$Cr(CO)_3$-Complexed, Silica-Bonded Polyphenylsiloxane As a Stereoselective Catalyst for Hydrogenation of Sorbate and Soybean Methyl Esters

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ABSTRACT

A silica-bonded complex was prepared by reacting polyphenylsiloxane with silylated Chromosorb and then with $Cr(CO)_6$. This complex catalyzed stereoselective hydrogenation of sorbate to *cis*-3-hexenoate. Soybean methyl esters were hydrogenated at 210 C in cyclohexane to form products high in *cis* unsaturation. The recovered catalyst could be recycled once with methyl sorbate. IR showed decreased $Cr(CO)_3$ in the recovered catalysts, and the hydrogenation products contained inactive Cr.

INTRODUCTION

Previous studies showed that arene-$Cr(CO)_3$ complexes and $Cr(CO)_6$ catalyze the stereoselective hydrogenation of polyunsaturates to *cis*-monoenes (1-3). The preparation of more practical $Cr(CO)_3$ catalysts was attempted by "heterogenizing" these soluble complexes. By reacting crosslinked polystyrene with $Cr(CO)_6$, a heterogeneous catalyst was made that was recyclable with methyl sorbate (4). However, this type of catalyst was ineffective for the hydrogenation of soybean oil and methyl esters (5). The polystyrene complex was too unstable at temperatures exceeding 180 C, which were required to conjugate soybean oil, a prerequisite for hydrogenation by $Cr(CO)_3$ complexes (1,2). Recently, several soluble $Cr(CO)_3$-complexed polyphenylsiloxanes were prepared that also catalyzed stereoselective hydrogenation of methyl sorbate and showed better thermal stability than the polystyrene complex (6). However, these polyphenylsiloxane complexes were too insoluble in cyclohexane and too reactive with such solvents as tetrahydrofuran, methylene chloride, or benzene to be practical for the hydrogenation of soybean oil.

Conan et al. (7) prepared a heterogeneous catalyst by reacting a rhodium complex with polyphenylsiloxane crosslinked on Chromosorb WAW, a diatomaceous silica, as support. This heterogeneous catalyst was more active than the homogeneous analogs and reacted by the same mechanism. On this basis we prepared a $Cr(CO)_3$-complexed polyphenylsiloxane crosslinked on Chromosorb as a hydrogenation catalyst for soybean oil and esters (Fig. 1). This paper reports the preparation and evaluation of this silica-bonded catalyst. Because our previous studies with the homogeneous arene-$Cr(CO)_3$ complexes supported a mechanism involving complete dissociation of $Cr(CO)_3$ (8-10), one purpose of this study was to establish whether polymer complexation and crosslinking on Chromosorb would provide a practical way of anchoring the active $Cr(CO)_3$ species to effectively heterogenize these complex catalysts.

EXPERIMENTAL

Materials and Methods

Chromosorb WAW (60-80 mesh) and Sylon BFT, a 99:1 mixture of bis(trimethylsilyl) trifluoroacetamide and trimethylchlorosilane, were purchased (Supelco, Inc., Bellefonte, PA). Except for those described below, all other regents were prepared and purified as previously reported (5,6).

Hydrogenation, catalyst recovery by filtration, and catalyst recycling procedures have been described previously (5,6). The removal of peroxide impurities from the sorbate and soybean substrates by alumina chromatography just before hydrogenation was essential to achieve rapid, reproducible hydrogenations with the silica-bound $Cr(CO)_3$ catalyst. Elemental Cr was analyzed by atomic absorption (Galbraith Laboratories, Inc., Knoxville, TN).

The procedure of Brown (11) was modified to increase the silanol content of the polyphenylsiloxane prepolymer. Phenyltrichlorosilane (150 g) in toluene (113 ml) was hydrolyzed the same way (11); but after removal of the aqueous, acidic layer and washing, the toluene was partially distilled to remove residual water and acid. A Barrett moisture trap was used and the water was drained off until the distillate (bp 109 C) was clear. The remaining toluene was effectively removed on a rotary evaporator at 70-75 C and reduced pressure. The residue was purified by dissolving in benzene, precipitating in methanol, and drying in vacuum at 80-90 C to produce a white, crystalline prepolymer (65.8 g). IR (CS_2): absorptions for bonds to Si were observed at 3700-3100 (-SiOH), 1130 (Si-O-Si), 1120-1025 (Si-O-Si), 995 (Si-Ph); other absorptions were noted at 3070, 3045, 3025 sh., 3005 sh., 880, 778, 737, 695, 583 and 492 cm^{-1}. IR (KBr disc): additional bands (not obsured by solvent) were observed at 1598 and 1433 (Si-Ph)cm^{-1}.

Silylated Chromosorb WAW

Chromosorb WAW (20 g), trimethylchlorosilane (60 ml) and pyridine (50 ml) were stirred at reflux for 2 hr. The Chromosorb was filtered, extracted 6 hr with tetrahydrofuran (THF) under dry N_2 and dried overnight in vacuum (yield: 19.6 g).

Polyphenylsiloxane on Silylated Chromosorb WAW

To polyphenylsiloxane prepolymer (5.0 g) in THF (20 ml) and Dowtherm A (1.25 ml) was added 0.1 ml KOH solution in CH_3OH (1.64 g/100 ml). The solution was transferred to a Morton flask containing silylated Chromosorb (10 g) in THF, and the solvent was removed slowly on a rotary evaporator. The impregnated Chromosorb was transferred to a glass resin kettle, partially evacuated and heated to 110 C. After one hr, N_2 was admitted to the kettle and the temperature was raised to 295 C for 2 hr. The resulting gray-white solid (14.6 g) was transferred to a Soxhlet thimble and extracted with dry benzene for 6 hr. The contents of the thimble were evacuated at 70 C for 2 hr and a white solid, a polyphenylsiloxane crosslinked on silylated Chromosorb (11.7 g), was obtained. IR (KBr) showed weak absorptions at 3070, 3045, 3005 sh., 1595, and 1430 cm^{-1}. The latter two bands were superimposed on a broad, strong absorption between 1500-850 cm^{-1} (max. ca. 1090 cm^{-1}) for Si-O-Si; medium bands for aromatic H's were evident at 788, 732 and 693 cm^{-1}, and weaker absorptions at 610 and 585 cm^{-1}.

Silylated Chromosorb-Bonded Polyphenylsiloxane

Polyphenylsiloxane on silylated Chromosorb (10.0 g) in benzene (50 ml) was stirred with Sylon BFT (10 ml), and the mixture was heated at reflux 2 hr. The filtered, silylated product was extracted with THF 6 hr under dry N_2 and dried in vacuum to produce a white, free-flowing solid (10.71 g). The IR (KBr disc) spectrum was the same as that of the unsilylated material, with the exception of perhaps weaker absorptions at 3650-3300 cm^{-1} and 1650-1600 cm^{-1}.

Cr Carbonyl Complexed with Silylated, Chromosorb-Bonded Polyphenylsiloxane

Silylated, Chromosorb-bonded polyphenylsiloxane (10 g) was reacted with $Cr(CO)_6$ (4 g) in refluxing glyme (150 ml) 24 hr as described previously (5) to produce a $Cr(CO)_3$ complex as a gray powder (10.22 g) containing 1.82% Cr. IR (KBr disc): 1982 and 1902 cm^{-1} (Cr bound CO). Unsilylated Chromosorb (20.0 g) was reacted with polyphenylsiloxane prepolymer (5.0 g) as above (yield: 22.3 g). $Cr(CO)_6$ (1.50 g) was reacted with this Chromosorb-bonded polymer (10.0 g) to prepare a $Cr(CO)_3$ complex (9.3 g) analyzing 0.94% Cr. IR (KBr disc): 1980 and 1900 cm^{-1} (Cr bound CO).

RESULTS AND DISCUSSION

Catalyst Preparation and Characterization

The method of Conan et al. (7) for polymerizing polyphenylsiloxane prepolymer on Chromosorb WAW was modified to prepare $Cr(CO)_3$-complexed, silica-bonded polyphenylsiloxane, as outlined in Fig. 1. Thermogravimetry (TG) showed that the polyphenylsiloxane on Chromosorb had 10-11% organic phase (Table I, run 3). A $Cr(CO)_3$ complex containing 0.94% Cr was prepared by the same procedure as previously used with polystyrene (5). Silylation of the Chromosorb improved thermal stability as indicated by less weight loss during TG (Table I, runs 1 and 2). Silylation after polymerization of the prepolymer on the silylated Chromosorb also reduced thermal weight loss (Table I, runs 5 and 6). More organic phase was bonded to the Chromosorb by first silylating, then polymerizing it with more prepolymer, and resilylating the product (Table I, runs 5 and 3). A bonded complex containing more Cr (1.82% Cr) was prepared by increasing the proportion of $Cr(CO)_6$. This complex showed better thermal stability (compare runs 7 and 4) than might be expected. Since the

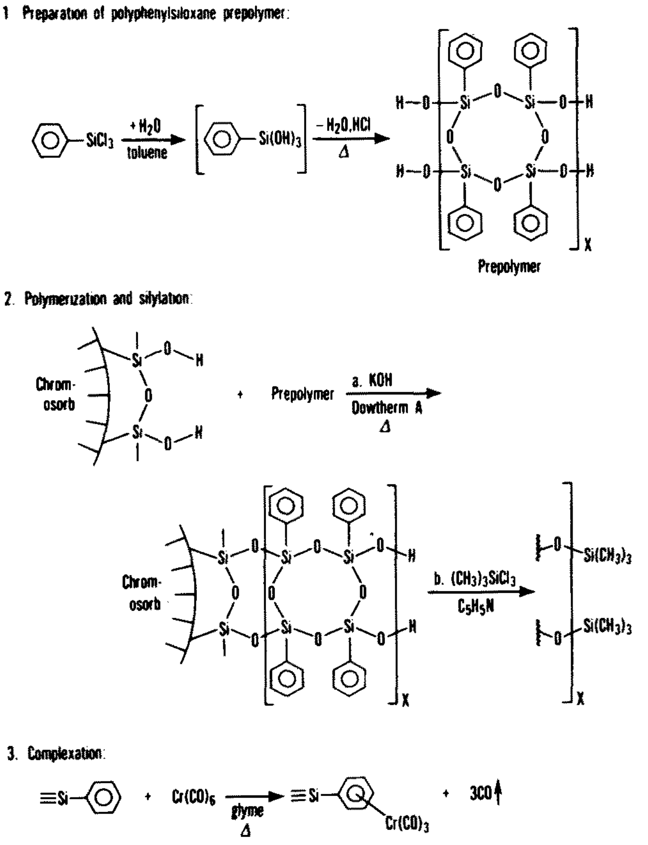

FIG. 1. Preparation of $Cr(CO)_3$-complexed, silica-bonded polyphenylsiloxane.

TABLE I

Thermal Characterizations by Dynamic Thermogravimetry[a]

Run no.	Sample description[b]	Weight loss (%)	Initial decomposition temperature (C)[c]	Temperature at 90% weight loss, C (est.)
1	Chromosorb WAW	0.59	710	?[d]
2	Silylated Chromosorb	0.36	450	?[d]
3	Polyphenylsiloxane-Chromosorb	10.7	450	710
4	$Cr(CO)_3$-Complex of sample 3	7.3	210	810
5	Polyphenylsiloxane-Silylated Chromosorb	15.0	450	710
6	Silylated Polyphenylsiloxane-Silylated Chromosorb	14.0	450	780
7	$Cr(CO)_3$-Complex of sample 6	10.9	280[e]	900

[a] Samples (4-8-mg) were heated (N_2 atm.; 30 ml/min) at 80 C/min from RT to 950 C and held 5 min; a Perkin-Elmer TGS-2 instrument was used.

[b] Cf experimental details.

[c] Estimated as initial departure of pen trace from the chart baseline, except as noted.

[d] The weight change with both silylated and unsilylated Chromosorb was too gradual to allow estimating of this temperature.

[e] Assuming a 1.3% weight loss below 150 C was from loss of adsorbed moisture (indicated also by isothermal TG).

silylated complex (run 7) had 3-4% more organic phase (compare runs 6 and 3) and twice as much Cr as the unsilylated complex, a greater weight loss would be expected in run 7 than in run 4. The higher decomposition temperatures may be due to the silylation of silanol groups to reduce side reactions.

Partial IR spectra of the silylated, Chromosorb-bonded polyphenylsiloxane and its $Cr(CO)_3$ complex are presented in Fig. 2. IR spectra for the silica-bonded $Cr(CO)_3$ complex showed carbonyl absorptions at 1982 and 1902 cm^{-1}. With the band at 1432 cm^{-1} (Si-Ph) as an internal reference, these CO absorptions were 2.3 times as intense as the CO absorptions of the unsilylated $Cr(CO)_3$ complex. Cr analyses of the silylated and unsilylated complexes agreed with the relative intensities of the CO bands.

Hydrogenation of Methyl Sorbate

The $Cr(CO)_3$ complex of the silylated, Chromosorb-bonded polyphenylsiloxane catalyzed 96% hydrogenation of sorbate at 200 C in 7 hr with a high degree of stereoselectivity for the formation of *cis*-3-hexenoate (Table II, run 1). The solid recovered by filtration showed very little activity when recycled (run 2). However, at a higher initial concentration, the recovered catalyst was moderately active and still selective for the formation of 3-hexenoate (Table II, runs 3 and 4). The silylated, silica-bonded complex was more active initially at lower Cr concentration than the unsilylated, bonded complex (compare runs 1 and 5). The catalyst recovered from the unsilylated complex was very active but no longer selective (run 6). A marked drop in activity was observed, however, when it was recycled again (run 7).

Hydrogenation of Soybean Methyl Esters

Hydrogenation with the $Cr(CO)_3$ complex of silylated Chromosorb-bonded polyphenylsiloxane at 0.67% Cr level and at 180 C resulted in only a small decrease in triene and diene (Table III, run 8). However, by raising the temperature to 210 C, the triene content was reduced with this catalyst to ca. 3% with only 5% *trans* unsaturation and no increase in saturates (run 9). When this hydrogenation was repeated at 210 C with fresh catalyst at 1.3% Cr concentration, the linolenate level had decreased to ca. 0.2% with 10% *trans* unsaturation after 4 hr (run 10). The products recovered from all runs were dark green, indicating that they contained solubilized inactive Cr. A weak absorption at 1981 cm^{-1} in the IR spectrum of product from run 9 suggested that a trace of chromium carbonyl was present.

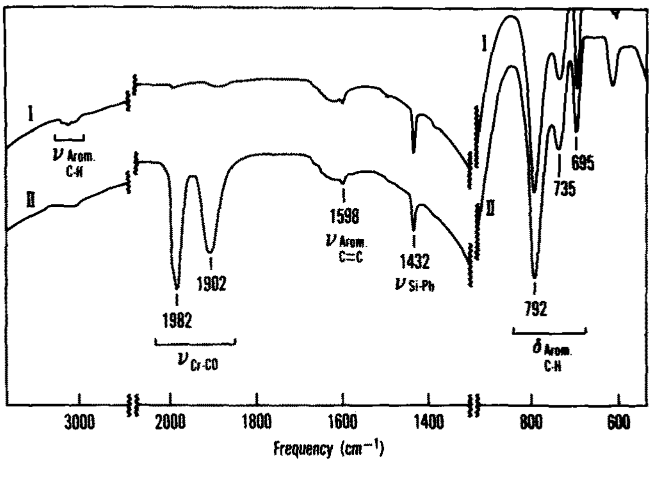

FIG. 2. Infrared spectra: I. Silylated polyphenylsiloxane on silylated Chromosorb WAW, II. $Cr(CO)_3$-complexed I.

TABLE II

Hydrogenations[a] of Methyl Sorbate with $Cr(CO)_3$-Complexed, Chromosorb-Bonded Polyphenylsiloxane

Run no.	$Cr(CO)_3$ catalyst[b]	Cr (%)[c]	Conversion (%)	Sample composition (% by GLC)[d]				
				Sorbate	2-Hexenoate	3-Hexenoate	4-Hexenoate	Hexanoate
1	Silylated Polyphenylsiloxane-Chromosorb	0.5	95.6	4.4	4.9	89.0	—	1.9
2	Run 1, recovered	ND	1.9	98.1	0.8	1.1	—	—
3	Silylated Polyphenylsiloxane-Chromosorb	2.0	99.8	0.2	2.9	88.7	—	7.7
4	Run 3, recovered	ND	77.0	23.1	2.4	73.4	—	1.1
5	Unsilylated Polyphenylsiloxane-Chromosorb	1.0	82.9	17.1	3.9	76.8	—	—
6	Run 5, recovered	ND	94.6	5.2	34.7	17.3	9.6	32.0
7	Run 6, recovered	ND	55.0	45.0	20.1	10.2	5.0	17.3

[a] A stainless steel Magne Dash autoclave (150-ml) was used. Conditions: 200 C, 500 psi, 7 hr; 1.50 g sorbate/50 ml cyclohexane.

[b] Cf experimental details.

[c] From elemental Cr analysis by atomic absorption. ND = not determined.

[d] GLC (gas liquid chromatography): Varian Aerograph Model 1440 gas chromatograph with FID and 6 ft. × 1/8 in. s.s. column of 10% SP-2330 on Chromosorb WAW. Operation: isothermal at 80 C (15 min) and programmed 8 C/min to 130 C (hold ca. 10 min).

TABLE III

Hydrogenations[a] of Soybean Methyl Esters with $Cr(CO)_3$-Complexed, Chromosorb-Bonded Polyphenylsiloxane[b]

Run no.	Cr (%)	Temperature (C)	Time (hr)	GLC analysis (%)[c]				*Trans* (by IR) (%)	IV[d]
				Triene	Diene	Monoene	Saturate		
–	–	–	0[e]	7.5	54.2	26.1	12.3	0	135.6
8	0.7	180	7	6.6	50.2	30.6	12.6	–	130.5
9[f]	0.7	210	5	3.0[g]	35.0	49.9	12.1	5.0	111.4
–	–	–	0[e]	6.4	50.3	25.9	17.4	0	126.1
10	1.3	210	2	0.6	19.2	63.3	16.9	–	89.3
			4	0.2[h]	16.0	67.4	16.4	10.1	86.2

[a] A Magne Dash autoclave (150-ml) was used. Conditions: 3.0 g soybean Me esters/50 ml cyclohexane; pressure, 500 psi at temperature.

[b] Cr analysis: 1.82%.

[c] GLC: Varian Aerograph Model 1440 gas chromatograph with FID and 6 ft × 1/8 in. s.s. column of 10% SP-2330 on 100/120 Chromosorb WAW. Operation: isothermal at 180 C.

[d] Iodine value (based on GLC).

[e] Initial oils.

[f] After 7 hr at 180 C (continued from run 8 by raising temperature and adjusting the pressure).

[g] Linolenate selectivity, 2.1.

[h] Linolenate selectivity, 2.6.

Results of Table III show that the silylated $Cr(CO)_3$ complex is sufficiently stable at 210 C to catalyze conjugation of polyunsaturated fatty acids in soybean methyl esters and selective hydrogenation to produce oils high in *cis* unsaturation. This result was not achieved previously with heterogenized chromium carbonyl catalysts (5). Further investigations are underway to determine if the new silica-bound polymer catalyst can be recycled satisfactorily in either batch or continuous hydrogenations.

The present evidence indicates that $Cr(CO)_3$ dissociated from the bonded polyphenylsiloxane during hydrogenation to form the homogeneous, catalytically active chromium carbonyl (8-10); some was partially decomposed into inactive species of chromium. Complexing $Cr(CO)_3$ to Chromosorb-bonded polyphenylsiloxane, rather than nonbonded polyphenylsiloxane (6), increased the surface exposure, allowing $Cr(CO)_3$ to more readily dissociate during hydrogenation. We previously suggested that $Cr(CO)_6$ also generates $Cr(CO)_3$ and functions as a homogeneous catalyst in the selective hydrogenation of sorbate or soybean methyl esters (3). Further investigations are necessary to determine if the $Cr(CO)_3$ remaining on the support is unaltered; however, undissociated $Cr(CO)_3$ would likely be less accessible for reaction.

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