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Advances in the understanding of molecular beryllium element bonding

Magnus R. Buchner

Molecular beryllium chemistry has made huge advances in the last ten years. Especially, low valent beryllium compounds and beryllium–element multiple bonds have emerged as highly investigated subjects. To understand these compounds and their reactivity, a detailed understanding of beryllium element bonding is necessary. Therefore, Be–C, Be–N, Be–P, Be–O, Be–S, Be–Se, Be–halide, Be–Be, Be–Al and Be–Mg bonds have been studied in detail in this review.

1 Introduction

Since the turn of the century, s-block chemistry, especially alkaline earth metal chemistry, has seen a huge resurgence and demonstrated that reactivities far beyond the known applications of lithium-organic compounds and Grignard reagents are possible.[1–13] However, one element was left aside. Due to the notorious "toxicity" of beryllium and its compounds, as well as the limited commercial availability of suitable precursors, very little research had been performed on its chemistry.[14] However, with more research into beryllium associated health hazards, a more concise picture on the underlying biological mechanisms liable for beryllium associated diseases emerged.[15,16] Based on this knowledge, a re-evaluation and update of the health and safety measurements necessary for safe handling of beryllium and its compounds were possible,[17] which allowed for a renaissance in chemical beryllium research roughly ten years ago. This led to detailed studies on N-donor beryllium complexes by the Schulz group,[18–21] while our group focused on the systematic investigation of beryllium chemistry with biologically relevant O-donor ligands and related systems.[22–31] This enabled the isolation and structural authentication of the first homoleptic beryllium carboxylate (**1Ph** Fig. 1).[24] Additionally, it can be shown that the speciation in water and anhydrous ammonia is similar and the latter leads to unprecedented adamantane shaped tetranuclear complex-cation **2**.[32–34] In the search for beryllium precursors with innocent leaving groups, we, additionally, performed some basic investigations into beryllium-organic compounds with anionic C-donor ligands in the hope of using these as Brønsted basic starting materials.[35,36] Similar compounds and their applications were also studied by the Schulz group,[37–39] while the Gilliard group concentrated on beryllium complexes with dative C-donor ligands.[40–43]

In parallel to the above mentioned research, a new field of beryllium chemistry evolved in the wake of the seminal Mg(I) dimer introduced by the Jones group,[1] which evolved as a quasi-universal reducing agent.[3] Therefore, numerous efforts were made to isolate low valent beryllium compounds. This led to cyclic alkyl amino carbene (CAAC) stabilised compounds with beryllium in the formal oxidation states 0[44] and I (**3** and **4**, Fig. 2).[45,46] However, the interpretation of the oxidation state in these compounds is heavily discussed,[47–49] which is also

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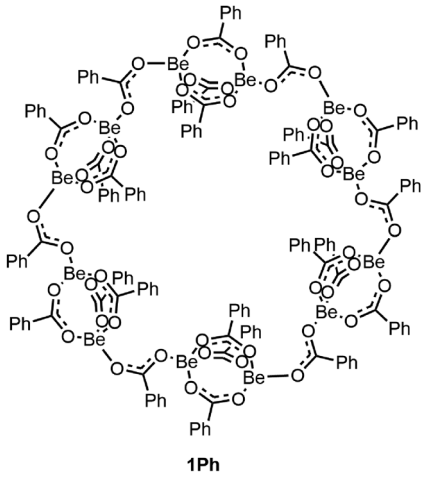


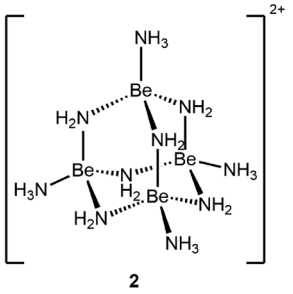


Fig. 1 O- and N-donor ligand based multinuclear beryllium complexes.[24,32]

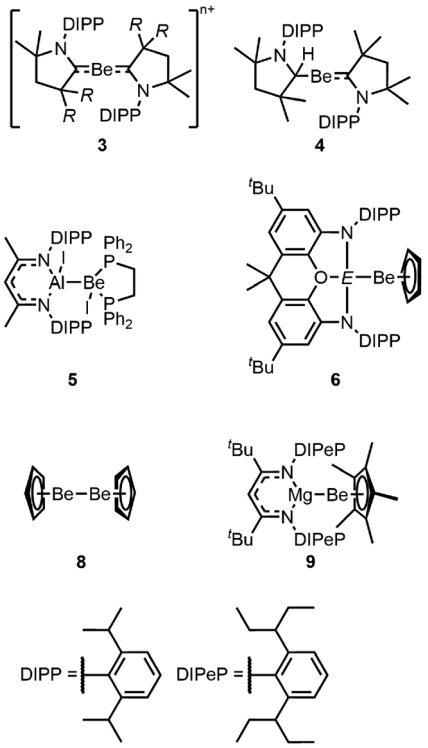
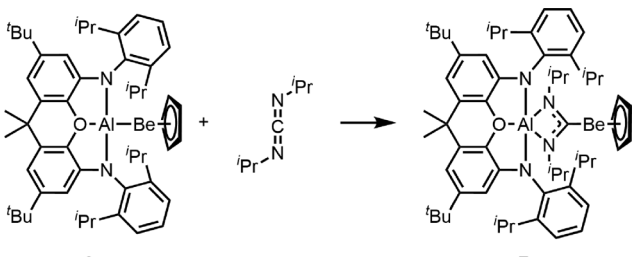


Fig. 2 Low valent beryllium compounds (n = 0 and 1; R = Me and Et; E = Al, Ga, and In).[44–46,51–55]

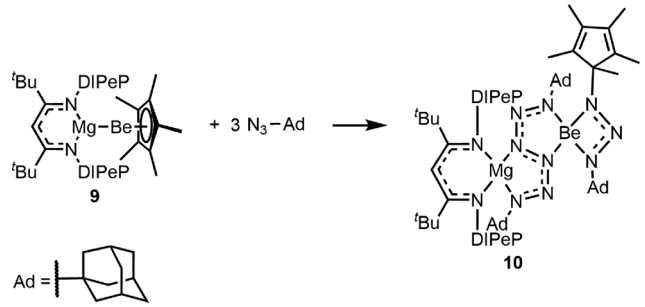
partially due to the observation that CAAC stabilised low valent Be compounds only show CAAC centred reactivity.[50]

An alternative approach to the realisation of low valent beryllium compounds is the formation of beryllium–element bonds with other main group metals with comparable electronegativity. In the case of aluminium as the bonding partner, this was first achieved by the Jones group (**5** Fig. 2),[51] while a more generalised solution could be realised by us in collaboration with the Aldridge group through employment of the 4,5-bis(2,6-di-iso-propylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene ligand (NON). With this NON ligand at a group 13 element, beryllium element bonds with aluminium, gallium and indium are accessible (**6**, Fig. 2).[52,54] The aluminium derivative of **6** features a non-nuclear attractor (NNA) on the Be–Al bond according to quantum theory of atoms in molecules (QT-AIM), which was the first time this was observed for a heterobimetallic bond.[52] Accordingly, **6** acts as a reducing agent and readily inserts carbodiimide into the Be–Al bond (**7**, Scheme 1). The fact that beryllium is bound to the carbon atom of the former carbodiimide suggests that the beryllium atom in **6** acts as a nucleophile and was therefore the first example of actual low valent behaviour in beryllium.[52]

A breakthrough was achieved by Boronski, Aldridge and co-workers when they isolated diberyllocene (**8**, Fig. 2)[53] and a derivative with one pentamethylcyclopentadienyl ligand,[56] which are only the second known homoleptic dimetallocenes besides the seminal dizincocenes reported by Carmona.[57,58] Interestingly, despite its homoleptic Be–Be bond, **8** only acts as a reducing agent when heteroleptic Be–metal bonds are formed.[53,59,60] Additionally, two examples of ligand exchange under retention of the Be–Be bond have been described so far.[56] In collaboration with the Harder group, we were able to synthesise the first compound with a Be–Mg bond (**9** Fig. 2).[55] **9** features a charge distribution, which is to date the closest to the formal oxidation state of Be(0). Furthermore, **9** is surprisingly stable towards heat and bulky molecules, while it readily reduces rod shaped molecules like organic azides. This results in the reductive coupling of two azide units to a hexazenediido ligand (Scheme 2).[55] A similar reductive coupling of azides was previously observed with the Jones Mg(I)-dimer.[61] However, the reaction of **9** with adamantyl azide does not stop with the hexazenediide formation but also one additional azide molecule is inserted into the Be–Cp* bond during the formation of **10**.[55] This insertion into a Be–Cp* bond is only the second



Scheme 1 Nucleophilic attack of the beryllium atom at the electrophilic site of a carbodiimide.[52]



Scheme 2 Reductive azide coupling at the Be–Mg bond and consecutive azide insertion into a Be–Cp* bond (Ad = adamantyl).[55]

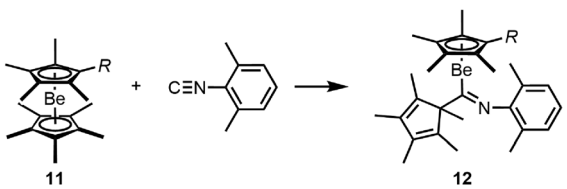
example of the activation of a beryllium–cyclopentadienyl bond. A related reaction was observed when sterically demanding beryllocenes reacted with an organic isocyanide, as depicted in Scheme 3.[62,63] This lack of knowledge on the reactivity of this fundamental bond is surprising considering the fact that beryllocenes are the organo-beryllium compounds for which, by far, the best understanding of bonding exists.[37,64–66]

Besides low valent beryllium chemistry, beryllium–element multiple bonds have also emerged as a novel research topic in the last five years (Fig. 3). This ranges from double dative Be=C bonds in **13** and **14**[67,68] to delocalised π-systems in **15** and **16**.[69] While evidence for partial Be=N double bonds has been known for decades,[70,71] this observation has been generalised with compounds like **17**[72] and **18**.[73] Based on these studies, the first Be≡C and Be≡O triple bonds were only recently realised in **19** and **20**.[74]

Considering the huge advances that were made in beryllium chemistry in recent years, my group has moved more into the investigation of principle beryllium element bonding to understand the underlying processes stabilising low valent beryllium species as well as beryllium–element bonds with the hope of rationalising the observed reactivity. In this article, our advances in the understanding of Be–C, Be–N, Be–P, Be–O, Be–S, Be–Se and Be–halide bonds are summarised in the context of the findings by other research groups during this time period.

2 C-donor ligands

While attempting to prepare the dinuclear beryllium chloride analogue to dilithiated hexacarbodiphosphorane **21** as a precursor for a compound with a Be–Be bond, we serendipitously



Scheme 3 Insertion of an isocyanide carbon atom into a beryllium–cyclopentadienyl bond (*R* = H and Me).[62,63]

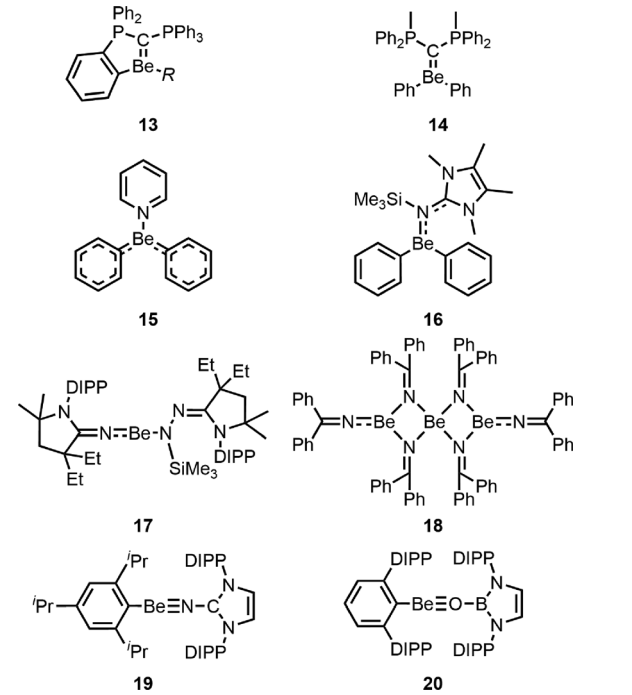
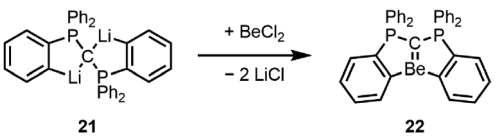


Fig. 3 Complexes with beryllium–element multiple bonds (*R* = Ph, Et, ^{n}Bu, and ^{i}Bu).[67–69,72–74]

obtained di-*ortho*-beryllated hexaphenylcarbodiphosphorane (**22**) according to Scheme 4. **22** features the first isolated Be=C double bond, and according to energy decomposition analysis in combination with the natural orbital for chemical valence (EDA-NOCV), the ligand interacts with the beryllium atom through one electron-sharing bond and three dative bonds.[67] The rigid geometry at the beryllium atom, which is enforced through di-*ortho*-beryllation, facilitates an efficient overlap between the second lone pair at the carbone carbon atom and the empty p-orbital of beryllium, which is not the case in hexaphenylcarbodiphosphorane adducts to beryllium halides, which show perpendicular orientation of these two orbitals.[75]

However, **22** shows extremely poor solubility in solvents which do not decompose the compound.[67] This low solubility is a property of all carbodiphosphorane adducts of beryllium, the origin of which is still unclear.[75,76] This low solubility meant that the reactivity of **22** could not be investigated.[67] These solubility issues could be mitigated by moving to mono-*ortho*-beryllated systems **13** (Fig. 3). These complexes can easily be prepared through the reaction of homoleptic organoberyllium compounds with hexaphenylcarbodiphosphorane as exemplified through the reaction with diphenyl beryllium (**23**),



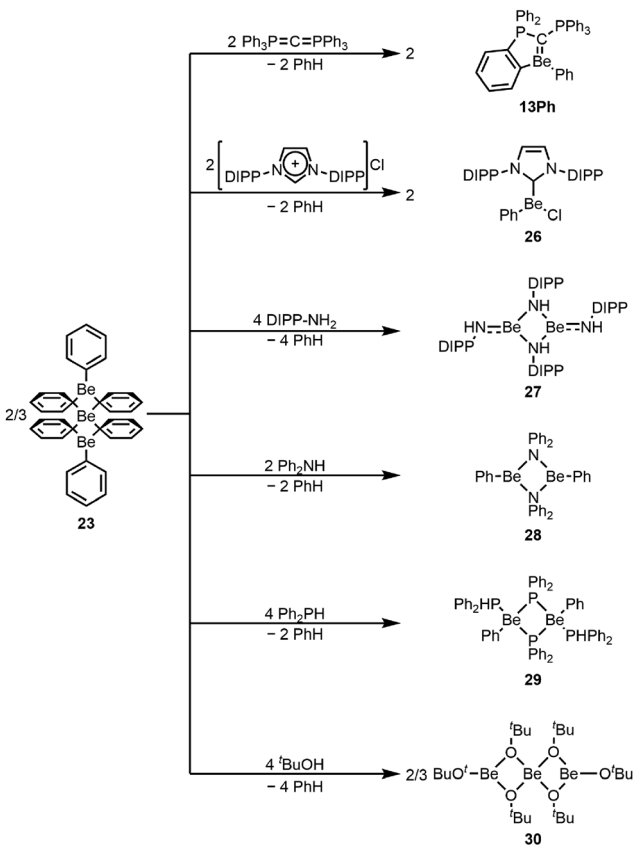
Scheme 4 Synthesis of di-*ortho*-beryllated hexaphenylcarbodiphosphorane.[67]

yielding phenyl derivative **13Ph** (Scheme 5). No di-*ortho*-beryllation occurs *via* this route and experiments with a less sterically demanding but more electron donating carbodiphosphorane confirm that the driving force for *ortho*-beryllation is the steric pressure in the system. Accordingly, with the latter carbodiphosphorane, no *ortho*-beryllation occurs and adduct **14** is formed (Fig. 3). Similar to **22**, **13** and **14** also feature a double dative bond from the carbone carbon atom to the beryllium atom. Despite their improved solubility, no reactivity of the Be=C bond with typical substrates could be observed, which is most likely due to strong steric shielding of this bond.[68] Efforts are ongoing to reduce the steric demand of the ligands in these systems to make the Be=C bond more accessible.

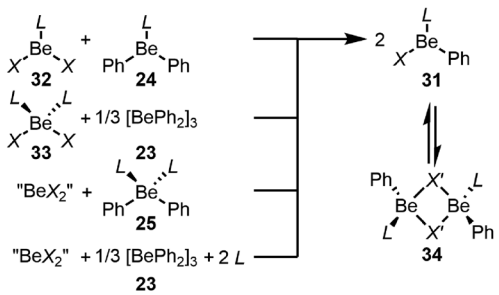
For comparison to the carbodiphosphorane adducts **13**, **14** and **22** the bonding in N-heterocyclic carbene (NHC) adducts to diphenyl beryllium and beryllium dibromide was also investigated. This revealed that in these NHC systems, a double dative bond is also present. However, the bonding is completely different, since in these cases, one dative bond is formed from the carbene's lone pair to the beryllium atom, while the other dative bond originates from the $BePh_2$ or $BeBr_2$ fragment donating to the empty p-orbital of the carbene carbon atom.[68,78] This interaction is the reason for the distinctive perpendicular orientation of the $BePh_2$ or BeX_2 (X = Cl, Br, and I) and the NHC plane found in all tri-coordinated NHC beryllium complexes.[79–82] Hyperconjugation of the π-systems of the phenyl rings into the empty p-orbital at the beryllium atom results in the formation of partial Be=C double bonds in Lewis base adducts of diphenyl beryllium (**15**, Fig. 3). However, if strong donor ligands like N-heterocyclic immines (NHIs) are used, these prevent partial Be=C double bonds through the formation of a partial Be=N double bond (**16** Fig. 3).[69] The hyperconjugation and the resulting delocalisation of the π-system are also probably the reason why tri-coordinated Lewis base adducts to diphenyl beryllium (**24**, Scheme 6) are more preferentially formed than the tetra-coordinated analogue (**25**, Scheme 6).[83,84]

Homoleptic diphenyl beryllium **23** acts as a versatile Brønsted base and can be used to directly prepare a wide range of beryllium complexes (Scheme 5). Through deprotonation of C–H acidic imidazolium salts, Grignard analogue beryllium complex **26** is accessible, while reaction with amines results in the formation of homo- (**27**) and heteroleptic (**28**) beryllium amides, depending on the sterics of the employed amines.[73,77] Also phosphines can be deprotonated to give beryllium phosphide **29**, while alcoholysis results in homoleptic beryllium *tert*-butoxide **30**, all of which could be structurally authenticated.[77]

Until recently Grignard analogue beryllium complexes were rare.[86,87] However, we could show that heteroleptic organo-beryllium halides (**31** Scheme 6) are actually the preferred species. This is evident from equilibria lying almost exclusively on the heteroleptic side if tri-coordinated Lewis base adducts of the beryllium halides (**32**) and **24** are mixed. The same observation was also made if either tetra-coordinated Lewis base adducts to the beryllium halides (**33**) and diphenyl beryllium or the beryllium halides and complexes **25** are allowed to react. Also simple mixing of beryllium halides, diphenyl beryllium and the desired donor ligand results in clean formation of Grignard analogues **31**.[85] Similar results were also obtained in parallel by the Jones group.[88] Depending on the steric bulk of the donor ligand L and the properties of the halido ligand, either mononuclear compounds **31** or dinuclear complexes **34** are formed (Scheme 6).[85] Similar observations have already been made in NEt_3 adducts of the beryllium halides.[31] At present, detailed studies on the bonding in dinuclear heteroleptic organo-beryllium halides are conducted to understand the mechanism of their formation from homoleptic precursors as well as the analogy to homoleptic organo-magnesium compounds, which can only be synthesised through an equilibrium shift *via* salt elimination.



Scheme 5 Versatile use of diphenylberyllium as a starting material.[68,73,77]



Scheme 6 Reactions yielding heteroleptic organo-beryllium halides (X = Cl, Br, and I; X' = Cl and Br; L = THF and NEt_3).[85]

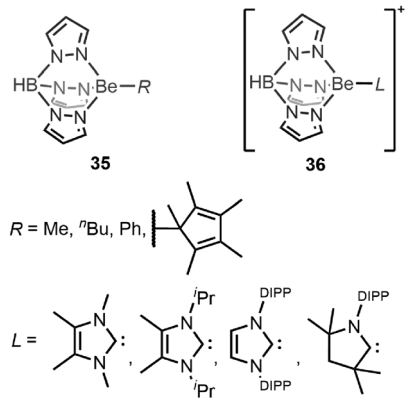


Fig. 4 Neutral and cationic 1-tris(pyrazolyl)borate organo-beryllium complexes.[89]

In beryllium chemistry, beryllium–element bond lengths determined in the solid state have extensively been used to analyse the bond strengths and bond order. However, often compounds with different coordination numbers at the beryllium center have been used. To investigate, whether solid state parameters are an appropriate tool to draw these conclusions we prepared a set of 1-tris(pyrazolyl)borate (Tp) organo-beryllium complexes with anionic and neutral C-donor ligands, as depicted in Fig. 4.[89]

Extensive solution and solid state analyses in combination with quantum chemistry revealed that all Be–C bonds are almost identical in nature. No discrimination into dative, covalent or ionic bonds could be made regardless whether the C-donor was a carbene or an alkyl or aryl. Furthermore, it was found that the structural parameters obtained from X-ray diffraction analysis were similar and that sterics plays the decisive role.[89] Therefore, solid state parameters can only be used with caution when deductions on bonding or oxidation states are drawn. This is only possible if systems with a similar steric demand and with the same coordination number at the beryllium center are compared. Also a quantum chemical analysis is crucial to understand the bonding mode.

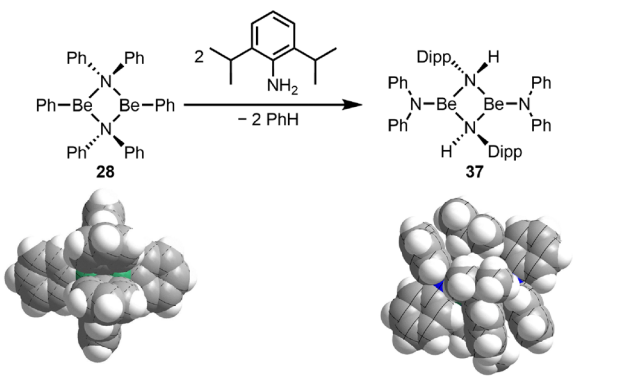
In summary, while the number of well characterised organo-beryllium compounds has increased significantly, there is still a lack of systematic investigations into their reactivity and ligand exchange processes. At present, we are investigating the reactivity of beryllocenes as well as the formation and application of beryllium Grignard compounds.

3 N-donor ligands

To study the differences between Be–C, Be–N, Be–O and Be–S bonding, we investigated the coordination behaviour of ambiphilic pseudo-halides at the rigid $[TpBe]^+$ fragment,[90] which we also used to study Be–C bonds (see the above section).[89] While cyanate and thiocyanate preferentially bind *via* the N-donor site, cyanide readily forms the cyanide and isocyanide beryllium complexes in a one-to-one ratio. Quantum chemical analysis of the bonding showed that N-coordination leads to strong polarisation of the pseudo-halido ligands, which result in charge accumulation at the nitrogen atoms. This partial negative charge is a strong stabilising factor for the highly polarised, mainly ionic Be–pseudo-halide bonds. However, in the case of cyanide, this polarisation has a significantly weaker influence on the bond towards metal atoms in general. The σ-donation is more effective if the C-donor site is coordinated, which is the reason why most metals form cyanide complexes. Only if strong orbital interactions, like with beryllium, are possible, N-coordination is preferred and then polarisation of the C≡N π-system additionally stabilises these isocyanide complexes.[90]

To gain insights into the electronic and steric effect onto Be–N bonds, a set of mono-, di- and trinuclear beryllium amide complexes have been synthesised (*e.g.* **27** and **28**, Scheme 5 as well as **37**, Scheme 7). In these compounds, the terminal N-donor ligands are mainly bound through a 2-electron-2-centre σ-bond, while the μ_2-N bridging interactions consist of 2-electron-3-centre σ-bonds. The electron deficiency at the tri-coordinated beryllium atoms is compensated through donation from the lone pairs of the terminal nitrogen atoms, which leads to partial Be=N double bonds. In contrast to this, the lone pairs at the bridging nitrogen atoms remain mainly N-located. Further electron delocalisation is present if the molecular geometry allows orbital overlap with an aromatic π-system or if imines are employed. In all explored compounds, the charge distribution between beryllium and nitrogen atoms is almost identical and seems to have no influence on the structure of the compounds. The decisive factor for the observed molecular structures is the steric demand of the ligands, as illustrated by the space filling models in Scheme 7.[73]

While we investigated the beryllium species present in liquid ammonia,[32–34] we realised that little is known about the solution behaviour of simple beryllium compounds in common organic N-donor solvents like acetonitrile, ethylenediamine or pyridine. Investigation of the solution behaviour of beryllium chloride, bromide, iodide and triflate in acetonitrile showed that in contrast to *N*,*N*-dimethyl formamide,[29] no halide dissociation occurs and, therefore, no ionic species are



Scheme 7 Conversion of organo-beryllium amide **28** into heteroleptic beryllium amide **37** (top) and respective space filling models of the compounds (bottom).[73]

formed. Only in the case of beryllium triflate, some indications for triflate dissociation were observed. Despite the lack of charged species in solution, halide exchange was observed as evident from the formation of heteroleptic berylliumhalide adducts of acetonitrile according to eqn (1)–(3), which predominantly lie on the right side.[91]

$$[(MeCN)_2BeCl_2] + [(MeCN)_2BeBr_2] \underset{(MeCN)}{\rightleftharpoons} 2[(MeCN)_2BeClBr] \quad (1)$$

$$[(MeCN)_2BeBr_2] + [(MeCN)_2BeI_2] \underset{(MeCN)}{\rightleftharpoons} 2[(MeCN)_2BeBrI] \quad (2)$$

$$[(MeCN)_2BeCl_2] + [(MeCN)_2BeI_2] \underset{(MeCN)}{\rightleftharpoons} 2[(MeCN)_2BeClI] \quad (3)$$

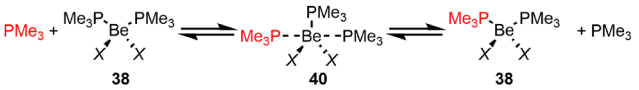
These observations indicate that no large differences between the anionic ligands, like in the heteroleptic organoberyllium halides (Scheme 6),[85] are necessary but rather small electronegativity and steric differences between anionic ligands facilitate the preferred formation of heteroleptic beryllium complexes.[91]

In contrast to acetonitrile, ethylenediamine readily replaces chloride, bromide and iodide from the first coordination sphere of beryllium during the formation of beryllium dications. The same reactivity is also observed for the pseudohalides N_3^-, CN^- and SCN^-, while ethylenediamine is not able to displace fluorido ligands.[92] This reactivity is closely related to liquid ammonia,[33,93] even though the solubility in ethylenediamine is significantly lower.[92] Similar solubility issues were also encountered when quinolino[7,8-*h*]quinoline complexes of beryllium were investigated in acetonitrile and pyridine.[94]

Besides the above-mentioned studies, N-donor ligands have been mainly employed as auxiliary ligands, like Tp[19–21,89,90,95] or 1,3-diketiminates,[96,97] to enforce a rigid coordination environment. Recently, a sterically demanding amido ligand has also been used to stabilise an anionic dinuclear hydrido beryllate with three μ_2-bridging hydrogen atoms.[98] Accordingly, still very little is known about the reactivity of Be–N bonds. Though, due to the high Be–N bond strength, this bond should be hard to break, let alone respective compounds utilised in the activation of other molecules. However, this assumption needs to be tested experimentally.

4 P-donor ligands

Phosphine complexes of beryllium halides have been shown to be a feasible precursor for the synthesis of beryllium-organic compounds[36] and are also capable of activating C–halide bonds,[99] while phosphine adducts to beryllium hydrides have been shown to activate CO and CO_2.[100] However, little was known about the underlying ligand exchange processes, the influence of the steric demand of the phosphines or the stability of the Be–P bonds. Therefore, we conducted an extensive study on ligand exchange processes in beryllium

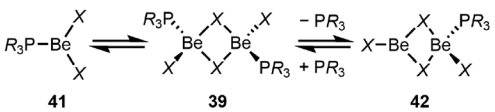


Scheme 8 Ligand exchange at trimethylphoshine complexes of the beryllium halides *via* an interchange mechanism (*X* = Cl, Br, and I).[101]

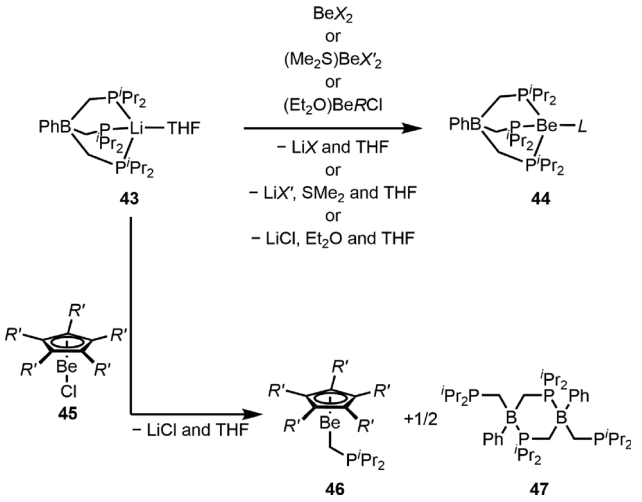
phosphine complexes. While readily two small PMe_3 ligands can coordinate with beryllium during the formation of tetracoordinated beryllium complexes **38** (Scheme 8), the coordination sphere of beryllium can only accomodate one larger PCy_3 (**39**, Scheme 9).[101] The threshold cone angle up to which two phosphines can be coordinated is between 136° and 145°.[102] The energy required for dissociation of a PMe_3 ligand in **38** rises from the chloride *via* the bromide to the iodide derivatives, since the respective Be–halide bonds become weaker and, therefore, the resulting electron deficiency at the beryllium atom needs to be compensated through stronger Be–P bonds. This increase in Be–P bond strength can be directly observed in solution *via* the $^1J_{PBe}$ coupling constants in the ^{9}Be and ^{31}P NMR spectra. In the case of the iodo-derivative, actually phosphine dissociation and iodide dissociation are equal in energy, which is the reason why in the iodo system cationic species are also non-negligible. Therefore, their reactivity differs from those of the other halido complexes.[101] While PMe_3 dissociation followed by solvent coordination plays a role in C–Cl bond activation processes by $[(PMe_3)_2BeCl_2]$,[99,101] this process is irrelevant for phosphine exchange, when an excess of phosphine is present.[101] This ligand exchange process proceeds *via* an interchange mechanism and involves penta-coordinated intermediate **40** (Scheme 8).[101]

In the case of dinuclear complexes **39** two significantly different dissociation processes take place. For PMe_3, homolytic cleavage to tri-coordinated intermediate **41** is energetically favoured, whereas for PCy_3, phosphine loss resulting in the formation of asymmetric dinuclear complex **42** is less energy demanding (Scheme 9).[101] The formation of **42** with its highly Lewis acidic tri-coordinated beryllium atom, which is not stabilised by a neutral donor ligand, is the explanation for the significantly higher reactivity of the PCy_3 beryllium halide complexes.[99,101]

Due to the observation that $^1J_{PBe}$ NMR coupling constants are a direct measure for the Be–P bond strength,[99,101] we developed a spectroscopic probe for the assessment of the base strength of various anionic ligands. Considering that the $^1J_{PBe}$ NMR coupling constant strongly depends on the Be–P distance, we employed a highly rigid monoanionic tridentate phosphaphenylborato ligand to facilitate a constant coordination environment at the beryllium atom. The reaction of the



Scheme 9 Dissociation processes at multinuclear beryllium phosphine complexes (*X* = Cl, Br, and I and *R* = Me and Cy).[101]



Scheme 10 Synthesis of phosphorus-based beryllium scorpionate complexes and transmetallation from boron to beryllium (X = Cl, Br, I, and OTf; X' = CN, N_3, NCO, and NCS; R = Ph and ^{n}Bu; L = Cl, Br, I, OTf, CN, N_3, NCO, NCS, Ph, and ^{n}Bu; and R' = H and Me).[103,104]

respective lithium salt **43** with a variety of homo- and heteroleptic beryllium (pseudo)-halides, triflate and beryllium-organic compounds gave the desired beryllium complexes **44**, as depicted in Scheme 10.[103,104] In these compounds the $^1J_{PBe}$ NMR coupling constant is a direct measure of the electron density of the beryllium atom and correlates with the base strength of the coordinated anionic ligand L. Furthermore, it was proven that the Be–P distances obtained from X-ray diffraction experiments are not suitable parameters for the assessment of the ligating properties of L.[103]

Attempts to synthesise derivatives of **44** with cyclopentadienyl ligands through the reaction of **43** with half-sandwich beryllocenes (**45**) failed. Instead, the unprecedented transmetalation of a $[CH_2P(^iPr)_2]^-$ group from boron onto beryllium was observed, which gave half-sandwich compounds **46** and neutral phosphaborane **47** (Scheme 10). This reaction shows that cyclopentadienyl as a six electron donor exhibits superior ligating properties compared to phosphaphenylborane. The formation of **46** is the first transmetalation reaction from a more to a less electronegative element, and similar reactivity can also be induced through steric overcrowding at the beryllium atom, withdrawal of electron density from the beryllium atom or weakening of the beryllium–scorpionate bond through oxidation of the phosphorus atoms.[104]

The Be–P bond strength seems to be in a sweet spot so that not only compounds can still be conveniently isolated but also bond cleavage is easily induced to facilitate further reactivity. At present, we investigate the properties of the Be–P bonds in detail and apply P-donor complexes of beryllium in Lewis acid–base reactions.[105]

5 O-donor ligands

Ethers, especially diethyl ether and tetrahydrofuran (THF), are among the most ubiquitous organic solvents. However, these solvents are rarely used in beryllium chemistry, except for the synthesis of the Et_2O adducts of $BeCl_2$, $BeBr_2$ and BeI_2 (**48** Fig. 5) from elemental beryllium.[106] Even though these etherates are applied for further synthesis[88] and their structures are well known,[86,106,107] little was known about the actual species in etheral solutions. In Et_2O, the diadducts **48** are present exclusively and no dissociation of halides occurs, which is analogous to the solution behaviour of the beryllium halides in acetonitrile.[91,108] μ_2-Halido bridged dinuclear complexes **49** can be prepared through the reaction of one equivalent Et_2O with the respective beryllium halide in aromatic solvents and the solid state structure of the chlorido derivative has been determined.[109] However, these dinuclear species play no role in diethyl ether solutions. Generally the etherates **48** do not dissolve well in diethyl ether, which is presumably the reason why this solvent is not commonly used.[108] Similar diadducts are formed in THF (**50**), and the chlorido and iodo derivatives are also only sparingly soluble in the solvent; interestingly, the bromido compound dissolves well. However, in the case of BeI_2, cationic species **51** and **52** are also presumably present in solution. These two complex cations are also observable in solutions of the THF diadduct of BeI_2 in benzene, together with μ_2-O bridged dinuclear **53**, which results from ring opening of THF.[108] Based on these results, ethers are non-ideal solvents for beryllium chemistry, since due to the high oxophilicity of beryllium, the formed ethrates show low solubility in ethers, while in the case of THF activation of the solvent also occurs. Nevertheless, diethyl ether complexes **48** are well soluble in aromatic solvents and the Be–O bond strength seems to be weak enough to remove the ether if desired.[88]

Ring opening also occurs if cyclic silaethers react with beryllium halides or diphenyl beryllium. Bromide, iodide and phenyl are selectively transferred onto the silicon atoms of hexamethylcyclotrisiloxane ($\mathbf{D_3}$) from $BeBr_2$, BeI_2 and **23**, respectively (Scheme 11). In the case of $BeCl_2$, no selective reaction occurs. The obtained trinuclear silanolates **54** are the first examples of α-bromo and α-iodo silanolates. However, only in the case of dimethylphenyl silanolate, hydroylsis gives free silanol $PhMe_2SiOH$, while free α-bromo and α-iodo silanols are

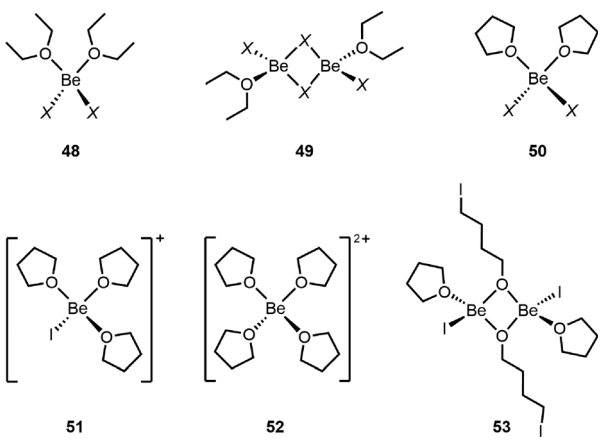
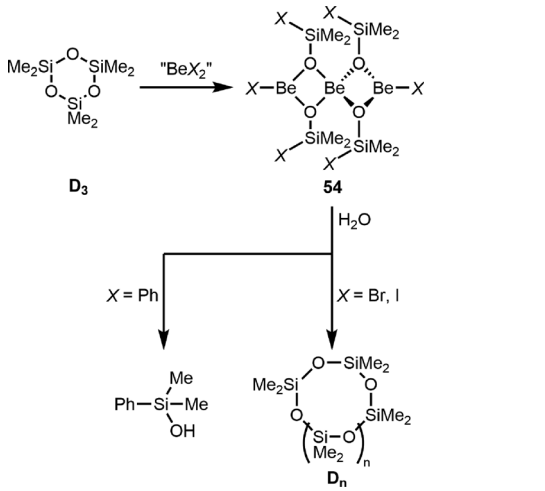


Fig. 5 Structures of beryllium etherates (X = Cl, Br, and I).[108]



Scheme 11 Beryllium mediated transfer of chloro-, bromo- and phenyl-groups onto silicon and their subsequent hydrolysis (*X* = Ph, Br, and I).[110]

not stable and react to a mixture of cyclic methylsiloxanes ($\mathbf{D}_n$).[110] The stabilisation of α-halido silanolates, in which the parent free silanols are not stable, is in analogy to the stabilisation of α-iodo alcoholates through beryllium coordination.[30]

In the hope of obtaining a beryllium precursor with a weakly coordinating and inert anionic ligand, we expanded our research into beryllium halide and pseudo-halide complexes onto triflate (OTf^-).[111] While $Be(OTf)_2$ can be readily prepared, triflate does not act as a weakly coordinating ligand in beryllium chemistry. While triflates show weaker coordination to beryllium atoms than chlorides and bromides, they exhibit better coordination properties than iodides. This is due to the high oxophilicity of beryllium and the good hard–hard match according to the hard and soft acids and bases (HSAB) concept. In contrast to this, the soft iodo ligand only forms weak bonds with beryllium atoms. According to this observation, the structural chemistry of beryllium triflates (Fig. 6) is closely related to that of $BeCl_2$ and $BeBr_2$ complexes. In the diethyl ether, complex **55** is formed, which is similar to the halides **48**,[108,111] while removal of the solvent results in the formation of one-dimensional polymer **56**, which is comparable to aldehyde adducts of $BeCl_2$.[30,111] With bulky ligands like NEt_3 triflate bridged dinuclear complexes **57**, similar to the respective $BeCl_2$ and $BeBr_2$ complexes, are formed.[31,111] Furthermore, autoionisation in the presence of 12-crown-4 to **58** occurs, which has also been observed for diphenyl beryllium and $BeCl_2$.[22,35,111] Eventually, SMe_2 activation and formation of hexatriflatodiberyllate **59** have also been encountered, in analogy to beryllium halides.[111,112]

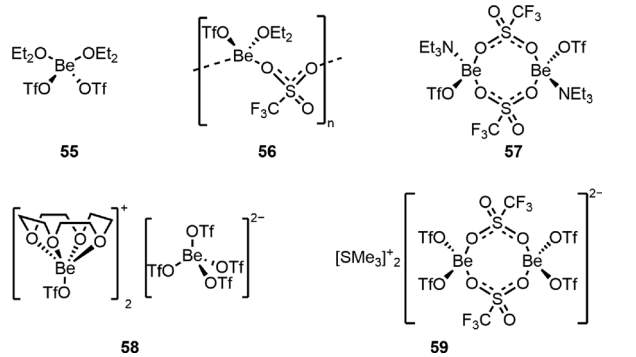
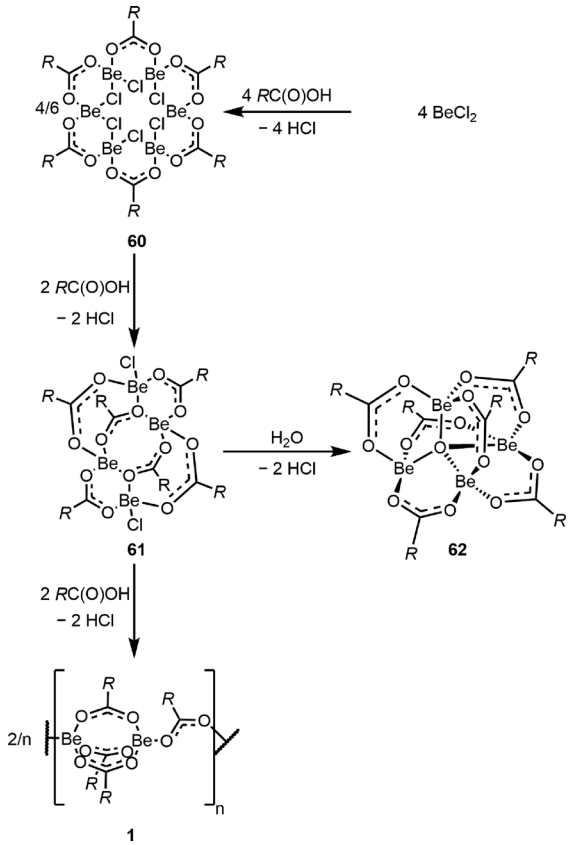
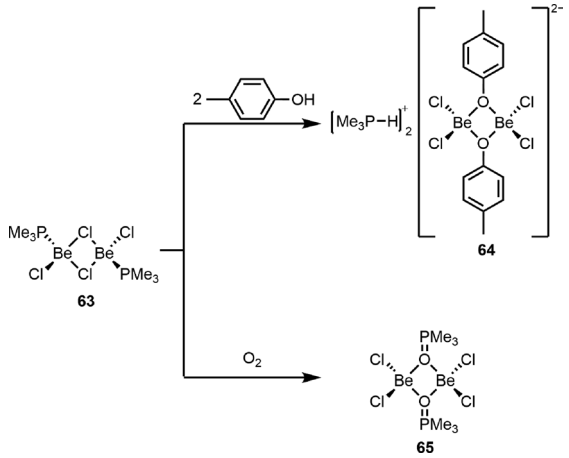


Fig. 6 Examples for the highly variable structures of neutral and cationic beryllium triflates as well as triflato beryllates.[111]

Based on our findings concerning the interaction of Be^{2+} ions with biologically relevant functional groups,[24] we concentrated on the interactions with carboxy functions. If beryllium chloride reacts with one equivalent of a carboxylic acid, hexanuclear beryllium chloro carboxylates **60** are formed (Scheme 12). **60** react with further carboxylic acid to give tetranuclear **61**, which is the precursor compound class to the well known beryllium oxo-carboxylates **62**[113] and rare homoleptic beryllium carboxylates **1**. This finding enabled a first rationalisation on how these two compound classes are formed.[114] Considering the assumption that **62** are the actual species liable for beryllium associated diseases,[115] we conducted an in-depth study on the electronic and steric influence of the carboxy ligands on the Be_4O core of **62**. This study revealed that only the steric demand of the carboxylic acid has an impact on the spectroscopic properties of **62**, while atomic distances are not affected by the carboxylic acids.[113]



Scheme 12 Formation of beryllium chloro carboxylates and subsequent formation of homoleptic beryllium carboxylates as well as oxo-carboxylates (*R* = Ph, *o*-Tol, and Mes).[114]



Scheme 13 Formation of μ_2-oxygen bridged dinuclear beryllium *p*-cresolate **64** and trimethylphosphine oxide complex **65**.[117]

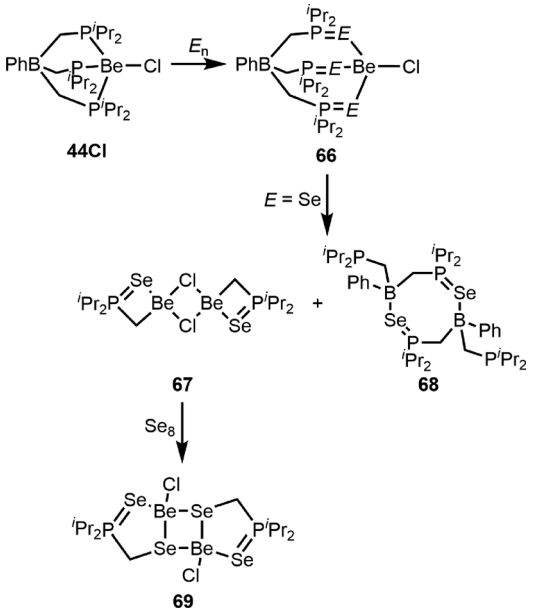
To evaluate whether the peptide backbone of proteins is a likely coordination site for Be^{2+} ions, beryllium carboxamide complexes were investigated.[116] The Be–O bonds in these compounds seem to be stronger than in related beryllium complexes with esters[25] or ketones.[116] However, an evaluation of the relative binding strength of carboxamides *versus* carboxy and hydroxy functions was not possible in organic solvents due to solubility issues. The low solubility of the beryllium carboxamide compounds is caused by the formation of extended and very strong hydrogen bond networks.[116] To overcome these issues, reactions in inorganic, water-related solvents are ongoing.

The high oxophilicity of beryllium is also highlighted by the fact that μ_2-O is preferred over μ_2-Cl bridging not only for anionic O-donor ligands but also for neutral phosphine oxides. This is highlighted by the reaction of dinuclear phosphine adduct **63** with *p*-cresol to give **64** and with Me_3PO to give **65**, as depicted in Scheme 13.[117] This oxophilicity can reach an extent, which prevents the isolation of beryllium compounds due to the formation of beryllium oxide under ligand decomposition.[118]

Unsurprisingly, O-donors form extremely strong bonds with beryllium atoms. This often results in low solubilities or reactivity. This limits the use of O-donor based solvent due to the competition between solvent and ligand coordination. While O-donor complexes are likely less relevant for the synthesis of low valent beryllium compounds, they are highly relevant to understand the physiological processes liable for beryllium metabolisation. Therefore, efforts are ongoing to better understand these compounds and their speciation in solution.

6 Further donor ligands

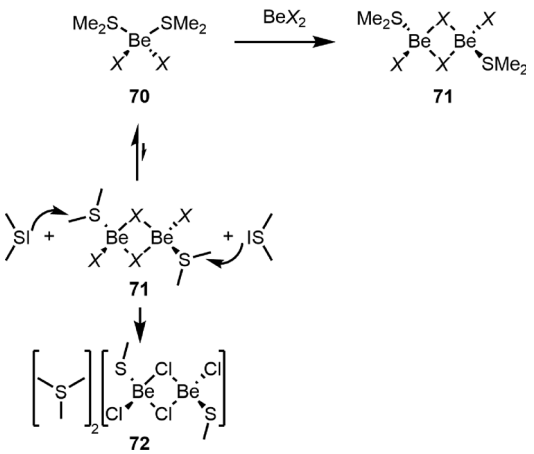
To evaluate the different Be–chalcogen bond strengths, **44Cl** was exposed to elemental oxygen, sulphur, selenium and tellurium (Scheme 14). With exception of tellurium, all chalcogens



Scheme 14 Insertion of chalcogens into the Be–P bond of **44Cl** and subsequent transmetalation and ring expansion in the case of selenium (E_n = O_2, S_8, and Se_8).[104]

were able to insert into the Be–P bonds of **44Cl**, which resulted in the formation of **66**. While the oxygen and sulphur derivatives of **66** are stable, the weak Be–Se bonds destabilise the complex to an extent that transmetalation from boron onto beryllium occurs. These reactions lead to the formation of dinuclear beryllium complex **67** and phospha-selena-bora heterocycle **68**. If an excess of selenium is present, ring strain in **67** is released through selenium insertion into the Be–C bond during the formation of five-membered phospha-selena-berylla cycle **69**.[104]

In contrast to the Be–S bonds in **66S**,[104] the respective bonds in thioether adducts to the beryllium halides (**70** and **71**, Scheme 15) are relatively weak.[112] For this reason SMe_2 is a versatile solubiliser for beryllium halides and their conversion



Scheme 15 Nucleophilic attack of non-coordinated SMe_2 at **71** during the formation of timethylsulfonium salt **72**.[112]

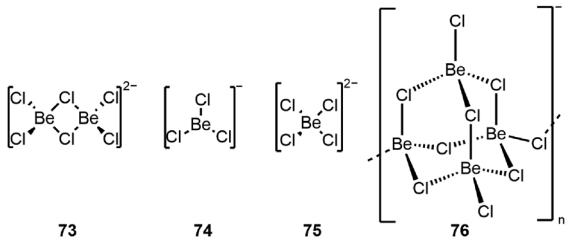


Fig. 7 Structures of chlorido beryllates.[99,117]

into pseudo-halides or triflate.[90,111] While in SMe_2 solutions only diadducts **70** are present, careful removal of SMe_2 *in vacuo* or reaction of **70** with an additional equivalent of the respective beryllium halide gives dinuclear complexes **71**.[112] This behaviour is closely related to beryllium etherates.[108] However, due to the weak Be–S bonds in **70**, SMe_2 partially dissociates during the formation of **71**. In **71**, the S–C bonds are highly polarised due to SMe_2 coordination to the strongly Lewis acidic beryllium atoms. If non-coordinated SMe_2 is present, it can nucleophilicly attack these carbon atoms, resulting in the formation of $[SMe_3]^+$ cations and thiolato beryllate **72**, as depicted in Scheme 15.[112] It is likely that similar processes are also accountable for the formation of triflato beryllate **59**, as shown in Fig. 6.[111]

During our research with the above-described ligand systems, we frequently encountered the formation of halido beryllate anions.[31,99,112,117] These anions can be understood as molecular, anionic fragments from the solid state modifications of beryllium halides,[119,120] as exemplified by the cholido beryllates **73–76**, depicted in Fig. 7.[99,117] Similar structural motifs have also been isolated by Dehnicke and colleagues.[121–126] While it is plausible that the Be–halide bond strength and the μ-bridging properties decrease from fluoride *via* chloride and bromide to iodide, still no systematic investigations on the reactivity of the beryllates have been conducted.

As expected, donor ligands with softer donor sites coordinate relatively weakly to beryllium atoms. Therefore, complexes with ligands based on heavier elements are more promising considering their application in bond activation processes. However, this, of course, makes these compounds harder to isolate. At present, efforts are ongoing to prepare beryllium complexes with heavier p-block donor ligands and explore their bonding and reactivity.

7 Conclusions

Beryllium element bonds are mostly covalent in nature but strongly polarised towards the ligand due to the higher electronegativity of the donating atom. Only in the case of very hard donor sites like in pseudo-halides, the bonding is mostly ionic. Electron deficiency at the beryllium atom is often reduced through hyperconjugation into empty atomic orbitals of beryllium, which results in the formation of (partial) beryllium–element multiple bonds. However, the electronic properties of the ligands have only a secondary effect on the structure of beryllium complexes, while the main factor is the steric demand. This is a direct result of the small size of the beryllium atom. Due to these strong steric influences, solid state parameters, like bond lengths, are not good descriptors for bond strengths. Therefore, these parameters can only be used cautiously when assessing charge distribution and reactivity of these complexes. A far superior probe for these properties is the NMR coupling constant obtained in solution. Unsurprisingly, beryllium forms the strongest bonds to other very hard elements, like oxygen, fluorine or nitrogen, which result in very stable compounds. However, the use of softer ligands like phosphines or thioethers results in well isolatable complexes, which show high reactivity in bond activation processes. Despite the advances in the understanding of beryllium–element bonds, still reactivity studies on fundamental compounds like beryllocenes are missing. Therefore, systematic investigations are required and ongoing. This is especially important for C-donor ligands, since these are the main substance class for the stabilisation of low valent beryllium complexes and also show unprecedented behaviour, as evident from the transmetalation from a more to a less electronegative element.

Conflicts of interest

There are no conflicts to declare.

Data availability

Since this is a review article, all the data are available in the study.

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