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Infrared Studies on Polymer-Bound Palladium–Phosphine Complexes

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The formation of Pd complexes in phosphinated polystyrene resins has been studied. By the use of $Cl_2Pd(pyridine)_2$ as the reacting complex it is shown that, depending on polymer properties such as BET surface area and phosphine content, varying amounts of the complex $Cl_2Pd(pyridine)(P—PS)_1$ are formed in the resin, together with the complex $Cl_2Pd(P—PS)_2$. It is found that the monosubstituted complex $Cl_2Pd(pyridine)(P—PS)$ exists even at formal ratios of $P/Pd > 2$. The presence of "inaccessible phosphine groups" in the resin contributes to this effect. Chemical analysis of the polymers treated with varying amounts of $Cl_2Pd(pyridine)_2$ has made it possible to calculate the "inaccessible phosphine concentration" in the three different polymers used in this study. This quantity is related to the BET surface area. The polymer with low surface area (1.5 m^2/g) has a higher amount of "inaccessible phosphine groups" than the polymer with the higher surface area (53.5 m^2/g). With $Cl_2Pd(benzonitrile)_2$ as the reacting complex, no analogous mixed complex is found in the resin. This system was studied by infrared spectroscopy in the M–Cl stretching region and in the spectral range of characteristic vibrations of some extra ligands (CO, 4-cyanopyridine) that were combined with the system. From these measurements we conclude that complexes of the type $(PS—P)-(PdCl_2)_n-(P—PS)$ where $n \geq 3$ are formed in the resin together with the bisphosphine complex. The role of the species $Cl_2Pd(pyridine)(P—PS)$ and $(PS—P)-(PdCl_2)_n-(P—PS)$ in catalytic applications of the resins is briefly discussed.

INTRODUCTION

Since the development of the technique of attaching soluble coordination catalysts to polymeric supports, this has become an active field of research. Most papers published in this area have, however, mainly dealt with catalytic reactions, i.e., studies on activity and selectivity. Studies with the primary interest to determine the constitution of the catalysts themselves have been rather scarce. As many of the systems that have been used behave similarly to their homogeneous counterparts, and as the latter ones often are well characterized, more detailed studies on heterogeneous systems have not been carried out. The assumption has been made that in both cases the same active species are operating. In those cases where the homogeneous and the heterogeneous systems give different results, and consequently a need for a deeper understanding exists, the investigator is often faced with major difficulties. The advantages of heterogenized systems, such as easier handling and more efficient product separation, are always accompanied by the disadvantage of more limited means by which structural information can be obtained. This is the same kind of problem as the one met in traditional heterogeneous catalysis.

Grubbs and Sweet (*1*) have used microprobe analysis to determine the distribution of metal and ligand atoms inside the polymer beads. Although important information is gained in this way, it gives no information of the metal–ligand arrangement in the polymer. Phosphorus (^{31}P) NMR has been used to study metal binding (Rh) to phosphinated polystyrene (*2*). By this technique the amount of phosphine complexed as a function of the amount of metal added could be determined. Very valuable information on molecular structure was actually gained in this study (*2*), namely, that a

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change from a trisphosphine complex to a bisphosphine complex took place on increased metal loading.

Photoacoustic spectroscopy (PAS) is a new technique that can be applied to materials unsuitable for study by conventional optical methods. PAS has been used to study and characterize the species formed on irradiation of $W(CO)_6$ in the presence of polyvinylpyridine (*3*). Yet another technique that has been successfully applied to determine the composition of heterogenized complexes is EPR. Using the method of paramagnetic probes, Russian scientists (*4*) were able to determine the distribution of complexes of palladium on silica.

Infrared spectroscopy is also a method that has been used for studying the metal–ligand arrangement in complexes and surface compounds. One can obtain much information from the frequency and absorption intensity of adsorbed carbon monoxide. In this way CO can be regarded as an ir probe for surface chemistry (*5–7*). Infrared spectroscopy together with chemical analysis has provided the information needed to determine the complex formed on reacting $Cl_2Pd(pyridine)_2$ with phosphinated polystyrene (*8*).

Palladium(II) chloride bound to phosphinated polystyrene is a system where major differences between the homogeneous and the heterogeneous system have been found (*9–12*). It is also a system where somewhat deviating suggestions have been made as to what complex actually is formed in the polymer. Thus in the work by Bruner and Bailar (*9, 10*) the polymer catalyst was synthesized by reacting $Cl_2Pd(benzonitrile)_2$ with the polymeric ligand and these authors suggest the formation of a bisphosphine complex in the matrix. Terasawa *et al.* (*12*) synthesized their catalyst by reacting the polymeric ligand with $PdCl_2$. From analytical, ir, and XPS results they suggest that the coordinatively unsaturated complex $Cl_2Pd(P{-}PS)$ is formed (P—PS is the polymeric ligand). This latter complex is somewhat similar to that found by us (*8*): when $Cl_2Pd(pyridine)_2$ was reacted with phosphinated polystyrene, only one phosphorus atom in the polymer was coordinated for each metal atom, the other coordination site being occupied by a pyridine ligand ($Cl_2Pd(pyridine)(P{-}PS)$).

The $X_2Pd(phosphine)_2$ type of catalyst has interesting applications as a hydrogenation catalyst. Meaningful discussion on its reactions cannot be carried out, however, if the constitution of the catalyst is unknown. Our previous investigations (*8*) on such systems have therefore been continued. In doing this we have synthesized a number of catalysts using different matrixes and various preparative methods, and used ir spectroscopy with several probes to elucidate the structure of the complexes formed in the matrix.

EXPERIMENTAL

Infrared spectra were measured with a Perkin Elmer 580B spectrometer equipped with PE Data Station. The catalysts were sampled as KBr or polyethylene pellet suspensions except for the CO-treated catalysts which were examined as Nujol mulls.

Materials. All chemicals and solvents used were of analytical grade. KBr and polyethylene used for the ir measurements were spectroscopically pure. Chloromethylated polystyrene was purchased from Merck (Merrifield Harz art. No. 805064) and from Pierce (No. 24600). Dichlorobisbenzonitrile palladium(II) $Cl_2Pd(benzonitrile)_2$ (*13*) and dichlorobispyridine palladium(II) $Cl_2Pd(pyridine)_2$ (*8*) were prepared by literature methods. *p*-Styrenediphenylphosphine $CH_2{=}CH{-}C_6H_4{-}P(C_6H_5)_2$ was prepared according to the method given by Rabinowitz and Marcus (*14*). Lithium diphenylphosphine Li $P(C_6H_5)_2$ was generated from Li and $P(C_6H_5)_3$ (*15*).

Preparation of phosphinated polymers. The chloromethylated polystyrenes (Merck, Pierce) were phosphinated by reacting the polymers with Li $P(C_6H_5)_2$ in dry THF under nitrogen (*4*). The styrene *p*-

styrenediphenylphosphine copolymer was prepared by rapid stirring of a solution of 12.5 ml styrene, 0.5 ml divinylbenzene solution (50%), and 8.0 g of *p*-styrenediphenylphosphine in water suspension at 70°C overnight. Azo-iso butyronitrile (250 mg) was used as initiator.

Work-up procedures for all polymers were the same as those given earlier (*8*). Phosphorus analyses are given in Table 1.

Preparation of polymer-bound palladium complexes. These were all carried out by the same general procedure. The calculated amount of palladium complex was dissolved in CH_2Cl_2 under nitrogen, and the calculated amount of the phosphinated polymer was then added to this solution. The mixture was shaken for 24 hr. The polymer was recovered by filtration and washed. It was then extracted with CH_2Cl_2 for 24 hr in a Soxhlet apparatus.

The methods of analysis have been given before (*8*). Data for all the preparations are given in Table 2.

Reactions with CO. Those samples which were selected for CO treatment were first finely ground and then placed in a glass vessel with a sidearm equipped with a membrane. The vessel was first evacuated to ca 0.1 Torr and then filled with dried CO to 600 Torr. After 12 hr contact time Nujol was injected through the membrane and the flask was gently shaken in order to let the Nujol carefully wet the polymer. The latter procedure is important, as the CO-complex formed is very moisture sensitive. Without protection the polymer darkens in a few minutes. If, however, the polymer is protected from moisture as described, the polymer can be easily handled and ir spectra taken. The reason for this darkening of the CO–Pd polymer in moist air will be discussed later together with the ir spectra of the CO complexes.

RESULTS AND DISCUSSION

Table 1 gives the data for the three different polymers that we have used in this study. They are all of the swellable, microporous type, although they differ quite considerably in surface area.

In Table 1 the phosphorus content represents total phosphorus. Some of the phosphines in the polymer will, however, presumably be located so that they are not easily accessible. The amount of the phosphines that can be used for metal binding depends on polymer properties such as porosity.

The method of preparation can also influence the amount of accessible phosphorus. An example from the chemistry of Rh may help to illustrate this. Thus if $ClRh[P(C_6H_5)_3]_3$ is reacted with the phosphinated polystyrene matrix, it needs only one phosphine in the polymer to form the

TABLE 1

Phosphorus Content and BET Surface Area for the Polymers

Polymer	Denoted	%P	$C_P{}^a$ (mmol/g)	BET area (m^2/g)	Cross-linking (%)	$C'_P{}^b$ (mmol/g)	$(C'_P/C_P) \times 100$
Merck	PI	2.5	0.81	53.5	2	0.28	34
Pierce	PII	1.9	0.62	1.5	2	0.46	74
Styrene–*p*-styrene diphenylphosphine copolymer	PIII	5.0	1.61	Too small to be determined	2	0.50	31

[a] C_P = total phosphine concentration.

[b] C'_P = concentration of inaccessible phosphine.

desired Wilkinson analog $ClRh[P(C_6H_5)_3]_2$ P—PS. In this way also isolated phosphines in the matrix can be used if there is enough space to accommodate the bulky complex at all. On the other hand, if the synthesis is carried out by reacting $[RhCl(C_8H_{12})]_2$ with the phosphinated polystyrene, three phosphines in the matrix are needed to form the desired $ClRh(P—PS)_3$ complex. In this way only those phosphine groups that are close together or which by chain deformation can be brought close together can be used. Isolated phosphine groups in the resin may result in the formation of other complexes, with different catalytic properties such as $RhCl(C_8H_{12})_2$ P—PS. The amount of phosphorus accessible for formation of a particular complex is accordingly in a way determined by the type of reaction.

In the present study we have touched upon these problems as we have used different polymers and different preparative routes. The two methods of preparation we have used are both based on ligand substitution reactions, that is to say substitution of a less strongly coordinating ligand (in this case an N-donor ligand such as pyridine or benzonitrile) by the polymeric phosphine. Both methods of preparation require that two P-groups must be supplied from the polymer to form the complex (Eq. (1))

$$Cl_2PdL_2 + 2\ PS—P \rightarrow (PS—P)_2PdCl_2 + 2L \quad (1)$$

(L = pyridine, or benzonitrile)

This in turn requires that the phosphines are, or can be, arranged so that a bisphosphine complex can be formed. We have previously shown (*8*) that, when a phosphinated polystyrene with 1.8% P and a Pd/P ratio of 1 : 2 was used, the substitution is not complete but that a mixed complex Cl_2Pd(pyridine)(P—PS) is the dominating species in the matrix. As the pyridine ligand in the matrix is easily detectable by ir spectroscopy or by analytical methods, the synthesis from $Cl_2Pd(pyridine)_2$ is one way in which it is possible to obtain an idea about the most favorable conditions for formation of the bisphosphine complex.

Synthesis from Cl_2Pd (pyridine)$_2$

By reacting the three different polymers with different amounts of $Cl_2Pd(pyridine)_2$ a set of preparations with different P/Pd ratios was obtained. The analytical results for these preparations are given in Table 2. Although the variation in the total phosphorus content between the various polymers is relatively small, a difference in complex formation can be seen. For instance, polymer PII with the lowest phosphorus content gives the formation of the mixed Cl_2Pd (pyridine)(P—PS) complex in spite of the ratio P/Pd used being such (2.3 : 1) that the bisphosphine complex might have been formed. Indeed, if the polymer PII is treated with an even larger quantity of the metal complex (P : Pd = 1.1 : 1), the amount of metal incorporated remains the same. This polymer reaches a state of saturation even though not all phosphorus is used (P/Pd = 4.7). It follows that the polymer PII holds a relatively large amount of nonaccessible phosphine groups. In a following section we discuss the concept of "inaccessible phosphine groups" and also show how this number can be calculated. For the polymer PII the relative amount of nonaccessible phosphine groups (C'_P/C_P) is very high (74%) (Table 1), and this polymer reacts quite differently compared to the others.

Polymers PI and PIII, which have a much lower but about the same relative amount of inaccessible phosphine groups (~30%, Table 1), both react according to the same pattern. That is, treatment of the polymers at high P/Pd ratios is accompanied by a formation of the bisphosphine complex $Cl_2Pd(P—PS)_2$ as the main species (see preparations 011, 037, 038). On synthesis at P/Pd ratios close to 2 the formation of the mixed complex Cl_2Pd(pyridine)(P—PS) is fully noticeable (preparation 039). Preparations carried out with lower P/Pd ratios

TABLE 2

Analytical Results for the Prepared Catalysts

Preparation	Polymer	Pd complex used	P : Pd[a]	%Pd	Pd (mmol/g)	%N	N (mmol/g)	$\%P_{corr}$[b]	P_{corr} (mmol/g)	P/Pd	N/Pd
011	PIII	Cl_2Pdpy_2	2.5 : 1	5.74	0.54	<0.1	—	4.5	1.46	2.22	—
012	PIII	Cl_2Pdpy_2	1.3 : 1	7.95	0.75	0.96	0.69	4.1	1.32	1.76	0.92
019	PIII	Cl_2Pdpy_2	0.6 : 1	8.56	0.80	1.11	0.79	4.0	1.29	1.61	0.99
014	PII	Cl_2Pdpy_2	2.3 : 1	1.36	0.13	0.15	0.11	1.9	0.61	4.7	0.85
015	PII	Cl_2Pdpy_2	1.1 : 1	1.37	0.13	0.16	0.11	1.9	0.61	4.7	0.85
037	PI	Cl_2Pdpy_2	6 : 1	1.23	0.12	<0.07	—	2.44	0.79	6.5	—
038	PI	Cl_2Pdpy_2	3 : 1	2.91	0.27	<0.08	—	2.38	0.77	2.8	—
039	PI	Cl_2Pdpy_2	2 : 1	3.49	0.33	0.22	0.16	2.31	0.75	2.3	0.49
040	PI	Cl_2Pdpy_2	1 : 1	4.19	0.39	0.50	0.36	2.23	0.72	1.8	0.91
034	PI	$Cl_2Pd(PhCN)_2$	3 : 1	2.58	0.24	—	—	2.41	0.78	3.2	—
035	PI	$Cl_2Pd(PhCN)_2$	2 : 1	3.64	0.34	—	—	2.35	0.76	2.2	—
036	PI	$Cl_2Pd(PhCN)_2$	1 : 1	6.64	0.62	—	—	2.22	0.72	1.2	—

[a] Stoichiometric ratio of phosphine (P) to Pd used at synthesis.

[b] Amount of phosphorus in the polymer determined by analysis. The weight of the polymer was corrected for metal uptake.

(preparations 012, 019, 040) result in a nearly complete formation of the mixed complex. From these observations one can rather safely state that the amount of accessible phosphine groups is one of the factors that determines the complex formation inside the polymers. Consequently it is important to be able to determine this quantity.

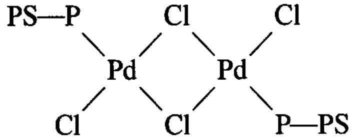
In the formation of the bisphosphine complex two phosphine groups in close proximity are needed. This can be achieved in two ways, either by increasing the phosphorus content and thereby decreasing the distance between the phosphine groups, or by changing polymer properties such as chain deformation ability, making the phosphine groups more mobile. However, the three polymers used in this study have the same degree of crosslinking (2%), and thus no great variation in phosphine mobility should be expected. Nevertheless, besides the degree of crosslinking one other effect that must be recognized in connection with phosphine mobility is that metal coordination can create a more rigid polymer. Such effects have been noted before (*16a*). The observation that PI and PII, which at low metal loadings both form mainly the bisphosphine complex, form the monophosphine complex at high metal loading, might be due to such an effect. The energy needed to change the chain conformation so that the bisphosphine complex can be formed increases for each metal atom coordinated in that case.

Synthesis from Cl_2Pd(benzonitrile)$_2$

Knowing how the polymer PI reacted on increased metal loading in the formation of the complex Cl_2Pd(pyridine)(P—PS), we found it interesting to study the same polymer reacting with Cl_2Pd(benzonitrile)$_2$. Also for such a preparative route Pittman *et al.* (*16b*) found that P/Pd ratios less than two can be achieved. No sign of benzonitrile present in the resin after reaction was found in our preparations (Table 2), nor have other studies (*10, 11*) showed the presence of benzonitrile in the polymers.

The first step in the substitution in the pyridine case as well as in the benzonitrile one is most probably the same. This means that, even in the last case, a mixed complex Cl_2Pd(benzonitrile)P—PS should be formed. Because of the low complex-binding ability of benzonitrile combined with the high trans-effect of the phosphine ligands, this is probably a very unstable complex. One can therefore assume that such a complex will react further. Different possible routes for further reactions exist, for example, the formation of a coordinatively unsaturated complex by release of the benzonitrile ligand. However, this is not a very likely reaction since it is well known that such coordinatively unsaturated complexes are mostly very reactive. A chemically more attractive way for further reactions from the unstable Cl_2Pd(benzonitrile)(P—PS) complex is a dimerization (Eq. (2)).

2 $Cl_2Pd(L)(P—PS) \rightarrow$



+ 2 L (2)

(L = benzonitrile)

From the analytical data in Table 2 no information as to which species is formed on high metal loading can be obtained. (At first sight, this is true. In a following section we will see that analytical data are nevertheless of value.) Analytical data do, however, inform us that a bisphosphine complex cannot be the only species in the resin at high metal loading since a P/Pd ratio less than two can be obtained. It does also inform us that if polymer PI is treated with either $Cl_2Pd(pyridine)_2$ or $Cl_2Pd(benzonitrile)_2$ in a P/Pd ratio of 1, the benzonitrile case gives a much higher metal incorporation (6.6% Pd compared to 4.2% Pd for the pyridine case). This must mean either that more phosphorus is accessible in the benzonitrile case, or that each accessible phosphorus atom is shared with more than one palladium atom.

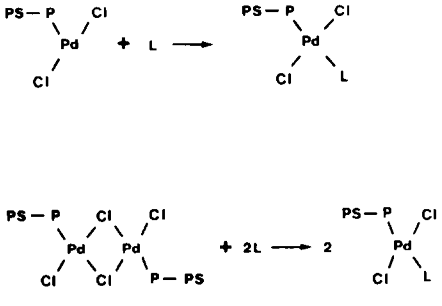
Infrared Studies

The coordinatively unsaturated complex as well as the bridged complex can be expected to behave chemically very similar. On treatment with a Lewis base L they will most probably give the same product according to Scheme 1. A suitable Lewis base, i.e., one that does not destroy the bisphosphine complexes, easy to detect by infrared spectroscopy, should therefore make it possible to show the existence of such species.

4-Cyanopyridine

For this purpose we have reacted preparation 036 with 4-cyanopyridine. This choice was made for two reasons. First, Cl_2Pd(pyridine)(P—PS) has been shown to be stable in the resin. Second, the cyano group on the pyridine ring permits an easy identification by infrared spectroscopy to be made, as the C≡N stretching absorption is strong and appears in a spectral region where resin absorption does not interfere.

On reacting preparation 036 with 4-cyanopyridine (Pd : 4-cyanopyridine = 1 : 1) in CH_2Cl_2 the original deep orange color of the resin changed to light yellow and palladium was extracted. (Cl_2Pd(4-cyanopyri-



SCHEME 1. Possible reaction routes on treatment with a Lewis base L.

dine)$_2$ could be identified in the solution.) Extraction of palladium down to a level comparable to the metal content of preparation 040 could perhaps be expected as the maximum possible content of Cl_2Pd(pyridine)(P—PS) is of that order. Much more was, however, extracted judged from the amount of Cl_2Pd(4-cyanopyridine)$_2$ formed although no quantitative measurements were made. This extraction of palladium does not make the results obtained with 4-cyanopyridine as conclusive as we hoped them to be. Taken together with other results of this study, however, even this extraction can be explained.

In the infrared spectra of the 4-cyanopyridine-treated polymers a very weak signal at 2239 cm^{-1} was present. On comparison with the spectra of the complex derived from reaction of $Cl_4Pd_2(P(C_6H_5)_3)_2$ with 4-cyanopyridine giving $Cl_2PdP(C_6H_5)_3$-(4-cyano)-pyridine, this can be assigned to the C≡N stretch in Cl_2Pd(4-cyanopyridine)(P—PS).

Infrared spectra thus show that the expected product is formed (Scheme 1) but to a rather small extent.

Carbon Monoxide

Another Lewis base useful as an infrared probe is CO. When preparation 036 suspended in solvents like acetone, ethanol, or CH_2Cl_2 was treated with CO, the polymer darkened and nothing but black polymers could be recovered showing no sign of carbonyl bands in their infrared spectra. We therefore changed to perform the CO treatment in the solid state under such conditions that moisture was carefully excluded. Using the method outlined in the experimental section, spectrum A given in Fig. 1 was obtained after 15 hr CO treatment. This spectrum shows two bands in the CO stretching region, one positioned at 2125 cm^{-1} and another at 1925 cm^{-1}, both with about equal intensity. If the Nujol mull was left in air the spectrum gradually changed and spectrum B was obtained. The peak at 2125 cm^{-1} in A has disappeared and a new peak at 1970 cm^{-1} is present instead. This new peak is of lower intensity than the one at 2125 cm^{-1}. It is also worth noting that the peak at 1925 cm^{-1} is unchanged by this treatment. However, on addition of a very moist solvent, such as dioxan with a small amount of water added, the polymer becomes black. The most likely explanation of the latter reaction is a reduction of the Pd–CO complex or complexes in the resin to form Pd metal. This is also evident from the infrared spectrum as it shows no carbonyl bands after treatment of the Nujol mull with moist solvents (spectrum C). In the following paper (*17*) it is shown that palladium metal is formed.

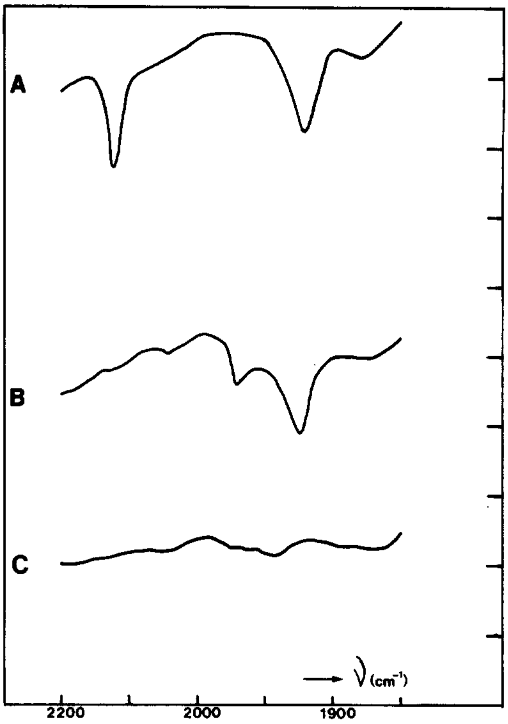


FIG. 1. Infrared spectra of preparation 036 treated with CO: (A) direct after treatment, (B) after storage in air, (C) after treatment with moist solvent.

Numerous workers have investigated the reaction of CO with Pd halides (*18–22*), with varying formulations of the complex formed. More recent studies (*23, 24*) however, have, established that CO reacts with Pd halides to form the complex $(PdXCO)_n$

with alternating CO and X bridges. This complex has the CO-stretching mode at about 1978 cm^{-1}. It can be isolated as a yellow (or yellow-green) solid, and it is unstable to heat and moisture. Goggin and Mink in their study (*24*) reacted $PdCl_4^{2-}$ with CO and initially observed a band at 2132 cm^{-1} corresponding to the ion $[Cl_3PdCO]^-$. On prolonged treatment this band decreased and new bands at 1966 and 1904 cm^{-1} (s) ((s) = strong) appeared. After reaction a solid phase of composition $Pr_4{}^nN$ $[PdCl_2CO]$ could be isolated on addition of $Pr_4{}^nNCl$ (Pr^n = *n*-propyl). The anion $PdCl_2CO^-$ (ν_{C-O} 1915 cm^{-1}) was formed on reaction of CsCl with $(PdClCO)_n$ (*23*) and $R_4N(PdCl_2CO)$ salts (ν_{C-O} 1963 cm^{-1} (vw), 1905 cm^{-1} (s)) could be prepared by reacting $(PdClCO)_n$ with the appropriate tetraalkylammoniumchloride. From this collected evidence we conclude that CO reacts with $PdCl_4^{2-}$ or $PdCl_2$ first to form the ion $PdCl_3CO^-$ (ν_{C-O} 2132 cm^{-1}) or $PdCl_2CO$. On further reaction involving reduction $(PdClCO)_n$ (ν_{C-O} 1978 cm^{-1}) is formed which on treatment with chloride containing salts gives the ion $PdCl_2CO^-$ (ν_{C-O} around 1910 cm^{-1}). Part of this pattern, i.e., the formation of a carbonyl complex absorbing at 2125 cm^{-1} which then reacts to give a peak at 1970 cm^{-1}, can also be observed in our spectra (A, B). The question now arises as to the source of $PdCl_4^{2-}$ or $PdCl_2$. As stated in the beginning of this section we suspected the existence of either the coordinatively unsaturated complex PS—P $PdCl_2$ or the bridged complex (PS—P) Pd_2Cl_4. In our opinion none of these structures can explain our CO spectra. If, however, the bridged complex is extended to contain more than two palladium atoms we arrive at a structure containing $PdCl_2$ units. We therefore suggest that at high Pd loadings the polymer contains species of the type (PS—P)–$(PdCl_2)_n$–(P—PS) with bridging Cl atoms.

On reaction with CO the chloride bridges are cleaved and $PdCl_2CO$ is formed from the $PdCl_2$ units in the chain, giving rise to the band at 2125 cm^{-1}. The band we observe at 1925 cm^{-1} is then arising from CO bonded to the two end groups. The position of this band corresponds to what is frequently observed for bridged CO in Pd(I) complexes (e.g., $\nu(C{\equiv}O)$ is at 1948 cm^{-1} for CO trans to PhCN in $(PdClCO)_3PhCN$ (*24*)). The assumption can therefore be made that Pd in this complex is reduced to Pd(I) and that the two end groups are bridged by CO to form a dimer. It is possible that CO acts as the reducing agent forming, for example, phosgene.

By keeping the Nujol mull open to air slow diffusion of moisture is a possible reaction. The changes in the spectra that we have observed (compare A and B) can therefore depend on a limited reduction of the $PdCl_2CO$ complex in the matrix to form the Pd(I) complex $(PdClCO)_n$ with CO absorption at 1970 cm^{-1}.

On treatment with larger amounts of water both CO complexes are reduced to Pd metal as judged by the color change and disappearance of the CO peaks in the spectrum. A complete scheme for the reactions discussed is given in Fig. 2. This scheme must not, however, involve the suggested long-chain bridged species. The same reaction scheme can also be applied to a case where excess palladium (compared to a stoichiometric ratio P/Pd = 2) is $PdCl_2$ deposited as such in the matrix, in addition to the coordinatively unsaturated species. But in such a case an explanation of the benzonitrile release and the $PdCl_2$ deposition is necessary.

It must be stressed that the bridged species $Cl_4Pd_2(P—PS)_2$ formulated above does not give rise to the CO spectra that we have observed. This can be deduced from the fact that $Cl_4Pd_2(C_6H_5)_3)_2$ does not react with CO although the Pt analog reacts and forms the complex $P(C_6H_5)_3PtCl_2CO$ (*25*). The same result concerning $Cl_4Pd_2(P(C_6H_5)_3)_2$ was also noted in another study published during the course of this work (*26*). These authors have prepared similar polymer-bound Pd-complexes and reacted them with

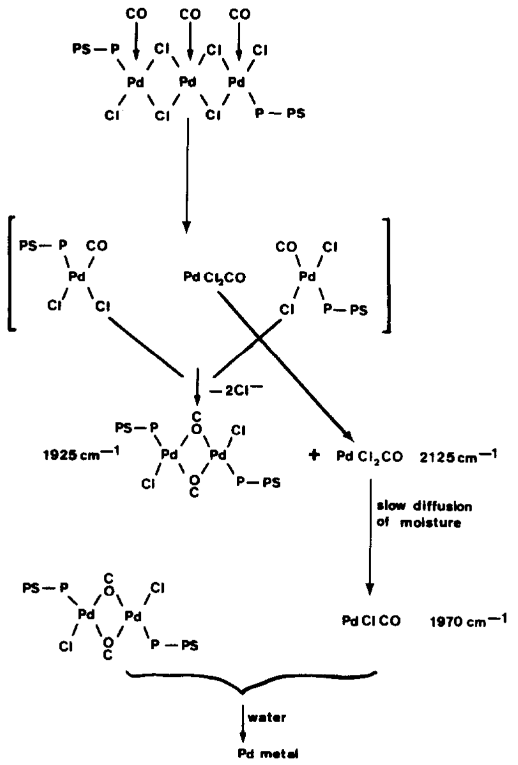


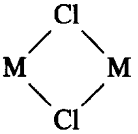
FIG. 2. Proposed reaction scheme for the CO-complexes formed in the resin.

CO. They report CO stretching frequencies in the region 1964–1947 cm^{-1} for polystyrene resins and around 1945 cm^{-1} for vinyl alcohol resins and suggest that $Cl_2Pd(CO)P$—PS species are formed. The rather low frequencies reported do however point to the fact that even in this case bridged Pd(I) complexes have probably been formed in the resins.

We can now return to the results obtained on treatment with 4-cyanopyridine. The extraction by 4-cyanopyridine of quite a large portion of the palladium in the resin is puzzling if only Cl_4Pd_2(P—PS)$_2$ or Cl_2Pd(P—PS) is present in the resin. Taking into account the presence of (PS—P)–$(PdCl_2)_n$–(P—PS) it is easy to imagine how this extraction occurs. Attack by the 4-cyanopyridine on the chloride bridges causes the interjacent $PdCl_2$ units to be released by the formation of (4-cyanopyridine)$_2PdCl_2$. Only a minor part of the palladium originally present is then left in the polymer, as Cl_2Pd(4-cyanopyridine)(P—PS).

Metal–Halide Vibrations

Further support for the formation of larger Pd aggregates can be derived from infrared spectra in the metal–chloride stretching region. Stretching frequencies for a large number of different palladium chloride complexes can be found in the literature (*25*), and assignments are reliable. Different problems, however, can arise if this method is applied to metal–chloride complexes in polymeric resins. First, as these complexes are often prepared in such a way that they are present in low concentrations in the matrix, the weak signals corresponding to M–Cl can be hard to detect and distinguish. Second, to our knowledge no study of intraligand deformation modes in polymeric phosphine ligands have been reported.

These problems, however, can be overcome. By the use of modern infrared spectrometers equipped with data handling facilities spectra can be expanded with retained signal to noise ratio. If necessary the background spectrum (matrix alone) can be subtracted. We have used this technique to study the complexes prepared from polymer PI in the region 400–180 cm^{-1}. Figure 3 shows a typical spectrum for the complexes prepared from Cl_2Pd(pyridine)$_2$ with the main peak at 353 cm^{-1}. This corresponds to a peak present in trans Cl_2PdL_2 complexes ranging from 357 to 353 cm^{-1} depending on phosphine. This peak is also found in $Pd_2X_4(PR_3)_2$ complexes (*27*) and is assigned to terminal Pd–X stretching. The small peaks at 295 and 265 cm^{-1} are present in all spectra with an intensity roughly independent of metal content in the polymer. This fact indicates that they are intraligand vibrations and not 

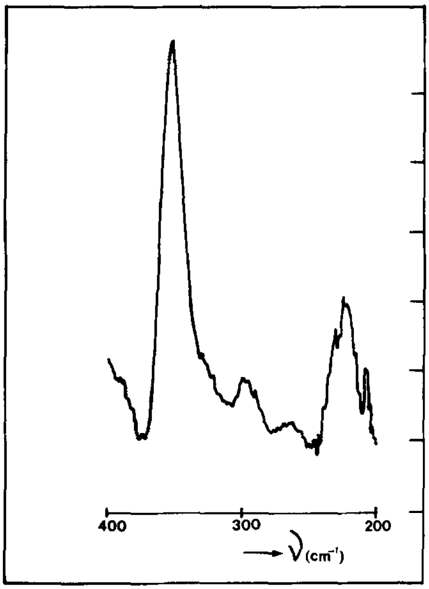


FIG. 3. Infrared spectrum of preparation 040 in the M–Cl region.

skeletal vibrations which are found at 297 and 260 cm^{-1}, e.g., in $Cl_4Pd_2(P(C_6H_5)_3)_2$. Another reason for this interpretation arises from the intensity ratio found for these two peaks. In all our spectra these are present in about equal intensity while in $Cl_4Pd_2(PR_3)_2$ complexes a ratio A_{260}/A_{297} of 2 has been found (*27*). The peak present at 220 cm^{-1} in our spectra however depends on the metal loading of the polymer and this fact indicates that it can be assigned to some kind of M–Cl vibration, possibly a combination mode of a bending mode and a M–P mode. As this band is not present for the complexes prepared from Cl_2Pd(benzonitrile)$_2$, however, an alternative explanation is that this band is due to coordinated pyridine.

If we now turn to the spectra obtained with the complexes prepared from Cl_2Pd (benzonitrile)$_2$ (Fig. 4) the same three peaks as in Fig. 3 are present at low Pd loading (spectrum A) with the peak at 353 cm^{-1} by far the most intense. Increasing the Pd loading (spectrum B) does not alter this situation much, but at the highest Pd loading (spectrum C) drastic changes occur. First, the absorption at ~353 cm^{-1} is broader and on 5 times abscissa expansion (spectrum E) it is clear that this absorption contains, in fact, two peaks, one at 353 cm^{-1} and the other at 340 cm^{-1}, the latter with a slightly lower intensity. Second, the intensity ratio of the two peaks at 295 and 258 cm^{-1} has changed, so that now the peak at low wavenumber is more intense (ratio about 2 : 1). The new peak appearing at 340 cm^{-1} is at the same position as the stretching vibration of the Pd–Cl bridges in solid $PdCl_2$ (*28*). $PdCl_2$ in the solid state consists of infinite chains of square-planar $PdCl_4$ units (*29*). We therefore conclude that this spectrum is consistent with the suggestion made earlier, that this polymer contains long chains of palladium atoms with chloride bridges. The changed intensity ratio for the two peaks at lower wavenumber might perhaps mean that even dimers are present in the polymer. However, this could also be due to the long chain species present.

A careful examination of the spectrum obtained with preparation 035 reveals that this also contains the peak at 340 cm^{-1} as a very weak shoulder (spectrum D). This can be seen more clearly if the difference spectrum (Fig. 5) between preparation 035–039 is formed.

Taken together, the studies on the complexes prepared from Cl_2Pd benzonitrile show clearly that in this case the polymer contains long-chain Pd species at high metal loading. We therefore suggest that the different reactions possible using different synthetic routes can be summarized in Scheme 2, with no implications to the actual mechanism of the reaction.

Calculations on the Analytical Data

Let us now once more turn to the interpretation of the analytical data left open in the introductory paragraph. Admittedly, we present a rather limited number of data but at least for two of the investigated resins, PI and PIII treated with the pyridine complex, we have a possibility of interpre-

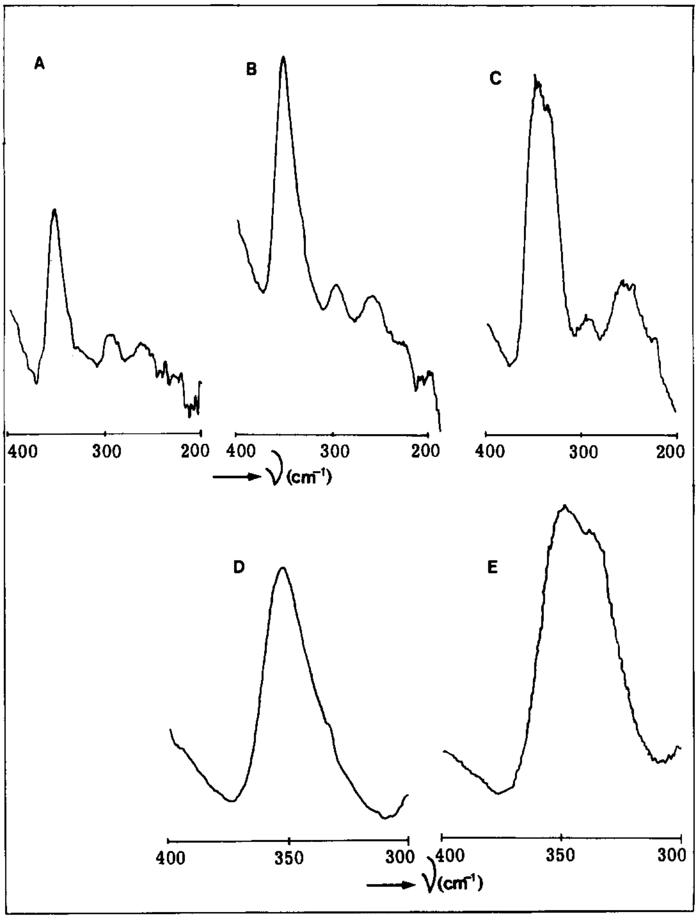


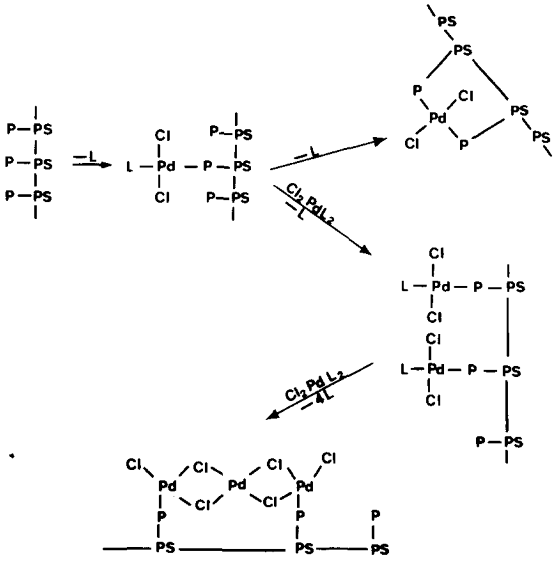
FIG. 4. Infrared spectra in the M–Cl region: (A) preparation 034; (B) preparation 035; (C) preparation 036; (D) spectrum B with 5 times expanded abscissa scale; (E) spectrum C with 5 times expanded abscissa scale.

tation. This interpretation will start from some concepts already introduced in the discussion above:

(1) The Pd complexes that are formed have a coordination number of four.

(2) There is only a certain part of the phosphine groups in the polymer that is accessible for coordination. Several reasons for this inaccessibility may exist, and one of them is most certainly the blocking by neighboring groups from the polymer units. As stated earlier the number of phosphines blocked may very well vary with degree of metal loading of the resin because of a change in conformation and superstructure. For the present analysis we neglect this possibility, however, and consider a certain concentration of inaccessible phosphine groups, C_p', as constant for one and the same preparation of polymer.

(3) The palladium(II) phosphine complexes are thermodynamically very stable. This means that the concentration of phosphine groups necessary to drive the equilibrium of the formation reaction to species of maximum coordination number is very small. Indeed, we will neglect this quantity in comparison with other terms. (This does not mean that there cannot exist "free" phosphine groups. If the metal loading of the resin is so low that the maximum coordination number is reached without con-



SCHEME 2. Proposed reaction scheme for the preparation of polymer bound Pd^{2+}-complexes.

suming all available groups, some must quite simply be left over.)

We further note that we have three different analytical quantities to deal with, namely, the total phosphine concentration C_P, the total metal concentration C_{Pd}, and the concentration of coordinated pyridine C_{py}.

Assuming that all metal atoms are kept in the resin because they are coordinated to one or two phosphines we can write the following mass balance equations:

$$C_P = C_P' + 2[Cl_2Pd(P—PS)_2] + [Cl_2Pdpy(P—PS)] \quad (3)$$

$$C_{py} = [Cl_2Pdpy(P—PS] \quad (4)$$

$$C_{Pd} = [Cl_2Pd(P—PS)_2] + [Cl_2Pdpy(P—PS)] \quad (5)$$

Eliminating the two unknown quantities we obtain the relation

$$C_{Pd} = \tfrac{1}{2}\,(C_P + C_{py} - C_P') \quad (6)$$

It is now pleasing to note that when plotting C_{Pd} against $C_P + C_{py}$ for the resins PI and PIII treated with $Cl_2Pd(pyridine)_2$, two straight lines result (Fig. 6). The slopes of these lines are 0.5 as in Eq. (6) and the intercept with the abscissa axis give a value for C_P'.

One of the points for the resin PI falls beside the line. This point corresponds to the lowest metal loading and one can rather safely assume there is unused ("free") phosphine groups present besides the $Cl_2Pd(P—PS)_2$ complexes. Hence Eq. (3) is not satisfied.

It is easily realized that the requirement for neglecting the "free" phosphine con-

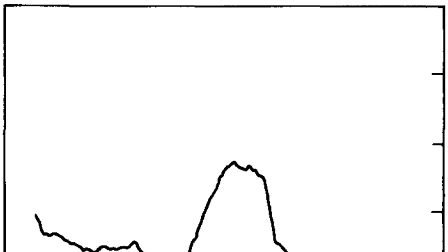


FIG. 5. Difference spectrum obtained on subtraction of the spectrum of preparation 039 from the spectrum of preparation 035.

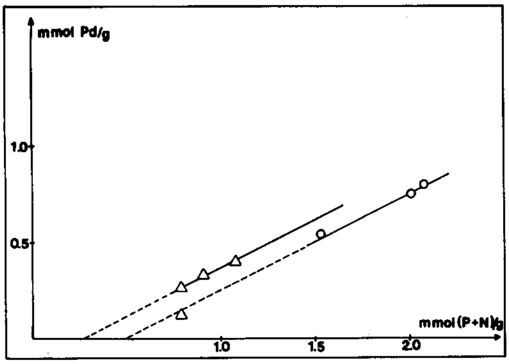


FIG. 6. Total palladium content plotted against the sum of total phosphine and pyridine content △, polymer PI; ○, polymer PIII.

centration is that $C_{Pd}^0 \geq \frac{1}{2}(C_P^0 - C'_P)$ where C_{Pd}^0 and C_P^0 are the starting values of the two concentrations.

Two interesting observations may now be made. The first one concerns the value of C'_P, the inaccessible phosphine concentration. Although we have only two points (or rather one, considering the final situation) for polymer PII it is possible to calculate C'_P for this resin supposing that the relations of Eqs. (3)–(5) hold. Such an assumption can be made rather safely as pyridine is detected to an appreciable extent. Thus introducing the analytical results into Eqs. (3)–(5) one obtains $C'_P = 0.46$ mmol/g.

One may now ask how the determined C'_P values correlate with the polymer structure. The determined BET surface area (Table 1) reflects the porosity of the polymer in the dry state, i.e., the higher the BET area the greater is the porosity. It is now good to note that the smaller the surface area (the lower the porosity) the larger is the relative concentration of shielded phosphine groups inaccessible for coordination (Table 1). This holds for polymers PI and PII, both of which are prepared by phosphination of a preformed polymer. Polymer PIII, which is prepared by copolymerization of the monomers styrene, divinylbenzene, and *p*-styrenediphenylphosphine does not, however, follow this pattern. Although this polymer has the lowest BET area the relative concentration of inaccessible phosphine groups is low. The reason for this might be the synthetic procedure. It is possible that the mode of preparation has created a polymer more prone to swell in the organic solvent used in the metal fixation. Hence the low porosity as reflected by the BET area in the dry state might be drastically changed by the action of the solvent.

The second observation concerns the PI resins treated with the benzonitrile complex. We assume that the value of C'_P is the same for the benzonitrile series as for the pyridine one. This is justified as the metal loading is about the same in the two cases. It is now possible to calculate the formal stoichiometric ratio Pd/P in the three experiments (Table 3). In all cases but the one with the lowest metal content one obtains more than one Pd for two P. The highest palladium content gives Pd : P = 2.8 : 2.

From these observations one can deduce that there exists one or more species in the resin with the general formulation (PS—P)–$(PdCl_2)_n$–(P—PS), where $n \geq 3$. The exact value of n cannot be determined without extra assumptions. Indeed, there might very well exist a series of complexes with $n = 3, 4, 5$ and so on. The important point is that this analysis of the total composition of the resins leads us to the same result as did the ir investigations on 4-cyanopyridine-treated resins as well as the ir investigations on the Pd—Cl vibration modes.

CONCLUSIONS

The degree of "inaccessible phosphine concentration" has been shown to vary with the properties of the resin, such as degree of crosslinking and surface area. It determines the type of complexes that form in the resin, and hence it influences the catalytic properties of the resin. An objective for further work is to investigate synthetic routes by which unutilized phosphines are minimized. A related question is

TABLE 3

Preparation	C_{Pd}[a] (mmol/g)	C_{P}[b] (mmol/g)	C'_{P}[c] (mmol/g)	Coordinated P[d] (mmol/g)	Coordinated N[e] (mmol/g)	ΣN + P (mmol/g)	Stoichiometric Pd : ΣN + P
011	0.54	1.46	0.50	0.96	—	0.96	1:2
012	0.75	1.32	0.50	0.82	0.69	1.51	1:2
019	0.80	1.29	0.50	0.79	0.79	1.58	1:2
037	0.12	0.79	0.28	—	—	0.51	—
038	0.27	0.77	0.28	0.49	—	0.49	1:2
039	0.33	0.75	0.28	0.47	0.16	0.63	1:2
040	0.39	0.72	0.28	0.44	0.36	0.80	1:2
034	0.24	0.78	0.28	0.50	—	0.50	1:2
035	0.34	0.76	0.28	0.48	—	0.48	1.4:2
036	0.62	0.72	0.28	0.44	—	0.44	2.8:2

[a] C_{Pd} = total palladium concentration.
[b] C_{P} = total phosphine concentration.
[c] C'_{P} = concentration of inaccessible phosphine.
[d] Coordinated P = $C_{\mathrm{P}} - C'_{\mathrm{P}}$.
[e] Coordinated N = amount of pyridine in the polymer.

whether the "inaccessible phosphine concentration" is constant or varies with the metal load or not.

Another very important discovery is that the resin can act as a host for $(\mathrm{PdCl_2})_n$ chains linked to phosphine groups. Such chains may have properties similar to crystallites of $\mathrm{PdCl_2}$ rather than to bisphosphine complexes and further work should investigate if such chains are formed for high metal loading also from other complexes than $\mathrm{Cl_2Pd}$ (benzonitrile)$_2$. The existence of these chains could be the reason for the easy reducibility of some of the Pd atoms in the resin.

The task for the catalyst designer is to combine the effects of crosslinking on diffusion of reactants and products with that on properties of the catalytically active metal complex.

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