

Dry, degassed 1-halopropane-*l*-<sup>13</sup>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 tube protected at the stem with 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.

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## <sup>31</sup>P Nuclear Magnetic Resonance Studies of Polymer-Anchored Rhodium(I) Complexes

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**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 (RhClL)<sub>2</sub> and with (RhClL')<sub>2</sub>, where L and L' are ethene and 1,5-cyclooctadiene, respectively. These complexes were added stepwise and during this process the <sup>31</sup>P NMR spectra were observed. <sup>31</sup>P chemical shifts and <sup>103</sup>Rh-<sup>31</sup>P coupling constants were compared with those of monomeric analogues which were treated in the same way.

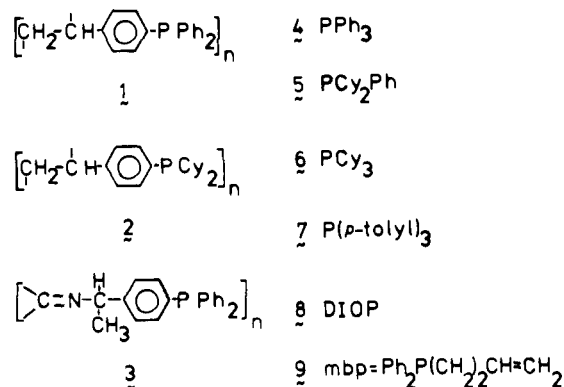
Recently, considerable interest has been shown in the anchoring of homogeneous catalysts to organic polymers.<sup>1,2</sup> For instance, polymer-bound rhodium complexes have been synthesized and used as hydrogenation catalysts. Apart from a recent EXAFS study<sup>3</sup> concerning the catalytic site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

It has been shown that <sup>31</sup>P NMR can help to elucidate the structures of metal-phosphine complexes.<sup>4</sup> Both the <sup>31</sup>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.<sup>5</sup> have tried to use <sup>31</sup>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 <sup>31</sup>P NMR signal<sup>5-7</sup> and therefore will have normal relaxation time, while coupling to rhodium is expected to decrease rather than increase the relaxation time.<sup>8</sup>

So far,<sup>2</sup> nearly all supports used to anchor homogeneous catalysts have a low phosphorus content and phosphine is un-

evenly distributed over the polymer chain. This is very unfavorable for a <sup>31</sup>P NMR study because the signal strength is low and appreciable variations occur in the environment of the phosphorus in the polymer. Therefore, we prepared three polymers which have a phosphine function in each repeating unit: poly(4-diphenylphosphinostyrene) (**1**), poly(4-dicyclohexylphosphinostyrene) (**2**), and poly[1-(4-diphenylphosphinophenyl)ethyliminomethylene] (**3**). These polymers were obtained by polymerization of their phosphine-containing monomers. Polymers **1** and **2** will have a more or less random



coil structure, whereas polymer **3** will have a rigid rod structure.<sup>9</sup>

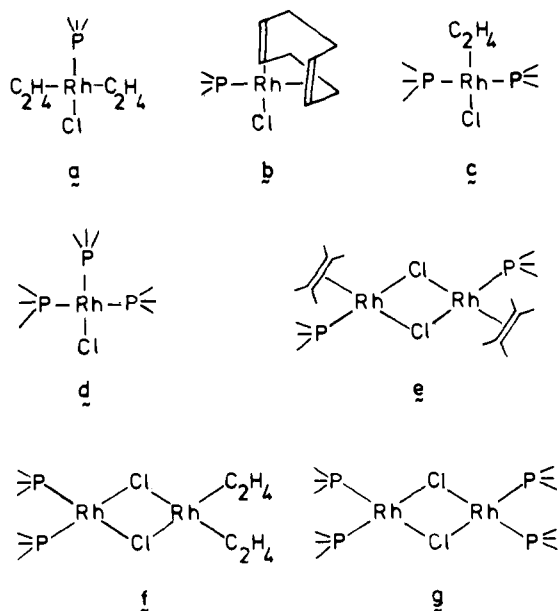
Addition of  $[\text{RhCl}(\text{COD})]_2$  and  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ , where COD = 1,5-cyclooctadiene, to polymers **1–3** gives rise to polymer rhodium complexes which are active hydrogenation catalysts.<sup>10</sup> This paper is concerned with the  $^{31}\text{P}$  NMR spectra of these complexes.

## Results

Addition of solutions of  $[\text{RhCl}(\text{COD})]_2$  or  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  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  $^{31}\text{P}$  NMR spectra in sealed tubes under a nitrogen atmosphere. When a  $^{31}\text{P}$  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  $^{31}\text{P}$  parameters. This spectrum required a long accumulation time because of the bad signal to noise ratio.

When  $[\text{RhCl}(\text{COD})]_2$  was added stepwise to polymers **1–3**, the  $^{31}\text{P}$  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**).



Stepwise addition of  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  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

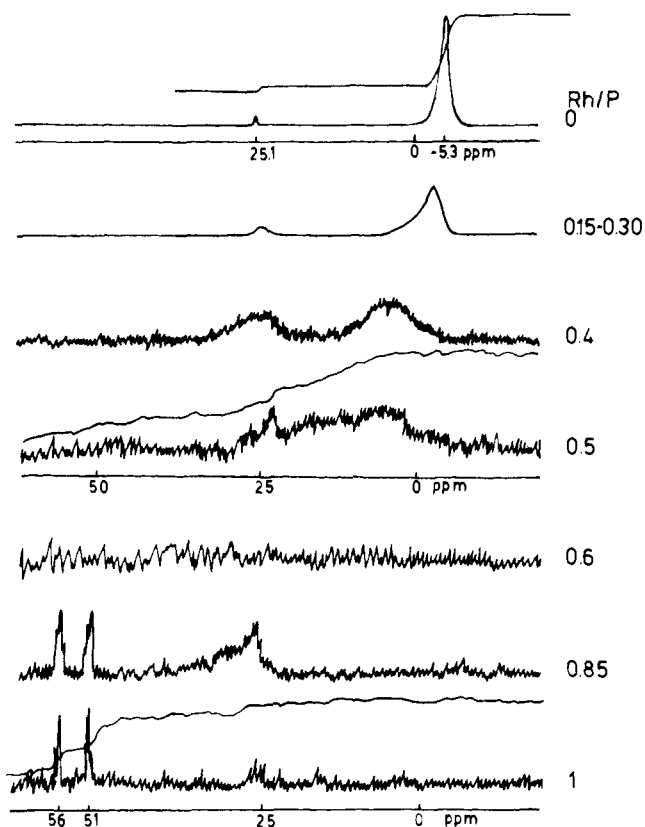


Figure 1.  $^{31}\text{P}$  NMR spectra during stepwise addition of  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  to polymer **1**.

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  $\text{H}_3\text{PO}_4$ . 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 dicyclohexylphenylphosphine (**5**). After three additions the rhodium to phosphorus ratio was 1.0. The shifts and the  $^{103}\text{Rh}$ – $^{31}\text{P}$  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  $[\text{RhCl}(\text{COD})]_2$  to triphenylphosphine or dicyclohexylphenylphosphine gave evidence of only one type

**Table I.**  $^{31}\text{P}$  NMR Data<sup>a</sup> of Polymer Phosphines and Their Complexes

compd	no.	$\delta^b$	$^1J(\text{Rh-P})$ , Hz
$[\text{Ph}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$	1	-5.3 (+25.1) <sup>c</sup>	
$[\text{Cy}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$	2	+2.2 (+43.5) <sup>c</sup>	
$[\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{N}=\text{C}<]_n$	3	-4.6 (+25.3) <sup>c</sup>	
$[\text{trans-RhCl}(\text{C}_2\text{H}_4)_2\cdot\text{Ph}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$	a1	+53.5 d	184
$[\text{trans-RhCl}(\text{C}_2\text{H}_4)_2\cdot\text{Cy}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$	a2	+52.3 d	184
$[\text{trans-RhCl}(\text{C}_2\text{H}_4)_2\cdot\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{N}=\text{C}<]_n$	a3	+54.1 d	185
$[\text{cis-RhCl}(\text{COD})\cdot\text{Ph}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$	b1	+30.9 d	147
$[\text{cis-RhCl}(\text{COD})\cdot\text{Cy}_2\text{PC}_6\text{H}_4\text{CHCH}_2]_n$	b1 <sup>d</sup>	+31.2 d	154
	b2	+29.1 d	169
	b2 <sup>d</sup>	+29.1 d	163
$[\text{cis-RhCl}(\text{COD})\cdot\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{N}=\text{C}<]_n$	b2 <sup>e</sup>	+29.1 d	146
	b3	+31.1 d	143

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

**Table II.**  $^{31}\text{P}$  NMR Data of Monomeric Phosphines and Their Complexes<sup>a</sup>

compd	no.	$\delta^b$	$^1J(\text{Rh-P})$ , Hz	ref
$\text{PPh}_3$	4	-5.6 (+24.6) <sup>c</sup>		
$\text{PCy}_2\text{Ph}$	5	+1.9 (+40.8) <sup>c</sup>		
$\text{PCy}_3$	6	+7.1 (+44.3) <sup>c</sup>		12
$\text{trans-RhCl}(\text{PPh}_3)(\text{C}_2\text{H}_4)_2$	a4	+53.3 d	184.4	
$\text{trans-RhCl}(\text{PCy}_2\text{Ph})(\text{C}_2\text{H}_4)_2$	a5	+53.6 d	181.5	
$\text{cis-RhCl}(\text{PPh}_3)(\text{COD})$	b4	+31.5 d	152	
$\text{cis-RhCl}(\text{PCy}_2\text{Ph})(\text{COD})$	b5	+29.9 d	146.3	
$\text{trans-RhCl}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$	c4 <sup>d</sup>	+35.4 d	128.8	
$\text{trans-RhCl}(\text{PCy}_2\text{Ph})_2(\text{C}_2\text{H}_4)$	c5	+31.2 d	123	
$\text{trans-RhCl}(\text{PCy}_3)_2(\text{C}_2\text{H}_4)$	c6	+47.2 d	113.7	15
$\text{RhCl}(\text{PPh}_3)_3$	d4 <sup>e</sup>	+47.3 dt	187.3	
	d4	+30.3 dd	143.4	
$\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$	d7	+46.2 dt	189	14
	d7	+30.2 dd	143	
$\text{mbp Rh}(\mu\text{-Cl})_2\text{Rh mbp}$	e9 <sup>f</sup>	+68.6 d	188	16
	e9	+69.6 d	189	
$(\text{PCy}_2\text{Ph})(\text{C}_2\text{H}_4)\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{PCy}_2\text{Ph})(\text{C}_2\text{H}_4)$	e5	+52.6 d	184.5	
$(\text{PCy}_3)(\text{C}_8\text{H}_{14})\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{PCy}_3)(\text{C}_8\text{H}_{14})$	e6	+45.1 d	182.9	12
$\text{diop Rh}(\mu\text{-Cl})_2\text{Rh}(\text{C}_2\text{H}_4)_2$	f8	+34.1 d	194	4
$(\text{PPh}_3)_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{PPh}_3)_2$	g4	+51.9 d	193.2	
$[\text{P}(p\text{-tolyl})_3]_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}[\text{P}(p\text{-tolyl})_3]_2$	g7	+49.5 d	196	14
$\text{diop Rh}(\mu\text{-Cl})_2\text{Rh diop}$	g8	+31.8 d	191	4
$(\text{PCy}_3)_2\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{PCy}_3)_2$	g6	+44.4 d	193.8	12

<sup>a</sup> The spectra are recorded in THF/ $\text{C}_6\text{D}_6$  at 298 K, except the spectra taken from the references. <sup>b</sup> Chemical shifts relative to  $\text{H}_3\text{PO}_4$ , calculated from external  $\text{PPh}_3$  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. <sup>c</sup> The resonance of the phosphine oxide is given in parentheses. <sup>d</sup> Reference 14 gives for c4 in toluene  $\delta$  +35.7 and  $^1J(\text{Rh-P})$  = 128 Hz. <sup>e</sup>  $J(\text{P-P}')$  is 38.1 Hz. <sup>f</sup> mbp is  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ .

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.<sup>11</sup> 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  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  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  $\text{PPh}_3$ . 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 this observation that at a Rh/P ratio of 0.3 the Wilkinson complex is not formed exclusively; the  $\text{PPh}_3$  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  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ , the same signals with the same relative intensities appeared in the  $^{31}\text{P}$  NMR spectrum. This indicates that with this phosphine all reaction steps are reversible.

After  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  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 **e5** 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.<sup>12,13</sup> 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

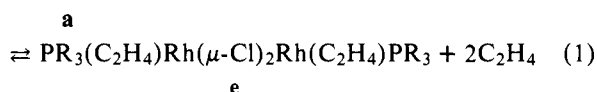
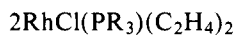
The polymer ligands **1–3** have  $^{31}\text{P}$  signals at positions which differ only slightly from those of their monomer counterparts. On coordination to rhodium the signals of both monomer and polymer ligands shift downfield. Information about the structures of the various complexes can be obtained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

**Complexes of the Monomers.** The value of  $^1J(\text{Rh-P})$  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.<sup>14</sup> From the values of the coupling constants it can also be shown that complexes **c4**, **c5**, **c6**, **d4**, and **d7** have two phosphines which are mutually trans.<sup>14,15</sup> 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  $^1J(\text{Rh-P})$  of the remaining phosphines.

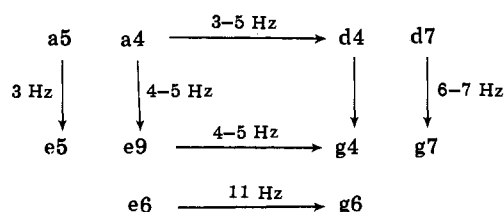
In the same manner, when in complexes **g** two phosphines are replaced by alkenes to yield complexes **e**, the remaining phosphines will have a lower coupling constant. This observation and others are presented in Scheme I. In this scheme ligand substitutions occur horizontally and monomer  $\rightleftharpoons$  dimer reactions vertically. From Scheme I 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**,<sup>16</sup> **g4**, **g7**). In the nonbridged case the  $^1J(\text{Rh-P})$  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**.



On the basis of the comparisons given above, assignment of structure **a4** to the doublet observed in the  $^{31}\text{P}$  NMR spectrum of the rhodium triphenylphosphine complex at Rh/P = 1.0 seems to be justified.<sup>17</sup> The two doublets in the  $^{31}\text{P}$  NMR spectrum of its dicyclohexylphenylphosphine 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

Scheme I



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.<sup>12,13</sup>

As complexes **a4** and **a5** are crucial for the elucidation of the structures of the polymer rhodium complexes, we also applied  $^1\text{H}$  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  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  and dicyclohexylphenylphosphine in  $\text{C}_7\text{D}_8$ , having a Rh/P = 1.0, showed in the  $^1\text{H}$  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  $^{31}\text{P}$  NMR spectrum.

On lowering the temperature to  $-45^\circ\text{C}$  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  $-80^\circ\text{C}$  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.<sup>18</sup>

At room temperature the  $^1\text{H}$  NMR spectrum of a mixture of  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  and triphenylphosphine (Rh/P = 1.0) showed only one very broad peak at 4 ppm. When the temperature was lowered to  $-80^\circ\text{C}$ , 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 (**a4**). These observations are in line with similar observations made by Wilkinson<sup>19</sup> on complex **c4**. The results obtained from the  $^1\text{H}$  NMR spectra of these phosphine rhodium ethene complexes support the assignment that was based on the  $^{31}\text{P}$  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  $^{31}\text{P}$  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  $\text{H}_3\text{PO}_4$  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  $^{31}\text{P}$  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 phosphine 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 **c5**.

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  $[\text{RhCl}(\text{COD})]_2$  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**  $^1J(\text{Rh-P})$  varies appreciably with the rhodium loading. For **b1** at Rh/P = 0.6  $^1J(\text{Rh-P})$  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  $^1J(\text{Rh-P})$  increases up to 169 Hz. A relatively high value for  $^1J(\text{Rh-P})$  has also been found for the complex  $\text{RhBr}(\text{PCy}_3)$  (norbornadiene), where  $^1J(\text{Rh-P}) = 160.8$  Hz.<sup>12</sup> In this complex too rhodium is surrounded by very bulky ligands.

In this study we have demonstrated that  $^{31}\text{P}$  NMR is a useful tool to investigate the structure of polymer-anchored 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  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  and  $[\text{RhCl}(\text{COD})]_2$  were synthesized according to the literature.<sup>20,21</sup> The monomers of polymers **1** and **2** have been synthesized according to the method described by Rabinowitz.<sup>22</sup> The structures of all phosphines were checked by  $^1\text{H}$  and  $^{31}\text{P}$  NMR and by IR.

**4-Diphenylphosphinostyrene:**  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6/\text{THF}$ )  $\delta$  -5.76.

**4-Dicyclohexylphosphinostyrene:**  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6/\text{THF}$ )  $\delta$  +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  $\text{N}_2$  with 0.03 g of AIBN in 30 mL of benzene. Sometimes the solution became too viscous to stir; then more benzene was added. At the end of the reaction the solution was concentrated to 10–20 mL and added to 150 mL of vigorously stirred hexane in an  $\text{N}_2$  atmosphere. The white precipitate which formed was collected by centrifugation under  $\text{N}_2$  and dried in vacuo, yield 50–70%.

**Poly(4-diphenylphosphinostyrene) (1):**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.5–2.5 (very br, 2 H,  $\text{CH}_2$ ), 6.6 (br, 1 H, CH), 7.03, 7.12, and 7.4 (m, 14 H, aromatic); IR (KBr) 515, 570, 700, 745, 830, 1085, 1405, 1435, 1480, 1495, 2900, 3020  $\text{cm}^{-1}$ . According to  $^{31}\text{P}$  NMR, the polymer contained less than 2% phosphine oxide. Another sample, which contained 30% phosphine oxide, was used for calibration purposes.

**Poly(4-dicyclohexylphosphinostyrene) (2):**  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.3–2.5 (very br, 24 H,  $\text{CH}_2$ , cyclohexyl), 6.2–7.8 (very br, 5 H, CH

and aromatic); IR (KBr) 522, 560, 760, 830, 1095, 1200, 1450, 1510, 1595, 2850, 2920, 3200  $\text{cm}^{-1}$ . According to  $^{31}\text{P}$  NMR, this polymer contained less than 3% phosphine oxide.

The syntheses of polymer **3** and its monomer have been described before.<sup>23</sup> The polymer contained less than 3% phosphine oxide. Another sample, which contained 10% phosphine oxide, was used for calibration.

Triphenylphosphine was purchased from Aldrich; dicyclohexylphenylphosphine was synthesized from  $\text{PhPCl}_2$  and  $\text{CyMgBr}$  in THF and recrystallized from EtOH/MeOH (under  $\text{N}_2$ ).

Samples for  $^1\text{H}$  NMR contained  $10^{-4}$  mol of compound in 0.6 mL of solvent and samples for  $^{31}\text{P}$  NMR  $(1-2) \times 10^{-4}$  mol of compound in 3–6 mL of solvent. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on Varian EM390 and Bruker WH90 spectrometers, respectively. All compounds were handled and all spectra were recorded in an  $\text{N}_2$  atmosphere. For the  $^{31}\text{P}$  NMR spectra pulse-FT NMR and broad-band noise decoupling techniques were used.

The  $^{31}\text{P}$  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 polymer 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  $^{31}\text{P}$  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  $\text{H}_3\text{PO}_4$  spectra of the suspension of complex **b1** were recorded using 2000–10 000 pulses instead of 1000 pulses for polymer **1** without rhodium.

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