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POLY(IMINOMETHYLENES).

8\*. CIRCULAR INSERTION MECHANISM OF NICKEL(II)-CATALYZED  
POLYMERIZATION OF ISOCYANIDES

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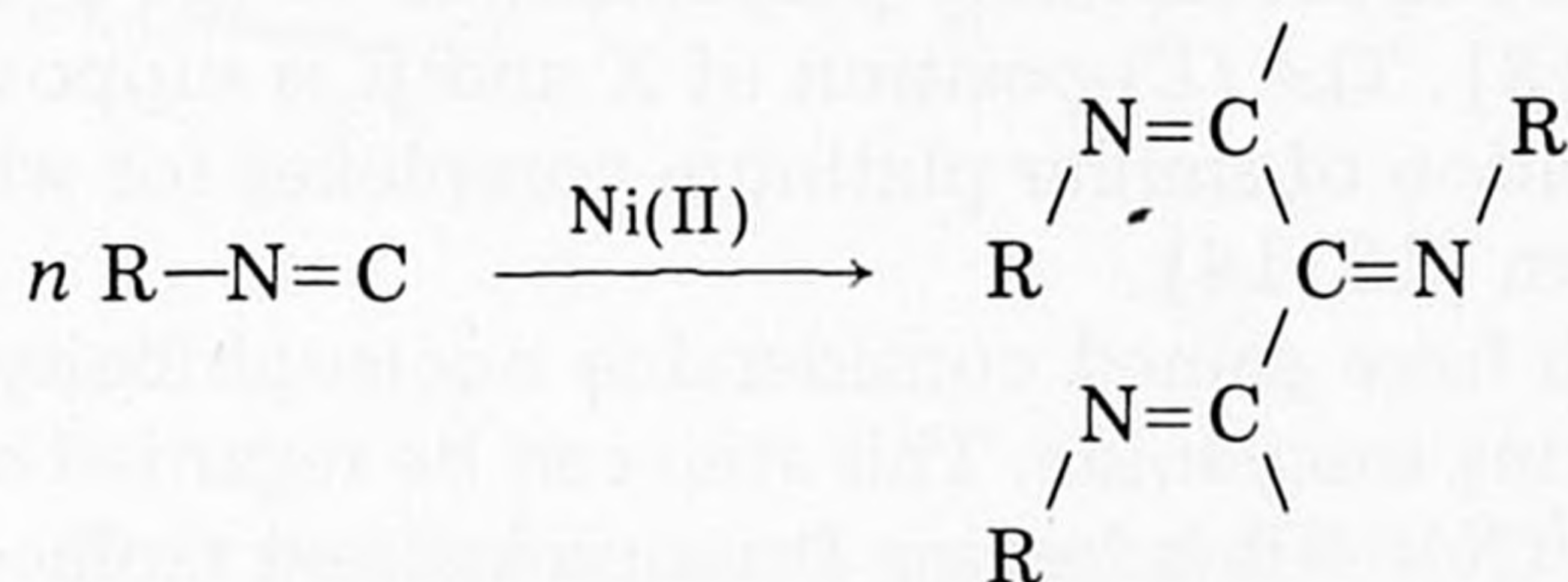
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Summary

A merry-go-round sequence of ligand insertions is proposed for the polymerization of isocyanides by nickel(II). The mechanism agrees with kinetic results as well as with data on the reactivity of coordinated isocyanides and on substitution at nickel(II).

Introduction

Transition-metal ions are active catalysts for the polymerization of isocyanides to a poly-Schiff-base, nickel(II) being particularly active [2 - 4]\*\*\*.



The driving force of this reaction undoubtedly is the conversion of carbon from a bivalent to a tetravalent species. The heat of polymerization is appreciable: 81.4 kJ/mol\*\*\*\*.

Poly(iminomethylenes) have the configuration of a tightly coiled helix with approximately four RNC units per turn [5 - 7]. Helices are chiral

\*Part 7. See ref. 1.

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\*\*\*Data on other methods of polymerization have been reviewed by F. Millich, *Chem. Rev.*, 72 (1972) 101.

\*\*\*\*Determined by Dr. J. C. van Miltenburg for isopropyl isocyanide dissolved in ethanol. Not yet corrected for heat of precipitation.

species. The property of chirality appeared from the resolution of poly(tert-butyliminomethylene) into its optically active enantiomers [6]. Also, the circular dichroism spectra of these enantiomers support a helical configuration [7]. The screw sense of the enantiomers has been assigned [7].

In continuation of our earlier, mainly kinetic study of the polymerization [4], we now present a more detailed mechanism which is in agreement with the reactivity of coordinated isocyanides, as well as with the stereochemistry of ligand substitution at nickel(II).

## Results and discussion

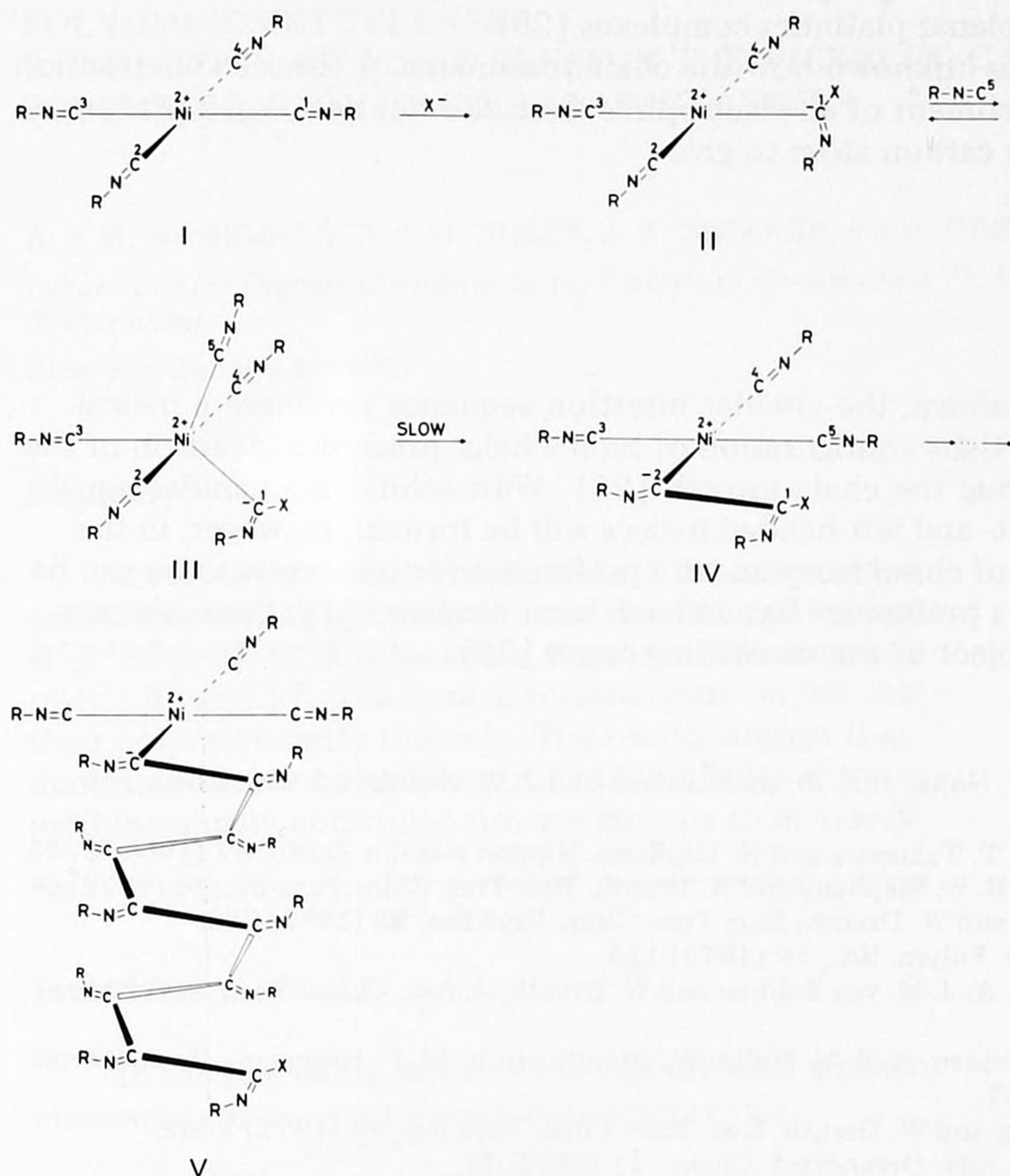
In an earlier paper [8] we showed that under anhydrous conditions, four equivalents of *t*-butyl isocyanide react with nickel(II) perchlorate to  $\text{Ni}(\text{CN-}t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$  in which the  $[\text{Ni}(\text{CN-}t\text{-C}_4\text{H}_9)_4]^{2+}$  ion has a square-planar arrangement. Addition of an excess of *t*-butyl isocyanide to nickel chloride in ethanol gives a red-colored solution with spectral characteristics similar to those of the above mentioned perchlorate\*. Therefore, it can be assumed that  $[\text{Ni}(\text{CNR})_4]^{2+}$  is the predominant nickel species under polymerization conditions.

A common reaction of a metal-coordinated isocyanide molecule is nucleophilic attack on its terminal carbon atom [9 - 11]. Therefore, a conceivable initiation step of the polymerization is attack of one of the four isocyanide ligands by a nucleophile, *e.g.*, a chloride ion [12] or an alcohol molecule [11] (step I  $\rightarrow$  II in Scheme 1). This nucleophile will come in either directly from the solution or through coordination at nickel. The plane of the ligand  $\text{C}^1(\text{X})=\text{NR}$  in II will be approximately perpendicular to the  $\text{C}^1\text{C}^2\text{-C}^3\text{C}^4$  plane for steric reasons [13]. The (*E*)-position of X and R is supposed to be analogous to the configuration of similar platinum complexes for which an X-ray determination is known [13, 14].

Carbon atom  $\text{C}^1$  of II will have gained considerable nucleophilicity, allowing it to attack a neighboring isocyanide. This step can be regarded as a ligand substitution at nickel:  $\text{C}^1(\text{X})=\text{NR}$  is leaving from nickel and replaced by an isocyanide monomer from the solution,  $\text{C}^5=\text{NR}$ . Such a substitution is supposed to be of the associative type, the new ligand coming in apically from above [15 - 18]. Concomitantly, the group  $\text{C}^1(\text{X})=\text{NR}$  is moving downwards, giving a trigonal-bipyramidal intermediate, III, having  $\text{C}^2=\text{N-R}$  and  $\text{C}^4=\text{N-R}$  as apical ligands. The slow step of the reaction would be attack of either  $\text{C}^2$  or  $\text{C}^4$  by  $\text{C}^1$ . Both these attacks have an equal chance of occurrence. In the Scheme we have chosen attack on  $\text{C}^2$ .

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\*Ethanol solutions,  $(0.2 - 9) \times 10^{-3}$  mol/l of  $\text{Ni}(\text{CN-}t\text{-C}_4\text{H}_9)_4\text{Cl}_2$  have: i.r.,  $\nu(\text{NC})$ : 2 235.9  $\text{cm}^{-1}$  (CO calibration); u.v. and visible spectrum,  $\lambda_{\text{max}}/\text{nm}$  ( $\log \epsilon$ ): 330 (3.10), 284 (3.58), 249 (3.58),  $< 220$ ;  $^1\text{H-n.m.r.}$  spectrum in  $\text{CD}_3\text{OD}$  relative to TMS as internal reference: 1.71 ppm (*t*- $\text{C}_4\text{H}_9$ );  $\Lambda_{\text{M}}$  ( $2.5 \times 10^{-4}$  mol/l, 25 °C) is 43  $\text{cm}^2 \text{ S mol}^{-1}$ .



Scheme 1.

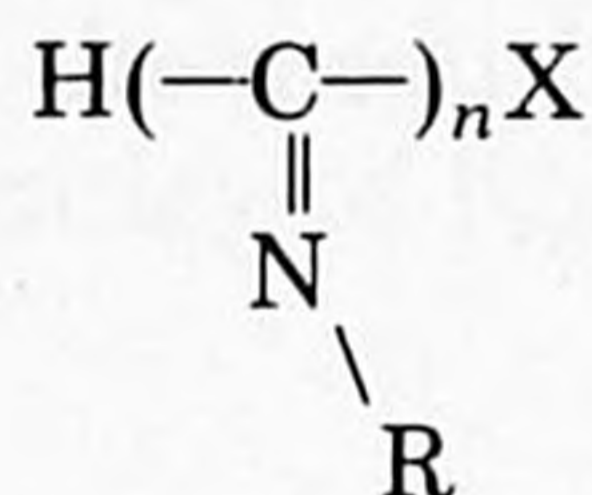
This mechanism is in agreement with the kinetic behavior [4]: first order in nickel chloride as well as in isocyanide. It is also in agreement with the high rate of coordination of ligands to nickel(II) [19]. In an alternative, but less likely mechanism the reactions  $\text{II} \rightarrow \text{III}$  and  $\text{III} \rightarrow \text{IV}$  occur simultaneously. In the next step  $\text{C}^2$  attacks  $\text{C}^3$  while the growing chain moves further downwards.

Since one turn of the helix contains approximately four repeating units, the subsequent insertion of four isocyanide ligands, *i.e.*, one rotation around nickel, increases the chain by one turn. Thus, apart from the coordination of isocyanide monomers, the rearrangement of atomic positions during polymerization is small. It involves a slight wobbling of the nickel plane and a movement of the chain downwards with respect to this plane (V).

A support for this mechanistic picture is the relatively low value of the entropy of activation. For isopropyl isocyanide in ethanol in the temperature

range 10 - 40 °C, with nickel chloride as catalyst,  $\Delta S^\ddagger = -54 \pm 13 \text{ J mol}^{-1} \text{ K}^{-1}$  [4]. This value is comparable with those observed for ligand substitutions in square planar platinum complexes [20].

Thus far it is unknown how the chain terminates. A conceivable reaction [11, 21] is attachment of an electrophile from the solution, *e.g.* a proton, to the last chain carbon atom to give



As shown above, the circular insertion sequence produces a helical chain. The very tight configuration of such a helix precludes inversion of the screw sense during the chain growth [22]. With achiral isocyanides equal amounts of right- and left-handed helices will be formed. However, in the polymerization of chiral isocyanides a preference for one screw sense can be expected. Such a preference has, indeed, been observed [1]; these observations are the subject of the succeeding paper [23].

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