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Lithium, Sodium and Potassium Magnesiate Chemistry: A Structural Overview

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Until recently, deprotonative metalation reactions have been performed using organometallic compounds that contain only a single metal (*e.g.*, organolithium reagents). Since the turn of the millennium, bimetallic compounds such as alkali metal magnesiates have begun to emerge as a new class of complementary metalating reagents. These have many benefits over traditional lithium compounds, including their enhanced stability at ambient temperatures, their tolerance of reactive functional groups and their stability in common reaction solvents. In recent years lots of attention has been focused on understanding the structure of alkali metal magnesiates in an effort to maximize synthetic efficiency and thus shed insight into approaches for future rational design. In this chapter, the diverse structural chemistry of alkali metal magnesiate compounds reported since 2007 will be summarized.

KEY WORDS:

Lithium, Sodium, Potassium, Magnesium, Magnesiate, X-ray Crystallography, Inverse Crowns

1.1 Introduction

The deprotonative metalation (deprotonation) of an aromatic ring (*i.e.*, the replacement of a hydrogen atom with a metal one) has been known since 1908 when Schorigin reported that a C-H bond of benzene could be cleaved by a mixture of sodium metal and diethylmercury, to yield phenylsodium.[1,2] Monometallic compounds, particularly organolithium reagents have historically been employed in deprotonation reactions.[3,4] In recent years, bimetallic variants (one metal being an alkali metal, the other magnesium, zinc, aluminum *etc*.) have come to the fore as a new class of compounds capable of smoothly performing deprotonation reactions.[5-12] These reagents often offer enhanced functional group tolerance, greater stability in common laboratory solvents, and also reactions can be performed at ambient temperature (rather than at −78°C). The bimetallic compounds are often referred to as *'ate' complexes*, a term coined by Wittig in 1951 when he studied bimetallic compounds such as the lithium magnesiate $LiMgPh_3$, lithium zincate $LiZnPh_3$ and 'higher-order' lithium zincate $Li_3Zn_2Ph_7$.[13] There was a window of almost five decades before chemists significantly exploited 'ate' chemistry. Since 2000, the number of structural and synthetic studies using bimetallic reagents has increased dramatically and due to their wide scope they continue to be a hot topic in modern chemistry. Several reviews have been published in this area.[6-12] In this chapter, an overview of the recent structural chemistry (from 2007-2015) is presented focusing specifically at the metal pairs utilized.

1.2 Lithium magnesiate complexes

In this section, the surprisingly diverse structural chemistry of recently published lithium magnesiate complexes, containing carbon- and/or nitrogen-based anions will be surveyed. Since 2007, several different structural motifs have been reported. In this section, these will be summarized according to the ligand sets within the lithium magnesiate framework.

1.2.1 Alkyl/Aryl lithium magnesiate complexes

Lithium magnesiates comprised completely of carbanionic ligands were amongst the first ate complexes reported. They are generally prepared by combining the two monometallic organometallic species in a hydrocarbon medium that also contains a Lewis base donor. Since 2007, contacted ion pair ‘lower order’ lithium (tris)alkyl magnesiates (and dimers of this motif) and ‘higher order’ dilithium (tetra)alkyl magnesiates, and solvent separated examples have been reported. Examples of each of these structural types will be discussed here.

The monomeric tris(carbanion) motif is the simplest structural form of a lithium all-carbanionic magnesiate. To isolate this particular form, the use of a multidentate Lewis basic donor compound is generally required. Hevia and co-workers have reported the PMDETA (*N*',*N*',*N*'',*N*''',*N*'''-pentamethyldiethylenetriamine) solvated monomeric lithium magnesiate (PMDETA)LiMg(CH_2SiMe_3)$_3$ **1** (Figure 1).[14] It has an open-motif, whereby a single CH_2SiMe_3 alkyl bridge connects the metals. This structure is intermediate between a solvent-separated ion pair and a molecule that consists of a closed four-membered Li-C-Mg-C ring (*vide infra*).

<FIGURE 1 HERE>

Figure 1: Molecular structure of (PMDETA)LiMg(CH_2SiMe_3)$_3$ **1**

When the denticity of the donor is lowered it is possible to completely change the structure of the isolated lithium magnesiate. For instance by using THF, a polymeric chain variant [(THF)LiMg(CH_2SiMe_3)$_3$]$_\infty$ **2** is isolated (Figure 2).[14] The monomeric unit of **2** consists of a closed Li-C-Mg-C ring, and polymer propagation occurs via an intermolecular interaction between the CH_2SiMe_3 group not present in this ring and a Li atom. Another interesting and unusual feature of **2** is that the molecule of THF that is present binds to the magnesium center.

<FIGURE 2 HERE>

Figure 2: Molecular structure of $[(THF)LiMg(CH_2SiMe_3)_3]_\infty$ **2**

When 1,4-dioxane is used in place of THF, two different lower order magnesiates can be formed depending on the quantity of the donor that is employed, higher quantities of donor lead to a polymeric complex which incorporates two molecules of 1,4-dioxane per monomeric unit, $[(1,4\text{-dioxane})_2LiMg(CH_2SiMe_3)_3]_\infty$ **3** (Figure 3).[14] In **3**, one 1,4-dioxane molecule binds solely to the lithium atom in a monodentate fashion (the other O atom does not participate in bonding). The polymeric arrangement is formed by a combination of Li-(1,4-dioxane)-Li and Mg-(1,4-dioxane)-Mg bridges to give a ‘head-to-head’ and ‘tail-to-tail’ repeating pattern.

<FIGURE 3 HERE>

Figure 3: Molecular structure of the simplest repeating unit of $[(1,4\text{-dioxane})_2LiMg(CH_2SiMe_3)_3]_\infty$ **3**

When a molar deficit of 1,4-dioxane is employed the polymeric ‘tetranuclear’ lower order magnesiate $[(1,4\text{-dioxane})Li_2Mg_2(CH_2SiMe_3)_6]_\infty$ **4** is isolated.[14] Each tetranuclear building block in **4** consists of three fused four membered metal-carbon rings: two are LiC_2Mg rings whilst the other is a Mg_2C_2 ring. The junctions occur at the Mg atoms.

<FIGURE 4 HERE>

Figure 4: Molecular structure of the simplest repeating unit of $[(1,4\text{-dioxane})Li_2Mg_2(CH_2SiMe_3)_6]_\infty$ **4**

The examples discussed thus far are classed as contacted ion pairs as both distinct metals are contained within the same molecule. Since 2007, one example of a solvent separated lithium *tris*(aryl) magnesiate (*i.e.*, the complex exists as distinct cationic and anionic moieties) has been reported. $[Li(THF)_4]^+[Mg(mesityl)_3]^-$, **5** (where mesityl is 2,4,6-trimethylphenyl) resembles many other trialkyl/aryl lithium magnesiates and consists of a tetrahedrally disposed tetra-THF solvated lithium cation and a trigonal planar magnesium *tris*(aryl) anion (Figure 5).[15]

<FIGURE 5 HERE>

Figure 5: Molecular structure of $[Li(THF)_4]^+[Mg(mesityl)_3]^-$ **5**

Another common motif in organomagnesiate chemistry occurs when the compound is rich in alkali metal with respect to magnesium. In general, two factors can lead to this scenario: 1) and most obviously, if the organolithium to organomagnesium reagent ratio employed in the synthesis is 2:1; 2) if the spatial nature of the lower order reagent (including steric bulk of anions and donor ligand) precludes the inclusion of a further molecule of ‘Li-R’ (R is alkyl/aryl). Since 2007, five complexes that can be classed as higher order lithium magnesiates have been reported. The first three are structurally similar and are the (trimethylsilyl)methyl-containing $(TMEDA)_2Li_2Mg(CH_2SiMe_3)_4$ **6** (Figure 6a);[14] the 1,4-buta-di-ide $(TMEDA)_2Li_2Mg[CH_2(CH_2)_2CH_2]_2$ **7** (Figure 6b)[16] and the heteroanionic 1,4-buta-di-ide, diphenyl-containing $(TMEDA)_2Li_2Mg(Ph)_2[CH_2(CH_2)_2CH_2]$ **8** (Figure 6c).[16] Complex **7** was prepared by treating 1,4-dilithiobutane with THF-solvated magnesium dichloride; whereas **8** was produced by combining 1,4-dilithiobutane with dioxane-solvated diphenylmagnesium.

<FIGURE 6 HERE>

Figure 6: Molecular structure of a) $(TMEDA)_2Li_2Mg(CH_2SiMe_3)_4$ **6**; b) 1,4-buta-di-ide $(TMEDA)_2Li_2Mg[CH_2(CH_2)_2CH_2]_2$ **7**; and c) $(TMEDA)_2Li_2Mg(Ph)_2[CH_2(CH_2)_2CH_2]$ **8**

The remaining two higher order magnesiates, have a subtly different structure and can be described as 'magnesiacyclopentadienes'.[17] By reacting substituted 1,4-dilithio-1,3-butadienes with 0.5 molar equivalents of $MgCl_2$ in the presence of TMEDA, the spiro-dilithio magnesiacyclopentadiene complexes $(TMEDA)_2Li_2Mg[CR^1{}_2(CR^2{}_2)_2CR^1{}_2]_2$ **9** and **10** (for **9**, $R^1 = SiMe_3$; $R^2 = Me$; and for **10**, $R^1 = SiMe_3$; $R^2 = Ph$) are formed (Figure 7).

<FIGURE 7 HERE>

Figure 9: Molecular structure of a) $(TMEDA)_2Li_2Mg[C(SiMe_3)_2(CMe_2)_2C(SiMe_3)_2]_2$ **9** and b) $(TMEDA)_2Li_2Mg[C(SiMe_3)_2(CPh_2)_2C(SiMe_3)_2]_2$ **10**

1.2.2 Amido lithium magnesiate complexes

In keeping with the chemistry discussed thus far, tris(amido) lithium magnesiate complexes can be grouped into lower order (contacted or solvent separated ion pairs) and higher order species. Since 2007, it appears that only one tris(amido) lower order lithium magnesiate has been synthesized namely the dimeric unsolvated lithium magnesium guanidinate $Li_2Mg_2(hpp)_6$ **11** (Figure 8) (where hpp is 1,3,4,6,7,8-hexahydro-2*H*-pyrimdo[1,2-a]pyrimidide).[18] The guanidinates anions adopt two different coordination modes – one bridging between two metal centers; the other between four metal centers.

<FIGURE 8 HERE>

Figure 8: Molecular structure of $Li_2Mg_2(hpp)_6$ **11**

Three solvent separated tris(amido) lithium magnesiates have been reported since 2007. All three are tris(HMDS) (1,1,1,3,3,3-hexamethyldisiliazide) complexes, $[Li\{(-)\text{-sparteine})_2]^+[Mg(HMDS)_3]^-$ **12** (Figure 9a),[19] $[Li\{(R,R)\text{-TMCDA}\}_2]^+[Mg(HMDS)_3]^-$ **13** (Figure 9b)[19] and $[Li(IPr)_2]^+[Mg(HMDS)_3]^-$ **14** (Figure 9c)[20] [where (*R*,*R*)-TMCDA and IPr are (*R*,*R*)-tetramethylcyclohexyldiamine and 1,3-bis(2,6-di-isopropylphenyl)imidazolyl-2-ylidene respectively] and have essentially identical $Mg(HMDS)_3$ anions.

<FIGURE 9 HERE>

Figure 9: Molecular structure of $[Li\{(-)\text{-sparteine}_2]^+[Mg(HMDS)_3]^-$ **12**; b) the cation of $[Li\{(R,R)\text{-TMCDA}\}_2]^+[Mg(HMDS)_3]^-$ **13**; and c) the cation of $[Li(IPr)_2]^+[Mg(HMDS)_3]^-$ **14**

Only one example $[Li_2Mg\{(NDipp)_2SiMe_2)_2]$ **15** (Figure 10) of a higher order heteroleptic amido magnesiate has been published between 2007-2015.[21] It incorporates the bulky dianionic bis(amido)silane ligand $[Me_2Si(DippN)_2]^{2-}$, (where Dipp is diisopropylphenyl). The Mg atom is tetrahedrally disposed - η^2 (*N*,*N*)-bound to two bis(amido)silane ligands – and the lithium atoms σ-bind to a N atom of each ligand. Further stabilization to the lithium atoms is provided by π-coordination to an arene-C atom (not shown in Figure 10).

<FIGURE 10 HERE>

Figure 10: Molecular structure of $[Li_2Mg\{(NDipp)_2SiMe_2\}_2]$ **15**. Li-Ar bonding not shown for clarity

1.2.3 Heteroleptic lithium magnesiate complexes

So far, only all carbanion or all amido lithium magnesiates have been discussed. In this section of the review, heteroleptic lithium magnesiates will be described. The section will begin by focusing on mixed carbanion/amido lithium magnesiates. Then magnesiates, which contain carbanions (or amido ligands) with other ligands, will be discussed. The structural chemistry for this set of molecules is diverse. The simplest example is the unsolvated lower order monomeric complex LiMg(HMDS)^{t}Bu **16** (Figure 11).[22] The HMDS ligands bridge between the two metals in the structure whilst the ^{t}Bu is terminally bound to the magnesium atom. Further stabilization of the lithium atom is achieved by two agostic-type interactions from a pair of CH_3-groups present on the HMDS ligands.

<FIGURE 11 HERE>

Figure 11: Molecular structure of LiMg(HMDS)^{t}Bu **16**

Redshaw and co-workers have recently reported the synthesis and structure of a monomeric bimetallic calixarene-containing complex (THF)LiMg^{n}BuR* **17** [where R* is 1,3-dipropoxy-*p*-*tert*-butylcalix[4]arendi-ide].[23] The Mg atom in **17** is five coordinate, adopting a distorted square pyramidal arrangement with the *n*-butyl ligand sits apically with respect to the four equatorially positioned oxygen atoms. The lithium atom has a trigonal planar coordination sphere and bonds to two anionic O centers and a THF molecule and it sits within the calixarene cone. Complex **17** has been successfully utilized in the ring-opening polymerization of *rac*-lactide.

<FIGURE 12 HERE>

Figure 12: Molecular structure of (THF)LiMg^{n}BuR* **17**

Two halide containing amido lithium magnesiates (THF)$_3$LiMg(TMP)Cl$_2$ **18** (Figure 13)[24] and the dimeric [(THF)$_2$LiMg(N^{i}Pr$_2$)Cl$_2$]$_2$ **19** (Figure 14)[25] have recently been reported. These are of particular importance to the well-developed synthetic area of turbo-Hauser metalation chemistry pioneered by Knochel.[26] Complex **18** is representative example of the most heavily utilized turbo-reagent and is dinuclear. The chloride anions bridge the two metals, the TMP anion adopts a terminal position on the Mg cation and three molecules of THF complete the structure – two binding to the Li cation and one to the Mg. In contrast, **19** is tetranuclear. A key structural, and synthetic difference between the two structures is that the diisopropylamide groups adopt bridging positions between two Mg cations at the center of the structure resulting in the formation of a dimer rather than a monomer, presumably due to the reduced steric influence of diisopropylamide versus TMP.

<FIGURE 13 HERE>

Figure 13: Molecular structure of (THF)$_3$LiMg(TMP)Cl$_2$ **18**

<FIGURE 14 HERE>

Figure 14: Molecular structure of [(THF)$_2$LiMg(N^{i}Pr$_2$)Cl$_2$]$_2$ **19**

Akin to their homoleptic analogues, higher order heteroleptic species have also been isolated. A series of higher order magnesiates which contain the dianionic (*rac)*-BIPHEN ligand have been reported. These include: (THF)$_3$Li$_2$Mg{(*rac*)-BIPHEN}(^{n}Bu)$_2$ **20** (Figure 15);[27] (THF)$_3$Li$_2$Mg{(*rac*)-BIPHEN}(CH$_2$SiMe$_3$)$_2$ **21**;[27]

$(THF)_2Li_2Mg\{(rac)\text{-BIPHEN}\}(^tBu)_2$ **22**;[27] and $(THF)_2Li_2Mg\{(rac)\text{-BIPHEN}\}(2\text{-pyridyl})_2$ **23** (Figure 16).[27] In **20-23** the biphenolate ligand stitches together the three metals forming a Li-O-Mg-O-Li zig-zag chain. The key structural framework is completed by the alkyl or pyridyl ligands adopting bridging positions between the metals. Interestingly **20** and **21** contain three THF molecules whilst **22** and **23** only contain two. The compounds were prepared by co-complexation of the dilithium biphenolate with the respective dialkyl (or dipyridyl)magnesium reagent. Also **23** could be prepared by reacting **20** with 2-bromopyridine showing that **20** is active in magnesium-halogen exchange reactions.

<FIGURE 15 HERE>

Figure 15: Molecular structure of $(THF)_3Li_2Mg\{(rac)\text{-BIPHEN}\}(^nBu)_2$ **20**. Complex **21** is isostructural except that ^{n}Bu groups are replaced by CH_2SiMe_3 groups

<FIGURE 16 HERE>

Figure 16: Molecular structure of $(THF)_2Li_2Mg\{(rac)\text{-BIPHEN}\}(2\text{-pyridyl})_2$ **23**. Complex **22** has a similar motif except that the pyridyl groups are replaced by ^{t}Bu groups

Two magnesium-rich species, which adopt cubane-type motifs have recently been isolated. The first is the tetranuclear lithium-trimagnesium alkyl alkoxide $(THF)LiMgMe_3(OC_6H_{11})_4$ **24** (Figure 17).[28] The metal cations and alkoxide anions occupy the corners of the cube, and the methyl ligands are terminally bound to the Mg centers. The coordination sphere of the Li cation is completed by a molecule of THF. Complex **24** has been employed as a molecular single-source precursor for the preparation of MgO nanoparticles which contains lithium. The second cubane thiol-containing $(^nBu_3N)LiMg_3\,^tBu_3\{S(^tBu)\}_4$ **25** (Figure 18) adopts a structural similar motif to **24** and was isolated by Schnöckel and co-workers whilst attempting to access Mg(I) complexes.[29]

<FIGURE 17 HERE>

Figure 17: Molecular structure of $(THF)LiMgMe_3(OC_6H_{11})_4$ **24**

<FIGURE 18 HERE>

Figure 18: Molecular structure of $(^nBu_3N)LiMg_3\,^tBu_3\{S(^tBu)\}_4$ **25**

Another lithium magnesiate structure has been reported. This structure arises from the double magnesiation of *N*-methyl-1,3-propylenediaminoboryl ferrocene (Fc^*-H_2).[30] The structural motif of the trimagnesium-bridged ferrocenophane $(THP)_2Li_2Mg_3(TMP)_2(Fc^*)_2$ **26** (Figure 19, where THP is tetrahydropyran) has been observed previously.[31]

<FIGURE 19 HERE>

Figure 19: Molecular structure of $(THP)_2Li_2Mg_3(TMP)_2(Fc^*)_2$ **26**

1.3 Sodium magnesiate complexes

1.3.1 Donor-free homo- and heteroleptic sodium magnesiate complexes

Tri organo sodium magnesiates can be prepared as solvates using common donor molecules (TMEDA, PMDETA, THF *etc.*) or as solvent-free complexes. The presence of polar alkali metals in their formulations is often required to increase their solubility in hydrocarbon solvents, often at the cost of altering their aggregation states in solution. If the anions within the magnesiate are judiciously chosen, polymeric (or highly oligomeric) aggregation states in the solid state can be achieved.

The polymeric sodium magnesiate $[NaMg(CH_2SiMe_3)_3]_\infty$ **27** is an example of a homoleptic tri-basic alkyl deprotonating agent.[32] Related species have been used in deprotonation reactions, for instance, its ^{n}Bu analogue $[NaMg(^nBu)_3]$[33] has been used as an effective deprotonating reagent of a certain sterically demanding ketone (2,4,6-trimethylacetophenone) for preparing mixed metal enolate complexes,[34] and more recently to deprotonate benzophenone imine to give sodium magnesium ate complexes containing ketimino anions.[35]

The homoleptic sodium magnesiate **27** (Figure 20) represents the first example of a structurally characterized solvent-free tris-alkyl sodium magnesium ate complex reported in the literature. Complex **27** exists as a solvent-free polymeric ate – prepared by a co-complexation approach by mixing the monometallic alkyls $NaCH_2SiMe_3$ and $Mg(CH_2SiMe_3)$ in an *n*-hexane/toluene solvent mixture.[32] The organo alkali metal reagent $NaCH_2SiMe_3$ interacts with the diorgano magnesium complex $Mg(CH_2SiMe_3)$ to formally give a '$NaMg(CH_2SiMe_3)_3$' moiety by electrostatic interactions (Figure 20a). The trigonal planar Mg atom is now bonded to three alkyl ligands, one bridges to the Na cation in the asymmetric unit cell whereas the other two bridging alkyls are linked to neighboring Na atoms. The absence of Lewis donor molecules is crucial in inducing polymerization by forcing the alkali metal Na to directly coordinate to a neighboring alkyl groups. This situation results in a 12-atom $[NaCMgC]_3$ fused ring which propagates as a honeycomb layered two-dimensional infinite network (Figure 20b) in which all CH_2SiMe_3 ligands are rendered equivalent. The bis(amido) alkyl sodium magnesiate $[NaMg(HMDS)_2(^nBu)]$ **28** (Figure 20c) is also polymeric;[36] however, it adopts a one-dimensional chain-like infinite polymer through an almost linear Na-C(^{n}Bu)-Mg bridge. Two bridging HMDS ligands complete the trigonal planar coordination sphere of both Mg and Na cations.

<FIGURE 20 HERE>

Figure 20: a) Molecular structure of [NaMg(CH_2SiMe_3)$_3$]$_\infty$ **27** showing the contents of the asymmetric unit. b) Section of the two-dimensional sheet network of **27**. c) Section of the extended polymeric framework of [NaMg(HMDS)$_2$(^{n}Bu)]$_\infty$ **28**.

Returning to **27**, it has been utilized in the promotion of catalytic hydroamination/trimerization reactions of isocyanates.[37] It also reacts with diphenylamine in a 1:3 molar ratio (albeit in the presence of THF) to yield [(THF)NaMg(NPh_2)$_3$(THF)] **29** (Figure 21). Complex **29** is a contacted ion-pair whereby the cationic [Na(THF)]$^+$ fragment exhibits π-interactions with two arenes groups (in a η^5 and η^2 fashion) from two distinct diphenyl amido PhN groups. The Mg binds to three di-diphenyl-amido ligands and one molecule of THF to complete its coordination sphere. Complex **29** acts as a pre-catalyst to selectively promote the hydroamination/trimerization reactions of isocyanates in good yields under mild conditions.[37] When it is reacted with three molar equivalents of *tert*-butyl isocyanate the reaction yields the novel tris(ureido)sodium magnesiate [(THF)$_3$NaMg(ureido)$_3$] **30**, resulting from the insertion of an heterocumulene molecule in each of the Mg–N bonds of **29**. In **30** each ureido ligand is *fac*-disposed and chelates to the octahedral Mg center via its O and N atoms forming a four-membered [Mg-O-C-N] ring, while the terminal Na atom is bonded to the three O atoms of the ureido ligands and to three THF molecules in an octahedral fashion.

<FIGURE 21 HERE>

Figure 21: a) Molecular structure of [(THF)NaMg(NPh_2)$_3$(THF)] **29** and b) [(THF)$_3$NaMg(ureido)$_3$] **30**

Complex **27** is also an ideal bimetallic precursor for novel solvent-free sodium magnesiate complexes which contain both alkyl and alkoxide ligands. When **27** is exposed to atmospheric oxygen in a controlled manner, the alkoxide containing complex $[Na_2Mg_2(OCH_2SiMe_3)_2(CH_2SiMe_3)_4]_n$ **31** is obtained (Figure 22a).[38] It features a dimeric rearrangement comprising two 'NaMgR_2(OR)' units giving rise to a face-fused double heterocubane structure with two missing corners. Alternatively, the complex can be described as a sodium magnesium inverse crown motif (see section 1.3.3 for definition) consisting of a cationic eight membered polymetallic $[NaCMgC]_2$ ring with four bridging CH_2SiMe_3 groups between Na and Mg atoms, and two alkoxide OCH_2SiMe_3 guests. Each alkoxide group is bonded to two Mg atoms and one Na. In absence of Lewis donor molecules discrete inverse crown units propagate in the two-dimensional space by long secondary Na···Me electrostatic contacts between the two Na atoms and CH_2SiMe_3 groups from neighboring inverse crown structures (Figure 22b).

<FIGURE 22 HERE>

Figure 22: a) Molecular structure of $[Na_2Mg_2(OCH_2SiMe_3)_2(CH_2SiMe_3)_4]_n$ **31** showing the contents of the asymmetric unit cell. b) Section of the two-dimensional network.

Interestingly, around the same time that the structure of [NaMg(HMDS)$_2$(^{n}Bu)] **27** was reported, Hill and co-workers[39] studied the reactivity of an *in situ* mixture of

[$NaMg(HMDS)_2(^{n}Bu)$] with $PhSiH_3$. The resulting novel higher metal hydride cluster is the heterododecametallic complex [$Na_6Mg_6\{N(SiMe_3)_2\}_8H_{10}$] **32** (Figure 23). Two distorted octahedral [MgH_6] units share two hydride ligands forming a [Mg_2H_{10}]. The remaining four Mg centers are coordinated to two HMDS and two hydride ligands in a tetrahedral fashion and six Na atoms occupy the terminal sites. The formation of **32** involves distinct metathesis of both ^{n}Bu and amide ligands present in **27**. This reactivity pattern indicates the under-represented utility of heteroleptic magnesiates for selective metathesis chemistry.

<FIGURE 23 HERE>

Figure 23: a) Molecular structure of the higher metal hydride cluster [$Na_6Mg_6\{N(SiMe_3)_2\}_8H_{10}$] **32**

1.3.2 Introducing donors to sodium magnesiate complexes

The mixed sodium magnesium compounds [$Na_2(HMDS)_2Mg(^{n}Bu)_2(donor)$]$_\infty$ (donor is TMEDA and (*R,R*)-TMCDA for **33** and **34** respectively, Figure 24) are isostructural and can be considered as the first examples of 'inverse sodium magnesium ate' complexes. They can be rationally prepared by combining HMDS(H) with a mixture of $^{n}BuNa$ and $^{n}Bu_2Mg$ in the presence of the corresponding donor molecule in a 2:2:1:1 molar ratio. Normally ate complexes are commonly associated with bimetallic systems, whereby one of the metals has higher Lewis acidity (i.e. Mg^{2+}) than the other (i.e. Na^{+}), thus the former metal captures mores Lewis basic anionic ligands (i.e. alkyl $^{n}Bu^{-}$ and amido $HMDS^{-}$). For **33** and **34**, this situation is reversed; these polymers can be better described as the $^{n}Bu_2Mg$ moiety formally acts as a Lewis base to solvate the dimeric [NaHMDS]$_2$ unit [*i.e.,* the (NaHMDS)$_2$ dimer acts as a

Lewis acidic entity], hence the new term '*inverse magnesiate*'. Both complexes are still polymeric despite the presence of TMEDA and (*R,R*)-TMCDA donors.

<FIGURE 24 HERE>

Figure 24: Section of the two-dimensional sheet network of a) $[Na_2(HMDS)_2Mg(^nBu)_2(TMEDA)]_\infty$ **33** and b) $[Na_2(HMDS)_2Mg(^nBu)_2(R,R\text{-TMCDA})]_\infty$ **34**

The two complexes [(donor)NaMg(TMP)(R)] **35** and **36** are isostructural (Figure 25), where donor and R are CH_2SiMe_3 and TMEDA or ^nBu and (–)-sparteine, respectively for **35** and **36**.[40] Complex **36** is an example of a chiral mixed-metal, mixed alkyl-amide sodium magnesiate and represents the first structural example whereby (–)-sparteine (a highly important ligand in asymmetric synthesis) is chelated to an alkali metal other than lithium. Both are discrete monomers consisting of four membered Na-N-Mg-C rings with one bridging TMP and alkyl ligand between Na and Mg, and one terminal TMP and bidentate chelating ligand, coordinated to Mg and Na, respectively. They contain the basic skeleton evident for many bimetallic synergic bases and indeed can be prepared by the typical co-complexation protocol in hydrocarbon solvent.

<FIGURE 25 HERE>

Figure 25: Molecular structure of a) $[(TMEDA)NaMg(TMP)(CH_2SiMe_3)]$ **35** and [{(–)-sparteine}NaMg(TMP)(^{n}Bu)] **36**

Complex **35** has been utilized in the metalation of furan, tetrahydrofuran, thiophene and tetrahydrothiophene. Several interesting deprotonation and cleave/capture mechanistic insights have been uncovered using this base. For instance, **35** reacts in a different fashion with thiophene and tetrahydrothiophene giving rise to different structural motifs. Towards the former, **35** behaves as a tri-basic reagent yielding [(TMEDA)Na(α-C_4H_3S)$_3$Mg(TMEDA)] **37** which contains three α-deprotonated thiophenyl moieties (Figure 26a).[41] It exhibits three α-deprotonated thiophenyl molecules that are bonded to Mg in a σ-fashion and Na is π-coordinated to the three thiophenyl moieties. TMEDA ligands are coordinated to both Na and Mg atoms, an exceptionally rare structural feature in the chemistry of sodium magnesiates.

When **35** reacts with an equimolar quantity of tetrahydrothiophene, the bis amido complex [(TMEDA)NaMg(TMP)$_2$(α-C_4H_7S)] **38** is obtained (Figure 26b). Complex **38** is structurally related to **35**, where an alkyl group has been replaced by the deprotonated tetrahydrothiophenyl unit and it represents the first structural example of a magnesiated tetrahydrothiophenyl molecule. Interestingly, now the Na atom is also interacting in a π-fashion with the softer S atom from the tetrahydrothiphenyl ligand providing addition stabilization for the α-deprotonated substrate.

<FIGURE 26 HERE>

Figure 26: Molecular structure of a) [(TMEDA)Na(α-C_4H_3S)$_3$Mg(TMEDA)] **37** and [(TMEDA)NaMg(TMP)$_2$(α-C_4H_7S)] **38**

When **35** reacts with furan, it mirrors the reactivity observed with thiophene acting as a dual alkyl-amido base; however, the unexpected dodecasodium hexamagnesium ate complex [{(TMEDA)$_3$Na$_6$Mg$_3$(CH_2SiMe_3)(2,5-C_4H_3O)(2-C_4H_3O)$_5$}$_2$] **39** (Figure 27a).[42] This structure is built upon a bridge network containing 10 α-deprotonated and 6 twofold α,α'-deprotonated furan ligands. The core of the structure represents a unique structural motif in mixed metal chemistry containing twelve Na and six Mg sites, being of the highest nuclearity uncovered via alkali-metal-mediated magnesiation.

Perhaps the most useful feature of **35** is its ability to induce cleavage and capture of highly sensitive and elusive molecules. The bimetallic butadiene-diide containing complex $[\{(TMEDA)NaMg(TMP)_2\}_2\{1,4\text{-}C_4H_4\}]$ **40** (Figure 27b) was isolated from the reaction of **35** with THF, to induce a unique example of cleave and capture chemistry through the fragmentation of THF.[43] The reaction of **35** with equimolar amounts of THF yields this complex as a result of breaking two C-O bonds and four C-H bonds of THF to produce the dianionic buta-1,3-diene ($C_4H_4^{2-}$) fragment which has been trapped by two terminal dinuclear $[(TMEDA)NaMg(TMP)_2]^+$ cationic residues of the original base $[(TMEDA)NaMg(TMP)_2(CH_2SiMe_3)]$ **26**.

<FIGURE 27 HERE>

Figure 27: a) Monomeric unit of $[\{(TMEDA)_3Na_6Mg_3(CH_2SiMe_3)(2,5\text{-}C_4H_3O)(2\text{-}C_4H_3O)_5\}_2]$ **30** with TMEDA and CH_2SiMe_3 groups omitted for clarity. b) Molecular structure of $[\{(TMEDA)NaMg(TMP)_2\}_2\{1,4\text{-}C_4H_4\}]$ **40**

The bis amido alkyl complexes $[(donor)_nNaMg(HMDS)_2(alkyl^-)]$ **41** (donor, diethyl ether; alkyl, ^{t}Bu; *n* = 1) and **42** (donor, TMEDA; alkyl, ^{n}Bu; *n* = 2) are discrete monomeric complexes (Figure 28).[44] Complex **41** is prepared *via* a metathetical approach by reacting NaHMDS with the Grignard reagent *t*BuMgCl in a 1:1 molar ratio in the presence of Et_2O in hydrocarbon solvent with concomitant NaCl elimination. Complex **42** is prepared by a different synthetic approach involving the deprotonative metalation of HMDS(H) by reacting BuNa, Bu_2Mg, in the presence of

TMEDA in 2:1:1:2 molar ratio in hydrocarbon solution. For **41,** its structure consists of a 4-membered Na-N-Mg-N ring with both the Na and Mg atoms occupying distorted trigonal planar arrangements. Two bridging HMDS ligands are connecting Na to Mg and a terminal *t*Bu group is bound to Mg completing its coordination sphere. Complex **42** is best described as a loosely contacted ion pair structure for where only a single ^{n}Bu group bridges Na to Mg. The chelation of two molecules of TMEDA to Na gives rise to a square pyramidal rearrangement, hampering the coordination of a second bridging HMDS amido molecule to Na and preventing the formation of a typical 4-membered Na-C-Mg-N ring.

<FIGURE 28 HERE>

Figure 28: a) Molecular structure of [(Et$_2$O)NaMg(HMDS)$_2$(^{t}Bu)] **41**. b) Molecular structure of [(TMEDA)$_2$NaMg(HMDS)$_2$(^{n}Bu)] **42**

The tris-amido sodium magnesium ate complex [(TMEDA)NaMg(*cis*-DMP)$_3$] **43** (Figure 29) was prepared by mixed-metalation approach.[45] Two *cis*-DMP ligands bridge the Mg and Na centers whilst one terminal amido ligand is coordinated to Mg completing its trigonal planar coordination sphere. One molecule of TMEDA ligand chelates to Na. The isolation of **43** has allowed structural comparisons with other related TMP and diisopropylamido magnesiates, and helped postulate that the chemistry of *cis*-DMP(H) resembles the latter amide.

<FIGURE 29 HERE>

Figure 29: Molecular structure of [(TMEDA)NaMg(*cis*-DMP)$_3$] **43**

1.2.4.6 Solvent-separated sodium HMDS amido magnesiate reagents

Several solvent-separated sodium magnesiates have been isolated. For instance, **44**-**47** are all well-defined charge separated ion pair magnesiates which have the generic formula $[(\text{donor})_2\text{Na}]^+[\text{Mg}(\text{HMDS})_3]^-$ (Figure 30).[46,47] The four magnesiates are constructed by a trigonal planar Mg center ligated to three bis(trimethylsilyl)amido ligands in a trigonal planar fashion $[\text{Mg}(\text{HMDS})_3]^-$. However, distinct Lewis donor molecules appears to be perfect donor in the isostructural cationic $[(\text{donor})\text{Na}]^+$ unit. The donor ligands are chelating Lewis basic molecules, TMEDA, (–)-sparteine and *R,R*-TMCDA, in **44**, **45** and **46**, respectively. For **45** and **46**, the coordination environment of the Na atom is distorted tetrahedral while unusual square-planar-like coordination environment is found in **44**. Being (*R,R*)-TMCDA and (–)-sparteine bidentate chiral donor molecules commonly used with alkali metals, interestingly in the case of **45**, the cationic $[\text{Na}\{(–)\text{-sparteine}\}_2]^+$ constitutes the first example in which the alkali metal center is sequestered by two (–)-sparteine molecules. In contrast, in **47** the Na atom is coordinated by two N-heterocyclic carbene (NHC) ligands, 1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene (IPr). N-heterocyclic carbenes are well known two electron σ-donor ligands which steric properties can be easily tuned by modification of the N-bound imidazolyl organic residues. They favor unusual bonding modes and low coordination numbers in complexes containing metals from across the entire periodic table. However, their use in s-block systems is relatively recent and crystallographic data of alkali metal containing examples is limited. Complex **47** is the first example in which a neutral NHC ligand is bound to sodium. The two IPr ligands are σ-bound through the sp^2-hybridized-carbenic C atom to the Na in almost a linear array while the harder bis(trimethylsilyl)amido ligands are coordinated to the harder Mg metal, in keeping with **44-46**.

In general terms, both the anionic $[Mg(HMDS)_3]^-$ and cationic $[Na(donor)_2]^+$ moieties are typical structural motifs for solvent-separated alkali metal containing bimetallic magnesium complexes.

<FIGURE 30 HERE>

Figure 30: Molecular structure of a) $[(TMEDA)_2Na]^+[Mg(HMDS)_3]^-$ **44**, b) [(*R,R*-TMCDA)$_2$Na]$^+$[Mg(HMDS)$_3$]$^-$ **45**, c) $[\{(–)\text{-sparteine}\}_2Na]^+[Mg(HMDS)_3]^-$ **46** and d) $[(IPr)_2Na]^+[Mg(HMDS)_3]^-$ **47**

A special case of solvent-separate sodium magnesiate complex is $[Na(THF)_6]^+[(THF)Mg(^nBu)\{(DippN)_2SiPh_2\}]^-$ **48** (Figure 31), where Dipp is 2,6-diisopropylphenyl,[48] prepared by reacting $[NaMgBu_3]$[34,49] with the bis(silyl)amine $Ph_2Si(NHDipp)_2$ in THF. In contrast to the previous examples **44**-**47**, the anionic $[MgN_2(^nBu)(THF)]^-$ moiety contains a Mg atom bonded to a bidentate bis amido ligand and to an alkyl group. The cationic moiety consists of a $[Na(THF)_6]^+$ unit.

<FIGURE 31 HERE>

Figure 31: Molecular structure of $[Na(THF)_6]^+[(THF)Mg(^nBu)\{(DippN)_2SiPh_2\}]^-$ **48**

The reactivity of **48** has been studied in magnesiation reactions and it has been discovered that this bulky magnesiate can induce complex magnesium-mediated transformations. For instance, simple organomagnesium reagents will deprotonate benzothiazole at 2-position; however, **48** initiates a remarkable cascade process with benzothiazole at ambient temperature comprising a sequence of C-H deprotonations, C-C coupling, ring-opening and nucleophilic addition reactions, forming the novel magnesiate **49** (Figure 32). Structural studies unveil that the molecular structure contains two similar Mg centers solvated by THF and connected by two newly generated trianionic fragments $[\{C_7H_4NS\}C\{NC_6H_4S\}]^{3-}$ as a result of this cascade event. The contacted-ion pair magnesiate **49** is completed by two $[Na(THF)_2]^+$ and $[Na(THF)_3]^+$ units.

<FIGURE 32 HERE>

Figure 32: Molecular structure of the sodium magnesiate **49**. THF molecules form the $[Na(THF)_2]^+$ and $[Na(THF)_3]^+$ units have been omitted for clarity

Complex **48** also reacts as a single mono-alkyl base with *N*-methylbenzimidazole to deprotonate the most acidic C2 site at ambient temperature in THF solution resulting in the solvent-separated ion pair derivative $[Na(THF)_5]^{+}{}_2[\{\{Ph_2Si(NDipp)_2\}Mg\{(N$-methylbenzimidazolyl)-2$\}\}_2]^{2-}$ **50** (Figure 33). The novel structure of **50** contains two Na cations solvated by only five THF molecules $[Na(THF)_5]^+$ and a dinuclear dianionic unit featuring two $[\{Ph_2Si(NDipp)_2\}Mg\{(N$-methylbenzimidazolyl$\}]^-$ units linked by two bridging *N*-methylbenzimidazolyl ligands via its N and C-metallated atoms forming a six-membered $[Mg\text{-}C\text{-}N]_3$ core ring. In addition, each Mg atom is bonded to a bulky bis(amido)silyl amide group $[Ph_2Si(NDipp)_2]$ which chelate the Mg atom forming a four-membered [Mg-N-Si-N] terminal ring.

<FIGURE 33 HERE>

Figure 33: Molecular structure of a) $[Na(THF)_5]^{+}{}_2[\{\{Ph_2Si(NDipp)_2\}Mg\{(N$-methylbenzimidazolyl)-2$\}\}_2]^{2-}$ **50** (cations not shown),

$[\{Na(THF)_2\}\{Mg(C_4H_4N)_2\{(DippN)SiPh_2(DippNH)\}\}]$ **51**, and

$[Na(THF)_6]^+[\{Ph_2Si(NDipp)(NHDipp)\}Mg(NHDipp)_2(THF)]^-$ **52**

Emphasizing the versatility and polybasic nature of **48**, it can act as a di-basic alkyl-amido reagent, using its single ^{n}Bu arm and one amido site of its bulky bis(amido)ligand to deprotonate certain substrates. For instance, the sodium magnesiate $[\{Na(THF)_2\}\{Mg(C_4H_4N)_2\{(DippN)SiPh_2(DippNH)\}\}]$ **51** (Figure 33b) is formed as a result of its deprotonation reaction with pyrrole.[50] Complex **51** is a contacted ion-pair tris(amido)magnesiate in which the sodium atom exhibits π-Na···C interactions with pyrrole ligands (η^5 fashion) whilst the Mg binds to three amido N atoms. Two molecules of THF complete the coordination sphere of Na. The Mg atom binds to two deprotonated pyrrole ligands and one monodeprotonated bis(amido)silyl ligand.

Highlighting the complexity of these deprotonation reactions, when **49** reacts with the primary amine 2,6-diisopropylaniline, the formation of the solvent-separated sodium magnesium ion pair complex $[Na(THF)_6]^+[\{Ph_2Si(NDipp)(NHDipp)\}Mg(NHDipp)_2(THF)]^-$ **52** (Figure 33c) occurred as the result of a double amination process involving both alkyl and amido basic groups of **49**. Despite their similar tris(amido) constitution, the sodium magnesiates **51** and **52** exhibit different structural features. In **52** the Mg atom adopts a distorted four-coordinate tetrahedral geometry bonded to one amido(silyl)amine $[Ph_2Si(NDipp)(NHDipp)]$ and two N(H)Dipp amido groups (where Dipp is 2,6-diisopropylphenyl group) and a solvating molecule of THF. Complex **52** exhibits a solvent separated structure where the Na is fully solvated by six molecules of THF in a distorted octahedral manner. The new N(H)Dipp amino group present in the amido(silyl)amine ligand of **52**, which is generated by protonation of one of the chelating N atoms of the bis-amido(silyl) ligand of **49**, does not coordinate to Mg.

Sodium-rich higher-order sodium magnesiates such as the tetra-alkyl magnesiate $[(TMEDA)_2Na_2Mg(^nBu)_4]$[49] can direct deprotonative metalation of 1-methylindole in a regioselective manner towards the 2-position. In keeping with the starting material, the product of this reaction is the sodium-rich tetraindol-2-yl magnesium complex $[(TMEDA)_2Na_2Mg\{(1\text{-methylindolyl})\text{-}2\}_4]$ **53** (Figure 34).[51] It can be prepared using a 4:1 molar ratio of 1-methylindole to base, mirroring the presence of four basic alkyl arms in the metallating reagent. The four basic *n*-butyl chains have been replaced by 2-metalated 1-methylindolyl groups giving rise to a tetrahedrally disposed Mg center. The two terminal Na atoms are linked to the 5 membered ring of the indolyl systems via electrostatic cation π-interactions in a η^2-manner with the C2 (deprotonated) and C3 (proton-bearing) atoms. Each Na atom is additionally solvated by a chelating TMEDA donor ligand completing their tetrahedral coordination spheres. This high order magnesium ate complex represents the first example of a structure of a C-magnesiate indolyl system.

<FIGURE 34 HERE>

Figure 34: Molecular structure of $[(TMEDA)_2Na_2Mg\{(1\text{-methylindolyl})\text{-}2\}_4]$ **53**

1.3.3 Inverse crown molecules

The donor-free sodium magnesium ate complexes of formula $[Na_4Mg_2(TMP)_6(\text{arene-di-ide})]$ (arene-di-ide = 2,5-C_6H_3OMe in **54**, 3,5-$C_6H_3NMe_2$ in **55**; and 3,5-C_6H_3Me in **56**; Figure 35) are representative structural motifs of inverse crown complexes.[52,53]

Those complexes are coined inverse crowns in view of their topological but inverse relation to conventional crown ethers in which the Lewis basic heteroatoms (*i.e.*, oxygen) of the host rings trap Lewis acid metal guests (*i.e.,* Li, Na, K *etc.*). Sodium magnesiates **54** and **55** are organometallic intermediates towards the regioselective functionalization via deprotonative metalation of aromatic substrates by the solvent-free sodium magnesium ate complex $[Na_4Mg_2(TMP)_6(^nBu)_2]$. They can ultimately be converted to organic products by reaction with appropriate Whilst the template base $[Na_4Mg_2(TMP)_6(^nBu)_2]$ reacts with anisole to give regioselective 2,5-di-metalation of the arene; with dimethylaniline (an arene which offers steric protection to both *ortho*-sites) yields di-metalation in a 3,5-regioselective fashion. Regioselective metalation in 3,5-positions of dimethylaniline **55** constitutes the first example in which the metalation at both *ortho*-sites of an aromatic substituted with a traditionally *ortho*-directing group has been overridden, breaking the dogma of Directed *ortho*-Metalation (D*o*M) effects. Similarly, the solvent-free combination of $^nBuNa/TMP(H)/Mg(CH_2SiMe_3)_2$ in 2:3:1 molar ratios reacts with toluene to give 3,5-di-metalation of the arene, **56**.

The three complexes **54-56** exhibit similar structural features, two Mg and four sodium cations within a 12-atom metal-TMP host ring, where the Mg cations anchor the corresponding guest arene-di-ide with four Na cations π-bonding in pairs to each metallated C position. However, as expected the structures of 2,5- (**54**) and 3,5-dimetallated arene (**55** and **56**) are subtly different due to the different metalation regioselectivities of the guest substrates.

<FIGURE 35 HERE>

Figure 35: Molecular structure of sodium magnesium inverse crowns a) $[Na_4Mg_2(TMP)_6(2,5\text{-}C_6H_3OMe)]$ **54**, b) $[Na_4Mg_2(TMP)_6(3,5\text{-}C_6H_3NMe_2)]$ **55**, and c) $[Na_4Mg_2(TMP)_6(3,5\text{-}C_6H_3Me)]$ **56**

Another example of a sodium magnesium inverse crown is the naphthalen-1,4-diide containing $[\{Na_4Mg_2(TMP)_4(TTHP)_2(1,4\text{-}C_{10}H_6)\}]$ **57** (where TTHP is 2,2,6-trimethyl-1,2,3,4-tetrahydropyridide) (Figure 36). It is obtained by reacting naphthalene with the aforementioned solvent-free sodium magnesium template base $[Na_4Mg_2(TMP)_6(n\text{Bu})_2]$.[54] Prior to this result, using conventional alkyllithium or alkali metal bimetallic bases naphthalene, had only been regioselective metalated at the 2-position[55] or di-metalated at the 2,6-positions.[56] The polymetallic twelve-membered $Na_4Mg_2N_6$ ring resembles that in **54**; however, two of the TMP ligands have been transformed into TTHP (2,2,6-trimethyl-1,2,3,4-tetrahydropyridide) ligand, formally by the loss of methane.

<FIGURE 36 HERE>

Figure 36: Molecular structure of sodium magnesium inverse crown $[Na_4Mg_2(TMP)_4(TTHP)_2(1,4\text{-}C_{10}H_6)]$ **57**

Another inverse crown molecule which has recently been reported contains benzophenone imine species $[Na_2Mg_2(PhC{=}N)_6(PhC{=}NH)_2]$ **58** (Figure 37). Its solid-state structure shows a bicyclic arrangement, centered on a planar $[Mg_2N_2]$ four-membered ring with both Mg atoms bridged both above and below the plane by N-Na-N linkers. All the N atoms of the ring system are ketimino anions and exocyclic ligands are neutral ketamine molecules which datively bond to the Na cations. The eight-membered dicationic $[(NaNMgN)_2]^{2+}$ ring hosts two $Ph_2C{=}N^-$ guest anions which sit above and below the center of the polymetallic ring and bridge the Mg cations.

<FIGURE 37 HERE>

Figure 37: Molecular structure of sodium magnesium inverse crown $[Na_2Mg_2(PhC{=}N)_6(PhC{=}NH)_2]$ **58**

Subjecting benzene to a bis-amido mono-alkyl mixture of NaTMP/^{t}BuMgTMP/TMEDA in a 1:2:2:2 molar ratios readily produces the open magnesiate complex $[\{(TMEDA)NaMg(TMP)_2\}_2(C_6H_4)]$ **59** (Figure 38). In this complex, benzene has been converted to a 1,4-dianion. Comparing this complex to compounds like **57**, it seems that the addition of TMEDA has resulted in the formation of an opening of the inverse crown molecule (with the extrusion of neutral NaTMP), whereby the TMEDA chelates to Na cations.

<FIGURE 38 HERE>

Figure 38: Molecular structure of the sodium magnesium ‘open’ inverse crown $[\{(TMEDA)NaMg(TMP)_2\}_2(C_6H_4)]$ **59**

1.3.4 Miscellaneous sodium magnesiate complexes

There are several other structural motifs which are prevalent in sodium magnesiate chemistry. The structure of $[(TMEDA)_2NaMg(CH_2SiMe_3)_2\{PhC(NSiMe_3)_2\}]$ **60** (Figure 39) displays two anionic alkyl bridging ligands between Mg and Na and a terminal bidentate benzamidinate ligand bound to the Mg cation.[57] Two bidentate TMEDA ligands coordinate to the alkali metal to form a discrete monomeric bimetallic contacted ion pair structure.

<FIGURE 39 HERE>

Figure 39: Molecular structure of $[(TMEDA)_2NaMg(CH_2SiMe_3)_2\{PhC(NSiMe_3)_2\}]$ **60**

The reaction of $[NaMg(N\mathit{i}Pr_2)_3]$ with two molar equivalents of phenylacetylene in the presence of TMEDA yields the bimetallic complex $[(TMEDA)_2Na_2Mg_2(PhC{\equiv}C)_4(N^iPr_2)_2]$ **61** (Figure 40).[58] This complex exists as a tetranuclear Na···Mg···Mg···Na near-linear chain stitched together by acetylido and amido bridges and is a contacted ion pair of two terminal $[Na(TMEDA)]^+$ cations and a heteroleptic dinuclear dianion $[Mg_2(C{\equiv}CPh)_4(N\mathit{i}Pr_2)_2]^{2-}$.

<FIGURE 40 HERE>

Figure 40: Molecular structure of $[(TMEDA)_2{\cdot}Na_2Mg_2(PhC{\equiv}C)_4(N^iPr_2)_2]$ **52**

1.4 Potassium magnesiate complexes

1.4.1 Inverse crown molecules

The final part of this chapter will focus on the recent chemistry which has been reported involving potassium magnesiate chemistry. The first examples to be discussed involve the characterization of solvent-free potassium magnesiates which contain two TMP and one *n*-butyl anion per potassium (or magnesium) cation [*i.e.,* '$KMg(TMP)_2{}^nBu$']. Three different oligomeric forms have been reported including polymeric $[KMg(TMP)_2{}^nBu]_\infty$ **62**, tetrameric $[KMg(TMP)_2{}^nBu]_4$ **63** and hexameric $[KMg(TMP)_2{}^nBu]_6$ **64** example (Figure 41). The structures of **63** and **64** are architecturally similar to the inverse crowns discussed in section 1.3.3; but they still retain the basic *n*-butyl arm, and as such they have been coined as pre-inverse-crowns. Pre-inverse crown **64** has been shown to function as a base towards naphthalene to induce regioselective mono-deprotonation of the arene at the 2-position producing inverse crown $[KMg(TMP)_2C_{10}H_7]_6$ **65**.[59] Complex **62** exists as an unusual helical polymer, the backbone of which is repeating [KNMgN] units. This chain is supported by $K\cdots CH_2(^nBu)\cdots K$ interactions generating a series of four-atom four-element [KNMgC] rings, fused together along the Mg-C edge to another ring of identical composition. Each K cation participates in a shared vertex that links neighboring pairs of doubly fused tetranuclear ring systems, favoring the propagation of the polymeric chain. The Mg center exhibits a distorted trigonal planar arrangement bonded to TMP N atoms of both bridging amido ligand, and the C atom of the *n*Bu anion. Tetrameric **63** and hexameric **64** consist of 16-atom and 24-atom polymetallic inverse crown-type rings respectively.

<FIGURE 41 HERE>

Figure 41: Molecular structure of a) **62** showing the contents of the asymmetric unit, which corresponds to a single turn of the helical chain, b) **63**, c) **64**, and d) **65**

1.4.2 Introducing donors to potassium magnesiate complexes

The deprotonation of anisole with the heteroleptic potassium magnesiate $[(PMDETA)KMg(TMP)_2(CH_2SiMe_3)]$ **66** (Figure 42) was found to serve as a perfect bimetallic system for 'structurally tracking' alkali metal mediated *ortho*-deprotonation transformations.[60] Starting from **66** and anisole, the first stage of the reaction produces an *ortho*-magnesiated anisole intermediate $[(PMDETA)KMg(2\text{-}C_6H_4OMe)(TMP)(CH_2SiMe_3)]$ **67**, but the ultimate product is the bis(amido) *ortho*-magnesiated anisole complex $[(PMDETA)KMg(2\text{-}C_6H_4OMe)(TMP)_2]$ **68** (*i.e.*, a TMP ligand has formally been reincorporated into the final product with the elimination of alkane). This structural study provided evidence that the heteroleptic base reacts kinetically through its TMP arm, but ultimately the alkyl group is the thermodynamically more basic ligand.

The molecular structures of **66**, **67** and **68** (Figure 42) contain the same [K-TMP-Mg] backbone unit, chelated by PMDETA at the K cations. Moving from **66** to **67**, the terminally disposed ligand on Mg changes from TMP to the alkyl CH_2SiMe_3. An *ortho*-deprotonated anisole ligand fills the vacated bridging position in **67**. Moving now from **67** to **68**, the terminal site on Mg loses the CH_2SiMe_3 ligand by reaction with TMP(H) and concomitant release of Me_4Si but gains a TMP anion.

<FIGURE 42 HERE>

Figure 42: Molecular structure of a) **66**, b) **67** and c) **68**

Mg adopts a distorted trigonal-planar geometry within **66**-**68** and binds to the *ortho*-C-site of the aromatic system in the deprotonated intermediates **67** and **68**. In addition, K engages long π-interaction with *ipso*/*ortho*-C atoms bonded to Mg in the anisolyl ligands.

A novel potassium tris(amido) magnesiate **69** (Figure 43) was prepared[61] by combining an equimolar mixture of benzylpotassium and di-*n*-butylmagnesium with three molar equivalents of diphenylamine in the presence of THF and PMDETA.

<FIGURE 43 HERE>

Figure 43: Molecular structure of **69**

The molecular structure of **69** comprises a monomeric dinuclear potassium magnesiate motif. The tetracoordinate (consisting of three amido groups and one THF molecule) Mg cation adopts a distorted tetrahedral arrangement. Two diphenyl amido ligands bridge Mg to K; however, perhaps surprisingly, not via the 'hard' amido N anions. Reflecting the soft nature of the heavier K metal, it engages π-interactions (η^6-bonding mode) with two phenyl rings, one from each bridging amido group. The second phenyl rings on the bridging diphenylamido ligands do not contribute to the stabilization of K.

Two novel potassium tris(amido) magnesiates, namely, $[\{(-)\text{-sparteine}\}K^+\{Mg(HMDS)_3\}^-]_n$ **70** and $[\{(R,R)\text{-TMCDA}\}K^+\{Mg(HMDS)_3\}^-]_n$ **71** (Figure 44) can be prepared from equimolar mixtures of KHMDS and ^{n}BuMg reacted with two further molar equivalents of HMDS(H) in a hydrocarbon medium with the corresponding addition of the chiral donor (–)-sparteine and (*R*,*R*)-TMCDA molecules, respectively.[62] Focusing on **70**, it has a polymeric structure. In the asymmetric unit two $[\{(-)\text{-sparteine}\}K^+\{Mg(HMDS)_3\}^-]$ ion pairs are linked by an agostic-type K···Me interaction with a $Me(SiMe_2)N$ unit. Both $[Mg(HMDS)_3]^-$ anions interact with the two K atoms within the asymmetric unit and a third neighboring K atom, acting as μ_3-bridges, hence supporting the formation of a polymeric arrangement. This is the first example of a metal complex which incorporates the chiral diamine (–)-sparteine as part of a polymeric framework, and also the first example of a K complex containing this chiral diamine.

<FIGURE 44 HERE>

Figure 44: Molecular structure of a) **70** and b) **71**

For **71**, mirroring the situation for **70**, its molecular structure consists of a contacted ion-pair potassium magnesiate $[\{(R,R)\text{-TMCDA}\}K\}^{+}\{Mg(HMDS)_3\}^{-}]_n$. The asymmetric unit comprises two unique anions $[Mg(HMDS)_3]^{-}$ and cations $[\{(R,R)\text{-TMCDA}\}K]^{+}$. Four K···Me agostic interactions result in the formation of a 12-membered ring motif. As for **70**, there are no K-HMDS N-amide interactions. Both $[Mg(HMDS)_3]^{-}$ units coordinate with two K atoms within the asymmetric unit and to a third neighboring K atom via long agostic-type interactions, promoting polymerization. In contrast to **70**, the extended framework of **71** forms a linear arrangement of alternating small 12-membered and larger 16-membered fused cyclic aggregates. It is the first K adduct containing (*R*,*R*)-TMCDA as a chiral donor ligand. Bis(benzene) chromium can act as a donor towards a potassium magnesiate HMDS amide complex. $[\{K\{(C_6H_6)_2Cr\}_{1.5}(Mes)\}]]^{+}[Mg(HMDS)_3]^{-}{}_{\infty}$ **72** was obtained from an attempt to deprotonate bis(benzene) chromium with a bimetallic KHMDS/$MgHMDS_2$ system in the presence of mesitylene.[63] As depicted in Figure 45, compound **72** contains $[Mg(HMDS)_3]^{-}$ anions and K^{+} cations that are coordinated to three bis(benzene)chromium and a mesitylene molecule. Mesitylene is coordinated to the K in a η^6-manner, whereas the metallocenes are best described as η^3-coordinated. Complex **72** is therefore a solvent-separated ion pair complex, where mesitylene solvates the metal center in the extended framework. All three of the bis(benzene)chromium molecules bridge to neighboring K cations, hence the K centers act as trigonal nodes to build two-dimensional framework with the

$[Mg(HMDS)_3]^-$ unit occupying the interstitial spaces between the layers of adjacent sheets.

<FIGURE 45 HERE>

Figure 45: Molecular structure of **72**. Anions are not shown in b)

In the solvent separated potassium magnesiate $[(IPr)_2K]^+[MgHMDS_3]^-$ **73** (Figure 46),**[20]** the K cation is coordinated by two IPr NHC ligands. Complex **73** represents a unique example whereby two neutral IPr ligands are σ-bound to a potassium in a near linear arrangement forming the $[(IPr)_2K]^+$ cation of **73**. This is the first example of a K complex where the metal is solely coordinated to NHC donor ligands.

<FIGURE 46 HERE>

Figure 46: Molecular structure of **73**

Three donor solvated potassium tris(alkyl) magnesiates have been characterized since 2007. They are: the polymeric lower order $[(C_6H_6)KMg(CH_2SiMe_3)_3]_\infty$ **74**, and the higher order $[(PMDETA)_2K_2Mg(CH_2SiMe_3)_4]$ **75** and $[(TMEDA)_2K_2Mg(CH_2SiMe_3)_4]$ **76** (Figure 47).[64] Complex **74** has a novel polymeric structure, which is formed by a combination of K–CH_2, Mg–CH_2 bonds and medium-long K···Me electrostatic interactions. Its monomeric unit comprises a trigonal planar Mg bonded to three trimethylsilylmethyl groups and a solvent free K^+ ion. Trimethylsilylmethyl groups link Mg to K, with K further engaging in interactions through a CH_2 unit and to one Me group. In addition, K π-engages interactions with a molecule of benzene in a η^6-manner and forms a long contact with a Me of neighboring trimethylsilylmethyl groups, propagating the polymeric two-dimensional network.

<FIGURE 47 HERE>

Figure 47: Molecular structure of a) and b) **74**, c) **75** and d) **76**

The addition of polydentate N-donors, PMDETA or TMEDA to **74** caused its deaggregation as well as inducing a redistribution process to yield the higher-order potassium magnesiates $[(PMDETA)_2K_2Mg(CH_2SiMe_3)_4]$ **75** and $[(TMEDA)_2K_2Mg(CH_2SiMe_3)_4]$ **76** respectively with the concomitant elimination of neutral $Mg(CH_2SiMe_3)_2$. The structures of **75** and **76** exhibit similar structural features. Both potassium magnesiates display a central distorted tetrahedral C_4-coordinated Mg center flanked by two terminal ionic $[(donor)_2K]^+$ units. However, the different denticities of the N-ligands impose different coordination modes of the K^+ ion resulting in subtly different metal arrangements. For **75**, a linear K⋯Mg⋯K arrangement is observed, whereas for **76**, a markedly non-linear K⋯Mg⋯K arrangement is evident.

Two further higher order potassium magnesiates have been reported, both containing a bulky bis(amido)silyl ligand. **77** and **78** (Figure 48).[65]

<FIGURE 48 HERE>

Figure 48: Molecular structure of a) **77** and b) **78**

Complexes **77** and **78** are monomeric where the central magnesium cation is (*N*,*N*)-coordinated (η^2) by two bulky di(amido) ligands. The K cations π-engage to the aromatic substituents of the amido ligand. The only difference between **77** and **78** are that the K cations in the former are also coordinated to THF molecules – one K cation to two, the other to one. The structures exhibit near linear K···Mg···K arrangements.

Reported by Hanusa, Okuda *et al.*[66] the potasium magnesiate allyl complexes [(THF)KMg(C_3H_5)] **79** and [$(THF)_2K_2Mg(C_3H_5)_4$] **80** (Figure 49) can be prepared from bis(allyl)magnesium [$Mg(C_3H_5)_2$] and one or two molar equivalent of allyl potassium [K(C_3H_5)], respectively, in THF. These potassium magnesium complexes have been investigated as initiators for butadiene polymerization and ethylene oligomerization.

<FIGURE 49 HERE>

Figure 49: Molecular structure of a) **79** and b) **80**

In **79**, the Mg center is tetrahedrally coordinated by the THF ligand and by three η^1-bonded allyl ligands forming [$Mg(C_3H_5)_3(THF)]^-$ units. The K center is coordinated by allyl ligands of four different [$Mg(C_3H_5)_3(THF)]^-$ units. The allyl ligands show η^3-, η^2-, and weak η^1-interactions with K resulting in a distorted octahedral coordination geometry. This is the first example of one metal center interacting with six allyl ligands. In **80**, the Mg center interacts with four allyl ligands in an η^1-fashion resulting in a distorted tetrahedral coordination geometry and in contrast to **79**, no Mg THF interactions are observed in the solid state. One of the crystallographically independent K atoms is coordinated by one THF ligand and by four allyl groups (η^2

and three η^3) resulting in distorted trigonal bipyramidal coordination mode with the η^2-allyl and the THF ligand in the axial positions. Interactions between K^+ ions and neighboring allyl ligands favors the propagation of the tridimensional network in both potassium magnesiate structures.

1.4.3 Miscellaneous potassium magnesiate complexes

Heterobimetallic potassium magnesium hydrides can be prepared by selective σ-bond metathesis route from the corresponding s-block amido alkyls bearing the utility amido group HMDS. For instance the potassium hydrido magnesiate **81** (Figure 50) can be obtained by reacting [KMg(HMDS)$_2$^{n}Bu], (*in situ* generated), with $PhSiH_3$ as a source of hydride. This protocol provides a powerful methodology for the selective Mg–C/Si–H σ-bond metathesis.[67]

<FIGURE 50 HERE>

Figure 50: Molecular structure of **81**

The molecular structure of **81** is a potassium magnesium hydrido species, which contains a Mg−H−Mg bridge and the eight-membered metal-amide ring of **81** is chair-shaped. The Mg atoms are forced into a highly distorted tetrahedral coordination environment by coordination to two HMDS bridging ligand and a hydrido group, and the 'naked' K^+ ion participates in the stabilization of the hydrido ligand by engaging long K⋯H interactions. Additionally, this hydrido species can be considered as an inverse crown complex as alluded to by Mulvey *et al.* previously in a similar scenario.[68] This complex constitutes the most recent addition of a hydrido species to the inverse crown family.

Metal−metal bonding constitutes an important area of chemistry, which attracts much attention. A number of metal–metal bonds involving both *p*- and *d*-block metals have been reported in recent years (silicon−silicon triple,[69] and chromium−chromium quintuple[70] bond). In 2004, Carmona and *co-workers* isolated the first stable compound containing a Zn−Zn bond.[71,72] In this context, the complex $[(THF)_3K]_2[LMg−MgL]$ **82**,[73] were L is $[(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NC(Me)}]_2^{2-}$, represents a new Mg−Mg-bonded compound stabilized by a doubly reduced α-diimine ligand exhibiting a Mg−Mg (Figure 51).

<FIGURE 51 HERE>

Figure 51: Molecular structure of **82**

It was prepared by reduction of a mixture of $MgCl_2$ and the ligand L with K metal in THF. Its molecular structure comprises a dimeric structure with a Mg−Mg bond length of 2.9370(18) Å, as a salient feature.

1.5 Summary

This chapter has demonstrated the recent progress made in understanding the solid-state structure of alkali metal magnesiates – key research as structure is inextricable linked to reactivity. The advantages that ate complexes have over conventional lithium reagents (use of milder reaction conditions, better functional group tolerance, and access to hitherto inaccessible synthetic chemistry *etc*.) ensure that this area of research will blossom further in the coming years. This chapter focused only magnesiate systems. In addition, alkali metal zincate, aluminate, manganate and cuprate systems are also the subjects of continual study and development, and it is highly likely that alkali metal ate chemistry will have an important future role in synthesis, and complement the massively important and longstanding role that single metal organometallic species such as organolithiums play in academia and industry.

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