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## INTERMEDIATE SPECIES IN THE POLYMERIZATION OF ISOCYANIDES

P. C. J. KAMER, R. J. M. NOLTE\*,\*\*, W. DRENTH\*\*

*Department of Organic Chemistry, University at Utrecht, Padualaan 8, 3584 CH Utrecht (The Netherlands)*

H. L. L. M. NIJS and J. A. KANTERS

*Laboratory for Crystal and Structural Chemistry, University at Utrecht, Padualaan 8, 3584 CH Utrecht (The Netherlands)*

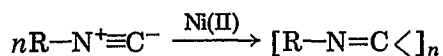
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### Summary

Isocyanides polymerize under the catalytic action of nickel(II) salts,  $nR-N^+\equiv C^- \rightarrow [R-N=C<]_n$ . The mechanism of the polymerization reaction has been investigated. The first intermediate is a square planar nickel(II) isocyanide complex. The general structure of this kind of complex was confirmed by an X-ray analysis of one particular complex, *viz.* tetrakis(2,6-diisopropylphenyl isocyanide)nickel(II) perchlorate. The polymerization is initiated by the attack of a nucleophile (in our case an amine) on a coordinated isocyanide. The initiation proceeds in two steps, (i) coordination of the amine to the nickel centre, and (ii) migration of the amine to the isocyano carbon atom. The resulting product is a nickel carbene complex. The propagation step is an insertion reaction of an isocyanide into the nickel-carbene bond. The polymerization propagates via a consecutive series of such insertion reactions around the nickel centre.

### Introduction

Isocyanides polymerize under the catalytic action of Ni(II) salts [1, 2]. The resulting polymers are called poly(isocyanides), poly(iminomethylenes) or poly(carbonimidoyls). The polymers have a rigid helical structure and



are, therefore, chiral. This chirality is caused by restricted rotation around the carbon-carbon single bonds of the polymer main chain. Stereoisomerism resulting from this type of chirality is called atropisomerism [3].

\*Present address: University at Nijmegen, 6525 ED Nijmegen, The Netherlands.

\*\*Authors to whom correspondence should be addressed.

In the past, a mechanism was proposed for the polymerization of isocyanides catalysed by nickel(II) [1]. Addition of an excess of isocyanide to nickel chloride in ethanol gives a red solution with spectral characteristics similar to those found for the square planar  $\text{Ni}(\text{C}\equiv\text{N})_4^{2-}$  ion. Therefore, we assumed that a similar complex (*i.e.*  $[\text{Ni}(\text{C}\equiv\text{N}-\text{R})_4]^{2+}$ ) is the predominant species under polymerization conditions [4, 5]. Kinetic measurements showed that the polymerization is first order in nickel chloride as well as in isocyanide [6, 7]. The activation entropy,  $\Delta S^\ddagger$ , of the polymerization of isopropyl isocyanide in ethanol was estimated to be  $-54 \pm 13 \text{ J mol}^{-1} \text{ K}^{-1}$  [6]. This value is of the same order of magnitude as those observed for ligand substitutions in square planar platinum complexes [8]. The activation enthalpy,  $\Delta H^\ddagger$ , was found to be  $61.4 \pm 4 \text{ kJ mol}^{-1}$  [6]. On the basis of these results, it was concluded that the polymerization is initiated by nucleophilic attack on a coordinated isocyanide, and proceeds via a series of consecutive insertion reactions around the nickel(II) centre. However, the intermediates of the polymerization reaction could not be isolated. The proposed structure of these intermediates was based on the structure of similar palladium and platinum complexes [9].

In the present paper we describe the isolation and characterization of the first intermediates in the polymerization of isocyanides.

## Results and discussion

As nucleophiles initiate the polymerization of isocyanides, we chose the non-nucleophilic  $\text{ClO}_4^-$  ion as the counterion for the preparation of our nickel isocyanide complexes. Stephany and Drenth [4] have already shown that complexes such as  $\text{Ni}(\text{CN}-t\text{-C}_4\text{H}_9)_4\text{X}_2$  can be isolated when  $\text{ClO}_4^-$  is the counterion (with  $\text{X} = \text{Cl}^-$  the polymerization process interfered).

The characterization of  $\text{Ni}(\text{C}\equiv\text{N}-t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$  is hampered by the low solubility of this complex. Therefore, we synthesized the complexes  $\text{Ni}(\text{C}\equiv\text{N}-t\text{-C}_5\text{H}_{11})_4(\text{ClO}_4)_2$  (1) and  $\text{Ni}[\text{C}\equiv\text{N}-2,6\text{-di}(i\text{-C}_3\text{H}_7)\text{C}_6\text{H}_3]_4(\text{ClO}_4)_2$  (2), which have better solubility and could even be crystallized. The crystal structure analysis of 2 confirms that the complex is centrosymmetric; the nickel(II) ion is the centre of the complex. The bond angle between the isocyanide carbons and nickel is  $92.3^\circ$ . Therefore, the complex has a square planar structure (see Fig. 1). The bond angles  $\text{C}\equiv\text{N}-\text{C}$  of the coordinated isocyanides show a deviation from linearity of only  $5.5^\circ$  ( $\text{C}^{11}\text{N}^1\text{C}^1$ ) and  $6.7^\circ$  ( $\text{C}^{21}\text{N}^2\text{C}^2$ ), which is in line with the high sp character of the N orbitals. The  $\text{N}\equiv\text{C}$  bond lengths, moreover, lie also in the range expected for sp hybridized atoms: 1.146 ( $\text{C}^1\text{N}^1$ ) and 1.160 ( $\text{C}^2\text{N}^2$ ) Å. The Ni-C bond lengths are 1.829 ( $\text{NiC}^1$ ) and 1.838 ( $\text{NiC}^2$ ) Å; the N-C bond lengths are 1.41 ( $\text{N}^1\text{C}^{11}$ ) and 1.42 ( $\text{N}^2\text{C}^{21}$ ) Å. The aromatic rings make angles with the plane formed by the nickel centre and the isocyanide carbon atoms. These angles amount to  $57.7^\circ$  (ring 1) and  $71.8^\circ$  (ring 2).

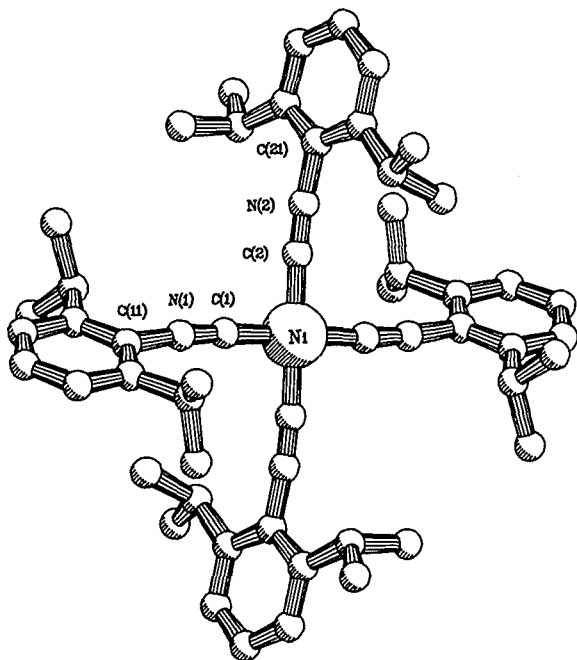


Fig. 1. X-ray structure of tetrakis(2,6-diisopropylphenyl isocyanide) nickel(II) perchlorate.

TABLE 1

IR stretching frequencies of the  $\text{N}\equiv\text{C}$  bond in free isocyanides and nickel(II) isocyanide complexes

R	$\nu(\text{N}\equiv\text{C})$ in $\text{R}-\text{N}^+\equiv\text{C}^-^{\text{a}}$ ( $\text{cm}^{-1}$ )	$\nu(\text{N}\equiv\text{C})$ in $\text{Ni}(\text{C}\equiv\text{N}^+-\text{R})_4(\text{ClO}_4)_2^{\text{a}}$ ( $\text{cm}^{-1}$ )
$t\text{-C}_4\text{H}_9$	2140	2245
$t\text{-C}_5\text{H}_{11}$	2131	2223
2,6-di-( $i\text{-C}_3\text{H}_7$ ) $\text{C}_6\text{H}_3$	2120	2222

<sup>a</sup>Measured in dry  $\text{CH}_2\text{Cl}_2$ .

Further information can be obtained from the infrared spectra of 1 and 2. The  $\text{N}\equiv\text{C}$  stretching frequencies of the free and coordinated isocyanides are given in Table 1. On coordination of the isocyanide, the  $\text{N}\equiv\text{C}$  stretching frequency shifts approximately  $100\text{ cm}^{-1}$  upwards, and is found at  $2223\text{ cm}^{-1}$  for complex 1 and at  $2222\text{ cm}^{-1}$  for complex 2. This is in the range of the  $\text{N}\equiv\text{C}$  stretching vibration of cyanides, which also have  $sp$  hybridized orbitals. The appreciable shift in  $\nu(\text{N}\equiv\text{C})$  means that of the two resonance structures  $\text{R}-\overset{\cdot}{\text{N}}=\text{C}:\leftrightarrow\text{R}-\text{N}^+\equiv\text{C}^-$ , the latter will become more important after coordination. The values of  $\nu(\text{N}\equiv\text{C})$  indicate that the isocyanide ligand in 1 and 2 is more a  $\sigma$  donor than a  $\pi$  acceptor, a

feature often observed when isocyanides coordinate to high-valent metal centres [10].

In the  $^{13}\text{C}$  NMR spectrum, the isocyanide carbon resonance has shifted from 155.1 in the free ligand [11] to 113.7 ppm in complex 1. This upfield shift is often observed when isocyanides coordinate to metal ions [12]. The UV spectrum of complex 1 shows two strong bands at  $\lambda = 239$  nm ( $\epsilon = 12\,300$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ),  $\lambda = 274$  nm ( $\epsilon = 7590$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ), and a weak broad band at about  $\lambda = 335$  nm ( $\epsilon = 40$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ). This UV spectrum is almost identical to that of the complex  $\text{Ni}(\text{C}\equiv\text{N}-t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$  isolated by Stephany and Drenth [4].

Coordinated isocyanides are sensitive to attack by a nucleophile [10]. Alcohols and amines are known to react with coordinated isocyanide to give carbene complexes [12]. We therefore presumed that the initiating step in the polymerization of isocyanides was the attack of a nucleophile on the coordinated isocyanide [5]. We treated complex 1 with one equivalent of (*S*)-(-)-1-phenylethylamine\* and observed that the reaction proceeded in two steps. When the reaction is carried out at  $-60^\circ\text{C}$ , intermediate 3 is formed, which is stable for some time (Fig. 2). Complex 3 is

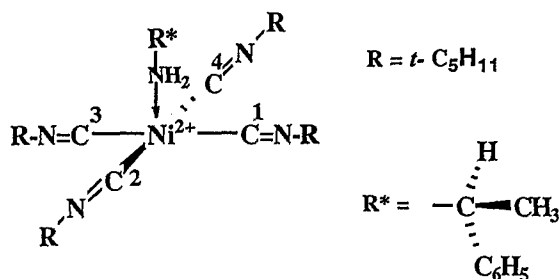


Fig. 2. Structure of intermediate 3.

red in colour, whereas complex 1 is yellow. In the IR spectrum of 3, two NH stretching frequencies are seen at 3300 and 3250  $\text{cm}^{-1}$ . These frequencies are  $\sim 30$   $\text{cm}^{-1}$  lower than those found for free 1-phenylethylamine. The two NH signals are indicative of a primary amine. Therefore, we concluded that in complex 3 the amine is coordinated to the nickel centre. On coordination of the amine, the symmetry of the nickel isocyanide complex changes, and as a result a different pattern of the  $\text{N}\equiv\text{C}$  stretching frequency will be observed. This is indeed the case. Complex 3 has a strong ( $\text{N}\equiv\text{C}$ ) absorption at 2233  $\text{cm}^{-1}$  and a shoulder at 2242  $\text{cm}^{-1}$ . A medium-sized absorption is present at 2202  $\text{cm}^{-1}$ , with a shoulder at 2188  $\text{cm}^{-1}$ . When the temperature is slowly increased, the IR spectrum changes. The two NH stretching frequencies gradually disappear and are transformed to one signal at 3280  $\text{cm}^{-1}$ , characteristic of a secondary amine. A new

\*An optically active amine was used in order to obtain optically active poly(isocyanides) using the described complex as catalyst, see also [13].

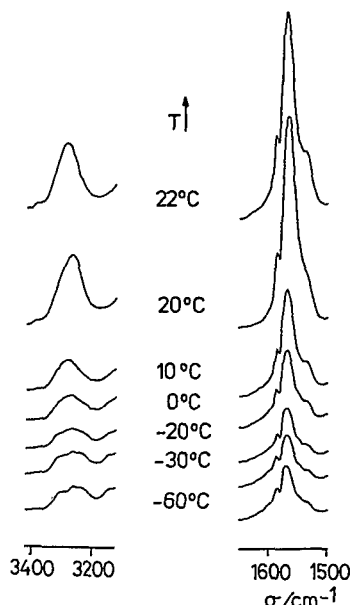


Fig. 3. Change in IR spectrum of complex 3 when raising the temperature from  $-60$  to  $22$  °C.

signal arises at  $1570\text{ cm}^{-1}$  with a shoulder at  $1585\text{ cm}^{-1}$ , while a medium peak is observed at  $1537\text{ cm}^{-1}$ . The change in these signals as a function of the temperature is shown in Fig. 3. Changes also occur in the  $\text{C}\equiv\text{N}$  stretching region. At  $20\text{ }^\circ\text{C}$  a strong absorption is observed at  $2220\text{ cm}^{-1}$ , with shoulders at  $2240$  and  $2190\text{ cm}^{-1}$ . The signals at  $1570$  and  $1585\text{ cm}^{-1}$  lie in the range observed for the  $\text{N}=\text{C}=\text{N}$  stretching vibrations in metal (Pd, Pt, Ni) carbene complexes [9]. We propose that at elevated temperatures a nickel carbene complex 4 is formed from 3. This would agree with the observation that a primary amine is converted into a secondary amine (Fig. 4).

If the conversion of complex 1 to 4 proceeds via complex 3, the UV spectrum of 1 will change and, because complexes 1 and 4 both have a square planar arrangement of ligands, will eventually return to approximately the original spectrum. In Fig. 5 the change is shown in the UV

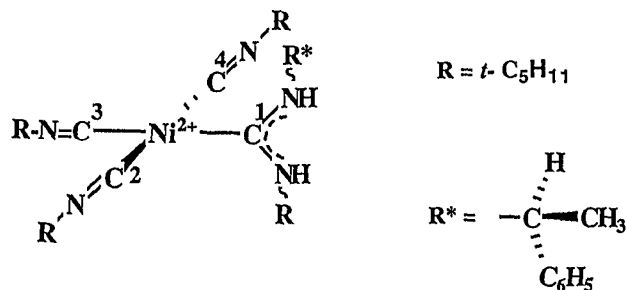


Fig. 4. Structure of the nickel carbene complex 4.

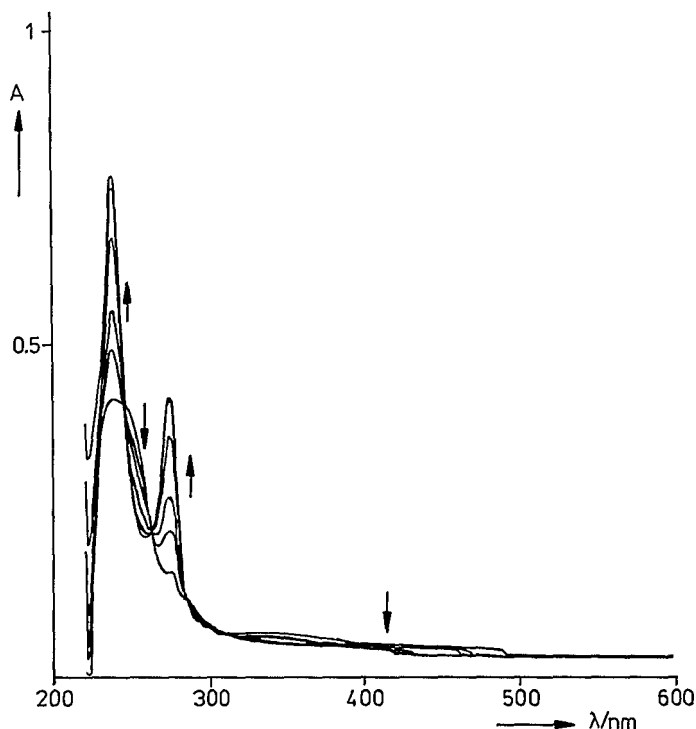


Fig. 5. Change in UV spectrum of complex 3 when raising the temperature from  $-60$  to  $22$  °C. Arrows indicate the main changes.

spectrum of the reaction mixture on increasing the temperature from  $-60$  to  $20$  °C. The UV spectrum at  $-60$  °C indeed is totally different from that of the starting complex 1. The UV absorptions appear at  $\lambda = 420$  nm (broad signal;  $\epsilon = 450$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>),  $\lambda = 340$  nm (broad signal;  $\epsilon = 820$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>),  $\lambda = 273$  nm ( $\epsilon = 2760$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>),  $\lambda = 250$  nm ( $\epsilon = 7880$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), and  $\lambda = 238$  nm ( $\epsilon = 8430$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). At  $20$  °C the spectrum of the reaction mixture is quite analogous to the spectrum of the starting complex 1. Several isosbestic points are observed, indicating that we are dealing with the transformation of one compound into another.

In analogy to similar known complexes, the plane of the ligand C{NH-CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>}NH-t-C<sub>5</sub>H<sub>11</sub> will be approximately perpendicular to the plane formed by the nickel ion and the isocyanide carbons [9].

The <sup>1</sup>H NMR spectrum of the five-coordinated complex 3 at  $-60$  °C showed only broad signals, suggesting that the complex is paramagnetic. The magnetic susceptibility of 3 was determined by the Evans method [14]. The  $\mu$ -value amounted to 1.2 BM, which corresponds to 0.56 unpaired electrons. Since an amine is a two-electron donor, the number of unpaired electrons is expected to be even. The observed low value of 0.56 may be ascribed to the reaction of complex 3 to form 4 during the preparation of the sample and the susceptibility measurement.

The carbene complex 4 is diamagnetic and showed well-resolved  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The  $^{13}\text{C}$  NMR spectrum was especially informative about the structure of the complex. Two  $^{13}\text{C}$  resonances, at 175.4 and 179.2 ppm, are observed in the region where carbenic carbon signals are to be expected [15 - 17]. The fact that two signals are present suggests that complex 4 occurs in two conformations. In line with this, two signals with almost the same intensity ratio are found for the other carbon atoms of the carbene ligand: 141.6 and 142.5 ppm ( $\text{C}^1$  of the phenyl ring); 54.1 and 61.1 (CH); 58.3 and 59.7 [ $\text{N}-\underline{\text{C}}(\text{CH}_3)_2\text{C}_2\text{H}_5$ ]; 33.3 and 35.5 ( $\text{CH}_2$ ); 26.5 and 28.2 [ $\text{C}(\underline{\text{C}}\text{H}_3)_2$ ]; 23.0 and 23.8 [ $\text{CH}(\underline{\text{C}}\text{H}_3)$ ]. A similar phenomenon was observed for the complex  $\text{Ni}(\text{C}\equiv\text{N}-t\text{-C}_4\text{H}_9)_3[\text{C}\{\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5\}\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$ , where the carbene ligand can have three conformations [18]. In principle four conformations are possible, which are shown in Fig. 6. Molecular models suggest that, for steric reasons, conformations 6B and 6D are not possible. When *t*-butyl isocyanide is used instead of *t*-pentyl isocyanide, conformation 6B is possible [18]. Similar observations have been reported by Crociani and Richards, who studied the conformations of palladium and platinum carbene complexes [19]. The most likely conformations are 6A and 6C. We believe that conformation 6A is more probable than 6C, because the phenyl ring can interact with the nickel centre.

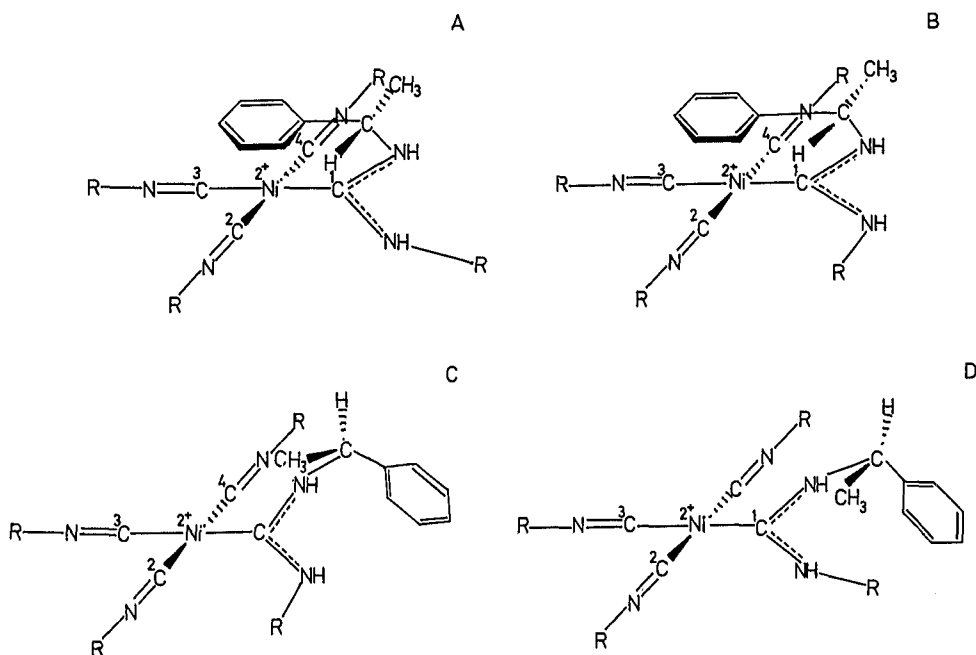


Fig. 6. Possible conformations of  $\text{Ni}(\text{C}\equiv\text{N}-t\text{-C}_5\text{H}_{11})_3[\text{C}\{\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5\}\text{NH}-t\text{-C}_5\text{H}_{11}](\text{ClO}_4)_2$  (complex 4).



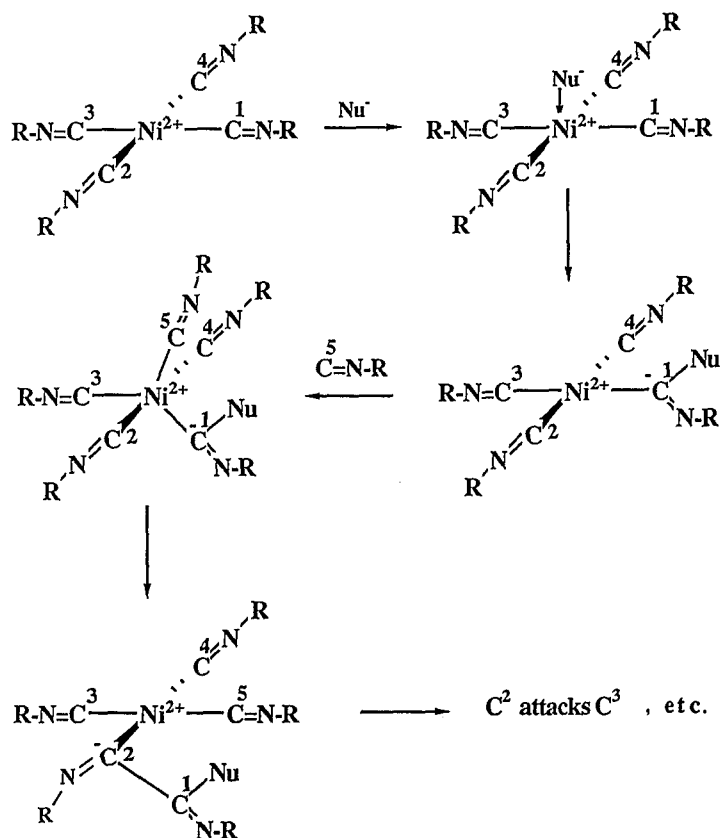


Fig. 7. Mechanism of the polymerization.

Moreover, the phenyl ring causes less steric hindrance than the *t*-pentyl substituent with respect to the bulky nickel centre\*.

The experiments described here confirm that the initiation step of the polymerization of isocyanides, resulting in a nickel carbene complex, is in line with the original proposal of Drenth and Nolte (see Fig. 7) [1]. Isocyanides are known to insert into metal-carbene bonds [12]. We therefore believe that a series of consecutive insertions is the most likely description of the propagation steps. However, attempts to isolate the intermediate formed in the first propagation step have so far been unsuccessful.

## Experimental section

### Analytical techniques

Infrared (IR) spectra were recorded on Perkin-Elmer 297 and 283 spectrophotometers. Ultraviolet (UV) spectra were recorded on a Perkin-

\*As a relative measure of steric hindrance, the  $\lambda$ -steric parameter can be used. See also [20], where (R,  $\lambda$ R): H, 0.00;  $\text{CH}_3$ , 1.00;  $\text{C}_6\text{H}_5$ , 1.23; *t*- $\text{C}_4\text{H}_9$ , 1.49.

Elmer 200 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.  $^1\text{H}$  NMR spectra were obtained on Varian EM 390 and Bruker WP 200 instruments.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker WP 200 instrument; chemical shifts ( $\delta$ ) are given in ppm downfield from internal tetramethylsilane. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Melting points were determined on a Mettler FP5/FP51 photoelectric melting point apparatus. Crystallographic data were collected with an Enraf-Nonius CAD 4 diffractometer.

#### *N-Formyl-t-pentylamine*

According to a literature procedure t-pentylamine was *N*-formylated with a 10% excess of ethyl formate in 67% yield. IR (neat) 1675 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.3 - 7.8 (m, 1H, CHO), 7.3 - 5.3 (br, 1H, NH), 1.60 (2  $\times$  q, 2H,  $\text{CH}_2$ ), 1.30 (2  $\times$  s, 6H,  $\text{CH}_3$ ), 0.90 (2  $\times$  t, 3H,  $\text{CH}_3$ ).

#### *t-Pentyl isocyanide*

This isocyanide was prepared from *N*-formyl-t-pentylamine by the method of Schuster *et al.* [21] but at a lower pressure (0.5 mmHg) than recommended. Yield 88%; IR ( $\text{CCl}_4$ ) 2131 (C=N)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.63 (3  $\times$  q, 2H,  $\text{CH}_2$ ), 1.37 (3  $\times$  s, 6H,  $\text{CH}_3$ ), 1.03 (t, 3H,  $\text{CH}_3$ ).

#### *N-Formyl-2,6-diisopropylaniline*

In 200  $\text{cm}^3$  of dry  $\text{CH}_2\text{Cl}_2$ , 60 g of 2,6-diisopropylaniline (0.34 mol) was dissolved and cooled in an ice bath. A mixture of 40  $\text{cm}^3$  of formic acid (1.06 mol) and 40  $\text{cm}^3$  of acetic anhydride was stirred for 1 h and then added to the above-mentioned solution at such a rate that the temperature remained between 5 and 10  $^\circ\text{C}$ . Subsequently, the reaction mixture was stirred for 60 h at room temperature and refluxed for 4 h. The solvent was evaporated under vacuum, and the residue was dissolved in  $\text{CHCl}_3$  and washed three times with a saturated aqueous  $\text{NaHCO}_3$  solution and with water. The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated in vacuum. The product was recrystallized from diethyl ether: yield 47 g (66%); m.p. 160  $^\circ\text{C}$ ; IR (KBr) 1660 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.2 - 7.6 (m, 2H, CH), 1.28 (d, 12H,  $\text{CH}_3$ ).

#### *2,6-Diisopropylphenyl isocyanide*

This isocyanide was synthesized from *N*-formyl-2,6-diisopropylaniline according to a modification of the method of Skorna and Ugi [22]. The procedure was as follows. Into a round-bottomed flask equipped with a magnetic stirrer and a  $\text{CO}_2$ /acetone reflux condenser kept at  $-30$   $^\circ\text{C}$ , were brought 17.9 g *N*-formyl-2,6-diisopropylaniline (87 mmol), 20  $\text{cm}^3$  of dry *N*-methylmorpholine (180 mmol) and 150  $\text{cm}^3$  of dry  $\text{CH}_2\text{Cl}_2$  as solvent. Over a period of 1 h, 3.9  $\text{cm}^3$  of diphosgene (45 mmol) in 50  $\text{cm}^3$  of dry  $\text{CH}_2\text{Cl}_2$  was introduced into the stirred reaction mixture at a temperature of  $-30$   $^\circ\text{C}$ . Stirring was continued for another hour. The cooling bath was

removed and 100 cm<sup>3</sup> of water was immediately added to the reaction mixture. The still cold organic layer was separated, washed three times with 100 cm<sup>3</sup> of an aqueous 5% NaHCO<sub>3</sub> solution and once with 100 cm<sup>3</sup> of water. The CH<sub>2</sub>Cl<sub>2</sub> layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The crude reaction product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>): yield 12.4 g (72%) of a colorless liquid; IR (CH<sub>2</sub>Cl<sub>2</sub>) 2120 (C=N) cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.06 (m, 3H, C<sub>6</sub>H<sub>3</sub>), 3.32 (m, 2H, CH), 1.17 (d, 12H, CH<sub>3</sub>).

*(S)-(-)-1-Phenylethylamine*

Racemic 1-phenylethylamine was resolved in its optical antipodes by a standard method [23]. The specific optical rotation of the (*S*)-enantiomer was:  $[\alpha]_D^{20} - 40.3^\circ$  (neat) [lit. [11]  $[\alpha]_D^{29} - 39.4^\circ$  (neat)].

*Tetrakis(t-pentyl isocyanide)nickel(II) perchlorate*

This complex was prepared according to a literature procedure by adding 4 equiv of *t*-pentyl isocyanide to a stirred 0.20 M solution of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 96% ethanol/ether 1:3 (v/v) at 0 °C [4]. The complex separated from the solution and was collected by filtration, washed with cold ethanol/ether and with cold ether. The complex was dried at 40 °C at 0.02 mmHg. Yield 80%: IR (CH<sub>2</sub>Cl<sub>2</sub>) 2223 (C=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.89 (q, 2H, CH<sub>2</sub>), 1.63 (s, 6H, CH<sub>3</sub>), 1.15 (t, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 113.71 (s, C=N), 64.91 (s, C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>), 34.29 (s, CH<sub>2</sub>), 26.97 (s, C(CH<sub>3</sub>)<sub>2</sub>), 8.14 (s, CH<sub>2</sub>CH<sub>3</sub>); UV (CH<sub>2</sub>Cl<sub>2</sub>) λ (ε) 335 (40), 274 (7590), 239 (12 300); elemental analysis: C<sub>24</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>4</sub>NiO<sub>8</sub> (646.25): calcd.: C, 44.61; H, 6.86; Cl, 10.97; N, 8.67; Ni, 9.08; O, 19.81%; found: C, 44.51; H, 6.83; Cl, 10.88; N, 8.63; Ni, 9.22; O, 19.81%.

*Tetrakis(2,6-diisopropylphenyl isocyanide)nickel(II) perchlorate*

This complex was prepared as described for Ni(C≡N-t-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>, but the solvent was 96% ethanol/ether 1:1 (v/v). The yield was 76%. A small sample of the product was dissolved in a minimum amount of tetrahydrofuran and the solution was stored at -30 °C. The product crystallized after one day and crystals were selected for X-ray analysis. Some crystallographic data: Space group P<sub>bca</sub> z = 4, with a = 19.15(1), b = 21.04(1), c = 15.91(1). Full details of the analysis will be published elsewhere [24]. IR (CH<sub>2</sub>Cl<sub>2</sub>) 2222 (C=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.1 (m, 3H, C<sub>6</sub>H<sub>3</sub>), 3.5 (m, 2H, CH), 1.25 (d, 12H, CH<sub>3</sub>); elemental analysis: C<sub>52</sub>H<sub>68</sub>Cl<sub>2</sub>N<sub>4</sub>NiO<sub>8</sub> (1006.81): calcd.: C, 62.03; H, 6.81; Cl, 7.04; N, 5.57; Ni, 5.83; O, 12.71%; found: C, 61.88; H, 6.67; Cl, 7.12; N, 5.50; Ni, 5.90; O, 12.70%.

*Tri(t-pentyl isocyanide([S]-(-)-1-phenylethylamino(t-pentylamino)-carbene] nickel(II) perchlorate*

In 10 cm<sup>3</sup> of dry CH<sub>2</sub>Cl<sub>2</sub>, 441.4 mg of tetrakis(*t*-pentyl isocyanide)-nickel(II) perchlorate (0.68 mmol) was dissolved. At 20 °C 86.9 × 10<sup>-3</sup> cm<sup>3</sup> of (*S*)-(-)-1-phenylethylamine (0.68 mmol) was added. The yellow solution turned orange-red and after a few minutes the color reverted to

yellow. After stirring for 15 min the  $\text{CH}_2\text{Cl}_2$  was removed under vacuum and the complex was dried at  $20^\circ\text{C}$  and 0.01 mmHg. Yield 100% of a yellow powder:  $[\alpha]_D^{20}$   $9.3^\circ$  ( $c$  0.45,  $\text{CHCl}_3$ ); IR ( $\text{CH}_2\text{Cl}_2$ ) 3280 (NH); 3059 (CH arom.); 2974, 2939 and 2880 (CH aliph.); 2220, 2240 (sh) and 2190 (sh) (C=N); 1570, 1585 (sh) and 1537 (N-C-N); 1090 and 620 ( $\text{ClO}_4^-$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.78 and 6.67 ( $2 \times d$ , 2H, CHNH), 8.02 and 6.33 ( $2 \times s$ , 2H, NH), 7.62 - 7.28 (m, 5H,  $\text{C}_6\text{H}_5$ ), 5.83 and 4.99 ( $2 \times m$ , 1H, CH), 1.92 - 0.47 (m, remaining H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  179.2 and 175.4 ( $2 \times s$ , C carbene), 142.5 and 141.6 ( $2 \times s$ ,  $\text{C}^1$  arom.), 129.3 - 126.1 (m, C arom.), 123.4 (br, C=N), 64.2 (br, C-N=C), 61.1 and 54.1 ( $2 \times s$ , CH), 59.7 and 58.3 ( $2 \times s$ , C-NH), 35.5 and 33.3 ( $2 \times s$ ,  $\text{CH}_2$ -C-NH), 34.5 (s,  $\text{CH}_2$ -C-N=C), 28.2 and 26.5 ( $2 \times s$ ,  $(\text{CH}_3)_2\text{CNH}$ ), 27.1 (s,  $(\text{CH}_3)_2\text{C-N=C}$ ), 23.8 and 23.0 ( $2 \times s$ ,  $\text{CH}_3\text{CH}$ ), 8.2 (s,  $\text{CH}_3\text{CH}_2\text{C-N=C}$ ), 7.8 (s,  $\text{CH}_3\text{CH}_2\text{CNH}$ ); FAB mass spectrum  $m/e$ : 666 ( $\text{M-ClO}_4^-$ ) $^+$ , 569 ( $\text{M-ClO}_4^-$ - $t\text{-C}_5\text{H}_{11}\text{NC}$ ) $^+$ , 505 ( $\text{M-2ClO}_4^-$ - $t\text{-C}_5\text{H}_{11}\text{NC} + \text{Cl}^-$ ) $^+$ , 373 ( $\text{M-2ClO}_4^-$ - $2t\text{-C}_5\text{H}_{11}\text{NC}$ ) $^+$ , 311 ( $\text{M-2ClO}_4^-$ - $3t\text{-C}_5\text{H}_{11}\text{NC} + \text{Cl}^-$ ) $^+$ , 276 ( $\text{M-2ClO}_4^-$ - $3t\text{-C}_5\text{H}_{11}\text{NC}$ ) $^+$ ; elemental analysis:  $\text{C}_{32}\text{H}_{55}\text{Cl}_2\text{N}_5\text{NiO}_8$  (767.43): calcd.: C, 50.08; H, 7.22; Cl, 9.24; N, 9.13; Ni, 7.65; O, 16.67%; found: C, 50.06; H, 7.29; Cl, 9.25; N, 9.10; Ni, 7.63; O, 16.65; UV ( $\text{CH}_2\text{Cl}_2$ )  $\lambda$  ( $\epsilon$ ): 248 (11800), 281 (5370), 330 (310).

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