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 compounds. Nevertheless, 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.

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magnesium hydride species could be mediated by σ-bond metathesis of hydrosilanes or pinacolborane with organo-magnesium complexes or counter ion metathesis between sodium hydride (NaH)\(^{36}\) 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-diketiminate magnesium hydride dimer 7 (ref. 23) performed anti-Markovnikov hydromagnesiation of...
unactivated aliphatic terminal alkenes in good efficiency to afford the corresponding organomagnesium complexes 8–10 (Scheme 3A). 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 PhSiH₃ 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).

Treatment of the 1,2-dimagnesioethane complex 23 with H₂ resulted in regioselective hydrogenation at the Mg–CPh₂ moiety to liberate alkylmagnesium 25 and magnesium hydride dimer 26, while the reaction of 23 with ethylene induced its insertion into the Mg–CPh₂ bond, providing 1,4-dimagnesiobutane 27 (Scheme 6A). Interestingly, in the reaction of 24 with CO, 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)
dimer 20 could reductively activate even inert ethylene, forming 1,4-dimagnesiobutane 29 in 43% yield (Scheme 7).

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 cyclopropane ring (Scheme 8A). A combination of hydro-magnesiation 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).
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). 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.

Rueping and Cavallo discovered that a catalytic amount of dibutylmagnesium (38) (Bu2Mg), 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). 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 Bu2Mg (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.

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) [MgH2]n, which could induce unprecedented anti-hydromagnesiation of arylalkynes such as diphenylacetylene (45) (Scheme 11A). 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 MgH2 dimer as a model active species suggested that the reaction via transition state TSanti 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 TSsyn, making the syn-hydromagnesiation unfavorable.
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 enabled engagement of propargylmagnesium species for the synthesis of nitrones (Chiba, 2021).
amination, resulting in the formation of \( \alpha \)-alkynyl nitrones (Scheme 13). The \( \alpha \)-alkynyl nitronite 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 \textit{in situ} generated magnesium(i) radical species.

Reduction of magnesium iodide complex 68 with a super bulky \( \beta \)-diketiminate ligand having 2,6-diisopentylphenyl groups on the imine nitrogen by sodium (Na) in the presence of tetramethylethylenediamine (TMEDA) in benzene generated cyclohexandiényl bridged magnesium complex 69 (dearomatized \( C_6H_5 \) dianion sandwiched between divalent magnesium cations) (Scheme 14A). 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 \( C_6H_5 \) dianion complex 69 in toluene at 120 \( ^\circ \text{C} \) for 3 days gave phenylmagnesium 73 and magnesium hydride species 74 (Scheme 14B).

The \( C_6H_5 \) 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 cyclohexadiényl bridged magnesium complex 79 (Scheme 15A). Similarly, 79 could be readily converted into phenylmagnesium 80 and magnesium hydride complex 7 upon gentle heating at 60 \( ^\circ \text{C} \) (Scheme 15A). Interestingly, the photoinduced magnesiation reactions of...
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. 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 alkenes 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 16 Hydrogenation of alkenes catalyzed by cationic calcium hydride dimer 85 (Maron and Okuda, 2017).

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

Scheme 18 Hydrometallation of non-activated terminal alkenes and the following SNAr 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 hydroisilylation of non-activated terminal alkenes such as 1-hexene (87) (Scheme 17B). It should also be noted that this catalytic system is amenable to the hydroisilylation 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 hydroisilylation.

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 C₆D₆ at ambient temperature to form alkylcalcium dimer 97 (Scheme 18). Further treatment of 97 at 60 °C liberated n-butylbenzene 99 along with the regeneration of the calcium deuteride dimer 95-d. 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 sp² hybridized carbon via the transition state 98.

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). Based on the

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

A. Catalytic hydrogenation of alkenes

95 (10 mol%) H₂ (2 bar) C₆D₆, 25 °C 14 days

99% conv. TOF: 0.03 h⁻¹

B. Proposed mechanisms

A. Generation of calcium hydride species

103 R

[Ca] = ½[Ca] + (Ar = 2,6-i-P₂C₆H₃)

109 (Ad = 1-adamantyl)

108 97%

B. With unactivated internal alkenes

109 (5 mol%) H₂ (10 bar) C₆D₆, 40 °C 72 h

112 90% conv.

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 H₂. Alternatively, the alkyl hydride dicalcium complex 103 can also undergo the second alkene insertion to generate the dialkyl complex 104, prior to deprotonation of H₂ to release the reduced alkane with the regeneration of the dimeric calcium hydride species 95.

Amidinato calcium hydride dimer complex 105 developed by Harder⁴⁷ 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 I₂ gave trans-stilbene (47) with calcium iodide dimer 107. In turn, the treatment of 106 under a H₂ 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 H₂. Thus, the organocalcium complex 105 could be employed as the catalyst for hydrogenation of diphenylacetylene (45) to 1,2-diphenylethane (108) under a H₂ atmosphere (6 bar) (Scheme 20B).

Cheng revealed that benzylcalcium complex 109 with a trispyrazolyl borate ligand is converted into the mononuclear calcium hydride complex 110 under a H₂ 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 C₆D₆ induces unprecedented hydride addition to C₆D₆ to form dearomatized anionic intermediate 116, which undergoes re-aromatization via elimination.

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

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**Scheme 23** Hydrogenation of non-activated alkenes and arenes with a barium hydride complex having a bis(trisopropylsilyl)amide ligand (Harder, 2020).
of deuteride to form strontium deuteride dimer 115-d₂ and 
C₆D₆H 117 (Scheme 22A). On the other hand, the strontium 
hydride dimer 115 performed fast deprotonative H–D exchange 
under a D₂ atmosphere (1.5 bar) at ambient temperature. Thus, 
these reactivities could be combined to develop catalytic 
deuteration of benzene under a D₂ atmosphere by 115 (Scheme 
22B). In turn, under an ethylene atmosphere (1 bar) in C₆D₆ 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 
C₆D₆ to form alkylated arenes 120 and 115-d₂ (Scheme 22C).

Harder recently exploited alkaline earth metal complexes 
121–124 having an extremely bulky bis(trisopropylsilyl)amidine 
ligand as the precatalyst for the alkaline earth metal hydrides 
capable of catalytic hydrogenation of alkenes under a H₂ 
atmosphere (Scheme 23A).²⁷ 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 naphtha-
lene (126) and biphenyl (128) to tetralin (127) and phenyl-
cyclohexane (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 H₂ 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 D₂ (10 bar) at 120 °C allowed for H/D 
exchange of benzene at 37% incorporation rate within 4 h.²²

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 mol-
ular magnesium(II) hydrides or magnesium(II) dimer complexes, 
which are supported by the sophisticated sterically hindered 
anionic ligands. The method for in situ generation of active 
magnesium hydrides via either o-bond metathesis between 
pinacolborane and dibutylmagnesium or counter ion metath-
esis between sodium hydride and magnesium iodide without 
the use of any supporting ligands also enabled concise trans-
formation of alkynes and 1,3-enynes into various scaffolds via 
ydromagnesiation 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 reactiv-
ities 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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