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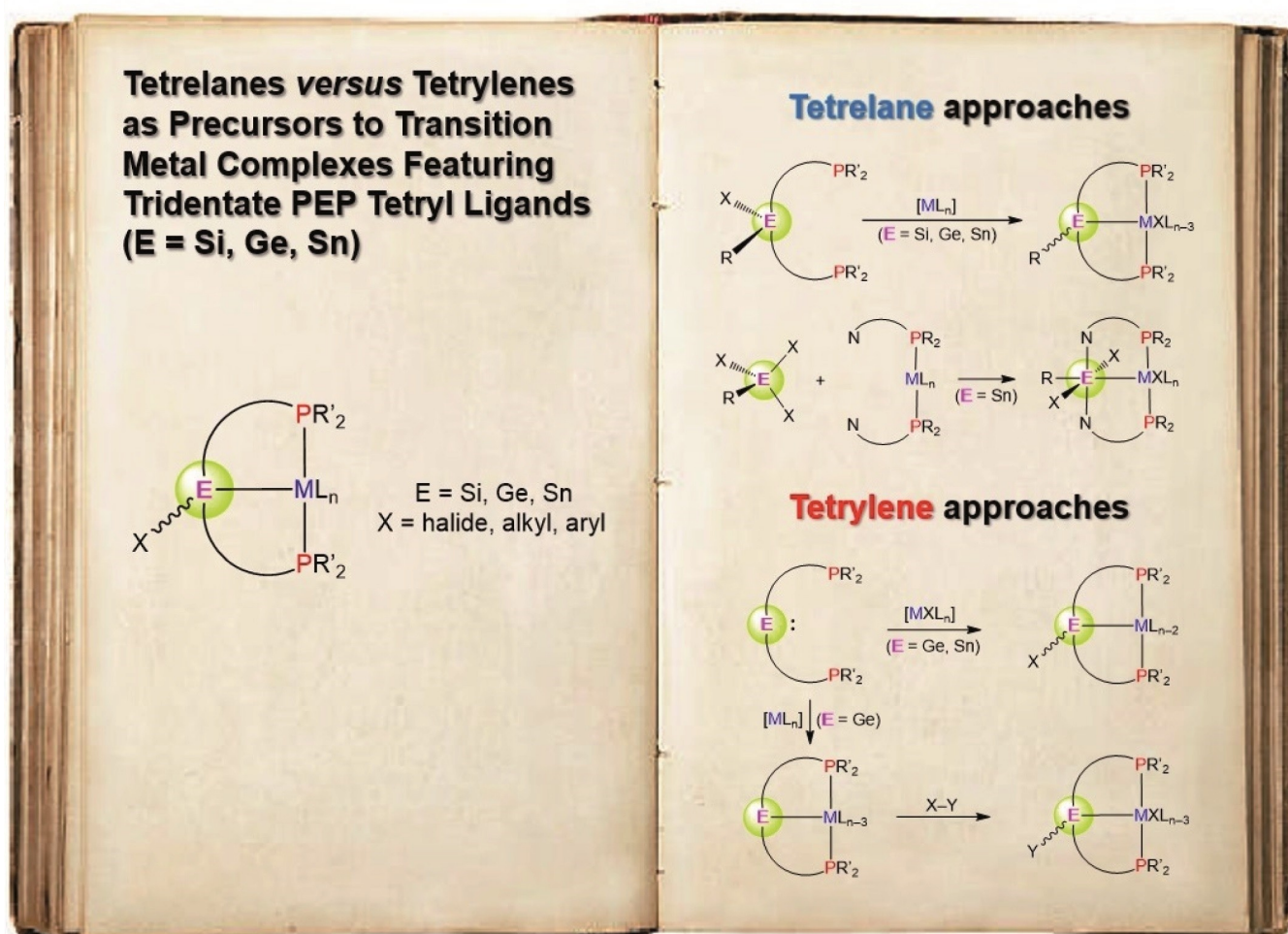


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Tetrelanes *versus* Tetrylenes as Precursors to Transition Metal Complexes Featuring Tridentate PEP Tetryl Ligands (E=Si, Ge, Sn)

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Abstract: Two synthetic approaches have until now been used to synthesize transition metal complexes having a tridentate (pincer or tripod) PEP tetryl (E=Si, Ge, Sn) ligand. These approaches differ in the metal-free precursor, tetrelane or tetrylene, that gives rise to the corresponding PEP tetryl ligand. Tetrelanes (PSiP silanes, PGeP germanes and PSnP stannanes and simple phosphane-free stannanes) have led to tetryl ligands by oxidatively adding an E–X bond (X=H, C or halogen in most cases) to the metal atom of a low-valent

transition metal complex, whereas tetrylenes (PGeP germynes and PSnP stannylenes) have led to tetryl ligands upon insertion of their E atom into an M–X bond (X=Cl in most cases) of the metal precursor or through a derivatization of the E atom after the tetrylene fragment is coordinated to the metal. For each synthetic approach, all the currently known types of PEP tetryl ligand frameworks that have been found in transition metal complexes are presented and discussed in this review.

1. Introduction

Mononuclear transition metal complexes featuring a heavier tetryl (silyl, germynyl or stannylyl) group as the internal fragment of a PEP (E=Si, Ge, Sn) tridentate (pincer or tripod) ligand (Figure 1) are currently an important class of complexes. In fact, despite their recent development, PEP tridentate heavier tetryl complexes have already been reported for most late transition metals (groups 8–12 of the Periodic Table), their metal atoms have been found in a variety of coordination numbers and environments, and some of them have already revealed an interesting catalytic activity.^[1,2] Their PEP ligands combine the convenient features of tridentate ligands, which generally provide enhanced kinetic and thermodynamic stabilities to their complexes, with those of phosphanes (easy steric and electronic tunability and easy reaction monitoring by ³¹P{¹H} NMR spectroscopy) and heavier tetryl ligands, which are stronger σ -donors on going up in the 14th column of the Periodic Table (tetrel atoms) and have an enhanced π -accepting character on going down in the group.^[1–4]

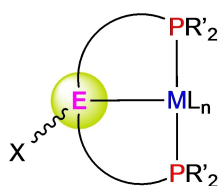


Figure 1. Schematic structure of the title complexes (E=Si, Ge, Sn; X = mono-anionic group).

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Prompted by the high interest that PEP pincer- or tripod-type heavier tetryl complexes are currently receiving, this article reviews the state-of-the-art of the synthesis of such complexes from their metal-free precursors, presenting and discussing the currently known synthetic approaches. The metal-centered derivative chemistry of these complexes, which has been extensively studied and reviewed in some cases,^[1,2] is not covered by this review.

2. Synthetic Approaches

To date, all reported metal complexes that are known to contain a PEP tridentate heavier tetryl ligand have been prepared using either tetrelanes (silanes, germanes, stannanes) or tetrylenes (silylenes, germynes, stannylenes) as metal-free precursors of the tetryl group. The toxicity of lead compounds may be behind the fact that PPbP tridentate plumbyls have not thus far been reported. Tetrelanes (PEP or phosphane-free) lead to tetryl ligands by oxidatively adding an E–X bond (X=H, halogen or C in most cases) to the metal atom of a low-valent transition metal complex (Figure 2), whereas PEP tetrylenes lead to tetryl ligands upon insertion of their E atom into an M–X bond (X=halogen in most cases) of the metal precursor or through a derivatization of the E atom after the tetrylene fragment is coordinated to the metal (Figure 3).

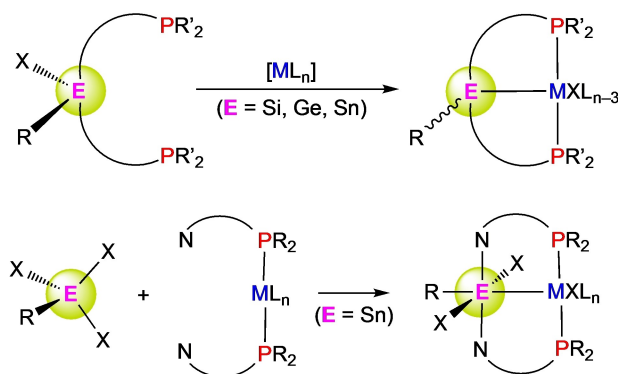


Figure 2. Tetrelane approaches to metal complexes containing a PEP heavier tetryl ligand.

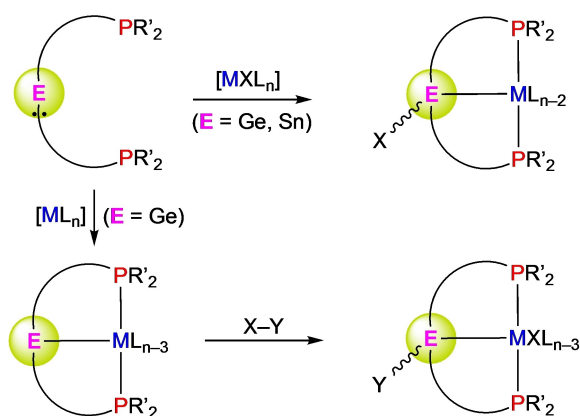


Figure 3. Tetrelene approaches to metal complexes containing a PEP heavier tetrel ligand.

2.1. Tetrelene Approaches

The first PSiP silyl complex was reported in 1996. It was prepared by treating silane **A** with $[\text{PtCl}_2(\text{cod})]$ (cod = 1,5-

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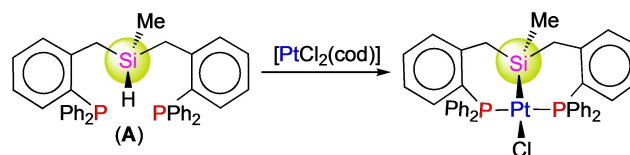
Pablo García-Álvarez obtained his PhD at the Univ. of Oviedo (2006) under the supervision of Javier A. Cabeza. After exploring some mixed-metal chemistry of representative elements in Strathclyde Univ. (Glasgow), working with Robert E. Mulvey, he returned to the Univ. of Oviedo in 2010 as a “Juan de la Cierva” research fellow. In 2014 he gained a position as a “Ramón y Cajal” researcher and in March 2021 he was promoted to Professor of Inorganic Chemistry. His research is focused on the coordination chemistry of heavier carbene analogues. In 2015 he received the “Young Researcher Award” from GEQO. He has authored more than 90 scientific publications.



cyclooctadiene) (Scheme 1).^[5] The synthesis of **A** (air sensitive liquid) was accomplished by treatment of SiCl_2MeH with a) $\text{BrMg-}o\text{-C}_6\text{H}_4\text{CH}_2\text{Br}$, b) $n\text{BuLi}$ and c) PPh_2Cl ^[5] or by reacting SiCl_2MeH with $[\text{Li}(\text{tmeda})][\text{CH}_2\text{PPh}_2]$ (tmeda = tetramethylethylenediamine).^[6]

The second family of PSiP silyl complexes was reported in 1997. Their syntheses involved reactions of silanes of type **B** ($\text{R}=\text{Me, Ph}$; $\text{X}=\text{H}$: $\text{R}'=\text{Ph, Cy}$; $n=1, 2$) with $[\text{PtCl}_2(\text{cod})]$, $[\text{Ir}_2\text{Cl}_2(\text{cod})_2]$, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Ru}_3(\text{CO})_{12}]$ (Table 1). While the platinum $[\text{PtCl}(\text{PSi}^{\text{R}}\text{P}_\text{B})]$ and iridium $[\text{IrHCl}(\text{PSi}^{\text{Me}}\text{P}_\text{B})]$ complexes were prepared in high yields, the ruthenium complexes $[\text{RuH}(\text{PSi}^{\text{Me}}\text{P}_\text{B})(\text{CO})_2]$ were minor reaction products.^[7a] The use of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ as starting complex allowed the synthesis of $[\text{RuCl}(\text{PSi}^{\text{Me}}\text{P}_\text{B})(\text{CO})]$ in high yield.^[7b] Some derivative chemistry of $[\text{IrHCl}(\text{PSi}^{\text{Me}}\text{P}_\text{B})]$ was subsequently developed.^[7c] The starting phosphane-silanes $\text{Si}\{(\text{CH}_2)_n\text{PR}'_2\}_2\text{RH}$ ($n=2, 3$) are air-sensitive liquids or gummy solids that were prepared by hydrophosphanylation $\text{Si}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}_2\text{RCI}^{[6]}$ or $\text{Si}\{(\text{CH}_2)_n\text{CH}=\text{CH}_2\}_2\text{RH}^{[8]}$ ($\text{R}=\text{O, 1}$) with $\text{PR}'_2\text{H}$ under UV irradiation (the chloridosilyl products of the former reactions were subsequently reduced with LiAlH_4 to the corresponding hydridosilyl derivatives). These complicated synthetic procedures have probably hampered the broadening of the transition metal chemistry of silanes of types **A** and **B**.

Silanes of type **C** (Table 2) were generally prepared by reacting dichloridosilanes SiCl_2RH ($\text{R}=\text{H, alkyl, aryl}$) with two equivalents of lithiated phosphanes $\text{Li}\{[o\text{-C}_6\text{H}_4]\text{PR}'_2\}$ ($\text{R}'=\text{Ph, }i\text{Pr, Cy, }t\text{Bu}$). This simple synthetic procedure and the easy availability of the starting materials have allowed a wide development of the transition metal chemistry of silanes of type **C** (Table 2).^[9–53] The formation of the metal complex involves the coordination of both P atoms and the oxidative addition of the Si–H bond to a low valent transition metal complex, the most common metal precursors being $[\text{Fe}(\text{PMe}_3)_4]$,



Scheme 1. Synthesis of the first PSiP silyl complex.

Table 1. PSiP silanes of type **B** that have been used as precursors to PSiP silyl complexes.

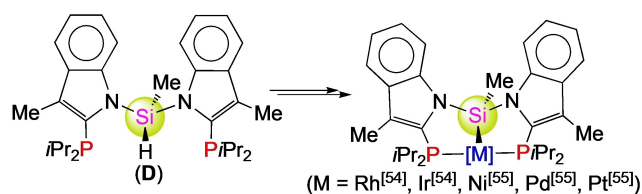
n	R	R'	M
0	Me	Ph	$\text{Pt}^{[7a]}, \text{Ru}^{[7a]}$
0	Me	Cy	$\text{Pt}^{[7a]}$
0	Ph	Cy	$\text{Pt}^{[7a]}$
0	Ph	Ph, Cy	$\text{Pt}^{[7a]}$
1	Me	Ph	$\text{Pt}^{[7a]}, \text{Ru}^{[7a,b]}, \text{Ir}^{[7a,c]}$
1	Me	Cy	$\text{Pt}^{[7a]}$
1	Ph	Ph	$\text{Pt}^{[7a]}$

Table 2. PSiP silanes of type C that have been used as precursors to PSiP silyl complexes.

R	R'	M
Me	<i>i</i> Pr	Fe ^[9,40b] , Ru ^[10–12] , Co ^[13–15] , Ir ^[16,27,53] , Ni ^[18] , Pd ^[19]
Me	Cy	Fe ^[20,25,52] , Ru ^[22,23] , Co ^[24,25,52] , Rh ^[17,26] , Ir ^[17,26,27] , Ni ^[28–30,32] , Pd ^[19,28,29,31] , Pt ^[19,37]
Me	<i>t</i> Bu	Ir ^[21,27]
Me	Ph	Fe ^[25,33,40,52] , Ru ^[34] , Co ^[15,33] , Rh ^[34,35] , Ir ^[35] , Ni ^[32,33,36c] , Pd ^[28,34,36] , Pt ^[34,36c,37]
Me	3,5-(CF ₃) ₂ C ₆ H ₃	Pd ^[36a,b]
Me	4-(CF ₃)C ₆ H ₄	Pd ^[36a,b]
Me	4-MeOC ₆ H ₄	Pd ^[36b]
Me	2-MeC ₆ H ₄	Pd ^[36b]
Me	2-furyl	Pd ^[36b]
Et	Ph	Rh ^[35] , Ir ^[35]
Ph	<i>i</i> Pr	Fe ^[9] , Co ^[14,15,38]
Ph	Ph	Fe ^[40b] , Co ^[15,38] , Rh ^[35] , Ir ^[35]
Ph	Cy	Fe ^[25,52]
H	Cy	Rh ^[41]
H	Ph	Fe ^[40] , Ru ^[42] , Co ^[15,38,43] , Rh ^[44]
H	<i>i</i> Pr	Fe ^[40] , Co ^[15,38,43,45] , Pt ^[46,47]
C ₆ H ₄ P <i>i</i> Pr ₂	<i>i</i> Pr	Pt ^[48]
C ₆ H ₄ PPh ₂	Ph	Pt ^[48]
C ₆ H ₄ SAd	<i>i</i> Pr	Fe ^[49]
O _{1/2}	<i>i</i> Pr	Ni ^[50]

[RuCl₂(PPh₃)₃], [Co₂(CO)₈], [M₂Cl₂(cod)₂] (M=Rh, Ir), [Ni(cod)₂], [NiCl₂(dme)] (dme = 1,2-dimethoxyethane), [PdCl₂(MeCN)₂] and [PtCl₂(cod)]. A Si–F bond cleavage was observed in the reaction of Si{(o-C₆H₄)PPh₂}₂F₂ with [IrH(CO)(PPh₃)₃], which led to [Ir{Si{(o-C₆H₄)PPh₂}₂F₂}(CO)(PPh₃)₃].^[39b] The oxidative addition of an Si–Cl bond of Si{(o-C₆H₄)PPh₂}₂Cl₂ to iridium has also been achieved.^[51] When the complexes contain an Si–H fragment (R=H), a subsequent derivatization at the Si atom, via silylene (Si=M) intermediates, to PSiP silyl derivatives is possible.^[40a,42,43–45,47] Curiously, the dihydrosilane Si{(o-C₆H₄)PPh₂}₂H₂ reacted with [Rh₂Cl₂(cod)₂] to give the chlorido-silyl complex [Rh{SiCl{(o-C₆H₄)PPh₂}₂}(cod)].^[44b] Many complexes derived from silanes of type C are efficient catalyst precursors for alkene hydrosilylation,^[15,38] carbonyl group hydrosilylation,^[33,40b] alkene hydrogenation,^[20,24,44a] alkyne hydrogenation,^[20] dinitrogen silylation,^[9,25,38,52] silane deuteration,^[50] organic azide carbonylation,^[13] allene carboxylation,^[31,36d,f] CO₂ hydroboration,^[31,32] alkene isomerization,^[32] alkene dehydrogenative borylation,^[36a,b] sila-Negishi coupling,^[39a] ketone transfer hydrogenation,^[21,34,40a] 2-butene isomerization and dimerization^[53] and arene borylation.^[27]

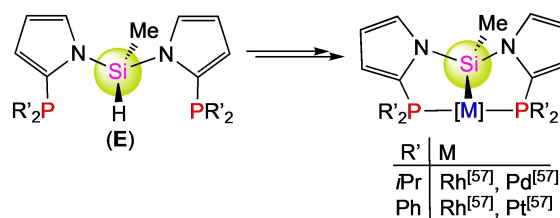
PSiP silyl complexes of Rh,^[54] Ir,^[54] Ni,^[55] Pd^[55] and Pt^[55] have been recently prepared from bis(indolyl)silane D (Scheme 2), reacting it with [M₂Cl₂(cod)₂] (M=Rh, Ir), [NiCl₂(dme)], [Pd₂Cl₂(allyl)₂] and [PtCl₂(SET)₂], respectively (Scheme 2). Silane D was synthesized in several steps from 3-methylindole: a) *n*BuLi, b) CO₂, c) *t*BuLi, d) *Pi*Pr₂Cl e) H₂O, f) *n*BuLi and g) 0.5 SiCl₂MeH.^[55,56] A hydridonickel complex has been successfully

**Scheme 2.** Synthesis of PSiP silyl complexes derived from silane D.

involved in CO₂ hydroboration.^[55] These indolyl-derived PSiP silyl ligands are sterically more demanding and weaker donors than their analogues derived from silanes of type C.

Diphenyl- and diisopropyl-2-pyrrolylphosphane have been recently used to prepare silanes of type E (Scheme 3) (from the corresponding lithium salts and SiCl₂MeH) together with some rhodium, palladium and platinum derivatives (from reactions with [Rh₂Cl₂(cod)₂], [RhH(CO)(PPh₃)₃], [Pd₂Cl₂(allyl)₂] and [PtCl₂(cod)], respectively) (Scheme 3).^[57] These pyrrolyl-derived PSiP silyl ligands are sterically similar but weaker donors than their analogues derived from silanes of type C.

N-Heterocyclic silanes of type F (Table 3), generally prepared by treating Li₂[(R'₂PCH₂N)₂(o-C₆H₄)] with the corresponding dichlorosilane SiCl₂RH, generated PSiP silyl derivatives (Table 3) upon treatment with [Fe(PMe₃)₄],^[58] [CoCl(PMe₃)₃],^[59] [CoMe(PMe₃)₄],^[59] [RuPhCl(CO)(PPh₃)₂],^[60] [RhCl(PPh₃)₃],^[60] [Ni(cod)₂],^[61] [Pd(PPh₃)₄]^[61] and [Pt(C₂H₄)(PPh₃)₂].^[61] The zero-valent group 10 metal precursors afforded dimetal(I) complexes having two silyl groups semibridging the M–M bond.^[61] Noteworthy, the reaction of dihydrosilane Si{(R'₂PCH₂N)₂(o-C₆H₄)}₂H₂

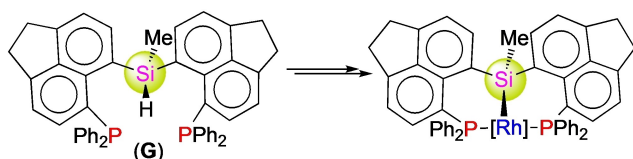
**Scheme 3.** Synthesis of PSiP silyl complexes derived from silanes of type E.**Table 3.** PSiP silanes of type F that have been used as precursors to PSiP silyl complexes.

R	R'	M
Me	Ph	Fe ^[58,59] , Co ^[59]
Ph	Ph	Fe ^[58] , Ru ^[60] , Rh ^[60] , Ni ^[61] , Pd ^[61] , Pt ^[61]
Ph	<i>i</i> Pr	Fe ^[58]
H	<i>t</i> Bu	Rh ^[44b]

with $[\text{RhCl}(\text{CO})(\text{PPh}_3)_3]$ has been shown to give the chloridosilyl complex $[\text{Rh}\{\text{Si}[(\text{R}'_2\text{PCH}_2\text{N})_2(\text{o}-\text{C}_6\text{H}_4)]\text{Cl}\}(\text{CO})]$ along with H_2 .^[44b] Some of these complexes have been satisfactorily involved in catalytic reactions, such as the dehydration of primary amines to nitriles^[58] and Kumada cross couplings.^[59]

The acenaphthyl-derived diphosphane-silane **G**, which was prepared by treating 5-diphenylphosphinoacenaphth-6-yl lithium with SiCl_2MeH ,^[62] reacted differently with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ and $[\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4]$ (Scheme 4). While the former gave the rhodium(I) dicarbonyl derivative $[\text{Rh}(\text{PSi}^{\text{Me}}\text{P}_6)(\text{CO})_2]$, the latter afforded a rhodium(III) complex, $[\text{RhHCl}(\text{PSi}^{\text{Me}}\text{P}_6)]$.^[63]

All PGeP tridentate germyl complexes that have thus far been prepared from metal-free germanes have used germanes of type **H** (Table 4),^[51,64–71] structurally analogous to silanes of



Scheme 4. Synthesis of PSiP silyl complexes derived from silane **G**.

Table 4. PGeP germanes (**H**) that have been used as precursors to PGeP germyl complexes.

X	R	R'	M
H	Me	Ph	$\text{Pd}^{[64,65]}$
H	Ph	Ph	$\text{Pd}^{[65]}$
Cl	Cl	Ph	$\text{Ir}^{[51]}$, $\text{Pt}^{[66]}$
Cl	Me	Ph	$\text{Pd}^{[67]}$
Cl	Me	4-MeOC ₆ H ₄	$\text{Pd}^{[67]}$
Cl	Ph	Ph	$\text{Pd}^{[69]}$, $\text{Pt}^{[68]}$
F	Ph	Ph	$\text{Pd}^{[69]}$
F	F	Ph	$\text{Ir}^{[70]}$
F	Ph	Ph	$\text{Ir}^{[70]}$
Me	Me	Ph	$\text{Rh}^{[71]}$, $\text{Ir}^{[71]}$
Ph	Ph	Ph	$\text{Ir}^{[70]}$

Table 5. PSnP stannanes of type **I** that have been used as precursors to PSnP stannyl complexes.

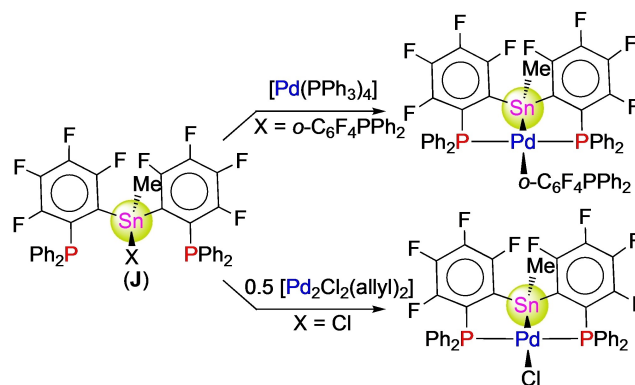
X	R	M
Me	Me	$\text{Rh}^{[71]}$, $\text{Ir}^{[71]}$
Me	Allyl	$\text{Pd}^{[65]}$
Ph	Allyl	$\text{Pd}^{[65]}$
Cl	Ph	$\text{Ir}^{[72]}$
F	Ph	$\text{Ir}^{[72]}$
F	C ₆ H ₄ PPh ₂	$\text{Ir}^{[72]}$
Cl	C ₆ H ₄ PPh ₂	$\text{Ir}^{[72]}$

type **C**. In all cases, germanes **H** were prepared by reacting $\text{Li}[(\text{o}-\text{C}_6\text{H}_4)\text{PR}'_2]$ with the appropriate dichloridogermane. Interestingly, the oxidative addition of the Ge–H bond of hydrido-germanes to low-valent metal complexes^[64,65] could not be satisfactorily achieved in most cases. Most complexes derived from germanes of type **H** were prepared by oxidatively adding Ge–X (X=F,^[69,70] Cl,^[51,66–69] Me,^[71] Ph^[70]) bonds to easily available low-valent metal complexes. Some of the resulting PGeP germyl complexes have been used as catalyst precursors for reductive aldol-type reactions^[65] and allene hydrocarboxylations.^[67]

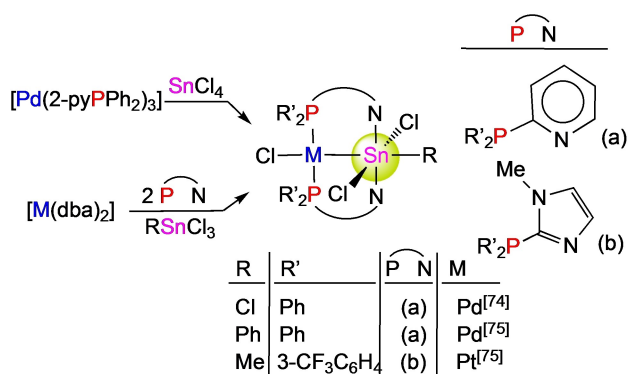
Two types of metal-free PSnP stannanes (**I** and **J**) have hitherto led to PSnP tridentate stannyl complexes. Curiously, stannanes of type **I** (Table 5) led to stannyl complexes through the oxidative addition of an Sn–C bond to a low-valent metal complex, such as $[\text{Pd}_2\text{Cl}_2(\text{allyl})_2]$ or $[\text{MH}(\text{CO})(\text{PPh}_3)_3]$ (M=Rh, Ir).^[65,71,72] For stannanes having both Sn–C and Sn–halogen bonds, the former are preferred over the latter.^[72] The participation of Sn–H and Sn–halogen bonds in these reactions has not been reported. One of the resulting PSnP stannyl complexes has been used as catalyst precursor for reductive aldol-type reactions.^[65]

Scheme 5 shows that stannanes of type **J** can lead to PSnP stannyl palladium(II) complexes via oxidative addition of Sn–C or Sn–Cl bonds.^[73] The oxidative addition of the Sn–C_{Me} bond of **J** was not observed.

A trichloridostannyl palladium(II) complex has been prepared by oxidatively adding an Sn–Cl bond of SnCl_4 to $[\text{Pd}(2\text{-pyPPH}_2)_3]$ (2-py = 2-pyridyl) (Scheme 6).^[74] This particular tetrelane approach (it does not involve a metal-free PEP tetrelane), which has been used only for E=Sn, was subsequently extended to platinum, trichloridoorganostannanes and other P–N phosphanes using $[\text{M}(\text{dba})_2]$ (M=Pd, Pt; dba = dibenzylidene acetone) as starting metal(0) precursors (Scheme 6).^[75] These complexes easily release a chloride anion from the tin atom, leading to cationic PSnP stannylene complexes.



Scheme 5. Synthesis of PSnP stannyl complexes derived from stannanes of type **J**.

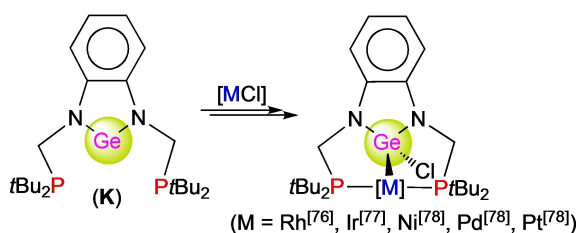


Scheme 6. P-SnP stannyl complexes derived from 2-pyridyl- and 2-imidazolyl-phosphanes.

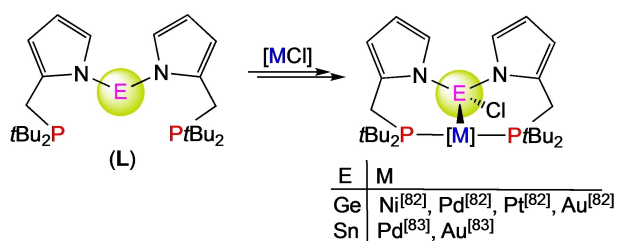
2.2. Tetrylene Approaches

These approaches, which start from metal-free PEP heavier tetrylenes as precursors of tetryl complexes (Figure 3), are only known for E=Ge, Sn.

Germylene **K**, which was easily prepared by sequentially reacting $(t\text{Bu}_2\text{PCH}_2\text{NH})_2(o\text{-C}_6\text{H}_4)$ with $n\text{BuLi}$ and commercial $\text{GeCl}_2(\text{dioxane})$,^[76] reacted with chlorido complexes, such as $[\text{M}_2\text{Cl}_2(\text{cod})_2]$ (M=Rh,^[76] Ir^[77]), $[\text{NiCl}_2(\text{dme})_2]$,^[78] $[\text{PdCl}_2(\text{MeCN})_2]$ ^[78] and $[\text{PtCl}_2(\text{cod})]$ ^[78] to give PGeP germyl complexes (Scheme 7). These reactions involved the insertion of the Ge atom into an M–Cl bond. The analogous metal-free stannylene Sn $\{(t\text{Bu}_2\text{PCH}_2\text{N})_2(o\text{-C}_6\text{H}_4)\}$ was similarly prepared using SnCl_2 as the tetryl atom precursor,^[79] but the P-SnP stannyl ligand that resulted from its reactions with chlorido complexes only behaved as a chelating ligand.^[79] The unexpected transformation of germylene **K** into a chelating PGeP germylene (a CH_2PtBu_2



Scheme 7. Synthesis of PGeP germyl complexes derived from germylene **K** and chloridometal complexes.



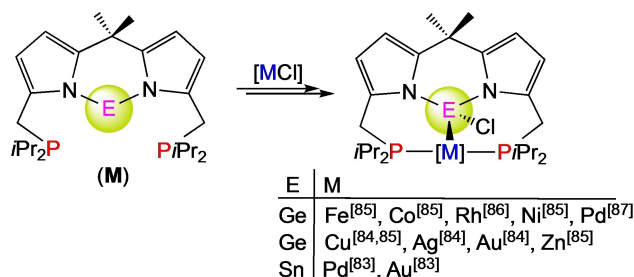
Scheme 8. Synthesis of PEP tetryl complexes derived from tetrylene **L**.

arm was converted into a CH_3 group and PHtBu_2) has been reported to occur upon reaction with the osmium hexahydride $[\text{OsH}_6(\text{P}i\text{Pr}_3)_2]$.^[80] A related metal-free PGeP germylene, $\text{Ge}\{\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{NCH}_2\}_2$, has been reported, but the P atoms of the resulting PGeP germyl complexes were attached to different metal atoms.^[81]

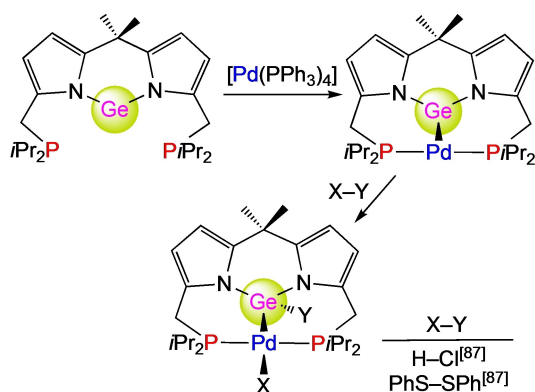
The pyrrolyl-derived PEP tetrylenes **L** (Scheme 8; E=Ge, Sn) were prepared by sequentially treating $\text{HpyrCH}_2\text{PtBu}_2$ (HPyr = 2-pyrrolyl) with $n\text{BuLi}$ and $\text{GeCl}_2(\text{dioxane})$ ^[82] or SnCl_2 .^[83] While their group 10 metal(II) derivatives (prepared from common dichlorides) have their metal atoms in typical square planar coordination, the gold(I) derivatives, prepared from $[\text{AuCl}(\text{tht})]$ (tht = tetrahydrothiophene), have an uncommon T-shaped metal coordination geometry. The low steric protection of the E atoms of these ligands and their high flexibility are responsible for the low stability of their complexes.^[82,83]

Aiming at increasing the stability of the final metal complexes, the dipyrromethane-derived PEP tetrylenes **M** were designed (Scheme 9; E=Ge, Sn). They were prepared in four steps from 5,5'-dimethyldipyrromethane by sequentially treating it with a) *para*-formaldehyde and $[\text{NH}_2\text{Me}_2]\text{Cl}$ in basic medium, b) $\text{PH}i\text{Pr}_2$, c) $n\text{BuLi}$ and d) $\text{GeCl}_2(\text{dioxane})$ ^[84] or SnCl_2 .^[83] Their reactions with common chloridometal precursors, such as MCl_2 (M=Fe, Co),^[85] $[\text{RhCl}(\text{cod})(\text{MeCN})]$,^[86] $[\text{RhCl}(\text{cod})(\text{PPh}_3)]$,^[86] $[\text{NiCl}_2(\text{dme})]$,^[85] $[\text{PdCl}_2(\text{MeCN})_2]$,^[87] $[\text{M}_4\text{Cl}_4(\text{PPh}_3)_4]$ (M=Cu, Ag),^[84] CuCl_2 ,^[85] $[\text{AuCl}(\text{tht})]$ ^[84] and ZnCl_2 ^[85] (not all possible combinations, Scheme 9) led to a variety of chloridotetryl metal complexes with the metal atoms in T-shaped tricoordinate,^[84] square planar,^[85–87] tetrahedral,^[85] trigonal bipyramidal^[86] and octahedral^[86] coordination environments. The Cl atom of chloridogermyl complexes can be easily replaced by anionic fragments (Me, OMe).^[86,88] Some rhodium(I) complexes have been found to be catalyst precursors for the hydroboration of styrenes.^[86]

The reaction of germylene **M** (M=Ge) with $[\text{Pd}(\text{PPh}_3)_4]$, which cannot lead to a chloridogermyl derivative, has been shown to give a rare T-shaped PGeP germylene palladium(0) complex (Scheme 10) in which the germylene fragment behaves as a Z-ligand (σ -acceptor).^[87] This complex is prone to undergo oxidative additions across its Ge–Pd bond to provide PGeP germyl palladium(II) derivatives (Scheme 9).^[87]



Scheme 9. Synthesis of PEP tetryl complexes derived from tetrylenes of type **M** and chloridometal complexes.



Scheme 10. Alternative synthesis of PGeP germyl complexes from a PGeP germylene.

3. Summary and Outlook

The above-reviewed results, the majority of which have been reported in the last 10 years, indicate that PEP tetryl complexes are currently receiving considerable attention from the chemical community.

The inexistence of metal-free PSiP silylenes is responsible for the fact that all the currently known PSiP silyl complexes have been prepared using a tetrelane approach from PSiP silanes (Schemes 1–4, Tables 1–3), which have in turn been prepared by functionalizing dichloridosilanes with two phosphane groups. Although the first PGeP germyl and PSnP stannyl complexes were also synthesized using this approach from the corresponding dichloridogermanes and -stannanes (Scheme 5, Tables 4 and 5), the recent appearance of stable metal-free PGeP germylenes and PSnP stannylenes, prepared from commercial GeCl_2 (dioxane) and SnCl_2 , has widely expanded the scope of PGeP germyl and PSnP stannyl complexes (Schemes 7–10). PSnP stannyl complexes have also been prepared from stannanes and metal complexes containing two uncoordinated pyridyl or imidazolyl fragments (Scheme 6), but this tetrelane approach has not been used to prepare PSiP silyl and PGeP germyl complexes, most probably because hexacoordinate (doubly donor-stabilized) tetryl species are much less stable for $\text{E}=\text{Si}$, Ge than for $\text{E}=\text{Sn}$.

Regarding future developments of this chemistry, the metal-centered reactivity of PSiP silyl complexes, which is currently being developed to a great extent, is expected to continue growing. In addition, it is desirable a) the design of new PSiP silyl ligand frameworks that will help drive/control the reactivity of the metal atoms and b) to achieve the synthesis of metal-free PSiP silylenes, which are currently unknown, probably with the Si atom sterically protected and stabilized by a strong and bulky donor. As studies on metal-centered reactivity and catalytic applications of PGeP germyl and PSnP stannyl complexes are much less abundant than those of the PSiP silyl relatives and many of them are in their initial stages (the existence of metal-free PGeP germylenes and PSnP stannylenes is still very short), new studies on these themes will no doubt appear in the near future. Another desirable target is the

synthesis of complexes containing PPbP plumbyl ligands (from the corresponding PPbP plumbanes or plumbylenes). These types of compounds are currently unknown despite the attachment of plumbylenes to transition metals^[89,90] and even the formation of PPbP plumbylene complexes have been described.^[90] In addition, regarding the applicability of PEP tetryl transition metal complexes, their successful participation in catalysis has already been demonstrated (many examples are mentioned in this review) and they might also present interesting medical/biological applications (yet to be investigated), which are currently being discovered for metal complexes supported by other pincer ligands.^[3a–c]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: germanium · pincer ligands · silicon · tin · tripod ligands

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