Hydroboration

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Asymmetric Magnesium-Catalyzed Hydroboration by Metal-Ligand Cooperative Catalysis

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Abstract: Asymmetric catalysis with readily available, cheap, and non-toxic alkaline earth metal catalysts represents a sustainable alternative to conventional synthesis methodologies. In this context, we describe the development of a first Mg^{II} -catalyzed enantioselective hydroboration providing the products with excellent yields and enantioselectivities. NMR spectroscopy studies and DFT calculations provide insights into the reaction mechanism and the origin of the enantioselectivity which can be explained by a metal-ligand cooperative catalysis pathway involving a non-innocent ligand.

The application of alkaline-earth metals in catalysis is a topical area. Most of the group 2 metals are abundant in the earth's crust and are characterized by their low cost and environmentally benign nature.^[1] However, despite their abundance and low toxicity, alkaline-earth metals such as Mg^{II} have only been used in a limited number of catalytic transformations.^[2] This limited use may be due to their propensity to undergo Schlenk-type equilibrium which results in catalytically inactive species. To avoid these problems, sterically demanding monoanionic ligands have been used to stabilize the alkaline-earth metals. In particular, β -diketimine ligands have been widely employed in group 2 catalysis as their bulkiness inhibits any kind of ligand redistribution. As a result, several magnesium-catalyzed transformations have been developed as a green alternative to transition metal catalyzed processes.^[3,4] These transformation include the impressive progress in the hydroboration of polarized and nonpolarized unsaturated bonds by use of β -diketiminato-stabilized magnesium complexes and the formation of magnesium hydride species.^[5] In addition, chiral magnesium-(II) binaphtholates as cooperative Brønsted/Lewis acid–base catalysts have been explored.^[6,7] Based on their unexpectedly high reactivity and sustainability, the use of chiral magnesium catalysts for the accomplishment of an asymmetric hydroboration would therefore be a desirable goal. However, to the

best of our knowledge, the onward development of an enantioselective hydroboration of polarized double bonds using a chiral magnesium catalyst has not been reported. Herein, we report an efficient method for the enantioselective synthesis of chiral alcohols by employing a readily available chiral magnesium complex (Scheme 1) and provide insight into the reaction mechanism and the origin of the enantioselectivity.

Magnesium-Ligand Cooperative Catalysis

Scheme 1. Magnesium-catalyzed asymmetric hydroboration of ketones.

The initial studies towards the development of an efficient magnesium-catalyzed hydroboration of ketones^[8] began with the evaluation of different chiral magnesium complexes derived from (*R*)-(+)-BINOL derivatives (**1a–h**), HBpin as hydroborating agent, and acetophenone (**2a**) as a model substrate (Table 1). With **1a** as ligand at room temperature, the transformation reached completion within less than 2 hours, affording, after protic quenching, the chiral alcohol **3a** with moderate enantioselectivity (entry 1). We were pleased to see that BINOL-Mg complexes were active in the hydroboration of **2a** given that to date only monoanionic ligands have shown to be active in the non-selective hydroboration of unsaturated bonds. By decreasing the temperature to -40°C , the enantiomeric ratio increased to 93:7, while the excellent activity was maintained (entry 1 vs. 2). Other solvents were tested, however, the selectivity did not improve (entries 2 vs. 3–6). From the different chiral (*R*)-(+)-BINOL scaffolds (**1a–h**) tested, magnesium complexes of ligand **1a** provided the best enantioselectivity (entries 2 vs. 7–13). Finally, we investigated the effect of alkali salt additives as they can have an influence on the performance. However, only a slight increase in enantioselectivity was observed (entry 14 vs. 2).

To evaluate the scope of our novel enantioselective magnesium-catalyzed hydroboration reaction a broad range of prochiral ketones were applied as substrates (Scheme 2). The use of differently substituted arylmethyl ketones afforded the corresponding chiral secondary alcohols **3a–e** in excellent yields and comparable selectivities. When other electron-

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Table 1: Optimization of the magnesium catalyzed hydroboration of acetophenone.^[a]

Entry	Solvent	Ligand	Conv. [%] ^[b]	<i>er</i> ^[c]
1 ^[d]	toluene	1a	> 99	76:24
2	toluene	1a	> 99	93:7
3	Et ₂ O	1a	> 99	71:29
4	THF	1a	> 99	54:46
5	DCM	1a	> 99	89:11
6	hexane	1a	50	50:50
7	toluene	1b	> 99	74:26
8	toluene	1c	> 99	59:41
9	toluene	1d	> 99	88:12
10	toluene	1e	> 99	89:11
11	toluene	1f	> 99	84:16
12	toluene	1g	> 99	63:37
13	toluene	1h	> 99	84:16
14 ^[e]	toluene	1a	> 99 (98)	95:5

[a] **2a** (0.5 mmol), HBpin (1.5 equiv), MgBu₂ (7 mol%, 1 M in heptane), **1a–1h** (7.5 mol%), solvent [0.4 M] at –40 °C for 2 h. [b] Determined by GC using n-dodecane as an internal standard. Yield after isolation in given within parentheses. [c] Determined by chiral-phase HPLC. Absolute configuration was assigned by comparison with literature values. [d] At 25 °C. [e] LiCl (20 mol%).

withdrawing groups were present on the aromatic ring (**2f–g**), enantioselectivities decreased while maintaining the excellent yields. It is important to highlight the excellent chemo- and enantioselectivities observed when **2h**, containing a methyl-ester group, was tested. We were pleased to see that substituents in the *ortho*-position of the aromatic ring were also tolerated (**3i–k**). Furthermore, different acetophenone derivatives containing polycyclic substituents (**2l**) and heterocycles (**2m,n**) could be reacted to the corresponding alcohols with high selectivities. Branched alkyl substituents (**2o**) as well a range of electronically different 1-indanones (**2p–s**) were hydroborated in excellent yields and enantioselectivities.

Generally, the hydroboration of α,β -unsaturated ketones is more challenging as chemoselectivity as well as enantioselectivity has to be taken into account. Therefore, to date only few successful examples for the selective 1,2-hydroboration of α,β -unsaturated ketones have been accomplished.^[8d,e] We were delighted to see that with our newly developed magnesium catalysis, only selective 1,2-addition occurred and that the corresponding allylic alcohols (**3t–z**) were obtained in good yields and with excellent enantioselectivities. It is important to notice that in the presence of a substituent in α -position (**3t** vs. **3u**), higher enantioselectivities are obtained while maintaining the excellent yields and regioselectivities. Likewise, different propargylic ketones

Scheme 2. Magnesium-catalyzed asymmetric hydroboration of ketones. General reaction conditions: **2** (0.5 mmol), HBpin (1.5 equiv), MgBu₂ (7 mol%, 1 M in heptane), **1a** (7.5 mol%), solvent [0.4 M] at –40 °C for 3 h. [a] 24 h [b] MgBu₂ (10 mol%), ligand (10.5 mol%). [c] Determined from the **3ad-Bz**, **3ae-Bz** and **3af-Bz** protected product. Absolute configuration was assigned upon the assumption of a common stereochemical mechanism.

underwent the magnesium-catalyzed hydroboration well and afforded the alkynols **3aa–ae** in excellent yields and enantioselectivities. This result surpassed the best results in the literature,^[9] showing the great efficiency of the enantioselective magnesium catalysis. Regarding the dialkyl ketone **3af**, excellent yield was obtained, albeit with very poor enantioselectivity, showing a limitation on the scope of this magnesium system.

To gain more information about the reaction mechanism, we decided to identify the catalytically active species. BINOLate-magnesium complexes form an equilibrium of monomeric BINOL-Mg and oligomeric Mg^{II} species.^[7a,d,g]

The oligomer can be dissociated into the active monomeric complex in the presence of any coordinating species. In our NMR spectroscopy studies we also observed this phenomenon (for detailed characterization, see the Supporting Information).

Importantly, in the previously reported Mg^{II}-catalyzed hydroborations of unsaturated bonds, a Mg–H species was been observed and can be formed from the alkyl magnesium precatalyst.^[5] However, in our case the reaction of dibutyl magnesium with **1a** did not lead to an Mg-alkyl precursor catalyst. For this reason, the formation of Mg–H is less likely and the reaction mechanism must be different. Thus, we decided to examine the mechanism in more detail.

In our **1a**/Mg catalytic system only one molecule of HBpin is necessary for the hydroboration and provides **3a** quantitatively in 15 minutes. To gain information about HBpin activation, we mixed **1a**/Mg with an equimolar amount of HBpin. ¹¹B NMR spectroscopy showed the complete conversion of HBpin ($\delta = 28.7$ ppm) into a new boron

species ($\delta = 34.6$ ppm). Moreover, ¹H NMR spectroscopy showed that the signal of HBpin disappeared. However, a Mg–H species was not formed.^[10] The groups of Nozaki and Hill reported several Mg–B activation modes.^[11] Based on the literature ¹¹B NMR values and the Lewis acidity/basicity affinity, the shift in the ¹¹B NMR activation of the HBpin is most probably due to a dual Mg–O and O–B coordination. In this regard, recently Graves and co-workers reported a similar activation mode of HBpin by tripodal trisnitroxide aluminum catalyst.^[12] Following the experimental results, we performed DFT calculations to gain insight into the reaction pathway and to define the origin of the enantioselectivity. Based on the calculated results, we propose the following reaction pathway. The reaction starts with the formation of the active catalyst by coordination of the ligand to MgBu₂ and synchronous elimination of butane, a step exergonic by 66.4 kcal mol^{−1} (see Scheme S1 in the Supporting Information). There is an equilibrium between **A** and the corresponding oligomeric species **A_n** as reported before. Coordination of the ketone results into intermediate **C** by two successive exergonic steps of 20.5 and 14.5 kcal mol^{−1} (Figure 1).

To proceed further along the reaction pathway a HBpin molecule is coordinated to **C**, endergonic by 1.1 kcal mol^{−1}, to generate **D** (see Figure S1). The hydroboration of the C=O bond could now occur from the coordinated HBpin molecule via a $[2\sigma + 2\pi]$ -addition-type transition state. This step requires an activation free energy of 33.0 kcal mol^{−1}, which is too high to be consistent with the reaction conditions used (see Figure S2). Thus, an alternative reaction pathway needs to be considered. Based on the above considerations the BINOL ligand could act as a non-innocent ligand and could

Figure 1. Computed energy profile for the magnesium catalyzed enantioselective hydroboration of ketones. Free energy values at M06(SMD)/Def2-TZVPP//BP86/Def2-SVP level of theory are presented.

be involved in the HBpin activation. Indeed, inserting the HBpin into the Mg–O(BINOL) bond via $[\mathbf{D-E_s}]^{\ddagger}$ with a free energy barrier of $9.3 \text{ kcal mol}^{-1}$ results in the intermediate $\mathbf{E_s}$. With the BINOL coordinating the HBpin becomes more electron rich and facilitates the hydride transfer to the C=O via the transition state $[\mathbf{E_s-F_s}]^{\ddagger}$, with an energy span of $14.0 \text{ kcal mol}^{-1}$ (with reference to intermediate $\mathbf{C}$) to give intermediate $\mathbf{F_s}$. The next step is the migration of the alkoxide from the magnesium to the boron center with a moderate activation barrier of $13.0 \text{ kcal mol}^{-1}$. The transition state $[\mathbf{F_s-G_s}]^{\ddagger}$ is characterized by concomitant B–O(alkoxide) and Mg–O(BINOL) bond formation. Finally, the liberation of the product $\mathbf{P_s}$ from the resulting intermediate $\mathbf{G_s}$ closes the catalytic cycle and regenerates the active catalyst.

The computed energy profile (Figure 1) reveals that the hydride transfer ($\mathbf{E_s} \rightarrow \mathbf{F_s}$) is predicted to be the rate-determining step. Therefore, the enantiocontrol occurs at the transition-state $[\mathbf{E_s-F_s}]^{\ddagger}$. To clarify the origin of the enantioselectivity we also investigated the competitive transition state $[\mathbf{E_R-F_R}]^{\ddagger}$ differing in the approach of the ketone towards the formation of the other enantiomer $\mathbf{P_R}$ (Figure 2). In comparison, $[\mathbf{E_s-F_s}]^{\ddagger}$ is $2.5 \text{ kcal mol}^{-1}$ more stable than $[\mathbf{E_R-F_R}]^{\ddagger}$, and explains the preference for the $\mathbf{P_s}$ formation. The DFT result is in good agreement with the experimental findings of 93:7 *er* (Table 1, entry 2). A closer inspection of the transition-state geometries shows that the less favorable $[\mathbf{E_R-F_R}]^{\ddagger}$ transition state arises from steric repulsion between the aryl residue of BINOL (the substituent at 3' position) and the aryl substituent of the ketone oriented perpendicularly (Figure 2). This particular repulsion is absent in the case of $[\mathbf{E_s-F_s}]^{\ddagger}$.

In summary, we have developed a new magnesium-catalyzed enantioselective hydroboration of prochiral

ketones. Excellent yields and enantioselectivities have been achieved for a wide range of ketones derived from acetophenone and 1-indanone. Moreover, the asymmetric magnesium catalysis can be applied to α,β -unsaturated ketones whereby the 1,2-addition is observed exclusively. Furthermore, even propargylic ketones could be used to provide the corresponding alcohols in excellent yields. Thus, the new methodology compares favorably with previously developed protocols. Following detailed spectroscopic and computational studies a plausible reaction pathway has been established which, in contrast to our expectations and previously described hydroborations, does not involve a magnesium hydride intermediate. Instead, the activation involves a new metal-ligand cooperative catalysis pathway in which BINOL acts as a non-innocent ligand. Thus, the newly developed magnesium catalysis protocol is not only of interest because of its wide scope and improved sustainability, but additionally because of the mechanistic insights which allow the design of further enantioselective procedures employing readily available magnesium catalysts.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: asymmetric reduction · DFT calculation · hydroboration · ketones · magnesium

Figure 2. Optimized geometries of transition states of the enantio-determining step, hydride transfer. Hydrogen atoms (except one) are omitted for clarity.

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Zuschriften

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Asymmetric Magnesium-Catalyzed
Hydroboration by Metal-Ligand
Cooperative Catalysis

HBpin-Aktivierung durch Mg-Ligand-Kooperation: Die enantioselektive, Magnesium-katalysierte Hydroborierung von Ketonen mit einem (*R*)-(+)-BINOL-Derivat als chiralem Liganden liefert exzellente Ausbeuten und Enantioselektivitäten. Experimente und DFT-Rechnungen geben Einblicke in den Reaktionsmechanismus und den Ursprung der Enantioselektivität.