Preparation of a Polymer Supported Cobalt (II) Schiff Base Catalyst

Spring 1979

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PREPARATION OF A POLYMER SUPPORTED COBALT(II) SCHIFF BASE CATALYST

BY

SUSAN L. FUHRMAN
B.S., Florida Technological University, 1977

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the degree of Master of Science: Industrial Chemistry in the Graduate Studies Program of the College of Natural Sciences at the University of Central Florida; Orlando, Florida

Spring Quarter
1979
Polystyrene bis(salicylaldehyde)-propylene-1,3-diiminato Cobalt(II) (salen) and Polystyrene bis(acetylacetone)-propylene-1,3-diiminato Cobalt(II) (BAE) were prepared stepwise from poly-styrl chloride. The reaction series included substitution of the chloride with a malononitrile carbanion, reduction to a diamine, condensation to form a Schiff base, and complexation with Co(II) acetate to form the active polymeric material. Optimum conditions with regard to time, temperature, reaction ratios, and solvent were determined for each reaction.

The ability of the polymer bound cobalt complex to oxidize 3-methyl indole was measured. The BAE catalyst yielded a large amount of the corresponding o-formylaminoacetophenone. However, the exact yield is not known because product could not be separated from the indole. The salen catalyst showed starting material with a small indication of product.
ACKNOWLEDGEMENTS

The author would like to thank Dr. John Idoux for his guidance and patience as he directed this research project. His friendly assistance helped me over many rough spots in the execution of this project.

I would also like to thank the rest of the Chemistry faculty and staff for their interest and instruction. I appreciate the time spent in discussion of the project and the personal assistance in areas unfamiliar to the author.

I would also like to thank my parents for their financial and moral support through the years.

Finally, I would like to thank the contributors to the FTU Foundation Grant, which made the chemical analyses possible.
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ABBREVIATIONS

The following is a list of abbreviations used in this report.

DMF  N,N Dimethyl Formamide
DVB  Divinyl Benzene
ESR  Electron Spin Resonance Spectroscopy
IR   Infrared Spectroscopy
NBS  N-bromosuccinimide
NMR  Nuclear Magnetic Resonance Spectroscopy
\( P \) or \( P^\theta \) Polystyrene - DVB Copolymer
TMED N,N,N',N' tetramethyl ethylenediamine
TrCl Trityl Chloride
INTRODUCTION

The use of polymeric backbones as supports for catalytic and synthetic reactions has increased tremendously in the last few years\textsuperscript{1-5}. This report will review these uses and present a synthesis of a polymer bound cobalt (II) Schiff base catalyst.

To accomplish this, the introduction will be divided into four sections. The first will give general information on polymer supports. The second will examine the use of polymer supports. Complexes of Schiff bases will be the focus of the third section, and the final section will give the background for this particular project.

General Information on Polymer Supports

Polymer supports are used for a diversity of purposes. Thus, many different variables must be considered in selecting the proper support. This section will be divided into four parts. The first will deal with the selection of the proper support. The second will examine the functionalization of that support. The third and fourth parts will examine some of the advantages and disadvantages of using polymeric backbones.

The Selection of the Support

To match the properties of the support to the end use, it is necessary to examine the chemical and mechanical parameters of the polymer. The chemical parameters will determine the lifetime and selectivity of the chemical species. Such properties as inertness
to reagents, degree of mobility of the attached species, polarity of support relative to reactants and products, and availability of the reaction sites to the reagents are necessary to tailor the backbone to the desired use.

The mechanical parameters will determine the effectiveness on a large scale operation. These include engineering properties such as the porosity of the support, the diffusion barrier of the reactant, the surface area of the support, the heat transfer properties, the mechanical stability, and the thermal stability of the polymer. These properties determine the practicality of using the support in the reaction.

Polystyrene crosslinked with divinylbenzene (DVB) is used almost universally in organic synthesis and catalysis. This medium provides an inert backbone with polar properties which can be modified by controlling the functional groups attached to the backbone or by selection of the proper copolymer. Polystyrene swells in solvents such as DMF, benzene, and methyl chloride. It offers a wide range of crosslink densities, surface areas, and porosities based upon the degree of crosslinking. For example, 2% DVB is a swellable, insoluble gel with mobile ligands that forms complexes with the support while maintaining its structural integrity under reaction conditions. On the other hand, 20% DVB is a brittle bead with a rigid structure that powders under laboratory conditions.
Polystyrene does have disadvantages such as poor heat transfer, poor mechanical stability, and poor thermal stability. For this reason, many engineers prefer clay supports which have better mechanical and thermal stabilities. Clays, however, do not have the flexibility of use of polystyrene. Thus, most research is being done on polystyrene supports.

The Functionalization of a Polystyrene Support

After choosing the proper support, it is important that a functional group be introduced that offers the flexibility of a variety of reactions. The purity of the polystyrene-DVB must be ascertained since minute amounts of surface impurities remaining from polymerization reactions may prevent even distribution of the functional groups.

The two methods used almost universally are shown in equations 1 and 2. The first is the chloromethylation of styrene.

Eq. 1. \[ \text{polystyrene} + \text{Cl}\text{-CH}_2\text{-O-CH}_2\text{-CH}_3 \xrightarrow{\text{SnCl}_2} \text{polystyrene-CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} \]

Eq. 2a. \[ \text{polystyrene} + \text{Br}_2 \xrightarrow{\text{FeCl}_3, \text{reflux CCl}_4} \text{polystyrene-Br} + \text{n-butyl lithium} + \text{n-butyl lithium} \]

Eq. 2b. \[ \text{polystyrene} + \text{n-butyl lithium} \xrightarrow{\text{TMED, quenched Co}_2} \text{polystyrene-Li} \]

This rapid, one step reaction often increases crosslinking due to
the formation of methylene bridges.

The second set of reactions is the bromo-lithiation of polystyrene. This reaction is more expensive, but the polymer backbone remains unchanged. Braun\textsuperscript{7} used the two step reaction shown in 2a. The bromination gave a 96% yield. The yield of the lithiation step depended upon the type of polymer used, the degree of bromination and the solvent. It gave 100% para-product. Chalk\textsuperscript{8} used a one step reaction in the presence of N,N,N',N' tetramethylethylene-diamine (TMED) to obtain a 0.6 to 0.9 milliequivalents (meq) gram product. The addition occurred at the meta- and para-positions.

Once the initial functionalization of the polymer support is accomplished, ordinary organic reactions can be used to link an organic compound to the support. The two major reaction pathways are nucleophilic and electrophilic substitution. Nucleophilic substitution utilizes the chloromethylated support and consists of substitution of the chloro group with a stronger nucleophile such as those seen in reactions 3a and 3b. Electrophilic substitution

\begin{equation}
\text{Eq. 3a.}
\end{equation}

\begin{equation}
\text{Eq. 3b.}
\end{equation}

utilizes the lithiated support and consists of substitution of the lithium group with a stronger electrophile such as those seen in
reactions 4a and 4b.

Eq. 4a.

There are three important analytical factors which must be considered for each link. The first, the percent substitution, is determined by elemental analysis. The chloromethylated support uses the wet analysis of chlorine\(^9\) to obtain the degree of functionalization. However, this method gives no information about the distribution of the linkages which is the second important analytical factor. Local concentrations of ligands are often important in the properties of a support. This parameter is often determined by the electron microprobe of a one to ten micron cross-section of the bead\(^10\).

The third important analytical factor is the chemical structure of the linking agent. Spectroscopy is the best method of determining this qualitative information\(^11\). If strong absorbing functional groups are present, IR may be used to determine the structure. When resin absorptions obscure functional groups, subtractive IR may dramatically simplify the spectra. NMR may be run during the course of the reaction to measure the formation of groups such as phosphine dichloride. ESR will measure the mobility.
of the resin pendant groups.

All of this information is combined to determine if the functionalization of the polymer support proceeded properly.

The Advantages of Polymeric Backbones

The use of polymeric supports simplifies multistep synthesis. By tying down the reactive groups, the backbone makes possible multistep synthesis and maximizes yields while minimizing time. This was first brought into the limelight by Merrifield with his synthesis of RNA\(^{12}\). The hooplane synthesis\(^{13}\), shown in equation 5 is an example of a synthesis made possible by the polymeric support.

$$\text{Eq. 5. } \text{repeat 70 times} \quad \begin{array}{c}
\text{NaHCO}_3 \\
\text{MeOH}
\end{array} \rightarrow \begin{array}{c}
\text{Ph}_3\text{CO} \\
\text{O}
\end{array} \quad \text{TrCl-1,10-decanediol}$$

The insoluble carrier allows many repetitions of the threading step. Unthreaded reactants are removed and recycled. Thus, the polymeric support is very useful in the synthesis of compounds with low yields due to statistical reasons.

The second advantage of polymer supports is that it allows automated synthesis in repetitious reactions. Chang\(^{14}\) demonstrated this by his synthesis of protected peptide hydrazide on a recycled
hydroxymethyl resin. The Edman Degradation of a peptide uses the same principle for the reverse of synthesis. A peptide is blocked and attached to a polymer support. It is then automatically degraded from the N-terminal end through twenty-one steps to give its components. In solution, it is difficult to separate the phenylthiohydantoin and the anilinothiazolidone from the residual peptide so each step has to be performed separately. Attachment to a polymer allows the reagents to be mechanically washed away so that automation is possible.

Polymer supports allow the use of excess reagents to enhance the rate of diffusion of the reactants to the reaction site. This increases the reaction rate. It also saturates the system with an excess of reaction sites to push the reaction to completion. This is the third advantage to be found in polymeric backbones.

The fourth advantage is the elimination of noxious or odorous vapors from the reaction. Equation 6 shows the synthesis of styrene oxide using a ylide reagent. The sulfur is attached to the polymer at all times so that there is no odor. Normally, special traps would be needed in the separation and recycle steps; but here, filtration is the only requirement.

\[
\text{Eq. 6. } \begin{align*}
\text{P-O-SMe} & \quad \text{MeBr} \quad \text{PhCHO} \\
\text{SMe} & \quad \text{Me} \\
\text{Ph} & \quad \text{CH} \\
\text{O} & \quad \text{CH}_2
\end{align*}
\]
The final advantage to polymer supports is its provision of a special environment around the reacting species which may favor one product over another\textsuperscript{18}. This environment is imposed by the diffusion of the species into the pores.

The construction of the pores and of the backbone will influence diffusion. If the pore is small, the internal channels will be selective for small molecules. Thus, larger molecules will not be able to diffuse to the reactive sites and product distribution is affected. If the pore is curvy, molecules with bulky groups will have a tendency to be blocked and not enter the inner sphere to react. Bulky substituents on the polymer backbone may block the entry of some components. The polarity of the backbone will control the swelling of the polymer. Polar solvents cause some polymers to swell and become less rigid. The pore sizes are reduced and the reactant site movement occurs. This will alter the internal movement of components and affect the product distribution. The bromination of cumene with NBS\textsuperscript{19} shows a change of mechanism when attached to a carrier. The carrier is a polar environment with interaction between neighboring succinimide units. The final product distribution was different than solution chemistry. To prove that the polarity of the carrier was causing this mechanism change, Yaroslavsky and associates ran the soluble bromination in a polar solvent. This yielded a product distribution similar to the polymer bound reagent and proved that the environment of the
polymer changed the normal mechanism of the reaction.

The Disadvantages of Polymeric Backbones

In order to obtain a pure product in a series reaction, all steps must go to completion. If they do not, cleavage of the product from the polymer at the end of the reaction will yield a mixture that is very difficult to separate. This is the first disadvantage of the use of polymeric backbones. This is most significant in biochemical reactions where one step may drastically alter the chain.

A second disadvantage is that cleavage of the products is often incomplete. This decreases the yield of the product and deactivates the polymer for further use. This effect has been attributed to steric hindrance of the polymer.

Steric hindrance is also blamed for the third disadvantage. This, coupled with incompatibility of the polymer and reactants, and absorption of the products on the resin, produces the lower yields observed with polymer bound reactants.

The fourth disadvantage is that the polymer will only swell in a small number of highly polar solvents. Before a synthetic scheme can be widely applied, a broad spectrum of solvents must be available for use. The polymer bound compound is most effective in its swollen state. Thus, many syntheses are not practical because of solvent effects.

Side reactions may occur in polymer bound reactions because
protecting groups are often inadequate\textsuperscript{20,21}. This is a minor problem involving a small number of reactions. The final disadvantage concerns mechanical problems. Some polymers partially disintegrate during the reaction and liberates fine particles which may contaminate the product. New methods of agitation need to be developed to overcome this problem.

**The Use of Polymeric Supports**

Polymer supports are beginning to be recognized as an economical alternative to solution chemistry. To date, applications fall into five major categories. Research is being done to expand the uses. Table I shows each of the categories.

The use of polymer supports can be conveniently divided into two areas: synthesis and catalysis. In these areas, the polymer backbone affects both the productivity and the economics of reactions.

**Organic Synthesis**

Reactions under this category fall into four areas.

A. Polymer Bound Organic Reagents

The use of polymer bound organic reagents is becoming more popular as energy costs rise. The reason is that at the end of the reaction, byproducts are linked to the polymer and easily separated by filtration. This eliminates costly solvent extraction and chromatography techniques and is especially useful in reactions where byproducts are difficult to separate from the main product.
<table>
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<th>Formula</th>
<th>Distinguishing Feature</th>
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<td>Polymer Bound Reagents</td>
<td>$\left{ P^{-A} + B \rightarrow \left{ P^{-A'} + P \right} \right.$</td>
<td>Byproduct remains attached to polymer.</td>
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<td>Polymers as Tying Agents in the Separation of mixtures</td>
<td>$\left{ P^{-A} + B + C + D \rightarrow \left{ P^{-A-B} + P^{-A} + B \right} \right.$</td>
<td>Polymer holds the compound while others are washed away. No reaction occurs.</td>
</tr>
<tr>
<td>Polymers as Transfer Agents</td>
<td>$\left{ P^{-A} + B \rightarrow \left{ P + P \right} \right.$</td>
<td>Polymer transfers one reagent to another. It remains unchanged during the reaction.</td>
</tr>
<tr>
<td>Polymers to Promote Intrapolymeric Reactions</td>
<td>$\left{ P^{-A} + P^{-B} \rightarrow \left{ P + P \right} \right.$</td>
<td>Both interaction molecules are attached to the polymer.</td>
</tr>
<tr>
<td>Polymers as Catalyst Carriers</td>
<td>$\left{ P^{-A} + B \rightarrow \left{ P^{-A} + P \right} \right.$</td>
<td>The bound catalyst causes reactions to occur.</td>
</tr>
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$A = \text{bound species} \quad P = \text{product} \quad A' = \text{byproduct} \quad B,C,D = \text{other reactants}$
One example is the Wittig reaction\(^5\). In the solution phase, separation of the byproduct triphenylphosphine oxide from the ketone product is difficult. By attaching the reagent to a polymer, the byproduct can simply be filtered out and a relatively pure product obtained. (Equation 7.)

\[
\text{Eq. 7.} \quad \begin{array}{c}
\text{P} - \text{O} - \text{P} \\
\text{O} - \text{C} - \text{R} \\
\hline
\text{RCH}_2X
\end{array}
\rightarrow
\begin{array}{c}
\text{P} - \text{O} - \text{P} \\
\text{O} - \text{C} - \text{R} \\
\hline
\text{RCH}_2RX
\end{array}
\]

The use of a polymer bound carbodimide as a condensing agent is another example of separation efficiency. In the liquid phase, there is often a problem of urea contamination in the product because of the separation difficulty. In the condensation of acids to anhydrides shown in equation 8, Weinshenker and Chen\(^22\) found that the polymeric reagent circumvents this difficulty since the urea is bound to the polymer\(^{23,24}\).

\[
\text{Eq. 8.} \quad \begin{array}{c}
\text{P} - \text{O} - \text{CH}_2 - \text{N} = \text{C} - \text{N} \\
\hline
\text{+ stearic acid}
\end{array}
\rightarrow
\begin{array}{c}
\text{stearic anhydride} \\
\text{+ P} - \text{O} - \text{CH}_2 - \text{NH} - \text{C} - \text{NHCH}_2(CH_3)_2
\end{array}
\]

Similar results were obtained using carbodimides in the Moffat oxidation of alcohols to aldehydes\(^{25}\).
The epoxidation of olefins by peracid reagents, shown in equation 9, further demonstrates this principle. Takagi \(^{26}\) and Helfferich \(^{27}\) found that the product yield was similar to that obtained with soluble phosphonium reagents. The acid byproducts remained attached to the polymer so that the epoxide was obtained by simple evaporation.

\[
\text{Eq. 9. olefin + } \overset{\text{O}}{\text{R} - \text{C-OOH}} \rightarrow \text{epoxide} + \overset{\text{O}}{\text{R} - \text{C-OH}}
\]

The polymer bound reagent also gave stereochemical control of the reaction by eliminating lithium ions in the reaction. Normally, lithium bases are used to form the ylide. These lead to trans-olefins. The polymer bound reagent eliminates lithium and gives a high yield of cis-olefins.

Thus, polymer bound reagents are useful for reactions where byproducts are difficult to separate from products and in reactions where residual ions from a previous step may affect the main reaction.

B. Polymer Backbones as Tying Agents in the Separation of Mixtures.

In the separation of a mixture of compounds, selective binding of one component to a polymer backbone will allow the other component to be washed away. Cleavage of the bound component yields the desired component in pure form.

This technique is especially useful in the resolution of an optically active mixture. A large functional group which contains
a template of the desired component is bound to a rigid, non-
swellable polymer. The template is removed leaving a fixed
stereochemistry inside the cavity of the polymer which corresponds
to the template. A recemic mixture is added. If access to the
inner channels of the polymer is adequate, the desired component
will penetrate and react with the polymer. The other enantiomer
will be washed away. The bound component is cleaved and obtained
in pure form. Wulff and associates\textsuperscript{28} used this technique to
separate D,L-glyceric acid and reported a resolving factor of
1.034.

As seen above, polymer backbones offer a relatively cheap,
simple, recyclable method of separating closely related compounds
without the expenditure of a large amount of energy.

C. Polymer Backbones as Transfer Agents.

In the course of an organic reaction, a polymer backbone may
be used to transfer a functional group to another reactant to form
the product. Equation 10 shows an example where this occurs in
the acylation of amines\textsuperscript{29}.

\[
\begin{align*}
\text{Eq. 10.} \\
\text{Recycle}
\end{align*}
\]

That is, the polymer backbone is unchanged by the reaction
and simply holds one reactant in a specific position available for
reaction. Polymer transfer reagents may be useful in situations where multiple reactions are possible. In the reaction above, the steric hindrance of the polymer prevents the second amine hydrogen from reacting. Thus a narrower distribution of products is obtained.

The halogenation of alkylaromatic compounds by halide polyvinyl pyridine complexes is another example of this principle. This reaction gives a high yield of mono-halogenated compounds. This results from the creation of a special micro-environment by the polar backbone. This effect has been previously discussed.

D. Polymer Backbones to Promote Intrapolymeric Reactions.

When two molecules that are both absorbed on a polymer react to form a product, an intrapolymeric reaction occurs. There are two kinds of reactions that fall under this heading, reactions that proceed because of proximity effects and reactions that proceed because of high dilution by the polymer.

Proximity effects are noticeable in rigid polymers that have high concentrations of pendent groups. The attached molecules are forced together in close proximity. This sometimes causes a fast, selective reaction to occur between the molecules. Equation 11 shows an example of a mixed ester condensation which typifies this situation. An aromatic ester is placed on a polymer backbone in high concentration. An aliphatic ester is added at low concentration. The polymer is then subjected to a base and cleaved with
hydrogen bromide to yield a polymer, a ketone, and an aromatic acid.

\[ \text{Eq. 11.} \quad \begin{array}{c}
\text{CH}_2\text{O-C-Ar} \\
\text{CH}_2\text{O-C-CH}_2\text{C} \\
\text{CH}_2\text{O-C-Ar}
\end{array}
\xrightarrow{(1) \text{Base}}
\begin{array}{c}
\text{CH}_2\text{Br} \\
\text{CH}_2\text{Br} \\
\text{CH}_2\text{Br}
\end{array}
\xrightarrow{(2) \text{HBr}}
\begin{array}{c}
\text{CH}_2\text{Br} \\
\text{Ar-C-OH} \\
\text{RCH}_2\text{-C-Ar}
\end{array} \]

This cannot be duplicated in solution because a complex mixture results from the self-condensation of the aliphatic ester. The polymer backbone separates the aliphatic esters and brings about close proximity of the aliphatic and aromatic ester groups. As expected, there is a strong relationship between the ketone yield and the ratio of the ester concentrations. If this ratio is over ten, the yield should be nearly quantitative. The polymer backbone must be rigid because a flexible lattice would not force the molecules together.

The complexation of alkali metal ions with crown ethers is another example of the proximity effect. Pederson and Frensdorf found that crown ethers form complexes with alkali metal ions in solution. Kopalow discovered that polymer bound crown ethers form complexes of the same stoichiometry as soluble crown ethers and that the polymer bound crown ethers have more complexing power than the corresponding soluble ethers. It was explained that the polymer matrix holds the two crown ethers in close proximity so that the 2:1 complex will form faster and easier than the three unit complex in solution. This cooperative effect shows that the
reaction of two pendent groups on a polymer backbone with a third reactant in solution mimics a bimolecular reaction which has less stringent entropy requirements than a termolecular reaction in solution\textsuperscript{36}.

The second effect that a polymer backbone has on an intrapolymeric reaction is that it provides an environment of high dilution. A rigid polymer at low concentration mimics an infinitely dilute solution. Intermolecular reactions are inhibited causing intramolecular reactions to occur more frequently\textsuperscript{5}. This limits the number of byproducts and allows selective transformations to occur which would require solutions that are too dilute to be feasible on a large scale. The preparation of macrocyclic compounds via the Dieckman condensation\textsuperscript{37,38} shown in equation 12, exhibits this property.

Eq. 12.

\[
\begin{align*}
&\text{P} \overset{\text{O}}{\underset{\text{O}}{\text{O}} \text{-O-C-Pep-NHZ} \rightarrow \text{P} \overset{\text{O}}{\underset{\text{O}}{\text{O}} \text{-O-C-Pep-NH}_{2} \rightarrow \text{P} \overset{\text{O}}{\underset{\text{O}}{\text{O}} \text{-OH} + \text{Pep}}
&\end{align*}
\]

In solution, this is a low yield reaction with many linear and cyclic byproducts. If the terminal ester of a protected peptide is attached to a polymer backbone and then the amino acid is deprotected, cyclization can be accelerated. The limited number of functional groups allows the formation of cyclic monomers over linear reaction products.
Crowley and Rapoport used this principle in the preparation of cyclic $\beta$-ketoesters using radioactive compounds to follow the reaction. From the reaction shown in equation 13, they obtained yields on the order of 30 to 40%. It has been found that in general, all cyclizations give good yields of pure products when forming five- and six-membered rings. Medium and large rings, however, show low yields because of the occurrence of intrapolar intermolecular reactions.

Eq. 13.

\[
\begin{align*}
\text{(P-O-CH}_2\text{O-)}_{2} & \text{CH}_2\text{O-CH}_2\text{O-C-(CH}_2\text{)}_3\text{CH}_2\text{O-C-(C}_2\text{H}_5\text{)}_3 + \text{OC}(C_2\text{H}_5)\text{ }_3 \\
\text{P-O-CH}_2\text{O-C-O-C-(C}_2\text{H}_5\text{)}_3 & \text{C}_2\text{H}_5 + \text{O-C-C-(C}_2\text{H}_5\text{)}_3
\end{align*}
\]

Another aspect of high dilution involves using polymers as blocking groups in the mono-reaction of symmetric bifunctional compounds. When a large excess of bifunctional compound is placed with a functionalized polymer, only one site of the compound will react and be blocked. The polymer separates sites and provides an environment of high dilution. The blocked polymer product can be filtered from the mixture and reacted further. Equation 14 shows the preparation of ethers from symmetrical diols using a polymeric acid chloride. Recycling of the polymer bound chloride results in a 50% reduction for each run because of incomplete
Eq. 14

\[
\begin{align*}
\text{P} - \text{CH}_2 - \text{C} - \text{O} - \text{Cl} + \text{HO(CH}_2)_n \text{OH} & \rightarrow \text{P} - \text{CH}_2 - \text{C} - \text{O} - (\text{CH}_2)_n \text{OH} \\
\text{P} - \text{CH}_2 - \text{C} - \text{OH} + \text{HO(CH}_2)_n \text{OTr} & \leftarrow \text{B} - \text{P} - \text{CH}_2 - \text{C} - \text{O} - (\text{CH}_2)_n \text{OTr}
\end{align*}
\]

cleavage of the ether. Thus, yields are still less than optimum for the individual situation.

A more successful reaction that typifies this approach involves the reaction of one aldehyde from a symmetrical dialdehyde\(^{44}\). The symmetrical dialdehyde was attached to a polymer by an acetal linkage via one of its aldehyde groups. The free aldehyde was run through a series of reactions and the products were cleaved from the polymer. Reaction of the aldehyde with excess hydroxylamine hydrochloride gave an oxime. A diarylpolyene was produced by the Wittig reaction using benzyl triphenyl phosphonium bromide in DMF and sodium methoxide. A crossed aldol condensation was run. The blocked aldehyde and benzaldehyde were condensed to give a mixed or crossed benzoin. Previous attempts to use benzoin condensation yielded a complex mixture because of the different aldehydes present in the starting mixture. With a polymeric blocking group, the insoluble resin which contains the crossed product is filtered out of the symmetrical benzoin and the excess reagent. The only problem with this synthesis is that the acetal linkage is only stable under basic conditions. This limits its use in the industrial
environment.

Even though most investigators agree that high dilution occurs, there is evidence that this effect is not consistent for all rigid polymers. There are reports that even with functionalizations as low as 0.5%, separation of sites does not occur. This is an area of current research and debate.

Catalysts
A. General Information

Catalysis may be carried out in a single phase, homogeneously, or in two phases, heterogeneously. Homogeneous catalysts usually have better defined active sites than heterogeneous catalysts. Under homogeneous conditions, all of the metal is usually available for catalysis and normally the steric and electronic environments about the metal atom can be varied at will. In addition, homogeneous catalysis is usually faster and more selective than heterogeneous phase catalysis.

Homogeneous catalysis does have several disadvantages. Under normal circumstances, some of the expensive metal is lost during separation. Thus, the separation of the catalyst from the product without loss of metal is complex and expensive. These catalysts are easily deactivated by the products or by extreme temperatures. Corrosion of the reactor is also common.

In an effort to use homogeneous catalysts under heterogeneous conditions, three approaches have been used. For gas phase reactions, the homogeneous catalyst has been dispersed in a high
boiling solvent inside the pores of a molecular sieve\textsuperscript{47}. For liquid reactions, the catalyst has been attached to an inorganic carrier such as silica gel\textsuperscript{48} by covalent bonds. The catalyst has also been covalently bonded to an insoluble polymer. The latter approach provides a number of advantages.

By binding a homogeneous catalyst to a solid support, the advantages of homogeneous catalysis are retained and most of the disadvantages are removed. Physically, the bound catalysts are heterogeneous because they are insoluble in the reactant and may be filtered out. Chemically, these catalysts are homogeneous since they are prepared from the same complexes as solution catalysts. The chemistry around the metal atoms is the same as in homogeneous catalysts so they are studied under conditions comparable to conventional homogeneous catalysts such as 100°C in liquid phase. All of the catalysts reported to date have retained their basic activity\textsuperscript{3}. For example, a Mobil Oil group\textsuperscript{49} has reported than an attached Rh(I) hydroformulation catalyst in a fixed bed reactor produces $4 \times 10^5$ moles of product per mole of catalyst. Lab scale research indicates that the catalyst can be used over eighty times in a batch reactor without loss of activity.

Common complexing groups are used as linkages between the polymer and the metal complex. These linkages are covalently bonded to the pendent groups of the polymer backbone.

One type of linkage contains phosphine groups\textsuperscript{50}. Linkage
must be established through more than one phosphine group or the complex is easily lost. Normally, multiple linkages are used as shown in the rhodium catalyst\textsuperscript{51} in equation 15. Amine linkages are more stable than phosphine linkages\textsuperscript{52}. Schiff bases are widely used as catalyst carriers and will be discussed in a later section.

Eq. 15.

\[
(\theta_3P)_5\text{RhCl} + 2 \text{P} \theta - \text{P} + \left( \text{P} \theta \text{O} \text{P} \right)_5 \theta \text{RhCl} + 3\theta_3 \text{P}
\]

Cyclopentadienyl\textsuperscript{53} linkages are also used. A classic example of this linkage is the titanocene dichloride catalyst which is attached to a 20% crosslinked polystyrene-DVB support. This reaction will be discussed in greater detail in a later section.

B. Advantages of Using Polymer Supported Catalysts

Some of the advantages of using solid supported catalysts parallels the use in organic synthesis such as separation. The separation of a solid catalyst from liquid reactants has obvious advantages from the viewpoint of time, energy and efficiency. There are other advantages that are unique to the polymer supported system.

The first advantage that stems directly from the polymer support is the enhancement of the catalyst's stability toward oxidation and hydrolysis. The addition of an aluminum chloride catalyst to a crosslinked polystyrene produces a catalyst that is more resistant to the atmosphere than the pure catalyst\textsuperscript{54}. Pittman
and Evans\textsuperscript{55,56} prepared this catalyst by swelling the polymer in a suitable solvent, attaching the catalyst to the inside pore structure of the polymer, contracting the polymer, poisoning the outside sites, and drying the finished catalyst. Equation 16 shows the execution of this method. The finished catalyst is a shelf stable acidic material with an active ingredient which can be called out by swelling in a solvent such a benzene, hexane, or carbon disulfide.

Eq. 16.

\[
P + \text{C}_2\text{S} + \text{AlCl}_3 \xrightarrow{\text{reflux}} \text{H}_2\text{O to hydrolize}} \xrightarrow{\text{wash ether}} \text{acetone, hot-i-propyl alcohol, ether}
\]

\[
\xrightarrow{\text{dry 8 hours}} \text{P-AlCl}_3
\]

The reaction of the polymeric catalyst gives a cleaner reaction than the monomer. It is thought that the polymer backbone mediates the effect of the strong Lewis Acid so that fewer byproducts of high molecular weight are formed. Neckers and coworkers\textsuperscript{55} supported this assertion with evidence that showed lower loadings of catalyst gave better results. Blossey\textsuperscript{57} found that the crosslinked styrene entraps the water so that the polymeric aluminum chloride is free to work. For this reason, the polymer bound reagent is preferred when the byproducts include water and when mild reaction conditions are necessary. For example when aluminum chloride is used to facilitate esterification\textsuperscript{54}, water is
always a byproduct. By using the polymer bound reagent, the water is entrapped and the reaction is pushed toward completion. The formation of ethers from carbinols, shown in equation 17, is a case where mildness and dehydration is desired. The mildness is necessary because of the strained nature of the molecule. The dehydration pushes the reaction to an 81% yield. This demonstrated that polymer attachment of catalysts protects many anhydrous and pyrophoric reagents.

\[
\text{Eq. 17. } 2\text{H-C-OH} \xrightarrow{\text{P-AlCl}_3} \text{H-C-O-C-H} + \text{H}_2\text{O}
\]

The unique polar and steric environment provided by the polymer in a polymer bound catalyst is the basis for the second major advantage. This environment, which is vastly different from solution chemistry, may enhance the specificity and activity of the catalyst.

When metal complexes are present, there may be localized steric congestion around the catalytic center. The complex may cause crosslinking in the immediate vicinity of the metal. This limits the way a molecule can approach the catalyst. Since selection of the size of the molecule that can approach the catalyst site is determined by the overall geometric and polar properties of the polymer, the steric environment will be a major factor in the type of product distribution. Haag supported this when
he found that the rate of a Ph(I) olefin hydrogenation catalyst was inversely proportional to the molecular size and the degree of cyclization. This also proved that most of the reduction occurred inside the polymer bed.

There are certain restrictions on the ligands used to complex the catalyst if this steric and polar environment is to be achieved. For example, if the polymer is sufficiently mobile to bring non-adjacent sites together, the phosphine ligands may chelate. This will destroy the steric environment and deactivate the catalyst. Thus steps must be taken to ensure clear catalytic sites.

This is the third advantage of using polymeric supports as catalyst carriers. The separation of sites achieved by the pendent groups tends to stop the aggregation of metallic catalysts which sometimes occurs in solution chemistry. A supported [Pd(NH₃)₄]⁺² catalyst was found to be more active than the homogeneous complex. In solution, aggregation of the palladium occurred to give a catalytically inactive, insoluble polymeric species of low surface area. The polymer support separated the sites and activated the catalyst.

The classic example of this principle is the titanocene catalyst. The preparation of this catalyst is shown in equation 18. The titanocene catalyst is a highly reactive catalyst in the reduction of olefins and acetylenes. Bonds group found that when the catalyst was supported on a 20% rigid crosslinked polymer and compared to solution chemistry, a 60 to 120 fold increase in
activity was observed. Grubbs and Kroll found similar results. The explanation that was offered contends that free titanocene complexes readily polymerize to form inactive materials of low solubility. Attachment to a rigid matrix with less than 10% substitution on the aromatic rings prevents metal-metal bond formation. Thus, more monomeric catalyst is available for reaction and efficiency increases. The distribution of the metal was measured by ESR.

Several types of supporting evidence was presented. Further evidence demonstrated that the activity was directly related to the amount of crosslinking. Bond and his coworkers found that if mobile ether links were incorporated, aggregation still occurred. Compilation of these results indicated that aggregation of metal occurred in mobile polymers but not in rigid polymers.

**Complexes of Schiff Bases**

Catalysts were attached to polymeric supports by many functional groups. This section will examine the functional group
in this study, the Schiff base. In recent years, much study has been directed towards these compounds because of their similarities to porphyrin and vitamin B-12 models.

Schiff base complexes are stable at room temperature and atmospheric conditions, insoluble in water, and soluble in carbon tetrachloride\textsuperscript{60}. The complexes are thought to be square planar simply because the metal cannot occupy two equilateral and axial positions at the same time\textsuperscript{61}. Since Schiff bases change structure under different pH conditions, pH control is necessary to form stable complexes\textsuperscript{62}.

It has long been known that Schiff bases will chelate metals\textsuperscript{62}. Cobalt(II) and Cobalt(III) are among these metals\textsuperscript{63,64}. These bases can be combined with other functional groups to form complexes. For example, a phenolic Schiff base will chelate copper ions\textsuperscript{65}.

Two of the most important Schiff bases used to chelate metals are the salicylaldehyde and acetylacetone groups. Since Co(II) is the complex formed in this study, the preparation of these two complexes with this metal will be examined.

The soluble Co(II) salicylaldehyde complex (Co-salen), shown in Figure 1, can be prepared in two ways\textsuperscript{66}. In the first, the formation of the Schiff base and the complexation is occurring simultaneously in solution. Salicylaldehyde, Cobalt acetate·4H\textsubscript{2}O, and an α-branched alkyl amine are heated in ethanol in the presence of 4 N sodium carbonate. The salicylaldehyde and amine react in solution to form the Schiff base and then the cobalt complexes.
Figure 1. The Co-salen Soluble Catalyst.
In the second preparation, the cobalt is already complexed with the salicylaldehyde and simply chelates with the amine. In this method, bis(salicylaldehyde)Co(II)·2H₂O and an excess of α-branched alkyamine were heated in methanol or ethanol. The products from both preparations were identical.

The Co(II) acetylacetone complex (Co-BAE), shown in Figure 2, was found to be insoluble in nonpolar solvents, but soluble in methanol. It was prepared by complexing the cobalt(II) salt with an acetylacetone Schiff base. Morgan and Smith reacted cobalt chloride, hot water, sodium hydroxide, and the acetylacetone Schiff base to recover the complex shown in Figure 2. Bigotto and coworkers eliminated the sodium hydroxide by reacting cobalt acetate and the acetylacetone Schiff base under a nitrogen blanket. The two complexes were then used to study the catalytic properties of cobalt.

Cobalt Schiff bases have long been known as active catalysts. The reduction of double bonds of a quadricyclane is one example of their use. In this reaction, there is some oxidation of the Co(II) to Co(III) upon repeated use, but treatment with a reducing agent reactivated the catalyst. Co-BAE and Co-salen have both been shown to be capable of reversibly taking up molecular oxygen in aprotic solvents to give 1:1 oxygen adducts. This property is currently under study as a method of isolating pure oxygen from air for use in the gasification of coal. Upon recycling, the
Figure 2. The Co-BAE Soluble Catalyst.
crystal dimensions of the catalyst change. This sets up strain and gradually results in fragmentation of the crystal.

Now that the general properties of cobalt Schiff base complexes are known, the questions that remains to be solved is whether the properties of these catalysts will change upon attachment to a polymer.

Kupchan and associates\textsuperscript{72} prepared the polymer bound Co(II) porphyrin shown in Figure 3. This complex was found to be an effective oxidizing agent for thiols. The polar bound catalyst did not show deactivation upon reuse and the activity depended upon the polymer support. Table II shows the activity ratios of the catalysts.

\begin{table}[h]
\centering
\caption{Activity of Polymer Bound Soluble Catalysts}
\begin{tabular}{ll}
Solution & 1.0 \\
Carrier #1 & 0.089 \\
Carrier #2 & 4.0 \\
\end{tabular}
\end{table}

The reason the second catalyst was more active than the first was than it swells more and diffusion is accelerated. The polar environment explains its increased activity when compared to solution.

Sasasaki and Matsunage\textsuperscript{73} prepared the hydrogen peroxide
Figure 3. The Polymer Supported Thiol Catalyst
decomposition catalyst shown in Figure 4. The polyethylene carrier increased the activity of the polymer. The polymer decreased the interaction between the cobalt and the nitrogen of the pyridine ring. This enhanced the catalytic activity. Infra-red studies of the bound catalyst have shown that bond distances are consistent with the monomer. Thus, the catalyst retains its structural integrity.

Gaul has found that when dealing with polymer bound salen catalysts, loading is more important in achieving site separation than crosslinking. This suggests that salen catalysts are subject to aggregation and that low loadings are desirable.

**Background For This Study**

From the preceding section, it is evident that Co(II) porphyrin catalysts have been attached to a polymer backbone and retained their catalytic activity. In those studies, the catalyst was obtained in soluble form and then attached to the polymer. In the current study, the aim is to build the complexing group stepwise on the polymer and then form the catalyst by chelating the polymer bound species. The Co-salen and Co-BAE groups will be used to complex the cobalt.

The main thrust of this work will be the synthesis of the catalyst since this differs from previous attempts. Some catalytic work will be done to determine if the catalyst retains its activity.

In 1975, Nishinaga reported that soluble bis(salicylidene)
Figure 4. The Polymer Supported Hydrogen Peroxide Decomposition Catalyst.
ethylenediamatocobalt(II) catalyzed the oxygenation of 3-substituted indoles to give the o-formylaminoacetophenone derivatives. The reaction scheme is shown in Equation 19. The reaction was quick and clean. The current study will deal with the polymer bound analog of the salen catalyst. Since a Co-BAE catalyst often mimics Co-salen catalysts, both will be prepared in the polymer found form. Figure 5 shows these polymeric materials.

Eq. 19.

Idoux, Bied-Charreton, and Gaudemer have reported the synthesis of a polymer bound Cobalt(II) salen Schiff base complex. However, no attempt was made to study the parameters of the reaction. In the current study, a number of reaction variables will be investigated in an attempt to optimize the synthesis of the polymer bound catalysts.
Figure 5. The Polymer Bound Co-salen and Co-BAE Catalysts
EXPERIMENTAL

The preparation of the catalyst carrier is initiated by the reaction of a chloromethylated polystyrene carrier with a mononitrile carbanion to yield the polymer-bound dinitrile. The nitrile is reduced to the corresponding diamine and condensed to yield a Schiff base. Cobalt is complexed into the functional group to complete the catalyst. The reaction sequence is shown in Figure 6. The specifications for reagents and instruments are shown in Table III.

Preparation of I (Polystyrene Malonitrile)

A hydrogen ion was extracted from malonitrile using a strong base, either sodium ethoxide or potassium tertiary butoxide. Sodium ethoxide was prepared by adding pure sodium to absolute ethanol. Tertiary butoxide was obtained in powder form. First base, solvent, and malonitrile were stirred and heated to reflux. Then, crosslinked chloromethylated 2% polystyrene-DVB was added and the reaction was stirred at reflux.

At the completion of the reaction, the polymer was filtered using suction. The polymer was washed with a series of acidic, basic, polar, and non-polar solvents to remove unreacted starting materials and impurities from the pores of the product. The polymer was placed in a vacuum desiccator at 80°C to dry. Infrared spectra (KBr Pellet) and elemental analysis were used to determine the
Figure 6. The Basic Reaction Sequence
### TABLE III
Specifications of Chemicals and Instruments

**Chemicals Used in the Reaction and Clean Up**

**Absolute Ethanol - Reagent Grade**

Anhydrous Ethyl Ether - Mallinckrodt, Lot DAJ, .01% H₂O, ACS Reagent Grade

Benzene - Fisher Scientific Co., Catalog B-243, Lot 745397, ACS Reagent Grade

Chloroform - Matheson, Coleman and Bell, CV 1055, CB 294, ACS Reagent Grade

Cobalt(II) 2,4-Pentanedionate - Alfa Products, Lot # 032276

Column Absorbent - Mallinckrodt Chem. Works, Silicar CC-7, 100-200 mesh, ACS Reagent Grade

DMF - Fisher Scientific Company, Lot 71230 with .1% H₂O, ACS Reagent Grade

**Ethanol - Reagent Grade**

Ethyl Acetate - MCB, Catalog CB 886, ACS Reagent Grade

Hexanes - Fisher Scientific Co., Lot 740909, Bp range 68.6 - 68.9°C, ACS Reagent Grade

Hydrochloric Acid - Mallinckrodt, Lot # 2612-6, ACS Reagent Grade

Lithium Aluminum Hydride (95%) - Alfa Products, Stock # 11111, Lot # G5

Malononitrile (99%) - Aldrich, Catalog # M 140-7, ACS Reagent Grade

Merrifield Resin (1.04 meq Cl/g) - Lab Systems Inc., Lot PPMR-27G, 200-400 mesh with 1% DVB

Merrifield Resin (4.04 meq Cl/g) - Bio-Rad Labs, Biobeads S-X1, Chloromethylated 200-400 mesh

**Methanol - Fisher Scientific Co., Lot 744609, Class 1B, ACS Reagent Grade**
### TABLE III (cont.)

3-Methyl Indole - Aldrich Chemical Co., Catalog # M5, 145-8, Lot # PC 082477

1-Methyl-2-Pyrrolidinone (98%) - Aldrich Chemical Co., Catalog # M7, 9603, Lot # LB 091577, ACS Reagent Grade

Nitrogen - Airco, Inc.

Oxygen - Airco, Inc.

2,4-Pentanedione - Matheson, Coleman and Bell, PX 210, 5103, Lot 12F09

Potassium-tertiary Butoxide - Aldrich Chemical Co., Catalog # 15, 667-1, Lot # BB 02777

Salicylaldehyde - Matheson, Coleman and Bell, SC 35, 2710, MP 1-2°C

Sodium - MCB, Catalog SX 240, CB 1035, ACS Reagent Grade

Sodium Hydroxide (98.6%) - Mallinckrodt, Lot 7708-5, ACS Reagent Grade

**Chemicals and Instruments Used in Analysis**

Carbon Tetrachloride - Norell Chemical Co., Catalog # DC 1070, Lot # 3178, NMR Grade

Deutero Chloroform (99.6%) - Aldrich Chemical Co., Catalog # 17,593-5, Lot # 040247, NMR Grade

Elemental Analysis of Cl and N performed by Robertson Laboratory; 73 West End Avenue; Florham Park, New Jersey 07932

Elemental Analysis of Co performed by Galbraith Laboratories; P.O. Box 4187; 2323 Sycamore Drive; Knoxville, Tennessee 37921

Infrared Spectrometer - Perkin Elmer 457 - Grating Infrared Spectrophotometer

Melting Point Apparatus - Thomas Hoover Capillary Melting Point Apparatus, Catalog # H 6406-K, Serial # 7IT-61

NMR - Varian T-60, NMR Spectrometer System
degree of substitution. Table IV shows the variables for each reaction.

Reduction of I to II (Polystyrene Diamine)

**Polymers with Low Loadings (1.04 meq/g)**

Anhydrous ethyl ether, lithium aluminum hydride, and I were added to a stirred vessel at room temperature. At the end of the specified reaction time (Table V), ethyl acetate was added in small quantities to destroy excess lithium aluminum hydride. A fine milky suspension was obtained which was difficult to filter. The suspension was filtered and stirred in 10% HCl for thirty minutes. The resulting solid was filtered and washed with the following series of solvent, twice consecutively: water, ethanol, ethyl acetate, chloroform, water, ethanol, and methanol. The polymer was dried overnight in a vacuum dessicator at 80°C and an infrared (KBr Pellets) was run. Table V shows the variables for each run.

**Polymers with High Loadings (4.04 meq/g)**

The reaction for the heavily loaded polymer was the same as that described above for low loaded polymers. The wash cycle differed because the large quantity of finely suspended particles clogged the paper and sintered glass filters. Thus, after the destruction of the excess hydride, the polymer was filtered. It was stirred in 10% HCl for twelve hours. If the resulting solid was difficult to filter, it was stirred in water overnight. When
<table>
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<th>Letter</th>
<th>Base Used</th>
<th>Malononitrile*</th>
<th>Malononitrile*</th>
<th>Base Polymer</th>
<th>Temp. °C</th>
<th>Time Hours</th>
<th>Solvent</th>
<th>Wash Sequence</th>
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<td>19.2</td>
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<td>19.2</td>
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<td>1.10</td>
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<td>96.4 218.0</td>
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<td>0</td>
<td>0</td>
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<td>80</td>
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<td>3.70</td>
<td>7.65</td>
<td>80</td>
<td>168.2 212.0</td>
<td>1-methyl 2-pyrr.</td>
<td>1,2,1,3,1,4,5,4,6</td>
</tr>
<tr>
<td>J</td>
<td>NaOEt</td>
<td>4.67</td>
<td>1.38</td>
<td>3.37</td>
<td>80</td>
<td>164.5 212.0</td>
<td>DMF</td>
<td>1,2,1,3,1,5,4,6</td>
</tr>
<tr>
<td>L</td>
<td>K-Ot-Bu</td>
<td>11.3</td>
<td>1.70</td>
<td>6.59</td>
<td>80</td>
<td>163.5 212.0</td>
<td>DMF</td>
<td>1,2,1,3,1,4,5,4,6</td>
</tr>
<tr>
<td>N</td>
<td>K-Ot-Bu</td>
<td>29.9</td>
<td>4.76</td>
<td>6.29</td>
<td>92</td>
<td>163.0 212.0</td>
<td>1-methyl 2-pyrr.</td>
<td>1,2,1,3,1,4,5,4,6,1,4,6</td>
</tr>
</tbody>
</table>

(See Continuation Page of Table IV for legends and notes)
TABLE IV (cont.)

\[ \text{N}≡\text{C-CH}_2\text{-C≡N} + \text{B}^- \rightarrow \text{N}≡\text{C-CH-C≡N} + \text{P-CH}_2\text{Cl} + \text{P-CH}_2\text{-CH} \]

Wash Sequence Legend
1 = Deionized Water
2 = 10\% (weight/volume) hydrochloric acid
3 = 10\% (weight/volume) sodium hydroxide
4 = Ethanol
5 = Benzene
6 = Methanol

* These are molar ratios. For example, in reaction A, if 5.0 g. of Polymer \((5.2 \times 10^{-3} \text{ mmCl})\) was used, 10.0 g. (.15 moles) malononitrile \((.15 = 28.8\) \(5.2 \times 10^{-3}\)), and 2.3 g (.10 moles) sodium \((.15 = 1.50 .10\)), were used in the reaction.

+ The starting material was poor yield trials from prior reactions.

# 4.04 Functionalization
### TABLE V
Reduction of Polystyrene Malononitrile

<table>
<thead>
<tr>
<th>Reaction</th>
<th>LiAlH₄ Polymer</th>
<th>Time (hours)</th>
<th>LiAlH₄ Polymer</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.08</td>
<td>2.25</td>
<td>2.84</td>
<td>18.0</td>
</tr>
<tr>
<td>B</td>
<td>28.21</td>
<td>10.00</td>
<td>1.30</td>
<td>90.9</td>
</tr>
<tr>
<td>D</td>
<td>20.02</td>
<td>2.00</td>
<td>5.50</td>
<td>11.4</td>
</tr>
<tr>
<td>F</td>
<td>5.08</td>
<td>23.00</td>
<td>2.61</td>
<td>71.25</td>
</tr>
<tr>
<td>H</td>
<td>3.58</td>
<td>48.00</td>
<td>5.48</td>
<td>141.0</td>
</tr>
<tr>
<td>I-1</td>
<td>4.75</td>
<td>70.20</td>
<td>5.58</td>
<td>10.6</td>
</tr>
<tr>
<td>I-2</td>
<td>6.33</td>
<td>24.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>4.00</td>
<td>142.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>6.59</td>
<td>142.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
an easily filtered solid was obtained, it was assumed that the polymer was in pure form. It was washed with the same series of solvents as the light polymer and dried overnight in a vacuum dessicator at 80°C. Table V shows the variables for each run.

Preparation of III (Polystyrene 2(bis-salicylaldehyde) propylene-1,3-diimine) and IV (Polystyrene 2(bis-acetylacetone) propylene-1,3-diimine)

Benzene and the condensing agent were stirred and heated to reflux in an apparatus that contains a dean stark tube and is protected from moisture by a calcium chloride drying tube. Polymer II was added and stirred at reflux. When the reaction was completed, the polymer was filtered. The benzene layer was usually green. The polymer was washed with the following series of solvents: ethanol, benzene, ethanol, water, 10% HCl, water, 10% NaOH, water, ethanol, and methanol. The product was dried in a vacuum dessicator at 80°C overnight and an infra-red spectrum (KBr Pellet) obtained. Tables VI and VII show the variables for the two condensing agents.

Preparation of V (Polystyrene bis(salicylaldehyde) propylene-1,3-diiminate Cobalt(II)) and VI (Polystyrene bis(acetylacetone) propylene-1,3-diiminate Cobalt(II))

Cobalt(II) acetate, polymer complexing group, and DMF were heated to reflux in a stirred reaction vessel under a nitrogen blanket followed by addition of the Schiff base. When the reaction
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Salicyl. Polymer</th>
<th>Time Hours</th>
<th>Solvent Salicyl.</th>
<th>Polymer Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>35.4</td>
<td>45.7</td>
<td>32.0</td>
<td>1.04</td>
</tr>
<tr>
<td>F</td>
<td>49.6</td>
<td>69.2</td>
<td>24.8</td>
<td>1.04</td>
</tr>
<tr>
<td>H</td>
<td>32.9</td>
<td>23.1</td>
<td>18.4</td>
<td>1.04</td>
</tr>
<tr>
<td>M</td>
<td>51.9</td>
<td>19.8</td>
<td>10.8</td>
<td>1.04</td>
</tr>
<tr>
<td>J-2</td>
<td>36.5</td>
<td>92.2</td>
<td>7.91</td>
<td>4.04</td>
</tr>
<tr>
<td>J-3</td>
<td>53.6</td>
<td>75.7</td>
<td>2.47</td>
<td>4.04</td>
</tr>
</tbody>
</table>
## TABLE VII

Condensation of II and Acetylaceton

\[
\text{II} + \text{CH}_3\text{-C-CH}_2\text{-C-CH}_3 \rightarrow \text{IV}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Acet. Polymer</th>
<th>Time Hours</th>
<th>Solvent Acet.</th>
<th>Polymer Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-2</td>
<td>85.6</td>
<td>95.0</td>
<td>18.7</td>
<td>1.04</td>
</tr>
<tr>
<td>J-2</td>
<td>83.4</td>
<td>95.2</td>
<td>33.0</td>
<td>4.04</td>
</tr>
<tr>
<td>J-3</td>
<td>103.0</td>
<td>75.7</td>
<td>107.0</td>
<td>4.04</td>
</tr>
<tr>
<td>K</td>
<td>80.6</td>
<td>185.8</td>
<td>5.18</td>
<td>1.04</td>
</tr>
<tr>
<td>M</td>
<td>99.0</td>
<td>19.8</td>
<td>4.15</td>
<td>1.04</td>
</tr>
</tbody>
</table>
was completed, the mixture was cooled and filtered. The polymer was washed with water, ethanol, and methanol and placed in a vacuum dessicator overnight at 80°C to dry and infra-red spectra (KBr Pellet) were run. Table VIII shows the variables for each run.

### Oxidation of 3-Methyl Indole Using Polymer Supported Catalyst

The basic procedure followed was that proposed by Nishinaga. Methanol, 3-methyl indole, and polymer bound catalyst were stirred in a vessel at room temperature. Oxygen was bubbled through the mixture. At the completion of the reaction, the catalyst was filtered and washed with methanol. The solvent was removed under vacuum and the residue taken through a series of recrystallizations to yield the products. Melting points, elemental analysis, infrared spectra (CCl₄) and NMR (CDCl₃) were used to analyze the fractions. Table IX shows the reaction parameters for each run.
### TABLE VIII

Complexation of Cobalt (II) with a Polymer bound Schiff base

(I) Salen:  \[ \text{III} + \text{Co}^{(II)} \rightarrow \text{V} \]  

(2) BAE:  \[ \text{IV} + \text{Co}^{(II)} \rightarrow \text{VI} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Comp. Agent Polymer</th>
<th>Solvent Comp. Agent</th>
<th>Time Hours</th>
<th>Polymer Loading</th>
<th>Cond. Agent</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.86</td>
<td>587</td>
<td>4.42</td>
<td>1.04</td>
<td>salen</td>
<td>Methanol</td>
</tr>
<tr>
<td>H-2</td>
<td>4.85</td>
<td>205</td>
<td>3.83</td>
<td>1.04</td>
<td>salen</td>
<td>NaOH</td>
</tr>
<tr>
<td>M</td>
<td>3.54</td>
<td>185</td>
<td>1.75</td>
<td>1.04</td>
<td>salen</td>
<td>NaOH</td>
</tr>
<tr>
<td>M</td>
<td>3.54</td>
<td>185</td>
<td>1.75</td>
<td>1.04</td>
<td>BAE</td>
<td>NaOH</td>
</tr>
<tr>
<td>J-2</td>
<td>2.15</td>
<td>125</td>
<td>14.00</td>
<td>4.04</td>
<td>salen</td>
<td>NaOH</td>
</tr>
<tr>
<td>J-2</td>
<td>3.20</td>
<td>125</td>
<td>14.00</td>
<td>4.04</td>
<td>BAE</td>
<td>NaOH</td>
</tr>
</tbody>
</table>
TABLE IX
Oxidation of 3-Methyl Indole Using A Polymer Supported Catalyst

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Condensing Agent</th>
<th>Time</th>
<th>Indole Residue Flash</th>
<th>Work Up</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>salen</td>
<td>5.0</td>
<td>3.99 Orange Crystal</td>
<td>R(H) → Fl →</td>
<td>Creamy Crystals</td>
</tr>
<tr>
<td>H-2</td>
<td>salen</td>
<td>48.0</td>
<td>13.3 Brown Oil</td>
<td>R(C) → Fl →</td>
<td>Brown Pellets</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>solid</td>
<td>R(C) → Fl →</td>
<td>Solid #1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R(M) → Fl →</td>
<td>Solid #2</td>
</tr>
<tr>
<td>M</td>
<td>salen</td>
<td>5.5</td>
<td>30.3 Brown Crystals</td>
<td>R(MW) → Fl →</td>
<td>Black Solid #5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R(M) → Fl →</td>
<td>Green Solid #4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fl → Fl →</td>
<td>Grey Powder #3</td>
</tr>
<tr>
<td>M</td>
<td>BAE</td>
<td>5.5</td>
<td>3.05 Orange Crystal</td>
<td>R(MW) → Fl →</td>
<td>Solid #1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fl → Fl →</td>
<td>Solid #2</td>
</tr>
</tbody>
</table>

R       Recrystallize
Fi      Filter
Fl      Flash
TLC     Mini-Column Chromatography
H       Hexanes
C       Carbon Tetrachloride
M       Methanol
MW      Methanol - H₂O
EA      Ethyl Acetate
W       Water
RESULTS AND DISCUSSION

This section is divided into two parts. The first deals with the preparation of the polymer bound catalyst, and those variables which affect the reaction are discussed relative to the optimum reaction conditions. The second part was designed to determine whether the polymer bound species retains its catalytic ability. No attempt was made to optimize the reactions involved in this section.

Preparation of the Polymer Bound Catalyst

Preparation of Polystyrene Malonitrile

The results from this section are shown in Table X. The elemental analysis of the first two columns should provide a quantitative measure of the substitution. Infrared analysis should determine what group substituted on the polymer. Ideally, all the chloride will be replaced by nitrile groups. Thus, chlorine bands at 1260 and 800-950 cm\(^{-1}\) will disappear while the nitrile stretch at 2200 cm\(^{-1}\) will appear. In reality, side reactions occur. The first is the reaction of the amide solvent with the polymer which provides a carbon-nitrogen stretch around 2800-3000 cm\(^{-1}\). The carbonyl band is obscured by the polymer. The reaction of the chloride with an alcohol is possible if alcohol is present to yield a carbon-oxygen band around 1085-1200 cm\(^{-1}\). In some samples, the polymer backbone obscured all but the strongest absorptions.

A comparison of reactions A, B, D and E show the effects of
### Table X

Experimental Data for the Preparation of I

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction time</th>
<th>% Cl</th>
<th>% N</th>
<th>C≡N 2200</th>
<th>1260 2800-3000</th>
<th>ether 1085-1200</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>800-950</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>53.5</td>
<td>0.0</td>
<td>67.9</td>
<td>small</td>
<td>none</td>
<td>slight</td>
</tr>
<tr>
<td></td>
<td>168.0</td>
<td>---</td>
<td>94.7</td>
<td>large</td>
<td>none</td>
<td>slight</td>
</tr>
<tr>
<td>B</td>
<td>98.0</td>
<td>---</td>
<td>212.4</td>
<td>large</td>
<td>none</td>
<td>slight</td>
</tr>
<tr>
<td></td>
<td>217.5</td>
<td>0.0</td>
<td>240.6</td>
<td>large</td>
<td>none</td>
<td>slight</td>
</tr>
<tr>
<td>D</td>
<td>97.8</td>
<td>---</td>
<td>52.5</td>
<td>large</td>
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<td>slight</td>
</tr>
<tr>
<td></td>
<td>216.5</td>
<td>---</td>
<td>61.8</td>
<td>large</td>
<td>none</td>
<td>slight</td>
</tr>
<tr>
<td>E</td>
<td>97.4</td>
<td>104.8</td>
<td>52.8</td>
<td>medium</td>
<td>none</td>
<td>slight</td>
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<tr>
<td></td>
<td>216.7</td>
<td>104.8</td>
<td>54.9</td>
<td>medium</td>
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<td>none</td>
</tr>
<tr>
<td>F</td>
<td>96.4</td>
<td>---</td>
<td>70.0</td>
<td>medium</td>
<td>none</td>
<td>slight</td>
</tr>
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<td>218.0</td>
<td>---</td>
<td>81.0</td>
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<td>none</td>
<td>none</td>
</tr>
<tr>
<td>G</td>
<td>97.7</td>
<td>95.3</td>
<td>7.6</td>
<td>none</td>
<td>smaller</td>
<td>medium</td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
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<td>+</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>K</td>
<td>162.5</td>
<td>---</td>
<td>58.0</td>
<td>medium</td>
<td>none</td>
<td>+</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>M</td>
<td>168.2</td>
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<td>154.8</td>
<td>medium</td>
<td>none</td>
<td>+</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>J</td>
<td>164.5</td>
<td>---</td>
<td>54.1</td>
<td>medium</td>
<td>none</td>
<td>+</td>
</tr>
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<td></td>
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<td>+</td>
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<td>L</td>
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<td>92.7</td>
<td>medium</td>
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<td>+</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>N</td>
<td>163.0</td>
<td>0.0</td>
<td>135.8</td>
<td>medium</td>
<td>+</td>
<td>+</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

+ spectra too obscure to analyze
- data not obtained
temperature on the reaction. As temperature increases, the substitution increases. At room temperature, only half of the chloride groups are replaced. On the other hand, at 112°C addition to the backbone occurs and a 200% replacement is obtained. Replacement of the chloride with an ether was also observed. The temperature which gave the greatest substitution with the least byproducts was 80°C. Thus, all other reactions were run at this temperature.

The effect of time can be seen by comparing reactions Al to A2, D1 to D2, and F1 to F2. In all three reactions, as time increased, yield of the nitrile increased. Even with times lower than fifty hours, the infrared peak due to the chloride disappeared. There was no change in the size of the ether peak for different times. At times lower than one hundred hours, yields of approximately sixty percent were observed. At times around two hundred hours, yields of approximately ninety percent were observed. Thus, as time increases, substitution increases. For the remainder of the study, times of about one week or 168 hours were used.

Reactions A and D show the effect of excess malononitrile on the reaction. Even with lower reaction times, an excess of malonitrile increases the amount of substitution. In fact, nearly quantitative results were observed when a 2880% excess of malonitrile was used.

Along similar lines, a mixture of products from reactions D and E with about 50% substitution was recycled through the first
step and labeled as reaction I. An analysis of the starting material showed 54.2\% substitution. The product showed a 71.6\% substitution or a 17\% increase. This increase was not large enough to warrant a second trial for each run when factors such as energy, chemical cost, and time are considered.

The nature of the hydrogen extractor also has a bearing on the reaction. Comparisons of reactions A, D, and F show this effect quite clearly. That is, the larger base, potassium tertiary butoxide, gave the higher yield. This would be opposite of what is expected until the presence of foreign chemicals is considered. Since sodium ethoxide was prepared by adding elemental sodium to excess ethanol, ethanol is present in all reactions utilizing this reagent. This could lead to the substitution of the chloride with the ethyl ether. The infrared confirms this in all reactions utilizing sodium as the extractor. Thus, potassium tertiary butoxide is the best base for this reaction.

The loading of the polymer does not seem to effect the reaction. Substitution was not affected by crowding of the mobile ligands.

The solvent, on the other hand, has a substantial effect on substitution. Dimethyl Formamide showed a tendency to add to the polymer. This was observed when a blank was run. In reaction G, the infrared shows absorption in the amide region which could only be caused by reaction of the polymer with DMF. 1-Methyl-2-
pyrrolidione showed an even greater tendency to cling to the backbone. Reaction M and N both show yields of over 100% which demonstrates this ability. Further reaction steps will displace this substance. Thus, DMF is the better of the two solvents. Further research into this area would be advantageous.

The conditions shown in Table XI can be considered "optimum" for the substitution of chloride by malonitrile on a polystyrene support.

**TABLE XI**

Optimum Conditions For the Preparation Of Polystyrene Malonitrile

<table>
<thead>
<tr>
<th>Temperature</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>Potassium t-butoxide</td>
</tr>
<tr>
<td>Time</td>
<td>1 week (168 hours)</td>
</tr>
<tr>
<td>Solvent</td>
<td>DMF</td>
</tr>
<tr>
<td>Malonitrile</td>
<td>Large Excess</td>
</tr>
</tbody>
</table>

**Reduction of Polystyrene Malonitrile**

The results from this section are shown in Table XII. The first three columns of this table provide a quantitative indication of the reaction through elemental analysis. The percent efficiency gives a measure of how much of the nitrogen previously reported was not covalently bonded to the polymer and was washed away during the reaction. Elemental analysis will determine the amount of nitrogen
### TABLE XII

Experimental Data for the Preparation of II

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Polymer Loading</th>
<th>% N initial</th>
<th>% N final</th>
<th>% efficiency</th>
<th>INFRARED (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CEN</td>
</tr>
<tr>
<td>A</td>
<td>1.04</td>
<td>94.7</td>
<td>55.6</td>
<td>58.7</td>
<td>none</td>
</tr>
<tr>
<td>B</td>
<td>1.04</td>
<td>240.6</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>D</td>
<td>1.04</td>
<td>61.8</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>F</td>
<td>1.04</td>
<td>75.5</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>H</td>
<td>1.04</td>
<td>50*</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>I-1</td>
<td>1.04</td>
<td>68.3</td>
<td>--</td>
<td>--</td>
<td>slight</td>
</tr>
<tr>
<td>I-2</td>
<td>1.04</td>
<td>68.3</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>K</td>
<td>1.04</td>
<td>58.0</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>M</td>
<td>1.04</td>
<td>154.8</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>J-1</td>
<td>4.04</td>
<td>54.1</td>
<td>54.1</td>
<td>100.0</td>
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</tr>
<tr>
<td>J-2</td>
<td>4.04</td>
<td>54.1</td>
<td>--</td>
<td>--</td>
<td>strong</td>
</tr>
<tr>
<td>J-3</td>
<td>4.04</td>
<td>54.1</td>
<td>--</td>
<td>--</td>
<td>none</td>
</tr>
<tr>
<td>L-1</td>
<td>4.04</td>
<td>92.7</td>
<td>--</td>
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<tr>
<td>N-1</td>
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<td>135.8</td>
<td>126.9</td>
<td>93.5</td>
<td>strong</td>
</tr>
<tr>
<td>N-2</td>
<td>4.04</td>
<td>126.9</td>
<td>--</td>
<td>--</td>
<td>strong</td>
</tr>
</tbody>
</table>

-- Data points not obtained

* Since the total of %Cl and %N is greater than 100%, it is assumed that all of the HCl used to wash the reaction was not removed and the overall is estimated at 50%.
in the product but not the form in which it exists. Since nitriles and amines have distinct bands in infrared, the IR was used to determine if reduction had occurred. The \( \text{C} \equiv \text{N} \) stretch around 2200 cm\(^{-1}\) should disappear as reduction progresses and the wide NH stretch around 3120 to 3620 should appear.

The IR of all 1.04 (low loaded) polymers shows that reduction occurred. This covered a range of reaction times that varied from two to twenty hours. Thus reaction occurs very quickly in this reaction. Reduction also occurred with reaction ratios as low as 4 to 1. Further research is suggested in order to determine the exact stoichiometry and reaction time.

Infrared analysis of the 4.04 (heavily loaded) polymer is puzzling at best. In reaction J, it took three runs until the nitrile peak disappeared. Reaction L only took one, and reaction N took over two. In all three reactions, the amine never appeared. On the surface, it appears that the polymer backbone masks the amine stretch. However, condensation reactions show the nitrile peak reappearing. Thus, reduction did not occur and the polymer masks the nitrile absorption. A possible explanation for this masking effect is that the lithium aluminum alkoxide complex blocks the pores of the polymer and restricts nitrile movement. Equation 20 shows the reaction between ethyl acetate and LiAlH\(_4\). The complex formed is rather large and may clog the smaller pores of the 4.04 polymer. The hydrogen ion cannot gain access and only
Eq. 20.

\[ \text{\(4\text{CH}_3\text{C-OC}_2\text{H}_5\) + 2\text{LiAlH}_4 \rightarrow \text{ether} \rightarrow 2\text{LiAl(OC}_2\text{H}_4\text{)_4} \rightarrow \text{H}^+ \rightarrow 2\text{CH}_3\text{CH}_2\text{OH}\)} \]

reacts with the free complex. This leaves the complex inside the bead blocking the pores. The reappearance of the nitrile peak after swelling the polymer in the next reaction step lends credence to this explanation. The pores of the 1.04 polymer are less crowded and allow access to the hydrogen ion to form ethanol.

The smaller pores in the 4.04 polymer could also explain why reduction did not occur. The LiAlH\(_4\) penetrated the outer pores and were blocked by the bulky functional groups. Thus reduction could only occur in the first portion of the polymer bead. Reduction in a solvent which swells the polymer would be further experimental proof that this occurs.

Elemental analysis of the 1.04 polymer suggests that about 40% of the nitrogen previously thought to be covalently bonded to the polymer was actually absorbed and was lost when another reaction step was taken. The 4.04 polymer produces contradicting results. Elemental analysis shows very little loss of nitrogen. A possible explanation is that the loss of nitrogen is not a result of absorbed nitrogen but is actually a measure of the extent of reaction. Very little 4.04 polymer was shown to reduce and very little nitrogen was lost. The LiAlH\(_4\)-nitrogen bond must be strong enough to rival the nitrile-carbon bond causing scission to occur.
in either place.

In summary, times of under two hours and reaction ratios of four to one are sufficient to reduce polymers with low loadings. Large pore sizes will be necessary for the same reaction to occur with polymers of higher loadings.

**Preparation of Polymer Bound Schiff Bases**

The results from this section are shown in Table XIII. In this reaction, elemental analysis was used to determine the efficiency of the reagent. Infrared was used to determine the functional groups present. If the Schiff base is formed, loss of the amine peak at $3120-3620 \text{ cm}^{-1}$ should occur. New peaks should appear at 1616-1637 and at 1280 due to the carbon-nitrogen stretch, and the phenolic carbon-oxygen stretch respectively.

Elemental analysis of most of the reactions showed a retention of eighty to ninety percent of the nitrogen. Two specific reactions, the salen and BAE derivatives of reaction M, merit special consideration. It was previously suggested that absorption of 1-methyl-2-pyrrolidinone solvent on the polymer was responsible for the yields above 100%. Two steps after this analysis, yields are reduced to around 100%. All of the absorbed species should be removed and only covalently bonded nitrogen should remain. Complexation data reveals that about 70% of the nitrogen is capable of reacting with cobalt and is existing in the Schiff base form. This suggests that thirty percent of the nitrogen on the polymer is actually 1-methyl-2-pyrrolidinone which is covalently bonded to the reaction sites.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Polymer Loading</th>
<th>Cond. Agent</th>
<th>% N Initial</th>
<th>% N Final</th>
<th>Efficiency</th>
<th>amine</th>
<th>C=N</th>
<th>C=O</th>
<th>C=EN</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1.04</td>
<td>salen</td>
<td>61.8</td>
<td>51.1</td>
<td>82.8</td>
<td>reduced</td>
<td>x</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>F</td>
<td>1.04</td>
<td>salen</td>
<td>75*</td>
<td>47.7</td>
<td>----</td>
<td>reduced</td>
<td>sidearm</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>H</td>
<td>1.04</td>
<td>salen</td>
<td>50*</td>
<td>54.9</td>
<td>----</td>
<td>reduced</td>
<td>sidearm</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>J-2</td>
<td>4.04</td>
<td>salen</td>
<td>54.1</td>
<td>48.1</td>
<td>89.1</td>
<td>small</td>
<td>none</td>
<td>none</td>
<td>large</td>
</tr>
<tr>
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<td>4.04</td>
<td>salen</td>
<td>54.1</td>
<td>----</td>
<td>----</td>
<td>small</td>
<td>none</td>
<td>none</td>
<td>large</td>
</tr>
<tr>
<td>M</td>
<td>1.04</td>
<td>salen</td>
<td>154.8</td>
<td>99.9</td>
<td>100*</td>
<td>reduced</td>
<td>x</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>I-2</td>
<td>1.04</td>
<td>BAE</td>
<td>68.3</td>
<td>34.0</td>
<td>49.0</td>
<td>reduced</td>
<td>sidearm</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>J-2</td>
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<td>BAE</td>
<td>54.1</td>
<td>50.7</td>
<td>93.8</td>
<td>small</td>
<td>none</td>
<td>none</td>
<td>large</td>
</tr>
<tr>
<td>J-3</td>
<td>4.04</td>
<td>BAE</td>
<td>54.1</td>
<td>----</td>
<td>----</td>
<td>small</td>
<td>none</td>
<td>none</td>
<td>large</td>
</tr>
<tr>
<td>K</td>
<td>1.04</td>
<td>BAE</td>
<td>58.0</td>
<td>49.4</td>
<td>85.2</td>
<td>none</td>
<td>x</td>
<td>x</td>
<td>none</td>
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<tr>
<td>M</td>
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<td>BAE</td>
<td>154.8</td>
<td>101.6</td>
<td>100</td>
<td>none</td>
<td>x</td>
<td>x</td>
<td>none</td>
</tr>
</tbody>
</table>

* See the explanation in the paper

--- Data points were not obtained

x Region is not distinct

* These samples were reruns of previously analyzed samples. Thus, the exact amount of initial % N is unknown. This number is an estimate.
DMF shows a lower proportion of nitrogen bonded and so is the better solvent.

Infrared analysis is not conclusive but strongly suggests that condensation occurs. In almost all low load polymers, the amine band decreased while the Schiff base and phenolic bands appeared. These bands were very faint and easily obscured by the polymer. This Schiff base band was a sidearm to an existing band. There appeared to be no relationship between time, reaction ratio, and band size. This suggests that at reflux, the reaction occurs in less than nineteen hours at reaction ratios of less than thirty. Further research is warranted to determine the lower limits of these two variables.

The nitrile absorption reappeared in all 4.04 polymers suggesting that swelling in benzene allowed the lithium complex to go into solution and unclogged the polymer canals.

There is little difference between condensing agents salen and BAE as demonstrated in reactions J2, J3, and M. Elemental analysis and IR spectra were similar. Thus, both Schiff bases should complex the cobalt and have similar characteristics. This will be discussed in the next section.

Preparation of the Cobalt(II) Schiff Base Complexes

Table XIV shows the results from this section. Elemental analysis of cobalt is used to determine the amount of Schiff base present. It is assumed that all of the Schiff base is complexed with cobalt. Previous studies 47,48 have determined IR absorptions
### TABLE XIV:

Experimental Data for the Preparation of V and VI

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Polymer Cond.</th>
<th>% N</th>
<th>% Co</th>
<th>% C=N</th>
<th>C-N (cm⁻¹)</th>
<th>C-O (cm⁻¹)</th>
<th>M-O</th>
<th>M-N</th>
<th>C≡N</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(MeTH)</td>
<td>1.04 salen</td>
<td>54.9</td>
<td>28.4</td>
<td>51.7</td>
<td>small</td>
<td>disappear</td>
<td>none</td>
<td>faint</td>
<td>none</td>
</tr>
<tr>
<td>H(NaOH)</td>
<td>1.04 salen</td>
<td>54.9</td>
<td>90.2</td>
<td>164.4</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>faint</td>
<td>none</td>
</tr>
<tr>
<td>M</td>
<td>1.04 salen</td>
<td>99.9</td>
<td>76.7</td>
<td>76.8</td>
<td>small</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>none</td>
</tr>
<tr>
<td>M</td>
<td>1.04 BAE</td>
<td>101.6</td>
<td>65.6</td>
<td>64.6</td>
<td>small</td>
<td>disappear</td>
<td>faint</td>
<td>faint</td>
<td>none</td>
</tr>
<tr>
<td>J-2</td>
<td>4.04 salen</td>
<td>48.1</td>
<td>5.1</td>
<td>10.6</td>
<td>reduced</td>
<td>reduced</td>
<td>none</td>
<td>none</td>
<td>large</td>
</tr>
<tr>
<td>J-2</td>
<td>4.04 BAE</td>
<td>48.1</td>
<td>5.1</td>
<td>10.6</td>
<td>reduced</td>
<td>same</td>
<td>none</td>
<td>none</td>
<td>large</td>
</tr>
</tbody>
</table>

* Spectra are too obscure to analyze this area
expected for the bound complex. These are shown in Table XV.

**TABLE XV**

Absorptions in Schiff Base Complexes

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Free Schiff Base</th>
<th>Metal Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡N stretch</td>
<td>1616-1637</td>
<td>1606-1656</td>
</tr>
<tr>
<td>Phendic C-O stretch</td>
<td>1280</td>
<td>1310-1390</td>
</tr>
<tr>
<td>Metal-O bend</td>
<td>--</td>
<td>660</td>
</tr>
<tr>
<td>Metal-N bend</td>
<td>--</td>
<td>590</td>
</tr>
</tbody>
</table>

The phenolic oxygen-hydrogen stretches above 3000 cm⁻¹ may not be observed because of intermolecular hydrogen bonding and may appear as a broad weak band at 2700-3100 cm⁻¹.

Cobalt analysis gave a final measure of the total efficiency of all reactions. In examining the cobalt analysis, it becomes evident from reactions H and H2 that basic conditions during the complexation give favorable results. Comparing the salen reactions H2 and M, it is found that DMF gives a 15% higher yield of cobalt. Some of this cobalt may not be covalently bonded. A comparison of the salen and BAE yields for reactions M and J2 shows very little difference between the complexing power of the species. This substantiates the IR data from the previous section. The low yields of the J2 reactions further demonstrate the lack of reduction from the second step.

Infrared spectroscopy substantiates these findings.
polymers showed obscured Schiff base and phenolic bands. No metal-oxygen band was visible and the metal-nitrogen band was faint. This would be expected if cobalt were complexed into the ligand. The complexed cobalt withdraws electrons from the ligand and weakens the signal. Since these peaks were faint at the start, the result would be an obscure peak. This result is noticed. The metal-oxygen band is weak under ideal conditions and masked under the polymer. The metal-nitrogen band is faint but present.

The 4.04 polymers show a mixture of nitrile and complexed products. The nitrile peak is strong showing that most of the product is in this form. The reduction of the Schiff base band suggests a small amount of complexation. This is borne out by elemental analysis. The failure of the phenolic peak, the metal-oxygen peak, and the metal-nitrogen peak to appear reflects the minute amount of complex formed.

Oxidation of 3-Methyl Indole Using A Polymeric Schiff Base

The purpose of this section is to determine if the polymer bound catalyst retained its activity. In order to achieve this aim, properties of the starting material and product must be obtained. These are shown in Table XVI. There should be a definite difference in the melting point of the two products. NMR should show loss of two peaks in the region of δ 1 to 2 and a gain around δ 2.63. The aromatic region should be shifted about .7 units. There is no significant difference in the infrared
of the two species. However, the region indicated should show some change due to different pendant groups.

Table XVII shows the results of the oxidation reaction. None of the runs resulted in a high yield of product. All runs showed a mixture of products. All attempts at resolving the mixture have failed.

A reference reaction was run using 3-methyl indole but without the catalyst to see if the new products were caused by an impurity in the starting material. As can be seen by the results, the end product exactly matches the starting material in appearance, melting point, IR, and NMR. Thus, all new peaks are due to the action of the polymer bound species.

Consider reaction H. The melting point is in the range of the product. However, NMR shows no trace of the product. IR shows the gain of a wide sidearm in the ketone and aromatic region. This suggests that the product is present but exists in very small

<table>
<thead>
<tr>
<th>Product</th>
<th>Melting Point</th>
<th>NMR</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methyl indole</td>
<td>97-98</td>
<td>1.06( ), 1.90(s), 6.20-7.50(m)</td>
<td>1632-1700</td>
</tr>
<tr>
<td>o-formylamino-acetophenone</td>
<td>79-80</td>
<td>2.63(s), 6.95-8.80(m)</td>
<td>1300-1630</td>
</tr>
</tbody>
</table>
### Experimental Results for the Oxidation of 3-methyl Indole

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cond. Agent</th>
<th>mp of Crude Product</th>
<th>% Co Initial</th>
<th>% Co Final</th>
<th>% Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>salen</td>
<td>82-86</td>
<td>90.2</td>
<td>32.8</td>
<td>36.4</td>
</tr>
<tr>
<td>H-2</td>
<td>salen</td>
<td>-----</td>
<td>32.8</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>M</td>
<td>salen</td>
<td>-----</td>
<td>76.7</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>M</td>
<td>BAE</td>
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</table>

--- Data was not obtained
### TABLE XVII (cont.)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>mp Reaction</th>
<th>mp Product</th>
<th>O C-CH$_3$ 2.63</th>
<th>O Ar-H NH CHO</th>
<th>NMR C-C-CH$_2$ 1.06</th>
<th>NMR Ar-CH$_2$ 1.90</th>
<th>INFRARED Ketone 1632-1700</th>
<th>INFRARED N Ring 1630-1500</th>
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</thead>
<tbody>
<tr>
<td>H</td>
<td>creamy crystals</td>
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<td>6.4-8.0 singlet</td>
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<tr>
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<td>brown crystals</td>
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<td>singlet</td>
<td>6.8-8.8 singlet</td>
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<td>+</td>
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</table>

---- Data not obtained + too obscure to determine
quantities.

Reaction H2 yielded three cuts. The first has a narrow melting point different from both of the desired species. The NMR contains the conjugated carbon of the starting material and the aromatic-ketone peaks of the product. This points to a mixture. Column chromatography was attempted to separate the two solids and yielded two more cuts. The last product's NMR matches the starting material. The second product resembles the mixture prior to the column. Thus, the chromatography separated some of the pure starting material but did not resolve the mixture. It is suggested that a longer column be employed for complete separation.

Reaction M was very difficult to separate. The melting points of all three samples were above either of the desired compounds. It is suggested that some fine polymer particles resulting from attrition due to the bubbling oxygen were present in the product. The black and green solids, samples 1 and 2, were insoluble in a range of solvents. Thus, no NMR or IR was taken. The grey powder showed a mixture of products. The NMR conjugated carbon area matches the starting material. The ketone area of the product is also present. The aromatic region is a combination of the two. Neither the first peak of the starting material nor the last peak of the product is present. IR is also inconclusive. Thus, this is most likely a mixture of products.
The reactions that have been discussed thus far utilized salen (V) catalysts. All have produced a mixture of products. Reactions H and M yielded the same product distribution but had different reaction ratios. Thus, diffusion of the indole to the catalyst is not the limiting factor. Reaction H2 was a rerun of reaction H and showed that time was not the limiting factor.

Reaction M was repeated using the BAE catalyst (VI). One of the products in this reaction had similar melting and solubility behavior to the salen M (V) which probably contains residual polymer. The second product however, contained a large amount of oxidized product. The melting point reveals that it is a mixture. The NMR shows strong product characteristics with a slight starting material contamination. The IR confirms this with a definite wide band in the amide-ketone region and the disappearance of the nitrogen ring stretch. Thus, the BAE catalyst seems to yield a fair amount of product with contaminating starting material.

From the above, it is concluded that the reduced catalytic ability of the salen catalyst is not a function of the reaction variables but reflects the effect of the backbone. Comparison with the BAE catalyst shows that the drastically reduced catalytic ability is unique to the salen system. The major difference in the two catalysts is the aromatic ring. This suggests that the aromatic rings of the polymer and catalyst
interact to form polar or steric environments incompatible with the entering indole. Thus, reaction does not occur. Further research using rigid polymers or larger pore sizes would confirm this supposition.

The salen polymer (V) lost a large portion of its cobalt during the reaction. This could be a factor in the reduced catalytic ability and should be investigated. The elemental analysis showed BAE polymer (VI) retained most of its cobalt. This suggests that BAE forms a stronger complex with the metal and is more stable. However, a reaction using the BAE polymer run under identical conditions with the omission of the oxygen showed losses of cobalt similar to the salen catalyst. Thus, the oxygen seems to stabilize the BAE complex as it is reacting. Further research is warranted in this area.

In summary, the BAE complex produces a better yield of oxidized product than the salen catalyst. Reaction ratio and reaction time are not the limiting factors in the reaction. Loss of cobalt and backbone effects seem to cause the loss of activity in the salen catalyst.
REFERENCES


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