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Generation of organo-alkaline earth metal complexes from non-polar unsaturated molecules and their synthetic applications

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Organomagnesium compounds, represented by the Grignard reagents, are one of the most classical yet versatile carbanion species which have widely been utilized in synthetic chemistry. These reagents are typically prepared *via* oxidative addition of organic halides to magnesium metals, *via* halogen–magnesium exchange between halo(hetero)arenes and organomagnesium reagents or *via* deprotonative magnesiation of prefunctionalized (hetero)arenes. On the other hand, recent studies have demonstrated that the organo-alkaline earth metal complexes including those based on heavier alkaline earth metals such as calcium, strontium and barium could be generated from readily available non-polar unsaturated molecules such as alkenes, alkynes, 1,3-enynes and arenes through unique metallation processes. Nonetheless, the resulting organo-alkaline earth metal complexes could be further functionalized with a variety of electrophiles in various reaction modes. In particular, organocalcium, strontium and barium species have shown unprecedented reactivity in the downstream functionalization, which could not be observed in the reactivity of organomagnesium complexes. This perspective will focus on the newly emerging protocols for the generation of organo-alkaline earth metal complexes from non-polar unsaturated molecules and their applications in chemical synthesis and catalysis.

1. Introduction

As part of the larger movement towards sustainable and green chemistry, transition-metal free methodologies have attracted much attention in the fields of synthetic chemistry and catalysis. In this context, leveraging of alkali/alkaline earth metals to drive desired synthetic processes is extremely attractive due to their abundance in nature and lower toxicity. Organomagnesium reagents, typified by the Grignard reagents, are one of the most classical yet versatile carbanion species, which have widely been utilized in synthetic chemistry.[1,2] These reagents are typically prepared *via* oxidative addition of organic halides to magnesium metals (Scheme 1A)[3] or *via* halogen–magnesium exchange between halo(hetero)arenes and alkylmagnesium

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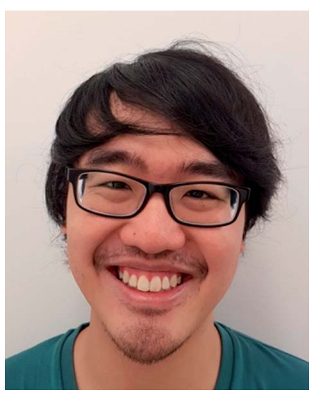

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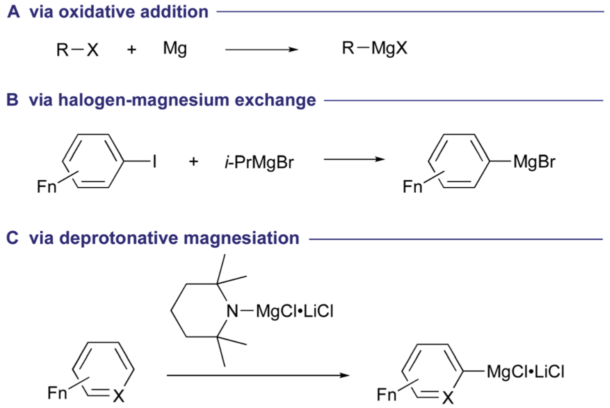

Scheme 1 Conventional preparation methods of organomagnesium reagents.

reagents (Scheme 1B).[4–8] Deprotonative magnesiation of (hetero)arenes has also been developed for the direct preparation of arylmagnesium reagents, while it commonly needs prefunctionalization at a suitable position of the (hetero)arene substrates (Scheme 1C).[9,10]

Recently, synthesis and structural characterization of various molecular magnesium(II) hydrides has successfully been achieved.[11] Employment of sterically hindered ligands (L) is the key to stabilize molecular magnesium(II) hydrides [L–Mg–H] kinetically from their Schlenk equilibrium to homoleptic magnesium-anionic ligand complexes [MgL_2] and insoluble magnesium hydride [MgH_2]$_n$ of the bulk lattice due to its higher lattice energy.[12] Thermally stable lower valent magnesium(I) dimers [L–Mg–Mg–L] could also be designed and synthesized with the aid of bulky anionic ligands.[13–15] The reactivity assessments of these magnesium(II) hydride and magnesium(I) dimer complexes have led to the discovery of unprecedented magnesiation processes of non-polar unsaturated carbon systems such as alkenes, alkynes and arenes, which could be applied in chemical synthesis and catalysis mainly *via* downstream functionalization of the resulting organomagnesium intermediates with various electrophiles. On the other hand, *in situ* generation of active magnesium hydride species could be mediated by σ-bond metathesis of hydrosilanes or pinacolborane with organomagnesium complexes or counter ion metathesis between sodium hydride (NaH)[16] and magnesium iodide (MgI_2) without the use of ligands, facilitating unique molecular transformations of non-polar unsaturated compounds. Moreover, heavier alkaline earth metal hydride complexes based on calcium, strontium and barium have also been designed and prepared.[17,18] These hydride complexes commonly display more hydridic reactivity for hydrometallation to non-polar unsaturated molecules to generate organo-heavier alkaline earth metal intermediates.[19,20] These species further perform unprecedented molecular transformations and catalysis, which are not often observed in the reactivities of organomagnesium complexes. The purpose of this perspective is to highlight recent advances in the development of new metallation methods of non-polar unsaturated systems with alkaline earth metal reagents and the applications of the resulting organo-alkaline earth metal intermediates in chemical synthesis and catalysis.[21] It should be noted that this perspective does not include the preparation methods of the key alkaline earth metal complexes that are used for the metallation of non-polar unsaturated systems. Readers can find the protocols in the corresponding references.

2. Organomagnesium complexes

2.1. Transformation of alkenes

The terminal magnesium hydride carbatrane complex **1** having a tris[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl ligand was recently synthesized by Parkin and it was found to serve as a catalyst for the Markovnikov hydrosilylation and hydroboration of styrene (**2**) through hydromagnesiation and ensuing σ-bond metathesis of the resulting alkylmagnesium intermediate with hydrosilane **3** ($PhSiH_3$) or pinacolborane (**4**) [HB(pin)] (Scheme 2).[22] The turnover frequency of the hydrosilylation was identified as 0.9 h^{-1}, whereas that of the hydroboration was 0.3 h^{-1}.

In contrast, β-diketiminato magnesium hydride dimer **7** (ref. 23) performed *anti*-Markovnikov hydromagnesiation of

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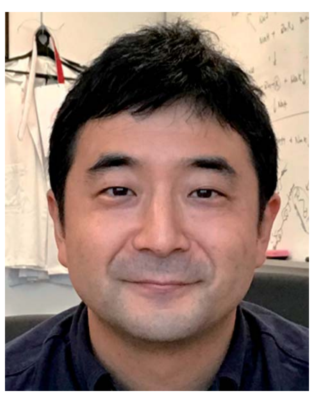
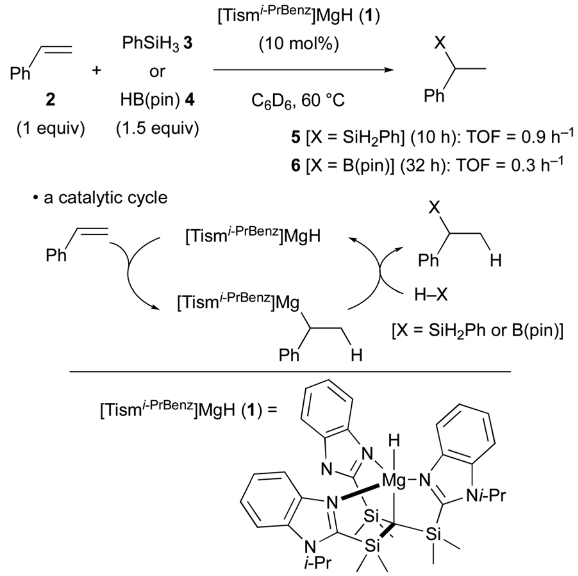


Shunsuke Chiba earned his PhD degree in 2006 under the supervision of Prof. Koichi Narasaka at the University of Tokyo. In 2007, he embarked on his independent career as the faculty of Nanyang Technological University (NTU), Singapore, where he is currently Professor of Chemistry. His research group focuses on methodology development in the area of synthetic chemistry and catalysis.



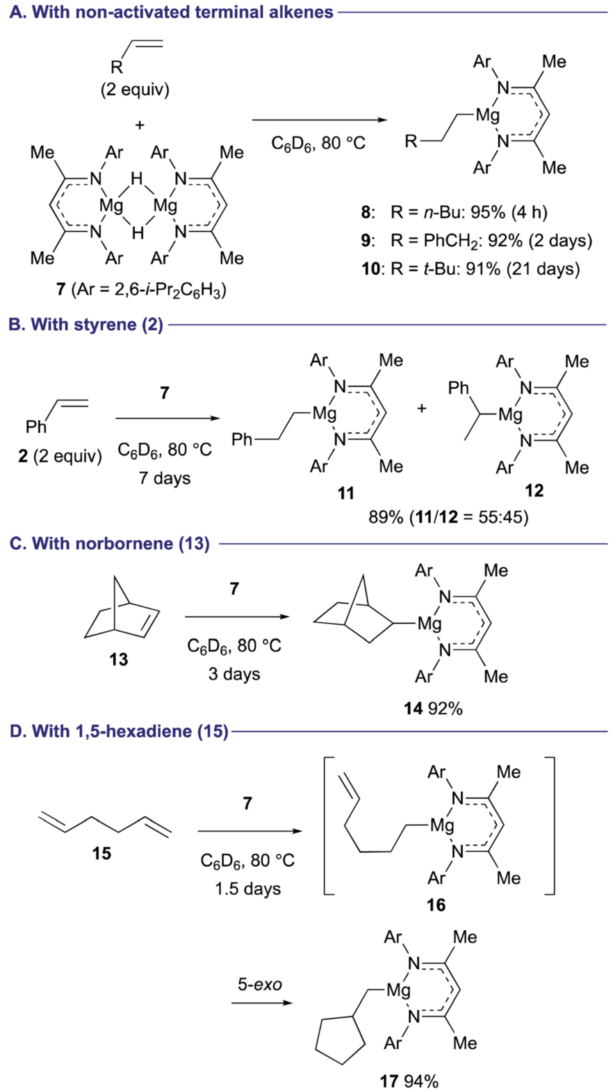
Scheme 2 Catalytic hydrosilylation and hydroboration of styrene (Parkin, 2017).

unactivated aliphatic terminal alkenes in good efficiency to afford the corresponding organomagnesium complexes **8–10** (Scheme 3A).[24] The *anti*-Markovnikov regioselectivity and the reaction rate are primarily governed by the steric effect. In turn, the hydromagnesiation of styrene (**2**) gave a 55 : 45 mixture of linear and branched organomagnesium species **11** and **12** (Scheme 3B). Although 1,2-disubstituted alkenes were generally inert toward hydromagnesiation, strained bicyclic alkene, norbornene (**13**) showed good reactivity with magnesium hydride **7** to afford 2-norbornylmagnesium **14** (Scheme 3C). A domino sequence of hydromagnesiation and 5-*exo* carbomagnesiation was observed in the reaction of 1,5-hexadiene (**15**), affording cyclopentylmethylmagnesium **17** *via* 5-hexenylmagnesium **16** (Scheme 3D).

Thus, this hydromagnesiation of non-activated alkenes with magnesium hydride **7** could be applied for the catalytic hydrosilylation using $PhSiH_3$ **3**, which is responsible to undergo rate-determining σ-bond metathesis with the organomagnesium intermediates generated by hydromagnesiation to maintain the catalytic turnover (Scheme 4).

Jones and Maron revealed that magnesium(I) dimers **20** (ref. 25) and **21** (ref. 26) supported by β-diketiminato ligands showed unprecedented reactivity toward alkenes. For example, 1,1-diphenylethylene (**22**) underwent oxidative insertion into the Mg(I)–Mg(I) bond of **20** and **21** to form 1,2-dimagnesioethane complexes **23** and **24**, respectively. At ambient temperature, this process was found reversible *via* reductive elimination of 1,1-diphenylethylene (**22**) (Scheme 5).[27]

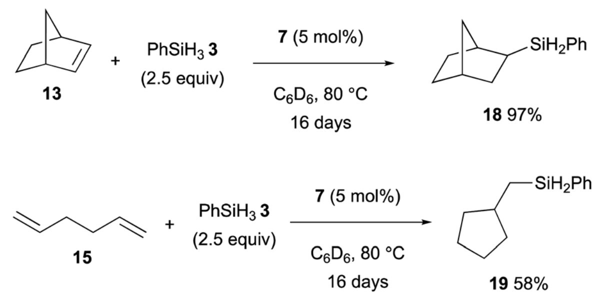
Treatment of the 1,2-dimagnesioethane complex **23** with H_2 resulted in regioselective hydrogenation at the Mg–CPh_2 moiety to liberate alkylmagnesium **25** and magnesium hydride dimer **26**, while the reaction of **23** with ethylene induced its insertion into the Mg–CPh_2 bond, providing 1,4-dimagnesiobutane **27** (Scheme 6A). Interestingly, in the reaction of **24** with CO,



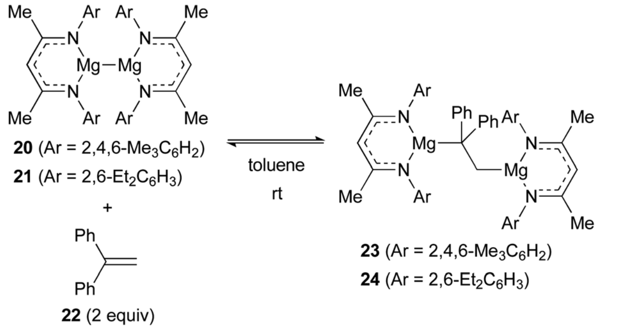
Scheme 3 Hydromagnesiation of alkenes with magnesium hydride **7** (Maron and Hill, 2019).

cyclobutenediolate **28** was formed *via* sequential incorporation of two molecules of CO and cyclization (Scheme 6B).

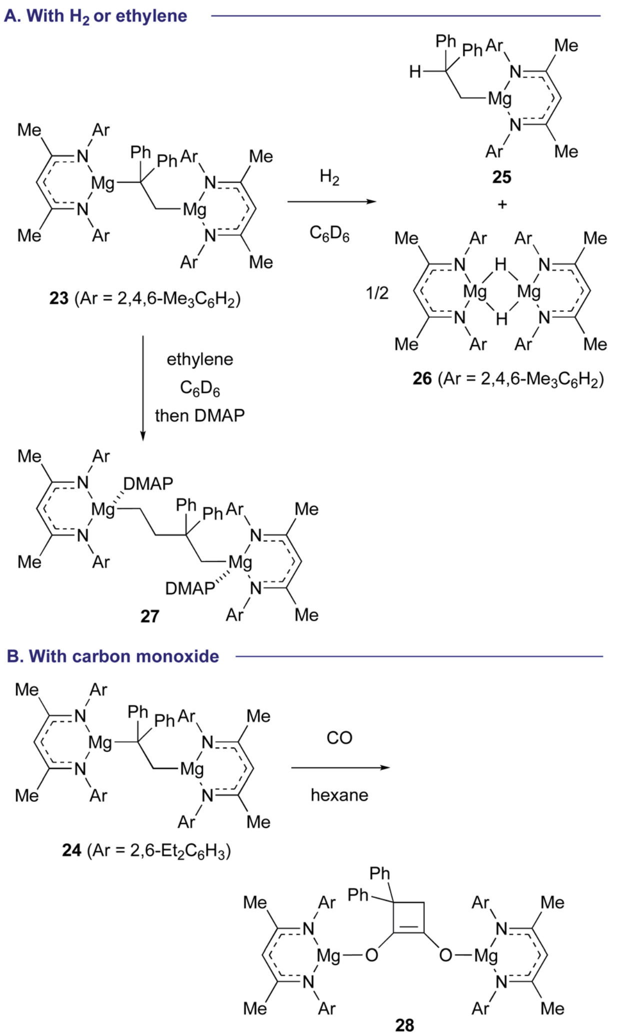
In the presence of an *N*-heterocyclic carbene ligand that can coordinate with Mg(I) centers as a Lewis base, the magnesium(I)



Scheme 4 Catalytic hydrosilylation of alkenes with **7** (Maron and Hill, 2019).



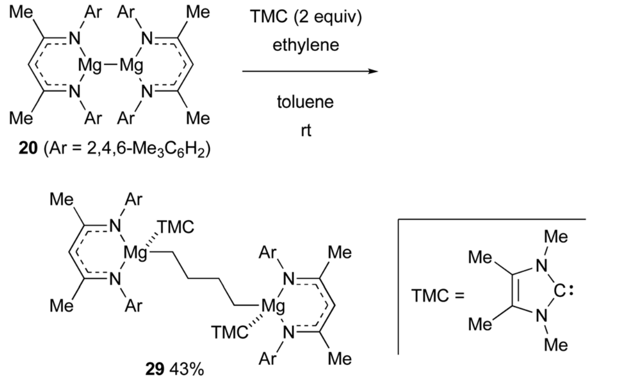
Scheme 5 Reversible insertion of 1,1-diphenylethylene into the Mg(I)–Mg(I) bond (Jones and Maron, 2017).



Scheme 6 Unique reactivity of 1,2-dimagnesioethane complexes **23** and **24** (Jones and Maron, 2017).

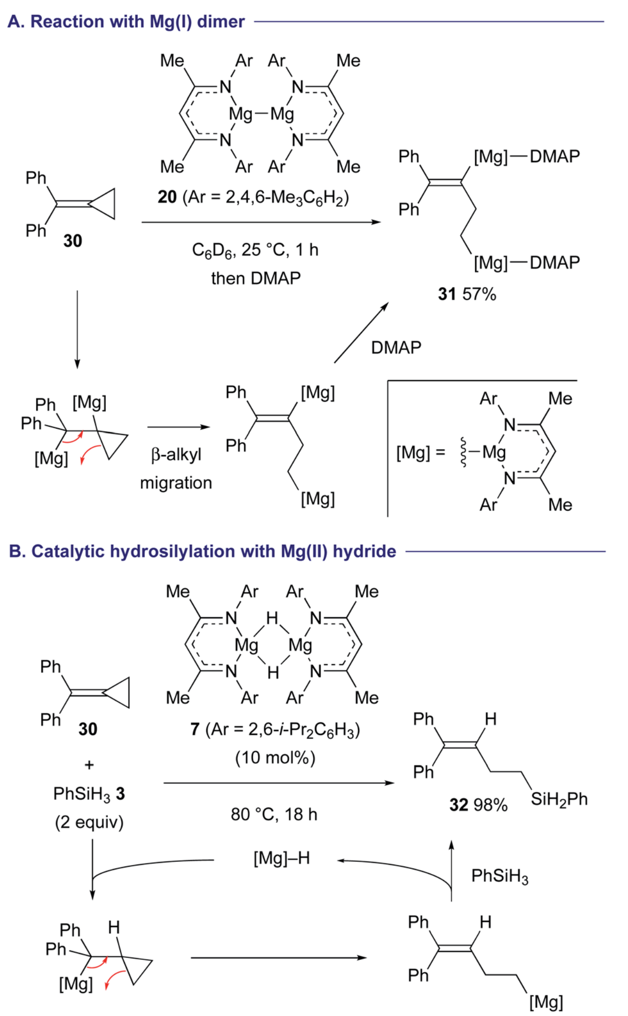
dimer **20** could reductively activate even inert ethylene, forming 1,4-dimagnesiobutane **29** in 43% yield (Scheme 7).[28]

Treatment of alkylidene cyclopropane **30** with magnesium(I) dimer **20** resulted in the formation of 1,3-dimagnesio-3-butene **31** *via* 1,2-dimagnesiation of the alkene moiety of **30** followed by β-alkyl migration associated with the ring-opening of the



Scheme 7 Reductive activation of ethylene with Mg(I) dimer **20** (Jones and Maron, 2020).

cyclopropane ring (Scheme 8A).[29] A combination of hydromagnesiation of alkenes and this β-alkyl migration led to the development of catalytic hydrosilylation of alkylidene cyclopropane **30** using magnesium hydride **7** and hydrosilane **3**, affording homoallylsilane **32** in high yield (Scheme 8B).



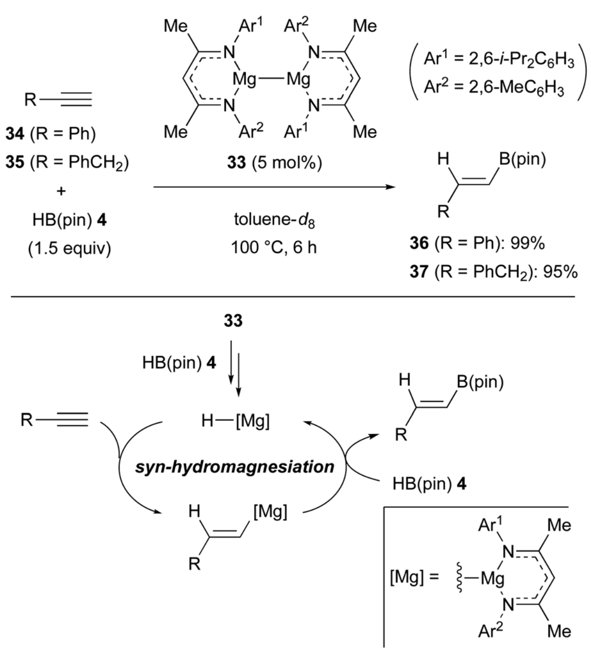
Scheme 8 1,2-Dimagnesiation of alkylidene cyclopropane **30** with Mg(I) dimer **20** followed by β-alkyl migration and its catalytic variant with Mg(II) hydride **7** (Crimmin, 2020).

2.2. Transformation of alkynes

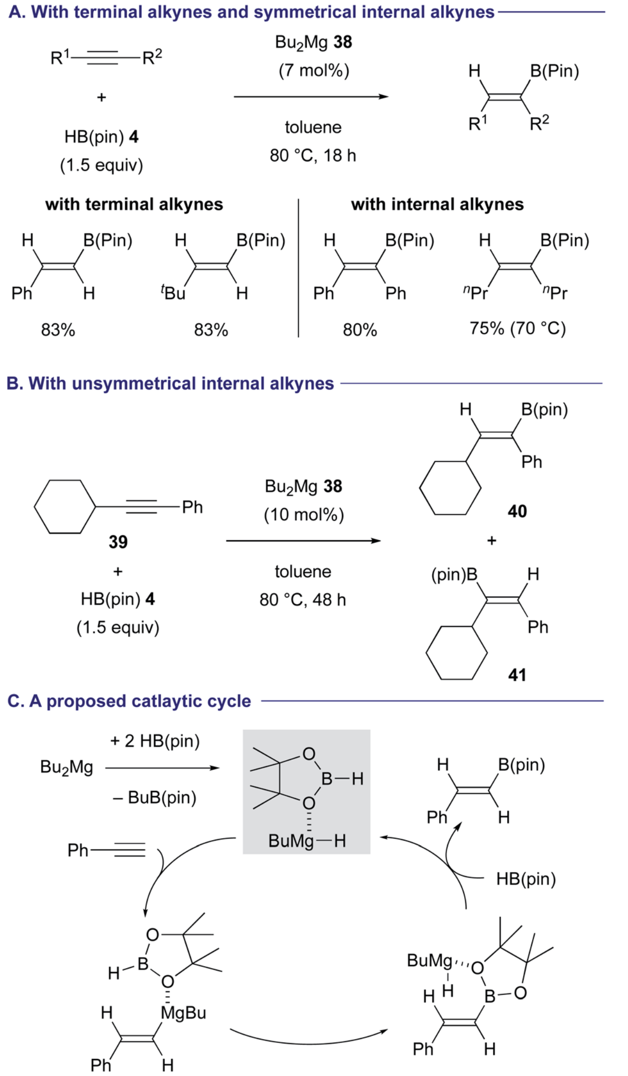
The magnesium(I) dimer **33** containing unsymmetrical β-diketiminate ligands was found to be an effective pre-catalyst for the *anti*-Markovnikov hydroboration of terminal alkynes such as **34** and **35** with pinacolborane (**4**) [HB(pin)] (Scheme 9).[30] In these processes, it was proposed that the magnesium(I) dimer pre-catalyst **33** is converted into magnesium hydride *via* the reaction with **4**, although the precise mechanism is unclear. The resulting magnesium hydride underwent *syn*-hydromagnesiation of the alkyne to form an alkenylmagnesium intermediate. Finally, σ-bond metathesis of alkenylmagnesium with HB(pin) **4** liberated the alkenylborane products such as **36** and **37** along with the regeneration of the magnesium hydride.[31]

Rueping and Cavallo discovered that a catalytic amount of dibutylmagnesium (**38**) (Bu_2Mg), in the presence of HB(pin) **4**, is able to effect the *syn*-selective hydroboration of both terminal and internal alkynes in good yields (Scheme 10A).[32] In the case of unsymmetrical internal alkynes such as (cyclohexylethynyl) benzene (**39**), the regioselectivity was controlled by the steric difference of the substituents (see Scheme 10B for the regioselective formation of **40** over **41**). The active catalytic species was estimated as butylmagnesium hydride coordinated with HB(pin) **4**, which could be generated *in situ* through σ-bond metathesis between Bu_2Mg (**38**) and HB(pin) **4** (Scheme 10C). The *syn*-hydromagnesiation of the alkyne generated the vinyl magnesium intermediate, which underwent another σ-bond metathesis with HB(pin) **4**, to regenerate butylmagnesium hydride species with the release of the hydroborated product.[33]

Solvothermal treatment of sodium hydride (**42**) with magnesium iodide (**43**) in THF was found to allow for counter ion metathesis, generating highly reactive magnesium hydride (**44**) $[MgH_2]_n$, which could induce unprecedented *anti*-

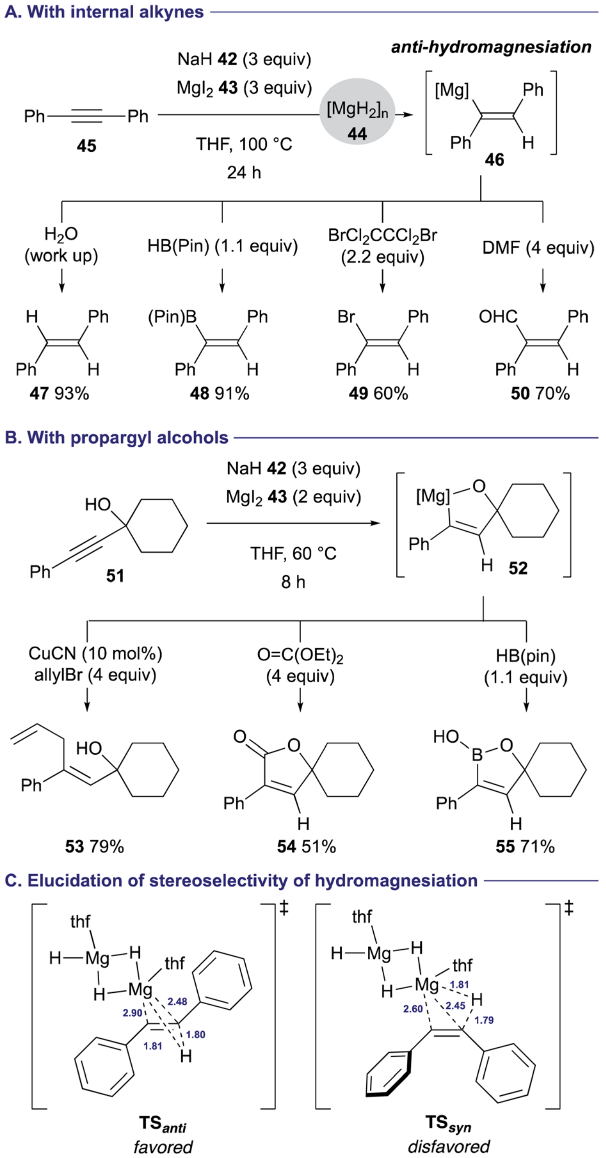


Scheme 9 Catalytic hydroboration of alkynes with unsymmetrical Mg(I) dimer **33** (Ma, 2018).



Scheme 10 Catalytic hydroboration of terminal and internal alkynes with Bu_2Mg (Rueping and Cavallo, 2019).

hydromagnesiation of arylalkynes such as diphenylacetylene (**45**) (Scheme 11A).[34] The resulting alkenylmagnesium intermediate **46** could be trapped with a series of electrophiles such as water (for **47**), HB(pin) **4** (for **48**), 1,2-dibromotetrachloroethane (for **49**) and dimethylformamide (DMF) (for **50**) to afford stereochemically well defined functionalized alkenes. In turn, the reactions of propargyl alcohols such as **51** underwent *anti*-hydromagnesiation with perfect diastereoselectivity *via* 5-membered ring magnesiocycles such as **52**, and ensuing treatment with electrophiles allowed for further downstream functionalization (see Scheme 11B for the synthesis of **53–55**). The DFT calculation using a MgH_2 dimer as a model active species suggested that the reaction *via* transition state $\mathbf{TS}_{anti}$ is the favored process, where the polar hydride transfer mechanism is involved, to afford the *anti*-alkenylmagnesium species (Scheme 11C). On the other hand, the large distortion of diphenylacetylene is required in $\mathbf{TS}_{syn}$, making the *syn*-hydromagnesiation unfavorable.

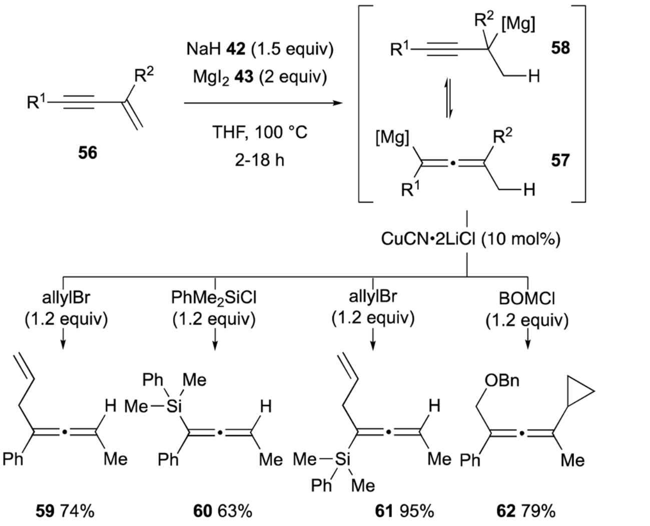


Scheme 11 *Anti*-hydromagnesiation of arylalkynes by *in situ* generated MgH_2 from NaH and MgI_2 (Chiba and Takita, 2020).

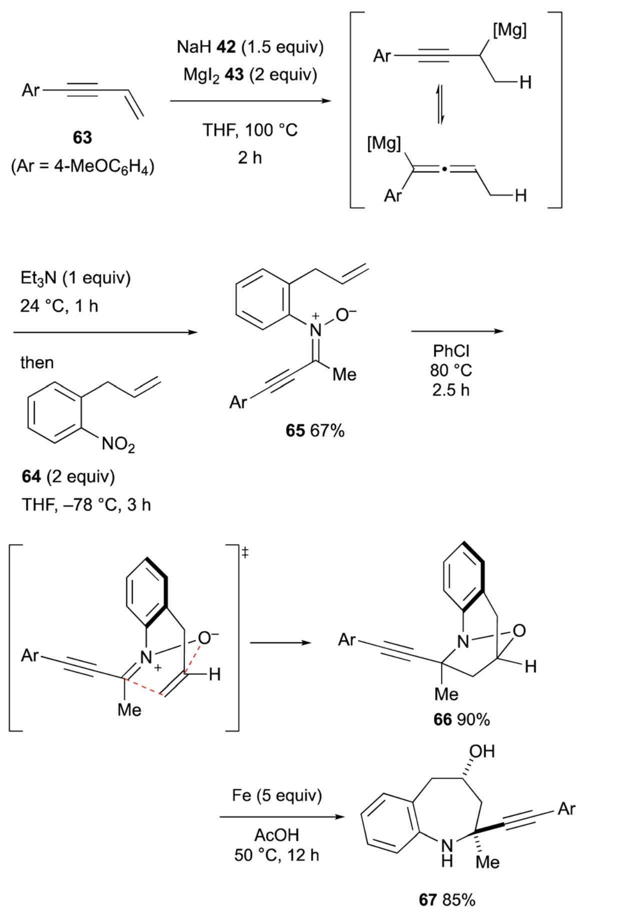
2.3. Transformation of 1,3-enynes

The unique hydridic reactivity of magnesium hydride (**44**) generated *in situ* from sodium hydride (**42**) and magnesium iodide (**43**) was extended further to regioselective hydromagnesiation of 1,3-enynes **56** to form an equilibrium mixture of allenylmagnesium **57** and propargylmagnesium **58** (Scheme 12).[35] Downstream functionalization of the resulting organomagnesium intermediates **57** and **58** was demonstrated by subsequent treatment with a series of alkyl and silyl halides in the presence of CuCN as a catalyst, affording polysubstituted allenes **59–62**.

In turn, downstream treatment of the allenyl/propargylmagnesium intermediates derived from hydromagnesiation of 1,3-enynes with organo nitro compounds[36,37] enabled engagement of propargylmagnesium species for the



Scheme 12 Hydromagnesiation of 1,3-enynes with MgH_2 and downstream functionalization for the synthesis of substituted allenes (Chiba and Takita, 2021).



Scheme 13 Hydromagnesiation of 1,3-enynes with MgH_2 and downstream functionalization for the synthesis of nitrones (Chiba, 2021).

amination, resulting in the formation of α-alkynylnitrones (Scheme 13).[38] The α-alkynylnitrone **65** derived from 1,3-enyne **63** and 1-allyl-2-nitrobenzene (**64**) underwent intramolecular 1,3-dipolar cycloaddition to afford tetrahydro-1,4-epoxybenzo[*b*]azepine **66** as the major product and the ensuing reductive N–O bond cleavage delivered diastereomerically pure tetrahydro-1*H*-benzo[*b*]azepin-4-ol **67**.

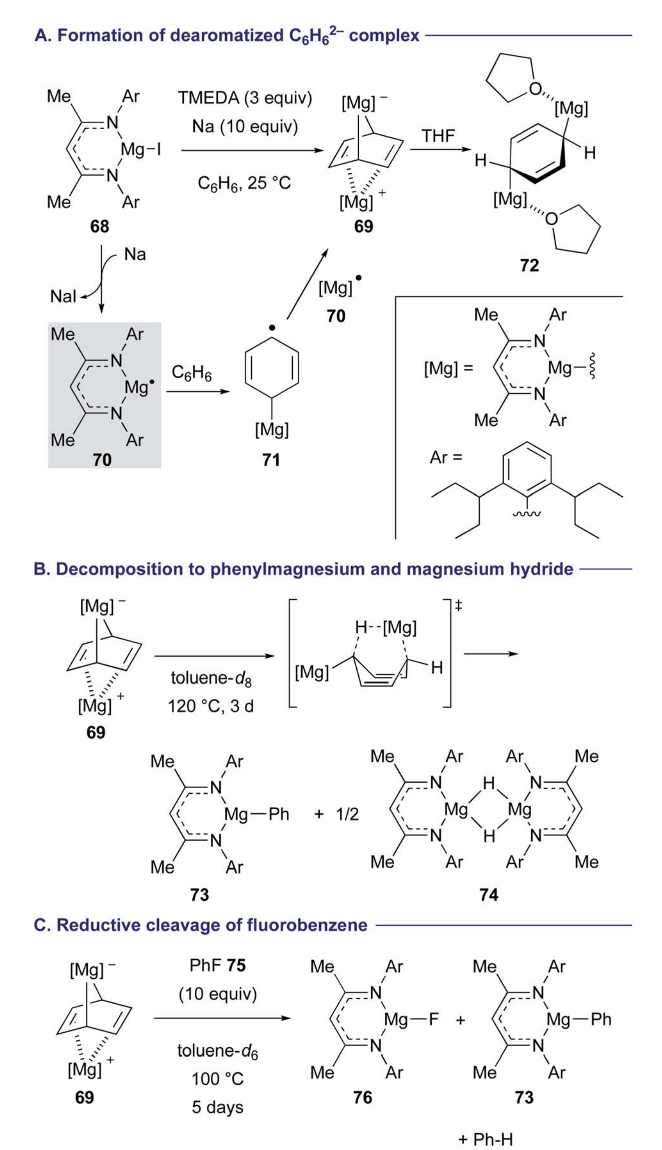
2.4. Transformation of arenes

Two new strategies have recently emerged to convert inert arenes into the corresponding arylmagnesium complexes with *in situ* generated magnesium(I) radical species.

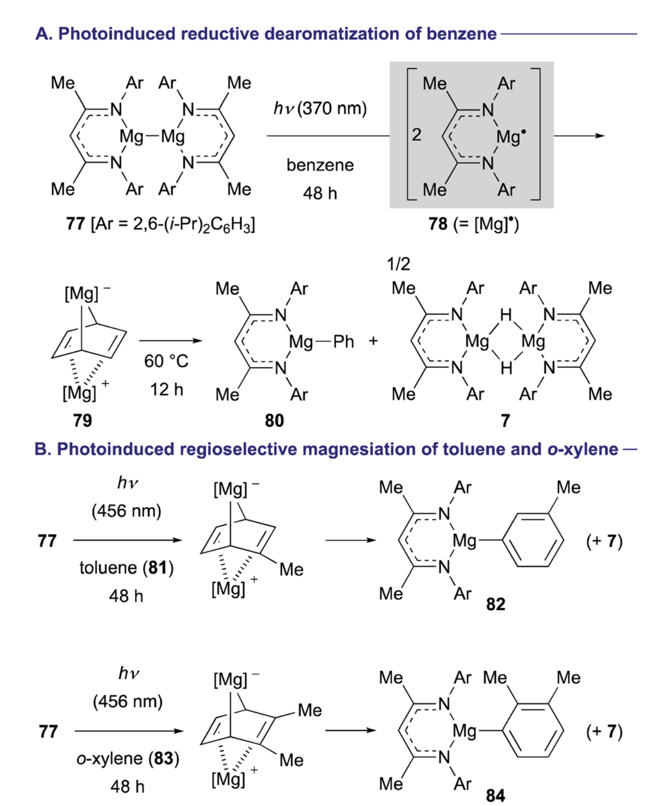
Reduction of magnesium iodide complex **68** with a super bulky β-diketiminate ligand having 2,6-diisopentylphenyl groups on the imine nitrogen by sodium (Na) in the presence of tetramethylethylenediamine (TMEDA) in benzene generated cyclohexandienediyl bridged magnesium complex **69** (dearomatized C_6H_6 dianion sandwiched between divalent magnesium cations) (Scheme 14A).[39] The reaction was initiated by the generation of doublet magnesium(I) radical **70** and its subsequent addition to benzene to form cyclohexadienyl anion radical **71**, which was further reduced by **70** to liberate **69**. The use of the bulky ligand and bidentate TMEDA is the key to kinetically stabilize the magnesium(I) radical **70** and prevent its dimerization. Addition of THF to **69** led to the formation of centrosymmetric flat C_6H_6 dianion THF adduct **72**. The reaction of this dearomatized C_6H_6 dianion complex **69** in toluene at 120 °C for 3 days gave phenylmagnesium **73** and magnesium hydride species **74** (Scheme 14B).

The C_6H_6 dianion complex **69** also displayed highly reducing reactivity. For example, addition of fluorobenzene (**75**) to **69** induced reductive cleavage of the C–F bond to give magnesium fluoride **76** and phenylmagnesium **73** with the release of benzene (Scheme 14C).

On the other hand, Maron and Jones discovered that photoexcitation of magnesium(I) dimer **77** induced homolysis of the Mg–Mg bond to generate a highly reactive magnesium(I) radical **78**, which could be used for reductive dearomatization of benzene to form cyclohexadienediyl bridged magnesium complex **79** (Scheme 15A).[40] Similarly, **79** could be readily converted into phenylmagnesium **80** and magnesium hydride complex **7** upon gentle heating at 60 °C (Scheme 15A). Interestingly, the photoinduced magnesiation reactions of



Scheme 14 Reductive magnesiation of benzene with magnesium(I) radical **70** (Harder, 2019).



Scheme 15 Reduction and C–H magnesiation of inert arenes using photochemically generated magnesium(I) radical **78** (Maron and Jones, 2021).

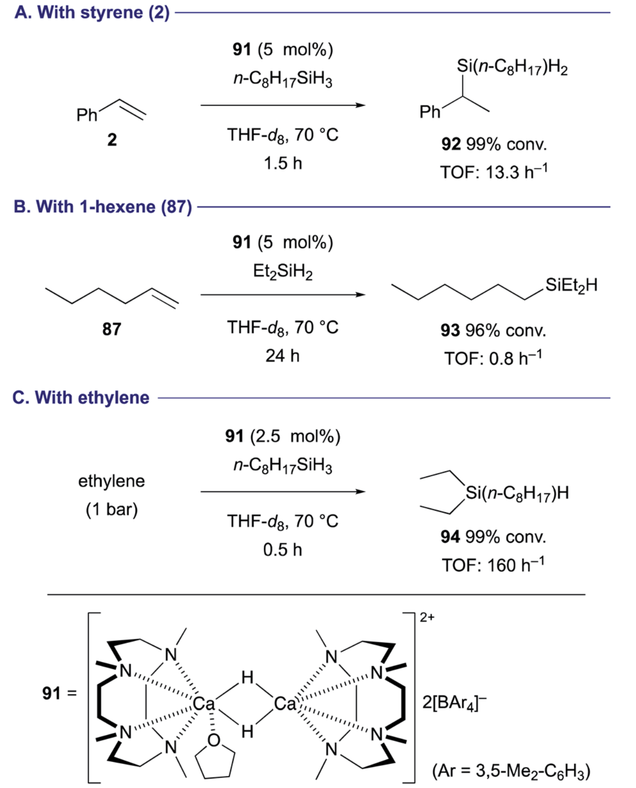
substituted arenes with **77** were observed to be regioselective. For example, the magnesiation of toluene (**81**) was observed at the *meta*-position to form **82**, whereas that of *o*-xylene (**83**) afforded *ortho*-magnesiated product **84** as a single product (Scheme 15B).

3. Organo-heavier alkaline earth metal complexes

This section highlights recent selected examples for the generation of organo-heavier alkaline earth metal complexes from non-polar unsaturated molecules and their exotic reactivities in chemical synthesis and catalysis.

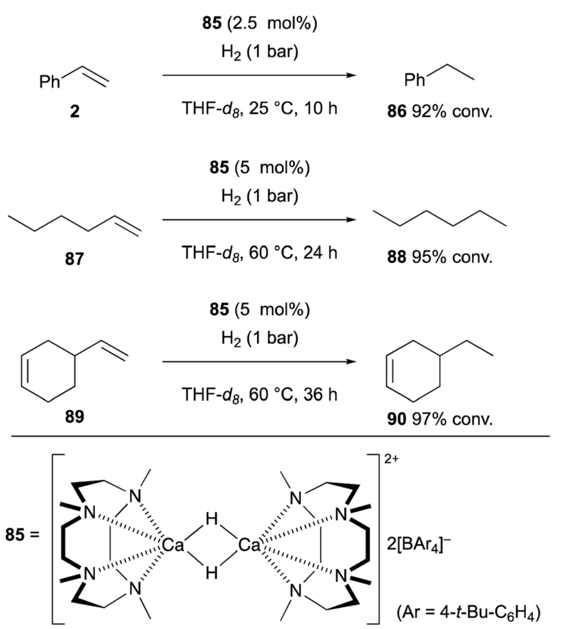
Maron and Okuda recently developed cationic dinuclear calcium hydride complex **85** supported by 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane as the neutral tetradentate macrocyclic nitrogen ligand and tetraarylborate as the counter anion.[41] This calcium hydride complex functioned as a catalyst for the hydrogenation of terminal alkenes such as styrene (**2**) and 1-hexene (**87**) under a hydrogen atmosphere, whereas internal alkenes could be kept intact (Scheme 16). Thus, in the reaction of skipped diene **89**, selective hydrogenation of the terminal alkene moiety was observed to afford **90** as the sole product. It was speculated that the process is initiated by hydrometallation of terminal alkenes by the cationic calcium hydride complex **85** to form organocalcium intermediates, which are subsequently protonated with molecular hydrogen *via* heterolysis of the H–H bond to give the hydrogenation products along with the regeneration of the calcium hydride complex **85** to maintain the catalytic turnover.

The regioselectivity of the hydrometallation of terminal alkenes is determined by the electronic nature of the alkenes.

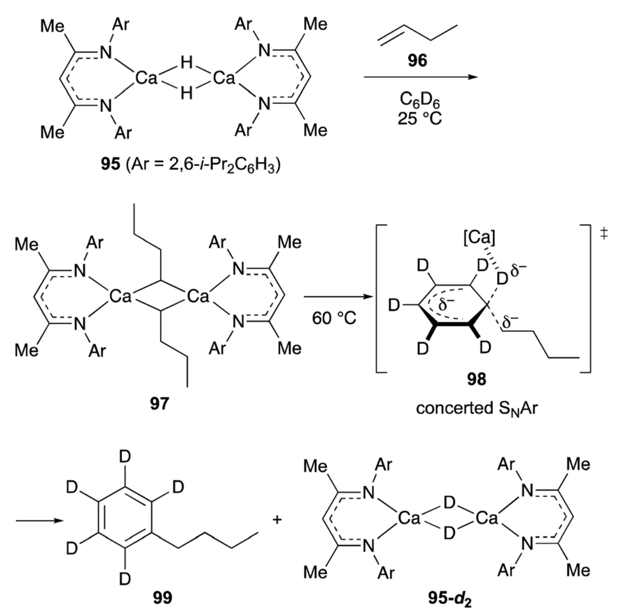


Scheme 17 Hydrosilylation of alkenes catalyzed by cationic calcium hydride dimer **91** (Okuda, 2020).

Okuda demonstrated hydrosilylation of terminal alkenes using the cationic dinuclear calcium hydride complex **91** as the catalyst in the presence of hydrosilanes (Scheme 17). The reaction with styrene (**2**) proceeded in the Markovnikov manner to form



Scheme 16 Hydrogenation of alkenes catalyzed by cationic calcium hydride dimer **85** (Maron and Okuda, 2017).

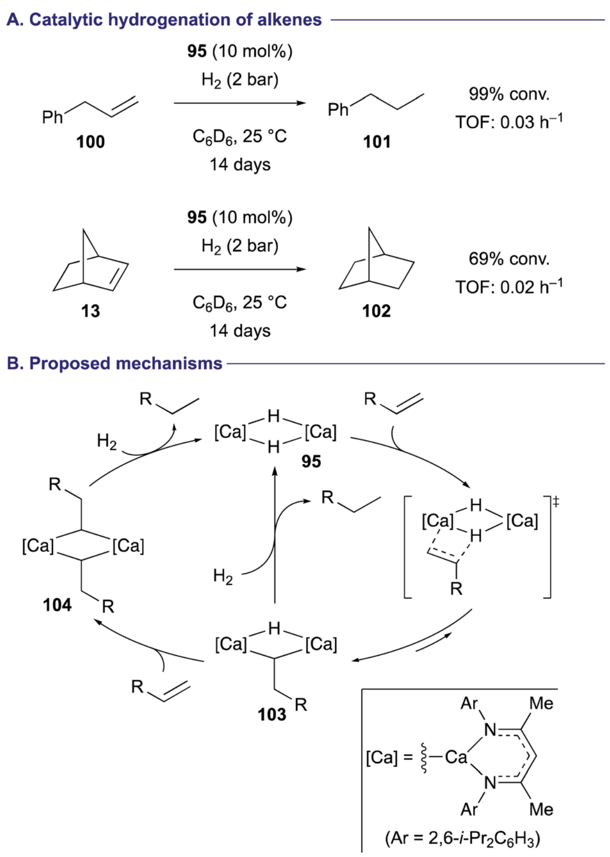


Scheme 18 Hydrometallation of non-activated terminal alkenes and the following S_NAr alkylation of benzene promoted by calcium hydride dimer **95** (Maron, 2017).

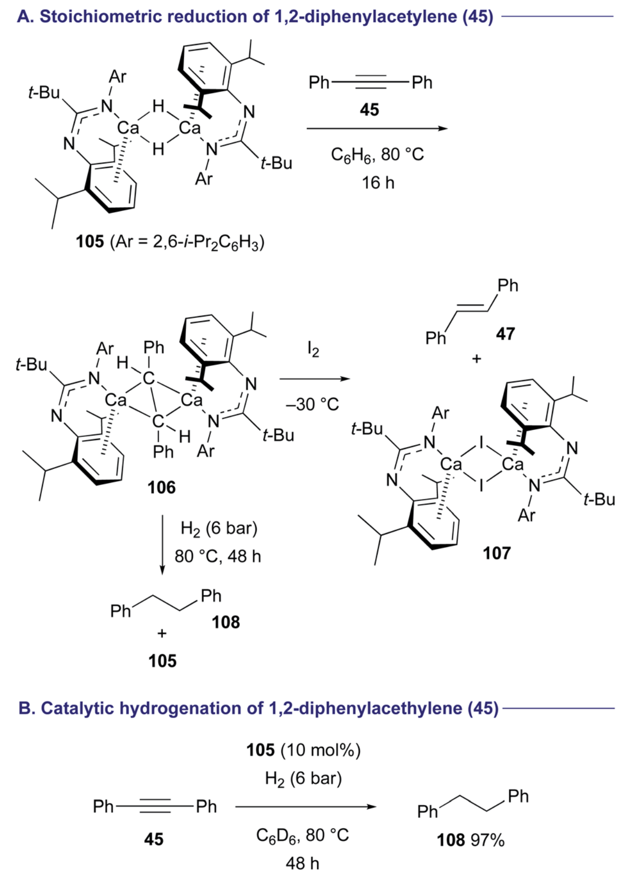
branched benzylsilane **92** as the product (Scheme 17A), whereas *anti*-Markovnikov selectivity was observed in the hydrosilylation of non-activated terminal alkenes such as 1-hexene (**87**) (Scheme 17B).[42] It should also be noted that this catalytic system is amenable to the hydrosilylation of ethylene (Scheme 17C). A more recent study revealed that the employment of 1,4,7,10,13-pentamethyl–1,4,7,10,13-pentaazacyclopentadecane as the pentadentate macrocyclic ligand could enhance the catalytic activity of the calcium hydride complex toward the hydrogenation and hydrosilylation.[43]

Maron discovered that β-diketiminato calcium hydride dimer **95** with no THF solvation on the calcium center undergoes hydrometallation of non-activated terminal alkenes such as 1-butene (**96**) in C_6D_6 at ambient temperature to form alkylcalcium dimer **97** (Scheme 18).[44] Further treatment of **97** at 60 °C liberated *n*-butylbenzene **99** along with the regeneration of the calcium deuteride dimer **95-*d*$_2$**. This unusual alkylation of benzene was characterized as the concerted nucleophilic aromatic substitution reaction where an alkyl carbanion is installed with concurrent elimination of a hydride on sp^2 hybridized carbon *via* the transition state **98**.[45]

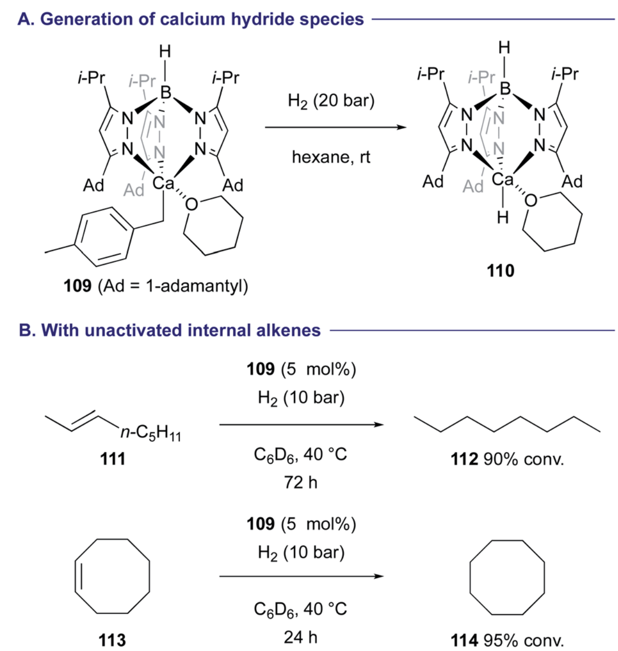
Hill and Maron demonstrated that under a hydrogen atmosphere, β-diketiminato calcium hydride dimer **95** could function as the catalyst for the hydrogenation of terminal alkenes such as allylbenzene (**100**) as well as some activated internal alkenes such norbornene (**13**) (Scheme 19A).[46] Based on the



Scheme 19 Hydrogenation of alkenes catalyzed by calcium hydride dimer **95** (Hill and Maron, 2018).



Scheme 20 Hydrogenation of alkynes with amidinato calcium hydride dimer **105** (Harder, 2017).



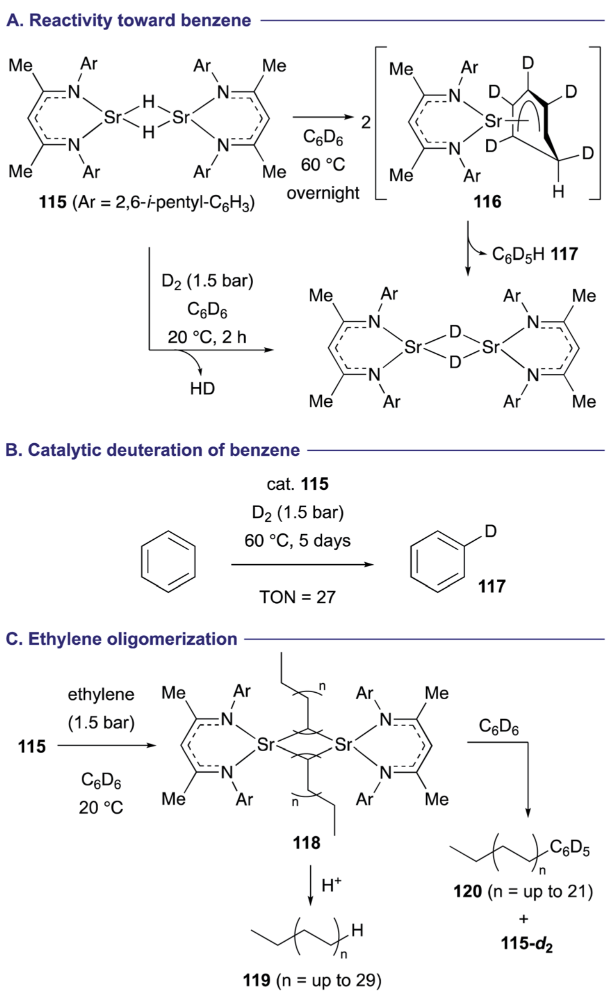
Scheme 21 Hydrogenation of alkenes with mononuclear calcium hydride **110** (Cheng, 2020).

experimental observations and the DFT calculations, it was proposed that the dimeric structure of the calcium complex is likely maintained during the catalytic cycle (Scheme 19B). Upon insertion of one molecule of alkene to calcium hydride dimer **95**, the resulting alkyl hydride dicalcium complex **103** liberates the reduced alkane *via* subsequent deprotonation of H_2. Alternatively, the alkyl hydride dicalcium complex **103** can also undergo the second alkene insertion to generate the dialkyl complex **104**, prior to deprotonation of H_2 to release the reduced alkane with the regeneration of the dimeric calcium hydride species **95**.

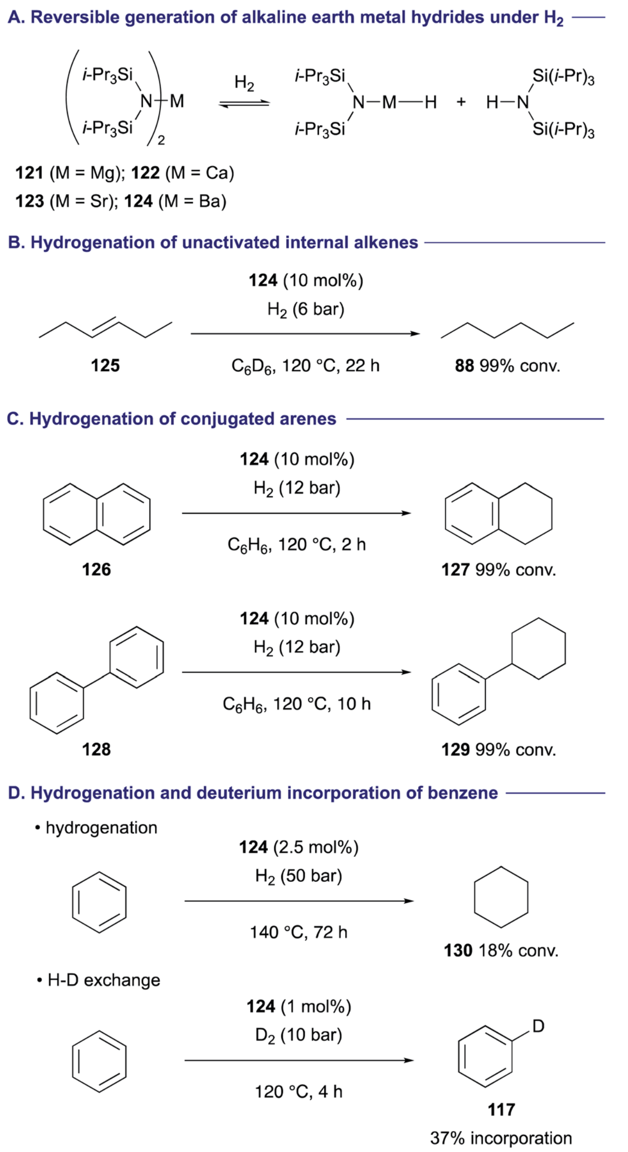
Amidinato calcium hydride dimer complex **105** developed by Harder[47] was found to react with diphenylacetylene (**45**) at 80 °C in benzene to form organocalcium complex **106** symmetrically bridged by a stilbene dianion (Scheme 20A).[48] Oxidation of **106** with I_2 gave *trans*-stilbene (**47**) with calcium iodide dimer **107**. In turn, the treatment of **106** under a H_2 atmosphere (6 bar) resulted in the formation of 1,2-diphenylethane (**108**) along with the regeneration of the calcium hydride dimer complex **105** *via* deprotonation of H_2. Thus, the organocalcium complex **105** could be employed as the catalyst for hydrogenation of diphenylacetylene (**45**) to 1,2-diphenylethane (**108**) under a H_2 atmosphere (6 bar) (Scheme 20B).

Cheng revealed that benzylcalcium complex **109** with a tris-pyrazolyl borate ligand is converted into the mononuclear calcium hydride complex **110** under a H_2 atmosphere (Scheme 21A).[49] The resulting calcium hydride **110** could serve as an active catalyst for the hydrogenation of alkenes including non-activated internal alkenes such as *trans*-2-octene (**111**) and cyclooctene (**113**) (Scheme 21B).

A strontium hydride dimer **115** having extremely bulky β-diketiminato ligands was found to display higher hydridic reactivity toward benzene by Harder (Scheme 22).[50] The stoichiometric reaction of **115** with C_6D_6 induces unprecedented hydride addition to C_6D_6 to form dearomatized anionic intermediate **116**, which undergoes re-aromatization *via* elimination



Scheme 22 Nucleophilic hydrogenation and alkylation of benzene promoted by strontium hydride dimer **115** (Harder, 2019).



Scheme 23 Hydrogenation of non-activated alkenes and arenes with a barium hydride complex having a bis(triisopropylsilyl)amide ligand (Harder, 2020).

of deuteride to form strontium deuteride dimer **115-*d*$_2$** and C_6D_5H **117** (Scheme 22A). On the other hand, the strontium hydride dimer **115** performed fast deprotonative H–D exchange under a D_2 atmosphere (1.5 bar) at ambient temperature. Thus, these reactivities could be combined to develop catalytic deuteration of benzene under a D_2 atmosphere by **115** (Scheme 22B). In turn, under an ethylene atmosphere (1 bar) in C_6D_6 at ambient temperature, the strontium hydride dimer **115** is quickly converted into alkylstrontium complexes **118** having ethyl, butyl, hexyl and higher ethylene oligomers, which could be confirmed by the detection of the corresponding alkanes **119** by GC-MS analysis. Furthermore, these alkylstrontium complexes **118** undergo nucleophilic aromatic substitution with C_6D_6 to form alkylated arenes **120** and **115-*d*$_2$** (Scheme 22C).

Harder recently exploited alkaline earth metal complexes **121–124** having an extremely bulky bis(triisopropylsilyl)amide ligand as the precatalyst for the alkaline earth metal hydrides capable of catalytic hydrogenation of alkenes under a H_2 atmosphere (Scheme 23A).[51] The barium complex **124** was found to be most reactive, performing hydrogenation of even unactivated internal alkenes such as *trans*-3-hexene (**125**) (Scheme 23B). Moreover, the barium amide **124** complex could perform hydrogenation of conjugated arenes such as naphthalene (**126**) and biphenyl (**128**) to tetralin (**127**) and phenylcyclohexane (**129**), respectively (Scheme 23C). This catalytic system was found to be amenable to the hydrogenation of benzene to cyclohexane (**130**) (Scheme 23D). With 2.5 mol% of **124** under higher H_2 pressure (50 bar) at 140 °C, 18% conversion of benzene to cyclohexane (**130**) was attained after 3 days. On the other hand, treatment of benzene with 1 mol% of **124** under milder pressure of D_2 (10 bar) at 120 °C allowed for H/D exchange of benzene at 37% incorporation rate within 4 h.[52]

4. Conclusions

In this perspective, we have highlighted the protocols for the generation of organomagnesium complexes from non-polar unsaturated compounds and their unique reactivities in chemical synthesis and catalysis. The key enabling advance in these transformations takes advantage of well-defined molecular magnesium(II) hydrides or magnesium(I) dimer complexes, which are supported by the sophisticated sterically hindered anionic ligands. The method for *in situ* generation of active magnesium hydrides *via* either σ-bond metathesis between pinacolborane and dibutylmagnesium or counter ion metathesis between sodium hydride and magnesium iodide without the use of any supporting ligands also enabled concise transformation of alkynes and 1,3-enynes into various scaffolds *via* hydromagnesiation and ensuing downstream functionalization with electrophiles. Engagement of heavier alkaline earth metal hydride complexes having well-defined bulky ligands allowed for metallation of non-activated internal alkenes and arenes including benzene. The resulting organo-heavier alkaline earth metal complexes have shown exotic and unique reactivities in the downstream functionalization. Given the versatile reactivities of organo-alkaline earth metal complexes to drive the unprecedented chemical processes which have been dominated by transition-metal catalysts, we view that more unique and capable synthetic methods, especially catalysis, that leverage organo-alkaline earth metal complexes as the key components, will be devised and engaged in various synthetic endeavours.

Author contributions

S. C. and R. T. conceived the contents of the perspective. All the authors contributed to the preparation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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