# 1 Introduction

1.1 Amidinates

Amidinates are a well-established class of monoanionic *N*-chelating ligand systems. The coordination chemistry of amidinate ligands has been reported with almost every metal or metalloid of the periodic table.[1] Amidinate anions with the general formula $[RC(NR^1)(NR^2)]^-$ can be considered as the nitrogen analogues of carboxylates $[RCO_2]^-$ (Figure 1.1). The ligand framework is rather versatile, as the substituents (R, R^1, R^2) present at the central carbon and nitrogen atoms can be widely varied, which allows a fine tuning of electronic and steric properties. Studies have revealed that, in order to stabilize compounds in elusive low-valent oxidation states, it was crucial to introduce a significant steric demand on the amidinate ligand backbone.[2] These interesting features of the amidinates make them contender of the ubiquitous cyclopentadienyl ligands.

Depending on the type of metals and substituents present on the central carbon and nitrogen atoms of amidinates, a variety of coordination modes with main group elements, transition metals, lanthanides and actinides are observed (B, Figure 1.1).[1a,3] Bulky substituents on the central carbon and nitrogen atoms typically induce a monodentate (κ^1) coordination mode (a),[4] although this mode is relatively rare in general.[5] The chelating (κ^2) coordination mode, in which delocalization of the double bond is commonly observed (b), forms a four-membered cycle with the coordinated element.[6]
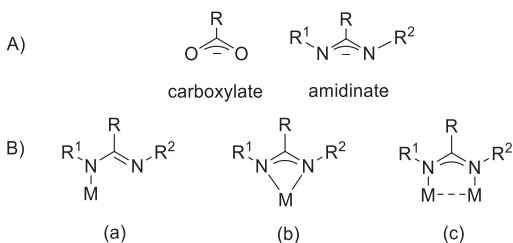
Figure 1.1 (A) Carboxylate and amidinate ligand frameworks, (B) possible coordination modes of amidinates.

The bridging coordination mode (c) is often found in paddlewheel-type coordination compounds with the general formula of $M_2(amidinate)_n$ (n = 2-4), in which three or four amidinates bridge two metal centres.[7] The potential for metal-metal interaction and the fascinating chemistry of these paddlewheel coordination compounds have been extensively

investigated and are still an actively pursued research field.[8] Owing to very small coordination pockets of amidinates, the latter offer very small bite angles (N-M-N angles) which lie in the range of 63-65°.[9]

Early reports have shown that amidinate metal complexes can be synthesized by heating metal carbonyls with a corresponding amidine.[10] Currently, the most widespread and routinely used methods include salt metathesis reactions between metal halides and alkali metal amidinates.[3] Deprotonation of amidines with metal alkyls or amides has also been used as an alternative approach to salt metatheses.[4b,11] However, this method is not commonly used which can be traced back to the low availability and stability of many metal alkyls. Additionally, direct insertion of carbodiimides (R-N=C=N-R') into M-C bonds has also been employed to synthesize metal amidinate complexes.[12]

The versatility of amidinates in coordination chemistry has led to a plethora of metal complexes and many of them have been applied in homogeneous catalysis or in material science to design novel materials.[12] Examples of application can be found in chemical vapor deposition (CVD), which requires metal precursors without any carbon in the direct coordination sphere in order to minimise carbide formation. Therefore, only coordinated by nitrogen atoms, the amidinate complexes of divalent Mg (Figure 1.2 (a)), trivalent Al and Ga have been used as CVD precursors to prepare metal nitride semiconductors (Figure 1.2 (b)).[13] As another example, cationic group 13 metal amidinate complexes have been utilized for olefin polymerization (Figure 1.2 (c)).[14] Prominent for the stabilization of reactive low-valent group 14 compounds, the amidinate ligand [PhC(^{t}BuN)$_2$]$^-$ was successfully used to access stable Si(II), Ge(II) and Sn(II) species (Figure 1.2 (d)).[15] More recently, our group has reported the first silicon analogue of the aromatic cyclobutadiene dication, [{PhC(^{t}BuN)$_2$Si}$_4$](BPh$_4$)$_2$ in which the four silicon centres adopt an almost square planar geometry.[16] Transition metal complexes of certain amidinates have been utilized as precursors in atomic layer deposition (ALD) where the crucial point is the volatility of the metal complexes, which can be controlled by taking advantage of substituent variation in the amidinate framework (Figure 1.2 (e)).[17] Moreover, the coordination chemistry of amidinates with rare earth metals was pioneered by the group of Edelmann more than two decades ago.[18] The amidinate ligand have been used to stabilize all available oxidation states (+2, +3, +4) of different lanthanides.[12]

In this regard, a series of homoleptic lanthanide complexes with various lanthanide metals have been reported in early studies using the $[RC_6H_4C(NSiMe_3)_2]^-$ amidinate anion (Figure 1.2 (f)).
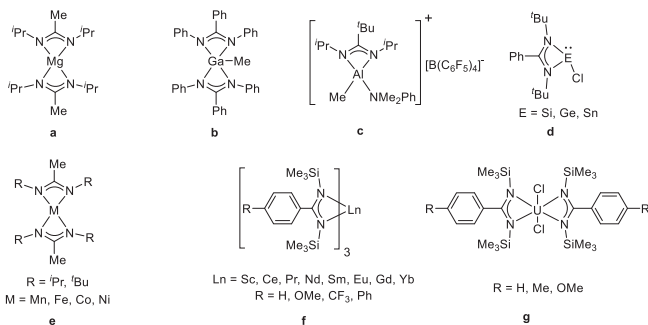
Figure 1.2 Selected examples of the amidinate-coordinated compounds.[12]

Since then, several other homoleptic lanthanide complexes have been synthesized and utilized as catalysts in the ring opening polymerization (ROP) of ε-caprolactone.[19] The most exciting application of a homoleptic lanthanide complex is the use of the erbium tris-amidinate complex $[\{MeC(N^tBu)_2\}_3Er]$ as a dopant source to prepare silicon nanocrystals.[12] The formation of mono-, bis-, or tris-amidinate substituted lanthanide complexes depends on the steric demand of the respective ligand and the ionic radius of the lanthanide, as described by the group of Teuben.[20] Additionally, the versatility of amidinate ligands can also be seen in the stabilization of actinide(IV) complexes and their use in ring opening polymerization of ε-caprolactone (Figure 1.2 (g)).[21]

1.2 Iminophosphonamide

In the monoanionic amidinate ligands described above (Section 1.1), a carbon corresponds to the central atom of the N-X-N motif. This central atom can be replaced by other elements and thus, a variety of N-X-N type bidentate chelating ligands are possible. Among those N-X-N ligands, boraamidinate (A), triazenide (B), sulfinamidinate (C) and iminophosphonamide (D) systems are known in the literature, where X = BR,[22] N,[23] SR,[24] and PR_2,[25] respectively (Figure 1.3). Not surprisingly, altering the central atom X, the electronic properties of the resulting ligands vary significantly.
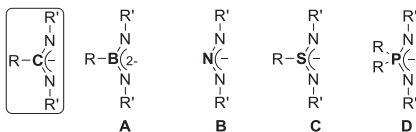
Figure 1.3 Various analogues of the amidinate ligand system.

At first glance, the coordination chemistry of these derived ligand systems can be expected to be similar. This is however not the case, as the respective bond lengths and bite angles differ, which has a considerable impact on the chemical behaviour in coordination compounds. Among the different classes of heteroatomic N-X-N type ligands, iminophosphonamides (X = PR$_2$) offer the longest X-N bond (1.60 Å), which leads to a wider bite angle in corresponding metal complexes. Furthermore, the phosphorus atom in the backbone of the iminophosphonamide ligand system serves as a spectroscopic "marker" for ^{31}P NMR spectroscopy, which allows a convenient monitoring of the reactions when using these ligands. In addition to this, the steric demand on the central X atom of the iminophosphonamide ligand backbone is comparatively greater than that in other NXN frameworks.

The iminophosphonamide ligand system [(R$_2$P(NR')$_2$]$^-$ can be considered as an analogue of the phosphinate anion (R$_2$PO$_2^-$) in which the oxygen atoms have been replaced by two amide groups. Three resonance forms can be depicted for this system (Figure 1.4). The nitrogen atoms in iminophosphonamides carry a negative charge and are σ-bonded to the positively charged phosphorus centre, thus making the NPN system a relatively stable zwitterionic framework.[26]
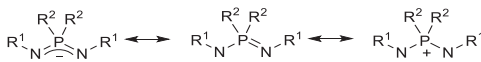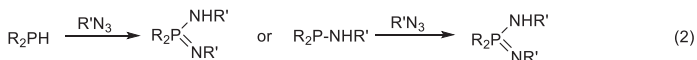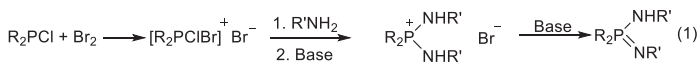

Figure 1.4 Resonance forms of the iminophosphonamide.

In general, iminophosphonamides can be synthesized by following two methods (Scheme 1.1):

(1) Kirsanov condensation: a reaction is carried out between tertiary phosphines R$_2$PX (X = Cl, Br) and primary amines (R'NH$_2$) leading to the formation of a diamino phosphonium salt, which, by using a strong base, is converted to the corresponding iminophosphonamide.[27]

(2) Staustinger reaction: a phosphonamine (R$_2$PNHR') or phosphine (R$_2$PH) is reacted with a stoichiometric amount of an organic azide (R'N$_3$), which directly leads to the protonated iminophosphonamine ligand *via* release of N$_2$.[28]

$$R_2PCl + Br_2 \longrightarrow [R_2PClBr]^+ Br^- \xrightarrow[\text{2. Base}]{\text{1. R'NH}_2} R_2P \underset{NHR'}{\overset{+}{\underset{}{\overset{NHR'}{<}}}} Br^- \xrightarrow{\text{Base}} R_2P \underset{NR'}{\overset{NHR'}{<}} \quad (1)$$

$$R_2PH \xrightarrow{R'N_3} R_2P \underset{NR'}{\overset{NHR'}{<}} \quad \text{or} \quad R_2P\text{-NHR'} \xrightarrow{R'N_3} R_2P \underset{NR'}{\overset{NHR'}{<}} \quad (2)$$

Scheme 1.1 Iminophosphonamide synthesis via Kirsanov (1) and Staudinger reaction (2).

Based on the above-mentioned methods, a variety of iminophosphonamines and their metal complexes has been reported in the literature. The respective metal complexes can be obtained either by salt metathesis reactions between alkali metal salts and metal halides or by deprotonation reactions (Scheme 1.2). Also, similarly to amidinates, iminophosphonamide ligands can also show the three types of coordination modes depicted in Figure 1.1.
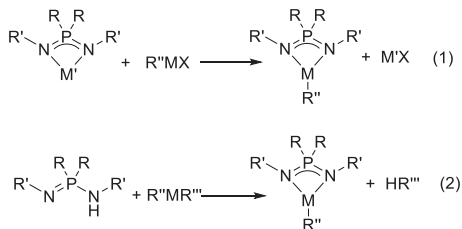

Scheme 1.2 Typical reaction pathways to synthesize iminophosphonamide metal complexes.

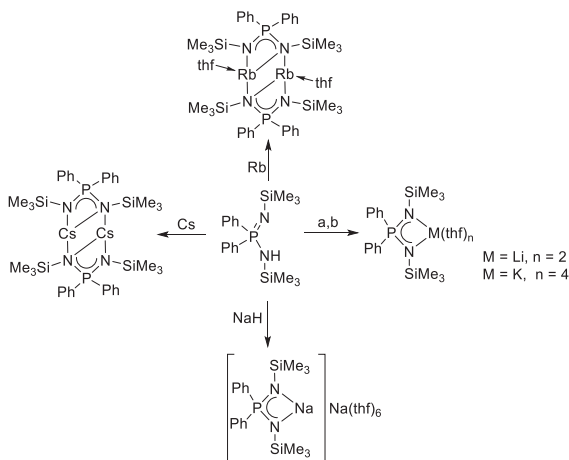### 1.2.1 s-Block metal complexes of iminophosphonamides

Alkali metal iminophosphonamide complexes are useful precursors for salt metathesis reactions. Treatment of the protonated iminophosphonamines with alkali metal bases such as *n*BuLi, NaH, [Na{N(SiMe$_3$)$_2$}] or KH, [K{N(SiMe$_3$)$_2$}] leads to the corresponding alkali metal complexes. A variety of alkali metal complexes have been reported and structurally characterized using various iminophosphonamines such as [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]H,[25c] [{(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$P(Ph$_2$)}]H, [{(2,4,6-Me$_3$C$_6$H$_2$N)$_2$P(Ph$_2$)}H],[26,29] [(2,4,6-Me$_3$C$_6$H$_2$N)$_2$P(Ph$_2$)]H and [{(2,6-*i*Pr$_2$C$_6$H$_3$NH)P(Ph$_2$)=N(C$_6$H$_2$-2,4,6-Me$_3$)}],[30] *rac*-[*trans*-1,2-C$_6$H$_{12}${NP(Ph$_2$)N(Ar)}$_2$].[31] Based on the structural investigation of the reported complexes, it can be anticipated that

the aggregation state of these metal complexes depends on the N-substituents and the ionic radii of the central metal atoms. For example, the potassium salt $[K\{(2,6\text{-}iPr_2C_6H_3N)_2P(Ph_2)\}]_n$ is polymeric in the solid state (Figure 1.5). Surprisingly, the potassium ion only shows coordination with the arene rings from two Dipp (Dipp = 2,6-$iPr_2C_6H_3$) substituents and two phenyl groups from a neighbouring ligand in the polymeric chain, instead of realizing one of the typical bonding motifs shown in Figure 1.1.
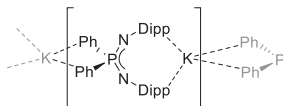

Figure 1.5 The polymeric chain of $[K\{(2,6\text{-}iPr_2C_6H_3N)_2P(Ph_2)\}].$[29]

In addition, the alkali metal complexes of the $\{Ph_2P(Me_3SiN)_2\}^-$ ligand show non-uniform coordination patterns throughout the series from Li to Cs.[32] These complexes were synthesized by deprotonation reactions of $\{PPh_2(Me_3SiN)_2\}H$ with n-BuLi, NaH, KH, Rb, and Cs (Scheme 1.3). The solid-state structures reveal that the lithium and potassium salts $[\{Ph_2P(NSiMe_3)_2\}Li(thf)_2]$ and $[\{Ph_2P(NSiMe_3)_2\}K(thf)_4]$ exist in monomeric forms. The sodium analogue shows an unusual, highly reactive example of a low melting sodium/sodiate ion pair $[\{Ph_2P(NSiMe_3)_2\}_2Na][Na(thf)_6]$. However, the corresponding Rb and Cs metal complexes exist in dimeric $[\{Ph_2P(Me_3SiN)_2Rb(thf)\}_2]$ and $[\{Ph_2P(Me_3SiN)_2Cs\}_2]$ forms.

Scheme 1.3 Synthesis of alkali metal iminophosphonamide complexes; (a) n-BuLi, (b) KH.[32]

M = Be, Mg, Ca, Sr, Ba
n = 0   2   2   2   2
m = 0   0   1   2   2
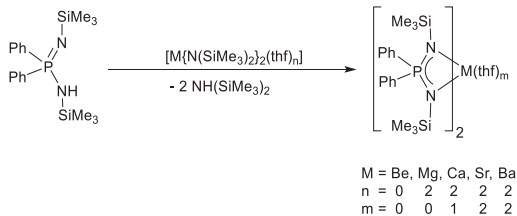
Scheme 1.4 Synthesis of alkaline earth metal iminophosphonamide complexes.[33]

Alkaline earth metal complexes supported by iminophosphonamides are typically synthesized by deprotonation of the corresponding iminophosphonamines by alkaline earth metal amides, $[M\{N(SiMe_3)_2\}_2]$. In contrast to the alkali metal complexes based on the $\{Ph_2P(Me_3SiN)_2\}^-$ ligand, the corresponding group-2 metal (M = Be, Mg, Ca, Sr, and Ba) complexes show a uniform coordination pattern (Scheme 1.4).[33] The common structural feature of all of these complexes is the coordination of two monoanionic ligands to the metal centre to form a mononuclear iminophosphonamide complex $[\{Ph_2P(NSiMe_3)_2\}_2M]$. Depending on the ionic radius of the respective metal, the incorporation of additional thf molecule(s) to satisfy the metal coordination sphere is observed. By utilizing sterically demanding iminophosphonamide ligands such as $\{(2,6\text{-}^iPr_2C_6H_3N)_2P(Ph_2)\}^-$, highly reactive $[Mg]^{+1}$ complexes have also been reported.[34] More recently, this complex was utilized to study the mechanistic insights of anionic ligand exchange and fullerene reduction.[35]

L = 4, 4'-bipyridine
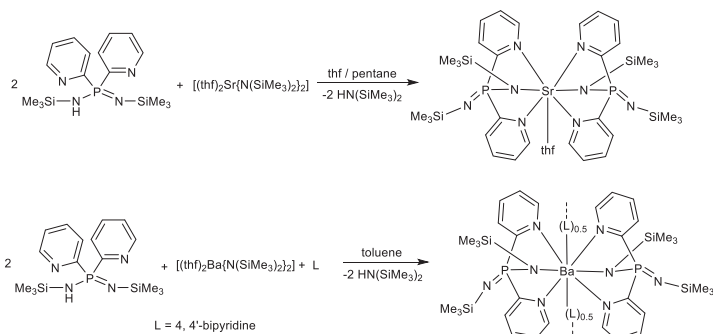
Scheme 1.5 Alkaline earth metal complexes based on *Janus head* iminophosphonamides.[36]

In order to introduce additional coordination sites in the $[Ph_2P(Me_3SiN)_2]^-$ iminophosphonamide ligand, a new *Janus head* $[Py_2P(Me_3SiN)_2]^-$ ligand has been reported where the phenyl groups on the phosphorus have been replaced by pyridyl substituents.[36]

This multi-dentate *Janus head* ligand exhibits two possible chelating coordination pockets based on (a) the NPN functionality and (b) two remote pyridyl substituents.

The reaction of the protonated Janus-type ligand with $[M\{N(SiMe_3)_2\}_2]$ (M = Sr or Ba) proceeds smoothly at room temperature, leading to the formation of the $[\{Py_2P(NSiMe_3)_2\}_2Sr(thf)]$ and $[\{Py_2P(NSiMe_3)_2\}_2Ba(4,4'-bipy)]_n$ complexes, where the solid state structure of barium complex show a zigzag polymeric arrangement assisted by 4,4'-bipyridine ligands.(Scheme 1.5).[36]

1.2.2 p-Block: group 13 and 14 compounds of the iminophosphonamides

1.2.2.1 Iminophosphonamide complexes of group 13 metals

Complexes containing group 13 metals have attracted a long-standing interest in various homogeneous catalyses involving polar substrates and have promoted Lewis acid mediated activation reactions.[37] In this regard, metal complexes containing M-X bonds (X = halide, alkyl, and hydride) are widely used catalysts in various reactions such as cationic polymerization,[14] hydroboration,[38] hydro functionalization,[39] Friedel–Craft and Diels–Alder reaction,[40] and epoxidation of alkenes.[41]

Typically, iminophosphonamides bearing medium-sized substituents show a chelating bonding mode with the group 13 metals and form four-membered metallacyclic rings. For example, Roesky *et al.* reported on aluminium complexes of the iminophosphonamide $\{Ph_2P(Me_3SiN)_2\}^-$. These complexes were obtained *via* salt metathesis reactions between the respective *in situ* generated lithium iminophosphonamide with group 13 metal precursors or *via* a direct base elimination reaction involving the iminophosphonamine $\{(Ph_2P(Me_3SiN)_2\}H$ (Scheme 1.6).[42]
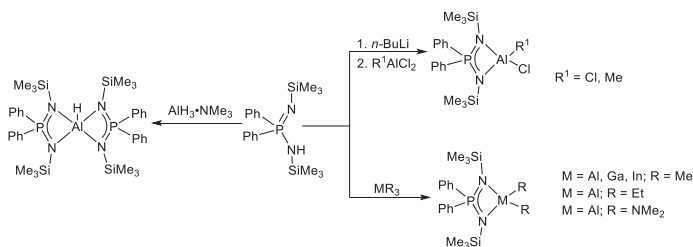
Scheme 1.6 Synthesis of group 13 iminophosphonamide complexes.[42]

Among the synthesized compounds, the tetracoordinated dimethyl complexes [{Ph$_2$P(NSiMe$_3$)$_2$}Me$_2$M] (M = Al, Ga, In) are thermally stable and show defined melting points. The monomeric nature of these metal complexes was confirmed by measuring the corresponding cryoscopic molecular weight.[42b] The aluminium centre in the aluminium monohydride complex is pentacoordinated and features a distorted trigonal bipyramidal geometry. In all of these complexes, the P-N contact lengths are in between single and double bonds.[43] Apart from the above mentioned examples, only few group 13 metal complexes based on other NPN backbones, e.g. {(2,6-^{i}Pr$_2$C$_6$H$_3$N)Ph$_2$P(N^{t}Bu)}$^-$,[25c,44] {(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$PH(^{t}Bu)}$^-$,[45] and rac-[trans-1,2-C$_6$H$_{12}${NP(Ph$_2$)N(Ar)}$_2$]$^-$ (where Ar = 2,4,6-Me$_3$C$_6$H$_2$ or 2,6-Me$_2$C$_6$H$_3$),[1b] have been structurally characterized. Interestingly, the sterically demanding iminophosphonamide {(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$Ph$_2$P}$^-$ ligand has been used to stabilize heavy monovalent group 13 (Ga(I), In(I), Tl(I)) metal complexes.[46]

1.2.2.2 Iminophosphonamide compounds of group 14 elements

Heavy divalent group 14 compounds are collectively termed as tetrylenes [R$_2$E:] with (E = Si, Ge, Sn and Pb with R = supporting ligand). In 1974, the group of Lappert reported that these compounds can be successfully stabilized by sterically demanding amido ligands (-NR$_2$) in which the lone pair of the amido group stabilizes the vacant p-orbital of the divalent group 14 elements by an effective P$_\pi$-P$_\pi$ interaction.[47] Following the first report of amidinate-stabilized divalent group 14 compounds [{(PhC(^{t}BuN)$_2$)ECl], (E = Si, Ge, Sn), the corresponding chemistry has been expanded drastically over the last two decades.[15b,15c,48]
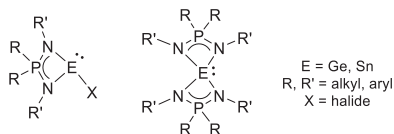

Figure 1.6 Literature-known tetrylenes based on iminophosphonamides.[49]

Compared to the well-established chemistry of amidinate-stabilized tetrylenes, only a few examples of tetrylenes based on iminophosphonamide ligands have been reported (Figure 1.6). Such examples include the germylene [Ph$_2$P(NtBu)(2,6-iPr$_2$C$_6$H$_3$N)GeX] (where X = Cl, O^{t}Bu, OTf)[49a] and stannylene [{Ph$_2$P(NSiMe$_3$)$_2$}$_2$Sn] and [{(Ph)(R)P(NtBu)$_2$}SnX] (where R = CH$_2$Ph or 8-C$_9$H$_6$N; X = Cl or N(SiMe$_3$)$_2$) compounds, which have been structurally
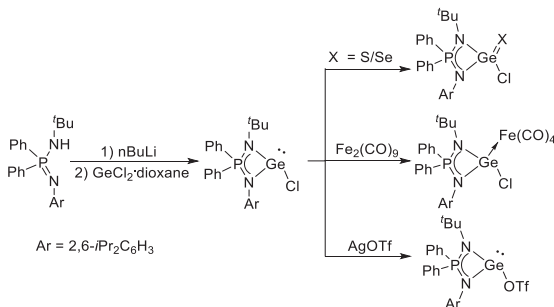
Scheme 1.7 Synthesis of an iminophosphonamide monochloride germylene and its reactivity.[49a]

characterized.[49-50] The general synthetic route for the preparation of the aforementioned low-valent compounds involve salt metathesis reactions using tetrylene halides. In this regard, the germylene monochloride [{(2,6-iPr$_2$C$_6$H$_3$N)P(Ph$_2$)(NtBu)}GeCl] can be synthesized by treatment of the *in situ* generated lithium salt of the ligand, **L**Li [**L** = (2,6-iPr$_2$C$_6$H$_3$N)P(Ph$_2$)(NtBu)], with one equivalent of GeCl$_2$·dioxane.[49a] The reactivity of the synthesized germylene monochloride was further studied towards oxidation, formation of adducts with transition metals and in salt metathesis reactions (Scheme 1.7). Additionally, the tetracoordinated iminophosphonamide complexes of Sn(II) and Pb(II), [{Ph$_2$P(NSiMe$_3$)$_2$}$_2$E] (where E = Sn, Pb), have also been reported.[49c] These homoleptic tetrylenes adopt a distorted trigonal bipyramidal geometry in which the respective lone pair occupies the equatorial position (Figure 1.6).

1.2.3 Transition metal complexes of the iminophosphonamide ligands

Transition metal complexes based on amidinate (NCN) ligands have been extensively studied, with reported catalytic applications in various organic transformations.[51] In contrast to the well-established chemistry of amidinate ligands, the corresponding chemistry of transition metal iminophosphonamides (NPN) is still in its infancy.[52] Nevertheless, in the past few decades, various transition metal complexes of iminophosphonamides have been employed as catalysts, e.g. in alkene polymerizations,[53] cyclopropanation reactions,[54] and in olefin oligomerizations.[55] In 1981, the group of Goddard reported the first nickel and palladium complexes starting with an (amino)bis(imino)phosphorane ligand (Scheme 1.8). The formation of these complexes occurred *via* unexpected allyl rearrangement of bis(η^3-allyl) Ni/Pd complexes involving the (amino)bis(imino)phosphorane ligand, leading to the