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. 11,12 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 further 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 exchange 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-C60H spectro­meter, 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 carried out 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 quaternized compound 1 being cooled at −30°C, about 0.5 ml of precooled (−30°C) 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°C. The measurements started 10–15 min after addition.

The pyrazoles 8a–d being obtained in the hydrazinolysis were isolated as described previously.

Acknowledgement

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Polym(iminomethylene), 71. Synthesis of diphenylphosphine-substituted poly[(1-phenylethyl)iminomethylene]

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Abstract. Polymer-anchored phosphine functions were obtained in two ways: by diphenylphosphinilation of poly[(1-4-bromophenylethyl)iminomethylene] and by polymerization of 1-[4(diphenylphosphino)phenyl]-1-isocyanooethane. 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 and polystyrene have frequently been used. This immobilization of a catalyst sometimes diminishes side-reactions 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 complexes is reduced, giving rise to lower activities. The degree of introduction of phosphine 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...
residual chlorine or bromine. In earlier papers Millich\cite{10,11} and we\cite{10,11} showed that poly(mimonomethylenes) have the configuration of a tightly coiled helix with side-chains protruding from a rodlike main chain. This property gives poly(mimonomethylenes) 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(mimonomethylenes). 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\cite{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\cite{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]\cite{14} to estimate the molecular weight, a value of 40,000 is calculated.

The introduction of diphenylphosphine functions into polymer 4 was realized through lithiation with butyllithium and subsequent coupling with chlorodiphenylphosphine. The effect of the reaction conditions on the degree of exchange of bromine in 4 was determined from the elemental analysis (Table I). The highest degree of functionalization, 50 %, was obtained in 5b. This value is appreciably higher than most of the values reported for polystyrene resins\cite{7,8}. An explanation for this difference could be the better accessibility of the side groups in poly(mimonomethylenes).

Table I  Lithiation of polymer 4 and coupling with chlorodiphenylphosphine.

<table>
<thead>
<tr>
<th>Polymer (a)</th>
<th>Polymer composition (b)</th>
<th>% Lithiation</th>
<th>% Coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>0.62 0.21 0.17</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>5b</td>
<td>0.40 0.11 0.49</td>
<td>90</td>
<td>55</td>
</tr>
</tbody>
</table>

\(a\) Reaction conditions 5a: 1.3 eq. BuLi, reaction time 2 h; 3.2 eq. Ph\(_2\)PCl, reaction time 4 h; 5b: 2.1 eq. BuLi, reaction time 3 h; 7.2 eq. Ph\(_2\)PCl, reaction time 96 h.

\(b\) \(m, n\) 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\cite{3}. Therefore, we decided to synthesize also a poly(mimonomethylene) with a phosphine function in each repeating unit (Scheme 2).

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 N-formyl[1-(4-diphenylphosphino)phenyl]ethyl]amine, 9, via a Leuckart synthesis\cite{15}. Initial attempts to synthesize 9 through reaction of the Grignard or lithium derivative of 2 with chlorodiphenylphosphine failed. The isocyanide 10 was obtained in a yield of 75-85 % by dehydration of 9 using either phosphoryl chloride\cite{16} or perchlormethyl formate\cite{17}, both in combination with triethylamine. Direct synthesis of 10 from isocyanide 3 by reaction with butyllithium 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 2142 and 1430 \(\text{cm}^{-1}\) indicative of the isocyanide and phenylphosphine functions. The structures of 10 and its precursors 8 and 9 were supported by elemental analysis, \(\text{H}^\text{1}, \text{C}^{13}, P\text{NMR}\) and mass spectrometry.

The isocyanide 10 was readily polymerized by treatment with nickel chloride. After isolation and fractionation, polymer 11 was obtained as a light yellow powder. The polymer was soluble in tetrahydrofuran, chloroform, benzene and toluene, and insoluble in the lower alcohols. The intrinsic viscosity of 11 was dependent on the amount of catalyst used: 5 mol % nickel chloride gave a polymer with \([\eta]\) = 0.02 dl/g. Lowering the amount of catalyst to 0.5 mol % increased this value to \([\eta]\) = 0.04 dl/g. Applying the Mark-Houwink equation as determined for poly(1-phenylethyliminomethylene), one calculates a molecular weight of 40,000.
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. Buis. NMR chemical shifts, δ, are given in ppm downfield from internal tetramethylsilane, unless otherwise stated.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cδ^1</th>
<th>Cδ^3</th>
<th>Cδ^5</th>
<th>Cδ^6</th>
<th>Cδ^8</th>
<th>Cδ^9</th>
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<tbody>
<tr>
<td>8</td>
<td>26.56</td>
<td>194.31</td>
<td>136.78</td>
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<td>134.22</td>
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</tr>
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<td>10</td>
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<td>53.44</td>
<td>138.84</td>
<td>125.46</td>
<td>134.11</td>
<td>137.21</td>
<td>136.67</td>
</tr>
</tbody>
</table>

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

Poly[(1-(4-bromophenyl)ethyl]iminomethylene] (4). A mixture of 4 g (0.13 mol) of 3 and 7 mg (0.03 mmol) of nickel chloride hexahydrate was added to 3 ml of benzene and poured into an excess of ether. A light-brown solid was obtained which was repeatedly extracted with ethanol. The residue was dissolved in tetrahydrofuran and added drop by drop to a hundredfold excess of ether. Collecting the solid and drying in vacuo afforded 3.2 g of creamish brown 5b. The calculated composition of 5b is given in Table I. It was based on the elemental analysis: C 73.80, H 6.23, Br 3.68, P 6.61; IR (KBr): 2000–1700 (mono- and disubst. arom.), 1620 (N=C), 1435 (P—Ph), 825 (disubst. arom.), 730 and 690 (monosubst. arom., C=Br) cm\(^{-1}\).

Polymer 5a was obtained in a similar way from 0.5 g (2.3 mmol) of 4, 3.1 mmol of butyllithium and 1.6 g (7.25 mmol) of chlorodiphenylphosphine. The reaction time for lithiation was two hours and for coupling with chlorodiphenylphosphine four hours. The calculated composition of 5a is given in Table I. It was based on: C 67.38, H 6.22, Br 9.54, P 2.90.

Acetal of 4-bromoacetophenone (6). This acetal was synthesized from 4-bromoacetophenone, 1, in a way similar to that described by Eliel. In 500 ml of benzene or toluene 199 g (1 mol) of 1, 68 g (1.2 mol) of 1,2-ethanediol and 0.01 g of 4-toluenesulfonic acid were dissolved and water was removed by azeotropic distillation for 30 h. After work up and drying over K₂CO₃, benzene was removed by distillation and the residue was distilled in vacuo; yield 75–85%; b.p. 88–90° (0.6 mm), or 134–136°C (28 mm); 1H-NMR (CDCl₃): δ 1.50 (s, 3H, CH₃), 3.60 and 4.00 (2 x m, 4H, CH₂—CH₂), 7.30 (4, 4H, arom.).

Acetal of 4-(diphenylphosphino)acetophenone (7). To 57 g (0.25 mol) of 6 in 200 ml of dry ether was added 200 ml (0.3 mol) of butyllithium in hexane at a temperature of −5° during two hours. The solution was stirred for another two hours at 0–5°, during which time a white precipitate was formed. At a temperature of −15°, 66 g (0.3 mol) of chlorodiphenylphosphine in 150 ml of dry ether were added during 30 minutes. The white precipitate disappeared and the solution became yellow. The reaction mixture was kept overnight at a temperature of 0–10°; 200 ml of satd. NH₄Cl solution was added and the organic layer separated. The aqueous layer was extracted with ether, the combined etheral layers were washed twice with small portions of water and dried over K₂CO₃; yield 74 g (85%) of 7. The product contained 4% of β-butyldiphenylphosphine. If HCl is used instead of NH₄Cl during work up, or when 7 is recrystallized from ethanol, part of the acetal function is hydrolysed. 1H-NMR (CDCl₃): δ 1.50 (s, 3H, CH₃), 3.60 and 3.90 (2 x m, 4H, CH₂—CH₂), 7.4 (br, 4H, arom.).

4-(Diphenylphosphino)acetophenone (8). To a small portion of 7 (0.54 g) were added 0.5 ml of formic acid, 0.5 ml of chloroform and 0.5 ml of acetic anhydride. The mixture was stirred for three hours. Subsequently, 18 ml (0.10 mol) of chlorodiphenylphosphine were added and stirring was continued for four days at room temperature; during this time the precipitate dissolved. After addition of 200 ml of satd. NH₄Cl solution, the organic layer was separated, washed and concentrated in vacuo. The resulting oil was dissolved in aceton and poured into an excess of ether. A light-brown solid was obtained which was repeatedly extracted with ethanol. The residue was dissolved in tetrahydrofuran and added drop by drop to a hundredfold excess of ether. Collecting the solid and drying in vacuo afforded 3.2 g of creamish brown 5b.
2 ml of water. This mixture was shaken for 30 minutes, water was decanted and the solution was concentrated. Crystallization from ethanol afforded 0.38 g (80%) of 8; m.p. 106-108°; IR (KBr): 3292, 1750 (C=O), 1600 (arom.), 1425 and 1370 (CH3) cm⁻¹; 'H-NMR (CDCl3): δ 2.00-1.70 (mono- and disubst. arom.), 1.68 (s, 1H, CH), 7.30 and 7.40 (br, 14H, arom.). For the 13C-NMR spectrum see Table II.

N-Formyl[1-[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° and at regular intervals 20 ml of a 7.5% NaHCO3 solution was added. The aqueous layers were decanted and the solution concentrated. Crystallization from cold water and with 75 ml of a 7.5% NaHCO3 solution. The dilute solution was heated to 180-190° and at regular intervals 20 ml of a 7.5% NaHCO3 solution was added. This mixture was shaken for 30 minutes, 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°. After cooling, the solution was poured into 400 ml of water/diethyl ether/THF (1:1:1 v/v). The aqueous layer was extracted 4 times with 150 ml ether/THF (1:1 v/v); the combined organic layers were washed 3 times with a 1% Na2CO3 solution and 3 times with water. The latter aqueous layers were extracted once with ether. The combined ether/THF solutions were dried over MgSO4. After filtration the solution was 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, 91 g of white crystals resulted; m.p. 125.3-124.5°; C21H20NOP (333.3); calc. C 79.98, H 5.75, N 4.26, P 9.18; found C 79.53, H 6.10, N 4.47, P 9.07. For the 13C-NMR spectrum see Table II.

1-[4-(Diphenylphosphino)phenyl]-1-isocyanooctane (10). The isocyanide 10 was obtained from 9 in two ways. The first method was analogous to the synthesis of 3; yield 70%. The second method used perchloromethyl formate: to 16.6 g (0.05 mol) of 9 and 10.7 g (0.01 mol) of triethylamine in 50 ml of dichloromethane were added 4.85 g (0.025 mol) of perchloromethyl formate in 30 ml of dichloromethane at a temperature of -10° during one hour. Stirring was continued for one hour while the temperature was allowed to rise to 20°. The solution was rapidly washed with 50 ml of cold water and with 75 ml of a 7.5% NaHCO3 solution. The dichloromethane solution was rapidly concentrated in vacuo (20°, 10 mm) and the residue dissolved in THF. This solution was dried over molsieve 4A, filtered and concentrated in vacuo (20°, 1 mm). The yield was 12.9 g (82%) of a yellow-brown solid. The solid was crystallized from ethanol (highest temp. 35°). The light yellow crystals were dried in vacuo (20°, 0.03 mm); m.p. 84.0-85.3°.

According to elemental analysis the crystals contained ethanol: C21H18NOP (315.3); calc. C 78.80, H 6.06, N 4.26, P 9.41; found C 78.62, H 6.04, N 4.41, P 9.35. For the 13C-NMR spectrum see Table II.

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