in the spectrum of the reaction mixture having reacted
overnight (see above), are assigned to the N—CH₃ and the
H—C= signals of 9 (R¹ = H), respectively. This was
confirmed when after an overnight reaction the ¹H-NMR
spectra of the solutions of 1b, 1c and 1d in N₂D₄-D₂O were
measured. In the case of 1c and 1d in the low field region a
peak is observed between δ 7.03-7.09 i.e. the HC= in 9
(R¹ = H) where in the case of 1b this low-field singlet is
absent but a peak is observed in the high field region at δ 1.87
i.e. the CH₃ in 9 (R¹ = CH₃) ¹³.

The three pyrazoles 8b, 8c and 8d which were isolated from
the analogous reaction of the pyrimidinium salts 1b, 1c
and 1d, are all deuterated at position 4. It was observed that
the 3,5-dimethyl-4-D-pyrazole (8c) also contains deuterium
in the methyl group as proved by the presence of peaks at
m/e = M, M + 1, M + 2, M + 3, M + 4 and M + 5 in the mass
spectrum. Apparently, in the open-chain compounds 3, 4
and 5 the methyl group participates in the
tautomerism since the alternative possibility — a H/D ex­
techange in the methyl group of 3,5-dimethyl-4-D-pyrazole
— does not take place under these mild conditions.

Experimental part
The ¹H-NMR spectra were recorded on a Jeol JNM-C60 H spectro­
meter, using TMS (δ = 0) as internal standard. In the case of adduct
measurements the apparatus was equipped with a JES-VT-3
variable temperature controller. Measurements of D contents were
conducted on an AEI-MS 902 mass spectrometer.

Preparation of the starting materials
1-Methylpyrimidinium iodide (1a), 1,2-dimethylpyrimidinium
iodide (1b), 1,4,6-trimethylpyrimidinium iodide (1c) and 4-
phenyl-1-methylpyrimidinium iodide (1d) were prepared as
described in the literature.

General procedure for measuring the ¹H-NMR spectra in N₂D₄-D₂O
To 50 mg of the quantemized compound 1 being cooled at ~ -30°,
about 0.5 ml of precooled (~ -30°) deuterated hydrazine hydrate
(Merck, 80% N₂D₄-D₂O, deuteration ratio >99%) was added.
A yellow-orange coloured solution was obtained. TMS was added
as internal standard. A sample of this solution was introduced in a
¹H-NMR tube being cooled at ~ -30°. The measurements started
10-15 min after addition.
The pyrazoles 8a-d being obtained in the hydrazinolysis were
isolated as described previously ³.

Acknowledgement
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Drs. C. A. Landheer for measuring the mass spectra.

Polym(aminomethylene), 7¹1. Synthesis of diphenylphosphine-substituted
dipoly[(1-phenylethyl)iminomethylene]

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Abstract. Polymer-anchored phosphine functions were obtained in two ways: by diphenylphosphina­tion
of poly[(1-4-bromophenylethyl)iminomethylene] and by polymerization of 1-[4(diphenyl­
phosphino)phenyl]-1-isocyanoethane. The synthesis of the monomers and polymers is described.

Introduction
Many efforts have been made at anchoring homogeneous
catalysts on insoluble supports. For this purpose materials
like silica ² and polystyrene ³,⁴ have frequently been used.
This immobilization of a catalyst sometimes diminishes
side-reactions ⁵ and extends its lifetime.
The anchoring of homogeneous catalysts on the usual types of
polymeric supports suffers from a number of disadvantages.
In most cases the secondary structure of the polymers
and the surroundings of the catalytic centres are unknown.
Often, the accessibility of the complex is reduced, giving rise
or lower activities.° The degree of introduction of phos­
phine groups, often used as interfaces between polymer and
metal ion, appears to be low: 1 per 3-20 polymer side
chains.° Moreover, the polymers usually contain some

¹ Part 6: R. J. M. Nolte, J. A. J. van Zomeren and J. W. Zwikkcr,
submitted for publication.
² K. G. Allum, R. D. Hancock, I. V. Howell, S. McKenzie, R. C.
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⁴ K. G. Allum, R. D. Hancock, I. V. Howell, R. C. Pitkethly and
Fr. 1163 and 1168 (1976).
(1976).
residual chlorine or bromine. In earlier papers Millich\textsuperscript{9} and we\textsuperscript{10,11} showed that poly(iminomethylenes) have the configuration of a tightly coiled helix with side-chains protruding from a rodlike main chain. This property gives poly(iminomethylenes) major advantages for catalyst attachment: the catalytic centres are more accessible and the secondary structure is more uniform and better defined. The chirality of the main chain might be attractive for asymmetric catalysis.

In this paper we describe the synthesis of two types of triphenylphosphine containing poly(iminomethylenes). The first type was made by diphenylphosphination of poly-[1-(4-bromo-phenyl)ethyl]iminomethylene. The second type was synthesized by polymerization of a triphenylphosphine containing isocyanide. Applications of these polymers in catalysis will be described in subsequent papers of this series.

Results and discussion

Millich has described the synthesis of 1-phenylethyl isocyanide and its polymerization by means of an acid-coated glass catalyst\textsuperscript{12}. We have synthesized 1-(4-bromophenyl)-ethyl isocyanide, (3), in an analogous way starting from 4-bromoacetophenone (Scheme 1). Polymerization of 3 was accomplished by nickel chloride\textsuperscript{13}. The intrinsic viscosity of the polymer obtained, (4), was 0.31 dl/g. If we use the values of the Mark-Houwink constants determined for poly[1-(phenylethyl)iminomethylene]\textsuperscript{14} to estimate the molecular weight, a value of 40,000 is calculated. The introduction of diphenylphosphine functions into the secondary structure is more uniform and better defined. The effect of the reaction conditions on the degree of attachment: the catalytic centres are more accessible and the side groups in poly(iminomethylene) have the conformation, 50\%, was obtained in a yield of 75-85\% by dehydration of 9 using either phosphoryl chloride\textsuperscript{16} or perchloromethyleneformate\textsuperscript{17}, both in combination with triethylamine. Direct synthesis of 10 from isocyanide 3 by reaction with butylthiolium and chlorodiphenylphosphine gave unsatisfactory results. The pale-yellow crystals of 10 were moderately soluble in ethanol and diethyl ether, and soluble in tetrahydrofuran, acetone, chloroform and dichloromethane. In chlorinated hydrocarbons slow decomposition was observed. In the infrared spectrum of 10 strong absorptions were visible at 1417 cm\textsuperscript{-1} indicative of the isocyanide and phenylphosphine functions. The structures of 10 and its precursors 8 and 9 were supported by elemental analysis, H\textsuperscript{1}, 13C-, 31P-NMR and mass spectrometry.

Table 1 Lithiation of polymer 4 and coupling with chlorodiphenylphosphine.

<table>
<thead>
<tr>
<th>Polymer\textsuperscript{a}</th>
<th>Polymer composition\textsuperscript{b}</th>
<th>% Lithiation</th>
<th>% Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>m = 0.62, n = 0.21, o = 0.17</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>5b</td>
<td>m = 0.40, n = 0.11, o = 0.49</td>
<td>90</td>
<td>55</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions 5a: 1.3 eq. BuLi, reaction time 2 h; 3.2 eq. Ph\textsubscript{2}PCl, reaction time 4 h; 5b: 2.1 eq. BuLi, reaction time 3 h; 7.2 eq. Ph\textsubscript{2}PCl, reaction time 96 h.

\textsuperscript{b} m, n and o are the fractions of unsubstituted, bromine substituted and phosphine substituted phenyl groups, respectively.

Just like functionalized polystyrene resins, polymer 5 suffers from two disadvantages: the distribution of phosphorus over the polymer chain is unknown and the presence of bromine can affect the behaviour of the support, e.g. by quaternization of phosphine with a possibility of cross-linking\textsuperscript{3}. Therefore, we decided to synthesize also a poly-(iminomethylene) with a phosphine function in each repeating unit (Scheme 2).

\[\text{Scheme 2}\]

Protection of the carbonyl function in 4-bromoacetophenone, 1, by 1,2-ethanediol gave the acetal 6. Its product of lithiation can be used as a synthon for coupling with many types of reagent. Reaction of this synthon with chlorodiphenylphosphine gave the substituted triphenylphosphine 7. This compound was hydrolyzed to give 8 which was directly converted to 1-[(1-4(diphenylphosphinopheno)phenyl]ethyl]amine, 9, via a Leuckart synthesis\textsuperscript{15}. Initial attempts to synthesize 9 through reaction of the Grignard or lithium derivative of 2 with chlorodiphenylphosphine failed. The isocyanate 10 was obtained in a yield of 75-85\% by dehydration of 9 using either phosphoryl chloride\textsuperscript{16} or perchloromethyleneformate\textsuperscript{17}, both in combination with triethylamine. Direct synthesis of 10 from isocyanide 3 by reaction with butylthiolium and chlorodiphenylphosphine gave unsatisfactory results.

weight in the range of 5,000–10,000. Usually, a molecular weight of 40,000–50,000 is found after polymerization of other isocyanides under these conditions. The lower values found for 11 might result from steric hindrance of polymerization by the bulky triphenylphosphine group.

Experimental part

Proton NMR spectra were obtained on Varian EM 360 and EM 390 spectrometers. The 13C- and 31P-spectra were recorded on a Varian CFT 20 and a Bruker WH 90 spectrometer, respectively. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Organic Chemistry TNO under supervision of W. J. Bais. NMR chemical shifts, δ, are given in ppm downfield from internal tetramethylsilane, unless otherwise stated. Abbreviations used are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and dist = distorted. All solvents and reagents were dried and distilled under a nitrogen atmosphere. Chlorodiphenylphosphine and butyllithium (1.5 mol/l in hexane) were purchased from Aldrich. All phosphorus-containing compounds were handled under rigorous exclusion of oxygen.

4-Bromoacetophenone (1) was synthesized as 82% yield in accordance with the literature. H-NMR (CCl4): δ 2.50 (s, 3H, CH3), 7.50 and 7.75 (2 x d, 4H, arom.). N-Formyl-[l-(4-bromophenyl)ethyl]amine (2) was obtained from 1 and ammonium formate. Yield 82%: b.p. 156–160° (0.6 mm); H-NMR (CDCl3): δ 1.40 (d, 3H, CH3), 5.05 (m, 1H, CH), 7.15 and 7.45 (2 x d, 4H, arom.). 1-(4-Bromophenyl)ethyl isocyanide (3). An amount of 30 g (0.13 mol) of 2 in 220 ml of dichloromethane and 88 ml of triethylamine was treated with 13.5 ml (0.15 mol) of phosphor chloride as described by Ugi and Millich for a similar compound. After work up and distillation in vacuo, 23 g (83%) of 3 were obtained: b.p. 95–98° (0.9 mm); IR (neat): 2140 cm–1 (ν=). H-NMR (CDCl3): δ 1.60 (d, 3H, CH3), 4.70 (q, 1H, CH), 7.10 and 7.40 (2 x d, 4H, arom.).

Poly[[(1-(4-bromophenyl)ethyl]iminomethylene] (4). A mixture of 4 g (20 mmol) of 3 and 7 mg (0.03 mmol) of nickel chloride hexa-hydrate was kept at 5° for one month. The resulting solid was dissolved in benzene and poured into a hundredfold excess of methanol/water (9:1, v/v). The precipitate was collected by filtration and dried over P2O5 at 50° (12 mm); yield 3.2 g (80%) of yellow-orange 4. As indicated by elemental analysis our sample of 4 contained some residual benzene: [%CH2Br(NH)(CH2)6OH], (216.3); calc. C 52.63, H 3.95, Br 36.94, N 6.48; found C 52.78, H 3.93, Br 36.81, N 6.48; [n] = 0.31 d/lg (THF, 30°); IR (KB): 1629 cm–1 (N=C); 1H-NMR (CDCl3): δ 0.9 and 1.3 (2J = 6.0 Hz, br, 3H, CH3), 5.0 (very br, 1H, CH), 6.7 (νC=O, 90 Hz, br, 4H, arom.).

Table II 13C chemical shifts and 13C-31P coupling constants of compounds 8, 9 and 10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cδ</th>
<th>Cγ</th>
<th>Cβ</th>
<th>Cα</th>
<th>C8</th>
<th>C9</th>
<th>C10</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>21.23</td>
<td>24.95</td>
<td>134.78</td>
<td>106.16</td>
<td>134.49</td>
<td>135.50</td>
<td>134.67</td>
</tr>
<tr>
<td>9</td>
<td>21.23</td>
<td>24.95</td>
<td>134.78</td>
<td>106.16</td>
<td>134.49</td>
<td>135.50</td>
<td>134.67</td>
</tr>
<tr>
<td>10</td>
<td>21.23</td>
<td>24.95</td>
<td>134.78</td>
<td>106.16</td>
<td>134.49</td>
<td>135.50</td>
<td>134.67</td>
</tr>
</tbody>
</table>

a The chemical shifts are in ppm relative to tetramethylsilane; the 13C-31P coupling constants are in Hz.

b The numbering of the carbon atoms is as follows: \[
\begin{array}{c}
\text{13C} \\
\Downarrow \\
\text{C}^\gamma \\
\Downarrow \\
\text{C}^\beta \\
\Downarrow \\
\text{C}^\alpha \\
\Downarrow \\
\text{C}^8 \\
\Downarrow \\
\text{C}^9 \\
\Downarrow \\
\text{C}^{10}
\end{array}
\]


2 ml of water. This mixture was shaken for 30 minutes, water was added and the solution was decanted and the content concentrated. Crystallization from ethanol afforded 0.38 g (80 %) of 8; m.p. 106-108°C; IR (KBr): 3480, 2960, 2870, 1720, 1650, 1450, 1410, 1240, 1160 and 1080 cm⁻¹; ¹H-NMR (CDCl₃): δ 7.2 (br, 14H, arom.), 7.1 (t, 3H, CH₃), 7.0 and 7.40 (br, 14H). For the ¹³C-NMR spectrum see Table II.

N-Formyl[l-[4-(diphenylphosphino)phenyl]ethyl]amine (9). This formamide was synthesized from 7 via a Leuckart synthesis. To 34.8 g (0.10 mol) of 7 were added, 100 ml of formamide, 25 ml of formic acid and 2 ml of water. This mixture was kept overnight; the solution was heated to 180-190°C and at regular intervals 20 ml portions of formic acid were added and water was distilled off. In this way 10 portions were added during 25 hours of heating. This procedure was followed by addition of two portions of 25 ml of toluene at a temperature of 200°C. After cooling, the solution was poured into 400 ml of water/diethyl ether/THF (1:1:1 v/v). The solution was heated to 180-190°C and at regular intervals 20 ml portions of formic acid were added and water was distilled off. The latter aqueous layers were extracted once with ether. The combined ether/THF solutions were concentrated in vacuo (50°, 0.1 mm) to give 29 g (85 %) of a white solid, 9, which was used without further purification for the synthesis of the isocyanide 10.

An amount of 13 g of 9 was recrystallized from ethanol. After drying in vacuo (0.1 mm) over P₂O₅, 9.1 g of white crystals resulted; m.p. 123.5-124.5°C; (C₂H₅₂OP)₃ (333.2); calc. C 78.80, H 6.06, N 4.26, P 9.29; found C 78.53, H 6.07, N 4.27, P 9.30. To 4.25 g (0.05 mol) of 9 and 10.5 (0.10 mol) of 4 were added 10 ml of DMSO and a solution of 6.5 g (0.05 mol) of 11 in 50 ml of methanol. This mixture was stirred rapidly. The resulting suspension was centrifuged; after decantation of the supernatant liquid the solid was twice suspended in methanol and isolated by centrifugation. Drying in vacuo (30°, 0.01 mm) afforded 1.65 g (70%) of polymer 11 as a light yellow powder. It was dissolved in 10 ml of THF, fractionated over a deactivated silica column and eluted with THF/ethanol (1:1, v/v); yield 1.60 g. The first fraction (1.50 g) was dissolved in 10 ml of THF and added drop by drop to 200 ml of pure methanol, which was stirred rapidly. The resulting suspension was centrifuged and the supernatant liquid decanted. After drying in vacuo (35°C, 0.05 mm) 1.19 g of 11 was collected; [η] = 0.04 dl/g (toluene, 30.0°C); (C₂H₅₂OP)₃ (315.3); calc. C 79.98, H 5.75, N 4.44, P 9.82; found C 79.53, H 6.12, N 4.47, P 9.70, no oxygen or nickel could be detected (<0.2%); IR (KBr): 3480-2960 (mono- and disubst. arom.), 1720, 1650 (C=O), 1450, 1410, 1240, 1160 and 1080 cm⁻¹; ¹H-NMR (CDCl₃): δ 0.8-1.8 (Av 30 Hz, br, 3H, CH₃), 4.5-5.7 (very br, 1H, CH), 6.3-8.0 (Av 22 Hz, br, 14H); ¹³C-NMR (CDCl₃): δ 4.6 (Av, 50 Hz, br), 36 (Av 75 Hz, br, intensity is 1/6 of main peak) ppm (relative to 85% H₃PO₄); the occurrence of the latter peak is neither due to the presence of triphenylphosphine oxide moieties nor due to the result of complexation of phosphate functions to nickel chloride as was shown in separate experiments.

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