Asymmetric β-Boration of α,β-Unsaturated Esters with Chiral (NHC)Cu Catalysts

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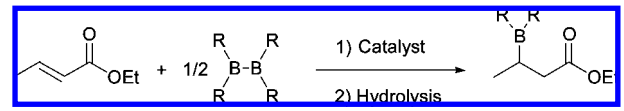
Summary: Copper complexes containing chiral N-heterocyclic carbene ligands catalyze the regioselective nucleophilic boryl attack at the β-carbon of α,β-unsaturated esters with enantioselectivities up to 74% ee, depending on the nature of the ester group.

In the past decade, the conjugate addition of boryl nucleophile to activated alkenes has opened up new perspectives in organoborane chemistry. The use of transition-metal-based catalysts to promote the heterolytic cleavage of diboron reagents, affording metal−boryl intermediates, is the key issue in these transformations. When employing α,β-unsaturated carbonyl compounds as starting materials, these boryl intermediates induce the regiocontrolled boryl migration to the β-position (Scheme 1).[1]

Most of the catalysts described for this transformation are based on copper;[2] however, other catalytic systems based on Pt,[3] Rh,[4] or Ni[5] are known and considered as attractive alternatives. This functionalization originates a stereogenic center at the β-carbon; therefore, the induction of enantioselectivity could be achieved with the appropriate catalyst.[6] However, to the best of our knowledge, there is only one example in the literature which achieves the successful enantioselective β-boration/oxidation of α,β-unsaturated esters and nitriles. This was described by Yun and co-workers[2c,7] using CuCl and the phosphines (*R*)-(*S*)-josiphos and (*R*)-(*S*)-NMe_2-PPh_2-mandyphos, with ee values up to 91%. Alternatively, Oestreich has recently reported the catalytic asymmetric addition of Me_2PhSi-Bpin across α,β-unsaturated acceptors to provide analogous chiral β-silyl carbonyl compounds.[8]

In a previous study, we found the catalytic capabilities of a series of copper complexes containing N-heterocyclic carbene (NHC) ligands in the selective diboration of alkenes and alkynes.[9] Recently, Hou and co-workers have also shown that related complexes effectively catalyze the carboxylation of organoboronic esters.[10] With the aim of contributing to the development of asymmetric induction in the β-boration of α,β-unsaturated carbonyl compounds, we describe in this paper the results obtained with a chiral copper catalytic system, matching the advantages that chiral NHC ligands provide on the catalyst (donor properties, ease of synthesis, and robustness).[11]

Scheme 1



Results and Discussion

First we investigated the potential of several complexes containing the (NHC)*Cu^+ core as the precursor of the catalyst for this reaction (Figure 1). The chiral NHC ligands display chirality either at the substituents at the nitrogen atom (L_1 and L_2) or at the backbone (L_3−L_5) of the NHC ring. The copper complexes employed as catalysts were those of general formulas (NHC)CuCl and [(NHC)Cu(NCMe)]BF_4 and were prepared in a manner similar to that for complexes **1**−**6**.[12]

These catalyst precursors were employed for the β-boration of the model substrate ethyl *trans*-crotonate with B_2pin_2. A 2% catalyst loading with regard to substrate was used in all cases, in the presence of 3 mol % of NaO*t*Bu and 2 equiv of MeOH, relative to alkene. In order to determine the degree of enantioselection, the initially formed organoboron compounds were derivatized into the acylated products, through consecutive oxidation and acylation steps (Table 1).

The use of chiral [(NHC)Cu($NCCH_3$)]BF_4 complexes containing the ligands L_1 and L_2 led to quantitative conversion, although enantiocontrol on the stereogenic β-carbon was low (Table 1, entries 1 and 2). However, those complexes with ligands L_3−L_5

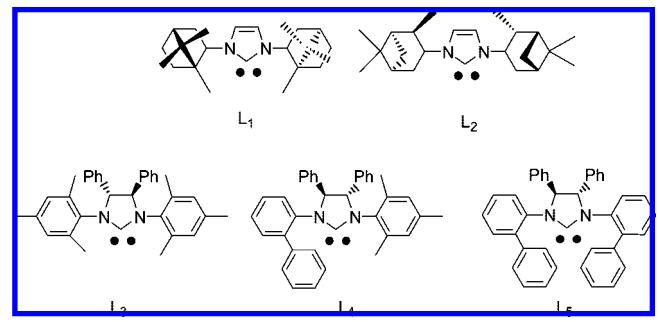


Figure 1. Chiral NHC ligands employed in this work.

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(1) (a) Marder, T. B. *J. Organomet. Chem.* **2008**, *34*, 46. (b) Dang, L.; Lin, Z.; Marder, T. B. *Organometallics* **2008**, *27*, 4443. (c) Kajiwara, T.; Terabayashi, T.; Yamashita, M.; Nozaki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 6606.
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(3) (a) Lawson, Y. G.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R. *Chem. Commun.* **1997**, 2052. (b) Ali, H. A.; Goldberg, I.; Srebnik, M. *Organometallics* **2001**, *20*, 3962. (c) Bell, N. J.; Cox, A. J.; Cameron, N. R.; Evans, J. S. O.; Marder, T. B.; Duin, M. A.; Elsevier, C. J.; Baucherel, X.; Tulloch, A. A. D.; Tooze, R. P. *Chem. Commun.* **2004**, 1854.
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(5) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2007**, *9*, 5031.
(6) (a) Burks, H. E.; Morken, J. P. *Chem. Commun.* **2007**, 4717. (b) Ramírez, J.; Lillo, V.; Segarra, A. M.; Fernandez, E. C. R. *Chimie* **2007**, *10*, 138.
(7) Lee, J.-E.; Yun, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 145.

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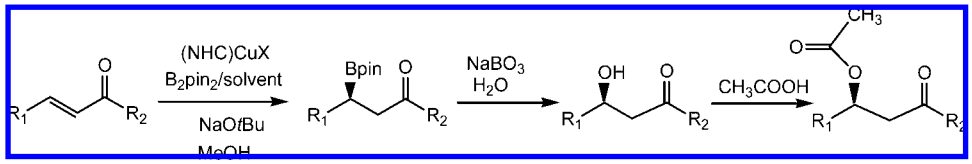
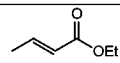
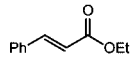
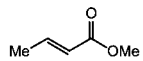
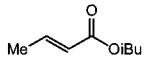
provided moderate ee values (e.g. 58% ee with L_4). It seems that the nature of the anion does not affect either the conversion or the enantioselectivity (Table 1, entries 3−6). This could be the result of a common catalytic species of composition (NHC)Cu^+ that could be reached from both starting materials. It seems obvious from these results that chirality at the backbone of the chiral NHC ligand plays an important role in inducing asymmetry in the β-boration reaction; therefore, the simultaneous contribution of IMes and biphenyl in L_4 provided the optimal benefits toward the asymmetric induction issue. Moreover, a comparison between the results obtained with L_4- and L_5-based catalysts indicate that C_1 symmetry provides better results than the corresponding C_2-symmetric catalyst, which will be interesting information for any further catalyst development.

This improvement in the enantiocontrol of chiral (NHC)Cu^+ complexes moved us to analyze the influence of the solvent and base on the β-boration of ethyl *trans*-crotonate. As inferred from data in Table 2, entries 8−10, the use of THF or toluene does not exert any effect on the reaction outcome. Similarly, when the base is changed from NaO*t*Bu to NaOMe, NaOAc, or NaOH, small differences can be detected in the catalytic activity of L_4CuCl (Table 1, entries 11−13). However, the absence of base in the β-boration of ethyl *trans*-crotonate with L_4CuCl and $[L_4Cu(NCCH_3)]BF_4$ decreases the conversion rate significantly but slightly improves the enantioselectivity (Table 1, entries 14 and 15). Yun et al.[2c] have postulated that the base is required to favor the formation of the LCu−-boryl catalytic species from the catalyst precursor and the diboron reagent. We have also previously shown that η^2-

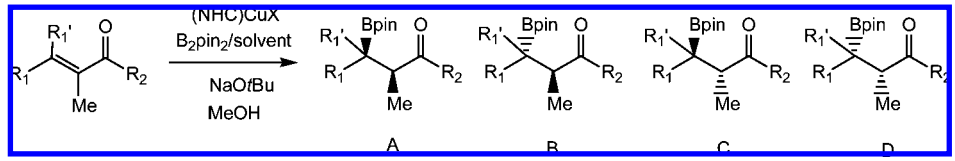
Table 1. Chiral (NHC)Cu^+ Complex Catalyzed β-Boration/Oxidation/Acylation of α,β-Unsaturated Esters[a]

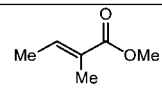
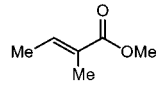
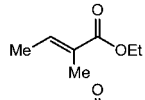
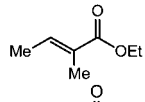
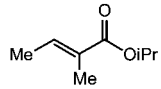
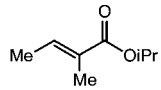
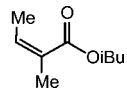
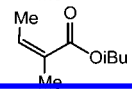


Entry	Substrate	Catalyst Precursor	Base	Solvent	Conv. (%)[b]	e.e. (%)[c]
1		$[L_1Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	93	10(R)
2	"	$[L_2Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	99	16(S)
3	"	$[L_3Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	99	25(S)
4	"	L_3CuCl	NaO*t*Bu	THF	96	31(S)
5	"	$[L_4Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	99	58(R)
6	"	L_4CuCl	NaO*t*Bu	THF	99	55(R)
7	"	L_5CuCl	NaO*t*Bu	THF	99	52(R)
8	"	L_4CuCl	NaO*t*Bu	Toluene	99	59(R)
9	"	L_4CuCl	NaO*t*Bu	CH_3CN	88	52(R)
10	"	L_4CuCl	NaO*t*Bu	CH_2Cl_2	99	57(R)
11	"	L_4CuCl	NaOMe	THF	99	51(R)
12	"	L_4CuCl	NaOAc	THF	73	50(R)
13	"	L_4CuCl	NaH	THF	99	53(R)
14	"	L_4CuCl	---	THF	<10	63(R)
15	"	$[L_4Cu(NCCH_3)]BF_4$	---	THF	25	62(R)
16		$[L_3Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	92	23(S)[d]
17	"	$[L_4Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	99	53(R)[d]
18	"	L_4CuCl	NaO*t*Bu	THF	99	61(R)[d]
19		$[L_3Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	96	31(R)[d]
20	"	$[L_4Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	96	48(R)[d]
21		$[L_3Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	99	15(R)
22	"	$[L_4Cu(NCCH_3)]BF_4$	NaO*t*Bu	THF	99	73(R)

[a] Standard conditions: substrate/Cu complex = 0.5/0.01, 3 mol % base, 1.1 equiv of bis(pinacolato)diboron (B_2pin_2), 2 equiv of MeOH, 2 mL of solvent, T = 25 °C, 6 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined on the acylated product by GC−MS equipped with the chiral column β-cyclodex. [d] Determined on the β-alcohols by HPLC-MS equipped with the chiral column Chiralcel OD-H.

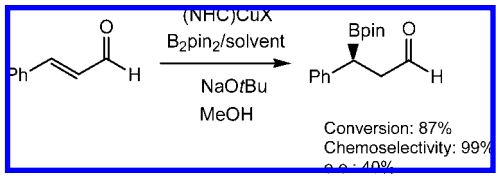
Table 2. Chiral (NHC)Cu$^+$ Complex Catalyzed β-Boration of α-Methyl α,β-Unsaturated Esters[a]



Entry	Substrate	Catalyst	Conv. (%)[b]	syn / anti [b]	syn e.e (%)[c]	anti e.e (%)[c]
1		L_4CuCl	99	60/40	54[d]	5[d]
2		L_5CuCl	97	52/48	68[d]	25[d]
3		L_4CuCl	94	64/36	57	11
4		L_5CuCl	99	60/40	35	8
5		L_4CuCl	65	55/45	70	20
6		L_5CuCl	82	53/47	56	37
7		L_4CuCl	93	70/30	74	5
8		L_5CuCl	99	65/35	39	42

[a] Standard conditions: substrate/Cu complex = 0.5/0.01, 3 mol % of NaO*t*Bu, 1.1 equiv of bis(pinacolato)diboron (B_2pin_2), 2 equiv of MeOH, 2 mL of solvent, T = 25 °C, 6 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined on the acylated product by GC−MS equipped with the chiral column β-cyclodex. [d] Determined on the β-alcohols by HPLC-MS equipped with the chiral column Chiralcel OD-H.

Scheme 2



diborane complexes can be involved in a pre-equilibrium step before the catalytic species (NHC)Cu-Bpin is formed.[9]

On the basis of the results obtained with the model ethyl *trans*-crotonate and with the aim of exploring the scope of this catalytic system, we did a series of experiments with a range of substrates under the optimized conditions. The reactions of ethyl *trans*-cinnamate with $[L_3Cu(NCCH_3)]BF_4$ and $[L_4Cu(NCCH_3)]BF_4$ provided quantitative conversion to the desired product (Table 1, entries 16 and 17), but again the enantioselectivity was better achieved when ligand L_4 was involved in the catalytic system, rising to 61% ee in the presence of the neutral catalyst precursor L_4CuCl (Table 1, entry 18). Similar catalytic performance was provided by $[L_3Cu(NCCH_3)]BF_4$ and $[L_4Cu(NCCH_3)]BF_4$ in the β-boration of methyl *trans*-crotonate ester (Table 1, entries 19 and 20). It is worth mentioning that the bulkiest species used, isobutyl *trans*-crotonate ester, behaved differently as far as the enantioselection induced by the metal center was concerned. Thus, the use of $[L_3Cu(NCCH_3)]BF_4$ afforded a 15% ee, whereas in the case of $[L_4Cu(NCCH_3)]BF_4$ this value rose to 73%. These results contrast with the tendency observed by Yun et al.,[2c,7] where enantioselectivity was independent of the nature of the ester moiety when CuCl/(*R*)-(*S*)-josiphos was used as catalytic system.

The metal-catalyzed β-boration of the most challenging α,β-unsaturated aldehydes has only been reported before in two examples through Rh[13a] and Pt[13b] catalysts, because this reaction suffers from a competitive 1,2-diboron addition reaction. Taking advantage of the benefits by copper-mediated B-addition reactions, we became motivated to carry out the (NHC)*Cu$^+$-catalyzed β-boration of cinnamaldehyde, as a model substrate. In that case the use of L_3CuCl afforded quantitative conversion and total chemoselectivity on the desired product with 40% ee (Scheme 2), whereas in the case of L_4CuCl and L_5CuCl this value did not reach more than 10% ee. Despite these moderate values, this is the first attempt to obtain enantioselectivity in the β-boration of α,β-unsaturated aldehydes.

We have also studied another variable that could affect the degree of enantioselection: the existence of substituents in the starting alkene (Table 2). We have carried out the β-boration reaction with a series of α-methyl-substituted esters, such as methyl tiglate (R_1 = Me, $R_{1'}$ = H, R_2 = OMe), ethyl tiglate (R_1 = Me, $R_{1'}$ = H, R_2 = OEt), isopropyl tiglate (R_1 = Me, $R_{1'}$ = H, R_2 = OiPr), and isobutyl angelate (R_1 = H, $R_{1'}$ = Me, R_2 = OiBu). These experiments have been carried out with L_4CuCl and L_5CuCl as the catalyst precursors. As shown in Table 2, we observed very high quantitative conversions into the β-boryl products in most cases (Table 2, entries 1−8) indicating that α-substitution does not

diminish the borylation pathway. The syn/anti product ratio slightly favored the syn diastereoisomers, and ee values were markedly higher for the enantiomeric mixture of the syn products than for the anti products: the bulkiest isobutyl angelate substrate can be borated at the β position, with the highest ee value (74%) on the syn diastereoisomers (Table 2, entry 7).

Conclusions

We have found that complexes containing the (NHC)Cu core catalyze the selective β-boration of α,β-unsaturated esters and aldehydes under mild conditions. The use of chiral NHC ligands induced a certain degree of enantioselection in the final products, in a reaction for which only one precedent with asymmetric induction is known. The nature of the different NHC ligands and substrates employed in this work serves as the basis for developing more enantioselective catalysts for such transformations.

Experimental Section

General Considerations. All reactions and manipulations were carried out under an atmosphere of dry nitrogen, and the necessary organic solvents were dried, distilled, and degassed before use. Bis(pinacolato)diboron was used as purchased from Lancaster. The rest of the reagents were purchased from SigmaAldrich. Complexes **1**−**6**[12] were prepared following literature procedures, as well as ligands L_1−L_4.[14] NMR spectra were recorded on Varian Gemini 300 and Varian Mercury 400 instruments. Chemical shifts are reported relative to tetramethylsilane for ^{1}H, 85% H_3PO_4 for ^{31}P, and BF_3−ether for ^{11}B.

Syntheses of the Ligand [L_5H][BF_4]. (a) Synthesis of (Bf)NHCH(Ph)CH(Ph)NH(Bf) (Bf = Biphenyl). $Pd_2(dba)_3$(91.6 mg, 0.1 mmol), BINAP (147 mg, 0.2 mmol), (−)-(*S*,*S*)-1,2-diphenylethylenediamine (212.3 mg, 1 mmol), 2-iodo-1,1′-biphenyl (560 mg, 2 mmol), and NaO-*t*-Bu (288 mg, 3 mmol) were placed into an ampule inside a glovebox. Toluene (20 mL) was added, and the mixture was stirred for 120 h at 100 °C outside the glovebox. The solution was then cooled to ambient temperature and was quenched by the addition of water (5 mL). The aqueous layer was washed with CH_2Cl_2 (3 × 5 mL), the organic layers were combined, dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum. Purification by silica gel chromatography (hexane−Et_2O 4:1) gave the diamine (Bf)NHCH(Ph)CH(Ph)NH(Bf) as a yellow solid (777 mg, 80%).

^{1}H NMR (CD_2Cl_2): δ 4.55 (d, J = 2.8 Hz, 2H, NCH), 4.64 (d, J = 2.8 Hz, 2H, NH), 6.13 (d, J = 7.6 Hz, 2H, arom), 6.66 (t, J = 7.5 Hz, 2H, arom), 6.92−6.95 (m, 2H, arom), 7.02−7.04 (m, 2H, arom), 7.07−7.09 (m, 4H, arom), 7.20−7.30 (m, 10H, arom), 7.48−7.57 (m, 6H, arom). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 63.9 (NH*C*), 111.8 (arom), 117.6 (arom), 126.9 (arom), 127.7 (arom), 128.4 (arom), 128.7 (arom), 128.8 (arom), 129.1 (arom), 129.7 (arom), 129.8 (arom), 139.1 (arom), 139.9 (arom), 143.9 (arom).

(b) Synthesis of [L_5H][BF_4]. A mixture of the diamine obtained as above (516.7 mg, 1 mmol), ammonium tetrafluoroborate (125.8 mg, 1.2 mmol), and triethyl orthoformate (1.5 mL) was heated at 120 °C for 12 h. The solution was then cooled to ambient temperature. Purification by silica gel chromatography (20:1 CH_2Cl_2−CH_3OH) afforded an off-white solid of [L_5H][BF_4] (540 mg, 88%).

^{1}H NMR (CD_2Cl_2): δ 4.74 (s, 2H, NCH), 6.69 (d, J = 8.0 Hz, 2H, arom), 7.22−7−41 (m, 20H, arom), 7.52−7.67 (m, 6H, arom), 8.98 (s, 1H, NCHN). ^{13}C NMR (CD_2Cl_2): δ 75.7 (NHC), 127.2 (arom), 128.0 (arom), 128.2 (arom), 128.6 (arom), 128.7 (arom), 129.0 (arom), 129.1 (arom), 129.3 (arom), 129.4 (arom), 129.5 (arom), 129.6 (arom), 129.8 (arom), 129.9 (arom), 130.0 (arom), 130.6 (arom), 132.1 (arom), 134.1 (arom), 138.4 (arom), 138.7(arom), 157.6 (NCHN).

Syntheses of the Neutral Complexes (NHC)CuCl and the Cationic Catalyst Precursors [(NHC)Cu(NCMe)]BF_4. The procedure was similar to that previously reported in the literature.[12] The imidazolium salt [LH][X] (X = Cl, BF_4) was dissolved (or suspended) in thf (5 mL), and 1.2 equiv of K^{t}OBu was added to the stirred solution at room temperature. The mixture was stirred until a clear solution was obtained (1 h), and then 1 equiv of CuCl was added. Further stirring for 4 h led to a suspension that was filtered through Celite; the filtrate was then taken to dryness and the residue dissolved in a 1:1 mixture of CH_2Cl_2 and petroleum ether. Upon concentration until cloudiness, cooling to −20 °C overnight afforded an off-white, microcrystalline material of composition (NHC)CuCl (NHC = L_1−L_5). The cationic complexes [(NHC)Cu(NCMe)]BF_4 employed as catalyst precursors were prepared in the following manner. A solution of the neutral complex in acetonitrile was treated with 1 equiv of $AgBF_4$. After 15 min of stirring, the mixture was filtered through Celite and the filtrate was dried under vacuum to yield a solid of general composition [(NHC)Cu(NCMe)]BF_4. The spectroscopic data of these neutral and cationic compounds are given in the Supporting Information.

Typical Catalytic β-Boration of α,β-Unsaturated Esters and Aldehydes. Bis(catecholato)diboron (1.1 equiv) was added to a solution of the catalyst (2 mol %) and base (3 mol %) in tetrahydrofuran (2 mL) under nitrogen. The solution was stirred for 5 min, and the substrate (0.05 mmol) was then added with 2 mL of MeOH. The mixture was stirred for 6 h at room temperature. The products obtained were analyzed by ^{1}H NMR spectroscopy to determine the degree of conversion and the nature of the reaction products.

Oxidation Protocol. A solution of sodium perborate (2.5 mmol) in THF−water (1:1, 4 mmL), was added to the mixture. The mixture was stirred vigorously for 4 h. After this time, it was quenched with a saturated solution of NaCl and then extracted into AcOEt (3 × 20 mL). The organic phase was dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The products obtained were analyzed by ^{1}H NMR spectroscopy to determine the degree of conversion and the nature of the reaction products. To determine the ee values of the β-alcohols, they were analyzed on an HPLC-MS instrument equipped with the chiral column Chiracel OD-H.

Acylation Protocol. A solution of 3 mL of acetic anhydride and 5 mL of acetic acid in 25 mL of $CHCl_3$ was added to the β-alcohol product. The reaction mixture was stirred overnight at 50 °C. The next day the mixture was extracted with AcOEt (3 × 20 mL). The organic phase was dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The solution was analyzed in a GC-MS instrument equipped with the chiral column β-cyclodex to determine the ee values.

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Supporting Information Available: Text giving spectroscopic data for the new copper complexes employed as catalyst precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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