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# PREPARATION AND PROPERTIES OF RHODIUM(I) COMPLEXES OF PHOSPHINATED POLY(METHYLSILOXANES)

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## Summary

A series of poly(methylsiloxanes) that contain carbon-functional diphenylphosphine groups were prepared and subsequently treated with $RhCl(CO)(PPh_3)_2$ to produce polymer-attached chlorocarbonylrhodium(I) complexes. The materials are soluble in a variety of organic solvents, and are easily precipitated from solution by the addition of excess methanol. The polymer complex A derived from a phosphinated silicone polymer containing one $PPh_2$ group per 60 siloxy units has a molecular weight of 21000 daltons and contains 0.8% Rh. In accord with its formulation, the polymer shows a $\nu$(CO) at 1970 $cm^{-1}$ and an ultraviolet absorption at 3625 Å. Similar rhodium(I) complexes derived from phosphinated silicones containing one $PPh_2$ group per 20 (complex B) and 8 (complex C) siloxy units were also investigated. Complexes A and B catalyze the hydroformylation of hex-1-ene at 100°C, 1000 psi $CO/H_2$ pressure yielding the linear/branched heptaldehyde in a ratio of 0.9 with 95% selectivity and an overall conversion of 97% to products in 3 h. Although the hydroformylation conditions do not lead to depolymerization, both Rh and P are lost from the polymers and the actual catalyst appears to be a free rhodium carbonyl species. Complex C is a less active hydroformylation catalyst (14% aldehyde conversion, normal/branched ratio 1.7) and the polymer undergoes extensive degradation in the reaction.

## Introduction

There is now current interest in attaching transition-metal complexes to solid macromolecular supports and in the potential use of these insoluble materials as "heterogenized" homogeneous catalysts [1—4]. Examples of supports are organic polymers such as cross-linked polystyrenes and inorganic materials such as high surface area silica. However, it has recently been pointed out that soluble polymeric supports may, in certain instances, offer certain advantages over the insoluble materials [5,6]. Soluble organic supports have been the subject of investigation in this regard [5,6], but very little information is available on possible soluble inorganic supports. As a class, the silicones are potential soluble inorganic support materials which could in certain respects be considered the soluble analogs of insoluble silica supports. However, there may be some problems with using derivatives of silicone polymers as supports for transition-metal complexes, particularly regarding possible polymer and/or catalyst degradation. Halogen-containing metal reagents could cleave the Si—O bonds of the silicones in solution and hence cause appreciable depolymerization with a concomitant alteration of the catalyst's activity. Even the metal carbonyl $Cr(CO)_6$ has been shown to cause considerable degradation of phenylsilicone polymers in glyme/diglyme solutions under certain not too drastic conditions [7].

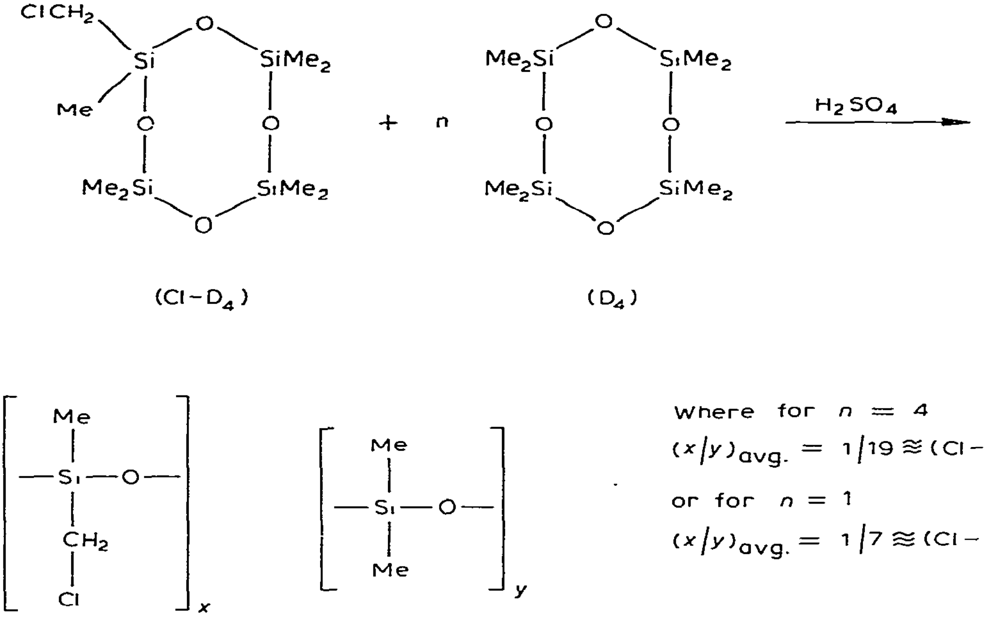
Only a few reports of well-characterized silicone polymers containing transition-metal groupings are available in the literature [7,8]. The best characterized are the ferrocene containing silicones [9] and the $\eta^6$-tricarbonylchromium-complexed arylenesiloxane polymers [7]. Phosphinated organosilicon polymers are known [10], but very little has been done regarding the study of metal complexes derived thereof, excluding the phosphinated organosilicon polymers covering silica [11]. In a previous communication, we described the preparation and hydroformylation properties of several soluble monomeric *trans*-halocarbonylrhodium(I)-bis-phosphine complexes that contained phosphinoalkyl organosilicon ligands [12]. In the present work, we have prepared a series of phosphinomethyl silicone polymers and observed their ability to function as polymer supports for the rhodium(I) complex. We have also examined the performance of these soluble macromolecular materials as hydroformylation catalysts.

## Results and discussion

### *Synthetic aspects*

Although there are many different types of phosphinated silicone polymers that could be studied as soluble support materials for metal complexes, we have investigated the synthesis and complexation properties of simple carbon-phosphinated poly(dimethyl silicone) polymers in the present work. The first step in the synthesis of the support material was the preparation of an appropriate chloromethyl silicone polymer by the sulfuric acid catalyzed room temperature polymerization of a mixture of $ClCH_2(Me)\overline{Si(OSiMe_2)_3O}$ and $(Me_2SiO)_3$ [13]. The ratio of $ClCH_2$ to $CH_3$ groups in the final polymer could be varied by using different ratios of the cyclic siloxanes and in our work, we studied two general

$ClCH_2$-polymer compositions: one with a functionalized group present with an average of twenty $Me_2SiO$ units, and the other with a functionality present with an average of eight $Me_2SiO$ units.



(Cl-$D_4$) (D$_4$)

Where for $n = 4$

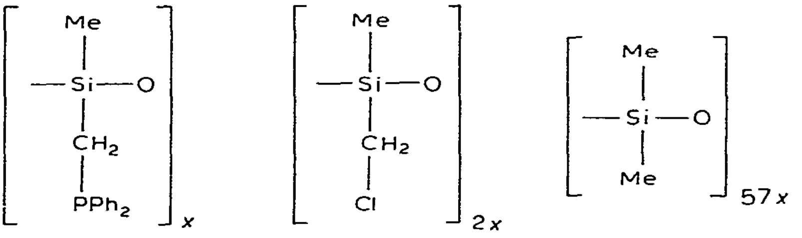
$(x/y)_{avg.} = 1/19 \approx (Cl-D_{20})_x$

or for $n = 1$

$(x/y)_{avg.} = 1/7 \approx (Cl-D_8)_x$

The polymers were colorless, extremely viscous liquids that were soluble in benzene, tetrahydrofuran, diethyl ether, heptane, toluene and chloroform, but insoluble in methanol and in water.

The two chloromethyl silicone polymers could not be phosphinated satisfactorily by their treatment with $LiPPh_2$ in tetrahydrofuran. The phosphination required several hours for completion after which time a gel permeation chromatography study indicated a significant decrease in the average molecular weight of the polymer. A much more satisfactory phosphination could be achieved by converting the $ClCH_2$-polymer to an $ICH_2$-polymer and treating the latter with $LiPPh_2$. The halogen conversion was achieved with no significant depolymerization by refluxing the $ClCH_2$-polymers with NaI in acetone [14]. For complete halogen exchange, the components were refluxed for ten days. Refluxing the Cl-$D_{20}$ polymer for two days with NaI in acetone, followed by phosphinating the product with $LiPPh_2$ produced a material which, from elemental analysis, appears to have about one-third of its $ClCH_2$ groups replaced by $ICH_2^-$ groups.



$\approx$ $PPh_2-D_{60}$

All the phosphinated polymers were viscous white liquids which retained the solubilities of their chloro (or iodo) precursors.

The phosphinated polymers were tested as supports for a metal complex by examining their reaction with $RhCl(CO)(PPh_3)_2$. This is a known general procedure for incorporating metal complexes into functionalized organic polymers (and silica) [15].

$$\textit{trans}\text{-}RhCl(CO)(PPh_3)_2 + 2\ (PPh_2\text{-polymer}) \xrightarrow{\text{benzene}} \textit{trans}\text{-}RhCl(CO)(PPh_2\text{-polymer})_2 + 2\ PPh$$

In our initial studies, we allowed the reaction to run as long as five days but later work indicated that the reaction was essentially complete within 48 h. The soluble rhodium-containing polymers were easily recovered by first reducing the reaction mixtures to about 1/2 their original volume and adding this to a twofold excess of absolute methanol. The products would precipitate out immediately as extremely viscous yellow oils. These oils were then dissolved in n-heptane and filtered to remove any *trans*-$RhCl(CO)(PPh_3)_2$ not bonded to the polymer since the monomeric complex is insoluble in heptane. The polymer product was then reprecipitated in methanol. Yellow-orange elastomeric gums were obtained after drying the materials in vacuo.

Analytical data and the stability of the materials suggested that both $PPh_3$ groups had been replaced by the polymer-$PPh_2$ groupings. The polymer attached complexes retained the solubility properties of the silicone support material so either little cross-linking occurred on complexation or the system was dilute enough to keep the material soluble. The three general polymers prepared by the above procedure are designated as: $[RhCl(CO)(PPh_2\text{-}D_{60})_2]_x$ (Complex A), $[RhCl(CO)(PPh_2\text{-}D_{20})_2]_x$ (Complex B) and $[RhCl(CO)(PPh_2\text{-}D_8)_2]_x$ (Complex C).

### *Characterization of the supports and their complexes*

The molecular weights ($\overline{M}$) of the silicone polymers and their derivatives could be estimated from $\overline{M}(\eta)$ values (Table 1) obtained from gel permeation measurements. The intrinsic viscosities ($\eta$) were not determined in each case but are expected to be in the range 0.2 dl/g to 0.1 dl/g [16]. A sample of a poly(dimethylsiloxane) oil having a known $\overline{M}$ of 30000 daltons had an experimental $\overline{M}(\eta)$ product of 6000, corresponding to a $\eta$ value of about 0.2 dl/g. The experimentally determined intrinsic viscosity of $RhCl(CO)(PPh_2\text{-}D_{60})_2$ in tetrahydrofuran was 0.115 dl/g. This gives a $\overline{M}$ for the polymer complex of about 21000 daltons.

The $\overline{M}(\eta)$ values given in Table 1 provide a qualitative means for determining if any significant changes in the polymer occur during the various synthetic operations. For example, the values indicate that the chloro-iodo halogen exchange reaction can be achieved without significant polymer degradation. During the phosphination of the $(I\text{-}D_{60})_x$ and $(I\text{-}D_8)_x$ polymers there is a reduction of $\overline{M}(\eta)$ of about 3 fold. This corresponds to a molecular weight decrease of about 2 fold on going from the iodo polymers to the phosphinated polymers if the usual Mark—Houwink—Sakurada exponent of 0.6 to 0.7 is assumed [17]. Few studies have ever been reported that concern the effect of phosphination

TABLE 1

SUMMARY OF GEL PERMEATION CHROMATOGRAPHY $\bar{M}(\eta)$ RESULTS FOR SOLUBLE POLYMERS [a]

| Sample | $\bar{M}(\eta)$ |
|---|---|
| Dow Corning $(Me_2SiO)_n$ | 6000 |
| Cl-$D_8$ | 9400 |
| Cl-$D_{20}$ | 9400 |
| I-$D_8$ | 9400 |
| I-$D_{20}$ | 9400 |
| $PPh_2$-$D_8$ | 3800 |
| $PPh_2$-$D_{60}$ | 3200 |
| $PPh_2$-$D_{20}$ | 1800 |
| $RhCl(CO)(PPh_2\text{-}D_8)_2$ | 710 |
| $RhCl(CO)(PPh_2\text{-}D_{60})_2$ | 2400 |
| $RhCl(CO)(PPh_2\text{-}D_{20})_2$ | 1800 |

[a] All measurements carried out in tetrahydrofuran.

on polymer molecular weights; however, appreciable polymer breakdown has been reported for the reaction of non-crosslinked poly(vinyl chloride) with $LiPPh_2$ [18]. Surprisingly, we found that the least amount of polymer breakdown appears to occur with the most highly phosphinated polymer. There also appears to be further polymer degradation when the rhodium complex is incorporated into the polymer. The extent varies and the data suggest that the highly phosphinated polymers are subject to the most degradation during this particular step. However, even in the polymer system with the lowest $\bar{M}(\eta)$ value, the molecular weight is about 3550 daltons, assuming the maximum value of 0.2 dl/g for $\eta$.

The complex *trans*-$RhCl(CO)(PPh_3)_2$ has a UV absorption at 3660 Å assigned to a metal—ligand charge transfer (MLCT) band involving the occupied molecular orbitals derived mainly from the rhodium *d* orbitals and the empty $\pi$-acceptor orbitals of the ligands [19]. While the band is not specifically assigned to either a M→P or M→CO MLCT we wanted to determine if it would change significantly when the $PPh_3$ ligands were replaced by the $PPh_2$-polymer ligands. Thus an exchange experiment involving *trans*-$RhCl(CO)(PPh_3)_2$ and a $(PPh_2\text{-}D_8)_x$ polymer having an initial $\bar{M}(\eta)$ value of 841 was carried out in which spectral and GPC measurements were obtained on representative samples taken at various intervals over a six day period. After 12 h, the $\bar{M}(\eta)$ value of the material fell to 473 while the UV absorption shifted to 3630 Å. After a 36 h reaction period, the $\bar{M}(\eta)$ value rose to 708, while the UV absorption shifted to 3625 Å. Aliquots of reaction products taken after 60 and 84 h produced the same results as obtained for the 36 h experiment. We conclude that the shift of the complex's MLCT absorption is due to the change of ligands from a triarylphosphine to a polymer-attached alkyldiarylphosphine system as the reaction proceeds. The decrease in the $\bar{M}(\eta)$ value after the 12 h period followed by its subsequent increase is somewhat surprising and could possibly be due to a change in the intrinsic viscosity of the system during the incomplete exchange, or to cleavage of the siloxane bonds initially, followed be recombinations of the cleavage products to some equilibrium state later. The overall results indicate that the phosphine exchange can be accomplished without serious polymer degradation in 36 h. The results also indicate that the rhodium complex has no major destabilizing effect on the polymer in solution at room temperature, once the exchange has occurred. This has been confirmed by long term studies which show that benzene solutions of the supported catalyst show no changes even after one year.

Infrared spectra were obtained for the polymer supports and the complexes derived thereof. The spectra of the phosphinoalkylsiloxane and the rhodium halocarbonyl polymer complexes were very similar other than for the presence of the characteristic $\nu$(CO) of the *trans*-rhodium(I) derivative at 1970 $cm^{-1}$. The carbonyl absorption is unobscured by other absorptions and can be used to estimate the extent of rhodium's being incorporated into the polymer. Other major absorptions were attributed to $(CH_3)Si$ (1250, 840—790 $cm^{-1}$) and Si—O—Si (1100—1020 $cm^{-1}$) groupings. The Si—O—Si absorption was split into two components, a characteristic feature of long chain siloxane polymers [20]. The C—H (aromatic) bands of the $PPh_2$ groups were just above the 3000 $cm^{-1}$ region.

The polymer-attached complexes appear to be very stable thermally and can be handled routinely in air without any noticeable decomposition. The $RhCl(CO)(PPh_2\text{-}D_{60})_2$ complex could be refluxed in benzene for several hours and recovered quantitatively. The material also remained unchanged when refluxed in benzene with a gentle stream of CO or $CO/H_2$ bubbling into the solution; however with $H_2$ alone, the refluxing solution darkened considerably. The material recovered from the latter reaction was not identified but contained new IR bands at 1940, 1775 and 1735 $cm^{-1}$. A sample of the material was heated at 100°C, 1000 psi $CO/H_2$ pressure without any olefin in the hydroformylation apparatus and was recovered unchanged. At no time in the above tests was there an indication that depolymerization took place or that rhodium was leached from the polymers.

*Hydroformylation study*

The three polymer-supported rhodium complexes along with $RhCl(CO)(PPh_3)_2$ were evaluated for catalytic activity in the liquid phase hydroformylation of hex-1-ene at 100°C, 1000 psi $CO/H_2$ pressures.

$$\text{hex-1-ene} + CO + H_2 \xrightarrow{\text{catalyst}} \text{n-heptanal} + \text{i-heptanal}$$

The results are given in Table 2.

The complexes containing the $PPh_2\text{-}D_{60}$ and $PPh_2\text{-}D_{20}$ ligands were very active catalysts with only traces of hex-1-ene remaining after the reaction. However the normal/branched aldehyde product ratios of 0.9 are more indicative of a rhodium carbonyl species acting as the catalyst in the reaction rather than a phosphinated rhodium species [21]. Thus it appears that under the conditions of the reaction, the rhodium is easily separated from these polymers and becomes converted to a rhodium carbonyl derivative. The carbonyl is also the likely catalyst in the recycle tests. The polymeric materials derived from the $PPh_2\text{-}D_{60}$ and $PPh_2\text{-}D_{20}$ complexes could easily be recovered from the hydroformylation products by dissolving the reaction residue in benzene and precipitating the polymer in methanol. Yields of the recovered polymer were at least 90% (based on the initial mass used) and gel permeation studies indicated

TABLE 2

PRODUCT DISTRIBUTION FOR THE HYDROFORMYLATION OF HEX-1-ENE CATALYZED BY $RhCl(CO)(PPh_3)_2$ AND SOME RHODIUM(I) COMPLEXES OF PHOSPHINATED POLY(METHYLSILOXANES)

| Catalyst | Product percent yield [a] | | | | | |
|---|---|---|---|---|---|---|
| | hex-1-ene | *cis trans* hex-2-ene | n-$C_7H_{14}O$ | i-$C_7H_{14}O$ | Other | n/i |
| $RhCl(CO)(PPh_3)_2$ | 0.6 | 1.7 | 61.8 | 35.0 | 0.9 | 1.8 |
| $[RhCl(CO)(PPh_2\text{-}D_{60})_2]_x$ [b] | 0.8 | 1.8 | 46.7 | 50.1 | 0.6 | 0.9 |
| $[RhCl(CO)(PPh_2\text{-}D_{20})]_x$ | 0.6 | 2.0 | 46.0 | 50.1 | 1.3 | 0.9 |
| $[RhCl(CO)(PPh_2\text{-}D_8)_2]_x$ | 42.8 | 24.6 | 19.0 | 10.9 | 2.7 | 1.7 |

[a] Yield determined by gas chromatographic analysis. [b] The catalyst material recovered after the reaction was recycled for two additional hydroformylation experiments. The results were essentially the same as found for the original material.

that essentially no depolymerization took place. However, in accord with the suggested nature of the catalyst mentioned above, analytical data for the material indicated that there was appreciable loss of the phosphorus and rhodium from the polymer. Furthermore, the carbonyl band in the infrared, originally present at 1970 $cm^{-1}$ was absent in the spent material and the electronic absorption band at 3625 Å is replaced by a broad band in the 4100—4500 Å region. Since traces of oxygen could be responsible for this behavior [22], the hydroformylation was repeated taking great care to exclude all traces of oxygen from the solvent, reactants, and pressure vessel. Even under these conditions, the results were the same as discussed above.

The rhodium(I) complex attached to the $PPh_2\text{-}D_8$ polymer produced different hydroformylation results than those observed with complexes of the other systems. In this case, about half of the hex-1-ene remained unreacted after the reaction and the normal/branched aldehyde product ratio (1.7) was just slightly less than that observed for $RhCl(CO)(PPh_3)_2$. Only 14% of the hex-1-ene was converted to aldehyde products while 24.5% was isomerized to a mixture of *cis*- and *trans*-hex-2-ene. In our previous work with hydroformylations catalyzed by analogous iodo complexes containing monomeric phosphinoalkylorganosilicon ligands we also observed that the best normal/branched aldehyde product ratios were obtained with the slower reactions [12]. This observation is consistent with the presence of phosphinated rhodium(I) complexes as the active catalyst and indeed this polymer material did contain the highest P/Rh ratio of the systems investigated. The coordinated phosphines of the active complex could be the phosphinated polymer material although they are more likely degradation products thereof, since no polymeric residue could be recovered at the end of the experiment in this particular case.

## Experimental

*Materials.* All solvents were dried and/or distilled prior to use. The silicon compounds were obtained from commercial sources and used as received. Lithium diphenylphosphide was prepared by the reaction of $ClPPh_2$ with lithium in tetrahydrofuran. The complex, *trans*-RhCl(CO)$(PPh_3)_2$ was prepared according to published procedures [23]. Elemental analyses were determined by Geller Laboratories.

*Equipment.* Infrared spectra of materials were taken with salt plates or KBr discs using a Perkin—Elmer spectrophotometer, Model 457. UV spectra of the polymers were taken on benzene solutions with a Cary-14 spectrophotometer. Gel permeation chromatography (GPC) experiments were carried out on a Waters Gel-Permeation chromatograph with columns of $3 \times 10^6$, $1.5 \times 10^5$, $10^4$ and $10^3$ $10^3$ Ångstrom ratings. Columns were used in the order given, with $3 \times 10^6$ Ångstrom column at the efflux end. THF was used as the carrier solvent in all GPC work. The flow rate was about 1 ml min$^{-1}$, the injection time was 1 min, and the sample concentration was 0.25% (wt) or less. The column system was calibrated by using a narrow molecular weight distribution polystyrene standard. Viscosity measurements were made on THF solutions of the polymer at 28.7—28.8°C by using a suspended level Ubbelholde Viscometer from Cannon Instrument Company. Viscosity calculations were made using accepted procedures [24]. Hydroformylation reactions were carried out in a 200 ml stainless steel Aminco rocking autoclave. Product distributions were determined on a Hewlett—Packard Model 5830 Gas Chromatograph by flame ionization detection.

### *Syntheses*

In general, reactions and operations were carried out in a glove box with a dry nitrogen atmosphere. However after the rhodium(I) complex was formed, all materials were handled under normal laboratory conditions.

### *Synthesis of the phosphinated silicone polymers*

Treating a neat mixture of octamethylcyclotetrasiloxane ($D_4$), 17.9 g (60 mmol) and chloromethylheptamethylcyclotetrasiloxane (Cl-$D_4$), 5.0 g (15 mmol) with 10 drops of concentrated $H_2SO_4$ produced, upon stirring for approximately 20 h, the desired chloromethylated polysiloxane, $(\text{Cl-}D_{20})_x$. The material is purified by adding an ether solution of the product to absolute methanol. The $(\text{Cl-}D_{20})_x$ polymer, 22 g, precipitates in essentially quantitative yield, 98%. The Cl-$D_8$ polymer is prepared in a similar manner using equimolar quantities of the cyclic siloxanes. Refluxing the $ClCH_2$-siloxanes with excess NaI in acetone for 10 days produced the corresponding $ICH_2$-siloxanes. A typical experiment calls for the reaction of $(\text{Cl-}D_{20})_x$ (15 g, 10 mmol $ClCH_2$-units) with NaI (15 g, 100 mmol) in refluxing acetone (200 ml) for 10 days. The bulk of the NaCl is removed by filtration and the $ICH_2$-polymer is obtained in 98% yield as a viscous oil when the filtrate is poured into methanol and the solution is cooled (the polymer is dried in vacuo). A typical phosphination involves treating the $(\text{I-}D_{20})_x$ polymer (3.0 g, 5 mmol $ICH_2$-units), dissolved in 40 ml of THF) with 30 ml of a 0.2 *M* solution of $LiPPh_2$. A pale orange color persists when the reaction is complete and a few drops of methanol are added to destroy the excess $LiPPh_2$. The mixture is evaporated to near dryness and added to 400 ml of methanol. When cooled, the $(PPh_2\text{-}D_{20})_x$ separates as a clear viscous oil in 82% yield.

If the halogen exchange reaction is allowed to proceed for 20 h, only partial halogen exchange is achieved. Treating a sample prepared in this manner with

$LiPPh_2$ as described above produced a phosphinated polymer in 80% yield having the following approximate composition $[PPh_2CH_2Si(Me)O]_x[ClCH_2Si(Me)O]_{2x}(Me_2SiO)_{57x} \approxeq PPh_2\text{-}D_{60}$ Anal. Found: C, 34.8, H, 7.8; P, 0.66. $C_{132}H_{367}Si_{60}O_{60}PCl_2$ calcd.: C, 33.8; H, 7.9; P, 0.66%.

*Synthesis of the polymer attached complexes*

*$PPh_2$-$D_{60}$ complex (A).* A solution of $(PPh_2\text{-}D_{60})_x$, (6.3 g, 3.8 mmol of $PPh_2CH_2Si$ groups) in 100 ml of dry, deoxygenated benzene was stirred for 5 days at room temperature with *trans*-$[RhCOCl(PPh_3)_2]$ (2 g, 3 mmol). After evaporating the mixture under vacuum to about 50 ml volume, the mixture is added to 400 ml of dry, absolute methanol at which time 7 g of a bright yellow, very viscous oil settles out. Upon drying under vacuum, the product darkens to a yellow-orange elastomeric gum. The purity of the product is checked by dissolving the polymer in heptane and filtering it to remove any insoluble $[RhCl(CO)(PPh_3)_2]$. It is then reprecipitated in methanol. Analysis of the material showed 0.50% P and 0.79% Rh (95 mol percent of $PPh_2$ groups complexed).

*$PPh_2$-$D_{20}$ complex, (B).* This was prepared and purified following the details given for the $PPh_2$-$D_{60}$ complex. Analysis of the material (90% yield) showed 1.67% P and 2.54% Rh (92 mol percent of the $PPh_2$ groups complexed).

*$PPh_2$-$D_8$ complex, (C).* This was prepared and purified following the details given for the $PPh_2$-$D_{60}$ complex. Analysis of the material (81% yield) showed 4.36% P and 2.97% Rh (41 mol percent of the $PPh_2$ groups complexed).

*Hydroformylation tests*

The pressure vessel is charged with an amount of catalyst which contains 0.05 mmol of rhodium (typically 0.5 g of a catalyst which is about 1% rhodium by weight), 42 g (500 mmol) of 1-hexene and 50 g of benzene as solvent, then sealed pressure tight. The vessel is positioned in the rocking mechanism, purged three times with 1/1 synthesis gas, then filled to the desired pressure (typically 1000 psi) with 1/1 synthesis gas. If necessary a diaphragm compressor is used to raise the available cylinder pressure to the predetermined level. The rocking mechansim and the heaters are activated and the progress of the reaction is followed on a temperature recorder and pressure gauge. The pressure drop, indicative of reaction, begins as the internal temperature approaches 90° C and continues throughout the run, which is normally held at an operating temperature of 100° C. At the run's completion, the rocker and heater are turned off and the autoclave cools overnight to room temperature. Gas samples are taken and analyzed by mass spectroscopy and GLC and the remaining gas is then vented to the atmosphere through a purge line. The pressure vessel is opened and the contents transferred to a rotating vacuum evaporator to remove the solvent. The products are analyzed on a Hewlett—Packard Model 5830 Gas Chromatograph by flame ionization detection. The catalyst is recovered by evaporating off as much volatile material as possible on a rotating vacuum evaporator and then pouring the residue (with a little benzene as solvent if necessary) into 200 ml of absolute methanol and refrigerating it for several hours. The polymer precipitates out and is recovered. The rhodium (phosphorus) analyses on the recovered polymer "complexes" were 0.22 (0.02) and 0.30 (0.90)% for the $PPh_2$-$D_{60}$ and $PPh_2$-$D_{20}$ complexes respectively.

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