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Polymeric cofactors which accelerate homogeneous rhodium(I) and ruthenium(II) catalyzed hydrogenations of alkenes

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Polymeric reagents prepared by exchanging silver(I) for H^+ on a macroreticular polystyrene sulfonate ion exchange resin are shown to be capable of selectively absorbing triphenylphosphine from solutions of triphenylphosphine complexes of rhodium(I) and ruthenium(II). Absorption of triphenylphosphine during alkene hydrogenations catalyzed by $RhCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ led to increased hydrogenation rates in hydrogenation of 1-hexene and other alkenes. Addition of this silver(I) polystyrene sulfonate to alkene hydrogenations catalyzed by $HRh(CO)(PPh_3)_3$, $RuH_2(PPh_3)_3$ and $RuH(OCOCH_3)(PPh_3)_3$ also led to modest rate accelerations. Catalyst activations seen in these alkene hydrogenations were shown to be due in some cases to triphenylphosphine absorption. In other cases, HCl or HCl plus triphenylphosphine absorption was responsible for the formation of a more active catalyst solution.

Keywords: Hydrogenation, catalysis, alkenes, rhodium, ruthenium, polymeric reagents

INTRODUCTION

Insoluble organic polymers have been used increasingly in recent years either to support homogeneous catalysts or as reagents in organic synthesis.[1-3] Such uses of insoluble polymers in catalytic reactions are usually based on the desire to achieve experimental advantages over conventional homogeneous systems. Easier product isolation, catalyst recovery, different reaction rates and different substrate selectivities have been cited as advantages of using insoluble polymers as ligands to bind homogeneous catalysts. These differences between a polymer-bound catalyst and its homogeneous counterpart are mainly due to the polymer bound catalyst's insolubility during and at the end of the reaction. In some cases, the decreased accessibility of such polymer-bound catalysts or reagents is responsible for altered substrate selectivity.[4,5] For example, the diffusional limitations encountered in use of solid polymeric reagents and catalysts has been shown to result in size dependent selectivity and enhanced reaction rates for smaller substrates. This paper describes our efforts to use this diminished accessibility of polymeric reagents as a way to activate homogeneous catalysts. Specifically, we have used soft acid and Bronsted base-containing polymers to selectively remove inhibitors or poisons from homogeneous catalytic reactions in situ. The utility of this strategy has been demonstrated in alkene hydrogenation reactions using rhodium and ruthenium triphenylphosphine ligated catalysts.

In many homogeneous transition metal catalytic systems the most active form of the catalyst results from dissociation of a ligand in an unfavorable equilibrium reaction like Eqn 1. Active catalysts are also often generated by oxidative addition of H_2 followed by reductive elimination of HX (Eqn 2).

$$ML_{n-1} \rightleftharpoons ML_{n-1} + L \qquad [1]$$

$$MX + H_2 \rightleftharpoons MH_2X \rightleftharpoons MH + XH \qquad [2]$$

$$(X = \text{halide, alkyl, aryl})$$

Decreasing the concentration of either the ligand L or HX in either of these equilibria increases the concentration of the active catalyst species ML_{n-1} or MH according to Le Chatelier's prin-

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ciple. Thus, it is possible to obtain increased hydrogenation rates if L or HX is removed in situ from solutions of transition metal catalysts. The common procedure of adding a base to produce a metal hydride catalyst exemplifies this idea. Here we describe the use of some common ion-exchange polymers to absorb PPh_3, HCl or both HCl and PPh_3 from a catalytic system. As a result of the diffusional limitations imposed on these absorption reactions by the resin matrix, the absorption phenomena is selective for the smaller products of equilibria 1 and 2. Absorption of the larger rhodium or ruthenium complex is less facile. As a result of shifting equilibria like 1 and 2, these polymeric reagents accelerate alkene hydrogenations using homogeneous catalysts such as $RhCl(PPh_3)_3$, $RuHCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, $HRh(CO)(PPh_3)_3$, $RuH_2(PPh_3)_3$ and $RuH(OCOCH_3)(PPh_3)_3$.

Other attempts to shift equilibria 1 and 2 have been made. One of the reasons $RhCl(PPh_3)_3$ was first supported on a polymer was in the hope of shifting equilibrium 1.[6] Several methods for removal of triorganophosphines from solution have also been tried. For example, reverse osmosis was used by Knoth, Gosser and Parshall to separate PPh_3 and other low molecular weight compounds from transition metal catalysts.[7] The selective reaction of dissociated PPh_3 with a Lewis acid would also consume PPh_3 and shift Eqn 1 to the right.[8,9] However, side reactions such as halide exchange or metal hydride formation limit the utility of this approach. Our procedure, which has been described in a preliminary report,[10] combines features of both of these approaches using insoluble porous functionalized polystyrene derivatives.

RESULTS AND DISCUSSION

We have prepared Lewis acid-containing polymers which selectively absorb PPh_3 in the presence of a homogeneous transition metal catalyst. This selectivity is a result of the diffusional limitations inherent in these cross-linked polymeric reagents which discriminate in favor of the smaller PPh_3 molecules.[4] In addition, the polymeric reagents we have designed meet several important criteria. Specifically, the polymers are not catalytically active themselves, nor do they interact too rapidly with the active catalyst. Further, these polymeric reagents are easily prepared, easily handled, and are air stable.

Table 1 Absorption of triphenylphosphine by metal-containing polystyrene sulfonate (macroreticular ion-exchange resin)[a]

Metal ion	Triphenylphosphine absorbed (mg)
Co^{3+}	0
Co^{2+}	10 (90)[e]
Ni^{2+}[b]	10
Cu^{2+}[b]	34 (104)[e]
Cu^{+}[c]	5
Ag^{+}[d]	104[f]
Na^{+}	0
$H_2NMe_2^{+}$	0
H^{+}	105[f]

[a] Absorption of PPh_3 by 1 g of resin from 10 cm^3 of a 0.04 mol dm^{-3} solution of PPh_3 in THF measured either by ^1H NMR spectroscopy using *p*-xylene as an internal standard or by GC on a fused silica capillary column using *n*-eicosane as an internal standard. [b] This resin also absorbed tri-*n*-butylphosphine from a benzene solution. [c] The copper(I) polystyrene sulfonate was present as the amine complex. [d] The extent of PPh_3 absorption varied with solvent and was highest in polar solvents like ethanol. [e] The value for absorption of PPh_3 using anhydrous copper(II) polystyrene sulfonate is shown in parentheses. [f] This resin absorbed 60 mg of PPh_3 within 15 min.

Polymeric reagents with these characteristics were successfully prepared from Amberlyst 15, a commercially available ion exchange resin. This sulfonated cross-linked polystyrene ($PS\text{-}SO_3H$) is a macroreticular resin designed for use in organic solvents and has a pore size of ca. 250 Å. Functionalization of $PS\text{-}SO_3H$ with metal ions was performed by conventional ion exchange techniques, and the efficacy of the resulting polymers for PPh_3 absorption is shown in Table 1. Several metal salts absorbed PPh_3. Among the most effective were copper(II)-exchanged $PS\text{-}SO_3H$ ($(PS\text{-}SO_3)_2Cu$) and silver(I)-exchanged $PS\text{-}SO_3H$ ($PS\text{-}SO_3Ag$). An increase in the phosphine-absorbing capacity of these polymeric metal sulfonates was noted in some cases when the salts were strictly anhydrous. This was especially true with $(PS\text{-}SO_3)_2Cu$ and $(PS\text{-}SO_3)_2Co$. The anhydrous Cu(II) and Co(II) sulfonates were both about as effective as the Ag(I) salt in absorption of PPh_3 over a 12 h period. However, the rate of PPh_3 absorption by $PS\text{-}SO_3Ag$ measured during the first 900 s was the greatest and this salt was consequently used in studies with catalyst systems. $(PS\text{-}SO_3)_2Cu$ was also briefly studied but was less effective (vide infra).

Control experiments showed that unfunctionalized macroporous polystyrene (PS-H) polystyrene sodium sulfonate ($PS\text{-}SO_3Na$) and dimethylammonium polystyrene sulfonate ($PS\text{-}SO_3H_2NMe_2^+$) did not absorb PPh_3. The polymer $PS\text{-}SO_3H$ also absorbed PPh_3.[11] All of these sulfonate derivatives of polystyrene absorb HCl from a toluene solution of HCl.

Having prepared the desired type of functionalized polymer, we next set out to use it to accelerate catalytic reactions. Unfortunately, no rate differences were seen in hydrogenations of the alkenes 1-octene, 1-hexene, cyclohexene, styrene and ethylacrylate using as catalysts $RhCl(PPh_3)_3$ only, versus either $RhCl(PPh_3)_3$ and $PS\text{-}SO_3^-H_2NMe_2^+$ or $RhCl(PPh_3)_3$ and $PS\text{-}SO_3Ag$. However, we were able to show that PPh_3 which had been added as an inhibitor was removed under conditions of an alkene hydrogenation. The final hydrogenation rate achieved was comparable to the rate observed in the absence of any added PPh_3.[10]

These effects are shown graphically in Fig. 1 for the case of styrene. In this figure, styrene hydrogenation in the absence of any added cofactor is shown to be the same as that of styrene in the presence of $PS\text{-}SO_3Ag$. While using $p\text{-}CH_3C_6H_4SO_3Ag$ similarly restores the rate of a PPh_3-poisoned styrene hydrogenation, the catalytic reaction eventually decreases in rate. When attempts were made to use the soluble $p\text{-}CH_3C_6H_4SO_3Ag$ in hydrogenations in the absence of added PPh_3, decreased hydrogenation rates were seen with hydrogen uptake eventually stopping completely. Premixed equimolar amounts of $p\text{-}CH_3C_6H_4SO_3Ag$ and $ClRh(PPh_3)_3$ also produced solutions that had no hydrogenation catalyst activity. This deactivation of the

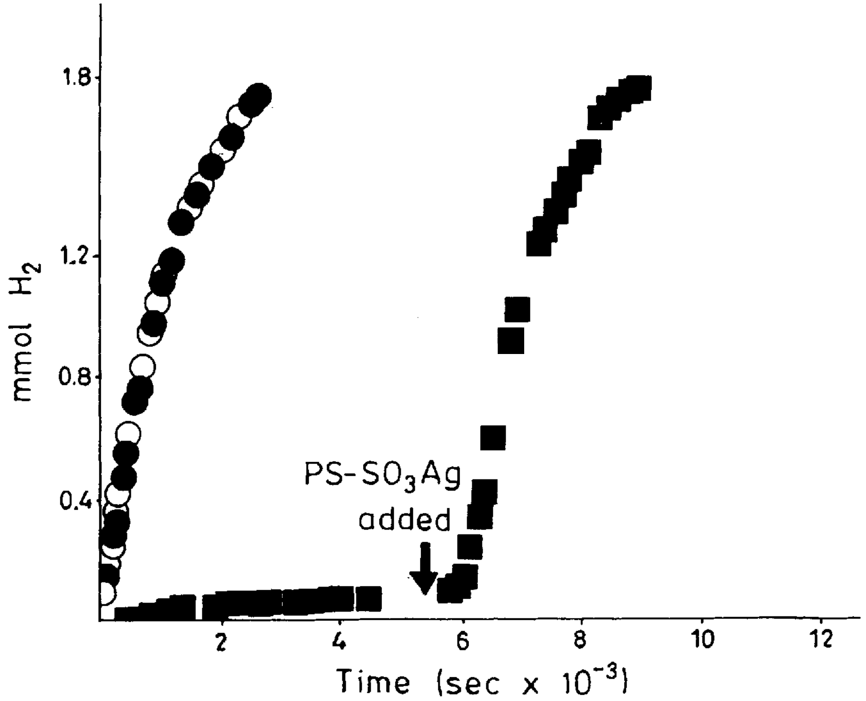

Figure 1 Hydrogenation of styrene (0.11 M) catalyzed by 2.3×10^{-3} M $RhCl(PPh_3)_3$ in toluene at 25°C: (a) in the absence of any cofactor (○); (b) in the presence of $PS\text{-}SO_3Ag$ (●); (c) in the presence of excess PPh_3 (1.6×10^{-2} M) with $PS\text{-}SO_3Ag$ added at 5400 s (■).

rhodium catalyst by a soluble silver species is reminiscent of that seen by Shriver using soluble Lewis acids and demonstrates the importance of using a polymeric cofactor.

The polymeric reagent PS-SO_3Ag clearly removes PPh_3 from organic solutions as shown by the above experiments where excess PPh_3 was selectively absorbed by the silver sulfonate resin without absorption of the rhodium complex. The presence of PPh_3 on the polymer was subsequently verified by analysis of an acidified methanol extraction of the polymer PS-SO_3Ag.[10] We presume that the lack of catalyst activation seen in the above reactions apparently resulted from the inability of PS-SO_3Ag to compete with the other species in solution for free PPh_3 during a $RhCl(PPh_3)_3$ catalyzed hydrogenation.

As described previously,[10] we found that addition of ethylene as a temporary ligand in the presence of PS-SO_3Ag was a successful strategy for inducing phosphine loss from a rhodium complex under conditions where absorption of PPh_3 by PS-SO_3Ag could occur. Rate accelerations of 196%, 135% and 580% were observed under such conditions for 1-hexene, cyclohexene and ethylene hydrogenations when the catalyst and substrate were treated with ethylene in the presence of PS-SO_3Ag for 900 s prior to removal of ethylene and addition of H_2. Rate accelerations in 1-hexene hydrogenations were also seen when $(PS\text{-}SO_3)_2Cu$ was used in place of PS-SO_3Ag in this ethylene pretreatment scheme. However, only an 11% increase in hydrogenation rate was seen. Since this metal sulfonate was less reactive kinetically at PPh_3 absorption, we did not further study it as a substitute for PS-SO_3Ag. In order to demonstrate that PPh_3 absorption was important in these ethylene pretreatment experiments, control experiments using HCl absorbers PS-$SO_3^-H_2N(CH_3)_2^+$, neutral alumina or KOH were performed. These experiments with HCl absorbers as cofactors did not lead to similar activations even when this ethylene pretreatment was performed, suggesting that HCl absorption (and shifting of equilibrium 2) was not the reason for catalyst activation. We also reported that addition of PS-SO_3Ag accelerated hydrogenation rates of norbornene by 3.7-fold and hydrogenation of norbornadiene by 550-fold. However, rate accelerations of these hydrogenations of 1.8-fold and 550-fold were also seen when PS-SO_3Na, PS-$SO_3^-H_2(CH_3)_2^+$ or neutral alumina were added as cofactors. HCl and PPh_3 absorption were both postulated as being important in activations of norbornene and norbornadiene hydrogenations.[10]

As mentioned above, soluble Lewis acids like p-$CH_3C_6H_4SO_3Ag$ were not useful as cofactors because they can easily react with the soluble rhodium complex. While studies of the simple reaction between $RhCl(PPh_3)_3$ and PS-SO_3Ag or PPh_3 and PS-SO_3Ag showed the absorption of the smaller PPh_3 was ca. 20-fold faster, absorption of the rhodium complex during hydrogenation experiments did occur after ca. 24 h. This slow reaction precluded the use of reactions with longer contact times between the polymeric cofactor and the homogeneous catalyst.

In order to further explore the potential of these polymeric metal salts as catalyst cofactors and to better understand the relationship between PPh_3 and HCl absorption as the cause of the observed catalyst activations of transition metal complexes, we turned our attention to hydrogenations catalyzed by $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$. The reactions between these complexes and various polystyrene sulfonic acid derivatives were also studied by ^{31}P NMR spectroscopy.

$RuCl_2(PPh_3)_3$ is not a good hydrogenation catalyst in the absence of added cofactors.[12] Hydrogen uptake occurs at a rate of about 4×10^{-4} mmol of $H_2\,sec^{-1}$. However, if PS-SO_3Ag, PS-SO_3H, PS-SO_3Na, PS-$CH_2N(CH_3)_3^+OH^-$ or neutral alumina were added to this solution, the solution gradually turned red and hydrogen uptake increased by as much as a factor of 11. It is known that addition of bases to $RuCl_2(PPh_3)_3$ forms $RuHCl(PPh_3)_3$ according to equilibrium 2.[13] This undoubtedly is part of the reason for the observed catalyst activation seen in the presence of alumina and these insoluble polystyrene sulfonic acid derivatives. However, experiments using PS-SO_3Ag and PS-SO_3Na or PS-SO_3H suggested that HCl and PPh_3 absorbtion were important in the former case. First, the activation seen using PS-SO_3Ag was greater than that seen using PS-SO_3Na or PS-SO_3H. Second, in hydrogenations using PS-SO_3Ag about three times as much isomerization of 1-hexene to 2-hexene occurred. $RuHCl(PPh_3)_3$ is a selective catalyst for hydrogenation of terminal olefins, plausibly because of the steric hindrance for coordination from the three phosphine ligands. It is reasonable that removal of phosphine might increase the isomerization ability of this catalyst. Finally, cyclohexene was hydrogenated nine times faster upon addition of PS-SO_3Ag and five times faster when PS-SO_3Na/PS-SO_3H was added. While these hydrogenations of cyclohexene are still slow, they are in agreement with the notion that $RuCl_2(PPh_3)_3$ formed $RuHCl(PPh_3)_3$ and $RuHCl(PPh_3)_2$ through a combination of HCl and phosphine absorption.

Since $RuHCl(PPh_3)_3$ was presumed to be the active catalyst in the above experiments, we briefly examined the effect of PS-SO_3Ag on 1-hexene hydrogenations using preformed $RuHCl(PPh_3)_3$. In these experiments, the PS-SO_3Ag was added to an ongoing 1-hexene hydrogenation. A small increase in hydrogenation rate from 6.6×10^{-2} to 11.6×10^{-2} mmol of H_2 s^{-1} mol^{-1} of catalyst was seen. This further corroborates the interpretation of the $RuCl_2(PPh_3)_3$ plus PS-SO_3Ag experiments described above, suggesting that PPh_3 absorption is indeed partly responsible for the observed catalyst activations seen using these ruthenium complexes and PS-SO_3Ag.

Spectroscopic evidence from ^{31}P NMR spectroscopy provided additional information about the interactions of $RuCl_2(PPh_3)_3$, PPh_3 and PS-SO_3Ag. After a 0.04 mol dm^{-3} $CDCl_3/CH_2Cl_2$ solution of $RuCl_2(PPh_3)_3$ and PPh_3 had been in contact with PS-SO_3Ag for 2 h, the peaks due to $RuCl_2(PPh_3)_3$ and PPh_3 at δ 42.3, 23.3 and -8.3 were gone. Instead, ^{31}P NMR spectroscopy of the resulting solution at -80°C contained a pair of doublets at δ 58.0 and 51.7 ($J_{P\text{-}P} = 42$ Hz) due to $[RuCl_2(PPh_3)_2]_2$.[14] A sharp singlet was also seen at δ 44.7. The latter singlet was tentatively assigned to $RuCl_2(PPh_3)_2$. Some $OPPh_3$ was also present in both spectra as an impurity. ^{31}P NMR spectroscopy of 0.008 mol dm^{-3} toluene solutions of $RuCl_2(PPh_3)_3$ in the presence of PS-SO_3Ag under a hydrogen atmosphere confirmed the postulated formation of $RuHCl(PPh_3)_3$ (δ 94.7, *t*, $J_{P\text{-}P} = 29$ Hz; δ 38.5, *d*, $J_{P\text{-}P} = 29$ Hz)[14] as the major ruthenium species present. The absence of a peak at $\delta -8$ indicates that PPh_3 was not present. A sharp singlet was seen at δ 46 and small peaks were also seen for $[RuCl_2(PPh_3)_2]_2$. Stirring this solution of ruthenium catalyst over PS-SO_3Ag for 12 h under H_2 did not lead to any diminution in the intensity of the phosphine signals of the presumed Ru-phosphine complexes. This suggested that absorption of the metal complex by the sulfonate resin was less of a problem in the Ru examples than in the Rh case discussed above. However, while most of the Ru-phosphine species remained in solution, the relative amounts of the various species changed appreciably. After this period of stirring, the peak at δ 46 was the major species present. Adventious oxidation of PPh_3 had evidently occurred to a minor extent and two small pairs of doublets were also seen at δ 15 and 6 and δ 12.2 and 3.6. These latter peaks might be due to dimers of $RuHCl(PPh_3)_2$. Taken together, these kinetic observations and observed changes in the ^{31}P NMR spectra suggest that addition of PS-SO_3Ag to alkene hydrogenations catalyzed by these ruthenium complexes are due to shifting both equilibria 1 and 2 by absorption of PPh_3 and HCl to form catalytically more active complexes.

Since some increases in catalytic activity for alkene hydrogenations were observed using PS-SO_3Ag and either $ClRh(PPh_3)_3$, $RuCl_2(PPh_3)_3$ or $RuHCl(PPh_3)_3$, we briefly surveyed the hydrogenation of 1-hexene by transition metal phosphine catalysts. None of these catalysts were extensively studied. Nonetheless, small activations in rate were noted in several cases listed in Table 2.

Table 2 Activations of alkene hydrogenations catalyzed by various metal phosphine complexes using silver(I) polystyrene sulfonate as a cofactor.[a]

Metal phosphine complex[b]	Alkene	Relative rate[c]
$RuH_2(PPh_3)_3$	1-Hexene	1.4
$RuH_2(PPh_3)_3$	Styrene	1.1
$RuH(OCOCH_3)(PPh_3)_3$	1-Hexene	1.4[d] (1.0)
$RuH(OCOCH_3)(PPh_3)_3$	Styrene	1.6
$HRh(CO)(PPh_3)_3$	Styrene	1.4[e]
$HRh(CO)(PPh_3)_3$	1-Hexene	1.0
$IrCl(CO)(PPh_3)_2$	Styrene	1.0

[a] Hydrogenations were carried out using Method 1 as described in the Experimental Section. [b] Typical catalyst concentrations were in the range of $2\text{–}8 \times 10^{-3}$ M and alkenes were typically 0.4–0.8 M. [c] The relative initial rates for a hydrogenation carried out in the presence of PS-SO_3Ag and in the absence of any cofactor using toluene as a solvent unless otherwise specified. [d] Higher catalytic activity was only seen in THF solution. [e] The extent of activation decreased as the catalyst concentration was decreased to less than 1×10^{-3} M until no detectable activation was seen.

EXPERIMENTAL SECTION

General methods

All solutions of air-sensitive catalysts were handled under nitrogen, argon, hydrogen or ethylene using standard Schlenk techniques.[15] Gases were used without further purification.

Toluene, diethyl ether, tetrahydrofuran, and pentane were freshly distilled under nitrogen from disodium benzophenone. Ethanol and methanol were purged with a strong flow of nitrogen for 1 h. 1-Hexene, 1-octene, cyclohexene, styrene, and norbornadiene were passed through neutral alumina to remove stabilizers and peroxides, carefully degassed, and then purged with nitrogen for 1/2 h. $RhCl(PPh_3)_3$ and $RhCl_3 . nH_2O$ were obtained from Strem Chemicals and used as received. Triphenylphosphine was obtained from Aldrich Chemical Co. and used as received. Macroreticular ion exchange resin, polystyrenesulfonic acid (Amberlyst 15), was purchased from either Aldrich or Chemalog and extracted for 48 h in a Soxhlet extractor with DMF (in which case PS-$SO_3^-H_2NMe_2^+$ forms) or with ethanol before use in order to remove any surfactants present. After ion exchange, the polymers were dried under vacuum for 24 h. The water content of the ion-exchanged resins was not measured. ^1H NMR spectra were taken on a Varian T-60 and ^{31}P NMR spectra were obtained using either a Varian XL-200 spectrometer or a Varian FT-80 spectrometer with ^1H noise decoupling. The temperatures in variable temperature ^{31}P NMR experiments were determined by use of the thermocouple which is part of the Varian XL-200 spectrometer. Chemical shifts in the ^{31}P NMR experiments are reported as ppm relative to an external H_3PO_4 standard. IR spectra were obtained using a Perkin–Elmer Model 297 IR spectrometer. UV/visible spectra were obtained from a Perkin-Elmer 552 UV/visible spectrometer equipped with an x-y recorder. Gas chromatography of hexane/hexenes was carried out using a Hewlett–Packard 5830A gas chromatograph with an FID detector on a 1.5-m *n*-octane/porasil column; a Hewlett–Packard 5880A gas chromatograph with an FID detector was used for PPh_3 analysis on a 10-m SE-30 capillary column. Reactions calling for shaking used a Burrell Model 75 wrist-action shaker. Melting points were determined in a Thomas/Hoover melting point apparatus and were uncorrected. Commercial analyses were done by Galbraith Laboratories, Knoxville, TN.

Preparation of PS-SO_3Ag

PS-SO_3H (Amberlyst 15, macroreticular sulfonated polystyrene, 44 g) was slurried with water (200 cm^3) and poured into a column (400 × 25 mm) which had a glass wool plug in the bottom. The resin as either the H^+ or $H_2NMe_2^+$ form was converted to PS-SO_3Na by flowing a solution of aqueous NaOH (1 mol dm^{-3}, 500 cm^3) through the column over a period of 1 h. The column was then washed with 2 dm^3 of water until the column effluent was neutral. An aqueous solution of $AgNO_3$ (41.1 g, 0.24 mol) in 2 dm^3 of H_2O was run through the column over a period of 16 h until considerable Ag^+ breakthrough occurred as indicated by heavy formation of AgCl ppt when an aqueous NaCl solution was used to receive the column effluent. Water (4 dm^3) was run through the column over a period of 5 h until no AgCl ppt was observed in the above test. The resin was then poured from the column and filtered on a glass frit, washed with EtOH (2 × 100 cm^3) and Et_2O (2 × 100 cm^3), and then air dried for 3 h. The polymer was dried under vacuum for 24 h or until a constant weight was achieved. IR analysis indicated that the resulting resin contains an undetermined amount of water (or ethanol). Commercial analysis of several PS-SO_3Ag batches showed 2.5–3.0 mmol of Ag^+ g^{-1} of PS-SO_3Ag. The starting PS-SO_3H had 4.7 mmol of H^+ g^{-1} of polymer. The same procedures used to prepare PS-SO_3Ag were followed for the other PS-SO_3M's.

Triphenylphosphine (PPh_3) absorption by polymers

Solutions of PPh_3 in tetrahydrofuran (THF), toluene, or acetone were prepared to cover a broad concentration range (0.0002–0.17 mol dm^{-3}). These solutions were then added to 1 g of the appropriate resin suspended in 10 cm^3 of the chosen solvent and analyzed periodically by removing 0.5 cm^3 aliquots. ^1H NMR experiments used *p*-xylene as an internal standard and employed more concentrated solutions. UV experiments and GC experiments both used more dilute solutions. The amount of PPh_3 was monitored by UV at 262 nm in UV-visible spectroscopy experiments.

Studies of the interaction of PS-$SO_3^-H_2^+$, PS-SO_3Ag and polystyrene (macroreticular) with $RHCl(PPh_3)_3$ by UV/visible spectroscopy

Solutions of $RhCl(PPh_3)_3$ (0.6×10^{-3} mol dm^{-3} or 1.66×10^{-3} mol dm^{-3}) in toluene were injected (10 cm^3) into 50 cm^3 flasks containing PS-SO_3Ag, PS-$SO_3^-H_2NMe_2^+$, or macroreticular polystyrene. Each of these resins had been under vacuum for 2 h. The mixtures were shaken in a shaker; control experiments in which no polymer was present were also run. The concentration of $RhCl(PPh_3)_3$ was monitored at 417 nm over a period of 19 h. Aliquots ($3\,cm^3$) removed from this solution were transferred using a cannula through the stopcock of gas adapter into 10.0 mm quartz UV cells fitted with ground glass joints. After a spectrum was obtained the samples were returned to the reaction flasks in the same manner and shaking was resumed. Results of these experiments are compared to the PPh_3 absorption studies in the text. Typical half-lives for $RhCl(PPh_3)_3$ absorption by $PS\text{-}SO_3Ag$ were 2–8 h at $RhCl(PPh_3)_3$ concentrations of $1.76 \times 10^{-3}\,mol\,dm^{-3}$. Triphenylphosphine absorption under similar conditions had a $t_{1/2}$ of ca. 10 min.

^{31}P NMR studies of $PS\text{-}SO_3Ag$, $PS\text{-}SO_3H$ and $PS\text{-}SO_3Na$ with $RuCl_2(PPh_3)_3$

A solution ($3\,cm^3$) of $RhCl(PPh_3)_3$ ($4.3 \times 10^{-2}\,mol\,dm^{-3}$ in $CDCl_3/CH_2Cl_2$, 10/90, v/v) was stirred for 19 h at 25°C and then transferred using a syringe into a N_2-filled flask containing the polystyrene sulfonate derivative (0.5 g) which had been under vacuum for 19 h. The resulting suspensions were shaken for the desired period of time and samples for ^{31}P NMR were withdrawn.

Hydrogenations

Hydrogenations were run at $25.0 \pm 0.1°C$ in a $200\,cm^3$ 3-necked flask equipped with a solid addition tube and a gas inlet tube covered with a serum cap. A 3.5 cm egg-shaped magnetic stirbar provided vigorous mixing. No more than 10 to $15\,cm^3$ of liquid was used in each hydrogenation reaction, and the flask was tilted so that the stirbar rested at the gas/liquid interface when the stirring motor was off. Changing the rate of stirring did not change the rate of the uptake of hydrogen. A Cole–Palmer 6 × 6 model stirring motor was used in all of these hydrogenation experiments. The flask was connected to a hydrogenation apparatus consisting of a two-way stopcock to vacuum and a three-way stopcock to the H_2 source and to a $50\,cm^3$ gas buret. A leveling bulb was connected to the bottom of the buret with rubber tubing and filled with dibutyl phthalate. Constant atmospheric pressure was maintained throughout the reaction by adjusting this leveling bulb as the reaction proceeded.

In order to ascertain the effects of various cofactors, typical hydrogenations were run in the three following ways: (1) the cofactor was added at the start of (or during) a hydrogenation; (2) the cofactor was present as the catalyst dissolved under H_2 and stirred with the solution of catalyst under H_2 before the addition of alkene; or (3) procedure (2) was followed, but under an ethylene atmosphere which was removed before hydrogenation commenced.

A typical hydrogenation using procedure (1) was as follows: The catalyst (10–60 μmol) was placed in the $100\,cm^3$ 3-necked flask and the cofactor (0.2 g or as noted) was put in the solid addition tube. The apparatus was carefully assembled, evacuated and flushed with H_2 three times, and then held under vacuum for 10 min. The apparatus was flushed with H_2 and evacuated three more times, then filled with H_2 and then the solvent ($10\,cm^3$ of toluene unless otherwise noted) was added. The solution was carefully degassed and filled with H_2 three times, and then stirred vigorously under H_2 until the catalyst was fully dissolved. At this point, stirring was stopped and alkene (2–20 mmol) was injected. When the cofactor was to be added at the beginning of a hydrogenation, it was added at this point by turning the solid addition tube. Hydrogenation was initiated by resumption of stirring. Alternatively, the cofactor was added after hydrogenation had been initiated.

Hydrogenations according to method (2) were run in essentially the same manner, except that the catalyst and the cofactor were both placed in the hydrogenation vessel as the reaction was set up. The solid addition tube was not used; a glass stopper was inserted in its place. All other procedures were identical to those used in procedure (1).

Hydrogenations were also run after utilizing an ethylene pretreatment. As in procedure (2), the catalyst and the cofactor were placed in the hydrogenation vessel. The third neck was fitted with a gas inlet valve connected to the ethylene source. The hydrogenation apparatus was evacuated and filled with ethylene three times. Toluene ($10\,cm^3$) was then added, and the resulting suspension was flushed with ethylene (3 ×). The resulting mixture was allowed to stir under ethylene for 900 s at which time the alkene to be hydrogenated (2–20 mmol) was injected. After an additional 100 s the apparatus was carefully evacuated and vigorously stirred for 15 s. During this time, the catalyst solution turned from yellow (the color of the ethylene complex) to red. Once the ethylene had been removed the apparatus was filled with H_2. After two more cycles consisting solely of filling with H_2 and careful evacuation, the apparatus was filled with H_2 and hydrogenation was begun by the initiation of stirring.

Hydrogenation rates were calculated by plotting the consumption of H_2 vs. time and fitting a straight line to the region where the rate was virtually constant; this region encompassed at least the first 50–500 s after introduction of alkene. Rates are reported as mmol of H_2 consumed s^{-1}.

In order to determine whether any catalytic activity resided upon the polymer beads, some hydrogenation experiments using $RhCl(PPh_3)_3$ and PS-SO_3Ag or $RuCl_2(PPh_3)_3$ and PS-SO_3Ag were stopped before alkene had been consumed. The polymer beads were allowed to settle and the supernatant was transferred by forced siphon to another H_2-filled hydrogenation apparatus and hydrogenation was resumed by turning on the stirring motor. The polymeric cofactors were stirred two times with toluene (15 cm^3) which was then removed by forced siphon. Fresh toluene (10 cm^3) and alkene (2–20 mmol) were injected and hydrogenation was initiated. No catalytic activity was observed to reside on the beads.

CONCLUSIONS

Using a readily available ion exchange resin we have successfully prepared silver(I) containing ion exchange polymers which selectively remove PPh_3 from solutions of a transition metal complex. In some cases where excess PPh_3 inhibits alkene hydrogenation, addition of such polymers restores the hydrogenation rate to its uninhibited value. In some cases involving representative aliphatic alkenes (1-hexene, cyclohexene), modest rate accelerations of $RhCl(PPh_3)_3$-catalyzed hydrogenations could be achieved only after ethylene pretreatment. In other cases such as $RhCl(PPh_3)_3$ catalyzed norbornene hydrogenation or $RuCl_2(PPh_3)_3$ catalyzed alkene hydrogenations, PS-SO_3Ag activated the hydrogenation by absorbing HCl and PPh_3. A survey of other transition metal phosphine complexes suggests these modest rate accelerations could be general.

These results describe a distinctly different way of using polymers to modify homogeneous catalytic reactions. Modification of the polymeric matrix or of the phosphine-absorbing agent could lead to more selective and/or more efficient ligand absorbing polymers. Application of these procedures to other catalytic systems could also result in more practicable activations of conventional homogeneous alkene hydrogenation reactions or the altering of a known catalyst's selectivity.

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REFERENCES

1. Pittman, CU, Jr In: *Comprehensive Organometallic Chemistry*, Wilkinson, G (ed) Pergamon Press, Oxford, 1982, 8: 553. Hartley, FR In: *Supported Metal Complexes. A New Generation of Catalysts*, D Reidel Publishing Co., Neth., 1985
2. Ford, WT *ACS Symposium Series*, 1986, 308: 1
3. Mathur, NK, Narang, CK and Williams, RE In: *Polymers as Aids in Organic Chemistry*, Academic Press, New York, 1980
4. Ford, WT and Tomoi, M *Adv. Polym. Sci.*, 1984, 55: 49
5. Pittman, CU, Jr and Wielmon, G *Ann. N.Y. Acad. Sci.*, 1980, 333: 67
6. Collman, JP, Hegedus, LS, Cooke, MP, Norton, JR, Dolcetti, G and Marquardt, DN *J. Am. Chem. Soc.*, 1972, 94: 1789
7. Gosser, LW, Knoth, WH and Parshall, GW *J. Mol. Catal.*, 1977, 2: 253
8. Hidai, M, Kuse, T, Hidita, T, Uchida, Y and Misono, A *Tetrahedron Lett.*, 1970, 1715
9. Strauss, SH and Shriver, DF *Inorg. Chem.*, 1978, 17: 3069
10. Bergbreiter, DE, Bursten, MS, Cook, K and Parsons, GL *ACS Symposium Series*, 1982, 192: 31
11. Triphenylphosphine is known to behave as a Bronsted base with strong acids, cf. Sasse, K In: *Methoden der Organischen Chemie*, Vol. XII/I, 4th edn., Muller, E, (ed), Georg Thieme Verlag, Stuttgart, 1963
12. Pignolet, LH (ed) *Homogeneous Catalysis with Metal Phosphine Complexes*, Plenum, New York, 1984
13. Hallman, PS, McGarvey, BR and Wilkinson, G *J. Chem. Soc.*, (*A*), 1968, 3143
14. Hoffman, PR and Caulton, KG *J. Am. Chem. Soc.*, 1975, 97: 4121
15. Shriver, DH *Manipulation of Air-Sensitive Compounds*, McGraw-Hill, New York, 1969