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Low Oxidation State and Hydrido Group 2 Complexes: Synthesis and Applications in the Activation of Gaseous Substrates

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Matthew J. Evans obtained his BSc degree in 2018 at Victoria University of Wellington – Te Herenga Waka in New Zealand. Following a research year with Associate Professor J. Robin Fulton, he completed his PhD degree in 2022 under the supervision of Professor Martyn Coles and Dr. Mathew Anker. Since 2022, Matthew has been working in Australia as a postdoctoral research associate for Professor Cameron Jones at Monash University. His research interests lie in the design of heterobimetallic main-group complexes for synergistic bond activation with a focus on mixed low oxidation state s-block complexes for small molecule activation.

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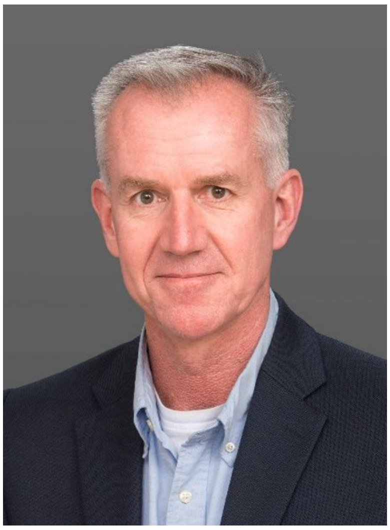


Professor Cameron Jones FAA obtained his BSc(Hons) degree at the University of Western Australia (1984). His PhD degree (1992) was gained from Griffith University, Brisbane, under the supervision of Professor Colin Raston FAA. He then moved to a postdoctoral fellowship (1992–1994) at Sussex University under the supervision of Professor John Nixon FRS. From 1994 he held a lectureship at The University of Wales, Swansea before moving to a Readership in Inorganic Chemistry at Cardiff University (1998). There, he was promoted to a Personal Chair in 2002. In 2007 he moved to Monash University, Melbourne, where he is currently the RL Martin Distinguished Professor of Chemistry. In 2017 he was elected as a Fellow of the Australian Academy of Science. His research interests include the stabilisation of low oxidation state and hydrido s- and p-block metal complexes, and their application to synthesis, small molecule activations and catalysis.

Abstract

Numerous industrial processes utilise gaseous chemical feedstocks to produce useful chemical products. Atmospheric and other small molecule gases, including anthropogenic waste products (*e.g.* carbon dioxide), can be viewed as sustainable building blocks to access value-added chemical commodities and materials. While transition metal complexes have been well documented in the reduction and transformation of these substrates, molecular complexes of the terrestrially abundant alkaline earth metals have also demonstrated promise with remarkable reactivity reported towards an array of industrially relevant gases over the past two decades. This review covers low oxidation state and hydrido group 2 complexes and their role in the reduction and transformation of a selection of important gaseous substrates towards value-added chemical products.

1. Introduction

Chemical transformations that exploit naturally occurring and abundant small-molecule synthons are pertinent to the development of sustainable and environmentally benign chemical processes. Gaseous small-molecule substrates can be used as building blocks in industry and academia to construct larger and more complex chemical commodities and materials. This has been exploited in a range of industrial processes using transition metals as catalysts to produce liquid hydrocarbons,[1, 2] ammonia,[3, 4] and other fundamental chemical products.[5, 6]

While the stoichiometric and catalytic functionalisation of these gaseous small molecule substrates was originally conceived to be a domain exclusive to the transition metals, an explosive and rapid development in the chemistry of the main-group elements in this area has seen a paradigm shift.[7, 8] Within this context, main-group element systems have been used successfully to cleave enthalpically strong polar and non-polar bonds, including those of dinitrogen[9] (N≡N, 946 kJ mol^{-1})[10] and carbon monoxide[11, 12] (C≡O, 1075 kJ mol^{-1}).[10] Molecular complexes of the terrestrially abundant s-block elements have been particularly successful in this regard and provide desirable alternatives to most transition metal-based reagents in the quest for next-generation, sustainable chemical practices.[13-15] The alkaline earth (group 2) metals, home to magnesium and calcium – rock-forming elements, have received considerable attention over the past few decades within the realm of small-molecule activation.[16-18] While the early chemistry of low oxidation state and hydrido alkaline earth metal complexes has been covered in several reviews, the explosive development of this field has seen significant recent breakthroughs that have placed the s-block at the forefront of main-group chemistry.[13-21]

This contribution provides an overview of the chemistry of structurally authenticated low oxidation state and hydrido group 2 complexes within the context of small molecule activation for the sustainable reduction and functionalisation of the industrially relevant gasses N_2, H_2, CO_2, N_2O, CO, C_2H_4 and SO_2. It is beyond the scope of this review to include other gaseous substrates, such as hydrocarbons and hydrofluorocarbons. The studies presented herein are limited to publications that have appeared before the beginning of 2024.

2. Low Oxidation State Group 2 Complexes

Main-group compounds that incorporate elements in low oxidation states have long been sought as targets for small molecule activation due to their propensity to readily undergo oxidation reactions with various organic and inorganic substrates.[7, 8] While low oxidation state chemistry involving the p-block elements has received considerable attention over the past few decades, molecular complexes of the group 2 elements in formally low oxidation states (+1 or 0) remain a significant synthetic challenge.[19-21] This is particularly true for the heavier members of the s-block, where no low oxidation state compounds have been reported for strontium and barium.

For beryllium, the lightest member of group 2, sub-valent beryllium(I) and beryllium(0) complexes are restricted to only a handful of examples (Figure 1, **1**–**4**).[22-26] Braunschweig and co-workers were the first to access a low oxidation state beryllium complex by utilising neutral cyclic (alkyl)(amino)carbene (CAAC) donors to stabilise a Be^0 centre ($\mathbf{1^R}$).[22] The reduction of the corresponding $BeCl_2$ supported CAAC adducts with KC_8 required an additional equivalent of the CAAC to give $\mathbf{1^R}$ (R = Me, Cy). This work was subsequently followed by the research group of Gilliard with the isolation of $\mathbf{1^{Et}}$ which was identified as a suitable reducing agent to access a rare example of a carbene–bismuthinidene complex.[23] Each complex ($\mathbf{1^R}$) possesses a linear geometry at the beryllium(0) centre with short Be–C bonds consistent with strong three centre two electron ($3c2e^-$) π-bonding across the C–Be–C moieties. The controlled oxidation of $\mathbf{1^{Et}}$ with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) provided a cationic beryllium(I) radical complex **2** supported by the $[Be(TEMPO^*)_3]^-$ (TEMPO* = 2,2,6,6-tetramethylpiperidin-1-olate) counterion.[24] The geometry at the Be(I) centre in **2** is slightly bent and the unpaired electron was calculated by density functional theory (DFT) to reside in a 2p orbital at beryllium. Further exploration of the chemistry of [**2**]$[Be(TEMPO^*)_3]$ with $NaBAr^F_4$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) resulted in exchange of the counter anion to give [**2**]$[BAr^F]$, where the identity of the radical cation remains unchanged. A neutral beryllium(I) radical (**3**) was isolated shortly after this report by employing mixed CAAC/CAAC–H ligands on a beryllium(II) monohalide precursor which could be subsequently reduced with lithium sand.[25] It is important to note that the assignment of these beryllium species as low oxidation state has been a debated topic,[27, 28] where recent computational studies have contradicted earlier findings and suggest that the unpaired spin density is significantly localised at the carbene donors, and as such, the +2 oxidation state for the metal centre in **1**–**3** may be a more appropriate description.[29, 30] While other attempts have been made to access 'true' low oxidation state mono-metallic beryllium(I) and beryllium(0) species using conventional organometallic ligands, isolation of the desired reduction products has not been forthcoming.[31, 32] Despite this, an array of complexes incorporating Be–metal bonds have been reported through coordination and salt metathesis approaches.[33-35] It was only recently that a diberyllocene complex (**4**), comprising of a Be–Be bond with each Be centre capped by η^5-Cp (Cp = cyclopenatadienyl) ligands, was reported by Aldridge and Boronski.[26] Key to the reduction of **4** is the utilisation of a mild reducing agent, namely the dimagnesium(I) complex **6** reported by our research group in 2007 (*vide infra*).[36] The isolation of **4** is perhaps surprising given that earlier attempts by Carmona *et. al.* to access sub-valent beryllium(I) species from the reduction of Be(Cp*)(Cl) (Cp* = 1,2,3,4,5-pentamethylcyclopenatadienyl) with potassium naphthalenide were unsuccessful and resulted in the formation of $Be(Cp^*)_2$.[37] This suggests that π-donor ligands to coordinatively saturate the Be(I) centre, appropriate choice of leaving groups (*i.e.* KCp *versus* KCl), and mild reducing agents, all play a pivotal role in the isolation of diberyllium(I) species. In an attempt to access an ionic beryllium(I) complex, Hill and co-workers reported that reactions of $[(SiN^{Dipp})BeClLi]_2$ (SiN^{Dipp} = $[(CH_2SiMe_2NDipp)_2]^{2-}$) with the heavier alkali metals gave reduction of the lithium(I) cation to lithium metal and formation of the corresponding $[(SiN^{Dipp})BeCl\mathbf{M}]_2$ complex (**M** = Na – Cs).[38] Each alkali metal (**M**) in $[(SiN^{Dipp})BeCl\mathbf{M}]_2$ was amenable to reduction by the successively heavier alkali metal reagent, further demonstrating the unusual characteristics of these beryllium(II) species under reducing conditions. In contrast, a wealth of low oxidation state dimagnesium(I) complexes (**5**–**34** and **40**) have been isolated using relatively simple *N*-chelating ligands.

The first molecular low oxidation state group 2 complexes were the dimagnesium(I) species **5** and **6** stabilised by a guanidinate or β-diketiminate ligand, respectively.[36] These complexes have since been exploited in modern main-group chemistry for their role as potent reducing agents to activate small-molecule substrates and to access other low oxidation state complexes,[17] including diberyllocene **4** (*vide supra*).[26] Since this initial study, numerous dimagnesium(I) complexes utilising variants of the β-diketiminate ligands have been reported (*e.g.* **5**–**24**).[36, 39-45] The general route to these dimagnesium(I) species involves the reduction of corresponding magnesium(II) iodide precursors ($[Mg(BDI^{Ar})(I)(OEt_2)_n]$, $BDI^{Ar} = [HC(MeCNAr)_2]^-$, Ar = arene, n = 0 or 1) with alkali metal reagents in toluene/diethyl ether mixtures. It is proposed that *in situ* generated magnesium(I) radicals combine to afford the Mg–Mg bond in these dimagnesium(I) complexes. Existence of transient radical intermediates is further supported by the mechanochemical reduction of magnesium(II) iodide $[Mg(BDI^{Dipp})(I)(OEt_2)]$ with K/KI to give a deep purple powder of "$[(BDI^{Dipp})Mg\bullet]$" which quickly assembles to $\mathbf{6^{Me}}$ when dissolved in solution.[46] Furthermore, scrambling of a mixture of **5** and $\mathbf{6^{Me}}$ under photolytic conditions (blue light radiation: λ=456 nm, 50 W) was observed to give the mixed guanidinate/β-diketiminate system **5'**.[47, 48] A similar scrambling reaction has also been observed between $\mathbf{6^{Me}}$ and **10** to yield $[(BDI^{Mes})Mg–Mg(BDI^{Dipp})]$ under thermal conditions.[49] The addition of Lewis bases (*i.e.* DMAP) to these dimagnesium(I) species induces an elongation of the Mg–Mg bonds by coordinatively saturating the Mg(I) centre(s) thereby lowering the bond dissociation energy and enhancing their reactivity (*vide infra*). For unsymmetrical dimagnesium(I) complexes, where, for example, only one Mg(I) centre is bound by a Lewis base, the reactivity is enhanced further through polarisation of the Mg–Mg bond. Although larger *N*-aryl substituents generally act to decrease reactivity, the combination of a large aryl group (Dipep) with a mild Lewis base (TMEDA) in the reduction of $[Mg(BDI^{Dipep})(I)]$ with Na (mirror) was shown to crowd the transient Mg(I) centre such that reduction of the reaction solvent occurs rather than the expected homo-coupling to **7**.[39] Thus, it was found that simple modifications to the β-diketiminate framework could be made to vary the stability and structure of these dimagnesium(I) complexes. In the case of $[Mg(BDI^{*Dipep})(I)]$ ($BDI^{*Dipep} = [HC(^tBuCNDipep)_2]^-$), potassium (mirror or K/KI) reduction gives an unusual dimagnesium(I) complex **24** comprising 2- and 3-coordinate magnesium(I) centres.[40] Exclusively 2-coordinate dimeric magnesium(I) systems have previously been accessed using bulky monoanionic, monodentate ligands (**25**–**27**), increasing diversity amongst the range of more commonly reported 3- and 4-coordinate neutral dimagnesium(I) complexes.[50] The reduction of $[Mg(BDI^{*Dipep})(I)]$ was later extended to use of 5% w/w

Na/NaCl as the reducing agent, providing facile access to the first mixed magnesium(0)/sodium(I) system **28**. This demonstrates that the reducing agent can have a profound influence on the outcome of the reaction (K/KI: **24**, Na/NaCl: **28**).[51] These alkali metal dispersions (5% w/w, Na/NaCl or K/KI), recently introduced by our research group, have been widely implemented in low oxidation state organometallic chemistry as effective stoichiometric reducing agents to access metal complexes that are susceptible to over-reduction.[52] Remarkably, benzene solutions of **28** were found to decompose at room temperature to give BDI^{*Dipep}Na, Na^0, Mg^0 and **29**, where the latter contains a Mg(0) centre sandwiched between two Mg(I) fragments.[51] Other examples of low oxidation state mixed s-block systems (**30**–**34**) utilise dianonic ligand sets to support the Mg(I) centres, where counter-cations are required to charge-balance the anionic Mg(I) components.[51, 53-56] These dianionic ligands have been comparatively less studied and are becoming increasingly popular to access heterobimetallic dimagnesium(I) complexes for synergistic small molecule activation. Recently, Hill *et. al.* detailed the isolation of an ionic dimagnesium(I) complex **33** where two [Mg(SiN^{Dipp})]$^{-}$ units are weakly bonded and contain bridging π(arene) interactions to two Na(I) cations.[55] A subsequent study showed that **33** is strongly reducing such that sodium metal and Mg$_2$(SiN^{Dipp})$_2$ are formed in the presence of mild bases (reduction to Na^0 also seen by **28**).[57] Our research group published a complementary ionic dimagnesium(I) complex **34** which is supported by the [NON^{Trip}]$^{2-}$ ligand system ([NON^{Trip}]$^{2-}$ = 4,5-bis(2,4,6-triisopropylanilido)-2,7-di-ethyl-9,9-dimethyl-xanthene) and potassium(I) counter-cations.[58] As these transient (neutral and anionic) magnesium(I) radicals couple in solution or undergo further reduction processes, mechanochemical methods (*i.e.* ball-milling) have been explored to access monomeric magnesium(I) systems. For example, **35** is supported by amidinate and CAAC ligands and was accessed by a ball-milling approach. While the majority of unpaired electron spin density resides on the CAAC ligand, a small contribution from the magnesium centre was noted.[30]

For calcium, the only example of an isolated low oxidation state species is the inverse sandwich complex **36**, reported by Westerhausen and co-workers.[59] While explicit examples of low oxidation state strontium(I) and other calcium(I) complexes have not yet been reported, synthons that render access to these fleeting low oxidation state species have been documented (*i.e.* **37** and **38**).[60-62] Noteworthy is a recent report by Harder *et. al.* on the activation of polyaromatics by an *in situ* generated Mg(I)–Ca(I) complex, [(BDI^{*Dipep})Mg–Ca(BDI^{Dipep})] (**39**).[63] This was subsequently followed by the reactions of the dimagnesium(0)/disodium(I) complex **28** with alkaline earth metal complexes **M**(HMDS)$_2$ to access homobimetallic (**M** = Mg) and heterobimetallic (**M** = Ca – Ba) alkaline earth metal-metal bonded systems **40**–**43**.[64] The heavier heterobimetallic complexes **41**–**43** contain Mg$^{\delta-}$–**M**$^{\delta+}$ bonds that are largely electrostatic, consistent with Mg(0) and **M**(II) metal centres. Currently, the reactivity of calcium(I) and strontium(I) intermediates remain only accessible by reactions with their corresponding synthons (*vide infra*).[60-62]

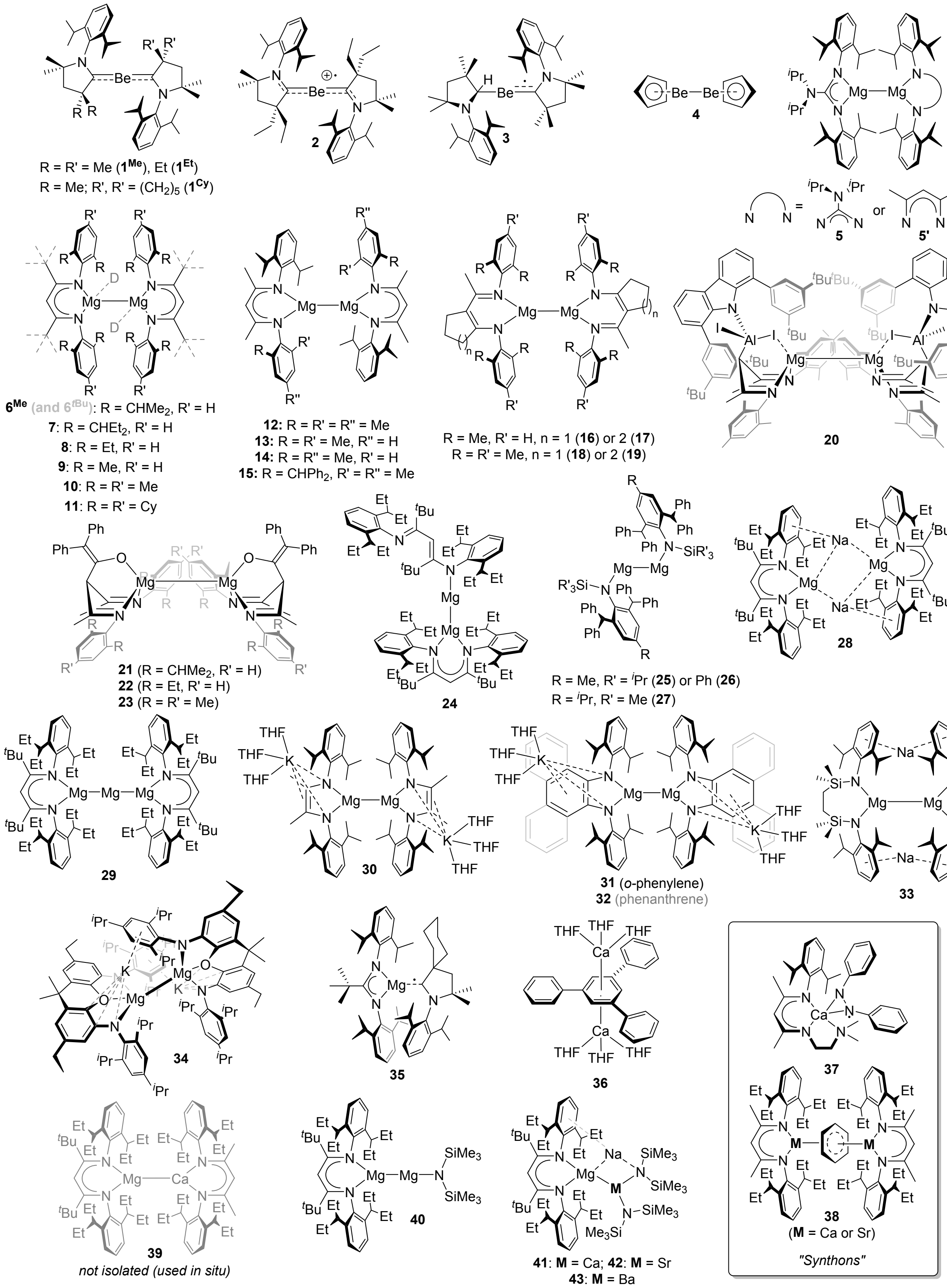


Figure 1: Library of reported low oxidation state group 2 complexes.

3. Group 2 Hydride Complexes

Molecular main-group hydrides have long been exploited by synthetic inorganic chemists for their ability to function as catalysts.[65] In contrast to transition metals, main-group elements display limited redox flexibility which challenges the catalytic reduction of small-molecules by low oxidation state systems. Main-group hydrides offer a viable route to design catalysts where the main-group element remains in a single oxidation state. The reduction of small molecule substrates by these hydrides is generally dominated by insertion and elimination processes, where the barrier for reduction and oxidation is not limited by the large ionisation energies of the main-group elements.[66] Within this context, the group 2 elements have received considerable attention and several group 2 hydride complexes have been implicated in catalysis (*vide infra*).[13-15, 65-67] Unlike low oxidation state group 2 systems, isolable hydrido complexes exist for each non-radioactive element of the alkaline earth metals. These group 2 hydride complexes can be accessed by utilising sterically demanding ligands to protect the M–H bond. This section will detail well-defined examples of molecular group 2 hydride complexes.

For beryllium, the smallest group 2 element, a limited array of hydride complexes has been reported (Figure 2, **44**–**54**). In 1983, the first structurally authenticated example of a terminal beryllium hydride (**44**) was isolated by Shearer and co-workers.[68] As an extension of this work, the same group reported the synthesis of an ionic beryllium(II) hydride complex **45** that assembles as a dimer with bridging hydride ligands.[69] These complexes remained as scientific curiosities until Parkin and Han later detailed a monomeric beryllium(II) hydride (**46**) supported by a tris(pyrazolyl)hydroborato ligand. The reactivity of **46** was explored towards halides (CH_3I, I_2) and chalcogenides (H_2S, S_8) to access insertion products indicating that these species could harness useful functionalities.[70]

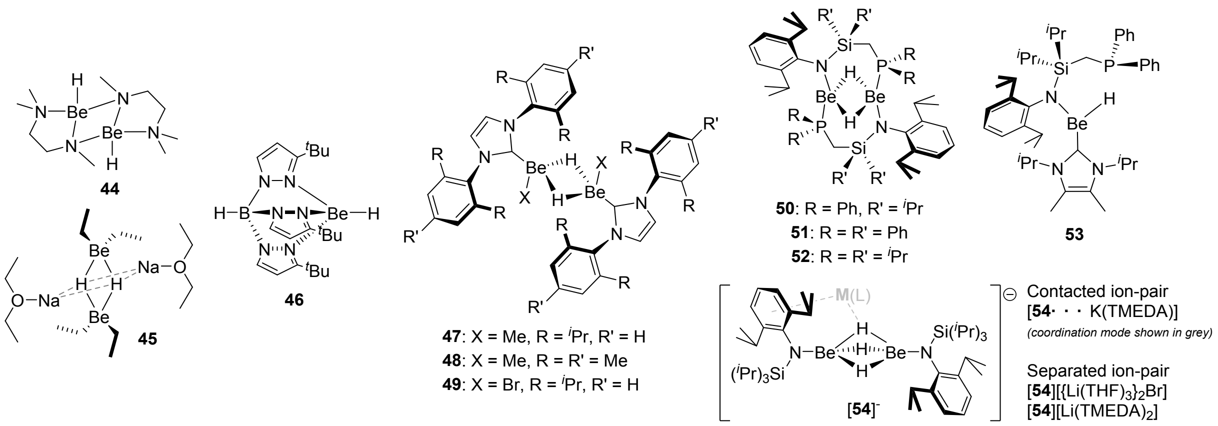


Figure 2: Library of reported beryllium(II) hydride complexes.

Despite these initial reports, structural investigations into the isolation of beryllium(II) hydride complexes remained dormant for almost two decades. It was only until Hill and co-workers isolated **47**, which comprised a 3-coordinate Be(II) centre coordinated by an *N*-heterocyclic carbene (NHC), methyl and hydride ligand, that these systems started to regain attention.[71] In an independent report by our research group, we showed that the architecture of the neutral NHC and monoanionic ligands could be modified to access similar beryllium(II) hydride complexes, **48** and **49**.[32] More recently, Hadlington and Szilvás demonstrated that tethered phosphine-functionalised amides were suitable ligand sets to access a range of beryllium(II) hydrides **50–52**.[72] Addition of an NHC to **50** was shown to furnish a monomeric complex **53** where the Be(II) centre is tricoordinate. These hydrides were shown to be potent reducing agents towards unsaturated small-molecules, such as carbon dioxide and carbon monoxide (*vide infra*). Hadlington and co-workers were also able to access ionic beryllium(II) hydrides utilising a bulky monanionic amide ligand to afford [**54**]$^-$ which contains a Be_2H_3 motif.[73] The structure of [**54**]$^-$ was influenced by the counter cation, where the potassium(I) or lithium(I) systems existed as contacted ion-pairs ([**54**···K(TMEDA)]) or separated ion-pairs ([**54**][$\{Li(THF)_3\}_2Br$] and [**54**][$Li(TMEDA)_2$]), respectively.

The chemistry of molecular magnesium(II) hydride systems remains an incredibly active area of scientific research and constitutes the majority of studies of hydrides of the alkaline earth metal complexes. Also, noteworthy is the extensive research into the application of MgH_2 and related polynuclear magnesium(II) hydride materials in hydrogen storage, which will not be covered here.[74-76] The successful utilisation of the β-diketiminate ligand system to stabilise magnesium(II) hydride complexes has been fundamental to the development of this field. Since the initial isolation of **55** by our research group,[43] combinations with Lewis bases and acids, variations in the aryl groups, and modifications to the ligand framework, have been explored to assess their implications on the structures and reactivities of formed neutral magnesium(II) hydride complexes (Figure 3, **55–81**). Most examples of magnesium(II) hydride complexes supported by β-diketiminate ligands form dimeric aggregates with tetracoordinate Mg(II) centres.[39, 41, 43, 77] Even in the presence of THF, the dimeric construct of **55** remains intact while the Mg(II) centres become pentacoordinate (L = THF, [**55**·$(THF)_2$]).[43, 78] However, the introduction of bulky Lewis bases (*i.e.* L = TMC[79] or L = DMAP[41], TMC = 1,3,4,5-tetramethylimidazol-2-ylidene) and/or tuning the steric bulk of the aryl group and backbone has been shown to enforce a monomeric arrangement in the solid-state.[51, 80] For example, modification of the backbone substituent from a methyl (**57**, BDI^{Dipep})[39] to a *tert*-butyl group (**63**, BDI^{*Dipep})[51] for the Dipep system inhibits the dimerization of two molecular units. In contrast, decreasing the steric profile of the aryl group can provide entry to larger aggregates, such as trimeric magnesium(II) hydride **61**.[81] Addition of the Lewis acid $B(C_6F_5)_3$ to $[Mg(BDI^{Dipp})(\mu\text{-}H)]_2$ (**55**) has been shown to render access to a cationic "$[Mg(BDI^{Dipp})]^+$" moiety ([**66**···$HB(C_6F_5)_3$]) with a weak Mg···H interaction that can facilitate the catalytic hydroboration of carbon dioxide (*vide infra*).[82] An alternative route to ionic hydride complexes [**67**][$Al(OC(CF_3)_3)_4$] and [**68**][$Al(OC(CF_3)_3)_4$] from [$BDI^{Dipp}Mg\cdots C_6D_6$][$Al(OC(CF_3)_3)_4$] has also been presented by Hill and co-workers.[83] Joining two *β*-diketiminate ligands through appropriate alkyl or aryl *N*,*N*-linkers has been exploited by the research groups of Harder and Kretschmer to access **69**,[75] **70**[74] and **74**,[84] and **71–73**,[85] respectively. A fused β-oxo-δ-diiminate ligand was recently used to gain entry to a tetranuclear magnesium(II) hydride complex (**75**) which contains a rare example of a four-coordinate hydride ligand in a near square planar geometry.[86] Variants of the β-diketiminate ligand that introduce chirality into the magnesium(II) hydride complex have also been reported (*e.g.* **76** and **77**).[87] Recently our research group detailed the isolation of mixed s-block hydrides **78–81** from the addition of **M**HMDS (**M** = K – Cs, HMDS = bis(trimethylsilyl)amide) complexes to [Mg(BDI$^{\mathrm{Dipp}}$)(μ-H)]$_2$ (**55**).[88] Surprisingly, the reaction between **55** and NaHMDS rendered access to a tetranuclear aggregate (**81**) instead of the target species (Na$_2$[Mg(BDI$^{\mathrm{Dipp}}$)(H)]$_2$). While the lighter complexes **78** and **79** were readily susceptible to decomposition, the structural identity of the cesium/magnesium system **80** remained intact in the solid-state and in solution under ambient conditions. Earlier reports of these mixed s-block hydride systems involved relatively simple ligand sets, such as the diisopropylamide (**82** and **83**)[89-91] and bis(trimethylsilyl)amide (**84–86**) ligands,[92, 93] where variation was achieved through the group 1 metal cation and its coordination environment. In an attempt to access a low oxidation state magnesium(I) complex, the reduction of magnesium(II) precursor [Mg(NON$^{\mathrm{Dipp}}$)(THF)] (NON$^{\mathrm{Dipp}}$ = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tertbutyl-9,9-dimethyl-xanthene) with KC$_8$ was shown to afford potassium hydrido-magnesiate **87**.[94] A rational synthetic route to **87** was presented from addition of an excess of potassium hydride to [Mg(NON$^{\mathrm{Dipp}}$)(THF)]. Phosphinimino amide ligands, which have a similar structural motif to the β-diketiminate framework, were introduced to magnesium(II) hydride systems **88–91** by Cui and co-workers.[95-97] Different variations in the *N*- and *P*-substituents were explored and the complexes were shown to be active catalysts in the hydroboration of pyridines and carbonyls. Alongside β-diketiminate systems, amidinate ligands have also seen success in the isolation of several hydride complexes (**92–96**).[87, 98, 99] Notably, complexes **92** and **93** have been implicated in the catalytic hydroboration of carbodiimides.[98] Other bidentate and tridentate ligands that have been used to stabilise magnesium(II) hydride complexes include the [Ph$_2$PCHPPh$_2$(fluorenylidene)]$^-$ (**97**)[100] and tris(pyrazolyl)methanide ligands (**98**).[101] Parkin and co-workers have detailed the use of the tris[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl (tism) ligand to give magnesium(II) hydride **99**,[102] which reacts with B(C$_6$F$_5$)$_3$ to form a cationic complex [Mg(tism)]$^+$ with no distinct Mg···H···B interaction to the counter-anion [HB(C$_6$F$_5$)$_3$]$^-$ unlike that in [**66**···B(C$_6$F$_5$)$_3$].[103] A series of polydentate ligands have been prepared by the research group of Okuda that afforded mono- and di-cationic magnesium(II) hydride complexes.[104-110] The monomeric penta- and tetra-coordinate Mg(II) hydrides, **100**[105, 106, 110] and **101**,[107] are complex ion-pairs with “[AlR$_3N$]$^-$” (R = Et, ^{i}Bu) and “[Al^{i}Bu$_3N$]$^-$” moieties, respectively. Similar to **99**, the addition of a Lewis acid (BPh$_3$) to **100** (R = ^{i}Bu) forms a separated ion-pair to render a [Mg(Me$_3$TACD·Al^{i}Bu$_3$)(thf)]$^+$ cation and a [HBPh$_3$]$^-$ anion.[105] A separated ion-pair was also formed for dicationic complex [**102**]$^{2+}$ which is charge-balanced by two [B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$^-$ anions.[109] For **103**[108] and **104** (Harder and co-workers),[111] the synthesis of magnesium(II) hydride complexes from Mg(HMDS)$_2$ and phenylsilane resulted in complexation of a molecule of Mg(HMDS)$_2$ to the MgH$_2$ unit, supported by the 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me$_4$TACD) or *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine (PMDTA) ligand, respectively. Hydride complexes **105–**

108 were also accessed by adopting a similar synthetic approach with neutral NHC or 1,4-diazabicyclo[2.2.2]octane (DABCO) ligands.[111, 112] By altering the reaction conditions that gave **104**, the PMDTA ligand has been used to give the larger magnesium(II) hydride aggregates, **109** and **110**.[111] Larger polynuclear magnesium(II) hydride and heavier alkaline earth hydride cluster complexes (*i.e.* **111**[113] and **112**[114]) have also been reported and will not be discussed in detail here.[115-117]

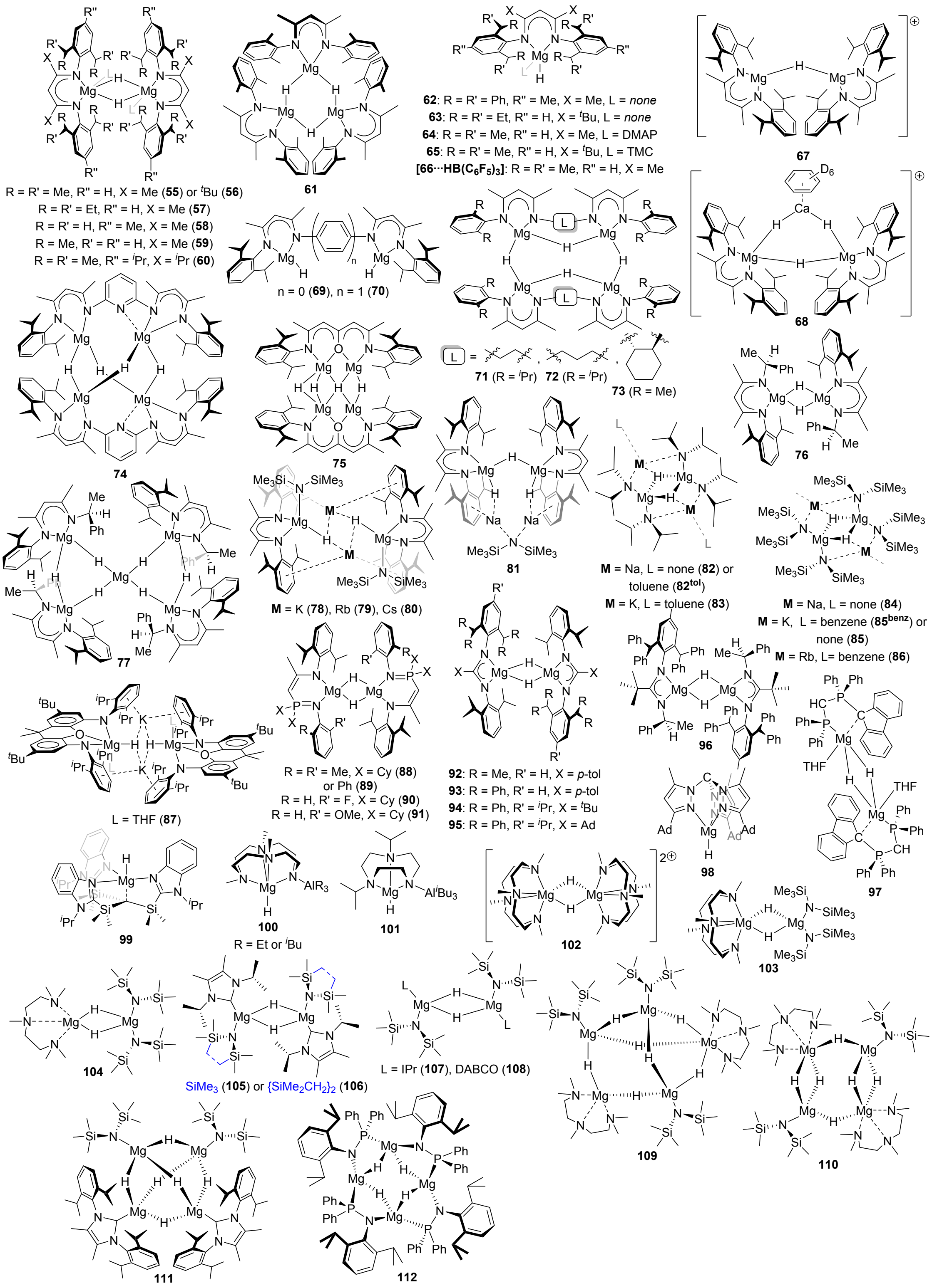


Figure 3: Library of reported magnesium(II) hydride complexes.

The quest for calcium(II) hydride complexes, and hydrides of the heavier members of the alkaline earth metals, is challenged by a higher degree of ligand specificity and competitive redistribution processes.[118-120] Although calcium(II) hydride complexes have been comparatively less explored than their magnesium(II) counterparts, they have also been implicated in a wide-range of catalytic applications.[66, 121-124] As for magnesium(II) hydride complexes, the β-diketiminate ligand framework has been implemented in the chemistry of heavier calcium(II) hydride systems to access **113–119** (Figure 4).[61, 125-128] While less success has been had through modification of the aryl substituents, the Dipp[126-128] and Dipep[61, 125] groups have proven effective to access non-solvated[61, 126] and solvated[125, 127, 128] calcium(II) hydride complexes. As with the analogous magnesium(II) hydride complex **55**, the addition of a Lewis acid to **115** provides facile entry to the contacted ion-pair [**120**···HBR_3] (R = C_6F_5).[82] For the amidinate ligand set, examples of dimeric and trimeric hydrido calcium(II) complexes have been reported.[129] In the absence of coordinating solvents, dimeric complexes **121** and **122** were formed,[129] where the ligand adopts an (*N*,aryl)-coordination mode, as opposed to the traditional *N*,*N*-coordination observed in related magnesium(II) hydride complexes **92**–**96**.[87, 98, 99] Contrastingly, the presence of ethereal solvents (*i.e.* Et_2O or THF) provided the corresponding trimers **123** and **124**.[129] Akin to magnesium(II) hydride **87**,[94] reduction of $[Ca(NON^{Dipp})(OEt_2)_2]$ with KC_8 afforded the heavier calcium(II) hydride analogue **125**, which could also be isolated from the reaction of $[Ca(NON^{Dipp})(OEt_2)_2]$ with an excess of KH. The utilisation of a sterically bulky cyclopentadienyl ligand in this area witnessed the isolation of a coordinatively saturated dimeric calcium(II) hydride complex, **126**.[130] The aforementioned neutral and monoanionic ligands reported by Okuda and co-workers have also been successfully applied to the chemistry of calcium(II) hydride complexes. Dicationic complexes [**127**]$^{2+}$ [131, 132] and [**128**]$^{2+}$ [124] comprise a dimeric Ca_2H_2 unit that is supported by the corresponding polydentate ligand and charge-balanced by two counter-anions ([**127**][$PhCHSiPh_3$]$_2$, [**127**][BAr_4]$_2$, [**127**(THF)][$B(C_6H_3\text{-}3,5\text{-}Me_2)_4$]$_2$, or [**128**][$BAr_4$]$_2$; Ar = C_6H_3-3,5-Me_2 or C_6H_3-4-^{n}Bu). For [**127**]$^{2+}$,[131] a monocationic variant [**129**][BAr_4] containing a dimeric Ca_2H_3 moiety was also isolated and its conversion to the dicationic complex could be achieved from a direct reaction with [NEt_3H][BAr_4].[133] In addition, a related monocationic trihydride supported by the Me_4TACD ligand has been reported by the same group ([**130**][$SiPh_3$]) and was shown to undergo exchange with deuterium (*vide infra*).[134] A monoanionic derivative of the ligand in [**130**]$^+$ was used to access complexes [**131**]$^+$[A]$^-$ as separated ion-pairs ([**A**]$^-$ = [$N(SiMe_3)(SiPh_3)$]$^-$, [Ph_3SiH_2]$^-$ and [$(Ph_2SiH)CHPh$]$^-$).[135] Recently, a tetranuclear calcium(II) hydride complex [**132**][BAr_4]$_2$ (Ar = C_6H_3-3,5-Me_2) was reported and shown to contain a highly symmetric $[Ca_4H_6]^{2+}$ core.[136]

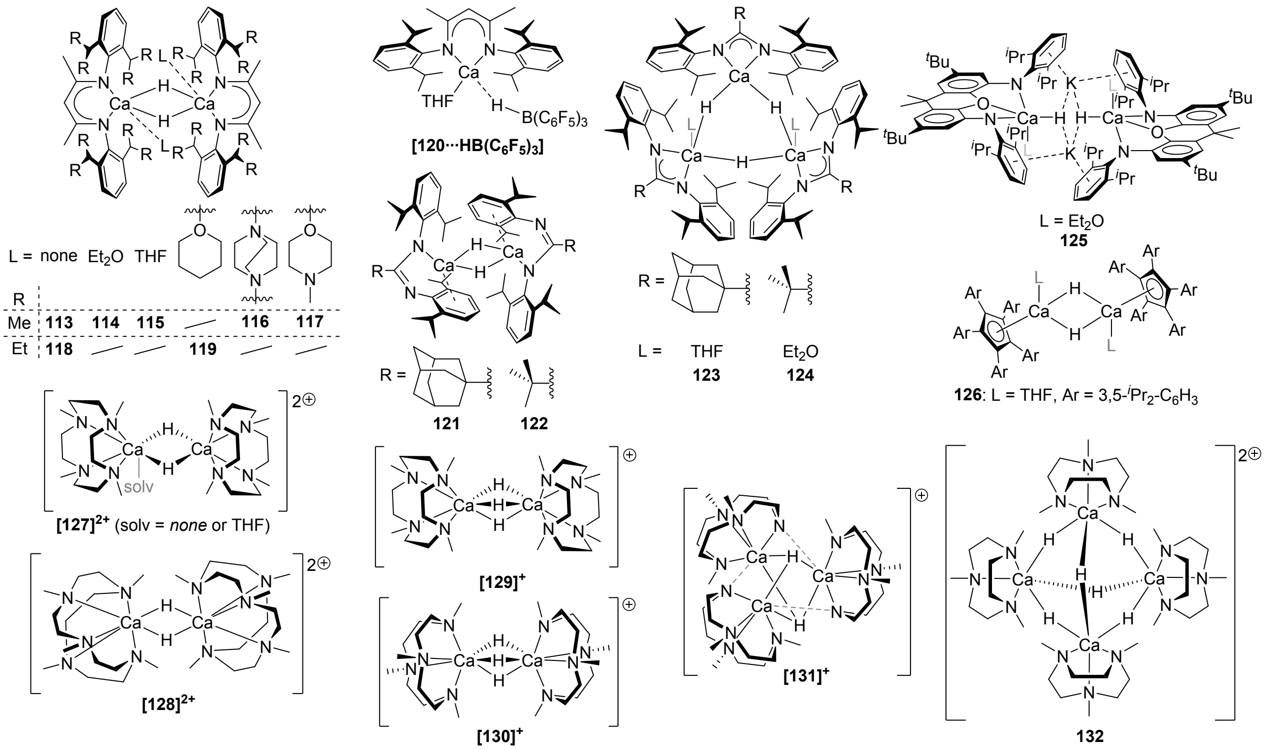
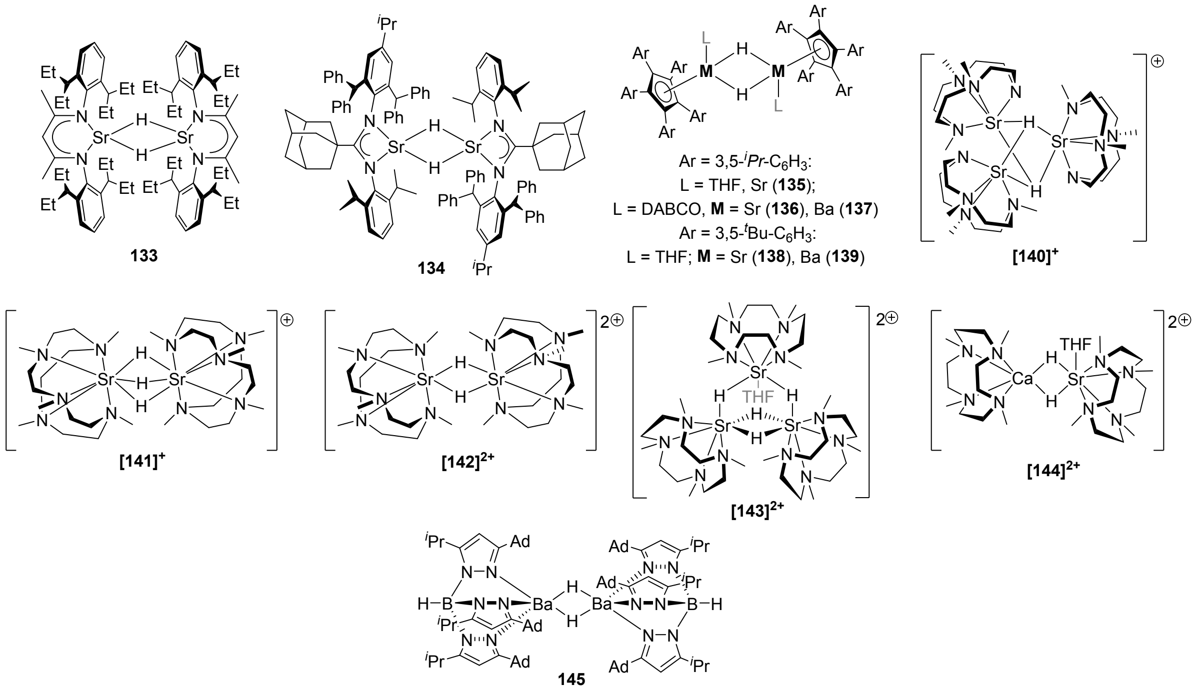


Figure 4: Library of reported calcium(II) hydride complexes.

Although outside the scope of this review, barium(II) and strontium(II) hydrides were initially restricted to large polynuclear cluster complexes (*e.g.* $[\mathrm{Sr_6H_9\{HMDS\}_3\bullet\{PMDTA\}_3}]$[115] and $[\mathrm{Ba_7H_7\{HMDS\}_7}]$),[116] with fewer examples of well-defined dinuclear–tetranuclear hydrides reported for these heavier group 2 elements relative to their lighter congeners. This is perhaps unsurprising due to their higher degree of ionicity and tendency to engage in Schlenk-type equilibria to give more stable saline hydrides, $\mathrm{AeH_2}$.[118-120] Within this context, the β-diketiminate and amidinate ligands have proven less effective with the only examples of neutral complexes being dimeric strontium(II) hydrides, **133**[137] and **134**.[99] In contrast, bulky cyclopentadienyl ligands have successfully stabilised an array of dimeric strontium(II) and barium(II) hydride complexes (**135**–**139**),[130] with the coordination sphere of the group 2 metal saturated by neutral THF or DABCO ligands. Okuda and co-workers have also applied neutral and monoanionic polydentate ligands to the chemistry of strontium(II) hydrides to access cationic and dicationic complexes **140**–**143**.[138-140] For [**140**]$^+$, a structure reminiscent of the lighter calcium(II) analogue[135] [**131**]$^+$ is formed with a $\mathrm{Sr_3H_2}$ trinuclear aggregate charge-balanced by the $[\mathrm{SiPh_3}]^-$ or $[\mathrm{(Ph_3Si)CPh_2}]^-$ counter-anions.[138] The cationic complexes [**141**]$^+$ and [**142**]$^{2+}$ could be formed from the addition of $\mathrm{H_2}$ (1 atm) to the precursor complexes $[\mathrm{(Me_5PACP)Sr(CH_2Ph)}][\mathrm{BAr_4}]$ ($\mathrm{Me_5PACP}$ = 1,4,7,10,13-pentamethyl-1,4,7,10,13-pentaazacyclopentadecane, Ar = $\mathrm{C_6H_3}$-3,5-$\mathrm{Me_2}$ or $\mathrm{C_6H_4}$-4-^{n}Bu), where [**141**]$^+$ converts to [**142**]$^{2+}$ in THF over 4 hours.[139] Utilising the $\mathrm{Me_4TACD}$ ligand system, a trinuclear aggregate [**143**]$[\mathrm{B(C_6H_3\text{-}3,5\text{-}Me_2)_4}]_2$ and a mixed calcium-strontium hydride complex [**144**]$[\mathrm{B(C_6H_3\text{-}3,5\text{-}Me_2)_4}]_2$ could also be isolated.[140] Cheng *et. al.* were the first to access a dinuclear barium(II) hydride complex by employing a sterically bulky tris(pyrazolyl)borate ligand (**145**), where the Ba–H bond was shown to be reactive towards unsaturated substrates including carbon monoxide (*vide infra)*.[141]



Ar = 3,5-^{i}Pr-C_6H_3:
L = THF, Sr (**135**);
L = DABCO, **M** = Sr (**136**), Ba (**137**)
Ar = 3,5-^{t}Bu-C_6H_3:
L = THF; **M** = Sr (**138**), Ba (**139**)

Figure 5: Library of reported strontium(II) and barium(II) hydride complexes.

4. Nitrogen Fixation

Nitrogen, an element essential to life and the primary constituent (~78 %) of the Earth's atmosphere, exists as a diatomic molecule in the gaseous phase with a strong non-polar N≡N bond (BDE = 946 kJ mol^{-1}).[10] While most living organisms do not possess the capability to reduce dinitrogen, a minority of bacteria have evolved to produce ammonia utilising nitrogenase enzymes.[142] Ammonia (NH_3) remains an essential feedstock in agriculture industries as a primary component in the production of fertilisers.[143] Current industrial processes for the production of ammonia from dinitrogen (*i.e.* the Haber-Bosch process) require harsh operating conditions, consume large amounts of energy, and generate CO_2 and N_2O as by-products, which are detrimental to the environment.[144, 145] Although the reduction of dinitrogen has been achieved by numerous d-block and f-block metal complexes,[146-151] limited success has been had by systems incorporating s-block or p-block elements.[9] Within this context, p-block systems that have been documented to activate N_2 are exclusive to low oxidation state boron[152-156] and carbon based species.[157] For the s-block, only three complexes (**146–148**)[56, 61, 158] have been able to facilitate the reduction of N_2, generating the N_2^{2-} ligand and overcoming the formidable energy barrier to partially cleave the N≡N bond (Figure 6).

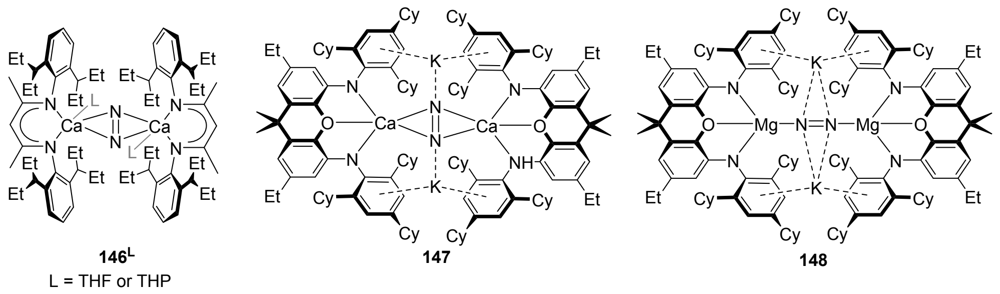
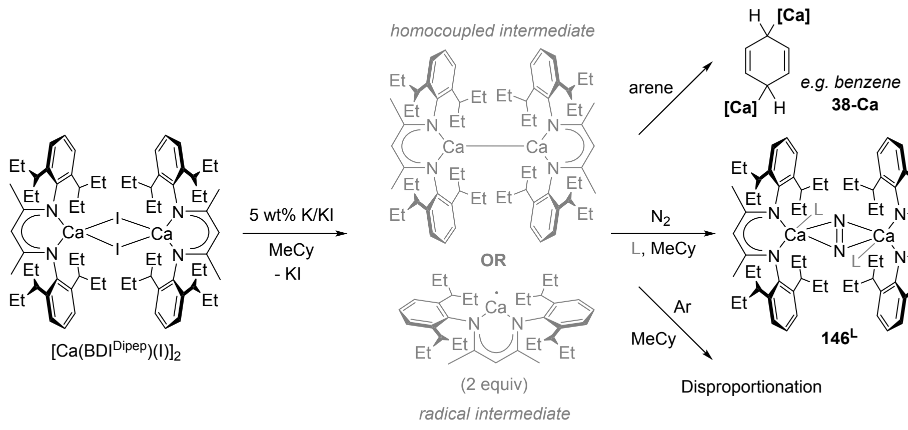


Figure 6: Nitrogen fixation by transient low oxidation state group 2 complexes to access **146–148**.

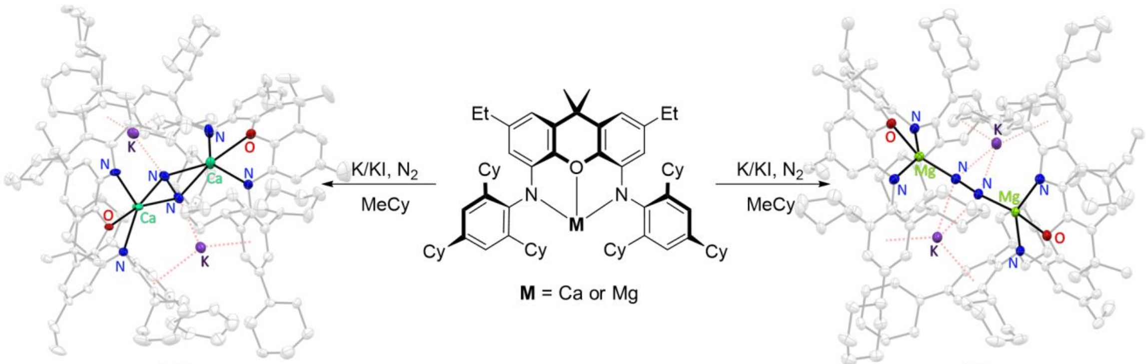
Harder and co-workers were the first to report the successful capture of dinitrogen by the reduction of $[Ca(BDI^{Dipep})(I)]_2$ with K/KI in methylcyclohexane (Scheme 1).[61] It is proposed that the initially targeted calcium(I) complex “$[Ca(BDI^{Dipep})]_2$” is an extremely potent reducing agent such that it reacts on formation to reduce the reaction medium (*i.e.* solvent or atmosphere). For example, reduction of $[Ca(BDI^{Dipep})(I)]_2$ in an arene solvent or under an atmosphere of argon resulted in the reduction of the arene or disproportionation processes, respectively. It is unclear whether the low oxidation state intermediate exists as a group 2 centred radical or a homo-coupled Ca–Ca bonded system. We suggest that by frustrating the homocoupling of the generated (and highly reactive) group 2 radicals by steric means, the opportunity to promote the cleavage of strong chemical bonds is expedited (*e.g.*, as in N_2). The N_2^{2-} ligand in **146^L** (L = THF or THP) could be protonated by THF (60 °C, 12 hrs) to form diazene N_2H_2 which subsequently undergoes disproportionation to N_2 and N_2H_4, showing promise for the successful conversion of nitrogen into value-added products *en route* to ammonia by alkaline earth metal complexes.



Scheme 1: Reduction of $[Ca(BDI^{Dipep})(I)]_2$ with K/KI in methylcyclohexane to access **146**.

Our research group wanted to assess the viability of accessing an ionic variant of **146** by using a rigid diamide ligand scaffold ($[NON^{TCHP}]^{2-}$ = 4,5-bis(2,4,6-tricyclohexylanilido)-2,7-di-ethyl-9,9-dimethyl-xanthene). As such, the reduction of “$[Ca(NON^{TCHP})]$” (solvate free) by K/KI (3 equivalents) was attempted in methylcyclohexane (Scheme 2).[158] Red crystals of the target species **147** were isolated and identified to contain an analogous N_2^{2-} ligand with side-on coordination to the Ca(II) centres.

Extension of this reduction protocol to the lighter magnesium(II) analogue "[Mg(NON^{TCHP})]" was also investigated.[56] Red crystals of **148** were isolated and shown in the solid-state to contain the N_2^{2-} ligand with an 'end-on' coordination mode to the Mg(II) centres. This was identified by DFT calculations to exist in a triplet ground-state where the N_2 π*-molecular orbitals (MOs) are singly occupied, resulting in appreciable paramagnetic character. It is noteworthy that repeating these reactions under argon does not provide entry to a low oxidation state complex, and instead leads to decomposition, indicating that transient radical intermediates are extremely susceptible to disproportionation or other complex processes. We also propose that the steric profile of the [NON^{TCHP}]$^{2-}$ ligand prevents homo-coupling of the transient radical intermediates, thereby promoting reactivity with dinitrogen. Evidence for this hypothesis was supported by the reduction of the smaller solvate free magnesium(II) complex "[Mg(NON^{Trip})]" which undergoes dimerization to access the dimagnesium(I)/dipotassium(I) system **34** (*vide supra*).[58] The exclusion of arene and ethereal solvents was also deemed essential in the aforementioned reduction procedures to prevent these decomposition pathways.



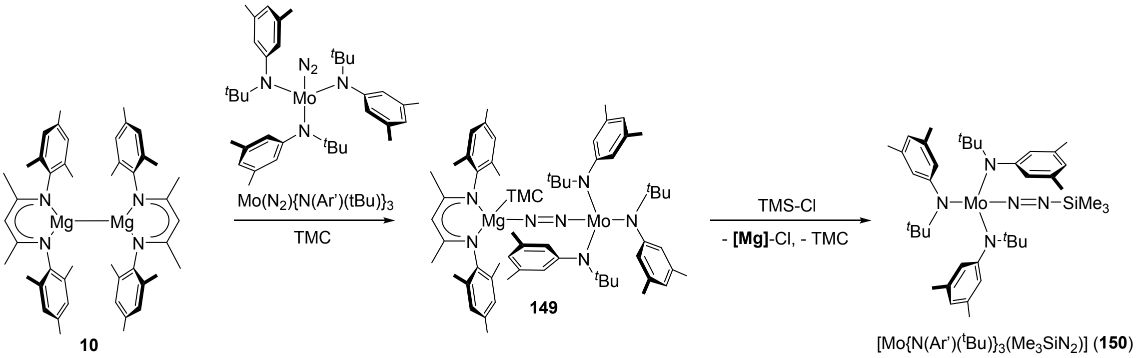
147
M = Ca, *side-on*

148
M = Mg, *end-on*

Scheme 2: Reduction of "[**M**(NON^{TCHP})]" with K/KI to access side-on (**M** = Ca) and end-on (**M** = Mg) N_2^{2-} containing products. Line-drawings of complexes **147** and **148** are presented in Figure 6.

Complexes **146–148** were characterised in the solid-state through single crystal X-ray diffraction measurements.[56, 61, 158] The N–N bonds lengths (1.255(3)–1.268(2) Å) within the reduced dinitrogen fragments are consistent with doubly reduced N_2^{2-} ligands. Further confirmation was provided by Raman spectroscopy, which in each case showed N–N stretching bands between 1376–1530 cm^{-1}, consistent with other examples of lanthanide complexes containing side-on or end-on bound N_2^{2-} ligands.[147, 148] Computational studies have also been investigated and support the proposed doubly reduced formalism for the N_2^{2-} ligand. [56, 61, 158, 159]

These complexes have demonstrated reactivity as masked low oxidation state species, where the release of dinitrogen provides clean access to highly reactive diradicals under thermal or photolytic conditions (*vide infra*). While attempts to functionalise the N_2^{2-} ligand with various electrophiles have failed thus far, our research group (and many others) are actively pursuing this area of research to develop next-generation and sustainable chemical practices for the production of ammonia and other value-added nitrogen-containing commodities. Noteworthy, and in contrast to the direct reduction of N_2 by alkaline earth metal complexes, the further reduction and functionalisation of N_2 has been achieved by dimagnesium(I) complex **10** within the coordination sphere of TMC and Cummins' molybdenum(III) tris(anilide) complex,[160, 161] $[Mo(N_2)\{N(Ar')(^tBu)\}_3]$ (Ar' = 3,5-dimethylphenyl).[162] In this case, an end-on complex **149** can be accessed and reacted with trimethyl silyl chloride to provide a previously reported silyldiazenido complex, **150** (Scheme 3).[163]

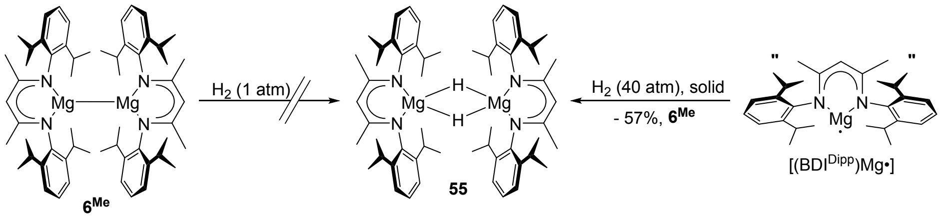


Scheme 3: Functionalisation of N_2 utilising dimagnesium(I) complex **10**.

Elemental magnesium and calcium have also been used as reducing agents in combination with other transition metal elements to form reduced dinitrogen species. Such reactivity is predominantly directed by the transition metal element, and thus, will not be discussed here further.[164-167]

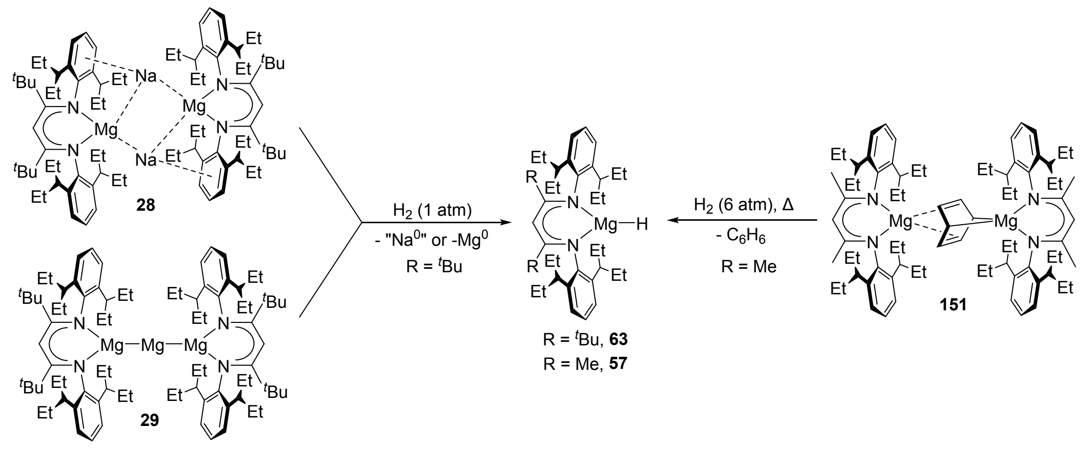
5. Dihydrogen Activation and Exchange

Dihydrogen, a non-polar diatomic gaseous molecule (H–H, BDE = 436 kJ mol^{-1}),[10] is widely used as a feedstock in numerous industrial processes for the reduction of unsaturated chemical substrates to access value-added products (*i.e.* hydrocarbons).[168, 169] Reactive sources of hydrogen can be accessed by cleavage of the H–H bond in dihydrogen to generate molecular complexes containing M–H bonds which act to deliver the hydrogen atom(s) to target molecules.[170] In industry, dihydrogen is often paired with other gaseous substrates (*e.g.* *syn*-gas, H_2/CO mixtures) to achieve atom efficient reductions of unsaturated substrates.[171] These hydrogenation processes are usually promoted by heterogeneous catalyst supports (*e.g.* palladium on carbon) that involve precious metals.[172] It is no surprise then that the direct control and manipulation of dihydrogen gas has become a widely researched topic relevant to both industry and academia. Homogeneous chemical systems (*e.g.* Wilkinson's catalyst)[173] for hydrogenation can offer greater selectivity over heterogeneous systems for the addition of hydrogen atoms to a target molecule, with relevant applications in the manufacture of asymmetric pharmaceuticals.[174] In contrast to transition metals which can destabilise the non-polar H–H bond through π-backdonation to the σ* orbital of H_2, the activation of dihydrogen by main-group complexes comprising access to only s- and p-orbitals remains a considerable endeavour.[7, 8] Indeed, the reduction of dihydrogen gas by neutral low oxidation state diberyllium(I) and dimagnesium(I) complexes (*i.e.* **4**[26] and **6^{Me}**[175]) has not yet been reported under ambient conditions. For example, the formation of magnesium(II) hydride **55** from **6^{Me}** requires a transfer hydrogenation reagent (1,3-cyclohexadiene) to achieve conversion.[175] However, a sample of "[(BDI^{Dipp})Mg•]" prepared by ball-milling undergoes hydrogenation in the solid-state (H_2, 40 bar) to give the hydride **55** (~43 %) and the homo-coupled product **6^{Me}** (~57 %),[46] indicating that reduction of the non-polar H–H bond by a radical pathway is more feasible (Scheme 4).



Scheme 4: Accessing magnesium(II) hydride **55** from "[(BDI^{Dipp})Mg•]"

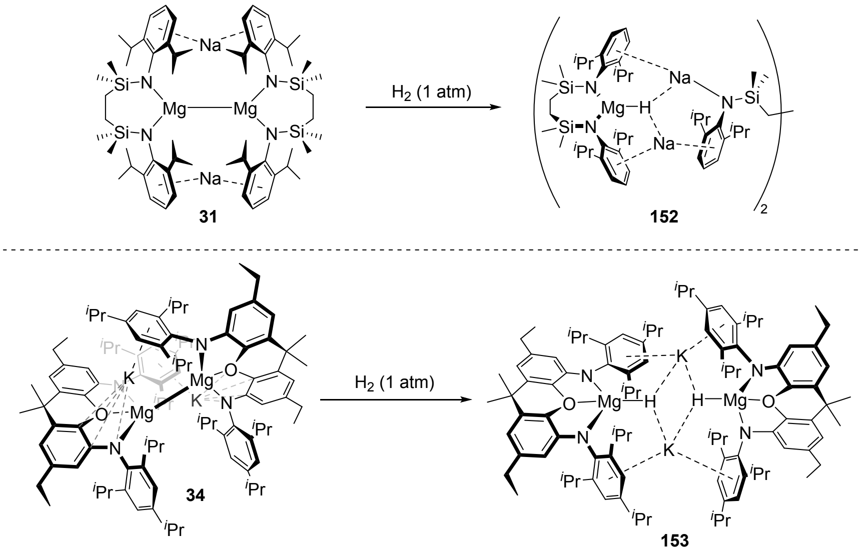
For low oxidation state homotrimetallic **29** and sodium/magnesium heterobimetallic **28**, which contain strongly reducing magnesium(0) centres, the activation of dihydrogen to give **63** was achieved under moderate conditions concomitant with loss of elemental sodium (1.5 atm, 20 °C, 2 days, C_6D_6) or magnesium metal (1.5 atm, 60 °C, 2 days, C_6D_6), respectively (Scheme 5).[51] In an alternative procedure to access a structurally related magnesium(II) hydride, benzene reduction product **151** was reacted with dihydrogen to afford **57** (6 atm, 120 °C, 5 days, toluene), where it was identified to act as a source of the corresponding magnesium(I) synthon (*i.e.* "[(BDI^{Dipep})Mg•]").[39]



Scheme 5: Reduction of dihydrogen using low oxidation state magnesium complexes. Note: **57** is dimeric but has been depicted above as a monomer for simplicity.

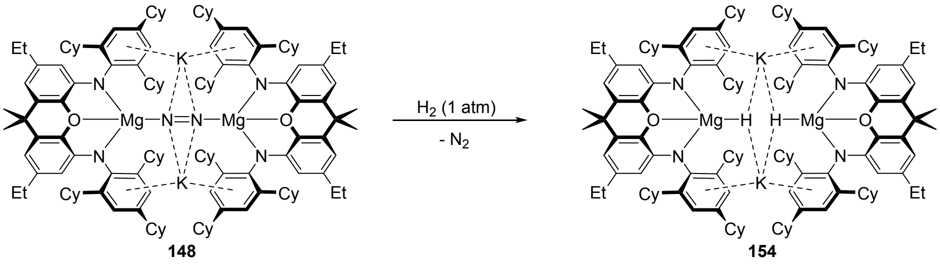
Ionic variants of dimagnesium(I) systems have also demonstrated utility in the reduction of dihydrogen. The sodium(I)/magnesium(I) heterobimetallic (**33**) reported by Hill and co-workers was found to reduce H_2 over 3 days (1.5 atm, 40 °C) to give **152** (Scheme 6).[176] The identity of **152** is complicated by a concomitant disproportionation process which leads to incorporation of a formal

"$Na_2[SiN^{Dipp}]_2$" unit in the final complex. In contrast, the reaction between **34** and H_2 (1 atm) proceeds cleanly at 80 ℃ over 3 days to afford the desired magnesium(II) hydride **153** in moderate yields (52% yield).[58] As has been previously observed in the chemistry of other mixed s-block/main-group complexes, the synergistic combination of two active metal centres can help promote reactivity not typically observed by their monometallic counterparts.[177-179]



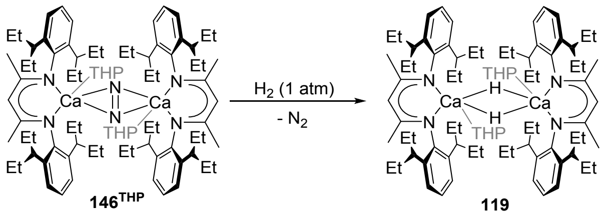
Scheme 6: Reduction of dihydrogen by a Mg(I)/**M**(I) (**M** = Na or K) ensemble.

In the case of **148**, the reduction of dihydrogen was possible in the solid-state (80 ℃, 1 atm, 24 hrs) and as a suspension in pentane (reflux, 1 atm, 24 hrs) to access the corresponding ionic hydride **154** (Scheme 7).[56] A mixed potassium(I)/magnesium(I) heterobimetallic low oxidation state complex was postulated as the intermediate for this redox event, formed by the favourable release of dinitrogen from the parent molecule.



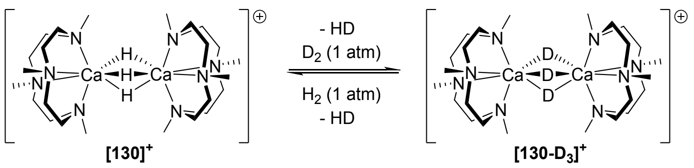
Scheme 7: Reduction of dihydrogen using a low oxidation state magnesium synthon.

A similar N_2 extrusion process was reported by Harder for the monometallic calcium complex **146^{THP}** in its reactivity with dihydrogen to form **119** (Scheme 8).[61] This reaction takes place instantaneously, suggesting a strongly reducing calcium(I) intermediate could be present, a feature derived from the susceptibility of the N_2^{2-} anion towards oxidation to form dinitrogen.



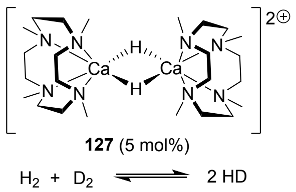
Scheme 8: Reduction of dihydrogen using a low oxidation state calcium synthon.

For molecular alkaline earth hydrides, reactions involving dihydrogen are generally restricted to hydrogen exchange/scrambling processes, a feat that was initially reserved for the heavier binary alkaline earth hydrides (**M**H_2, **M** = Ca–Ba) and their solid-state reactions with deuterium gas under forcing conditions (200 °C).[180-182] Early examples of hydrogen exchange were documented for the neutral THF-solvated dimeric magnesium(II) and calcium(II) deuterides $[Ae(BDI^{Dipp})(\mu\text{-}D)(THF)]_2$ in their reactions with dihydrogen under mild conditions to give H–D (**55-D₂**•$(THF)_2$: 60 °C, **115-D₂**: room temperature).[75, 183] More recently, Okuda and co-workers have shown that the exposure of a homogeneous solution of [**130**]$[SiPh_3]$ to an atmosphere of deuterium (1 atm, 25 °C) resulted in the reversible exchange of the hydride ligands for deuteride ligands (Scheme 9).[134] The proposed mechanism for this process suggested cooperation between the cation and anion to achieve cleavage of the H–H/D–D bond which is likely essential for the exchange to occur.



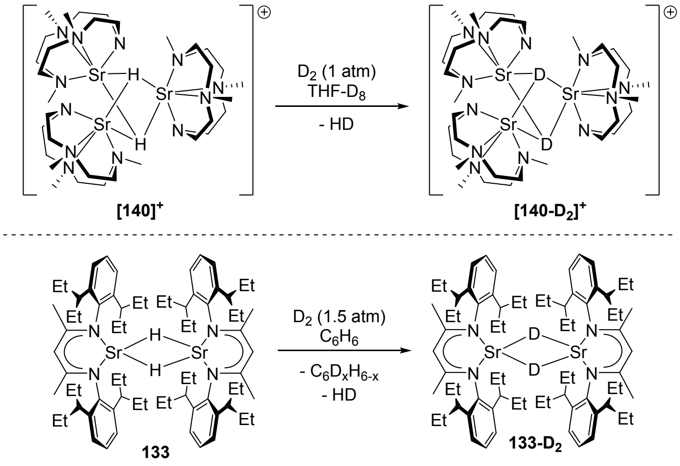
Scheme 9: D_2 exchange by a cationic calcium hydride complex.

A similar scrambling reaction was noted for [**127**]$[B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ in the presence of an equimolar amount of H_2 and D_2 (Scheme 10).[133] In this case, the reaction is catalytic and reaches equilibrium rapidly (*ca.* 5 mins).



Scheme 10: H_2/D_2 scrambling by a cationic calcium hydride complex.

Strontium(II) hydride systems $[\mathbf{140}]^+$ and **133** have also been documented to undergo H/D exchange in the presence of D_2 gas to give the corresponding deutero-analogues $[\mathbf{140\text{-}D_2}]^+$ and **133-D₂**, respectively (Scheme 11).[137, 138] For [**140**]$[SiPh_3]$, the authors noted that the silicon-containing anion degrades over the course of the H_2/D_2 activation process while the cationic component remains surprisingly unaffected.[138] In contrast, neutral strontium(II) hydride system **133** was found to engage in H/D exchange with D_2 in benzene.[137] It was hypothesised that this H/D exchange could happen through a Meisenheimer intermediate (cyclohexadienyl anion) where the arene helps to facilitate the process. This was supported by the initial formation of **133-D$_2$** and C_6H_5D in excess D_2 (1.5 atm), followed by further deuteration to give C_6D_6 with an appreciable turnover (TON = 27) over 5 days. As such, **133** was noted as a viable catalyst for the deuteration of C_6H_6 by D_2 gas, albeit with a slow turnover frequency (TOF = 0.23 h^{-1}). This has also been achieved by an *in situ* generated barium(II) hydride of the type "[Ba(N{Si^{i}Pr$_3$}$_2$)(H)]" with a marked improvement in turnover number (TON = 134) and frequency (TOF = 268 h^{-1}).[184] These complexes represent rare examples of hydrogen exchange processes promoted by homogeneous main-group hydride systems.

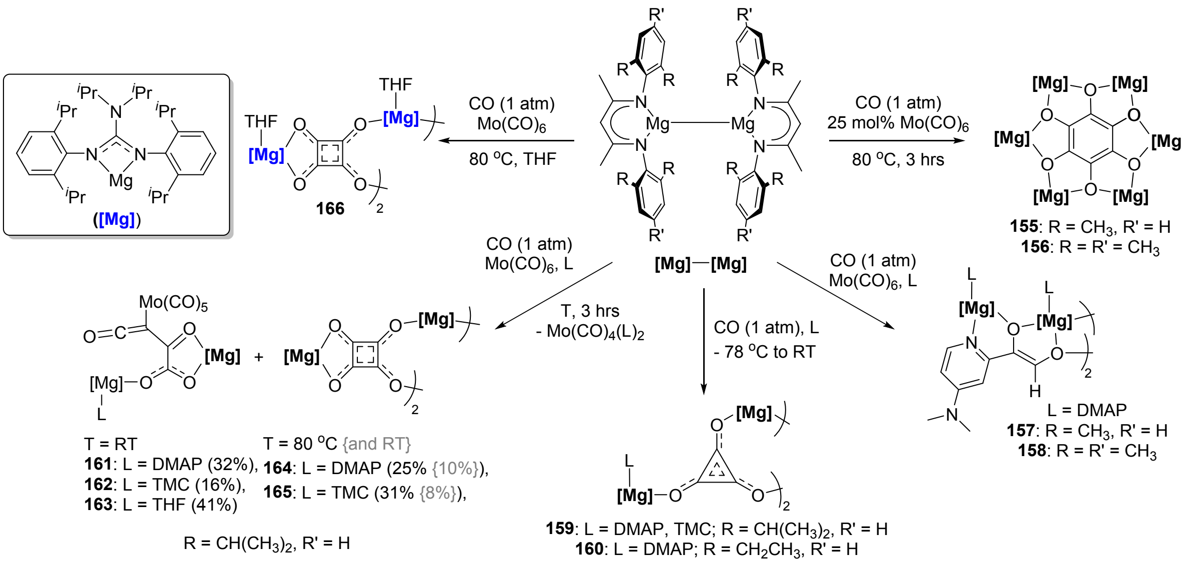


Scheme 11: H–D exchange by cationic and neutral strontium(II) hydride complexes.

6. Homologation and Reduction of Carbon Monoxide

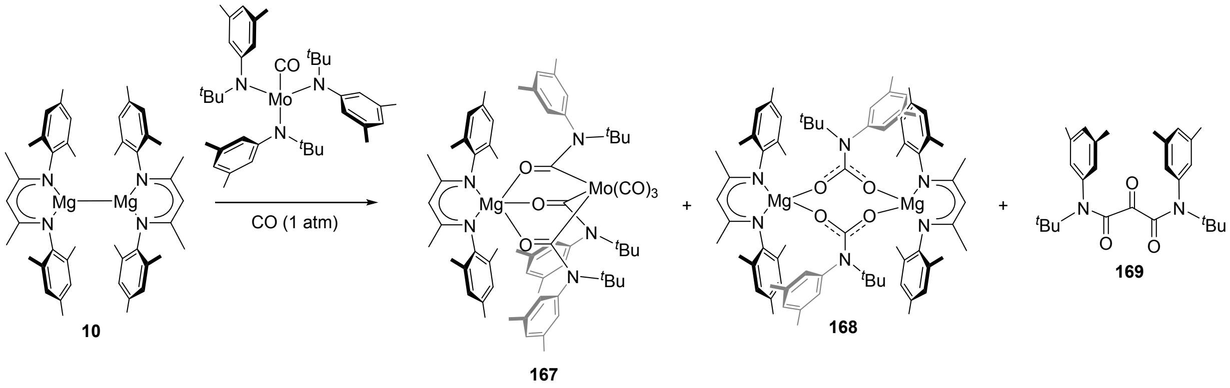
Carbon monoxide (C≡O, BDE = 1075 kJ mol^{-1}),[10] which contains the strongest bond in nature, is a polar diatomic gaseous molecule that is widely utilised in industry.[185, 186] These applications range from simple carbonylation reactions to complex homologation processes. For example, carbon monoxide and dihydrogen can be combined (aforementioned *syn*-gas) in the Fischer-Tropsch process to produce value-added liquid hydrocarbons – a sustainable method for the production of fuel from renewable resources.[187, 188] This contrasts with current (and unsustainable) methods to produce fuel that rely upon extraction and cracking of crude oil from natural reservoirs within the upper continental crust.[189] The artificial production of fuel utilising the Fischer-Tropsch process generally requires heterogeneous catalysts that give a broad mixture of hydrocarbons (solid catalyst/gas).[190, 191] Soluble models of the Fischer-Tropsch process can provide a more detailed mechanistic insight into the synthesis at a molecular level, which remains complicated for heterogeneous systems where the polymerisation reaction takes place on the surface of the catalyst,[192, 193] ultimately aiding in the design of chemoselective homogeneous metal complexes to produce well-defined hydrocarbon products. Within main-group chemistry, the reduction and homologation of carbon monoxide remains an incredibly active area of research, such that C_1–C_6 fragments (C_n, n = number of incorporated CO molecules) have been stabilised within the coordination sphere of main-group metals.[11, 12, 194, 195]

For low oxidation state alkaline earth metal complexes, the reduction of CO by neutral dimagnesium(I) systems has been comprehensively investigated (Scheme 12). In each case, the reactivity of a dimagnesium(I) system with CO is promoted by $Mo(CO)_6$ and/or a Lewis base to activate the Mg–Mg bond. While only previously accessible for alkali metals under highly forcing conditions (180 °C, molten metal), dimagnesium(I) complexes **9** and **10** react with CO under ambient conditions in the presence of 25 mol% $Mo(CO)_6$ to form the corresponding benzenehexaolate ($[C_6O_6]^{6-}$) complexes **155** and **156**, the largest structurally authenticated cyclic oligomers of CO formed by molecular main-group species.[195] These homologation processes can be mediated through numerous factors, including reaction conditions, stoichiometry, and the steric profile of the dimagnesium(I) complex. For example, the reaction of **9** and **10** with CO, 25 mol% $Mo(CO)_6$ and 4-dimethylaminopyridine (DMAP) results in the reductive dimerization of CO, followed by the rapid *ortho*-C–H activation of DMAP to afford moderate yields of **157** and **158**, respectively.[196] Utilising the bulkier dimagnesium(I) systems $\mathbf{6^{Me}}$ and **8**, reactions at low temperature (–78 °C) with CO in the presence of a Lewis base (*i.e.* DMAP or TMC) resulted in the reductive trimerization of CO to afford the deltate ($[C_3O_3]^{2-}$) complexes **159** and **160**, respectively.[197] For $\mathbf{6^{Me}}$, reactions with CO, $Mo(CO)_6$, and a Lewis base at room temperature resulted in the formation of two major isolable products, metallo-ketene complexes **161**–**163** and squarate complexes **164** and **165** ($[C_4O_4]^{2-}$).[198] At elevated temperatures (80 °C), only the formation of squarate systems **164** and **165** could be observed, highlighting the specificity of the homologation process for these neutral dimagnesium(I) complexes. A related squarate complex (**166**) was also isolated from the reaction of the guanidinate stabilised dimagnesium(I) complex **5** with $Mo(CO)_6$ and CO (1 atm) at 80 °C.



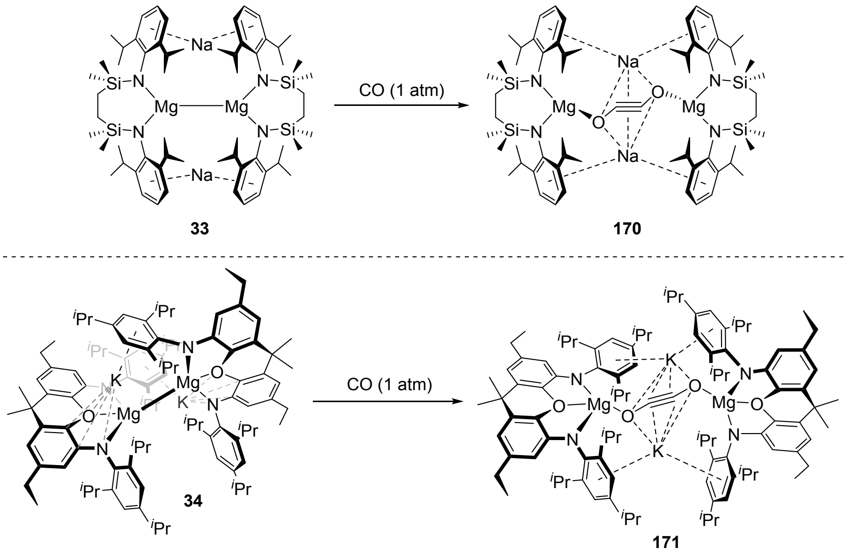
Scheme 12: Diverse reactivity of dimagnesium(I) complexes with CO in the presence of $Mo(CO)_6$ and/or Lewis bases.

In an alternative procedure, dimagnesium(I) complex **10** was reacted with Cummins' molybdenum(III) tris(anilide) $[Mo(CO)\{N(Ar')(^tBu)\}_3]$ to afford a broad mixture of products (**167**–**169**, Scheme 13).[162] Complex **167** is postulated to arise from the insertion of CO into the Mo–N bonds, along with complexation of CO at the molybdenum(III) centre. In contrast, **168** and **169** form through complex reaction pathways independent from that which afforded **167**.



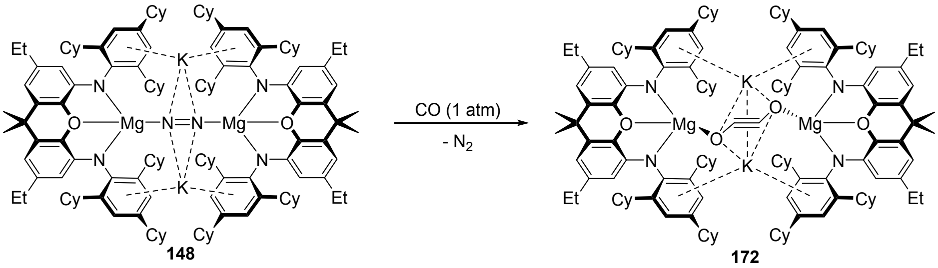
Scheme 13: Reactivity of a dimagnesium(I) complex with CO in the presence of $Mo\{N(^tBu)(C_6H_4Me_2)\}_3(CO)$.

For ionic dimagnesium(I) systems, **33** and **34** have been shown to facilitate the reduction of carbon monoxide to yield ethynediolates ($[C_2O_2]^{2-}$) **170** and **171**, respectively (Scheme 14).[55, 58] This reactivity diverges from the neutral systems, where in these cases, one well-defined product was isolated (79% {**170**} and 61% {**171**} isolated yield), characteristic of mixed metal cooperativity. The reaction mechanism for **33** with CO was studied using computational methods and suggests involvement of both the magnesium(I) and sodium(I) centres in the formation of the ethynediolate fragment.[55]



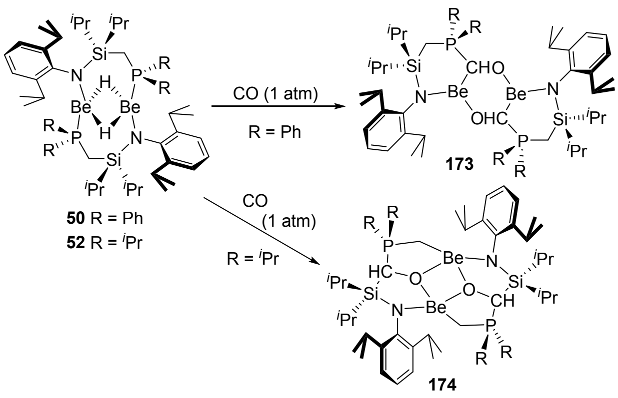
Scheme 14: Homologation of CO by Mg(I)/**M**(I) (**M** = Na or K) ensembles.

Moreover, a similar outcome was observed for the reaction between **148** and CO affording the corresponding ethynediolate complex **172** in modest yields (61% yield, Scheme 15). In this case, formation of **172** is mediated by magnesium(I) and potassium(I) metal centres, postulated to proceed through a transient low oxidation state intermediate. The dimeric construct of **172** is akin to that observed in **170** and **171**.[56]



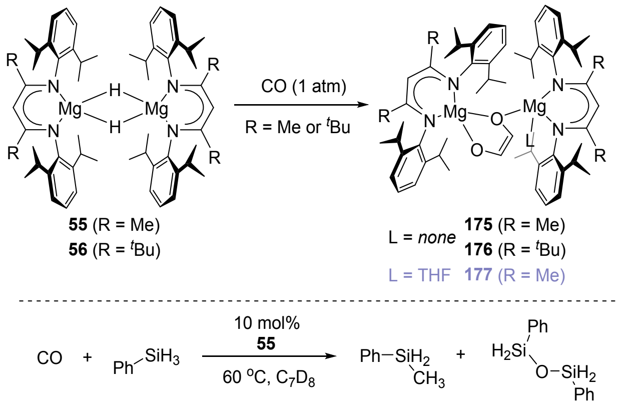
Scheme 15: Homologation of CO by a low oxidation state magnesium synthon.

While the reduction of carbon monoxide by low oxidation state alkaline earth metal(I) complexes has been largely restricted to complex homologation reactions that afford a broad mixture of products, reactions with alkaline earth metal(II) hydrides have shown more promise in regards to stoichiometric and catalytic transformations. For beryllium(II) hydrides, Haddlington and co-workers have recently demonstrated the reduction of CO by **50** and **52** to give complexes **173** and **174**, respectively (Scheme 16).[72] In **173**, insertion of CO into the Be–H bonds yield formyl ligands ($[CHO]^-$), where the phosphine arms of the phosphanamido ligand bind the formyl carbon. While **174** contains a similar formyl moiety, a further ligand activation process ensues to give a pentacyclic structure, where the $[CHO]^-$ fragments adopt an unusual binding mode.



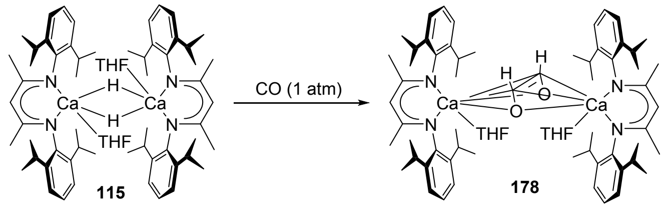
Scheme 16: Reduction of CO by beryllium(II) hydride complexes.

In contrast to the formyl ligands observed in **173** and **174**, the derivatisation of CO by the heavier alkaline earth metal hydrides has been documented to primarily form stable complexes containing either ethenediolate ligands ($[C_2H_2O_2]^{2-}$) or propanetriolate ($[C_3H_3O_3]^{3-}$) ligands through reductive dimerization or trimerization processes, respectively. For magnesium(II) hydrides **55** and **56**, the reactions with CO afford the corresponding ethenediolate complexes **175**[199] and **176**,[200] respectively (Scheme 17). Each complex exists as a dimer with a *cis*-ethenediolate ligand that adopts a κ^2-μ_2-bridging mode with a three- and four-coordinate magnesium(II) centre. In the presence of THF, a similar structure could be obtained (**177**) where a single molecule of THF is present at the formerly three-coordinate (in **175**) magnesium(II) centre.[175]



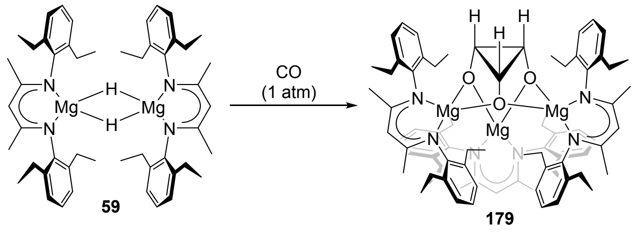
Scheme 17: Reductive coupling of CO by magnesium(II) hydride complexes (top). Catalytic deoxygenation of CO by **55** (bottom).

These reactions were proposed to proceed through formyl intermediates, "$[Mg(BDI^{Ar})(CHO)]$", which have previously been observed in the reactions of magnesium(II) hydrides with transition metal carbonyl complexes,[201] prior to engaging in dimerization processes.[199, 200] Indeed, the reaction of **55** with CO in the presence of phenylsilane has been shown to facilitate the catalytic deoxygenative conversion of CO into $O(SiPhH_2)_2$ and phenylmethylsilane, supporting the intermediacy of these formyl species. It is worth noting that no evidence for C_2– or higher homologation products could be identified under the reaction conditions implemented for catalysis. In contrast to **55**, the catalytic deoxygenation of CO by phenylsilane and the related calcium(II) hydride **115** did not proceed even under forcing conditions (100 °C). Instead, complex **178** was isolated where the ethenediolate ligand is bound symmetrically in an η^4-fashion to each calcium(II) centre (Scheme 18).[200]



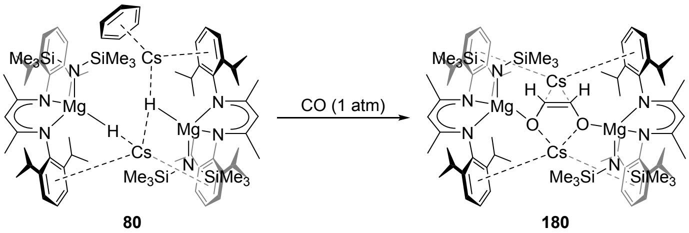
Scheme 18: Reductive coupling of CO by a calcium(II) hydride complex.

Decreasing the steric bulk of the aryl groups on the β-diketiminate framework has been shown to influence the selectivity of the insertion process.[175] Utilising the smaller magnesium(II) hydride **59**, the reaction with CO afforded a propanetriolate complex **179**, resulting from the trimerization of CO by three Mg–H fragments (Scheme 19).



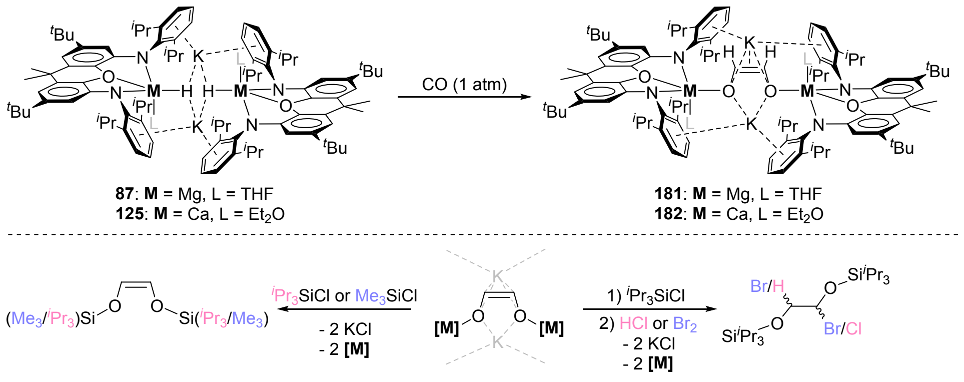
Scheme 19: Reductive coupling of CO by a magnesium(II) hydride complex.

Additionally, the combination of extensively studied magnesium(II) hydride **55** with CsHMDS was shown to promote the formation of a mixed s-block hydride **80**, which engages in the cooperative activation of CO to access ethenediolate complex **180** (Scheme 20).[88] While **180** is essentially an ionic variant of **175**, the coordination mode of the ethenediolate ligand is different due to the influence of the Cs cations in the dimeric construct. These combinations show an effective method to establish synergistic bond activation through the use of simple group 1 reagents.



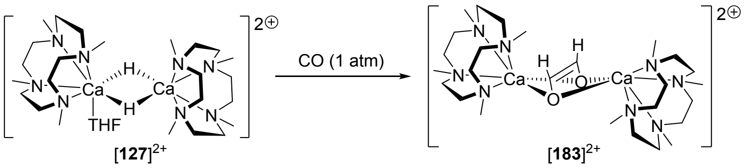
Scheme 20: Reductive coupling of CO by a Mg(II)/Cs(I) hydride complex.

The mixed s-block magnesium(II) and calcium(II) hydrides **87** and **125** reported by Hicks and co-workers have been shown to form similar ethenediolate moieties (**181** and **182**, respectively)[94] to that observed in **180** (Scheme 21, top).[88] In these cases, the ethenediolate fragment could be further functionalised to saturated and unsaturated disilyl ethers using appropriate silyl chlorides (*i.e.* Me_3SiCl or $^iPr_3SiCl$), demonstrating the stoichiometric conversion of CO into value-added organic products by mixed s-block complexes (Scheme 21, bottom).[94]



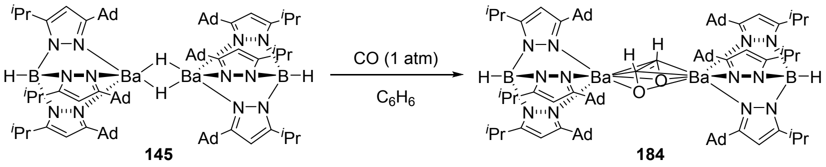
Scheme 21: Reductive coupling of CO by Mg(II)/K(I) and Ca(II)/K(I) hydride complexes. Conversion of the ethenediolate fragment into unsaturated and saturated silyl ethers using silyl chloride electrophiles.

The cationic calcium(II) hydride complex [**127**][$B(C_6H_3\text{-}3,5\text{-}Me_2)_4$]$_2$ reported by the research group of Okuda was also shown to react with CO under ambient conditions to give the corresponding ethenediolate complex, [**183**][$B(C_6H_3\text{-}3,5\text{-}Me_2)_4$]$_2$ (Scheme 22).[132] In this case, DFT calculations suggested dissociation of the dimer prior to activation of CO and subsequent dimerization of two monomeric formyl moieties, unlike the mechanism leading to **178** from **115** where the reaction occurs within the confines of the dimeric aggregate.[200]



Scheme 22: Reductive coupling of CO by a cationic calcium(II) hydride complex.

Barium(II) hydride complex **145** has been shown to facilitate the reduction of CO to ethenediolate complex **184** (Scheme 23).[141] Surprisingly, no other examples of CO reduction products have been reported in the chemistry of strontium(II) and barium(II) hydrides, a testament to their poor stability and synthetic inaccessibility relative to the lighter congeners.

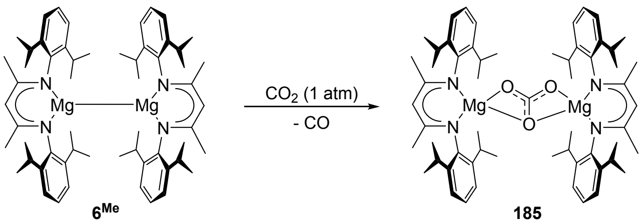


Scheme 23: Reductive coupling of CO by a barium(II) hydride complex.

7. Reduction of Carbon Dioxide

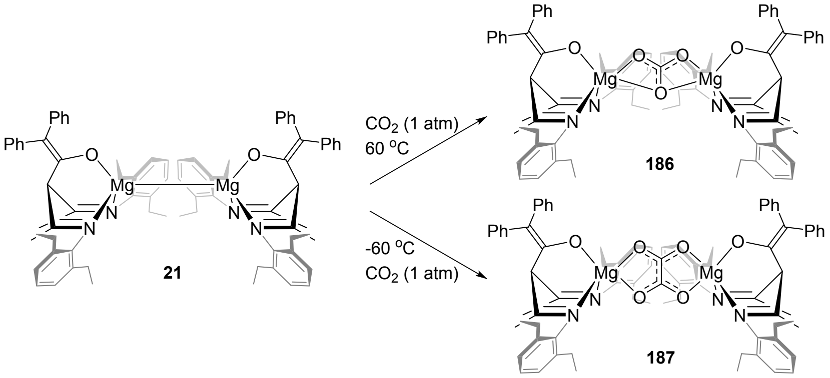
Carbon dioxide (CO_2), a greenhouse gas and a waste product of industrial processes and the combustion of fossil fuels, remains a global issue as a primary contributor to anthropogenic global warming.[202] It is estimated that >30 billion metric tons of carbon dioxide are released into the atmosphere every year, and as such, mitigation is required to prevent the devastating impacts of climate change.[203-205] Establishing chemical methods to convert carbon dioxide into non-volatile and useful value-added products is of industrial and academic interest.[206-208] Consequently, the stoichiometric reduction of carbon dioxide has received considerable attention in molecular main-group chemistry, while effective catalytic applications remain comparably rare.[209, 210] Within this context, low oxidation state and hydrido alkaline earth metal complexes have established themselves as potent reductants of carbon dioxide.[13, 66]

For example, the reaction between dimagnesium(I) complex **6^{Me}** and CO_2 was shown to afford a magnesium(II) carbonate complex **185** (Scheme 24).[211] The reduction of CO_2 was postulated to proceed through a magnesium(II) oxide complex, concomitant with the release of CO, and the subsequent addition of CO_2 across the Mg–O bond to access the Mg-bound CO_3^{2-} ligand. Similar reactivity has recently been reported for heterobimetallic Al–Mg[212] and Mn–Mg[213] bonded systems, and for the tripodal ligand supported dimagnesium(I) complex **21** to give **186** at elevated reaction temperatures (Scheme 25, >60 °C).[42]



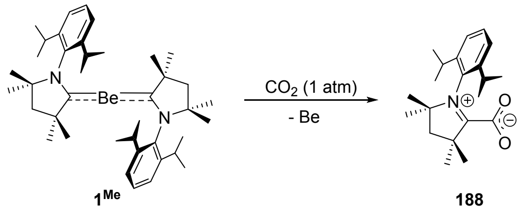
Scheme 24: Extrusion of CO from CO_2 by a dimagnesium(I) complex to access carbonate **185**.

A computational mechanistic study into the formation of **185** later suggested that a magnesium(II) oxide intermediate is energetically unfavourable, and that an alternative concerted mechanism through a complex metallacycle is more likely.[214] It was also noted that **185** was a kinetic product while an oxalate ($C_2O_4^{2-}$) product was calculated to be the thermodynamic product. Experimentally, this oxalate product was only observed in trace amounts and could not be isolated in sufficient quantities.[211] For the reaction between **21** and CO_2 at lower temperatures (–60 °C), the only isolable product was a magnesium(II) oxalate complex **187** formed through a reductive dimerization process.[42, 44] In this case, computational studies suggested that **186** was the thermodynamic product while **187** was the kinetic product, which is likely influenced by the larger steric constraints of the tripodal ligand set. As observed for **185**, the formation of magnesium(II) carbonate **186** was only feasible through a concerted mechanistic pathway involving a carbocyclic intermediate.[44]



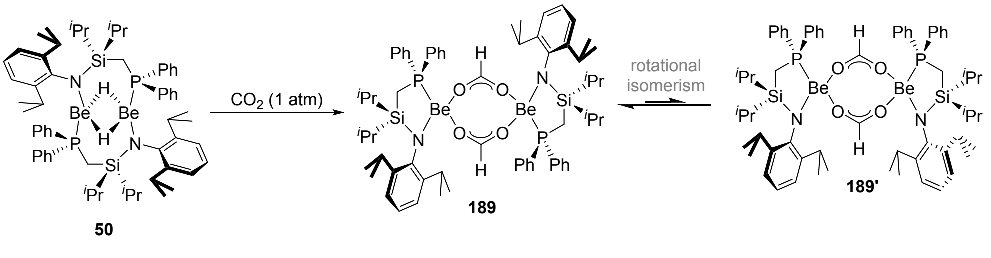
Scheme 25: Homologation of CO_2 by a tripodal dimagnesium(I) complex.

In contrast to the reactivity reported for low oxidation state magnesium(I) complexes, the reduction of CO_2 by beryllium(0) complex $\mathbf{1^{Me}}$ proceeds *via* deposition of beryllium metal and the formation of zwitterionic **188** (Scheme 26).[22] This suggests ligand-based reactivity instead of direct reaction at the beryllium(0) metal centre.



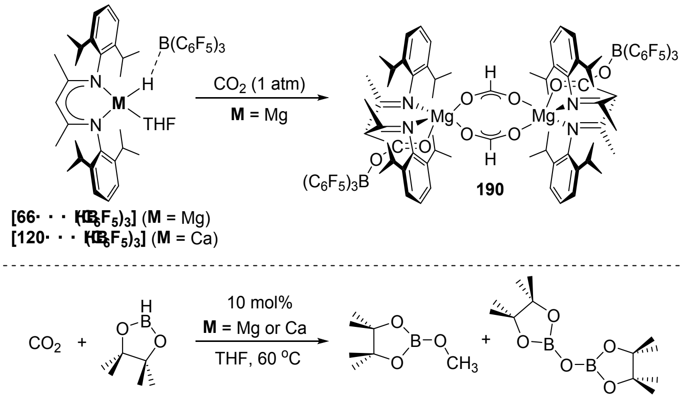
Scheme 26: Reactivity of a low oxidation state beryllium complex with CO_2.

Beryllium(II) hydrides (*e.g.* **50**) have, however, recently been shown to react with CO_2 to give beryllium(II) formate complexes (**189**, Scheme 27). Upon dissolution, **189** underwent solution-state equilibria to give a mixture containing the related rotational isomer **189'**. While **189**/**189'** arises from a neutral alkaline earth metal hydride complex, most examples of CO_2 reduction by the heavier members (> Mg) involve 'ionic' complexes.



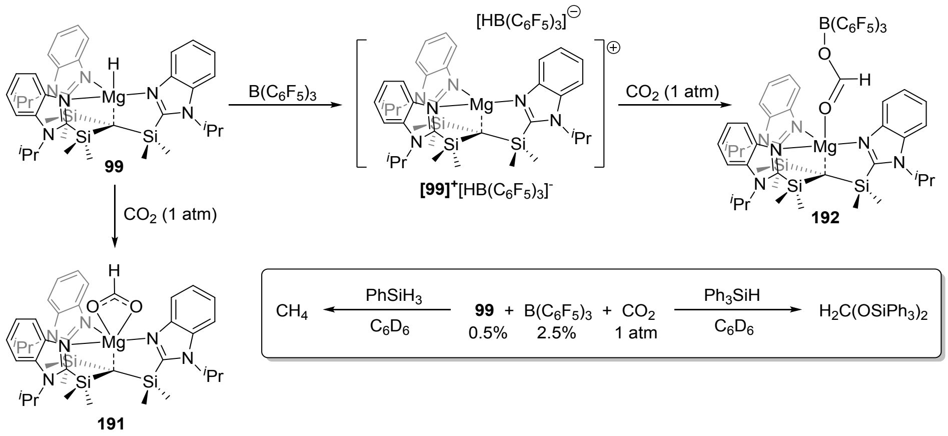
Scheme 27: Reduction of CO_2 by a beryllium(II) hydride complex.

The stochiometric reduction of CO_2 by [**66**···$HB(C_6F_5)_3$] afforded magnesium(II) formate complex **190** (Scheme 27).[82] Interestingly, an additional molecule of CO_2 is incorporated in the structure of **190**, where a molecule of CO_2 adds across the β-diketiminate ligand to render a tripodal ligand that stabilises the magnesium(II) formate. While a solid-state structure was not reported for the product of the reaction of the related calcium(II) hydride [**120**···$HB(C_6F_5)_3$], it was characterised by solution-state multi-nuclear NMR spectroscopy as the corresponding calcium(II) formate complex with no evidence for CO_2 addition across the β-diketiminate ligand. The catalytic hydroboration of CO_2 could be achieved using 10 mol% of [**66**···$HB(C_6F_5)_3$] or [**120**···$HB(C_6F_5)_3$] in the presence of HBpin to give a methanol (CH_3OBpin) and water (O{Bpin}$_2$) equivalent. While the full consumption of HBpin was identified as a slow process and required elevated temperatures (**M** = Mg, 6 days, 60 °C; **M** = Ca, 4 days, 60 °C), the reactivity illustrated the synthetic utility of alkaline earth metal hydrides in the catalytic reduction of carbon dioxide.



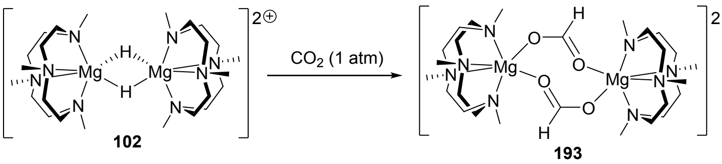
Scheme 28: Catalytic reduction of CO_2 by cationic magnesium(II) and calcium(II) hydride complexes.

Examples of stoichiometric CO_2 reduction to access magnesium(II) formate complexes have been reported utilising a range of other polydentate ligand sets. For example, **99** reacts with CO_2 to afford a formate complex (**191**) that is bound in a κ^2-O_2CH fashion (Scheme 29).[103] This binding mode is different when the reaction is repeated in the presence of $B(C_6F_5)_3$ to give the terminally bound formatoborate **192**. The structure of $[\mathbf{99}]^+[HB(C_6F_5)_3]^-$ was characterised in the solid-state and shown to exist as a separated ion-pair which explains the contrasting reaction products. Perhaps more interesting, the combination of **99** (0.5 mol%) and $B(C_6F_5)_3$ (2.5 mol%) was demonstrated to facilitate the catalytic hydrosilylation of CO_2 by phenylsilane or triphenylsilane to give methane or $H_2C(OSiPh_3)_2$, respectively. These advances provide a means to tune the degree of reduction of CO_2 through judicious choice of a silane reagent. However, this process was suggested to be largely directed by the $[HB(C_6F_5)_3]^-$ ion, where the direct insertion of CO_2 into the Mg–H bond was not implicated as an intermediate in the catalytic cycle.



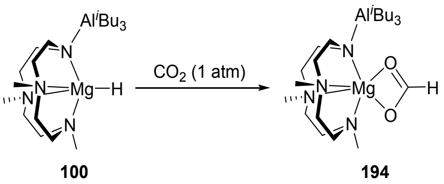
Scheme 29: Stoichiometric and catalytic reduction of CO_2 by a polydentate magnesium(II) hydride complex.

The activation of CO_2 by the dicationic magnesium(II) hydride complex [**102**][B(3,5-Me_2-C_6H_3)$_4$]$_2$ yields the corresponding dicationic magnesium(II) formate complex [**193**][B(3,5-Me_2-C_6H_3)$_4$]$_2$ (Scheme 30).[109] The cationic and anionic components in [**193**][B(3,5-Me_2-C_6H_3)$_4$]$_2$ contain no formal interactions, where the structure of the cationic component ([**193**]$^{2+}$) contains two "[Mg(Me_4TACD)(OCHO)]$^+$" fragments that assemble as a dimer through Mg–O interactions to the formate ligands in the solid-state.



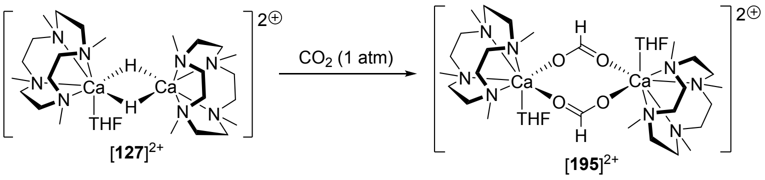
Scheme 30: Reduction of CO_2 by a cationic magnesium(II) hydride complex.

Similar reactivity has been observed in the reaction of **100** with CO_2 which affords the monomeric magnesium(II) formate complex **194** (Scheme 31).[105, 110] The formate ligand in **194**[105] is bound in a κ^2-O_2CH fashion akin to that observed in the structure of **191**.[103]



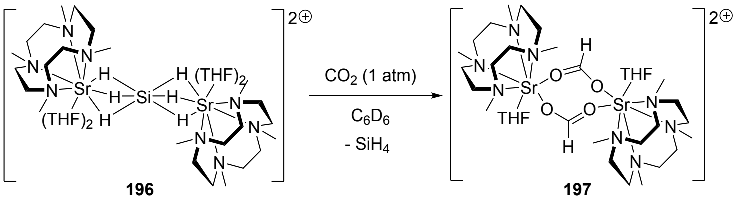
Scheme 31: Reduction of CO_2 by a magnesium(II) hydride complex.

Very few carbon dioxide reduction products have been structurally characterised for the heavier alkaline earth metal hydrides. Complex [**127**][B(3,5-Me_2-C_6H_3)$_4$]$_2$ remains the only structurally authenticated calcium(II) hydride complex that reduces CO_2, yielding the corresponding calcium(II) formate complex, [**195**][B(3,5-Me_2-C_6H_3)$_4$]$_2$ (Scheme 32).[132] Similar to [**193**]$^{2+}$, the complex [**195**]$^{2+}$ is a separated ion-pair and the cationic component exists as a dimeric aggregate comprising two "[Ca(Me$_4$TACD)(OCHO)]$^+$" moieties in the solid-state.



Scheme 32: Reduction of CO$_2$ by a cationic calcium(II) hydride complex

While no examples of CO$_2$ reduction have been provided for well-defined strontium(II) and barium(II) hydrides, the reaction of [**196**][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ with CO$_2$ was shown to afford the strontium(II) formate complex [**197**][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ which is structurally analogous to the calcium derivative[132] [**195**][B(3,5-Me$_2$-C$_6$H$_3$)$_4$]$_2$ (Scheme 33).[215] In this case, [**196**]$^{2+}$ was shown to act as a masked strontium(II) hydride *via* expulsion of silane gas, as demonstrated by its reactivity with CO$_2$.

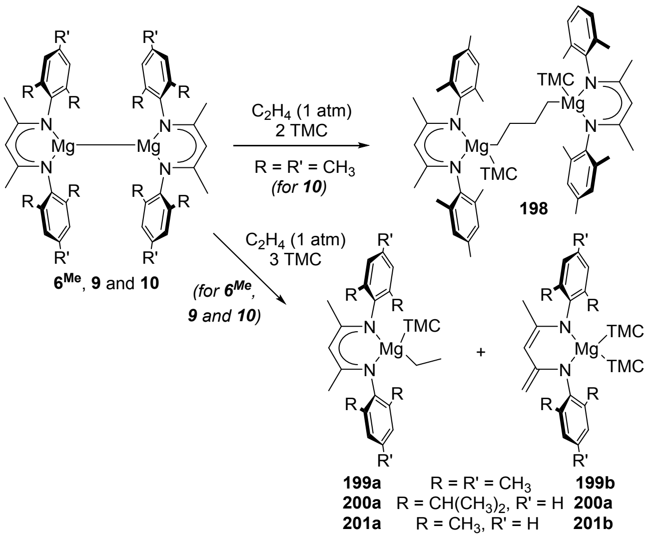


Scheme 33: Reduction of CO$_2$ by a cationic strontium(II) hydride synthon

8. Functionalisation and Reduction of Ethene

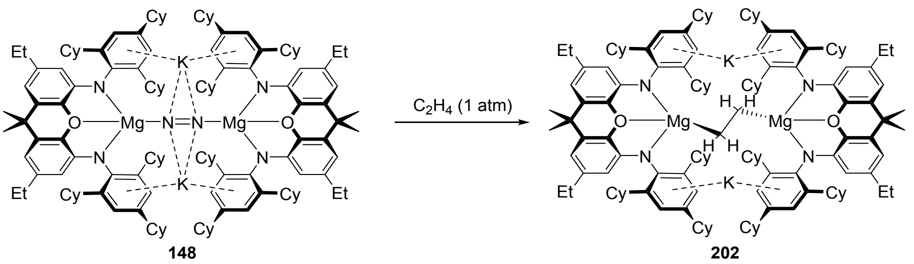
Ethene (C$_2$H$_4$) is a small non-polar unsaturated hydrocarbon that is found in the environment and generated naturally by plants and microorganisms.[216] While ethene can be derived from these natural sources, industrial sources of ethene are generally accessed through the steam cracking of longer-chained hydrocarbons.[217] Within industry and academia, ethene remains an essential *C$_2$*–synthon to produce polymers (*e.g.* polyethylene) and other value-added chemical commodities.[218, 219] Although the coordination and reaction chemistry of ethene has been widely explored by use of transition metal systems,[220-223] comparatively fewer studies involving main-group species have been reported. For low oxidation state and hydrido alkaline earth metal complexes, chemical applications involving the stoichiometric and catalytic transformation of ethene have begun to emerge (*vide infra*).

The first examples of ethene reduction by low oxidation state alkaline earth metal complexes were the reactions of dimagnesium(I) complexes **6^{Me}**, **9** and **10** with ethene (Scheme 34). Each reaction involved TMC which was deemed necessary to improve the solubility of the isolated products. For **10** in the presence of 2 equivalents of TMC, the magnesium(II) alkyl **198** was isolated through the installation of a C–C bond between two reduced ethene units yielding a C$_4$H$_8$$^{2-}$ ligand fragment.[79] A similar product was observed for the addition of ethene across a Mg–C bond of the magnesium(II) alkyl, [(BDI^{Mes})Mg–CPh$_2$–CH$_2$–Mg(BDI^{Mes})], which was prepared from **10** and 1,1-diphenylethene.[224] This suggests that both reactions proceed through a similar mechanism involving initial insertion of one alkene into the Mg–Mg bond, followed by insertion of the second alkene into the Mg–C bond. In contrast, the reaction between **10** and ethene in the presence of 3 equivalents of TMC affords the corresponding monomeric complexes **199a** and **199b**.[79] Analogous products are also isolated for the reactions of **6^{Me}** (**200a** and **200b**) and **9** (**201a** and **201b**) with ethene, where the stoichiometry of TMC was shown to have no impact on the outcome of the reaction. In these cases, it is proposed that insertion of ethene into the Mg–Mg bond occurs, followed by a rapid β-diketiminate ligand activation event to give the observed products.



Scheme 34: Reduction of ethene by dimagnesium(I) complexes.

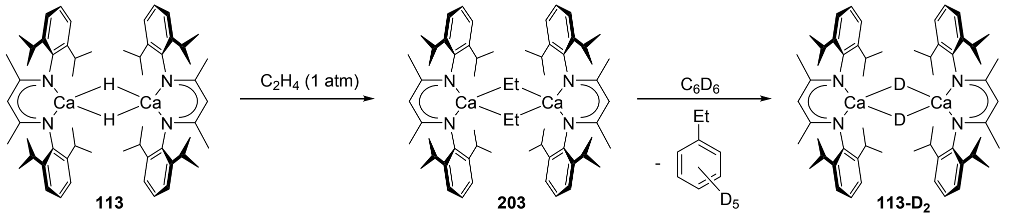
This work was recently extended to masked ionic dimagnesium(I) variants which do not require a Lewis base co-reactant. The masked dimagnesium(I) synthon **148** was shown to react with ethene at 80 °C to give the corresponding $C_2H_4^{2-}$ coordinated complex **202** (Scheme 35).[56] In this case, only one molecule of ethene is incorporated into the product, reminiscent of the computationally modelled intermediate proposed in the formation of **198**. Complex **202** presents itself as a unique example of ethene double reduction by a heterobimetallic main-group system.[225-227]



Scheme 35: Reduction of ethene by a low oxidation state magnesium(I) synthon.

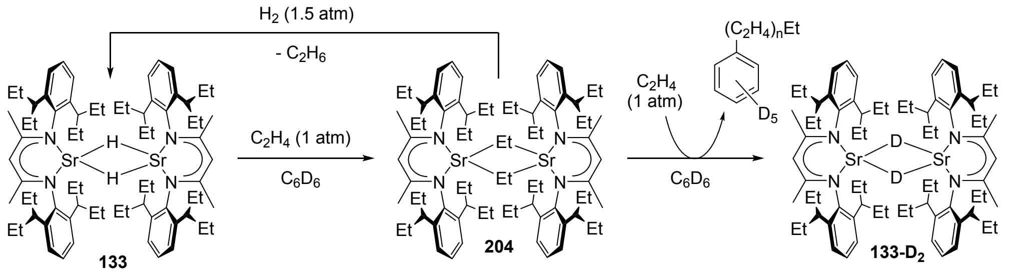
Within the realm of the alkaline earth metal hydrides, a range of catalytic and stoichiometric reductions of ethene have been established. For example, the addition of ethene to calcium(II) hydride

113 gives the calcium(II) ethyl complex **203** (Scheme 36).[126] It is noteworthy that the corresponding magnesium(II) hydride complex (**55**), and its related TMC adduct, "[Mg(BDI^{Dipp})(H)(TMC)]", do not react with ethene even at elevated temperatures (>50 °C).[79] Complex **113** was found to facilitate the nucleophilic alkylation of benzene in the presence of ethene to give d_5-ethylbenzene and **113**–D_2 at 60 °C.[126] This process was not exclusive to ethene and was also shown effective for longer-chained alkenes which were exploited further in subsequent studies (*i.e.* 1-butene and 1-hexene).[228, 229]



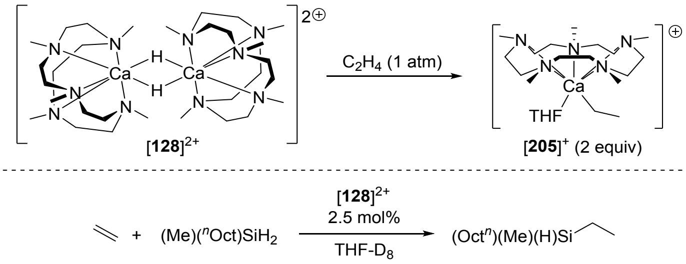
Scheme 36: Reduction of ethene and nucleophilic alkylation of benzene by a calcium(II) hydride complex.

A similar process was identified for the related strontium(II) hydride complex, **133** (Scheme 37).[137] In this case, the larger steric profile of the β-diketiminate ligand system was deemed necessary to isolate and study the strontium(II) hydride. The reaction between **133** and ethene in hexane was shown to give the corresponding strontium(II) ethyl complex, **204**. In contrast to the related calcium(II) system **203**,[229] the reaction of **204** with dihydrogen returns the strontium(II) hydride complex **133** and ethane, demonstrating its capability to facilitate the hydrogenation of ethene.[137] A benzene solution of **133** held at 20 °C for 12 hours or 60 °C for 5 minutes gives full conversion to d_5-ethylbenzene and **133**–D_2. However, catalytic applications for the nucleophilic alkylation of benzene with ethene by **133** or **204** are limited by competing processes that give rise to a range of ethene oligomers, $(C_2H_4)_nC_6D_5$ (n = 0 - 10) and $(C_2H_4)_nH_2$ (n = 5 - 18).



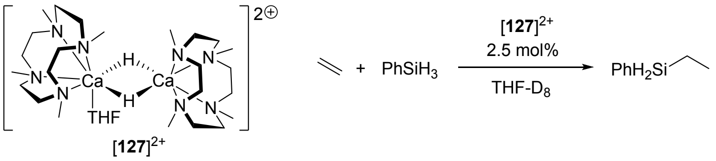
Scheme 37: Reduction of ethene by a strontium(II) hydride complex and nucleophilic alkylation of benzene.

Okuda's cationic calcium(II) hydride complex, [**128**][B(4-^{n}Bu-C_6H_4)$_4$]$_2$, was found to activate ethene to give the corresponding monomeric calcium(II) ethyl complex, [**205**][B(4-^{n}Bu-C_6H_4)$_4$] (Scheme 38).[124] While the direct hydrogenation of [**205**][B(4-^{n}Bu-C_6H_4)$_4$] with dihydrogen was not reported, the catalytic hydrosilylation of ethene by [**128**][B(4-^{n}Bu-C_6H_4)$_4$]$_2$ and ^{n}OctMeSiH$_2$ was shown to proceed at room temperature.



Scheme 38: Stoichiometric and catalytic reduction of ethene by a cationic calcium(II) hydride complex.

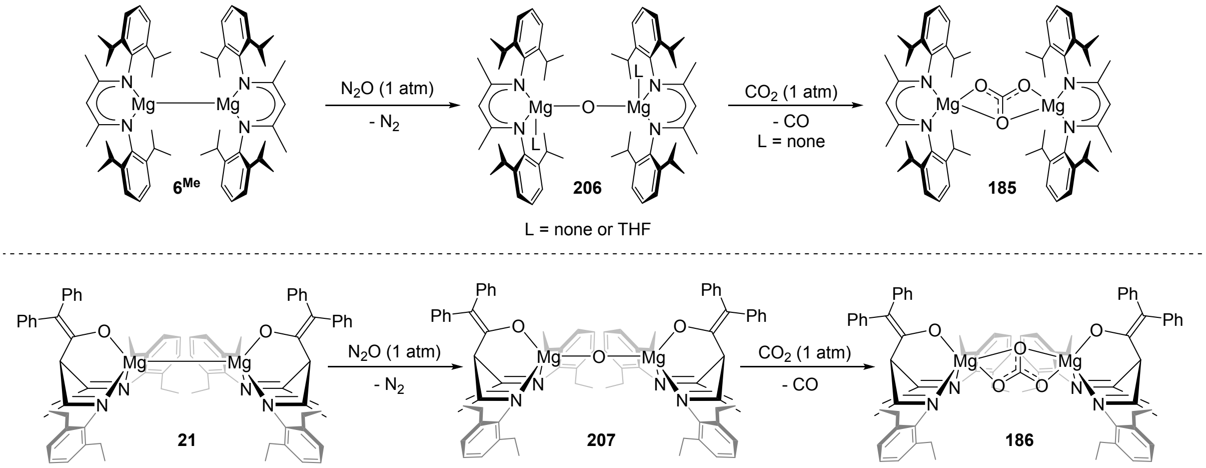
In contrast to [**128**][B(4-^{n}Bu-C_6H_4)$_4$]$_2$,[124] the exposure of cationic calcium(II) hydride [**127**][B(3,5-Me_2-C_6H_3)$_4$]$_2$ to ethene resulted in the formation of an intermediate calcium(II) ethyl complex, followed by rapid oligomerisation to higher *n*-alkyl calcium species (C_2–C_6) and other unidentified products.[131] Although the intermediate ethyl complex could not be isolated (*cf.* [**205**]$^+$), [**127**][B(3,5-Me_2-C_6H_3)$_4$]$_2$ was identified as a viable catalyst in the hydrosilylation of ethene using a range of aryl and alkyl silane reagents (Scheme 39, phenylsilane shown as an example). This represents an example of facile ethene reduction by a homogeneous s-block catalyst under ambient conditions.



Scheme 39: Catalytic hydrosilylation of ethene by a cationic calcium(II) hydride complex.

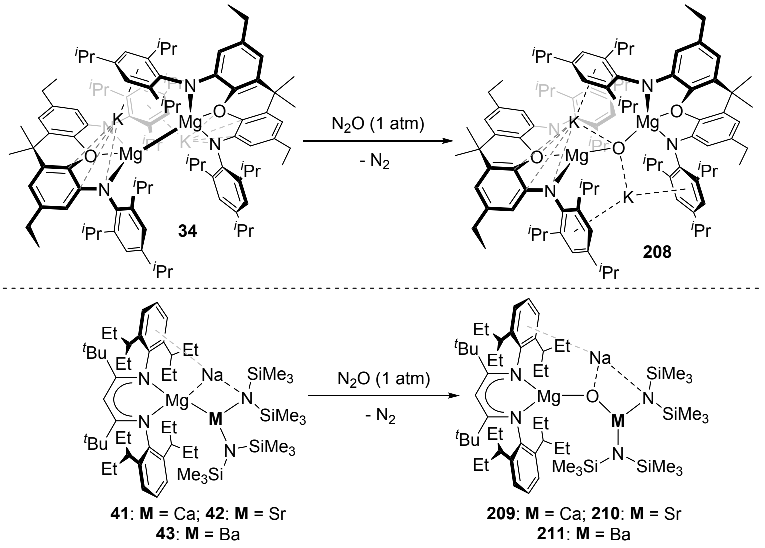
9. Nitrous Oxide and Sulfur Dioxide Activation

Nitrous oxide (N_2O) and sulfur dioxide (SO_2) are often utilised in academic and industrial chemical processes. For example, nitrous oxide is used in the hydroxylation of arenes or the carbonylation of alkenes.[230] Nitrous oxide, or 'laughing gas', has also been widely utilised in the medical industry as an anaesthetic. While often neglected, nitrous oxide is the third-most prevalent greenhouse gas (after CO_2 and CH_4), emitted as an industrial by-product in the production of adipic acid and nitric acid.[231] As such, the chemical transformation of N_2O into less harmful substrates is pertinent to mitigating climate change. In this respect, low oxidation state alkaline earth metal complexes have been successfully used in the activation of N_2O to N_2 and O^{2-} (Scheme 40). Dimagnesium(I) complex **6^{Me}** reacts with N_2O at room temperature to afford the corresponding magnesium(II) oxide complex **206**, which itself reacts with CO_2 to form the magnesium(II) carbonate complex **185**.[211] While **206** was initially suspected as an intermediate in the reduction of carbon dioxide to **185**, mechanistic studies suggested that a different concerted mechanism was more plausible (*vide supra*).[214] The related tripodal dimagnesium(I) system **21** follows the same reactivity pattern with N_2O to afford magnesium(II) oxide **207**.[42] Similar to **206**, the reaction of **207** with CO_2 affords the corresponding magnesium(II) carbonate complex **186**.



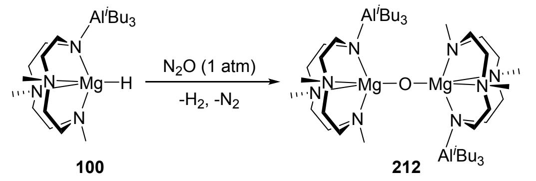
Scheme 40: Reduction of N_2O by dimagnesium(I) complexes to form magnesium(II) oxides and their subsequent reactivity with CO_2.

An ionic variant of a magnesium(II) oxide complex (**208**) was recently isolated by our research group from the reaction of **34** with N_2O (Scheme 41, top).[58] In this case, the magnesium(II) oxide exists as an unsymmetrical contacted dimeric ion pair due to the different coordination environments of the potassium(I) cations. Similar ionic magnesium(II) oxide complexes **209–211** were subsequently synthesised by Harder and co-workers from the reactions of heterotrimetallic magnesium(I) complexes **41–43** with N_2O (Scheme 41, bottom).[64]



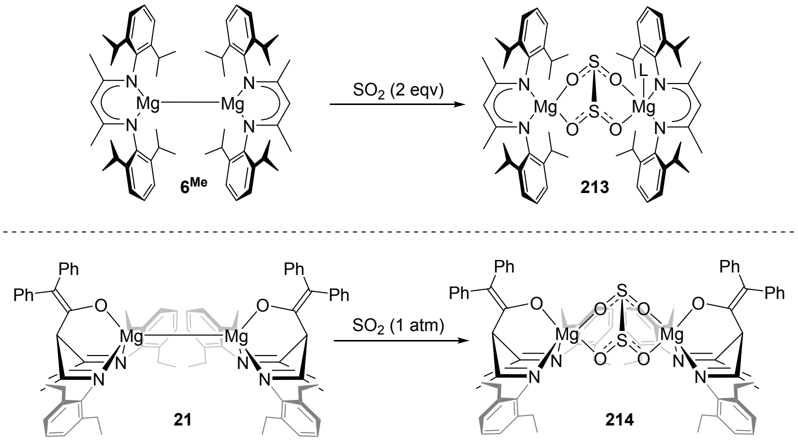
Scheme 41: Reduction of N_2O by heterobimetallic and heterotrimetallic magnesium(I) complexes.

A magnesium(II) hydride complex **100** has been shown to react with N_2O to give a magnesium(II) oxide complex **212** (Scheme 42).[105] It was postulated that the reaction proceeds through a transient hydroxide complex, "Mg(Me_3TACD·Al^iBu_3)(OH)", which reacts with itself or another equivalent of the hydride (**100**) liberating H_2O or H_2 to generate **212**.



Scheme 42: Reduction of N_2O by a cationic magnesium(II) hydride complex.

Sulfur dioxide is also used industrially to prepare fine chemicals.[232] While sulfur dioxide is not listed as a greenhouse gas, it remains a major pollutant that is responsible for acid rain, often released during oil production and the combustion of fossil fuels.[233] Recent applications of sulfur dioxide include the preparation of sulfur-containing polymers for the design of next generation thermoplastics.[234] In low oxidation state alkaline earth metal chemistry, the reduction of SO_2 by dimagnesium(I) complexes **6$^{\mathbf{Me}}$** and **21** has been shown to yield **213** and **214**, respectively (Scheme 43).[42] In both instances, two molecules of SO_2 have been reductively coupled through the installation of an S–S linkage. For **213**, the reaction stoichiometry was critical to prevent decomposition that was suspected to occur because of secondary reactivity with the β-diketiminate ligand backbone, not possible in the case of **214**.



Scheme 43: Reductive coupling of SO_2 by dimagnesium(I) complexes.

10. Conclusion and Future Outlook

An overview of well-defined low oxidation state and hydrido alkaline earth metal complexes has been detailed. The role of these species in the reduction of small-molecule substrates has been presented within the context of a selection of industrially relevant gases. These complexes can effectively facilitate the stoichiometric reduction of N_2, H_2, CO, CO_2, C_2H_4, N_2O and other gaseous substrates. The catalytic reduction of CO, CO_2 and C_2H_4, has also received considerable attention and suitable alkaline earth metal catalysts have been developed towards this end. Research in this area continues to expand the scope of these stoichiometric and catalytic chemical transformations to achieve the sustainable production of value-added chemical commodities and materials. The further advancement of this field may realise the activation of saturated hydrocarbons (*e.g.* CH_4, C_2H_6), a challenging feat that is yet be to achieved. Currently, the thermodynamic barrier to bond formation and bond cleavage in these small-molecule activation processes remains a large synthetic challenge that impedes direct catalytic applications. As such, methods need to be developed that enable the capture, functionalisation and release of gaseous substrates by catalytically active low oxidation-state or hydrido alkaline earth metal complexes. By expanding on the systems presented in this review, it may be possible to design next-generation catalysts to reimagine and improve current industrial processes.

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