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PREPARATION AND CHARACTERIZATION OF
HYBRID PHASE CATALYSTS

presented by

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has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Organic Chemistry

A handwritten signature in dark ink, appearing to be "R. H. H. Su", written over a horizontal line.

Major professor

Date _____



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PREPARATION AND CHARACTERIZATION OF HYBRID PHASE CATALYSTS

By

Shiu-Chin H. Su

A DISSERTATION

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ABSTRACT

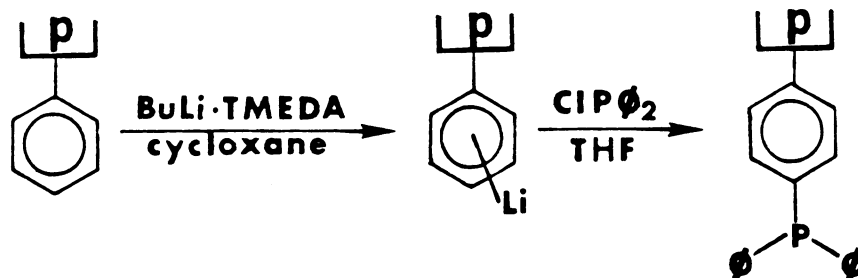
PREPARATION AND CHARACTERIZATION OF HYBRID PHASE CATALYSTS

By

Shiu-Chin H. Su

Polymer-supported phosphines have been used as ligands in hydrogenation¹, hydrosilylation² or hydroformylation³ reactions involving various transition metals. In all cases, the insoluble catalyst could be filtered from the reaction mixture and reused without appreciable loss of activity. In most cases, styrene-divinylbenzene copolymer "beads" have served as the polymer support.

An easily-controlled and convenient route for functionalizing polystyrene polymers was developed⁴. Styrene crosslinked with divinylbenzene (2 or 20%) was converted to polystyrene-lithium by treatment with a 1:1 complex of butyllithium-tetramethylethylenediamine in cyclohexane. The lithiated polymer was allowed to react with chlorodiphenylphosphine to produce polystyryldiphenylphosphine.



Cumene was used as a low molecular weight model molecule for examining the position of metalation. ^1H and ^{13}C NMR revealed that only meta and para trimethylsilane substituted cumene derivatives were obtained. Glc analysis indicated that the ratio of meta/para was the statistical, 2:1.

The radial distribution of phosphorus and the percent phosphorus substitution could be varied over a wide range by controlling the reaction time and temperature.

Tris(triphenylphosphine)chlororhodium polymer-supported catalysts were prepared from these polymeric ligands and gave a rate of reduction of cyclohexene of 7.65 ml/min./mmol of Rh which is better than that observed with a similar batch of material prepared by the bromination route^{1b}.

Lithiated polymer was reacted with chlorotrimethyltin, tetrachlorotin, diethylaluminium chloride and ethylaluminium dichloride to give respectively polymer-supported trimethyltin(IV), polymer-supported trichlorotin(IV), polymer-supported diethylaluminium and polymer-supported ethylaluminium chloride.

Phosphorus-31 NMR spectroscopy provides a useful tool for characterizing the polymeric organophosphorus ligands and their transition metal catalysts. The ^{31}P NMR measurements of phosphinated beads can be performed in a variety of swelling solvents, such as THF, benzene, toluene, xylene, chlorinated hydrocarbon, ethylacetate, acetone, diethyl ether, chlorobenzene and nitrobenzene. Since

toluene has a wide temperature range for the liquid state, it served as the main swelling solvent in these studies.

The chemical shift of polymeric triphenylphosphine (δ 5.93 ppm vs. 85% H_3PO_4) is essentially the same as that of triphenylphosphine. Polymeric triphenylphosphine oxide (δ -24.5 ppm vs. 85% H_3PO_4) is very easily detected by ^{31}P NMR. The extent of phosphination can be routinely measured by employing a sample of known phosphorus concentration and an external reference (tri-n-butylphosphine).

The ^{31}P -NMR peak of the metal complexed polystyrylphosphine is too broad to be observed. Comparison of the relative peak areas of the external reference and the rhodium complexed copolymer revealed the concentration of uncomplexed polymeric phosphine. The maximum coordination number per rhodium atom by polymeric phosphines $[\text{P}]-\text{P}_\text{C}/\text{Rh}$ was calculated from the ^{31}P -NMR measurements. These $[\text{P}]-\text{P}_\text{C}/\text{Rh}$ values revealed multiple binding of polymeric phosphine to the rhodium(I). $([\text{P}]-\text{P}\phi_2)_3\text{RhCl}$ was proposed if the catalyst was prepared by equilibration with $\text{RhCl}(\text{P}\phi_3)_3$. However, in the case of $[\text{Rh}(\text{cyclooctene})_2\text{Cl}]_2$ equilibration, the presence of dimer was indicated. The $[\text{P}]-\text{P}_\text{C}/\text{Rh}$ values of samples prepared from $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ equilibration were increased to 3 or greater by treatment with $\text{P}\phi_3$ at high temperature. Both electron microprobe analysis and scanning electron microprobe data support the conclusion that the polymeric phosphine break the chlorine bridge to form a monomer.

^{31}P spin-lattice relaxation times (T_1) of polymeric triphenylphosphine (1.9 seconds) were obtained by applying a $180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence. The reorientational correlation time (τ_c) was estimated to be 5.7×10^{-10} seconds at room temperature. Temperature dependence of the ^{31}P T_1 of the polymeric $\text{P}\phi_3$ indicated that dipole-dipole interactions provide the dominant relaxation mechanism within the studied temperature range. In sharp contrast to Regen's⁵ results, the rotational correlation times (τ_c) of polymeric $\text{P}\phi_3$ calculated from the ^{31}P T_1 are not sensitive to the swelling properties of the solvents.

The temperature dependence of ^{31}P -NMR spectra of polymer-supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$, prepared by equilibrating polystyrylphosphine with $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ or $[\text{RhCl}(\text{CO})_2]_2$, indicated that free polymeric $\text{P}\phi_3$ exchanges with complexed polystyrylphosphine.

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TO

**MY PARENTS , MY HUSBAND ,
MY BROTHERS and MY SISTER**

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LIST OF ABBREVIATIONS

COE = cyclooctene, C_8H_{14}

ϕ = phenyl, C_6H_5

$P\phi_3$ = triphenylphosphine, $P(C_6H_5)_3$

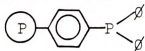
TMEDA = N,N,N',N'-tetramethylethylenediamine

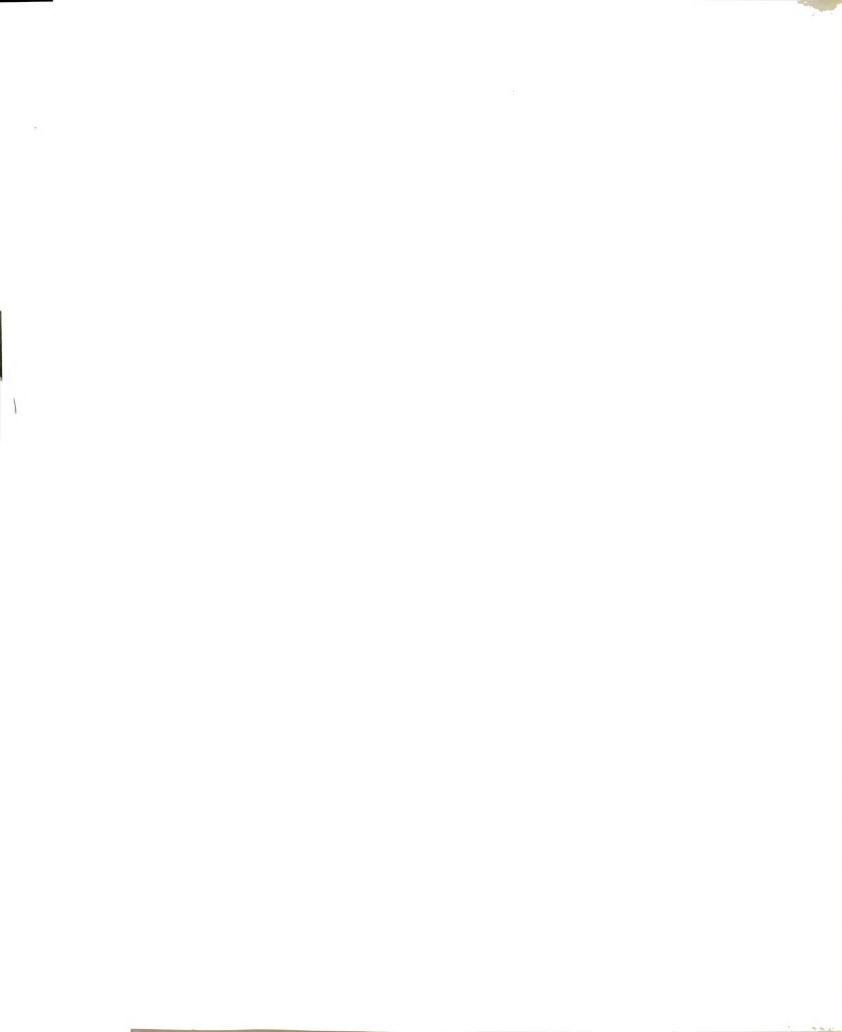
meq = mini equivalent

mmol = mini mole

$P]-P_c$ = polymer-supported triphenylphosphine
coordinated to metal

$P]-P\phi_2$ = polymer-supported triphenylphosphine,





PART I

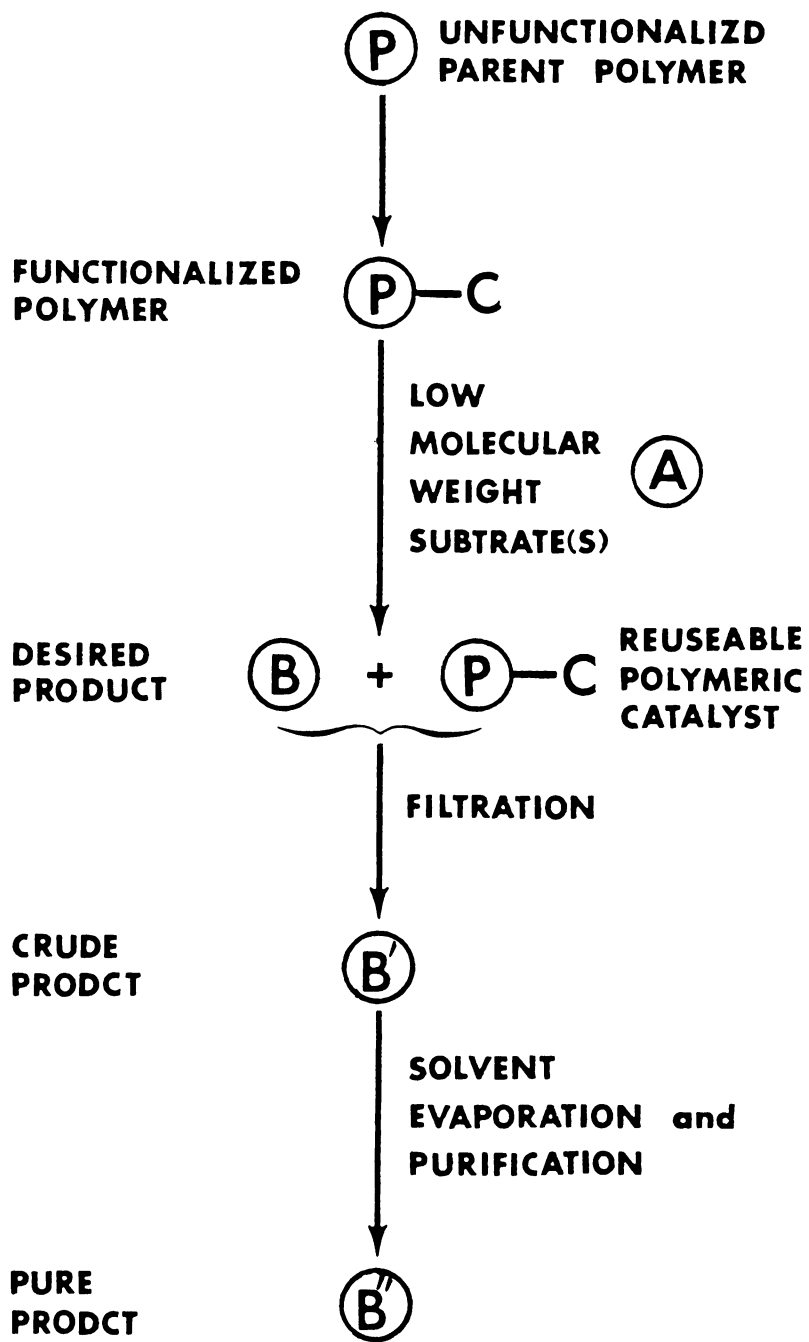
THE PREPARATION OF POLYSTYRENE-ATTACHED PHOSPHINE LIGANDS,
ORGANOMETALLIC COMPOUNDS AND HYBRID PHASE CATALYSTS

I. INTRODUCTION

Over the past decade, many highly active and selective catalysts have been derived from transition metal complexes. However, in the use of a soluble catalyst, a problem of practical importance is encountered : the separation of the catalyst from the reaction products often requires special treatment which usually results in deactivation.

One way of overcoming this problem, while retaining the advantage of the transition metal complex catalyst, is to attach the complex to the surface of a solid support. In this case, the workup procedure for the isolation of the product is very much simplified, since the support may be removed from the reaction mixture by simple filtration. A general scheme whereby a polymeric catalyst would be used in a synthesis is presented in Scheme I¹.

In addition to the ease of separation from products, polymer-supported catalysts (polymeric catalysts) can have other advantages over their homogeneous counterparts, such as (A) enhanced size² and positional selectivity, (B) ability to carry out sequential catalytic reactions³, (C) the potential isolation of reactive catalytic species, with a resulting increase in reaction rate⁴.



Scheme I – Syntheses Using Polymeric Catalysts

The improvement in reaction yields and the speed with which reactions may be completed by using polymer-supported catalysts has generated widespread interest in the application of polymer-bound metal complexes⁵⁻⁹. These polymer complexes can be considered as simple models for enzyme catalysts, and are expected to provide a key to understanding the nature of bio-catalysts.

In one of the earliest studies of polymer-bound tris(triphenylphosphine)chlororhodium(I), it was demonstrated that the swollen polymer was an active hydrogenation catalyst that could be "reused" repeatedly with no loss of activity. After each use it was separated from the reaction products by simple filtration. Furthermore, this catalyst was capable of selectively hydrogenating small olefins while rejecting large ones. Evidently, large molecules were not able to permeate into the resin channels to reach the catalyst sites. The following results are typical².

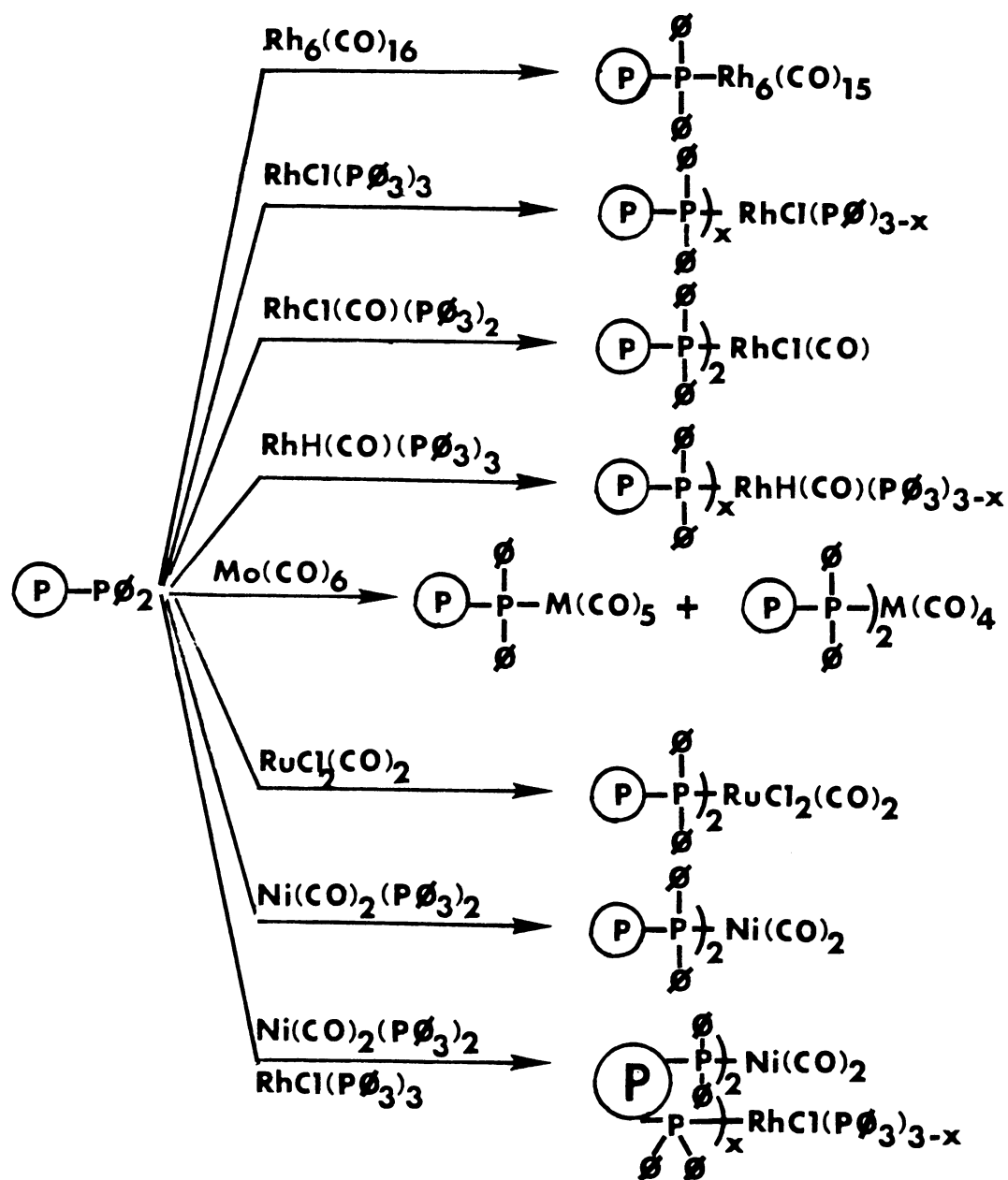
Olefin	Beads rel rate	RhCl(P ϕ) ₃ rel rate
Cyclohexene	1.0	1.0
Cyclododecene	1.0/4.45	1.0/1.5
Δ^2 -Cholestene	1.0/32	1.0/1.4

The Preparation of Polymeric Organophosphorus
Ligands for Catalyst Attachment

The most satisfactory way of supporting transition metal complex catalysts involves the formation of a chemical bond between the surface of the support, usually a polystyrene copolymer, and a ligand group involved in the metal complex. The major ligand used for homogeneous catalysts is triphenylphosphine. Thus, a variety of polymeric catalysts have been prepared by attaching the catalyst center to a phosphine^{2,8-12}. Some examples are summarized in Scheme II.

There are essentially two general methods of preparing polymer-bound ligands. This involves either chemically bonding ligand groups to a preformed polymer, in most cases a divinylbenzene-styrene copolymer, or polymerization of a ligand monomer¹³. The first of these two methods has been the more widely used, and two approaches have been used to prepare polymer-supported phosphines.

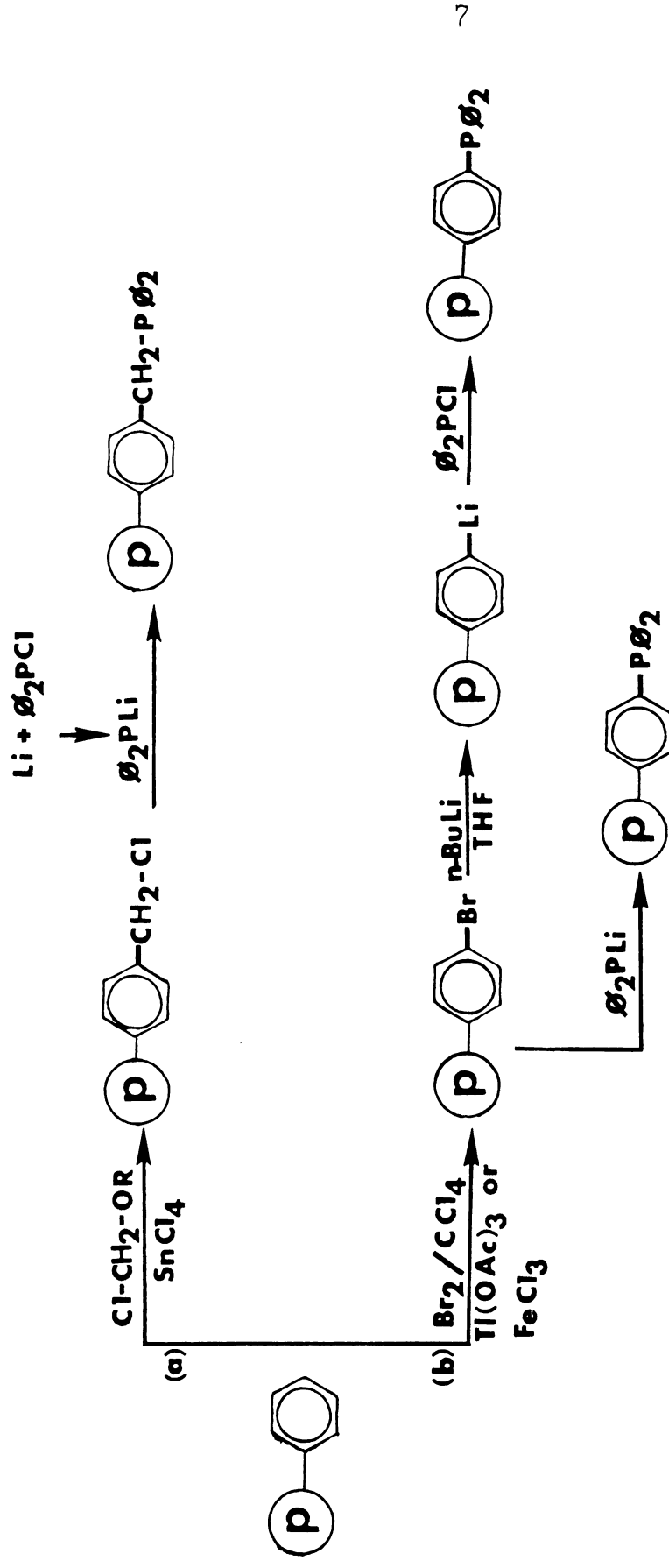
In the first route, polystyrene was functionalized by chloromethylation², and then the chloromethylated polymer was treated with a tetrahydrofuran solution of lithiodiphenylphosphine. In the second route, resin-substituted triphenylphosphine was prepared by ring bromination (Br_2/CCl_4 , FeCl_3 or $\text{Tl}(\text{OAc})_3 \cdot 1.5 \text{ H}_2\text{O}$) and phosphination of the bromination product by lithiodiphenylphosphine¹¹. Alternatively, a two stage procedure involving lithiation



$(P-P\phi_2)_n = \text{Polymer-supported } P\phi_3 \text{ or } \phi CH_2 P\phi_2$

Scheme II – Preparation of Polymeric Catalyst



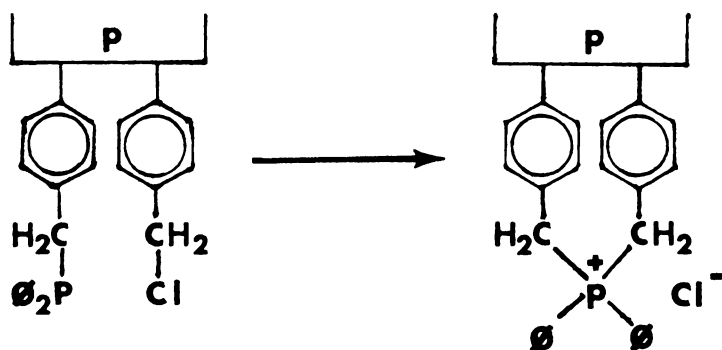


Scheme III – Methods have been used in preparation of polymeric organophosphorus ligands.



of the polymer with n-butyllithium followed by reaction with chlorodiphenylphosphine¹² could be used. These two routes are outlines in Scheme III.

The first of these procedures is the simpler, requiring fewer steps and less operation under inert atmosphere. However, it suffers from a number of disadvantages. The resulting phosphine is a resin analog of benzyldiphenylphosphine. The major ligand used for homogeneous catalysts is triphenylphosphine. Thus, the resin-bound catalyst system prepared using this functionalization procedure are different from the homogeneous catalysts normally used. Mitchell and Whitehurst¹⁴ have shown that the preparation of phosphine-rhodium complexes attached to polymers leads, in some cases to quaternization as shown in Scheme IV.



Scheme IV



In view of these results, Mitchell and Whitehurst point out that the synthesis of polymer-bound catalysts may not lead to the expected product and, hence, that the behavior of such a catalyst does not necessarily parallel that of the monomeric, homogeneous catalyst. Another disadvantage of the first route is that chloromethyl ethers are carcinogenic.

Several procedures for brominating polymers have been tried¹⁵, but a long work-up is required to remove the catalysts. Furthermore, phosphination by the reaction of lithium diphenylphosphine with brominated polymer results in a significant amount of residual bromine. This may be ascribed to the inherent difficulty in carrying out nucleophilic displacement on halogenated arenes. During the bromination of highly cross-linked polymers, the vinyl groups remaining after polymerization take up bromine.

In order to overcome these problems, an easily-controlled and convenient route for functionalizing polystyrene copolymers has to be developed¹⁶.

It has been reported¹⁷ that tertiary aliphatic amines influence markedly the reactivity of the organolithium component. The coordination of two ligands by lithium was indicated by the unusually high activity observed with bidentate ligands such as N,N',N'-tetramethylethylenediamine (TMEDA) and sparteine. The greater stability of



these complexes is ascribed to the chelation capability commonly associated with bidentate ligands. A number of reactions have been carried out with the n-butyl-lithium·TMEDA complex¹⁸. For example, metalation of dimethyl sulfide to give methylthiomethylolithium; transmetalation 4-bromo-N,N-dimethylaniline to give p-dimethylaminophenyllithium; metalation of olefins; and selective metalation of limonene, the latter being used for the synthesis of several bisabolane sesquiterpenes and monocyclic diterpene, α -artemisene.

Eberhardt's important discovery of the unusual reactivity of n-butyllithium in the presence of TMEDA made possible the direct metalation of the aromatic rings of polystyrene. There have been many reports of the direct lithiation of polystyrene on the aromatic rings by n-BuLi·TMEDA complex¹⁹⁻²¹. Broadus carries out a study of the metalation of alkylbenzenes with n-BuLi·TMEDA complexes²². His results showed high yields of ring substitution, particularly in the meta and para positions. Evans reported²⁰ a study of the kinetics and mechanism of the lithiation of polystyrene by n-BuLi·TMEDA. The infrared spectra of carboxyl and methyl derivatives of lithiated polystyrene indicate the reaction occurred at both meta and para positions on the phenyl ring. Comparison of the carbon-13 NMR spectrum of ¹³C enriched methyl derivative of metalated polystyrene sample with that of the



characterized poly(α , ortho, meta and para-methylstyrenes) confirmed that metalation of polystyrene by n-BuLi·TMEDA occurs at the meta and para positions on the aromatic ring. No detectible metalation occurs either at the ortho position or at the α -carbon²¹.

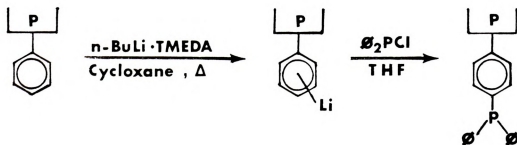
To explore the possible application of the direct lithiation procedure to insoluble cross-linked polystyrene polymers. We carried out a series of reactions of n-BuLi·TMEDA with 2 and 20% divinylbenzene-styrene copolymers.

During this study Leznoff reported²³ the direct lithiation of cross-linked polystyrene with n-BuLi·TMEDA as a means of attaching organic reagents to polymers.

II. RESULTS AND DISCUSSION

The Preparation of Polymeric Organophosphorus Ligands for Catalyst Attachment

The synthesis of polymer-supported triphenylphosphine was accomplished in a single reaction vessel by the application of a direct lithiation procedure¹⁹. Cross-linked divinylbenzene(DVB)-styrene copolymer were treated with n-butyllithium and TMEDA in purified cyclohexane. At the end of the reaction period, the dark red polymer, presumed to be lithiated on the phenyl ring, was separated and washed with more solvent. The phenyl-lithiated beads were then allowed to react with chlorodiphenylphosphine, as shown in Scheme V, and the pale-yellow product was analyzed for phosphorus. The distribution of phosphorus in the beads was determined by electron microprobe analysis²⁴.



Scheme V

A random polymer bead from each reaction was cut in half with a razor blade under a low power microscope. A narrow (0.5 micron diameter) beam of high energy (10 to 25 KV) electrons was focused on the sample, causing X-rays characteristic of phosphorus ($PK\alpha$) to be emitted from a 1 to 10 micron diameter volume. The intensity of this emission was taken as a measure of the phosphorus density in that part of the bead.

The bead cross-section was scanned by moving it across the electron beam at constant speed. X-ray intensities were plotted on the y axis of a stripchart recorder driven at constant speed. Thus distance on the chart was directly related to the distance across the bead, and the phosphorus density was determined as a function of distance from the edge of the bead. A radial distribution of phosphorus in the polymer bead could be determined from the intensity of the emission from each point in the cross sectional surface. Representative spectra are presented in Figures 1 through 5.

Comparison of the spectra in Figure 1 and 2, shows that heating the beads in cyclohexane for an extended period before the reagents were added results in a more even distribution of the reagents throughout the polymer. As shown in Figure 3, the reaction of 20% macroreticular DVB-styrene copolymer under similar conditions, gave phosphinated beads in which the phosphorus was evenly distributed throughout the bead.

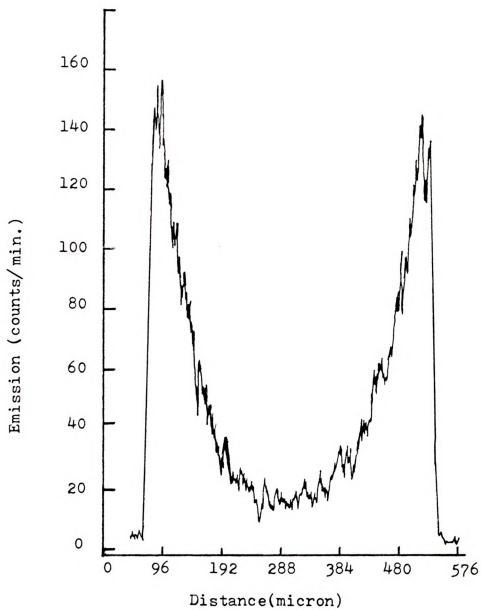


Figure 1. Phosphorus microprobe spectrum of batch 3, 16 KV, 0.023 μ A.



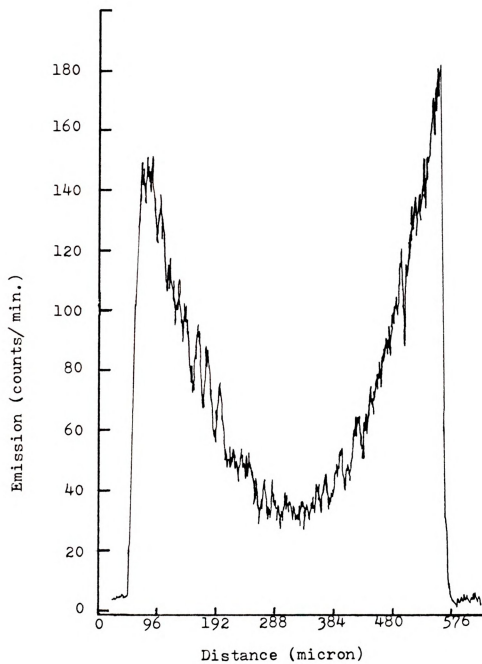


Figure 2. Phosphorus microprobe spectrum of batch 4,
16 KV, 0.023 μ A.

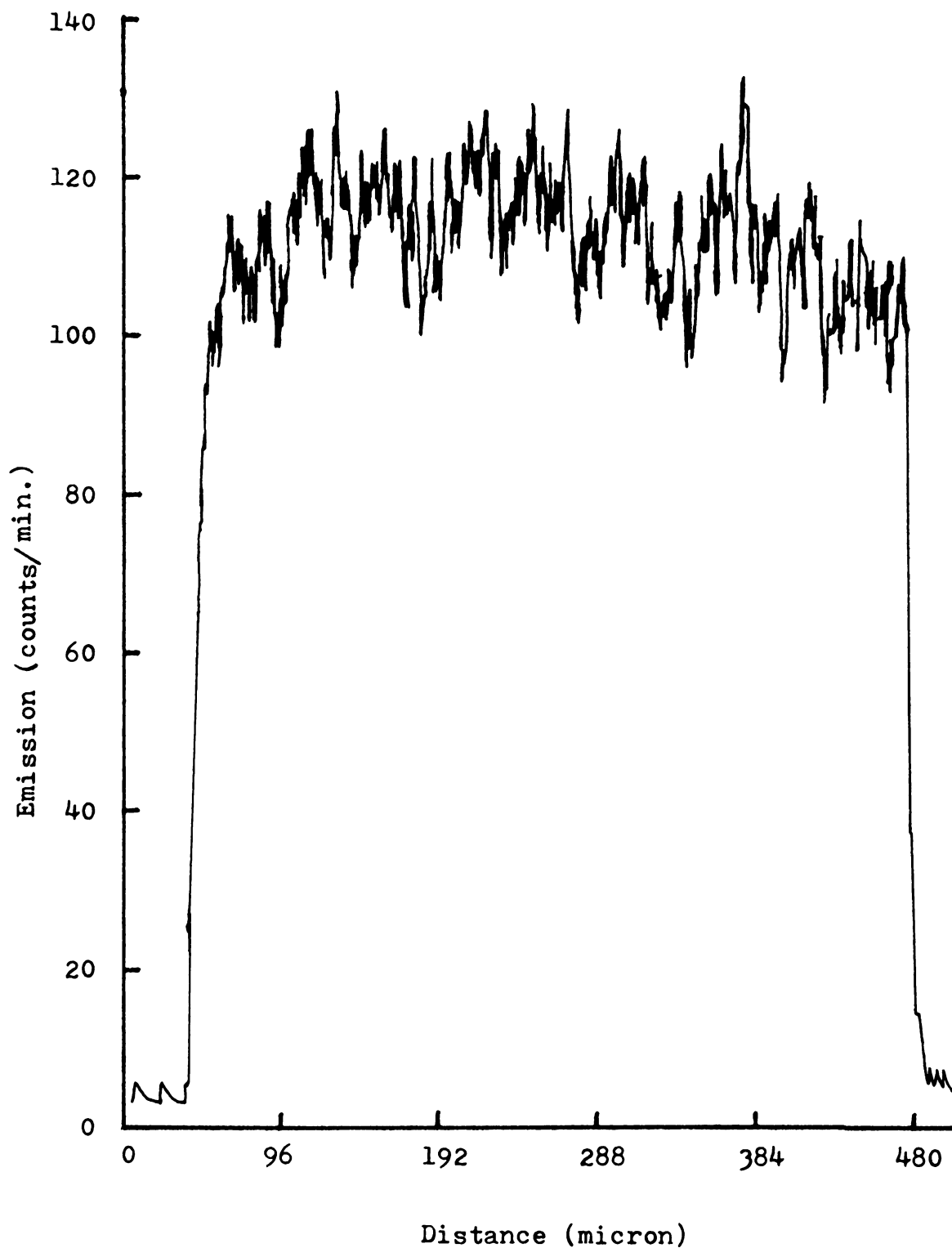


Figure 3. Phosphorus microprobe spectrum of batch 20, 16 KV, 0.023 μ A.

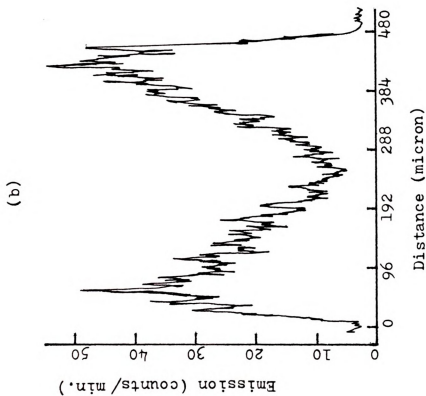
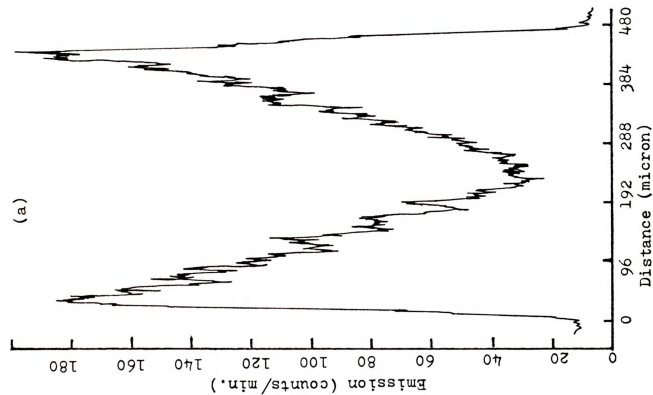


Figure 4.

(a) Phosphorus microprobe spectrum of batch 1, 15 KV, 0.023 μ A.

(b) Rhodium microprobe spectrum of batch 1, 15 KV, 0.023 μ A.

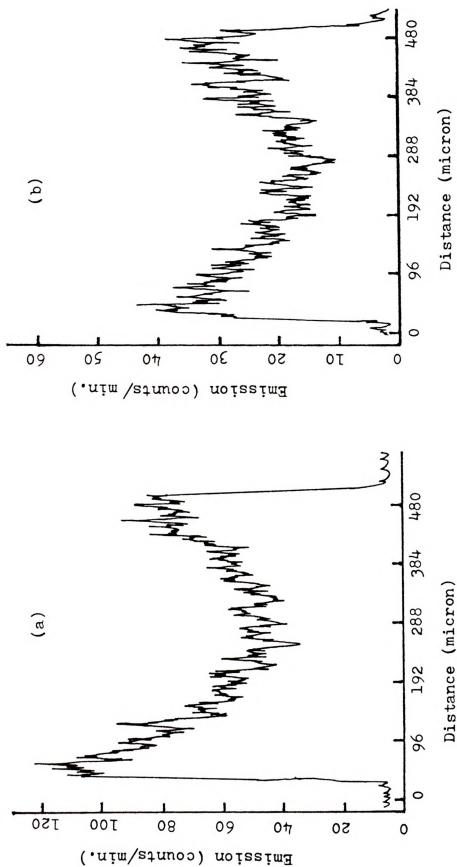


Figure 5. (a) Phosphorus microprobe spectrum of batch 10, 15 KV, 0.023 μ A.

(b) Rhodium microprobe spectrum of batch 10, 15 KV, 0.023 μ A.



A factor I_c is used to compare the distribution of phosphorus in samples from each reaction. The I_c is defined as the ratio of the intensity of radiation at the center of the bead divided by the maximum intensity.

Since reactions involving polymeric beads progress from the surface into the center, the factor I_c varies between 0 and 1.0. A zero I_c value indicates that all the phosphorus is located at the outer edge of the bead and a value of 1 is characteristic of beads which have phosphorus evenly distributed throughout. In this work, the beads used were 425-500 μ in diameter. Beads with a low I_c contained the majority of the phosphorus in the first 100-150 μ from the surface.

The variation of the radial distribution of phosphorus and the percent phosphorus substitution has been examined as a function of a number of variables. The results of a study in which time and relative ratios of reactants were varied are presented in Table 1. As can be seen, this reaction provides a route to polymers having substitution percentages ranging from 0.50 to 15.6, and distributions of $I_c=1$ to 0.1. Cyclohexane is a poor solvent for polystyrene and requires heating for maximum swelling to be reached. It was observed that heating the beads in cyclohexane for an extended period before the reagents were added increased the rate of the reaction.

The table indicates that the percent substitution increases to a maximum and then falls off with extended

Table 1. Effect of reaction conditions on the phosphorus substitution and the radial distribution of phosphorus.

Batch	% Cross-linkage	% n-Buli	Time (hr)	Temp. (°C)	Swelling ^a	Substitution ^b	meq/gbeads ^c	I _c ^d
1	1.8	100	48	RT	15 mins.	10.77	0.8652	0.072*
2	1.8	100	4	81	None	13.29	1.030	--
3	1.8	100	1	60	None	9.87	0.8039	0.10
4	1.8	100	1	60	24 hrs(60°)	11.20	0.8943	0.15
5	1.8	100	8	60	None	15.02	1.1398	0.30
6	1.8	100	12	60	None	11.97	0.9493	--
7	1.8	100	24	60	None	15.62	1.1753	0.13
8	1.8	50	22(RT)	60(3hr)	24 hrs(60°)	8.02	0.6715	0.28
9	1.8	40	3	60	18 hrs(60°)	11.73	0.9298	0.37*
10	1.8	20	18(RT)	60(5hr)	24 hrs(60°)	8.41	0.7006	0.362*
11	1.8	10	1	60	None	3.82	0.3422	0.18
12	1.8	10	12	60	None	11.78	0.9330	0.40
13	1.8	10	19	60	None	0.51	0.049	--
14	1.8	10	24	60	None	1.21	0.113	--

* From rhodium microprobe spectrum.



Table 1. (continued)

Batch	% Cross-linkage	% n-BuLi	Time (hr)	Temp. (°C)	Swelling ^a	Substitution ^b	meq/g. beads ^c	Ic ^d
15	1.8	10	43	60	None	5.24	0.459	1.00
16	1.8	10	48	RT	15 mins. (60°C)	5.57	0.4876	0.21
17	20	100	4	81	None	9.56	0.7819	--
18	20	100	40	60	24 hrs (60°C)	8.50	0.7070	1.0
19	20	100	38	81	None	12.54	0.9334	--
20	20	100	48	RT	15 mins (60°C)	--	--	1.0

^a Time and temperature of treatment of dry beads with cyclohexane before the addition of the reagents.

^b Calculated from equation % sub. = $(M \times 10^{-1}) / [(1 - M \times 288.3) / 104.7 + M \times 10^{-3}]$,
M = meq/g. beads.

^c meq/g. beads = (% P/30.974) x 10, % P from elemental analysis.

^d Ic = The ratio of the intensity of radiation at the center of the bead divided by the maximum intensity.



reaction time. This is apparently due to the slow decomposition of TMEDA by the alkyllithium reagents.

Many batches of phosphinated beads have been prepared by utilizing this route in this group. By experience, around ten percent substitution is very easy to achieve by using 30-40% lithiating reagent and heating the reaction at 60°C for about 12 hours.

Two batches of the phosphinated polymer (batch 1 and 10) were equilibrated with tris-(triphenylphosphine)chlororhodium, and the attached catalysts were then used to reduce various olefins. Rhodium and phosphorus microprobe spectra of both batches are presented in figures 4 and 5. In batch 10, significant amounts of rhodium was present in the very center of the bead ($I_c=0.36$), while in batch 1, only very small amount of rhodium was present in the very center of the bead ($I_c=0.07$).

The results of hydrogenation using these two batches are presented in Table 2. Relative rates are taken with the average cyclohexene rate equal to 1. These two batches with a P/Rh ratio of 4.22 and 4.29 gave a rate of reduction of cyclohexene of 7.60 and 7.65 ml/min/mmol of rhodium. These rates are much better than that observed with a similar batch of material prepared by the bromination route. For example, one sample prepared by the bromination route with a P/Rh ratio of 4.2 reduced cyclohexene at a rate of 2.8 ml/min/mmol Rh.



Table 2. Rates of hydrogenation for samples of polymer-bound $\text{RhCl}(\text{P}\phi_3)_3$ of various preparations.

<u>Batch</u>	<u>P/Rh</u>	<u>Olefin</u>	<u>Initial rate</u> (ml/min/meq Rh)	<u>Relative rate</u>	<u>I_c</u>
1	4.22	Cyclohexene	7.60	1.0	0.072
		1-Hexene	15.42	2.70±0.20	
		Cyclooctene	5.90	0.59±0.04	
		1-Dodecene	6.92	0.92±0.10	
		β-Pinene	3.10	0.52±0.03	
10	4.29	Cyclohexene	7.65	1.0	0.362
		1-Hexene	6.65	0.95±0.06	
		Cyclooctene	5.37	0.82±0.07	
		1-Dodecene	15.19	1.80±0.20	
		β-Pinene	4.63	0.53±0.03	



The unusually high rates of reduction of 1-hexene for batch 1 and 1-dodecene for batch 10 seemed strange. The change in order of relative rate, from 1-hexene greater than cyclohexene for batch 1 to cyclohexene greater than 1-hexene for batch 10 was similar to what E.M. Sweet observed, although it was puzzling¹⁵.

Studies Regarding the Position of Metalation

The question of the position of metalation was considered. It was decided to use cumene as a low molecular weight model molecule.

The purified cumene was treated with n-BuLi·TMEDA in cyclohexane at 65° to give a dark red solution. The lithiated cumene was then quenched with chlorotrimethylsilane. The light tan milky looking mixture was then washed with water and aqueous hydrochloric acid, and dried over anhydrous calcium chloride followed by drying over molecular sieves. The two products were separated and purified by gas-liquid phase chromatography (glpc). These two pure samples were then examined by mass spectroscopy, proton magnetic resonance spectra and carbon-13 FT magnetic resonance spectra.

The mass spectra for both fraction had a very strong parent peak at $m/e = 192$ (calculated for trimethylsilyl substituted cumene is 192.38). Major peaks also occurred at $m/e = 177, 18, 28, 73$ (decreasing magnitude). The ^1H noise-decoupled ^{13}C NMR spectra were recorded using a



Varian CFT-20 spectrometer. Assignment of the spectral lines is very straight forward. The chemical shifts are presented in Table 3. As Figures 6-8 show, all the lines are well-resolved.

Thus, the treatment of cumene with $n\text{-BuLi}\cdot\text{TMEDA}$ followed by quenching with chlorotrimethylsilane gave meta and para derivatives. The ratio of meta/para derivatives was statistical, 2:1. No detectible metalation occurs either at the ortho position or at the α -carbon.

The experiments by Evans et al²¹ on lithiation of soluble polystyrene also showed that both meta and para lithiation occurred, with a meta/para ratio of 2:1. It is likely that a considerable amount of lithiated copolymer is actually in the meta position.

Phenyl-Supported Titanocene Dichloride

It has been found⁴ that titanocene dichloride was activated dramatically as a hydrogenation catalyst by coordinating an analog of TiCp_2Cl_2 to the 20% DVB-styrene copolymer beads using a benzyl linkage to give 1 on the polymer of a phenyl linkage to give 2 on the polymer.

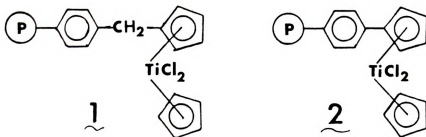
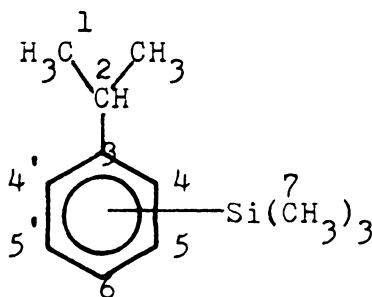


Table 3. Chemical Shifts in ^{13}C -NMR Spectra of Cumene, and Trimethylsilyl-substituted Cumene.



Carbon Atom Number	Chemical Shift-ppm downfield from Internal TMS.		
	I ^a	II ^b	III ^c
1	24.05	25.13	24.94
2	34.23	35.36	35.14
3	148.76	148.80	150.52
4	} 126.41	132.47	} 126.99
4'		127.79	
5	} 128.36	141.15	} 134.50
5'		128.54	
6	125.83	131.89	138.36
7	--	1.00	1.06

^aI = Purified Cumene

^bII = $\text{Si}(\text{CH}_3)_3$ group on C₅(meta-)

^cIII = $\text{Si}(\text{CH}_3)_3$ group on C₆(para-)

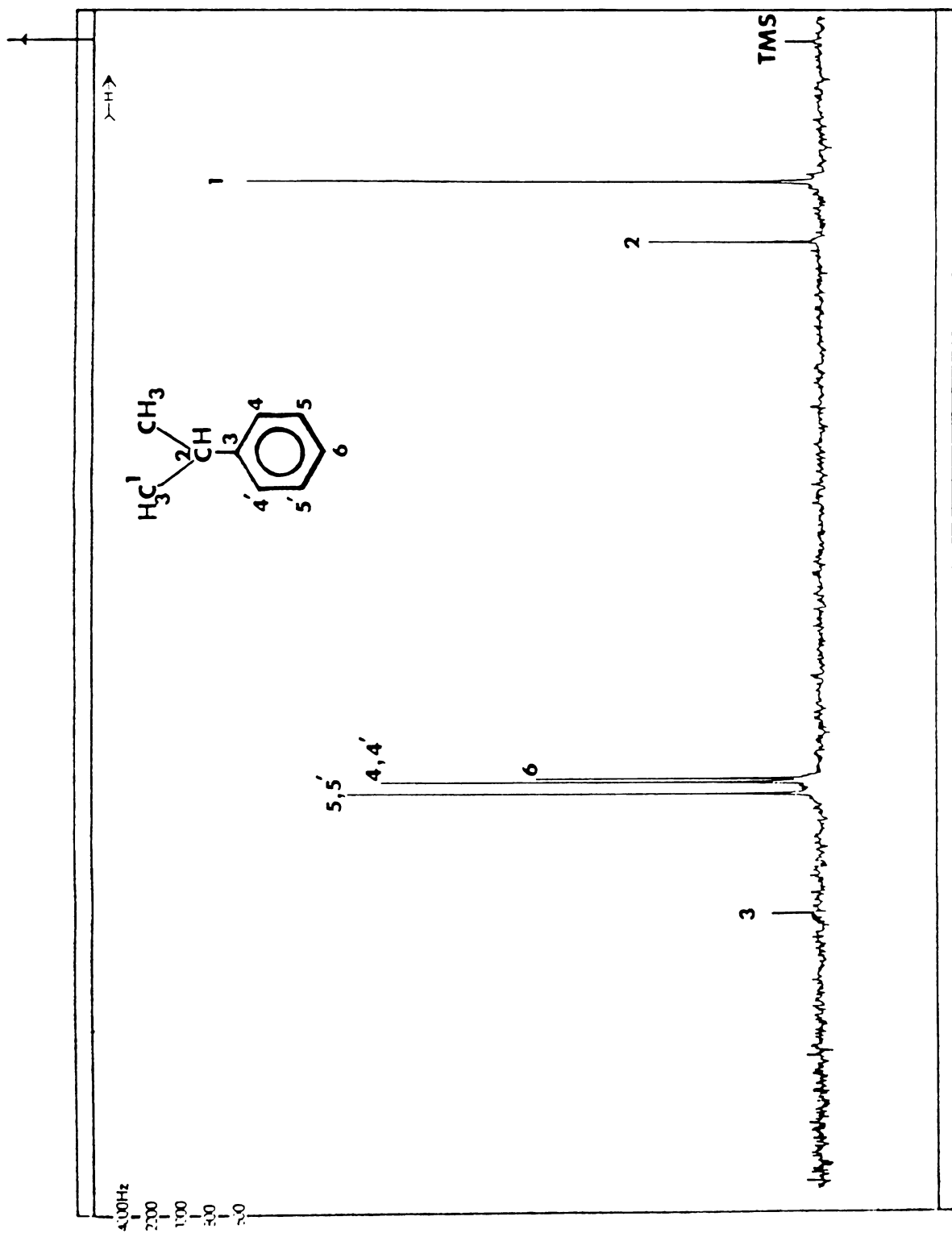


Figure 6. ^1H noise-decoupled ^{13}C -NMR spectrum of cumene.

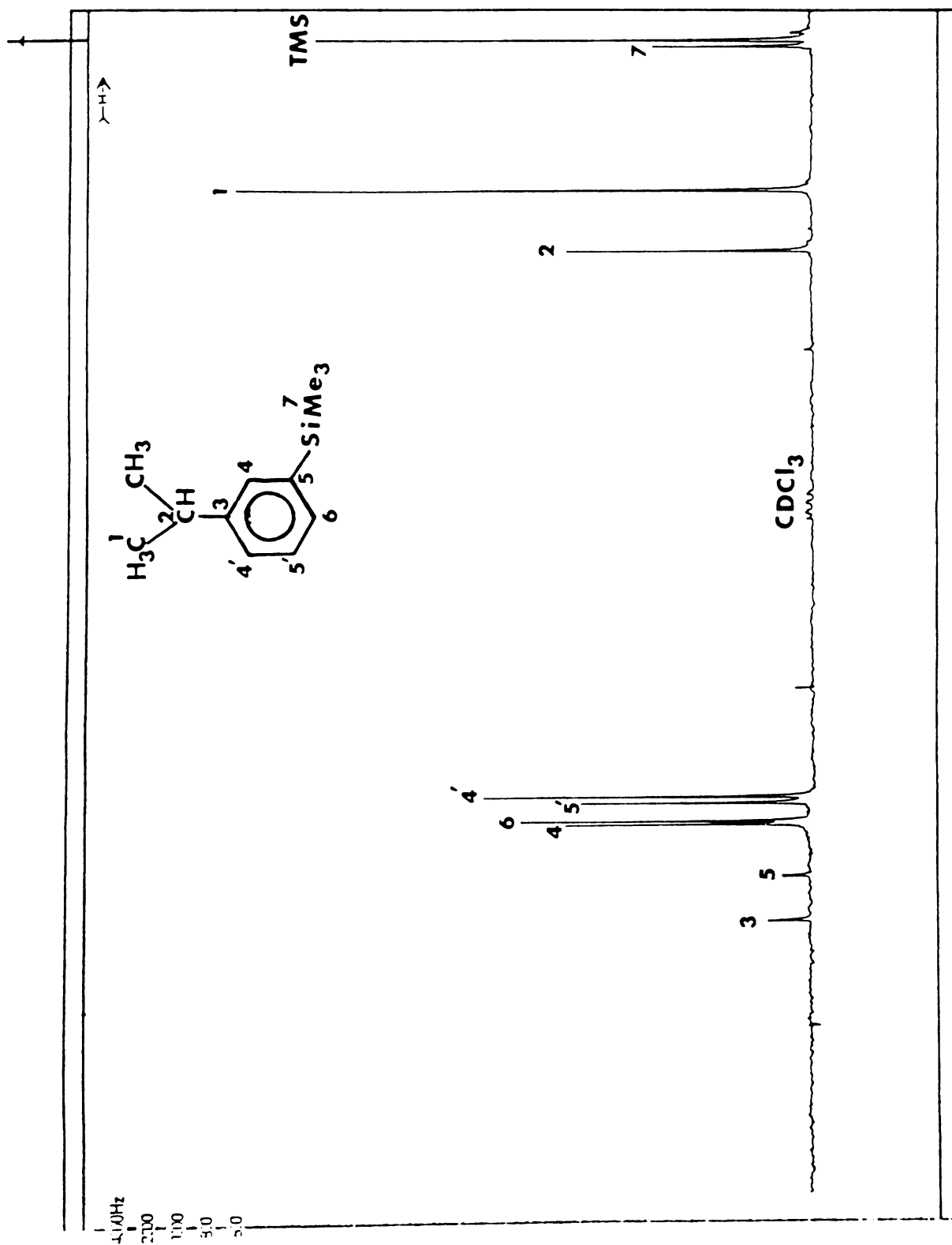


Figure 7. ^1H noise-decoupled ^{13}C -NMR spectrum of m-trimethylsilyl cumene.



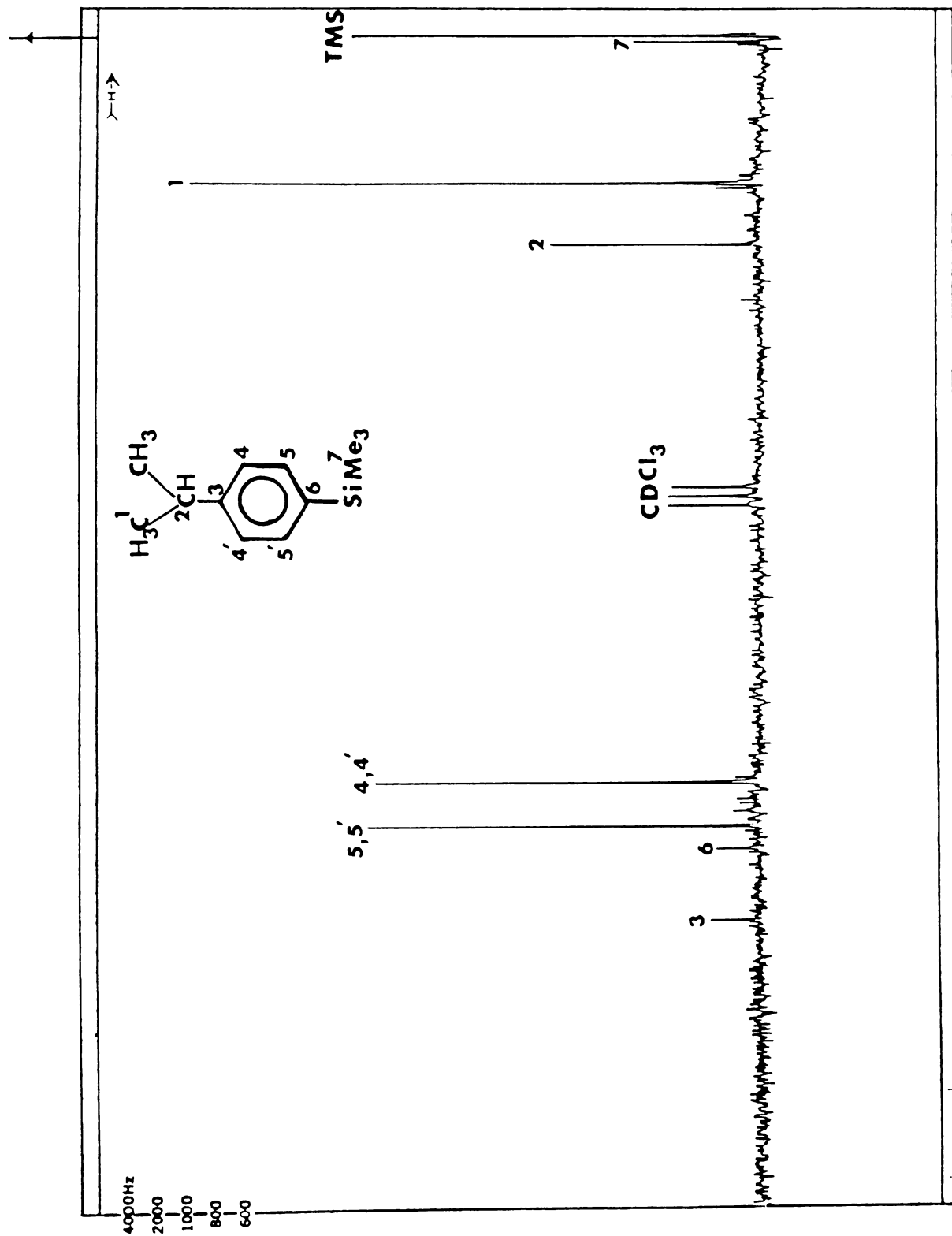
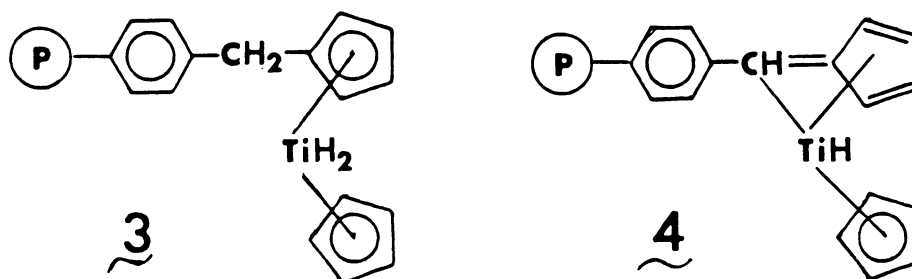
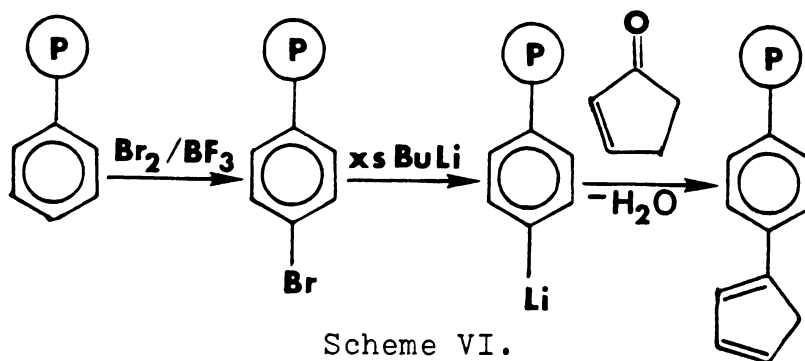


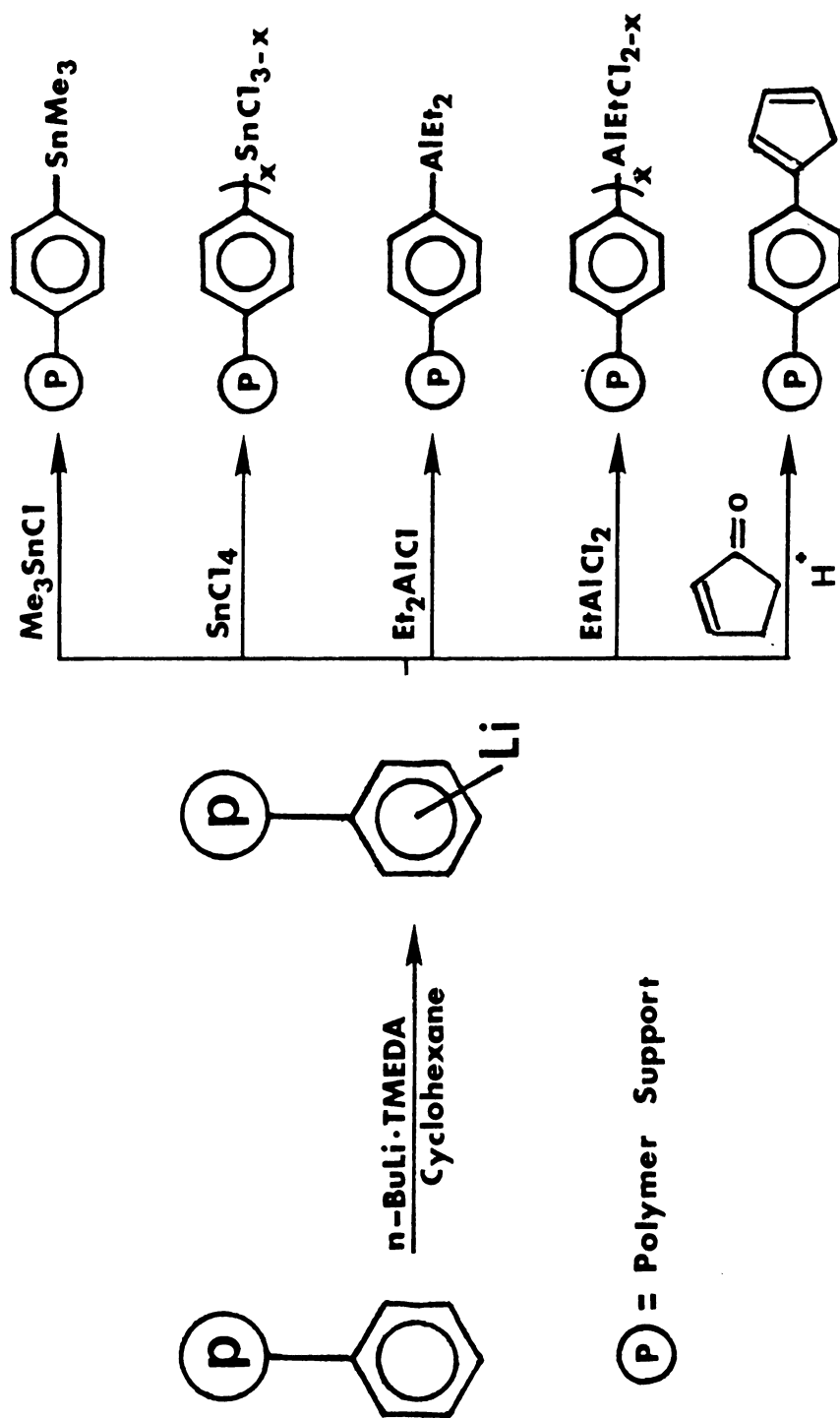
Figure 8. ^1H noise-decouple ^{13}C -NMR spectrum of p-trimethylsilyl cumene.

The removal of the benzylic methylene group from a position adjacent to the cyclopentadienyl ring activated the supported complex more, probably due to the elimination of the formation of 4 from 3.



The synthetic route for attaching titanocene dichloride to the polymer with a phenyl linkage also had been developed as shown in Scheme VI. However, the bromination reaction was a long work-up procedure and difficult to control to give reproducible results. It was decided to utilize the direct metalation of the copolymer on the phenyl rings by *n*-BuLi·TMEDA for attaching cyclopentadienyl groups to a polymer backbone. Several other functionalized copolymers were also prepared by this direct lithiation procedure. They are summarized in Scheme VII.





Scheme VII- Bead Functionalization.

2% or 20% divinylbenzene-styrene copolymer was lithiated using the 1:1 complex of n-butyllithium and TMEDA in purified cyclohexane. Treatment of these dark-red polymer beads with chlorotrimethyltin, tetrachlorotin, diethylaluminium chloride, ethylaluminium dichloride, and 2-cyclopentene-1-one gave polymer bound trimethyltin(IV); polymer-bound trichlorotin(IV); polymer-bound diethylaluminium, ethylaluminium chloride; and polymer-supported cyclopentadiene respectively. This polymer-supported cyclopentadiene was used to prepare phenyl-supported dicyclopentadienyldichlorotitanium(IV) by the method developed by earlier workers. Samples containing 0.8935 meq of titanium per g. of beads and 0.075 meq of titanium per g. of beads were obtained. The ability of these two phenyl-supported titanocene to catalyze the hydrogenation of olefin was tested. These are listed in Table 4. The rate of hydrogen uptake was determined by the use of an electronic monitoring device, SAM¹⁵.

In order to test the proposal that the increase in activity for olefin hydrogenation with polymer-supported titanocene resulted from site isolation on the polymer, several different loading of catalysts were prepared. The loading was controlled by the amount of lithiating reagent used. Thus supported titanocene with loading values of 0.1649, 0.1441, 0.0835, 0.0543 mmole of titanium per g. of polymer was achieved, as indicated in Table 5.

Table 4. Hydrogenation of Cyclohexene by Polymer-Supported
 Cp_2TiCl_2 at room temperature^a.

Catalyst	meq-Ti/g. beads	Rate of H ₂ reduction	
		ML/min./mmol Ti	ML/min./g beads
Attached-TiCp ₂ Cl ₂			
Batch A	0.8935	4.9	4.4
Attached-TiCp ₂ Cl ₂			
Batch B	0.0752	37.2	2.8

^a 1 ml. of cyclohexene in 20 ml. of cyclohexane



Table 5. Hydrogenation of Olefin by Polymer-Supported
 Cp_2TiCl_2 at room temperature^a.

Batch	Loading		Rate of H_2 reduction ^b		
	% Ti	mmol of Ti/g of beads	ml/min./mmol Ti	ml/min./g beads	
I	0.79	0.1649	48.3 ± 0.5	7.97 ± 0.09	
II	0.69	0.1441	54.3 ± 0.4	7.83 ± 0.06	
III	0.40	0.0835	$(52.8 \pm 0.3)^c$	$(7.61 \pm 0.04)^c$	
IV	0.26	0.0543	--	--	

^a 0.5 M of cyclohexene or 1-hexene in cyclohexane with 20 ml. of total volume

^b The rate of hydrogen uptake was determined by the use of an electronic monitoring device, SAM.

^c Value in bracket is the hydrogenation rate for 1-hexene



On the course of this study, a similar study has been accomplished by C.P. Lau²⁵. It was decided not to continue this test. Obviously, the results in Table 5 are consistent with the site isolation approach²⁵.



III. EXPERIMENTAL

Materials

<u>Compound</u>	<u>Source</u> ^a	<u>Treatment</u> ^b
n-Butyllithium	1	(N)
Carbon monoxide	7	(N)
Chlorodiphenylphosphine	1	(A)
Chlorotrimethylsilane	1	(N)
Cumene	1	(B)
Cyclohexene	6	(C)
Cyclooctene	3	(C)
Cyclopentadienyltitaniumdichloride	1	(N)
2-Cyclopentene-1-one-ethyleneketyl	1	(N)
Diethylaluminium chloride	2	(N)
Divinylbenzene-styrene copolymer	4	(D)
Ethylaluminium dichloride	2	(N)
Ethylene	7	(N)
1-Hexene	3	(C)
Methylolithium	1	(N)
Rhodium trichloride ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$)	5	(N)
Tetrachlorotin	2	(N)
TMEDA	1	(E)
Titanium butoxide	2	(A)
Titanium cresylate	2	(A)
Titanium methoxide	2	(N)
Trimethylchlorotin	1	(N)
Triphenylphosphine	8	(F)

^a The following code is used for the various sources of materials.



- 1 - Aldrich Chemical Company
 - 2 - Alpha Inorganics
 - 3 - Chemical Samples Company
 - 4 - Dow Chemical Company
 - 5 - Engelhard Industries Incorporated
 - 6 - Matheson, Coleman & Bell Company
 - 7 - Matheson Gas Product
 - 8 - Pressure Chemical Company
- b (N) Chemical were used as obtained
- (A)-(F) Chemicals were purified prior to use as follows:

Purifications

(A) Chlorodiphenylphosphine, titanium butoxide and titanium cresylate were distilled under vacuum and stored in an inert atmosphere.

(B) Cumene was purified by stirring with concentrated sulfuric acid, removing the acid layer. The procedure was repeated until darkening became slight. The purified cumene was washed with water, aqueous sodium hydroxide, water and saturated sodium chloride and dried over calcium chloride, 4A molecular sieves, and refluxed with sodium for 5 hours before distilling.

(C) Cyclohexene, and cyclooctene were distilled from sodium under nitrogen.

(D) all divinylbenzene-styrene copolymers were a gift of the Dow Chemical Company. The 1.8% crosslinked beads used for the experiment were 35-32 mesh (425-500 μ) fraction

which was obtained by the use of sieves to separated the sample of 25-60 mesh 2% divinylbenzene-styrene copolymer (1.8% crosslinked). This selected polymer was refluxed with a large excess of benzene for 24 hours, filtered, and then washed with 1:3, 3:1, 1:1, 1:3 and 0:1 benzene-methylene chloride mixtures. The purified polymer was dried for 24 hours at 60°C in vacuo before use. The 20% crosslinked macroreticular polystyrene-divinylbenzene copolymer was washed with 10% hydrogen chloride solution, 10% sodium hydroxide solution, water, 3:1, 1:1, 1:3 water-methanol mixtures, 3:1, 1:1, 1:3, and 0:1 methanol-methylene chloride mixtures. The purified beads were dried 24 hours at 40°C in vacuo before use.

(E) N,N,N',N'-tetramethylethylenediamine (TMEDA) was dried over molecular sieves and refluxed with sodium for at least 2 hours before distilling under nitrogen or argon.

(F) Triphenylphosphine was recrystallized twice from 95% ethanol. The purified triphenylphosphine was stored under an inert atmosphere.

All solvents were reagent grade. The aprotic solvents used were distilled under nitrogen from sodium or potassium, benzophenone ketyl. Protic solvents were dried over molecular sieves, then distilled under argon.

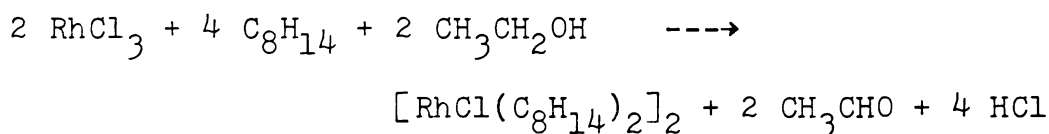
Argon was passed through BASF-BTS catalyst heated to 140°C and 4A molecular sieves. Nitrogen was used as received.

Hydrogen was purified by passing through two columns (40 mm by 0.9m) of BASF-BTS catalyst heated to 140°C and two columns of 4Å molecular sieves at room temperature. The purified hydrogen was then passed through two gas washes containing sodiumbenzophenoneketyl in toluene.

Preparations

Biscyclooctenerhodium(I) Chloride Dimer $[\text{RhCl}(\text{COE})_2]_2$

The title compound was prepared by a method similar to that reported by Porri et. al.²⁶.



Rhodium trichloride, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, (2.3329 g.) and freshly distilled cyclooctene (7ml) were dissolved in 55 ml. of degassed absolute ethanol. The solution was stirred under an inert atmosphere for seven days. The resulting precipitate was filtered from the solution of a frit under argon(as shown in Figure 9), washed four times with degassed ethanol, once with degassed diethyl ether, and dried under vacuum for twelve hours. A yellow microcrystalline powder was obtained (2.3227 g., 70.0% yield). A second crop of 0.54 g. was obtained after stirring for another seventeen days, giving a total yield of 2.8627 g. (86.3% yield based on rhodium trichloride).

Note : This reaction is very slow, in order to get a good yield six to seven days of reaction time was required.

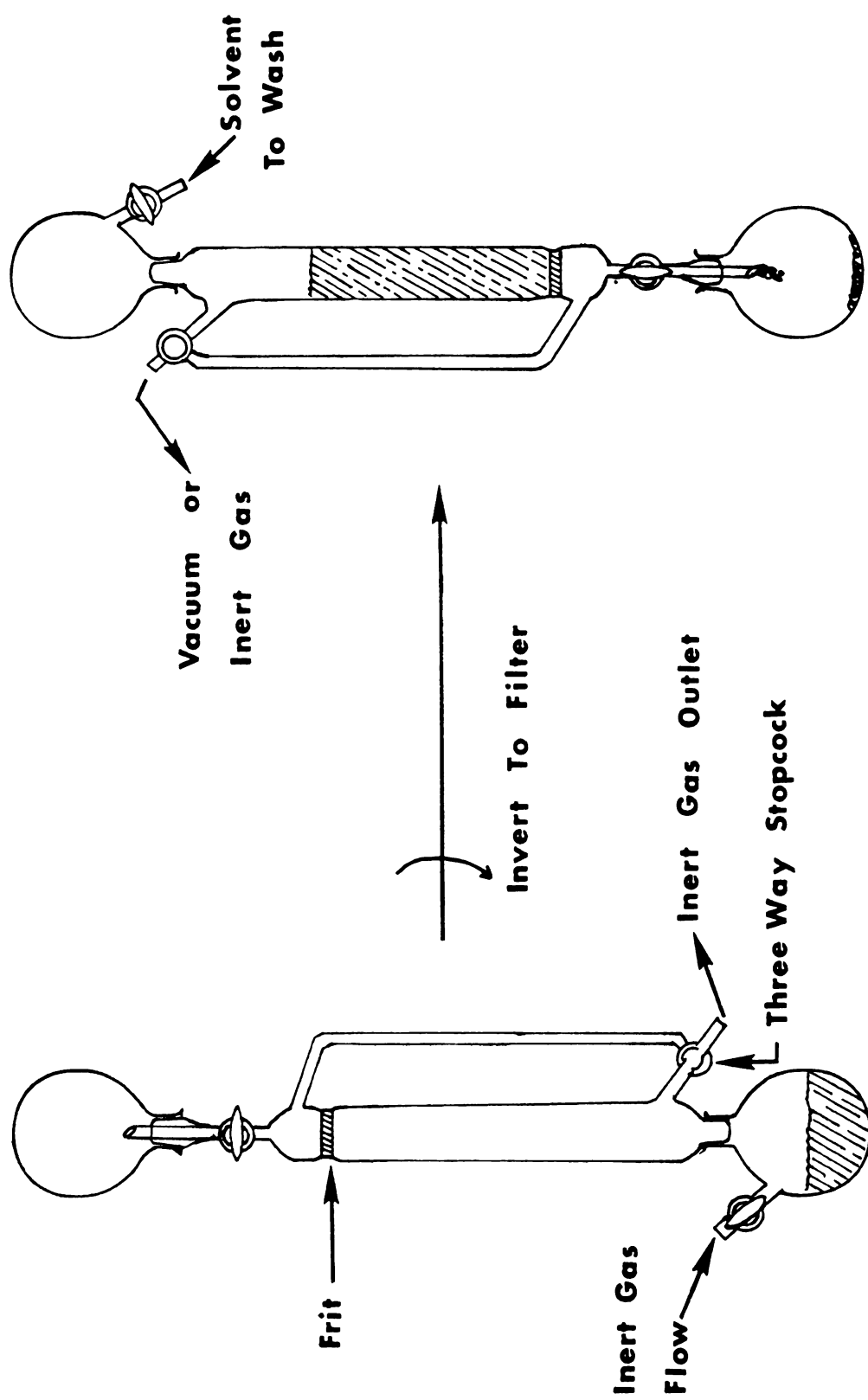
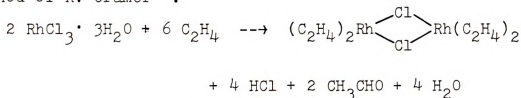


Figure 9. Apparatus for filtering under an inert atmosphere.



μ -Dichlorotetraethylenedirrhodium(I), $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$

μ -Dichlorotetraethylenedirrhodium was prepared by the method of R. Cramer²⁷.



Rhodium trichloride, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, (3.0092 g. was placed into a 250 ml. two side armed flask containing a Teflon-covered magnetic stirring bar, and one glass stoppers. Ten ml. of water was added to the round-bottomed flask and was stirred until the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ had dissolved before 100 ml. of methanol was added.

The flask was freed of oxygen by evacuation and pressuring with ethylene to 1 atmosphere three times. Ethylene was bubbled through the stirred methanolic solution at room temperature.

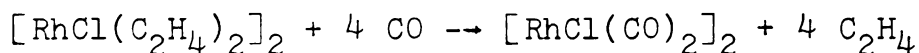
After about 7 hours, the dark-rust-colored solid was collected by filtration under vacuum on a sintered-glass funnel. The solid was washed with methanol and ether, and dried in vacuo. The yield was 1.0604 g. (47.6%).

A second crop was recovered by neutralizing the acid generated during synthesis. A solution of half a gram of sodium hydroxide in 2 ml. of water was added to the filtrate and washings from the first crop. The solution was treated with ethylene as before to recover 0.3088 g. of the title compound. This gave a combined yield of 1.3692 g. (61.6%)

based on $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$). The red product was stored under an inert atmosphere at 0°C .

μ -Dichlorotetracarbonyldirrhodium(I), $[\text{Rh}(\text{CO})_2\text{Cl}]_2$

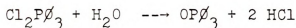
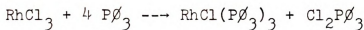
μ -Dichlorotetracarbonyldirrhodium(I) was prepared by the method of R. Cramer²⁸.



Forty ml. of freshly distilled diethyl ether was added to 0.9113 g. (4.689 mmol) of μ -dichlorotetraethylenedirrhodium in a 250 ml. round-bottomed flask under argon. Then carbon monoxide was bubbled through the solution at a rate of about a bubble per second. (Caution: The reaction must be run in a well-ventilated hood.) After one and half hours, the orange-red solution was transferred to a 100 ml. flask with a syringe under argon leaving a solid which was saved for second crop. The solution was concentrated to about 10 ml. and chilled to 0°C . The yellow liquid was transferred into a 25 ml. Bantamware with a syringe under argon. The solid was vacuum dried giving 0.5723 g. (47.3% yield) of red-needle crystals. Evaporation of ether from the yellow solution left 0.1069 g. of less pure title compound. Thirty ml. of diethyl ether was added to the residue in a 250 ml. flask. Treatment of the residue solution as before gave 0.3628 g. of $[\text{RhCl}(\text{CO})_2]_2$. The compound was stored in an inert atmosphere at 0°C .

Tris(triphenylphosphine)chlororhodium(I), [RhCl(P ϕ)₃]

Tris(triphenylphosphine)chlororhodium(I) was prepared by the procedure of O'Conner and Wikinson²⁹.



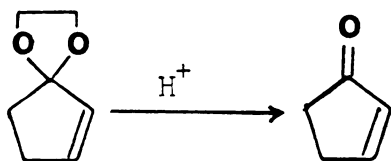
Rhodium trichloride trihydrate (1.3274 g., 5.222mmol) was placed into a 1 liter 3-neck round bottomed flask fitted with gas inlet tube, reflux condenser, and gas exit bubbler. This flask was then thoroughly purged with nitrogen before fifty ml. of oxygen free ethanol(95%) was added. A solution of 8 g. of triphenylphosphine (freshly recrystallized in ethanol) in 250 ml. of hot ethanol was then added.

The flask was then closed except for the gas inlet system and the gas exit bubbler. The mixture was then stirred and refluxed for at least three hours.

The mixture was cooled to room temperature, and then filter through a frit under nitrogen, as shown in Figure 9. The product was washed with four 50 ml. portions of oxygen-free ethanol and once with 30 ml. of dry diethyl ether. The solid was then dried under vacuum for 10 hours to yield 4.5332 g. (93.8% based on Rh) of deep-red micro-crystalline solid.

2-Cyclopentene-1-one

The method of DePuy, et.al.³⁰ was used to prepare 2-cyclopentene-1-one via its ethylene glycol ketal.

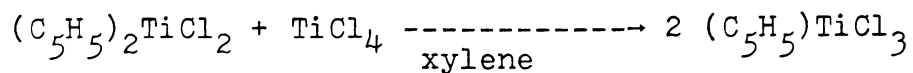


2-Cyclopentene-1-one ethylene ketal 6.5 g. was added slowly to 100 ml. of 2N hydrochloric acid. The resulting solution was stirred at room temperature for 30 minutes before 20 ml. of methylene chloride was added. After cautious saturation of the aqueous layer with sodium bicarbonate, the mixture was filtered and the organic layer was separated.

The aqueous layer was extracted with two 20 ml. portions of methylene chloride and twice with ether. The organic layers were combined, dried over anhydrous sodium sulfate, and distilled at 150-155°C before use.

Cyclopentadienyltitanium Trichloride, $[\text{C}_5\text{H}_5\text{TiCl}_3]$

The most convenient and efficient method for preparing cyclopentadienyltitanium trichloride appears to be the redistribution reaction between the sandwich compound, bis-(cyclopentadienyl)-titanium dichloride(II) and titanium tetrachloride in xylene solution³¹.



Titanium tetrachloride (25.1 g., 0.136 mol) was added to 12.0 g. (0.048 mol) of biscyclopentadienyltitanium dichloride in 90 ml of dry xylene contained in a three-necked flask under an inert atmosphere. The solution was



stirred with a magnetic stirrer and heated at the boiling point (ca. 140°C) for 2½ hours. The reaction mixture was then allowed to cool to room temperature. The resulting crystals were filtered under an inert atmosphere, washed with dry hexane, and dried briefly under nitrogen.

The crude product was purified by recrystallization from hot benzene. For this a modified method was used, due to the low solubility of cyclopentadienyltitanium trichloride in benzene. Charcoal was added to the crude product, which was then put into a thimble in a Soxhlet extractor equipped with a condenser, gas inlet tube, a side-armed flask and a magnetic stirrer. Dry benzene (300 ml.) was introduced to the flask by means of a syringe. The extraction was continued until the benzene solution in the Soxhlet extractor was very light in color. Removal of the benzene on a rotary evaporator left an yellow solid of 13.3875g. (Yield 65%). The solid was further purified by sublimation.

Cyclopentadienyltitanium trichloride forms yellow to orange yellow crystals which are very sensitive to hydrolysis.

Preparation of Polymeric Organophosphorus Ligands for Catalyst Attachment

All operations were performed under nitrogen with solvents prepared as previously described.

Lithiation

Impurities such as water, air and carbon dioxide must be excluded since they rapidly react with organolithium compounds. In a typical preparation, 3g. of purified crosslinked polystyrene (2%DVB-styrene copolymer or 20% DVB-styrene copolymer) was suspended in 20 ml. of freshly distilled cyclohexane in a side-armed flask fitted with magnetic stir bar, condenser, gas inlet tube and gas outlet bubbler. The mixture was heated to 60°C for the required swelling period. To this mixture the required amount of purified TMEDA and n-butyllithium (1.6M in hexane) were added by means of a syringe. The reaction mixture rapidly turned red and was then heated with stirring for the required time period.

After cooling, the liquid was removed by forcing it out under nitrogen pressure through a gas dispersion tube inserted through a rubber stopper. A rubber tube leading to a flask was attached to the dispersion tube. The copolymer was then washed with 30 ml. portion of cyclohexane (four times) and three times with oxygen-free dry THF. The solvent was removed after each wash by the method described above.

Phosphination

The lithiated copolymer (dark-red in color) from above was suspended in 50 ml. of dry THF under nitrogen. To this mixture, 6 ml. of chlorodiphenylphosphine was added with a syringe. The copolymer rapidly decolorized during

this addition. On completion of addition, the flask was sealed and the slurry stirred for two days. The solution was then removed with a gas dispersion tube and the copolymer was washed with 30 ml. portions of the following solvents or solvent mixtures :

(a) degassed THF (3 times), (b) 1:1 10% aqueous NH_4Cl (oxygen free): THF (3 times), (c) 1:1 THF : H_2O (3 times), (d) THF, (e) 3:1, 1:1, 1:3, THF : benzene, and (f) benzene. Solvent removal was by the gas dispersion tube method described above. The beads were dried under vacuum for 24 hours at room temperature. They were analyzed for phosphorus by elemental analysis and microprobe analysis.

Metalation

All operations were conducted under nitrogen to exclude atmospheric moisture. All solvents were transferred by syringe.

Batch 1

Copolymer (3g. of 2% DVB-styrene copolymer) was phosphinated by the method described above. To these phosphinated beads, in a side-armed flask, 1.85 g. of tris-(triphenylphosphine)chlororhodium(I) (2 meq Rh) was added. The flask was evacuated and filled with nitrogen, 100 ml. of freshly distilled benzene added and the flask was sealed and the mixture stirred for seven days. The solution was removed and the copolymer was repeatedly washed with benzene until a wash remained clear for 24 hours and stored under nitrogen.

Analysis : 2.68% P (0.865 meq P/g.beads)
2.11% Rh(0.205 meq Rh/g.beads)
Ic = 0.0723 (rhodium)

Batch 10

The 2% DVB-styrene copolymer (7.75 g.) was phosphinated as described above to contain 2.17% phosphorus (0.701 meq P/g.beads). The entire batch of phosphinated beads was equilibrated with 2.76 g. of tris(triphenylphosphine)-chlororhodium(I) in 120 ml. of benzene for 16 days under nitrogen. This solution was removed and the copolymer was washed with benzene until no coloration of the rinses was noted. The copolymer was then dried under vacuum for 24 hours.

Analysis : C, 87.33%; H, 7.48%; P, 2.18% (0.704 meqP/g.beads); Cl, 1.01%; Rh, 1.69% (0.167 meq Rh/g.beads).
Ic = 0.362 (rhodium)

Preparation of Polymer-Supported Titanocene Dichloride

A 20 g. sample of washed 20% DVB-styrene copolymer beads were suspended in 100 ml. of freshly distilled cyclohexane in a side-armed flask equipped with a magnetic stir bar, condenser, gas inlet tube and gas outlet bubbler. To this mixture 28.5 ml of TMEDA (0.19 mol) and 100 ml. of 1.6 M n-butyllithium (0.20 mol) were added by a syringe. The mixture was heated to 50°C and stirred for 42 hours.

Excess methanol was added, while the slurry was chilled in an ice bath and the solution was removed by means of gas dispersion tube. The beads were then washed with methanol 1:1 aqueous HCl: THF; THF; 3:1, 1:1, 1:3 THF : CH₂Cl₂; CH₂Cl₂ and dried in vacuo for ten hours.

All the following were carried out with oxygen-free dry solvents under a nitrogen atmosphere.

These saturated beads were suspended in 100 ml. of cyclohexane in a 500 ml. side-armed flask. The mixture was treated with 5.7 ml of TMEDA (0.04 mol) and 20 ml. of n-butyllithium (0.04 mol) and then refluxed for 38 hours.

After removing the solution, the resulting tan beads were washed seven times with THF, then 40 ml. of THF was added to suspend the beads. While the mixture was stirred and cooled in an ice bath, 3.5 g. of freshly distilled 2-cyclopentene-1-one (0.042 eq) was added. The beads immediately decolorized, and turned to light tan after being stirred for 72 hours. The beads were washed five times with THF, six times with aqueous THF and twice more with dry THF and were then dried in a vacuum.

Batch A

A 7.5 g. sample of cyclopentadiene-substituted copolymer was weighed into a 250 ml. side-armed flask maintained under nitrogen. THF (25 ml.) was added to suspend the copolymer and the mixture was treated with 10 ml. of 2.06 M methyllithium in diethyl ether for two days. They were washed three times with 50 ml. THF and twice with

50 ml. benzene. Cyclopentadienyltitanium trichloride (7.2 g., 0.032 mol) was added to the beads with 80 ml. of benzene. The mixture was stirred for 8 days, washed with benzene twice and extracted with benzene overnight in a soxhlet extractor. The vacuum dried beads were brownish pink in color.

Analysis : 4.28% Ti (0.8935 meq Ti/g. beads)

Batch B

A suspension of the cyclopentadiene-substituted copolymer in THF was treated with 14 ml of 2.06 M methyl-lithium in diethyl ether. After 5 days, the solvent was removed and the beads were washed three times with THF, twice with benzene. A portion of the resulting polymer was stirred with 6.30 g. of cyclopentadienyltitanium trichloride (0.028 mol) in 130 ml. of benzene for three days. The beads were treated with benzene in soxhlet extractor for 24 hours, vacuum dried, and analyzed for titanium content.

Analysis : 0.36% Ti (0.0752 meq Ti/g.beads)

Preparation of Polymer-supported Trimethyltin(IV)

A sample of 2.04 g. of 1.8% crosslinked polystyrene beads was weighed into a 250 ml. side-armed round-bottomed flask equipped with a stirring bar, a condenser and a gas inlet tube. The system was evacuated and filled with argon. Purified cyclohexane (20 ml.) was introduced by a syringe, and the mixture was heated to 60°C. To the mixture

was added 4 ml. TMEDA followed by 16 ml. of 1.6 M n-butyl-lithium in hexane. After stirring for $5\frac{1}{2}$ hours at 60°C , the slurry was allowed to cool to room temperature, and the solution was removed by the use of a gas dispersion tube. The dark red beads were washed with cyclohexane five times and THF three times. The beads were then treated with a solution of 0.6 g. of chlorotrimethyltin in 15 ml. of freshly distilled THF. The color of the dark polymer faded in about 10 minutes. After three days of stirring under argon, the solution was removed and the copolymer was washed with THF; 1:1 oxygen-free 10% aqueous NH_4Cl : THF; 1:1 oxygen-free H_2O : THF; THF; 3:1, 1:1, 1:3, 0:1 THF : benzene. The beads were vacuum dried.

Analysis : 7.07% Sn (0.596 meq Sn/g.beads)

Preparation of Polymer-supported chlorotin(IV)

A 5.75 g. sample of 2% DVB-styrene copolymer was suspended in 35 ml. of purified cyclohexane in a 250 ml. sidearm round-bottomed flask under argon. The temperature was raised to 75°C and maintained at that temperature for 1 hour. TMEDA 8.5 ml and 35 ml. of 1.6M n-butyllithium were added and the mixture was stirred for 2 hours at 75° . After removing the solution, the copolymer was washed with cyclohexane four times and THF three times. The dark red pure copolymer was then suspended in 45 ml. of freshly-distilled THF. Pure tetrachlorotin 2.2 ml. was added while the slurry was chilled in an ice bath. The mixture

was allowed to warm up to room temperature, and stirred for three days. After washing the copolymer with THF; 1:1 oxygen-free aqueous NH_4Cl : THF; 1:1 oxygen-free H_2O : THF; THF; Benzene, the copolymer was vacuum dried, and analyzed for the content of tin and chlorine.

Analysis : 2.10% Cl (0.592 meq Cl/g.beads)

6.13% Sn (0.5165 meq Sn/g.beads)

Preparation of Polymer-supported Aluminum Compound

n-Butyllithium (1.6M, 19 ml.) and TMEDA (5 ml.) were used to lithiate 10.64 g. of 1.8% crosslinked DVB-styrene copolymer suspended in 45 ml of freshly distilled cyclohexane at 70°C for 10 hours. The red beads were washed with cyclohexane until no coloration in the rinses and twice with freshly distilled benzene. After suspending the beads in 20 ml. of benzene, diethylaluminum chloride (25% in hexane, 8 ml.) was added to the slurry while they were cooled in an ice bath. The ice bath was then removed, and the mixture was stirred under argon for 31 hours. The milky looking solution was removed and the light red beads were washed six times with freshly distilled benzene. Benzene(50 ml.) and 25% diethylaluminum chloride in hexane (8 ml.) were added. The beads turned to pale yellow in one hour. The beads were stirred under argon for two days. After removing the solution. the beads were washed with benzene until the rinses were clear. The beads were then vacuum dried, analyzed and stored under argon.

Analysis : 2.52% Al (0.934 meq Al/g.beads)

Some other polymer-supported aluminum compounds were prepared similarly and they are summarized in Table 6.

Analysis

The percent of phosphorus, titanium, chlorine, rhodium, tin, and aluminum was determined by elemental analysis by Galbraith Laboratory or Schwarzkopf Microanalytical Laboratory. Microprobe spectra were determined on an American Research Laboratories EMX-SM microprobe.

Preparation of Beads for Microprobe Analysis

Beads were placed on the stage of a low power binocular microscope. They were held in place with small tweezers and cut in half with a razor blade. They were then attached to a graphite disk using the adhesive from freezer tape. The bead and disk were then coated with carbon from an arc and inserted into the microprobe.

Determination of Elemental Radial Distribution within a Bead

A selected bead was identified in the microprobe microscope. Using the secondary electron emission scan, at fast scan rate, the bead was aligned so that the X axis of the microprobe corresponded to a bead diameter. The X-ray detector was set to obtain a maximum reading on the required wavelength for the desired element.



Table 6. The Preparation of Polymer-Supported Aluminum Compounds.

Sample	Beads % cross- linked	Amount used (mmol)	% Lithiating reagent	Aluminum reagent	mmol of Al added	<u>Analysis of Aluminum</u>	
						<u>% Al</u>	<u>mmol/gbeads</u>
Al-2-I	1.8	102.3	30	Et ₂ AlCl	23.76	2.52	0.934
Al-20-I	20	182.7	50	Et ₂ AlCl	72.02	2.07	0.767
Al-2-II	1.8	144.5	30	EtAlCl ₂	44.1	3.69	1.366
Al-20-II	20	192.7	50	EtAlCl ₂	83.2	2.42	0.896

Beads were scanned by moving the stage at a constant speed in the X direction while the electron beam location remained fixed. Scans were started and ended about 50 microns from the bead edge. X-ray intensity (counts/min.) was plotted on a stripchart recorder driven at constant speed.

Hydrogenation

All hydrogens used were purified as the manner described in the materials section. Solvents and solutes were transferred by the use of syringes.

Hydrogenation rates were monitored by use of the automatic hydrogenation apparatus, SAM¹⁵. SAM automatically allowed a fixed amount of gas to enter the system whenever a chosen partial vacuum was reached, giving an electric pulse with each aliquot. The pulse was fed to a strip-chart recorder, and thus gave a measure of the time at which each aliquot was introduced.

Temperature was maintained by placing the reaction vessel in a water bath maintained in equilibrium with water bath. All reactions were run at $25^{\circ} \pm 0.2$ C. All reductions were stirred using magnetic stirrers with stir bar of the appropriate size in the reaction vessels.



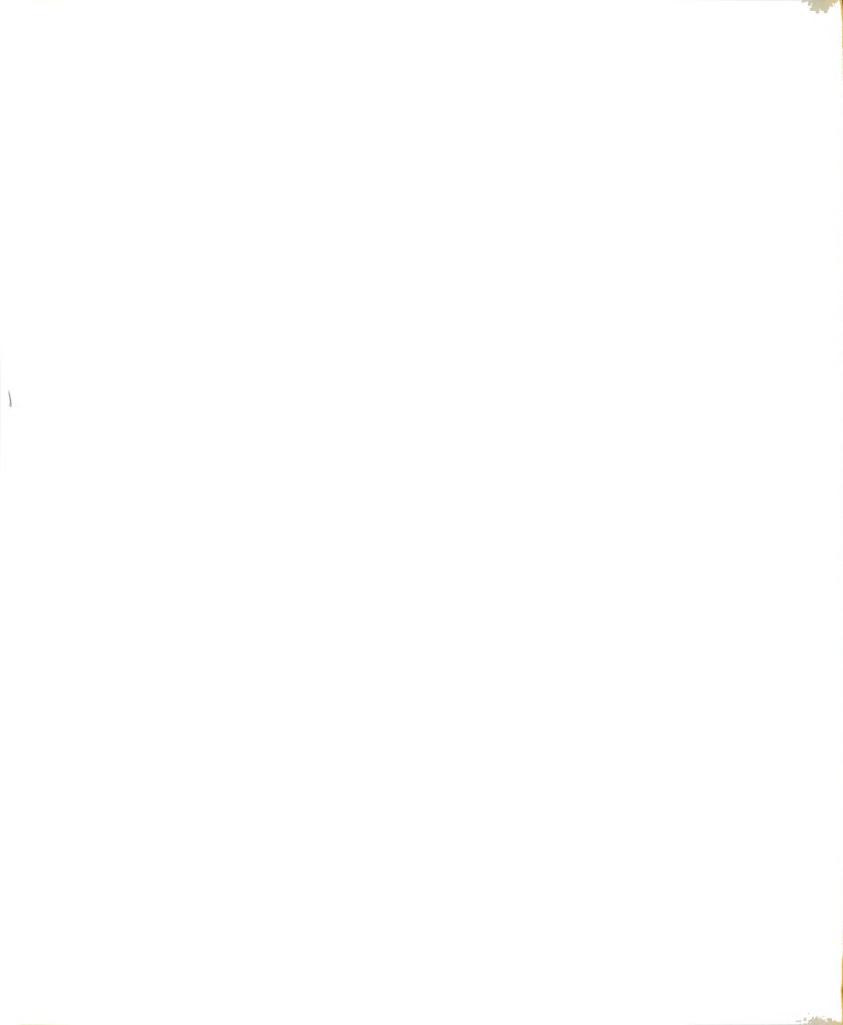
Supported Wilkinson's Catalyst Hydrogenation

All hydrogenations were performed in 1.0 M of toluene solution. This is calculated by assuming the volumes of alkene and solvent are additive.

The supported Wilkinson's catalysts were weighed into 100 ml. sidearm round-bottomed flasks equipped with stirring bars and reaction vessel adaptor. This total apparatus which is referred as the reaction vessel, was attached to the hydrogenation apparatus. After hydrogen flushing, sufficient toluene was then introduced so that upon adding the required amounts of alkene, a 1.0 M solution in alkene would produce a total volume of 30.0 ml. After ca. 15 minutes of stirring under hydrogen, the required amount of alkene was injected, and data collection started.

Cyclohexene was used as the reference compounds, reduced before and after each run of other alkene. The beads were rinsed with toluene between each run. The process "hydrogen flushing" consisted of a minimum of three vacuum cycles of about 0.1 torr vacuum with alternate hydrogen addition to remove virtually all oxygen from the system before solvent addition.

The data was obtained as volume of hydrogen used versus time at which the apparatus added and additional known volume of hydrogen to the system was recorded. The output times were converted to volume versus time data using program SAMV¹⁵. This was then entered into program



KINFIT³². Initial rates were obtained by fitting the equation

$$V = Rt + At^2 + B$$

The initial rate is R. The additional parameters allowed deviation of rate in time and deviation of the initial volume from zero.

The absolute rate for a given alkene run was divided by the absolute rate for the two standard runs immediately preceding and following the run. This gives a total of four comparisons for each hydrogenation, which reduces the effect of the variance in standard absolute rates. The average of these comparisons and the standard deviation of their mean are reported.

Polymer-supported Titanocene Hydrogenation

A sample of 0.46 g. of Batch A polymer-supported TiCp_2Cl_2 (0.55 g. for batch B) were weighed into a 100 ml. side-armed flask. A stirring bar was inserted and a reaction vessel adaptor attached. The reaction vessel was purged with argon before 2.0 ml. of 1.6 M of n-butyl-lithium (2.5 ml. for Batch B) and 10 ml. of cyclohexane were introduced by a syringe.

After stirring for 8 hours, the light yellow solution was removed and the dark grey, air-sensitive beads were washed with four 10 ml. portions of freshly distilled cyclohexane to remove excess butyllithium. The beads were vacuum dried and then attached to the hydrogenation



apparatus SAM. After hydrogen flushing, 20 ml. of cyclohexane followed by 1 ml. of cyclohexene were injected, and data collection started. The methods described above were used to get the initial rates.

Studies Regarding the Position of Metalation

The ^1H NMR spectra were run on a Varian T-60 spectrometer using internal TMS in a solvent of deuteriochloroform. Mass spectra were run on a Hitachi Perkin-Elmer RMU-6. The carbon-13 NMR spectra were run on a Varin CFT-20 spectrometer operating at 20 M Hz in Fourier Transform mode, using deuteriochloroform as solvent and tetramethylsilane as an internal reference.

Metalation of Cumene

Cumene (7 ml., 0.05 mol) and TMEDA (7.5 ml., 0.05 mol) were added to 20 ml. of cyclohexane contained in a side-armed flask under an inert atmosphere at 65 °C. The solution was stirred with a magnetic stirrer. To the solution 1.6 M of n-butyllithium in hexane (28 ml.) was added by means of a syringe. The reaction mixture turned to dark-red.

Quenching of the Lithiated Cumene

After two hours of further stirring, the solution was cooled to room temperature. Trimethylchlorosilane (8 ml., 0.06 mol) was added slowly to the reaction mixture, while the mixture was chilled in an ice bath. The resulting reaction mixture was allowed to stir at room temperature



for two days.

The light tan mixture was washed with water, dilute aqueous hydrogen chloride to give milky looking solution. After rinsing with water, the organic layer was separated and dried over anhydrous calcium chloride and molecular sieves. The resulting silanes were analyzed and separated by gas-liquid phase chromatography (glpc) with a carbowax column at 115°C. The mass spectra, proton magnetic resonance spectra and carbon-13 magnetic resonance was recorded from samples collected from the glpc.



PART II

CHARACTERIZATION OF POLYSTYRENE-RHODIUM(I)
COMPLEXES BY PHOSPHORUS-31 NMR SPECTROSCOPY
AND ELECTRON MICROPROBE ANALYSIS



I. INTRODUCTION

(A) Concepts in NMR

Nuclear Magnetism

When a nucleus was placed in a static magnetic field H_0 , it may undergo nuclear magnetic resonance (NMR) if it posses an angular momentum p . This angular momentum is referred to as nuclear spin. The component of p in the direction of H_0 , denoted as p_0 , can only take on half-integral or integral multiples m of $h/2\pi$:

$$p_0 = mh/2\pi; \quad m = \pm n\frac{1}{2}; \quad n = 0, 1, 2, 3, \dots$$

where m is the spin quantum number, the values of m are further limited by the total spin quantum number I :

$$m = I, I-1, I-2, \dots, -I.$$

I is a constant, characteristic of the ground state of every nucleus.

Nuclei with a total spin quantum number $I \neq 0$ interact with magnetic fields due to their magnetic moment μ . The magnitude of μ is related to the spin ; by the equation $\mu = \gamma p$, where γ is a constant, called the gyromagnetic ratio. The component of μ in the direction of H_0 , μ_0 , is also quantized.

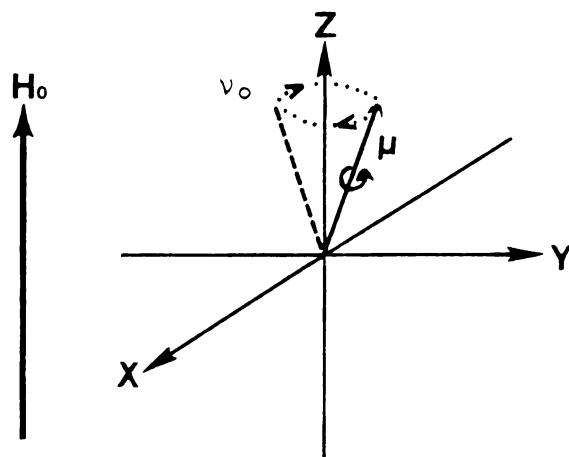
$$\mu_0 = \gamma I h / 2\pi$$



Nuclear Precession

When a spinning nucleus is exposed to a homogeneous magnetic field H_0 , it behaves like a gyroscope in a gravitational field.

The spin axis, which coincides with the magnetic moment vector μ , precesses about H_0 .



The frequency of precession, ν_0 , is known as the Larmor frequency of the observed nucleus. In contrast to bar magnets, the magnetic moments of spinning nuclei do not align in the direction of H_0 , no matter how strong this field is. Instead, the Larmor precession is accelerated by increasing the strength of the field.

Nuclear Magnetic Energy Levels

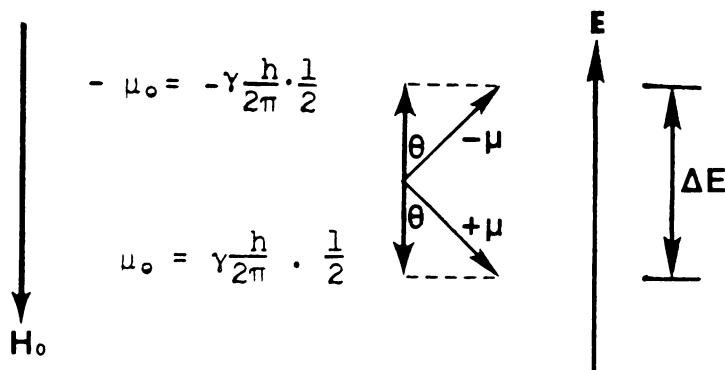
The energy of a magnetic moment μ in a field H_0 is given by the product of H_0 and μ_0 ; i.e.,

$$E = -\mu_0 H_0 = -\gamma(h/2\pi)IH_0$$

According to quantum mechanical rules, a nucleus with total spin quantum number I may occupy $(2I+1)$ different energy levels when placed in a magnetic field. For nuclei with



$I = \frac{1}{2}$, e.g. ^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P , two spin alignments relative to H_0 arise :



The energy difference ΔE between the two levels is $\gamma \frac{h}{2\pi} H_0$.

Nuclear Magnetic Resonance

The energy difference ΔE is the difference between the energies of precession in the direction of and opposite to H_0 . By recalling that ΔE also equals $h\nu_0$, the Larmor precession frequency ν_0 of nuclei with $I = \frac{1}{2}$ can be calculated :

$$\nu_0 = \frac{\gamma}{2\pi} H_0$$

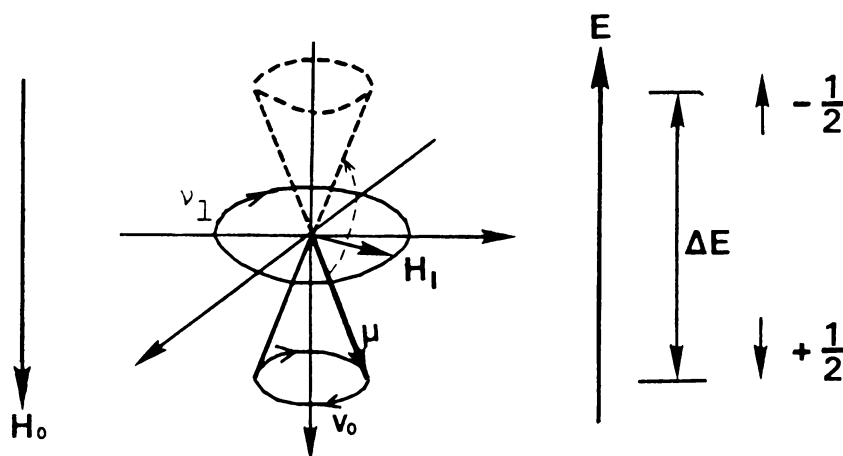
The value of γ for ^{31}P is such that for a typical magnetic field of 14,100 gauss, the corresponding value of ν_0 is around 24.3 MHz, much lower than that of ^1H (60 MHz).

An alternating magnetic field H_1 with frequency ν_1 , irradiating an ensemble of nuclear spins precessing in the static field H_0 , may overcome the energy difference ΔE if it meets two conditions : The vector of the alternating

field H_1 must rotate in the plane of precession with the Larmor frequency ν_0 of the nuclei to be observed.

$$\nu_1 = \nu_0$$

As a result, the spins originally precessing in the direction of H_0 flip over, and now precess against H_0 . Absorption of energy ΔE from H_1 takes place (Nuclear Magnetic Resonance).



In order to observe NMR, a sample containing nuclear spins (e.g. ^1H , ^{31}P) is placed in a static magnetic field H_0 . An alternating field with radio-frequency ν_1 is applied perpendicularly to H_0 . Usually, ν_1 is increased or decreased slowly and continuously during observation. When ν_1 matches the Larmor frequency of the nucleus to be observed, an absorption signal is recorded in the receiver of the NMR spectrometer.

At equilibrium, the population of the nuclear magnetic energy levels will be governed by a Boltzmann distribution with the parallel or lower energy state occupied by a

very slightly larger number of nuclei at 25°. Thus, in some cases the sensitivity of NMR can be slightly increased by lowering the sample temperature. However, care must be taken with temperature dependent spectra.

Relaxation and Saturation

If there were no processes by which nuclei in the upper state could return to the lower state, the continuous irradiation by the radio-frequency H_1 would soon cause all nuclei to precess against H_0 , and no further absorption of energy would occur. This condition is referred to as saturation. In fact, energy absorption from radio-frequency fields due to NMR is observed for long periods if the rf power is not too high. The processes responsible are referred to as relaxation. These relaxation processes are radiationless mechanisms.

There are two kinds of relaxation to be distinguished. The relaxation that establishes the equilibrium value of the nuclear magnetization along the direction of the external field is called longitudinal relaxation. It follows a kinetic law that is first order, in that the rate of relaxation depends on the first power of the excess (over the equilibrium value) of the number of nuclei in the upper state.

$$N - N_e = (N - N_e)_0 e^{-k_1 t} = (N - N_e)_0 e^{-t/T_1}$$

The reciprocal of the rate constant k_1 is called T_1 , the longitudinal relaxation time or spin-lattice relaxation time. It is due to the interaction of the nuclear spins

with various fluctuating local fields resulting from the motions of the electrons and of neighboring atoms. Addition of any paramagnetic substance to the solution can greatly shorten T_1 . The other kind of relaxation process is called transverse relaxation or spin-spin relaxation (characterized by a relaxation time T_2). If the nuclei precessing about a field direction are in phase with one another, there will be a net component of magnetic moment in a plane XY normal to the axis Z of the magnetic field. Any disturbing field that tends to destroy this phase coherence will cause relaxation of the XY component of magnetic moment. One such process is spin-spin relaxation, in which a nucleus in a higher spin state transfers energy to a neighboring nucleus by exchanging spins with it.

According to the Heisenberg uncertainty relationship the line width is $\Delta\nu_{\frac{1}{2}} = 1/(\pi T_2)$. The observed line width of an NMR signal depends additionally on the field inhomogeneity ΔH_0 , whose contribution to $\Delta\nu_{\frac{1}{2}}$ arises from

$$\Delta\nu_{\frac{1}{2}}(\text{inhom.}) = \frac{\gamma\Delta H_0}{2\pi} = \frac{1}{\pi} \left(\frac{\gamma\Delta H_0}{2} \right)$$

Therefore, the observed line width $\Delta\nu_{\frac{1}{2}}(\text{obs.})$:

$$\Delta\nu_{\frac{1}{2}}(\text{obs.}) = \Delta\nu_{\frac{1}{2}} + \Delta\nu_{\frac{1}{2}}(\text{inhom.}) = \left(\frac{1}{\pi} \right) \left(\frac{1}{T_2} + \frac{\gamma\Delta H_0}{2} \right) = \frac{1}{\pi T_2^*}$$

Chemical Shift

The environment surrounding the nucleus has a small but definitely measurable effect on the field sensed by the nucleus. The electrons surrounding a nucleus are acted upon by the external field to produce an induced



diamagnetism which partially shields the nucleus. The resulting change in resonance frequency is called chemical shift. In order to measure chemical shifts, the absorption signal of a reference compound R appearing at frequency ν_{0R} is assigned a shift of zero. The chemical shift of equivalent nuclei of a sample, having their signal at frequency ν_{0S} , may then be measured as a frequency difference $\Delta\nu_S$ in Hz. Because the frequency difference $\Delta\nu_S$ is proportional to the swept radio-frequency ν_1 (in MHz). Chemical shifts $\Delta\nu_S$ obtained at different radio-frequency ν_1 have to be adjusted to a common radio-frequency before comparison. In order to get chemical shift values which are independent of the frequency used, the δ scale of chemical shifts is introduced. δ values are obtained by dividing the frequency differences $\Delta\nu_S$ (in Hz) by the frequency of ν_1 (in MHz = 10^6 Hz).

$$\delta_S = \frac{\nu_{0S} - \nu_{0R}}{\nu_1} \times 10^{-6}$$

The shifts on the δ scale are given in ppm (parts per million = units of 10^{-6}).

A common reference compound used for calibrating ^1H and ^{13}C NMR spectra is tetramethylsilane (TMS), $\text{Si}(\text{CH}_3)_4$. For ^{31}P NMR spectra, the reference substance is traditionally 85% H_3PO_4 .

The chemical shift with respect to H_3PO_4 is defined :

$$\delta = \frac{H_{\text{obs.}} - H_{\text{H}_3\text{PO}_4}}{H_{\text{H}_3\text{PO}_4}} \times 10^{-6} \quad \text{or}$$

$$-\delta = \frac{\nu_{\text{obs.}} - \nu_{\text{H}_3\text{PO}_4}}{\nu_{\text{H}_3\text{PO}_4}} \times 10^{-6}$$

where, $H_{\text{obs.}}$ is the strength of the external field at the observed resonance and $H_{\text{H}_3\text{PO}_4}$ is the strength of the field at the resonance of H_3PO_4 . So, positive chemical shifts indicate greater nuclear shielding than in H_3PO_4 , while negative shifts indicate lesser shielding.

Reference compounds can be added to the sample solution (internal reference) or kept separate from the sample in a sealed capillary (external reference). If an external reference is necessary, a correction term accounting for the difference between the bulk susceptibility of reference (X_R) and sample solution (X_S) must be added to the observed shift, $\delta_{\text{obs.}}$:

$$\delta_{\text{corrected}} = \delta_{\text{obs.}} + \frac{2\pi}{3} (X_R - X_S)$$

(B) Introduction to Fourier Transform NMR

In the conventional NMR experiment, the sample is irradiated with a slowly changing radio-frequency and the absorption of energy observed. The resulting continuous wave (CW) NMR spectrum is simply a plot of this absorption vs. frequency. This is known as a spectrum in the frequency domain.

If the available sample size is very small, then the signal response will only be of the same order of magnitude as the "noise" inherently associated with the instrument.

The spectrum must then be scanned many times and the information from each scan stored in a digital computer capable of averaging the noise. This technique is known as the CAT method (Computer Averaged Transients). Noise, being of random nature, will be averaged out, while the signals associated with the sample will add up. If N is the number of sweeps, then the signal to noise ratio obtained is given by

$$\frac{\text{signal enhancement}}{\text{noise enhancement}} = \frac{N}{\sqrt{N}} = \sqrt{N}$$

The signal to noise is therefore a function of the square root of the number of sweeps.

Although repeated scanning can lead to a good spectrum from a very small amount of material, it suffers from the significant drawback that the time required to performed the experiment is extremely long. This problem is more serious if we are dealing with a nucleus having low sensitivity due to low natural abundance or a small gyromagnetic ratio or both. For instance, the sensitivity for ^{13}C is only about 10^{-4} of that observed for ^1H , and the sensitivity for ^{31}P is only 6.63% of that observed for ^1H though the natural abundance for ^{31}P is 100%.

It would be more efficient if instead of irradiating at one frequency at a time, we could irradiate at all frequencies in the range of interest at once. Spectrometers incorporating a large number (M) of transmitter frequencies each matched by a suitable receiver channel

can be built, but rapidly becomes uneconomical as M increases. The Fourier transform technique³³ accomplishes the same thing in a much more satisfactory manner.

In a pulsed FT NMR experiment, the sample is irradiated by a short intense radio-frequency (rf) pulse. If Δ Hz is the entire range of chemical shifts to be recorded in the spectrum, the pulse length, (t_p seconds) for a 90° pulse must be chosen such that

$$t_p(90^\circ) \ll 1/4\Delta$$

Pulse lengths for ^{31}P spectra may be of the order of microseconds.

In conventional FT-NMR, the single 90° pulse is used to tip the magnetization of all the nuclei to be studied. Following this pulse, the system begins to return to equilibrium by the processes of spin-spin (T_2) and spin-lattice (T_1) relaxation. Thus, the signal detected in the spectrometer following the perturbing pulse tends to decay and is called a free induction decay (FID).

The FID for a single resonance frequency, where the pulse is applied exactly on resonance, is (as shown in Figure 10b) an exponentially decaying function with a time constant T_2^* related to the transverse relaxation time T_2 and the magnetic field inhomogeneity ΔH_0 :

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma \Delta H_0}{2}$$

If the spectrum consists of only a single frequency, but the rf pulse is applied somewhat off resonance, the FID

The first part of the paper discusses the importance of maintaining accurate records of all transactions, including sales, purchases, and expenses. It emphasizes the need for a systematic approach to record-keeping, such as using a ledger or accounting software, to ensure that all financial data is properly documented and organized. This section also highlights the benefits of regular reconciliation and auditing to identify any discrepancies or errors in the records.

The second part of the paper focuses on the importance of budgeting and financial planning. It explains how a well-defined budget can help a business or individual manage their finances effectively, allocate resources wisely, and achieve their financial goals. This section provides practical tips and strategies for creating a realistic budget, monitoring progress, and making adjustments as needed. It also discusses the importance of setting financial priorities and understanding the impact of various financial decisions on the overall financial health.

The third part of the paper explores the importance of understanding and managing cash flow. It explains how cash flow is the lifeblood of any business, and how a positive cash flow is essential for maintaining liquidity and meeting financial obligations. This section provides insights into the factors that can affect cash flow, such as sales volume, payment terms, and operating expenses, and offers strategies for improving cash flow management. It also discusses the importance of maintaining a healthy cash flow buffer to应对 unexpected expenses or downturns in business.

The fourth part of the paper discusses the importance of understanding and managing debt. It explains how debt can be a double-edged sword, providing access to capital but also increasing financial risk. This section provides guidance on how to evaluate the costs and benefits of different debt options, such as loans, credit cards, and bonds, and offers strategies for managing debt responsibly. It also emphasizes the importance of maintaining a good credit rating and avoiding excessive borrowing.

The fifth and final part of the paper discusses the importance of understanding and managing taxes. It explains how taxes are a significant financial obligation for businesses and individuals, and how proper tax planning can help minimize tax liability and maximize financial resources. This section provides an overview of the basic principles of taxation, including income tax, corporate tax, and sales tax, and offers practical advice on how to stay compliant with tax laws and take advantage of available tax deductions and credits.

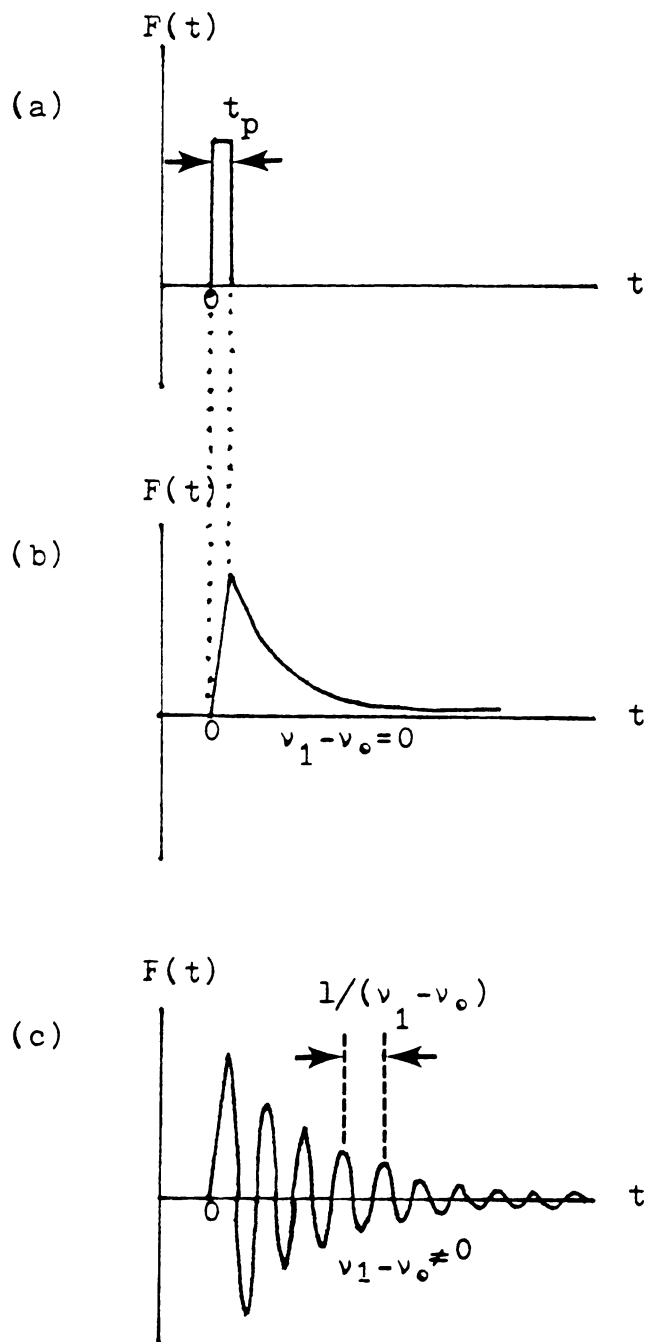
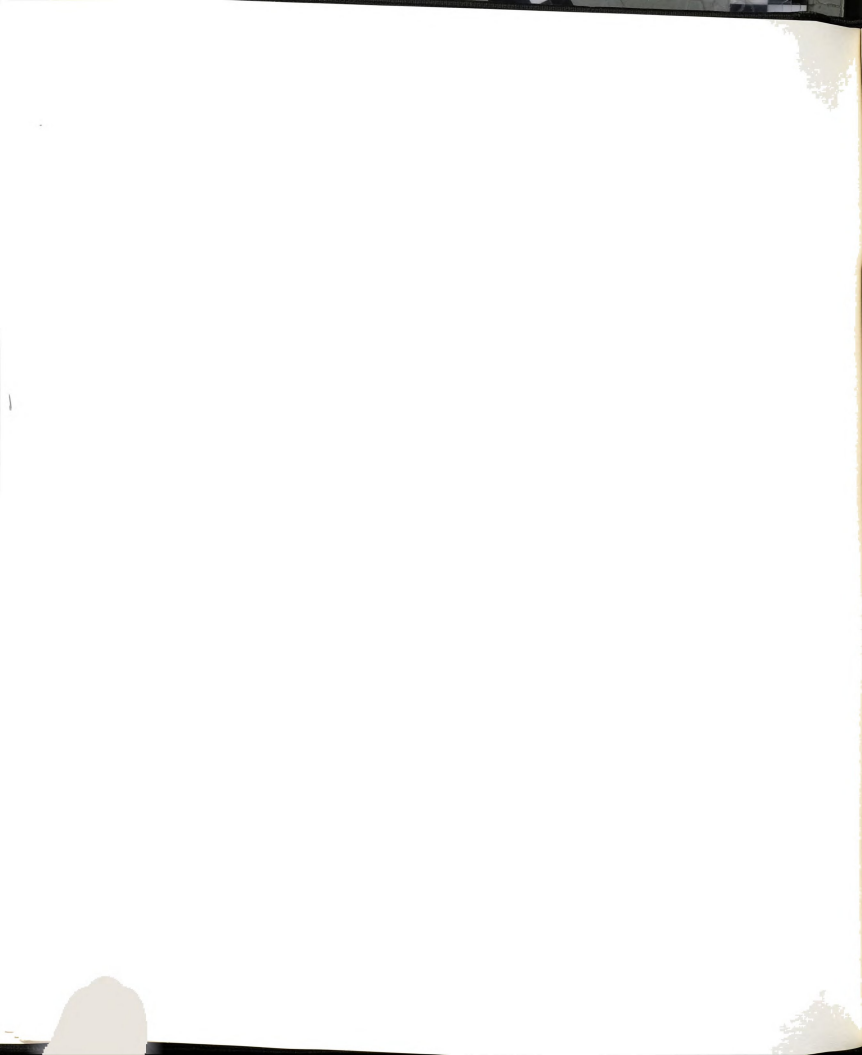


Figure 10. Free induction decay

(a) rf as input signal

(b) output signal for rf at resonance

(c) output signal for rf off resonance



observed in the receiver coil is a decaying sine wave (Figure 10c) analogous to the wiggles of CW high resolution NMR spectra. This damped sine wave is a plot of signal intensity vs time and is thus called a time domain spectra. Now if there are several precession frequencies due to chemical shifts and spin-spin coupling, then the FID is a complex interference pattern. The time domain spectrum contains all the information about the frequencies and their relative intensities, but it is present in a form that is not directly interpretable. This information can, however, be reproduced by Fourier transformation of the FID in a digital computer, as a frequency spectrum equivalent to that obtained from a conventional technique.

$$F(\omega) = \int_0^{\infty} f(t) e^{i\omega t} dt$$

where $f(t)$ is the FID and $F(\omega)$ is the resultant spectrum, ω represents the difference between the frequency ω_1 and the Larmor frequency distribution $\omega_0 + \Delta\omega$, $\omega_0 = \omega_1 - (\omega_0 + \Delta\omega)$.

The advantage of the FT method is that the entire process of excitation and detection of the FID occurs very rapidly. In FT-NMR experiments, pulses are usually applied to the sample repetitively, with coherent addition of the FID's, and the result is a dramatic improvement in signal/noise for a given expenditure of time.

For nuclei other than protons the FT method is especially valuable, since signals are generally very weak, and a large number of repetitive scans would be



needed. Furthermore, chemical shift ranges tend to be quite large, (e.g. the known ^{31}P chemical shifts range from about -225 ppm to +460 ppm relative to 85% H_3PO_4), so that extremely long times might be required for a conventional scan. With the pulse FT method the time needed for data acquisition is independent of the spectral range. (The acquisition time can be calculated by the equation $2 \times \text{SW} \times \text{AQT} = \text{DP}$ where SW is the spectral range, AQT the acquisition time and DP the number of data points in the FID.)

With the advent of improved instrumentation and pulse and Fourier transform techniques, chemical applications of ^{31}P NMR, ^{13}C -NMR, and other nuclei (e.g. ^{113}Cd , ^{109}Hg , ^{207}Pb , ^{205}Tl , . . . etc.) grew rapidly.

(C) General

The nuclear magnetic resonance (NMR) phenomenon was first observed by Bloch et al³⁴ in 1946. NMR has become one of the most widely applied physical methods, although it is only about twenty years since the first commercial instrument became available. Recent advances in NMR technology have improved the sensitivity, stability, and resolution of commercially available instruments to such a degree that nuclear magnetic resonance spectroscopy has become a powerful tool for investigations of molecular structure, the structure of solids, and also of phenomena of molecular motion in liquids and solids.

The three elements to which high-resolution NMR is particularly adaptable are hydrogen, phosphorus, and fluorine, since for each an isotope exhibiting a nuclear spin of one-half is present at or near 100% natural abundance and these nuclei have large magnetic moments. By far, the greatest effort has been devoted to ^1H NMR. However, among the three elements - hydrogen, phosphorus, and fluorine - only one, the phosphorus, is a central or backbone atom in molecular structures. Thus, nuclear magnetic resonance of the ^{31}P nucleus is suitable not only for the structural elucidation of phosphorus compounds, but also for analytical and kinetic studies.

By 1955, commercial instrumentation was in use and ^{31}P NMR began to be of practical value as a tool for the study of molecular structure and analytical applications. Chemical shift data on several hundred phosphorus compounds was soon published^{35,36}. As instrumentation improved and became more generally accessible, chemical applications of ^{31}P NMR grew rapidly and the literature on ^{31}P chemical shift data for phosphorus compounds continue to accumulate in the literature and in unpublished private compilations 35-38.

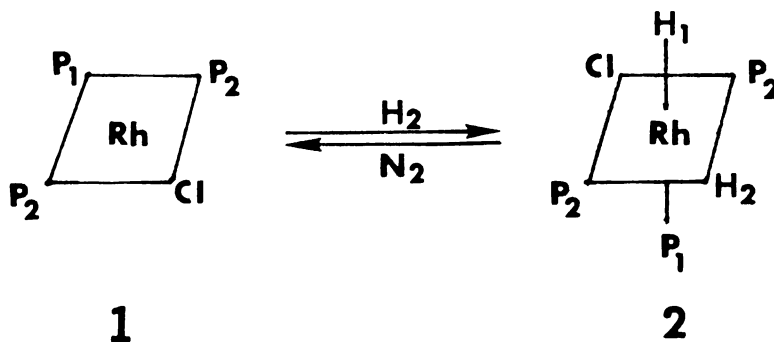
^{31}P -NMR of Transition Metal Phosphine Complexes

The important role of transition metal phosphine complexes in homogeneous catalysis has prompted their study in recent years. The discovery that nuclear magnetic resonance "virtual coupling" in bisphosphines is apparently



related to the geometry of the complex has been important to solution structure work in this area. Among these, the most studied one is the solution of chlorotris(triphenylphosphine)rhodium(I), or so-called Wilkinson's catalyst, which is the most efficient hydrogenation catalyst yet discovered.

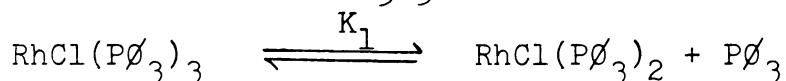
$\text{RhCl}(\text{P}\emptyset_3)_3$ is readily detected in solution using ^{31}P NMR³⁹. The phosphorus spectra supported a square-planar structure (configuration 1). The spectra^{39c} consist of four lines at high field ($\delta\text{P}_2 = -32.21$), due to the mutually trans phosphorus (labeled P_2) and six lines at lower field ($\delta\text{P}_1 = -48.94$) due to cis phosphorus atom (labeled P_1), where chemical shifts are in parts per million relative to external 80% H_3PO_4 , a negative value being to low field. The coupling constant data are $J_{\text{P}_1\text{P}_2} = -37.5\text{Hz}$, $J_{\text{P}_1\text{Rh}} = -192\text{ Hz}$ and $J_{\text{P}_2\text{Rh}} = -146\text{ Hz}$.



The dissociation of $\text{RhCl}(\text{P}\emptyset_3)_3$ in solution (into $\text{RhCl}(\text{P}\emptyset_3)_2$ and $\text{P}\emptyset_3$) has been a subject of considerable



interest and controversy, particularly in view of the indications of the importance of such dissociation to distinctive chemical properties of $\text{RhCl}(\text{P}\phi_3)_3$, e.g., as a hydrogenation catalyst and as a reagent for the decarbonylation of aldehydes. NMR measurements⁴⁰ and chemical evidence indicate that the degree of dissociation in solvents such as benzene and chlorinated hydrocarbons is much smaller than suggested by early molecular weight measurements⁴¹. The equilibrium constant, K_1 , for the dissociation of $\text{RhCl}(\text{P}\phi_3)_3$ according to the reaction,



has been determined⁴² spectrophotometrically to be 1.4×10^{-4} M in dilute benzene solution. By using the Fourier transform NMR technique, Tolman et al^{39c} detected a weak free phosphine resonance in a solution of 0.05M complex in CH_2Cl_2 with an intensity about 3% of that of the principle species.

It has also been demonstrated^{39c} that in addition of molecular H_2 to a solution of $\text{RhCl}(\text{P}\phi_3)_3$, the dihydride, which contains three phosphorus ligands, was formed almost quantitatively. The structure was assigned as configuration 2. The equilibrium may be reversed by passing N_2 through the solution. Again no resonance for free triphenylphosphine was observed.

NMR Study on Polymers, Exchange Resins and Gels

Nuclear magnetic resonance spectroscopy has proved to be a method of considerable interest and importance for the study of physical and chemical properties of polymers⁴³. Analysis⁴⁴⁻⁴⁶ of the width and detailed shape of absorption resonances and studies of magnetic relaxation times have yielded valuable information concerning the nature and frequency of molecular motions, such as the rotation of methyl groups and the onset of segmental motion of polymer chains. Results from such studies are affected to a great extent by the internal mobility of the polymer chains.

It is well known⁴⁷ that the line width in NMR spectra of swollen crosslinked polymers is larger than the line width in NMR spectra of analogous linear soluble polymers at equal concentration and temperature. The increased line width in conventionally measured NMR spectra of crosslinked polymers is due to a number of effects :

- (1). Insufficient averaging of dipolar interactions as a consequence of slow or anisotropic internal motions.
- (2). Anisotropy of magnetic susceptibility caused by simple physical heterogeneity of the sample. Both these effects can be suppressed by measurement of NMR spectra with rapid spinning of the sample about an axis inclined at the so called "magic angle" with respect to the direction of the stationary magic field (MAR-NMR).

Nuclear spin relaxation is a phenomenon which directly senses motional behavior of molecule. Doskocilova et al⁴⁸ have used magic-angle sample rotation to investigate internal motions in crosslinked poly(methyl methacrylate) gels swollen in CHCl_3 , as a function of crosslinking agent. From the temperature dependence of the limiting line widths of the OMe, α -Me and skeletal CH_2 groups, the activation energy ΔE of the corresponding motions were determined. They found that ΔE increased slightly with increasing crosslinked densities.

Tao et al⁴⁹ noted that in resins composed of relatively large microparticles, about a micron in size, the internal water line is broadened by kinetic processes in the resin phase. In small particles (ca. 10 nm) inter-particle heterogeneity was shown by multiple peaks. In a bead copolymer of styrene and technical divinylbenzene two signals were observed with a chemical shift difference which was a function of the internal molality of H^+ . On spinning, the line width of the external water was less than that of the internal water, which differed in different types of resin.

With the development of the pulse Fourier-transform nuclear magnetic resonance (FT-NMR) technique, relaxation time measurements have become feasible on biopolymers. K. Akasaka⁵⁰ measured proton and phosphorus-31 nuclear spin-lattice relaxation times (T_1) on single-stranded polyriboadenylic acid (poly(A)) in a neutral D_2O solution



with the Fourier-transformed method.

Analytical Problems in Solid-Phase Synthesis
& Hybrid Phase Catalysts

Analysis of hybrid phase catalysts, as well as polymer-supported reactants and products has suffered severe limitations. The most informative direct method employed now is infrared spectroscopy. The advantages of infrared are associated with the possibility of making unambiguous transmission mode measurements on insoluble polymers with approximately the same sensitivity as that attained with low molecular weight compounds. However, the complex spectrum of the resin tends to obscure the spectral features of the attached moiety. Fortunately, J.I. Crowley et al⁵¹ found that difference spectra, using purified unreacted co(polystyrene-2% divinylbenzene) in the reference beam, dramatically simplify the spectra of many polymer-supported compounds. They were able to routinely quantify the extent of chloromethylation by such a procedure, employing a standard curve prepared from resins of known percentages of chlorine.

ESR has been used to analyze the mobility of a spin-labeled resin⁵² and to evaluate the paramagnetism of the polymer-supported titanocene catalyst³⁶.

Electron microprobe spectroscopy has been used³¹ to investigate the structure of rhodium-phosphinated polystyrene.

Raman⁵³ and ¹³C NMR spectroscopy⁵⁴ appears to be at, or



nearing, the level of development sufficient to encourage attempts at resin analysis. The alkyl and aromatic carbons of the co(polystyrene-2% divinylbenzene) can be easily indentified by natural abundance ^{13}C NMR⁵¹. Use of specific enriched ^{13}C functionality on the resin could permit observation of concentrations of the magnitude now being used in solid-phase reactions. However, ^{13}C enrichment is not very economical and practical. In the polymer-supported homogeneous catalysts, phosphorus is an important linking ligand. Since phosphorus is a central atom in the functional group, nuclear magnetic resonance of ^{31}P nucleus would provide a most economic and informative tool. The application of pulsed and Fourier-transform techniques and the improvements of modern instrumetation make ^{31}P NMR of phosphinated beads (1.8% crosslinked) possible⁵⁵.

In the research area of polymer-supported homogeneous catalysts, one question which is still open concerns the exact structure of the catalytic site in the heterogeneous system as compared with the homogeneous one. Does the polymeric carrier inflict changes on the microenvironments of the catalytic site which might be determinal for catalytic activity ? The only study, which tries to find an answer to this question is one by Collman and coworkers¹². They showed that when phosphine containing polymers are exchanged with Rh/phosphine complexes, two phosphine ligands are released per Rh-ion taken up by the polymer.

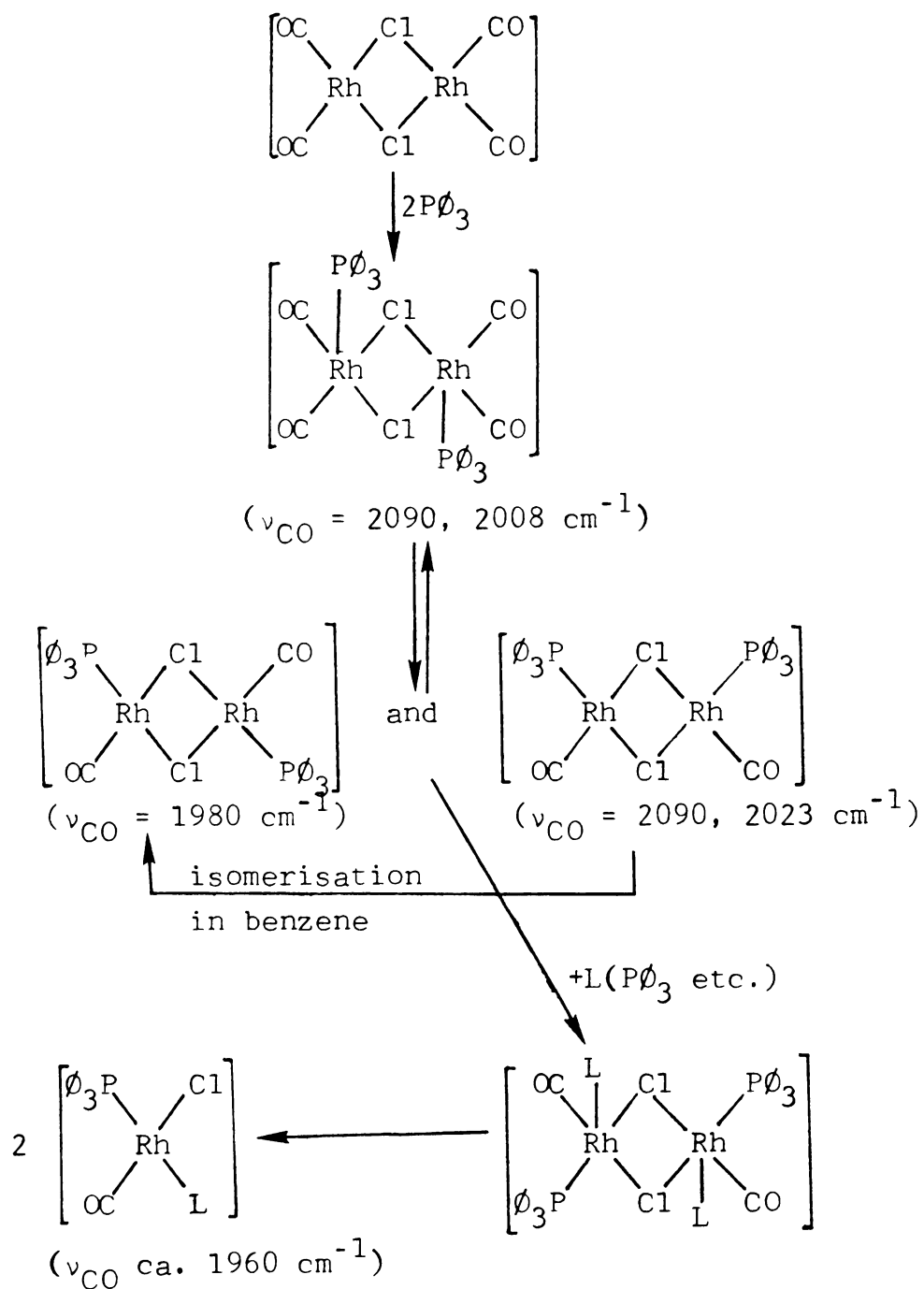


In other words in the polymeric complex every Rh-ion seems to be surrounded by two ligands. The crosslinked polymer seems to be sufficiently mobile in that it can bring non-adjacent phosphine sites together.

Bridge-Splitting Reactions of Rhodium Carbonyl Chloride

It has been reported that reaction of $[\text{RhCl}(\text{CO})_2]_2$ with excess triphenylphosphine gave the well-known trans- $[\text{RhCl}(\text{CO})(\text{P}\phi_3)_2]$. The reaction of $[\text{RhCl}(\text{CO})_2]_2$ with triphenylphosphine (1:2 molar ratio) was first reported to give the complex trans- $[\text{RhCl}(\text{CO})_2\text{P}\phi_3]$ ⁵⁶. However, T.A. Stephenson⁵⁷ found evidence that the above trans- $[\text{RhCl}(\text{CO})_2\text{P}\phi_3]$ should be reformulated as the dimer complexes trans- $[\text{RhCl}(\text{CO})\text{P}\phi_3]_2$. A mechanism for the reaction of $[\text{RhCl}(\text{CO})_2]_2$ with $\text{P}\phi_3$ was proposed (as shown in Scheme VIII) on the basis of detailed i.r. studies.

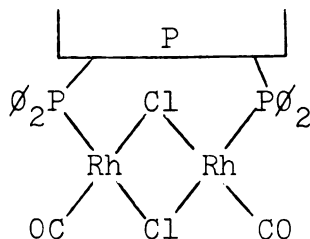
L.D. Rollmann⁵⁸ also reported that IR and NMR data provided structural evidence for the cis- $\text{Rh}(\text{CO})_2(\text{PR}_3)\text{Cl}$ made from stoichiometric amounts of phosphine monomers to CH_2Cl_2 solutions of the carbonyl chloride ($\text{Rh}/\text{P} = 1$) under CO. The polymer phosphine analog of cis- $\text{Rh}(\text{CO})_2(\text{PR}_3)\text{Cl}$ was prepared by the addition of PPBu_2 phosphine resin to the carbonyl dimer solution. In the presence of high CO and H_2 pressure, the trans isomer was proposed. Rollmann thought the crosslinking species, trans- $\text{Rh}(\text{CO})(\text{PPBu}_2)_2\text{Cl}$ was unlikely due to structural constraints in the resin. In contrast to this conclusion, G. Strathdee et al⁵⁹ suggested (on the basis of the i.r. band) that on addition



Scheme VIII. Proposed mechanism for reaction of $[\text{RhCl}(\text{CO})_2]_2$ with $\text{P}\phi_3$.



of triphenylphosphine substituted polystyrene beads (ground to a powder) to the benzene solution of dimer, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, most of the Rh(I) was present as trans- $\text{Rh}(\text{CO})\text{Cl}(\text{P}^-\text{O})_2$, some might also be present as a dimer, perhaps as



Very recently⁶⁰, it was reported that tri-tert-butylphosphine reacted with tetracarbonyl- μ -dichlorodirhodium(I) to form carbonylchlorobis(tri-tert-butylphosphine)rhodium (I), existing in an equilibrium with dicarbonyl- μ -dichlorobis(tri-tert-butylphosphine)rhodium in pentane solution.

The ^{31}P spectrum (CH_2Cl_2) of the yellow solid obtained from the reaction of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ with $\text{P}(\text{OMe})_3$ indicates the presence of $\text{Rh}_2\text{Cl}_2[\text{P}(\text{OMe})_3]_4$ ⁶¹.



II. RESULTS AND DISCUSSION

Phosphorus-31 NMR spectra of polystyrylphosphine

A sample of 35-32 mesh (425-500 micron) 2% Divinylbenzene(DVB)-styrene copolymer ($\approx 1.8\%$ crosslinked) was lithiated with n-BuLi·TMEDA complex followed by treatment with chlorodiphenylphosphine¹⁶. The ^{31}P NMR spectra of these phosphinated beads were then measured in swelling solvents. As Figure 11 shows, spectra of good quality are obtained in a reasonable time (about 15 minutes) on the phosphinated beads sample swollen with toluene in a 10mm NMR tube. Disregarding the line broadening, which is due to restricted mobility in the bead, this spectrum is comparable with that for triphenylphosphine.

The chemical shift ($\delta=5.93$ ppm) is essentially the same as that of a triphenylphosphine solution ($\delta=5.83$ ppm). The tube interchange method was used for referencing. The chemical shift (δ) with respect to 85% orthophosphoric acid is defined as

$$\delta = \frac{H_{\text{obs.}} - H_{\text{H}_3\text{PO}_4}}{H_{\text{H}_3\text{PO}_4}} \times 10^6$$

where $H_{\text{obs.}}$ is the strength of the external field at the observed resonance and $H_{\text{H}_3\text{PO}_4}$ is the strength of the field at the resonance of H_3PO_4 .





Figure 11. ^{31}P pulse FT spectra of triphenylphosphine and phosphinated beads. Chemical shifts (parts per million) are relative to 85% H_3PO_4 . Exponential multiplication yielding 1.94 Hz line broadening was applied to the free-induction decays.

(A) A 1.5 M solution of $\text{P}\phi_3$ in toluene in a 10 mm NMR tube. Result of one pulse. Acquisition time: 0.82 sec. Chemical shift: 5.83 ppm. Spectrum line width: 25.6 Hz.

(B) 12% phosphinated DVB-Styrene copolymer in toluene in a 10 mm NMR tube. Result of 200 pulses with 3.5 seconds between pulses. Total accumulation time: 860 seconds. Chemical shift : 5.93 ppm. Line width : 78 Hz.

(C) Phosphinated beads which were oxidized. The low field signal is due to oxidized polymeric triphenylphosphine (polymeric phosphine oxide). Result of 200 pulses with 3.5 seconds between pulses. Total accumulation time: 860 seconds. Chemical shift: low field one, -26.44 ppm; high field one, +5.93 ppm. Line width: low field one, 76 Hz; high field one, 82 Hz. Sample was in a 15 mm NMR tube.

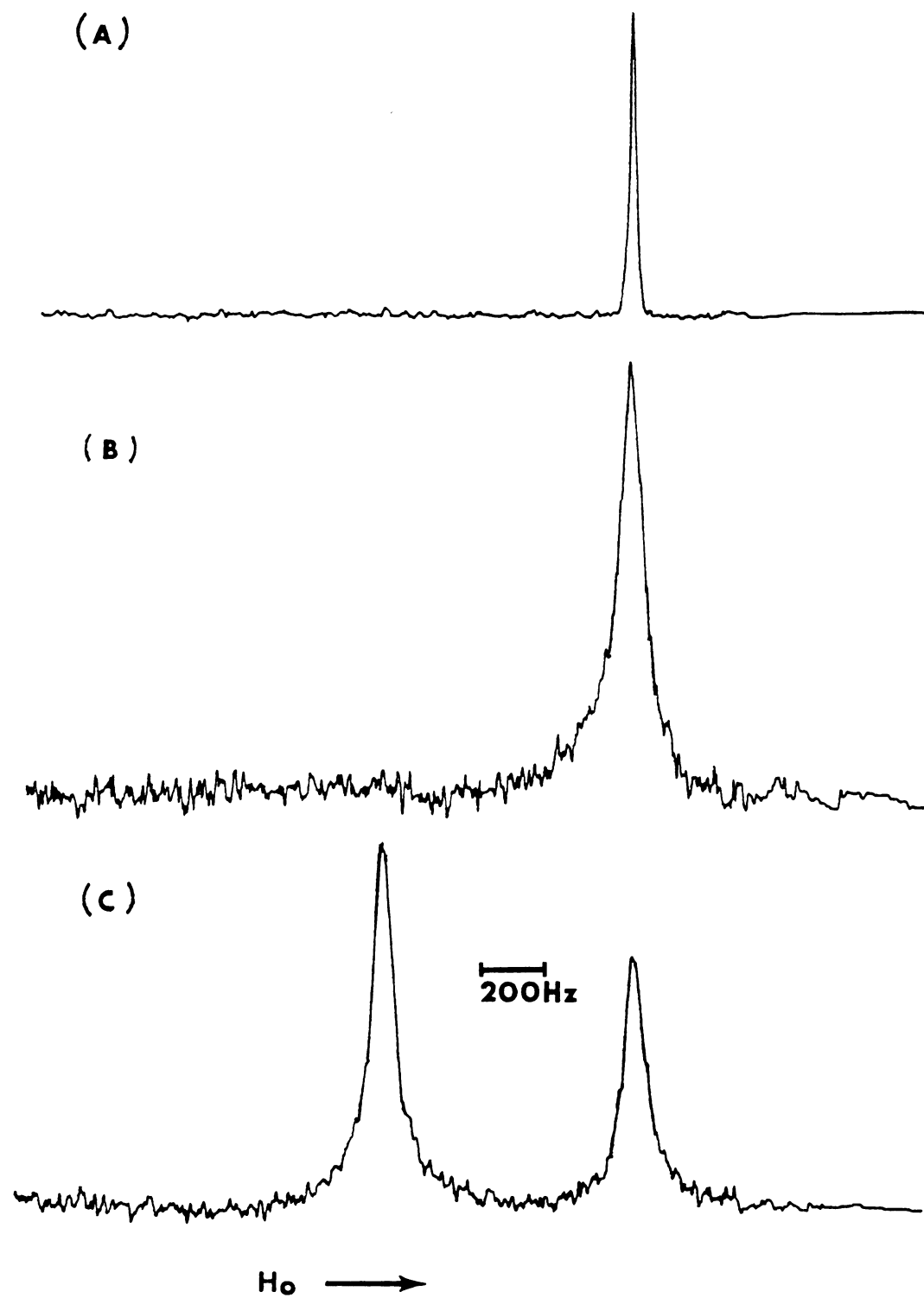


Figure 11.



The line width of the ^{31}P signal of triphenylphosphine in solution is about 24 Hz. The unresolved spin-spin splitting by the β -hydrogen of the phenyl group is the cause of this peak broadening. Thus decoupling the ^1H - ^{31}P spin interactions sharpens the ^{31}P signal of a triphenylphosphine solution to a line width of about 7 Hz.

The ^{31}P NMR measurements of phosphinated beads can be performed in a variety of swelling solvents, such as tetrahydrofuran(THF), benzene, toluene, xylene, chlorinated hydrocarbon, ethylacetate, acetone, diethyl ether, chlorobenzene and nitrobenzene. The solvent effects on the chemical shifts are only about ± 0.5 ppm. In low swelling solvents, e.g. cyclohexane and nitromethane, elevated temperatures are necessary in order to observe the ^{31}P NMR spectra of phosphinated beads. However, in solvents that shrink the pore sizes of the beads, such as ethanol, no ^{31}P signal was observed even at temperatures as high as 70°C . The degree of swelling (q) of phosphinated beads in a variety of solvents are listed on page 146.

A sample of 20% DVB-polystyrene copolymer was also phosphinated to give 0.78 meq P per g. beads. At room temperature, no phosphorus resonance signal was observed in toluene. However, very broad triphenylphosphine resonance was obtained at elevated temperature and the S/N ratio was improved by increasing the temperature.

The Detection of Polymeric Phosphine Oxide by ^{31}P NMR

As Figure 11 shows, the chemical shift of polymeric triphenylphosphine oxide is about -24.5 ppm from 85% phosphoric acid. In order to test the nature of polymeric triphenylphosphine, a sample of 11% phosphine-substituted polystyrene beads (1.8% crosslinked) was exposed to air. A small peak corresponding to triphenylphosphine oxide resonance was observed after 2 days. After refluxing the sample for 12 hours in toluene about 40% of the polymeric phosphine was oxidized. The results are summarized in Figure 12. Polymeric phosphine was very easily oxidized during phosphination, as well as in the presence of transition metal complexes, if oxygen is not excluded. The color of the phosphinated beads does not reflect their purity. Consequently, the synthesis of polymer-bound catalysts may not lead to the expected product, and the behavior of such catalysts does not necessarily parallel that of the monomeric homogeneous catalyst. Phosphorus-31 NMR spectroscopy provides a useful tool to characterize the polymeric organophosphorus ligands and their transition metal catalysts.

Quantitative Analysis of the Content of the Polymeric Phosphines

The extent of phosphination can be routinely measured by employing a sample of known phosphorus concentration.

A sample of phosphinated beads was analyzed for the

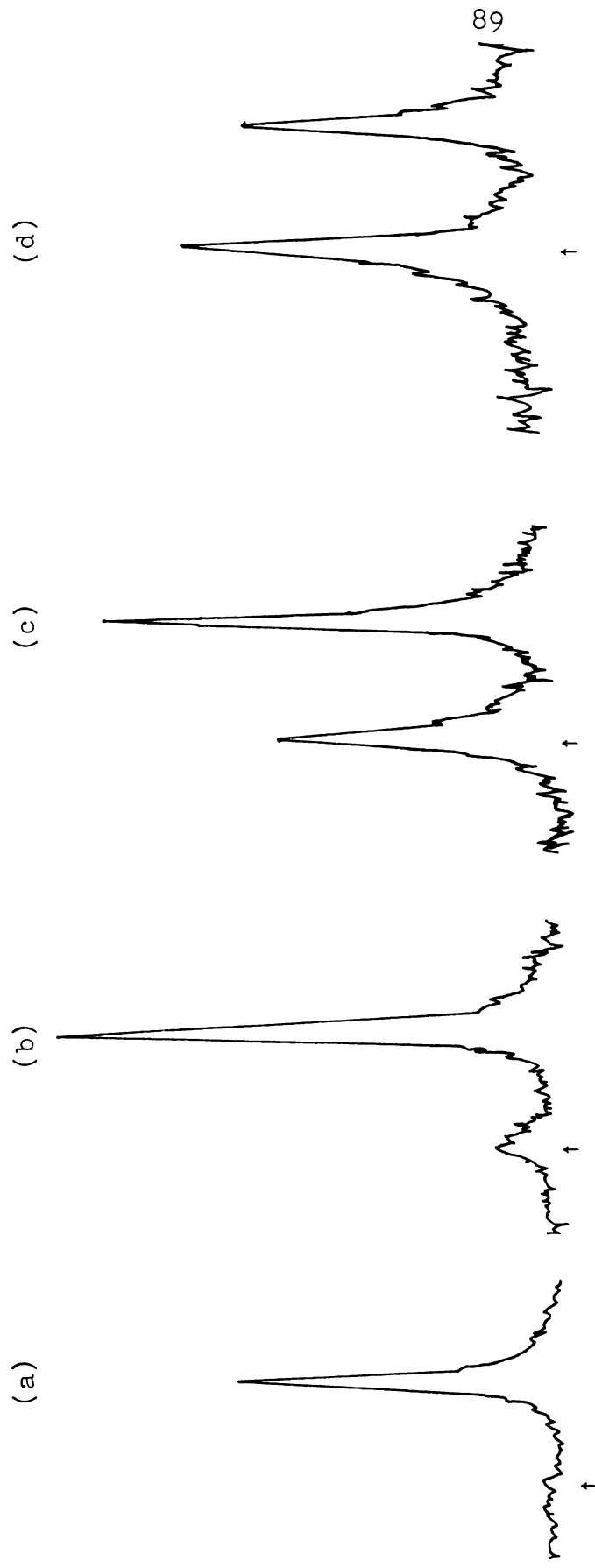


Figure 12. ^{31}P pulse FT spectrum of 11% phosphinated beads swollen with toluene.

(a) before oxidized

(b) sample of (a) exposed to air for 2 days

(c) sample of (b) exposed to air and refluxed in toluene for 12 hours
area ratio 1:1.45

(d) sample of (c) exposed to air for another two weeks.

↑ shows the growing of phosphine oxide peak.

content of phosphorus by elemental analysis. This standard was then swelled in toluene in a 15 mm NMR tube. The external reference (tri-n-butylphosphine), sealed in a 5 mm NMR tube, was inserted and this assembly was carefully lined up with a mark on the probe. The ^{31}P NMR spectrum was then measured and the integration was recorded. The peak area ratio (I) of polystyrylphosphine to the tri-n-butylphosphine was then calculated. The same reference tube was used for the measurement of ^{31}P -NMR spectrum of the sample of unknown phosphine content. The percentage of phosphorus was then calculated from the known percentage of phosphorus value and the relative peak areas.

$$\%P(\text{unknown}) = \frac{\%P(\text{standard})}{I(\text{standard})} \times I(\text{unknown})$$

Two to three measurements were made for each sample and the average value was used for the calculation of the percentage of phosphorus with an accuracy of about $\pm 5\text{-}10\%$.

The effect of the delay time (time between pulses) on the results was considered. The ^{31}P -NMR measurements of a sample and a standard were carried out with a delay time of 3.5 seconds. The phosphorus content of the sample was calculated to be 60.8% that of the standard. The experiments were then repeated with a delay time of 100 seconds and the percentage of phosphorus of the sample was calculated to be 63.8% that of the standard. Thus the delay time parameter does not effect the obtained results (within error). In order to save time and get a better

signal to noise ratio, a 3.5 seconds delay time was used in this study unless otherwise mentioned.

The ^{31}P NMR Spectra of Polystyrylphosphine Metal Complexes

The 1.8% crosslinked DVB-styrene copolymer was phosphinated by the standard technique¹⁶. The phosphinated beads were then reacted with rhodium complexes, such as $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (COE is the abbreviation for cyclooctene) and $\text{RhCl}(\text{P}\phi_3)_3$, in benzene. After equilibration, the beads were washed with benzene until no coloration showed in the rinse solution. The beads were then vacuum dried.

The metal complexed copolymer was swelled in toluene, and ^{31}P -NMR measurements of the polystyrylphosphine metal complexes and the phosphinated copolymer were then carried out under the same conditions.

The ^{31}P -NMR peak of the metal complexed polystyrylphosphine is too broad to be observed due to the strong interaction of the rhodium electrons and the phosphine nuclei as well as the insufficient averaging of dipolar interactions. The polymeric phosphine oxide peak might have been mistaken for the metal complexed polystyrylphosphine peak due to their similar chemical shifts. However, these signals were not hard to distinguish when a standard sample was employed. As can be seen from Figure 13, the uncomplexed polymeric phosphine peak slowly decreased as the ratio of rhodium complexes to the phosphines was increased, until no peaks other than the

Figure 13. ^{31}P NMR spectra of phosphinated beads and polystyrylphosphine metal complexes. The high field signal is due to the reference sample, tri-n-butylphosphine.

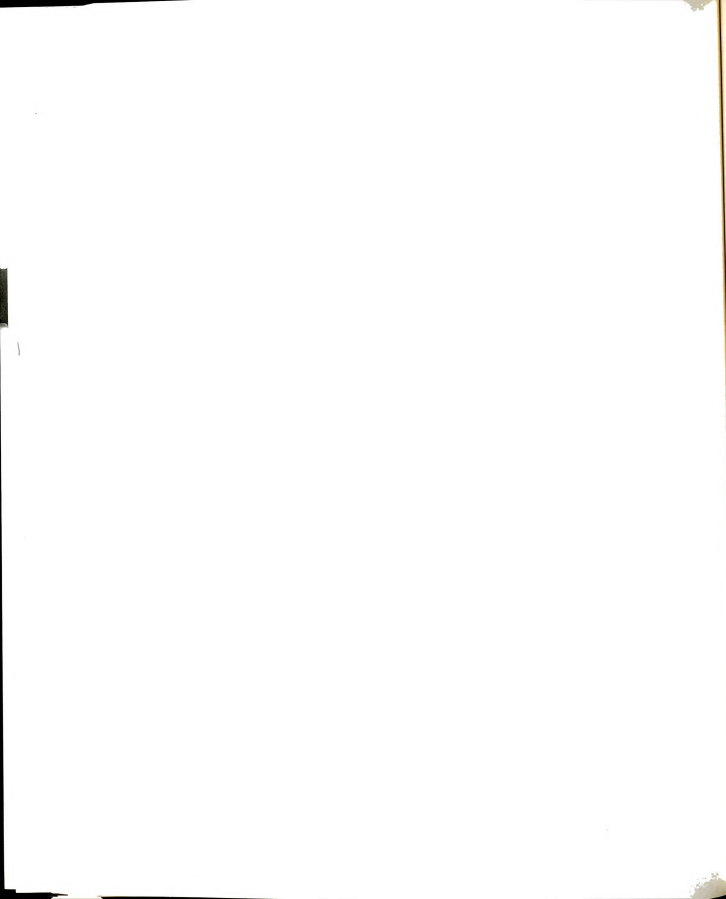
Spectrum from bottom to top is batch 4 phosphinated beads, complexes of IVB, IVD, IVE, IVF and IVG.

reference sample ($P(n-Bu)_3$) were observed. The uncomplexed polymeric phosphine does not show a significant change in chemical shift or line width during this series of measurements. The amount of uncomplexed polymeric phosphine in the metal complexed copolymer can be calculated by comparing the relative peak areas by the previously described method.

T. Mizoraki et al.⁶² observed a sharp absorption of ^{31}P (32.4 ppm lower in field than free triphenylphosphine) for methylene chloride solution of soluble polystyryl nickel complexes ($[P]-\phi-Ni(P\phi_3)_2Br$) which were prepared from tetrakis(triphenylphosphine)nickel and brominated polystyrene. The ^{31}P chemical shift was independent of the nickel content of the polystyryl complex. An analogous polystyryl platinum complex ($[P]-\phi-Pt(P\phi_3)_2I$), prepared from iodinated polystyrene and tetrakis(triphenylphosphine)-platinum, also shows one sharp absorption of ^{31}P (26.7 ppm) and a large coupling constant of J_{Pt-P} (3065 Hz) in methylene dichloride. In hexane, however, neither of the above complexes showed absorption. The explanation suggested is that, when the polystyryl metal complex swells in a polar solvent such as methylene dichloride, the environment around the metal site is analogous to that of homogeneous bis(triphenylphosphine)-arylmatal(II)halide, which gives one sharp ^{31}P -NMR absorption. In a non-polar solvent, such as n-hexane, the coordination sites of metal

atoms are blocked by either the halogen atoms or phenyl rings of the polystyrene, resulting in the ^{31}P -NMR absorption becoming too broad to be detected.

At the present time there is considerable controversy about the isolation of catalytic sites in the resin-bound chemistry. A resin-analog of tris(triphenylphosphine)-chlororhodium has been prepared by exchanging the phosphine in the complex with polymeric phosphines (resin-bound phosphines). Originally, a single bond was assumed to be involved in the attachment of the polymer to each rhodium¹. If this is the case, then the complex could be easily lost from the support. It has been found that use of low crosslinked polystyrene allows multiple binding to the polymer¹². When polymeric triphenylphosphine was treated with bis(triphenylphosphine)carbonylchlororhodium, analysis of the filtrate from reactions using measured quantities of polymeric triphenylphosphine and the homogeneous complex showed that at least two triphenylphosphines were always released for each metal atom incorporated. The formation of new cross-links during repeated usage processing of the polymer-supported catalysts has also been ascribed to the multiple binding of bound catalysts. Two rhodium(I) complexes, $\text{RhCl}(\text{P}\phi_3)_3$ and $[\text{Rh}(\text{COE})_2\text{Cl}_2]_2$, and five batches of phosphinated polystyrene beads (1.8% crosslinked with divinylbenzene) with different levels of ring substitutions were used in these studies.



$\text{RhCl}(\text{P}\phi_3)_3$ Studies

The six samples of beads (IA-IF) used in this study, were all prepared by equilibration of $\text{RhCl}(\text{P}\phi_3)_3$ with phosphinated beads containing 0.95 mmole of phosphine per g. of beads in benzene. They were then swelled in toluene prior to the phosphorus-31 NMR measurement. The content of free phosphine was determined from the relative peak areas by the method described above. The maximum possible content of polymeric phosphine coordinated to the rhodium per g. beads, $[\text{P}]-\text{P}_\text{C}/\text{g. beads}$, was determined by subtracting the free phosphine content of the complex sample from the phosphine content of the original beads. The maximum number of coordinations per rhodium atom in the complexed polymer by polymeric phosphines, $[\text{P}]-\text{P}_\text{C}/\text{Rh}$, was then calculated. The results are summarized in Table 7.

$[\text{Rh}(\text{cyclooctene})_2\text{Cl}]_2$ Studies

Four batches of 2% divinylbenzene-styrene copolymer beads were phosphinated by the standard techniques, to contain 1.237, 0.878, 0.560 or 0.379 mmole of phosphine per g. of beads. Each phosphinated beads sample was used to prepared six to seven batches of rhodium complexed copolymer by equilibration the copolymer with $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ in benzene with different rhodium to phosphorus ratio. These samples were then analyzed for free phosphine content by phosphorus-31 spectroscopy.

Table 7 . The complexation of polymeric triphenylphosphine with rhodium(I).-- $\text{RhCl}(\text{P}\phi_3)_3$ Equilibration

Sample	meq Rh/g. beads (added)	meq P_c /g.beads ^a (calculated)	$\text{P}] - \text{P}_c / \text{Rh}$ ^b
IA	0.0725	0.371	5.1
IB	0.1018	0.485	4.8
IC	0.1322	0.554	4.2
ID	0.1524	0.584	3.8
IE	0.2655 (0.2225) ^c	0.860	3.2 (3.8) ^d
IF	0.3624 (0.2546) ^c	0.816	2.3 (3.2) ^d

^a The maximum possible content of polymeric phosphine coordinated to the rhodium per g. beads.

^b The maximum number of coordination per rhodium atom by polymeric phosphine.

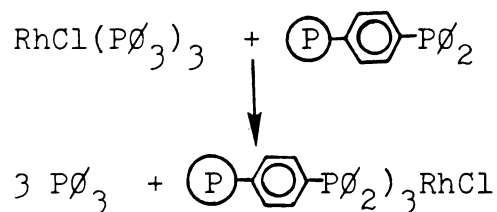
^c From elemental analysis.

^d The elemental analysis of rhodium content was used.



The maximum mmole of phosphine coordinated to the rhodium per g. of beads ($P]-P_c/g.\text{beads}$) and the maximum amount of phosphines complexed to each rhodium atom were calculated. The results are summarized in Table 8-11. A plot of mmole $P_c/g.$ beads vs. Rh/P is presented in Figure 14.

As can be seen from Table 7, the maximum possible number of coordinations per rhodium atom by polymeric phosphine ($P]-P_c/Rh$) is always no less than three. The belief that the phosphine substituted co(polystyrene-2% divinylbenzene) is sufficiently mobil to bring nonadjacent sites together seemed to be clearly supported by this result.



It has been demonstrated that the multiple patterns of the ^{31}P spectra of tris(triphenylphosphine)rhodium(I) complexes collapse and eventually show only a single phosphorus line as the temperature is raised or as an excess triphenylphosphine is added to the solutions.

So, a plausible explanation for the $P]-P_c/Rh$ ratio greater than three is that a portion of polymeric phosphine sites were flexible enough to provide fast ligand exchange with the polymeric complex by the nmr criterion.

The decrease of the $P]-P_c/Rh$ ratio with increasing

Table 8 . The complexation of polymeric triphenylphosphine with rhodium(I).-- $[\text{RhCl}(\text{COE})_2]_2$ Equilibration (1.237 mmole phosphine/g. beads)

Sample	meq Rh/g. beads (added)	meq P_c /g. beads ^a (calculated)	$\text{P}]-\text{P}_c/\text{Rh}$ ^b
IIA	0.083	0.137	1.7
IIB	0.142	0.224	1.6
IIC	0.181	0.268	1.5
IID	0.237	0.314	1.3
IIE	0.440	0.523	1.1
IIF	0.704 (0.364) ^c	0.739	1.1 (2.0) ^d
IIG	1.052 (0.415) ^c	0.987	0.9 (2.4) ^d

^a The maximum possible content of polymeric phosphine coordinated to the rhodium per g. beads.

^b The maximum number of coordination per rhodium by polymeric phosphine.

^c From elemental analysis.

^d The elemental analysis of rhodium content was used.



Table 9 . The complexation of polymeric triphenylphosphine with rhodium(I).-- $[\text{RhCl}(\text{COE})_2]_2$ Equilibration-- (0.878 mmole phosphine/g. beads)

Sample	meq Rh/g. beads (added)	meq P_c /g. beads ^a (calculated)	$\text{P}]/\text{P}_c/\text{Rh}^b$
IIIA	0.046	0.158	3.4
IIIB	0.077	0.214	2.8
IIIC	0.106	0.280	2.6
IIID	0.207	0.449	2.2
IIIE	0.375 (0.316) ^c	0.625	1.7 (2.0) ^d
IIIF	0.830 (0.441) ^c	0.878	1.1 ^d (1.5)

^a The maximum possible content of polymeric phosphine coordinated to the rhodium per g. beads.

^b The maximum number of coordination per rhodium by polymeric phosphine.

^c From elemental analysis.

^d The elemental analysis of rhodium content was used.

Table 10. The complexation of polymeric triphenylphosphine with rhodium(I).-- $[\text{RhCl}(\text{COE})_2]_2$ Equilibration-- (0.560 mmole phosphine/g. beads)

Sample	meq Rh/g. beads (added)	meq P_c /g.beads ^a (calculated)	$\text{P}] - \text{P}_c / \text{Rh}$ ^b
IVA	0.039	0.016	0.4
IVB	0.044	0.075	1.7
IVC	0.070	0.091	1.3
IVD	0.108	0.203	1.9
IVE	0.185	0.294	1.6
IVF	0.311	0.469	1.5
IVG	0.488 ^c (0.383)	0.560	1.1 ^d (1.5)

^a The maximum possible content of polymeric phosphine coordinated to the rhodium per g. beads.

^b The maximum number of coordination per rhodium by polymeric phosphine.

^c From elemental analysis.

^d The elemental analysis of rhodium content was used.

Table 11. The complexation of polymeric triphenylphosphine with rhodium(I).-- $[\text{RhCl}(\text{COE})_2]_2$ Equilibration-- (0.379 mmole phosphine/g. beads)

Sample	meq Rh/g.beads (added)	meq P_c /g.beads ^a (calculated)	$\text{P}]/\text{P}_c/\text{Rh}^b$
VA	0.021	0.036	1.8
VB	0.033	0.063	1.9
VC	0.057	0.105	1.8
VD	0.105	0.164	1.6
VE	0.135	0.210	1.6
VF	0.218	0.320	1.5
VG	0.322 ^c (0.286)	0.379	1.2 ^d (1.3)

^a The maximum possible content of polymeric phosphine coordinated to the rhodium per g. beads.

^b The maximum number of coordination per rhodium by polymeric phosphine.

^c From elemental analysis.

^d The elemental analysis of rhodium content was used.

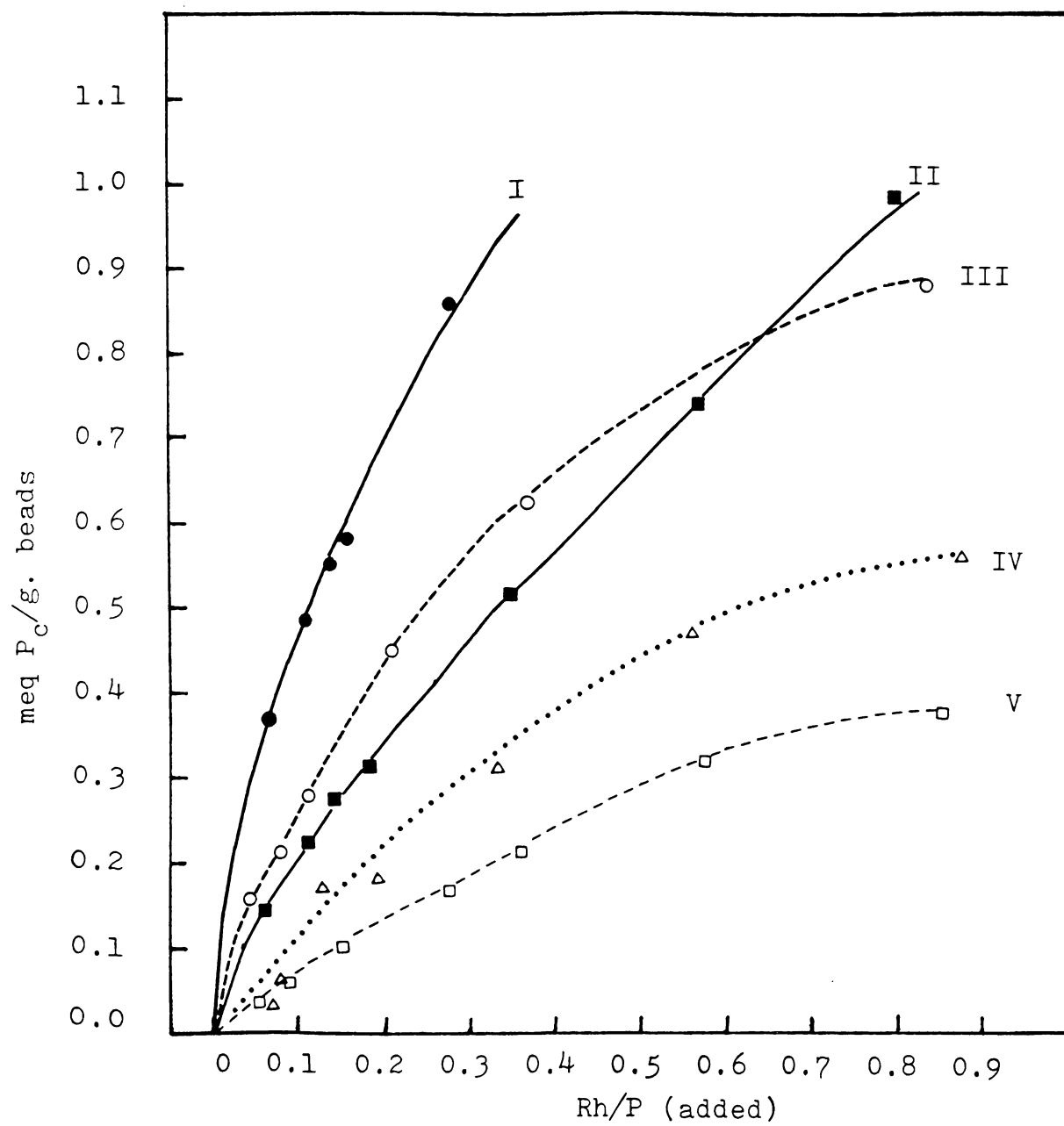


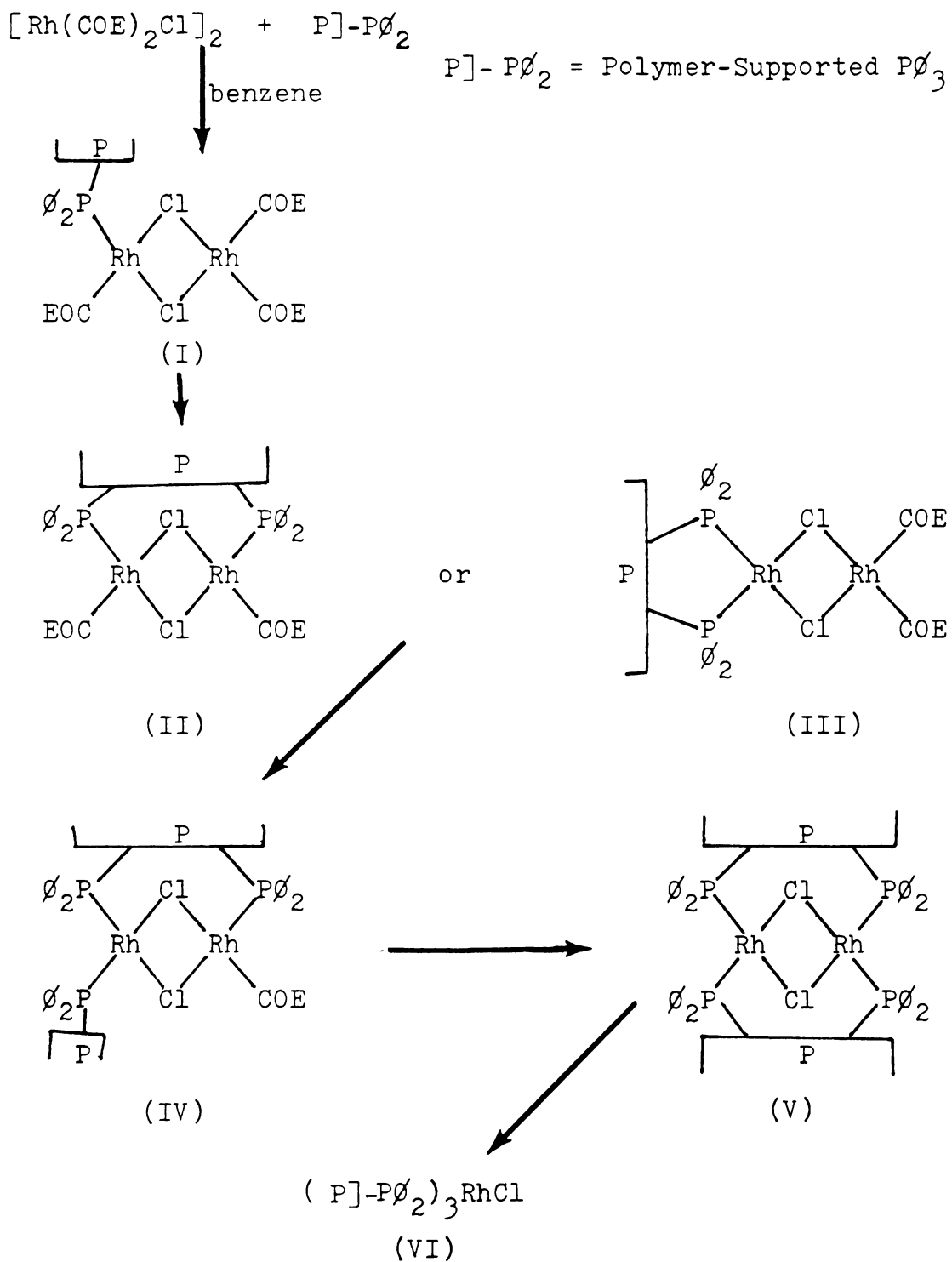
Figure 14. Plot of meq P_c /g.beads vs. Rh/P.

ratio of the starting complexes to the polymeric phosphines may be ascribed to the lower concentration of available free phosphines.

In order to test whether dimerization of supported Wilkinson's catalyst occurs, sample IF was refluxed for 2 days in toluene. This sample was then analyzed for the phosphine content. Polymeric phosphine oxide was detected, and the $\text{P]}-\text{P}_\text{C}/\text{Rh}$ was calculated to be 2.1. Cyclooctene was readily displaced from the dimer $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ by polymeric triphenylphosphine in benzene. From Table 8-11, it is seen that most of the $\text{P]}-\text{P}_\text{C}/\text{Rh}$ values are less than three. This suggested that most of the Rh(I) was present as a dimer, while the analogous homogeneous reaction with triphenylphosphine gives monomer, $\text{RhCl}(\text{P}\phi_3)_3$.

A plausible pathway is presented in Scheme IX.

The rhodium complex was first attached to the polymer by replacing one of the cyclooctene ligands on chlorobis-(cyclooctene)rhodium(I) dimer with polymeric phosphine. The other cyclooctene ligand on the dimer (I) was then displaced by the polymeric phosphines which were close to the rhodium metal center to give (II), (III), (IV) or (V). The possibility of obtaining (I), (II), (III), (IV) and (V) in the rhodium complexed copolymer would account for the $\text{P]}-\text{P}_\text{C}/\text{Rh}$ value which is between 1 and 2. As the metal loading increased, the relative amount of available polymeric phosphines decreased, consequently the $\text{P]}-\text{P}_\text{C}/\text{Rh}$ decreased (Figure 14).



Scheme IX.

Samples of series III(IIIA-IIIG) were crushed. The increase of surface area resulted in the increase of polymeric phosphine concentration around the metal center. Consequently, the $P]/P_c/Rh$ value is much higher than the other series. In addition, a low loading of monomeric complexed copolymer $(P]-P\phi_2)_3RhCl(VI)$ was also obtained.

Characterization by Electron Microprobe Analysis

Random beads were selected from batch II, III, IV, V, IIB, IIF, IIIA, IIIF, IIIG, IVA, IVC, IVD, IVF and IVG. The beads were then cut in half under a microscope. Each of the samples was subjected to electron microprobe analysis.

The I_c values (as defined on page 19) for batch II, III, IV and V of phosphinated beads and IIIF, IIIG, IVG were calculated from the spectra as described in part I and they are as follows :

<u>Sample</u>	II	III	IV	V	IIIF	IIIG	IVG
<u>I_c</u>	0.22	0.28	0.41	0.46	0.32	0.33	0.24
<u>Trace Element</u>	P	P	P	P	Rh	Rh	Rh

When the attached catalysts were prepared by equilibrating with $[Rh(COE)_2Cl]_2$, using a deficiency of the complex (e.g. IIB, IIF, IIIA, IIIC, IIID, IVC) the metal was distributed locally in the first few micron of the bead with no metal in the center of the bead, as shown in Figure 15. The percentage of volume containing the metal was calculated and they are as follows :

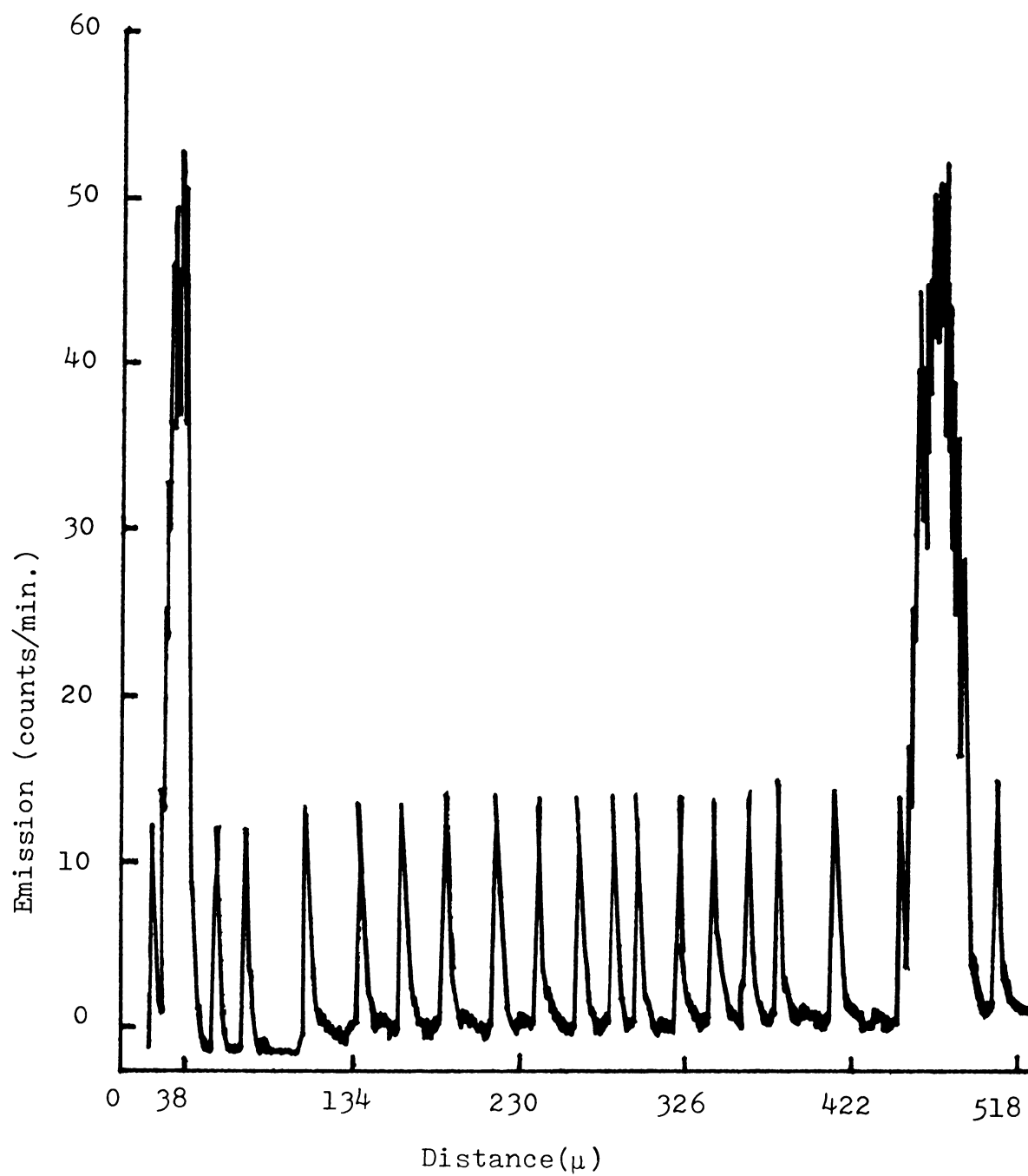


Figure 15. Microprobe spectrum of batch IVC, Rh
L α , 15kV, 0.027 μ A.

<u>Sample</u>	IIB	IIG	IIIA	IVA	IVC	IVD	IVF
<u>V_{Rh}/V_{total}</u>	0.68	0.78	0.28	0.33	0.31	0.44	0.77

An attempt was made to obtain the elemental ratios of rhodium to phosphorus within the shell where rhodium was distributed. This is of interest, because the $P]/P_C/Rh$ have been calculated from ^{31}P NMR analysis.

On the basis of phosphorus electron microprobe spectra of batch III and IV beads, the counts within the rhodium containing shell and the total counts in the whole bead were calculated. The ratios (C_R) were obtained on several bead samples. The phosphorus content of the rhodium containing shell was obtained by multiplying the ratio C_R by the elemental analysis data of the phosphorus content. The results are presented in Table 12.

It is interesting to find that, the electron microprobe analysis and ^{31}P NMR spectroscopy both gave a P/Rh value of about 1.6 on sample IVF. The electron microprobe data clearly show that in the case of high metal loading, the content of phosphorus within the rhodium containing shell is less than twice the content of rhodium. Consequently, the $P]/P_C/Rh$ ratio is smaller than two. In the case of low metal loading, due to the inaccuracy of edge position, it is quite possible to have overcalculated by 50% the content of phosphines within the rhodium containing shell. In spite of this uncertainty, the trend of increased P/Rh ratio as the loading decreases is apparent.

Table 12. The P/Rh ratio calculated from the electron microprobe data.

Sample	ratio ^a (C _R)	meq P/g.beads ^b (calculated)	meq Rh/g.beads (added)	P/Rh ^c	P]-Pc/Rh ^d
IIB ^e	0.844	1.044	0.142	7.4	4.5
IIG ^f	0.901	1.115	0.415	2.7	2.4
IIIA	0.371	0.326	0.046	7.1	3.4
IVA	0.408	0.229	0.039	5.8	
IVC	0.408	0.229	0.070	3.3	1.3
IVD	0.528	0.295	0.108	2.7	1.9
IVF	0.912	0.511	0.311	1.6	1.6

^a see text

^b within the rhodium containing shell

^c calculated from the microprobe data

^d calculated from the ³¹P NMR analysis data

^e treated with 0.09 meq PØ₃/g.beads at 92°C for 12 hours

^f have been treated with 0.1 meq PØ₃ at 92°C for 12 hours

The Effect of Triphenylphosphine on Polymer
Bound Ligand Coordination

Several samples were used in these studies, most were from the $P]-P_c/Rh$ ratio study.

A bead sample, prepared by equilibration of chlorobiscyclooctenerhodium(I) dimer with phosphinated beads, was subjected to ^{31}P NMR analysis, and then treated with a measured quantity of triphenylphosphine. This slurry was heated with occasional shaking for a designated time, followed by washing with toluene at least four times to remove the excess triphenylphosphine. The sample was then subjected to ^{31}P NMR analysis again. As can be seen from Figure 16, the free phosphine peak was decreased after the above treatment. The maximum coordination numbers per rhodium atom, $P]-P_c/Rh$, was calculated as described before. The results are summarized in Table 13.

In another test, 6.01 g. of batch 1 phosphinated beads containing 0.95 m mole phosphine per g. of beads was equilibrated with 1.972 meq of chlorobiscyclooctenerhodium dimer in benzene. The excess dimer complex was removed by washing with benzene, and the beads were vacuum dried and divided into four 15 mm NMR sample tubes. Each sample was swollen with toluene and then subjected to ^{31}P NMR analysis. The $P]-P_c/Rh$ value for the sample was determined by averaging the results of four samples. To one of these samples was added 0.48 meq of purified triphenylphosphine, and the mixture was heated at 90°C for 8½ hours. After

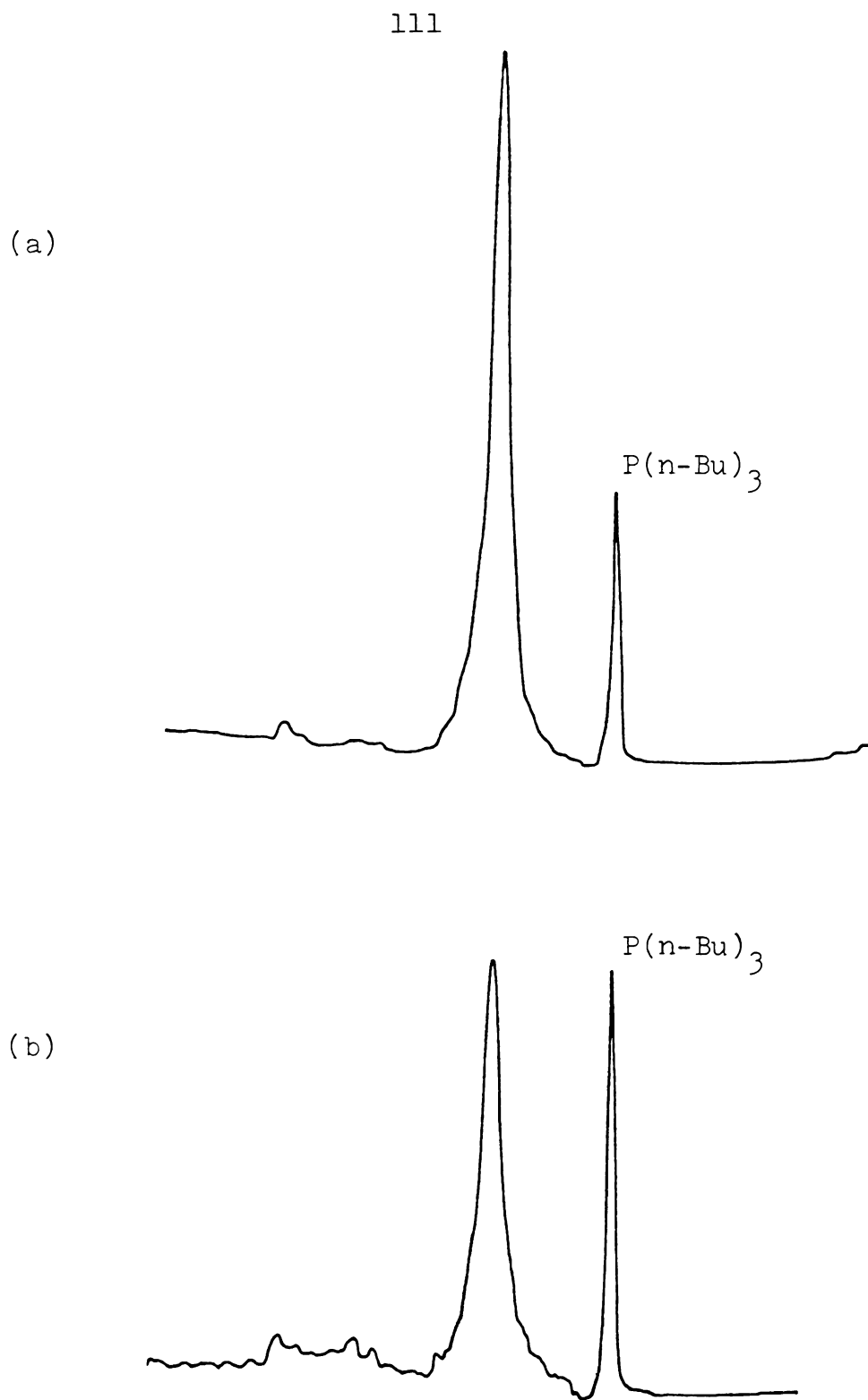


Figure 16. ^{31}P NMR spectra of polystyrylphosphine rhodium complex.

(a) spectrum of sample IID.

(b) above sample after P_2O_3 treatment.



Table 13. The effect of triphenylphosphine on polymer bound ligand coordination.

Sample	meq Rh/ ξ .beads (added)	meq P ϕ_3 /g.beads (added)	Temp. (°C)	Time (hr)	P]-P ϕ_3 /Rh (before)	P]-P ϕ_3 /Rh (after)
VA	0.021	0.17	80	5½	2.3	4.9
IIA	0.083	0.09	92	12	1.7	5.8
IIB	0.142	0.09	92	12	1.6	4.5
IID	0.237	0.09	92	12	1.3	3.7
IIE	0.440	0.09	92	12	1.1	2.2
IIF	0.704 (0.364) [*]	0.08	80	9	2.0	2.2
IIF ^{ab}	0.2896 ^c	Excess (ca. 5)	92	10	2.2	3.1 ^d
IIG	0.4149 ^c	0.10	92	12	0.9	2.6 ^d
IIG ^{ab}	0.3945 ^c	0.20	95	2	2.6	2.9 ^d

^a Orange-red precipitate was found after the treatment.

^b Second treatment. ^c From elemental analysis after treatment with P ϕ_3 .

^d The elemental analysis of rhodium content was used. ^{*} Analysis before the P ϕ_3 treatment.

cooling the slurry to room temperature, the excess triphenylphosphine was washed away before ^{31}P analysis. Another of the four samples was used as a standard reference for comparison. The results are summarized as follows :

<u>Sample</u>	<u>Treatment</u>	<u>$\text{P}] - \text{P}_c / \text{Rh}$</u>
VI-Rh-1	None	2.1
VI-Rh-2 ^a	add 0.48 meq $\text{P}\phi_3$, heat at 90°C for $8\frac{1}{2}$ hours.	2.8
VI-Rh-3	heated at 90°C for 9 hours	2.3
VI-Rh-4 ^b	add hydrogen	2.1

^a The P-31 absorption was barely detectable.

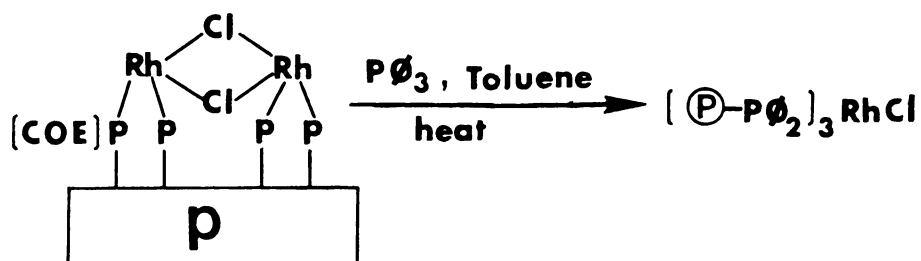
^b No other changes was detected.

It was found that the above four samples had been crushed to a powder during the equilibration with rhodium complex. This may have affected the coordination of polymer-supported triphenylphosphine, therefore another batch of beads was prepared by equilibration of 2.27 g. of phosphinated beads containing 0.94 meq of phosphine per g. of beads with 0.563 m eq of chlorobiscyclooctenerhodium dimer in benzene. After removing the excess dimer complex, these beads were subjected to ^{31}P NMR analysis. The $\text{P}] - \text{P}_c / \text{Rh}$ value was 1.5, and it was found to be unchanged after heating at 90°C for 12 hours. However, the $\text{P}] - \text{P}_c / \text{Rh}$ value was increased to 3.1 by adding 0.036 meq of triphenylphosphine per g. of beads and heating at 90°C for 48 hours.

^{31}P -NMR analysis was determined after removing the excess triphenylphosphine.

As can be seen from Table 13, the $\text{P}] - \text{P}_\text{C} / \text{Rh}$ value was increased to around three after the triphenylphosphine treatment. Interestingly, in the case of low rhodium loading, the final $\text{P}] - \text{P}_\text{C} / \text{Rh}$ value is greater than 3 (for example, $\text{P}] - \text{P}_\text{C} / \text{Rh}$ of IIA was increased from 1.7 to 5.8).

Added triphenylphosphine catalyzed the replacement of the cyclooctene ligand and the cleavage of the chlorine bridges by polymeric phosphines.



This monomer complex, produced by cleavage of the chlorine bridges, then exchanges with nearby polymeric phosphines. In the case of high metal loading, for example sample IIF, the final $\text{P}] - \text{P}_\text{C} / \text{Rh}$ value (2.2) was limited by the available polymeric phosphine within the bead. However, on addition of a large excess of triphenylphosphine, some homogeneous phosphines replaced the polymer-supported triphenylphosphine in the polymer complex and formed an orange-red complex, presumably $[\text{RhCl}(\text{P}\phi_3)_2]_2$, which precipitated on the bottom of the NMR tube. On the basis of elemental analysis of the rhodium content and the amount of complexed polymeric phosphine from ^{31}P -NMR

measurement, the $P]-P_c/Rh$ value of this polymer complex was calculated to be 3.1 (Table 13).

If the beads were crushed during complex equilibration, the $P]-P_c/Rh$ value was a little higher (2.1 for VI-Rh-1 compare to 1.5 for the uncrushed sample). This is not unexpected, since an increase in surface area would make more polymeric phosphine available around the metal centers since the metal concentrates at the surface of the polymer beads. In addition, the $P]-P_c/Rh$ value increased even further on heating although the $P]-P_c/Rh$ value of uncrushed beads was found unchanged after heating at 90°C for 12 hours. Again, this may be ascribed to the increase in polymeric phosphine concentrations around the metal centers.

The above conclusions were supported by an electron microprobe analysis. Random beads were selected from sample IIF's (before and after the triphenylphosphine treatment). As we can see from Figure 17 and Figure 18, before the $P\phi_3$ treatment, electron microprobe spectra of cross-section of a bead sliced in half shows that the metal was distributed mainly in the outer regions (ca. 70 micron from the edge), and no metal was detected near the center (Figure 17). However, after a second treatment with $P\phi_3$, the metal was distributed throughout the bead (Figure 18). The I_c value of the rhodium is comparable to that of phosphorus. Samples from IIG's gave similar electron microprobe spectra.

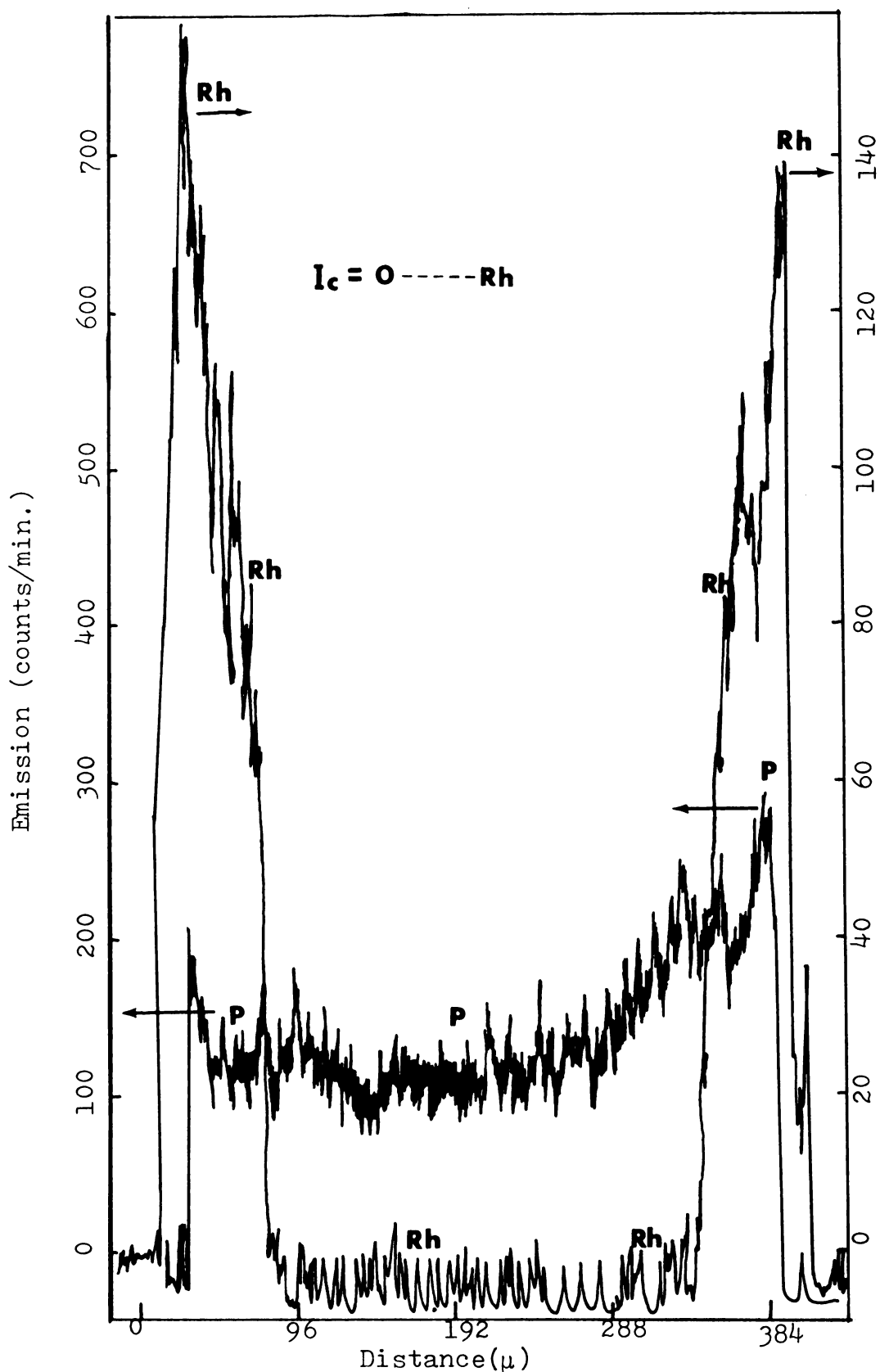


Figure 17. P & Rh microprobe spectra of batch IIF.
(before $P\phi_3$ treatment)

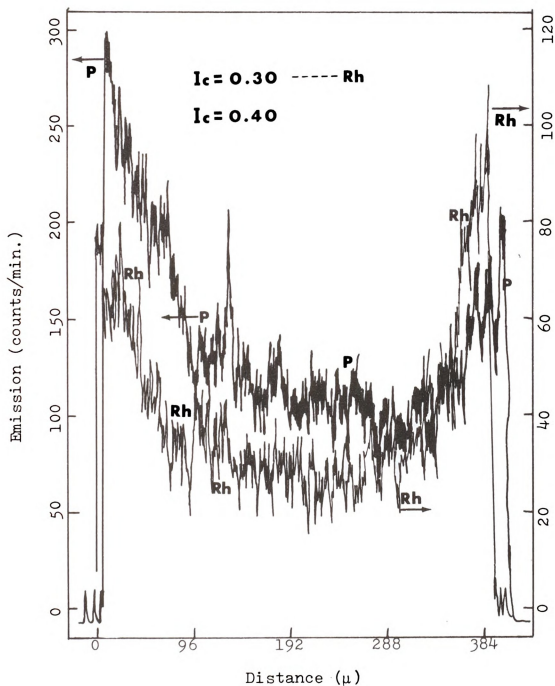


Figure 18. Microprobe spectra of batch IIF(after $P\phi_3$ treatment). P K α , Rh L α , 15 KV, 0.027 μ A.

Photographs of the scanning electron microprobe of sample IIF and IIG are presented in Figure 19-20. As can be seen from Figure 19(a), when sample IIF (before $P\emptyset_3$ treatment) was examined under a microscope, most of the beads were observed to be dimpled. However, after the treatment with $P\emptyset_3$, the dimples were shallower (Figure 19 (b) & 20(a)) and eventually perfect spheres were observed.

The results from electron microprobe analysis and scanning electron microprobe are consistent with the pathway (Scheme IX) we have proposed. The cyclooctene rhodium dimer attaches to the polymer whenever one or two cyclooctene ligands are replaced by polymeric phosphines. The rhodium then tries to find other available polymeric phosphines to replace the cyclooctene ligands. Thus the bead becomes dimpled. In the presence of triphenylphosphine under high temperature, the free homogeneous $P\emptyset_3$ may replace polymeric $P\emptyset_3$ temporarily, thus allowing the metal center to rearrange to a lower energy conformation. Consequently, the beads return to their original spherical shape.

^{31}P Spin-Lattice Relaxation Study of Polymeric Triphenylphosphine

^{31}P spin-lattice relaxation times (T_1) of polymeric triphenylphosphine were obtained by applying a 180° - τ - 90° pulse sequence. The intensity A of peaks obtained from sets of such spectra (for example Figure 21) was used to determine T_1 according to the expression

Figure 19. Photographs of the scanning electron microprobe of sample IIF.

Magnified 25 X

(a) Before the $P\emptyset_3$ treatment, containing
0.364 meq Rh/g.beads, $P]-P_c/Rh = 2.0$

(b) After second treatment with $P\emptyset_3$,
containing 0.2896 meq Rh/g.beads,
 $P]-P_c/Rh = 3.1$

(see Page 112)

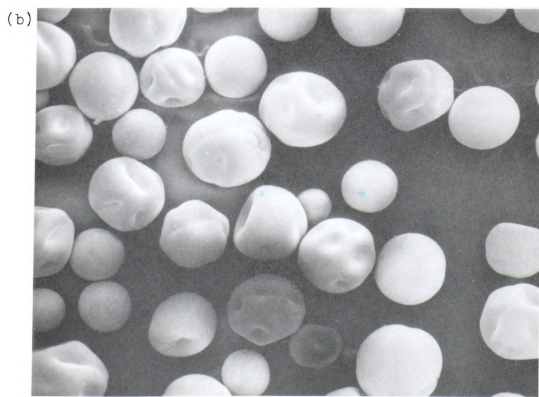
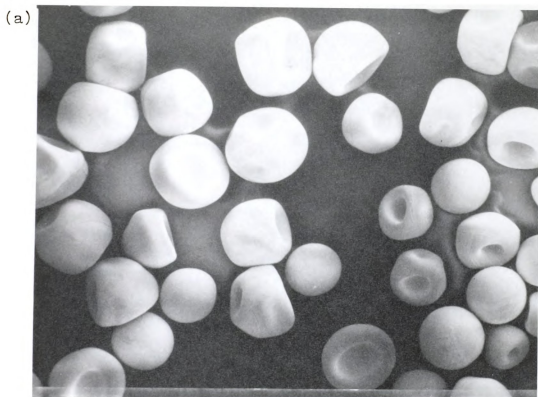


Figure 19.

Figure 20. Photographs of the scanning electron microprobe of sample IIG.

Magnified 25 X

- (a) After first treatment with $P\phi_3$,
 $P]-P_c/Rh = 2.6$
- (b) After second treatment with $P\phi_3$,
 $P]-P_c/Rh = 2.9$

(see also Page 112)

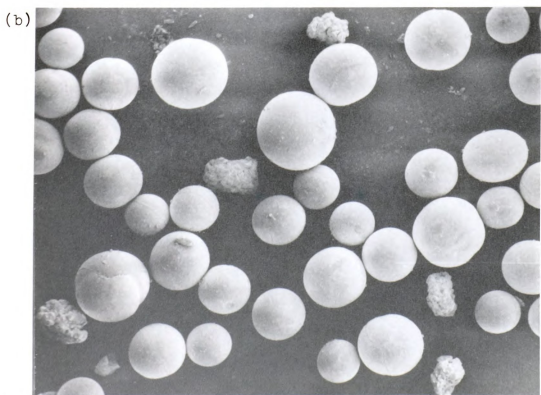
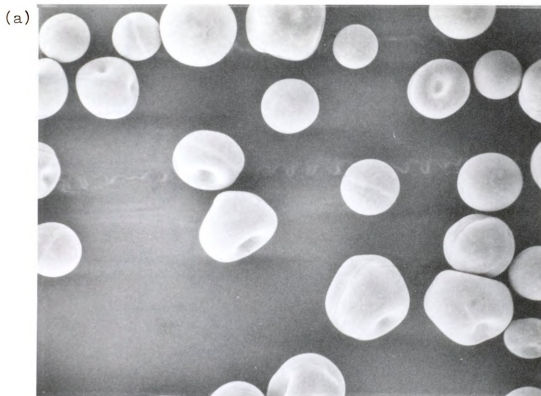


Figure 20.

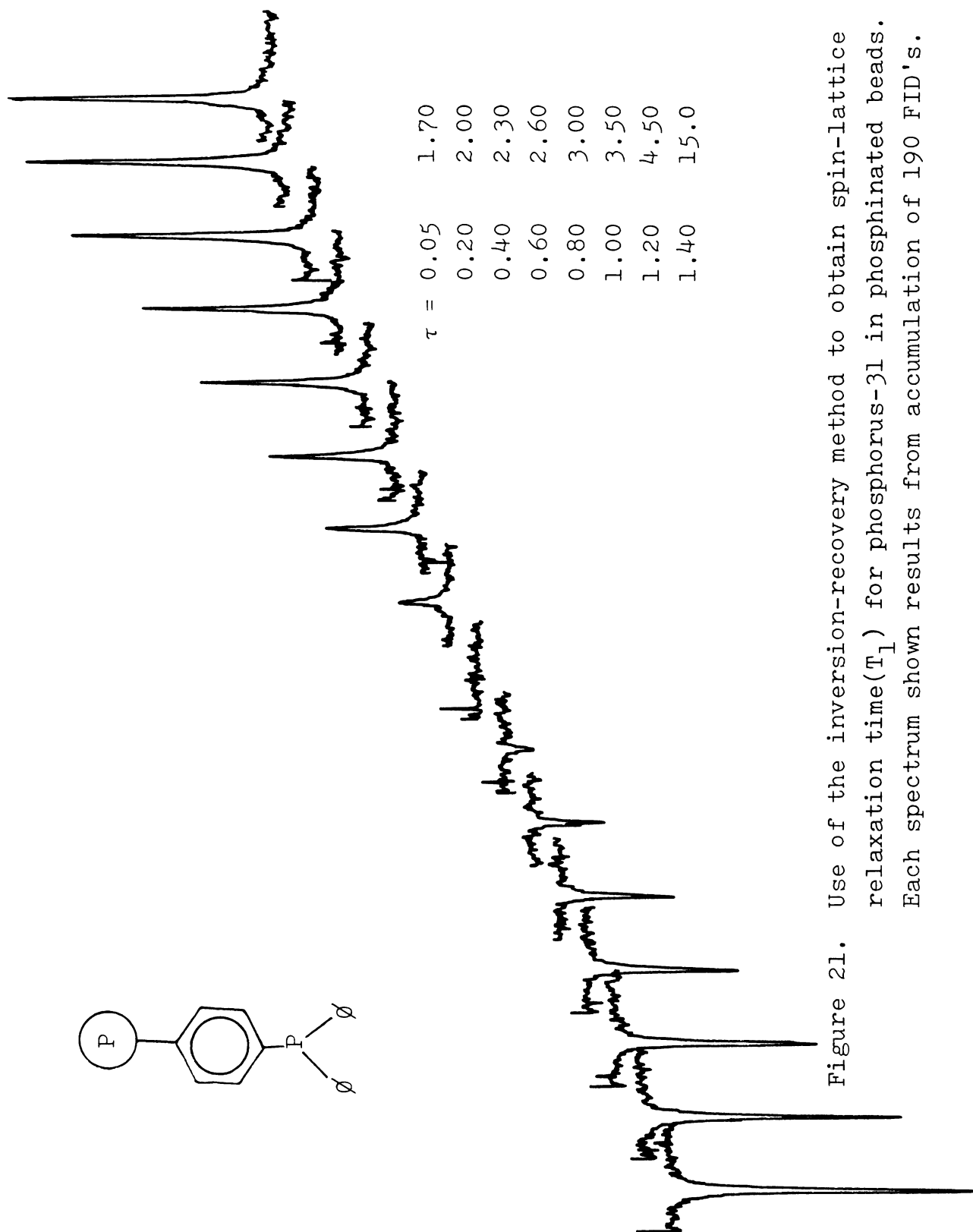


Figure 21. Use of the inversion-recovery method to obtain spin-lattice relaxation time(T_1) for phosphorus-31 in phosphinated beads. Each spectrum shown results from accumulation of 190 FID's.

Table 14. The temperature dependences of the ^{31}P spin-lattice relaxation times(T_1) of polymeric triphenylphosphine in toluene.

Temperature ($^{\circ}\text{K}$)	$1/T \times 10^3$ (deg^{-1})	T_1 (sec.)	$\ln T_1$
377.5	2.649	3.68 ± 0.05	1.303
357	2.801	3.03 ± 0.09	1.109
337.5	2.963	2.74 ± 0.08	1.008
320	3.125	2.29 ± 0.07	0.829
301.5	3.317	1.94 ± 0.02	0.663
286	3.497	1.80 ± 0.07	0.588
275	3.636	1.64 ± 0.07	0.495

$$A = A_{\infty} [1 - 2 \exp (-\tau/T_1)]$$

where A_{∞} is the equilibrium intensity of the spectrum.

The T_1 's were calculated by the least-squares method.

The temperature dependence of the measured phosphorus spin-lattice relaxation times (T_1) of polymeric triphenylphosphine (batch I) swollen with toluene are presented in Table 14 and depicted in Figure 22 as a plot of $\ln T_1$ vs. $1/T$. Figure 22 indicates that within the temperature region studied (2-106°C), the dipole-dipole interactions with the nearest protons provide the dominant relaxation mechanisms. This observation is consistent with the results of J. Jonas et al.⁶³ on the T_1 study of triphenylphosphine within the temperature range of 90-160°C.

Since dipolar interactions provide the main relaxation mechanisms, the reorientational correlation time, τ_c , can be estimated by assuming

$$\frac{1}{T_1} = \frac{6 \hbar^2 \gamma_P^2 \gamma_H^2}{r_{P-H}^6} \tau_c$$

where $\hbar$ is the Planck's constant divided by 2π , γ_P is the gyromagnetic ratio for phosphorus, γ_H is the gyromagnetic ratio for hydrogen, r_{P-H} is the interatomic distance of P and H, and τ_c is the reorientational correlation time in seconds.

If $PC = 1.83\text{\AA}$, $CC = 1.39\text{\AA}$ and $CH = 1.10\text{\AA}$, the calculated r_{P-H} is $2.92\text{\AA}$. On the basis of this interatomic distance of P and H, the reorientational correlation time,



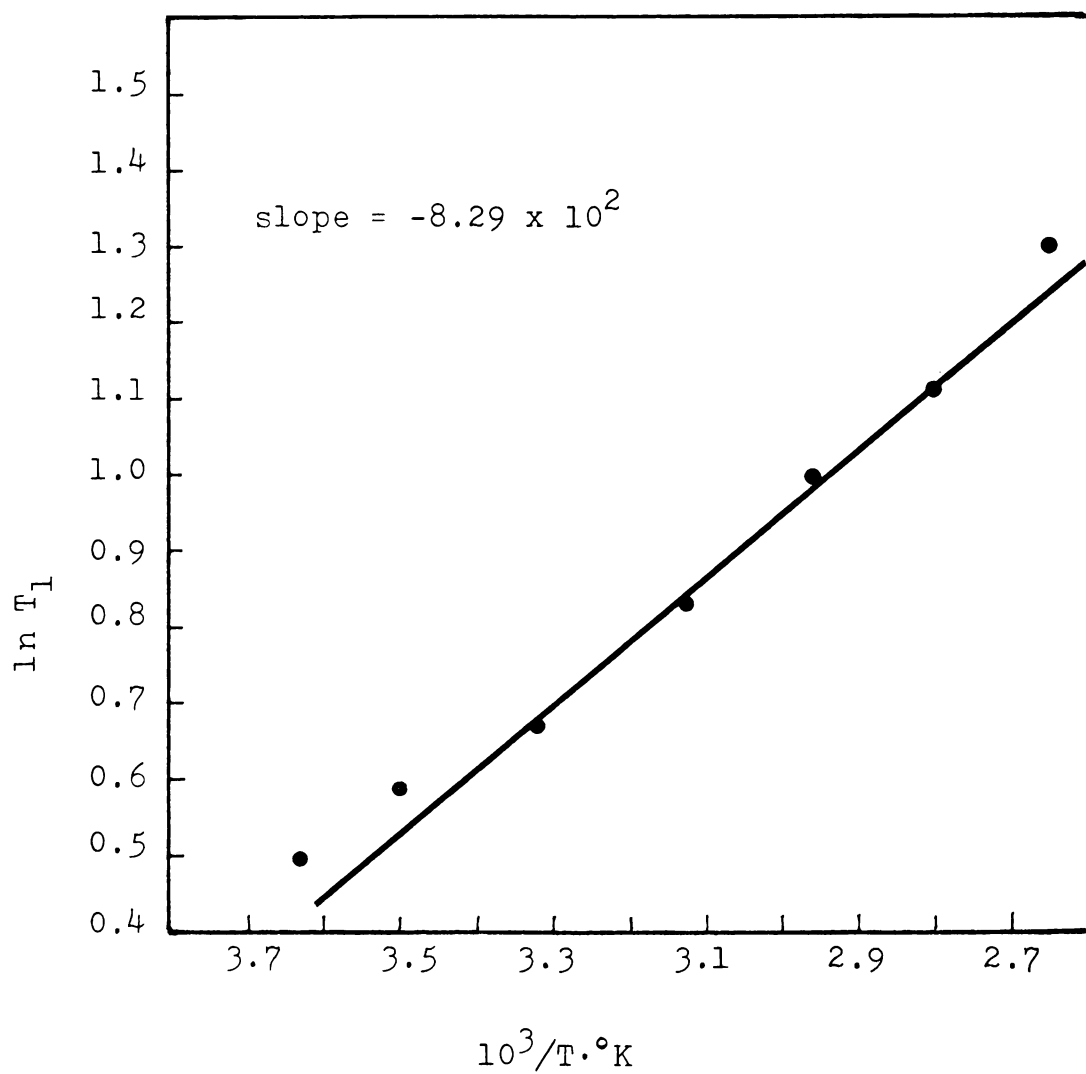


Figure 22. Plot of $\ln T_1$ vs. $1/T$ ($^\circ\text{K}^{-1}$) for polymeric triphenylphosphine swollen with toluene.

τ_c , was calculated to be 5.7×10^{-10} seconds at room temperature. For comparison, the spin-lattice relaxation time (T_1) of a solution of a 1.5 M triphenylphosphine in toluene was measured to be 11 seconds at room temperature. By applying the above bond lengths and equation, the approximate τ_c was calculated to be 10^{-10} seconds. In other words, the mobility of polymeric triphenylphosphine swollen with toluene is only one sixth that of 1.5 M triphenylphosphine in toluene. Jonas et al⁶³ considered both the intramolecular and intermolecular dipolar contributions to the ^{31}P relaxation, and obtained a value of 0.75×10^{-10} seconds for the reorientational correlation time of neat triphenylphosphine.

By assuming $1/T_1$ proportional to τ_c , the activation energy of motion was estimated to be 1.65 Kcal/mole. This is much lower than expected. In single-stranded polyribonucleic acid⁵⁰ an activation enthalpy ΔH of 8.1 Kcal/mole was obtained for the molecular motion of the sugar-phosphate backbone, as deduced from the phosphorus relaxation data. The activation energy for triphenylphosphine was found⁶³ to be 6.2 Kcal/mole from the ^1H T_1 plot. In contrast, by assuming $1/T_1$ proportional to τ_c , the activation energy we estimate from their ^{31}P data is 2.3 Kcal/mole, which is much closer to our results. This seems to tell us that the motion hindrance of polymeric triphenylphosphine is comparable to that of neat triphenylphosphine.



A comparison of the temperature dependence of T_1 of a triphenylphosphine solution with this work would probably give us more information, however, no extensive work was tried.

An attempt was made to investigate the influence of solvent on the motion of polymeric triphenylphosphine. This would be of interest, since S.L. Regen⁵² found that the degree of swelling of the polymer supports is an important factor in determining the mobility of the attached spin label (examined by electron paramagnetic resonance spectroscopy).

As we can see from Table 15, in sharp contrast to Regen's results, the rotational correlation times (τ_c) of polymeric triphenylphosphine calculated from ^{31}P spin-lattice relaxation times (T_1) are not sensitive to the swelling properties of the solvents. Interestingly, diethyl ether, which is a poor swelling solvent, had about the same effect on the motion as toluene which swelled the polymer lattice appreciably.

No absorption was observed on the ^{31}P FT-NMR of polymeric triphenylphosphine swollen in hexane at room temperature. At a higher temperature (55°C) a sharp absorption was obtained.

Table 15. The ^{31}P spin-lattice relaxation times(T_1) as a function of q (degree of swelling values).

Sample	Solvent	T_1 (sec.)	$\tau_c(10^{-10}\text{sec.})^a$	q^b
Batch 1 ^c	Toluene	1.94±0.02	5.7	2.95±0.08
	Et_2O	2.17±0.03	5.1	1.35±0.04
		2.18±0.03	5.1	
B ^d	Acetone	2.05±0.03	5.4	1.68±0.02
		2.01±0.02	5.5	
	Toluene	2.09±0.03	5.3	
Batch 4 ^c	Cumene	1.79±0.04	6.2	1.98±0.07
	Toluene	1.90±0.05	5.8	
Batch S ^e	Toluene	1.72±0.07	6.4	
	THF	1.71±0.07	6.5	3.05±0.08
	Benzene	1.76±0.07	6.3	3.06±0.04
Oxidized ^f S	Toluene	1.80±0.05	6.2	
		1.36±0.02 (P=0)		
1.5M $\text{P}\phi_3$	Toluene	11.29±0.49	1.0	
0.4M $\text{P}(\text{n-Bu})_3$	Toluene	9.84±0.85		

^a Calculated by assuming $(T_1)^{-1} = 6\pi^2 \gamma_H^2 \gamma_P^2 \tau_c / (r_{\text{P-H}})^6$.

^b See page 146 Table 17.

^c Phosphinated beads for multiple binding studies.

^d 12% phosphinated beads, half of the phosphine complexed to rhodium. ($[\text{RhCl}(\text{COE})_2]_2$) Equilibration.

^e 14% phosphinated beads, ca. 5% phosphine was oxidized.

^f Swelled in toluene and exposed to air for days.

Phosphine Exchange in Carbonylchlorobis(triphenylphosphine)rhodium(I), $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$

The phosphorus-31 spectrum of trans-carbonylchlorobis(triphenylphosphine)rhodium(I) consists of a doublet due to rhodium-phosphorus coupling^{39b,61,64}. The chemical shift was reported to be -29.1 ppm^{39b} in chloroform solution vs. 85% H_3PO_4 ; -28.9 ppm⁶¹ in CH_2Cl_2 vs. 85% H_3PO_4 and the coupling constant $J_{\text{Rh-P}}$ was reported to be -124 Hz or 129.4 Hz respectively.

Since it has been found that the phosphine exchange in $\text{RhCl}(\text{P}\phi_3)_3$ is a dissociative mechanism^{39a}, we decided to carry out a ligand exchange study of $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ as a model for the analogous polymer complex.

The ^{31}P spectrum of a chloroform solution $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ in a 15 mm NMR tube showed a chemical shift of -34.6 ppm vs. free triphenylphosphine (or -28.9 ppm vs 85% H_3PO_4) and a coupling constant of 129.4 Hz. Three samples of different complex to phosphine ratios were used in the temperature studies. Approximate methods⁶⁵ were used to evaluate the rate constants.

As we can see from Table 16, the ligand exchange is very fast and only one broad peak was observed at temperatures as low as -44°C. The rate data are presented in the form of an Arrhenius plot in Figure 23 and may be described by the equation

$$\text{rate}(T) = 10^{6.62} e^{-3600/RT}$$

The calculated activation parameters are :

$$E_a = 3.6 \text{ Kcal/mole}, \Delta G^\ddagger = 12.0 \text{ Kcal/mole},$$

$$\Delta H_{298}^\ddagger = 2.4 \text{ Kcal/mole}, \Delta S_{298}^\ddagger = -32.2/\text{mole}\cdot\text{deg}$$

A plot of $\ln k$ vs. $\ln [P\phi_3]$ gave a straight line with 0.23 as the slope. In other words, the exchange rate is proportional to the concentration of triphenylphosphine to a power of 0.23.

Table 16. The temperature dependence of ^{31}P -NMR data of 0.05M $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ and 0.2M $\text{P}\phi_3$ in CHCl_3 . (complex/phosphine = 1/4)

Temperature		half-width(Hz)	$k(\text{sec}^{-1}) \times 10^{-4}$
$^{\circ}\text{C}$	$^{\circ}\text{K}$		
61	334	75.68	2.69
28	301	96.44	1.79
10	283	135.50	1.10
0	273	150.79	0.96
-10	263	193.37	0.70
-26	247	278.28	0.46
-34	239	380.14	0.32
-44	229	436.29	0.28

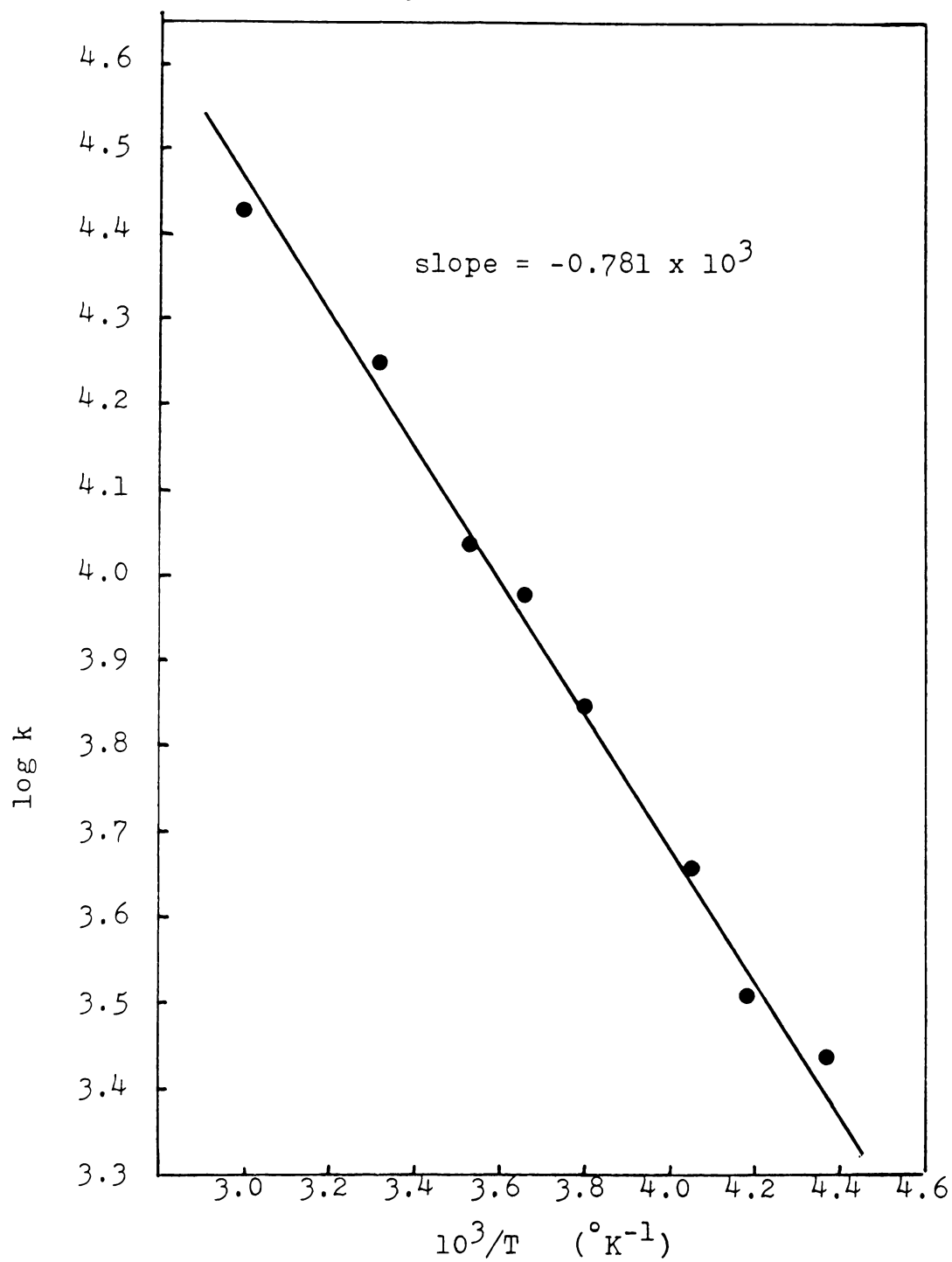


Figure 23. Plot of $\log k$ versus $10^3/T$ ($^{\circ}\text{K}$).

Phosphine Exchange in Polymer-supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$

The temperature dependence of ^{31}P NMR spectra of polymer-supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ (RhV_1 - RhV_3) are presented in Figure 24-26. These spectra indicate that an exchange phenomena is associated with this system, and that the exchange rate increases with the rhodium to phosphine ratio.

From previously study, it has been demonstrated that the ^{31}P NMR spectrum of rhodium complexes of polymer-supported triphenylphosphine ligands is too broad to be observed. However, polymer-supported free phosphine may exchange with rhodium complexed monomeric phosphine, $(\text{P}] - \text{P}\phi_2)\text{RhCl}(\text{CO})(\text{P}\phi_3)$. In an effort to prove this, chlorodicarbonylrhodium(I) dimer was used to prepare the polymer-supported complex (RhV_4). The temperature dependence of ^{31}P NMR spectra of this polymer complex is presented in Figure 27. As can be seen from Figure 27(a)-(c), exchange did not occur or it is too slow to be detected by this method. Triphenylphosphine (0.037 meq per g of beads) was added to RhV_4 under argon and this slurry was heated at 90°C for 6 hours with occasional shaking. After washing away the triphenylphosphine with toluene, the ^{31}P NMR was measured at room temperature and 94°C . Figure 27(d)&(e) clearly show that the ligands exchange. This result supports the belief that free polymer-supported triphenylphosphine exchanges with

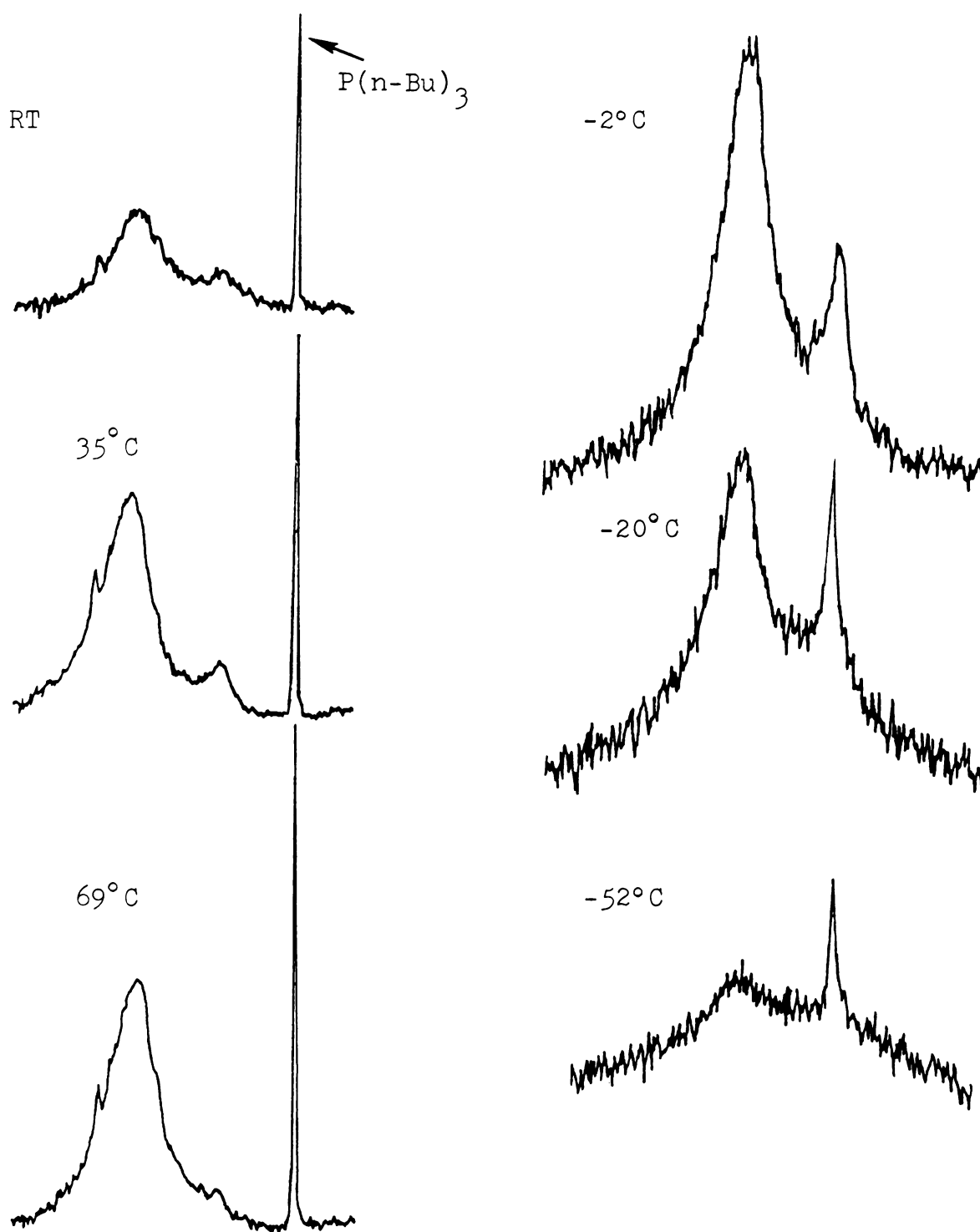


Figure 24. Variable temperature Phosphorus-31 NMR spectra of polymer-supported $RhCl(CO)(P\phi_3)_2$ --Sample RhV₁

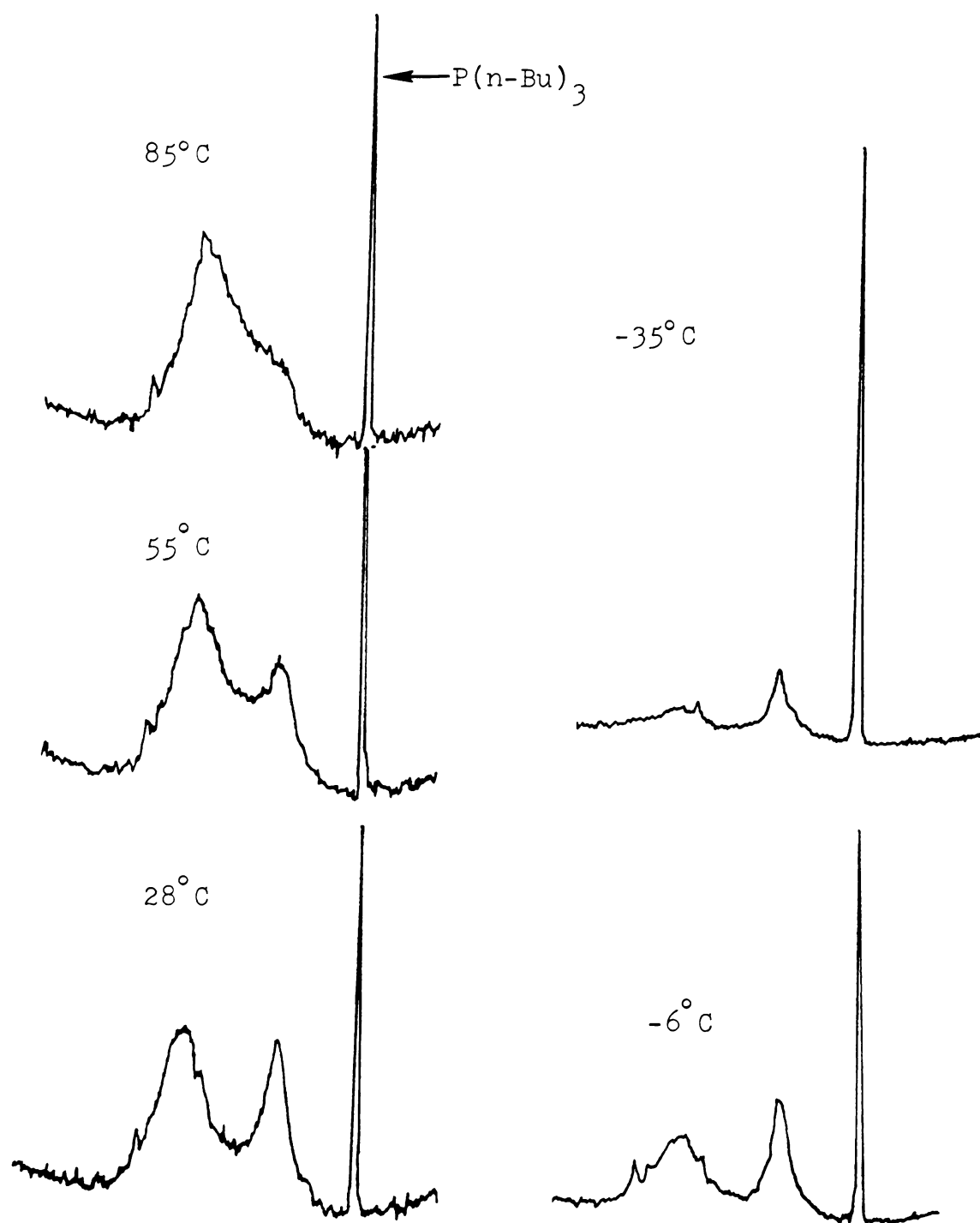


Figure 25. Variable temperature Phosphorus-31 NMR spectra of polymer-supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ --Sample RhV_2 .

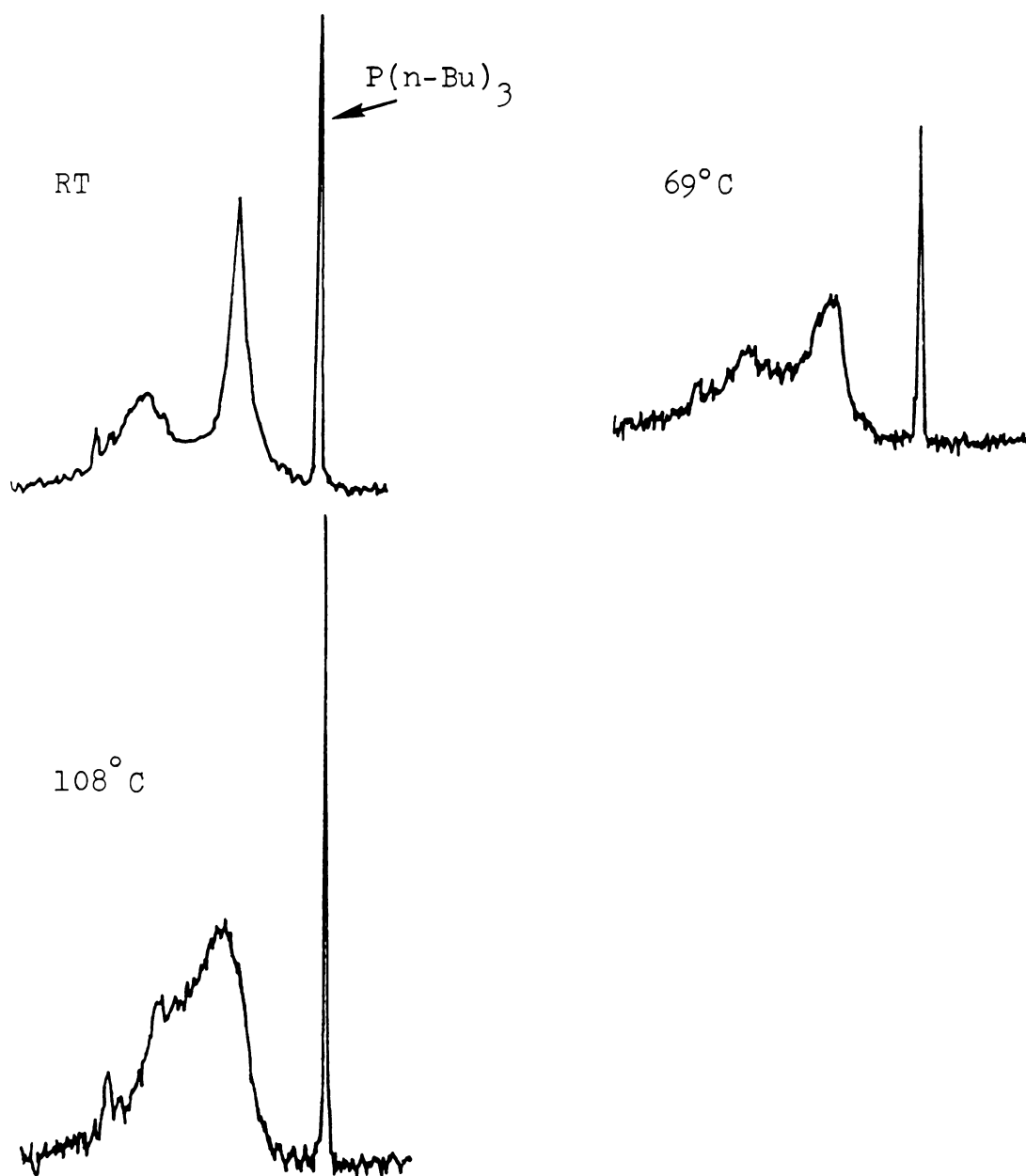


Figure 26. Variable temperature phosphorus-31 NMR spectra of polymer-supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ -- Sample RhV_3 .



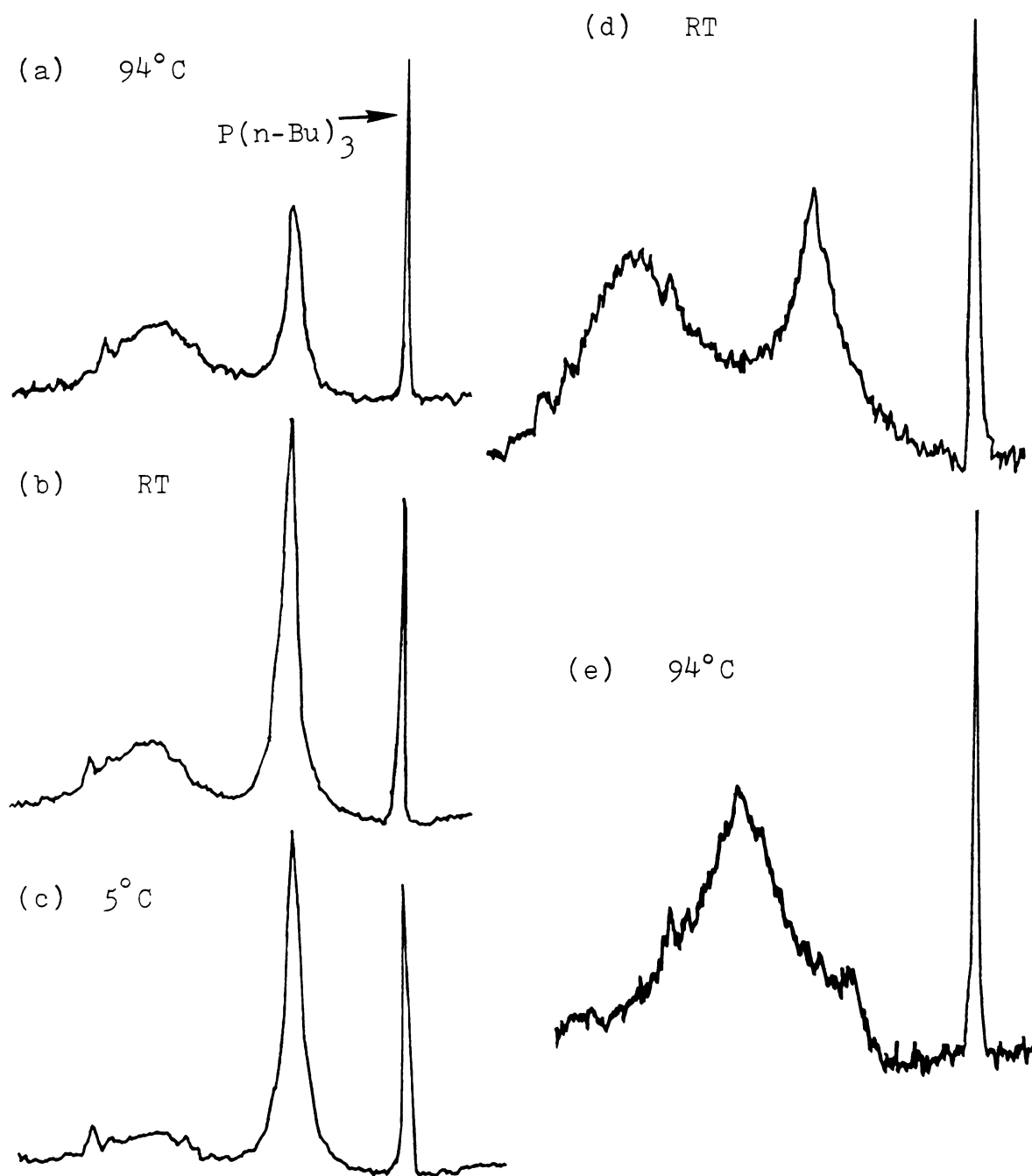


Figure 27. Variable temperature ^{31}P NMR spectra of polymer-supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ --Sample RhV_4 .
 a,b,c-- before the $\text{P}\phi_3$ treatment
 d,e-- after the $\text{P}\phi_3$ treatment

coordinated monomeric phosphine. In order to obtain additional information about this reaction, another sample, RhV₅, was also prepared by the chlorine bridge splitting reaction of $[\text{RhCl}(\text{CO})_2]_2$ with phosphinated beads in benzene. After unreacted complex was removed, the copolymer was dried and then divided into two parts (RhV₅-1 and RhV₅-2) before swelling with toluene. RhV₅-1 was retained as a reference sample. Triphenylphosphine (ca. 0.012 meq per g. beads) was added to RhV₅-2 and this mixture was heated at 90°C for 5 hours. After removing excess triphenylphosphine, the ^{31}P NMR spectra at room temperature and at 94°C were measured. RhV₅-1 was also heated at 90°C for 6½ hours and a comparison of ^{31}P NMR spectra at room temperature and 93°C is given in Figure 28. About 0.1 meq of triphenylphosphine per g. of beads was again added to RhV₅-2 and this slurry was heated at 90°C for 24 hours. The triphenylphosphine was again removed and variable temperature ^{31}P NMR spectra were measured. The results are presented in Figure 29.

Both RhV₅-1 and RhV₅-2 were then subjected to electron microprobe analysis of phosphorus and rhodium. The results are summarized in Figures 30 and 31. As can be seen from Figure 30, the rhodium in sample RhV₅-1 was distributed only in the outer regions (ca. 150 μ from the edge), and no metal was detected near the center. However, after the second $\text{P}\phi_3$ treatment the metal was distributed throughout

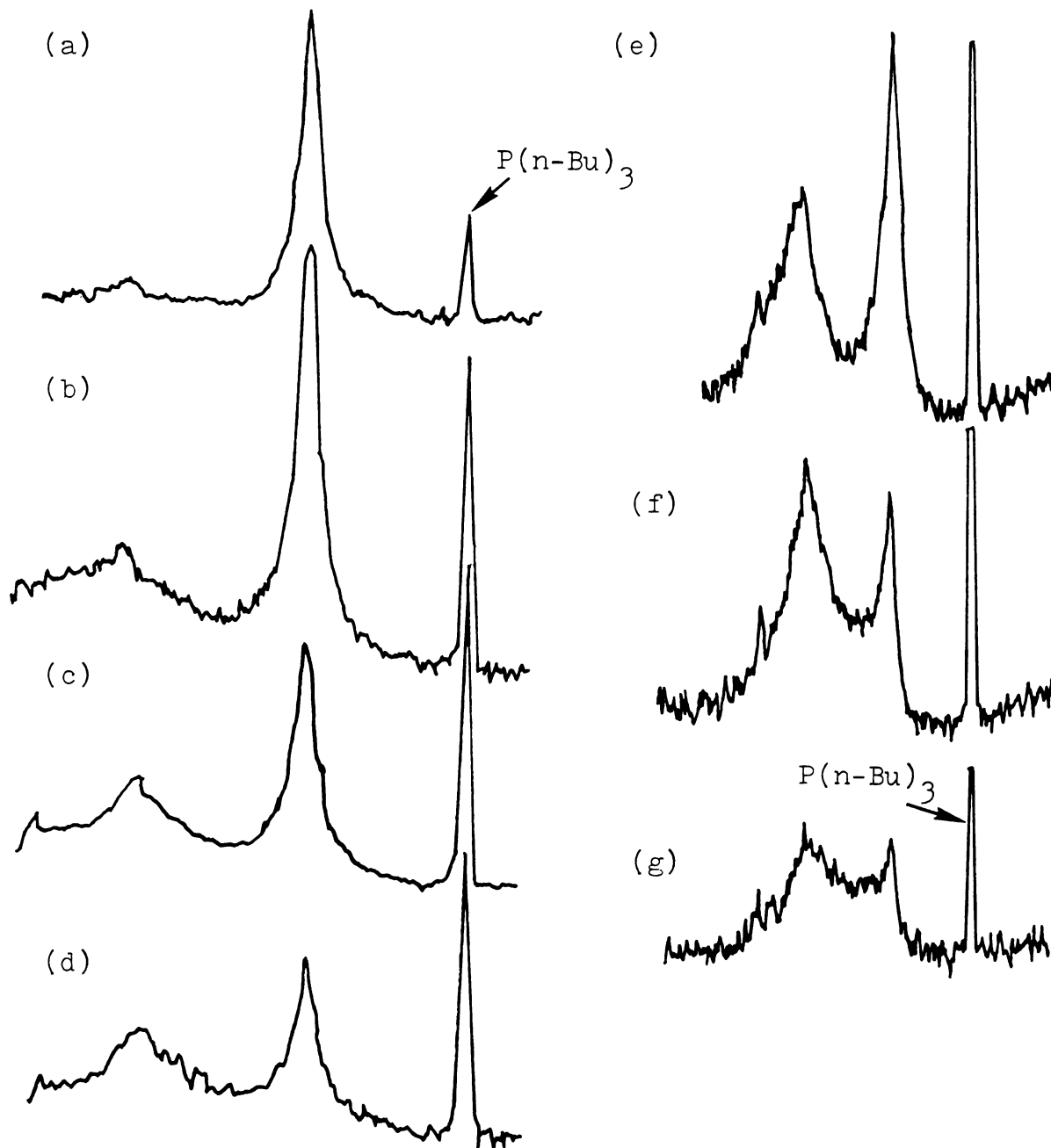


Figure 28. Variable temperature phosphorus- 31 NMR spectra of polymer supported $\text{RhCl}(\text{CO})(\text{P}(\text{O})_3)_2$ --Sample RhV_5

(a) phosphinated beads before metalation, at RT
 (b) RhV_5 -1 at RT
 (c) RhV_5 -1 at 93°C (after heating at 90° for $6\frac{1}{2}$ hrs)
 (d) RhV_5 -2 at 93°C (after treating with 0.012 meq of triphenylphosphine at 90°C for 5 hrs)
 (e) RhV_5 -2 at 33°C (d sample heat 24 hrs, 90°C)
 (f) RhV_5 -1 at 92°C (c sample heat 24 hrs, 90°C)
 (g) RhV_5 -2 at 92°C (e sample)

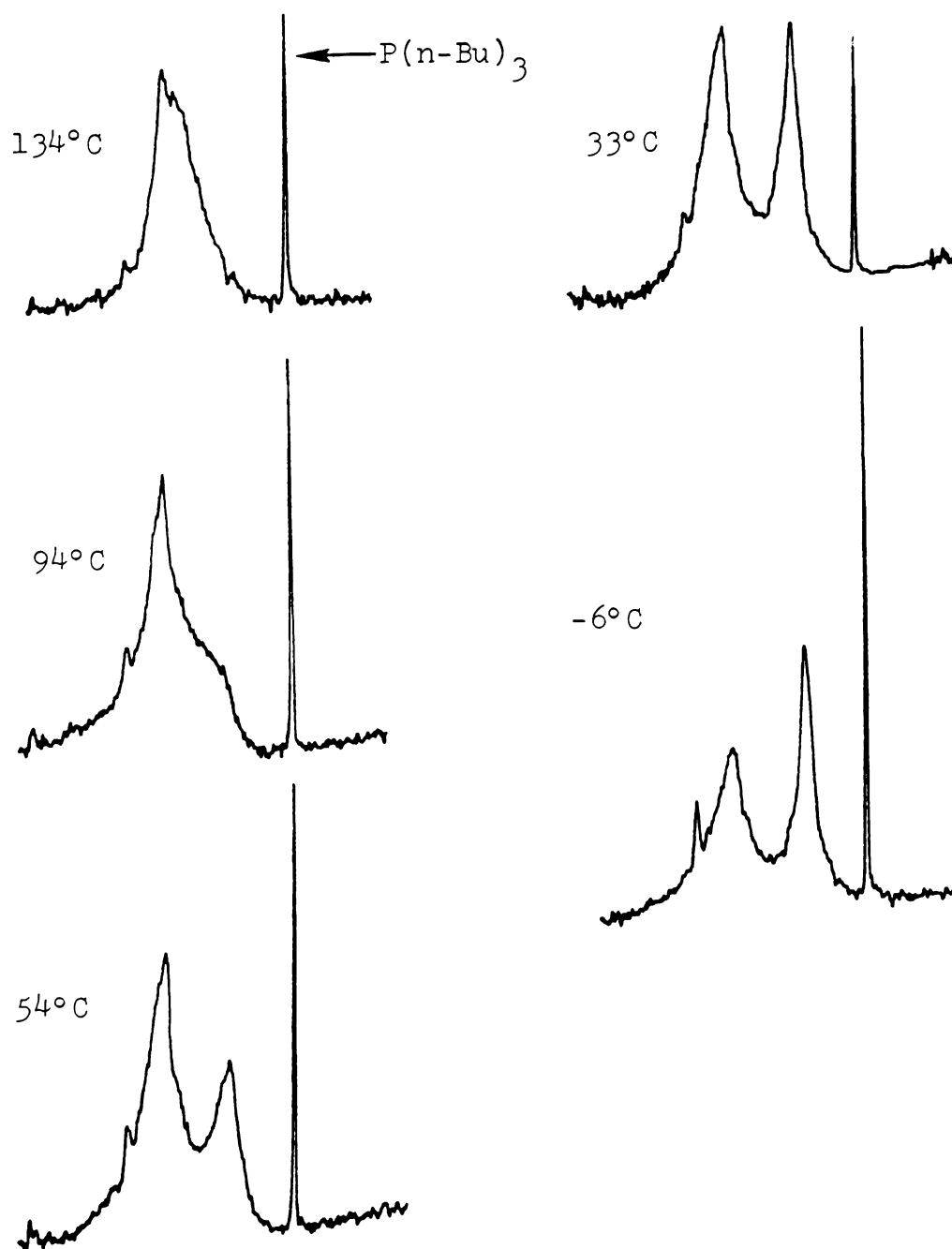


Figure 29. Variable temperature ^{31}P -NMR spectra of polymer-supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ -- $\text{RhV}_5\text{-2}$ (after treating 0.1 meq of $\text{P}\phi_3$ per g. beads at 90°C for 24 hours).

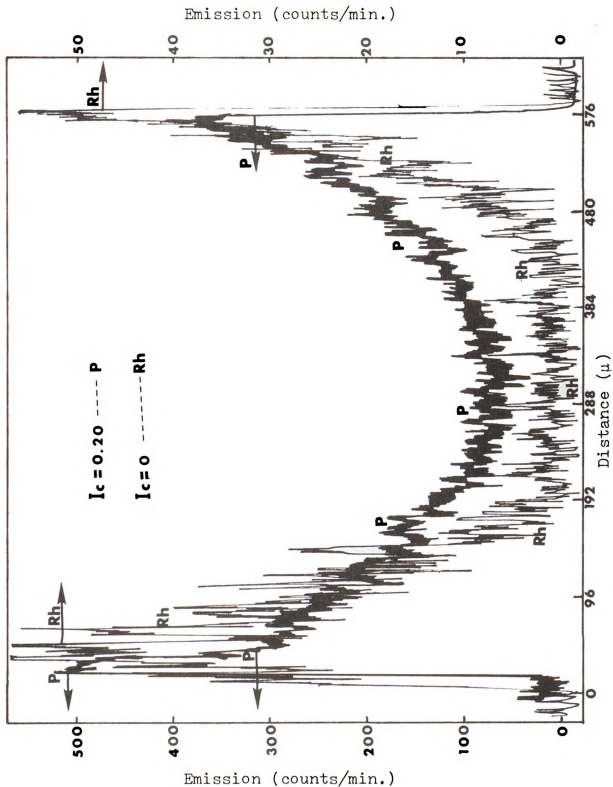


Figure 30. P & Rh eleclectron microprobe spectra of RhV₅-1



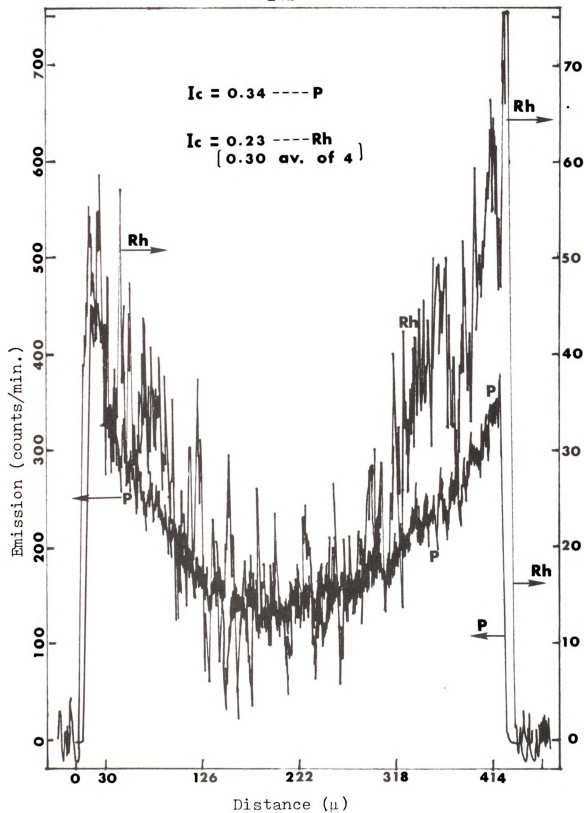


Figure 31. P & Rh electron microprobe spectra of RhV₅₋₂, after second treatment with P₂O₃.



the bead, as shown in Figure 31. Figure 31 also shows that the I_c value of the rhodium is comparable to that of the phosphorus. The rhodium microprobe spectra of RhV_1 gave an I_c value of 0.40.

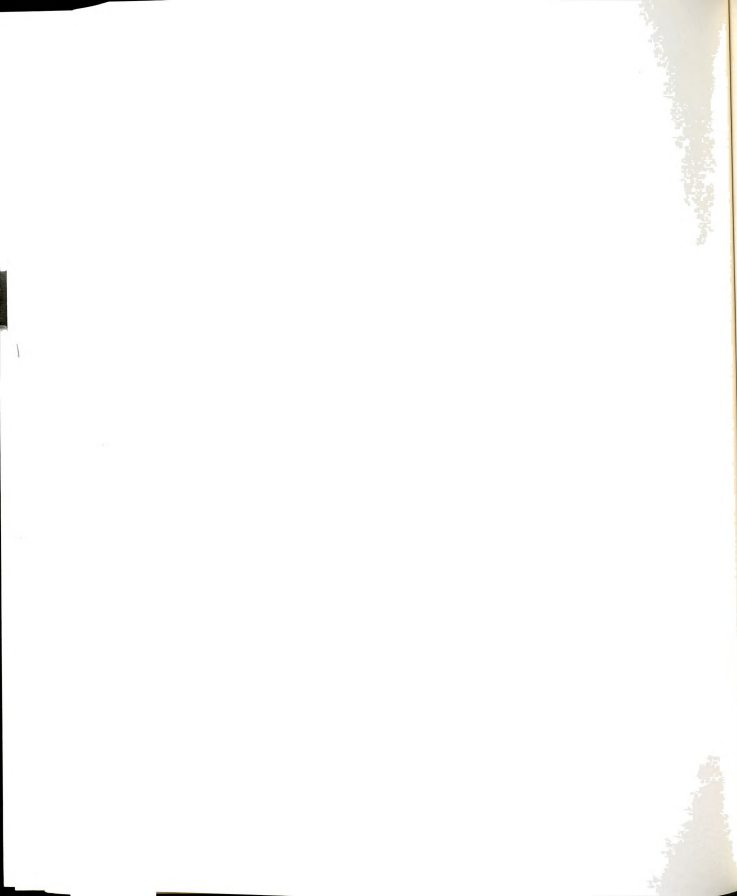
In the case of RhV_5 -1 the only phosphine source is polymer-supported triphenylphosphine. However, Figure 28 indicates that the exchange is fast enough to be detected by ^{31}P -NMR in RhV_5 -1. Therefore, this is some question about the proposal that polymer-supported free phosphine exchanges with complexed monomeric phosphine. Also, the $P]-P_c/Rh$ value, which was estimated from the decrease of free polymeric phosphine, is 1.85 for RhV_2 , 1.95 for RhV_3 , 2.3 for RhV_4 , and 2.2 for RhV_5 . These $P]-P_c/Rh$ values revealed that most of the catalyst is present as $(P]-P\phi_2)_2RhCl(CO)$.

In the case of RhV_1 , RhV_2 and RhV_3 , samples prepared by ligand exchange reactions of $RhCl(CO)(P\phi_3)_2$ with phosphinated beads, the peak area ratio (I_M) of the free polymer-supported phosphine and the complexed phosphine to the external reference sample (tri-n-butylphosphine) is about the same as the peak area ratio (I_p) of polystyrylphosphine (prior to metalation) to the external reference sample. In the case of RhV_4 and RhV_5 , samples prepared by the reaction of the phosphinated beads with $[RhCl(CO)_2]_2$ in benzene have an I_M much smaller than I_p , and the value of I_M increased after the $P\phi_3$ treatment. In other words,

the relative peak area of the low field resonance increased after treatment with triphenylphosphine.

The above experimental results support the conclusion that the polymeric triphenylphosphines react with $\text{RhCl}(\text{CO})(\text{P}\emptyset_3)_2$ or $[\text{RhCl}(\text{CO})_2]_2$ to form $(\text{P})-\text{P}\emptyset_2)_2\text{RhCl}(\text{CO})$ by ligand exchange and chlorine bridge splitting respectively. The complexed polymeric phosphine then exchanges with the free polymeric phosphine. However, in the case of $[\text{RhCl}(\text{CO})_2]_2$ equilibration, the rhodium was distributed only in the outer region of the bead (Figure 30) due to the ease of ligand substitution of CO by $\text{P}\emptyset_3$. The local crosslinking is dramatically increased. Thus, a very broad resonance for complexed phosphine was observed. Most of the free polymer-supported phosphine detectable by ^{31}P NMR is in the center part of the bead. Consequently, the exchange rate is extremely limited by the mobility of free polymeric phosphine in the bead center. Since added $\text{P}\emptyset_3$ catalyzed redistribution of the metal throughout the whole bead (Figure 31), polymer-supported free phosphines must exist around the metal complexes and exchange with them. The increased relative area peak of the very low-field signal resonance might be due to increased mobility resulting from a reduction of local crosslinking.

The coupling constant $J_{\text{Rh-P}}$ in $\text{RhCl}(\text{CO})(\text{P}\emptyset_3)_2$ was reported to be -124 Hz. In $\text{RhCl}(\text{P}\emptyset_3)_3$, the coupling constants are $J_{\text{P}_1-\text{Rh}} = -192$ Hz, $J_{\text{P}_2-\text{Rh}} = -146$ Hz, where P_1



is the phosphine trans to chlorine. The strong interaction between phosphines and rhodium in $\text{RhCl}(\text{P}\phi_3)_3$ may be the cause of the disappearance of the complexed polystyryl-phosphines ^{31}P resonance.

As we can see from Figure 24-26, ligand exchange in sample RhV_3 occurs more slowly than in sample RhV_1 . The coalescence temperatures are 70° for RhV_1 , 85° for RhV_2 and 110° for RhV_3 . A homogeneous system shows that the exchange is associative and the rate proportional to the concentration of triphenylphosphine to 0.23 power. The difference of the exchange rate between RhV_1 and RhV_3 , which have the same phosphine concentration but different rhodium loading, may be ascribed to this rate relationship.

The Swelling Values--q

The degree of swelling values for phosphinated beads (1.8% crosslinked) were obtained by measuring the swelled volume and dry volume of the beads in a graduated cylinder. The swelling value, q , is defined as the relative increase in volume of beads on adding solvent ($q = V(\text{swelled})/V(\text{dry})$). Some q values for 32 to 35 mesh phosphinated beads with 1.8% crosslinked are presented in Table 17. Some q values which were measured by E.M.Sweet, for unfunctionalized beads are also presented in this table for comparison. The smaller q values of the functionalized beads may be ascribed to the increase of crosslinking during functionalization.

Table 17. The degree of swelling values-q.

Solvent	q^a (phosphinated beads)	q^a (unfunctionalized) ^b
Benzene	3.05±0.08	3.90±0.20
THF	3.06±0.04	3.65±0.12
Toluene	2.95±0.08	3.45±0.18
Dichloromethane	3.27±0.13	
Cumene	1.98±0.07	
Ethylacetate	1.98±0.05	
Acetone	1.68±0.02	
Diethylether	1.35±0.04	2.05±0.11
Nitrobenzene ^c	2.59±0.08	2.35±0.13
Cyclohexane	1.00	1.95±0.10

^a $q = V(\text{swelled})/V(\text{dry})$.

^b Data of E.M. Sweet.

^c Beads float.

III. EXPERIMENTAL

Materials

Solvents such as cyclohexane, benzene, toluene and xylene were reagent grade and were distilled under nitrogen from sodium or potassium benzophenone ketyl. Solvents for measuring the degree of swelling values were used as obtained, except for nitrobenzene. Acetone was dried over anhydrous CaSO_4 and distilled under argon. Dichloromethane was distilled from CaSO_4 and stored in the dark. Chloroform was washed with water to remove ethanol. After drying over CaCl_2 it was distilled and stored under argon in the dark. Ethylacetate was purified by washing with aqueous 5% Na_2CO_3 , then with saturated CaCl_2 and drying over CaSO_4 . The solvent was then further dried with molecular sieve before distillation. Nitrobenzene was purified by crystallization from absolute ethanol (by refrigeration). The ethanol was then removed at reduced pressure and the nitrobenzene was stored in the dark under inert atmosphere. It is very hygroscopic.

Argon was purified by passing through BASF-BTS catalyst heated to 140°C and $4\text{\AA}$ molecular sieves.

Biscyclooctenerhodium(I) chloride dimer and chlorotris(triphenylphosphine)rhodium(I) were prepared as

described in part I. Bis(triphenylphosphine)carbonylrhodium(I)chloride was prepared by L.C. Kroll.

The other reagents were obtained and treated as described in part I.

Instrumentation

(I) DA-60 NMR spectrometer

A modified Varian DA-60 NMR spectrometer was used to do all the phosphorus-31 studies except the studies of the ^{31}P spin-lattice relaxation times (T_1), for which a Bruker HFX-90 NMR spectrometer was used. The spectrometer consists of a modified specilities MP-1000 spectrometer, a Nicolet 1083 computer with 12K of memory, and a home-built interface⁶⁶. The configuration is shown in the form of a block diagram in Figure 32.

The frequency source of the RF unit is 56.44 MHz. The resonance frequency of the sample can be obtained by changing the synthesizer frequency, instead of changing the magnetic field. By utilizing the mixing network and tunable probe, this spectrometer can be used to observe NMR signals in the range of about 2 to 35 MHz.

Before each experiment, the probe and image filter were well tuned to the phosphorus-31 resonance frequency, which is 24.289 MHz at this field. The homogeneity was also well adjusted, so that a 1.5 M solution of triphenylphosphine in toluene will give 29.3 Hz (or smaller) of half width. Exponential multiplication yielding 3.89 Hz

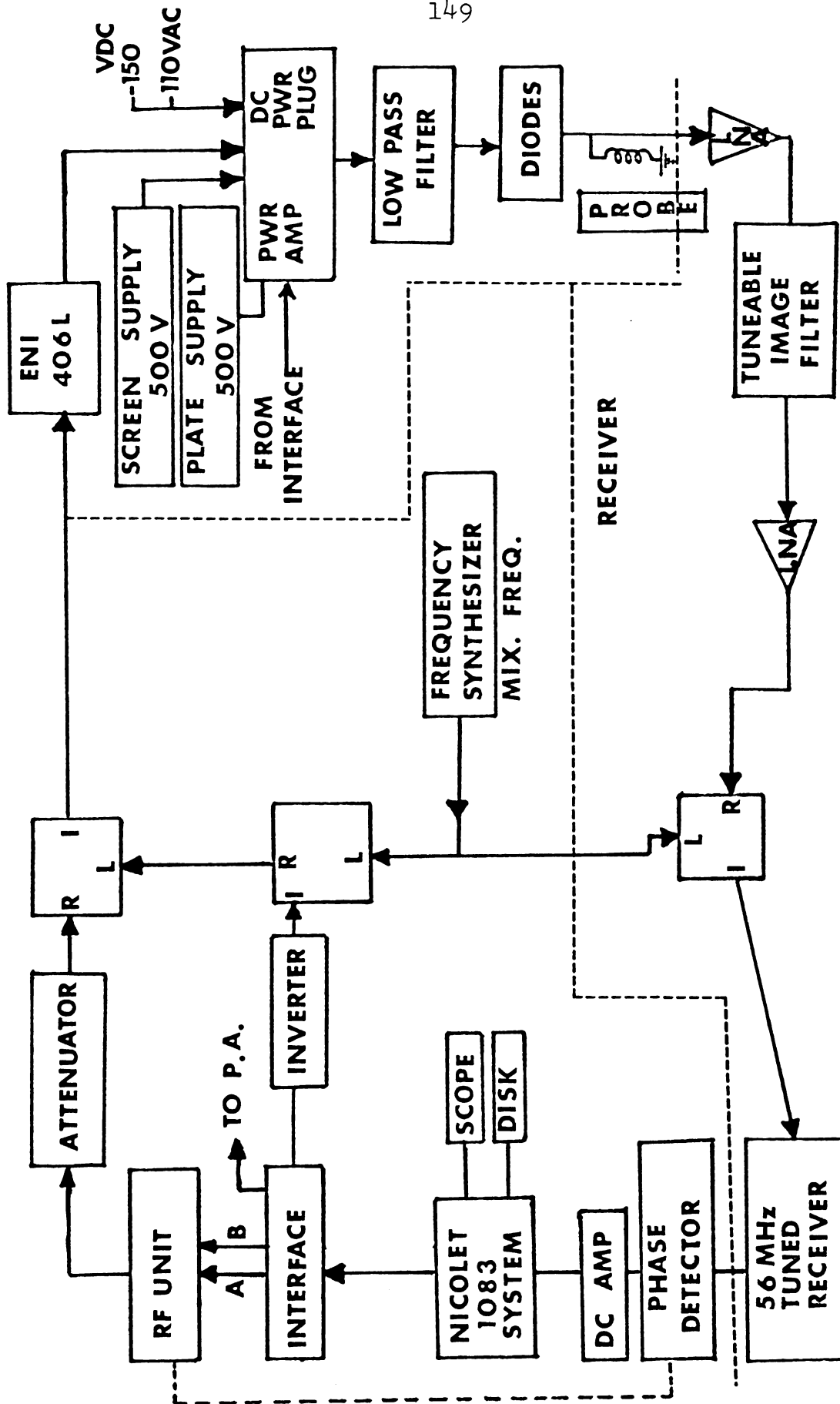


Figure 32. The block diagram of DA-60 multi-nuclear NMR spectrometer.



line broadening was applied to the free-induction decays.

The External Lock

The field is locked by a home-built lock probe, which uses the DA-60 console to lock on the proton resonance of the upfield sideband of H_2O .

A 3 mm O.D. quartz capillary was filled with water doped with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to give a linewidth of c.a. 4Hz. The lock probe slides into the back of the pulse probe. Since the lock probe was not thermally insulated, it tended to follow the temperature of the experimental sample. With the lock inserted to its fullest extent into the pulse probe, it was determined that the lock sample attained a temperature of 0.1°C when the experimental sample was at approximately -170°C . In order to go to lower temperatures while still using the lock, the lock probe must be partially withdrawn from the pulse probe to decrease the thermal contact. In this manner locked operation was possible down to the lowest attainable temperature.

Temperature Control and Measurement

The temperature was regulated by a heater-sensor and the Varian V-4343 variable temperature controller. The temperature were measured by a copper-constantan thermocouple. Thermal gradients in the probe were measured⁶⁶ and they were not found to be strongly dependent on the actual temperature. The magnitude of

these gradient was not greater than 2.20°C in 4.0 cm. The average gradient was about 0.2°C across a 0.5 cm sample.

Samples were allowed 20-30 minutes of equilibrium time between each experiment. During the experiments the temperature was very stable.

Sampling and Referencing

The probe in the DA-60 requires 5, 10 or 15 mm o.d. tube. In most of the studies, a 15 mm o.d. Wilmad NMR tube was employed. In order to keep the sample free from oxygen, the NMR tube was equipped with a 24/40 Knotes inner joint and a side arm with $\frac{1}{2}$ " 2A glass stopcock.

A coaxial type of reference tube was used. The design of the sample tube and the reference tube are shown in Figure 33. The reference sample (tri-n-butylphosphine in toluene) was put into the 5 mm o.d. NMR tube, and the whole reference tube was sealed off.

The sample tubes and the reference tube were made by the glass shop in Michigan State University. The reference tube may be not exactly coaxial, therefore marks on the sample tube and reference tube were used.

During these studies, the samples were not spun.

(II) Bruker HFX-90 NMR spectrometer

The phosphorus-31 spin-lattice relaxation times (T_1) were measured by using a Bruker HFX-90 NMR spectrometer equipped with a Nicolet 1083 computer with 12K of memory, a Diablo disk memory unit, and a Nicolet 293 I/O controller.

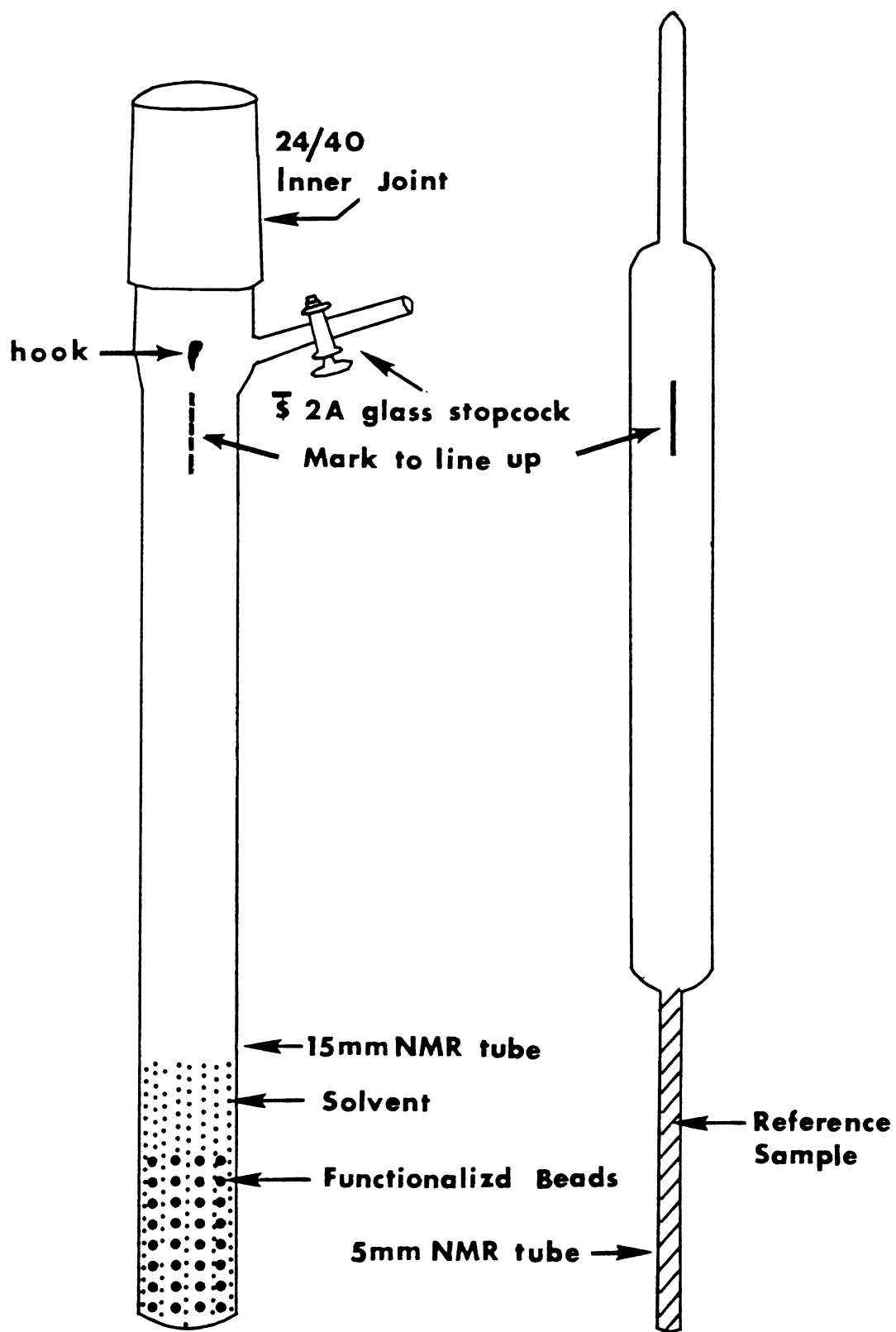


Figure 33. The sample and reference tube for $P-31$ measurements.

The spectra were obtained at a frequency of 36.44 MHz.

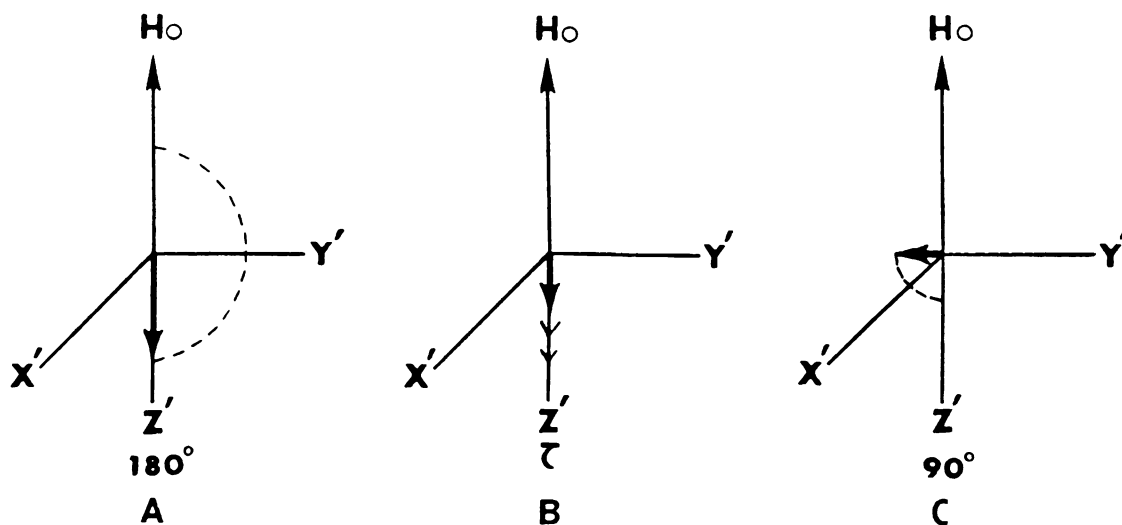
Probe temperature were measured by inserting a copper-constantan thermocouple directly into a solvent filled tube in the NMR probe and reading the temperature from a 25-Doric Trendicator 400 digital output. A thermocouple fastened near the bottom of the sample tube regulated the flow of cooled nitrogen gas.

The Measurement of Spin-Lattice Relaxation Times (T_1)

Various experiments have been designed to measure spin-lattice relaxation times. The most common method of measuring T_1 is the so-called inversion-recovery method or partially relaxed NMR spectroscopy. This method consists of the application of pulse sequence $180^\circ, \tau, 90^\circ$, where τ is waiting period between the two pulses. The pulse sequence then, is abbreviated $[180-\tau-90-(\text{sample})-T]_n$ where n is the number of FID to be summed and τ is the delay time which must be at least 5 times the longest T_1 in the system, to allow for complete recovery.

As shown in Figure 34-[1]A and [2]A, the 180° pulse inverts the magnetization along the $-Z'$ axis. After a time τ , spin-lattice relaxation has caused M to decrease (Figure 34-[1]B through zero if τ is long enough to increase toward its positive equilibrium value (Figure 34-[2]B). The 90° pulse applied at time τ samples the value of M at the instant by turning M to Y' axis where it generates a FID. Fourier transformation of the FID gives a partially

[1] $\tau < T_1$



[2] $\tau > T_1 \ln 2$

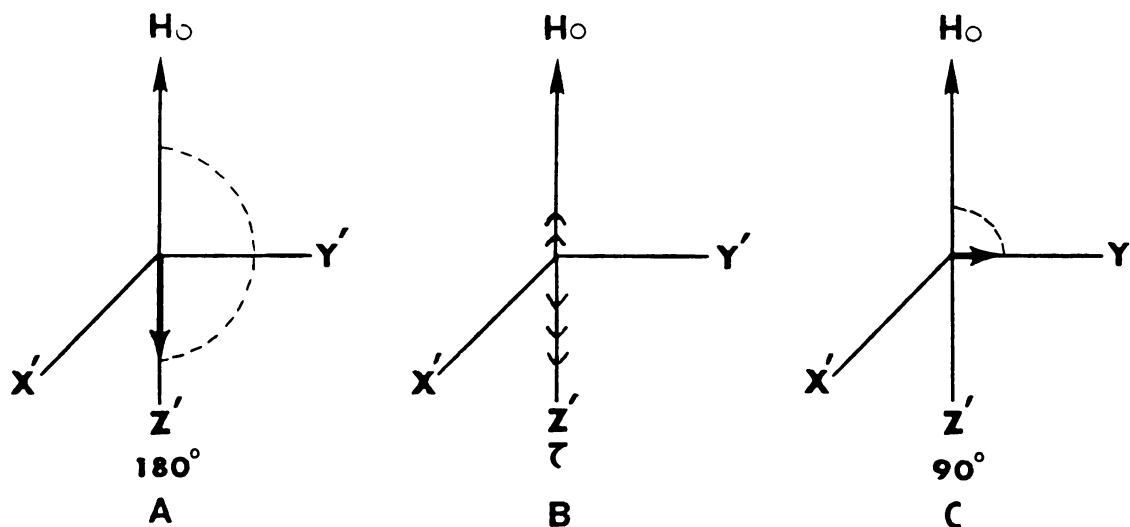


Figure 34. Representation of an inversion method for T_1 measurement.

(A) A 180° pulse is applied.

(B) The system is allowed to relax for a period of τ .

(C) A 90° pulse is applied.

The magnetization vector then returns to equilibrium.



relaxed spectrum in which the intensity of the resonance line is proportional to the Z magnetization at the time of the 90° pulse (nonequilibrium state). The system is then allowed to relax back to equilibrium and the pulse sequence repeated with another value of τ . Thus a series of spectra was measured as a function of τ and stacked in such a way as to create the impression of a three dimensional plot of frequency and time. Accurate T_1 's can be calculated from a plot of τ versus the log of the difference between the intensity of each line and its equilibrium value.

The phosphorus-31 T_1 measurements were performed using the $[180^\circ-\tau-90^\circ-T]_n$ sequence. In a typical experiment, eight tau values were utilized, with the initial and final τ value being equal to T, which was chosen to be 4-5 times the value of T_1 . The spectra were measured over a 10000 Hz spectral width.

The pulse width required to flip the spins 180° was determined by pulsing a sample of 85% H_3PO_4 near the resonant frequency. The value of the pulse width was then varied until the experimental FID or FT signal had minimum intensity. A 90° pulse is exactly half the value of a 180° pulse. About 200 pulses for each τ value were necessary to achieve a sufficiently good signal to noise ratio to calculate T_1 values.

Since the signal to noise ratio of a frequency domain spectrum can be improved by the application of a



multiplication exponential with a negative exponent, the eight FID's acquired during each T_1 experiment were subjected to an exponential multiplication with -5 as the exponent and then Fourier transformed under identical conditions. The frequency domain spectra were plotted and the T_1 was calculated by the T_1 program which performed a least squares analysis to fit a straight line to the equation

$$\ln (1-A/A_\infty) = -\tau/T_1 + \ln 2$$

where A, A_∞ is the intensity of spectra with τ values equal to τ, τ_∞ . Thus, a plot of $\ln(1-A/A_\infty)$ vs. τ gives a line with slope $-1/T_1$ and a theoretical intercept of 0.693.

Much has been published concerning the errors involved in the measurement of relaxation times by the various pulse procedures available. Errors arise from a variety of sources, principally inhomogeneities in H_0 and H_1 , incorrect pulse powers, incorrect timing, and inaccuracies in phasing.

Preparation of Reference Sample

A 0.4 M of tri-n-butylphosphine solution in toluene was used as a reference sample. A 25 ml. pear-shape flask with side arm was equipped with a gas inlet tube. Tri-n-butylphosphine (density 0.812 g./ml.) 1.15 ml was transferred into the flask after it has been purged with argon and mixed with 10.35 ml. of dry, oxygen-free toluene.

The concentration of this solution is 0.4 M, if the mixture is additive. About 1 ml. of this solution was then placed into the reference tube under argon, and the tube was sealed off under vacuum. All the samples and solvent were transferred by means of syringes.

General Preparation of the Samples for P-31 NMR Measurements

A 0.9-1.2 g. sample of the beads was put into the sample tube under argon and sealed with a 24/40 outer type of stopper. The system was evacuated and flushed with argon three times. Then three to four ml. of the desired solvent was added from the top while the tube was under argon pressure. The tube was sealed off and the beads were allowed to swell for at least 2 hours before the P-31 spectra were measured. However, in most cases the beads sample were allowed to equilibration for more than 24 hrs.

In order to obtain the content of polymeric phosphine present in the beads, the reference tube was put into the sample tube and the marks were lined up. They were then lined up with a guide mark on the probe. During this studies, a 3.5 seconds of delay time (time between pulses) was used. The area ratio of a sample and a reference was changed with the delay time used due to the longer T_1 of tri-n-butylphosphine sample.

Note : The height of the swelled beads in the NMR tube must be greater than the length of the coil of the probe.



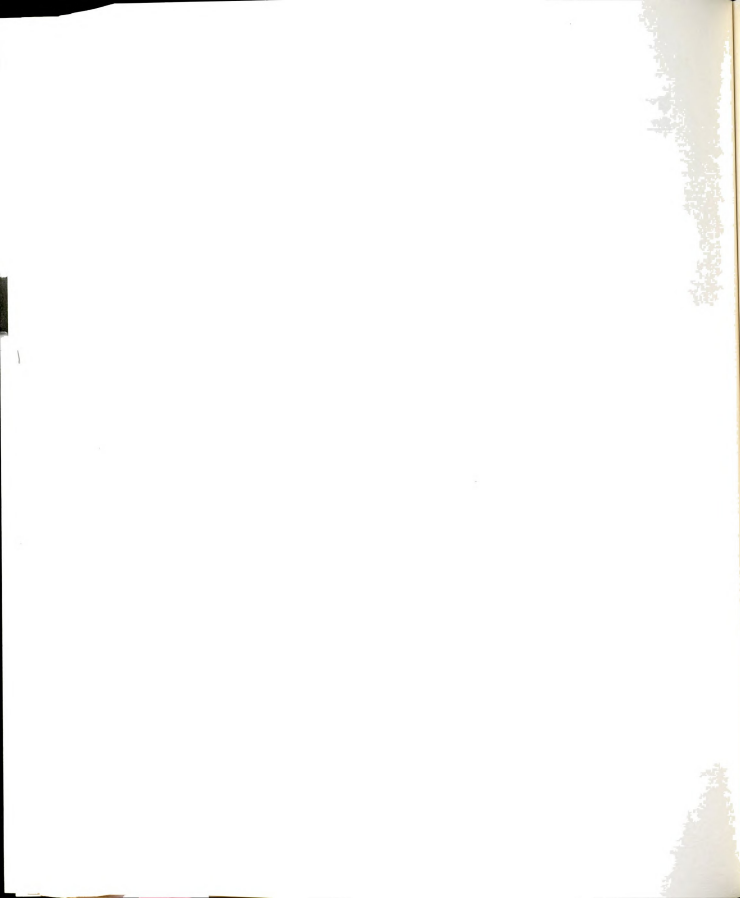
Preparation of Polymeric Triphenylphosphine
for Chelation Studies

All operations were carried out under argon with solvents prepared as previously described. The standard method, described in part one was used to prepare the phosphine substituted polystyrene copolymer. Five batches of different per cent substitution of phosphinated beads were prepared by varying the relative ratios of reactants and the reaction time. The amount of copolymer used, relative amount of reactants and time for the lithiation are summarized as follows :

Batch	Beads(g.)	%n-BuLi·TMEDA	Temp. (°C)	Time (hr)	ml of ClP ϕ ₂	%P
1	19.62	50	67	7	26	2.84
2	13.40*	20	65	6		
		40	65	12	23	3.83
3	14.93	20	74	6	17	2.72
4	10.02	10	70	11	10	1.73
5	12.19	5	65	1½	6	1.27

* The beads were treated with a solution of 20% lithiating reagents, washed with cyclohexane and then treated with a solution of 40% lithiating reagents.

The above beads were used to prepare the following metal complexes for P-31 studies.



Preparation of Polystyrylphosphine Metal
Complexes for Phosphorus-31 Studies

All solvents were dry and oxygen-free, and all reactions were carried out under argon. Solvent transfer was carried out by means of a syringe.

$\text{RhCl}(\text{P}\phi_3)_3$ studies

A 1-2 g. sample of phosphinated beads from batch 1 containing 0.95 meq phosphine per g. of beads was treated with $\text{RhCl}(\text{P}\phi_3)_3$ in benzene for several days. The beads were then washed with benzene until the rinses were colorless. They were then vacuum dried and stored under argon. Sample of IA-IF were prepared as summarized in Table 18 .

$[\text{Rh}(\text{COE})_2\text{Cl}]_2$ studies-- Series II-V

In a typical preparation, approximately 1 g. of a phosphinated beads sample were weighed into a 50 ml. side-armed flask equipped with gas inlet tube. The required amount of biscyclooctenerhodium(I)chloride dimer was added. After evacuating and flushing with argon (three times), 15-30 ml. of benzene was added. The mixture was stirred under argon with a magnetic stirrer or with a shaker for a designated time. The copolymer was then washed with benzene until no coloration shown in the rinses. The copolymer was then vacuum dried with or without heating and stored under argon.

Batch 2(1.237 mmole P/gbeads), 3(0.878 mmole P/gbeads), 4(0.560 mmole P/gbeads) and batch 5(0.379 mmole P/gbeads) of above phosphinated beads were equilibrated with $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ in benzene to provide sample of series II-V respectively. They are summarized in Table 19-22.

The dried samples were placed into a 15 mm of NMR tube and swollen in toluene as previously described. The content of free phosphine was then analyzed by P-31 NMR spectroscopy.

Phosphine Exchange in $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$

DA-60 was used for this study.

$\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$, 0.2986 g.(0.4321 mmole) was placed in a 25 ml. bantamware flask equipped with a gas inlet tube and a septem stopper. The system was vacuumed and flushed with argon three times. Chloroform 5.4 ml. was added to make 0.08 M of yellow solution.

Purified triphenylphosphine , 0.5985 g. in a 25 ml. bantamware flask equipped with a gas inlet tube was vacuumed and flushed with argon three times. Chloroform 3.8 ml. was then added to make a 0.6 M solution triphenylphosphine.

The 15 mm NMR tube equipped with side-arm and stopper was vacuumed and flushed with purified argon three or four times. 2.1 ml. of 0.08 M of $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ and 1.1 ml. of 0.6 M $\text{P}\phi_3$ were introduced by the means of syringes. The solution was well mixed and it contained 0.052 M of $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ and 0.202 M of $\text{P}\phi_3$ ($\text{Rh}/\text{P}\phi_3 = 3.9/1$).



Table 18. The preparation of samples IA-IF.

Sample	Beads used (mmol P)	$\text{RhCl}(\text{P}\phi_3)_3$ (mmol)	Rh/P	Equilibration time (day)	color (soln.)
IA	1.79	0.137	0.076	9	faint yellow
IB	1.00	0.107	0.107	18	yellow
IC	1.36	0.189	0.139	9	yellow
ID	1.00	0.162	0.162	18	yellow
IE	1.41	0.395	0.280	28	red
IF*	1.52	0.579	0.385	8	dark red

* Reflux in benzene for $5\frac{1}{2}$ hours.

Analysis : IE- Rhodium 2.29% (0.2225 mmol/g.beads)

IF- Rhodium 2.62% (0.2546 mmol/g.beads)
Phosphorus 2.73% (0.8814 mmol/g.beads)

Table 19. The preparation of samples IIA-IIG.

Sample	Beads used (mmol P)	$[\text{RhCl}(\text{COE})_2]_2$ (meq Rh)	Rh/P	color of soln. before washing
IIA	1.404	0.094	0.067	clear
IIB	1.419	0.163	0.115	clear
IIC	1.328	0.188	0.142	faint yellow
IID	1.493	0.286	0.193	faint yellow
IIE	1.423	0.506	0.356	yellow
IIF	1.622	0.924	0.569	yellow
IIG	1.827	1.554	0.851	yellow

Analysis : IIF* Rhodium 2.98% (0.2896 mmol/gbeads)

IIG1-Rhodium 4.27% (0.4149 mmol/gbeads)

IIG2-Rhodium 4.06% (0.3945 mmol/gbeads)
Phosphorus 3.41% (1.101 mmol/gbeads)

* Analysis performed after the second treatment with $\text{P}\phi_3$

Table 20. The preparation of samples IIIA-IIIG.

Sample	Beads used (mmol P)	$[\text{RhCl}(\text{COE})_2]_2$ (meq Rh)	Rh/P	color of soln. before washing
IIIA	2.05	0.107	0.052	clear
IIIB	1.492	0.121	0.081	clear
IIIC	1.278	0.112	0.088	clear
IIID	1.386	0.1678	0.121	clear
IIIE	1.259	0.2963	0.235	clear
IIIF	2.375	1.013	0.427	faint yellow
IIIG	0.822	0.822	1.000	yellow

Analysis : IIIF- Rhodium 3.25% (0.316 mmol/g.beads)
Phosphorus 2.24% (0.723 mmol/g.beads)

IIIG- Rhodium 4.54% (0.441 mmol/g.beads)
Phosphorus 1.78% (0.575 mmol/g.beads)

Table 21. The preparation of samples IVA-IVG.

Sample	Beads used (mmol P)	$[\text{RhCl}(\text{COE})_2]_2$ (meq Rh)	Rh/P	color of soln. before washing
IVA	0.668	0.047	0.070	clear
IVB	0.696	0.055	0.079	clear
IVC	0.660	0.083	0.125	clear
IVD	0.893	0.172	0.192	clear
IVE	0.844	0.279	0.330	faint yellow
IVF	0.780	0.433	0.556	yellow
IVG	0.962	0.837	0.870	yellow

Analysis : IVF- Rhodium 2.70% (0.2624 mmol/g.beads)
Phosphorus 1.23% (0.3971 mmol/g.beads)

IVG- Rhodium 3.94% (0.3829 mmol/g.beads)
Phosphorus 1.23% (0.3971 mmol/g.beads)

Table 22. The preparation of samples VA-VG.

Sample	Beads used (mmol P)	$[\text{RhCl}(\text{COE})_2]_2$ (meq Rh)	Rh/P	color of solution before washing
VA	0.622	0.034	0.054	clear
VB	0.630	0.055	0.087	clear
VC	0.579	0.088	0.151	clear
VD	0.500	0.138	0.276	clear
VE	0.425	0.152	0.357	faint yellow
VF	0.447	0.257	0.576	yellow
VG	0.397	0.338	0.851	yellow

Analysis :

VG- Rhodium 2.94% (0.2857 mmol/g. beads)



Preparation of Polymer-Supported $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$
for Phosphine Exchange Studies

Poly(styrene-divinylbenzene)copolymer(1.8% crosslinked), in bead form, was phosphinated by the previously described technique¹⁶. The functionalized beads were then equilibrated with $\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$ or $[\text{RhCl}(\text{CO})_2]_2$ in benzene. The nonattached complexes were removed by washing with benzene until no coloration shown in the rinses. The preparation of sample RhV_1 - RhV_5 are listed in Table 23. The vacuum dried complexed copolymer was swollen with toluene in a 15 mm NMR tube (as shown in Figure 33).

The DA-60 multi-nuclei spectrometer was used for the ^{31}P NMR measurements. A 3.5 seconds of delay time (time between pulses) was used for all the measurements.

Table 23. The preparation of sample RhV_1 - RhV_5 .

<u>Sample</u>	<u>meqP/gbeads</u>	<u>meq Rh/gbeads</u>	<u>Equilibration</u>	
			<u>Complex</u>	<u>P/Rh</u>
RhV_1	0.878	0.548	$\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$	1.60
RhV_2	0.894	0.314	$\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$	2.85
RhV_3	0.878	0.161	$\text{RhCl}(\text{CO})(\text{P}\phi_3)_2$	5.45
RhV_4	0.894	0.263	$[\text{RhCl}(\text{CO})_2]_2$	3.40
RhV_5	0.894	0.234	$[\text{RhCl}(\text{CO})_2]_2$	3.82



Scanning Electron Microprobe Analysis

The beads (about 150 mg.) were mounted on an aluminum stub using scotch double stick tape. The sample was then coated with 400 to 500 Å of gold in a model EMS-41 sputter coater. The beads were then examined in a Super III scanning electron microprobe (International Scientific Instruments) operating with 10 KV accelerating voltage and zero degree specimen tilt.

The Degree of Swelling Values, q

The degree of swelling values were measured by the method developed by E.M. Sweet¹⁵. About 2 ml. of phosphinated (ca. 13% substituted) beads were put into a 10 ml. graduated cylinder. After recording the volume of dry beads, the cylinder was filled with solvent. The volume of beads was taken periodically. The final volume was noted over a 24 hours period. Equilibrium was usually attained within a 2-hour period. The degree of swelling value, q, was then calculated.

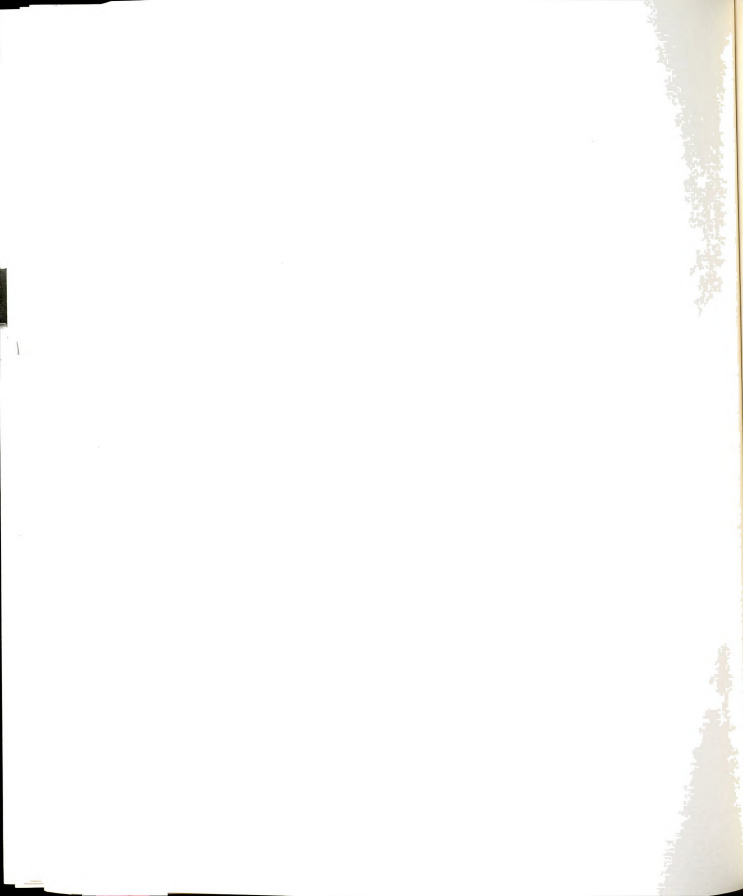
$$q = \text{Swelled volume} / \text{dry volume}$$

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