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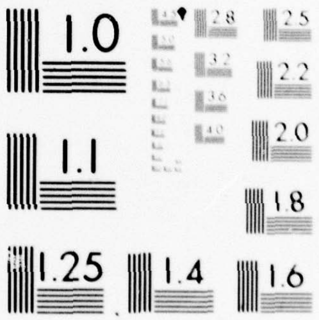

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Synthetic procedures for attaching multidentate amines to organic polymers are described. These materials form the basis for the preparation of a wide variety of macrocyclic and chelating ligands that can be covalently attached to polymers. The reaction to produce Schiff base chelates is described and a series of covalently attached metal complexes prepared and identified. These systems have potential as catalysts for organic oxidations.

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Preparation and Catalytic Oxidizing Potential of Polymer Supported Chelating Amine and Schiff Base Complexes

by

Russell S. Drago, John Gaul, Alan Zombeck, and Darel K. Straub

ABSTRACT

A new versatile high yield synthesis for covalently attaching multidentate chelates to polystyrene is described. Polymeric substrates containing bound polydentate amines as discrete units can be obtained by reacting chloromethylated polystyrene with bis-(2-cyanoethyl)amine, followed by BH_3/THF reduction, to provide polymer attached bis-(3-aminopropyl)amine, Ⓟ-DPT. These materials form the basis for the preparation of a wide variety of chelating ligands; for example, through the Schiff base reaction with various aldehydes and ketones. In order to demonstrate the feasibility of these polymer reactions, the entire sequence of reactions was carried out in solution using benzyl chloride as the starting material. A series of polymer bound metal complexes were prepared and characterized. ESR spectra of the polymer bound Cu(II)SalDPT and Co(II)SalDPT$\cdot O_2$ complexes were very similar to their respective frozen glass spectra. Mössbauer of the polymer bound Fe(II)SalDPT was similar to the powder spectrum. The Fe(II)bound complex was irreversibly oxidized upon exposure to air. The Co(II)SalDPT bound complex was found to be an active catalyst for the oxidation of 2,6-dimethylphenol. A large enhancement in product selectivity is obtained with the polymer Co(II) complex over the solution analog.

INTRODUCTION

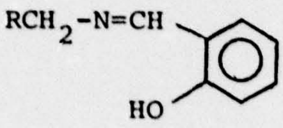
The use of polymers as supports for chelates and catalysts, as well as synthetic reagents, has grown tremendously since Merrifield demonstrated their use in peptide synthesis. Excellent reviews on these applications have been reported.[1] Varying degrees of success have been reported for incorporation of metal ions or metal complexes into polymers containing chelating groups of various sizes and donor sets. Polymers with nitrogen, oxygen, sulfur, and phosphorus donors are commonly found as monodentate or bidentate ligands. The polymer analog of triphenylphosphine has seen the largest application as a bound monodentate ligand used to immobilize transition metal catalysts. Most of the monodentate ligands used to immobilize metal complexes suffer from the disadvantage of the metal complex leaching into solution. Accordingly, there has been considerable interest in covalently attaching multidentate ligands to the polymer. Several bidentate ligands have been attached to a polymer support; the most recent is Neckers' poly(styrl)bipyridine.[2] A few tridentate and quadridentate chelate types have been investigated such as bound phathalocyanines[3] and porphyrins.[4]

We became interested in developing a procedure for covalently attaching multidentate amines to polymers. Since these materials have provided the building blocks for a good deal of chelate and macrocycle chemistry, covalently attached polymer bound multidentate amines would be valuable as the starting material for synthesizing many polymer bound chelates and macrocycles.

In addition to providing a basic building block for chelates and macrocycles, the polymer bound tridentate ligands have potential uses as chelating resins in the recovery of Cu(II) from aqueous solutions containing other transition metals. This is an industrially important process and in view of the known chelating tendencies of polydentate amines to copper(II), synthesis of resins with this functionality is an important objective. An example of a resin[5] used for this purpose is a polymer based on derivatives of N,N'-bis(2-pyridylmethyl)-2,2-diaminobiphenyl.

Our goal in preparing these materials was to obtain chelating ligands for cobalt(II), copper(II), and iron(II) that would yield systems with potential for catalytic oxidations of organic substrates. We were interested in determining if the polymer matrix could stabilize iron(II) systems with respect to oxidation by inhibiting the rate controlling step in the oxidation; the formation of a peroxo bridged iron dimer, Fe-O-O-Fe. For these applications, we selected the Schiff base derivatives.

The oxidation of substituted phenols in homogeneous solutions of cobalt(II)-Schiff base complexes has been investigated[6] and commercial processes based on these complexes exist. Copper(II) Schiff base complexes are homogeneous catalysts for the oxidative coupling of phenols.[7] The advantages to be gained in heterogenizing homogeneous catalysts through polymer attachment have been described.[8] A few examples which utilize a Schiff base linkage are Stanberg's α dioxane type chelate polymer[9] and Kalalova's[10] polymer containing the following salicylidenimine ligand.



No attempts were made to isolate chelating sites in the preparation of these polymers. More recently,[11] Idoux, et at., have produced a polymer bound Schiff base complex from the condensation of aldehydes with polymer attached 1,3-diamines. The yields were 25%-60% with respect to the parent chloromethylated polystyrene and tetradentate chelates were obtained.

We report herein the synthesis and characterization of polymer bound tridentate amine and pentadentate Schiff base complexes. The versatile and high yield synthesis utilizes nitrile groups as a blocking function to provide polymer attached polydentate amines. The Schiff base reaction with these amines produces polymer bound five coordinate chelates of unambiguous structure capable of binding many transition metals. The physical and chemical properties of these resins are discussed as well as the catalytic activity of the cobalt(II) bound complexes.

RESULTS AND DISCUSSION

Synthesis of Supported Multidentate Amines

Chloromethylated polystyrene is a convenient substrate for studies of polymer supported ligands because it is readily available and has been thoroughly studied. Chloromethylated polystyrene, as a gel resin, can be prepared with varying amounts of substitution and crosslinking by copolymerization of styrene (STY), vinylbenzylchloride (VBC), and divinylbenzene (DVB).[12] Macroreticular polystyrene[13] can be chloromethylated with chloromethylmethyl ether, using $SnCl_4$ as a catalyst,[14] though this method is no longer advised because of the noted potential carcenogeneity of side products from this reaction. The chloromethyl group is a reactive functional group that is readily converted to many other functional groups.

The attachment of a polydentate amine to polystyrene by reaction of the chloromethylated polymer with the nucleophilic amine would lead to a wide range of products as a result of the different amine groups in the molecule reacting in varying amounts with intrastrand and interstrand chloromethyl residues. Accordingly, a general scheme, illustrated in Figure 1, for polymer attachment of dipropylenetriamine (DPT), was developed for incorporation of substrates containing pendant multidentate amine groups.

Formation of dicyanoethylamine, DCEA, can be readily achieved through cyanoethylation of ammonia.[15] The chloromethylated resin can be reacted with di(cyanoethyl)amine

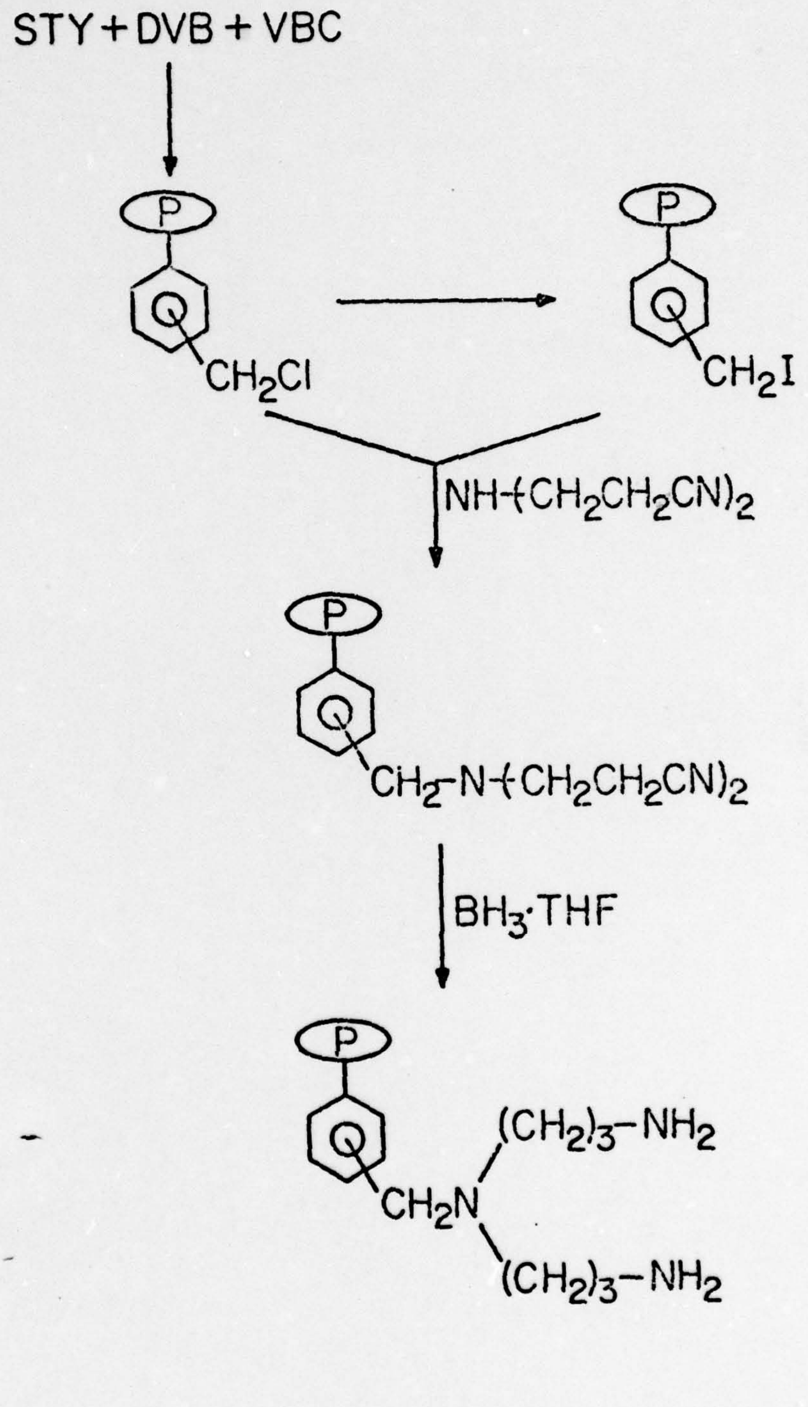


Figure 1. Reaction scheme for the incorporation of dipropylenetriamine (DPT) in chloromethylated polystyrene.

directly or indirectly by first converting the chloro group to an iodo group through reaction with NaI. If the chloromethylated resin is reacted directly with DCEA, a 30-50 fold excess of DCEA is needed. The DCEA is acting as the base to neutralize the hydrochloride and a large excess of DCEA is needed to drive the reaction to completion. Conversion of the resin bound chloromethyl group to an iodomethyl group allows the incorporation of the DCEA, without use of a large excess of this reagent.

The reduction of nitrile groups can be accomplished with a number of reagents.[16] $NaBH_4$, $LiAlH_4$, and Raney Ni are just a few. All of these are highly efficient if the nitrile is in solution. However, since in our system the nitrile is in a solid polymer phase, reagents that are insoluble in a swelling solvent are not efficient. Diborane, (B_2H_6), reduces nitriles readily, is a gas and is freely soluble in THF with which it forms an adduct, $BH_3 \cdot THF$. THF is also an excellent swelling solvent for the resin. A slurry of the nitrile containing resins with $BH_3 \cdot THF$ in a dry inert atmosphere leads to the desired product, resin bound DPT, after workup (see Experimental).

Other than the N analysis, there is no convenient way to follow the reaction sequence described above in the polymer. For this reason, the solution analogues of the resin products were synthesized to ascertain if the desired reactions could take place. Under comparable conditions the desired sequence of reactions occurred in solution (see Experimental).

By using a similar reaction sequence, malononitrile can be used to form polymer bound propylenediamine and bis-(2-cyanoethyl)-phosphine can be used to form di-(3-aminopropyl)phosphine (see Experimental).

Reactions of Polymer Bound Amines

In order to further characterize the polymer bound reaction products and to establish the reactivity of the bound amine, Schiff base condensation reactions were attempted and some metal complexes synthesized. The resin bound DPT may be reacted with any number of aldehydes and ketones at this stage. Excess aldehyde is usually used and the water of condensation removed by distilling off an azeotrope. Extractions with ethanol or methanol/THF yield the characteristically colored resin bound ligand.

For the [P]-SalDPT system, the resin bound complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) were prepared. The reactions were facile and yielded various colored resins whose colors compared favorably to the analogous crystalline complexes (see Table I).

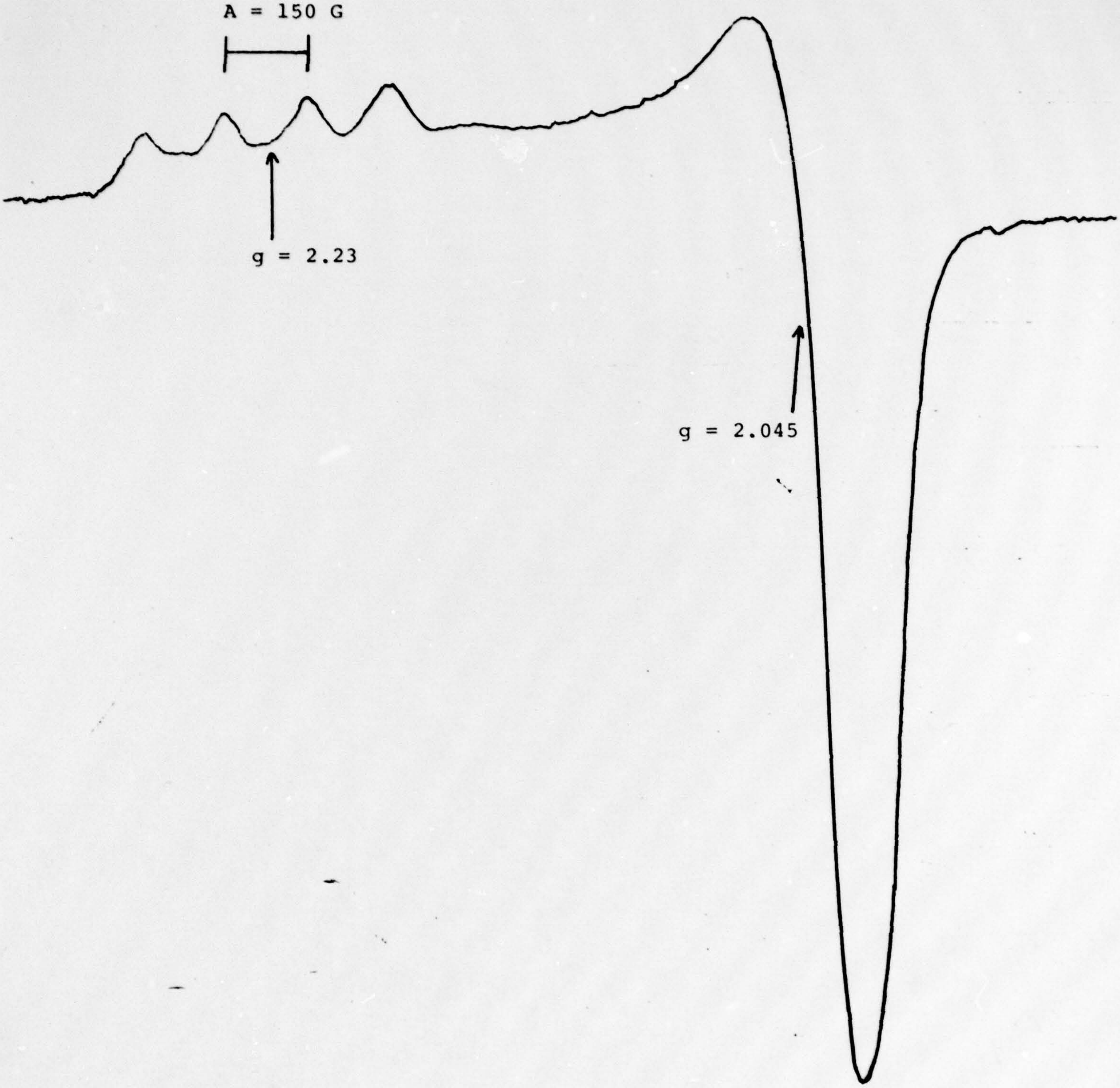


Figure 2. ESR spectrum (Q-band) of Cu(SalDPT) on polymer GR-X15S3 at 77K.

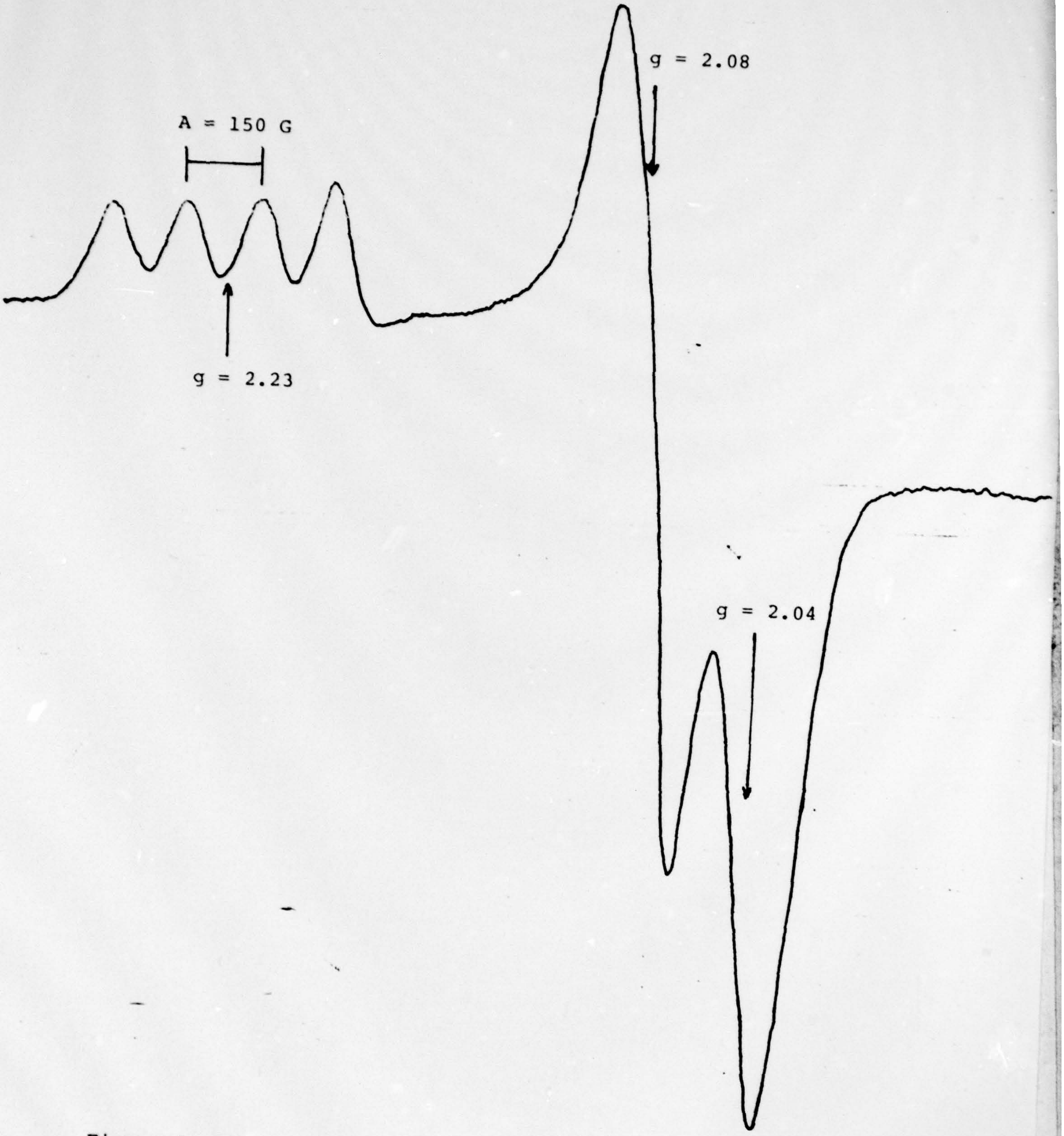


Figure 3. ESR spectrum (Q-band) of parent complex, Cu(SalMeDPT) at 77K in a toluene glass.

Table I. Comparison of Colors of Parent and Polymer Bound H_2SalDPT Complexes

	Parent Complex	Polymer Complex
Mn(II)	orange	orange
Fe(III)	black	dark brown
Co(II)	gold	gold
Ni(II)	light green	light green
Cu(II)	dark green	dark green
Zn(II)	white	pale yellow

Additional documentation to indicate that the desired reactions had been carried out was obtained by investigating the esr spectra of the polymer bound Schiff base complexes. The esr spectra of the polymer bound Cu(II) complex is shown in Figure 2. Nitrogen hyperfine is not resolved but the similarity in the g values and the copper hyperfine to those obtained from a toluene-CH_2Cl_2 glass of the parent compound, Figure 3, establishes the existence of this complex on the polymer. Computer simulation of these spectra led to a solution g values of $g_1 = 2.04$, $g_2 = 2.08$, $g_3 = 2.235$ with A values of $A_1 = 20$, $A_2 = 30$ and $A_3 = 150$. The polymer bound material gave $g_1 = 2.04$, $g_2 = 2.04$, $g_3 = 2.236$, $A_1 = 50$, $A_2 = 50$, $A_3 = 150$. These results compare reasonably well with the values $g_1 = 2.04$, $g_2 = 2.07$, $g_3 = 2.23$, $A_1 = 66$, $A_2 = 38$ and $A_3 = 150$ reported from a single crystal epr investigation.[17] An angular overlap calculation was employed to show that distortions from a square pyramid to a trigonal pyramid have a pronounced effect upon the epr parameters. The differences in the A values from the spectra of the glass and polymer could result from minor changes in the distorted, trigonal bipyramidal geometry of the complex. The main difference arises in the $g_\perp$ region. The frozen glass spectrum results in the resolution of g_x and g_y, whereas inthe polymer the spectrum is axial. This could result from "pockets" in the polymer that permit motion of the complex at the temperatures employed.

The esr spectrum of [P]-Co(SalDPT) yielded no signal even at -100°C as is to be expected for high spin Co(II). However, exposure of the resin at low temperature to pure O_2 resulted in the spectrum seen in Figure 4. The g values and cobalt hyperfine of this complex compare exactly in structure and shape to that obtained from a methylene chloride-toluene glass of the dioxygen adduct of crystalline Co(SalDPT).[18]

The iron(II) (SalDPT) complex can be prepared by either of the two methods indicated in the Experimental section. Both of these analytically pure complexes were submitted for Mössbauer analysis, the results of which are shown in Table II. Comparison of these (1 & 2) with the reported parameters for high spin Fe(Salen) and Fe(SalOPH) indicate that the complexes are indeed normal high spin Fe(II).

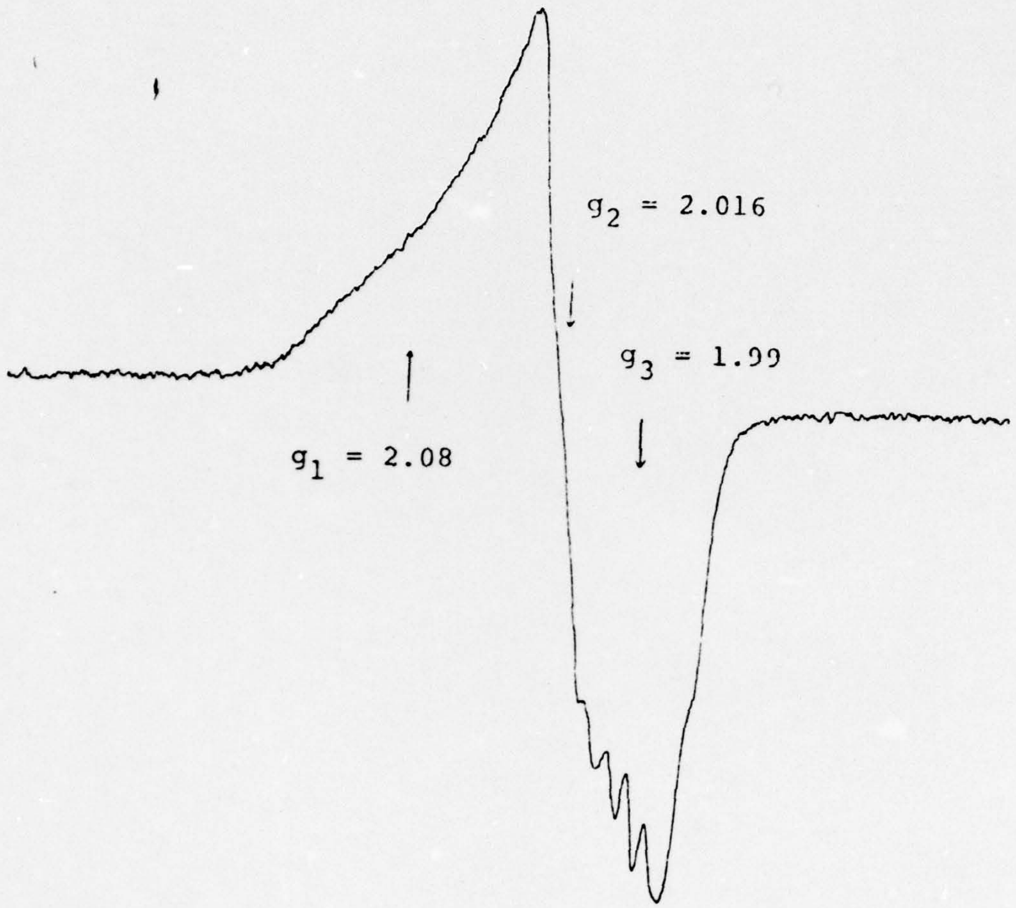


Figure 4. ESR spectrum of the oxygen adduct of Co(SalDPT) on polymer GR-X15S9 at liquid N_2 temperatures.

Table II. Comparative Mössbauer Data for Crystalline and Polymer Bound Fe(SalDPT)

		Peak	I.S. mm/sec	Q.S.	fwhm[c] mm/sec
1.[a]	Fe(SalMeDPT) from Fe(CO)$_5$	doublet	1.20	2.80	0.377
2.[a]	Fe(SalMeDPT) from Fe(OAc)$_2$	doublet	1.25	2.80	0.377
3.[a]	[P]-Fe(SalDPT) from Fe(CO)$_5$	complicated doublets	1.48	2.44	---
4.[a]	[P]-Fe(SalDPT) and excess O$_2$	doublet	0.63	0.72	0.68
5.[a]	[Fe(SALEN)–]$_2$O[23]	doublet	0.58	0.92	
6.[a]	[Fe(SALEN)]$_2$ O py$_2$[23]	doublet	0.71	0.92	
7.[a]	[Fe(TPP)]$_2$O[23]	doublet	0.55	0.62	
8.[a]	[Fe(protoporph)]$_2$O[23]	doublet	0.66	0.66	
9.[b]	Fe(SALEN)[24]	doublet	1.24	2.50	
10.[b]	Fe(SALOPH)[24]	doublet	1.20	2.42	
11.[b]	Fe(SAL)$_2$[24]	doublet	1.43	2.51	
12.[b]	Fe(salicylaldoxime)[24]	doublet	1.56	2.53	
13.[b]	Fe(picket fence porphyrin)O$_2$[25]	---	0.54	2.00	
14.[b]	HbO$_2$[26]	---	0.52	2.19	

ALL ISOMER SHIFTS ARE VS. SODIUM NITROPRUSSIDE.

[a] = room temperature

[b] = 77°K

[c] = full width at half maximum

After incorporation of Fe(II) into the [P]-SalDPT system under strict anaerobic conditions, a purple resin was obtained. The Mossbauer results (Table II, #3) indicate the iron is most likely high spin iron(II). The slight difference between the crystalline and polymer bound complexes could also be due to slight conformational changes imposed on the complex by the polymer environment. Exposure of the resim to air results in oxidation of the iron as shown in line four of Table II. The Mössbauer data are typical of Fe(III) oxo bridged species or many h.s. Fe(III) cases. It has been shown that the oxidation of iron(II) by O_2 is a process that is second order in iron(II).[27] Since the iron is extensively chelated, leaching of iron(III) into solution is not expected to be the cause of this oxidation by O_2. Instead we conclude that we have not been able to attain site separation in this polymer.

Cobalt-Polymer Oxidation Catalysts

In recent years there have been several reports of the use of cobalt Schiff base complexes as oxidation catalysts.[6] The cobalt(II) complexes have been reported to catalyze the synthetically important reaction of substituted phenol oxidations. So far, no attempts have been made to heterogenize these solution catalysts. We therefore tested [P]-Co(SalDPT) as a catalyst in the oxidation of 2,6-dimethylphenol (2,6-DMP). Several resins were functionalized with Co(SalDPT), including a macroreticular resin.

Table III. Comparison of Yield Ratios for Phenol Oxidations Using Co(SalMeDPT), (HMG, homogeneous) and the Macroreticular (MR) and Microreticular (GR) Polymer Bound Analogs.

Type	[Co] $\times 10^{-2}$	[Phenol] $\times 10^{-1}$	Sub/ Co	Conv.	BQ/DPQ
HMG	1.7	3.3	20	67	6.6
HMG	3.3	3.3	10	100	9.6
HMG	1.7	6.6	40	57.4	5.7
HMG	3.3	6.6	20	87.4	10
MR	1.7	3.3	20	52.1	5.5
MR	3.3	3.3	10	42.8	3.6
MR	1.7	6.6	40	35.1	5.0
MR	3.3	6.6	20	46.5	4.0
GR	2.4	3.3	14	71	16
GR	1.7	3.3	20	53.9	4
GR	1.1	3.3	30	34	0.63

Both the gel and macroreticular resins catalyze the oxidation as indicated by product analysis for benzoquinone and diphenoquinone. Rates of reaction were monitored by following the rate of absorption of O_2. In all instances the rates of the O_2 absorption and therefore the catalytic activity of the bound catalyst is reduced over that observed for the homogeneous catalysis by the parent complex at comparable conditions. Some very significant changes in product distributions were observed with variation of the cobalt(II) complex on the gel resin. The results are summarized in Table III. In looking at the data for the parent compound (indicated by type HMG), it can be seen that high concentrations of catalyst regardless of substrate concentration favors both high conversions of substrate (∿90-100%) and a high selectivity towards BQ (Bq/DPQ = 10). Lower catalyst concentrations regardless of phenol concentration results in lower conversions (∿60-70%) and a greater relative production of DPQ. The results with the MR resin do not show a discernible trend in product conversion or any great difference in the BQ/DPQ ratio. Since this resin was obtained commercially only one resin loading was used in this study. Three different cobalt loadings were investigated for the gel resin corresponding to 0.29, 0.20 and 0.14 mmole Co(II) per gram of resin (these correspond to the [Co] x 10^{-2} values of 2.4, 1.7 and 1.1, respectively). The general trends are the same as those observed for the homogeneous system. The primary difference is the enhanced selectivity accompanying slight changes in the resin loading. Doubling the resin loading (from 0.8 mmole Co/g resin to 1.7) doubles substrate conversion but increases BQ selectivity 25 fold. A similar doubling of the cobalt concentration in the homogeneous case (from 1.7 x 10^{-2} M to 3.3 x 10^{-2} M) increases conversion 1.5 times and BQ selectivity 1.5 times. The proposed mechanism of oxidation involves formation of phenoxy radicals.[6] The low concentrations of cobalt in the polymer increase the probability of two radicals combining to form DPQ. At higher cobalt concentrations and in solution the probability of organic radical encounters is decreased and an increased BQ ratio results.

Free radical reactions have the serious disadvantage of yielding a variety of products. As illustrated in this study, polymer attachment of the catalyst offers considerable potential for enhancing selectivity.

EXPERIMENTAL

Manipulations involving air-sensitive materials were performed under argon in Schlenk-type glassware. All elemental analyses were performed by the Microanalytical Laboratory at the University of Illinois. The ESR spectra were collected on a Varian Model E-9 spectrometer equipped with a Hewlett-Packard frequency counter.

Mössbauer spectra[19] were obtained with a scanned-velocity spectrometer operating in the time mode and calibrated with sodium nitroprusside and ^{57}Fe foil. Spectra were fitted with a least squares approximation assuming two Lorentian line shapes of equal width. Estimated error limits on the isomer shift and quadropole splitting ±0.03 mm/sec.

A 20% crosslinked macroreticular resin was a gift from Dr. Carl Brubaker. p-Chloromethylation of the macroreticular resin and preparation of the gel polystyrene resins has previously been described.[12]

(i) Preparation of 3,3'-iminodiproprionitrile (DCEA = dicyanoethylamine). This compound was prepared according to a published procedure.[15]

Calc for $C_6H_9N_3$: $HN-(CH_2CH_2CN)_2$: C, 58.51; H, 7.37; N, 34.13. Found: C, 58.31; H, 7.56; N, 34.01.

(ii) Preparation of 3,3'-benzyliminodiproprionitrile (benzylDCEA). Benzyl chloride was converted to benzyl iodide using sodium iodide in a refluxing mixture of acetone-dioxane. (Caution: Benzyl iodide is an intense lachrymator.) DCEA, 18.9 g (0.15 moles) was added dropwise to 16.7 g (0.075 moles) of benzyl iodide in 250 ml of THF. The reaction mixture was refluxed 1 hr, cooled and allowed to stir overnight. The precipitate, $C_6H_9N_3 \cdot HI$ was filtered and washed with ether. The filtrate was rotovaped to give an oily residue that was dissolved in CH_2Cl_2. This was extracted with 3.0 M HCl, separated, and the aqueous phase made basic with 6.0 M NaOH. This aqueous phase was extracted with CH_2Cl_2, dried (K_2CO_3), filtered, and rotovaped to yield a pure colorless liquid. The identity of the 3,3'-benzyl-iminodiproprionitrile was verified by IR and C, H, and N analysis.

Calc for $C_6H_5CH_2N(CH_2CH_2CN)_2$, $C_{13}H_{15}N_3$: C, 73.20; H, 7.09; N, 19.71. Found: C, 72.97; H, 7.01, N, 19.90.

(iii) Preparation of bis-(3-aminopropyl)benzylamine (BenzylDPT). 3,3'-benzyliminodiproprionitrile, 2.0 g in 5 ml of THF was added over 15 min to 75 ml of a 0.94 molar diborane in THF solution under argon. (Note: This solution is commercially available from Aldrich as ∿1.0 molar solution of the $BH_3 \cdot THF$ adduct in THF). If higher concentrations of the reducing agent are needed or a different solvent is desired, B_2H_6 gas can be conveniently generated by the method of H. C. Brown[20]. The reaction mixture was refluxed overnight. The clear solution was cooled, exposed to air and excess methanol added CAUTIOUSLY to destroy any remaining $BH_3 \cdot THF$. The solution was then distilled at atmospheric pressure until almost all of the solvent was gone. Concentrated HCl (∿50 ml) was added and the solution refluxed 24 hr, then stirred at room temperature 24 hr. The aqueous phase was separated and filtered to remove insolubles. The water was removed on a rotovap and the solid residue dissolved in 2.0 M NaOH. The water was removed until two layers separated. Benzene was added and the aqueous phase removed in a separatory funnel. The benzene layer was dried (K_2CO_3) and rotovaped to give an oil that was vacuum distilled (b.p. = 117-125 at 0.025 mm of Hg). The identity of the benzyldipropyltriamine (benzylDPT) was verified by its IR and mass spectra and by C, H and N analysis.

Calc for $C_6H_5CH_2N$-$(CH_2CH_2CH_2NH_2)_2$, $C_{13}H_{23}N_3$: C, 70.53; H, 10.47; N, 18.99. Found: C, 70.10; H, 10.45; N, 18.33.

(iv) Preparation of polymer bound 3,3'-iminodiproprionitrile [P]-DCEA.

Method A. 10 g of a chloromethylated resin and 30 g of 3,3'-iminodiproprionitrile were slurried in 75 ml of dioxane and refluxed under an argon atmosphere for three days. The resin was then washed with copious amounts of dioxane, dioxane-H_2O, H_2O, H_2O-THF and finally extracted with THF for 24 hr. The resin was washed with ethanol and dried at 80°C.

Method B. 25 g of chloromethylated polymer was refluxed for 2-4 days in an acetone-dioxane mixture (3:1 v/v) containing 15-20 g of sodium iodide. The resin was cooled, filtered and extracted with acetone 24 hr, then dried at 80°C. The dried resin was added to enough THF to make an adequate slurry and 10 g of 3,3'-iminodiproprionitrile added. This was heated at reflux for 4 days, cooled and extracted with THF until the filtrate was colorless. For example, a macroreticular resin which analyzed for 4.55% Cl, produced a nitrile containing resin with 2.20% N.

(v) Preparation of polymer bound bis-(3-aminopropyl)amine [P]-DPT. Aminated resin (about 20 g) prepared as above, was slurried in 150 ml of $BH_3 \cdot THF$ solution (1.0 molar) under an argon atmosphere. This was stirred for 1-2 days followed by refluxing 24 hr and cooled. The excess borane was destroyed with methanol (cautiously), then refluxed for several hrs. The resin was then filtered and slurried in a 50/50 mixture of 3 M HCl/dioxane and heated 24 hr. It was then cooled, filtered and slurried in H_2O/dioxane for several hr and washed with water. The washed resin was slurried in either 1.0 M NaOH/dioxane (50/50) or a concentrated dioxane solution of pyridine, 2,6-lutidine or triethylamine, and stirred for 24 hr. The resin was then filtered and washed with dioxane and dried to yield polymer bound DPT. The nitrile absorbance in the infrared spectrum of the unreduced polymer was completely eliminated upon treatment with BH_3-THF. Approximately 80% of the benzyl halide is convered to [P]-DPT with this technique. The BH_3 reduction is a quantitative step. Unreacted halomethylated sites were removed by treatment with NaOMe/MeOH, for example, found %N = 2.00, %Cl, 0.05, %I = 0.23.

(vi) Preparation of polymer bound bis-(2-cyanoethyl)-phosphine and polymer bound di-(3-aminopropyl) phosphine [P]-DAPP. Bis-(2-cyanoethyl)phosphine was a gift from the

American Cyanamid Co. It was incorporated into chloromethylated polystyrene in a fashion similar to the analogous amine compound above (see (iv), Method A) and reduced as in Section (v) to yield [P]-DAPP.

(vii) Addition of malonitrile to chloromethylated resin. Malonitrile as its potassium or sodium salt, can be added to the chloromethyl group. The sodium salt of DMSO is prepared by adding 80 ml of dry DMSO to 21 g of 57% NaH that has been washed with hexane under an argon atmosphere and heating for 1.5 hr. Malonitrile, 3.30 g in 20 ml of DMSO was added and the resulting solution filtered under argon onto 25 g of a chloromethylated resin. Stirring and heating at 70°C continued for three days. The resin was cooled, washed with DMSO and water, then extracted with THF. About 35-40% of the active sites are functionalized by this procedure.

(viii) Preparation of polymer bound diaminopropane [P]-DAP. The polymer (vii) above can be reduced in the usual fashion (v) to yield polymer bound diaminopropane.

(ix) Condensations of aldehydes and ketones with polymer bound polyamines to prepare the Schiff bases. Any of the three types of resins above may be used: [P]-DAP, [P]-DPT or [P]-DAPP. All of these are typically white or slightly offwhite. To the desired resin in a sufficient amount of benzene to form a slurry, is added a large excess of the aldehyde or ketone, *e.g.*, salicylaldehyde. The slurry is heated to reflux and the water of condensation removed in a Dean-Stark trap. The resin is then cooled and extracted with ethanol overnight, then dried at 80°C. If salicylaldehyde is used, the resulting resins are bright yellow. Their designations are [P]-SalDAP, [P]-SalDPT, and [P]-SalDAPP, respectively. Aldehydes and ketones used in addition to salicylaldehyde (SAL), are acetylacetone (acac), 2-pyridine-aldehyde and 2,3-butanedione (biacetyl). All were successful except for 2,3-butadione. Barring such special cases, any aldehyde or ketone can be used.

(x) Incorporation of metal ions into resin bound Schiff base ligands. The metal (Mn, Co, Ni, Cu, Zn), as the acetate, was dissolved in dry DMF and this used to slurry the resin bound ligand. After 1-3 days, the resin was filtered and washed with large quantities of DMF, then extracted with acetonitrile and dried. For Co and Mn, this reaction was carried out in dry degassed solvents under argon.

Incorporation of Fe(III) was accomplished in the following way for [P]-SalDPT. Excess $FeCl_3$ (anhydrous) was dissolved in 50 ml of a dry 1:1 (v/v) pyridine/DMF mixture and this used to slurry 5 g of [P]-SalDPT. Within ∿1 hr, the resin was filtered and washed with pyridine/DMF until the filtrate was colorless, then extracted with ethanol. The very dark brown beads were then filtered and dried. A 6% substituted resin analyzed for 2.60% Fe.

(xi) Preparation of polymer bound di-[3-(2-picolynyl)-aminopropyl]amine [P]-PicDPT. 2-pyridinealdehyde was condensed with [P]-DPT to form the pentadentate Schiff base containing two imine linkages. These imine linkages were reduced using the procedure outlined above in (v) to yield a linear pentamine capable of coordinating metal ions to form salt-like complexes. The resin bound copper complex was prepared.

(xii) Preparation of Mn, Co, Ni, Cu, Zn(SalMeDPT). These five metal complexes were prepared according to published literature methods.[21] All the analyses were within experimental error. E.g.,

Calc for $C_{21}H_{25}N_3O_2Co$: C, 61.45; H, 6.09; N, 10.24; Co, 14.36. Found: C, 61.20; H, 5.95; N, 10.05; Co, 14.57.

(xiii) Preparation of Fe(III)(SalMeDPT)Cl. This complex was prepared according to a published literature method.[22]

Calc for $C_{21}H_{25}N_3O_2FeCl$: C, 56.97; H, 5.69; N, 9.49; Cl, 8.01; Fe, 12.61. Found: C, 56.67; H, 5.45; N, 9.70; Cl, 8.97; Fe, 12.74.

(xiv) Preparation of anhydrous ferrous acetate. Iron powder (∿5 g) was added to 90 ml glacial acetic acid and 10 ml of acetic anhydride. The system was flushed with argon and refluxed overnight. The resulting white powder was filtered by suction and dried under vacuum. The compound is moisture sensitive.

Calc for $C_4H_6O_4Fe$: Fe, 32.11. Found: Fe, 30.71.

(xv) Preparation of Fe(II)(SalMeDPT). Method A. Using $Fe(CO)_5$. Salicylaldehyde, 2.44 g (0.02 moles) was added to 1.45 g (0.01 moles) of MeDPT in 15 ml of DMF. Benzene, 10 ml, was added and the water from the condensation removed with a Dean-Stark trap. After complete removal of water, the benzene was distilled away from the DMF. The resulting dry solution of the ligand was thoroughly deoxygenated by successive evacuation-refill cycles using argon. It is necessary to pump for ∿5 min during each of these repetitive cycles. Freshly distilled $Fe(CO)_5$, 1.96 g (0.01 moles) was syringed into the deoxygenated solution of the ligand. This was heated at 100°C for 2-3 hr, then at 95°C overnight. The dark red solution was cooled and filtered under an argon atmosphere. The filtrate was cooled (<0°C) for two days whereupon the complex was obtained as black crystals. The crystalline material was suction filtered and washed with 20-30 ml of dry toluene, then pumped to dryness. The dry complex is not air sensitive.

Calc for $C_{21}H_{25}N_3O_2Fe$: C, 61.92; H, 6.19; N, 10.32; Fe, 13.71. Found: C, 62.04; H, 6.20; N, 10.16; Fe, 13.66.

The oxidation state of the iron center was verified in the following way. 2.00 ml of a dry degassed DMF solution containing 7.85×10^{-4} moles of Fe(SalMeDPT) was equilibrated at 30°C and exposed to a pure oxygen atmosphere in an oxygen buret. The deep red solution turned brown during the oxygen uptake (∿5 min). 1.82×10^{-4} moles of oxygen were consumed. The iron to oxygen mole ratio of 4.31/1 indicates an irreversible oxidation of Fe(II) to Fe(III).

Method B. Using $Fe(OAc)_2$. The anhydrous ligand H_2SalMePDT in acetonitrile was dripped into an acetonitrile slurry of $Fe(OAc)_2$ under dry anaerobic conditions over 20 min at room temperature. The dark red solution was stirred overnight. The crystals formed were collected on a Schlenk funnel and washed with ~30 ml of dry deoxygenated CH_3CN, then pumped to dryness. The red-brown microcrystals were analyzed as follows.

Calc for $C_{21}H_{25}N_3O_2Fe$: C, 61.92; H, 6.19; N, 10.32; Fe, 13.71. Found: C, 61.43; H, 5.78; N, 10.20; Fe, 13.67.

(xvi) Incorporation of $Fe(CO)_5$ into MR-X20S8 containing H_2SalDPT. 6.0 g of the MR-X20S8 H_2SalDPT polymer was slurried in 30 ml of DMF and this degassed. Freshly distilled $Fe(CO)_5$, 2.0 ml, was injected into this slurry under an argon atmosphere. No immediate change occurred. The reaction vessel was sealed under argon and protected from light. The slurry was stirred overnight during which time the solution above the beads turned deep red (a DMF complex?). At this time the temperature was raised to 100°C and held there 24 hr. The slurry was cooled, filtered and Sohxlet extracted with THF under argon. The beads were pumped to dryness to yield a violet colored resin.

(xvii) Oxidation of 2,6-Dimethylphenol. The resin bound and parent complexes were prepared as described above. The catalyst used for the phenol oxidations is Co(SalMeDPT) and the resin bound analog. A variety of polymers containing this cobalt complex were prepared and include the following: MR-X20S8, GR-X15S9, GR-X15S6 and GR-X15S3. In general, the loadings in the polymer will be designated by the code number's.[28] The polymer is of the type [P]-Co(SalDPT) at the various loadings indicated.

The test phenol used for the catalytic oxidation is Aldrich Gold label 2,6-dimethylphenol (2,6-DMP), and the solvent used is benzene. The reaction was monitored by the oxygen uptake using a gas buret filled with mercury. A benzene manometer was connected to the buret. (The oxygen absorbed could be measured by adjusting the mercury leveling bulb until the benzene manometer indicated that the internal and external pressures were equalized. The level in the buret could then be read.) As oxygen, was used up in the reaction, the internal pressure would drop and the benzene layer in the internal side of the manometer would begin to rise. By raising the mercury leveling bulb and thereby pushing mercury into the buret (displacing oxygen), the internal pressure would be raised. If the mercury level inside the buret is raised until internal and external pressures are equalized, the amount of O_2 consumed can be read from the buret. This enables one to carry out the reaction at a constant pressure of oxygen. The reaction was allowed to proceed until the O_2 uptake was complete, as indicated by only very small changes in O_2 pressure over long periods or until a predetermined amount of time had elapsed.

In a typical experiment, enough catalyst to contain 2×10^{-4} moles of cobalt was added to the reaction vessel (25 ml R.B.) and the system thoroughly flushed with oxygen. Benzene, 10 ml, was then injected through the top of the reaction vessel and the stopcocks closed so that the benzene solution was exposed only to the oxygen in the buret. After the reaction mixture was equilibrated to the proper temperature, the system was vented to equalize internal and external pressures. After equilibrium was reached and internal and external pressures equalized (usually 0.5 hr), 4×10^{-3} moles of 2,6-DMP in 2.0 ml of benzene were injected, the system closed and the oxygen uptake monitored.

The products of the oxidation were analyzed by either dry column chromatography or thin layer chromatography. Generally three or four bands were obtained in this way, depending on whether the resin bound or parent catalyst, respectively, was used. The bands were labeled A, B, C and D in order of decreasing R_f value, A > B > C > D.

Band A, which moved the furthest down the column, is colorless. The compound readily sublimed at 30°C. It was identified by its melting point and C and H analysis, as the starting 2,6-dimethylphenol. Literature melting point = 45-46°C; found 45.5°C.

Calc. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.62; H, 8.32.

Band B, which moved second furthest down the column, is a bright yellow color. It readily sublimed at ∿80°C to give yellow needles. It was identified by its color and melting point as 2,6-dimethyl-1,4-benzoquinone (BQ). Literature melting point = 72-73°C. Found: 71-72°C.

Band C, which remained near the top of the column (small R_f) was bright yellow in solution. The solid product, however, was bright red. It was identified as 3,3',5,5'-tetramethyldiphenoquinone by its C and H analysis and mass spectrum.

Calc for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.86; H, 6.66. Molecular weight from mass spectrum: molecular weight = 240. Theoretical molecular weight for $C_{16}H_{16}O_2$ = 240.23.

Band D which was only present when the parent catalyst Co(SalMeDPT) was used instead of the resin bound analog, remained at the top of the column ($R_f = 0$). This band was dark brown in color and analyzed in the following way after recrystallization from CH_2Cl_2/hexane. C, 52.33; H, 5.69; N, 8.28; Co, 11.38. This analysis does not correspond to any immediately obvious cobalt complex which this reaction might produce.

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