precipitate the polymer.

The number-average and weight-average molar masses (Mn and Mw, respectively) and molar mass distributions (Đ) of the polymer samples were determined by size exclusion chromatography (SEC) at 35 °C with a Waters 712 WISP high-speed liquid chromatograph equipped with a R410 refractometer detector. Tetrahydrofuran was used as the eluent, and the flow rate was set up at 1.0 mL/min. A SHODEX precolumn (polystyrene AT806M/S Mw = 50000000 g/mol) and two STYRAGEL columns (HR1, 100–5000 g/mol, and HR 4E, 50–100000 g/mol) were used. Calibrations were performed using polystyrene standards (400–100000 g/mol).

V. Notes and references

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Conclusion

Conclusion

Conclusion

During this thesis, we have developed: (i) the synthesis of two-generations of hemilabile germylene-sulfoxide ligands and their corresponding transition metal complexes, (ii) the elaboration of new homoleptic metallylenes stabilized by sulfonimidamides and (iii) the application of the previous complexes and metallylenes in hydrogen transfer or polymerization catalysis.

A novel germylene - α - sulfoxide ligand has been investigated in the first place and successfully obtained even if sulfoxides are well known oxidant. The versatility of the methodology has been extended to a wide range of (i) structural architectures, by modification of the amidinate or the sulfoxide group, and (ii) oxidation state of sulfur with the introduction of thioether or sulfone. These ligands have been used in coordination chemistry with group IV and two different ruthenium (II) precursors to obtain several monodentate, bis-monodentate and bidentate complexes. The formation of a bidentate ruthenium (II) complex with a coordination through germanium and oxygen atoms showed a potential hemilability of the sulfoxide ligand. The ruthenium complexes have been applied in hydrogen transfer reaction of acetophenone in ^{*i*}PrOH to form the corresponding alcohol. The optimal conditions at 25 °C allowed to fully reduce various carbonyl compounds such as arylmethylketones, bis(aryl)ketone and arylaldehyde in a reaction time of 4 to 72 hours. The asymmetric reduction of acetophenone has been also investigated starting with enantiopure ligands to obtain a moderate ee of 21 %.

Then, the formation of germylene $-\beta$ - sulfoxide ligand has been investigated with a larger spacer between the metallylene and the sulfoxide moieties. The influence of the spacer showed different properties on the coordination chemistry of the ligand. Indeed, the complexation behavior toward group IV and nickel (0) was surprisingly different and resulted in the formation of bidentate complexes with germanium and sulfur coordinated to the metal center. The formation of a nickel (0) complex allowed to obtain another nickel (0) tricarbonyl complex, by addition of carbon monoxide, which was used for a TEP comparison. The result showed that the σ -donation strength of the germylene was between the σ -donation strength of phosphines and NHCs. Surprisingly, the formation of a new bis-ruthenium complex has been observed with a μ -SO bridge.

Conclusion

The synthesis of several symmetric and dissymmetric sulfonimidamides has been performed. They were used for the stabilization of germylenes and stannylenes. Homoleptic metallylenes were obtained after protonolysis reaction of the sulfonimidamides and the bis(HMDS) metallylene. Their electronic properties have been investigated by DFT calculations. Finally, stannylenes have been applied in the polymerization of ε -caprolactone, showing an interesting activity, especially for the dissymmetric sulfonimidamide stannylene.

Listing of products

Chapter II:







-265-



Chapter III:



6f





Chapter IV:

11b









Résumé

Ce travail présente la synthèse de ligands mixtes germylène-sulfoxyde qui ont été utilisés en chimie de coordination avec plusieurs métaux de transitions et finalement appliqués en catalyse de transfert d'hydrogène. Une seconde partie de ce travail est axée sur la synthèse de nouveaux métallylènes stabilisés par un sulfonimidamide qui ont été appliqués en catalyse de polymérisation. Le premier chapitre présente l'état de l'art des germylènes avec leurs synthèses, modes de stabilisations et finalement leur chimie de coordination et leurs applications en catalyse. Les sulfoxydes seront aussi décrits pour leur application en tant que ligands hémilabiles.

Le second chapitre décrit la synthèse de ligands germylène-α-sulfoxide avec une diversité structurale (cyclohexyle, ^{*t*}Bu, tolyle..) et avec différents degrés d'oxydation du souffre (thioéther, sulfoxyde et sulfone). La chimie de coordination a permis la synthèse de complexes bis-germylène du groupe IV, bidentes du ruthénium ainsi que monodentes du ruthénium.

Le troisième chapitre présente l'extension de la méthodologie à la formation de ligands germylène- β -sulfoxide. L'influence du groupement espaçant les deux entités sur la chimie de coordination a été étudiée et montre la formation de complexes bidentates du groupe IV. La coordination du ruthénium a mené à la surprenante synthèse d'un complexe bis-ruthénium caractérisé par diffraction des rayons X. Finalement, la nouvelle architecture a permis d'obtenir des complexes de nickel (0) dont une structure avec des ligands carbonyles permettant une comparaison TEP.

Le chapitre quatre présente la synthèse de nouveaux ligands, analogues des amidinates, pour la stabilisation des métallylènes avec un atome central soufré. L'effet apporté sur les métallylènes par ces nouveaux ligands sulfonimidamides a été étudié par calcul DFT.

Le dernier chapitre est centré sur l'application de plusieurs complexes de ruthénium en catalyse de transfert d'hydrogène avec plusieurs substrats carbonylés. L'utilisation de stannylènes stabilisés par des ligands sulfonimidamides a été étudiée en catalyse de polymérisation de la ɛ-caprolactone.

Mots clés : Germylène, sulfoxyde, ligand hémilabile, réaction de transfert d'hydrogène, sulfonimidamide, polymérisation de la ɛ-caprolactone.

Abstract

This work concerns the synthesis of mixed germylene-sulfoxide ligands that were involved in coordination chemistry with several transition metals and finally applied in hydrogen transfer catalysis. In a second part, the synthesis of new metallylenes stabilized by a sulfonimidamide group was develop, which were applied in polymerization catalysis. The first chapter is centered on the state of the art of germylenes with their synthesis, their stabilization and finally their coordination chemistry and applications in catalysis. Sulfoxides will also be described for their potential as hemilabile ligands.

The second chapter describes the synthesis of germylene- α -sulfoxide ligands as structurally tunable structures (cyclohexyl, ^{*t*}Bu, tolyl..) and with different oxidation states of the sulfur atom (thioether, sulfoxide and sulfone). The coordination chemistry led to the formation of bis-germylene group IV complexes, bidentate-ruthenium and monodentate ruthenium complexes.

The third chapter shows the extension of the methodology to the formation of germylene- β -sulfoxide ligands. The influence of the spacer between the two entities on the coordination chemistry was studied and shows the formation of bidentate group IV complexes. Coordination to ruthenium led to obtain a surprising bis-ruthenium complex characterized by X-ray diffraction analysis. Finally, the novel architecture allowed to obtain two nickel (0) complexes, one of them including carbonyl ligands permitting a TEP comparison.

The fourth chapter is centered on the synthesis of new ligands, analogue of amidinate substituents for metallylene stabilization with a central sulfur atom. The effect brought to the metallylene center by the sulfonimidamide was studied by DFT calculations.

The last chapter concerns the application of several ruthenium complexes in hydrogen transfer reaction with various carbonyl compounds. The use of sulfonimidamide stannylenes was also investigated in polymerization catalysis of ε -caprolactone.

Keywords: Germylene, sulfoxide, hemilabile ligand, H-transfer reaction, sulfonimidamide, ε-caprolactone polymerization.