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A nickel–carbene complex as an intermediate in the polymerization of isocyanides[≠]

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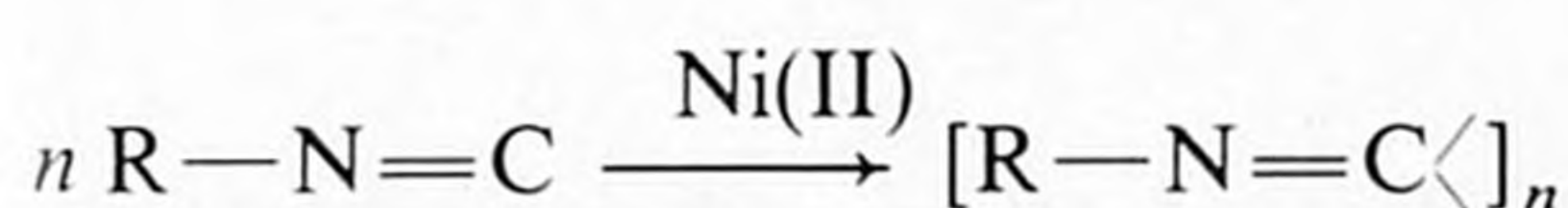
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Abstract. An intermediate in the polymerization of isocyanides, catalysed by nickel(II), has been isolated and characterized. The polymerization starts by nucleophilic attack of (*S*)-(–)-(1-phenylethyl)amine on the terminal carbon atom of a coordinated isocyanide of tetrakis(*tert*-butyl isocyanide)nickel(II) perchlorate. The resulting intermediate was isolated and shown to be a nickel–carbene complex: $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3 [\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$. 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}.



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 atropisomerism³.

In our laboratory, several methods have been developed for the preparation of optically active polymers of isocyanides⁴⁻⁹. A mechanism of polymerization has also been proposed^{1,5a}. The polymerization is initiated by a nucleophilic 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 (see Fig. 1). The structure of the complex formed after the initiating step was supported by the fact that analogous structures of palladium and platinum complexes are known⁵. The intermediate nickel complex, however, has never been isolated. In the present paper, we describe the isolation and characterization of this complex, *viz.* $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3 [\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$, which was prepared from $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$ ¹⁰ and (*S*)-(–)-(1-phenylethyl)amine*.

Results and discussion

Racemic (1-phenylethyl)amine was resolved into its optical antipodes using a standard method¹¹. *tert*-Butyl isocyanide was prepared by *N*-formylation of *tert*-butylamine¹² and subsequent dehydration with 4-toluenesulphonyl chloride¹³. $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$ was prepared as previously described¹⁰. 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: *i.e.* $\text{Ni}[\text{C}=\text{N}-2,6\text{-di}(i\text{-C}_3\text{H}_7)\text{C}_6\text{H}_3]_4(\text{ClO}_4)_2$ ¹⁴. $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3 [\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$ was synthesized by adding one equivalent of (*S*)-(–)-(1-phenylethyl)amine to a suspension of $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$ in dry CH_2Cl_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 $\text{C}_{28}\text{H}_{47}\text{Cl}_2\text{N}_5\text{NiO}_8$. Its IR spectrum shows an N–H stretching frequency at 3280 cm^{-1} . Since a primary amine such as (1-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)¹⁵. 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: α -methylbenzenemethanamine.

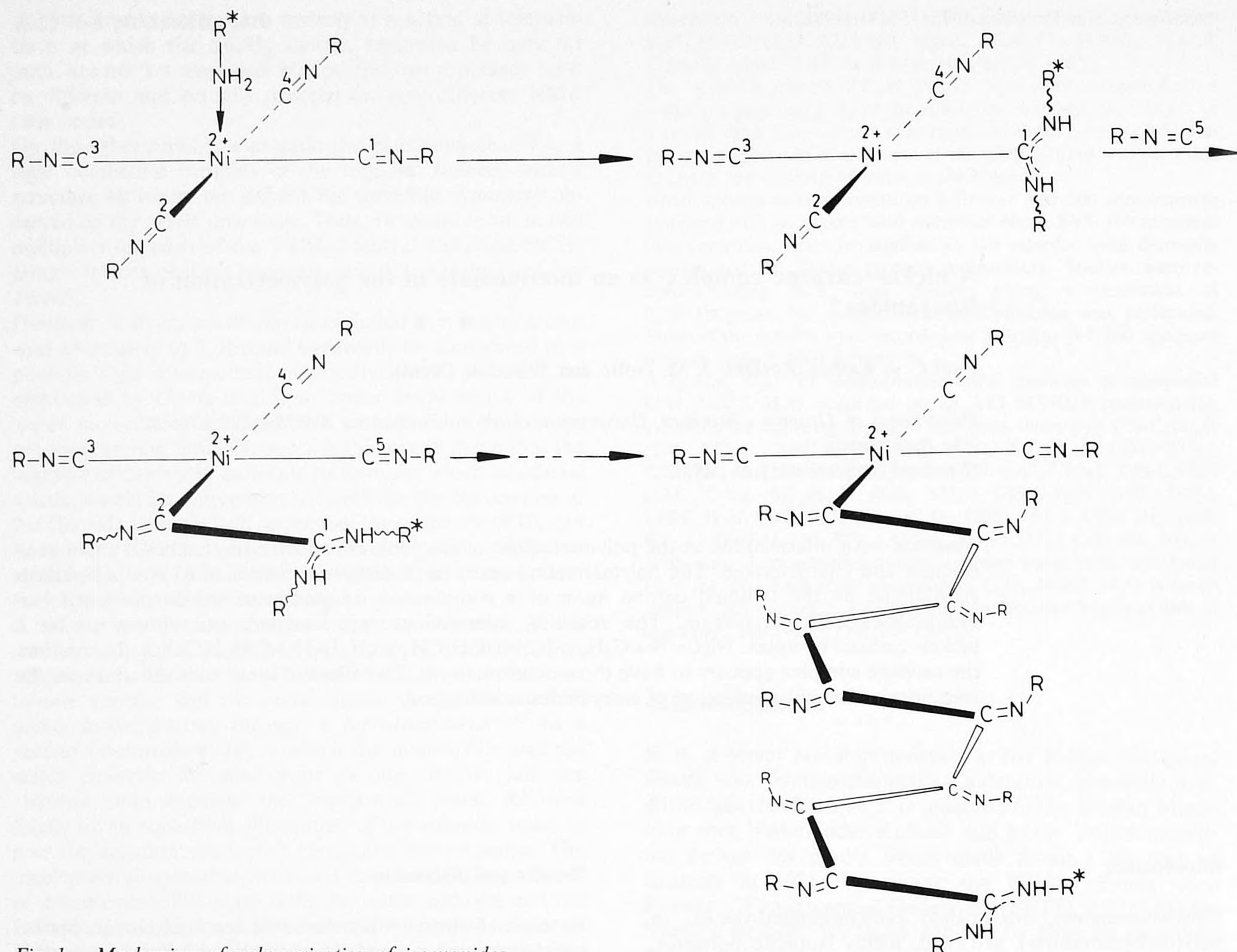


Fig. 1. Mechanism of polymerization of isocyanides.

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 $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$ ¹⁰, 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 $\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9$ 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 $\text{Ni}(\text{C}=\text{N}-t\text{-C}_5\text{H}_{11})_4(\text{ClO}_4)_2$ ^{16,17}. In the carbene complex formed after reaction of $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_4(\text{ClO}_4)_2$ 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 $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{NH}$ 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 $\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9$ is almost perpendicular to the plane of the isocyanide carbons and nickel^{15c,15e,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.

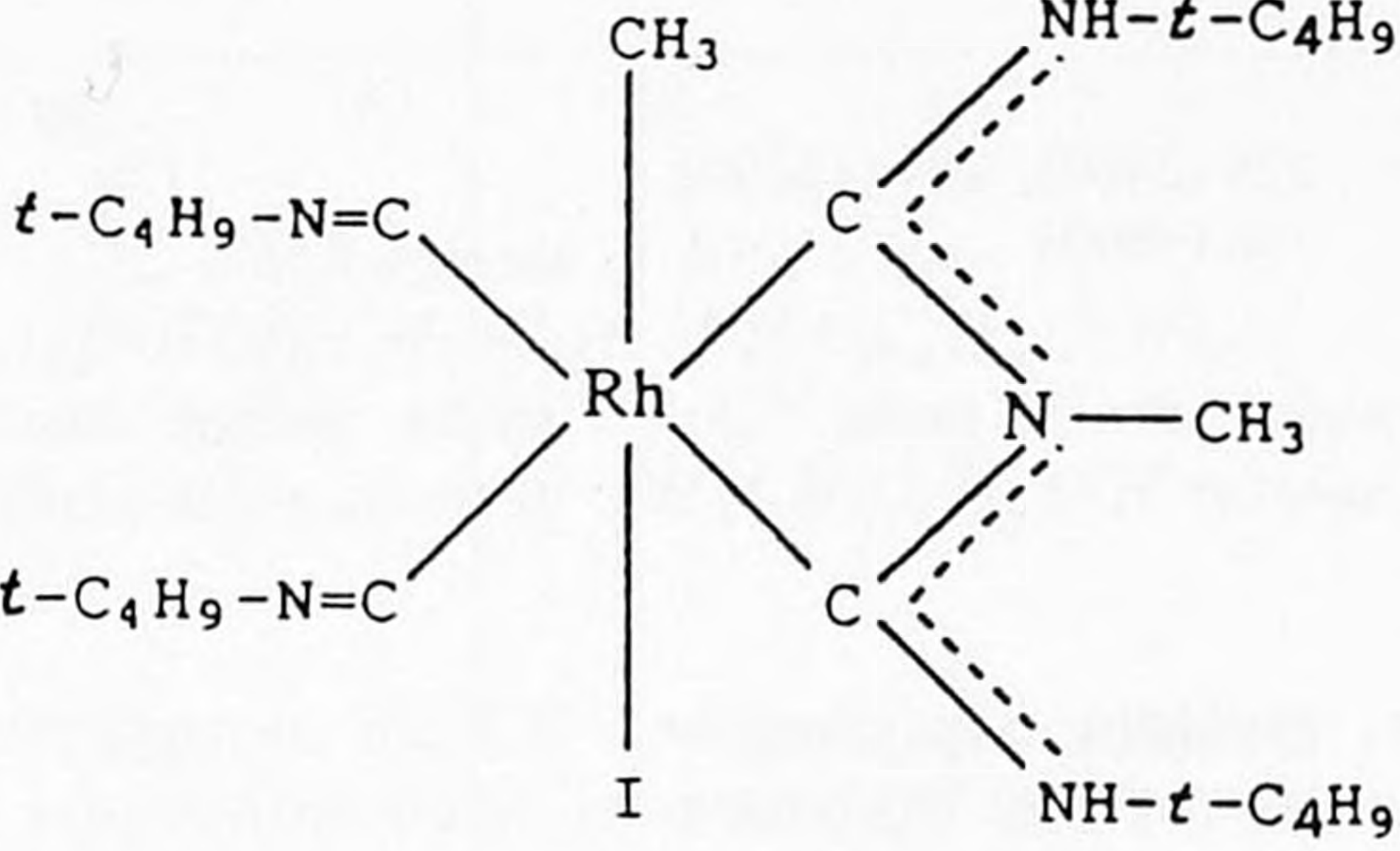
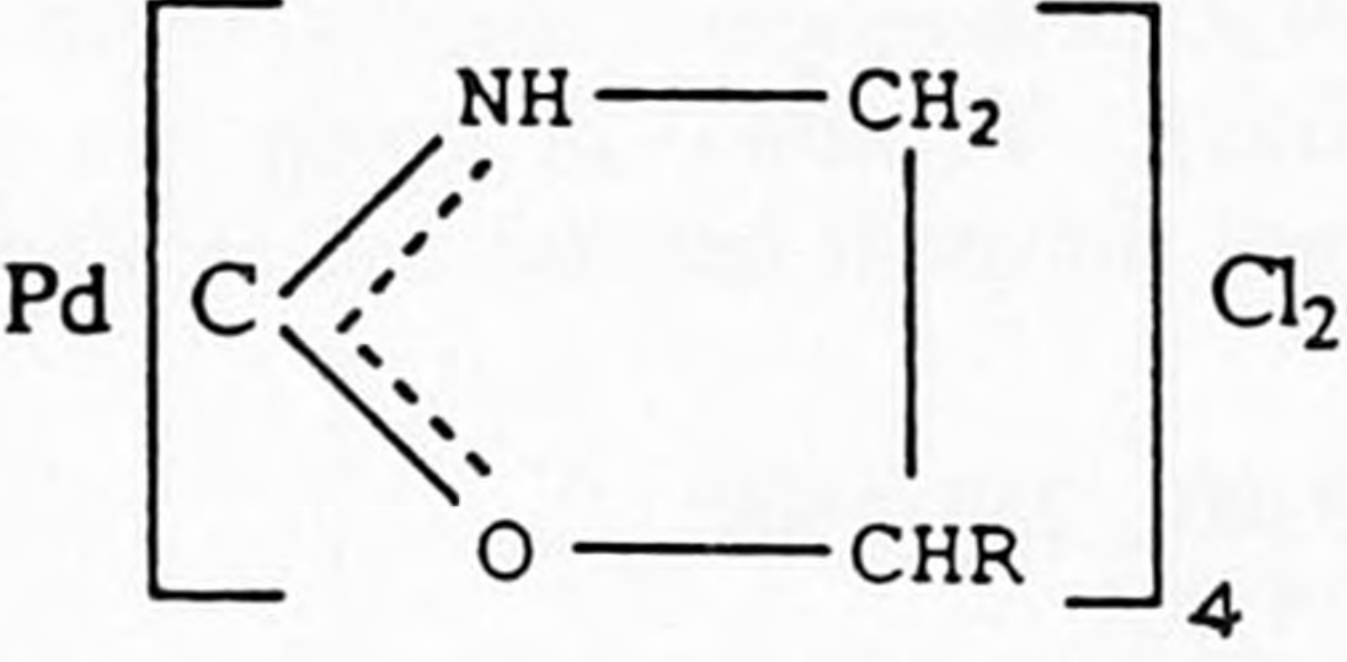
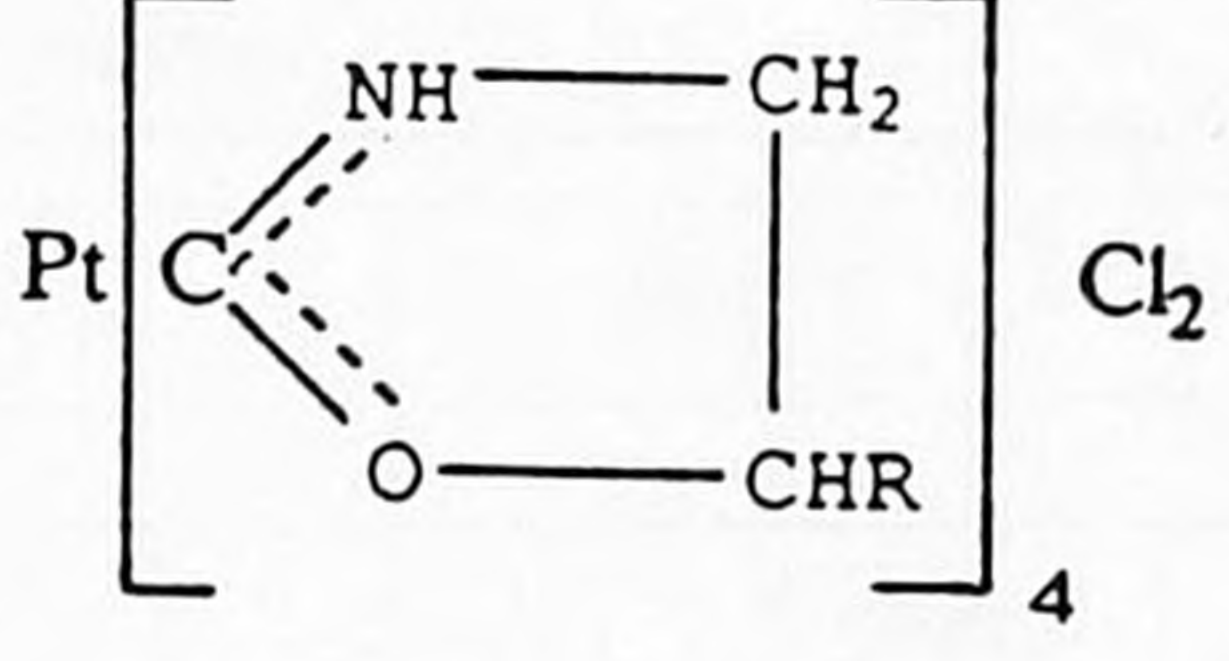
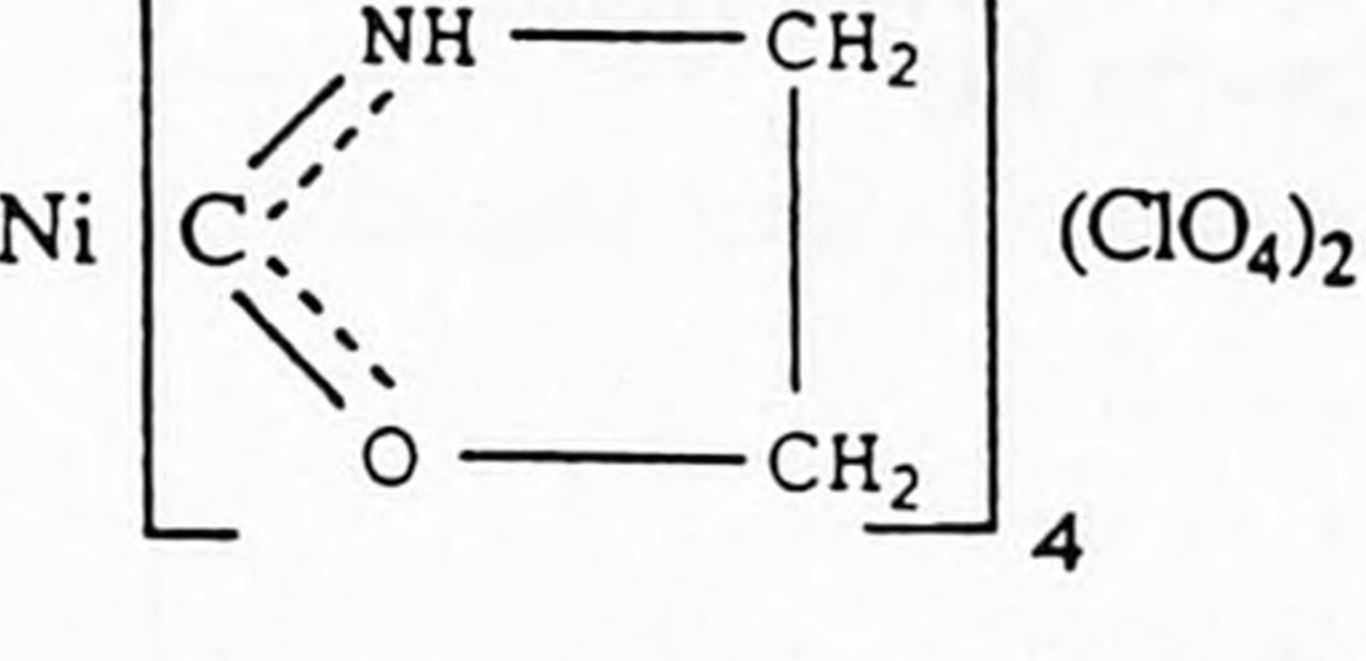
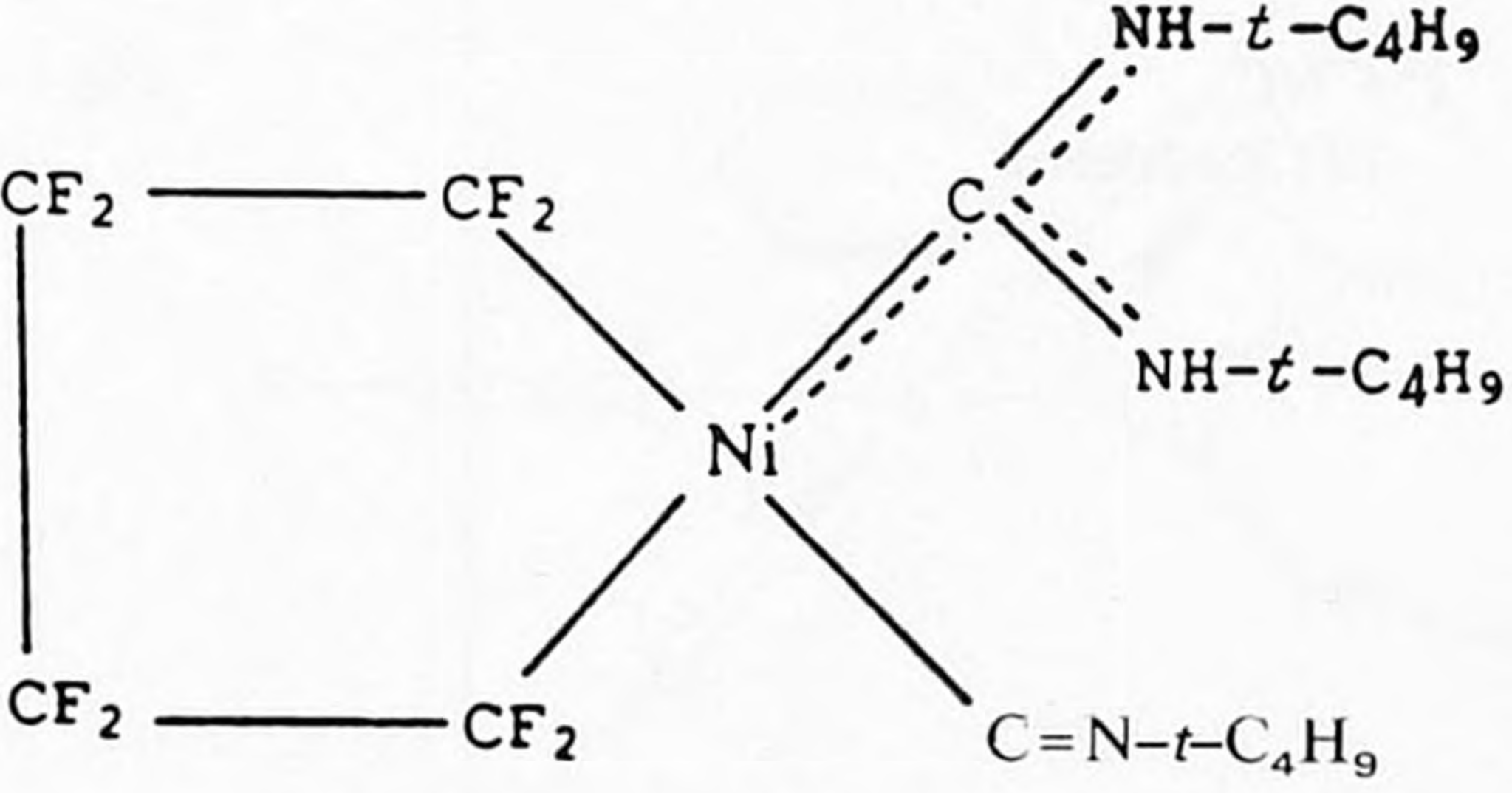
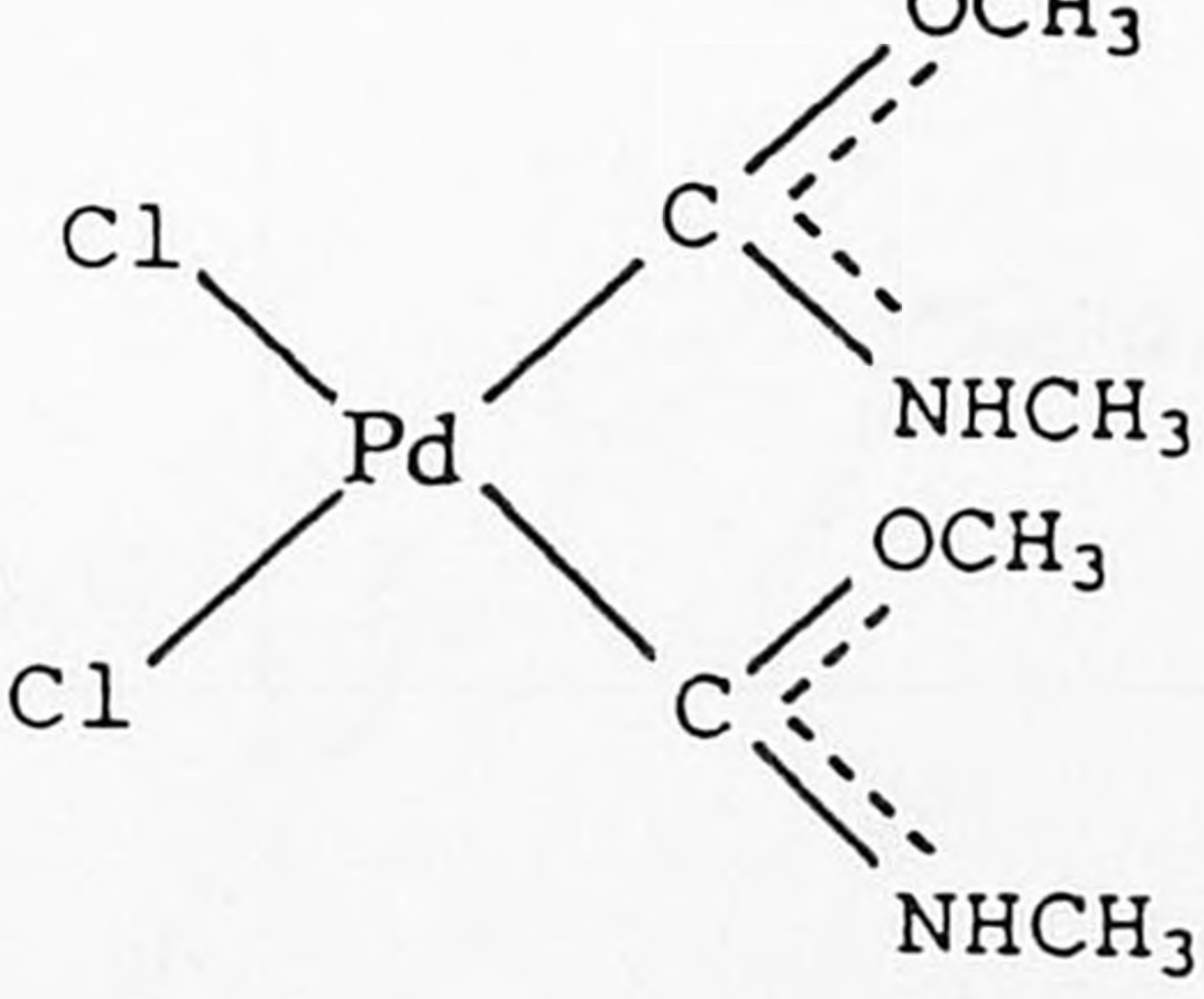
Complex	Wave number/cm ⁻¹	Ref.
<p data-bbox="140 320 959 365">$\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3[\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$</p> 	<p data-bbox="1110 320 1591 396">2226, 2250 ($\nu\text{N}=\text{C}$); 1588, 1570, 1558, 1542 ($\nu\text{N}-\text{C}-\text{N}$)</p> <p data-bbox="1110 607 1390 683">2205, 2185 ($\nu\text{N}=\text{C}$); 1552 ($\nu\text{N}-\text{C}-\text{N}$)</p>	<p data-bbox="1757 320 1887 356">this work</p> <p data-bbox="1798 607 1846 644">15d</p>
<p data-bbox="292 991 762 1037">$\text{Pd} \left[\text{C} \begin{array}{l} \text{NH}-\text{CH}_2 \\ \text{O}-\text{CHR} \end{array} \right]_4 \text{Cl}_2$</p> 	<p data-bbox="1110 976 1442 1052">1562 ($\nu_{\text{as}}\text{N}-\text{C}-\text{O}$); 1170, 1155 ($\nu_{\text{s}}\text{N}-\text{C}-\text{O}$)</p>	<p data-bbox="1798 976 1846 1013">15c</p>
<p data-bbox="333 1285 762 1330">$\text{Pt} \left[\text{C} \begin{array}{l} \text{NH}-\text{CH}_2 \\ \text{O}-\text{CHR} \end{array} \right]_4 \text{Cl}_2$</p> 	<p data-bbox="1110 1270 1442 1345">1565 ($\nu_{\text{as}}\text{N}-\text{C}-\text{O}$); 1172, 1155 ($\nu_{\text{s}}\text{N}-\text{C}-\text{O}$)</p>	<p data-bbox="1798 1270 1846 1306">15c</p>
<p data-bbox="333 1578 810 1623">$\text{Ni} \left[\text{C} \begin{array}{l} \text{NH}-\text{CH}_2 \\ \text{O}-\text{CH}_2 \end{array} \right]_4 (\text{ClO}_4)_2$</p> 	<p data-bbox="1110 1563 1379 1639">1555 ($\nu_{\text{as}}\text{N}-\text{C}-\text{O}$); 1155 ($\nu\text{ClO}_4$)</p>	<p data-bbox="1798 1563 1846 1599">15c</p>
<p data-bbox="167 1826 882 2113">$\text{Ni} \begin{array}{l} \text{NH}-t\text{-C}_4\text{H}_9 \\ \text{NH}-t\text{-C}_4\text{H}_9 \\ \text{C}=\text{N}-t\text{-C}_4\text{H}_9 \end{array}$</p> 	<p data-bbox="1110 1902 1348 1977">2191 ($\nu\text{N}=\text{C}$); 1546 ($\nu\text{N}-\text{C}-\text{N}$)</p>	<p data-bbox="1798 1902 1846 1938">15b</p>
<p data-bbox="147 2174 478 2219">$\text{Pd}[\text{C}(\text{NHCH}_3)_2]_4(\text{PF}_6)_2$</p>	<p data-bbox="1110 2174 1348 2210">1583 ($\nu\text{N}-\text{C}-\text{N}$)</p>	<p data-bbox="1798 2174 1846 2210">15a</p>
<p data-bbox="147 2249 478 2295">$\text{Pt}[\text{C}(\text{NHCH}_3)_2]_4(\text{PF}_6)_2$</p>	<p data-bbox="1110 2249 1348 2286">1586 ($\nu\text{N}-\text{C}-\text{N}$)</p>	<p data-bbox="1798 2249 1846 2286">15a</p>
<p data-bbox="281 2310 768 2718">$\text{Pd} \begin{array}{l} \text{OCH}_3 \\ \text{NHCH}_3 \\ \text{OCH}_3 \\ \text{NHCH}_3 \end{array}$</p> 	<p data-bbox="1110 2491 1307 2567">1565 ($\nu\text{N}=\text{C}$); 1255 ($\nu\text{C}=\text{O}$)</p>	<p data-bbox="1798 2491 1846 2528">15e</p>

Table II UV data of some relevant metal carbene complexes.

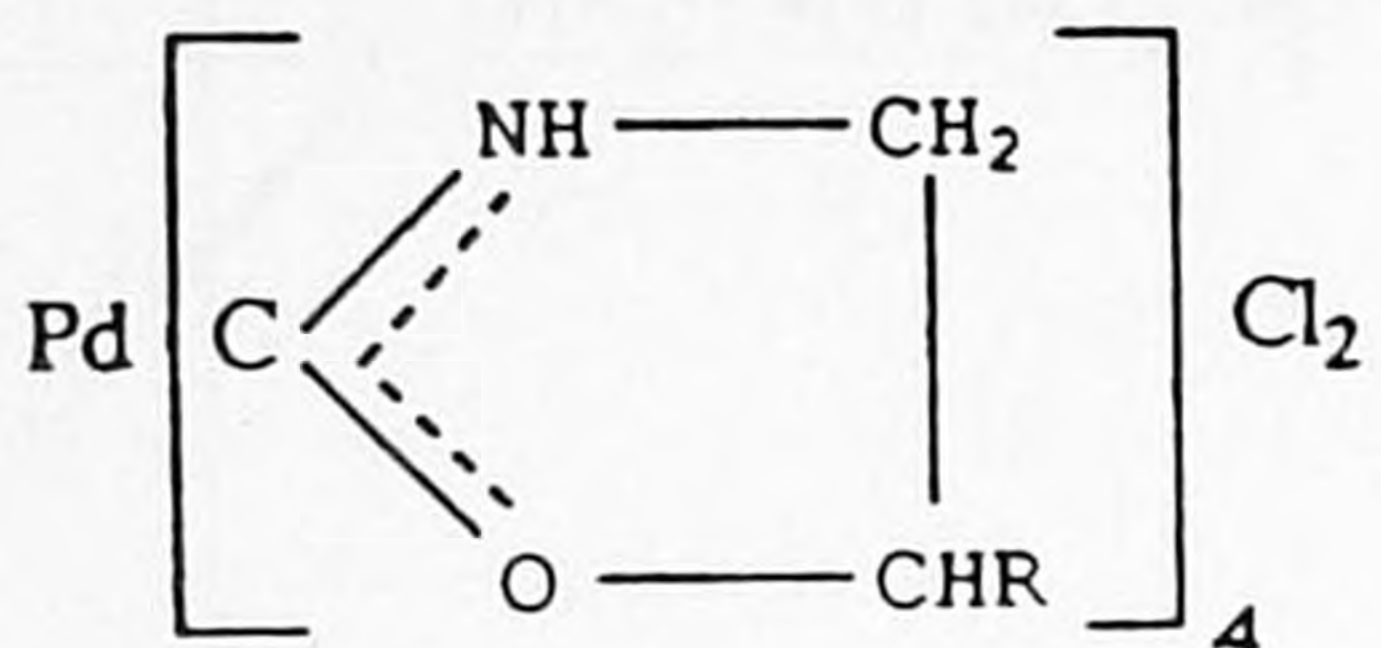
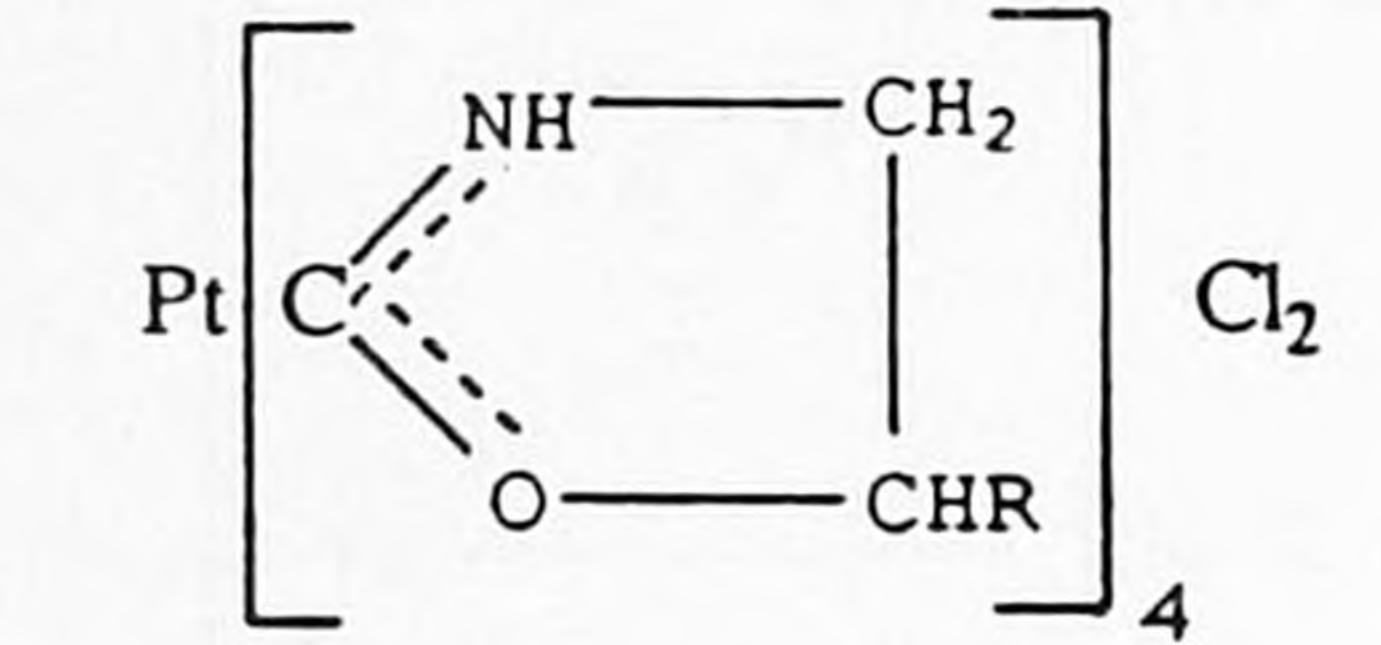
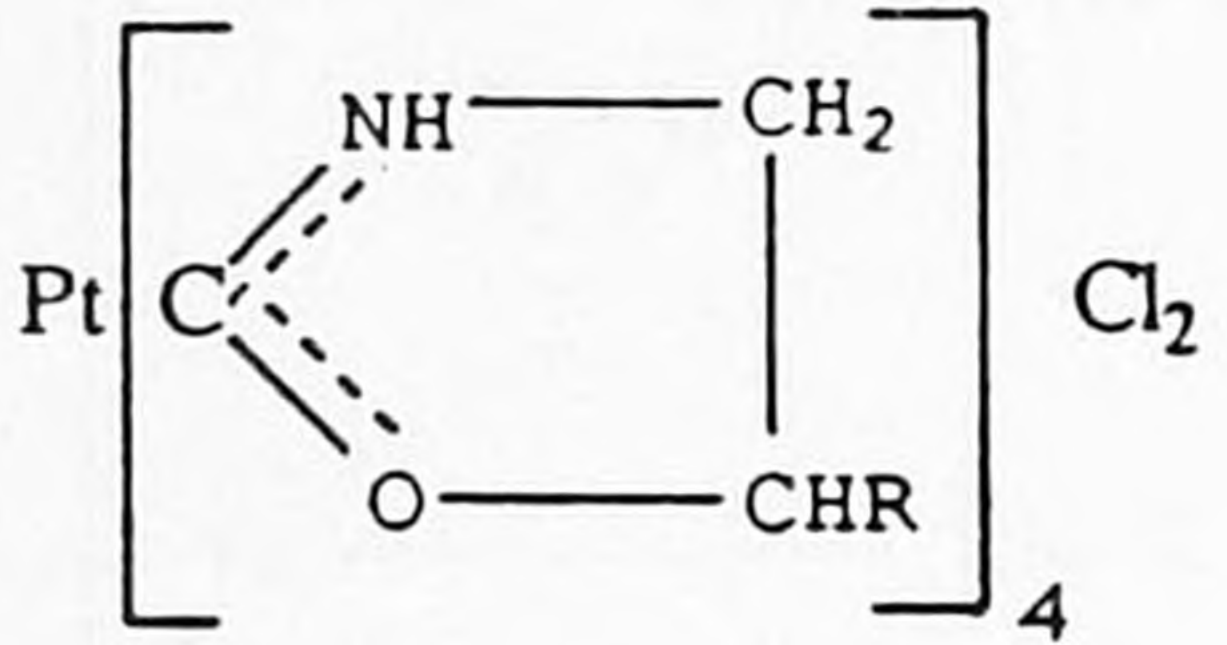
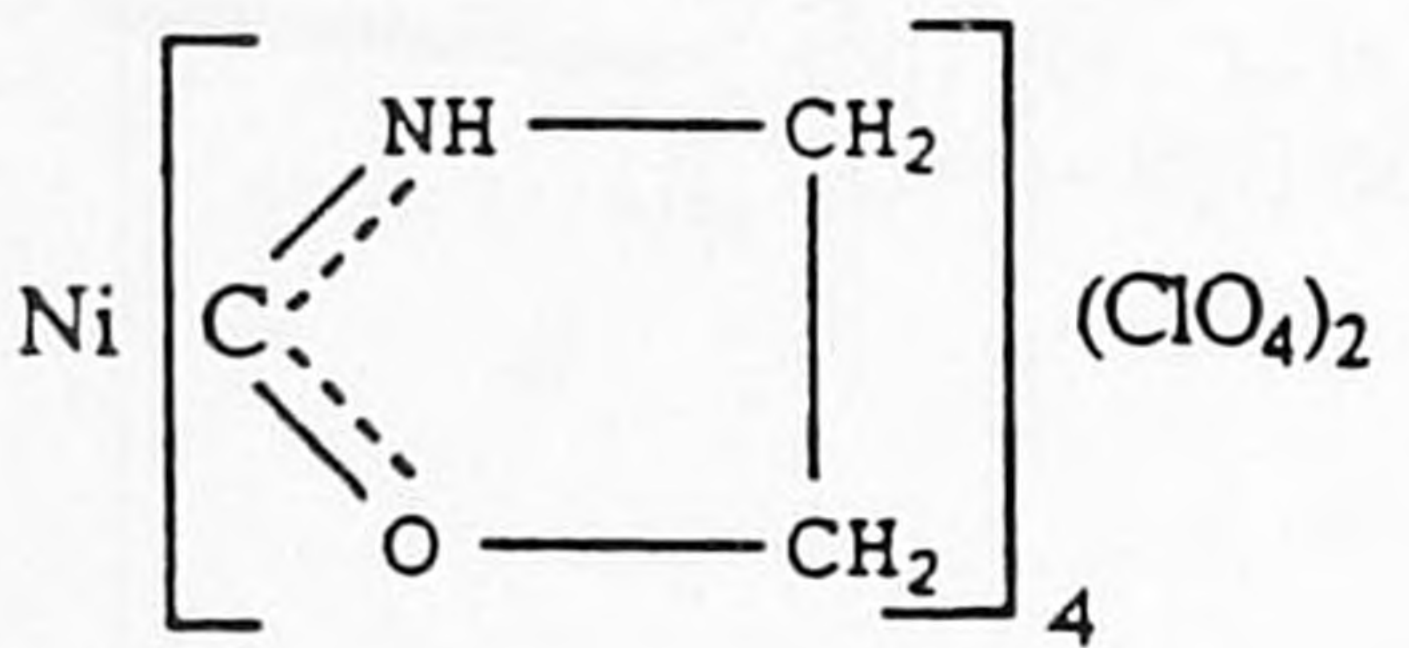
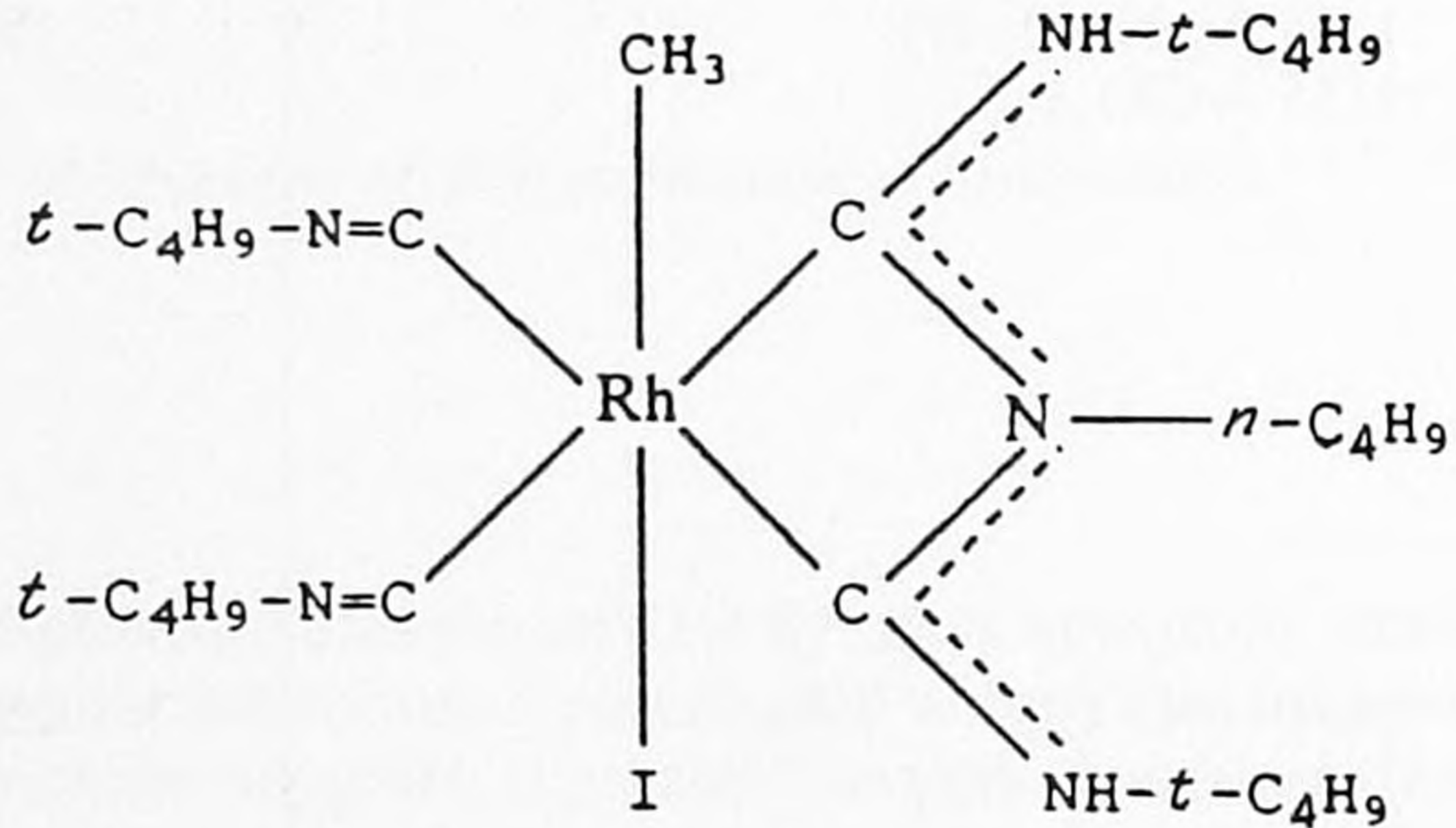
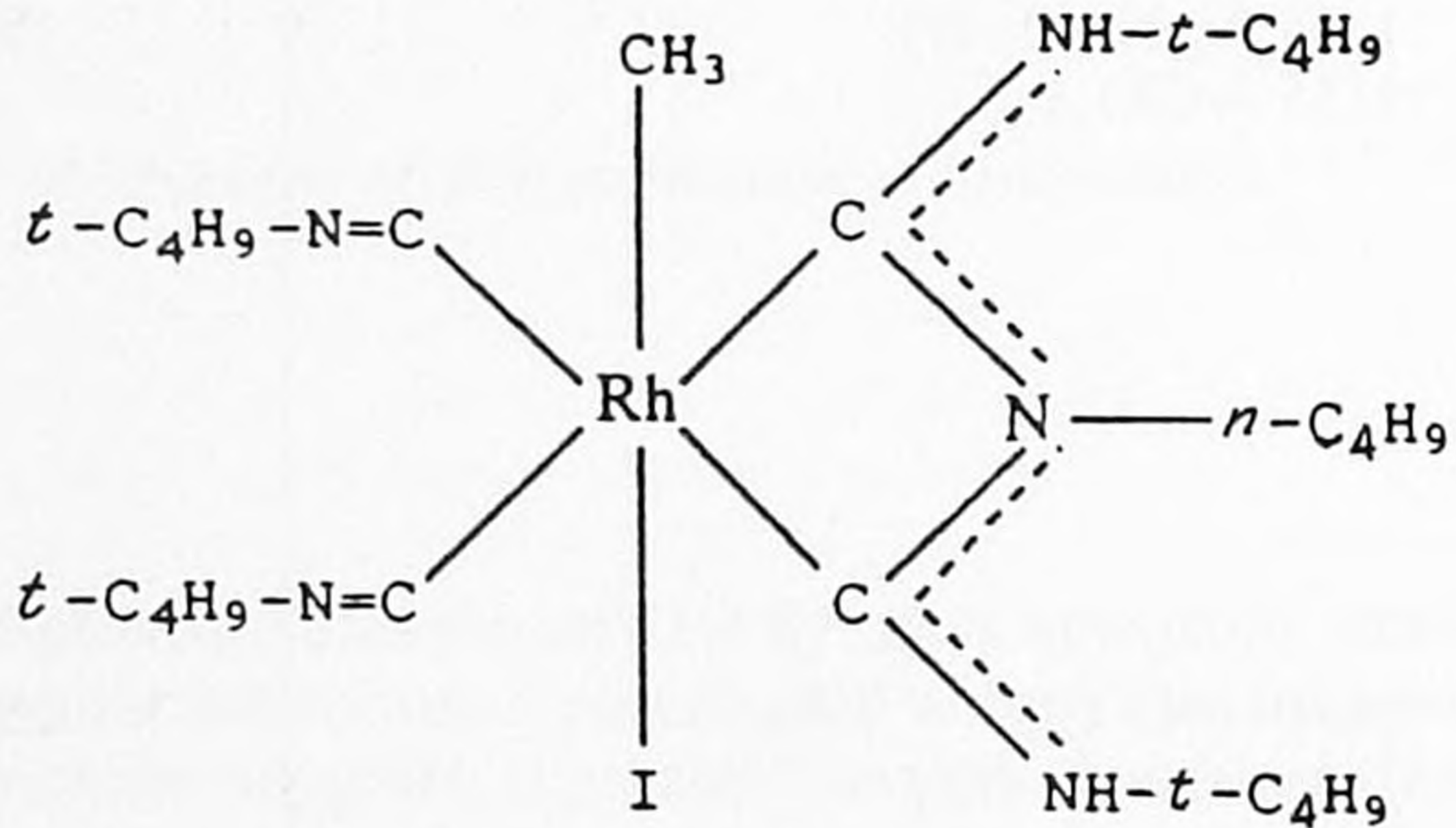
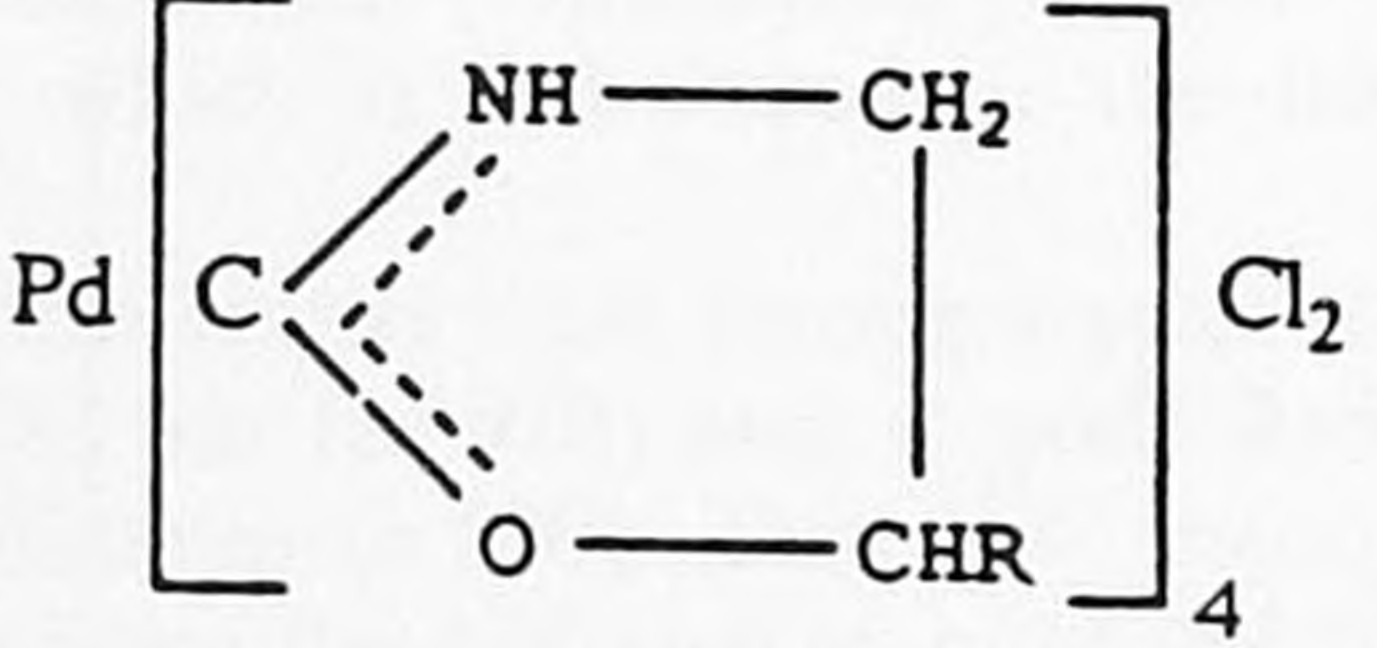
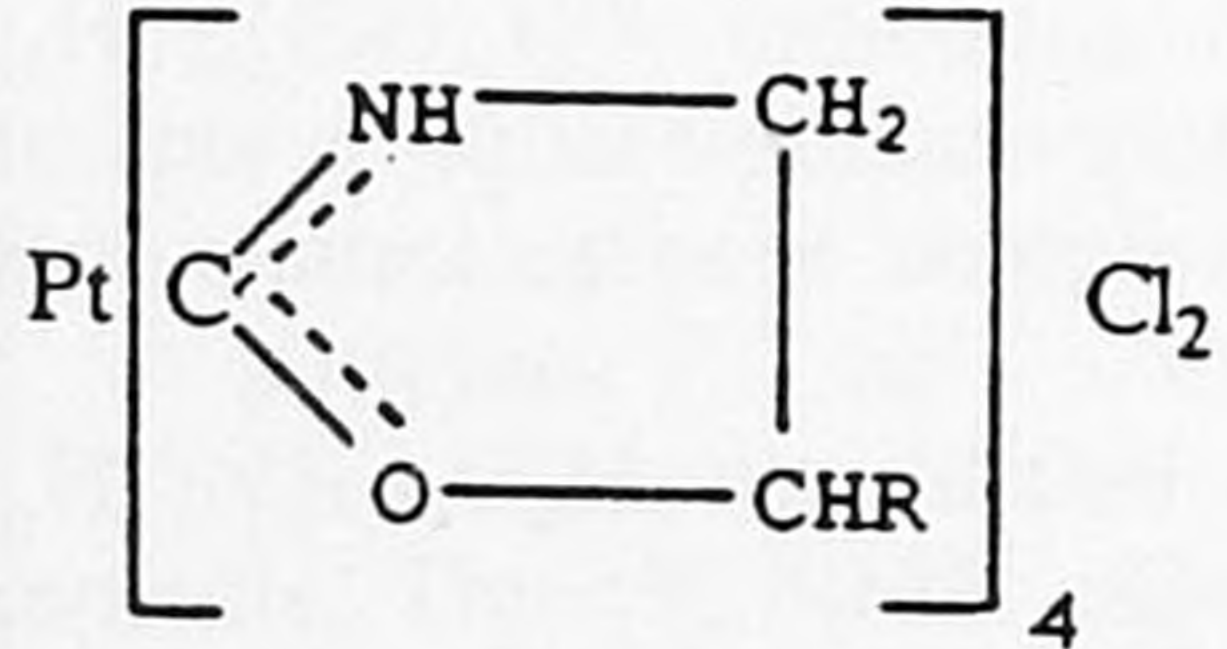
Complex	λ_{\max}/nm (ϵ)	Ref.
$\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3[\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$ 	330 (520), 283 (5070), 249 (10390)	this work
	226 (2400), 204 (13200), 196 (9600)	15c
	287 (600), 243 (8100), 208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

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

Complex	δ/ppm	Ref.
$\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3[\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$ 	181.4, 179.2, 175.2 carbene 120–124 NC	this work
	154 NC 187.2 carbene	15d
	206.4 carbene	15c
	198.9 carbene	15c

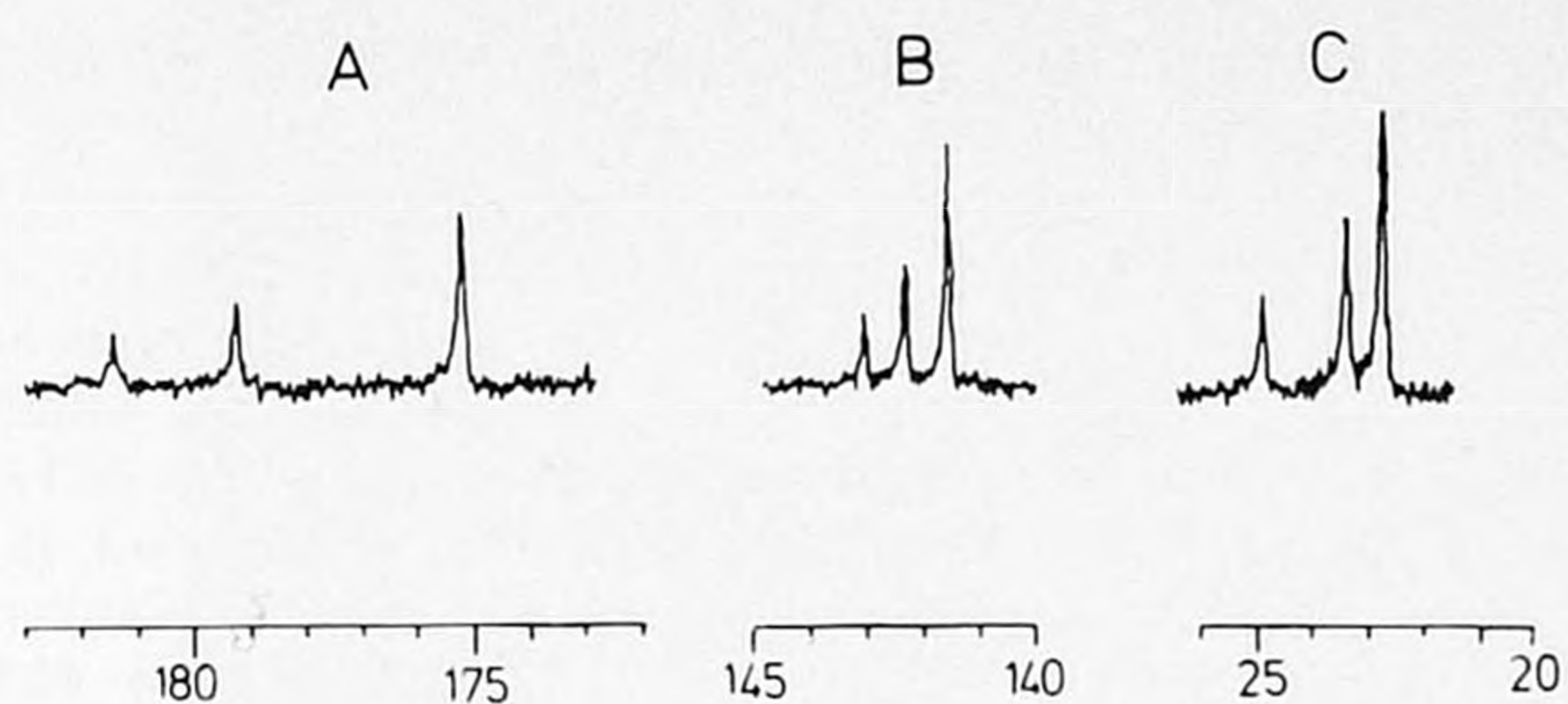


Fig. 2. ^{13}C NMR signals of $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$.
A: carbenic-carbon atom; B: C^1 atom of the phenyl ring;
C: methyl-carbon atom of $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{NH}$ residue.

For comparison, the CD spectrum of completely resolved (*M*)-(+)-poly(*tert*-butyl isocyanide)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 $\text{R}-\text{N}=\text{C}$ using $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3[\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$ as catalyst.

R in $[\text{R}-\text{N}=\text{C}]_n$	$[\alpha]_D^{20}$ ^a	Screw sense ^b
<i>t</i> -C ₄ H ₉	-28.7	<i>P</i>
<i>t</i> -C ₅ H ₁₁	-9.7	<i>P</i>
α,α -dimethylbenzyl	-5.9	<i>P</i>
2,6-di-Cl-C ₆ H ₃	-70	<i>P</i>

^a c 0.02–0.1, CHCl_3 . ^b Derived from CD spectra of the polymers.

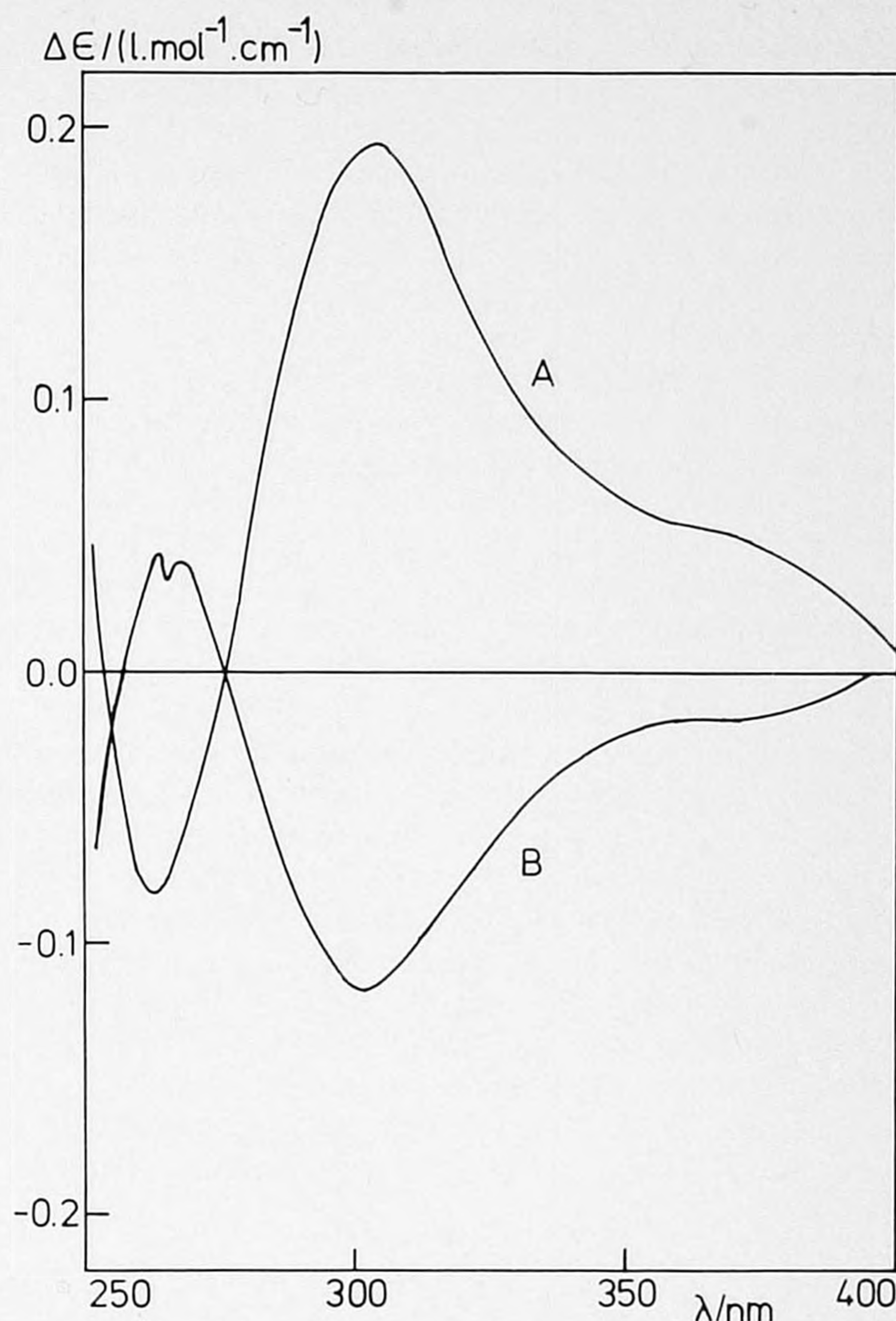


Fig. 4. CD spectra of poly(*tert*-butyl isocyanide): (A) optically pure *M*-polymer, (B) polymer obtained with (*S*)-(-)-(1-phenylethyl)amine as the initiator. The additional bands at 260 nm are caused by the phenyl rings of the (1-phenylethyl)amine end groups.

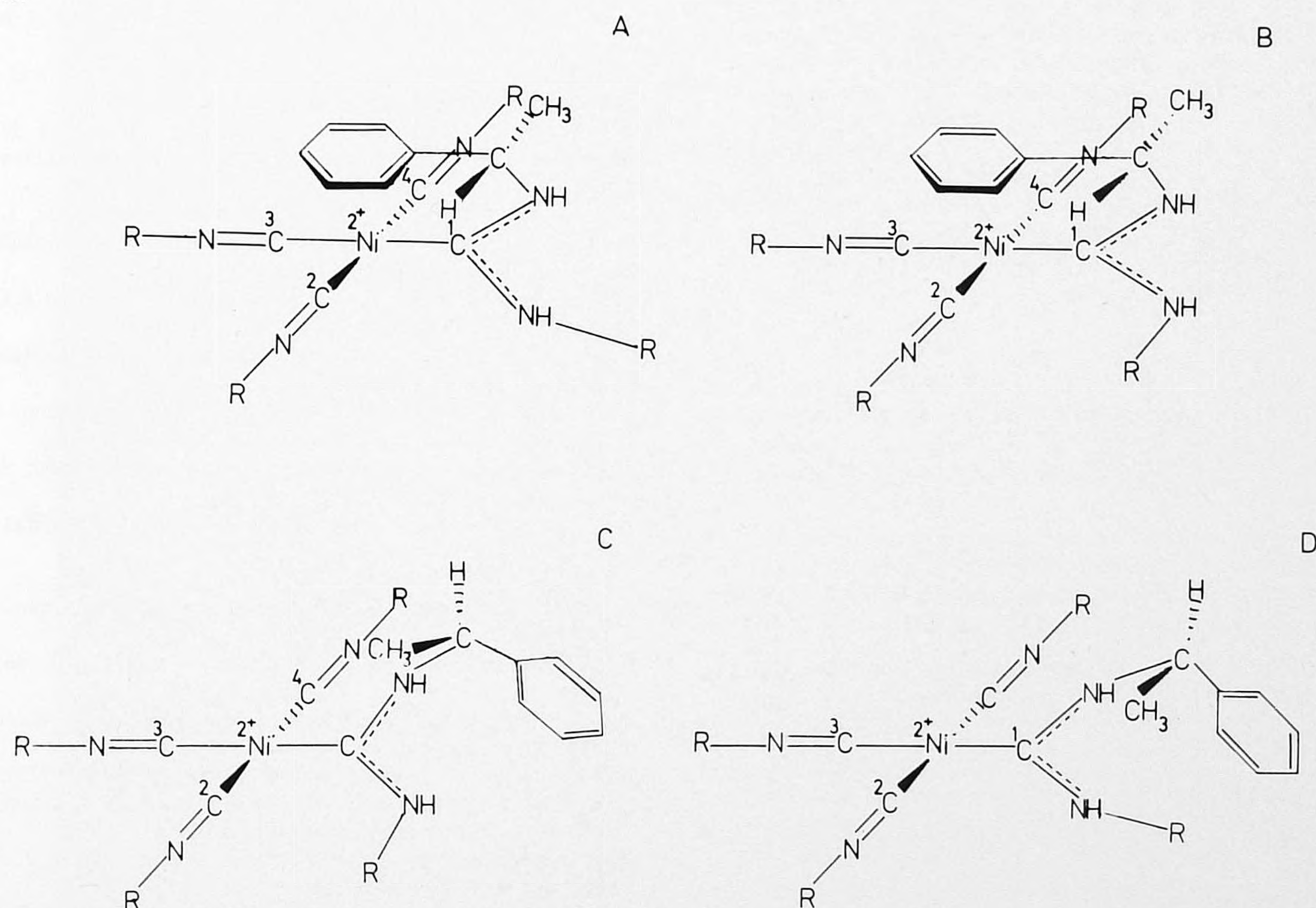


Fig. 3. Possible conformations of $\text{Ni}(\text{C}=\text{N}-t\text{-C}_4\text{H}_9)_3[\text{C}[\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5]\text{NH}-t\text{-C}_4\text{H}_9](\text{ClO}_4)_2$.

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 nickel⁹. The first C–C bond is formed when the carbon atom C¹ of the carbene ligand attacks one of its neighbours, C² or C⁴. This attack is facilitated when a new isocyanide C⁵=N–R is substituted for the carbene ligand (Fig. 1). This fifth ligand will enter from below the complex, since the other side is shielded by the phenyl ring. The nucleophilic attack by C¹ 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.

In the case of conformation 3B, the fifth ligand can approach the nickel both from below and above. According to molecular models, entry from below will have preference since, at this side, the steric hindrance is less than at the upper side. This will result in the formation of an excess of right-handed helices. In conformation 3C, the fifth ligand will preferentially enter the complex from above and the nucleophilic attack will take place on C⁴. This again results in the formation of a right-handed helix. The relatively high chiral induction in the polymerization initiated by (1-phenylethyl)amine is due to the fact that the prevailing conformations of the intermediate induce the same screw sense.

Experimental

Analytical techniques

Infrared (IR) spectra were recorded on Perkin-Elmer 297 and 283 spectrophotometers. Ultraviolet (UV) spectra were measured on a Perkin-Elmer 200 spectrophotometer and optical rotations on a Perkin-Elmer 241 Polarimeter. ¹H NMR spectra were obtained using a Varian EM 390 apparatus and ¹³C NMR spectra using a Bruker WP 200 instrument. Chemical shifts (δ) are given in ppm downfield from internal tetramethylsilane. Abbreviations used are s = singlet, d = doublet, m = multiplet, br = broad. Mass spectra were recorded on a VG ZAB 2f mass spectrometer using FAB ionisation (7 kV, 1 mA) and 3-nitrobenzyl alcohol as matrix. Circular Dichroism (CD) spectra were recorded on a Jobin Yvon Dichrographe III apparatus. Elemental analyses were carried out at TNO, Zeist (Holland).

Compounds

N-*tert*-Butylformamide. *tert*-Butylamine was *N*-formylated with a 10% excess of ethyl formate¹² in an almost quantitative yield; b.p. 94–95°C/21 mm Hg. IR (neat) 1660 (C=O) cm⁻¹. ¹H NMR (CDCl₃) δ: 8.0 (m, 1H, CHO), 6.8 and 5.9 (2 × br, 1H, NH), 1.28 (3 × s, 9H, CH₃).

tert-Butyl isocyanide. This isocyanide was prepared using the method of Casanova¹³, but a lower pressure (0.5 mm Hg) than recommended; yield 78% of a colourless liquid. IR (CH₂Cl₂) 2140 (C=N) cm⁻¹. ¹H NMR (CDCl₃) δ: 1.43 (3 × s, CH₃).

(*S*)-(-)-(1-Phenylethyl)amine. Racemic (1-phenylethyl)amine was resolved in its optical antipodes using a standard method¹¹. The specific optical rotation of the (*S*) enantiomer was: [α]_D²⁰ –40.3° (neat) [lit.¹¹ [α]_D²⁹ –39.4° (neat)].

Ni(C=N-*t*-C₄H₉)₄(ClO₄)₂. This complex was prepared according to a procedure previously described by us¹⁰. Yield 92% of a white solid. IR (CH₂Cl₂): 2245 (C=N) cm⁻¹. ¹H NMR (CD₃CN) δ: 1.63 (s, CH₃).

Ni(C=N-*t*-C₄H₉)₃[(*S*)-C/NHCH(CH₃)C₆H₅]NHC(CH₃)₃]/(ClO₄)₂. Ni(C=N-*t*-C₄H₉)₄(ClO₄)₂ (1.93 mmol) was suspended in 45 cm⁻³ of dry CH₂Cl₂ under N₂. To this light yellow suspension (*S*)-(-)-(1-phenylethyl)amine (1.93 mmol) was added at room temperature. The yellow suspension turned into a homogeneous, orange solution. Within a few minutes, the colour of the solution returned to yellow. The solvent was removed in vacuum and the complex was dried at 0.01 mm Hg; yield 100%; yellow solid; [α]_D²⁰ 13.7° (c 0.22, CHCl₃). IR (CH₂Cl₂): 3280 (NH), 2250 (sh) and 2226 (C=N), 1570 (N–C–N) cm⁻¹. ¹³C NMR (CDCl₃) δ: 22.77, 23.40 and 24.90 (3 × s, CHCH₃); 28.55–30.78 (m, C(CH₃)₃); 53.02–61.66 (m, C(CH₃)₃ + CH); 120.23–123.71 (m, C=N); 125.97–129.15 (m, C arom.); 141.55, 142.32 and 143.03 (3 × s, substituted C arom.); 175.18, 179.20 and 181.37 (3 × s, C carbene). ¹H NMR (CDCl₃) δ: 8.57 + 6.89 (2 × d, 1H, CHNH), 8.04 + 7.75 + 6.46 (3 × s, 1H, NH), 7.7–7.0 (m, 5H, C₆H₅), 5.92 + 5.66 + 5.01 (3 × m, 1H, CH), 1.70 (d, 3H, CH), 1.6–0.8 (m, 36H, CH₃). FAB mass spectroscopy; *m/e* 610 (M – ClO₄⁻)⁺; 527 (M – ClO₄⁻ – *t*-C₄H₉–N=C)⁺; 454 (M – ClO₄⁻ – HClO₄ – C₄H₈)⁺; 444 (M – ClO₄⁻ – 2*t*-C₄H₉–N=C)⁺; 427 (M – ClO₄⁻ – HClO₄ – *t*-C₄H₉–N=C)⁺; 361 (M – ClO₄⁻ – 3*t*-C₄H₉–N=C)⁺; 345 (M – 2ClO₄⁻ – 2*t*-C₄H₉–N=C)⁺; 288 (M – ClO₄⁻ – HClO₄ – 2*t*-C₄H₉–N=C – C₄H₈)⁺; 262 (M – 2ClO₄⁻ – 3*t*-C₄H₉–N=C)⁺. Elemental analysis: C₂₈H₄₇Cl₂N₅NiO₈ (711.31) calcd.: C 47.28, H 6.67, Cl 9.97, N 9.85, Ni 8.25, O 18.00; found: C 47.00, H 6.73, Cl 9.97, N 9.73, Ni 8.27, O 18.36%.

References

- ^{1a} W. Drenth and R. J. M. Nolte, *Acc. Chem. Res.* **12**, 30 (1979);
- ^b R. J. M. Nolte and W. Drenth in "Advances on Mechanistic and Synthetic Aspects of Polymerization", A. Guyot and M. Fontanille, eds. D. Reidel, Dordrecht, in the press.
- ² F. Millich, *Macromol. Rev.* **15**, 207 (1980).
- ³ E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p. 156.
- ⁴ R. J. M. Nolte, A. J. M. van Beijnen and W. Drenth, *J. Am. Chem. Soc.* **96**, 5932 (1974).
- ^{5a} R. J. M. Nolte, J. W. Zwikker, J. Reedijk and W. Drenth, *J. Mol. Catal.* **4**, 423 (1978);
- ^b A. J. M. van Beijnen, R. J. M. Nolte, J. W. Zwikker and W. Drenth, *J. Mol. Catal.* **4**, 427 (1978).
- ^{6a} A. J. M. van Beijnen, R. J. M. Nolte, W. Drenth, A. M. F. Hezemans and P. J. F. M. van de Coolwijk, *Macromolecules* **13**, 1386 (1980);
- ^b A. J. M. van Beijnen, R. J. M. Nolte, A. J. Naaktgeboren, J. W. Zwikker, W. Drenth and A. M. F. Hezemans, *Macromolecules* **16**, 1679 (1983).
- ^{7a} R. J. M. Nolte, J. A. J. van Zomeren and J. W. Zwikker, *J. Org. Chem.* **43**, 1972 (1978);
- ^b H. G. J. Visser, R. J. M. Nolte, J. W. Zwikker and W. Drenth, *J. Org. Chem.* **50**, 3133 (1985).
- ⁸ T. Harada, M. C. Cleij, R. J. M. Nolte, A. M. F. Hezemans and W. Drenth, *J. Chem. Soc., Chem. Commun.* 726 (1984).
- ⁹ P. C. J. Kamer, R. J. M. Nolte and W. Drenth, *J. Chem. Soc., Chem. Commun.* 1789 (1986).
- ¹⁰ R. W. Stephany and W. Drenth, *Recl. Trav. Chim. Pays-Bas* **91**, 1453 (1972).
- ¹¹ A. Ault, *Org. Synth.* **49**, 93 (1969).
- ¹² J. Moffat, M. V. Newton and G. J. Papenmeier, *J. Org. Chem.* **27**, 4058 (1962).
- ¹³ R. E. Schuster, J. E. Scott and J. Casanova, *Org. Synth.* **46**, 75 (1966).
- ¹⁴ P. C. J. Kamer, R. J. M. Nolte, W. Drenth and J. A. Kanters, manuscript in preparation.
- ^{15a} J. S. Miller and A. L. Balch, *Inorg. Chem.* **11**, 2069 (1972);
- ^b C. H. Davies, C. H. Game, M. Green and F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* 357 (1974);
- ^c W. P. Fehlhammer, K. Bartel, U. Plaia, A. Völkl and A. T. Liu, *Chem. Ber.* **118**, 2235 (1985);
- ^d P. R. Branson, R. A. Cable, M. Green and M. K. Lloyd, *J. Chem. Soc., Chem. Commun.* 364 (1974);
- ^e P. Domiano, A. Musatti, M. Nardelli and G. Predieri, *J. Chem. Soc. Dalton Trans.* 2165 (1975).

- ¹⁶ ¹³C NMR measurements on Ni(C=N-t-C₄H₉)₄(ClO₄)₂ were not possible, due to the low solubility of this complex.
- ¹⁷ P. C. J. Kamer, R. J. M. Nolte and W. Drenth, unpublished results.
- ^{18a} E. M. Badley, J. Chatt, R. L. Richards and G. A. Sim, J. Chem. Soc., Chem. Commun. 1322 (1969);
- ^b W. M. Butler and J. H. Enemark, Inorg. Chem. **12**, 540 (1973);

- ^c R. F. Stepaniak and N. C. Payne, Inorg. Chem. **13**, 797 (1974);
- ^d K. P. Wagner, P. M. Treichel and J. C. Calabrese, J. Organometal. Chem. **71**, 299 (1974);
- ^e A. Modinos and P. Woodward, J. Chem. Soc. Dalton Trans. 2065 (1974).
- ¹⁹ A. J. M. van Beijnen, R. J. M. Nolte, W. Drenth and A. M. F. Hezemans, Tetrahedron **32**, 2017 (1976).
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