A nickel–carbene complex as an intermediate in the polymerization of isocyanides*  

Paul C. J. Kamer, Roeland J. M. Nolte and Wiendelt Drenth

Department of Organic Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands  
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Abstract. An intermediate in the polymerization of isocyanides, catalysed by nickel(II), has been isolated and characterized. The polymerization starts by nucleophilic attack of \((S)-(\_)-(1\text{-phenylethyl})\)amine to the terminal carbon atom of a coordinated isocyanide of tetrakis(tert-butyl isocyanide)nickel(II) perchlorate. The resulting intermediate was isolated and shown to be a nickel–carbene complex: \(\text{Ni}(\text{N}=-\text{C}(\text{H})_{10})_{4}\text{[C[NHCH(CH}_{3}]_{2}\text{C}_{6}\text{H}_{5}]\text{NH-t-C}_{6}\text{H}_{5}}\text{(ClO}_{4})_{2}\). In solution, the carbene complex appears to have three conformations. The effect of these conformations on the enantioselective polymerization of isocyanides is discussed.

Introduction

Poly(isocyanides), also called poly(iminomethylenes) or poly(carbonimidoyls), are rigid, highly isotactic polymers, which are prepared from isocyanides by the catalytic action of Ni(II) salts \(^1,2\).  

\[ \text{R-
N\overline{C}\text{Ni}(\text{II})}\text{R} \longrightarrow \text{[R-N=C(\text{\_})]n} \]

The polymers consist of right-handed \((P)\) and left-handed \((M)\) helices and, therefore, are chiral. The chirality of these polymers is the result of restricted rotation around the single bonds that connect the main-chain carbon atoms. This kind of stereoisomerism is called atropisomerism \(^3\).

In our laboratory, several methods have been developed for the preparation of optically active polymers of isocyanides \(^4\). A mechanism of polymerization has also been proposed \(^1,5\). The polymerization is initiated by a nucleophile attack, in our case by an amine, on an isocyanide, coordinated to Ni(II). The propagation proceeds via a series of insertion reactions around a square-planar nickel complex: \([\text{Ni}(\text{N}=-\text{C}(\text{H})_{10})_{4}\text{[C[NHCH(CH}_{3}]_{2}\text{C}_{6}\text{H}_{5}]\text{NH-t-C}_{6}\text{H}_{5}}\text{(ClO}_{4})_{2}\] \(\rangle\). The square-planar structure of this complex, which was derived from its UV spectrum, has recently been confirmed by the crystal structure of another nickel isocyanide complex: \(\text{i.e. Ni}[\text{N}=-\text{N}_{2}, \text{Cl}-\text{N}_{2}\text{H}_{4}]_{4}\text{[ClO}_{4})_{2}\) \(\rangle\). \(\text{Ni}(\text{N}=-\text{C}(\text{H})_{10})_{4}\text{[C[NHCH(CH}_{3}]_{2}\text{C}_{6}\text{H}_{5}]\text{NH-t-C}_{6}\text{H}_{5}}\text{(ClO}_{4})_{2}\) was synthesized by adding one equivalent of \((S)-(\_)-(1\text{-phenylethyl})\)amine to a suspension of \(\text{Ni}(\text{N}=-\text{C}(\text{H})_{10})_{4}\text{[ClO}_{4})_{2}\) in dry CH\(_2\text{Cl}_2\). The resulting complex was isolated by removing the solvent in vacuum. A complete elemental analysis proved this complex to be in agreement, within experimental error, with the formula \(\text{C}_{25}\text{H}_{45}\text{Cl}_{2}\text{N}_{2}\text{NiO}_{4}\). Its IR spectrum shows an N–H stretching frequency at 3280 cm \(^{-1}\). Since a primary amine such as \((1\text{-phenylethyl})\)amine shows two NH bands, the presence of only one band suggests that a secondary amine has been formed. The aromatic and aliphatic C–H stretching frequencies are found at 3052 and 2985 cm \(^{-1}\). The isocyanide stretching frequency has shifted from 2245 to 2226 cm \(^{-1}\), a shoulder is present at 2250 cm \(^{-1}\). A very strong absorption at 1098 cm \(^{-1}\) is caused by the perchlorate ion. The complex also shows an absorption at 1570 cm \(^{-1}\) with a shoulder at 1558 cm \(^{-1}\) and two weak absorptions at 1588 and 1542 cm \(^{-1}\). These frequencies around 1570 cm \(^{-1}\) are in the range of the N–C–N stretching frequency of carbene complexes of Ni, Pd and Pt (see Table I) \(^13\). Thus, the infrared data suggest that we are dealing with a nickel–carbene complex.

Results and discussion

Racemic \((1\text{-phenylethyl})\)amine was resolved into its optical antipodes using a standard method \(^11\). \(\text{t}-\text{Butyl isocyanide was prepared by N-formylation of tert-butyl isocyanide}\) \(^12\) and subsequent dehydration with 4-toluenesulphonyl chloride \(^13\). \(\text{Ni}(\text{N}=-\text{C}(\text{H})_{10})_{4}\text{[ClO}_{4})_{2}\) was prepared as previously described \(^10\). The square-planar structure of this complex, which was derived from its UV spectrum, has recently been confirmed by the crystal structure of another nickel isocyanide complex: \(\text{i.e. Ni}[\text{N}=-\text{N}_{2}, \text{Cl}-\text{N}_{2}\text{H}_{4}]_{4}\text{[ClO}_{4})_{2}\). The isocyanide complex was isolated by removing the solvent in vacuum. A complete elemental analysis proved this complex to be in agreement, within experimental error, with the formula \(\text{C}_{25}\text{H}_{45}\text{Cl}_{2}\text{N}_{2}\text{NiO}_{4}\). Its IR spectrum shows an N–H stretching frequency at 3280 cm \(^{-1}\). Since a primary amine such as \((1\text{-phenylethyl})\)amine shows two NH bands, the presence of only one band suggests that a secondary amine has been formed. The aromatic and aliphatic C–H stretching frequencies are found at 3052 and 2985 cm \(^{-1}\). The isocyanide stretching frequency has shifted from 2245 to 2226 cm \(^{-1}\), a shoulder is present at 2250 cm \(^{-1}\). A very strong absorption at 1098 cm \(^{-1}\) is caused by the perchlorate ion. The complex also shows an absorption at 1570 cm \(^{-1}\) with a shoulder at 1558 cm \(^{-1}\) and two weak absorptions at 1588 and 1542 cm \(^{-1}\). These frequencies around 1570 cm \(^{-1}\) are in the range of the N–C–N stretching frequency of carbene complexes of Ni, Pd and Pt (see Table I) \(^13\). Thus, the infrared data suggest that we are dealing with a nickel–carbene complex.

* Dedicated to Prof. Dr. G. J. M. van der Kerk on the occasion of his 75th birthday.
* Chem. Abstr. name: \(\alpha\)-methylbenzenemethanamine.
The fast-atom-bombardment (FAB) mass spectrum shows the molecular ion minus a perchlorate anion. The fragmentation pattern suggests that the complex contains three coordinated tert-butyl isocyanide molecules. The fourth isocyanide has reacted with (1-phenylethyl)amine to form the carbene ligand, which is not found in the fragmentation pattern.

The UV spectrum shows two strong bands at λ 249 nm (ε 10400) and 283 nm (ε 5070) and a weak broad band at approximately 330 nm (ε 520). This UV spectrum is only slightly different from the UV spectrum of the starting complex Ni(C=NR-C4H9)4(C104)22,16,17, indicating that the carbene complex also has a square-planar configuration. In Table II, UV data of related carbene complexes are given.

The carbenic structure of the ligand C[NHCH(CH3)C6H5]NH-C4H9 was further supported by 13C NMR measurements. The 13C NMR chemical shift of the isocyano carbon atom of coordinated tert-butyl isocyanide is expected at 118 ppm, since this value is observed for Ni(C=NR-C4H9)4(C104)216,17. In the carbene complex formed after reaction of Ni(C=NR-C4H9)4(C104)2 with (S)-(−)-(1-phenylethyl)amine, the 13C chemical shifts of the isocyano carbons are found at 120–124 ppm. Moreover, three carbon signals appear at 181.37, 179.20 and 175.18 ppm. These values are in the region where carbenic-carbon signals can be expected; see for comparison Table III, where NMR data of other carbene complexes are listed.

The presence of three carbene signals suggests that the complex can adopt more than one conformation. In line with this suggestion is the presence of three signals for the methyl-carbon atom of the CH3CH(C6H5)NH residue (22.77, 23.40 and 24.90 ppm) and for the number-1 carbon of the phenyl ring (141.55, 142.32 and 143.03 ppm). In all these sets, the three signals have almost equal intensity ratio (see Fig. 2). Free rotation around the N–C bonds in the carbene ligand is unlikely as a consequence of the double-bond character in the N–C–N moiety. This means that four conformations can be expected for the complex. These conformations are given in Fig. 3. Crystal structures of similar palladium and platinum complexes suggest that the plane of the ligand C[NHCH(CH3)C6H5]NH-C4H9 is almost perpendicular to the plane of the isocyanide carbons and nickel15,15c,18. Molecular models show that conformation 3D is not very likely, because of steric hindrance. Therefore, the three conformations which actually exist in solution will be 3A–C.

The complex described here has been used as a catalyst in the enantioselective polymerization of isocyanides9. From tert-butyl isocyanide, optically active poly(tert-butyl isocyanide) with a prevailing right-handed screw sense was prepared in an enantiomeric excess of 61%. This number is calculated from the (CD) spectrum, which is given in Fig. 4.
Table I  IR data of some relevant metal carbene complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Wave number/cm$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(C=N-t-C$_4$H$_9$)$_3$<a href="ClO$_4$">C[NHCH(CH$_3$)$_2$C$_6$H$_5$]NH-t-C$_4$H$_9$</a>$_2$</td>
<td>2226, 2250 ($\nu$N=C); 1588, 1570, 1558, 1542 ($\nu$N-C-N)</td>
<td>this work</td>
</tr>
<tr>
<td>Rh$^4$</td>
<td>2205, 2185 ($\nu$N=C); 1552 ($\nu$N-C-N)</td>
<td>15d</td>
</tr>
<tr>
<td>Ni$^4$</td>
<td>1562 ($\nu_{as}$N-C-O); 1170, 1155 ($\nu_{as}$N-C-O)</td>
<td>15c</td>
</tr>
<tr>
<td>Pt$^4$</td>
<td>1565 ($\nu_{as}$N-C-O); 1172, 1155 ($\nu_{as}$N-C-O)</td>
<td>15c</td>
</tr>
<tr>
<td>Ni$^4$</td>
<td>1555 ($\nu_{as}$N-C-O); 1155 ($\nu$ClO$_4$)</td>
<td>15c</td>
</tr>
<tr>
<td>Ni$^{10}$$_4$</td>
<td>2191 ($\nu$N=C); 1546 ($\nu$N-C-N)</td>
<td>15b</td>
</tr>
<tr>
<td>Pd[CNH$_3$]$_2$(PF$_6$)$_2$</td>
<td>1583 ($\nu$N-C-N)</td>
<td>15a</td>
</tr>
<tr>
<td>Pt[CNH$_3$]$_2$(PF$_6$)$_2$</td>
<td>1586 ($\nu$N-C-N)</td>
<td>15a</td>
</tr>
<tr>
<td>Pd[CNH$_3$]$_2$(PF$_6$)$_2$</td>
<td>1565 ($\nu$N=C); 1255 ($\nu$C=O)</td>
<td>15e</td>
</tr>
</tbody>
</table>
Table II  UV data of some relevant metal carbene complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \lambda_{\text{max}}/\text{nm (} \epsilon \text{)} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni((=\text{N-t-C}_4\text{H}_9)\text{)[C[NHCH(CH}_3\text{)C}_6\text{H}_5\text{]NH-t-C}_4\text{H}_9\text{]}(\text{ClO}_4\text{)}_2)</td>
<td>330 (520), 283 (5070), 249 (10390)</td>
<td>this work</td>
</tr>
<tr>
<td>Pd</td>
<td>226 (2400), 204 (13200), 196 (9600)</td>
<td>15c</td>
</tr>
<tr>
<td>Pt</td>
<td>287 (600), 243 (8100), 208 (11700), 195 (1050)</td>
<td>15c</td>
</tr>
<tr>
<td>Ni</td>
<td>285 (3300), 230 (5400), 195 (19700)</td>
<td>15c</td>
</tr>
</tbody>
</table>

Table III  \(^{13}\text{C NMR data of some relevant metal carbene complexes.}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \delta/\text{ppm} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni((=\text{N-t-C}_4\text{H}_9)\text{)[C[NHCH(CH}_3\text{)C}_6\text{H}_5\text{]NH-t-C}_4\text{H}_9\text{]}(\text{ClO}_4\text{)}_2)</td>
<td>181.4, 179.2, 175.2 carbene 120–124 NC</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>154 NC 187.2 carbene</td>
<td>15d</td>
</tr>
<tr>
<td>Pd</td>
<td>206.4 carbene</td>
<td>15c</td>
</tr>
<tr>
<td>Pt</td>
<td>198.9 carbene</td>
<td>15c</td>
</tr>
</tbody>
</table>
For comparison, the CD spectrum of completely resolved (M)-( +)-poly(tert-butyl isocyanide)\textsuperscript{19} is also given. Similarly, the complex can be used for the asymmetric polymerization of other achiral isocyanides. Some representative examples are given in Table IV. According to CD, right-handed helices are formed from all these achiral isocyanides.

Table IV Enantioselective polymerization of achiral isocyanides

\[
\begin{array}{|c|c|c|}
\hline
R & [\mathbf{R-N=C}(\textit{\textsuperscript{1}})] & \lambda_{\text{CD}} \text{ (deg cm}^{-1} \text{ mol}^{-1}) \\
\hline
\text{t-C}_{4}H_{9} & -28.7 & P \\
\text{t-C}_{4}H_{9} & -9.7 & P \\
\alpha, \alpha\text{-dimethylbenzyl} & -5.9 & P \\
2,6\text{-di-Cl-C}_{4}H_{3} & -70 & P \\
\hline
\end{array}
\]

\textsuperscript{a} c 0.02–0.1, CHCl\textsubscript{3}.  \textsuperscript{b} Derived from CD spectra of the polymers.

\[\Delta \varepsilon = (l \text{ mol}^{-1} \text{ cm}^{-1})\]

\[
\text{Fig. 3. Possible conformations of Ni(C-N-t-C}_{4}H_{9})(\mathbf{C}\text{[NHCH(CH}_{3}\text{)}C_{6}H}_{5}\text{]}\text{NH-t-C}_{4}H_{9})(\text{ClO}_{4})_{2}.
\]
The screw sense of the polymers can be predicted by considering the conformations of the complex, as shown in Fig. 3. The most probable conformation of the complex is 3A, since in this conformation the bulky tert-butyl group is pointing away from the nickel centre and the phenyl group can have some bonding interaction with the nickel. The first C–C bond is formed when the carbon atom C1 pointing away from the nickel centre and the phenyl group will preferentially take place on C2, since this is the sterically substituted for the carbene ligand (Fig. 1). This fifth ligand attack is facilitated when a new isocyanide C5 = N–R is formed. Since in this conformation the bulky tert-butyl group is shielded by the phenyl ring. The nucleophilic attack by C1 will preferentially enter the complex from above and the a right-handed helix is formed.

In the case of conformation 3B, the fifth ligand can attack one of its neighbours, C2 or C4. This first C–C bond is formed when the carbon atom C1 pointing away from the nickel centre and the phenyl group will preferentially take place on C2, since this is the sterically least hindered reaction path. The polymerization proceeds consecutively by attack on C3, C4, etc. In this way, a right-handed helix is formed.

References


16 $^{13}$C NMR measurements on Ni(C=N-C$_5$H$_5$)$_2$(ClO$_4$)$_2$ were not possible, due to the low solubility of this complex.


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R. F. Stepaniak and N. C. Payne, Inorg. Chem. 13, 797 (1974);


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