Benzosuberyl Substituents as a "Sandwich-like" Function in Olefin Polymerization Catalysis

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Electronic Supplementary Information

Abstract For the rational design of metal catalyst in olefin polymerization catalysis, various strategies were applied to suppress the chain transfer by bulking up the axial positions of the metal center, among which the "sandwich" type turned out to be an efficient category in achieving high molecular weight polyolefin. In the α-diimine system, the "sandwich" type catalysts were built using the typical 8-aryl-naphthyl framework. In this contribution, by introducing the rotationally restrained benzosuberyl substituent into the ortho-position of N-aryl rings, a new class of "sandwich-like" α-diimine nickel catalysts was constructed and fully identified. The rotationally restrained benzosuberyl substituents played a "sandwich-like" function by capping the nickel center from two axial sites. Compared to the nickel catalyst NiI bearing freely rotated benzhydryl substituent, NiII featuring benzosuberyl substituent enabled the increase (8 times) of polymer molecular weights from 8 kDa to 65 kDa in the polymerization of ethylene. By further increasing the steric bulk of another ortho-site of the N-aryl ring, the polymer molecular weight even reached an ultrahigh level of 833 kDa (Mn = 1857 kDa) using the optimized NiIII. Notably, these nickel catalysts could also mediate the copolymerization of ethylene with methyl 10-undecenoate, with NiIII giving the highest copolymer molecular weight (88 kDa) and the highest incorporation of comonomer (2.0 mol%), along with high activity of up to 105 g·mol−1·h−1.

Keywords Olefin polymerization; Benzosuberyl substituent; Sandwich; Nickel catalyst; Polar monomer

INTRODUCTION

Molecular weight is one of the most important parameters to evaluate the different application of polyolefin. For example, polyethylene with high molecular weight, especially ultrahigh molecular weight, has been widely used as plastic in daily life. For the benchmark α-dimine catalyst, the key to affording polymers with high molecular weight is to suppress the chain transfer by blocking the axial positions of the active metal center.[1–3] The extensively adopted method in catalyst design is to incorporate sterically bulky substituents into the ortho-positions of N-aryl rings.[6–41] For instance, the α-dimine nickel catalysts bearing terphenyl moieties produced polyethylene with Mn up to 4.5×106 g·mol−1 (Chart 1, I).[27,29] Derived from this platform, we developed a concerted double-layer steric strategy to construct a blockage around the nickel center by interlocking the axial faces, resulting in ultrahigh molecular weight polyethylene (Mn = 4.2×106 g·mol−1) (Chart 1, II).[37] Another representative example of α-dimine nickel catalysts is those featuring dibenzhydryl units (Chart 1, III), forming polyethylenes with Mn at the level of 105 g·mol−1.[21–23] This class of catalysts has been further extended to unsymmetrical systems, which also showed excellent behavior on enhancing polymer molecular weight.[32,36,38] Besides the above mentioned rigid steric substituents, flexible bulky substituents have recently been introduced into the α-dimine ligands (Chart 1, IV), leading to the formation of high molecular weight (Mn up to 1.2×106 g·mol−1) polyethylene.[14]

In addition to the introduction of ortho-steric substituents, alternative approaches have been developed. "Rotated restriction" is an efficient manner to increase the polymer molecular weight by prohibiting the N-aryl rotation, which slows down the associative chain transfer.[6–10,42–46] In this context, the cyclophane-based α-dimine nickel catalyst containing a macrocycle could generate polyethylene with constant high molecular weight (in the range of 106 g·mol−1) even at elevated temperature (Chart 1, V).[29,40] The pentapyracyl substituent was also found to be a beneficial fragment to retard the N-aryl rotation (Chart 1, VI), compared to the free dibenzhy-
“Sandwich” type α-diamine nickel catalysts based on 8-aryl-naphthylimino moieties (Chart 1, VII) occurred as another way to shield the axial sites, by capping the nickel center from the above and below the five-membered square place, using the nearly parallel aryl rings.[47–51] This type of catalysts exhibited superior performance on giving rise to high polymer molecular weights.

The “sandwich” type framework was a marvellous tool to enhance the molecular weight, which also achieved remarkable outcome of ultrahigh molecular weight polyethylene in the phenoxy-imine systems.[52–57] In the iminopyridine system, rotationally restrained benzosuberyl substituents were introduced to increase the polymer molecular weight, by effectively blocking the axial position of the metal center.[58,59] Recently, we have also reported the application of benzosuberyl groups to form a sandwich configuration on the nickel active center (Chart 1, VIII). We envisioned that tension of the seven-membered cycle in benzosuberyl substituents might inhibit the rotation of phenyl rings to shield the nickel center from two axial sites, thus improving polymerization performance, especially polymer molecular weight.

EXPERIMENTAL

General Considerations

All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were recorded on a Bruker AV400 (1H: 400 MHz, 13C: 100 MHz, 19F: 376 MHz) or a Bruker AV500 (1H: 500 MHz, 13C: 125 MHz, 19F: 470 MHz). The molecular weights and molecular weight distributions (Mn/Mw) of polyethylene and copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. Melting points (Tm) of polyethylene and copolymers were measured through DSC analyses, which were carried out on a Mettler TOPEM TM DSC Instruments under nitrogen atmosphere at heating and cooling rates of 10 °C/min (temperature range: 0–160 °C). Mass spectra of the complexes were recorded on an Acquity UPLC & Quattro Premier. Elemental analysis was performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry. Stress/strain experiments were performed at 5 mm/min on an Electromechanical Universal Testing Machine (E43.140) at room temperature. Polymers were melt-pressed at 150 °C to obtain the test specimens, which have 41-mm gauge length, 17-mm width, and 1.5-mm thickness. At least three specimens of each polymer were tested.

X-ray Diffraction

Data collections were performed at –100 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Ka radiation (λ=0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[60] The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[61] All structures were solved by direct

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methods and refined by full-matrix least-squares procedures on F using Olex2. Refinement was performed on F anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. Exceptions and special features: for NiBr₄, the program SQUEEZE was used to remove mathematically the effect of the solvent. The quoted formula and derived parameters do not include the szezide solvent molecules.

**Synthesis of Ligands and Nickel Complexes**

**Synthesis of ligand L1**
To the solution of 2-benzhydryl-6-fluoro-4-methylaniline (1.80 g, 6.18 mmol) in methanol (50 mL) at 80 °C was added 2,3-butadione (253 mg, 2.94 mmol) and three drops of formic acid. The reaction mixture was stirred for 2 days at 80 °C. The formed yellow suspension was cooled to room temperature and concentrated to a half of its original volume. The yellow precipitate was collected by filtration, washed with methanol and dried in vacuum (1.03 g, 56% yield). ¹H-NMR (500 MHz, 298 K, CDCl₃, 7.26 ppm): δ = 7.25–7.23 (m, 8H, aryl-H), 7.19–7.16 (t, J = 7.3 Hz, 4H, aryl-H), 7.06–7.04 (d, J = 7.0 Hz, 8H, aryl-H), 6.84–6.82 (d, J = 10.6 Hz, 2H, aryl-H), 6.35 (s, 2H, aryl-H), 5.42 (2H, =C=CH₂), 2.25 (s, 6H, aryl-Me), 1.49 (s, 6H, N=C=Me). ¹³C-NMR (125 MHz, 298 K, CDCl₃): δ = 170.78 (N=C=Me), 151.02, 149.08, 142.46, 136.96, 134.17 (J=30 Hz), 134.45 (J=55 Hz), 129.53, 128.29, 126.32, 125.21, 125.19, 114.33 (J= 80 Hz), 52.18 (CHAr), 21.16 (aryl-Me), 15.62 (Me-C=N). ¹⁹F-NMR (470 MHz, 298 K, CDCl₃): δ = −127.98. Elemental analysis: Anal. Calcd. for C₂₀H₁₄F₂N₂: C, 83.52; H, 6.05; N, 4.43. Found: C, 83.64; H, 6.10; N, 4.35.

**Synthesis of ligand L2**
To the solution of the corresponding aniline (2.0 g, 6.30 mmol) in methanol (50 mL) at 80 °C was added 2,3-butadione (258 mg, 2.30 mmol) and three drops of formic acid. The reaction mixture was stirred for 3 days at 80 °C. The formed yellow suspension was cooled to room temperature and concentrated to a half of its original volume. The yellow precipitate was collected by filtration, washed with methanol and dried in vacuum (0.96 g, 47% yield). ¹H-NMR (500 MHz, 298 K, CDCl₃, 7.26 ppm): δ = 7.19 (br, 16H, aryl-H), 6.86–6.83 (d, J = 10.6 Hz, 2H, aryl-H), 6.62 (s, 2H, aryl-H), 5.12 (2H, =CH=CH₂), 3.44 (br, 4H, —CH₂), 2.97 (br, 2H, —CH₂), 2.50 (br, 2H, —CH₂), 2.25 (s, 6H, aryl-Me), 1.55 (s, 6H, N=C=Me). ¹³C-NMR (100 MHz, 298 K, CDCl₃, 77.16 ppm): δ = 171.51 (N=C=Me), 150.95, 143.55, 140.95, 134.35, 135.27, 135.25, 133.91 (J=56 Hz), 132.98 (J=32 Hz), 131.62, 131.30, 129.12, 127.10, 126.35, 126.33, 126.20, 124.10 (J=80 Hz), 56.13 (CHAr), 33.47 (CH₂), 30.48 (CH₂), 21.28 (aryl-Me), 15.74 (Me-C=N). ¹⁹F-NMR (470 MHz, 298 K, CDCl₃): δ = −128.00. Elemental analysis: Anal. Calcd. for C₂₀H₁₄Br₂F₂N₂: C, 63.82; H, 4.69; N, 3.10. Found: C, 63.94; H, 4.77; N, 3.16.

**Synthesis of complex N1**
Ligand L1 (200 mg, 0.32 mmol) was used, and the product was obtained as an orange solid (220 mg, 82% yield). MALDI-TOF-MS (m/z): 769.1 [M−Br]⁺. Elemental analysis: Anal. Calcd. for C₂₀H₁₄Br₂F₂N₂: C, 62.08; H, 4.50; N, 3.29. Found: C, 62.39; H, 4.57; N, 3.22.

**Synthesis of complex N2**
Ligand L2 (200 mg, 0.32 mmol) was used, and the product was obtained as an orange powder (204 mg, 77% yield). MALDI-TOF-MS (m/z): 821.2 [M−Br]⁺. Elemental analysis: Anal. Calcd. for C₂₀H₁₄Br₂F₂N₂: C, 63.82; H, 4.69; N, 3.10. Found: C, 63.94; H, 4.77; N, 3.16.

**Synthesis of complex N3**
Ligand L3 (130 mg, 0.16 mmol) was used, and the product was obtained as an orange powder (82 mg, 50% yield). MALDI-TOF-MS (m/z): 937.3 [M−Br]⁺. Elemental analysis: Anal. Calcd. for C₂₀H₁₄Br₂F₂N₂: C, 70.68; H, 5.14; N, 2.75. Found: C, 70.81; H, 5.18; N, 2.66.

**General Procedures for the Ethylene Polymerization**
In a typical experiment, a 350 mL gas pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 98 mL of toluene and MMAO was added to the reactor under N₂ atmosphere, and then the desired amount of Ni catalyst in 2 mL of CH₂Cl₂ was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 0.8 MPa of ethylene. After 15 min, the pressure reactor was vented and the polymerization was quenched via the addition of 100 mL of acidic MeOH (5% HCl in MeOH) and dried in a vacuum oven to constant weight.

**General Procedures for the Ethylene Copolymerization**
In a typical experiment, a 150 mL gas pressure reactor conn-
lected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 20 mL of toluene with MMAO and polar monomer were added to the reactor under N₂ atmosphere, and then the desired amount of Ni catalyst in 2 mL of CH₂Cl₂ was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at desired ethylene pressure. After 1 h, the pressure reactor was vented and the polymerization was quenched by adding 20 mL of acidic MeOH (5% HCl in MeOH) and dried in a vacuum oven to constant weight.

RESULTS AND DISCUSSION
Preparation and Identification of Ligands and Nickel Complexes
To construct the target α-diamine ligands, treatment of benzhydryl or benzosuberol with aniline derivatives readily gave the 2-benzhydryl-6-F-disubstituted aniline or 2-benzosuberetyl-6-R-disubstituted anilines (R=F, Ph) in high yields, respectively (Scheme 1). Preparation of α-diamine ligands L₁–L₃ was accomplished by the reaction of 2,3-butanedione with the synthesized 2,6-disubstituted anilines, respectively. The prototypical nickel dibromide complex Ni₁, and the desired nickel counterparts Ni₂ and Ni₃ were obtained by the reaction of the corresponding ligands with NiBr₂(DME) in good isolated yields. These α-diamine ligands L₁–L₃ were comprehensively characterized by ¹H- and ¹³C-NMR spectroscopy, and elemental analysis, while the three nickel complexes Ni₁–Ni₃ were identified by mass spectrometry and elemental analysis.

Molecular structures of Ni₁ and Ni₂ were further determined by X-ray diffraction analysis. As shown in Fig. 1 and Fig. 2, complexes Ni₁ and Ni₂ both possess a distorted tetrahedral geometry around the nickel center, with two phenyl rings locating on the above and below axial positions of the metal center to form a capping blockade. The angles between the two phenyl rings and the five-membered coordinate plane of the nickel center in Ni₁ and Ni₂ are 24.3°, 18.6°, and 20.4°, 18.6°, respectively, indicative of a “sandwich-like” configuration. In the solid-state structures, Ni₂ only featured a slightly smaller dihedral angle than Ni₁ (20.4° versus 24.3°). With regard to the compared polymerization results (as shown below), we assumed that the rotationally restrained effect of benzosuberyl groups should be more obvious in the solution state. In addition, the distances between the fluorine atoms and the nickel center (>3.7 Å) were beyond the range of van der Waals radii of the fluorine and the nickel atom (3.3 Å),[65] indicating of no direct ligand metal interaction in the solid state.

Effect of the Aluminum Activator on Ethylene Polymerization
Three representative aluminum activators (MMAO, MAO and AlEt₂Cl) were selected for ethylene polymerization at temperatures from 30 °C to 70 °C, using Ni₂ as a model catalyst (Table 1). Overall, MMAO and MAO were preferred for ethylene polymerization. With the activation of MMAO or MAO at 30 °C, Ni₂ exhibited high activities of 10⁶ g·mol⁻¹·h⁻¹, which remained a high level (>10⁶ g·mol⁻¹·h⁻¹) at elevated temperatures of 50 and 70 °C. In terms of molecular weight, MMAO had an advantage on obtaining polyethylene with higher molecular weight, compared to MAO. Moreover, these aluminum reagents showed no obvious effect on the branching density.

Ethylene Polymerization by Nickel Complexes
The catalytic properties of dibromo nickel complexes Ni₁–Ni₃ were studied (Table 2). With the in situ activation of MMAO, Ni₁ exhibited the highest activities and the lowest polymer molecular weight among these three nickel catalysts, in the temperature range of 30–70 °C (Fig. 3). Taking the temperature of 30 °C as an example (Fig. 4), activity of Ni₂ was approximate 1.7 times lower than that of Ni₁, while the polymer molecular weight generated by Ni₂ was 8 times higher than that by Ni₁. We speculated that the free rotation of one of the two phenyl rings in the benzosuberyl fragment, fixed by the seven-membered ring, was restrained to some extent in the solution state. This rotationally restrained effect might compel the

Scheme 1  Synthesis of α-diamine ligands and the corresponding nickel complexes.

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phenyl rings to stay in the “sandwich-like” geometry, which could retard chain transfer to enhance the molecular weight, and slow down ethylene insertion to lower activity. Moreover, the branching density produced by Ni2 was close to that by Ni1.

The enhancement of polymer molecular weight enabled by benzoxyster groups propelled the study of Ni3. With the replacement of fluorine atoms by phenyl units (Ni3), the steric hindrance on the axial positions of the nickel center was further increased. Consequently, the activity of Ni3 dropped dramatically by nearly 10 times (1.76×10^6 g·mol⁻¹·h⁻¹ versus 17.58×10^6 g·mol⁻¹·h⁻¹), but the molecular weight of polyethylene significantly increased by two orders of magnitude (1857 kDa versus 22 kDa), compared to those of Ni1 at 30 °C (Fig. 4). It is worth noting that polyethylene produced by Ni3 at 30 °C shows bimodal GPC curves (Fig. S45 in the electronic supplementary information, ESI). We assumed that this might be caused by the two existing forms of the unsymmetrical Ni3 at 30 °C in the solution. In previous reports, unsymmetrical α-dimine catalysts were usually comprised of the α-dimine and a nickel complex.
anti and syn isomers, which played different steric impacts on the metal center to differentiate polymerization performances.\cite{16,66–68} As far as Ni3, the anti form with benzosuberyl moieties on the opposite sides of the N^N-Ni coordination plane, namely the “sandwich-like” configuration, existed. The syn form with two benzosuberyl moieties on the same side of the N^N-Ni coordination plane was the outcome of N-aryl rotation. At low temperature as 30 °C, the interconversion was slow, so that an equilibrium occurred between the anti and syn isomers, leading to polyethylene with bimodal GPC curves. In view of branching density, a descending trend (Ni3 < Ni2) at 30 °C was observed, which should be the statistical results of polyethylenes produced by anti-Ni3 and syn-Ni3. Notably, in comparison with the highly branched polyethylene generated by the traditional “sandwich” nickel catalyst,\cite{51} polymer obtained by Ni3 was of moderate branching density.

With elevating temperatures, decrease on polymer molecular weight using Ni3 was found (also for Ni1 and Ni2). Furthermore, polyethylene produced at 50 °C showed unimodal GPC curve, along with a small shoulder. These results suggested that the interconversion of the anti and syn isomers was promoted at higher temperature. To further verify the effect of temperature, ethylene polymerization by Ni3 at 70 °C was further performed (Fig. S71 in ESI). Unimodal distribution ($M_w/M_n$=1.44) was observed as anticipated (Fig. 5). In addition, time-dependence studies of Ni3 were carried out at 70 °C, demonstrating almost constant activity in the polymerization time range from 15 min to 60 min (Fig. S70 in ESI).

In the case of branching density, from 30 °C to 70 °C, polyethylene produced by Ni3 at 70 °C was further performed (Fig. S71 in ESI). Unimodal distribution ($M_w/M_n$=1.44) was observed as anticipated (Fig. 5). In addition, time-dependence studies of Ni3 were carried out at 70 °C, demonstrating almost constant activity in the polymerization time range from 15 min to 60 min (Fig. S70 in ESI).
As branching density increased, these three samples were further tested for strain recovery. Stretched to over 20 times of its original length without break values ranging from 87% to 1105%. Note that the break values ranging from 3.0 MPa to 26.6 MPa, and strain at break values of 90/1000C, all entries are based on at least two runs, unless noted otherwise; Activity is in unit of g·mol⁻¹·h⁻¹; determined by GPC in 1,2,4-trichlorobenzene at 150 °C using a light scattering detector; c Determined by DSC (second heating); d Determined by GPC in 1,2,4-trichlorobenzene at 150 °C using a light scattering detector; e Determined by 1H-NMR spectroscopy; f Determined by 13C-NMR spectroscopy; g Determined by MS. Polyethylene branching density generated by Ni1 were similar, and remained comparably moderate branched structures. Strikingly, for Ni3, when rising 30 °C to 50 °C, the branching density drastically increased from 31/1000C to 82/1000C and was even higher than those of Ni1 and Ni2. This outcome further implied that polyethylene branching density generated by anti-Ni3 and syn-Ni3 differentiated largely, and thus the total branching density was dependent on the interconversion of these two isomers.

**Polyethylene Microstructures**

As a representative example, the microstructure of polyethylene with the highest branching density (96/1000C) (Table 2, entry 9) generated by Ni3 was characterized by 13C-NMR spectroscopy to verify the branching patterns based on assignments reported previously.[69-72] The unsaturated chain end groups were not found in either 1H- or 13C-NMR spectra (Figs. S27 and S31 in ESI). As shown in the 13C-NMR spectrum, this polyethylene structure contained mostly methyl branches, and a small amount of ethyl and propyl branches.

**Mechanical Properties of Polymer**

To investigate the mechanical properties, tensile tests were carried out for polyethylenes with different branching densities (Fig. 6). The three selected polyethylenes displayed stress at break values ranging from 3.0 MPa to 26.6 MPa, and strain at break values ranging from 87% to 1105%. Note that the moderate branched (65/1000C) polyethylene could be stretched to over 20 times of its original length without breaking which is beyond the limitation of the instrument used. These three samples were further tested for strain recovery (Fig. 6, Figs. S72 and S73 in ESI). As branching density increased, stain recovery (SR) value showed an increased trend from 38% to 76%. Polyethylene with high branching density (90/1000C) possessed the SR value of 76%, indicating the feature of elastomer.

**Copolymerization of Ethylene and Polar Monomer by Nickel Complexes**

All three nickel catalysts Ni1–Ni3 were further studied toward the copolymerization of ethylene and the biorenewable monomer methyl 10-undecenoate (UA).[73] In the presence of 0.2 mol·L⁻¹ of UA, Ni1 copolymerized ethylene and UA with the highest activity (3.2×10⁵ g·mol⁻¹·h⁻¹), but the lowest molecular weight (Mₚ=2.2×10⁴ g·mol⁻¹) and incorporation ratio (0.39 mol%) at 30 °C (Table 3, entry 1), among these three catalysts. As the temperature increased to 50 °C, activity and molecular weight by Ni1 reduced by approximately 2 times, while the incorporation of polar monomer remained unaltered (Table 3, entry 2). Under otherwise identical conditions, Ni2 improved the incorporation of UA and the molecular weight of copolymer to some extent, compared to Ni1; however, Ni3 afforded the highest copolymer molecular weight (8.8×10⁴ g·mol⁻¹), along with the highest incorporation of UA (2.0 mol%). These results based on copolymerization reaction again indicated the preference of benzosuberyl group in these nickel catalysts.

**CONCLUSIONS**

In summary, we have constructed “sandwich-like” α-dimine nickel catalysts by installing the rotationally restrained benzosuberyl substituents into the ortho-positions of N-aryl...
rings. The benzosuberyl substituents were probably fixed in the capping orientation to block the two axial sites of the nickel center, which differed from the previously reported “sandwich” type α-diamine nickel catalysts based on 8-arylnaphthyl groups. Compared with the freely rotated benzhydryl substituents, the rotationally restrained benzosuberyl substituents demonstrated superior polymerization behavior in terms of polymer molecular weight, by significantly suppressing the chain transfer. As a consequence, molecular weights of polyethylene gradually increased from the low level of 10^4 g mol^-1 to the ultrahigh level of 10^6 g mol^-1. However, the more crowded environment generated by the benzosuberyl substituents also caused the decrease of activity. In addition, these nickel catalysts were capable of copolymerizing ethylene with polar monomer, such as methyl 10-undecenoate. This utilization of the rotationally restrained strategy to create a “sandwich-like” geometry might shed light on catalyst design in an easier manner to manufacture polyolefin with the desired properties.

Electronic Supplementary Information
Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-021-2562-7.

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