PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/16270

Please be advised that this information was generated on 2017-07-16 and may be subject to change.
Dry, degassed 1-halopropane-\( _{-1}^{13} \text{C} \) (0.63 g, 0.0049 mol) was introduced by syringe. The reactant mixture was stirred at room temperature for 14 h, by which time it had turned purple and developed a large amount of finely divided gray solid. The solution was centrifuged and the supernatant liquid transferred by syringe for modified Gilman titration, purification procedures on the vacuum line, and NMR investigation. Modified Gilman titration showed 92% conversion to propyllithium with <2% alkoxide present.

All propyllithium samples were evacuated to a solid on the vacuum line to remove unreacted halide and coupling products. In certain cases propyllithium was distilled across an inverted Y-shaped lube protected by a straight-bore stopcock. Pure cyclopentane was distilled into the receiver side of the Y and this solution transferred via syringe to the 8-mm NMR tube, protected by a straight-bore stopcock. This assembly was transferred to the vacuum line, and the solution degassed by four freeze-thaw cycles and then sealed off.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE76-10909A02.

References and Notes

(1) (a) The Ohio State University, (b) Eastman Kodak.

31P Nuclear Magnetic Resonance Studies of Polymer-Anchored Rhodium(I) Complexes

Aart J. Naaktgeboren, Roeland J. M. Nolte, and Wiendelt Drenth*

Contribution from the Department of Organic Chemistry of the University, 3522 AD Utrecht, The Netherlands. Received April 18, 1979

Abstract: Poly(4-diphenylphosphinostyrene) (1), poly(4-dicyclohexylphosphinostyrene) (2), and poly[1-(4-diphenylphosphinophenyl)ethyliminomethylene] (3) were obtained by polymerization of the corresponding monomers. The polymers were treated with (RhCl\( _2 \))\( _2 \) and with (RhCl\( _2 \)), where L and L' are ethene and 1,5-cyclooctadiene, respectively. These complexes were added stepwise and during this process the \( ^{31} \text{P} \) NMR spectra were observed. \( ^{31} \text{P} \) chemical shifts and \( ^{103} \text{Rh} \)\( ^{31} \text{P} \) coupling constants were compared with those of monomeric analogues which were treated in the same way.

Recently, considerable interest has been shown in the anchoring of homogeneous catalysts to organic polymers.\(^{1,2}\) For instance, polymer-bound rhodium complexes have been synthesized and used as hydrogenation catalysts. Apart from a recent EXAFS study\(^3\) concerning the catalytic site of the polymer-bound Wilkinson catalyst, there has been hardly any other study relating to characterization of anchored catalysts.

It has been shown that \( ^{31} \text{P} \) NMR can help to elucidate the structures of metal–phosphine complexes.\(^4\) Both the \( ^{31} \text{P} \) chemical shift and the metal–phosphorus coupling constant can provide information concerning the stereochemistry of these complexes and their coordination number.

Grubbs et al.\(^5\) have tried to use \( ^{31} \text{P} \) NMR as a tool for studying polymer-supported rhodium complexes, but failed to observe any signals of coordinated phosphines. They attributed this failure to increased relaxation times due to complexation of the phosphine to the metal center. We consider this explanation to be less likely, because without rhodium the phosphine in polystyrenes gives a clear \( ^{31} \text{P} \) NMR signal\(^6,7\) and therefore will have normal relaxation time, while coupling to rhodium is expected to decrease rather than increase the relaxation time.\(^8\)

So far,\(^2\) nearly all supports used to anchor homogeneous catalysts have a low phosphorus content and phosphine is unevenly distributed over the polymer chain. This is very unfavorable for a \( ^{31} \text{P} \) NMR study because the signal strength is low and appreciable variations occur in the environment of the phosphine. Poly(4-diphenylphosphinostyrene) (1), poly(4-dicyclohexylphosphinostyrene) (2), and poly[1-(4-diphenylphosphinophenyl)ethyliminomethylene] (3) were obtained by polymerization of their phosphine-containing monomers. Polymers 1 and 2 will have a more or less random structure of the phosphine groups along the polymer backbone, while the phosphine group is more or less evenly distributed over the polymer chain.
coil structure, whereas polymer 3 will have a rigid rod structure.9

Addition of [RhCl(COD)]2 and [RhCl(C2H4)2]2, where COD = 1,5-cyclooctadiene, to polymers 1-3 gives rise to polymer rhodium complexes which are active hydrogenation catalysts.10 This paper is concerned with the 31P NMR spectra of these complexes.

Results

Addition of solutions of [RhCl(COD)]2 or [RhCl(C2H4)2]2 in THF to solutions of the polymers in the same solvent gave suspensions of polymer rhodium complexes which were insoluble not only in THF, but also in benzene, alcohol, etc. In general, short centrifugation of the suspensions afforded the polymer rhodium complex quantitatively; only traces of non-volatile matter remained in the supernatant.

We recorded 31P NMR spectra in sealed tubes under a nitrogen atmosphere. When a 31P spectrum was taken of the clear and homogeneous supernatant, the signals were very much weaker than those of the freshly prepared suspensions. Thus, the signals of the polymer complex suspensions are almost entirely of the insoluble material. After mixing, two spectra were recorded: a survey spectrum with an accumulation time of 0.5-1 h and a final one with an accumulation time of 8-24 h. The survey spectrum was essentially different from the final spectrum. Apparently, it took 0.5-1 h for ligand exchange to reach equilibrium. The final spectrum was used to derive the 31P parameters. This spectrum required a long accumulation time because of the bad signal to noise ratio.

When [RhCl(COD)]2 was added stepwise to polymers 1-3, the 31P NMR spectrum consisted of a doublet of phosphine coordinated to rhodium at approximately +30 ppm and a signal caused by uncoordinated polymer phosphine at the same position as in the starting polymers. The latter signal diminished on addition of more of the rhodium complex and disappeared when the rhodium to phosphorus ratio was 1.0. The signals at the latter ratio and at some lower ratios are given in Table I (entries b1-b3; the structural type of the rhodium complexes is denoted by the letter a-g and the phosphine by the numbers 1-9).

Figure 1. 31P NMR spectra during stepwise addition of [RhCl(C2H4)2]2 to polymer 1.

Stepwise addition of [RhCl(C2H4)2]2 to a sample of polymer 1 gave a series of spectra which are shown in Figure 1. On addition of the rhodium complex the resonance of the free polymer phosphine, initially present at -5.3 ppm, broadens and disappears at a loading of 0.3-0.4 equiv of rhodium per phosphorus. When 0.4-0.6 equiv of rhodium is added, the spectra show a very broad envelope of signals covering the regions from 0 to +30 and from +40 to +60 ppm. These signals vanish at about 0.6 equiv of rhodium. At 0.8-1 equiv of rhodium per phosphorus a new signal is clearly present as a doublet at +53.5 ppm. Polymers 2 and 3 behaved in the same way as polymer 1. The signals observed at a rhodium to phosphorus ratio of 1.0 are given in Table I (entries a1-a3). In the case of a2 there was evidence of other signals besides the doublet listed in Table I.

In order to determine how much of our phosphorus was visible in the NMR spectra we calibrated the spectrum of the suspension of insoluble complex b1 against the spectrum of the dissolved polymer 1 with external H3PO4. The experiments were performed under such conditions that saturation was avoided. The data revealed that 30 min after mixing the spectrum of the suspension showed 5% of the phosphorus present; this value slowly decreased with time. Moreover, we made an intramolecular calibration. As an intramolecular standard we took the phosphine oxide peak. We used a batch of polymer 1 with a phosphine oxide content of 30% and of polymer 3 with a phosphine oxide content of 10%. At a Rh/P ratio of 1.0 the integral of the doublet at approximately 54 ppm and of the phosphine oxide peak at 25 ppm gave values which are, within 10%, in agreement with the amount of phosphine oxide initially present in the polymers.

In order to facilitate the interpretation of the spectra of the polymer rhodium complexes, the procedure described above was repeated for monomeric analogues of the polymers, viz., triphenylphosphine (4) and dicyclohexylphosphinephosphine (5). After three additions the rhodium to phosphorus ratio was 1.0. The shifts and the 131Rh-31P coupling constants observed during the additions as well as their assignments are given in Table II, together with data of comparable complexes taken from the literature.

Stepwise addition of [RhCl(COD)]2 to triphenylphosphine or dicyclohexylphosphine gave evidence of only one type
Table I. $^{31}$P NMR Data$^a$ of Polymer Phosphines and Their Complexes

<table>
<thead>
<tr>
<th>compd</th>
<th>no.</th>
<th>$\delta^b$</th>
<th>$^1J$(Rh–P), Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ph}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>1</td>
<td>5.3 (+25.1)$^c$</td>
<td></td>
</tr>
<tr>
<td>$[\text{Cy}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>2</td>
<td>2.2 (+43.5)$^c$</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ph}_2\text{PC}_6\text{H}_4\text{CH(CH}_3\text{)N}==\text{C}&lt;]_n$</td>
<td>3</td>
<td>4.6 (+25.3)$^c$</td>
<td></td>
</tr>
<tr>
<td>$[\text{trans-RhCl}((\text{C}_2\text{H}_4)_2\text{PhPC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>a1</td>
<td>53.5 d</td>
<td>184</td>
</tr>
<tr>
<td>$[\text{trans-RhCl}((\text{C}_2\text{H}_4)_2\text{Cy}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>a2</td>
<td>52.3 d</td>
<td>184</td>
</tr>
<tr>
<td>$[\text{trans-RhCl}((\text{C}_2\text{H}_4)_2\text{PhPC}_6\text{H}_4\text{CH(CH}_3\text{)N}==\text{C}&lt;]_n$</td>
<td>a3</td>
<td>54.1 d</td>
<td>185</td>
</tr>
<tr>
<td>$[\text{cis-RhCl}((\text{COD})\text{PhPC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>b1</td>
<td>30.9 d</td>
<td>147</td>
</tr>
<tr>
<td>$[\text{cis-RhCl}((\text{COD})\text{Cy}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>b1$^d$</td>
<td>31.2 d</td>
<td>154</td>
</tr>
<tr>
<td>$[\text{trans-RhCl}((\text{COD})\text{PhPC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>b2</td>
<td>29.1 d</td>
<td>169</td>
</tr>
<tr>
<td>$[\text{trans-RhCl}((\text{COD})\text{Cy}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$</td>
<td>b2$^d$</td>
<td>29.1 d</td>
<td>163</td>
</tr>
<tr>
<td>$[\text{trans-RhCl}((\text{COD})\text{PhPC}_6\text{H}_4\text{CH(CH}_3\text{)N}==\text{C}&lt;]_n$</td>
<td>b3</td>
<td>31.1 d</td>
<td>146</td>
</tr>
</tbody>
</table>

$^a$ The spectra are recorded in THF/C$_6$D$_6$ at 298 K. The P/Rh ratio is 1.0. $^b$ Chemical shifts relative to H$_3$PO$_4$, calculated from external PPh$_3$ at ~5.6 ppm. The chemical shifts are in parts per million; downfield is positive; d = doublet. $^c$ The resonance of the phosphine oxide is given in parentheses. $^d$ At Rh/P = 0.6. $^e$ At Rh/P = 0.3.

Table II. $^{31}$P NMR Data of Monomeric Phosphines and Their Complexes$^a$

<table>
<thead>
<tr>
<th>compd</th>
<th>no.</th>
<th>$\delta^b$</th>
<th>$^1J$(Rh–P), Hz</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$_3$</td>
<td>4</td>
<td>5.6 (+24.6)$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCy$_2$Ph</td>
<td>5</td>
<td>1.9 (+40.8)$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCy$_3$</td>
<td>6</td>
<td>7.1 (+44.3)$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-RhCl(PPh$_3$)((C$_2$H$_4)_2$</td>
<td>a4</td>
<td>53.3 d</td>
<td>184.4</td>
<td></td>
</tr>
<tr>
<td>trans-RhCl(PCy$_2$Ph)((C$_2$H$_4)_2$</td>
<td>a5</td>
<td>53.6 d</td>
<td>181.5</td>
<td></td>
</tr>
<tr>
<td>cis-RhCl(PPh$_3$)(COD)</td>
<td>b4</td>
<td>31.5 d</td>
<td>152</td>
<td></td>
</tr>
<tr>
<td>cis-RhCl(PCy$_2$Ph)(COD)</td>
<td>b5</td>
<td>29.9 d</td>
<td>146.3</td>
<td></td>
</tr>
<tr>
<td>trans-RhCl(PPh$_3$)((C$_2$H$_4)_2$</td>
<td>c4$^d$</td>
<td>35.4 d</td>
<td>128.8</td>
<td></td>
</tr>
<tr>
<td>trans-RhCl(PCy$_2$Ph)((C$_2$H$_4)_2$</td>
<td>c5</td>
<td>31.2 d</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>trans-RhCl(PCy$_3$)((C$_2$H$_4)_2$</td>
<td>c6</td>
<td>47.2 d</td>
<td>113.7</td>
<td></td>
</tr>
<tr>
<td>RhCl(PCy$_3$)((C$_2$H$_4)_2$</td>
<td>d4$^c$</td>
<td>47.3 d</td>
<td>187.3</td>
<td></td>
</tr>
<tr>
<td>RhCl(P[t-p-tolyl]$_3$)</td>
<td>d7</td>
<td>46.2 dt</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>RhCl(P[t-p-tolyl]$_3$)</td>
<td>d7</td>
<td>30.2 dd</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>mbp Rh(µ–Cl)Rh mbp</td>
<td>e9$^f$</td>
<td>68.6 d</td>
<td>188</td>
<td></td>
</tr>
<tr>
<td>(PCy$_2$Ph)((C$_2$H$_4)_2$)Rh(µ–Cl)Rh(PCy$_2$Ph)((C$_2$H$_4)_2$</td>
<td>e5</td>
<td>52.6 d</td>
<td>184.5</td>
<td></td>
</tr>
<tr>
<td>(PCy$_3$)((C$_2$H$_4)_2$)Rh(µ–Cl)Rh(PCy$_3$)((C$_2$H$_4)_2$</td>
<td>e6</td>
<td>45.1 d</td>
<td>182.9</td>
<td></td>
</tr>
<tr>
<td>dioph Rh(µ–Cl)Rh(C$_2$H$_4)_2$</td>
<td>f8</td>
<td>34.1 d</td>
<td>194</td>
<td></td>
</tr>
<tr>
<td>(PPh$_3$)((µ–Cl)Rh(PPh$_3$)$_2$</td>
<td>g4</td>
<td>51.9 d</td>
<td>193.2</td>
<td></td>
</tr>
<tr>
<td>[P[t-p-tolyl]$_3$][Rh(µ–Cl)Rh[P[t-p-tolyl]$_3$],</td>
<td>g7</td>
<td>49.5 d</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>dioph Rh(µ–Cl)Rh</td>
<td>g8</td>
<td>31.8 d</td>
<td>191</td>
<td></td>
</tr>
<tr>
<td>dioph Rh(µ–Cl)Rh(PCy$_3$)$_2$</td>
<td>g6</td>
<td>44.4 d</td>
<td>193.8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The spectra are recorded in THF/C$_6$D$_6$ at 298 K, except the spectra taken from the references. $^b$ Chemical shifts relative to H$_3$PO$_4$, calculated from external PPh$_3$ at ~5.6 ppm. The chemical shifts are in parts per million; downfield is positive; d = doublet, dd = doublet of doublets, dt = doublet of triplets. $^c$ The resonance of the phosphine oxide is given in parentheses. $^d$ Reference 14 gives for c4 in toluene $\delta = 35.7$ and $^1J$(Rh–P) = 128 Hz. $^f$ J(P–P') is 38.1 Hz. $^g$ J(P–P') for mbp = 138 Hz.

of complex, viz., b4 and b5, respectively. The excess of phosphine present at rhodium to phosphorus ratios of 0.3 and 0.6 was not able to break the coordination bond between the rhodium and the 1,5-cyclooctadiene ligand. The signals of the excess phosphine were found at the positions expected for noncoordinated phosphines. On additions of more rhodium complex the latter signals disappeared at a Rh/P ratio of 1.0.

When $[\text{RhCl}((\text{C}_2\text{H}_4)_2]$ was added stepwise to triphenylphosphine, the spectra were much more complex. Apparently, more than one type of phosphine rhodium complex is formed; the relative amounts of these complexes depend on the Rh/P ratio. When this ratio was 0.3, two complexes were present: c4 and d4 (the Wilkinson complex), besides noncoordinated PPh$_3$. At a Rh/P ratio of 0.6 the major part of the rhodium was present as complex a4 and a minor part as complex c4, while the complex d4 had disappeared. At a Rh/P ratio of 1.0 also complex c4 had disappeared and only complex a4 was left. We may conclude from these observations that at a Rh/P ratio of 0.3 the Wilkinson complex is not formed exclusively; the PPh$_3$ ligand is not able to expel the ethene ligand completely under these conditions. When the addition was reversed, i.e., tri-
phenylphosphine was added stepwise to a solution of [RhCl(C2H4)2]2, the same signals with the same relative intensities appeared in the 31P NMR spectrum. This indicates that with this phosphine all reaction steps are reversible.

After [RhCl(C2H4)2]2 had been added to solutions of dicyclohexylphenylphosphine the equilibrium of ligand exchange was established relatively slowly. At a Rh/P ratio of 0.3 complex a was formed besides uncoordinated phosphine. The Wilkinson-type complex with three phosphines around the rhodium was not formed with this phosphine, apparently for steric reasons. This behavior is in line with the behavior of the tricyclohexylphosphine ligand, for which this complex is not known either.1 2, 1 3 At a rhodium to phosphorus ratio of 1.0 two complexes, a5 and e5, were observed in a ratio of 86:14. Under similar conditions triphenylphosphine gave only one complex, a4.

Discussion

The polymer ligands 1–3 have 31P signals at positions which differ only slightly from those of their monomer counterparts. On coordination to rhodium the signals of both monomer and polymer ligands shift downfield. Information about the structures of the various complexes can be obtained from a mutual comparison of the 31P parameters in Tables I and II.

Complexes of the Monomers. The value of 1J(Rh–P) is appreciably lower in complexes b4 and b5 than in complexes a4 and a5. This is because the phosphine in the former complexes is trans to alkene and not trans to chlorine, as dictated by the cyclooctadiene ligand, which occupies two positions cis to each other.

The values of the coupling constants (181.5–189 Hz) of the complexes a4, a5, d4, and d7 indicate that each of these complexes has a phosphine ligand trans to chlorine.14 From the values of the coupling constants it can also be shown that complexes c4, e5, c6, d4, and d7 have two phosphines which are mutually trans.15 It can be concluded from a comparison of the various complexes, for instance, of d4 with c4, that replacement of a phosphine by an alkene at the same ligand position causes a lowering of the 1J(Rh–P) of the remaining phosphines. In the same manner, when in complexes g two phosphines are replaced by alkynes to yield complexes e, the remaining phosphines will have a lower coupling constant. This observation and others are presented in Scheme 1. In this scheme ligand substitutions occur horizontally and monomer 1 2 dimer reactions vertically. From Scheme 1 it is clear that in these square-planar rhodium phosphine complexes one can discriminate between phosphine trans to a nonbridged chlorine (a4, d4, d7) and trans to a bridged chlorine (e9, 16 g4, g7). In the nonbridged case the 1J(Rh–P) is lower. For triphenylphosphine complexes this lowering is 4–7 Hz and for dicyclohexylphosphine complexes it is 3 Hz.

Two structures could be assigned to the spectra at a rhodium to phosphorus ratio of 1.0, viz., a and e. Complex e may be formed via dimerization of complex a.

2RhCl(PR3)(C2H4)2

\[ \Rightarrow \text{PR}_3((\text{C}_2\text{H}_4)\text{Rh}(\mu-\text{Cl})_2\text{Rh}(\text{C}_2\text{H}_4))\text{PR}_3 + 2\text{C}_2\text{H}_4 \] (1)

On the basis of the comparisons given above, assignment of structure a4 to the doublet observed in the 31P NMR spectrum of the rhodium triphenylphosphine complex at Rh/P = 1.0 seems to be justified.17 The two doublets in the 31P NMR spectrum of its dicyclohexylphosphine analogue at Rh/P = 1.0 can be attributed to the presence of both the monomeric species a5 and the dimeric species e5. The doublet with the lowest coupling constant (181.5 Hz) is assigned to a5 and the one with the highest coupling constant (184.5 Hz) to e5. The absolute value of the latter coupling constant is in close agreement with the value of the coupling constant of the tricyclohexylphosphine derivative, e6, reported by Van Gaal.12, 13

As complexes a4 and a5 are crucial for the elucidation of the structures of the polymer rhodium complexes, we also applied 1H NMR in order to get additional information about the structures of these rhodium complexes.

The proton spectra of these monomer rhodium phosphine ethene complexes have been recorded to see whether at a Rh/P ratio of 1.0 the solutions of these complexes contain free as well as coordinated ethene. According to eq 1 1 equiv of ethene is liberated when complete dimerization of complex a occurs.

At room temperature a solution of [RhCl(C2H4)2] and dicyclohexylphenylphosphine in C2D6, having a Rh/P = 1.0, showed in the 1H NMR spectrum two broad signals, at 3.0 and 5.1 ppm, which can be assigned to complexed and free ethene, respectively. From the intensity ratio the amount of dimer is found to be 18%. This value does not deviate significantly from the value of 14% calculated from the 31P NMR spectrum.

On lowering the temperature to −45 °C the signal of the free ethene sharpened and shifted to 5.25 ppm and the signal of the complexed ethene was split into two broad peaks, which on cooling to −80 °C further resolved into two doublets at 3.50 and 2.55 ppm. These doublets, which have fine structure, are caused by restricted rotation of the complexed ethene in these rhodium complexes at this low temperature.18

At room temperature the 1H NMR spectrum of a mixture of [RhCl(C2H4)2] and triphenylphosphine (Rh/P = 1.0) showed only one very broad peak at 4 ppm. When the temperature was lowered to −80 °C, two poorly resolved peaks became visible at about 4.5 and 3.7 ppm. Apparently, rotation of ethene is much less restricted in these rhodium complexes. The proton spectra of these phosphine rhodium ethene complexes support the assignment that was based on the 31P NMR spectra.

Complexes of the Polymers. The data in Tables I and II reveal a close agreement between the shifts and coupling constants in the 31P NMR spectra of complexes a1, a2, and a3 and those of their monomeric analogues a4 and a5 when the rhodium to phosphorus ratio is 1.0. This agreement strongly suggests a similarity in structure and, since the structures of the monomers have been well determined, those of the polymers are very probably correct. Although the calibration with H2PO4 reveals that only 5% of the phosphorus present is visible, we assume that the doublet, observed for polymers 1 and 3 at Rh/P = 1.0, represents the main species present (see Table I). This assumption is based on the behavior of the 31P spectrum when small portions of rhodium are subsequently added to the polymer. The spectrum is changing until—just as with the monomers—it gets its final form at a rhodium to total phosphorus P ratio of 1.0. The detectable phosphorus could be present in a more solvated and the remainder of the sample in a less solvated ("more solid") state.

In the case of polymer 2 the main species we observe at a
Rh/P ratio of 1.0 is complex a2, but additional signals are also present. These additional signals cannot be assigned to specific structures because of the complexity of the spectrum. It should be noted that at a Rh/P ratio of 1.0 the monomer analogue showed other signals, in addition to those of a5. These additional signals could be assigned to e5 and, depending on the reaction time, also to e5.

A comparison of the spectra of monomer rhodium ethene complexes with those of the polymer rhodium ethene complexes at Rh/P ratios lower than 1.0 is hampered by the broadness of the signals in the latter spectra. The different species obviously present in the spectra of the monomer complexes, and listed in Tables II, cannot be recognized directly in the spectra of the polymer complexes (Figure 1).

The spectra of the polymers and monomers at various loadings of [RhCl(COD)]2 are relatively simple and always show the doublet of complex b in addition to the signal of the remaining uncoordinated phosphine. The simplicity of the spectra is due to the presence of only one type of complex, viz., complex b, and to the reduced exchangeability of the bidentate 1,5-cyclooctadiene ligand as compared to the monodentate ethene ligand.

It can be seen from Table I that for compounds b1 and b2 1J(Rh-P) varies appreciably with the rhodium loading. For b1 at Rh/P = 0.6 1J(Rh-P) is almost equal to the coupling constant of the monomer analogue b4. At Rh/P = 1.0 this coupling constant has decreased by 7 Hz. Also the coupling constant of 143 Hz observed for b3 is relatively low with respect to the coupling constant in the monomer analogue b4.

For complex b2 a different behavior is found. At a Rh/P ratio of 0.3 a normal value of 146 Hz for the rhodium-phosphorus coupling constant is observed. This value is equal to the value of the coupling constant in the monomer analogue b5. At higher rhodium loadings 1J(Rh-P) increases up to 169 Hz. A relatively high value for 1J(Rh-P) has also been found for the complex RhBr(PCy3) (norbordiene), where 1J(Rh-P) = 160.8 Hz. In this complex too rhodium is surrounded by very bulky ligands.

In this study we have demonstrated that 31P NMR is a useful tool to investigate the structure of polymer-anched rhodium complexes. An important conclusion is that the ligand cyclooctadiene, in contrast to the widely used ethene, gives only a single type of complex which could be an advantage in catalytic studies.

Experimental Section

The complexes [RhCl(C2H4)2] and [RhCl(COD)]2 were synthesized according to the literature.20,21 The monomers of polymers 1 and 2 have been synthesized according to the method described by Rabinowitz.22 The structures of all phosphines were checked by 'H and 31P NMR and by IR.

4-Dicyclohexylphosphineoxystyrene: 31P NMR (CD2Cl2/THF) δ = 5.76. 4-Dicyclohexylphosphinoxystyrene: 31P NMR (CD2Cl2/THF) δ = +1.6.

These monomers were polymerized to yield polymers 1 and 2 by stirring an amount of 10 g of the monomer for 24 h at 65 °C under N2, to which 0.3-2.5 (very br, 2H, CH2), 6.0 (br, 1H, CH), 7.0, 7.12, and 7.4 (m, 1H, aromatic); IR (KBr) 515, 570, 700, 745, 830, 1085, 1405, 1435, 1480, 1495, 2900, 3020 cm-1. According to 31P NMR, the polymer contained less than 2% phosphate oxide. Another sample, which contained 30% phosphate oxide, was used for calibration purposes.

Poly(4-dicyclohexylphosphinoxystyrene) (2): 1H NMR (CDCl3) δ 0.3-2.5 (very br, 24H, CH2, cyclohexyl), 6.2-7.8 (very br, 5H, CH and aromatic); IR (KBr) 522, 560, 760, 830, 1095, 1200, 1450, 1510, 1595, 2850, 2920, 3200 cm-1. According to 31P NMR, this polymer contained less than 3% phosphate oxide.

The synthses of polymer 3 and its monomer have been described before.23 The polymer contained less than 3% phosphate oxide. Another sample, which contained 10% phosphate oxide, was used for calibration.

Trienes prepared from Aldrich: dicyclohexyl-phenylphosphine was synthesized from PhPCl3 and CyMgBr in THF and recrystallized from EtOH/MeOH (under N2).

Samples for 1H NMR contained 10-4 mol of compound in 0.6 mL of solvent and samples for 31P NMR (1-2) × 10-4 mol of compound in 3-6 mL of solvent. The 1H and 31P NMR spectra were recorded on Varian EM390 and Bruker WH90 spectrometers, respectively. All compounds were handled and all spectra were recorded in an N2 atmosphere. For the 31P NMR spectra pulse-FT NMR and broadband noise decoupling techniques were used.

The 31P NMR spectra of the monomer phosphines were recorded using 100-500 pulses with a flip angle of 40-50° and a repetition rate of 0.5-1 Hz. For the rhodium phosphines 300-1000 pulses were used with a flip angle of 40-90° and a repetition rate of 0.3-3 Hz. The spectra of the complexes of the monomer phosphines with rhodium were recorded 5 min after mixing; we used the same number of pulses and the same flip angles. The 31P NMR spectra of the rhodium complexes of the polymers were recorded with a 65-90° flip angle and a repetition rate of 0.8-3 Hz. The number of pulses varied from 10 000 to 20 000 for the polymer COD complexes and from 50 000 to 200 000 for the polymer ethene complexes. For the survey spectra taken during the first 0.5-1 h, 5000-10 000 pulses were used. Changing the flip angle or the repetition rate did not alter the spectra of the polymer complexes. In the calibration experiments with H3PO4 spectra of the suspension of complex b1 were recorded using 2000-10 000 pulses instead of 1000 pulses for polymer 1 without rhodium.

Acknowledgment. This research was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank Miss Vera Richters and Mr. R. Bokhorst for experimental assistance and Drs. M. J. A. de Bie and R. J. J. Ch. Louwsberg for helpful suggestions.

References and Notes

(2) Grubbs, R. H. Chemtech. 1977, 7, 512.
(8) For instance, this is observed when monomeric phosphines are complexed to rhodium: Naaktgeboren, A. J., unpublished results.
(10) Naaktgeboren, A. J.; Nolte, R. J. M.; Drenth, W., to be published.
(17) As far as we are aware, complexes of type a have not been described before. A complex of composition [RhCl2(C6H4H2P)]2 has been reported to be an intermediate in the Rh(catalyzed) tetramerization of allene. This complex was not characterized, however. Cf. Otsuka, S.; Nakamura, A.; Mimardma, H. Chem. Commun. 1969, 191.