LIGAND MODIFICATION AND CATALYSIS:
WATER-SOLUBLE PHOSPHINES AND CHIRAL CYCLOPENTADIENES

by

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"If the catalyst is heterogenized by linking it to a polymer, one may look upon the heterogenized catalyst as consisting of the insoluble, polymeric portion, which is the catalyst support, and the catalytic portion, which projects into the solution and is solvated and, in a sense, dissolved by it. The combination may be likened to soap in an oil-water system in which the nonpolar, hydrocarbon portion of the molecule dissolves in the oil and the polar portion in the water. Each of these must be tailored to suit the needs of the reaction which is to be catalyzed."

J. C. Bailar, Jr.
Cat. Rev.-Sci. Eng., 10, 17 (1974)

"A 'heterogenized' catalyst may in fact be prepared by the use of a properly designed soap."

David Feitler
5th North American Meeting of the
Catalysis Society
April 24, 1977
Pittsburgh, Pennsylvania

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Submitted to the Department of Chemistry at the Massachusetts Institute of Technology, May 23, 1977, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Abstract

Part I: A New Method for Immobilization of Homogeneous Catalysts. Homogeneous Catalysis in Water by Rhodium-Water-Soluble Phosphine Complexes.

A new method for immobilization of homogeneous catalysts, Surfactant Catalysis, is proposed. Water-soluble phosphines were prepared by the following two methods:

a. $$\mathrm{Me(OCH_2CH_2)_{12}OH} \xrightarrow{\mathrm{SOCl_2}} \mathrm{Me(OCH_2CH_2)_{12}Cl} \qquad (1)$$

$$1 + \mathrm{Ph_2PK} \longrightarrow \mathrm{Me(OCH_2CH_2)_{12}PPh_2} \qquad (2)$$

b. $$\mathrm{Me(OCH_2CH_2)_{12}OH} + \underline{\mathrm{p}}\text{-}\mathrm{BrCH_2PhBr} \xrightarrow{\mathrm{KH}}$$

$$\mathrm{Me(OCH_2CH_2)_{12}OCH_2PhBr}\text{-}\underline{\mathrm{p}} \qquad (3)$$

$$3 \xrightarrow[\mathrm{Ph_2PCl}]{\mathrm{BuLi}} \mathrm{Me(OCH_2CH_2)_{12}OCH_2PhPPh_2} \qquad (4)$$

These phosphines have been used as ligands for cationic Rh complexes in homogeneous organic and aqueous media, and the complexes were shown to be active hydrogenation catalysts. The polyethylene glycol chain was found to have little effect on catalysis. Water had variable effects on rates of catalysis, and a neutral, hydroxy-ligated Rh species was probably present in equilibrium with the cationic Rh species. Two-phase hydrogenation was demonstrated using an aqueous catalyst solution to hydrogenate cyclohexene. A third, interfacial phase appeared in water/catalyst/cyclohexene systems. The interface and aqueous layers carried more than 95% of the catalytic activity, with the interface carrying a surprisingly large portion thereof. A moderate decrease in rates of hydrogenation in two-phase systems from homogeneous organic systems was attributed to surface equilibrium effects and not to mass transport problems.

Part II: Appendices

Appendix I: Chiral Cyclopentadienes

Attempted syntheses for chiral cyclopentadienes by methods previously developed are described.

Appendix II: Reductive Oligomerization of Carbon Monoxide

The use of one-electron reductants as a means of obtaining organic derivatives from carbon monoxide was explored. Evidence for the existence of novel ketenes of the form (RO)RC=C=O was obtained.

Thesis Supervisor: George M. Whitesides

Title: Professor of Chemistry

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PART I

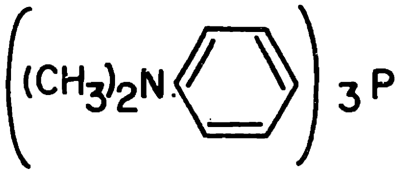
A NEW METHOD FOR IMMOBILIZATION OF HOMOGENEOUS CATALYSTS. HOMOGENEOUS CATALYSIS IN WATER BY RHODIUM-WATER-SOLUBLE PHOSPHINE COMPLEXES.

Introduction

Homogeneous catalysis possesses inherent advantages over heterogeneous catalysis, among which are counted reproducibility,[1] selectivity,[1,2] efficiency,[1] rate,[3,4,5] mass and thermal transport properties,[6,7] and characterizability.[1] Two major difficulties with homogeneous catalysis are (1), the failure thus far to find homogeneous catalysts which will activate carbon-carbon sigma bonds, carbon-hydrogen bonds, or dinitrogen,[2] and (2) the problems of recovering or at least separating the catalyst from the reaction mixture.[1] The first difficulty is being addressed by investigation of the catalytic properties of small metal clusters.[2,8,9] The second has been approached by heterogenizing the homogeneous catalyst.[1,5,10,11] The most productive ventures have been ones which immobilized catalysts on a solid support: polystyrene, alumina, silica and glass beads. As might be expected, a homogeneous catalyst bound to a solid support does not carry its properties intact with it down to the support. Dramatic changes in rate,[5,10] selectivity,[5,10] and stability,[12] have been observed. In many cases the process of immobilization is beneficient, but the changes effected are in any case unpredictable. In addition to the problems with characterization and with mass and thermal transport properties incurred by immobilization on a solid support, the immobilization of a catalyst is a non-trivial matter and the synthetic procedures can be complex. By anchoring a catalyst to a soluble polystyrene, Bayer has shown that most of these problems can be overcome.[13] Bayer's catalyst must, however, be separated from reaction mixtures by ultrafiltration, a technique not suitable for large scale preparations. Parshall[14] and others[15,16] have used selectively permeable membranes to remove catalyst from solutions of substrate. Again the rates of separation discourage large scale use. It is evident therefore that an alternative method for immobilization is desirable. Such a method should:

1. Be synthetically facile
2. Render the catalyst readily separable
3. Render the catalyst highly dispersable (hence providing good mass and thermal transport properties)
4. Transfer catalytic properties intact to the immobilized system
5. Allow characterization of the catalyst by the unusual methods.

The use of a second liquid phase as a means of immobilization has received very little attention. Rony[17] and Parshall[18] investigated the use of molten salts as media for metal ions. Unfortunately, this technique has not gained popularity, perhaps due to the instabilities and expenses associated with molten salts (although improvements have been made[19]). Capitalizing on the exclusive N-protonation of 1,[20] Gregorio and Andreeta[21] patented the use this ligand in hydroformylation systems with $Co(CO)_4H$ catalysts. Extraction of the Oxo solution with aqueous acid removed both the ligand and the cobalt. Neutralization and extraction of the aqueous phase with fresh olefin conserved 100% of the original activity. This procedure has also attracted little attention, perhaps in this case because of the multistep nature of the recovery, or the unfavorable properties of the ligand towards catalytic activity.[22] More recently, Ollis has reported the



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development of a liquid membrane bubble reactor.[6] Here, a water-soluble catalyst is carried in a membrane around a gaseous reactant. This bubble floats upwards through an organic layer as the reactants diffuse into the catalyst membrane and the products diffuse out of the membrane into the surrounding organic phase. This system is limited to processes such as Wacker oxidations, where the catalyst is water soluble. Taking these three examples together it seems clear that binary liquid phase systems have potential as alternatives to insoluble polymer supports. Mass transport effects should be controllable by agitation and/or the addition of surfactants and thermal transport problems should be nonexistent. Behavior of the catalysts should be amenable to classical methods of investigation. Separation of the two liquids should be a simple matter of decanting one phase.

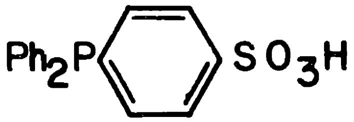
Pollak and Whitesides have recently described a two-liquid-phase system for immobilizing enzymes.[23] Enzymes are preferentially solvated by one of the phases of a system containing two immiscible aqueous solutions of different high polymers such as dextran/water and polyethylene glycol/ water.[23,24] The high partition coefficients of some enzymes were exploited to produce an enzyme reactor in which the enzyme was immobilized in one of the two immiscible aqueous polymer solutions (dextran/water), while substrates and products could be extracted with the other (PEG/water). If a piece of polymer (PEG) was attached covalently to the enzyme, the partition coefficient of the active modified enzyme would reflect a preference for the aqueous polymer solution (PEG/water) that was previously avoided. The signal significance of this inversion of partition coefficients was that the solubility of a catalyst could be modified by an attached polymer chain while retaining activity. The facile nature of this modification suggested applications to homogeneous transition metal catalysts. Many important homogeneous transition metal catalysts are soluble in organic solvents. Modification of the ligands of these catalysts to give them an affinity for an organic-immiscible solvent (such as water, various high polymers or molten salts), could promote liquid-liquid systems for immobilized homogeneous catalysis. Such a modified catalyst would posses affinities for both phases of the liquid-liquid system, and thus possess, to some extent, surfactant properties. We call such a method Surfactant Catalysis.

To demonstrate these concepts, we prepared nonionic water-soluble phosphines (by incorporating short polyethylene glycol chains) and used them as ligands for rhodium-based hydrogenation catalysts. We investigated the properties of these rhodium complexes with three objectives in mind: (1) establishing that water-soluble catalysts can be prepared and are stable; (2) showing that Surfactant Catalysis constitutes a usable method of catalyst immobilization; (3) determining in as general ways as possible the degree to which Surfactant Catalysis based on polyethylene glycol phosphines in water provides a new method of catalyst immobilization which meets the ideal criteria mentioned earlier.

Results and Discussion

Water-Soluble Phosphines. Water-soluble phosphines have long been a missing member of the family of ligands associated with transition metal catalysts. The only attempt to prepare nonionic species was made by Chatt *et al.*[25] These investigators found that 2 would not stabilize a metal ion towards reducing conditions. There are two examples of ionic water-soluble phosphines in association with a metal. The amine-phosphine of Gregorio and Andreeta[20] (1) is soluble in aqueous acid, and carries with it a cobalt hydridocarbonyl. No homogeneous aqueous catalysis using this ligand has been reported. Joo and Beck[26] have reported the use of the anionic sulfonic acid phosphine 3. They proposed that a ruthenium (III) complex of this phosphine hydrogenated pyruvic acid in aqueous HCl under one atmosphere of dihydrogen. While there is no reason to doubt this result, the authors have failed to demonstrate that the complex is actually responsible for hydrogenation. The complex is reported to be unstable, reducing to a ruthenium (II) species. In view of the reported activity of aqueous ruthenium species[27] towards unsaturated carboxylic acids and the very low activities of the new systems, the actual role of the phosphine remains open to question. Joo and Beck were unable to obtain stable rhodium complexes. Another cationic water-soluble phosphine has been reported by Eschenmoser[27] (4) but there is as yet no report of its use as a water-soluble ligand.

$(HOCH_2)_3P$ 2

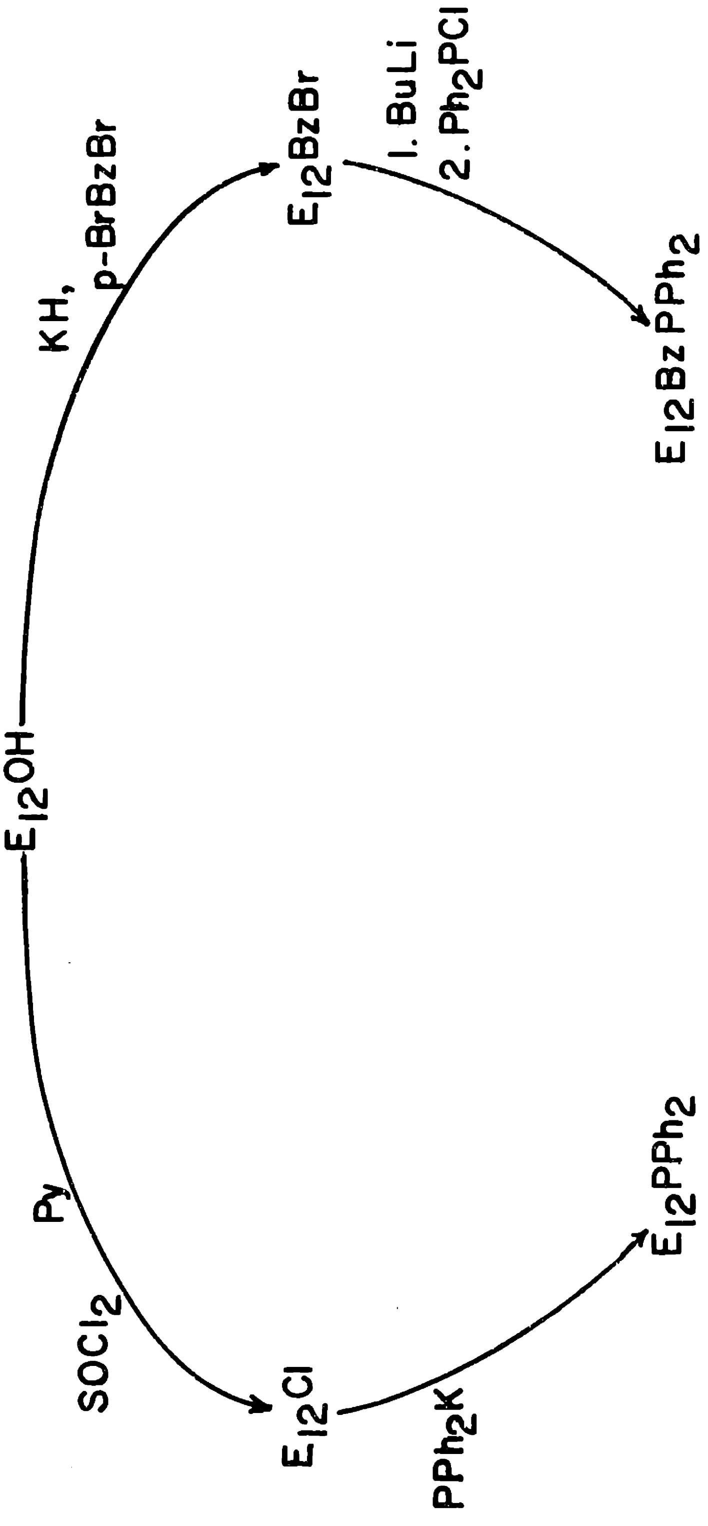


3

$Ph_2PCH_2CH_2N(CH_3)_2$ 4

The synthetic methods used to prepared water-soluble phosphines are outlined in Figure 1. Polyethylene glycol monomethyl ethers (PEGs) were chosen as the water solubilizing group for four reasons. First, the synthetic and physical chemistry of PEGs is well understood.[29,30] Second, interference by reactive functionality either in synthesis or catalytic application is minimized by the use of ether linkages. Third, PEGs and other polyethers can themselves be used as an immiscible second liquid phase with organic solvents,[28] thus generalizing the method to non-aqueous systems. Fourth, the monomethyl ethers are monofunctional and commercially available in a variety of molecular weight ranges. PEG monomethyl ethers were purchased as polydisperse

Figure 1: Preparations of Water-Soluble Phosphines


$E_{12}OH$
KH,
p-BrBzBr
$E_{12}BzBr$
1. BuLi
2. Ph_2PCl
$E_{12}BzPPh_2$
Py
$SOCl_2$
$E_{12}Cl$
PPh_2K
$E_{12}PPh_2$

materials having average molecular weights of 350, 550, and 750 (or average chain lengths of 8, 12, and 16 ethylene glycol units). Derivatives of the two lower molecular weight materials were easier to characterize and manipulate than those of the higher molecular weight ether, and since there is a chain conformation transition[28] starting at about 12 ethylene glycol units which increases water solubility, we have restricted our studies to derivatives of $CH_3(OCH_2CH_2)_{12}OH$. We abbreviate this substance as $E_{12}OH$, and name its derivatives accordingly.

Reaction of $E_{12}OH$ with thionyl chloride in pyridine provides moderate yields of the analogous chloride. Diphenylphosphine was prepared[32,33] and treated with potassium hydride to give potassium diphenylphosphide. The potassium salt of diphenylphosphide was superior to the lithium salt for displacement of chloride from $E_{12}Cl$ and the reaction proceeded cleanly to $E_{12}PPh_2$ provided that one-to-one stoichiometries were maintained. The reaction of $E_{12}OH$ with p-bromobenzyl bromide was readily promoted by KH in THF. The conversion of the resulting benzylic ether to $E_{12}BzPPh_2$ required transmetallation with BuLi at -78° and reaction with Ph_2PCl.[34] This sequence works well only if the individual steps were performed rapidly at low temperatures. Our best preparations used a slight excess of distilled $ClPPh_2$ which was added no more than 5 minutes after the addition of the BuLi solution. $E_{12}BzBr$ and $E_{12}BzPPh_2$ precipitated at -78° but this precipitation did not appear to interfere with the

Table 1: Analytical Data for Water-Soluble Phosphines

Elemental Analyses	Calculated	Found
$E_{12}Cl(C_{25}H_{51}ClO_{12})$	C, 51.84; H, 8.89; Cl, 6.12	C, 51.07; H, 8.78; Cl, 5.46
$E_{12}BzBr(C_{32}H_{57}BrO_{13})$	C, 52.69; H, 7.88; Br, 11.10	C, 52.20; H, 7.75; Br, 11.91
$E_{12}PPh_2(C_{37}H_{61}O_{12}P)$	C, 60.97; H, 8.44; P, 4.25	C, 60.50; H, 8.45; P, 3.06
$E_{12}BzPPh_2(C_{44}H_{67}O_{13}P)$	C, 63.29; H, 8.09; P, 3.71	C, 59.20; H, 7.74; P, 3.49

^{1}H NMR Chemical Shifts in PPM δ relative to tetramethylsilane

$E_{12}PPh_2$	7.35 (s, 10), 3.68 (s, 48), 3.37 (s, 3), 2.37 (t, 2, J = 7 Hz)
$E_{12}BzBr$	7.37 (q, 4), 4.50 (s, 2), 3.68 (s, 48), 3.37 (s, 3)
$E_{12}BzPPh_2$	7.35 (d, broad, 14), 4.58 (s, approx. 1), 4.53 (s, approx. 1), 3.68 (s, 48), 3.35 (s, 3)

^{31}P NMR Chemical Shifts in PPM downfield from 85% phosphoric acid in water

	Solvent	tert.-Phosphine (%)	Other Absorptions
$E_{12}PPh_2$	Acetone	-23.84 (94%)	
	Water	-22.96 (94%)	
$E_{12}PPh_2$*	Water	-22.81 (86%)	-10.96, -12.17, -21.05 unknown origin
$E_{12}BzPPh_2$	Water	-6.93 (60%)	6 peaks from 36 to 25 ppm

*Another batch

reaction. The phosphines were stored without abnormal precautions and ^{31}P nmr showed that aqueous solutions were stable for three weeks. Using $EtOCH_2CH_2OCH_2CH_2OH$ in place of $E_{12}OH$ in the above reactions, distillable compounds were obtained. Unfortunately, sufficient purity still could not be obtained (as evidenced by elemental analysis) to use these as model systems.

The phosphines obtained from these sequences were not pure, and they resisted purification. Physically, the phosphines were viscous oils which could not be crystallized, but could be precipitated at low temperature from methylene chloride-ether mixtures. Precipitation failed to purify the oil as proton nmr spectra showed that impurities coprecipitated. Distillation proved futile as well, as the thermal stability of the phosphines agreed with previous reports of similar phosphines containing β-ethoxy groups.[35] The air sensitivity of the phosphine moiety in solution and the polydisperse character of the ethylene glycol oligomers used made chromatography difficult. The principle impurities in $E_{12}PPh_2$ seemed to be oxides of excess potassium phosphide. The impurities in $E_{12}BzPPh_2$ were principally $E_{12}Bz$-derived species. These species may have been generated by the attack of phosphide on the benzylic ether position (although attack is at most 10% by examination of the ^{31}P nmr) or protonation of the phenyllithium species. Proton nmr did show a large percent of benzylic protons which did not have the correct frequency for $E_{12}BzPPh_2$, although the peaks were too close together for quantitative estimates.

Since we were primarily interested in the ability of these phosphines to form water-soluble complexes with transition metals rather than the details of their composition, we have used crude products directly in catalytic studies. Approximate assays of the compositions could be obtained by a combination of elemental analysis and ^{31}P nmr spectroscopy; given the total phosphorus content by elemental analysis, integration of Fourier transform ^{31}P nmr spectra showed the fractional distribution of phosphorus between the desired tert.-phosphine and the various impurities. For $E_{12}PPh_2$, this fraction ranged from 85-95%; for $E_{12}BzPPh_2$, the fraction ranged from 55-60%. Details of these analyses are summarized in the experimental section.

Model Systems. New methods of catalyst immobilization are often demonstrated using rhodium-based hydrogenation catalysts as model systems. Hydrogenations by insoluble polymer-bound rhodium complexes were among the first demonstrations of the potentials of homogeneous catalyst immobilization.[1] Pittmann[36] is investigating a phosphinated version of Regan's[37] polymeric phase transfer catalyst as a means of binding rhodium for aqueous substrates. Pinnavaia is using smectite clays to immobilize cationic rhodium complexes by ion exchange.[38] We have chosen to use the cationic rhodium system of Schrock and Osborn[39] as a basis for studying Surfactant Catalysis. The catalysts are readily prepared in situ, have a reasonably well understood character, and have been shown to be tolerant of water.

Catalyst solutions were prepared by weighing out the appropriate amount of phosphine into a sealed-off 19/38 female ground glass joint (thimble) adding a magnetic stirring bar, wiring a No-Air stopper in place, purging with argon and adding a solution of norbornadienyl rhodium (I) perchlorate in acetone. For aqueous systems the acetone was evaporated under a stream of argon before water was added. The catalyst precursor solution was activated by flushing with H_2 for 3-5 minutes and stirring under 8 lbs. of H_2 for 20-60 minutes. A visible color change was observed during activation, although the color and intensity were dependent on the ligand and its concentration. Solutions of orange $(E_{12}PPh_2)_2Rh(\text{norbornadiene})^+ClO_4^-$ faded under a hydrogen atmosphere to pale yellow. Solutions of yellow $(E_{12}BzPPh_2)_2Rh^+ClO_4^-$ under hydrogen turned orange. We found that norbornadienyl rhodium perchlorate was not stable to H_2 without at least two equivalents of phosphine present, and the addition of polyethylene glycols without phosphines did not prevent the formation of metallic rhodium. If a strongly complexing substrate (maleic acid) was present, phosphine deficits were tolerated to some extent. After the activation period, olefin (which had been freshly distilled from Ph_3P under argon) was added.

Interpretation of Data. Homogeneous hydrogenation by rhodium complexes has historically been a difficult area to quantify with precision. The catalysts are highly sensitive to impurities and most appear to have finite lifetimes even under the best of circumstances. James devoted considerable space to the evaluation of the kinetic data reported at the time:[40]

> It should be noted at this stage that the reproducibility of kinetic data for the hydrogenation of substrates by these rhodium (I) systems is generally inadequate. Candlin and Oldham[40] report a value of ±10%; a discussion involving small differences in constants derived from kinetic data should therefore, be considered guardedly. From reading the literature, this ±10% figure seemingly refers to the same catalyst sample and solvent batch. Variation in rates reported by different workers for similar systems is sometimes larger than this, which will become evident as these systems are discussed.

James goes on to discuss the factors to which variations in rates can be attributed: purity of the olefin with regard to peroxide content, the presence of Rh (II) species, the sensitivity of the systems to dioxygen, the dependence of this sensitivity on the solvent and the unpredictable changes in the rate expression that can occur promoted by a change in the conditions.

Because of these known variances, data of a more qualitative nature was sought. Rather than seeking rate constants, which would be impossible to determine for multi-phase systems anyhow, comparisons were made on a standard system (defined in the previous section) for a standard length of time (6 hrs.) (although in many cases other time intervals have been examined). Crude rates are reported as turnover numbers (moles product/mole rhodium) at this standard time.

Two kinds of variance were observed in this work. The first kind can be classed as fluctuations of less than 30%

around the anticipated values. The second kind can be classed as decreases by larger factors.

Variances of the first kind were attributed to leniency in experimental design. We were interested in observing large numbers of systems, varying ligand, solvent and substrate with minimum difficulty. The apparatus designed for kinetic experiments[39] was too cumbersome and expensive to be used for a screening program. We were able to obtain qualitatively informative data using syringe and cannula techniques. One further factor may have been the lack of temperature regulation. Experiments were run at ambient temperatures, which over the course of months probably fluctuated in a 10° range.

Variances of the second kind were attributed to experimental error. As noted above, experiments typically consisted of 5 mL of a 1.6 mM solution of rhodium (10 μmol). 1 mL of air contains enough O_2 to poison a typical experiment. If the full oxidative capacity of dioxygen is used then 0.25 mL of air can lead to total deactivation (4 Rh (I) + O_2 = 4 Rh (II)). Numerous transfers via syringe and cannula were made for each preparation. The avoidance of dioxygen contamination was dependent on accurate technique, and contamination occurred from time to time.

Most of the data obtained in this work has been plotted in Figures 2a (for catalysis based on $E_{12}PPh_2$) and 2b (for catalysts based on E_{12}-$BzPPh_2$). For systems where many values are plotted, the large majority of the points were taken from separate batches of catalyst, and even from separate batches

Figure 2a: Reproducibility of Rates of $(E_{12}PPh_2)Rh^+$ Hydrogenations

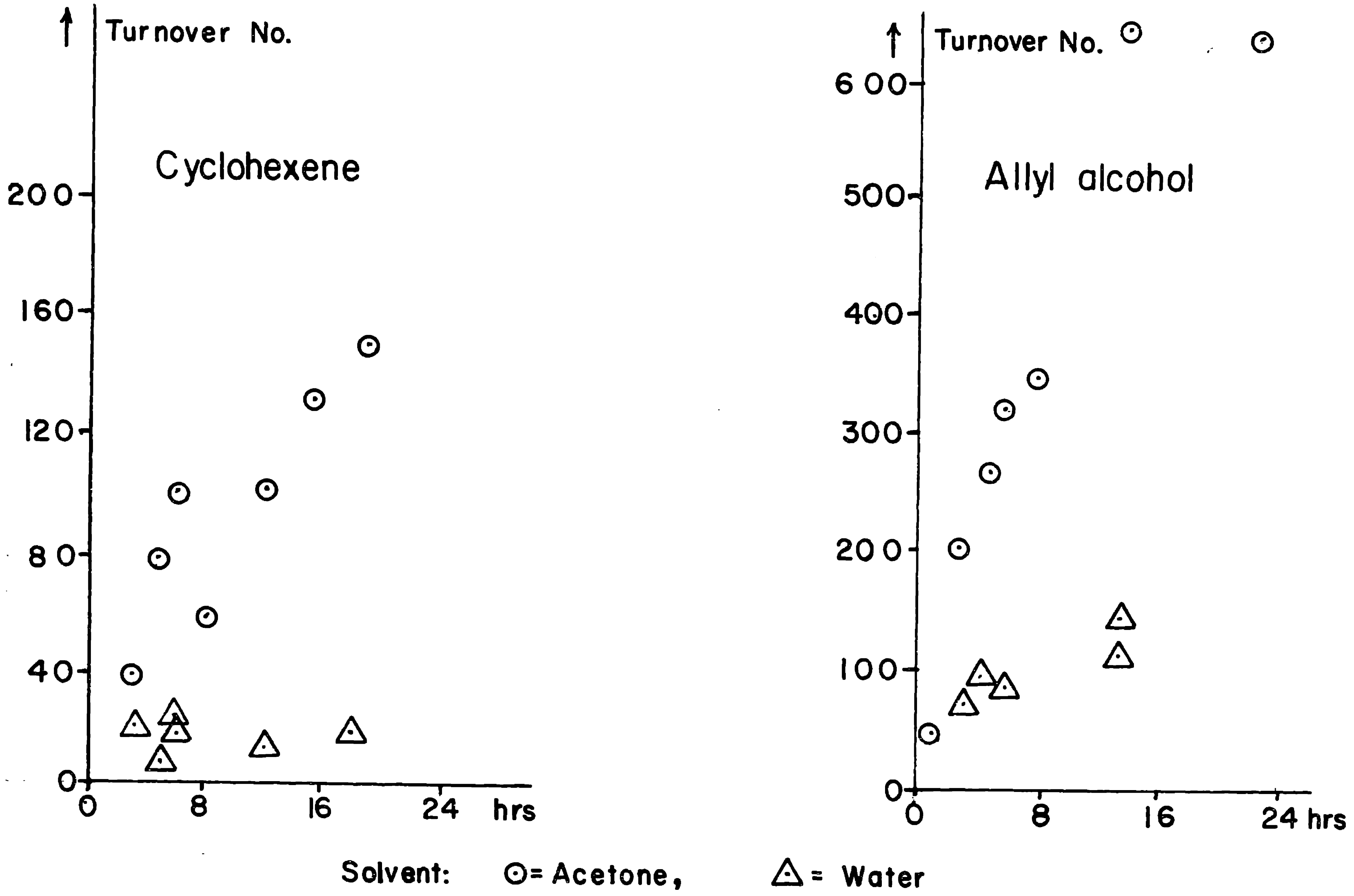
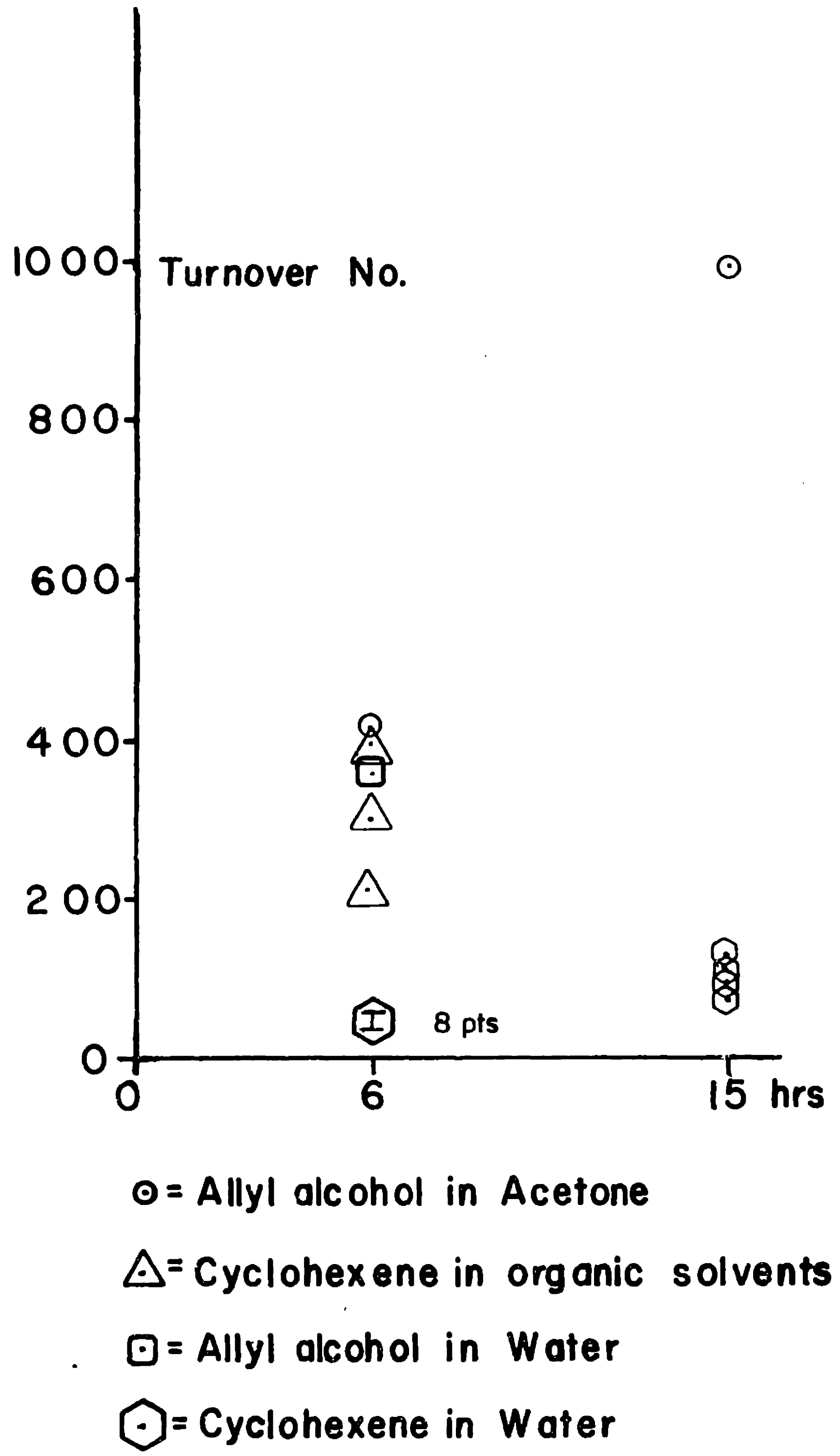

Turnover No.
Cyclohexene
200
160
120
80
40
0
0
8
16
24
hrs
Turnover No.
Allyl alcohol
600
500
400
300
200
100
0
0
8
16
24 hrs
Solvent: ⊙= Acetone, △ = Water

Figure 2b: Reproducibility of Rates of $(E_{12}BzPPh_2)_2Rh^+$ Hydrogenations


1000
800
600
400
200
0
Turnover No.
8 pts
0
6
15 hrs
⊙ = Allyl alcohol in Acetone
△ = Cyclohexene in organic solvents
⊡ = Allyl alcohol in Water
⬡ = Cyclohexene in Water

of phosphine. A consistent picture is obtained for all experiments, that is, we see clearly different rates for the two catalysts and for each of the basic conditions (homogeneous aqueous, homogeneous organic and heterogeneous systems). Data are shown from certain experiments which were not repeated _per se_, but their qualitative agreement with similar experiments lends them acceptable reliability. For example, the activity of $E_{12}BzPPh_2$-based catalysts towards cyclohexene in organic solution is given by experiments in three different organic solvents. None of the experiments were duplicated, yet taken together they are good evidence for a high level of activity in homogeneous organic systems as compared with heterogeneous organic systems which were extensively duplicated. Activity towards allyl alcohol in acetone for the $E_{12}BzPPh_2$-based catalyst was not repeated, but the nearly linear behavior over 15 hrs. up to 1000 turnovers indicates a valid experiment and a high rate. Because the rate approaches that which was repeatedly obtained for Wilkinson's Catalyst it seems reasonable to assume that repetition of the experiment will not yield significantly higher rates. The reactions on which the most repetitions were done, heterogeneous systems (water/cyclohexene) show good consistency.

Data having the uncertainty of the data obtained in this work are normally not considered usable for drawing mechanistic or kinetic conclusions. Indeed, since most of the rate data obtained for homogeneous rhodium catalysts reported in the literature shows variations of less than two orders of magnitude, and often, repeatable differences between systems that are less than a factor of two have been observed, it is difficult to conceive of using even perfectly reproducible data to draw any kind of mechanistic conclusion.

The questions we have to answer (p. 13 this draft) are simple compared to most physical-organic questions:

1. Do we have catalysis?
2. Are predominant effects attributable to the polyethylene glycol chain?
3. Does water exert an abnormal solvent effect?
4. Are Surfactant Catalysis systems different from homogeneous systems?

The data that we have obtained are sufficiently accurate to answer these questions. They are also sufficient to be used as a foundation for speculation, hypothesis and further experiments.

Catalysis. Our early work established that $E_{12}PPH_2$ was capable of ligating rhodium (I) cations in aqueous solution to give a stable homogeneous catalyst. Maleic acid and allyl alcohol were both hydrogenated with good turnover numbers. Later, turnover numbers of 600 were obtained for allyl alcohol using an $E_{12}BzPPh_2$ catalyst (Table 2). Some isomerization of allyl alcohol to propionaldehyde was observed, but isomerization was a minor reaction. Two-phase hydrogenation was also possible. Our work here focused exclusively on cyclohexene,

Table 2: Hydrogenation of Olefins by $(E_{12}PPh_2)_2Rh^+$ (A) and $(E_{12}BzPPh_2)_2Rh^+$ (B) Complexes

Homogeneous Solutions: Water

Catalyst[a]	Substrate	Time	Turnover No.
$(E_{12}PPh_2)_2Rh^{+}$[b]	maleic acid	15 hrs.	100[c]
A	allyl alcohol	6 hrs.	140
B	allyl alcohol	6 hrs.	350
Homogeneous Solutions: Acetone			
A	allyl alcohol	6 hrs.	320
		15 hrs.	640
B	allyl alcohol	6 hrs.	420
		15 hrs.	1000
A	cyclohexene	6 hrs.	100
B		6 hrs.	300
$(E_{12}BzPPh_2)_2RhCl$		6 hrs.	460
Homogeneous Solutions: Toluene			
A	cyclohexene	6 hrs.	80
B		6 hrs.	400
Heterogeneous Systems: Water/Cyclohexene[d]			
A	cyclohexene	6 hrs.	20
B		6 hrs.	50
$(E_{12}BzPPh_2)_2RhCl$		6 hrs.	30

[a] 1.6 μM in Rh, 1.6 mM in substrate

[b] 43.4 mol Rh in 5 cc of water

[c] 4.35 mmol of maleic acid, quantitative hydrogenation

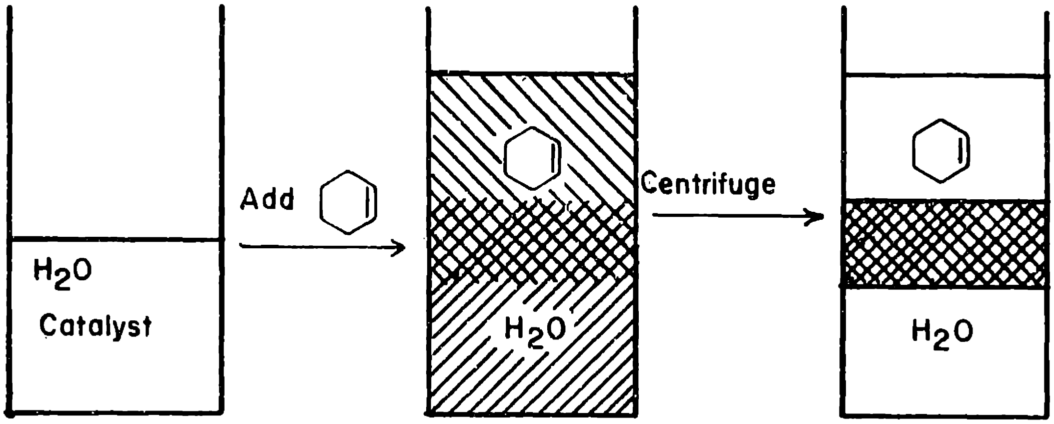
[d] 1.6 μM in Rh, 1 mL of cyclohexene (1000/Rh), 5 mL of water

as 1-hexene and 1-decene were both isomerized. Turnover numbers for binary phase hydrogenations are much lower than the corresponding homogeneous systems, the best results being about 100 turnovers in 6 hours for an $E_{12}BzPPh_2$ catalyst. This sharp decrease in rate will be discussed later.

The vital question for Surfactant Catalysis is whether active catalyst can be recovered. We were unable to address this question in as thorough a manner as we would have liked because the low activity of the two-phase systems and the sensitive nature of the catalyst made it very difficult to show that specific activities were conserved in any experiment that involved transferring material. Very few systems maintained a constant level of activity, or even showed a generally predictable decline in activity, so the total activity expected in a system after a transfer or separation was not comparable to the total activity found. The origin of the discrepancy could not be assessed. The situation was complicated by the appearance of a third phase. Cyclohexene is a known cloudpoint depressant[28,29] for non-ionic surfactants, and addition of cyclohexene to a solution of surfactant catalyst in water resulted in an emulsion, which could be broken by means of centrifugation into three phases (Figure 3). The interface consisted mostly of surfactant with some trapped water and olefin.

In light of the above problems we chose to assay the activities of the three phases by decanting them and measuring the relative rates of hydrogenation of an added aliquot of

Figure 3: Separation of a Surfactant Catalysis System into Three Phases



allyl alcohol. Two additional problems were encountered with this assay. Because of possible solvent effects it was difficult to interpret the results (Table 3). While experiments dealing only with transferred activity are not satisfying, they are the best that can be obtained at present. The rhodium concentration (or for that matter the form of the rhodium) was unknown and the low initial activities raised the possibility that rhodium might be inactive in one phase of a heterogeneous system but regain activity under the homogeneous conditions of the assay. It was also considered possible for permanently deactivated rhodium to collect in one phase. The unknown nature of the variety of rhodium species made rhodium concentration data of limited use and the unpredictable solvent effects in the assay rendered evaluation of the innate and transferred activity in each phase a very

Table 3: Distribution of Catalytic Activity in Multiphase Systems

Experiment 1: Determination of the Activity Distribution in a System Containing 100 μmol of $(E_{12}PPh_2)_2Rh^+$, 5 mL of Water and 5 mL of Cyclohexene.

	% Activity[a]		
Time	Cyclohexene (2.5 mL)	Interface (1.25 mL)	Water (5 mL)
4 hrs.	8	66	26
6 hrs.	6	43	51
Differential (4-6 hrs.)	3	19	78

Experiment 2: Determination of the Activity Distribution in a System Containing 100 μmol of $(E_{12}PPh_2)_2Rh^+$, 5 mL of Water and 5 mL of Cyclohexene and in the Extracts of the Interface with Water and Cyclohexene.

% Activity after 18 hrs.[a]				
Cyclohexene (1 mL)	Water (4 mL)	Extracts of the Interface (Original volume, 3 mL)		
		Cyclohexene (0.5 mL)	Water (6 mL)	Interface (0.5 mL)
0	36	0	48	15

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[a] Percent activity means the percent proponol produced in a given separated phase of the total propanol produced in all the phases.

qualitative matter.

For experiment 1 in Table 3, a disproportionate amount of activity seemed to be transferred with the interface. This amount of activity is plausible if we expect that the rhodium-phosphine complex is more likely to be 'desolubilized' by cyclohexene than the free ligand. On the other hand, the interface-allyl alcohol solution might have been a better medium for hydrogenation than water-allyl alcohol. Cyclohexene-allyl alcohol might be a particularly poor medium for homogeneous hydrogenation. Cyclohexene can be hydrogenated neat with $E_{12}PPh_2$-based catalysts with turnover numbers better than binary systems, (Table 6), and allyl alcohol is hydrogenated in wet cyclo<u>hexane</u>.[41] In experiment 2 the interfacial layer was partitioned between fresh water and olefin, stirred, centrifuged, and the three phases separated and assayed for activity along with the original aqueous and organic phases. Here, activity in the cyclohexene phases was not detected and the activity of the aqueous phase, and the interface-derived aqueous phase and the second interface was high. Again a large amount of activity was carried by the interface. While the precision of these experiments was not great, they provided a demonstration that activity could be transferred in the organic-immiscible phases.

We have briefly compared our operating systems with those reported in the literature (Table 4). We have expressed literature values for first- or second-order rate constants in terms of turnover numbers/six hours. While our systems compare

Table 4: Hydrogenation by $(Ph_3P)_3RhCl$ (A), $(Ph_3P)_2Rh^+$ (B), and Ⓟ-Rh[a] (C)

Time = 6 hrs.

Catalyst	Solvent	Substrate	Turnover No.	Ref.
A	benzene	cyclohexene	2880	1
	various		3200-6400	2
B	2-methoxyethanol	1-hexene	21,600	3
	acetone		2,200	3
A	acetone	cyclohexene	570	4
B			210	4
C			80	4
A	benzene	allyl alcohol	1060	5
A	acetone		800	4,5
C			60	4

---

1. F. H. Jardine, J. A. Osborn , and G. Wilkinson, J. Chem. Soc., A, 1968, 1064.

2. A. S. Hussey and Y. Takeuchi, J. Am. Chem. Soc., 91, 672 (1969).

3. R. R. Schrock and J. A. Osborn , J. Am. Chem. Soc., 98, 2134 (1976).

4. This work, 1.6 mM Rh in 5 mL of solvent and 1 mL of substrate.

5. Extrapolated from a shorter run.

[a] 2.9% Rhodium on a 2% divinyl benzene cross-linked polystyrene resin.

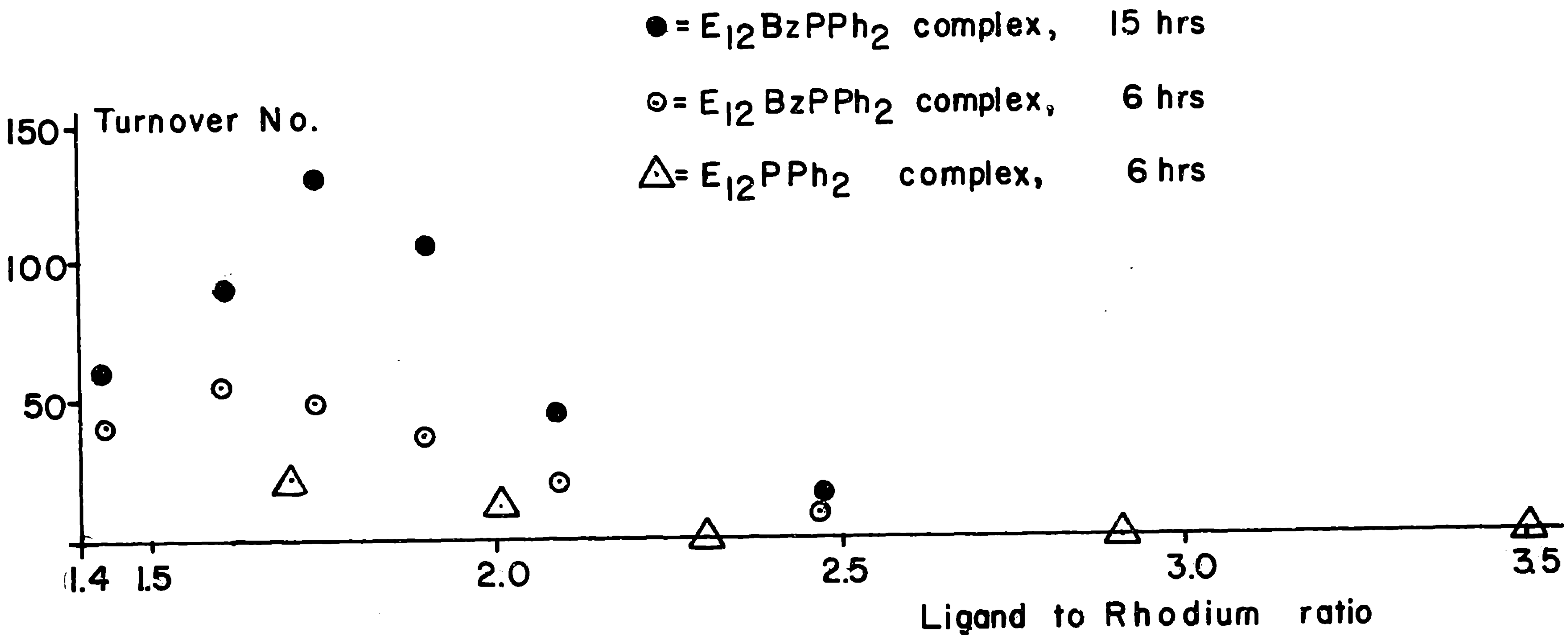
well with our own use of Wilkinson's catalyst,[4] we see at least an order of magnitude difference between our results and the literature. We also see that choice of solvents can considerably affect the performance of a catalyst. We have included some numbers from samples of polystyrene-bound Wilkinson's catalyst. The polymer-bound catalyst was probably not fully activated during our short reaction durations, but the relative values fit well with Grubb's original observations comparing the relative rates of homogeneous and 2% cross-linked polystyrene-bound systems.[5]

Characterization. The ideal criteria for a new method of immobilization of homogeneous catalysts mentioned earlier can be restated as specific questions about polyethylene glycol phosphines and aqueous Surfactant Catalysis: (1) Does the PEG chain exert a major influence on the catalyst? (2) Does water have a major effect on the catalyst? (3) Does the existence of two phases have a major effect on the catalyst?

The Effect of Polyethylene Glycol. One of the first characteristics of rhodium-based hydrogenation catalysts to be discovered was the almost universal requirment that two equivalents of ligand per rhodium be used for maximum catalyst activity and stability.[40] R. B. King found that if a phosphine had attached to it other functional groups such as amines (King examined the triaminephosphine used by Gregorio and Andreeta,[20] as well as the di-, and the monoamine homologues)

Figure 4: Effect of Variation of L/Rh on Catalyst Activity

Hydrogenation of Cyclohexene in Water



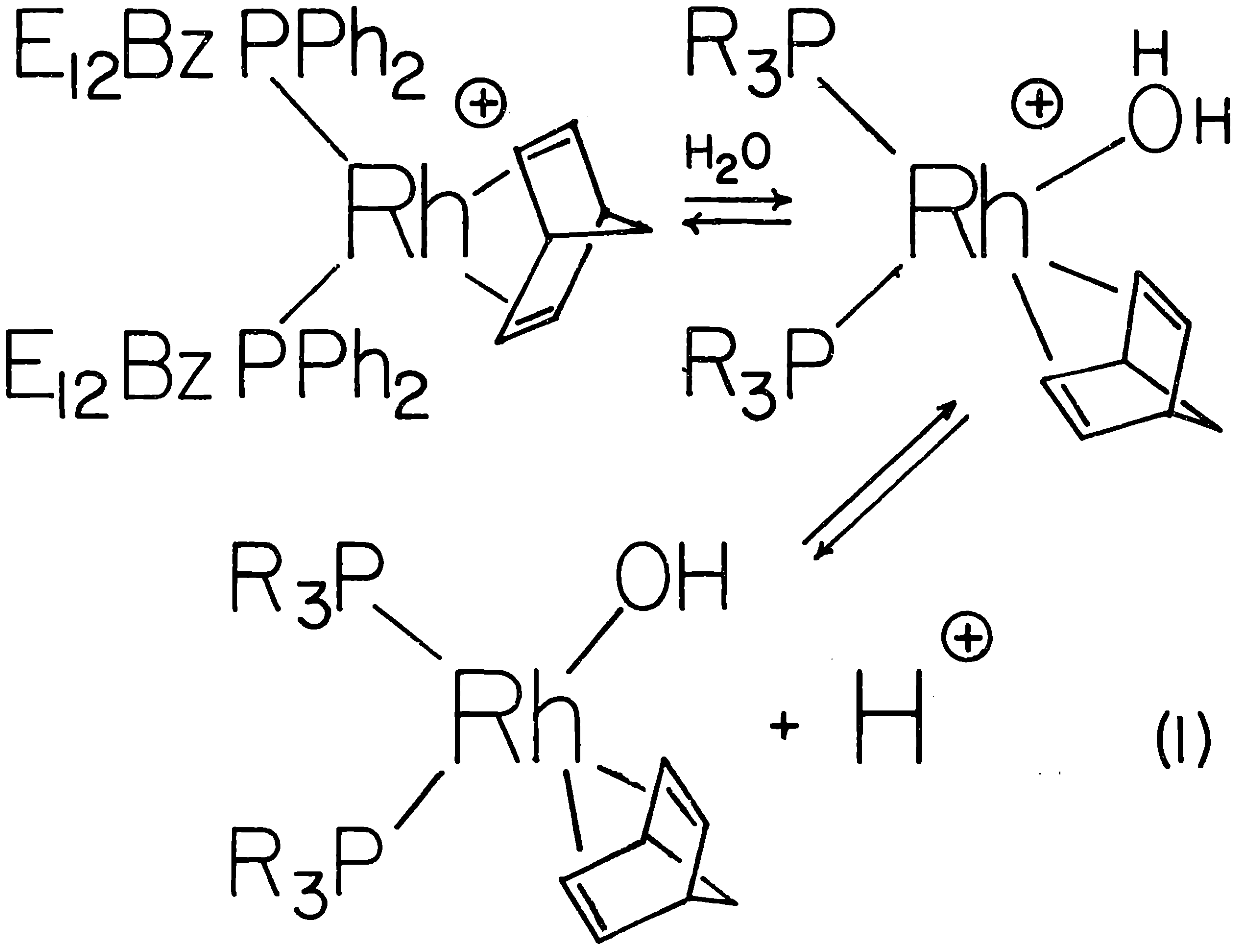
then reduction in the required amount of phosphine occurred accompanied by decreased activity.[21] We investigated the optimum ligand/rhodium ratio for both $E_{12}PPh_2$ and $E_{12}BzPPh_2$. We found that the optimum ratio was slightly less than two in both cases (Figure 4), although the degree to which this was true was unclear because of the uncertainty in the actual amount of useful tert.-phosphine in a given experiment.

Consideration of the structural differences between $E_{12}PPh_2$ and $E_{12}BzPPh_2$ leads to the expectation that catalysis by $E_{12}PPh_2$-rhodium complexes ought to be slower than catalysis by $E_{12}BzPPh_2$ complexes due to chelation. Comparison of activities under a variety of conditions listed in Tables 2 and 6 shows that the $E_{12}PPh_2$ complexes are slower. The relative rate ratio for the two systems holds constant at about three except for the case of allyl alcohol, where it decreases to about 1.3. (One may speculate that this singularity may be due to a rate enhancement for allyl alcohol in non-protic solvents through hydrogen-bonding between the substrate and the polyethylene glycol chain in $E_{12}PPh_2$ complexes but not in $E_{12}BzPPh_2$ complexes. In water the ability of the chain to hydrogen-bond to substrate is limited because of preferential hydrogen-bonding to water, thus restoring the relative rates to norm.) The origin of this difference in rates could lie with the difference in basicities of the phosphines. For example, the cationic-rhodium complexes based on PPh_3, $PPhMe_2$, had relative rates hydrogenation of 1-hexene of 1, 3.6, in 2-methoxy ethanol and PPh_3, PPh_2, and $PPhMe_2$ had relative rates of 0.1, 3.0 and 6.0 in acetone.[38]

From this series one would predict that $E_{12}PPh_2$ ought to generate better catalysts than $E_{12}BzPPh_2$. Whether basicity is responsible for the rate differences is thus unclear. Further evidence for chelation by $E_{12}PPh_2$ will be presented in the following section. The conclusion to be drawn from the rate differences is that the bulk polyethylene glycol does not dominate the chemistry of these catalysts: If complexation by PEG chains did predominate, then the consistent differences in the rates between the two kinds of catalysts should not be observed.

The Effect of Water. Water can act in two fashions beyond solvating Surfactant Catalyst systems: coordination by rhodium as an aquo or a hydroxy ligand. While the first may be expected to be innocuous, the second species, being neutral, would be a departure from the cationic rhodium complexes we started with. The activity of the catalyst for hydrogenation might be unimpaired, but such a change in catalyst charge is a definite departure from the non-immobilized system and therefore Surfactant Catalysis would be less than the desired ideal method of immobilization sought. Examination of the rates of hydrogenation of allyl alcohol by the two catalysts in homogeneous aqueous and acetone solutions showed mixed evidence for any solvent effect of water (Table 2). The $E_{12}BzPPh_2$ complexes seem aloof from rate retardation by water but the $E_{12}PPh_2$ complexes suffer a rate decrease of a factor of three. Similar variations in rate with change in solvents have been observed in strictly organic systems[38,39] and our results are thus not indicative of any unique solvent effect for water. The presence of absence of a hydroxy ligand may not measurably affect the rate of hydrogenation. Other evidence for such a species must be sought.

Table 5 lists the pH values of various aqueous solutions of phosphine, catalyst precursor and activated complexes. $E_{12}BzPPh_2$ systems are acidic <u>prior</u> to activation to the extent of 0.25 to 0.4 equivalents of H^+ per rhodium. $E_{12}PPh_2$ systems remain about neutral. This phenomenon provides inferential evidence that the 4-coordinate $E_{12}BzPPh_2$ complex can and does equilibrate to the 5-coordinate hydroxy complex.



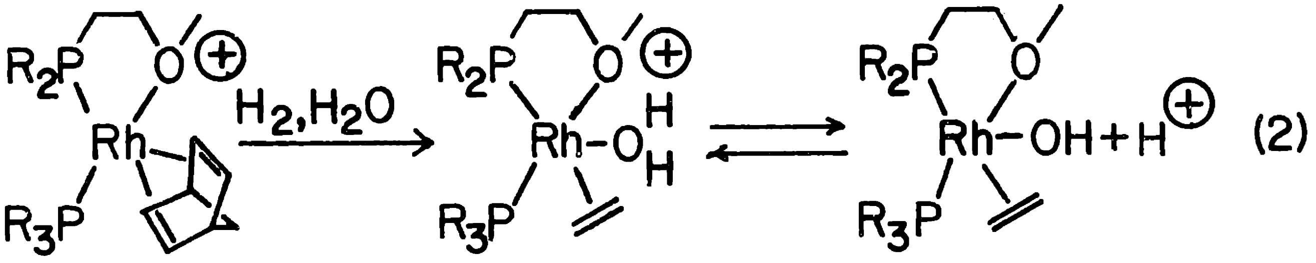
(1)

Table 5: pHs of Aqueous Catalyst Systems

System	pH	Equiv. H^+/Rh
Degassed Water	6.9	
20 mM $E_{12}BzPPh_2$	4.3	
$(E_{12}BzPPh_2)_2Rh^+$ (rxn mixtures, 1.6 mM in Rh)	2.6-3.2	1.2-0.3
$(E_{12}PPh_2)_2Rh^+$ 1.6 mM	3.1	0.4
$(E_{12}BzPPh_2)_2Rh(norbornadiene)^+$ ClO_4	3.1[a]	0.4
$(E_{12}BzPPh_2)_2Rh^+$ (above entry after exposure to H_2)	3.1[a]	0.4
$(E_{12}PPh_2)_2Rh(norbornadiene)^+$ ClO_4	5.3[a]	
$(E_{12}PPh_2)_2Rh^+$ (above entry after exposure to H_2)	3.1[a]	0.4
$(E_{12}BzPPh_2)_2Rh(norbornadiene)^+$ ClO_4^- 16 mM	2.3	0.25
$(E_{12}BzPPh_2)_2Rh^+$ (above mixture after exposure to H_2)	2.3	0.25

[a] 1.6 mM in Rh

This equilibrium might be blocked by chelation with a proximal



ether in an already 5-coordinate $(E_{12}PPh_2)_2Rh(norbornadiene)^+$ ClO_4^- complex (equation 2). The pH of a solution of the $E_{12}BzPPh_2$ complex does not change on introduction of H_2 while the pH of the $E_{12}PPh_2$ complex drops to similar values to those observed for the $E_{12}BzPPh_2$ complex before H_2. Schrock and Osborne[39] have identified two distinct catalytic species arising from cationic rhodium (1) complexes:

$$\underset{\underline{A}}{L_nRhS_mH_2^+} \rightleftharpoons \underset{\underline{B}}{L_nRhS_mH} + H^+ \qquad (3)$$

Species B was presumed to be a powerful hydrogenation catalyst and an even more powerful isomerization catalyst. Species A was less active than B as a hydrogenation catalyst and nearly inactive as an isomerization catalyst. Added base (triethylamine) drove the equilibrium to the right and resulted in predominant isomerization. Added acid (70% aqueous $HClO_4$) resulted in hydrogenation without isomerization. Because 70%

aqueous $HClO_4$ contains two equivalents of water per mole of acid, the question of whether a hydroxy complex was formed arises. 2-Methoxyethanol was found to be a solvent in which cationic rhodium complexes were very active, and the possibility of alkoxy complexes being formed here exists. Wilkinson's Catalyst[4] ($(Ph_3P)_3RhCl$) is a powerful non-isomerizing hydrogenation catalyst. It is conceivable that the hydroxy or alkoxy analogues of Wilkinson's complex might have similar properties. We have observed that our catalysts isomerize 1-olefins in aqueous binary media. However, isomerization could be due to cationic rhodium (I) complexes. No subsequent changes in pH are noted as the reactions progress, therefore the participation of the equilibrium in equation 3 cannot be assessed. These brief observations show that homogeneous aqueous systems have important differences from their homogeneous organic counterparts; thus direct transfer of properties may be the exception rather than the rule. It should be noted at this point that failure to directly transfer properties does not mean that satisfactory properties cannot be obtained.

Two-Phase Systems. Two problems of major concern with two-phase water/olefin systems are: (1) Where does catalytic activity lie? and (2) Why do we see a consistent decrease in rate for two-phase systems in contrast to homogeneous systems? The question of location is important because a true surfactant catalyst could be a useful model system for the growing area of surface chemistry. The origin of the decrease in hydrogenation rate is of importance to the practicality of Surfactant Catalysis. Unfortunately, the answers we can provide at this time are, at best, educated guesses. In the following discussion we will make some assumptions. First, the questions of catalyst location and catalyst activity are interrelated. An explanation of one must fit both. Second, the explanation, whatever it is, will not require two or more coincident effects. Third, the essential chemistry of our two catalyst systems is the same and both ought to respond to changes in about the same way. These assumptions are of course dangerous. However, in the absence of any data to contradict them, they will be used as the basis for the following discussion.

(1) The location of catalytic activity. In order to attack this question, we must make one temporary assumption: that catalytic activity has one predominant location. Without (for the moment) considering the effects of the appearance of the third (that is, interfacial) phase, we can postulate that the catalyst will act in a homogeneous organic phase (cyclohexene), or in a homogeneous aqueous phase, or at an interface between the phases. We can eliminate both cases of homogeneous activity.

If the catalyst acted only in a homogeneous cyclohexene phase then the rates for a two-phase system ought to be the same as those for neat cyclohexene. For both catalyst systems however, the rates are lower, and by roughly the same factor of three to four (Table 6). Although factors of three and four are not normally considered significant variances, the comparison between homogeneous organic and two-phase systems is a thoroughly reproducible one, and the difference appears real. The lowered activity might be explained by supposing that some amount of catalyst resides in the organic phase, with the catalyst at the interface and in the aqueous phase being dormant. The negligible activity transferred in the organic phase (Table 3) makes this explanation implausible, but better experiments are needed to prove this point. The experiments listed in Table 3 were designed to show that large amounts of activity could be manipulated away from a second-phase substrate. They were not designed to show the presence of a small amount of activity in the organic phase. The difference between the maximum activity observed in the organic phase (8%) and amount needed to give the rates of catalysis observed in two-phase systems (Table 6) (20-25%) is only a factor of three. Tentatively we accept this factor as real, and conclude that activity is not located principally in a homogeneous organic phase.

A similar argument applies to homogeneous catalysis in the aqueous phase. Homogeneous catalysis in the aqueous phase can be viewed in two fashions, one which involves an equilibrium argument and one which invokes kinetics. It can easily be demonstrated that there is insufficient cyclohexene dissolved in the aqueous phase of a two-phase system to support the observed rate of reaction.

Table 6: Comparison of the Rates of Hydrogenation of Cyclohexene by $(E_{12}PPh_2)_2Rh^+$ (A) and $(E_{12}BzPPh_2)_2Rh^+$ (B) in Homogeneous and Heterogeneous Systems

Medium	Catalyst[a]	No. of Phases	Turnover No. (6 hrs.)
5 mL of toluene and 1 mL of cyclohexene	A B	1 1	80 400
4 mL of toluene, 4 mL of water and 1 mL of cyclohexene	A B	2 2	12 68
5 mL of cyclohexene	A B	1 1	60 210
5 mL of water and 1 mL of cyclohexene	A B	2 2	17 48
0.5 mL of water and 1 mL of cyclohexene	B	3	56
1.0 mL of water and 1 mL of cyclohexene	B	3	48
5.0 mL of water and 1 mL of cyclohexene	B	3	38
10.0 mL of water and 1 mL of cyclohexene	B	3	55
5 mL of acetone and 1 mL of cyclohexene	A B	1 1	100 300
4 mL of acetone and 1 mL of water and 1 mL of cyclohexene	B	2	280
3 mL of acetone and 2 mL of water and 1 mL of cyclohexene	B	?	214
2 mL of acetone and 3 mL of water and 1 mL of cyclohexene	B	3	71
1 mL of acetone and 4 mL of water and 1 mL of cyclohexene	B	3	62
5 mL of water and 1 mL of cyclohexene	B	3	54

[a] 10 μmol of rhodium

Cyclohexene is soluble in pure water to the extent of 2 μM,[42] and the measured solubility of cyclohexene in our systems is 1 mM. The maximum predicted solubility of cyclohexene in water using a good PEG-surfactant in similar concentration is 5 mM.[28,29] Homogeneous catalysts are normally run at substrate concentrations of about 1 M.[40] Wilkinson found[4] that the rate of hydrogenation of 1-heptene, among other olefins, was linear with a slope of 1 up to a 1-heptene concentration of 1 M and leveled off slowly as the concentration increased to 2.5 M. Our reactions were run in homogeneous media at about 1.6 M, 1000 times the concentration of cyclohexene found in the aqueous phases of two-phase systems. One would expect then that the rates of hydrogenation in two-phase systems should be 1000-times slower than homogeneous systems if the reactions were taking place in a homogeneous aqueous medium. Since the rate decrease is, at most, a factor of 10, it is unlikely that catalyst dissolved in water is hydrogenating cyclohexene dissolved in water. It is possible, however, that cyclohexene is hydrogenated as fast as it diffuses into the aqueous phase. If diffusion of cyclohexene is the rate limiting step, then both of the catalyst systems should have the same rates in two-phase systems. As can be seen in Table 6, the relative rates of the two catalysts are unaffected by the choice of solvent system, and whether the system has one or two phases. One expects that a pair of reactions whose rates are different will aquire identical rates as diffusion becomes the rate-limiting step due to experimental modifications. Table 6 provides no evidence that the rates of reaction are converging. Thus, neither diffusion of cyclohexene nor equilibrium concentrations of cyclohexene provide a basis for the aqueous phase being the primary location of catalysis in two-phase systems.

Having ruled out the two homogeneous phases we are left with the catalyst acting at the interface. Two further pieces of evidence support this hypothesis: (1) The rate of hydrogenation seems to be independent of olefin concentration in the organic phase (Table 6). The concentration of neat cyclohexene was 10 M, the concentration of cyclohexene in toluene, 2 M. Although the response of rate to changes in concentration of olefin above 1 M is less than directly proportional,[4] we would still expect to see some decrease in rate associated with the change in cyclohexene concentration. (2) The rate of hydrogenation seems to be independent of concentration of catalyst in the aqueous phase (Table 6). Variation of the volume of water from 0.5 to 10 mL while holding the amount of rhodium and cyclohexene constant did not significantly affect the turnover number after 6 hours. Granted that the catalysts operate at an interface, what sort of interface do they operate at?

One kind of interface that might be involved would be micellular; that is, a monolayer of surfactant-catalyst molecules surrounding a droplet of cyclohexene in water. Neither the appearance of the system nor some simple calculations support this model. Micellular emulsions are generally stable,[28,29] that is, separation of the emulsion takes place, if at all, over a period of months. The surfactant catalyst emulsions spontaneously separate in minutes. Further, the emulsions, even when stirred contain macroscopic particles. Simple calculations based on estimated sizes of catalyst molecules imply that the minimum and maximum areas for a monolayer coverage by our catalysts is between 1.5×10^{4} cM^{2} and 12×10^{4} cM^{2}. These areas require dispersal of 1 mL of cyclohexene into 10^{15} particles 20-200 Å in diameter. The appearance of many macroscopic particles would seem to exclude this possibility.

Another option is location of some of the catalyst at the interface, operating at a normal rate while the balance of the catalyst lies dormant in the aqueous phase. Alternatively, all of the catalyst could be loosely organized in multilayers around the interface, and the activity of all the catalyst molecules regulated by a reduced apparent concentration of cyclohexene at the interface. Both of these hypotheses are compatible with the observed appearance of a third insoluble phase at the interface of a "two-phase" system. We believe the former hypothesis to be correct because activity was transferred by both the aqueous and interfacial phases, suggesting that considerable amounts of potentially active catalyst reside away from the interface. Regan has recently demonstrated "tri-phase" catalysis.[36] A polyethylene glycol-grafted polystyrene resin was found to catalyze the aqueous solvolysis of 1-bromoadamantane. The kinetics of this three phase system (water, resin, and 1-bromoadamantane) were independent of stirring rate. If surfactant catalysts are really tri-phase catalysts then two results can be expected· (1) The surfactant catalyst systems should also be independent of the rate of stirring. (2) The rate of hydrogenation would be expected to be proportional to the amount of catalyst in the interfacial phase and efforts to increase this amount should lead to increased rates of hydrogenation in "two-phase" systems.

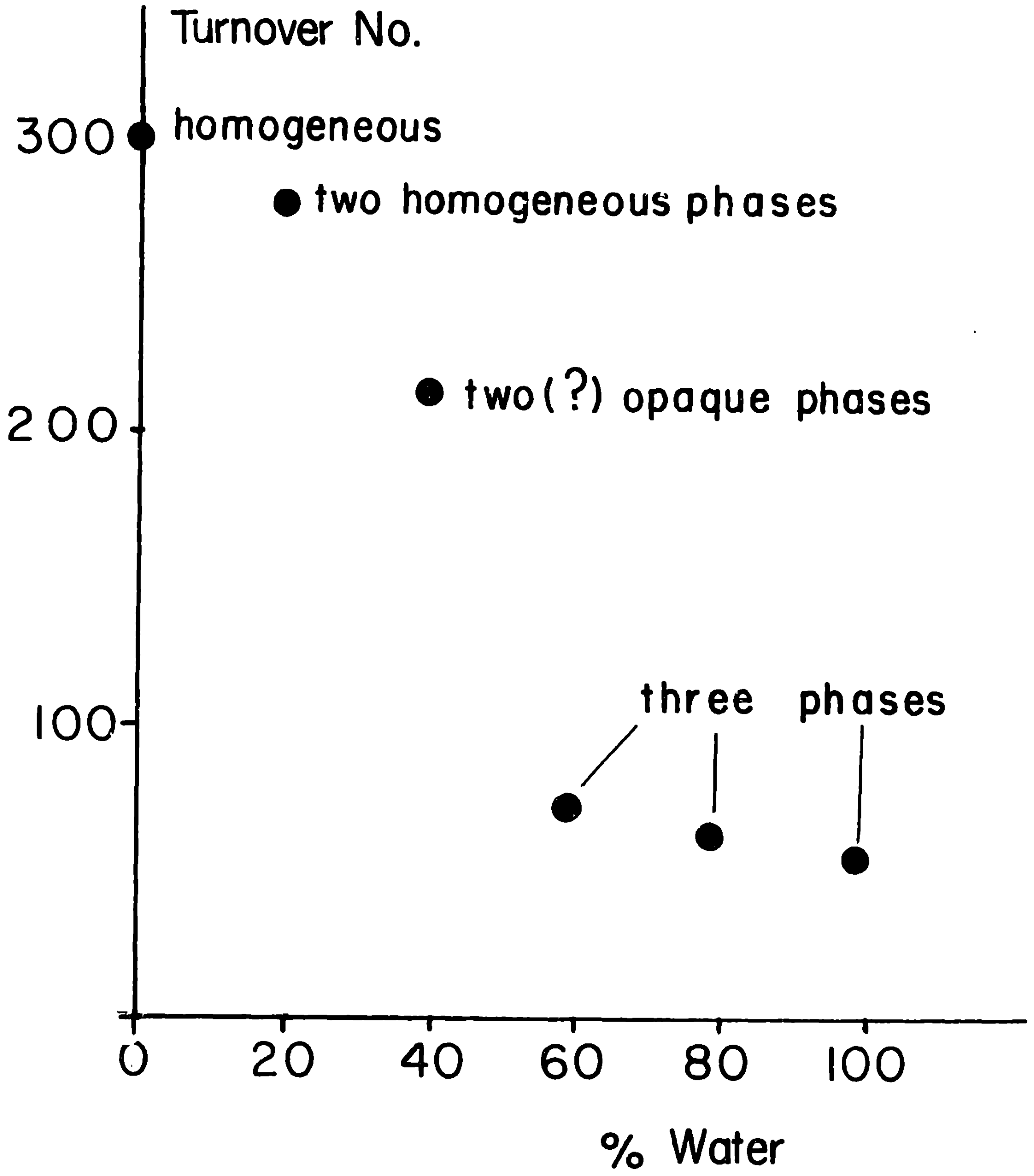
(2) Origin of the rate decrease. In discussing the location of catalytic activity we made use of the decrease in rate from homogeneous to two-phase systems. To claim that we see this decrease because the catalysis takes place at the interface would be an example of circular logic, although it is reasonable to expect the phenomena to be in fact related in causal fashion.

We can hope to bring some independent observations to the question of the origin of the rate decrease. We have already established in discussing the location of catalyst activity that a change to diffusion as the rate limiting step is not the case. It is possible that solvent effects (such as are observed for homogeneous systems, when switching from THF to acetone) are responsible for the drop in rate. (Admittedly, defining such a thing as a solvent effect for a two-phase system is difficult. What we mean by solvent effect here is that if cyclohexene and water were miscible the rate decrease would still be observed.) There is a paucity of data on whether water does in general exhibit a solvent effect compared to acetone. Collecting these data posed more complex problems than could be quickly solved. The choice of olefins which are water soluble and useful in a screening program is limited. The inclusion of organic acids, especially acrylic acids raises the question of the effect of aqueous pH. We believe however, that the results for homogeneous hydrogenation of allyl alcohol by $E_{12}BzPPh_2$-rhodium complexes in water and acetone (Table 2) indicate that a solvent effect is not necessarily present. The constancy of relative rates of catalyst systems A and B in Table 6 argues against a solvent effect. A solvent effect would not be expected to alter both catalyst's rates equally. Published data support this contention: Schrock and Osborn found in the hydrogenation of 1-hexene that catalysts based on cationic-rhodium complexes of Ph_3P turned over ten times faster in 2-methoxyethanol than in acetone; complexes using $PhPMe_2$ turned over only twice as fast.[39]

One approach to ruling out a solvent effect and establishing that the multiplicity of phases creates substrate and catalyst concentration differences would be to investigate the rate of hydrogenation as a function of water concentration in mixed solvent systems. We would expect that in totally homogeneous systems rate would be a continuous function of solvent composition. As a system became heterogeneous, as a result of increased water concentration, a discontinuity in this function would be expected. Discontinuity would not in this case disprove a solvent effect, since catalyst activity could be located in a phase with a discontinuously increased water concentration. However, if it could be established for a homogeneous system that small variations in composition in predominantly aqueous systems gave variation in rate, and if the rate of hydrogenation in a discontinuous two-phase system did not show variation in the rate away from the discontinuity, then a solvent effect could be ruled out. Figure 5 shows a preliminary experiment testing this approach (the results are listed in Table 6 also). Use of pure acetone as a solvent (5 mL) and 1 mL of cyclohexene gave a clear homogeneous solution and maximal activity. In 80% acetone: 20% water with 1 mL of cyclohexene two clear immiscible liquid phases were present; no major drop in activity was observed. A 60/40 mixture was opaque and had an indeterminate number of phases; the decrease in activity was significant. For the remaining three concentrations, 40/60, 20/80, and 100% water, three phases were present and the rates were all near those already found in water/cyclohexene systems.

These results suggest that the appearance of the third phase is associated with the drop in rate. A two-phase system was found to be very active. On the other hand, the two-phase system could have had catalyst located in both phases. It is clear that this sort of experiment will have to be done in association with experiments showing the location of activity as a function of solvent composition. While all the evidence accumulated thus far supports the use of

Figure: Hydrogenation of Cyclohexene in Mixed Solvent Systems by $(E_{12}BzPPh_2)_2Rh^+$


Turnover No.
300
200
100
homogeneous
two homogeneous phases
two(?) opaque phases
three phases
0
20
40
60
80
100
% Water

Regan's "tri-phase catalysis" as a model for two-phase Surfactant Catalysis, both for explaining the location of the catalyst and the reason for the decrease in rate, a number of experiments need to be done before these questions are settled.

Conclusions

In this work we have developed easy preparations for water-soluble phosphines. These phosphines are the first water-soluble phosphines which are genuinely useful as ligands for homogeneous catalysis in aqueous systems. Preliminary evidence was obtained for the existence of significant phosphine-transition metal complex chemistry in aqueous systems which differs in non-trivial ways from chemistry in other solvents. Aqueous solutions of water-soluble phosphine complexes proved to be hydrogenation catalysts for water-immiscible olefins, supporting the use of liquid-liquid systems as a means of catalyst immobilization. Evidence was found that the catalysts in these systems act at the interface between the aqueous phase and the organic phase.

Experimental Section

Synthetic Methods. Chemicals were purchased from the following sources: Polyethylene glycol monomethyl ethers (Polysciences Inc.); p-bromobenzyl bromide, cyclohexene, allyl alcohol, maleic acid, triphenylphosphine, chlorodiphenylphosphine (Aldrich); silver perchlorate, butyllithium (Alfa); norbornadienylrhodium chloride and polymer-bound Wilkinson's catalyst (2% cross-linked polystyrene-divinylbenzene copolymer, 2.9% Rh) (Strem Chemical Co.). Diphenylphosphine was prepared from triphenylphosphine by the action of lithium aluminum hydride,[32] isolated by distillation (bp 95-98° at 0.07 torr) and stored in a Schlenck tube. Tetrahydrofuran was distilled from idsodium benzophenone dianion under argon and stored in a Schlenck tube. Proton nmr were taken on either a Perkin-Elmer R-20 or a Varian T-60 spectrometer. Phosphorus nmr spectra were taken on a modified[44] Brucker 90-HX spectrometer with proton decoupling. pH measurements were made using a Sensorex Inc. S200C combination pH electrode and an Instrumentation Laboratory Inc. Model 165 pH meter. Elemental analyses were performed by Robertson Laboratories, Florham Park, N.J.

Catalytic Methods. An all-metal gas line was constructed of copper and brass pieces. Coils of 1/8" copper tubing extended from the manifold to needle valves which were connected to Luer-lock adapters fitted with stainless steel needles (22 gauge, 4"). Welding grade hydrogen (less than 1 ppm 0_2) and argon (less than 1 ppm 0_2) were used without further effort to remove 0_2. Water was drawn from a polyethylene reservoir of deionized water distilled using a Corning model Ag-1b glass still and degassed by bubbling argon through it for two hours. Reagent grade acetone and toluene were purified by passage through alumina and distillation from triphenylphosphine under argon and stored in a Schlenck tube. Cyclohexene and allyl alcohol were purified in a similar manner, but fresh material was distilled before each use, and a trace of dicyclooctenyl rhodium chloride or tris-triphenylphosphine rhodium chloride was added to the still pot to act as an additional scavenger for catalyst poisons. Maleic acid was used as received.

Hydrogenations were carried out in reaction vessels ("thimbles") fashioned from 19/38 female ground glass joints sealed off immediately after the ground glass, fitted with Teflon-coated magnetic stirring bars and sealed with securely wired 19/38 No-Air stoppers. Argon and hydrogen were admitted into the thimbles through the stainless steel needles described above, and reagents, solvents and catalysts were added, and samples removed using syringe and cannula techniques. After each use the thimbles and stirring bars were soaked in chromic acid cleaning solution, rinsed in water, in a 10% solution of ammonium hydroxide in water, water and acetone. Further details will be supplied under the heading of <u>Catalyst Preparation and Hydrogenation</u>.

Analytical Methods. Analysis of reaction mixtures containing cyclohexane and cyclohexene was performed on a 12 ft. 25% $AgNO_3$ in tetraethylene glycol impregnated 80-90 mesh Chromosorb W(AW) column, and mixtures containing allyl alcohol and 1-proponol were analyzed on a 10 ft. 10% 20 M Carbowax on Chromosorb W column. Nonane was used as an internal standard for cyclohexene reaction mixtures and 1-butanol for allyl alcohol reaction mixtures. Gas chromatography was performed on Perkin-Elmer 990 or 3920 instruments equipped with flame ionization detectors. Peak integration was performed by an Auto Lab Minigrater. Analysis of mixtures of maleic and succinic acids was performed using an HPLC system consisting of a Waters 1000 pump, a Watman Partisil 10-SAX column, and Waters differential refractance and UV (254 nm) detectors. An aqueous buffer solution (10 mM $NaHSO_4$, pH adjusted to 2.84 using sulfuric acid) served as the mobile phase. Typical flow rates were 1.9 mL/min.

$E_{12}Cl$. $Me(OCH_2CH_2)_{12}OH$ (59 g, 0.107 mol, avg. mol wt. 550) was dissolved in pyridine from a freshly opened bottle (100 mL). Thionyl chloride (10 mL, 0.14 mol) was added dropwise over 10 min. to the rapidly stirred mixture. After an initial exothermic reaction had ceased, the mixture was heated at 70°, poured cautiously while still hot into ether (500 mL), and the ether decanted from an insoluble residue. The residue was extracted with ether (1.5 L). The combined ethereal solutions were neutralized by stirring with 10 mL of a saturated aqueous solution of $NaHCO_3$, and an additional 20 g of $NaHCO_3$ until the evolution of carbon dioxide ceased (2-4 hrs.). Filtration, evaporation and heating at 170° for 1 hr. at 0.05 torr gave a clear brown oil. The oil was taken up in 200 mL of ether and refluxed with 5 g of activated charcoal for 10 min. On filtration, white crystals formed in the receiving flask. These crystals were collected, dissolved in methylene chloride and passed through a short column (40 g) of Woelm activity grade I neutral alumina. Evaporation at reduced pressure gave a white oil (20.8 g, 31%).

Characterization of this oil proved difficult. Because of the hygroscopic nature of the oil, and the low visibility of a hydroxyl stretch in the ir spectrum of $E_{12}OH$, ir was useless as a measure of chlorination. NMR was equally useless as the hydroxyl proton could not be observed in $E_{12}OH$, nor could $C\underline{H}_2Cl$ or $C\underline{H}_2OH$ be distinguished against the large $-OC\underline{H}_2C\underline{H}_2O-$ signal. Rather than wait for elemental analysis, the material was used to good effect in the following reaction as if it were 100% pure. Subsequent elemental analysis showed that 89% of the theoretical amount of chloride was incoporated.

Anal. Calcd. for $C_{25}H_{51}ClO_{12}$: C, 51.84; H, 8.89; Cl, 6.12. Found: C, 51. 07; H, 8.78; Cl, 5.46.

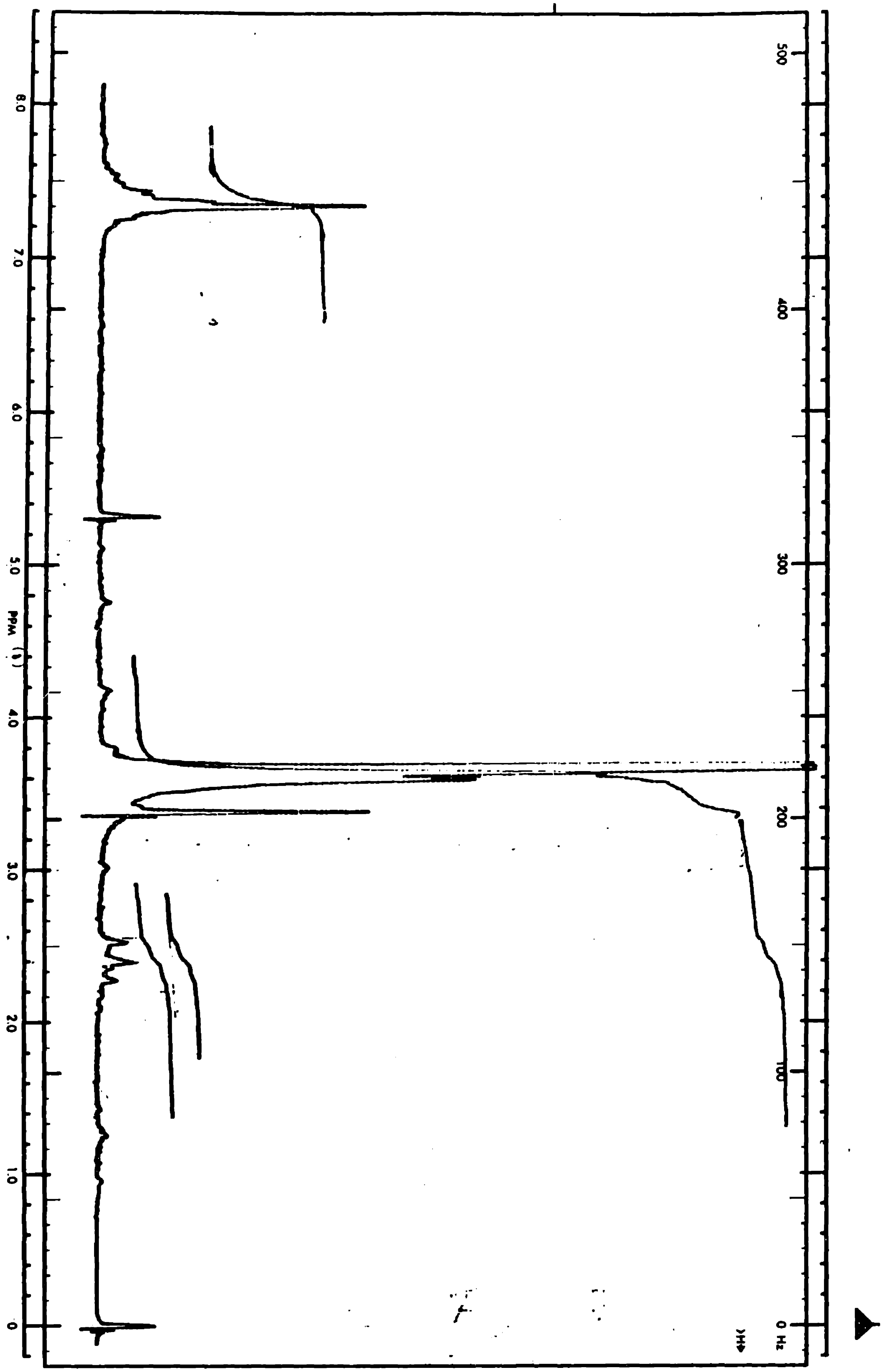
$\underline{E_{12}PPh_2}$. Diphenylphosphine (ca. 3.5 mL, 3.73 g, 0.020 mol) was transferred from a storage tube by means of a syringe to a tared, flame-dried, argon-purged 25 mL round-bottomed flask fitted with a septum stopper and a magnetic stirring bar.

After determining the exact weight of the phosphine, THF (10 mL) was added by means of a syringe, and the solution was transferred by forced syphon through a stainless steel cannula into a previously prepared suspension of potassium hydride (5 g, excess) in THF (20 mL). $E_{12}Cl$ (12 g, 0.021 mol) was added as a solution in THF (30 mL) dropwise over 1 hr. to the deep red solution of $KPPh_2$ and stirred a further 0.5 hr. after the addition was complete. The faded (orange) solution was quenched with water (2 mL), poured into 500 mL of ether, filtered, passed through about 100 g of neutral Woelm activity grade I alumina, and crystallized at -70° from ether, giving in three batches (totaling 11 g, 75%) a pale yellow oil at room temperature (after evaporation of entrapped ether at reduced pressure). Elemental analysis of this oil indicated the presence of significant levels of impurities:

Anal. Calcd. for $C_{37}H_{61}O_{12}P$: C, 61.06; H, 8.46; P, 4.30. Found: C, 60.50; H, 8.45; P, 3.06.

^1H nmr spectroscopy (Figure 6) indicated that a carbon-phosphorus bond had been formed by the appearance of a new signal at 2.37 δ as a triplet characteristic of $PC\underline{H}_2CH_2$, J = 7 Hz. The area ratio of these protons to the aromatic protons (δ = 7.35) from $\underline{Ph}_2P$ was 0.19, as compared to an expected value of 0.20. The ratio of the $PC\underline{H}_2$ protons to the PEG protons ($\delta = 3.5$ $OC\underline{H}_2$, δ = 3.38, $OC\underline{H}_2$) was 0.036 as compared to an expected value of 0.039. ^{31}P nmr was carried out in both acetone and water. A peak at 23.84 ppm (downfield from external 85% H_3PO_4 in water) in acetone and a peak at 22.96 ppm

Figure 6: $E_{12}PPh_2$- ^1H NMR Spectra


8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0
500
400
300
200
100
0 Hz

in water were assigned to ROCHCH$_2$ ^{31}PPh$_2$.[45] Integration of the total ^{31}P spectrum showed this resonance to have an intensity of 94%. Using the weight percent phosphorus from elemental analysis and the fraction of ROCH$_2$CH$_2$ ^{31}PPh$_2$ identified by P nmr spectroscopy a purity 67% was computed. Other samples prepared using analogous procedures had purities by this criterion ranging from 50-70%. A ^{31}P spectra shown in Figure 7, has various amounts of unidentified phosphorous containing impurities. The ^{31}P spectrum shown in Figure 8 is of the same solution after standing 3 weeks, and is unchanged.

E$_{12}$BzBr. Potassium hydride (21.7 g of a 22.1% suspension in mineral oil, 0.12 mol) was washed free of mineral oil with three 20-mL portions of reagent grade pentane, taken up in 30 mL of THF, and added to a solution of p-bromobenzyl bromide (25 g, 0.10 mol) in THF (500 mL). The mixture was refluxed and E$_{12}$OH (55 g, 0.10 mol) added. The solution was refluxed 16 hrs., cooled, filtered, and evaporated to a brown oil. This oil was taken up in CH$_2$Cl$_2$, treated with decolorizing charcoal (3 g), passed through 50 g of neutral activity grade I Woelm alumina and evaporated at reduced pressure to a light yellow oil (72 g, 80%).

This material was characterized by nmr (Figure 11). The benzyl position was clearly 100% ether linked. nmr (CDCl$_3$): TMS 7.37 (q, 40); 4.50 (s, 2), 33.68 (s, broad, 58); 3.37 (s, 3). The oil was used without purification in the next step.

Figure 7: $E_{12}PPh_2$- ^{31}P NMR Spectrum

Peak	PPM	%
1	-10.96	4.5
2	-12.17	2.6
3	-21.05	5.7
4	-22.81	86.1

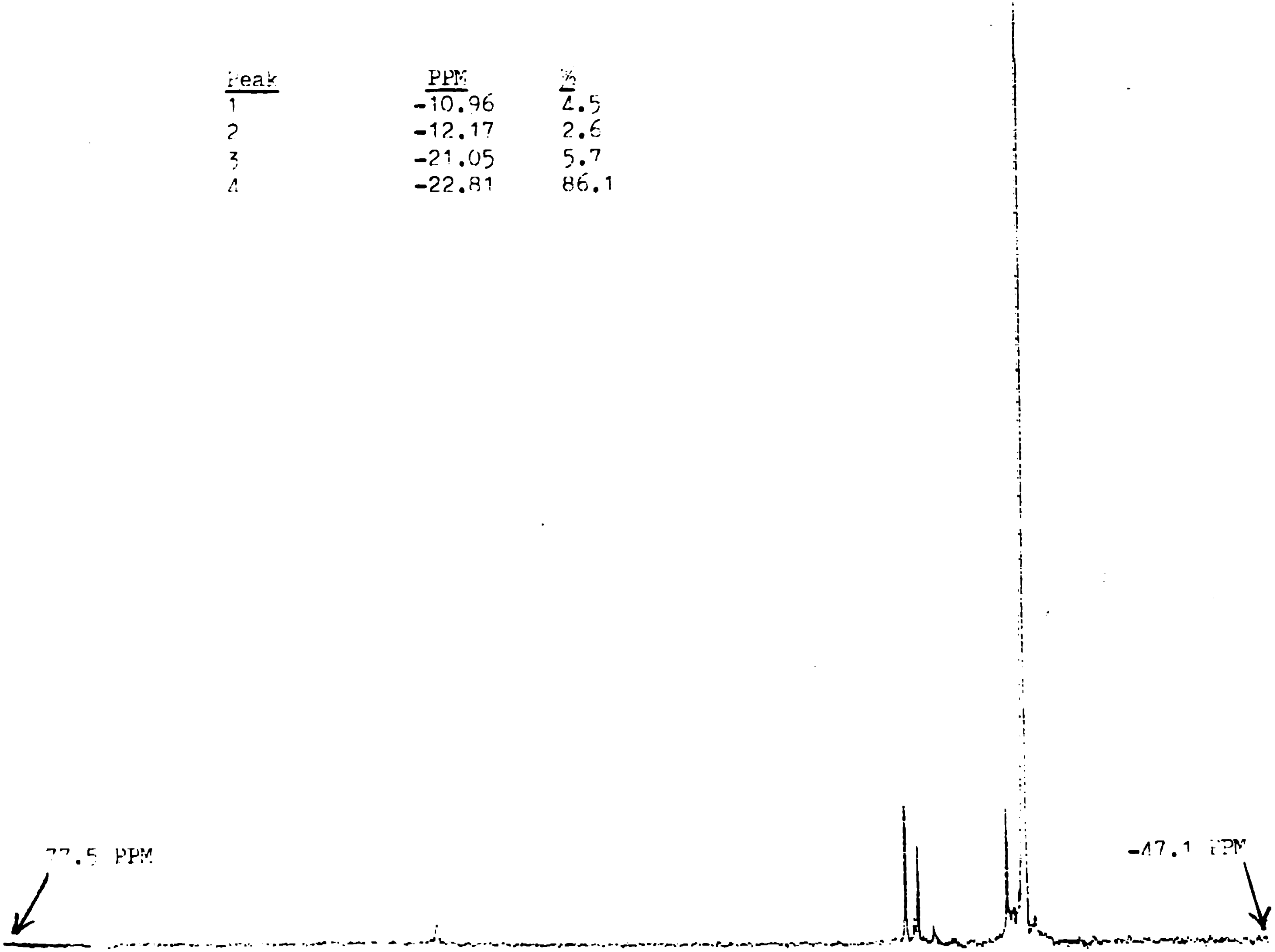
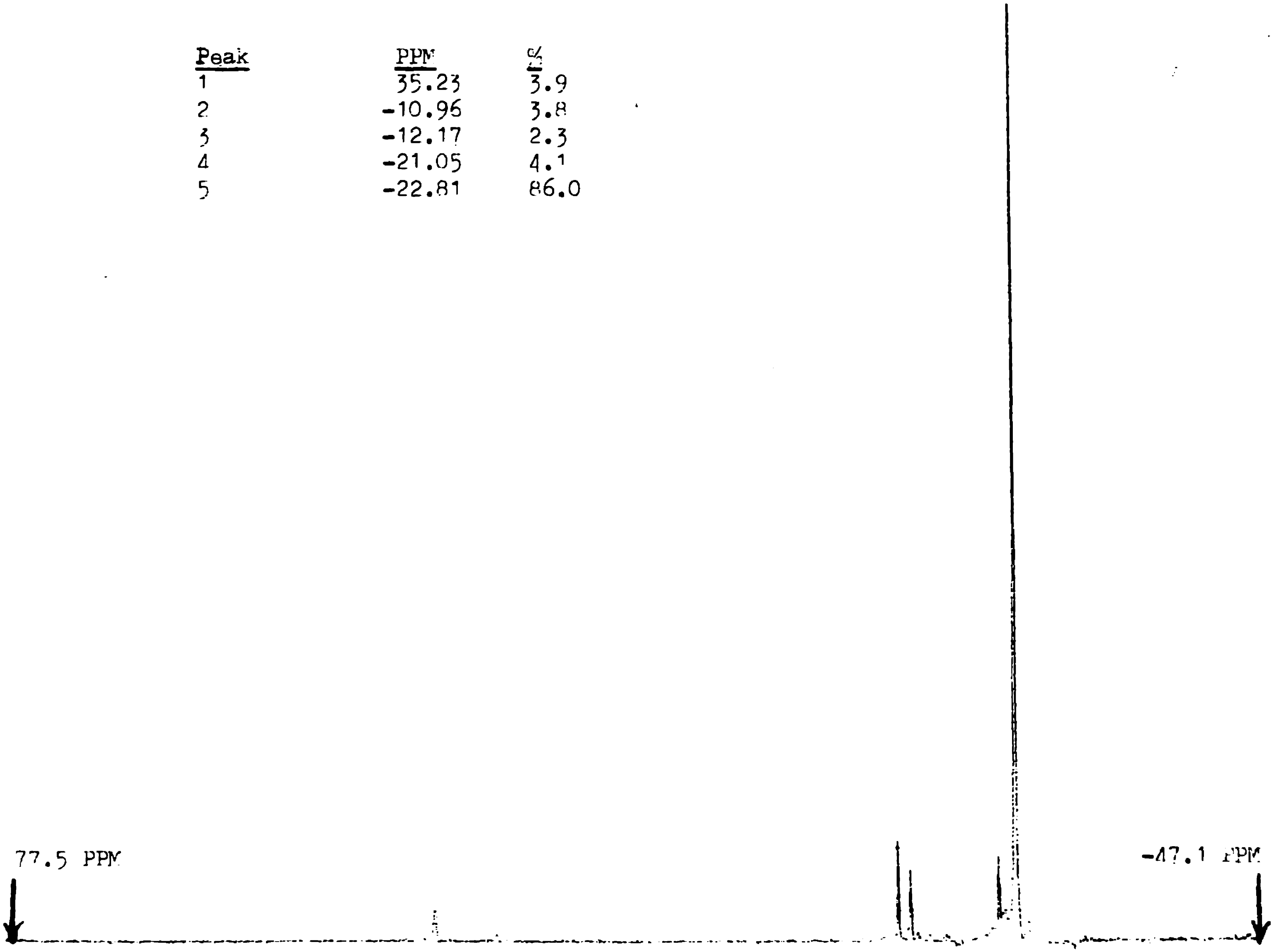


Figure 8: $E_{12}PPh_2$- ^{31}P NMR Spectrum After Storage for Three Weeks

Peak	PPM	%
1	35.23	3.9
2	-10.96	3.8
3	-12.17	2.3
4	-21.05	4.1
5	-22.81	86.0



Anal. Calcd. for $C_{32}H_{57}BrO_{13}$: C, 52.69; H, 7.88; Br, 11.10. Found: C, 52.20; H, 7.75; Br, 11.91.

$E_{12}BzPPh_2$. A solution of crude $E_{12}BzBr$ (12.3 g, 17 mmol) in THF (250 mL) was cooled under argon to -78°. n-Butyllithium (7.2 mL, 2.4 N solution in hexene) was added via syringe, followed 5 min. later by Ph_2PCl (3.4 mL, 22 mol). The solution was allowed to warm to room temperature, quenched with water (1 mL), evaporated to an oil at reduced pressure, taken up in CH_2Cl_2, filtered, and again concentrated to an oil at reduced pressure. Low boiling impurities were removed by heating to 140° at 0.02 torr in Kugelrohr for 2 hrs. The residue was taken up in CH_2Cl_2, passed through 40 g of Woelm activity grade I alumina, and reduced to an opaque yellow oil (7.4 g). This material resisted further purification by conventional means.

Anal. Calcd. for $C_{44}H_{67}O_{13}P$: C, 63.29; H, 8.09; P, 3.71. Found: C, 59.22; H, 7.74; P, 3.49.

^1H nmr spectroscopy suggested the presence of $R-CH_2Ph$ moieties as a significant impurity. $E_{12}BzBr$ showed a distinct aromatic quartet, and while phosphorus coupling would be expected to broaden the signal, collapse to the doublet seen in Figure 10 must be attributed to a large amount of mono-substituted benzyls. nmr ($CDCl_3$): δ (TMS): 7.35 (d, broad, 14), 4.58 (s, $\sim$1), 4.53 (s, $\sim$1), 3.68 (s, broad, 48), 3.35 (s, 3). The total integral of the benzyl signals (two) is satisfactory, but the division of this area between two

Figure 9: $E_{12}BzBr$ ^1H NMR Spectrum

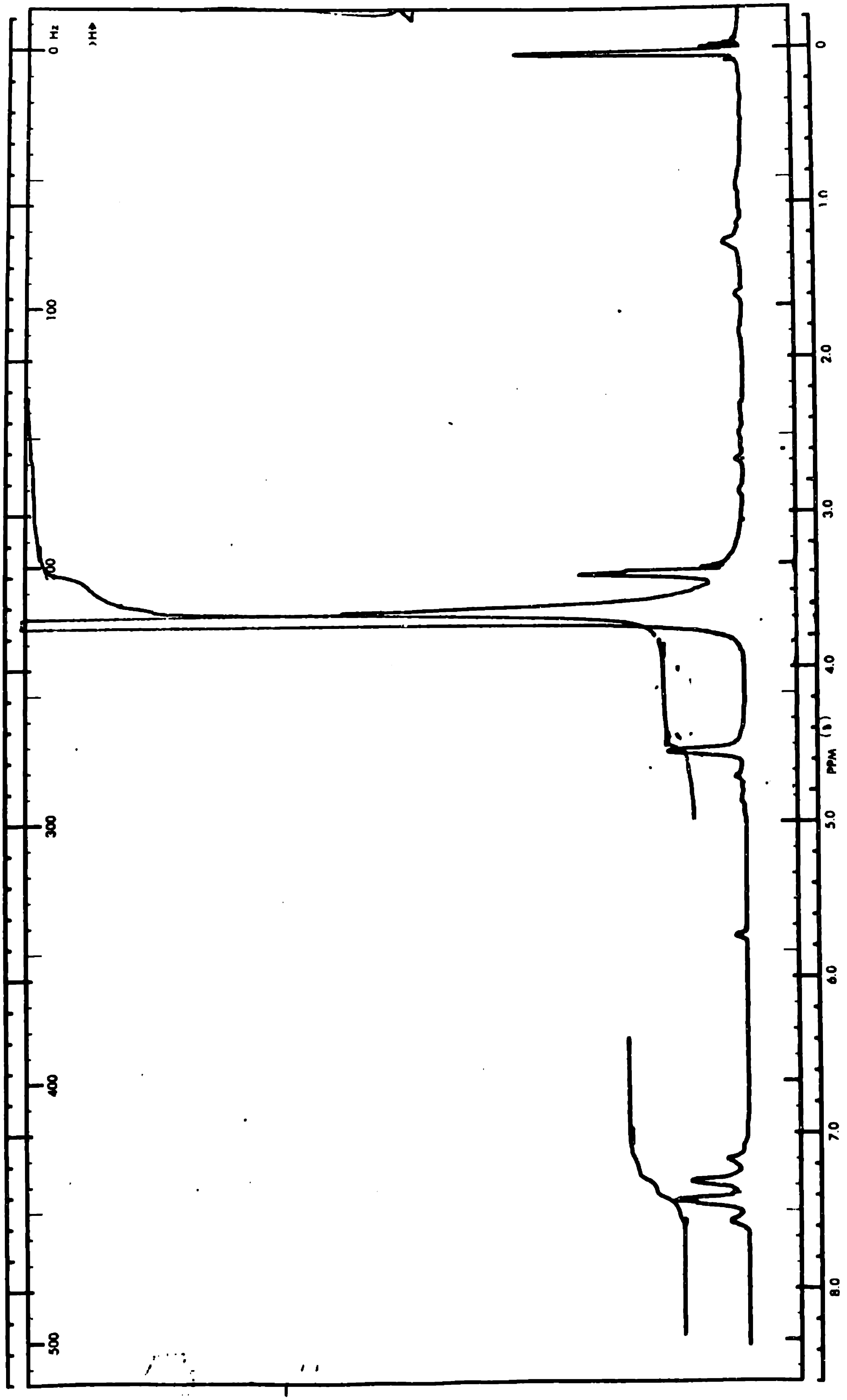
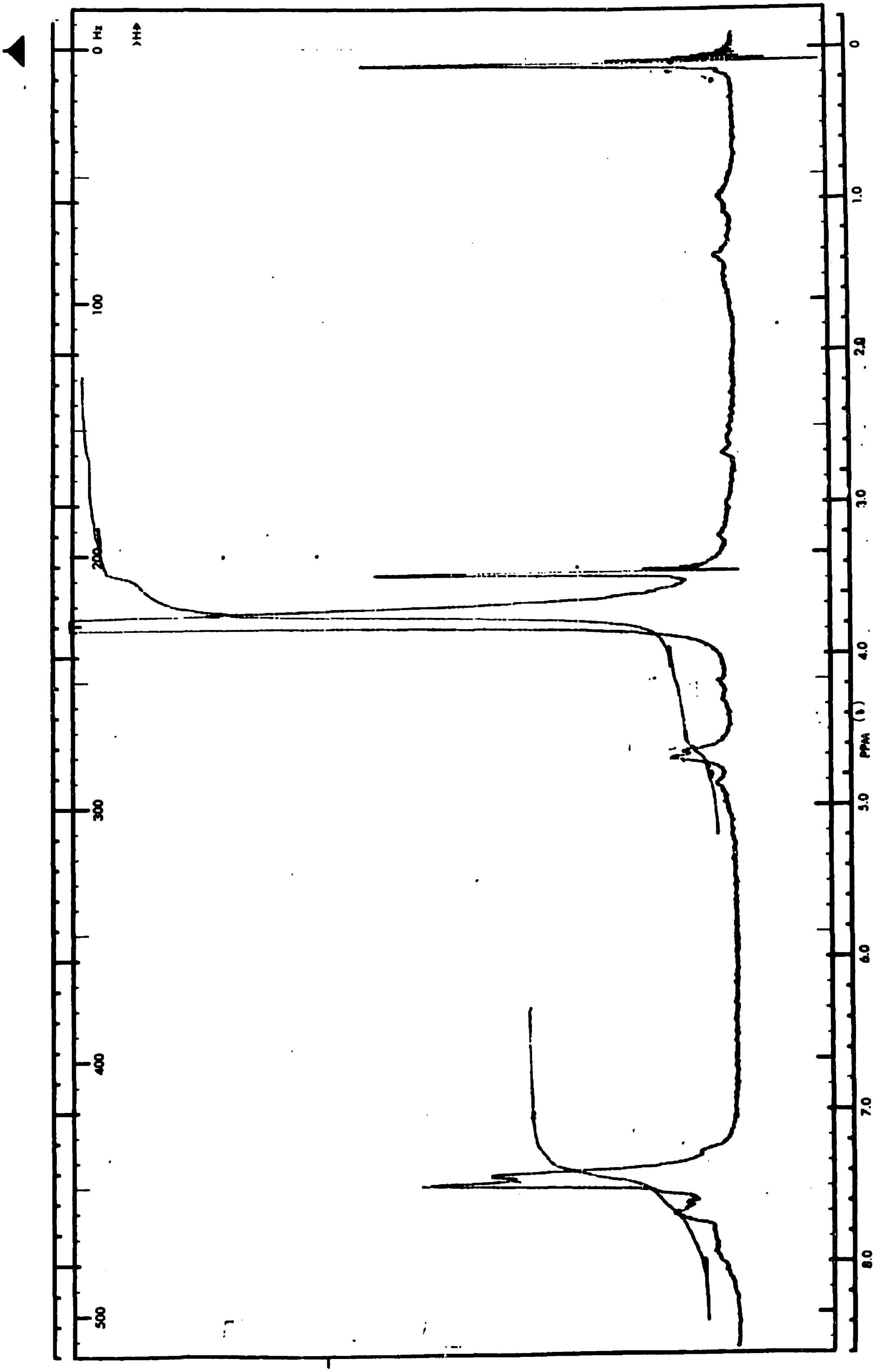

0 Hz
100
200
300
400
500
0
1.0
2.0
3.0
4.0
PPM (δ)
5.0
6.0
7.0
8.0

Figure 10: $E_{12}BzPPh_2$- ^1H NMR Spectrum



0 Hz
100
200
300
400
500
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
PPM (δ)

Figure 11: Purified $E_{12}BzPPh_2$- ^{31}P NMR Spectrum

Peak	PPM	%
1	36.01	1.7
2	31.50	4.7
3	24.20	14.8
4	23.47	--
5	-5.13	1.6
6	-5.34	4.3
7	-5.78	--
8	-5.98	1.6
9	-6.58	60.1
10	-7.43	--
11	-7.62	2.2
12	-8.03	--
13	-15.82	--
14	-17.10	6.7

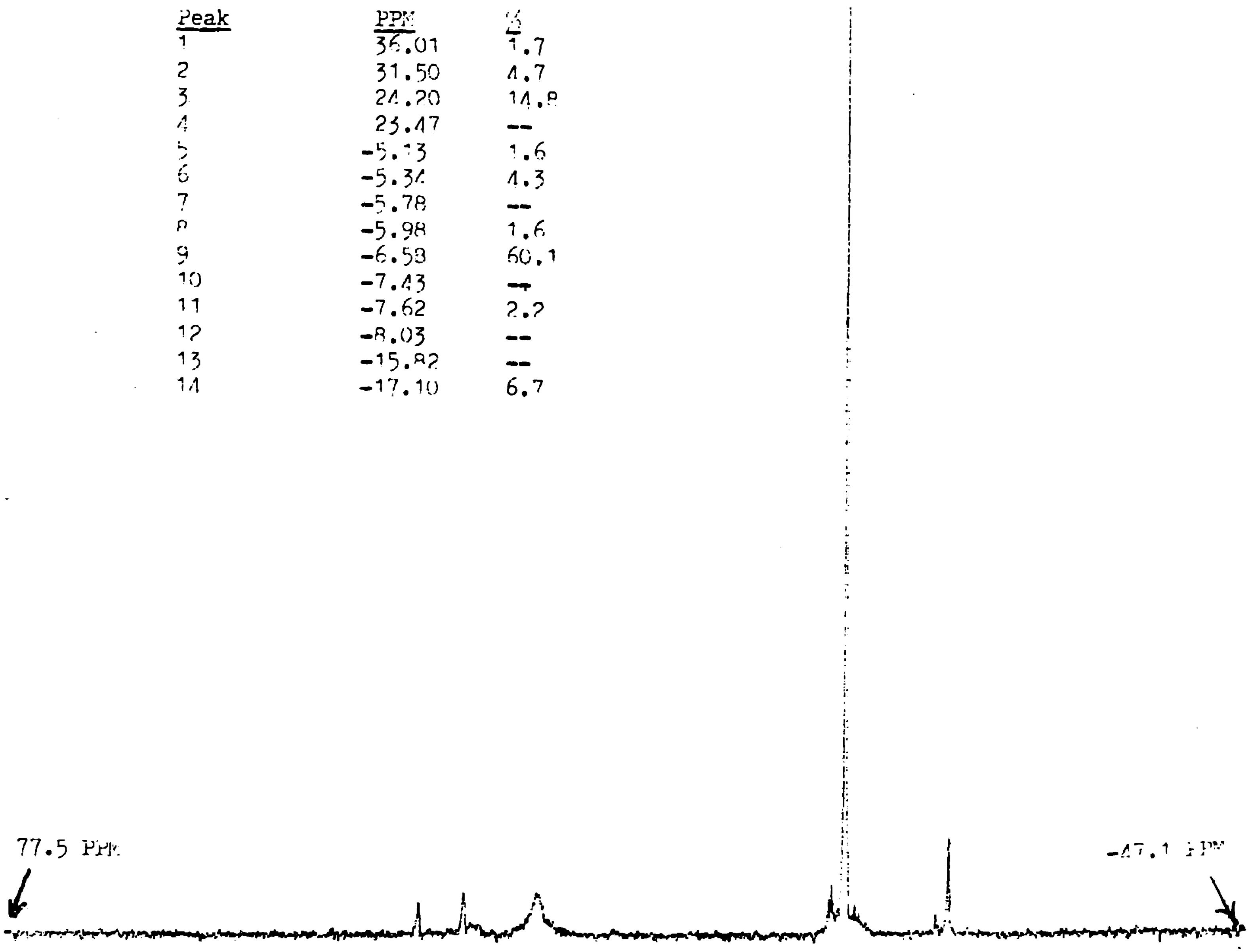


Figure 12: Unpurified $E_{12}BzPPh_2$

Peak	PPM	%
1	36.24	1.5
2	33.74	3.9
3	32.05	1.8
4	31.94	3.5
5	25.25	1.8
6	25.11	1.9
7	24.81	11.9
8	-5.29	8.7
9	-5.84	1.9
10	-6.38	59.7
11	-18.01	3.2

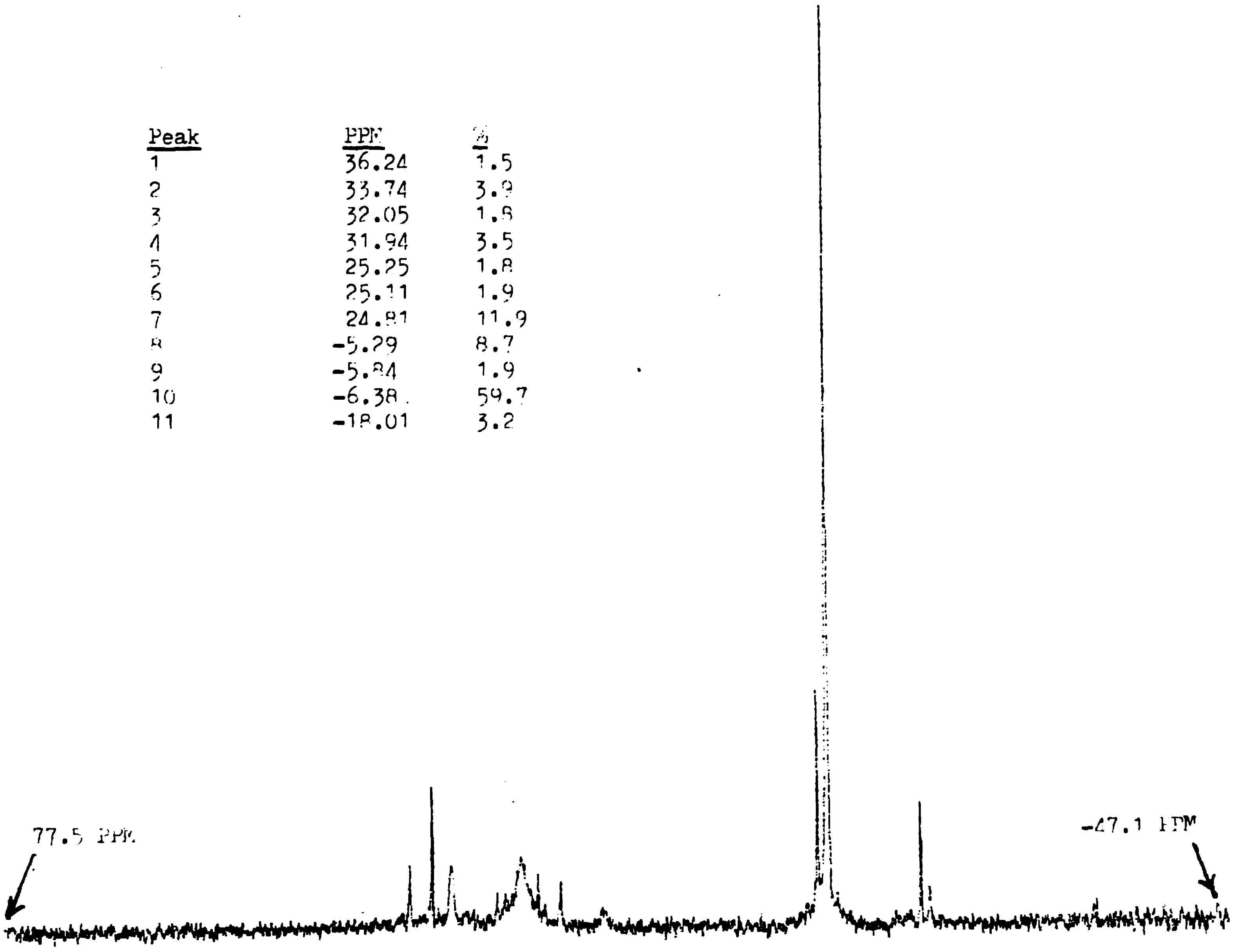
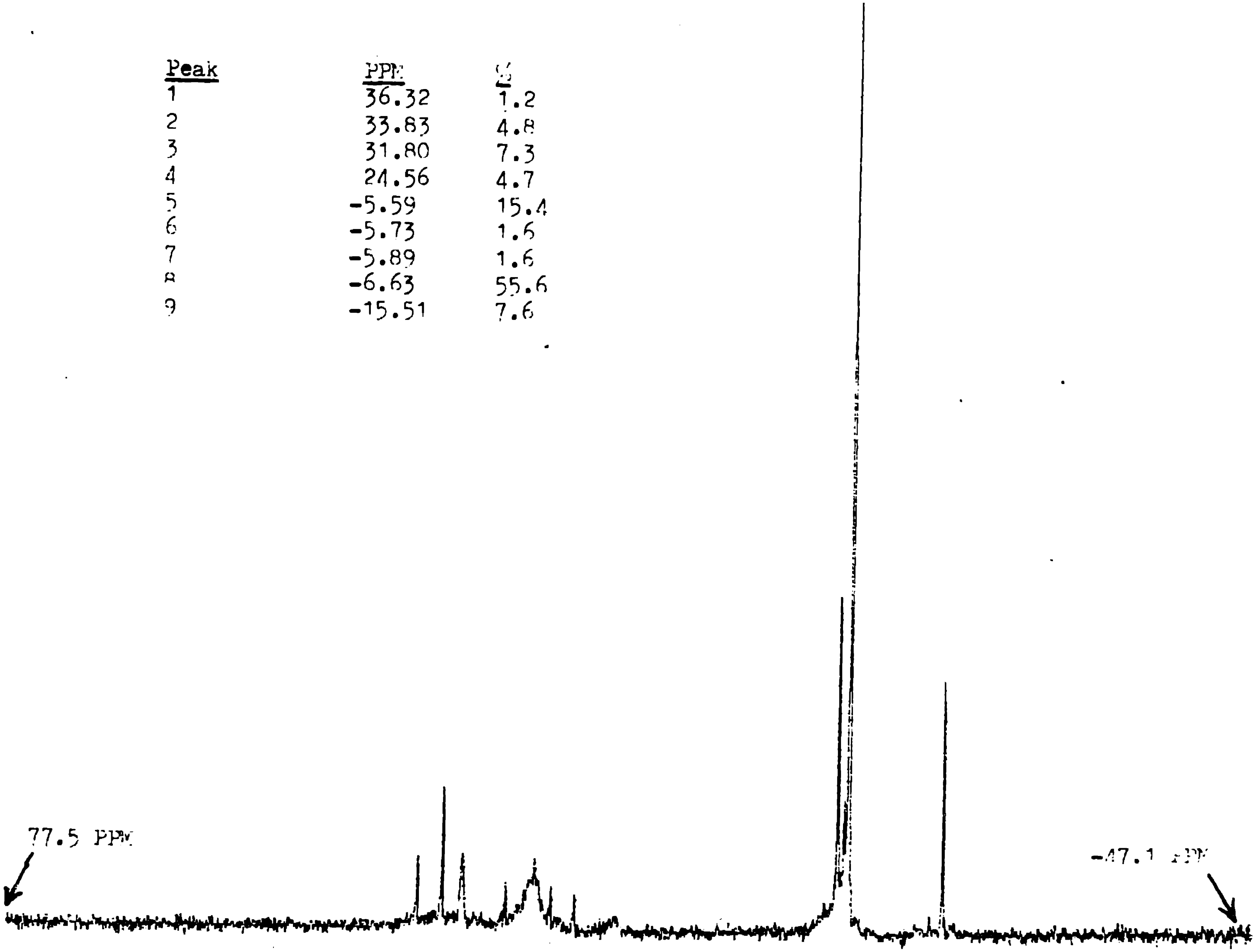


Figure 13: Unpurified $E_{12}BzPPh_2$- ^{31}P NMR Spectrum After Storage for Three Weeks

Peak	PPM	%
1	36.32	1.2
2	33.83	4.8
3	31.80	7.3
4	24.56	4.7
5	-5.59	15.4
6	-5.73	1.6
7	-5.89	1.6
8	-6.63	55.6
9	-15.51	7.6



different signals indicates that some forms of $E_{12}Bz$ and PPh_2 not chemically linked must be present. ^{31}P nmr (Figure 12) showed a principle resonance (60%) of -6.4 ppm in water relative to 85% H_3PO_4 which was assigned to triaryl phosphine.[46] Based on the weight percent of phosphorus and the ^{31}P nmr purity of 55% was estimated. Treatment with decolorizing charcoal and passage of the methylene chloride solution through 20 g of Woelm activity grade I neutral alumina, improved in the ^{31}P spectrum (Figure 11) to give the principle resonance 60% of the area. Allowing the unpurified sample to stand for three weeks in aqueous solution gave evidence of a very slow loss of purity to a peak at -16.06 ppm. This peak has not been identified (Figure 13).

Catalyst Preparation and Hydrogenation. Norbornadienerhodium (I) chloride (23 mg, 100 μmol) and silver perchlorate (21 mg, 100μmol) were dissolved in separate 40-mL centrifuge tubes in 2 mL of acetone under argon. The $AgClO_4$ solution was added by forced syphon through a stainless steel cannula to the rhodium-containing solution. The mixture was stirred for three min., and the precipitated silver chloride separated by centrifugation. The supernatant was decanted by forced syphon into an argon-purged 10-mL volumetric flask, and the volume adjusted with additional acetone to 10.00 mL. Water-soluble phosphine (23 mg of $E_{12}PPh_2$, 2 equiv., or 23 mg of $E_{12}BzPPh_2$, 1.5 equiv.) was weighed into a reaction thimble, a Teflon-coated magnetic stirring bar added, and a No-Air stopper wired firmly in place. After purging the thimble with argon for 10 min., 1 mL of the standard solution of norbornadiene rhodium (I) perchlorate was added. If the reactions were to be performed in acetone the volume was made up to 5 mL. If the reaction was to be performed in another solvent (i.e., toluene, water), the acetone was removed by evaporation in a stream of argon. The appropriate solvent (5 mL) was added to the remaining oil. The manifold was switched to hydrogen, and the solution were flushed for 5 min. before sealing the systems at 8 lbs. of dihydrogen. After an activation period of 0.3-1.0 hrs, 1 mL of olefin was added, along with 50 μL of the appropriate internal standard. The reaction was allowed to proceed with stirring for a selected interval (usually 6 hrs.) and a sample was then removed and analyzed.

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42. $(E_{12}PPh_2)_2Rh^+$ gave 50-60 turnovers in three hours of allyl alcohol in wet cyclohexane (0.25 mL water in 5 mL of cyclohexane) compared with 70 turnovers for allyl alcohol in water and 200 for allyl alcohol in acetone. This shows that cyclohexane is comparable to water as a solvent for allyl

alcohol hydrogenation under conditions similar to those which were found in allyl alcohol assays for activity of cyclohexene solutions. Since cyclohexene was not used the evidence is only inferential.

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PART II

APPENDICES

APPENDIX I

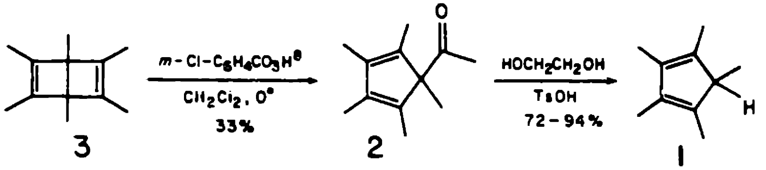
CHIRAL CYCLOPENTADIENES

Introductory Note

Pentaalkylcyclopentadienes, until recently, were a highly desired and highly inaccessible cyclopentadiene congener for transition metal complexes. The desirability of pentaalkylcyclopentadienes as modifiers of catalyst activity has been called into question because of the steric bulk they possess. Recent results of ours[1] and Schrock's[2] suggest that the steric bulk of these ligands often renders the complexes inert, rather than more selective. The pentaalkylcyclopentadienes are not inaccessible anymore, as work of Burger,[3] ourselves,[4] and Bercaw[5] has provided a wide assortment of methods by which to prepare them (Figure 1), all improvements on the original deVries synthesis.[6] Each of the methods has some problem as an ideal synthetic route. Method 1 of the Swiss group depends on costly starting materials (2) and Method 2 is long despite its inexpensive starting materials and easy manipulations. One of our methods (Method 3) is moderately expensive (due to the cost of tiglic acid (8)), while the other (Method 4), although very practical can be faulted for a lack of generality. Bercaw's most recent effort (Method 5) depends on the availability of 2-bromo-2-butene and the necessary skills to convert this vinyl bromide to the lithium reagent in good yield. Because 2-bromo-2-butene is no longer commercially available, its preparation must be counted as an extra step. The techniques needed to prepare 5-L batches of a vinyllithium reagent are not common knowledge.

Figure 1: Preparations of Pentaalkylcyclopentadienes

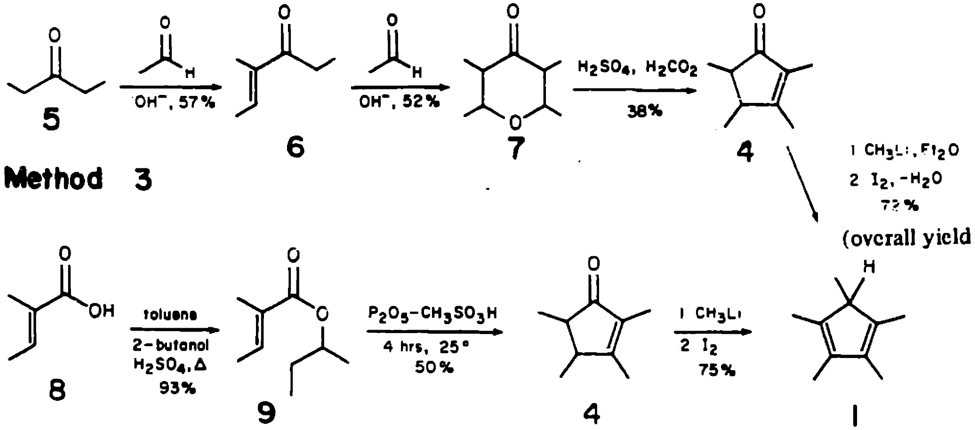
Method 1



(overall yield 24% on preparative scale)

Method 2

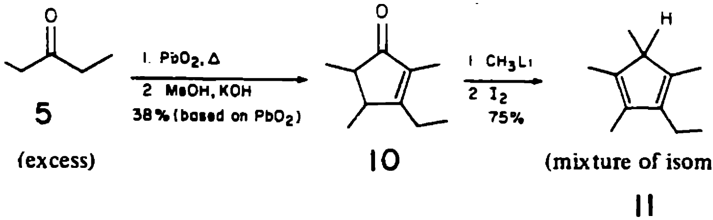
Method 3



(overall yield 8%)

(overall yield 34%)

Method 4

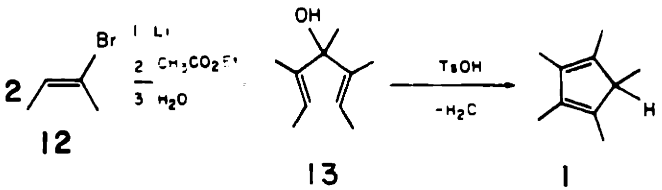


(excess)

(mixture of isomers)

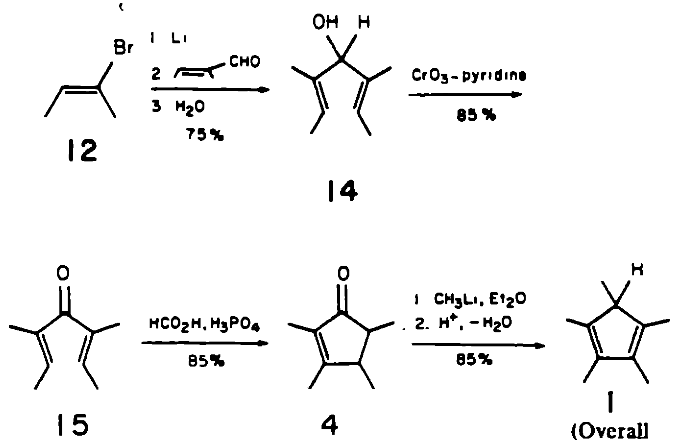
(overall yield 28%)

Method 5



(overall yield 75%)

Method 6



(Overall yield 46%)

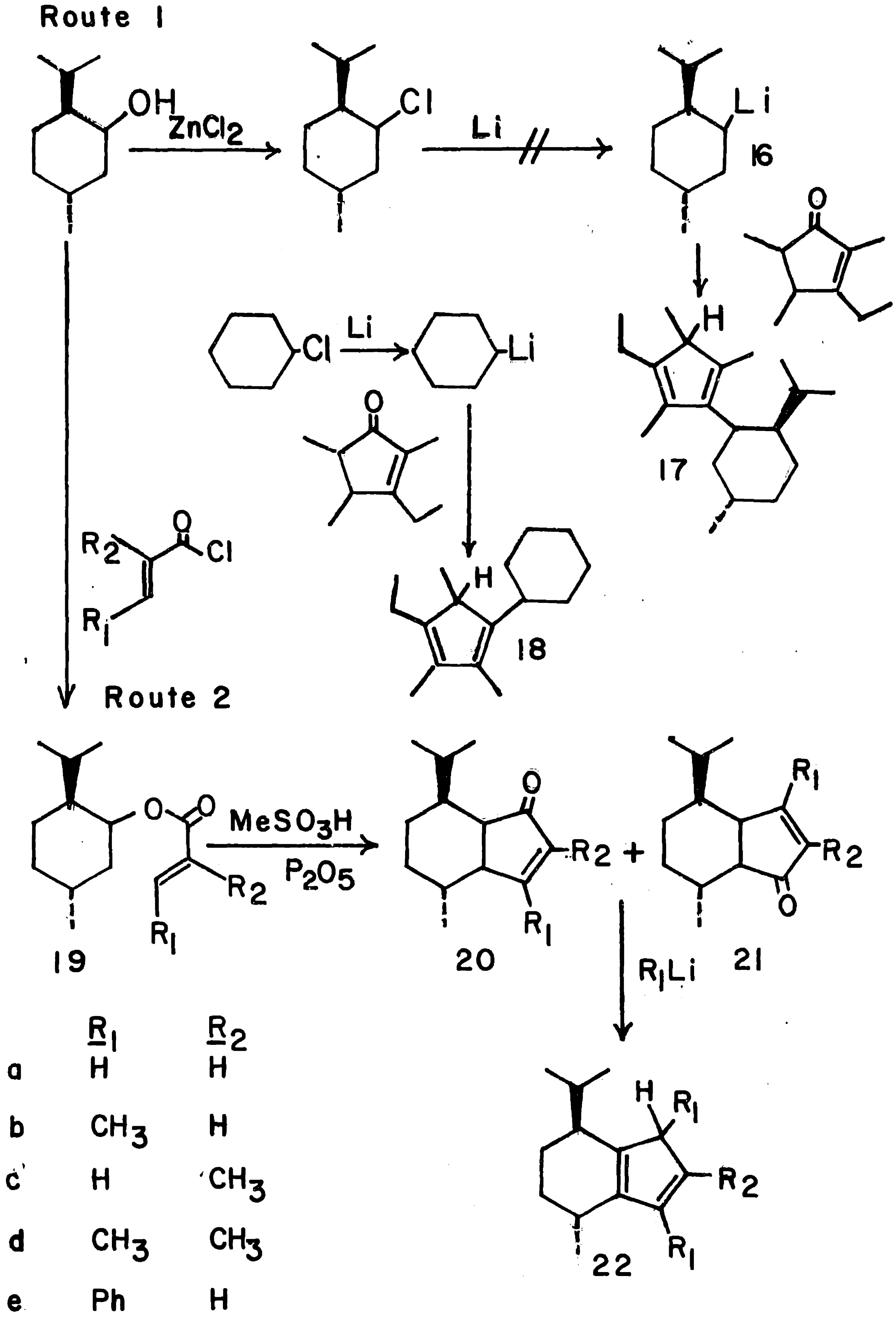
Because our work[4] has already been published, further details will not be supplied. However, several projects (one of which will be discussed here) were undertaken which derived from that work. The projects were terminated on the basis that the experimental data suggested that too much work would be required to make successful projects of them. What follows is a brief description of the tactics and strategies of one project and the essential findings.

Attempted Syntheses of Chiral Cyclopentadienes

Effective chiral catalysis by chiral transition metal complexes is a domain reserved nearly exclusively for noble metals coordinated by chiral phosphines.[7] Our ability to prepare highly functionalized cyclopentadienes lead us to attempt to alter this monopoly. Biscyclopentadienyltitanium dichloride is a precursor to both hydrogenation and polymerization catalysts.[8,9] Successful efforts to obtain chiral polymers have been made by using tetramenthoxy titanium,[10,11] but no examples are known for hydorgenation or isomerization. Biscyclopentadienylzirconium hydridochloride[12] has been used by Schwartz to migrate double bonds away from sterically crowded positions. Hydrogenation, isomerization, and polymerization all invite chiral induction, should a chiral metal-Cp complex become available.

Development of chiral Cp-metal complexes was hindered on two counts. We found that our syntheses were somewhat naive, and that extensive substitution on the cyclopentadiene hindered

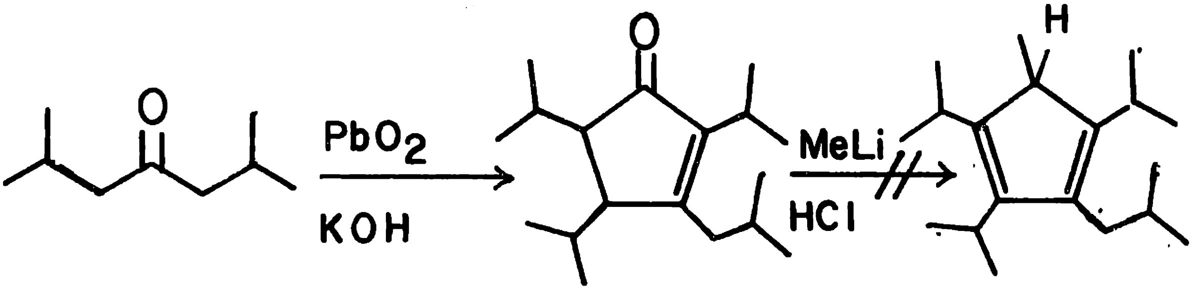
Figure 2: Routes to Chiral Cyclopentadienes



	$\underline{R}_1$	$\underline{R}_2$
a	H	H
b	CH_3	H
c	H	CH_3
d	CH_3	CH_3
e	Ph	H

hydrogenation by a titanocene catalyst.

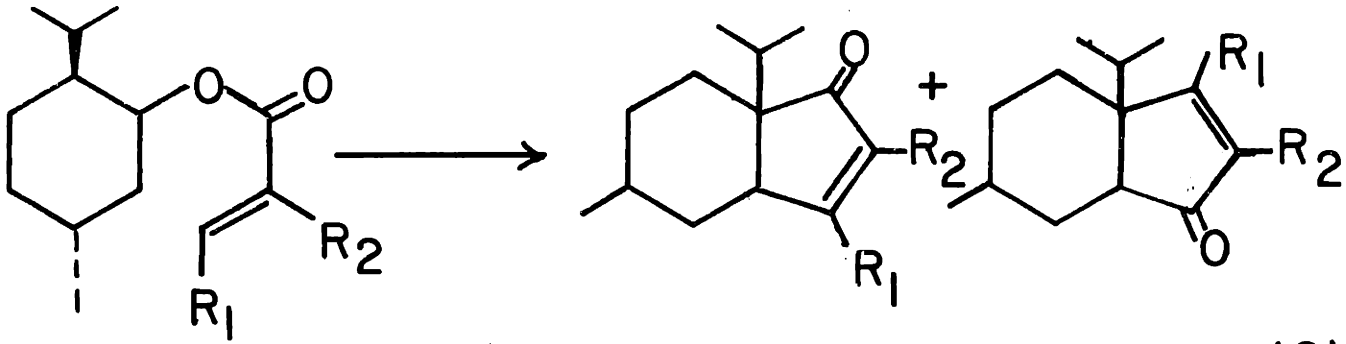
We though that the adaptation of our previous work shown in Figure 2 would readily generate chiral cyclopentadienes. In the first route, we found that menthyllithium[13] was nearly impossible to prepare. We had also found earlier that the highly hindered ketone shown in equation 1 could not be reacted with methyllithium. We prepared and successfully reacted cyclohexyllithium[14] with 3-ethyl-2,4,5-trimethylcyclopent-2-enone to give the cyclopentadiene (18). This appears to be the first example of a carbonyl reaction of a cyclohexyllithium exclusive of carbon dioxide. Since menthyllithium could not be prepared, and menthyl magnesium chloride did not add to the cyclopentenones this route was abandoned.



(1)

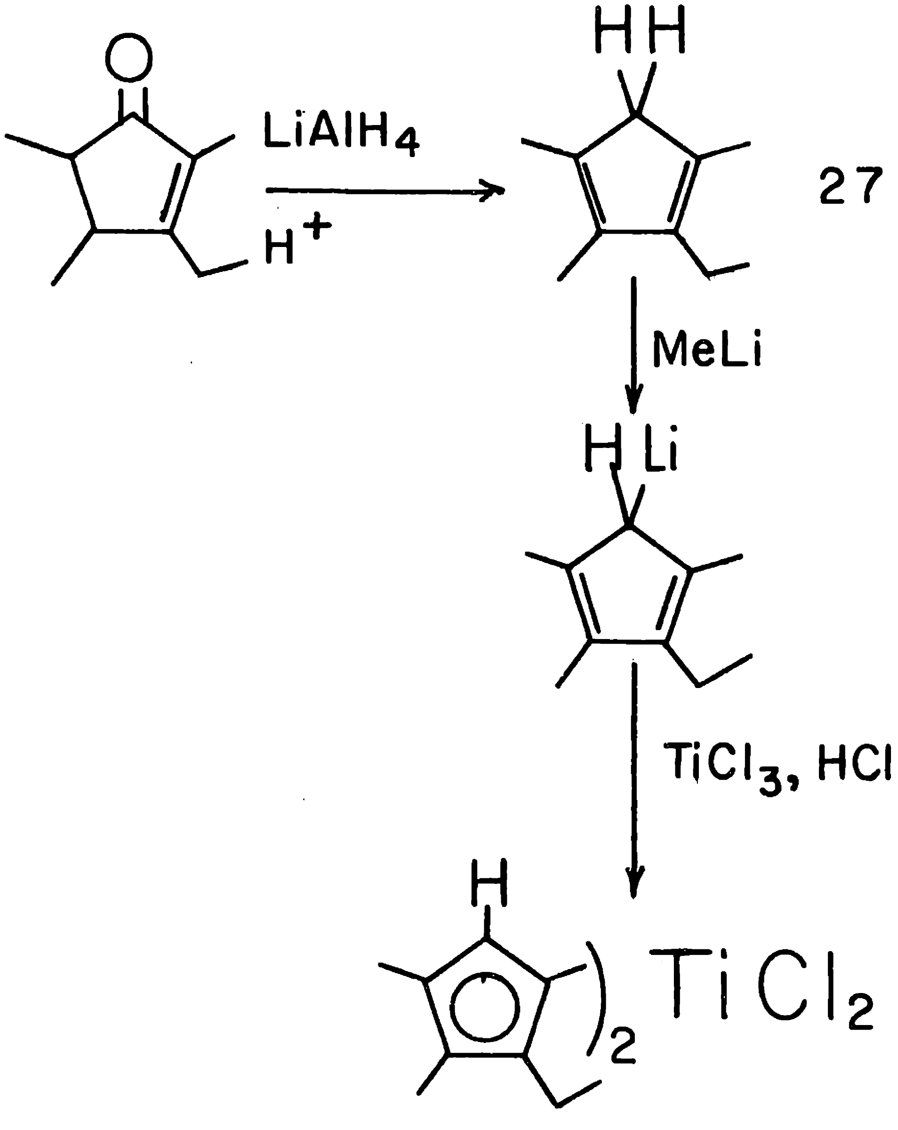
The second route suffered from the possibility of isomerization as in equation 2. Isomers of types 25 and 26 were found in all reaction mixtures (this was deduced by examination of vpc data), as well as the desired isomers, and varying the substituents as listed in Figure 3 did not seem to alter the distribution of isomers. We attempted to react the mixture of isomers with methyllithium, and carry the products all the way through to lithium cyclopentadienide. It was hoped that the lithium cyclopentadienides could be obtained in amounts large enough to isolate the titanocene derivatives, and it was hoped that these derivatives could be separated from the cyclopentadienes of isomers of types 27 and 28 which could not form cyclopentadienides due to their having a tertiary carbon in the ring. These efforts were also unsuccessful.

A key cause for the abandonment of this project was the discovery that $(EtMe_4Cp)_2TiCl_2$ generated a far less active hydrogenation catalyst than did Cp_2TiCl_2. Since we required a highly substituted cyclopentadiene in order to obtain a rigid, non-rotating system, this result seemed to us fatal. $(EtMe_3Cp)_2TiCl_2$ was prepared (Figure 3) and characterized, but the project was terminated before this compound could be tested.



19 25 26 (2)

Figure 3: Preparation of Bis-1-ethyl-2,3,5-trimethylcyclopentadienyltitanium Dichloride



28

Experimental Section

1-Ethyl-2,3,5-trimethylcyclopentadiene (27). 2-Ethyl-1,3,5-trimethylcyclopent-2-enone (76 g, 0.5 mol) dissolved in 100 mL of dry ether, was added to a suspension of $LiAlH_4$ (7.6 g, 0.2 mol) in 500 mL of ether, maintained at 0°. Workup after Fieser,[15] dehydration with aqueous HCl, and distillation (74° at 23 torr) gave 18.4 g (27%) of (27). nmr ($CDCl_3$): δ (TMS) 2.73 (s, 2), 2.30 (q, 2), 1.94 (s, 6), 1.83 (s, 3), 1.01 (t, 3).

Bis-1-ethyl-2,3,5-trimethylcyclopentadienyltitanium dichloride (28). 27 (10 g, 73 mmol) dissolved in THF (100 mL) was treated with MeLi (38 mL, of 1.92 M solution in hexane) sufficient to form the lithium cyclopentadienide. $TiCl_3$ (4.62 g, 30 mmol) was weighed out and transferred to a three-necked round-bottomed (500 mL) flask in a dry box. The flask was removed from the dry box, THF (100 mL) added, the mixture cooled to 0°, and the solution of lithium cyclopentadienide added by forced syphon through a stainless steel cannula. After the addition was complete, the flask was fitted with a reflux condenser and the mixture refluxed overnight. After cooling to room temperature, the mixture was quenched with 15 mL of concentrated aqueous HCl, extracted with chloroform (3 x 100 mL), the organic layer extracted with brine (100 mL), dried (Na_2SO_4) and crystallized by the addition of ether (100 mL) giving 4.5 g (39%) of purple-red crystals. mp 214.5-216.5. nmr ($CDCl_3$): δ (TMS): 5.97 (s, 1), 2.53 (quartet of doublets, 2, J = 7 Hz), 2.1 (s, 3), 1.98 (s, 3), 1.93 (s, 3), 1.01 (t, 3, J = 6.5 Hz).

Anal. Calcd. for $C_{20}H_{30}Cl_2Ti$: C, 61.73; H, 7.71; Cl, 18.24. Found: C, 61.73; H, 7.95, Cl, 18.29.

Cyclohexyllithium. Cyclohexyl chloride (14 g, 0.1 mol) eluted from alumina was mixed with 100 mL of hexane and added over 5 hrs. via a constant rate addition funnel to a magnetically stirred suspension of 0.23 mol of lithium dispersion (from mineral oil, 2% Na) in 100 mL hexane under a positive argon pressure at reflux. About 10% of the halide was added to initiate the reaction, which could be observed by discoloration of the lithium, and turbidity of the solution. The solution was allowed to settle and about 10 mL was cannulated into a flame dried storage vessel. The solution was titrated at 0.19 M by the Gilman procedure[16] (20%).

1-Cyclohexyl-3-ethyl-2,4,5-trimethylcyclopentadiene (18). 3-Ethyl-2,4,5-trimethylcyclopent-2-enone (1.14 g, 7.5 mmol) was dissolved in 50 mL of THF and cooled under argon to -78°. Cyclohexyllithium (100 mL, 10 mmol) in hexane was added slowly via cannula. The solution was allowed to warm to room temperature overnight and carefully quenched by pouring into 200 mL of water. Extraction with pentane and concentration to 25 mL gave a yellow solution; a sample was dried and ir showed hydroxyl and carbonyl stretching, 3460 broad, 1692, 1640 cm^{-1}. Dehydration with 0.5 mL of 12 N HCl, drying (Na_2SO_4) and distillation gave two fractions: 30-35° (0.06 torr), 0.5 mL; ir 1710, 1642, unreacted cyclopentenone by vpc; and 61° (0.06 torr), 0.61 g (2.7 mmol, 38%), ir, only C-H and C-C, 93% pure by vpc, mass spec. M^+ 2.8, bicyclohexyl 166, M-C_6H_{11} 135.

Hydrogention Experiments

In a 40 mL centrifuge tube 1 mmol of $(EtMe_4Cp)_2TiCl_2$ or Cp_2TiCl_2 was suspended in 10 mL of olefin free, dry pentane, and 1 mL (10 mmol) of cyclohexene. The mixture was stirred and flushed with hydrogen, then 1.09 mL (2 mmol) of lithium napthalide in THF added. The black-grey solution was stirred 5 hrs. under a hydrogen atmosphere and then quenched with water. Analysis of the mixture by vpc (10 ft. TCEP) showed 80% hydrogenation of cyclohexene by the Cp_2Ti system and none by the $(EtMe_4Cp)_2Ti$ system.

In a 40 mL centrifuge tube 1 mmol of $(EtMe_4Cp)_2TiCl_2$ was dissolved in 10 mL of THF and cooled under a hydrogen blanket to -78°. Cyclohexene (1 mL, 10 mmol) and 2 mmol of BuLi in pentane were adeed. The mixture was allowed to warm to room temperature overnight and then quenched with water. Analysis by vpc (10 ft. TCEP) showed 13% hydrogenation of cyclohexene.

Figure 4: 1-Ethyl-2,3,5-trimethylcyclopentadiene-^{1}H NMR Spectrum

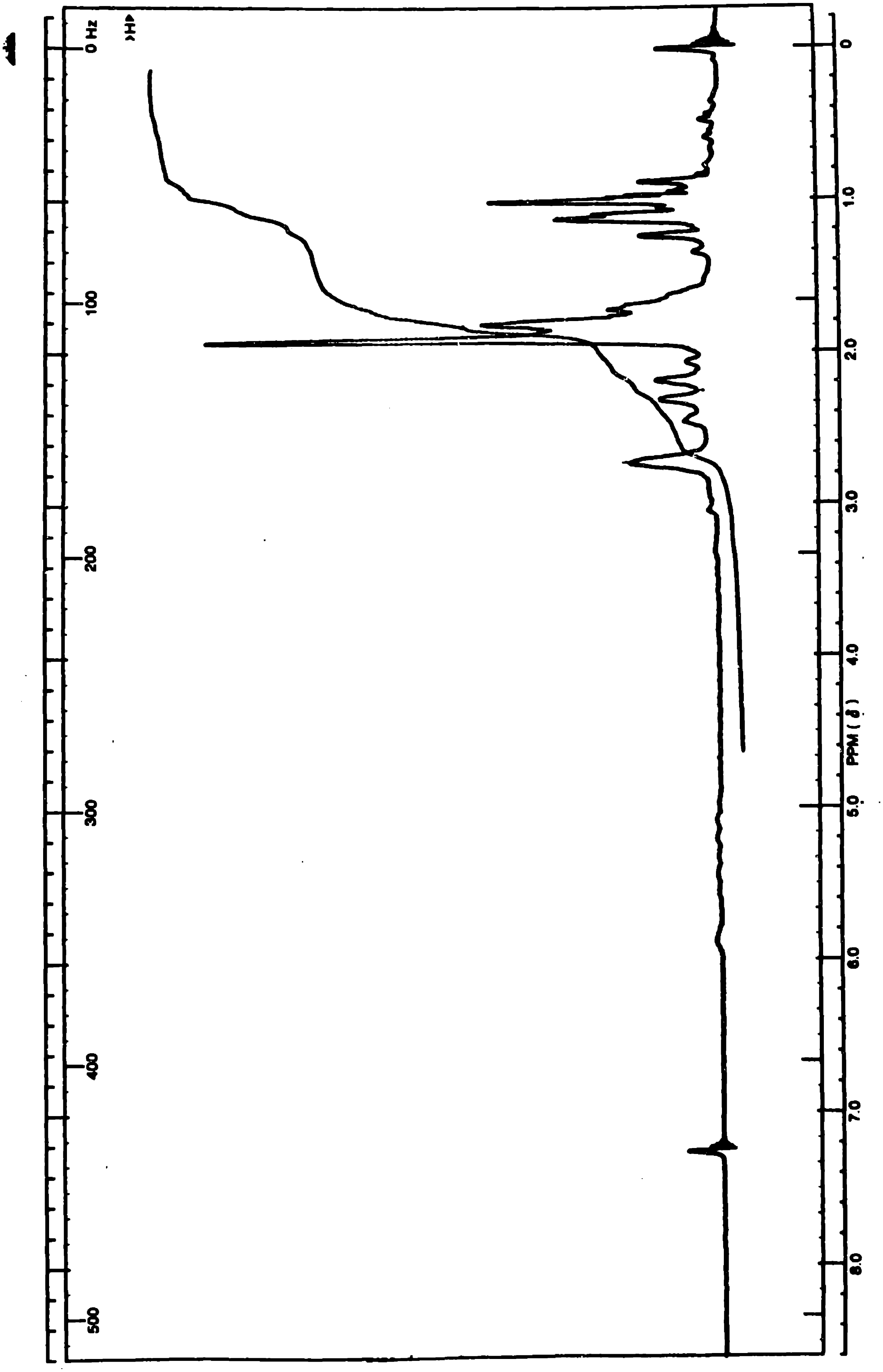
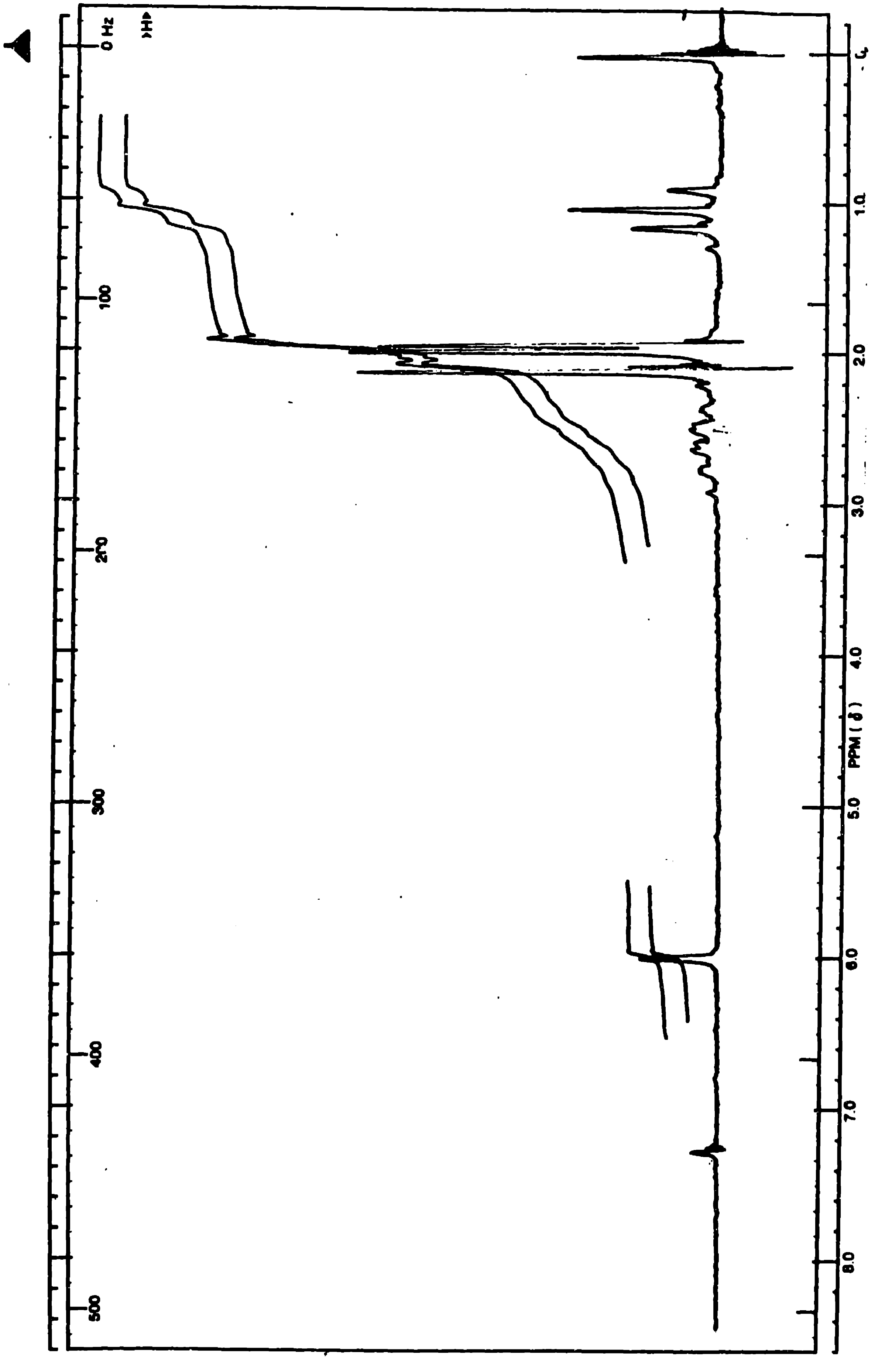

0 Hz
100
200
300
400
500
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
PPM (δ)

Figure 5: Bis-1-ethyl-2,3,5-trimethylcyclopentadienyltitanium Dichloride



0 Hz
100
200
300
400
500
1.0
2.0
3.0
4.0
PPM (δ)
5.0
6.0
7.0
8.0

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APPENDIX II

REDUCTIVE OLIGOMERIZATION OF CARBON MONOXIDE

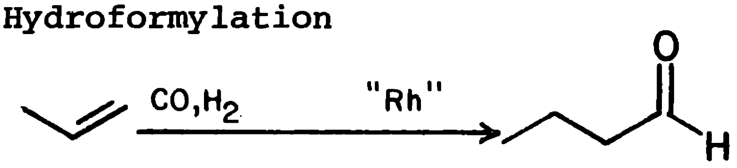
Introductory Note

The depletion of fossil fuel reserves, specifically oil, if forcing consideration of schemes for conserving organic carbon. Organic carbon is lost through formation of carbon monoxide and carbon dioxide. Carbon dioxide is naturally recycled by photosynthesis, but carbon monoxide has no direct counterpart. (Oxidation of carbon monoxide to carbon dioxide is not an attractive method of disposal or utilization.) Current technology provides several outlets:

1. The Water Gas Shift Reaction[1]

$$CO + H_2O = CO_2 + H_2$$

2. Hydroformylation



3. Reduction to Methanol[3]

$$CO + 2H_2 \longrightarrow MeOH$$

4. Acetic acid Synthesis[4]

$$CO + MeOH \xrightarrow{Rh(CO)_2I_2^-} CH_3COOH$$

5. Ethylene glycol synthesis[5]

$$CO + H_2 \xrightarrow{\text{Rh Cluster}} HOCH_2CH_2OH$$

6. Gasoline Synthesis from Methanol[6]

$$MeOH \xrightarrow{\text{shape selective zeolite}} \text{alkanes, aromatics} \leq C10$$

7. The Fischer-Tropsch Reaction[7]

$$CO + H_2 \longrightarrow MeOH,\ ROH,\ \text{alkanes}$$

All of these reactions depend on the reduction of CO with hydrogen except the first, which serves as a source of hydrogen. The two primary reducing agents of the future are carbon (coal) and the electrochemical electron. Controlled combustion of coal is not of great interest. Electrochemical reduction of carbon monoxide produced only squaric acid.[8,9] Chemically modified electrode technology will probably have to advance considerably before electrochemical process will produce anything else.[9] Both coal and e^- can be used to produce other reducing agents: hydrogen, Na, K, Mg and various transition metals.

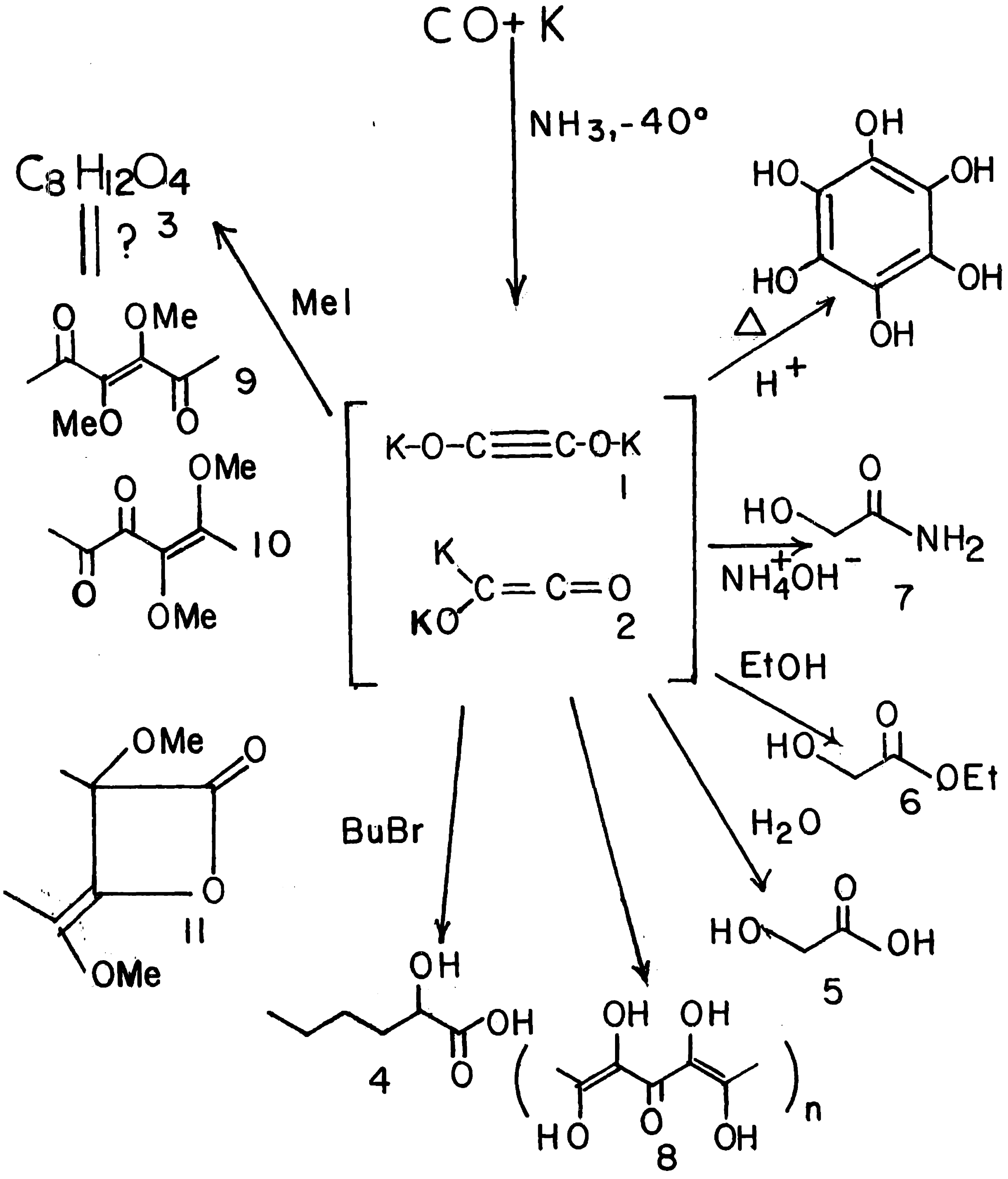
Reduction of carbon monoxide with alkalai metals has been known for 140 years. Liebig reported the reaction of K and CO in 1834.[10] The discovery that the potassium salt of hexahydroxy benzene was a principle product came 50 years later.[11] Joannis first reported the dissolving metal reduction of CO and isolated a two-carbon fragment, glycolic acid[12] after hydrolysis. Buchner published a classic series of papers concerning these reactions in the 1960's.[13-22] The primary product of the reaction of CO with an alkalai metal at low temperature, or with an alkalai metal in liquid ammonia was $M_2C_2O_2$ (Figure 1).

Evidence for structure 1 was provided by powder diffraction studies, and 2 by infra-red spectra of the powder. The former is supposed to be the predominant isomer. Heating $M_2C_2O_2$ or heating M and CO lead to (after workup) hexahydrobenzene. Hydrolysis, amminolysis or ethanolysis of $M_2C_2O_2$ lead to glycolic acid, glycolamide and ethylglycolate. Reaction of $M_2C_2O_2$ with MeI gave an unidentified material $C_8H_{12}O_4$. Reaction of $M_2C_2O_2$ with BuBr and hydrolysis gave 2-hydroxycaproic acid.[15] A polymeric product, an aci-reductone,[8] was isolated as a lead salt and was found in differing amounts depending on reaction and workup conditions. The kinetics of the reaction of liquid sodium and potassium with CO were investigated by various Atomic Energy Commission workers, the intent here being to obtain data useful for nuclear reactor core cooling studies.

Low valent titanium (Ti^{+2}) was also reported to reduce CO[24], however, the products were not well defined.

We re-investigated these reactions on the basis that sufficient demand could produce a secondary reducing agent, even potassium, at low cost, and with the goal of obtaining useful chemistry.

Figure 1: Products from the Reaction of Potassium and Carbon Monoxide


CO+K
NH3,-40°
C8H12O4
? 3
MeI
O OMe
9
MeO O
OMe
10
OMe
K-O-C≡C-O-K
1
K
C=C=O
KO
2
OH
HO OH
HO OH
OH
Δ
H+
O
HO NH2
NH4+OH-
7
EtOH
O
HO OEt
6
H2O
O
HO OH
5
OMe
O
O
11
OMe
BuBr
OH
OH
4
O
OH OH
HO O OH
8
n

Results and Discussion

Titanium Chemistry. Low valent titanium, prepared by the action of magnesium amalgam on $TiCl_4$ unambiguously reduced CO in a THF solution. However, the reaction proceeded only if the solution was slowly warmed to room temperature from an initial -78° and did not occur in any solvent other than THF. THF, unfortunately, was decomposed by the action of low valent Ti,[25] and in no case were the CO reduction products distinguishable by any technique from those resulting from warming a solution of $TiCl_4$ in THF in the presence of magnesium amalgam under an inert gas. This approach was abandoned.

Reduction with K and Na. Reduction of CO with potassium metal is a highly exothermic reaction, a fact to which the cracks on the bottom of a pressure bottle will attest. Further experiments were carried out as dissolving metal reductions. We considered three possible avenues for obtaining useful chemistry from $K_2C_2O_2$: oxidation, reduction and alkylation.

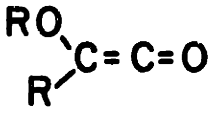
Oxidation of potassium carbonyl could be conceived to give squaric acid or oxalic acid. Neither is a particularly attractive target. Reduction of $K_2C_2O_2$ could be interesting, but it is a highly insoluble material and catalytic reduction with hydrogen or reduction with a metal hydride seemed improbable, especially since $K_2C_2O_2$ is itself stable to potassium in ammonia. Alkylation offered good prospects for success. Buchner[15] had reported small amounts of hydroxy caproic acid from $K_2C_2O_2$ and BuBr, and both Buchner and Sager[23] observed a $C_8H_{12}O_4$ species from the reaction of $K_2C_2O_2$ with MeI.

Reexamination of the MeI reaction showed that Sager's linear structures (9, 10) were not the only possible ones. An oil was obtained following the procedures in both Buchner's and Sager's papers and the data obtained (boiling point and IR) agreed roughly with what they reported. The IR carbonyl absorbtion was so broad however, that assignment of the value was difficult, and it became understandable that different values were reported by both groups. Proton nmr showed large numbers of peaks, although one spectrum did show as its principle features peaks that could be ascribed to *cis-trans* isomers of a linear structure. Given Buchner's solid identification of *alpha*-hydroxycaproic acid (4) as the alkylation product of potassium carbonyl with n-butylbromide, the possibility of a ketene dimer (11) formed from a similar intermediate is raised. The data found are in as much agreement with a ketene dimer structure as with Sager's linear structures.

Either

$$ROC\equiv COR$$

or



should be useful materials. Other reactive alkylating reagents, which would also render the products less reactive were considered. Trimethylsilyl chloride was tried first, and a dark red liquid which showed ketene absorbtion could be obtained on bulb-to-bulb distillation at reduced pressure of the reaction mixture. NMR and vpc studies of this material showed it to be a complicated mixture of compounds, and carbonyl ir absorbtions suggestive of ketene dimers and absorbtions suggestive of hydrolyzed trimethylsilyl ethers were also observed. Benzoyl chloride gave another liquid having ketene frequencies in the ir, but the material was even less homogeneous than that obtained by the use of TMSCl. Diphenyl phosphorus chloride gave an off-white powder, which showed ketone absorbtion, and mass spectroscopy of the bulb-to-bulb distilled material showed a molecular ion corresponding to

$$(Ph_2P(O))_2C_2O_2$$

Unfortunately, the samples were badly contaminated by the reaction products of ammonia and Ph_2PCl as well as an apparent reductive dimer $(Ph_2P)_2$. The origin of the extra oxygen is not clear. Pure samples have not at this data been obtained.

Experimental Section

Preparation of $K_2C_2O_2$. Ammonia (125 mL-150 mL) was evaporated from the top of a #4 cylinder of C.P. grade ammonia and condensed into a flame-dried 3-necked 250 mL flask fitted with a mechanical stirrer and a polyethylene paddle, a dry ice condenser and gas inlet tubes, and maintained at -60° by means of a CO_2/i-proponal slush bath. Potassium (1-2 g) was weighed out under mineral oil, rinsed in hexane and transferred in small pieces into the ammonia. A blanket of carbon monoxide (Matheson, C.P.) was maintained until the blue solution faded to an off-white, leaving a thick slurry. Evaporation of ammonia and evacuation to 0.02 torr gave an off-white highly pyrophoric powder.

Reaction of $K_2C_2O_2$ with Ph_2PCl. A batch of $K_2C_2O_2$ was prepared from 1.1 g of K, suspended in THF (50 mL), cooled to -78° with a dry ice/i-propanol slush bath and Ph_2PCl (6.0 mL) added. After warming to room temperature the mixture was filtered, THF evaporated at reduced pressure and the resulting oil bulb-to-buld distilled (140-180°, 0.01 torr) to give a white oil which crystallized in the receiver. Mass Spectral m/e$^+$ 458 (corresponding to $(Ph_2P(O))_2C_2O_2$), and m/e$^+$ at 418 and 370 (corresponding to Ph_2P-PPh_2 and $Ph_2P(O))_2NH$). ir, 2300 cm^{-1}.

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Afterword

A Ph.D. thesis has the obvious, traditional and principle function of recording in detail a body of research. Four or so years are devoted to this research and a few months to setting it down on paper. Time is rarely devoted officially to the aesthetic, moral and political question the research raises. There is a tacit understanding that what we do is good, although we're not sure that what they do is good also. They certainly have their doubts about us, for the last few decades have seen increased distrust of science commensurate with the increased impact of technology on our lives.

The questions that we face though, are political ones: What do we want to do that meets our collective moral and aesthetic desires? Research is not a politically neutral endeavour. Research can be scientifically objective and simultaneously politcally biased. All research represents an advocacy of some sort, even so-called pure research requires a diversion of resources, a diversion without guarantee of return.

This afterword is in part intended as a ballot for the kind of research reported in this thesis, so that this thesis is not just a tacit vote, but an active vote for what may be loosely called the status quo. (That is, present society, with its capacity for ordered growth and change, regardless of the specific changes necessary.) In the past four years I have worked on projects where the knowledge produced would hopefully have practical applications in the petrochemical industry. The petrochemical industry is a quietly controversial one, and touches people's lives more frequently and intensely than the more thoroughly publicized nuclear industry. The questions that are raised by the petrochemical industry are going to be basic to the debates on public policy in the future; a few of them are relevant to this thesis:

> Is the oil consumed to produce chemicals better used as fuel? Are the products worthwhile?
>
> Does the pollution caused by the petrochemical industry cost more than its worth?

These questions reflect on the kind an quality of life that we desire. I have little hesitation in endorsing the general lifestyle held by consensus in this country: A society of great individual mobility and opportunity.

The petrochemical industry is an inextricable but under appreciated and mostly invisible part of the technological base that supports our lifestyle. I support the petrochemical industry, not necessarily as it is, but as it can and ought to be. Petrochemicals are worth their cost in fuel. The propriety of the displacement of wood, metal and glass products can only be determined fairly on the free market. The petrochemical industry can and should become non (not <u>less</u>) polluting, but cleaning up takes time and we cannot afford disruption of our economy for marginal gains in environmental cleanliness.

Having established my political persuasion, I wish to cover two other areas in this afterword: 1. To set the research problems in a general petrochemical context and 2. To set down a special sort of gratitude.

Three areas of research are covered in this thesis. All deal with problems less academic than has been normal. Part I and Appendix I deal with the title subject of this thesis.[22] The improvement of catalysts by design rather than endurance is a noble task in this regard. Part I deals with improvements in homogeneous catalysis. The work was most satisfying because it brought together previously unassociated chemical specialities and produced intriguing results having commercial import and at the same time opened doors for new kinds of chemistry. Appendix I deals with some support work done for this groups organo-titanium catalyst research. The successful portions of the work are reported elsewhere. The work reported here is instructive in supporting the idea that an advance in one project offers opportunities for the solution of standing problems. Appendix II deals with a basic problem of the petrochemical industry, utilization of carbon monoxide. While the project was frustrating for its lack of clean-cut results it was the most stimulating for the same reasons.

I have acknowledged my debt to George Whitesides already. But in the spirit of this afterword I must acknowledge one facet not previously mentioned: the ethical quality of the work. It would be sufficient to work for 4 years on nearly any problem in preparation to do useful work. It is unusual and praiseworthy to have an opportunity to prepare to do useful work by doing useful work, and in my case to have worked on so many important problems. I am grateful most of all for this aspect of my experience at MIT and the credit belongs to George Whitesides.

Biographical Note

The author was born in Chicago, Illinois on October 5, 1952 to Herbert and Shirley Feitler. He was taken by his parents to Southern California where he completed his primary education and entered U.C.L.A. At U.C.L.A. he worked under M. F. Hawthorne and Jules Rebek and cultivated a number of outside interests as well. On graduating from U.C.L.A. he ventured East to M.I.T. and George M. Whitesides. He married Suzanna in the spring of 1977 and has accepted employment at Air Products in Allentown, Pennsylvania.

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3. "Polymer-Bound Tosyl Azide," W. R. Roush, D. Feitler and J. Rebek, *Tetrahedron Letters*, 1391 (1974).

4. "Peptide Synthesis with Carbodiimide III. Racemization," J. Rebek and D. Feitler, *Int. J. Pept. and Prot. Res.*, *7*, 167 (1975).

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