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Polydentate Amidinato-Silylenes, -Germylenes and -Stannylenes

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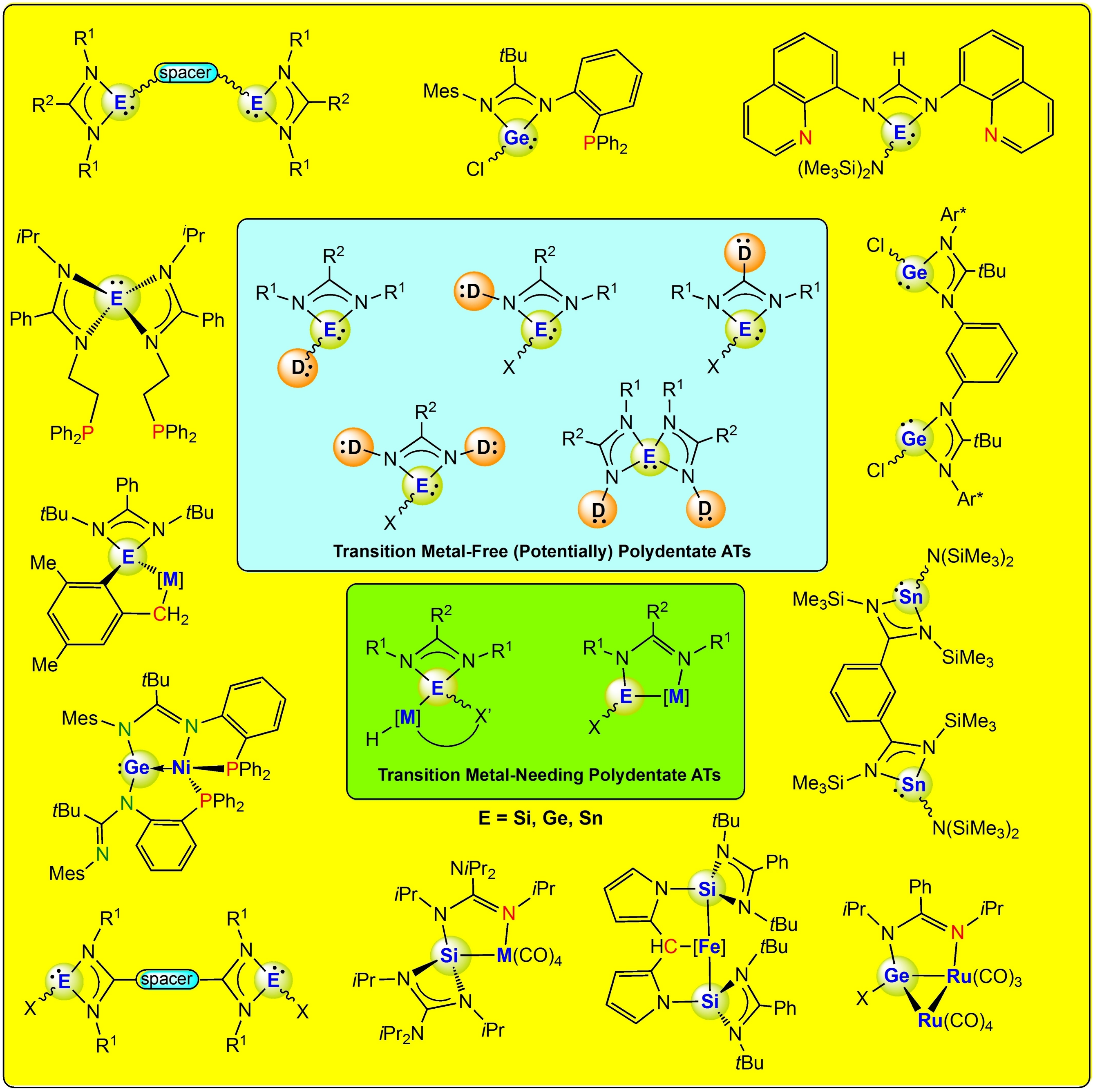
Dedicated to Professor José M. Fernández-Colinas, wishing him the best for his retirement.



This review article focuses on amidinatotetrylenes that potentially can (or have already shown to) behave as bi- or tridentate ligands because they contain at least one amidinatotetrylene moiety (silylene, germylene or stannylene) and one (or more) additional coordinable fragment(s). Currently, they are being widely used as ligands in coordination chemistry, small molecule activation and catalysis. This review classifies those that have been isolated as transition metal-free compounds into five families that differ in the position(s) of the donor group(s) (D) on the amidinatotetrylene moiety, namely: $ED\{R^1NC(R^2)NR^1\}$, $EX\{DNC(R^2)NR^1\}$, $EX\{R^1NC(D)NR^1\}$, $EX\{DNC(R^2)ND\}$ and $E\{R^1NC(R^2)ND\}_2$ (E = Si, Ge or Sn). Those that do not exist as transition metal-free compounds but have been observed as ligands in transition metal complexes are cyclometallated and ring-opened amidinatotetrylene ligands. This article presents schematic descriptions of their structures, the approaches used for their syntheses and a quick overview of their involvement (as ligands) in transition metal-catalysed reactions. The literature is covered up to the end of 2023.

1. Introduction

The chemistry of heavier carbene analogues (silylenes, germylenes, stannylenes and plumbylenes, also known as heavier tetrylenes, HTs) has been extensively developed in the last two decades (excluding that of plumbylenes).[1–6] Among the currently known HTs, those containing at least a bulky amidinate fragment (amidinatotetrylenes, ATs; Figure 1) have played a predominant role not only for their intrinsic interest as low-valent main group compounds[3] but also because their kinetic stability (the bulky R^1 substituents of the amidinate fragment protect the low-valent tetrel atom) has allowed an extensive use as ligands in coordination chemistry[2–4] and catalysis.[5,6] In addition, ATs have been recognized as very strong electron donors, even stronger than most phosphanes and *N*-heterocyclic carbenes,[7] and this property is of crucial importance for ligands of complexes involved in small molecule activation and catalysis. In this article, the acronym AT also includes guanidinatotetrylenes (guanidines are amidines that have $R^2 = NR_2$).

The general, coordination and transition-metal catalytic chemistries of ATs have been previously, but not recently, reviewed.[3–6] The last comprehensive review on the transition-metal chemistry of ATs was published in 2015.[4] Polydentate ATs (those having one (or more) additional coordinable fragment(s)) were then scarce. However, the last decade has witnessed an increasing interest in these potentially bi- or tridentate ATs (*vide infra*). This currently very active research field has been stimulated by the excellent catalytic properties shown by many of the transition metal complexes that use these di- or tridentate AT-containing ligands (particularly, silylenes; *vide infra*). Prompted by these facts and encouraged by the rising interest that the chemical community is currently devoting to HTs in general, we decided to classify in this review the structural types of the currently known donor-functionalized ATs, also overviewing the synthetic approaches used for their syntheses and their involvement (as ligands) in transition metal-catalysed reactions.

2. Types of Polydentate Amidinatotetrylenes: Structures and Syntheses

From a structural point of view, the currently known transition metal-free polydentate ATs can be organized into five families of compounds that differ in the position(s) of the donor group(s) on the AT fragment (Figure 2). Thus, compounds of type $ED\{R^1NC(R^2)NR^1\}$ (**I**) have a 2-electron-donor group D dangling from the E atom, whereas compounds of types EX

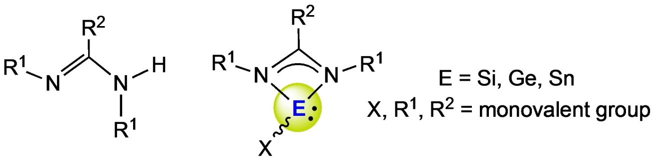


Figure 1. Generic structures of an amidine (left) and an amidinatotetrylene (right).

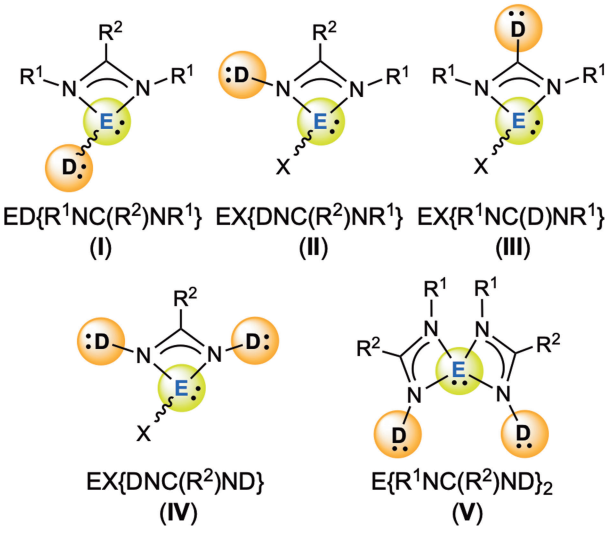


Figure 2. Generic types of transition metal-free donor-functionalized ATs (E = Si, Ge, Sn; D = 2-electron-donor group).

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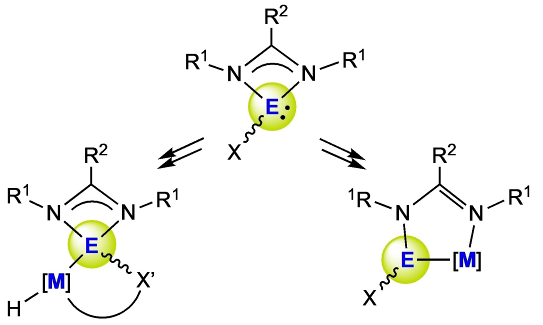
{DNC(R^2)NR^1} (**II**) and EX{R^1NC(D)NR^1} (**III**) have a donor group attached to an N or the C atom, respectively, of the amidinate fragment. Compounds featuring two donor groups in addition to the AT moiety are those of types EX{DNC(R^2)ND} (**IV**), which have each amidinate N atom connected to a donor group D, and E{R^1NC(R^2)ND}$_2$ (**V**), which contain the E atom attached to two amidinate fragments, each having a donor group D on an N atom.

There are two additional families of polydentate ATs. They comprise ATs that are not stable as transition metal-free species, but that have been found as ligands in some transition metal complexes, namely, cyclometallated ATs (**VI**) and ring-opened ATs (**VII**) (Figure 3). Their precursors are ATs that do not necessarily contain an additional 2-electron-donor group.

The following sections of this review deal with all these families of ATs.



(Cyclometallated AT)
(**VI**)

(Ring-opened AT)
(**VII**)

Figure 3. Generic examples of cyclometallated and ring-opened ATs.

2.1. Polydentate Mono(amidinatotetrylenes)

These compounds have one AT fragment. Therefore, although they also contain one (or more) donor group(s) D, they do not contain an additional AT fragment as part of the donor group.

2.1.1. Mono(amidinatotetrylenes) of Type ED{R¹NC(R²)NR¹} (I)

The synthesis of donor-functionalized ATs of this type usually requires the previous preparation of the corresponding chlorido-AT ECl{R^1NC(R^2)NR^1} (E = Si, Ge, Sn), which generally involves two steps in the case of germylenes and stannylenes (Figure 4): a) synthesis of symmetric amidinates, generally as lithium salts of the type Li[R^1NC(R^2)NR^1], by reacting symmetric carbodiimides R^1NCNR^1 with lithiated groups LiR^2, and b) reactions of Li[R^1NC(R^2)NR^1] with $GeCl_2$(dioxane)[8] or $SnCl_2$.[8a,9] Due to the absence of readily available silicon(II) precursors, the syntheses of the most widely used amidinatosilylene, SiCl{*t*BuNC(Ph)N*t*Bu}, have always used silicon(IV) precursors. It was first prepared in low yield by sequentially treating Li[*t*BuNC(Ph)N*t*Bu] with $SiCl_4$ and potassium metal,[10] but its most convenient synthesis involves the treatment of Li[*t*BuNC(Ph)N*t*Bu] with $SiHCl_3$, to give $SiHCl_2${*t*BuNCPh)N*t*Bu}, and the subsequent dehydrochlorination of the latter with LiN($SiMe_3$)$_2$ (Figure 4).[11]

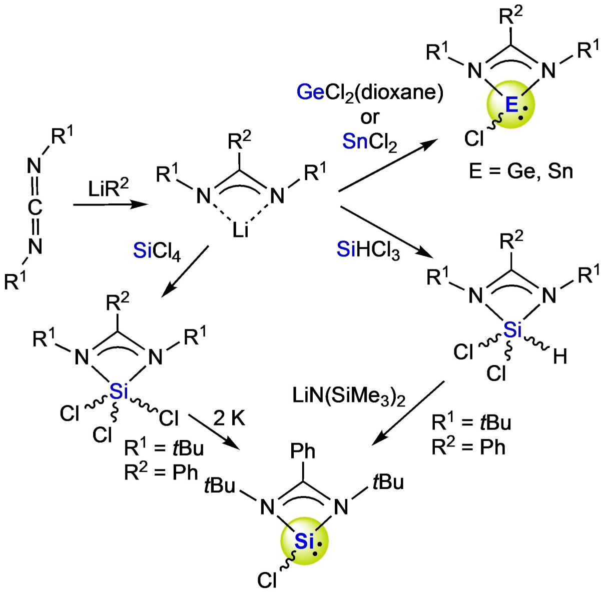


Figure 4. Syntheses of chlorido-ATs ECl{R^1NC(R^2)NR^1} (E = Si, Ge, Sn).

ATs of type **I**, which have the donor group D dangling from the E atom, are the most widely represented polydentate ATs.

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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 new developments of the coordination chemistry and catalytic applications of heavier tetrylenes. In 2015 he received the GEQO "Young Researcher Award". He has authored more than 100 scientific publications.

Figure 5 shows the currently known mono-ATs of this type (they do not contain an additional AT fragment in the donor group D).[12–23] Compounds having two AT fragments (bis-ATs) are considered later in this manuscript (Section 2.2.1). The reason behind the abundance of these compounds is that their syntheses are in most cases very easy, as they generally involve a transmetallation reaction between the readily available and long known chlorido-ATs $ECl\{R^1NC(R^2)NR^1\}$ (Figure 4) and the anionic form of the corresponding donor group precursor (generally as a Li^+ salt). This is the case for ATs **A** (E=Ge) and **C**–**L** (Figure 5). The exceptions are commented below.

ATs of type **A** with E=Si were prepared by treating $SiHCl_3$ with two equivalents of $Li[R^1NC(R^2)NR^1]$, to give $SiHCl\{R^1NC(R^2)NR^1\}_2$, and subsequent dehydrochlorination of the latter with $KN(SiMe_3)_2$ (Figure 6).[12a,b]

ATs of type **B** (E=Si, Ge) were prepared by condensing $ECl\{tBuNC(Ph)NtBu\}$ with germylene $Ge\{(NDipp)_2C(CH_2)C(H)CMe\}$, *via* (formal) insertion of the later into the E–Cl bond of the former (Figure 7).[13]

There are examples of ATs that are not *a priori* functionalized with additional coordinable groups but that they have occasionally behaved as polydentate ligands by coordination of an aryl group forming part of the X group. This is the case for the examples shown in Figure 8.[24]

2.1.2. Mono(amidinatotetrylenes) of Type $EX\{DNC(R^2)NR^1\}$ (II)

ATs of type **II** are very scarce. In fact, the only known example of this kind is germylene **O** (Figure 9). Its synthesis implied the construction of its asymmetric amidine precursor by treating N-

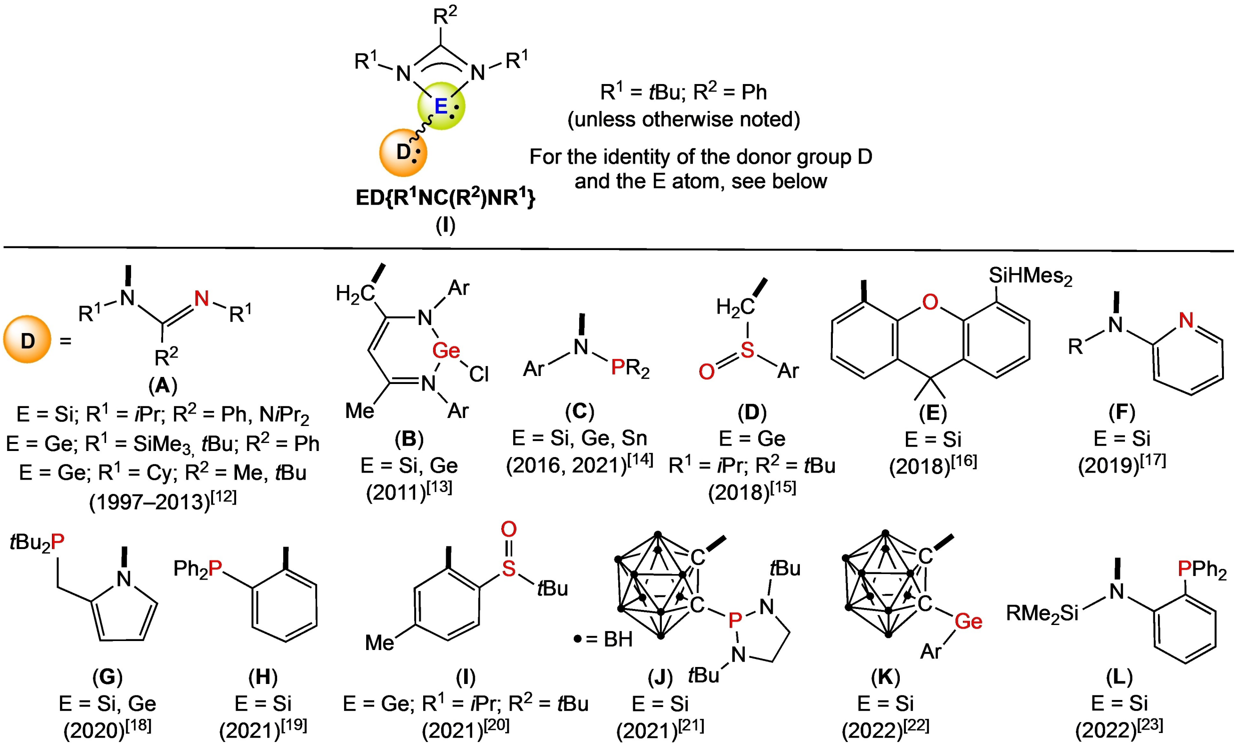


Figure 5. Currently known bidentate mono-ATs of type **I**. The thicker black segment on each spacer indicates the atom that is attached to the amidinate fragment.

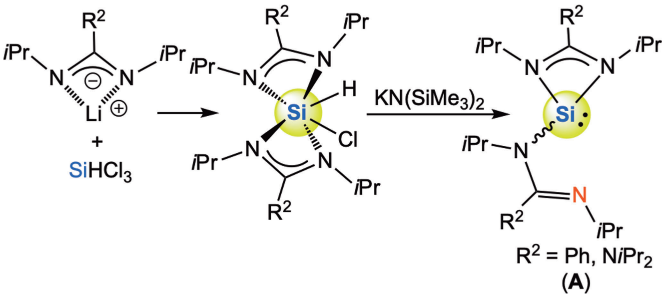


Figure 6. Synthesis of silylenes of type **A**.

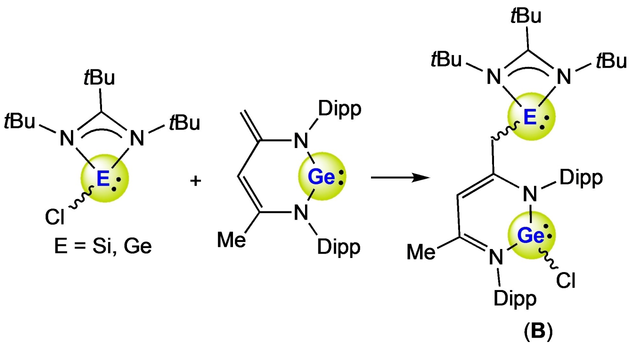
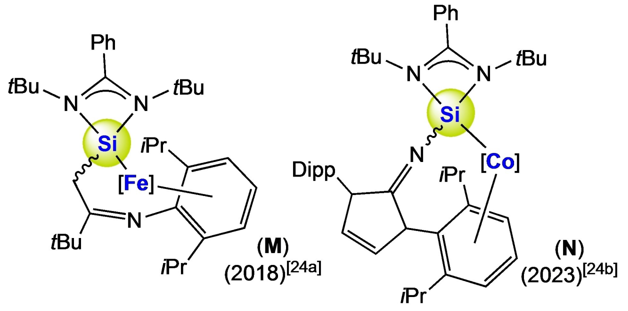


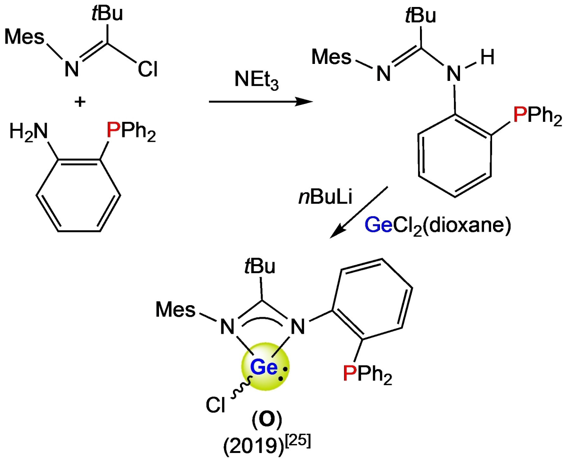
Figure 7. Synthesis of Si–Ge and Ge–Ge ATs of type **B**.



(M) (2018)[24a]

(N) (2023)[24b]

Figure 8. Arene-coordinated ATs **M** and **N** in their metal complexes.



(O) (2019)[25]

Figure 9. Synthesis of germylene **O**.

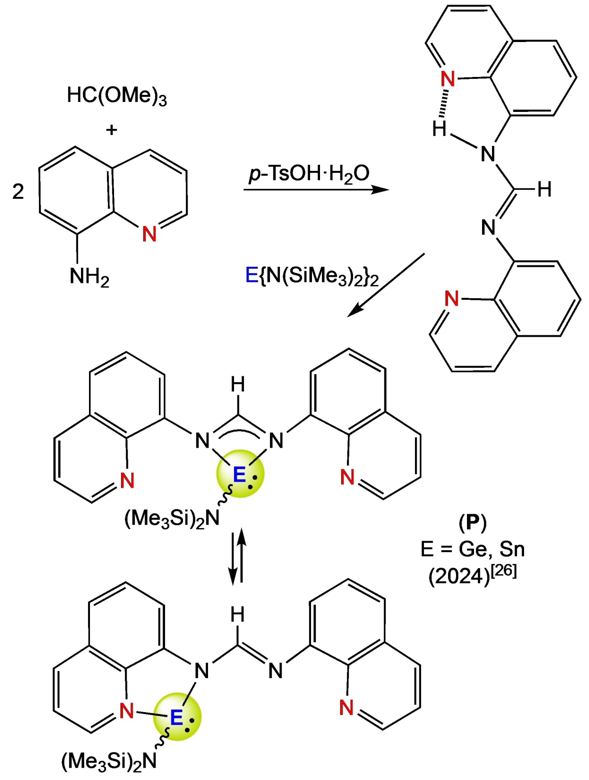
mesitylpivalimidoyl chloride with 2-(diphenylphosphanyl)aniline and the subsequent reaction of the resulting amidine with nBuLi and $GeCl_2$(dioxane).[25]

2.1.3. Mono(amidinatotetrylenes) of Type EX{DNC(R^2)ND} (IV)

The known examples of these tridentate ATs have been reported very recently.[26] Their preparations involve reactions of the doubly-donor-functionalized amidine *N,N'*-bis(quinol-8-yl)formamidine (for E=Ge) or its lithium salt (for E=Sn) with Lappert's tetrylenes E{$N(SiMe_3)_2$}$_2$ or SnCl{$N(SiMe_3)_2$}, respectively (E=Ge, Sn) (Figure 10).[26] Compounds **P** are fluxional in solution and DFT studies have shown that the symmetric structure depicted in Figure 10 is isoenergetic (and is in equilibrium in solution) with other one in which the E atom is chelated by an amidinate N atom and its closest quinolyl N atom. The formamidine was obtained by condensing trimethylorthoformate with two equivalents of 8-aminoquinoline.[27]

2.2. Polydentate Bis(amidinatotetrylenes)

All known compounds of this type have two symmetry-related AT fragments, generally separated by a spacer. Therefore, for bis-ATs, the D groups of the generic formulas shown in Figure 2 contain another AT fragment (generally attached to a spacer). The following subsections classify these compounds according to the AT fragment position to which the donor group (or the spacer) is attached.



(P)
E = Ge, Sn
(2024)[26]

Figure 10. Synthesis of doubly-donor-functionalized ATs **P**.

2.2.1. Bis(amidinatotetrylenes) of Type ED{R^1NC(R^2)NR^1} (I)

Compounds this type have the E atoms of two AT fragments (D also contains an AT group) connected to each other with or without a spacer between them. Figure 11 displays the currently known compounds of this type that have a spacer between the E atoms.[28–44]

Compounds of types **Q** and **R** were prepared by synthetic routes that are very different from those used for the remaining members of the family (*vide infra*). Bis-silylene **Q** was obtained by dehydrochlorinating with $LiN(SiMe_3)_2$ the siloxane [SiHCl{tBuNC(Ph)NtBu}]$_2$O,[28] which was previously prepared by controlled hydrolysis of $SiHCl_2${tBuNC(Ph)NtBu} (Figure 12). Bis-germylenes of type **R** (Figure 13) were prepared following one pot-two step procedures starting from GeCl{DippNC(tBu)NDipp}. The initial reduction with KC_8 (it was believed to give a germanium(I) intermediate that was not isolated) was followed by treatment with Me_3NO of S_8 to render the corresponding oxo- or sulfide-bridged bis-germylene.[29]

Bis-ATs of types **S**–**AC** (Figure 11) have in all cases been prepared by treating two equivalents of the corresponding chlorido-AT with the doubly lithiated form of the corresponding spacer (Li_2spacer) (Figure 14), which arises from either the

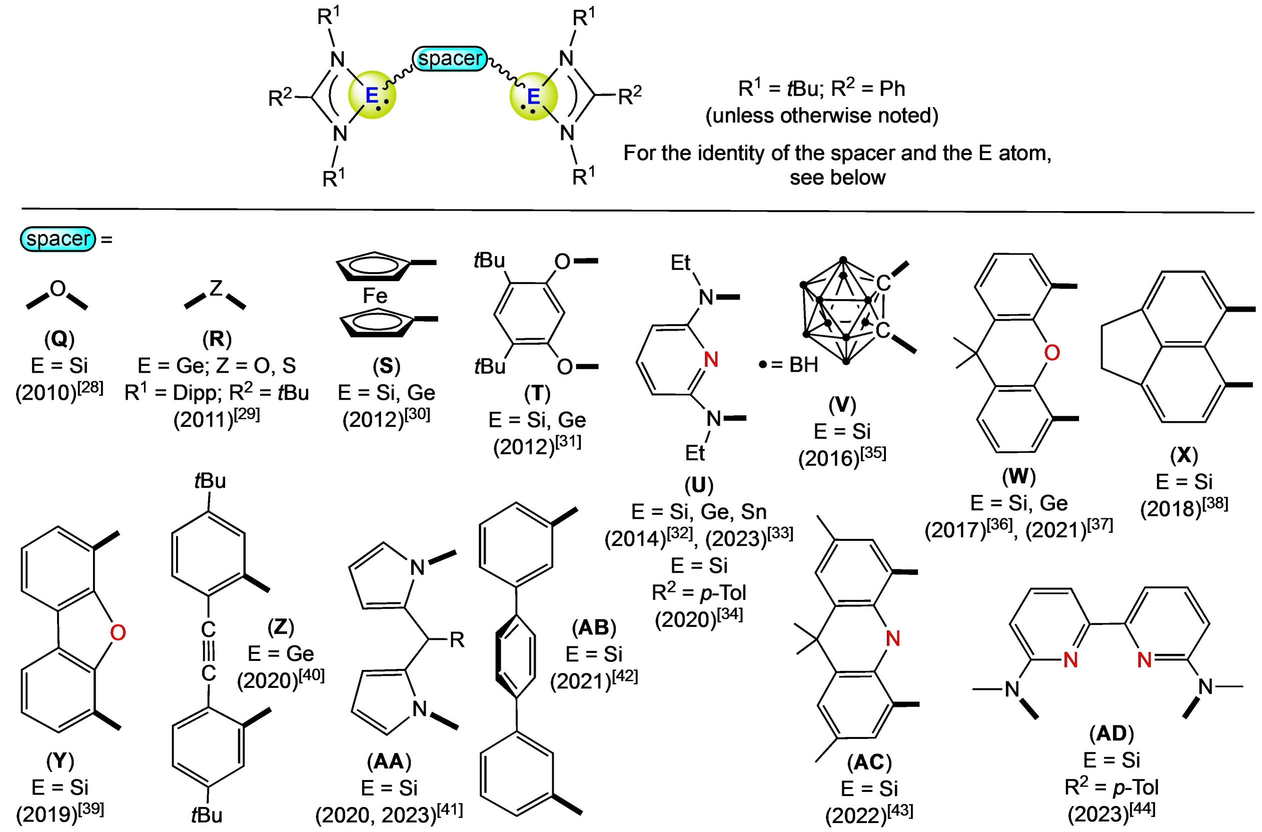


Figure 11. Currently known bis-ATs containing a spacer between their E atoms. The two thicker black segments on each spacer indicate the atoms that are attached to the amidinate fragments.

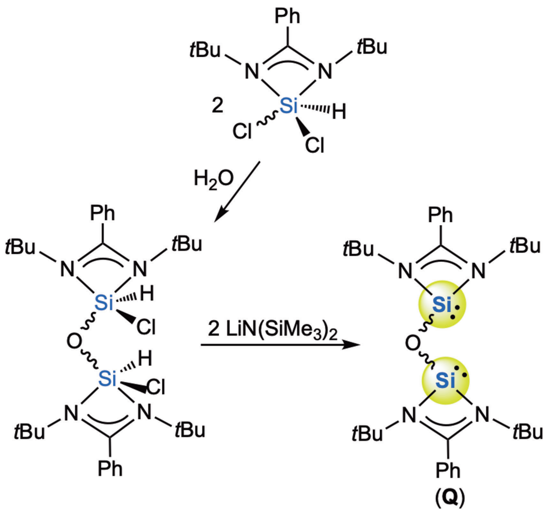


Figure 12. Synthesis of bis-silylene **Q**.

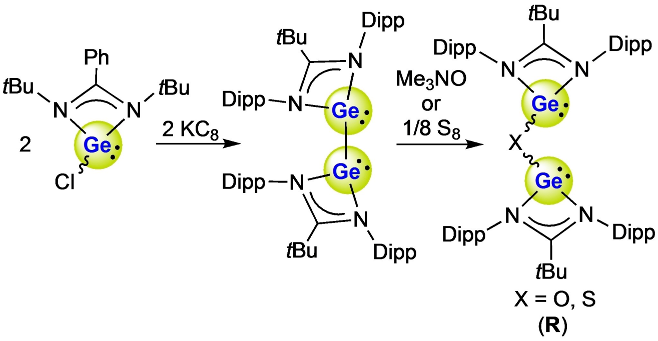


Figure 13. Synthesis of bis-germylenes of type **R**.

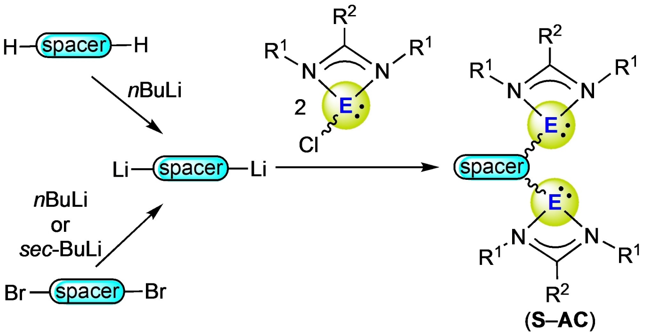
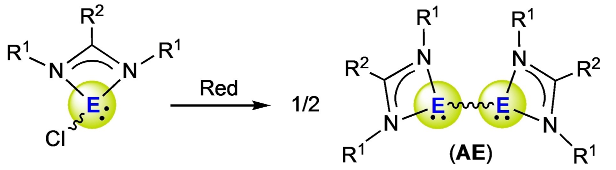


Figure 14. Syntheses of bis-ATs of types **S**-**AC**.

deprotonation of H_2spacer species with *n*BuLi (**S**–**V**,[30–35] **AA**[41]) or from the lithiation of Br_2spacer species with *n*BuLi (**X**,[36,37] **X**,[38] **AC**[43]) or *sec*-BuLi (**Y**,[39] **Z**,[40] **AB**[42]). The synthesis of bis-silylene **AD** involved the deprotonation of the corresponding H_2spacer with benzyl potassium.[44]

Although the formal oxidation state of the E atoms of the E–E bonded dimeric compounds $E_2\{R^1NC(R^2)NR^1\}_2$ (**AE** in Figure 15) is one (they have no spacer between the E atoms), they



Red = K; E = Ge; R^1 = Dipp; R^2 = *t*Bu, NMe_2 (2006)[45a]
Red = K; E = Ge; R^1 = *t*Bu; R^2 = Ph (2008)[45b]
Red = KC_8; E = Si; R^1 = *t*Bu; R^2 = Ph (2009)[46]
Red = $[Mg\{CH(MesNCMe)_2\}]_2$; E = Si, Ge, Sn;
R^1 = Dipp; R^2 = 4-*t*BuC_6H_4 (2011)[47]

Figure 15. Synthesis of dimeric compounds of type **AE**.

can also be considered as bis-ATs. Their syntheses involve a one-electron reduction of chlorido-ATs of the type $ECl\{R^1NC(R^2)NR^1\}$ with potassium,[45] potassium graphite[46] or a magnesium(I) dimer.[47]

2.2.2. Bis(amidinatotetrylenes) of Type $EX\{DNC(R^2)NR^1\}$ (II)

The members of this family have two AT fragments connected to a spacer through one of their amidinate N atoms (D also contains an AT fragment). Only one example of this type has so far been reported (**AF**, Figure 16). It was prepared by condensing 1,3-$C_6H_4\{NC(Cl)tBu\}_2$ with Ar^*NH_2 (Ar^* = 2,6-bis(diphenylmethyl)-4-(isopropyl)phenyl) and subsequent treatment of the resulting bis(amidine) with *n*BuLi and $GeCl_2$(dioxane).[48]

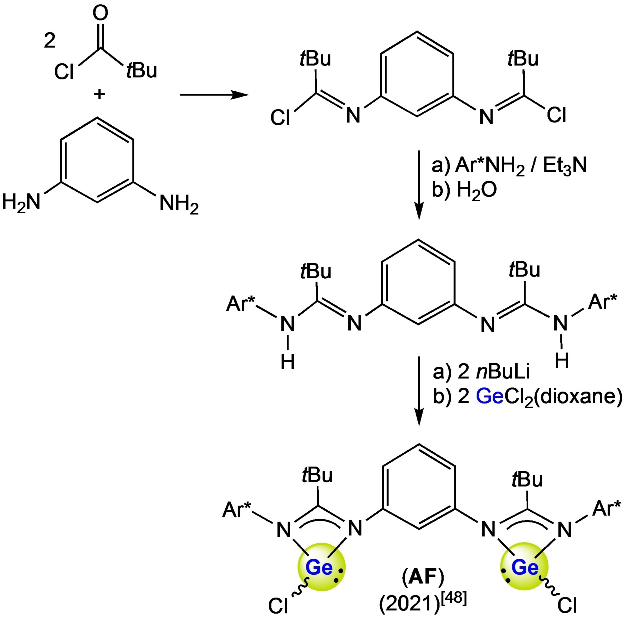


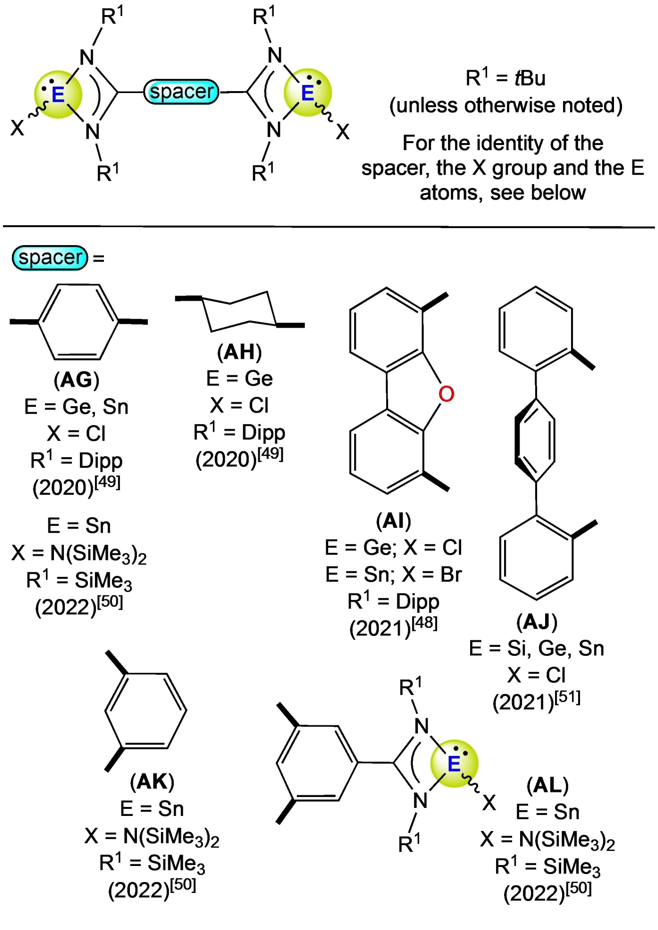
Figure 16. Synthesis of bis-AT **AF**.

2.2.3. Bis- and Tris(amidinatotetrylenes) of Type $EX\{R^1NC(D)NR^1\}$ (III)

Compounds of this type have two or three AT fragments connected to a spacer through their amidinate central C atom (D also contains one or two AT groups) (Figure 17).[48–51]

The syntheses of ATs **AG**–**AL** (Figure 17) require the attachment of two or three C-bonded amidinate fragments to the corresponding spacer prior to the final reaction with the appropriate tetrel atom precursor. Two different approaches have been used. The most general approach, used for bis-ATs of types **AG** (R^1 = Dipp),[49] **AH**,[49] **AI**[48] and **AJ**,[51] involves reactions of carbodiimides with the appropriate dilithiated spacers, previously generated by treating the corresponding neutral H_2spacer[48,49] or Br_2spacer[51] with *n*BuLi (Figure 18). Subsequent reactions of the dilithium diamidinates with $GeCl_2$(dioxane) or SnX_2 (X = Cl, Br) allow the isolation of the corresponding germylenes or stannylenes. Bis-AT **AJ** with E = Si has been prepared by sequential treatment of the deprotonated diamidine with $SiHCl_3$ and $Li\{N(SiMe_3)_2\}$ (as dehydrochlorinating reagent).[51]

An alternative route to bis- and tris(amidinatostannylenes) of type $SnX\{R^1NC(D)NR^1\}$ (the D group contains one or two additional amidinatostannylene fragments) consists of the



R^1 = *t*Bu
(unless otherwise noted)
For the identity of the spacer, the X group and the E atoms, see below

(AG)
E = Ge, Sn
X = Cl
R^1 = Dipp
(2020)[49]
E = Sn
X = $N(SiMe_3)_2$
R^1 = $SiMe_3$
(2022)[50]

(AH)
E = Ge
X = Cl
R^1 = Dipp
(2020)[49]

(AI)
E = Ge; X = Cl
E = Sn; X = Br
R^1 = Dipp
(2021)[48]

(AJ)
E = Si, Ge, Sn
X = Cl
(2021)[51]

(AK)
E = Sn
X = $N(SiMe_3)_2$
R^1 = $SiMe_3$
(2022)[50]

(AL)
E = Sn
X = $N(SiMe_3)_2$
R^1 = $SiMe_3$
(2022)[50]

Figure 17. Bis- and tris-ATs containing a spacer between their amidinate C atoms. The two thicker black segments on each spacer indicate the atoms that are attached to the amidinate fragments.

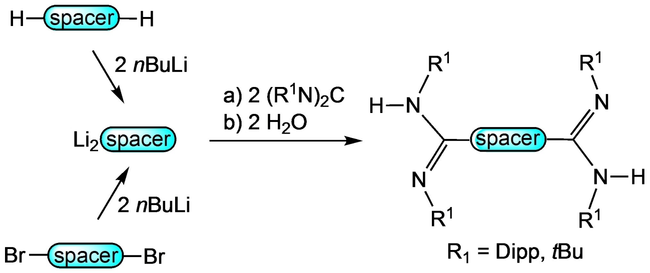


Figure 18. Synthetic routes used to prepare the diamidines that are precursors to bis-ATs **AG**–**AJ**.

reactions of aromatic di- or trinitriles with the appropriate amount of Sn{N(SiMe$_3$)$_2$}$_2$. This approach has also been used to prepare ATs **AG** (E=Sn; X=N(SiMe$_3$)$_2$), **AK** and **AL** (Figure 19).[50]

2.3. Polydentate Bis(amidinato)monotetrylenes of Type E{R^{1}NC(R^2)ND}$_2$ (V)

These compounds have two donor-functionalized amidinate fragments but only one tetrel atom. The first specimens of this type have been very recently prepared in two steps from *N*-isopropylbenzimidoyl chloride, 2-(diphenylphosphanyl)ethylamine, LiN(SiMe$_3$)$_2$ (as deprotonating reagent) and GeCl$_2$(dioxane) or SnCl$_2$ (Figure 20).[52]

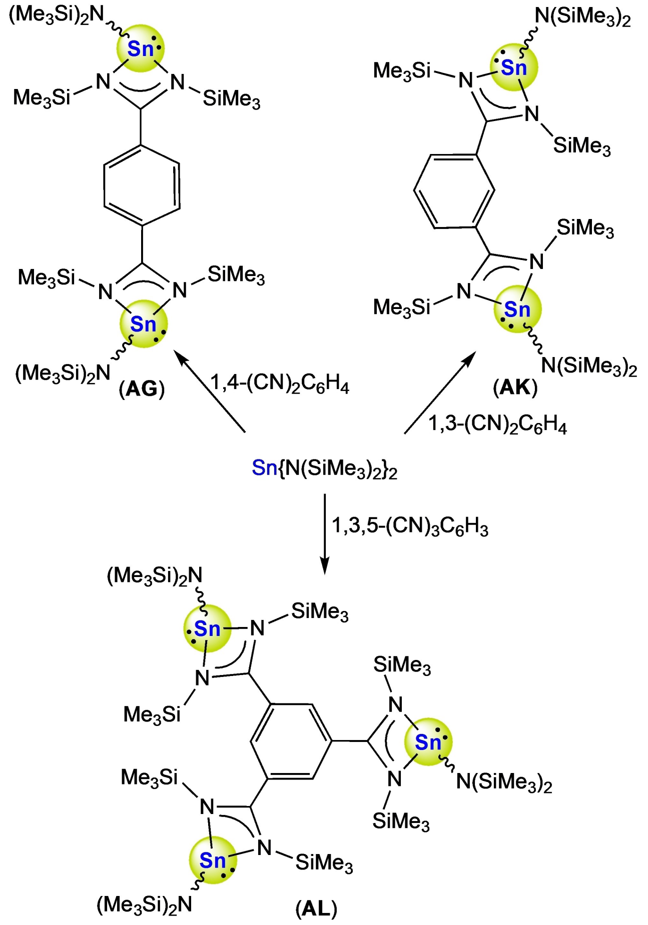


Figure 19. Syntheses of bis-ATs **AG** and **AK** and tris-AT **AL**.

2.4. Cyclometallated Amidinatotetrylenes (VI)

These ATs have been observed as ligands in transition metal complexes but are not stable as transition metal-free compounds. Figure 21 shows the currently known cyclometallated AT ligands as found in their transition metal complexes. While the transition metal-free precursors of **AO** are simple monodentate ATs, namely, E(Mes){*t*BuNC(Ph)N*t*Bu} (E=Ge, Sn),[54,55] those of **AN**,[31] **AP**[17a] and **AQ**[41] are donor-functionalized,

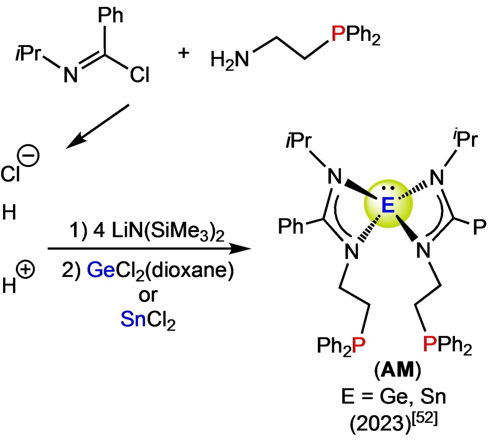


Figure 20. Synthesis of ATs **AM**.

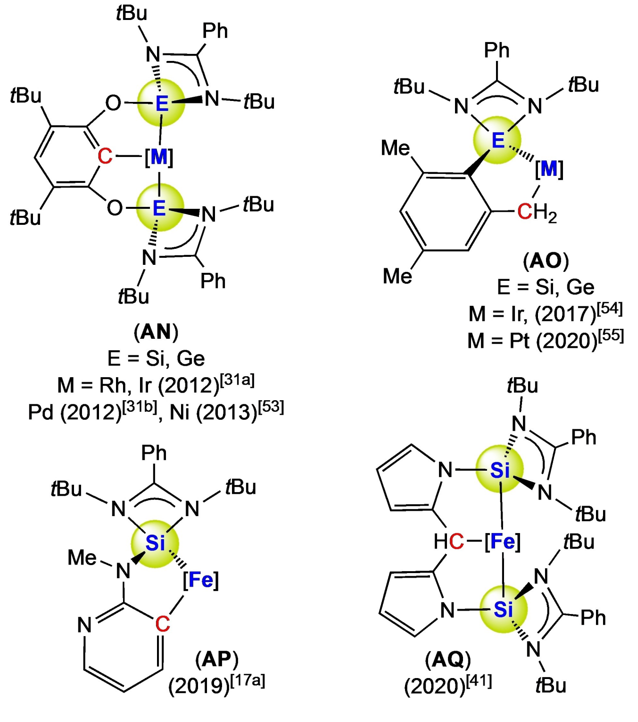


Figure 21. Currently known cyclometallated bi- or tridentate AT ligands, as found in their transition metal complexes.

potentially bidentate, ATs (**T**, **F** and **AA**, respectively) whose syntheses have already been presented in this article.

2.5. Ring-Opened Amidinatotetrylenes (VII)

These ATs are also known only as ligands in transition metal complexes. The precursors to the ligands of complexes **AR** and **AS** (Figure 22) are simple ATs,[8c,56–58] whereas those of complexes **AT**–**AW** (Figure 23) are donor-functionalized ATs.[25,26,52] The ligands of complexes **AR**–**AW** arise from a simple (formal) insertion of a metal atom into an E–N bond of a metal-free AT. However, that of **AW** arises from the displacement of both cod ligands of [Ni(cod)$_2$] by two ATs **O** (Figure 9), to give [Ni**O**$_2$], and a subsequent reduction of the latter with KC$_8$.[25] Interestingly, the ATs of complexes **AU**[52] and **AW**[25] behave as σ-acceptor *Z*-ligands.

3. Polydentate Amidinatotetrylenes Involved in Metal-Catalysed Reactions

The transition metal coordination chemistry of the ATs on which this review is focused has been developed to a great extent and many are the resulting transition metal complexes that have been involved in catalytic reactions. Table 1 summarizes the catalytic reactions that have so far been performed using catalyst precursors that contain di- or tridentate ATs. It is noteworthy that the great majority of these catalytic transformations use silylenes (entries 1–10, 12 and 14–28) and that many of them are bis-silylenes (entries 6–10, 12 and 14–26), probably because amidinatosilylenes are more electron-donating than their heavier congeners.[7] It is also relevant that most catalyst precursors are complexes of first-raw transition metals (entries 2–7, 9–11 and 14–26) and that some of them are efficient for challenging catalytic C–H activation transformations, such as borylation of arenes (entries 12, 13, 18 and 28) and terminal alkynes (entry 20), or the silylation of dinitrogen (entries 4 and 23). Cooperation between the tetrel atom and the metal has been observed in some occasions (entries 10, 11, 16, 24 and 26). Interestingly, a nickel(0) complex with AT **AB** (entry 24) has been claimed to be the most active homogeneous nickel-based catalyst for the hydrogenation of olefins (TON = 9800, TOF = 6800 h^{-1}).

Polydentate amidinatogermylenes have seldom been used as part of catalyst precursors (Table 1, entries 11 and 13). In some examples (entries 7 and 8), while the silylene complexes are catalytically active, the analogous germylene complexes are inactive under the same reaction conditions. It should also be

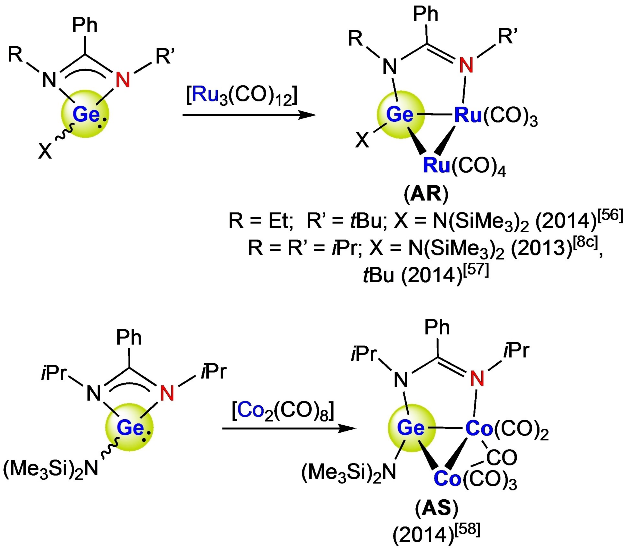


Figure 22. Currently known ring-opened bidentate AT ligands arising from simple ATs, as found in their transition metal complexes.

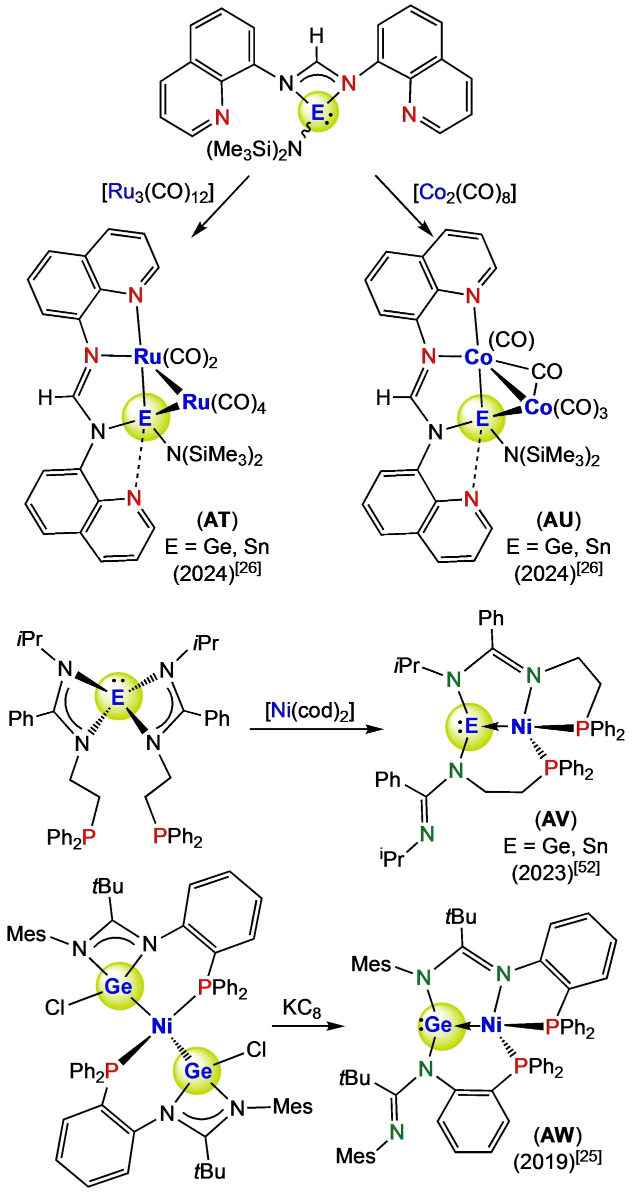


Figure 23. Currently known ring-opened bi- or tridentate AT ligands arising from donor-functionalized ATs, as found in their transition metal complexes.

noted that Table 1 does not contain any entry involving tin as the tetrel atom.

4. Discussion and Future Outlook

The above-reviewed results, the majority of which have been reported in the last 10 years, indicate that ATs functionalized with additional potentially coordinable groups are currently receiving considerable attention from the chemical community.

ATs of the type ED{R^{1}NC(R^2)NR^1} (**I**), in which the donor group is attached to the E atom, are well represented in the chemical literature, both as potentially bidentate or tridentate ligands (Figures 5, 11 and 15), but most of them are silylenes probably because their transition metal complexes soon demonstrated their efficiency in catalysis (Table 1), prompting the synthesis of more amidinatosilylenes of this type. Therefore, much work involving amidinatogermylenes and, especially, amidinatostannylenes of this type is still needed to equilibrate the situation.

Regarding ATs of the types EX{DNC(R^2)NR^1} (**II**) (Figures 9 and 16), EX{DNC(R^2)ND} (**IV**) (Figure 10) and E{R^{1}NC(R^2)ND}$_2$ (**V**) (Figure 20), in which the donor group(s) is (are) attached to one or both amidinate N atoms, their syntheses are more challenging because they involve the assembling of the donor-functionalised amidine prior to the reaction with the tetrel precursor. Currently, they are still very few (**O**,[25] **P**,[26] **AF**,[48] and **AM**[52]), their preparations have been reported very recently, and the catalytic properties of their transition metal complexes are yet to be investigated. It is noteworthy that none of them is an amidinatosilylene, probably because the syntheses of ATs with E = Ge, Sn are much easier, as they utilize commercially available tetrel(II) precursors, such as $GeCl_2$(dioxane) or $SnCl_2$, whereas, as no silicon(II) reagents are commercially available, the syntheses of amidinatosilylenes involve more steps and require challenging reductions of silicon(IV) precursors (Figure 4). This situation is comparable to that of ATs of type EX{R^{1}NC(D)NR^1} (**III**) (Figure 17), which have the donor group attached to the central C atom of the amidinate scaffold. Therefore, many more synthetic and catalytic investigations involving ATs of these types will be welcome.

Table 1. Catalytic Reactions Promoted by Transition Metal Complexes Containing Di- or Polydentate ATs.

Entry	AT	E	Metal	Catalytic reaction	Ref.
1	**E**	Si	Rh^{III}	Alkylation of 2-phenyl pyridine with norbornene	16
2	**F**	Si	Fe^{II}	Hydroboration of ketones and aldehydes	17a
3	**F**	Si	Cu^{I}	Click cycloaddition	17b
4	**M**	Si	Fe^{0}	Silylation of dinitrogen	24a
5	**N**	Si	Co^{I}	Olefin hydrogenation	24b
6	**Q**	Si$_2$	Ni^{0}	Organozinc and Grignard coupling with aryl halides	62
7	**S**	Si$_2$	Co^{I}	2+2+2 Cycloaddition of phenylacetylene with MeCN	30
8	**S**	Si$_2$	Rh^{I}	Hydroformylation of styrene	63
9	**S**	Si$_2$	Fe^{0}	Ketone hydrogenation	60
10	**T**	Si$_2$	Ni^{0}	Shonogashira cross coupling	53
11	**T**	Ge$_2$	Ni^{0}	Shonogashira cross coupling	53
12	**T**	Si$_2$	Rh^{I}, Ir^{I}	C–H Borylation of arenes	31a
13	**T**	Ge$_2$	Rh^{I}, Ir^{I}	C–H Borylation of arenes	31a
14	**U**	Si$_2$	Fe^{II}	Ketone hydrosilylation	32
15	**U**	Si$_2$	Co^{III}	C–H Borylation of furan and 2,6-lutidine	34
16	**U**	Si$_2$	Co^{III}	H/D Exchange of sterically hindered C–H bonds	61
17	**U**	Si$_2$	Mn^{II}	Transfer semi-hydrogenation of alkynes	64
18	**U**	Si$_2$	Co^{II}	C–H Borylation of arenes	65
19	**U**	Si$_2$	Fe^{0}	Carbonyl group hydrosilylation	59
20	**U**	Si$_2$	Mn^{II}	C–H Borylation of terminal alkynes	66
21	**V**	Si$_2$	Ni^{II}	Arene amination	35
22	**W**	Si$_2$	Ni^{0}	Olefin hydrogenation	36
23	**AA**	Si$_2$	Fe^{II}	Silylation of dinitrogen	41
24	**AB**	Si$_2$	Ni^{0}	Olefin hydrogenation	42
25	**AC**	Si$_2$	Fe^{II}	Reduction of nitrocompounds to aminoboranes with HBPin	43
26	**AC**	Si$_2$	Fe^{II}	Decomposition of N_2O to N_2 and H_2 with HBPin	43
27	**AO**	Si	Ir^{III}	H/D Exchange of arene C–H bonds	54a
28	**AO**	Si	Ir^{III}	C–H Borylation of arenes	54a

The reason behind the currently scarce use of polydentate amidinatogermylene and amidinatostannylene ligands in transition metal catalysis is not yet clear, but it may have nothing to do with catalytic activity; simply and most probably, they have been relegated by the prompt discovery of the excellent catalytic activity of their silicon analogues and, in addition, the very recent discovery of many of these polydentate ATs (particularly those with $\mathrm{E}=\mathrm{Sn}$) has not yet allowed subsequent catalytic studies.

Therefore, although the field of polydentate ATs (synthesis, transition metal chemistry and catalytic applications) has already been widely developed, much work is still needed, particularly if it involves amidinatogermylenes and amidinatostannylenes.

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Conflict of Interests

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 analysed in this study.

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