Magnesium Pincer Complexes and Their Applications in Catalytic Semihydrogenation of Alkynes and Hydrogenation of Alkenes: Evidence for Metal–Ligand Cooperation

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ABSTRACT: The development of catalysts for environmentally benign organic transformations is a very active area of research. Most of the catalysts reported so far are based on transition-metal complexes. In recent years, examples of catalysis by main-group metal compounds have been reported. Herein, we report a series of magnesium pincer complexes, which were characterized by NMR and X-ray single-crystal diffraction. Reversible activation of H₂ via aromatization/dearomatization metal–ligand cooperation was studied. Utilizing the obtained complexes, the unprecedented homogeneous main-group metal catalyzed semihydrogenation of alkynes and hydrogenation of alkenes were demonstrated under base-free conditions, affording Z-alkenes and alkanes as products, respectively, with excellent yields and selectivities. Control experiments and DFT studies reveal the involvement of metal–ligand cooperation in the hydrogenation reactions. This study not only provides a new approach for the semihydrogenation of alkynes and hydrogenation of alkenes catalyzed by magnesium but also offers opportunities for the hydrogenation of other compounds catalyzed by main-group metal complexes.

INTRODUCTION

The importance of catalysts in organic and inorganic transformations is indisputable. Currently, the most commonly used catalysts are derived from transition metals due to their efficiency in substrate activation and reaction acceleration. However, the costly and, in some cases, toxic characteristics of transition-metal compounds have become significant driving forces to explore alternative catalysts. In this respect, the earth-abundant, nontoxic, and environmentally friendly main-group metals, it is still in its infancy compared to that of transition metals.

In 2016, potassium and lithium dearomatized so-called pincer-type complexes is a versatile strategy for chemical bond activation (Figure 1a). One significant feature of this process is that the oxidation state of the metal center does not change since the bond activation process has been dominated by costly and precious transition metals. In the last few years, increasing attention has been paid to the cheaper first-row transition metals such as Fe, Mn, and Co. With respect to the application of main-group metals, it is still in its infancy compared to that of transition metals.

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pincer complexes were synthesized and characterized by Danopoulos and co-workers, but activity studies have not been demonstrated. Recently, zinc dearomatized complexes were prepared supported by a (PNP)T Bu pincer ligand and applied to N−H and H−H bond activation via the MLC process.

Inspired by these significant advances, we envisioned designing new complexes with other abundant main-group metals, such as magnesium, and extending the main-group metal complexes to more challenging catalytic reactions by employing the MLC activation process.

Catalytic semihydrogenation of alkynes is an important reaction in organic chemistry. Homogeneous catalysts using transition metals and frustrated Lewis pairs have been developed in recent years to efficiently access Z- or E-alkenes. On the contrary, homogeneous main-group metal-catalyzed semihydrogenation of alkynes has never been reported. Indeed, the main-group metal-catalyzed hydrogenation of unsaturated C−C bonds using H2 is rare, presumably because of the challenging H−H bond activation. In 2008, Harder and co-workers reported the hydrogenation of conjugated alkenes by alkaline earth metal complexes under relatively mild conditions, indicating that the early main-group metal-catalyzed hydrogenation of C−C unsaturated bonds is possible. In continuation of our work

Figure 1. Overview of this work. (a) Metal–ligand cooperation by the aromatization/dearomatization of pincer complexes for reversible bond activation and the development of Mg pincer complexes. (b) Application of magnesium pincer complexes in semihydrogenation of alkynes and hydrogenation of alkenes.

Figure 2. Synthesis of magnesium pincer complexes. (a) Synthesis of Mg-1 and Mg-2 with a PNP-type ligand. (b) Synthesis of Mg-3 with a PNN-type ligand. (c) Synthesis of Mg-4 with an NNN-type ligand.
on the activation of small molecules by MLC, we hypothesized that dearamatized magnesium complexes may activate H\textsubscript{2} via the same MLC process as that of transition metals, perhaps leading to the semihydrogenation of alkenes catalyzed by main-group metals.

Herein, we report a series of magnesium pincer complexes based on PNP-, PNN-, and NNN-type ligands, prepared under mild conditions and characterized by NMR and X-ray crystallography. These complexes undergo H–H bond activation via the MLC process without changing the metal oxidation state. The new complexes are applied to the catalytic semihydrogenation of alkenes, generating Z-alkenes with up to >99% yield and >99:1 stereoselectivity. The complexes also catalyze the hydrogenation of alkenes under similar reaction conditions. A possible mechanism clearly demonstrating the catalytic process is proposed based on control experiments and DFT studies.

**RESULTS AND DISCUSSION**

**Preparation and Characterization of Magnesium Pincer Complexes.** The dearamatized magnesium complex Mg-1 was prepared by the reaction of 2,6-bis(di-tert-butylphosphinomethyl)pyridine and Et\textsubscript{3}Mg-dioxane in toluene at room temperature. The color of the solution changed from colorless to yellow after stirring for 10 min, indicating product formation. Unlike the preparation of the known lithium, potassium, and sodium analogues of Mg-1, the magnesium complex was obtained as an orange solid after removing the excess solvent at room temperature for 2 h, and a dimer of two magnesium pincer complexes, supporting the structure of five-coordinate Mg-1 (Figure 3, left). The X-ray structure exhibits a dimer of two magnesium pincer complexes, supporting the observation by NMR. The magnesium center and PNP/Bu ligand form a distorted plane, which results in the different bond lengths of Mg1–P1 (2.66 Å) and Mg1–P2 (2.93 Å). As such, it is understandable that the 31P\textsuperscript{1}H NMR spectrum of Mg-1 exhibits two doublets with a small coupling constant. The dearamatized structure is clearly confirmed by the considerably shorter C1–C2 bond (1.39 Å) compared to the C6–C7 bond (1.51 Å). The result also matches the observation by NMR. Following a similar procedure using Ph\textsubscript{3}Mg-dioxane as a reactant, Mg-2 was obtained with a phenyl group coordinated to the magnesium center. The 31P\textsuperscript{1}H NMR spectrum shows two singlets at a higher field (16.41 and –6.34 ppm) compared to that of Mg-1. The larger steric hindrance of the phenyl group compared to the ethyl group possibly resulted in longer Mg–P bonds, which led to the formation of singlet phosphorus resonances. The 1H NMR spectrum also exhibits characteristic methine (CH) and methylene (CH\textsubscript{2}) peaks of the side arm, which confirm the dearamatized structure. NMR signals assigned to the phenyl group are observed, confirming the presence of the phenyl ligand. Similar chemical shifts and integration are observed in the 1H NMR spectrum, indicating the formation of a structure similar to Mg-1.

Mixing the PNN-type ligand (PNN = 6-(di-tert-butylphosphinomethine)-2-(N,N-diethylaminomethyl)-1,6-dihydro-pyridine) and Et\textsubscript{3}Mg-dioxane at room temperature for 2 h resulted in the formation of Mg-3 as an orange solid after removing the excess solvent. The 31P\textsuperscript{1}H NMR spectrum exhibits a singlet at 0.43 ppm, suggesting the generation of a single product. A dearamatized pyridine backbone was observed in the 1H NMR spectrum, indicating the formation of a structure similar to Mg-1.

Complex Mg-3 was also formed as a dimer with two (PNN)MgEt units bridged by dioxane, as displayed by its X-ray structure (Figure 3, middle). Similar to Mg-1, the PNN ligand and magnesium center exhibit a distorted plane due to steric hindrance. The Mg1–P1 bond length (2.75 Å) is slightly longer than that of Mg-1 (2.66 Å).

The successful preparation of Mg-3 indicates that tertiary amines are proper ligands for dearamatized magnesium complexes displayed as wireframes for clarity. Selected bond lengths (Å) and angles (deg): (Mg-1) Mg1–P1 2.656(2), Mg1–P2 2.928(2), Mg1–N1 2.140(5), Mg1–O1 2.171(4), C1–P1 1.770(7), C1–C2 1.393(9), C7–P2 1.852(6), C6–C7 1.509(8), N1–C2 1.404(7), N1–C6 1.363(7), C24–Mg1–N1 165.5(2), C24–Mg1–O1 100.5(2). (Mg-3) Mg1–P1 2.7516(6), Mg1–N1 2.1440(12), Mg1–N2 2.3011(13), Mg1–C22 2.1783(14), Mg1–O1 2.1288(10), C1–C2 1.382(2), C6–C7 1.510(2), and C22–Mg1–O1 104.98(5). (Mg-4) Mg1–N1 2.0333(12), Mg1–N2 2.4354(12), Mg1–N3 2.2943(11), Mg1–C33 2.1507(14), C1–C2 1.5023(18), C6–C7 1.3658(18), and N1–Mg1–C33 173.71(5).
complexes. Thus, \( \text{Mg-4} \) was prepared to investigate its structure and activity using an NNN-type ligand (Figure 2c). The complex \( \text{Mg-4} \) exhibits three signals at 6.41, 5.97, and 4.95 ppm for the pyridine protons in the \(^1\text{H}\) NMR spectrum. These signals shifted to low frequencies, signifying the formation of a dearomatized NNN ligand. Unlike the other complexes described above, dioxane is not coordinated in this case, possibly because of the steric hindrance of the bulky substituents on the amines. This indicates that the four-coordinate magnesium complex is stable, which is in accord with reports in the literature.\(^{37,40}\) Single crystals of \( \text{Mg-4} \) suitable for X-ray diffraction studies were obtained by slow evaporation of a mixed solvent of \( \text{Et}_2\text{O} \) and pentane at room temperature. The structure reveals a slightly distorted plane geometry (Figure 3, right). The angle between the ethyl group and amine of the pyridine ring is 173.7° (N1–Mg1–C33). The bond length of Mg1–N2 (2.44 Å) is longer than Mg1–N3 (2.29 Å). The different bond lengths of C1–C2 (1.50 Å) and C6–C7 (1.37 Å) further confirm the dearomatized structure of \( \text{Mg-4} \).

Hydrogen Activation by Magnesium Pincer Complexes. Upon treatment of a toluene solution of \( \text{Mg-1} \) with \( \text{H}_2 \) in a J. Young NMR rotating tube with 5 bar of \( \text{H}_2 \) at room temperature for 24 h, only a trace amount of decomposition was observed by \(^{31}\text{P}\{\text{H}\} \) NMR (Figure S34). After heating at 65 °C for another 36 h, two new broad peaks at 31.77 and −3.14 ppm were observed by \(^{31}\text{P}\{\text{H}\} \) NMR, in addition to the free ligand resulting from partial decomposition (Figure S35). Increasing the temperature to 120 °C, \( \text{Mg-1} \) was fully transformed into a new species and free ligand after 36 h (Figure 4a). The \(^1\text{H}\) NMR spectrum of the solution exhibited new signals associated with the pyridine ring at a high field, suggesting that the dearomatized structure still remained. Both the dioxane ligand and the ethyl group disappeared and were replaced by a hydride. The hydride signal overlapped with the tertiary butyl groups of the ligand, but upon treatment of \( \text{Mg-1} \) with \( \text{D}_2 \), a deuteride signal was observed by \(^2\text{H}\) NMR (vide infra). Notably, ethane was detected by \(^1\text{H}\) NMR and GC, in line with the formation of a magnesium hydride species. DOSY NMR experiments suggest that the species is a dimer (Figures S43 and S44), in line with previously reported dimeric magnesium hydride complexes.\(^{73,74}\) Finally, the new structure was determined as a dearomatized magnesium hydride \( \text{Mg-5} \). However, the NMR signals of \( \text{Mg-5} \) gradually disappeared and converted to the free ligand under high temperature and \( \text{H}_2 \) pressure.

Formation of the free ligand and \( \text{Mg-5} \) upon treatment of \( \text{Mg-1} \) with \( \text{H}_2 \) might derive from an unstable aromatized magnesium hydride intermediate through the addition of \( \text{H}_2 \) to the dearomatized side arm and the magnesium center (that is, activation of \( \text{H}_2 \) via the MLC process). The active intermediate partially decomposed to generate the free ligand and the rest converted to \( \text{Mg-5} \) via the elimination of the ethyl group and a proton on the side arm. To prove the assumption that \( \text{H}_2 \) addition to \( \text{Mg-1} \) occurs via an MLC process, 5 bar of \( \text{D}_2 \) was added to a toluene solution of \( \text{Mg-1} \) in a J. Young NMR tube.
After heating at 65 °C for 16 h, partial decomposition of the complex to the free ligand was detected by $^{31}$P{$^{1}$H} NMR (Figure S45). Interestingly, the phosphorus signals of the free ligand and Mg-1 were split into multiplets. A more remarkable split could be observed upon prolonging the reaction time to 36 h. Such a phenomenon implies the incorporation of deuterium into both side arms of the ligand of Mg-1, leading to the formation of different types of phosphorus nuclei. Mg-1-D was consequently formed as Mg-1 with the deuterium-labeled pincer ligand under the current conditions. Mg-5-D, with deuteride coordinated to the magnesium center and incorporated into both side arms of Mg-5, was also generated, as determined by $^{31}$P{$^{1}$H} NMR and $^{2}$H NMR spectroscopy. Notably, after the solution was heated at the same temperature for 3 days, Mg-1-D was completely converted to Mg-5-D together with the elimination of CH$_3$CH$_2$D. A Mg-D signal appears at 1.32 ppm in the $^{2}$H NMR spectrum, further confirming the structure of Mg-5 and Mg-5-D. These results suggest that D$_2$ (H$_2$) is reversibly activated by Mg-1 via the MLC process. To determine the deuterated ratio of the side arm at the end of the reaction, higher temperature and longer reaction time were employed to ensure the full decomposition of Mg-5-D to the free ligand (PNP)Bu-D. Integration of the methylene protons in the $^{1}$H NMR spectrum confirmed that 95% deuterium was incorporated into the side arms of the free ligand. This result further supports the reversible activation of D$_2$ (H$_2$) via the MLC process.

Table 1. Catalytic Semihydrogenation of Alkynes$^a$

| R$^1$-R$^2$ | Mg-1 (3 mol %) | H$_2$ (5 bar) | toluene (0.5 mL) | 120 °C, 24 h | H$ceil$H | H$ceil$H |
|------------|---------------|---------------|-----------------|--------------|-------|-------|
| Ph-C$_6$H$_{11}$ | 2a | 98% (92%)$^b$ | 29:1 Z/E | | |
| Ph-C$_6$H$_{11}$ | 2b | 99%, 30:1 Z/E | | |
| Ph-Me | 2c | 93%, 29:1 Z/E | | |
| Ph-Cy | 2d | 99%, >99:1 Z/E | | |
| Ph-CH$_2$Br | 2e | 99%, 39:1 Z/E | | |
| Ph-CH$_2$F | 2f | 99%, >99:1 Z/E | | |
| C$_6$H$_{11}$ | 2g | 99%, >99:1 Z/E | | |
| C$_6$H$_{11}$ | 2h | 83%, 25:1 Z/E | | |
| C$_6$H$_{11}$ | 2i | 88%, 8:1 Z/E | | |
| C$_6$H$_{11}$ | 2j | 82%, 22:1 Z/E | | |
| C$_6$H$_{11}$ | 2k | 85%, 16:1 Z/E | | |
| C$_6$H$_{11}$ | 2l | 99%, >99:1 Z/E | | |
| C$_6$H$_{11}$ | 2m | >99%, >99:1 Z/E | | |
| C$_6$H$_{11}$ | 2n | 93%, >99:1 Z/E | | |
| C$_6$H$_{11}$ | 2o | 93% (93%) | >99:1 Z/E | | |
| C$_6$H$_{11}$ | 2p | 99%, 15:1 Z/E | | |
| C$_6$H$_{11}$ | 2q | >99% (99%) | 30:1 Z/E | | |
| C$_6$H$_{11}$ | 2r | 99% (98%) | 33:1 Z/E | | |
| C$_6$H$_{11}$ | 2s | >99% (98%) | 30:1 Z/E | | |
| C$_6$H$_{11}$ | 2t | 97%, 28:1 Z/E | | |
| C$_6$H$_{11}$ | 2u | 95%, 28:1 Z/E | | |
| C$_6$H$_{11}$ | 2v | 93% (99%) | 27:1 Z/E | | |
| C$_6$H$_{11}$ | 2w | 99%, >99:1 Z/E | | |
| C$_6$H$_{11}$ | 2x | 99%, 29:1 Z/E | | |

$^a$Reaction conditions: 1 (0.3 mmol), Mg-1 (3 mol %), H$_2$ (5 bar), toluene (0.5 mL), 120 °C, 24 h. Reaction yields were determined by $^{1}$H NMR using 1,3,5-trimethoxybenzene as the internal standard. Isolated yields are in parentheses. The Z/E ratio was determined by $^{1}$H NMR of the crude solution. The over-reduction products were less than 3% in all cases unless noted otherwise. $^b$Yield in parenthesis was obtained from a 6 mmol scale reaction. $^c$5 mol % catalyst, 8 bar of H$_2$, and 36 h reaction time. $^d$With 5% over-reduction product. $^e$With 7% over-reduction product, the isolated yield in parenthesis contains 7% over-reduction product.
activate D$_2$ (H$_2$) via the MLC, as supported by the observation of Mg-5-D formation when Mg-5 was pressurized with D$_2$ (Figure 4c and also see Figure S53). Finally, to further confirm that deuterium incorporation proceeds via the MLC process, the free ligand (PNP)$_{tBu}$ was treated with D$_2$ under similar conditions in the absence of the magnesium precursor, resulting in no incorporation of deuterium into the side arms (Figure S55). This result is also in line with our previous work involving zinc pincer complexes.

### Catalytic Semihydrogenation of Alkynes

As the reversible activation of H$_2$ (D$_2$) by Mg-1, Mg-2, and Mg-5 via the MLC process was shown to be feasible, the hydrogenation of C–C multiple bonds catalyzed by the new magnesium complexes might be possible. We first tested the semihydrogenation of internal alkynes hept-1-yn-1-ylbenzene (1a) with 3 mol % of Mg-1 as a catalyst. Alkene was generated in 98% yield and 29:1 Z/E selectivity after heating at 120 °C for 24 h under 5 bar of H$_2$. The over-reduction byproduct amounted to less than 2%, according to $^1$H NMR using benzyl benzoate as the internal standard. Isolated yields are in parentheses.

| entry | alkene | product | yield (%)$^b$ |
|-------|--------|---------|---------------|
| 1 | R = H, 3a | 4a | >99 |
| 2* | R = 2-Me, 3b | 4b | 98 |
| 3 | R = 3-OMe, 3c | 4c | 99 |
| 4 | R = 4-Me, 3d | 4d | >99 |
| 5 | R = 4-OMe, 3e | 4e | 95 |
| 6 | R = 4-$t$Bu, 3f | 4f | >99 (96) |
| 7 | R = 4-F, 3g | 4g | 83 |
| 8 | 3h | 4h | >99 (99) |
| 9 | 3i | 4i | >99 (97) |
| 10 | 3j | 4j | >99 |
| 11 | 3k | 4k | 87 |
| 12 | 3l | 4l | 97 |
| 13 | 3m | 4m | 97 |
| 14* | 3n | 4n | 70 |

| Reaction conditions: $^a$3 (0.3 mmol), Mg-1 (4 mol %), H$_2$ (5 bar), toluene (0.5 mL), 120 °C, 24 h. $^b$Reaction yields were determined by $^1$H NMR using benzyl benzoate as the internal standard. Isolated yields are in parentheses. $^c$Reaction time was 48 h. $^d$7 bar of H$_2$ and 5 mol % Mg-1 were used. |

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 activate D$_2$ (H$_2$) via the MLC, as supported by the observation of Mg-5-D formation when Mg-5 was pressurized with D$_2$ (Figure 4c and also see Figure S53). Finally, to further confirm that deuterium incorporation proceeds via the MLC process, the free ligand (PNP)$_{tBu}$ was treated with D$_2$ under similar conditions in the absence of the magnesium precursor, resulting in no incorporation of deuterium into the side arms (Figure S55). This result is also in line with our previous work involving zinc pincer complexes.

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However, the bulky tertiary butyl substituted alkyne \(1h\) generated product \(2h\) with only 83% yield and 25:1 Z/E selectivity. Next, diaryl alkynes were further evaluated. Hydrogenation of diphenylacetylene \(1i\) gave \(\text{cis}\)-stilbene in 55% yield. Increasing the pressure of \(H_2\) to 8 bar and prolonging the reaction time to 36 h, \(2i\) was obtained in 88% yield and 8:1 Z/E stereoselectivity. The conditions were also suitable for the semihydrogenation of \(F\)- and \(t\)Bu-substituted diaryl alkynes \(1j\) and \(1k\), generating products in 82 and 85% yields, respectively. Surprisingly, bis(trimethylsilyl)acetylene, a challenging substrate under most other homogeneous catalyses, smoothly converts to Z-bis(trimethylsilyl)ethene \(2l\) in 99% yield and >99:1 stereoselectivity. In addition, the semihydrogenation reaction can proceed with dialkyl alkynes, generating the desired alkenes \(2m−2o\) in up to >99% yield and >99:1 stereoselectivity. Next, the substituents on the phenyl ring of arylalkyl alkynes were evaluated. The position of the substituent did not influence the reaction yield but had an impact on the selectivity. For example, all of the \(ortho\), \(meta\), and \(para\)-methyl substituted alkynes successfully generated the...
desired alkenes 2p–2r with excellent yields under the standard conditions, but the stereoselectivity was affected when the methyl group was placed at the ortho position of the triple bond. The electron density of the alkenes has no impact on the yield and selectivity of the reaction. Both electron-rich alkenes (1w) and electron-deficient alkenes (1s–1u) can generate desired products with excellent yields. It is worth mentioning that electron-rich naphthyl substituted alkyl ether efficiently transformed into product 2x in 99% yield and 29:1 stereoselectivity. These results indicate the compatibility of the developed catalysis for different types of alkenes and different functional groups. However, the current catalysis is not suitable for the hydrogenation of terminal alkenes due to the incompatibility of the magnesium catalyst with the acidic proton of terminal alkenes.

**Catalytic Hydrogenation of Alkenes.** To the best of our knowledge, magnesium-catalyzed hydrogenation of alkenes remains challenging, which may be due to the lack of efficient catalysts for H₂ splitting. Considering the efficiency of the developed complexes in the semihydrogenation of alkenes, we explored if they are also suitable for the hydrogenation of alkenes. Indeed, styrene 3a was smoothly converted to the desired product 4a in >99% yield using 5 bar of H₂ and 4 mol % Mg-1 at 120 °C for 24 h. Other substituted styrenes were also tested under the optimal conditions (Table 2). The sterically hindered ortho-methyl styrene 3b required longer heating, 48 h, to generate the product in high yield (98%). When a variety of styrenes bearing functional groups, i.e., OMe, Me, Bu, and F, at the meta- and para-position of the phenyl ring were utilized, the reaction gave the corresponding products 4c–4g in high yields (83–99%). Interestingly, the reaction yield was slightly affected by the electron density of the double bonds. For example, fluorosubstituted alkenes 3g gave a lower yield than the neutral (3a) and electron-rich (3c and 3e) alkenes. As expected, electron-rich 2-vinyl naphthalene 3h smoothly generated the desired product 4h in 95% yield. Aliphatic terminal alkenes were further evaluated under the optimal conditions. Monosubstituted alkenes with different chain lengths were efficiently transformed into saturated products (4i–4m) in excellent yields (87–99%) catalyzed by Mg-1. Finally, we turned our attention to the more challenging internal alkene 3n. It was not surprising that only 10% yield was obtained under the optimal conditions. After increasing the pressure of H₂ to 7 bar and Mg-1 loading to 5 mol % and extending the reaction time to 48 h, the reaction yield was improved to 70%. The above results indicate that the developed magnesium complexes are not only suitable for the semihydrogenation of alkenes but also efficient in the hydrogenation of alkenes.

**Mechanistic Studies.** The new magnesium complexes were first tested to compare their effect on the catalytic semihydrogenation of 1a (Figure 5a and also see Table S10). Mg-2 gave a slightly lower yield than Mg-1, probably because the Mg-phenyl group led to a less stable complex. Mg-3 and Mg-4 supported by PNN- and NNN-type ligands generated a trace amount of the product since they are unstable at high temperatures. Interestingly, using the dearamoritized hydride complex Mg-5 as a catalyst, the alkene product was obtained in 98% yield and 32:1 stereoselectivity, a similar result to that of using Mg-1. Likewise, the hydrogenation of styrene 3a catalyzed by Mg-5 also generated the desired product in >99% yield (Table S12). Considering the fact that Mg-5 is derived from Mg-1 upon treatment with H₂, Mg-5 may act as the active catalyst in the hydrogenation reaction. Next, to demonstrate the importance of the dearamoritized PNP ligand to the hydrogenation reaction, various simple magnesium compounds were further evaluated. According to previous reports, a magnesium hydride intermediate can be formed as active catalytic species in the combination of Bu₃Mg with PinBH. However, the generated magnesium hydride species was unable to catalyze the hydrogenation of alkyn 1a. Other magnesium compounds, including Bu₃Mg, Et₂Mg-dioxane, and MgBr₂, were also examined as catalysts in the semihydrogenation of alkyn 1a, but no conversion of 1a was observed. These results suggest that the dearamoritized ligands are essential for the hydrogenation reaction.

To investigate the active catalytic species and reaction intermediates, Mg-1 was dissolved in toluene-d₈ and combined with 1-phenylpropyne 1c in a 1:6 ratio in a J. Young NMR tube and pressurized with 3 bar of H₂ to monitor the reaction (Figure S56). Interestingly, after only 10 min at 120 °C, two new singlets appear at 24.89 and −3.51 ppm in the 3¹P{¹H} NMR spectrum in a 1:1 ratio, suggesting the formation of a new complex as the reaction intermediate. The complete conversion of Mg-1 to the new species was observable when the reaction time was prolonged to 2 h. We then replaced 1c with the aliphatic alkyn 6-dodecyn (1n) to avoid the overlap of arene signals in the ¹H NMR spectrum and increased the concentration of alkyn to determine the structure of the generated intermediate (Figure 5b, left). The ¹H NMR spectrum supported the structure of the generated intermediate as Mg-6, with a cis-alkyne bound to the magnesium center considering the Z-configuration of the generated alkene product. In addition, two singlets at 26.54 and −2.42 ppm in the 3¹P{¹H} NMR spectrum suggest two different phosphorus nuclei of the formed complex. The protons of methine and methylene of the side arms were observed by ¹H NMR, indicating that the dearamoritized structure still remained. A triplet (J = 6.2 Hz) assigned to the alkyn proton, derived from the addition of magnesium hydride to the alkyn, was detected at 5.87 ppm. H–H COSY spectrum exhibits the correlation with its vicinal CH₂ protons. An sp² carbon bound to the Mg center appears at 172.7 ppm (J = 23.0 Hz) in the DEPT-Q spectrum. The HMBC spectrum further confirms the observation (see the SI for more characterization data). Meanwhile, the semihydrogenation of alkyn 1n catalyzed by Mg-5 was also investigated to further confirm the reaction intermediate (Figure 5b, right, and also see Figure S71). The same species Mg-6 was formed upon combining Mg-5 with 6-dodecyn 1n in a 1:6 ratio under 3 bar of H₂. Notably, Mg-6 was also formed in the absence of H₂. Upon consumption of the alkyn, the regeneration of Mg-5 was observed. Thus, we can conclude that Mg-5 is generated in situ from Mg-1 as the active catalyst, and Mg-6 is formed as a reaction intermediate, which originates from the addition of the Mg–H bond to the triple bond.

Similarly, the hydrogenation of styrene catalyzed by Mg-1 was also monitored under similar conditions (Figure S72). The formation of an active intermediate via the addition of the Mg–H bond to the styrene double bond was detected as well, indicating an analogous mechanism in the hydrogenation of alkenes. However, internal alkenes exhibit lower reactivity, and their hydrogenation is more challenging. As noticed, the internal alkyn 3n can convert to the alkane in 70% yield when increasing the loading of Mg-1 and the pressure of H₂ and prolonging the reaction time. This result prompted us to...
investigate why E-alkenes and alkanes were generated with low yields in the catalytic semi-hydrogenation of alkynes. We thus prolonged the reaction time for the hydrogenation of 1c to 48 h (page S65). It was found that the yield of E-alkene and alkane increased to 9 and 17%, respectively. Prolonging the reaction time to 60 h did not significantly improve their yields. These results suggest that Mg-I can slowly catalyze the isomerization of Z-alkenes to the more stable E-alkenes and the hydrogenation of internal alkynes to alkanes. However, the gradual decomposition of Mg-I to the free ligand led to catalyst deactivation. Therefore, in most cases of the semi-hydrogenation of alkynes, the E-alkenes and over-reduction products can be avoided if the reactions are terminated after 24 h.

On the basis of the control experiments and previous studies on bond activation via MLC involving the aromatization/dearomatization, a mechanistic cycle is proposed (Figure 5c). Initially, Mg-I is converted to Mg-S as the active catalytic species by reaction with H2. Mg-S can further dissociate into the monomer Mg-S′, which provides a vacant site for alkyne coordination to generate intermediate A. The coordinated alkyne then inserts into the Mg-H bond to generate a magnesium vinyl intermediate B. Next, addition of H2 to intermediate B via the MLC process results in the aromatization of the pincer ligand to form the vinyl hydride intermediate C. Deprotonation of the side arm by the vinyl ligand generates the Z-alkene products and the magnesium hydride intermediate (Mg-S″)′, which provides a vacant site for alkyne coordination to form the magnesium pincer complexes supported by PNP, PNN, and PNN types of ligands. The complexes were well characterized by NMR and X-ray single-crystal diffraction. The reversible activation of H2 by the dearomatized complexes via the MLC process was shown to be feasible. The obtained magnesium pincer complexes catalyze the semi-hydrogenation of internal alkynes, affording Z-alkenes in excellent yields and stereo-selectivities. To the best of our knowledge, this is the first example of homogeneous main-group metal-catalyzed semi-hydrogenation of alkynes, representing significant advances in semi-hydrogenation of alkynes and main-group metal catalysis. Besides, the developed complexes are suitable for the hydrogenation of alkynes, which have long been dominated by transition metals. Mechanistic studies indicate that a magnesium hydride complex is first formed as the active catalyst for the transformation. The aromatization/dearomatization MLC process is likely to play a significant role in achieving the reaction, as supported by control experiments and DFT studies. We believe that this study will provide new routes for the hydrogenation of other compounds catalyzed by main-group metal complexes.

### CONCLUSIONS

In summary, we have prepared a series of dearomatized magnesium pincer complexes supported by PNP, PNN, and PNN types of ligands. The complexes were well characterized by NMR and X-ray single-crystal diffraction. The reversible activation of H2 by the dearomatized complexes via the MLC process was shown to be feasible. The obtained magnesium pincer complexes catalyze the semi-hydrogenation of internal alkynes, affording Z-alkenes in excellent yields and stereo-selectivities. To the best of our knowledge, this is the first example of homogeneous main-group metal-catalyzed semi-hydrogenation of alkynes, representing significant advances in semi-hydrogenation of alkynes and main-group metal catalysis. Besides, the developed complexes are suitable for the hydrogenation of alkynes, which have long been dominated by transition metals. Mechanistic studies indicate that a magnesium hydride complex is first formed as the active catalyst for the transformation. The aromatization/dearomatization MLC process is likely to play a significant role in achieving the reaction, as supported by control experiments and DFT studies. We believe that this study will provide new routes for the hydrogenation of other compounds catalyzed by main-group metal complexes.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c08491.

Experimental procedures, NMR spectra, and computational details and X-ray crystallographic coordinates for the structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2174062, 2174063, and 2174064 (PDF).

#### Accession Codes

CCDC 2174062–2174064 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Notes**

The authors declare no competing financial interest.

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