

Poly(styryl)bipyridine: Synthesis and Formation of Transition-Metal Complexes and Some of Their Physical, Chemical, and Catalytic Properties

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Poly(styryl)bipyridine, **1**, is produced from the reaction of lithiated polystyrene with bipyridine in tetrahydrofuran. Under our conditions, bipyridine becomes bound to 10–15% of the phenyl residues. The reaction of **1** with a variety of transition-metal salts can be carried out in a variety of swelling solvents and results in formation of polymer-bound bipyridine transition-metal complexes. The extent of metal incorporation depends on solvent, metal ion concentration, and the identity of the metal species. Zerovalent metal complexes such as $\text{P-Ph-bpy-M}(\text{CO})_4$ ($\text{M} = \text{Cr, Mo, W}$) are readily prepared from the reaction of **1** with the metal hexacarbonyl complexes. (Poly(styryl)bipyridyl)palladium acetate is an active catalyst for the hydrogenation of olefins at ambient pressure and temperature. It can also be used to catalyze the acetoxylation of benzene; however, the percent conversion in this case is rather low.

I. Introduction

Polymer-based organo transition metal catalysts offer several advantages in synthetic and industrial chemistry.² Of these, the ease of separation of the catalyst from the desired reaction product(s) and the ease of recovery and reuse of the catalyst are most important. In polystyrene-based systems, the ability to control the pore size, either through the amount of cross-linking or through choice of the solvent system, allows some steric selectivity not observed in analogous homogeneous systems. Such selectivity has been demonstrated in the relative rate of olefin hydrogenation³ and in the regioselectivity of the hydroformylation process⁴ when polymer-supported transition metals are used as catalysts.

Work in this area has shown several significant advances during the past 7 years, though, with time and the continued efforts of several groups, a few deficiencies of the commonly used polymer systems have become apparent. Moffat, for example, reported that a cobalt carbonyl complex of poly(vinyl)pyridine is too labile to be used as a heterogeneous catalyst for hydroformylation.⁸ Pittman et al. have reported that palladium complexes of polymeric phosphine ligands are also labile under certain conditions.⁶ Although conditions in both cases were quite severe, there appears to be a need for less labile polymer-bound transition-metal reagents.

Therefore, it seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand which would be able to form complexes with a wide variety of transition metals and, therefore, have a large range of applications. Potential advantages of such a system would include greatly decreased metal complex lability, nearly distortion-free binding of this multidentate ligand to a metal, different catalyst selectivity if chelating ligand atoms other than phosphorus were used, and the ability to prepare different stereoisomers than would be possible from the binding of more than one unidentate polymer-bound ligand to the metal.

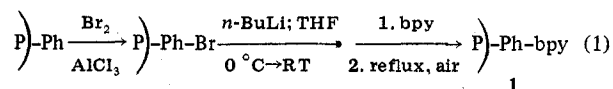
A few examples of polymer-bound chelating ligands have been reported. Most of these were designed for special purposes, and, therefore, their use is subject to some limitations.^{7–12} (A notable exception involves the preparation of $\text{P-C}_6\text{H}_4\text{-P}(\text{Ph})\text{CH}_2\text{CH}_2\text{P}(\text{Ph})_2$ which was reported by Pittman's group after we had begun this work.¹³) In order to be generally useful the chosen ligand must be readily available, be relatively inexpensive, be able to bind to a large variety of transition-metal species, be able to be bound to the polymer support smoothly and efficiently, and be chemically inert under a wide variety of potential reaction conditions. 2,2'-Bipyridine was selected as most closely fitting these qualifications.

We report herein the synthesis of our polystyrene-based bipyridine system. The versatility of this polymer is demonstrated by the wide variety of transition-metal complexes

which can be prepared. And, some of the physical, chemical, and catalytic properties of these very promising reagents are presented.

II. Results and Discussion

A. Preparation and Physical Properties of Polymer-Bound Bipyridine. Bipyridine is attached to phenyl residues of polystyrene-2% divinylbenzene (PS-2% DVB) copolymer beads through the reaction sequence shown in eq 1. Ring



bromination and lithiation are commonly used in the preparation of polystyrene derivatives.¹⁴ In our system the stoichiometry of the ring bromination is controlled so that less than 25% of the phenyl residues are brominated. Solid bipyridine is added to a tetrahydrofuran (THF) suspension of the lithiated polymer, and the resulting solution is brought to reflux. After a few hours, the solution is allowed to cool to room temperature and air is bubbled through the solution until a color change from dark purple to yellow-gold is observed. The polymer is separated by filtration and washed with copious amounts of various solvents.

Because the polymer beads are totally insoluble in organic solvents, only infrared spectral data (KBr pellet) could be obtained. New bands, in addition to those of PS-2% DVB, are observed at 1580, 1560, 1430, 1115, 1020, 825, and 785 cm^{-1} , entirely consistent with the assigned structure.¹⁵ No change in the intensity of these, or any other, bands was observed even after washing small amounts of the polymer with liters of benzene, ethyl acetate, or THF.

Elemental analysis for C, H, and N has been obtained for several batches of **1** but is not useful in defining the amount of incorporation of bipyridine.¹⁶ However, results from metal binding studies (vide infra) indicate that the polymer contains one bipyridyl group for each seven to eight phenyl residues. Therefore, conversion from the brominated phenyl residues to bipyridylphenyl residues occurs in greater than 50% yield. This is a substantial improvement over the 9% yield reported for the formation of 2-phenylbipyridine from phenyllithium and bipyridine.¹⁷

The swelling factor of **1** in various solvents has been examined (Table I) and is considerably different from that observed for the original PS-2% DVB copolymer.¹⁸ In general, **1** swells much less than PS-2% DVB. This may be due to some expansion of the polymer beads upon incorporation of the bipyridyl moiety or to cross-linking which may have occurred during the synthetic sequence.¹⁹

B. Preparation and Physical Properties of Transition-Metal Complexes of **1.** A wide range of transition-metal complexes

Table I. Swelling Factors for **1** and PS-2% DVB

Solvent	Swelling factor ^a	
	PS-2% DVB	1
Methanol	1.1	1.0
Acetonitrile	2.8	1.4
Ethyl acetate	2.9	2.4
Tetrahydrofuran	2.3	2.6 ^b
Chloroform	5.2	2.8
Benzene	5.5	2.9
Benzene-ethyl acetate (1:1)		3.2

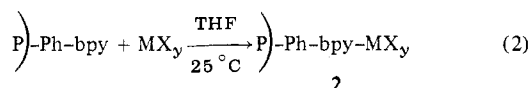
^a Ratio of volume of swollen polymer to the volume of dry polymer. ^b Value determined in freshly distilled (over LiAlH₄) THF; this value is sensitive to traces of water in the solvent.

Table II. Amounts of Various Metal Salts Which Become Bound to Polymer **1** in Tetrahydrofuran

Metal salt	Quantity bound, mequiv of metal/g of polymer	Metal salt	Quantity bound, mequiv of metal/g of polymer
Cr(NO ₃) ₃	0.22	CoCl ₂	0.35
MnI ₂	0.14	Ni(NO ₃) ₂	0.70
FeCl ₂	0.36	Pd(O ₂ CCH ₃) ₂	0.69 ^a
FeCl ₃	0.83	CuBr ₂	0.34 and 0.37 ^b
RuCl ₃	Not determined	AgNO ₃	Not determined

^a Determined by elemental analysis for Pd. ^b Two different batches of polymer were used.

of **1** can be easily prepared. In the standard procedure, polymer **1** is added to a THF solution of the desired metal salt (eq 2). The resulting solution is then stirred for a short period



of time and the resulting polymer-metal complex is removed from the solution by filtration. This metal-containing polymer is washed thoroughly with a variety of solvents to remove any uncomplexed metal salts.

Most of these reactions are accompanied by an obvious change in color intensity of the reaction solution. This color change can be monitored spectrophotometrically and can be used to determine the amount of metal bound to the polymer. Table II presents some of the metal complexes prepared and the amount of metal incorporation as determined in this manner.

The amount of metal incorporation determined in this manner appears to be entirely consistent with the amount of metal incorporation determined by elemental analysis for the metal. In one example, spectrophotometric analysis indicated 0.4 mequiv of Fe(III)/g of polymer: this is equivalent to 2.2% iron. Elemental analysis indicated 2.22% Fe, in close agreement with the spectrophotometric value.

The factors which determine the amount of metal incorporation are not yet entirely understood. However, several important trends can be observed.

First, the amount of metal incorporation decreases as the initial concentration of metal ion in solution decreases. This is readily apparent from the data in Table III. Polymer **1** was stirred in a constant volume of THF solution containing various concentrations of iron(III) chloride ranging from 1×10^{-7} to 1×10^{-2} M. The resulting polymers were isolated and thoroughly washed, and the amount of iron incorporation was determined by elemental analysis. The difference in color of the resulting polymers was observable by the naked eye and ranged from a very pale yellow to dark brown.

This result suggests that the polymer may prove to be useful in analytical applications where direct analysis of the amount of metal species present in an organic solution is not possible or convenient.

Table III. Effect of Metal Ion Concentration on the Amount of Metal Incorporation in **1**

Initial concn of FeCl ₃ , M	Amt of Fe incorpn	
	% Fe	mequiv of Fe/g of polymer
1×10^{-2}	1.65	0.29
4×10^{-3}	0.69	0.12
2×10^{-3}	0.28	0.05
4×10^{-4}	0.12	0.02
8×10^{-5}	0.04	0.007
1×10^{-5}	<0.01	
1×10^{-6}	<0.01	
1×10^{-7}	<0.01	

Table IV. Effect of Solvent on the Quantity of FeCl₃ Bound to **1**

Solvent	Swelling factor ^a	Quantity bound, mequiv/g
Methanol	1.0	0.002
Acetonitrile	1.4	0.25
Tetrahydrofuran ^b	2.2	0.83
Ethyl acetate	2.4	1.2 ^c
Ethyl acetate-benzene (1:1)	3.2	1.2 ^c

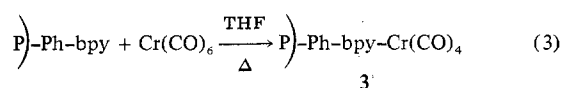
^a The ratio of volume of swollen to nonswollen polymer **1**. ^b Reagent grade; not dried. ^c See ref 16.

The amount of metal incorporation also depends on the solvent system used (Table IV). From the study involving iron(III) chloride in a variety of solvents, it appears that the extent of metal incorporation increases with the swelling factor of the solvent system until a maximum metal incorporation is reached, in this case at ethyl acetate.

Several points should be noted from this data. First, in methanol (nonswelling solvent) coordination of only those bipyridyl groups on the bead surface should be possible. If complete binding to these surface groups occurs, the very low binding observed indicates that greater than 99% of the bipyridyl groups are located inside the bead. And the incorporation of 1.2 mequiv of Fe/g of polymer requires that there must be at least one bipyridyl group for each ca. eight phenyl residues. If this level of incorporation results from complete complexation of all bipyridyl residues, the extent of incorporation of most metal ions in the polymer should be nearly the same in the most swelling solvent—benzene-ethyl acetate. Unfortunately, the very low solubility of most metals in this system prevents testing of this hypothesis.

The infrared spectra of these metal complexes are very similar to each other and differ from that of **1** by the addition of a weak, broad band at ca. 1700 cm⁻¹ and an increase in the intensity of the bands at 1100 and 905 cm⁻¹ relative to those at 700 and 755 cm⁻¹. Reasonable absorption bands for other ligands are also observed.

Zerovalent transition-metal complexes are also readily prepared. For example, when polymer **1** and hexacarbonylchromium are brought to reflux in THF and maintained at reflux for a few hours, a new polymer is obtained. This polymer, **3**, is filtered from the reaction solution and washed



thoroughly. The infrared spectrum includes bands at 2010, 1895, and 1850 cm⁻¹, entirely consistent with the formation of the expected *cis*-L₂Cr(CO)₄ system.²⁰

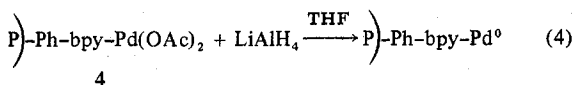
Similar complexes have also been prepared from molybdenum and tungsten hexacarbonyls. In the case of molybdenum, elemental analysis of the black polymer indicates 0.65 mequiv of Mo/g of polymer. Similar amounts of metal incorporation are expected for the other carbonyl complexes.

All of the transition-metal complexes prepared above are stable to air and moisture for at least several months. As expected, the metal complexes do not show any electrical conductivity.

C. Chemical and Catalytic Properties of Polymer-Metal Complexes, 2. One of the potential advantages of the use of a polymer-bound chelating ligand involves the expected decreased metal complex lability due to the chelation effect.²¹ Polymer **1** does, indeed, form impressively stable metal complexes.

When an iron(III) chloride complex of **1** was stirred in the presence of 100 equiv of potassium cyanide in 1:1 benzene-methanol for 48 h, 39% of the iron remained bound to the polymer. When the palladium acetate complex of **1** was treated under similar conditions for 8 h, 64% of the palladium remained bound to the polymer.

Transition-metal complexes, **2**, can be oxidized or reduced while remaining bound to the polymer. Reaction of (poly(styryl)bipyridine)palladium acetate, **4**, with lithium aluminum hydride results in the formation of (poly(styryl)bipyridine)-palladium(0). The reaction is accompanied by a color change



from brown to black and a loss of the acetate bands in the IR spectrum. The palladium(0) complex can be reoxidized to the +2 oxidation state by treatment with dilute nitric acid or ceric ammonium nitrate. The color of the polymer changes back from black to brown, and bands due to nitrate ligands are observed in the IR spectrum of the product.

In beginning to examine the catalytic properties of some of the transition-metal complexes of our polymer-bound bipyridine ligand, work with polymer **4** was most attractive. First, a large number of catalytic processes are known for various palladium species. The cost of palladium makes easy recovery and reuse of the catalytic species attractive financially. And, the low lability of **4** in comparison to other polymer-palladium systems should be an important asset.

Polymer **4** is an active hydrogenation catalyst which has properties different from those of both palladium acetate and palladium on carbon. (Poly(styryl)bipyridine)palladium acetate appears to be selective for the reduction of carbon-carbon multiple bonds. Palladium acetate is not useable under these conditions because of the formation of palladium metal.

The hydrogenation of simple olefins occurs readily at ambient temperature and 1 atm of hydrogen. The hydrogenations were carried out in dry tetrahydrofuran. The rate of hydrogen consumption was monitored as a function of time. With one exception, plots of total hydrogen consumed vs. time were linear for at least the first 80% of the hydrogenation or the first 180 min. (The exception was 1-octene.) The rate of hydrogen consumption in the hydrogenation of 1-hexene (2.5 mL/min) was assigned the relative rate of 1.0. The relative rates of the hydrogenation of a variety of olefins are presented in Table V. In the case of 1-octene the relative rate listed is the initial rate of hydrogen consumption (vide infra).

In general, it appears that hindered olefins are reduced less rapidly than less hindered olefins, and very hindered species such as α -pinene are not reduced. It is interesting that the relative rates of hydrogenation presented in Table V are very similar to those observed by Grubbs and Kroll in their use of a polymer-based rhodium catalyst.²² Unfortunately, comparison with homogeneous examples is not possible under our conditions.

The hydrogenation of olefins containing hydrogen on the carbon α to the π bond is accompanied by olefin isomerization. This is shown clearly in the hydrogenation of 1-octene. After consumption of 0.5 equiv of hydrogen, the reaction was stopped

Table V. Relative Rates and Product Yields of Olefin Hydrogenation^a

Olefin	Rel rate	Reacn time, min	Cnvrsn to alkane, ^b %
2-Methyl-3-buten-2-ol	2.7	60	>95
1-Octene	2.0	150	50 ^c
<i>p</i> -1-Propenylanisole	1.3	80	88
Cyclohexene ^d	1.0	60	64
<i>trans</i> -Stilbene	0.8	205	86
Cyclooctene	0.3	180	40
Cyclododecene	0.2	180	27
α -Pinene		120	None
Oleic acid		300	None

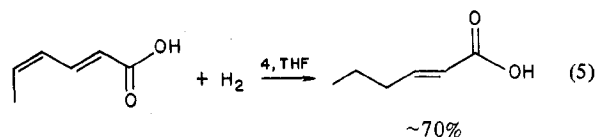
^a 100 mg of **1**, 10 mmol of olefin, 10 mL of dry tetrahydrofuran, 1 atm of hydrogen at room temperature. ^b Determined by nuclear magnetic resonance spectroscopy. No effort was made to maximize the yields. The reactions were stopped at an arbitrary time—often before uptake of hydrogen had ceased. ^c A 50% yield of 2-octene was also received; longer reaction time results in increased conversion to octane. ^d An ether workup with water washes was used to remove the tetrahydrofuran.

and the solution analyzed by NMR. A 1:1 mixture of 2-octene and octene was observed. Thus, the nonlinear consumption of hydrogen observed in this case is due to competing isomerization followed by the slower hydrogenation of the resulting 2-octene.

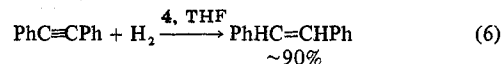
A turnover number greater than 2800 is observed in the hydrogenation of 3-methylbuten-3-ol. A lower turnover number (~800) is observed in the hydrogenation of 1-octene, presumably due to the presence of the competing isomerization process.

The amount of leaching of metal during the hydrogenation is dependent on the reaction conditions. In the atmospheric hydrogenation of 2-methyl-3-buten-2-ol the amount of palladium incorporation of the polymer decreased from 7.30 to 7.27%. In another experiment, 16.7 g of 2-methyl-3-buten-2-ol, 30 mL of dry THF, and 100 mg of (poly(styryl)bipyridine)palladium acetate were placed in a Parr apparatus and shaken at 30 psi for 3 h. In this case the amount of palladium incorporation decreased from 7.30 to 5.63%.

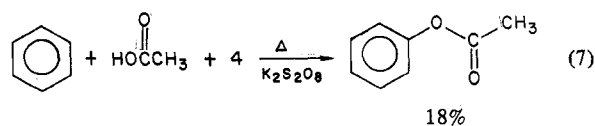
Hydrogenation of acetylenes and polyfunctional molecules is currently under study. An interesting example of the selectivity which can be observed involves the net hydrogenation of the terminal double bond of sorbic acid.



The reduction of an internal acetylene to an olefin has been observed without modification of the catalyst, but a mixture of *cis* and *trans* isomers is observed.



(Poly(styryl)bipyridine)palladium acetate also serves as a catalyst for the acetoxylation of benzene (eq 7). The yields



are lower than those observed for the analogous homogeneous reaction.²⁴ No sign of decomposition of the polymer is observed after several hours of reflux in glacial acetic acid.

Further investigations of these and other catalytic processes are currently under active study in these laboratories.

III. Summary

We have reported, herein, the synthesis of a generally useful, readily prepared polymer-bound chelating ligand. Poly(styryl)bipyridine readily forms complexes with a large range of transition-metal salts. Alternatively, polymer-bound complexes may be prepared via the reaction of poly(styryl)bipyridine with metal carbonyl complexes. In the former case, the amount of metal incorporation can be controlled through choice of the solvent system or by control of the initial concentration of metal ion in the reaction solution. Our results suggest that poly(styryl)bipyridine may have important applications in the quantitative and/or qualitative analysis of metal ions in organic solutions.

The use of our polymer-bound chelating system in the preparation of polymer-bound transition-metal complexes appears to result in a decrease in metal lability. And, some of these complexes have interesting catalytic properties.

IV. Experimental Section

Unless otherwise indicated, all elemental analyses were performed by Spang Microanalytical Laboratory. Infrared spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer, ultraviolet-visible spectra on a Beckman Acta MIV spectrophotometer, and nuclear magnetic resonance spectra on a Varian Associates CFT-20 or A-60 NMR spectrometer.

Polymer-Bound Bipyridine, 1. Polystyrene-2% divinylbenzene copolymer beads (50 g, ca. 0.4 mol of phenyl residues), 6 mL (0.1 mol) of bromine, and 1 g (8 mmol) of aluminum trichloride were added to 500 mL of chloroform, and the resulting red solution was stirred at room temperature for 48 h. Aqueous sodium bisulfite was carefully added to the solution until nearly all of the unreacted bromine was converted to bromide. The supernatant aqueous layer was periodically decanted and discarded. The resulting chloroform suspension was filtered through fritted glass. The polymer was washed extensively with benzene, acetone, water, hexane, and ether. The pale yellow polymer was dried in a vacuum oven at ca. 60 °C for 6–8 h.

The brominated polymer (8 g, ca. 0.02 mol of bromophenyl residues) was added to 100 mL of dry THF in a three-neck, 500-mL round-bottom flask fitted with a condenser, nitrogen inlet, and rubber septum. The system was purged with nitrogen and maintained under a positive nitrogen pressure. The solution was cooled to 0 °C and *n*-butyllithium (20 mL of a 2.2 M solution in hexane, 0.044 mol) was added via syringe to yield a pinkish solution. The solution was allowed to stir at 0 °C for 45 min and was then allowed to warm to room temperature. After the solution was stirred for 1 h at room temperature, bipyridine (7.5 g, 0.048 mol) was added as a solid. An immediate color change from red brown to dark purple was observed. The solution was brought to reflux and maintained at reflux for 3 h. The reaction solution was allowed to cool to room temperature and air was bubbled through the solution until the entire solution had become golden yellow. The resulting polymer was separated by filtration through fritted glass and was thoroughly washed with THF, benzene, and ethyl acetate.

Elemental analysis has been obtained for a number of batches of polymer.¹⁶ The data indicate that there is approximately one bipyridyl group for each nine phenyl residues.

Formation of Metal Complexes of 1. Method A. Polymer-Bound (Bipyridine)palladium(II) Acetate, 4. Palladium acetate (1 mmol, 0.22 g) was dissolved in 50 mL of THF in a 100-mL round-bottom flask. Polymer 1 (1 g) was added, the flask stoppered, and the solution stirred at room temperature overnight. The resulting polymer was isolated by filtration through fritted glass and was thoroughly washed with THF, benzene, and ethyl acetate in repeated cycles until at least three complete cycles were color free.

Elemental analysis indicates 7.30% palladium, equivalent to 0.69 mequiv of palladium/g of polymer. The elemental analyses of different batches differ slightly but are usually within 5% of this value.

The presence of the acetate ligands is evident from the IR spectrum which includes bands at 1560 and 1545 cm⁻¹.²⁴

Method B. Polymer-Bound (Bipyridine)(tetracarbonyl)molybdenum. Hexacarbonylmolybdenum (0.22 g, 1 mmol) and 1 g of 1 were added to 50 mL of THF, and the resulting solution was refluxed under nitrogen for 6 h. The polymer was separated from the resulting solution

by filtration through fritted glass. The polymer was thoroughly washed with THF, benzene, and ethyl acetate.

Elemental analysis indicates 6.20% molybdenum or 0.65 mequiv of molybdenum per gram of polymer. The IR spectrum includes bands at 2010, 1905, 1870, and 1835 cm⁻¹, very similar to that observed for (bipyridine)(tetracarbonyl)molybdenum.²⁵

Spectrophotometric Determination of Metal Incorporation. In a typical procedure, 67.5 mg (0.25 mmol) of iron(III) chloride hexahydrate was added to a volumetric flask and tetrahydrofuran was added to make a total volume of 250 mL. Solutions which were 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , and 8×10^{-4} M in ferric chloride were prepared from the original solution by dilution. These solutions were then used to prepare a calibration curve by plotting absorbance vs. concentration at 405 nm.

Polymer 1 (200 mg, 0.24 ± 0.02 mmol of bipyridyl) was added to a 250-mL Erlenmeyer flask and titrated with the remaining 10^{-3} M ferric chloride solution. The ferric chloride solution was added in 5–10-mL portions by pipet, and the resulting solution was shaken for 10–15 min. The polymer was allowed to settle to the bottom of the flask and part of the supernatant solution was removed and the absorbance determined. This solution was then returned to the Erlenmeyer flask and the titration continued until no further change in total absorbed metal ion was observed.

The amount of metal incorporation was determined according to the equation $(C_i - C_s)V/0.2$ g of polymer = mequiv of Fe/g of polymer. In this equation C_i is the initial molar concentration of iron(III) chloride, C_s is the molar concentration of iron(III) chloride in the supernatant solution, and V is the total volume of solution added in mL.

The results from this work have been presented in Tables II and IV.

In a separate run, a polymer 1–ferric chloride complex was prepared which contained 0.4 mequiv iron/g of polymer as determined by this method. Elemental analysis indicated 2.22% iron. These values are equivalent.

Reaction of Metal Complexes of Poly(styryl)bipyridine with Cyanide. Attempted Leaching of the Metal. The desired metal-complexed polymer, 2 (200 mg), and potassium cyanide (0.7 g, 0.01 mol) were added to 50 mL of a 1:1 mixture of benzene and methanol. In the case of (poly(styryl)bipyridine)palladium acetate, the reaction was stirred for 8 h. The incorporation of palladium decreased from 7.77 to 5.04%. In the case of (poly(styryl)bipyridine)iron(III) chloride, the reaction was stirred for 48 h. The incorporation of iron decreased from 0.87% to 0.30%. In each case, the polymer was isolated by filtration through fritted glass and was thoroughly washed and then dried *in vacuo* before analysis.

Reduction of (Poly(styryl)bipyridine)palladium Acetate. Lithium aluminum hydride (76 mg, 2 mmol) was added to 50 mL of dry tetrahydrofuran. Polymer 4 (1 g, 0.69 mmol) was added and the resulting solution was stirred for 2 h. The black polymer was isolated by filtration through fritted glass and washed thoroughly with ethyl acetate, tetrahydrofuran, dilute acetic acid, and aqueous sodium bicarbonate. The IR spectrum of the product was similar to that of 4 except for the loss of the bands at 1560 and 1545 cm⁻¹.

Oxidation of (Poly(styryl)bipyridine)palladium(0). (Poly(styryl)bipyridine)palladium(0) (100 mg, 0.069 mmol) was added to 25 mL of 2 M aqueous nitric acid. The resulting solution was stirred for 1 h and the resulting polymer isolated by filtration through fritted glass. The polymer was washed with dilute aqueous sodium hydroxide, tetrahydrofuran, and ethyl acetate. The product was identified on the basis of the IR spectrum which included new bands at 1601, 1290, and 985 cm⁻¹, indicative of nitrate ligands.²⁶

Olefin Hydrogenation. In a typical procedure, 2-methyl-3-buten-2-ol (0.86 g, 10 mmol) and 100 mg of 4 (0.069 mmol Pd) were added to 10 mL of dry THF in a 100-mL round-bottom flask. The flask was attached to a 1-atm hydrogenation apparatus, the system purged with hydrogen, and the solution stirred under 1 atm of hydrogen. The hydrogen consumed was measured as a function of time, and the reaction was stopped when no further uptake of hydrogen was observed. The catalyst was separated by filtration through fritted glass, the solvent removed by distillation at reduced pressure, and the product identified by NMR spectroscopy (DCCl₃): δ 2.4 (s, 1) (OH), 1.48 (m, 2) (CH₂), 1.23 (s, 6) ((CH₃)₂), 0.91 (m, 3) (CH₂CH₃). Complete conversion to 2-methyl-2-butanol was observed.

Elemental analysis for palladium of the polymer before reduction under these conditions showed 7.30% palladium compared with 7.27%

after the hydrogenation. The results are from a single determination in each case.

Kinetics of Olefin Hydrogenation. All hydrogenations were conducted under the conditions described directly above. The reaction was stirred until hydrogen consumption began. The amount of hydrogen consumed was then measured as a function of time. The rate of hydrogen consumption in the hydrogenation of cyclohexane was assigned as 1.0 and the relative rates of hydrogenation are given in Table V. The rates of hydrogen consumption were constant up to at least 80% conversion or 180 min, at which point the slower hydrogenations were terminated. The other data presented in Table V provide an indication of the actual time required for the hydrogenation of these compounds under these conditions.

In most cases several runs were made. The data is reproducible to $\pm 10\%$.

Hydrogenation of Sorbic Acid. Sorbic acid (2.24 g, 0.02 mol) and 100 mg of **4** (0.069 mmol Pd) were added to 25 mL of THF. The solution was purged with hydrogen and then stirred under 1 atm of hydrogen. After ca. 2 h, a significant decrease in the rate of hydrogen uptake was observed. The reaction was terminated at this point. The reaction solution was filtered through fritted glass and the solvent removed by distillation at reduced pressure. NMR (DCCL₃): δ 11.6 (m, 20), 7.5–6.9 (m, 13), 6.0–5.3 (m, 17), 2.5–1.1 (m, 94), 0.94 (m, 52). These data are consistent with a product mixture consisting of 71% 2-hexenoic acid, 18% hexanoic acid, and 11% 3-hexenoic acid. Hydrogenation for longer periods of time led to complete conversion to hexanoic acid.

Hydrogenation of Diphenylacetylene. Diphenylacetylene (1.78 g, 0.01 mmol) and 100 mg of **4** (0.069 mmol Pd) were added to 25 mL of THF. The solution was purged with hydrogen and then stirred under hydrogen at room temperature and atmospheric pressure. After 40 min a decrease in the rate of hydrogen uptake was observed and the reaction was terminated. The solution was filtered and the solvent removed at reduced pressure. NMR (DCCL₃): δ 7.24–7.0 (m, 90), 6.50 (s, 10), 2.84 (s, 3). These data are consistent with a mixture containing 32% *trans*-stilbene, 59% *cis*-stilbene, and 9% diphenylethane. Continued hydrogenation led to conversion to diphenylethane in greater than 90% yield.

Acetoxylation of Benzene. Benzene (4 g, 0.05 mol), **4** (1.0 g, 0.69 mmol of Pd), and potassium persulfate (13.8 g, 0.05 mol) were added to 50 mL of glacial acetic acid. The reaction was brought to reflux and stirred at reflux for 12 h. The reaction was allowed to cool and then added to ether–water. The layers were separated and the ethereal layer was washed with water and aqueous sodium bicarbonate. The resulting solution was dried over anhydrous magnesium sulfate and filtered, and the solvent and unreacted benzene were removed at reduced pressure. NMR (DCCL₃): δ 7.24 (m, 5), 2.29 (s, 3). This is identical with that of a commercial sample of phenyl acetate. The product was obtained in 18% yield.

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Registry No. 1, 9003-53-6; Cr, 7440-47-3; Mn, 7439-96-5; Fe, 7439-88-5; Ru, 7440-18-8; Co, 7440-48-4; Ni, 7440-02-0; Pd,

7440-05-3; Cu, 7440-50-8; Ag, 7440-22-4.

References and Notes

- (1) For preliminary communications of some of this work see R. J. Card and D. C. Neckers, *J. Am. Chem. Soc.*, **99**, 7733 (1977).
- (2) For recent reviews see: (a) D. C. Neckers, *CHEMTECH*, **8**, 108 (1978); (b) E. C. Blosser and D. C. Neckers, Ed., "Solid Phase Synthesis", Dowden, Hutchinson and Ross, 1975; (c) J. C. Bailer, Jr., *Catal. Rev.-Sci. Eng.*, **10**, 17 (1974).
- (3) E. S. Chandrasekaran, R. H. Grubbs, and C. H. Brubaker, Jr., *J. Organomet. Chem.*, **120**, 49 (1976), and references cited therein.
- (4) C. U. Pittman, Jr., and R. M. Hanes, *J. Am. Chem. Soc.*, **98**, 5402 (1976).
- (5) A. J. Moffat, *J. Catal.*, **18**, 193 (1970); **19**, 322 (1970).
- (6) C. U. Pittman, Jr., S. K. Wu, and S. E. Jacobson, *J. Catal.*, **44**, 87 (1976).
- (7) For example, chiral ligands have been synthesized for use in hydrogenation and hydrosilylation of olefins⁸ and reduction of ketones.⁹ Other chelating ligands have been reported for the selective chelation of certain metal ions¹⁰ and polymer-bound crown ethers have been prepared.¹¹ An example involving phenanthroline linked to the polymer via a sulfamide residue has also appeared.¹²
- (8) W. Dumont, J. C. Poulin, T. P. Dang, and H. B. Kagan, *J. Am. Chem. Soc.*, **95**, 8295 (1973).
- (9) N. Takaishi, H. Imai, C. A. Bertelo, and J. K. Stille, *J. Am. Chem. Soc.*, **98**, 5400 (1976).
- (10) L. R. Melby, *J. Am. Chem. Soc.*, **97**, 4044 (1975).
- (11) (a) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); (b) S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **4**, 395 (1971).
- (12) J. Rebeck, Jr., and F. Gavina, *J. Am. Chem. Soc.*, **97**, 3453 (1975).
- (13) C. U. Pittman, Jr., A. Hirao, R. Hanes, Q. Ng, and J. J. Yang, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **22**, 1196–1750 (1977).
- (14) (a) J. P. Collman, L. S. Hegehus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquart, *J. Am. Chem. Soc.*, **94**, 1789 (1972); (b) E. S. Chandrasekaran, R. H. Grubbs, and C. H. Brubaker, Jr., *J. Organomet. Chem.*, **120**, 49 (1976).
- (15) Sadtler Research Laboratories, Inc., "Standard Grating Spectra", 1967, spectrum 8616K.
- (16) Samples of the same batch of polymer were submitted to two micro-analytical laboratories (Spang and Midwest) for duplicate elemental analysis. The following range of data was received: C, 83.65–84.20; H, 6.81–6.99; N, 2.15–2.49. These data suggest there is one bipyridyl residue per 1120–1280 mass units. This same batch of polymer was used to determine the data in Table II. In ethyl acetate 1.2 mequiv of Fe/g of polymer binding was observed. These data require at least one bipyridyl group for each 830 mass units. In another example, a sample of polymer and its palladium acetate complex were submitted to Midwest Microlabs for elemental analysis. The results for the polymer (and its palladium complex) were the following: C, 89.82 (76.77); H, 7.40 (6.22); N, 1.25 (1.28). Note that the palladium acetate complex analyzed for more nitrogen than the original polymer!
- (17) R. F. Knott and J. G. Breckenridge, *Can. J. Chem.*, **32**, 512 (1954).
- (18) H. Javaheripour, Ph.D. Thesis, University of Toledo, 1976.
- (19) We thank the reviewers for calling the latter explanation to our attention.
- (20) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).
- (21) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley, New York, N.Y., 1972, pp 650–652.
- (22) R. H. Grubbs and L. C. Kroll, *J. Am. Chem. Soc.*, **93**, 3062 (1971).
- (23) L. Ebersson and L. Jonsson, *J. Chem. Soc., Chem. Commun.*, 885 (1974).
- (24) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).
- (25) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).
- (26) C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Q. Rev., Chem. Soc.*, **25**, 289 (1971).