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Main Group Organometallic Chemistry

Structurally Defined Allyl Compounds of Main Group Metals: Coordination and Reactivity

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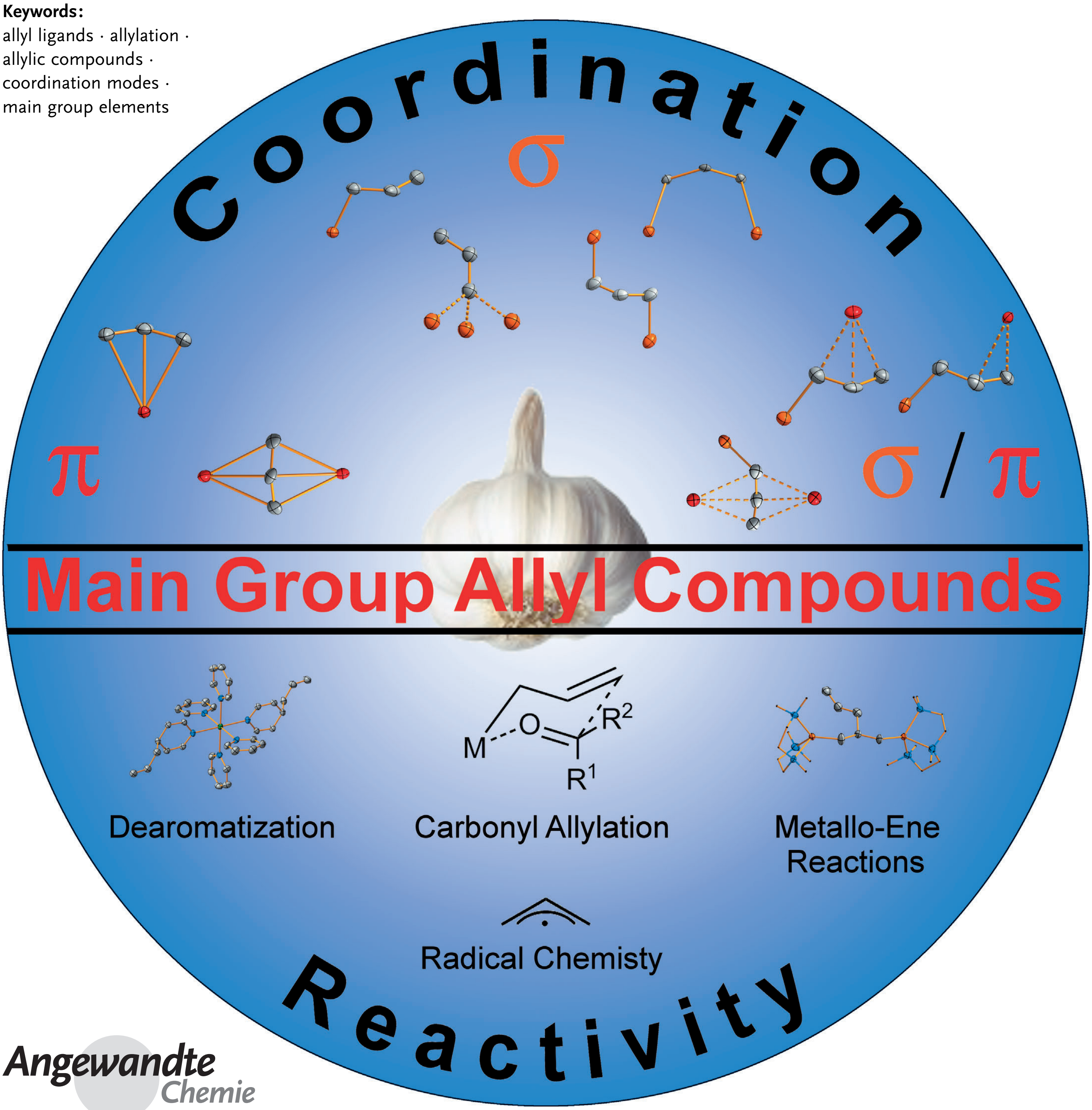
allyl ligands · allylation · allylic compounds · coordination modes · main group elements



Angewandte Chemie

Organometallic allyl compounds are important as allylation reagents in organic synthesis, as polymerization catalysts, and as volatile metal precursors in material science. Whereas the allyl chemistry of synthetically relevant transition metals such as palladium and of the lanthanoids is well-established, that of main group metals has been lagging behind. Recent progress on allyl complexes of Groups 1, 2, and 12–16 now provides a more complete picture. This is based on a fundamental understanding of metal–allyl bonding interactions in solution and in the solid state. Furthermore, reactivity trends have been rationalized and new types of allyl-specific reactivity patterns have been uncovered. Key features include 1) the exploitation of the different types of metal–allyl bonding (highly ionic to predominantly covalent), 2) the use of synergistic effects in heterobimetallic compounds, and 3) the adjustment of Lewis acidity by variation of the charge of allyl compounds.

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1. Introduction

In 1844, steam distillation of one hundred-weight (ca. 56 kg) of garlic led to the isolation of the first allyl compound in about 0.2% yield (*m*/*m*), which was later shown to be bis(allyl)disulfide.[1] Derived from the Latin name for garlic (*allium sativum*), the term "allyl" has since become established in chemical terminology for the unsaturated C_3H_5 group. Allylmetal complexes have proved to be a prominent class of compounds in the fields of organic, organometallic, and coordination chemistry. In early studies triggered by the synthesis of $[Ni(C_3H_5)_2]$ by Wilke et al., allyl compounds of a wide range of transition metals were studied with respect to σ/π bonding.[2] Allyl compounds of main group metals were subsequently also investigated, especially those of some Group 1 and 2 metals,[3] boron,[4,5] silicon,[5,6] and tin.[5,7] Allyl compounds of Group 3 elements and the lanthanoids were later studied in detail.[8]

Overall, a rich arsenal of organometallic allyl-transfer reagents and catalysts has been developed that covers a broad spectrum of applications.[9] Key findings include that allylmetal compounds are pivotal intermediates in rearrangement reactions[10] and in catalyzed olefin oligo-[11] and polymerizations.[12] They have also been applied as unique initiators for the polymerization of olefins and cyclic esters.[8a,12a,b,13] Moreover, the transfer of an allyl group (catalyzed and non-catalyzed) is of tremendous importance in organic synthesis, for example, in chemo- and regioselective reactions,[14] in diastereo- and enantioselective reactions,[15] including umpolung of the allyl ligand,[15g,16] in (de)protection of diverse functional groups[17] as well as in tandem,[18] cascade,[19] and multicomponent reactions.[20]

Allyl complexes of main group metals find frequent application in many of the above-mentioned transformations. Striking differences in the chemo-, regio-, and stereoselectivity are often observed depending on the metal center, but cannot be explained satisfyingly in all cases. Attempts to rationalize the reactivity patterns in such reactions are often hampered by the allyl compounds being generated in situ. This inherently causes potential salt contamination, which can dramatically influence the reactivity of the organometallic species.[21] Fundamental investigations of metal–allyl interactions in isolated compounds should help to overcome this lack of understanding. Some of the allyl compounds of main group metals that have long been used as in situ reagents have only recently been isolated and characterized. Others have been reinvestigated, and have led to a modification of our view of metal–allyl interactions in text book examples, such as bis(allyl)zinc. Moreover, allyl compounds of main group metals, which had previously rarely been considered by the organic and organometallic community (e.g. those of heavy Group 2 elements), have more recently been isolated and have broadened the spectrum of allyl-transfer reagents. Based on these investigations, recent advances in the field have revealed new types of metal–allyl bonding modes. Furthermore, new allyl-specific reactivities have been uncovered in metallo-ene reactions, dearomatizations, and oxidatively induced coupling reactions. In addition to the conventional approach of investigating neutral compounds, formally charged species have attracted increased interest. These include well-defined and highly Lewis acidic cationic compounds as well as heterobimetallic compounds whose characteristics can be exploited in terms of synergistic effects. This Review covers recent advances in the chemistry of allyl compounds of main group metals including Group 12 elements. It is restricted to homoleptic compounds of the parent $[C_3H_5]^-$ moiety and their solvent adducts, as well as a few exceptions where important findings have so far only been observed for derivatives.[22] The bonding situation of these compounds in solution and in the solid state is described. Trends in the periodic table of the elements are discussed, since some gaps have recently been closed, thereby resulting

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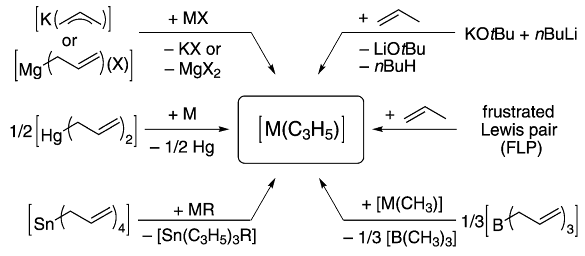
in a more-thorough understanding. Allyl-specific reactivities are also presented.

2. Synthesis of Allylmetal Compounds

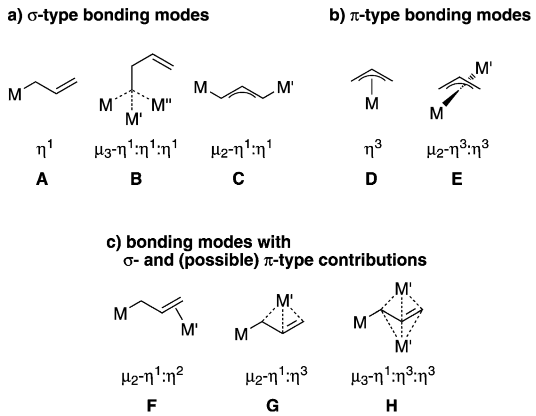
The most important type of reaction for the synthesis of allyl compounds of main group metals is salt elimination (Scheme 1). (Allyl)magnesium halides and (allyl)potassium are frequently used allyl-transfer reagents. The Grignard compound offers the advantage of easy accessibility, whereas preparation of the potassium compound requires an increased experimental effort. As a consequence of its pronounced ionic character, the potassium compound shows a higher tendency to transfer the allyl group, and the resulting potassium halides are easier to separate. Metal/metal exchange and transmetalation represent two other general reaction routes for the synthesis of allyl complexes, but their use is limited due to the high toxicity of the related reagents tetrakis(allyl)tin and bis(allyl)mercury. If the homoleptic methyl complex of an element is easily accessible, the related allyl species can potentially be obtained by transmetalation with tris(allyl)boron. Other methods such as direct synthesis and metalation of propene are limited to special cases. Recently, the first preparation of an allyl compound by use of a frustrated Lewis pair (FLP) was reported (see Section 4.4).[24]



Scheme 1. Methods for the synthesis of homoleptic allylmetal compounds. A monovalent target compound is shown for simplicity; X = halide.

3. Structure of Allylmetal Compounds

Understanding the interactions of delocalized π-electron systems with metal centers spanning the entire range from ionic to covalent bonding is of fundamental interest in organometallic chemistry. The allyl group represents the simplest delocalized π-electron system and is, therefore, an ideal model ligand for such investigations. In recent years, the allyl ligand has been shown to possess a rich coordination chemistry (Scheme 2). This is remarkable bearing in mind that this ligand consists of only three non-hydrogen atoms. The bonding mode of the allyl ligand is in the first place determined by the frontier orbitals of the metal center. They are influenced by factors such as the presence and donor strength of neutral ligands and the charge of the metal center. The type of counterion (if present) can also have a crucial impact. A thorough understanding of the coordination chemistry of a class of compounds can contribute to understanding its reactivity. This has been achieved in the case of (allyl)palladium compounds, in which the allyl ligand reacts as a nucleophile when bonded in an η^1 fashion or as an electrophile when bonded in an η^3 fashion.[16]



Scheme 2. Structurally authenticated bonding modes of the allyl ligand; a *cis* and a *trans* isomer can be realized for **C**.

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3.1. Structure in the Solid State

IR and Raman spectroscopy as well as solid-state CP MAS ^{13}C NMR measurements have been used to investigate the bonding mode of allyl ligands in the solid state.[66,68] These analytical techniques allow differentiation between bonding modes with localized or delocalized π-electron systems. However, only limited information can be obtained about the nature of the metal–allyl interaction, as allyl ligands with delocalized π-electron systems can show σ-type M−C^{allyl} (M = metal) bonding (Scheme 2, type **C**) and allyl ligands with localized π-electron systems can be involved in π-type M−C^{allyl} bonding (Scheme 2, types **F**–**H**). Single-crystal X-ray analysis is necessary for a precise experimental distinction between the eight bonding modes of the allyl ligand that have been structurally authenticated for main group elements to date. Theoretical calculations provide additional helpful information (see e.g. Section 3.1.3).

3.1.1. σ-Type Bonding Modes

Three different bonding modes have been reported in which the allyl ligand shows σ-type interactions with the metal center(s) exclusively. The archetypical σ-type coordination mode is η^1 bonding (**A**), with localized single and double bonds in the allyl group. In a closely related coordination mode, one carbon atom of an allyl ligand with localized single and double bonds bridges three metal centers (μ_3-η^1:η^1:η^1, **B**).[55b] Notably, an analogous bridging of two metal centers by an allyl ligand in the solid state has not been reported to date. Instead, the bridging of two metal centers by an allyl group is realized by the interaction of the two terminal carbon atoms with one metal center each (μ_2-η^1:η^1, **C**).[40,55a,60,65] Delocalization of the π electrons within the allyl ligand is usually observed for this bonding mode.[25] Thus, without the aid of single-crystal X-ray analysis, this coordination mode cannot be distinguished from others, such as μ_2-η^3:η^3 coordination (**E**, see Section 3.1.2).[26] The type **C** coordination mode can be realized as a *cis* isomer with both metal centers on the same side of a plane defined by the three carbon atoms of the allyl ligand or as a *trans* isomer with the two metal centers on different sides of this plane.[65] It leads to cyclic oligomeric as well as one- and three-dimensional polymeric arrangements in the solid state.[55a,60,65]

3.1.2. π-Type Bonding Modes

η^3 Coordination of the allyl ligand (**D**) is the archetypical bonding mode showing only π-type M−C^{allyl} interactions.[40,57a] Similarly, the bridging μ_2-η^3:η^3 coordination mode (**E**) also shows π-type M−C^{allyl} bonding exclusively.[61] Mode **E** leads to oligomeric cyclic[42] as well as one-[43] and two-dimensional[61] polymeric arrangements in the solid state. For both coordination modes, **D** and **E**, the π electrons in the allyl ligand are delocalized. Different extents of delocalization have been observed and are expressed by different degrees of asymmetry in the metal–allyl bonding (e.g. differences in M−C^{terminal} and C^{allyl}–C^{allyl} bond lengths).

3.1.3. Bonding Modes with σ- and (Possible) π-Type Contributions

μ_2-η^1:η^2 Coordination of the allyl ligand (**F**) involves σ-type interactions of the allyl ligand with the first metal center M. Interactions of the allyl ligand with the second metal center M′ are realized by donation of electron density from the C=C bond to empty orbitals of M′. This is a σ-type M′–allyl interaction, although π electrons of the C=C bond are involved. Only if there is significant back bonding by donation of electron density from metal-centered orbitals to the π* orbital of the C=C bond, can this M′–allyl bonding be classified as a π-type interaction. However, such back donation has not been reported for allyl compounds of main group metals.[27] In general, the C−C bonds of allyl ligands adopting a μ_2-η^1:η^2 coordination mode (**F**) are localized. Slight elongation of the coordinating C=C bond has been predicted by ab initio calculations for M = M′ = Zn, but has not been observed experimentally for M = Ga, M′ = K.[65,76] In one case, a distorted **F**-type bonding has been observed and discussed in terms of a possible intermediate μ_2-η^1:η^1 coordination (**C**).[66] Whereas π bonding in addition to the metal–allyl σ interactions is possible in coordination mode **F**, a π-type contribution is certain for recently reported coordination modes **G** (μ_2-η^1:η^3) and **H** (μ_3-η^1:η^3:η^3).[51,56] Localized single and double C−C bonds within the allyl ligand are found in the few examples of type **G** and **H** coordination modes. This, together with the fact that single-crystal X-ray analysis is so far the only experimental technique able to detect these bonding modes, sometimes makes differentiation from type **F** coordination difficult.[28] Additional DFT calculations have been helpful for a more reliable distinction.[51] Allyl compounds showing type **G** and **H** coordination modes form coordination oligo-[56] or polymers[51] in the solid state.

3.2. Structure in Solution

Whereas a large number of coordination modes of the allyl ligand has been observed in the solid state, less have been described for the bonding situation in solution. This is probably due to the fact that many of the interactions of an allyl ligand with more than one metal center are not kinetically stable in solution.[29] If they do occur, they are usually difficult to classify experimentally due to dynamic phenomena and/or rapid ligand-exchange reactions (see Section 3.3). DFT calculations have been used to overcome experimental limitations.[37e] The main experimental techniques used for investigating the bonding of allyl ligands to main group metals in solution are IR, Raman, and NMR spectroscopy.[30] The former two methods allow discrimination between allyl ligands with localized and delocalized π electrons, as described in Section 3.1. The band ascribed to the asymmetric stretching of the allyl ligand is usually used as a diagnostic tool (localized type: $\tilde{\nu} = 1590$–$1660\,\mathrm{cm^{-1}}$; delocalized type: $\tilde{\nu} = 1450$–$1580\,\mathrm{cm^{-1}}$).[68] More detailed information can be obtained by NMR spectroscopy (see also Section 3.3). Three different situations can be differentiated by ^{1}H NMR spectroscopy at ambient temperature:

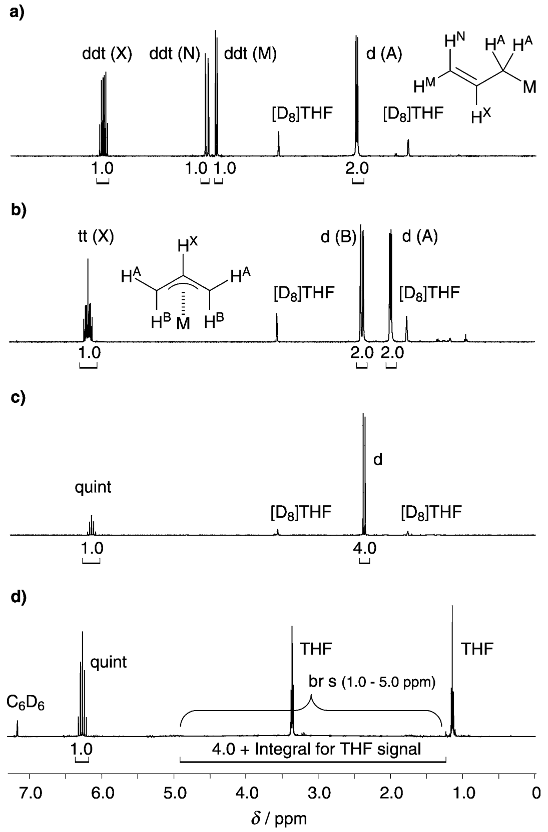


Figure 1. Ambient-temperature ^{1}H NMR spectra of compounds containing a) η^1-bonded allyl ligands (A_2MNX; example: $[Bi(C_3H_5)_3]$);[109] b) η^3-bonded allyl ligands (A_2B_2X; example: $[K(C_3H_5)]$);[37d] c) fluxional allyl ligands (A_4X; example: $[Mg(C_3H_5)_2]$);[53] d) allyl ligands with a coordination behavior intermediate between (a) and (c) (example: $[Ga(C_3H_5)_3(thf)]$).[76] Integrals are set to values corresponding to one allyl ligand.

1) The allyl ligands can show η^1 bonding with localized single and double bonds, thereby resulting in an A_2MNX coupling pattern (Figure 1 a). The chemical shift of the aliphatic methylene group does not directly correlate with the electronegativity of the metal center and has been discussed in terms of the diamagnetic anisotropy of the M−C and C=C bonds.[93] The chemical shifts of the methine and the terminal methylene protons are affected to a lesser extent by the nature of the central atom.
2) The second bonding situation that can be detected in solution is η^3 coordination. In this case, rotation around both C−C bonds of the allyl ligand is hindered, thereby giving rise to an A_2B_2X coupling pattern (Figure 1 b).
3) The third bonding situation refers to an allyl ligand that shows fluxional behavior; that is, the four methylene protons formally exchange their positions (for a discussion of the mechanisms, see Section 3.3). Such processes have been reported for compounds with η^1- or η^3-allyl ligands in the ground state.[31,57a,68] If these exchange phenomena are fast on the NMR time scale, an equivalence of all four methylene protons is observed, thus resulting in an A_4X coupling pattern (Figure 1 c). If they take place on a time scale that is approximately equal to the corresponding resolution of the NMR experiment, the resulting spectra reflect intermediates between the ground state (η^1 or η^3 bonding) and the fluxional situation (A_4X pattern). In the case of η^1-bound allyl ligands, this can result in one extremely broad signal for the methylene groups that virtually disappears into the base line, whereas the resonance attributed to the methine proton remains sharp (Figure 1 d).[76,85]

Identification of the ground state of the allyl coordination for compounds that show fluxional behavior at ambient temperature is commonly achieved by means of low-temperature NMR spectroscopy. If the exchange rate at low temperature is still too high to allow determination of the ground-state coordination or if this information needs to be obtained at a higher temperature, Saunders' isotopic perturbation technique can be applied.[37a–c] For this purpose, the compound of interest must be monodeuterated at a terminal position of the allyl ligand. This makes the methylene carbon atoms distinguishable by ^{13}C NMR spectroscopy (one singlet, one 1:1:1 triplet). The deuteration will also cause a so-called static isotope effect $\Delta\delta_{stat}$, which is expressed by a slight upfield shift (ca. $\delta = 0.4$ ppm) of the signal for the deuterated carbon atom. These are the only relevant changes in the ^{13}C NMR spectrum that will occur compared to that of the nondeuterated compound if the ground state of the allyl coordination is η^3 (Figure 2 a). However, another effect becomes apparent if the ground state of the allyl coordination is η^1. The equilibrium shown in Figure 2 b is in favor of the CHD group as an olefinic unit rather than an aliphatic methylene unit due to the lower zero-point vibrational energy of the C−D bond compared to that of the C−H bond. This causes a downfield shift of the signal for the deuterated carbon atom in the ^{13}C NMR spectrum (and an upfield shift of the signal for the CH_2 carbon atom). This dynamic isotope effect, $\Delta\delta_{dyn}$, overcompensates the static isotope effect. Thus, discrimination between η^1- and η^3-bonding modes as the ground states of allyl coordination in fluxional systems is possible. For η^3-type bonding modes, cases ranging from perfectly symmetric to nonsymmetric π-type coordination have been discussed.[37a–c,e]

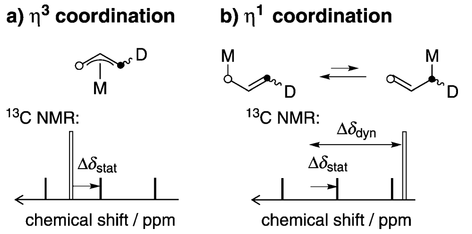
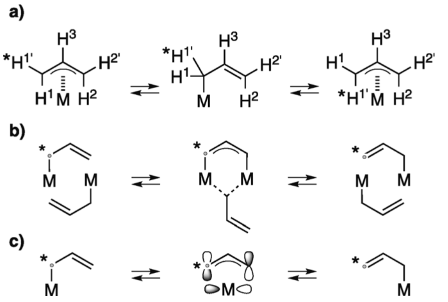


Figure 2. Saunders' isotopic perturbation technique for determination of the ground-state coordination modes of fluxional allyl ligands; situations found for a) η^3 coordination and b) η^1 coordination, with schematic representations of the methylene region in the ^{13}C NMR spectra (signals of CH_2 and CHD groups are shown as white or black filled lines, respectively).

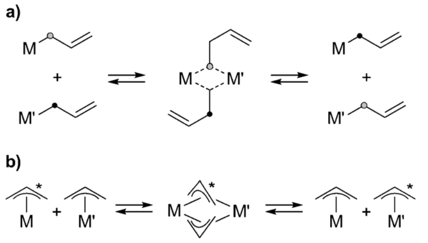
3.3. Dynamics and Mechanisms of Allyl Exchange

The first suggestion to explain the fluxional behavior of allyl ligands mechanistically dates back more than 50 years, and was made on the basis of the NMR spectra of allylpalladium chloride compounds.[32] It involves intramolecular π-σ-π (or σ-π-σ) rearrangements of the allyl ligand, and is thus only plausible for compounds that facilitate π-type metal–allyl interactions (Scheme 3 a).[33] Free rotation around the C–C single bond in the σ form is the key feature of this mechanism. The isolation of η^1- and η^3-allyl complexes of the alkali/alkaline earth metals Li,[40,41] Mg,[51,56] and Ca[57a,59,60] has been reported, and corroborates this mechanism for such compounds. A second mechanism has been suggested, as there are allyl compounds of main group metals that seem not to favor π-type metal–allyl interactions (Scheme 3 b).[65,68] Consequently, this bimolecular mechanism involves only σ-type metal–allyl interactions, and a transition state featuring a μ_2-η^1:η^1 coordination mode has been suggested (see Scheme 2, **C**). Determination of the molecularity of the exchange reaction is required to differentiate experimentally between these two mechanisms.[68] In addition, activation parameters of the allyl-exchange reactions have been determined by means of variable-temperature (VT) NMR spectroscopic measurements in combination with line-shape analysis. Low values for the activation entropy $\Delta S^{\neq}$ indicate an ordered transition state, but the interpretation in terms of the molecularity of the allyl exchange is controversial.[80–82,109] A third mechanism accounting for allyl exchange is the thermally induced suprafacial [1,3]-sigmatropic rearrangement (Scheme 3 c). It is relevant for semimetals and goes along with inversion of the stereocenter at M (if applicable). This has been investigated in detail only for allylsilicon compounds (see Section 4.5).[97,98]



Scheme 3. Mechanisms accounting for the fluxional behavior of allyl ligands ("structure-altering" allyl exchange): a) unimolecular mechanism involving π-type metal–allyl interactions; b) bimolecular mechanism featuring exclusively σ-type metal–allyl interactions; c) [1,3] sigmatropic rearrangement (relevant for semimetals).

The processes described above can be termed "structure altering", since they occur with alteration of the chemical environment of two or four methylene protons. This characteristic makes these processes observable by analytical techniques such as NMR spectroscopy. In addition, there are also "structure-preserving" allyl-exchange processes. These cause exchange of allyl ligands between metal centers, but the protons of the allyl ligands remain in their original chemical environments. Thus, such phenomena cannot be observed by NMR spectroscopy. Two fundamentally different mechanisms are possible for the "structure-preserving" allyl exchange. The process can take place via a transition state featuring two-electron three-center bonds (or related bonding situations) with σ-type metal–allyl interactions (Scheme 4 a).[34] Alternatively, allyl ligands could be exchanged via a transition state with a bridging μ_2-η^3:η^3 coordination of the allyl ligand (Scheme 4 b).[35] This includes a switch of the allyl face that interacts with a metal center: prior to exchange, the allyl ligand coordinates to the metal center M with one face, and after exchange has taken place it coordinates to M′ with the other face. Such exchange mechanisms have never been reported for allylmetal compounds. However, evidence for their viability can be deduced from solid-state structures of a small cluster featuring allyl ligands in a bridging μ_3-η^1:η^1:η^1 coordination[55b] and a cyclic tetramer with allyl ligands coordinating in a μ_2-η^3:η^3 fashion.[42] It is highly possible, although not proven, that such processes take place in solution in addition to the "structure-altering" allyl exchanges.



Scheme 4. Schematic representation of a plausible σ-type (a)[34] and π-type (b)[35] mechanism for "structure-preserving" allyl exchange.

4. Trends in the Periodic System of the Elements

For a generalization of trends in the periodic system of the elements (PSE) regarding allylmetal complexes it is helpful to distinguish between compounds featuring π- or σ-bonded allyl ligands (Figure 3). On the one hand, known compounds of Group 1 and heavier Group 2 elements mostly favor π-bonded $(C_3H_5)^-$ groups. This tendency increases as the ionic character of the M–C interaction increases, that is, it increases from the top to the bottom and from right to left in Groups 1 and 2 of the PSE. As a consequence, the rates of allyl exchange according to a π-σ-π rearrangement (Scheme 3 a) follow the opposite trend. On the other hand, compounds of Groups 12–16 (semi)metals favor σ-type metal–allyl interactions because of the more covalent character of the M–C bond. Here, the rates of allyl exchange mostly increase from top to bottom in the PSE as a result of the decreasing M–C bond strength.[36]

Recently, there has been considerable progress in the preparation and characterization of homoleptic allyl complexes and their solvent adducts. Compounds that have not been isolated to date are associated with problems of

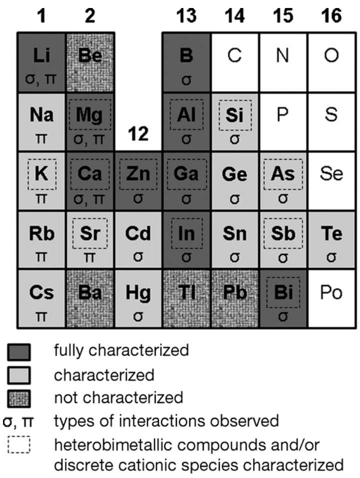
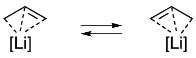


Figure 3. Section of the periodic table of the (semi)metals considered in this Review. This Figure exclusively refers to homoleptic allyl compounds and their solvent adducts.

solubility (Ba), stability (Pb), toxicity (Be, Tl, Pb), or combinations thereof.

4.1. Group 1 (Li–Cs)



Scheme 5. Schematic representation of unsymmetric η^3 bonding in $[\{Li(C_3H_5)(thf)_2\}_2]$ in THF solution.

Investigations of allyl compounds of Group 1 elements represent a detailed case study of allyl bonding in solution.[37] Saunders' isotopic perturbation method in combination with VT NMR experiments, cryoscopic measurements, and DFT calculations showed that allyllithium is a dimer in THF solution, with the allyl ligand showing unsymmetric η^3 bonding and partially localized C–C bonds (Scheme 5).[37] This bonding situation in solution is unique for allyl compounds of lithium. Higher homologues of the alkali metals show symmetrical η^3 bonding in solution.[37a,c,d] In THF, the rotational barrier of the allyl ligand (see Scheme 3a) increases as the atomic number of the alkali metal increases.[37d,38] As expected, the ionic character of the metal–allyl interactions shows the same trend.[38b] Although allyl compounds of the alkali metals have been isolated and analyzed in detail by NMR spectroscopy,[39] only lithium compounds have been fully characterized. In the solid state, the allyl ligands in $[Li(C_3H_5)(L)]$ show μ_2-η^1:η^1 (L = tmeda)[40] or η^3 coordination modes (L = pmdta)[41] depending on the denticity of the neutral donor ligand. Purely π-type metal–allyl interactions (η^3 or μ_2-η^3:η^3) in the solid state can be anticipated for the higher homologues Na–Cs, as observed for the analogous species bearing bis(silylated) allyl ligands.[42–45] Allyl compounds of the alkali metals can be obtained by deprotonation of propene because of the high Brønsted basicity of the relevant organometallic precursors.[38a,39b,46] In the case of a propene derivative, CH_2CHCH_2-$\{SiMe_2(CH_2NC_5H_{10})\}$, even the dilithiated species is accessible.[47] Metal/metal exchange and transmetalation are other reliable routes to allyl species of Group 1 elements, but require the use of toxic $[Sn(C_3H_5)_4]$ or $[Hg(C_3H_5)_2]$. Halogen/metal exchange and direct synthesis are hampered by Wurtz coupling. The high ionic character of Group 1 organometallic compounds makes them extremely potent allyltransfer reagents,[3,15d] which has frequently also been exploited for the preparation of heterobimetallic compounds (see Sections 4.2–4.4). However, they are usually substituted by the more-easily accessible Grignard reagent when possible (cf. Section 4.2).

4.2. Group 2 (Be–Ba)

One attempt aiming at the synthesis of bis(allyl)beryllium has been reported, but the pure compound has never been isolated.[48] DFT calculations predict a small energy difference between η^1 and η^3 bonding for $[Be(C_3H_5)X]$ (X = H, Br) in the absence of additional donor ligands. The diethyl ether adduct of the related bis(trimethylsilyl)allyl compound, $[Be(Me_3SiCH(CH)CHSiMe_3)_2(Et_2O)]$, has been fully characterized and shows η^1 coordination of the allyl ligands.[49]

The higher homologue, bis(allyl)magnesium, was synthesized early on,[50] but its structure still remains elusive. A Lewis base adduct of this compound has recently been analyzed by single-crystal X-ray diffraction, and revealed the expected η^1 coordination mode of the allyl ligands (Figure 4a).[51,52] In general, σ-type bonding of the allyl ligand is widely preferred for magnesium compounds in solution (with

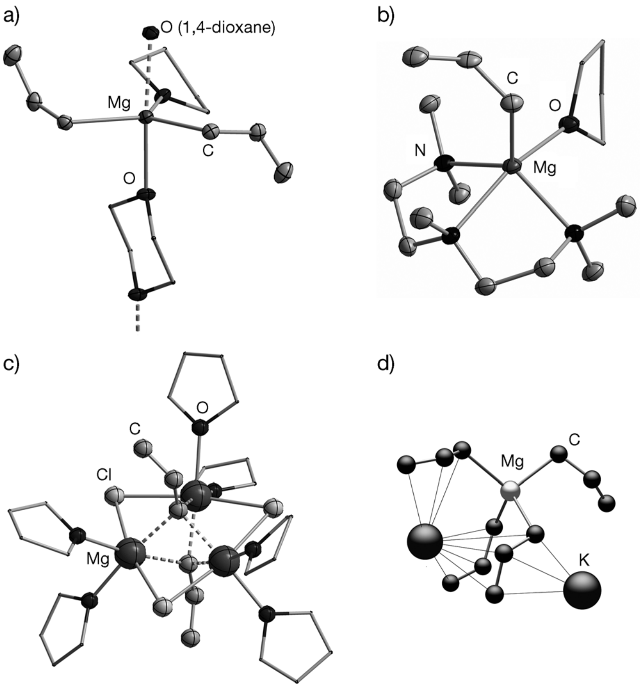


Figure 4. Molecular structures of a) $[Mg(\eta^1\text{-}C_3H_5)_2(thf)(\mu\text{-}1,4\text{-dioxane})]$[51] b) cationic part of $[Mg(\eta^1\text{-}C_3H_5)(thf)(pmdta)]\,[B(C_6F_5)_4]$[51] c) cationic cluster $[\{Mg(\mu\text{-}Cl)(thf)_2\}_3(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}C_3H_5)_2]^+$[55b] d) fragment $[K_2(Mg(C_3H_5)_4]$ featuring a μ_3-η^1:η^3:η^3-allyl coordination, which is part of $[K_2Mg(C_3H_5)_4(thf)_n]$ (isolated: $n = 2$; calculated: $n = 3$).[51] Ellipsoids set at 50% probability (a,b); stick-and-ball model (c).

fluxional behavior being observed even at low temperature) and in the solid state.[37a,53,54] When heteroleptic compounds are included, allylmagnesium species cover a broad range of σ-type metal–allyl interactions, including examples of μ_2-η^1:η^1 and μ_3-η^1:η^1:η^1 bonding (Figure 4c).[55] In the absence of donor solvents, however, π-type coordination is also possible, as shown experimentally for the dimer $[\{Mg(Me_3SiCH(CH)CHSiMe_3)_2\}_2]$ (μ_2-η^1:η^3 coordination) and by DFT calculations for the parent compound $[Mg(C_3H_5)_2]$.[56] More recent developments also consider the rational synthesis of formally charged allylmagnesium compounds, that is cationic (Figure 4b), anionic, and dianionic species. In addition to new reactivity (see Sections 5.2 and 5.4), these complexes also revealed a novel coordination mode of the allyl ligand in the solid state, namely μ_3-η^1:η^3:η^3 bonding (Figure 4d; see Scheme 2, **H**).[51] Overall, magnesium complexes show the greatest structural diversity of the allyl compounds of all the main group elements. This is probably due to the unique balance between covalent and ionic bonding combined with the fact that compounds with charges between +1 and −2 at the magnesium center as well as cluster compounds are accessible.

Allyl compounds of heavier alkaline earth metals have only recently been investigated in more detail. In contrast to its lighter magnesium homologue, bis(allyl)calcium shows η^3 coordination of the allyl ligands in the presence of donor ligands in solution and in the solid state (Figure 5a).[57] In allylcalcium compounds with unsymmetrically substituted allyl ligands (butenyl or hexenyl), unsymmetric η^3 coordination is observed in the solid state.[58] ^{13}C NMR spectroscopic data for these compounds hint at a similar bonding situation in solution. A σ-type coordination of the allyl ligand to calcium is possible with [18]crown-6 ([18]c-6) bound to the metal center. This has been demonstrated for thermally unstable $[Ca(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)([18]c\text{-}6)]$[59] and for monocationic $[Ca(C_3H_5)([18]c\text{-}6)][Zn(C_3H_5)_3]$, which forms a linear coordination polymer in the solid state with the allyl ligand in a bridging μ_2-η^1:η^1 coordination mode (Figure 5b,c).[60] The former species is the only allyl compound of a main group metal that shows two fundamentally different coordination modes of the allyl ligand at one metal center.

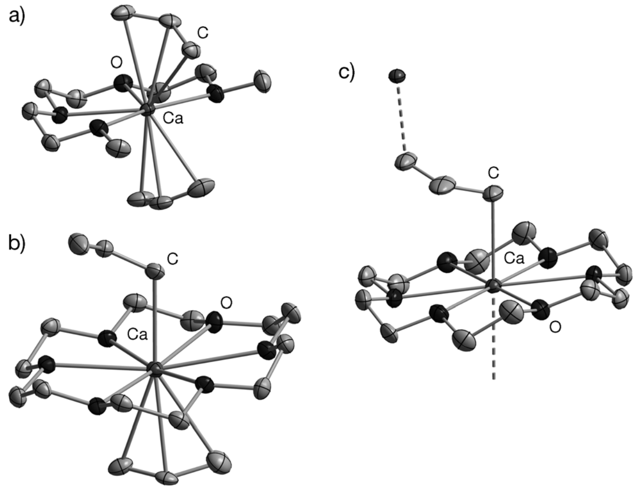


Figure 5. Molecular structures of a) $[Ca(\eta^3\text{-}C_3H_5)_2(\text{triglyme})]$[57a] b) $[Ca(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)([18]c\text{-}6)]$[59] c) cationic part of $[Ca(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}C_3H_5)([18]c\text{-}6)][Zn(\eta^1\text{-}C_3H_5)_3]$.[60] Ellipsoids set at 50% probability.

The isolation of bis(allyl)strontium and bis(allyl)barium has been reported in a patent, but these compounds were only analyzed spectroscopically.[57b,c] Recent reinvestigation of the preparation of $[Sr(C_3H_5)_2]$ by a different synthetic route, namely the reaction of $[K(C_3H_5)]$ with different strontium precursors, led to the ate complex $[KSr(C_3H_5)_3]$ regardless of the stoichiometry.[61] The THF adduct $[KSr(C_3H_5)_3(thf)_3]$ forms a coordination polymer in the solid state, with the allyl ligands showing μ_2-η^3:η^3 coordination modes. Comparable observations have been made in the case of the related barium compound $[KBa_2(Me_3SiCH(CH)CHSiMe_3)_5(thf)]$.[62]

As a consequence of their broad spectrum of M−C interactions ranging from mainly covalent to highly ionic, allyl compounds of Group 2 metals show a delicate balance between σ- and π-type coordination of the allyl ligand. Allyl bonding can further be influenced by the presence and nature of donor ligands and the charge of the metal center. Although homoleptic allyl compounds of beryllium and barium have not been fully characterized, yet, the trend shows that σ bonding is preferred for the lighter alkaline earth elements and π bonding is preferred for the higher homologues.

4.3. Group 12 (Zn–Hg)

Bis(allyl)zinc[63] is a valuable alternative to allyl-Grignard reagents in organic synthesis, as it shows distinct selectivities in some cases.[63b,64] The allyl ligands of the sublimable compound were believed to show η^3 bonding in the solid state, until recent single-crystal X-ray analysis revealed a μ_2-η^1:η^1 coordination mode (Figure 6a).[65] This suggests that π-type Zn–allyl interactions are generally not favorable. For the closely related compound bis(methallyl)zinc, a distorted μ_2-η^1:η^2 coordination has been reported and discussed in the context of an intermediate μ_2-η^1:η^1 coordination (Figure 6b).[66] σ-Type coordination modes in bis(allyl)zinc have also been predicted in the gas phase by ab initio calculations.[65] In solution, the allyl ligand shows fluxional behavior at ambient temperature, but an η^1 coordination mode can be frozen out at low temperatures.[67,68,150] σ-Type zinc–allyl

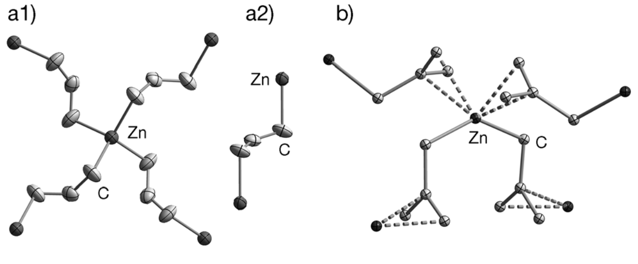


Figure 6. Sections of the solid-state structures of a1) $[Zn(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}C_3H_5)_2]$ with a view of *trans*-μ_2-η^1:η^1-allyl coordination (a2)[65] and b) $[Zn(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}CH_2CMeCH_2)_2]$.[66] Ellipsoids set at 50% probability.

interactions are also found for monocationic[69] and monoanionic[60,150] allylzinc compounds in the solid state. In solution, the allyl-exchange rate follows the order cationic < neutral < anionic. In the case of tris(allyl)zincates, the dynamic behavior of the allyl ligand cannot be frozen out at low temperatures.[60,150]

The allyl-exchange mechanism for bis(allyl)zinc has been investigated in some detail. It was shown to follow second-order kinetics, which were associated with an intermolecular allyl-exchange mechanism (see Scheme 3b).[68] This interpretation is corroborated by the reluctance of allylzinc compounds to undergo π-type metal–allyl interactions.[65] Bis(allyl)zinc is thermally unstable in solution. The main degradation pathway at elevated temperatures of ≥ 100 °C is radical coupling of allyl ligands with concomitant formation of Zn^0.[70,71] At lower temperatures of 30 °C to 50 °C, bis(allyl)zinc undergoes an oligomerization in a metallo-ene reaction.[63b] This type of reaction was studied in detail for the allylzinc monocation[69] (see Section 5.3.2). In general, bis(allyl)zinc is more reactive than di(alkyl)zinc reagents, as evidenced by the clean and rapid formation of vinylacetic acid from the reaction of bis(allyl)zinc with CO_2 followed by aqueous workup.[63a]

Bis(allyl)cadmium is a pyrophoric solid that decomposes above 0 °C with formation of Cd^0, and is light-sensitive even at temperatures below 0 °C.[72] It is monomeric in benzene solution and the allyl ligand shows dynamic behavior in THF solution at temperatures as low as −100 °C. It is expected, although not proven, that bis(allyl)cadmium would show a bonding situation similar to its lighter zinc congener.[72] Bis(allyl)cadmium shows a higher reactivity than other di(organo)cadmium compounds. It consumes CO_2 at −20 °C in THF solution to give the expected vinylacetic acid after aqueous workup. The use of bis(allyl)cadmium in organic and organometallic chemistry is extremely limited due to its toxicity and the difficulties in handling the pure compound.[73]

Bis(allyl)mercury is a distillable liquid.[74] Its allyl ligands are bonded at the metal center in an η^1 fashion in the pure compound and in solution.[75] Fluxional behavior was not observed in THF solution up to 108 °C. NMR spectroscopic studies suggested that allyl exchange mainly proceeds intermolecularly. Although the compound can be expected to be light-sensitive,[72] no comment concerning this characteristic is found in the literature.[74,75] Bis(allyl)mercury is, in principal, a reliable allyl-transfer reagent for the synthesis of Group 1 and 2 allyl compounds in transmetalation reactions,[37d,57b,c] but its use is limited due to the high toxicity of organomercury species.

4.4. Group 13 (B–Tl)

Of the allyl complexes of Group 13 elements, only tris(allyl)borane has been isolated as a homoleptic compound. In the case of the aluminum congener, such attempts were shown to be hampered by organometallic oligomerization, that is, carbalumination of the C=C bond of an allyl ligand by an allylaluminum species.[48] Similar processes are expected to also be relevant for Lewis base adducts of the higher homologues. This is corroborated by the observation that $[Ga(C_3H_5)_3(thf)]$ has a much higher stability in the donor solvent THF compared to benzene, thus hinting at intermolecular degradation pathways.[76] For compounds $[M(C_3H_5)_3(L)]$ ($M = B$, Al, Ga, In), the thermal stability decreases in the order $B \approx Al > Ga > In$. The tendency of the allyl ligand to show fluxional behavior increases in the order $B \approx Al < Ga < In$.[77] Allyl compounds of Group 13 elements show a higher reactivity than other tris(organo)species of the triels in addition reactions with organic substrates (see Sections 5.1 and 5.2).

Tris(allyl)borane is an air-sensitive, distillable colorless liquid (b.p. = 62–65 °C at $p = 20$ mbar).[78] Gas-phase electron diffraction experiments in combination with quantum-chemical calculations revealed the expected η^1 coordination mode of the allyl ligand and a slight pyramidalization of the boron atom.[79] In the liquid phase, the allyl ligands are bonded at the metal center in an η^1 fashion, as evident from NMR spectroscopic analysis at −40 °C, but show fluxional behavior at higher temperatures.[80] Activation parameters of the exchange process have been determined ($\Delta G^{\neq,298} = (61.65 \pm 3.08)$ kcal mol^{-1}).[81] An intramolecular allyl-exchange mechanism has been suggested. However, the negative activation entropy of this process[81] and the fact that the exchange rate decreases upon dilution in the case of $[B(C_3H_5)_3(Py)]$[82] favor an intermolecular mechanism.

Stable Lewis base adducts of tris(allyl)aluminum, $[Al(C_3H_5)_3(L)]$ (L = thf, $OPPh_3$, etc.), have recently been isolated and fully characterized along with their monocationic and monoanionic derivatives.[83] The allyl ligands in all of these species show η^1 bonding in solution (without fluxional behavior being observed at ambient temperature) and in the solid state. The neutral donor ligands in these species are labile in solution. Whereas allyl compounds of Group 13 elements are usually prepared from activated olefins (e.g. allyl halides or other allylmetal compounds), the generation of an allylaluminum species from a non-activated olefin has been demonstrated by using the frustrated Lewis pair (FLP) approach. Deprotonation of isobutylene with a P/Al-based FLP led to the ion pair $[P(t\text{Bu})_3H][(C_6F_5)_3Al(CH_2(CCH_3)CH_2)Al(C_6F_5)_3]$, which features a methallyl ligand in a bridging μ_2-η^1:η^1 coordination mode in solution and in the solid state.[84]

The investigation of Lewis base adducts of tris(allyl)gallium revealed differences in the thermostability and allyl-exchange rates compared to the aluminum congener (see above).[76] Both of these characteristics are strongly solvent dependent. The gallium–allyl interactions in the neutral compound as well as in cationic and anionic derivatives are of σ type in solution and in the solid state. For the potassium tetrakis(allyl)gallate, a bridging μ_2-η^1:η^2 coordination mode of an allyl group revealed the non-innocence of the counterion in the solid-state coordination chemistry with respect to the $(C_3H_5)^-$ group (Figure 7). This characteristic was confirmed for the reactivity of this gallate in solution (see Section 5.1).

Indium is the heaviest Group 13 element for which Lewis base adducts of tris(allyl) compounds have been isolated and fully characterized.[85] The allyl ligands show fluxional behav-

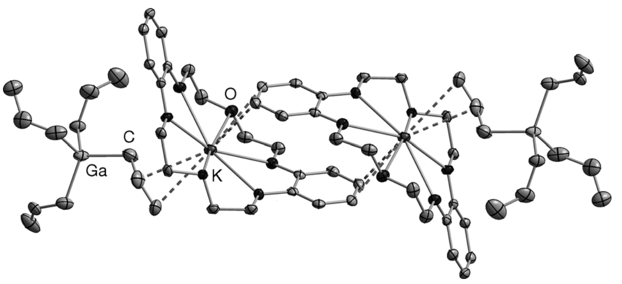


Figure 7. Dimeric arrangement of ([K(dibenzo[18]c-6)][Ga(C_3H_5)$_4$])$_2$[76] featuring a μ_2-η^1:η^2-allyl ligand bridging Ga and K. Ellipsoids set at 50% probability.

ior in solution at ambient temperature. The η^1 coordination mode is revealed at low temperature in solution and in the solid state. Cationic and anionic derivates of tris(allyl)indium have also been reported.[85,86] Tris(methallyl)indium can even be prepared free of additional donor ligands. One of the methallyl ligands in this compound shows a bridging μ_2-η^1:η^1 coordination mode in the solid state which is not preserved in solution. Allylindium(I) species have been discussed controversially with respect to their role in indium-mediated allylations.[87] However, such compounds have never been isolated.

Homoleptic allyl compounds of thallium(I) or -(III) have not been reported to date. This is somewhat surprising, considering that the easily accessible cyclopentadienyl compound [Tl(C_5H_5)] is a reliable cyclopentadienyl-transfer reagent.[88] Methyl(allyl)thallium compounds such as [Tl(CH_3)(C_3H_5)(Cl)] have been prepared and show an η^1-bonded allyl ligand in solution.[89]

4.5. Group 14 (Si–Pb)

Homoleptic allyl compounds of silicon,[90] germanium,[91] and tin[92] are distillable liquids. They show only modest air-sensitivity,[93] which is advantageous for their application in organic synthesis. In all three cases, the allyl ligands coordinate to the central atom in an η^1 fashion in the pure compounds and in solution.[93–95] The corresponding ^{1}H NMR spectra are invariant from −60 °C to 150 °C. Mass spectrometric studies revealed distinct fragmentation patterns for [M(C_3H_5)$_4$] (M = Si, Ge, Sn), which were explained by the stability of the M−C bond decreasing in the order Si > Ge > Sn.[96] The inversed trend (Si < Ge < Sn) can be expected for the tendency of the above-mentioned compounds to undergo allyl-exchange reactions. For silanes, allyl exchange was shown to proceed in a unimolecular [1,3]-sigmatropic rearrangement only at high temperatures of 275 °C to 500 °C (depending on the conditions; see Scheme 3 c).[97] The reaction takes place with inversion of the configuration at the silicon atom, as shown by the use of optically active allylsilanes.[98] In contrast, allyl exchange in stannanes even proceeds below room temperature, as demonstrated by the isomerization of trimethyl(butenyl)tin compounds.[99] Lewis bases or acids accelerate these rearrangements.[99,100] Single-crystal X-ray diffraction data on tetrakis(allyl) compounds of Group 14 (semi)metals is only available for Si in heterobimetallic [Cu_5Cl_5(C_3H_5)$_4$Si], which features allyl ligands in μ_2-η^1:η^2 coordination modes (Figure 8).[101]

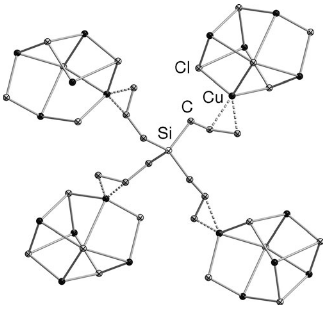


Figure 8. Section of the solid-state structure of [Cu_5Cl_5(C_3H_5)$_4$Si], which forms a three-dimensional coordination polymer in the solid state.[101] Ellipsoids set at 50% probability.

Allyllead compounds are significantly less stable than their lighter homologues. This has so far prevented the isolation of tetrakis(allyl)lead. Decomposition pathways presumably include radical coupling of allyl ligands. This has been observed for [Pb(C_6H_5)$_2$(C_3H_5)$_2$], which disproportionates into Pb^0, 1,5-hexadiene, and [Pb(C_6H_5)$_4$].[102] Only monoallyl derivatives such as [Pb(C_6H_5)$_3$(C_3H_5)] have been reported as isolable compounds.[103]

In Group 14 compounds of the general formula [M(C_3H_5)X_3] (M = Si-Pb, X = H, Me, C_3H_5, etc.), experimental and/or theoretical evidence has been found for a weakening of the C=C bond of the allyl ligand compared to that in vinyl derivatives.[95,104] This has been interpreted in terms of a so called β effect, that is interactions between σ_{M-X} and $(\pi_{C=C})^*$ orbitals.[104,105]

4.6. Group 15 (As–Bi)

The homoleptic allyl compounds of Group 15 with the general formula [M(C_3H_5)$_3$] (M = As,[106] Sb,[107] Bi)[108,109,110c] are distillable liquids used for metalorganic chemical vapor deposition and related processes (see Section 5.5).[110] The main decomposition pathway is the coupling of allyl ligands to give 1,5-hexadiene with concomitant formation of M^0.[109,110b] The allyl ligands show an η^1 bonding mode in the liquid phase[94,106,109] and a weak β effect has been suggested for derivatives of As and Sb (see Section 4.5).[111] A dynamic behavior of the allyl ligands has not been reported for the homoleptic compounds, although high-temperature scenarios have not been investigated. However, rearrangement reactions have been observed in the case of butenyl and prenyl dihaloarsines and stibines. Such compounds with the Group 15 fragment at the less-substituted terminus of the allylic system are the thermodynamically more-stable isomers.[111] In halogenated or cationic derivatives of allyl bismuth, [Bi(C_3H_5)$_2$(I)] and [Bi(C_3H_5)$_2$(thf)$_2$]$^+$, the allyl ligands show dynamic behavior in solution.[109] In the latter case, an intramolecular mechanism has been suggested on the basis of the activation entropy being significantly higher than in intermolecular allyl-exchange processes. In the solid state, η^1 coordination of the allyl ligands has been revealed for heterobimetallic $[\mathrm{PdX_2\{As(C_3H_5)_3\}_2}]$ (X = Cl, Br),[112] homoleptic $[\mathrm{Bi(CH_2CMeCH_2)_3}]$,[109] and cationic $[\mathrm{Bi(C_3H_5)_2(thf)_2}]^{+}$[109] by single-crystal X-ray analyses (Figure 9). In none of these cases are intra- or intermolecular interactions of the C=C bond of the allyl ligands with a metal center observed.[113]

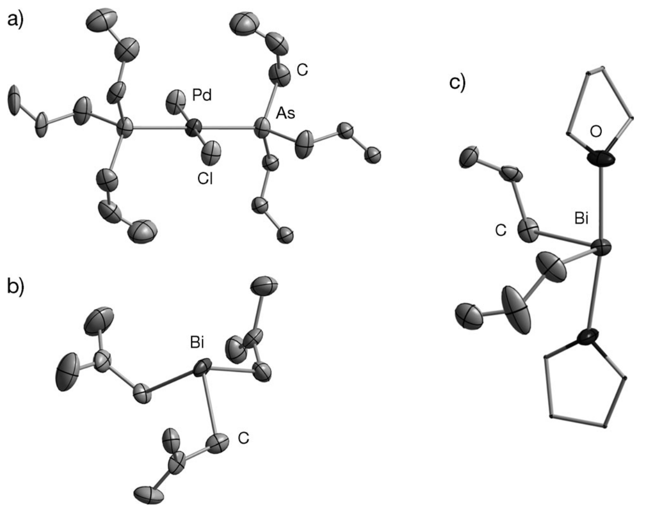


Figure 9. Molecular structures of a) $[\mathrm{PdCl_2\{As(C_3H_5)_3\}_2}]$,[112] b) $[\mathrm{Bi(CH_2CMeCH_2)_3}]$[109] and c) cationic part of $[\mathrm{Bi(C_3H_5)_2(thf)_2}][\mathrm{B(C_6H_3Cl_2)_4}]$.[109] Ellipsoids set at 50% probability.

4.7. Group 16 (Te)

Bis(allyl)tellurium(II)[114] is a light-sensitive, distillable liquid with η^1-bound allyl ligands, and is used for metalorganic chemical vapor deposition (see Section 5.5).[115] Fluxional behavior of the allyl ligand was not observed and no indications for allyl exchange at higher temperatures was found in studies on bis(butenyl)tellurium.[116] Thermal decomposition of bis(allyl)tellurium proceeds through a radical coupling of allyl ligands to give Te^0 and 1,5-hexadiene.[114,116] The homoleptic compound with Te in the oxidation state of +IV, tetrakis(allyl)tellurium, is unstable with respect to disproportionation into $[\mathrm{Te(C_3H_5)_2}]$, 1,5-hexadiene, and Te^0.[117] However, heteroleptic compounds such as $[\mathrm{Te(C_3H_5)_2(X)_2}]$ (X = Cl, Br) and $[\mathrm{Te(C_3H_5)(Ph)_2}][\mathrm{BF_4}]$ are isolable.[118] The allyl ligand adopts an η^1 coordination mode in such compounds in the solid state, as shown by single-crystal X-ray analysis.[118a,b]

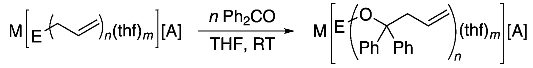
5. Allyl-Specific Reactivities

A unique and well-known property of allylmetal compounds is their ability to react with electrophiles at both C termini. Reaction at the γ terminus allows simultaneous Lewis acid activation of the substrate in a cyclic, six-membered transition state.[119] For some substrates, this leads to low-energy reaction pathways that are accessible only for allyl compounds. In this section, such reactions are presented along with new concepts in allylation reactions.[120] Furthermore, allyl compounds as reagents in metalorganic chemical vapor deposition and polymer chemistry are briefly discussed.

5.1. Allylation of Aldehydes, Ketones, and Imines

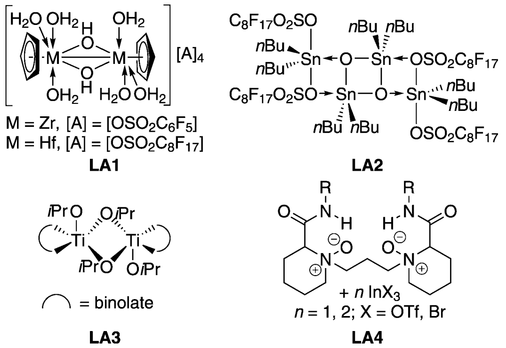
The allylations of aldehydes, ketones, and imines are of great importance in organic synthesis.[4a,6a,7,14a,b,15a–f,i,20] The influence of the charge at the metal center on reactivity was investigated for a series of well-defined cationic, neutral, and anionic allylaluminum and -gallium compounds.[76,83a] The rates of reaction in the allylation of benzophenone follow the order cationic ≈ neutral ≫ anionic, thus revealing the importance of Lewis acid activation and/or precoordination of the substrate (Table 1, entries 1–6). The neutral compound proved to be most sufficient for this type of allylation reaction in both cases (Table 1, entries 2 and 5). In the case of the anionic gallium compounds, counterion effects were shown to be important for the number of allyl substituents that can be transferred ($\mathrm{K}^+ < [\mathrm{PPh_4}]^+$; Table 1, entries 6 and 7).[76]

Table 1: Allylation of benzophenone with well-defined cationic, neutral, and anionic allyl compounds of aluminum and gallium.



Entry	M	E	*n*	*m*	A	*t* [h]	Conv. [%]	Sel. [%]
1	–	Al	2	2	$\mathrm{BPh_4}$	0.17	> 99	90
2	–	Al	3	1	–	0.17	> 99	> 99
3	K	Al	4	0	–	9	> 99	> 99
4	–	Ga	2	2	$\mathrm{B(C_6F_5)_4}$	0.17	50	> 99
5	–	Ga	3	1	–	0.17	> 99	> 99
6	K	Ga	4	0	–	53	50	> 99
7	$\mathrm{PPh_4}$	Ga	4	0	–	53	75	> 99

$[\mathrm{Sn(C_3H_5)_4}]$ is highly toxic, but is still used for the allylation of Lewis acid activated carbonyl compounds, as it is commercially available and can be handled under atmospheric conditions. Recent developments include the exploitation of new cationic Lewis acids for these reactions, such as Group 4 metallocene derivatives $[\mathrm{M(\eta^5\text{-}C_5H_5)_2(H_2O)_{\mathit{n}}}][\mathrm{OSO_2C_8F_{17}}]_2\cdot(\mathrm{THF})_2$ (M = Ti, Zr; $n = 2, 3$)[121] and $[(\mathrm{M(\eta^5\text{-}C_5H_5)(H_2O)_3})_2(\mu_2\text{-}\mathrm{OH})_2][\mathrm{A}]_4\cdot(\mathrm{L})_6$ (**LA1**; Scheme 6; [A] = counterion; L = solvent molecule),[122] stannoxane $[(\mathrm{PfOBu_2SnOS}n\mathrm{Bu_2OPf})_2]\cdot(\mathrm{H_2O})_n$ (**LA2**; Scheme 6; Pf = $\mathrm{SO_2C_8F_{17}}$),[123] and a chelated di(aryl)bismuth species $[\mathrm{C_6H_{11}N(CH_2C_6H_4)_2Bi}][\mathrm{BF_4}]$.[124] Some known Lewis acids have now also been investigated as catalysts in the allylation of carbonyl compounds with $[\mathrm{Sn(C_3H_5)_4}]$. These approaches mostly focus on factors such as atom economy,[125] reducing the amount of or avoiding organic solvents,[126–132] catalyst immobilization,[128,129,131] catalyst reusability,[121,122,126,128,130,131] reducing reaction times by applying microwave conditions,[131] and new concepts in one-pot reactions.[133] $[\mathrm{Nb_2O_5(H_2O)_{\mathit{n}}}]$,[129] $[(\mathrm{NH_4})_2\mathrm{Ce(NO_3)_6}]$,[134] $\mathrm{Sc(OTf)_3}$ (Tf = triflate),[125] [GdCl3-



Scheme 6. Lewis acidic catalysts employed for the allylation of carbonyl compounds with $[Sn(C_3H_5)_4]$.

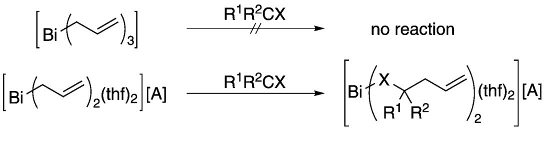
$(H_2O)_6]$,[135] and mesoporous silica-supported Lewis acids[131] have been studied in these contexts.

An ongoing challenge in the allylation of carbonyl compounds with $[Sn(C_3H_5)_4]$ is the development of enantioselective reactions. Low levels of chiral induction can be achieved by the addition of one equivalent of the amino acids L-proline or L-aspartic acid.[136] Two general catalyst systems based on a titanium binolate (**LA3**; Scheme 6)[137–139] and on the combination of an indium salt with one or two equivalents of *N,N'*-dioxides (e.g. **LA4**; Scheme 6)[140] have been reported. The substrate scope includes a broad range of ketones (with cyclic enones) in the first case,[137,139] and ketones,[140a] α-ketoesters,[140b] as well as α-ketophosphonates[140c] in the second case. The first bismuth-catalyzed enantioselective allylation of aldehydes was achieved by using $[Bi(OTf)_3]$ and Trost's prophenol as a chiral ligand under basic conditions.[141] An undefined cationic or dicationic bismuth compound was suggested as the catalytically active species.

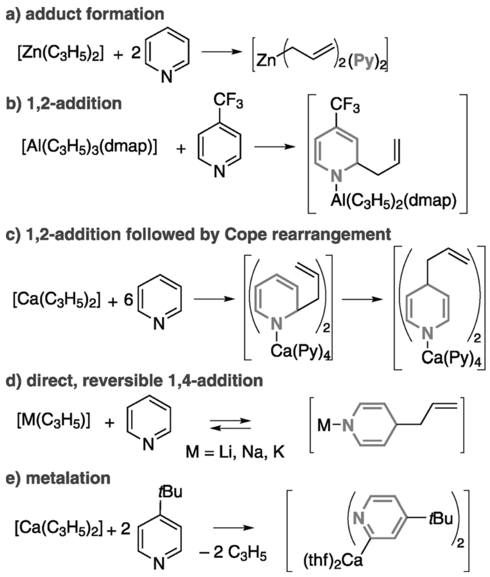
An influence of the charge at the metal center on the reactivity was found for simple allylbismuth compounds in the absence of any other co-reagents. Whereas neutral tris(allyl)bismuth fails to react with benzaldehyde without additional Lewis acids, the structurally defined bis(allyl)bismuth cation readily allylates aldehydes, ketones, and imines under mild conditions with a high functional group tolerance (Scheme 7).[109]

5.2. Dearomatization of N-Heteroaromatic Compounds

Dihydropyridines (DHPs) are pharmacologically active compounds[142] and can be synthesized by using stepwise procedures such as the Hantzsch DHP synthesis.[143] Alternatively, N-metalated DHPs are accessible in one-pot reactions from the dearomatization of pyridines by the addition of an organometallic compound to pyridines. Five types of reactions can be distinguished in reactions between allylmetal compounds and pyridine. Some of them can also take place consecutively. Coordination of pyridine at the metal center is considered as the initiating step (Scheme 8a). Subsequent 1,2-carbometalation of pyridine (a metala-Claisen rearrangement) gives an N-metalated 1,2-DHP (Scheme 8b). A subsequent Cope rearrangement leads to the N-metalated 1,4-DHP (Scheme 8c). Direct 1,4-addition to pyridine is also possible (Scheme 8d). Metalation of the pyridine core at the 2-position was only reported for pyridine derivatives (Scheme 8e). Some of the above-mentioned processes can be reversible (e.g. Scheme 8d). The nature of the metal center plays a crucial role in these reactions, but the substitution pattern at the pyridine core also influences the outcome of these reactions.



Scheme 7. Influence of charge on the reactivity in the allylation of carbonyl and imine substrates with bismuth reagents; $[A]=[B(C_6H_3Cl_2)_4]$; $R^1=$ aryl, $R^2=$ H, aryl; X = O, NTosyl.



Scheme 8. Five different types of reactivity between main group allyl compounds and pyridine (derivatives); DMAP = *N,N*-dimethylaminopyridine.

Adduct formation or ligand-exchange reactions between pyridine and allyl compounds of main group metals without subsequent carbometalation have been reported for $[Zn(C_3H_5)_2]$,[144] $[B(C_3H_5)_3]$,[82] and $[Ga(C_3H_5)_3(thf)]$[76] (Scheme 8a). In the case of $[Al(C_3H_5)_3(thf)]$, ligand substitution of THF for pyridine proceeds readily, but carbometalation of the coordinating pyridine does not take place in the absence of coordinating solvents.[83b]

For allyl complexes of Group 13 elements, 1,2-additions to pyridine without subsequent Cope rearrangements can be observed. In such reactions, the allyl compounds are significantly more reactive than the corresponding alkyl compounds.[76,83b] In the case of $[B(C_3H_5)_3]$, the presence of protic solvents is needed to ensure an addition reaction. Bis(allylation) is the favored reaction pathway under these conditions to give a 2,6-bis(allyl)tetrahydropyridine as the major product.[145,146] A reversible 1,2-carbometalation of 3-bromopyridine has been reported for the closely related tris(methallyl)boron.[147] An aprotic polar solvent is needed to trigger the 1,2-addition reaction in the case of $[Al(C_3H_5)_3(thf)]$. The carbometalation proceeds more readily with electron-poor pyridines and is inhibited in the case of electron-rich pyridines.[83b] The neutral ligand at the aluminum center can be utilized for fine-tuning of the reaction conditions (Scheme 8b). The higher homologue $[Ga(C_3H_5)_3(thf)]$ does not carbometalate pyridine, but the activated N-heteroaromatic quinoline.[76] The gallate $K[Ga(C_3H_5)_4]$ undergoes the same reaction at a slower rate, which might prove advantageous when selectivity issues come into play. 1,2-Carbometalation of pyridine was also observed for $[Mg(C_3H_5)(thf)_5][B(C_6F_5)_4]$, but rapid decomposition prevented isolation of the product.[51]

Bis(allyl)calcium reacts under 1,2-carbometalation with pyridine, followed by a Cope rearrangement to give the N-metalated 1,4-DHP quantitatively (Scheme 8c).[148] In the case of α- or γ-methylpyridines as the substrates, deprotonation of the methyl group is the thermodynamically favored reaction pathway. A 2-metalated pyridine compound is the thermodynamically controlled product when a sterically demanding *tert*-butyl group is the γ substituent of the pyridine substrate (Scheme 8e). 1,2- and 1,4-addition products were observed as intermediates.[149]

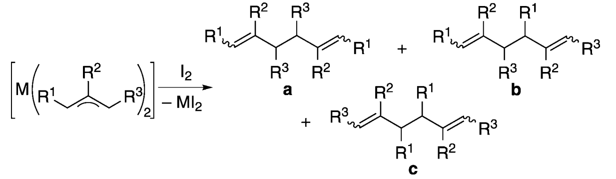
A reversible 1,4-carbometalation of pyridine was reported for allyl compounds of Group 1 metals $[M(C_3H_5)]$ (M = Li, Na, K).[150] It proceeds as a direct 1,4-carbometalation, as shown for M = K, and is thus mechanistically distinct from the reaction between pyridine and bis(allyl)calcium. The resulting N-metalated 1,4-DHPs were stabilized by formation of the corresponding zincates or magnesiates while maintaining reversibility—a result of synergistic effects in heterobimetallic compounds.

5.3. Allyl Coupling Reactions

5.3.1. Oxidatively Induced Allyl Coupling

Oxidatively induced coupling of allyl ligands is known to proceed at redox-active Fe^{II} or Mo^{III} metal centers.[151] Recently, the same reactivity pattern has been observed for allyl compounds of the alkaline earth metals Ca–Ba, by using iodine as the oxidizing agent (Table 2).[57a,58,62] The reactions proceed instantaneously and quantitatively. When unsymmetrically substituted allyl ligands are used, formation of the coupling products with the sterically demanding substituents in the terminal positions is favored (Table 2, entries 3 and 4). The addition of iodine to the isoelectronic bis(allyl)aluminum cation also triggers oxidatively induced allyl coupling, but is much slower and shows a lower selectivity of 80% (Table 2, entry 8).[83a] A two-step mechanism has been suggested for this type of reaction on the basis of DFT calculations for bis(allyl)calcium. The mechanism involves electrophilic addition of I_2 to one allyl ligand to give $[Ca(\eta^3\text{-}C_3H_5)(I)(\eta^2\text{-}C_3H_5I)]$ followed by an intramolecular S_N2' reaction to release the coupling product 1,5-hexadiene and CaI_2.[57a] The second step, that is reaction of an allylmetal compound with allyl halides, has been studied in more detail for the bis(allyl)aluminum cation.[83a]

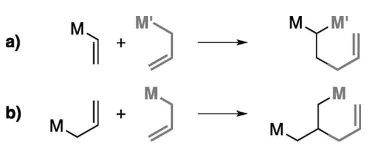
Table 2: Oxidatively induced allyl coupling reactions.



Entry	M	R^1	R^2	R^3	**a** [%]	**b** [%]	**c** [%]
1	Ca	H	H	H	**a** = **b** = **c**		
2	Ca	H	Me	H	**a** = **b** = **c**		
3	Ca	H	H	Me	29	29	42
4	Ca	H	H	*n*Pr	10	45	45
5	Ca	$SiMe_3$	H	$SiMe_3$	**a** = **b** = **c**		
6	Sr	$SiMe_3$	H	$SiMe_3$	**a** = **b** = **c**		
7	Ba	$SiMe_3$	H	$SiMe_3$	**a** = **b** = **c**		
8	Al^+	H	H	H	**a** = **b** = **c**		

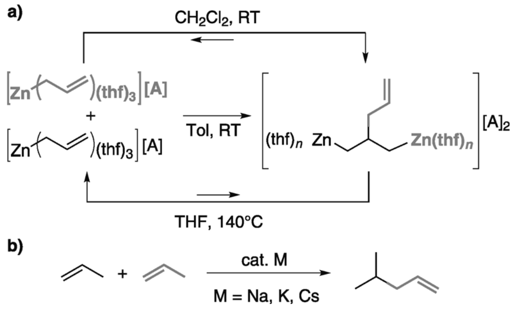
5.3.2. Allyl Coupling in Metallo-Ene Reactions

Metallo-ene reactions between vinylmetal species and allylmetal species are established synthetic methods (Gaudemar–Normant reaction; Scheme 9a).[152,153] This type of reaction is also possible between two allylmetal compounds (Scheme 9b), but has received much less attention. It was first reported as a side reaction preventing the isolation of $[Be(C_3H_5)_2]$ and $[Al(C_3H_5)_3]$.[48] Metallo-ene reactions of neutral $[Zn(C_3H_5)_2]$ ("organometallic oligomerization") were investigated in some more detail by analysis of the organic compounds that were obtained after quenching with electrophiles.[63b,71] The C–C bond formation always takes place between the β- and the γ-carbon atom; the opposite regioselectivity (bond formation between C^β and C^α) is not observed. However, these reactions only proceed sluggishly with radical coupling of the allyl ligands as the major side reaction, which becomes dominant at elevated temperatures (see Section 4.3).



Scheme 9. Metalo-ene reactions between a) a vinyl and an allylmetal species or b) two allyl compounds of main group metals.

Recently, it was shown that this drawback can be overcome by using more Lewis acidic cationic allylzinc compounds instead of neutral species.[69] These compounds dimerize in solvent-dependent, reversible reactions (Scheme 10a), for which key thermodynamic and kinetic data were determined. The dimetalated dimerization products were isolated in near quantitative yields. This reaction is a model for the alkali metal catalyzed dimerization of propene to give



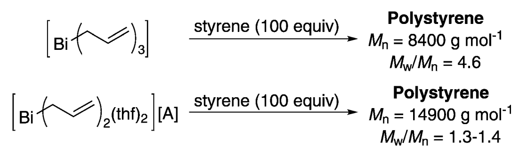
Scheme 10. a) Dimerization of an allylzinc cation in a metallo-ene reaction showing solvent-dependent characteristics; [A] = [B(C_6F_5)$_4$]; $n = 2$ (isolated and dried compound), 3 (in situ reaction);[69] b) alkali metal catalyzed dimerization of propene to give 4-methylpent-1-ene.[154]

4-methylpent-1-ene (Scheme 10b),[154] which is an industrially relevant (co)monomer.[155]

5.4. Olefin Polymerization

The use of allylmetal compounds as catalysts in polymerization reactions occurring through anionic or coordination/insertion mechanisms is well-documented.[2a,8] The influence of the charge at the metal center on the polymerization was investigated for the polymerization of butadiene (BD) in the presence of allylmagnesium initiators.[51] Whereas cationic and neutral allylmagnesium compounds did not initiate BD polymerization, anionic and dianionic compounds gave polybutadiene (PDB) with low polydispersity indices (PDIs) of 1.04–1.10 and high 1,2-PDB contents of 69–77%. Rates of reaction followed the order monoanionic < dianionic, with a pronounced counterion effect (Ca ≪ K). When used as initiators for BD polymerization, the heterobimetallic ate compounds were superior to their monometallic components in terms of aspects such as activity, control of molecular weight distribution, and robustness.

The use of allyl compounds of main group metals as initiators for the controlled radical polymerization of activated olefins such as styrene has only recently been reported through the use of bismuth species.[109] A key finding was that the activity and the control of the molecular weight distribution could be improved by applying cationic [Bi(C_3H_5)$_2$(thf)$_2$][B($C_6H_3Cl_2$)$_4$] as an initiator rather than neutral [Bi(C_3H_5)$_3$] (Scheme 11).



Scheme 11. Improvement of the control of molecular weight distribution in the radical polymerization of styrene by cationization of an allylbismuth initiator; [A] = [B($C_6H_3Cl_2$)$_4$]; PDI = polydispersity index (M_w/M_n).[109]

5.5. Metalorganic Chemical Vapor Deposition (MOCVD)

Two crucial properties for compounds used in metal-organic chemical vapor deposition (MOCVD) are their volatility and the metal–ligand bond strength. Small hydrocarbon ligands ensure suitable volatility of the organometallic compound and prevention of carbide inclusion in the resulting material. Of these small ligands, the allyl ligand has a low homolytic bond dissociation energy (BDE) because of resonance stabilization of the resulting radical (Table 3).[156]

Table 3: Homolytic C–H bond dissociation energies (BDEs) for alkanes and propene.[156]

Compound	BDE [kcal mol^{-1}]	Compound	BDE [kcal mol^{-1}]
Me-H	105.1 ± 0.2	*i*Pr-H	95.1 ± 1
Et-H	98.2 ± 1	*t*Bu-H	93.2 ± 1
*n*Pr-H	97.9 ± 1	allyl-H	86.3 ± 1.5

This makes homoleptic allyl compounds of Ge, Sb, Bi, and Te useful precursors for low-temperature MOCVD processes. [Ge(C_3H_5)$_4$] and [Sb(C_3H_5)$_3$] were reported to be precursors for metal thin film deposition.[107b] The latter compound decomposes in the temperature range 100–160 °C, with 1,5-hexadiene as the only organic decomposition product detected.[110b] A radical mechanism and an Sb–C_3H_5 BDE of 21.6 kcal mol^{-1} were suggested for this process, although reductive coupling could not be ruled out. The higher homologue [Bi(C_3H_5)$_3$] was investigated as a new liquid source of bismuth for MOCVD and low-temperature (< 300 °C) MOCVD of bismuth-containing superconductor films, such as $SrBi_2Ta_2O_9$.[110c,d] The decomposition of [Bi(C_3H_5)$_3$] in solution gave 1,5-hexadiene as the only detected organic decomposition product, thus suggesting a radical mechanism.[109] The synthesis of "electronic grade" bis(allyl)tellurium was recently reported.[114] This compound was used for the low-temperature deposition of semiconductors CdTe and HgTe.[115] Low temperatures are beneficial in these processes, as diffusion or evaporation of the Group 12 component can be reduced. Mechanistic studies on bis(butenyl)tellurium revealed radical pathways for the decomposition reactions.[116]

6. Summary and Perspective

We have presented an overview of the allyl compounds of main group metals that have been isolated as pure substances. Recent progress in this field has left allyl compounds of only a few elements unknown (Be, Ba, Tl, Pb), thus allowing a comprehensive understanding of metal–allyl bonding trends across the periodic table of the elements. The analytical techniques used for differentiating between the possible metal–allyl bonding situations in solution and in the solid state have been summarized along with their scopes and limitations. This could be transferred to heteroleptic allyl compounds, which are not covered in this Review. Fundamental characteristics of the allylmetal compounds have been systematized according to the periodic table of the elements. This should help chemists searching for allyl compounds with certain characteristics to meet the requirements of their synthetic challanges.

Finally, allyl-specific reactivities have been discussed, including allylation of carbonyl compounds and N-heteroaromatic compounds, allyl coupling reactions, MOCVD processes, and polymerization catalysis. This section focused on new or little-exploited concepts or little-explored areas in main group organometallic chemistry. Some studies dedicated to the influence of charge on the reactivity have provided new insights. In this respect, the exploitation of the increased Lewis acidity of cationic species and of synergistic effects in heterobimetallic ate chemistry have been important results. Furthermore, reports on selective C−C coupling reactions based on well-defined complexes of abundant heavy alkaline earth metals or nontoxic bismuth should trigger future research studies.

We hope that the findings presented in this Review will contribute to inspire the development of new applications based on the abundant main group metals. Future advances are expected in the fields of stoichiometric and catalytic allylation reactions and of polymerization catalysis.

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showing allyl ligands in μ_2-η^1:η^1 coordination modes with localized C–C bonds at low temperature (as determined by single-crystal X-ray analysis), electron delocalization in the allyl ligand at higher temperatures has been reported (determined by IR and CP-MAS ^{13}C solid-state NMR spectroscopy): Refs. [65,66,68].

[26] Transfer of Saunders' isotopic perturbation technique (Section 3.2) from solution ^{13}C NMR experiments to solid-state ^{13}C NMR experiments are most likely not possible due to lower resolution of the solid-state experiments.

[27] This phenomenon has been reported for the mixed main group/transition metal allyl compound [$Cu_5Cl_5(C_3H_5)_4Si$]; see Ref. [101].

[28] In [$KSn(Me_3SiCH(CH)CHSiMe_3)_3(thf)$], a relatively small K–C distance without significant K–C bonding interactions has been reported (μ_2-η^1:η^2 versus μ_2-η^1:η^3 bonding): R. A. Layfield, F. García, J. Hannauer, S. M. Humphrey, *Chem. Commun.* **2007**, 5081 – 5083.

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[30] Comparison of the solution analytical data of a series of closely related compounds has also been used as a strategy to investigate the nature of metal – allyl interactions, as reported for [$MZn(Me_3SiCH(CH)CHSiMe_3)_3$] (M = Li, Na, K): C. K. Gren, T. P. Hanusa, A. L. Rheingold, *Organometallics* **2007**, *26*, 1643 – 1649.

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[35] A bimolecular transition state was chosen for space-saving reasons. The smallest oligomer of allylmetal compounds with μ_2-η^3:η^3 coordination of the allyl ligand is a tetramer (Ref. [42]).

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