Asian Journal of Chemistry Vol. 1, No, 1 (1989), 1–6

Polystyrene Functionalized with Sulfoxide Groups as a Macromolecular Ligand for Iridium(III) and Palladium(II)

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In the present work the preparation and characterization of coordination complexes of iridium(III) and palladium(II) with some polymeric sulfoxides have been described. The experimental data shows that polymeric sulfoxide is capable of coordinating hard metal ions through O-bonding of macromolecular sulfoxide groups. The complex of iridium (III) system has utility in hydrogen transfer catalysis but palladium(II) system does not effectively catalyze acetylene cyclotrimerization, apparently because of steric inhibition.

INTRODUCTION

In a recent series of papers we have described the preparation[1], spectroscopy[2], and thermal chemistry[3] of a variety of functionalized polystyrenes bearing pendant, sulfur-containing Lewis base groups capable of ligating transition metal ions. Interest in this area of chemistry stems from the extensive coordination chemistry of sulfur donor ligands such as thioethers[4] and sulfoxides[5], where applications in catalysis may benefit from studies of polymer-supported systems[6]. Following our reported work on the preparation[1] and characterization[2] of platinum(II) complexes of polystyrenes bearing pendant benzyl ethyl sulfide and benzyl ethyl sulfoxide functional groups, we here describe the coordination chemistry of iridium (III) and palladium(II) with the macromolecular sulfoxide ligand and report our initial investigations of catalytic experiments.

RESULTS AND DISCUSSION

A complete description of the synthesis[1] and characterization[1,2] of the sulfoxide-functionalized polystyrene, **1**, used in this study has been reported previously. To summarize, biological grade linear polystyrene was chloromethylated under conditions designed to minimize crosslinking, yielding an 85% chloromethylated product (Found: 20.5% Cl; Calc. for 85% chloromethylation: 20.6%). This material was treated with the sodium salt of ethanethiol causing almost quantitative replacement of chloride (Found: 10.1% S; $\leqslant$0.4% Cl) and generating the thioether linkage. Oxidation with m-chloroperoxybenzoic acid produced the sulfoxide, **1**,

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which has been characterized by IR ν(SO) = 1018, 1048 cm^{-1}), nmr, and other methods[1-3].

The polymeric sulfoxide, **1**, was reacted with iridium(III) chloride in hot isopropanol and the reaction progress monitored at time intervals by IR-spectroscopy. After 2 hrs., no change in the ν(SO) region of the IR spectrum was observed. After 26 hrs., the IR spectrum of the polymer showed that free sulfoxide groups were still present (ν(SO) = 1019, 1048 cm^{-1}) but new bands had appeared at 1154 cm^{-1} and 1119 cm^{-1}, indicating coordination of iridium via the sulfoxide sulfur. No evidence for oxygen-bonding of the sulfoxide groups was found in the spectrum. Interestingly a new band was observed at 2204 cm^{-1}, indicative of the formation of an iridium hydride. Further monitoring after 75 hrs. showed a slight increase in intensity of the bands due to coordinated sulfoxide groups and also an increase in intensity of the iridium-hydride band. After a total reaction time of 200 hrs., the IR spectrum showed no further change in intensity for the free and coordinated sulfoxide groups, but clearly showed an increase in intensity of the iridium-hydride band.

These observations allow a qualitative description of the reaction of **1** with iridium(III) chloride to be proposed. Thus, considering the related chemistry of dimethyl sulfoxide (DMSO) with iridium(III), we find a wide array of known[7] structural types including *cis*- and *trans*-$[Ir(S\text{-}DMSO)_2Cl_4^-]$; $[Ir(S\text{-}DMSO)_3Cl_3]$, *mer*-$[Ir(S\text{-}DMSO)_2(O\text{-}DMSO)Cl_3]$, $[Ir(S\text{-}DMSO)_3Cl_2H]$, and $[Ir(S\text{-}DMSO)_3ClH_2]$. Our data allow us to assign structures for the immobilized iridium complexes that involve S-bonding of sulfoxide groups with no O-bonding, and the presence of Ir-H groups. The immobilized complexes thus appear to be of the form $[Ir(S\text{-}DMSO)_x(H)_y(Cl)_z]$ (where $x + y + z = 6$).

The reaction of the polymeric sulfoxide, **1**, with sodium tetrachloropalladate for 24 hrs. in a mixed chloroform/methanol medium produced a yellow polymeric material. The IR spectrum of this material showed the presence of unreacted sulfoxide groups (ν(SO) = 1047, 1019 cm^{-1}) and new bands due to both S-bonded sulfoxide groups (ν(SO) = 1158, 1124 cm^{-1}) and O-bonded sulfoxide groups (ν(SO) = 932 cm^{-1}). The observation of a new band at 932 cm^{-1} indicative of O-bonding was entirely unexpected since the complex *trans*-$[PdCl_2(BzS\{O\}Et)_2]$ contains two S-bonded sulfoxide ligands. We interpret this observation as an indication that more than one type of immobilized complex may be present (e.g., S,S-; S,O-; O,O-isomers), perhaps resulting from the special spatial requirements imposed by the macromolecular ligand.

The polymer-supported iridium complex has been examined as a potential catalyst for hydrogen transfer from acyclic secondary alcohols to cyclic ketones and compared with the related homogeneous catalyst[7], $[Ir(S\text{-}DMSO)_2(O\text{-}DMSO)Cl_3]$. In hydrogen transfer from isopropanol to cyclohexanone, producing acetone and cyclohexanol, the homogeneous

catalyst gave a turnover of 7.2 moles of substrate consumed per mole of catalyst per hour during the first 90 hrs. of a 140 hr. experiment. During the last 50 hrs. the turnover number decreased as the substrate approached complete consumption. Addition of further substrate led to renewed catalysis at a slightly reduced turnover of 4 mol/mol/hr. Reaction conditions are described in the Experimental Section. With the polymer supported iridium complex, under comparable conditions, we find a rate decrease in the hydrogen transfer reaction of about one order of magnitude, with a maximum observed turnover of 0.7 moles of substrate consumed per mole of catalyst per hour. We also noted some variation in rate between sequential experiments using fresh portions of catalyst which was not observed for the homogeneous system. While the rate decrease was entirely expected since polar solvents tend to collapse polystyrene matrices, denying substrate access to the metal sites, the rate variation between experiments is an inconsistency that we are unable to explain.

Since palladium(II) compounds are known[8] to catalyze the cyclotrimerization of diphenylacetylene to hexaphenylbenzene, we have examined the polymeric palladium(II) sulfoxide complex as a potential catalyst and compared it with the homogeneous analogs $[PdCl_2L_2]$ (where L= BzS{O}Me or BzS{O}Et. In each experiment, 0.08 mol of diphenylacetylene and 0.0025 mol of metal complex were taken in CD_2Cl_2 and monitored by ^1H nmr spectroscopy. Yields of hexaphenylbenzene were estimated by integration and are presented in Table 1. The palladium (II) complex of BzS{O}Me was found to be most active, effecting a 26% conversion over 298 hrs. The complex of BzS{O}Et, a marginally bulkier ligand, was found to be about half as active when compared after 48 hrs. The complex of the massive polymeric ligand, **1**, displayed almost no activity, with only a trace (~2% conversion) of hexaphenylbenzene formed after 720 hrs. It seems likely, therefore, that this reaction is sensitive to steric effects and that the design of suitable polymer supported catalysts may be problematic.

Conclusions

The macromolecular sulfoxide ligand, **1**, coordinates iridium(III) and palladium(II). The iridium(III) system has utility in hydrogen transfer catalysis, operating at rates about one order of magnitude lower than analogous homogeneous catalysts. The supported palladium(II) system does not effectively catalyze acetylene cyclotrimerization, apparently because of steric inhibition.

Preliminary experiments indicate that the polymeric sulfoxide, **1**, is also capable of coordinating hard metal ions (e.g. copper (II), see Experimental Section) through O-bonding of the sulfoxide groups. Future experiments will focus on the utilization of **1** as a medium for selective separation of metal ions through competitive binding.

EXPERIMENTAL

^1H nmr spectra were obtained for $CDCl_3$ solutions (or solvent swollen gels of polymer samples) at 89.56 MHz on a JEOL FX90Q nmr spectrometer operating in the Fourier transform mode. Chemical shifts are relative to internal TMS with more positive values of the chemical shift representing deshielding.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained using a Nicolet 5DX FTIR spectrometer equipped with a 64K × 20 bit high speed data processor, a DTGS room temperature pyroelectric bolometer with KBr window, a Harrick "preying mantis" diffuse reflectance accessory and a Zeta 8 printer/plotter. The spectrometer has f5 optics and the spectra were recorded with a resolution of 4 cm^{-1} over the spectrometer range, 4600–400 cm^{-1}, at a maximum gain setting. Happ-Ganzel apodization was applied.

The samples for DRIFT analysis were prepared by dilution with dried potassium bromide (*ca* 1 : 20) and the spectra were obtained for solid solutions by ratioing against a potassium bromide background using a dry nitrogen or dry air purge system.

A Hewlett Packard 5720A gas chromatograph and a Variant Aerograph model 90-P gas chromatograph, both fitted with columns packed with 10% Carbowax 20M adsorbed on chromosorb, were used for chromatographic analyses.

Preparation of Ir(III) Complex of Polymeric Sulfoxide

The polymeric sulfoxide (0.102 g) and iridium(III) chloride (0.050 g, 0.14 mmol) in isopropanol (25 ml) were refluxed with stirring for up to 200 hrs. (see results and discussion). The polymer was precipitated with hexane, filtered off, washed with hexane, dried and its IR spectrum was recorded. IR after 200 hrs.: ν(S=O) = 1157, 1119, 1049, 1020 cm^{-1}; ν(Ir-H) = 2202 cm^{-1}.

Preparation of Pd(II) Complex of Polymeric Sulfoxide

To a solution of the polymeric sulfoxide (0.044 g) in chloroform (25 ml) was added sodium tetrachloropalladate(II) (0.925 g, 0.085 mmol) in methanol (5 ml). Immediately after addition a yellow solid separated out from the solution. The reaction mixture was stirred at room temperature for 24 hrs. The polymer was filtered off, washed with water, methanol and dried under vacuum. IR : ν(S=O) = 1158, 1124, 1047, 1019 and 932 cm^{-1}.

Preparation of Cu(II) Complex of Polymeric Sulfoxide

The polymeric sulfoxide (0.098 g) and copper(II) chloride (0.070 g, 0.41 mmol) in chloroform were refluxed with stirring for 1 hr. The solid

was precipitated with hexane from the decanted solution, filtered off, washed with hexane and dried under vacuum. IR : ν(S=O) = 942 cm^{-1}.

Preparation of (S,S,O)-[$IrCl_3(DMSO)_3$]

Iridium(III) chloride (0.10 g, 0.283 mmol) and DMSO (0.066 g, 0.85 mmol) in isopropanol (5 ml) were refluxed with stirring for 1 hr. The product was precipitated with hexane, filtered, washed with hexane, air dried and recrystallized from methanol. ^1H nmr : δ 3.54 ppm (*S*-DMSO), 2.34 ppm (*O*-DMSO) in the ratio 2 : 1. IR : ν(S=O) = 1142 cm^{-1} (S-coordinated), 985 cm^{-1} (*O*-coordinated).

Preparation of [$PdCl_2L_2$] (L = Benzyl methyl sulfoxide, benzyl ethyl sulfoxide).

To a solution of sodium tetrachloropalladate(II) (0.147 g, 0.5 mmol) in water (1 ml) was added the ligand, L (1.0 mmol), and the mixture was stirred at room temperature for 24 hrs. The solid precipitate was filtered, washed with water and dried under vacuum. The complexes were characterized by DRIFT spectroscopy: [$PdCl_2(BzS\{O\}Me)_2$] : IR ν(S=O) = 1110, 1154 cm^{-1}; [$PdCl_2(BzS\{O\}Et)_2$] : IR ν(S=O) = 1125, 1257 cm^{-1}.

Reduction of Cyclohexanone by Homogeneous Complexes

A solution of cyclohexanone (2.45 g, 25 mmol), dimethyl sulfoxide (2 drops) and (S,S,O)-trichlorotris(dimethyl sulfoxide) iridium(III) (0.030 g, 0.056 mmol) in isopropanol (25 ml) containing extra water (0.5 ml) was heated under reflux. The solution remained clear and after 140 hrs. the ketone was completely reduced to cyclohexanol as determined by gas chromatography. Twice more cyclohexanone (2.45 g, 25 mmol) was added to this reaction mixture. Both times the reduction was complete within 146 hrs.

Reduction of Cyclohexanone by Supported Complex

A solution of cyclohexanone (2.45 g, 25 mmol), polymeric sulfoxide, **1**, (0.015 g) and the Ir(III) complex of the polymeric sulfoxide (0.050 g, 0.056 mmol) in isopropanol (25 ml) containing extra water (0.5 ml) was heated under reflux. After 295 hrs. the yield of cyclohexanol was 46%. In the absence of uncomplexed polymeric sulfoxide the conversation after 295 hrs. was 18% and in absence of both polymeric sulfoxide and the Ir(III) complex, no formation of cyclohexanol was detected by gas chromatography after 295 hrs.

Oligomerization of Diphenylacetylene

Diphenylacetylene (0.08 mmol) and the appropriate palladium complex (0.0025 mmol) in deuterated dichloromethane were taken in an nmr tube and the progress of the reaction was monitored by ^1H nmr spectroscopy. The results are given in Table 1.

TABLE 1

CYCLOTRIMERIZATION OF DIPHENYLACETYLENE USING PALLADIUM(II) SULFOXIDE COMPLEXES AS CATALYSTS

Time/hrs	% Conversion of diphenylacetylene[a] ligand		
	BzS{O}Me	BzS{O}Et	Polymer I
4.75	—	9	0
9.5	16	—	—
24	20	10	0
48	21	10	—
168	25	—	—
298	26	—	—
720	—	—	2

[a]See Experimental Section for reaction conditions.

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[Invited Article. *Received* : 20 October, 1988]