Helical Configuration of Poly(iminomethylenes). Synthesis and CD Spectra of Polymers Derived from Optically Active Isocyanides


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ABSTRACT: Each of nine chiral isocyanides, R*-N=C, in enantiomerically pure or almost pure form, is polymerized to the corresponding poly(iminomethylene), [R*-N=C<]n. The group R* either contains at least one substituent (carboxylic ester, phenyl, phosphinyl) or is unsaturated (C=C, C≡C). The polymers are of the rigid-rod type with a helical main chain of carbon atoms. Because of the chirality of R*-N=C either the P or the M helix is preferentially formed. CD spectra and optical rotation at 578 nm are determined and compared with those of the model compounds R*-N=CH(t-C4H9) and the monomers. This comparison and earlier calculations on [t-C4H9-N=C<]n allowed the assignment to each polymer of the excess screw sense. The screw sense is also theoretically predicted by two approaches, a thermodynamic and a kinetic one. The latter approach gives an appreciably better fit with the experimental results.

Introduction

Stereoisomerism due to restricted rotation around single bonds (atropisomerism) is a well-known phenomenon in organic chemistry. In polymer chemistry this type of isomerism is very rare. Restricted rotation around the single bonds connecting the main-chain carbon atoms of a macromolecule can give rise to the formation of a stable helix. One condition is that the polymer is highly isotactic; that is, the configuration around all main-chain single bonds should be the same, e.g., all R or all S.

As far as we know, only three examples of atropisomerism in polymers have been reported in the literature. There is indirect evidence that polychloral prepared from chloral with a chiral initiator forms a stable helix with preference of one helical screw sense over the other. It has been shown that triphenylmethyl methacrylate, when polymerized by chiral anionic catalysts, yields an isotactic, optically active polymer. The optical activity is attributed to the presence of a rigid helix, which is stable because of the bulky triphenylmethyl ester functions. The third example of atropisomerism is found in polymers of isocyanides. These polymers, also called poly(iminomethylenes) or, more properly, poly(carbonimidoyls), are obtained by polymerization of isocyanides with several catalysts, among them nickel(II) catalysts.

The polymers have a rigid helical structure with four monomeric units per helical turn. Poly(tert-butyliminomethylene) has been resolved into right-handed (P) and left-handed (M) helices by column chromatography. These helices show negative and positive signs of optical rotation at λ = 578 nm, respectively. The resolution of poly(tert-butyliminomethylene) indicates that polymerization of isocyanides is stereoselective with respect to screw sense. Thus, when the monomer is nonchiral a racemic mixture of P and M screws is formed. However, when the monomer is one enantiomer of a chiral isocyanide, its polymer will be a mixture of diastereoisomers, and P and M screws will not be obtained in equal amounts. In a previous paper we compared the CD spectra of polymers of optically active alkyl isocyanides with those of model compounds. This comparison, although restricted to three examples, supported the hypothesis that optically active isocyanides yield polymers with an excess of one helical chain over the other. In the present paper we describe the synthesis and CD spectra of an additional number of nine optically active poly(aminomethylenes), compounds 3a–i (Scheme I), which have different side chains R. The CD spectra of these polymers are compared with the CD
spectra of representative model compounds. A major goal of our investigations is the development of chiral supports, such as deoxygenated 3I, which can bind metal complexes. These polymeric systems are of interest as chiral catalysts, e.g., in hydrogenation reactions.12

Results and Discussion

Synthesis. Polymers 3a–i were prepared according to the general procedure of Scheme I. Optically active N-formylamines served as starting materials. L-(S)-N-Formylalanine ethyl ester (1a) was obtained from L-alanine by esterification with HCl and subsequent reaction with sodium formate, formic acid, and acetic anhydride. (S)-N-Formyl-0-acetyl-2-amino-3-methyl-l-butanol (1b), (S)-N-formyl-0-acetyl-2-amino-3-methyl-1-butanol (1c), and (R)-N-formyl-O-acetyl-2-amino-2-phenylethanol (1d) were prepared from L-alanine, L-valine, and D-phenylglycine, respectively, as outlined in Scheme II. The carboxylic function of the latter compounds was esterified and subsequently reduced to the hydroxymethyl group during the reduction process. The latter group was removed by hydrogenolysis with palladium on carbon. The unprotected alcohols 5j and 5k were treated with formic acid-acetic anhydride to give N,O-diformylated products. The latter compounds were selectively deformylated at oxygen by reaction with sodium hydrogen carbonate in 10% aqueous methanol to give 6j and 6k. Formamide 6j was obtained from 5j with excess of ethyl formate. Compounds 6 were O-acetylated using acetic anhydride and pyridine. (S)-TV-Formyl-l-amino-l-phenylethane (le), (S)-Af-formyl-2-amino-l-phenylethanol (lf), and (S)-N-formyl-2-amino-2-phenylethanol (lg) were prepared from (S)-l-amino-l-phenylethane using acetic anhydride and pyridine. (S)-TV-Formyl-l-amino-l-phenylpropane (1f) was prepared from (S)-l-amino-l-phenylpropane (lf) and (S)-3-amino-l-pentene, respectively. Reaction of sodium acetylide in liquid ammonia with propionaldehyde provided alcohol 7. Compound 7 was converted with p-toluenesulfonyl chloride into the corresponding tosylate 8. When 8 was treated with excess liquid ammonia in an autoclave at room temperature for 24 h, amine 9 was formed in 85% yield. No reaction was observed at the boiling temperature of ammonia (−33 °C). In the literature, the reaction of a tosylate similar to 8 with sodium amide in liquid ammonia has been described.13 This procedure gives amine in a much lower yield (40%). The racemic amine 9 was resolved through crystallization of its bitartrate from water. After two crystallizations 1H NMR shift experiments showed that 9 was optically pure with [α]D +14.2°. After we had completed this experiment, Scandinavian workers14 published the resolution of 9 by a similar procedure. Their optically pure amine had [α]D +14.4°, and its absolute configuration was established to be S. A sample of optically pure (S)-9 was converted into amine (S)-10 by catalytic hydrogenation using a deactivated Lindlar catalyst.15

\[\text{HC=CN}_{\text{H}_{2}}\text{CHO} \rightarrow \text{HC=CC}(\text{H}_{2})\text{OH} \rightarrow \text{HC=CC}(\text{H}_{2})\text{OTs} \rightarrow \text{HC=CC}(\text{H}_{2})\text{NH}_{2} \rightarrow \text{H}_{2}\text{C=CHCH}(\text{H}_{2})\text{NH}_{2} \]

(S)-N-Formyl-1-amino-2-(diphenylphosphinyl)propane (1) was prepared according to Scheme IV. L-Alanine (4j) was converted into its methyl ester and, subsequently, protected at its amine function with two benzyl (Bn) groups. For the introduction of the latter groups we used the combination benzyl bromide and solid sodium carbonate in acetonitrile as solvent. We found this procedure more convenient than the literature procedure,16 which makes use of benzyl chloride and KOH in ethanol–water as solvent. The double-protected L-alanine ester was reduced with LiAlH₄ to give alcohol 11. Compound 11 was treated with p-toluenesulfonyl chloride in pyridine with the purpose of preparing the O-tosyl derivative 15. However, the expected reaction product was not formed. Instead the chloride 12 and pyridine salt 16 were obtained in approximately 45% and 30% yield, respectively. Substitution of N-methylimidazole for pyridine gave chloride 12 in an even higher than 95% yield. The latter compound could also be obtained by using thionyl chloride as reagent, albeit in lower yields (<70%) and longer reaction time. The rearrangement, which takes place during the synthesis of 12 from 11 by the procedures mentioned above, is not unexpected and has some precedents in literature.18 It probably proceeds via the following three-membered-ring intermediate:

The optical rotation of chloride 12 amounted to [α]D +19.3°. The structure of 12 was confirmed by 1H and 13C NMR and mass spectrometry. Chiral shift reagents gave no signal splitting in the 1H NMR of 12, which might indicate that this compound is optically pure. The absolute configuration of 12 would be R if during the conversion 11 → 12 inversion occurs at the chiral center. Chloride 12 was treated with Pb₂P₃Li in THF to give its phosphine derivative, which was oxidized with hydrogen peroxide to yield phosphine oxide 13. The benzyl groups in the latter compound were removed by hydrogenolysis with palladium on carbon as the catalyst. Attempts to remove the benzyl groups in the phosphine stage were unsuccessful, probably because the phosphine–amine acts as a strong bidentate
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3
17
70.6
74.0
-458
27.6
CH(i-C,HJ
-910
-190
-172
72.5
35.3
-355
164x98
strongly depends on the amount of catalyst used. For
observed that the molecular weight of the polymers
condition that the optical rotation and CD spectrum are
ultimate that their viscosity-average molecular weights range
octyliminomethylene
chloroform, 30.00 °C). If we apply the Mark-Houwink
the polymers varied from 0.06 to 0.70 dL/g (toluene or
solvents (alcohols, water). The intrinsic viscosities \([\eta] \) of
isocyanides are given in
Table I: A low molecular weight polymer sample serves as
model compound, MW = 1100 (tetramer).
ligand to the metal catalyst. Compound 14 was converted
into formamide II using formic acid as formylating agent.
Scheme IV

<table>
<thead>
<tr>
<th>R</th>
<th>([M]^{\theta}_{\infty \text{a}, \text{b}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, (S)-C,H,O,CCH(CH,.)</td>
<td>+21.2</td>
</tr>
<tr>
<td>b, (S)-CH,CO,CH,CH,CH,</td>
<td>+74.0</td>
</tr>
<tr>
<td>c, (S)-CH,CO,CH,</td>
<td>+72.5</td>
</tr>
<tr>
<td>d, (R)-CH,CO,CH,CHPh</td>
<td>-129</td>
</tr>
<tr>
<td>e, (S)-PhCH(CH,.)</td>
<td>-55.0 \text{c}</td>
</tr>
<tr>
<td>f, (S)-PhCH,CH,CH,</td>
<td>+70.6</td>
</tr>
<tr>
<td>g, (S)-HC=C(CH,R,.)</td>
<td>-11.9 \text{e}</td>
</tr>
<tr>
<td>h, (S)-H,C=CCH(CH,.)</td>
<td>+90.2 \text{f}</td>
</tr>
<tr>
<td>i, (S)-Ph,P(0)CH(CH,JCH,CH,</td>
<td>+55.3</td>
</tr>
</tbody>
</table>

\text{a In (deg cm\(^{-1}\))g. The molar rotations of the polymers are expressed per polymer repeat unit. \text{b In chloroform as solvent, unless otherwise stated; 2, c 1-4; 17, c 1-3; 3, e 0.005-1.0. \text{c} In methanol, c 5. \text{d} Model compound is R-N=C(CH,.) \text{e} Neat. \text{f} Both neat and in methanol, c 1. \text{g} A low molecular weight polymer sample serves as model compound, MW = 1100 (tetramer).}

Isocyanides 2 were obtained from formamides 1 by dehydration with trichloromethyl chloroformal (CICOO-CCl\(_3\)) and \(N\)-methylmorpholine at low temperatures (compounds 2a-d),\(^{19}\) by (Ph\(_3\)P)CCl\(_3\) in situ from triphenylphosphine and carbon tetrachloride (compound 2e),\(^{20}\) and by phosphorus oxychloride and triethylamine or \(N\)-methylmorpholine (compounds 2f-i).\(^{21}\) The yields varied from 50 to 75%. The infrared absorption spectra of compounds 2a-i showed characteristic isocyanide stretching vibrations in the region \(2140-2145 \text{ cm}\(^{-1}\)). The molar optical rotations of the isocyanides are given in Table I.

The monomers were polymerized at room temperature by 0.1-5 mol % of NiCl\(_2\)-6H\(_2\)O either in methanol solution or without solvent. The yields of isolated polymer ranged from 60 to 95%. The polymers were pale yellow or yellow solids. Polymer 3g was a brown solid. In general, the solids were soluble or sparingly soluble in apolar solvents (chloroform, benzene, petroleum ether) and insoluble in polar solvents (alcohols, water). The intrinsic viscosities \([\eta] \) of the polymers varied from 0.06 to 0.70 dL/g (toluene or chloroform, 30.00 °C). If we apply the Mark–Houwink equation \([\eta] = 1.4 \times 10^{-3} \text{M}^{1.72} \), determined for poly(2-octyliminomethylene),\(^{10}\) to the present polymers, we estimate that their viscosity-average molecular weights range from 25 000 to 95 000. We did not aim at high molecular weights. On the other hand, the samples should fulfill the condition that the optical rotation and CD spectrum are independent of molecular weight. The latter situation is attained when the average chain length of the polymers is larger than approximately 20 monomer units (molecular weight >2000), as we showed in a previous study.\(^{8}\) We observed that the molecular weight of the polymers strongly depends on the amount of catalyst used. For
instance, if \(\alpha\)-phenylethyl isocyanide (2e) is polymerized neat with 0.015, 0.2, and 100 mol % of nickel chloride, the molecular weights of the polymer samples amount to \(M_c = 175 000, M_c = 95 000, M_c = 30 000, \) and \(M_c(VPO) = 2000\), respectively. Polymers 3a-i showed \(N\)=C stretching vibrations in the infrared spectrum at 1620-1650 cm\(^{-1}\). Their optical rotation values are given in Table I.

As low molecular weight model compounds for the polymers a number of \(N\)-neopentylidene amines, RN=CH-(t-C\(_2\)H\(_5\)) (17), were synthesized. The molar optical rotations of these compounds are also included in Table I.

**CD Spectra.** Polymers 3a-i have various side chains R. For convenience, we will divide these polymers into classes that have ester functions only in their side chain (compounds 3a-c, model compounds are 17a,b), compounds that have a phenyl substituent or a phenyl substituent in addition to an ester function in their side chain (compound 3d-f, model compound is 17e), compounds that have a triple or double bond in their side chain (compounds 3g,h, model compound is 17h), and a compound that has a diphenylphosphinyl substituent in its side chain (compound 3i, model compound is a corresponding low molecular weight polymer sample 17i). The CD spectra of the various polymers and model compounds will be discussed below. Before doing so, we will recall some features of the CD spectrum of (\(M\)=(+)poly(\( tert\)-butyliminomethylene), which serves as a general reference spectrum.\(^{9}\) This spectrum is presented in Figure 1 together with the UV absorption spectrum. The shoulder in the latter spectrum at about 290 nm corresponds to the n–\(\pi^*\) transition of the imino group.\(^{9}\) This n–\(\pi^*\) transition is responsible for the CD spectrum in the region 240-400 nm. Two CD bands centered at the wavelength of this shoulder are observed, forming a so-called “exciton couplet.”\(^{22}\) The sign sequence of this couplet is characteristic of the screw sense of the polymer. It was shown that a positive band at higher and a negative band at lower wavelength (positive couplet) in poly(iminomethylene) corresponds to an \(M\)-helical configuration.\(^{9}\) The reverse situation (negative couplet) corresponds to a \(P\)-helical configuration.

The UV and CD spectra of the first class of polymers (3a-c) are presented in Figure 2a-c. The UV and CD data of model compounds 17a and 17b are listed in Table II. Both 17a and 17b show an absorption band in the UV at 220-230 nm. These bands probably include the n–\(\pi^*\) transition of the imino group as well as that of the carbonyl
group. The transition of the latter group should be at the shorter wavelength side, as carbonyl groups normally show their n-\pi* transition at about 210-220 nm (\(\varepsilon \approx 50 \text{ L-mol}^{-1} \text{cm}^{-1}\)).\(^2\)\(^3\) In the CD spectra of 17a and 17b a Gaussian band centered at 235 nm is visible with \(\Delta \varepsilon\) values of -4.0 and -0.29 L-mol\(^{-1}\)cm\(^{-1}\), respectively. The relatively high wavelength position of the band suggests that the chirality of the carbonyl group is not pronounced in the CD.

The UV spectra of polymers 3a-c reveal the n-\pi* transition of the imino group as a broad band in the region 290-330 nm. This transition is considerably shifted to longer wavelengths with respect to the model compounds. Such a shift has also been observed for poly(imino-methylenes) derived from simple alkyl isocyanides.\(^1\)\(^0\) In polymers of optically active isocyanides both the chiral center in the side chain of the helical structure of the main chain will induce rotational power in the imino chromophore. The contribution by the chiral side chain in polymers 3a-c is manifested in the CD spectrum as a relatively large negative band at 240-400 nm. The helicity of the main chain is obscured due to overlap with this negative band. Careful inspection of the curves, however, shows that negative couplets are present for compounds 3b and 3c. The positive parts of these couplets are lowered by the negative band of the side chain. Also for polymer 3a a negative couplet might well be present; the asymmetry of the CD curve is an indication, as is supported by a simulated spectrum (Figure 2d). For an accurate curve analysis the CD spectra should also be recorded and interpreted in the short-wavelength region. However, this is difficult to realize because of solvent absorption and unfavorable \(\Delta \varepsilon\)/\(\varepsilon\) ratios. The occurrence of negative couplets in 3a-c indicates an excess of right-handed or \(P\) helices in these polymers. An estimate of the excess percentage from the intensity of the couplets, as we were able to make in case of polymers of simple optically active alkyl isocyanides,\(^1\)\(^0\) would be too unreliable at this time. The molar rotation data for polymers 3a-c show appreciable shifts to negative values as compared to the rotations of the model imines and also to the rotations of the isocyanide monomers. These shifts to negative rotations suggest a levorotatory contribution by the helices. The combination of \(P\) screw and negative optical rotation was found earlier for poly(tert-butyliminomethylene) (vide supra).

The UV and CD spectra of the model compound of polymers 3d-f, compound 17e, are presented in Figure 3a. In these spectra the typical pattern of a phenyl group is
visible between 250 and 280 nm. The band due to the n-π* transition of the imino chromophore is partly masked by the phenyl pattern. This n-π* transition can be located at about 250 nm. In n-hexane as well as in chloroform as solvent it gives rise to a negative CD band. The intensity of the latter band in n-hexane is lower than in chloroform. This difference in intensity might be caused by conformational changes due to solvation.

In the UV spectra of polymers 3d–f (Figure 3b–d) the n-π* transitions are located as very weak bands in the range from 300 to 350 nm. The absorption bands of the phenyl group can be recognized as shoulders at about 275 nm. The CD spectrum of polymer 3f (Figure 3d) clearly reveals the CD bands of the phenyl group, as found in the model compound, and a negative couplet at 320 nm, indicative of a P helix. Very remarkably, no negative CD band due to the side-chain induction in the imino chromophore is visible. On the contrary, polymers 3d and 3e do show the side-chain bands. The latter bands in 3d and 3e probably are of opposite sign, as judged by the intensity difference of the CD spectra, in line with the opposite R and S absolute configuration of the side chains of the polymers. No clear-cut couplets are present for 3d and 3e. However, the CD spectra are rather asymmetric, just as in case of polymers 3a–c. This asymmetry in the CD spectrum of polymer 3e is simulated in Figure 3e by the summation of a negative couplet, a negative CD band due to the side-chain induction in the imino chromophore, and a positive phenyl band. Thus, also 3d and 3e will have P-helical structures. The optical rotation data of polymers 3d–f are in agreement with these structure assignments: going from monomer or model compound to polymer the molar optical rotation becomes more negative (see Table I, entries d–f).

The CD spectrum of polymer 3g in the region around 300 nm could not be measured due to a very unfavorable Δε/ε ratio (the polymer has a dark brown color). The molar optical rotation of this polymer shows a shift to negative value as compared to the isocyanide monomer (Table I). Assuming the isocyanide to be a correct reference for this polymer, the presence of an excess of P helices can be derived.

The UV and CD spectra of polymer 3h and the corresponding data for model compound 17h are given in Figure 4 and Table II, respectively. The model compound shows a UV n-π* absorption band at 247 nm and a single negative Cotton effect at the same wavelength position in the CD. The polymer has an absorption band at 320 nm in the UV spectrum. The CD spectrum reveals a negative band due to the side-chain contribution as well as a positive couplet due to the helical main chain. The latter couplet indicates the presence of an excess of M helices in polymer 3h. A comparison of molar optical rotation values (Table I, entry h) leads to the same conclusion, provided imine 17h is used as model compound. Taking isocyanide 2h as a reference, the wrong screw sense is predicted. This demonstrates that an isocyanide occasionally is an inadequate model for its polymer (compare also ref 11).

Polymers 3g and 3h have side chains from which, in principle, the chirality can be removed by reduction. With (M) (+)-poly(tert-butylinomethylenes) as a calibration standard, the chiroptical properties of the “dechiralized” polymers will give information about the excess P or M screw present in the original polymers. Unfortunately, however, we were not able to get this information, as polymers 3g and 3h resisted all reduction methods tried. These methods included catalytic hydrogenations with 10% palladium on carbon, platinum oxide, W-6 Raney nickel, and Rh(PPh3)3Cl (Wilkinson catalyst) and dissolving-metal reductions with lithium in ethylenediamine and sodium in liquid ammonia. Probably, the unsaturated groups in 3g and 3h are well protected against reduction by steric hindrance.

The UV and CD spectra of polymer 3i and its model compound, a low molecular weight polymer sample, 17i (Table I), are given in Figure 5. In these spectra the pattern of the phenyl group is visible between 250 and 280 nm (compare also Figure 3a). The chirality of the main chain in 3i is manifested by the positive couplet at 320–420 nm, indicating the presence of an excess of M helix. Inspection of Table I (entry i) indicates that this M helix has a negative contribution to the total optical rotation. In this respect polymer 3i is different from the other optically active poly(iminomethylenes) studied so far. At the moment we cannot offer an explanation for this deviating behavior.

Table II

<table>
<thead>
<tr>
<th>Compd</th>
<th>λ_{max}/nm</th>
<th>ε/ε</th>
<th>Δε_{max}/ε</th>
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<tr>
<td>17a</td>
<td>220^{b,c}</td>
<td>100</td>
<td>-4.0^{b,c}</td>
</tr>
<tr>
<td>17b</td>
<td>230^{b,c}</td>
<td>100</td>
<td>-0.29^{b,c}</td>
</tr>
<tr>
<td>17e</td>
<td>250</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>17h</td>
<td>247</td>
<td>94</td>
<td>-1.57</td>
</tr>
</tbody>
</table>

* Compound, solvent (concentration in mol L^{-1}); 17a, n-hexane (2.45 × 10^{-4}), CHCl3, (2.14 × 10^{-4}); 17b, n-hexane (3.48 × 10^{-4}), CHCl3, (5.56 × 10^{-4}); 17e, n-hexane (3.67 × 10^{-4}), CHCl3, (2.96 × 10^{-4}); 17h, n-hexane (7.02 × 10^{-4}).

b In chloroform the UV and CD cannot be measured below 245 nm. Down to the latter wavelength the intensities in this solvent are of the same order of magnitude and of the same sign as when n-hexane was used as solvent.

c The bands due to the n-π* transition of the imino group and the carbonyl group are not completely separated in the UV spectrum. In the CD spectrum, Δε_{max} lies at 235 nm.

d The band due to the n-π* transition of the imino group is masked by the phenyl bands. See Figure 3a.
thermodynamically controlled process. The question which screw, P or M, is the most favorable one for a given chiral side chain R, can be answered by inspecting Figure 6. In this figure a projection along the \( C-N= \) bond of a side chain, \( R_1 R_2 R_3 \), of a \( P \)-helical poly(iminomethylene) is given. The relative steric requirements of the substituents \( R_1, R_2, \) and \( R_3 \) at the chiral carbon atom are denoted by S (small), M (medium), and L (large), respectively. Poly(iminomethylenes) have four repeating units per helical turn.\(^7,9\) The most severe steric hindrance for a substituent at the chiral carbon atom of repeating unit \( C_n \) comes from the \( R-N=C \) moiety. This moiety is close to and has its \( C_1 \) nearly on top of \( C_A \). A lesser but still important hindrance is that with the vicinal \( C_4 =N \) moiety. The most favorable side-chain position will be that position in which the largest substituent L points away from the helix, while substituents S and M are placed in the direction of \( C_2 \) and \( C_4 \), respectively. Vice versa one can conclude that an arrangement of substituents as shown in Figure 6 will favor a \( P \)-helical main chain. In Table III the thermodynamically predicted screw senses are derived by following the procedure outlined above. Also given in Table III are the experimentally determined screw senses. A comparison of the two reveals that there are many disagreements. This result suggests that the induction of screw sense is not a thermodynamically governed process.

We will now consider a kinetically controlled process at the catalyst center. Polymerization of isocyanides by nickel(II) salts proceeds via a sequence of insertion reactions around the nickel center (Scheme V).\(^6\) Reaction starts from the square-planar complex Ni(CNR)\(_4\)\(^{2+}\) . A coordinated isocyanide in the latter complex is easily attacked by a nucleophile \( X \) (e.g., Cl\(^-\) of nickel chloride) to

![Figure 6. Projection of the side chain (SML)C–N= along the C–N= bond in a P-helical poly(iminomethylene).](image)

**Table III**  
Experimental and Predicted Screw Sense of Poly(iminomethylene) (R\(^1\)R\(^2\)R\(^3\)CN–C<)\(_n\))

<table>
<thead>
<tr>
<th>polymer</th>
<th>( R_1, R_2, R_3 )</th>
<th>exptl</th>
<th>kinetically</th>
<th>thermodynamically</th>
</tr>
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<tbody>
<tr>
<td>3a</td>
<td>H (S), CH(_3) (L), COOC(_2)H(_5) (M, Y)</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>3b</td>
<td>H (S), CH(_3) (M), CH(_2)O CCH(_3) (L, Y)</td>
<td>P</td>
<td>P</td>
<td>M</td>
</tr>
<tr>
<td>3c</td>
<td>H (S), iC(_3)H(_7) (L), CH(_2)O CCH(_3) (M, Y)</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>3d</td>
<td>H (S), CH(_2)O CCH(_3) (M, Y), Ph (L, Y)</td>
<td>P</td>
<td>P</td>
<td>M</td>
</tr>
<tr>
<td>3e</td>
<td>H (S), CH(_3) (M), Ph (L, Y)</td>
<td>P</td>
<td>P</td>
<td>M</td>
</tr>
<tr>
<td>3f</td>
<td>H (S), CH(_3) (M), CH(_2)Ph (L, Y)</td>
<td>P</td>
<td>P</td>
<td>M</td>
</tr>
<tr>
<td>3g</td>
<td>H (S), C(_2)H(_5) (L), C–CH (M, Y)</td>
<td>P</td>
<td>P</td>
<td>M</td>
</tr>
<tr>
<td>3h</td>
<td>H (S), C(_2)H(_5) (L), CH–CH(_3) (M, Y)</td>
<td>P</td>
<td>P</td>
<td>M</td>
</tr>
<tr>
<td>3i</td>
<td>H (S), PPh(_2)O (L, Y), CH(_3) (M)(^d)</td>
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<td>P</td>
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</tbody>
</table>

\(^a\) In parentheses are the relative bulkiness and coordinative property. The substituents \( R_1, R_2, \) and \( R_3 \) are ranked according to their anticlockwise sequence in Newman projection i. They are numbered according to their relative steric requirements as expressed by the \( \lambda \)-steric parameters (see ref 27); \( R, \lambda R \): H, 0.00; CO, C\(_2\)H\(_5\), 0.90; CH\(_3\), 1.00; C\(_2\)H\(_5\), 1.05; CH\(_2\)O CCH\(_3\), \( \approx 1.1 \); CH\(_2\)Ph, 1.15; Ph, 1.23; iC\(_3\)H\(_7\), 1.27; PPh\(_2\)O, \( \approx 1.27 \); the steric parameters for \( \text{CH–CH}_2 \) and \( \text{C–CH} \) are unknown, but will be \( \approx 1 \), with \( \lambda_{\text{CH–CH}_2} < \lambda_{\text{CH–CH}} \) (see ref 28). \(^b\) P screw if Ph coordinates to nickel, \( M \) screw if CH\(_2\)O CCH\(_3\) coordinates to nickel. \(^c\) In a previous paper\(^11\) we reported a \( P \) screw for this polymer based on a comparison of optical rotation data (see also text). Both the kinetically and thermodynamically predicted screw sense disagree with the experimental one. At the moment, we cannot give a satisfactory explanation for this result. \(^d\) R\(^1\)R\(^2\)R\(^3\) are the substituents at the chiral 1-carbon atom. The kinetically predicted screw sense is derived from the Newman projection ii of 18z along the –NCH\(_2\)-CH\(_2\)PPh\(_2\)O bond.
give ion 18. The plane of the ligand C(X)=NR in 18 is approximately perpendicular to the plane of the isocyanide carbons and nickel, with R either in the E or in the Z position with respect to the nickel center. There is no free rotation around the bond from C1 to nickel for steric reasons. Carbon atom C1 has gained in nucleophilicity, allowing it to attack a neighboring ligand. Such an attack is facilitated when a new isocyanide ligand C3=NR is substituted for C1(X)=NR. Attack can occur on either C2 or C4. In 19 it has occurred on C2. When the sequence of attacks continues in the direction C1 → C2 → C3 → C4, a left-handed helix is obtained (20). In a similar way the sequence of attacks C1 → C4 → C3 → C2 will result in a right-handed helix.

In the case of an achiral isocyanide the transition states for attack of C1 on C2 and on C4 are the same. On the contrary, in case of a chiral isocyanide these transition states differ and will depend on the steric interactions between ligands C1 and C2, and C3 and C4, respectively. With regard to these interactions the E or Z position of -CR2R3 in C1(X)=NCR2R3 is of interest as well as the relative sizes and arrangement of the substituents R1, R2, and R3 on the chiral carbon atom. It is known from the literature that in metal complexes comparable to 18 as well as in imines, the E/Z ratio varies with temperature, solvent, and substituents. The present ligands C1(X)=NCR2R3 all contain substituents (denoted by Y) that can interact with the nickel center and thus favor a Z position (18z) over an E position. In 18z Y is coordinated to the nickel center and the remaining substituents at the chiral carbon atom are S and M or L. For a given arrangement of substituents attack by C1 will preferentially occur on the least hindered side. In 18z with S pointing backward this is on C4 and with S pointing to the front this is on C2. A P screw and an M screw will be formed, respectively. In Table III the kinetically predicted screw senses, based on intermediate 18z, of polymers 3a-i are given. In general, these screw senses are in good agreement with experiment. In view of this finding we can say that the induction of screw sense in the polymerization of optically active isocyanides is most likely a process kinetically controlled at the catalyst center.

Experimental Section

Analytical Techniques. Infrared (IR) spectra were recorded on a Perkin-Elmer 297 and 283 spectrophotometers. Ultraviolet (UV) spectra were obtained on a Perkin-Elmer 200 spectrophotometer. CD spectra were recorded on a home-built apparatus. This instrument measures the difference in absorbance (ΔA) with a sensitivity better than 1 x 10^-6. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. 1H, 13C, and 31P spectra were obtained on a Varian EM 390, a Varian CFT 20, and a Bruker WH 90 instrument, respectively. Chemical shifts (δ) are given in ppm from internal tetramethylsilane or external H3PO4. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under the supervision of W. J. Buis. Melting points were determined on a Mettler FP5/FP51 photoelectric melting point apparatus. Solution viscosity data were obtained with a Cannon-Ubbelohde viscometer. Mass spectra were recorded on an AEI MS-902 mass spectrometer. Field desorption (FD) mass spectra were obtained with a Varian MAT 711 mass spectrometer with a combined EI/FI/FD ion source and coupled to a spectrometry MAT 100 data acquisition unit.

N-Formyl-L-alanine Ethyl Ester (1a). L-Alanine (4j) was esterified with dry HCl and dry HCl, according to a standard procedure.29,30 Subsequent reaction with formic acid, sodium formate, and acetic anhydride31 afforded 1a as a colorless liquid in quantitative yield: [α]D25 = 69.0° (c 4, ethanol); IR (neat) 1740 (CO), 1675 (NCO) cm^-1; 1H NMR (CDCl3) δ 8.24 (s, 1 H, CHO), 7.75 (br, 1 H, NH), 4.61 (m, 1 H, CH), 4.22 (q, 2 H, CH2), 1.43 (d, 3 H, CH3), 1.25 (t, 3 H, CH3). (S)-1-Carbethoxethyl Isocyanide (2a). This isocyanide was synthesized from 1a according to a modification of the method of Skorna and Ugi.19 The procedure was as follows: Into a round-bottomed flask, equipped with a magnetic stirrer and a CO2-acetone reflux condenser kept at -30 °C we were brought 4.35 g (30 mmol) of 1a, 7.05 mL (63.0 mmol) of dry N-methylmorpholine, and 50 mL of dry CH2Cl2 as a solvent. At a temperature of -30 to -40 °C, 1.81 mL (15.0 mmol) of dihydrogen in 10 mL of dry CH2Cl2 was introduced into the stirred reaction mixture over a period of approximately 2 h. The reaction was followed by TLC (silica gel, CH2Cl2). The chromatograms were developed with a NiCl2-H2O solution in ethanol; with this reagent isocyanides give a red-brown spot. In this way it could be determined that the minimum temperature for reaction was between -30 and -40 °C. After reaction was complete (3 h) the cooling
bath was removed, and immediately 25 mL of water was added to the mixture. The still cold organic layer was separated, washed with 35 mL of an aqueous 7.5% NaHCO₃ solution, again separated, and dried over Na₂SO₄. The crude reaction product was purified by column chromatography (silica gel, CHCl₃): yield 2.86 g (75%); [α]₂₅⁰+16.7° (c 3.7, chloroform); IR (CCl₄) 1740 (C=O), 2140 (N=C) cm⁻¹; H NMR (CCl₄) δ 4.30 (q, 2 H, CH₃), 2.45 (m, 1 H, CH), 1.63 (s, 3 H, CH₃), 0.67 (d, 3 H, CH₃). From the optical purity of the racemization-sensitive compound 2α we hydrolyzed a sample with a solution of 0.01 mol/L HCl in water−tetrahydrofuran (1:2 (v/v)). The thus obtained formamide had, after chromatographic purification, almost the same optical rotation value, viz., [α]₂₅⁰ −68.0° (c 1.7, ethanol), as the formamide 1α from which the isocyanate was prepared. Thus racemization had not occurred during the formation and purification of the isocyanate.

Poly(S)-(1-carboxethoxy)liminomethylene (3a). Iso­cyanide 2α was polymerized with 0.2 mol % of NiCl₂·6H₂O at ambient temperature and without solvent. After 5 days the glassy reaction mixture was dissolved in a small amount of chloroform and added dropwise to an excess of vigorously stirred methanol−water (4:1 (v/v)). The precipitated yellow-colored polymer and added dropwise to an excess of vigorously stirred methanol−water (1:4 (v/v)) at 60 °C, compound 3a was obtained as a colorless liquid: yield 75%; bp 168.6 °C (0.02 mm); [α]₂₅⁰+14.25° (c 5.5, CHCl₃); IR (KBr) 1745 (OCO), 1655 (NCO) cm⁻¹. Anal. Calcd for C₉H₁₄NO₂: C, 73.68; H, 9.54; N, 9.66; found: C, 73.58; H, 9.60; N, 9.70; O, 5.85; 9.50; O, 25.70.

(S)-2-Aminopropanol (1α). N-Benzoyl-1-alanine and N-benzoyl-1-alanine methyl ester were prepared starting from 1α according to standard procedures.²⁹ N-Benzyl-1-alanine was prepared from the above ester with an excess of LiAlH₄ in boiling diethyl ether. After hydrogenolysis in water−ethanol (1:4 (v/v)) at 60 °C, compound 5α was isolated as its HCl salt in an overall yield of 90%: [α]₂₅⁰−14.5° (c 2.0, H₂O); IR (KBr) 1740 (OCO), 1655 (NCO) cm⁻¹. Anal. Calcd for C₁₀H₁₅NO₂: C, 73.71; H, 9.08; N, 9.00; found: C, 73.65; H, 9.02; N, 8.95.

(S)-N-Formyl-2-amino-3-methylbutanol (6α). This compound was obtained starting from 1-­valine (4k) as indicated for the synthesis of 5α and isolated as its HCl salt from methanol−ether: mp 120 °C [lit.²⁷ mp 117−118 °C]; [α]₂₅⁰ +14.5° (c 2.0, H₂O); IR (KBr) 1740 (OCO), 1655 (NCO) cm⁻¹.Anal. Calcd for C₆H₁₂NO₃Cl: C, 56.68; H, 7.14; N, 11.02; O, 21.65. Found: C, 56.65; H, 7.65; N, 11.08; O, 21.85.

(S)-N-Formyl-2-amino-3-methylbutanol (6α). This compound was obtained from 5α as described for the synthesis of 6α. It was used directly for the synthesis of 1α.

(S)-N-Formyl-O-acetyl-2-amino-3-methylbutanol (1α). Alcohol 6α was acetylated with acetic anhydride and pyridine in quantitative yield. The resulting oil had the following properties: [α]₂₅⁰−48.6° (c 2.5, chloroform); IR (KBr) 1740 (OCO), 1670 (NCO) cm⁻¹; H NMR (CDCl₃) δ 7.0−8.5 (m, 2 H, CH₃), 4.0−4.6 (m, 2 H, CH₂), 2.05 (s, 3 H, CH₃), 1.9 (m, 1 H, CH), 0.97 (d, 6 H, (CH₃)₂).

(S)-O-Acetyl-2-isocyno-3-methylbutanol (2c). This isocyanide was obtained from the latter formamide as described for 2α. The reaction temperature was kept between −15 and −25 °C. After chromatographic purification (silica gel, CHCl₃) the yield was 70% of a colorless liquid: [α]₂₅⁰+46.8° (c 1.6, chloroform); IR (CCl₄) 2148 (NC), 1740 (CO) cm⁻¹; H NMR (CDCl₃) δ 4.14 (m, 2 H, CH₂), 3.63 (m, 1 H, CHN), 2.07 (s, 3 H, CH₃), 1.9 (m, 1 H, CH), 1.01 (d, 6 H, (CH₃)₂).

Poly(S)-(1-acetoxyethyl)liminomethylene (3b). Monomer 2b was polymerized with 0.3 mol % of NiCl₂·6H₂O in methanol. Polymer 3b was obtained as a yellow solid in a yield of 90%: [α]₂₅⁰ = 0.42 deg/g (chloroform, 30.00 °C); [α]₂₅⁰ −150° (c 1.2, chloroform); IR (KBr) 1735 (CO), 1630 (CN) cm⁻¹. Anal. Calcd for C₆H₁₂NO₃C: C, 56.68; H, 7.14; N, 11.02; O, 21.75. Found: C, 56.29; H, 6.87; N, 11.08; O, 25.65.

Poly(S)-(1-acetoxyethyl)liminomethylene (3b). Monomer 2b was polymerized with 0.3 mol % of NiCl₂·6H₂O in methanol. The polymer was obtained as a bright yellow powder in a yield of 70%: [α]₂₅⁰ = 0.076 deg/g (chloroform, 30.00 °C); [α]₂₅⁰ −82° (c 0.5, chloroform); IR (KBr) 1745 (CO), 1622 (CN) cm⁻¹.

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Amine was resolved into its optical antipodes by a standard method. Subsequently, the excess of ammonia was allowed to evaporate. The specific optical rotation of the 8-antipode was: \( [\alpha]_{D}^{25} = 3.86^\circ \) (neat). This amine was N-formylated with a 10% excess of ethyl formate in dry methanol; \( [\alpha]_{D}^{23} = +22.5^\circ \) (c, 2 H2 O) [lit. 21 \( [\alpha]_{D}^{23} = +22.8^\circ \) (c, H2 O)]. The amine was converted into the isocyanide according to a modified literature method: \( [\alpha]_{D}^{25} = +15.0^\circ \) (neat, c 4, ethanol) [lit. 21 \( [\alpha]_{D}^{25} = +20.9^\circ \) (neat, c 0.813 g/mL, c 14.4°, d 1.0, ethanol)].

**Poly(S)-(1-phenylethyl)iminomethylene (2e).** This isocyanide was obtained by fractional crystallization from its salt by treating it with an excess of aqueous KOH solution and subsequently converted into the formamide with a 50% excess of ethyl formate. The product was obtained as a white solid in almost quantitative yield: mp 44–46 °C; \( [\alpha]_{D}^{25} = -17.0^\circ \) (c 2.0, chloroform); IR (KBr) 1670 (CO) cm\(^{-1}\); \( ^1\)H NMR (CCl\(_4\)) \& 7.30 (s, 5 H, CH\(_3\)), 7.13 (s, 5 H, C6H5), 4.18 (m, 1 H, CH2), 2.4–2.9 (m, 2 H, CH2), 1.07 (d, 3 H, CH3).

**Poly(S)-(1-benzyl)iminomethylene (1f).** This compound was synthesized starting from a sample of optically pure (S)-1-benzyliminomethylene-2,6-lutidine solution and subsequently converted into the formamide with a 50% excess of ethyl formate. The product was obtained as a white solid in almost quantitative yield: mp 44–46 °C; \( [\alpha]_{D}^{25} = -17.0^\circ \) (c 2.0, chloroform); IR (KBr) 1670 (CO) cm\(^{-1}\); \( ^1\)H NMR (CCl\(_4\)) \& 7.30 (s, 5 H, CH\(_3\)), 7.13 (s, 5 H, C6H5), 4.18 (m, 1 H, CH2), 2.4–2.9 (m, 2 H, CH2), 1.07 (d, 3 H, CH3).

**Poly(S)-(1-benzyl)iminomethylene (3f).** This isocyanide was obtained as a colorless liquid in 55% yield after column chromatography (silica gel, CHCl\(_3\)); mp 46–48 °C; \( [\alpha]_{D}^{25} = +48.7^\circ \) (c, 1.0, methanol) [lit. 24 \( [\alpha]_{D}^{25} = +14.4^\circ \) (c, ethanol)]. A sample of the amine was liberated from its salt as an orange formamide with a specific optical rotation \( [\alpha]_{D}^{20} = +14.4^\circ \) (c 1.2, ethanol) [lit. 24 \( [\alpha]_{D}^{20} = +20.9^\circ \) (neat, d 8.216 g/mL, c 14.4°, d 1.0, ethanol)].

**Poly(S)-(1-ethyl-2-propynyl)iminomethylene (3g).** This isocyanide was polymerized with 0.3 mol % of NiCl\(_2\)-6H\(_2\)O in methanol. After 24 h the reaction mixture was concentrated under vacuum. The residual liquid was dissolved in chloroform, washed with water, dried over MgSO\(_4\), and concentrated to a small volume. The polymer was obtained as a white solid in 50% yield: mp 192–194 °C; \( [\alpha]_{D}^{22} = +23.3^\circ \) (c 2, H2 O) [lit. 24 \( [\alpha]_{D}^{22} = +23.8^\circ \) (c 1, H2 O)].

**Poly(S)-(1-ethyl-2-propynyl)iminomethylene (3h).** This formamide was obtained in almost quantitative yield from the amine by a literature method: \( [\alpha]_{D}^{25} = -122^\circ \) (c 20, CHCl\(_3\)); IR (CCl\(_4\)) 2140 (NC) cm\(^{-1}\). The amine was prepared from 2l in a yield of 50% according to a standard procedure: \( [\alpha]_{D}^{25} = -56^\circ \) (neat, d 0.005 g/mL, c 1.0, methanol) [lit. 25 \( [\alpha]_{D}^{25} = -56^\circ \) (c, ethanol)]. A sample of the amine was liberated from its salt as a colorless liquid with a specific optical rotation \( [\alpha]_{D}^{20} = +21.1^\circ \) (c 2.5, methanol) [lit. 25 \( [\alpha]_{D}^{20} = +21.6^\circ \) (c, methanol)].

**Ethylene-propynylamine (4).** This compound was prepared from 1g in a yield of 50% according to a standard procedure: \( [\alpha]_{D}^{25} = -12.8^\circ \) (neat, d 0.224 g/mL, c 20, CHCl\(_3\)); IR (CCl\(_4\)) 2140 (NC) cm\(^{-1}\); \( ^1\)H NMR (CCl\(_4\)) \& 1.70 (s, 3 H, CH3). The colorless liquid became dark on standing at room temperature on air oxidation.

**Poly(S)-(1-ethyl-2-propynyl)iminomethylene (1h).** This formamide was obtained from the HCl salt of 10 with 50% sodium formate, formic acid, and acetic anhydride: yield almost 100% of light yellow oil; \( [\alpha]_{D}^{25} = -24.2^\circ \) (c, 2.5, methanol) [IR (neat) 3080, 990, 925 (CH=CH2), 1610–1630 (C=CH) cm\(^{-1}\)]; \( ^1\)H NMR (CCl\(_4\)) \& 7.6–8.2 (br, 1 H, NH), 8.1 (s, 1 H, CHO), 5.6–6.0 (d, 1 H, NH), 5.0–5.3 (m, 2 H, CH=CH2), 3.74 (s, 3 H, CH3).
The product was crystallized from ethanol; \( \delta \) 22 d -26.6° (c 0.7, 90%: bp 140-150 °C (0.005 mm); \([\alpha]_20^D\) -49.9° (c 1.8, chloroform); \(\delta\) H NMR (CDCl_3) \(\delta\) 7.5 (m, 10 H, aromatic H), 3.2-3.9 (m, 5 H, NCH_2, CH), 3.61 (s, 3 H, OCH_3), 1.25 (d, 3 H, CH_3). The latter ester was reduced with an excess of LiAlH_4 in THF. The latter solution was made from Ph_2 PLi in 50 mL of THF. The latter solution was made from 17 g (0.06 mol) of pivaldehyde and L-alanine ethyl ester according to a procedure described in the literature (19). This amine was obtained in 94% yield from 14 and formic acid in benzene by azetotropic distillation. The formamide was purified by column chromatography: \([\alpha]_20^D\) +7.7° (c 0.7, chloroform); IR (KBrs) 1860 (CO), 1440 (PPh) cm\(^{-1}\); \(\delta\) H NMR (CDCl_3) \(\delta\) 7.5-7.9 (m, 10 H, aromatic H), 3.5 (m, 2 H, CH), 2.8 (m, 1 H, CHP), 1.35 (m, 3 H, CH_3); 13C NMR (CDCl_3) \(\delta\) 132.32, 132.27 130.94, 130.75, 129.11, 129.78 (aromatic C), 43.36 (CH_3N), 33.42 (CHP), 11.12 (CH_3), no signal for the isocyanate carbon atom was observed; \(\delta^2\) NMR (CD_3OD/THF) \(\delta\) +28.6.

POLY[S]-(1-ethyl-2-propenyl)iminomethylen) (3h). Iso- cyanide 2h was polymerized with 0.4 mol % of NiCl_2&H_2O in methanol. The yellow, static polymer was obtained in 80% yield: \(\eta = 0.064 \text{DL/g}^{\text{c}}\) (chloroform, 30.00 °C), \([\alpha]_22^D\) +29° (c 0.2, chloroform); IR (KBrs) 3090, 1658, 990, 925 (CH=CH), 2141 (NC cm\(^{-1}\); \(\delta\) H NMR (CDCl_3) \(\delta\) 5.55-5.95 (m, 1 H, \(-CH=\)), 5.2-5.5 (m, 2 H, \(-CH=\)), 4.10 (m, 1 H, CH), 1.65 (m, 2 H, CH_2), 1.02 (t, 3 H, CH_3).

Poly[S]-(1-ethyl-2-propenyl)iminomethylen) (3h). Iso-

\([\alpha]_20^D\) +8.69° (c 1.4, chloroform); \(\delta\) H NMR (CDCl_3) \(\delta\) 7.3 (m, 10 H, aromatic H), 3.15 and 3.79 (\(\delta_{gem}\) = 13.8 Hz, 2 d, 4 H, NCH_2), 3.25 and 3.48 (J = 5.1 and 9.1 Hz, \(\delta_{gem}\) = 13.5 Hz, 2 H, CH_2O), 3.1 (s, 1 H, OH), 3.0 (s, 1 H, OH), 1.0 (s, 9 H, 

This compound was synthesized from 17a: \(\delta\) 13.4 Hz, dd, 3 H, CH_3); \(\delta\) 13.2 Hz, dd, 3 H, CH_3); the off-resonance spectrum confirmed this assignment; \(\delta^2\) NMR (CD_2D) \(\delta\) -5.6.

The hydrophosphor hydroxide was converted into the phosphine oxide hydroxide chloride with 1.1 equiv of HCl in ethanol at 0 °C. The product was crystallized from ethanol; \([\alpha]_20^D\) -26.6° (c 0.7, chloroform). The amine was liberated from its HCl salt by treatment of a chloroform solution of this compound with NH_3 gas. Compound 13 had the following: \(\delta\) H NMR (CDCl_3) 7.7-7.2 (m, 20 H, aromatic H), 3.3 and 3.7 (J = 13.8 Hz, 2 d, 4 H, CH_2Ar), 2.3-2.8 (m, 3 H, CHCH_2N), 1.15 (J = 6.5 Hz, J\(^{H-H}\) = 17 Hz, dd, 3 H, CH_3); \(\delta^2\) NMR (CD_3OD/EtOH) \(\delta\) +3.10. Poly[S]-(1-diphenylphosphinyl)propylamine (14). This amine was obtained after debenzylation of 13-HCl in acidic ethanol using Pd/C as a catalyst. The product was purified by column chromatography over silica gel using CHC_3 and CHCl_3/CH_3OH (5:1 (v/v)) as eluents: \([\alpha]_20^D\) +28.0° (c 0.7, chloroform); \(\delta\) H NMR (CDCl_3) \(\delta\) 7.5-8.0 (m, 10 H, aromatic H), 3.0 (m, 2 H, CH_2N), 2.5 (m, 1 H, CHP), 1.83 (s, 2 H, NH), 1.18 (s, 3 H, CH_3).

Poly[S]-(2-diphenylphosphinyl)propyl isocyanide (2i). Iso-

This compound was obtained in 94% yield from 14 and formic acid in benzene by azetotropic distillation. The formamide was purified by column chromatography: \([\alpha]_20^D\) +7.7° (c 0.7, chloroform); IR (KBrs) 1860 (CO), 1440 (PPh) cm\(^{-1}\); \(\delta\) H NMR (CDCl_3) \(\delta\) 7.8-7.9 (m, 10 H, aromatic H), 3.5 (m, 2 H, CH), 2.8 (m, 1 H, CHP), 1.35 (m, 3 H, CH_3); 13C NMR (CDCl_3) \(\delta\) 132.32, 132.27 130.94, 130.75, 129.11, 129.78 (aromatic C), 43.36 (CH_3N), 33.42 (CHP), 11.12 (CH_3), no signal for the isocyanate carbon atom was observed; \(\delta^2\) NMR (CD_3OD/THF) \(\delta\) +28.6.

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References and Notes

(13) Part of this work has been published as a Note: Beijin, A. J. M. van; Nolte, R. J. M.; Zwikker, J. W.; Drenth, W. J. Mol. Catal. 1981, 11, 343.
(17) The structure of this compound was proven by spectroscopic techniques and a single-crystal X-ray analysis. Apparently, no rearrangement takes place when pyridine is the nucleophile.