Cis-Unsaturated Fatty Acid Products by Hydrogenation with Chromium Hexacarbonyl[1]

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ABSTRACT

The use of $Cr(CO)_6$ was investigated to convert polyunsaturated fats into *cis* unsaturated products. With methyl sorbate, the same order of selectivity for the formation of *cis*-3-hexenoate was demonstrated for $Cr(CO)_6$ as for the arene-$Cr(CO)_3$ complexes. With conjugated fatty esters, the stereoselectivity of $Cr(CO)_6$ toward the *trans,trans* diene system was particularly high in acetone. However, this solvent was not suitable at elevated temperatures required to hydrogenate *cis,trans*- and *cis,cis*-conjugated dienes (175 C) and nonconjugated soybean oil (200 C). Reaction parameters were analyzed statistically to optimize hydrogenation of methyl sorbate and soybean oil. To achieve acceptable oxidative stability, it is necessary to reduce the linolenate constituent of soybean oil below 1-3%. When this is done commercially with conventional heterogeneous catalysts, the hydrogenated products contain more than 15% *trans* unsaturation. By hydrogenating soybean oil with $Cr(CO)_6$ (200 C, 500 psi H_2, 1% catalyst in hexane solution), the product contains less than 3% each of linolenate and *trans* unsaturation. Recycling of $Cr(CO)_6$ catalyst by sublimation was carried through three hydrogenations of soybean oil, but, about 10% of the chromium was lost in each cycle by decomposition. The hydrogenation mechanism of $Cr(CO)_6$ is compared with that of arene-$Cr(CO)_3$ complexes.

INTRODUCTION

One aim of our hydrogenation research is to develop new procedures for minimizing *trans* isomers formed in vegetable oils by conventional heterogeneous catalysts. The unique property of $Cr(CO)_3$ complexes, as homogeneous hydrogenation catalysts, to convert polyunsaturates into *cis* unsaturated products without the formation of saturates (1–4) makes them particularly desirable today (5).

We investigated $Cr(CO)_6$ as a homogeneous catalyst because it is cheaper and more available than the $Cr(CO)_3$ complexes. Also we had previously found $Cr(CO)_6$ to be effective in conjugating 1,4- to 1,3-polyunsaturated fatty esters (6)–a necessary step for hydrogenation. A preliminary report was presented on the activity of $Cr(CO)_6$ for the hydrogenation of methyl sorbate to 3-hexenoate, achieved at 150–165 C in either acetone or cyclohexane (7). In this paper, we report a hydrogenation study of various fatty acid substrates with $Cr(CO)_6$ with the goal of preparing *cis* unsaturated products that can be readily freed from the catalyst. Because of its low fat solubility and its high volatility, $Cr(CO)_6$ was expected to be relatively easy to remove from the hydrogenated products by sublimation, a property that could be exploited in catalyst recycling with vegetable oils.

EXPERIMENTAL SECTION

Methyl sorbate, soybean oil, soybean methyl esters, and conjugated methyl linoleate were prepared as described elsewhere (8). The catalyst $Cr(CO)_6$ was purchased from Strem Chemicals, Inc., Newburyport, MA, and sublimed before use. Methods for gas chromatography (GC), and infrared spectrometry (IR) were also as described previously (1). *Trans* unsaturation was determined in a few samples by GC using a column capable of separating oleate from elaidate (20 ft x 4 mm, 10% Silar 10 C). For GC analyses, hydrogenated soybean oil was transesterified with 0.5 N $NaOCH_3$ in methanol-ether solution.

Hydrogenations were carried out in a stainless steel Magne Dash autoclave (150 or 300 ml) with a sampling tube. After sealing, the hydrogenation mixtures were purged three times with H_2 (500 psi) before agitating and heating to reaction temperature. At the end of reaction, the contents were cooled to room temperature and transferred with solvent into a round bottom flask. Removal of solvent and soluble $Cr(CO)_6$ was done by evacuation with a rotating evaporator (50–60 C). The resulting hydrogenated products showed no evidence of $Cr(CO)_6$ ($\lambda 1975\ cm^{-1}$) but contained varying amounts of decomposed catalyst as indicated by their greenish color and by atomic absorption analyses.

RESULTS

Selective Hydrogenation of Methyl Sorbate

Hydrogenation parameters were investigated for maximum selectivity and conversion. The same high selectivity for the formation of *cis*-3 hexenoate from methyl sorbate was achieved with $Cr(CO)_6$ as with the $Cr(CO)_3$ complexes (9). With hexane solvent up to 93.5% 3-hexenoate was obtained at 160 C with 1% $Cr(CO)_6$ in 6 hr (Table I, run 3). With acetone, $Cr(CO)_6$ was active at lower temperatures, but more catalyst was required at 150 C to achieve 98% conversion (Table I, run 8).

Hydrogenation runs were analyzed statistically (10) to test the effect and any interactions of several factors upon conversion. Table II shows the means for levels of factors computed on 24 measurements from 8 runs. Based on the least significant difference (95% level) for comparing means, temperature, catalyst concentration and acetone, solvent had significant effects in increasing conversion of methyl sorbate to 3-hexenoate. Significant interactions influenced this conversion. Catalyst concentration and temperature interactions resulted in increased conversion at 2 and 4 hr reaction times but no significant effect at 6 hr. With both solvents, conversion increased at high temperature and catalyst concentration. When acetone is compared with hexane as solvent, the effect of temperature was not significant at 4 and 6 hr, but the effect of catalyst concentration was significant at all reaction times.

Hydrogenation of Conjugated Fatty Esters

Methyl *trans*-9,*trans*-11-octadecadienoate was very selectively hydrogenated to the *cis*-monoene at 150 C in acetone solution, leaving the *cis,trans*-diene impurity unreacted (Table III, run 12). With commercial conjugated methyl linoleate consisting of 41% *cis,trans*, 16% *trans,trans* and 6% *cis,cis* isomers, only 43–44% conversion to monoene occurred at 150–160 C in acetone (Table III, runs 13,14).

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TABLE I

Hydrogenation of Methyl Sorbate with $Cr(CO)_6$[a]

Run no.	Solvent	Catalyst %	Temp. C	Time hr	GC Analysis, % 3-Hexenoate	2-Hexenoate	Sorbate
1	Hexane	1	150	2	9.5	tr	90.5
				4	17.3	tr	82.7
				6	23.5	tr	75.6
2	Hexane	2	150	2	32.0	tr	68.0
				4	52.0	tr	48.0
				6	64.5	tr	35.5
3	Hexane	1	160	2	53.4	1.1	45.5
				4	81.5	2.2	16.5
				6	93.5	1.9	4.6
4	Hexane	2	160	2	71.7	1.6	26.7
				4	90.5	2.2	7.3
				6	96.5	1.8	1.7
5	Acetone	2	120	4	3.9	tr	96.1
				6	6.0	tr	94.0
6	Acetone	2	140	2	34.5	0.2	65.3
				4	52.0	0.6	47.4
				6	63.9	tr	36.1
7	Acetone	1	150	2	26.4	tr	73.6
				4	44.8	0.8	54.4
				6	56.3	1.1	42.6
8	Acetone	2	150	2	97.6	1.7	0.7
				4	96.6	2.3	1.1
				6	98.2	1.8	0.0
9	Acetone	0.5	160	2	29.7	0	70.3
				4	41.8	0	58.2
				6	48.2	1.2	50.6
10	Acetone	1	160	2	69.6	1.6	28.8
				4	84.0	2.1	13.9
				6	92.9	2.1	5.0
11	Acetone	2	160	2	95.2	2.0	2.8
				4	97.1	2.5	0.4

[a]Conditions: 10g substrate, 40 ml solvent, 500 psi H_2, 150 ml Magne Dash autoclave.

Most of the *trans,trans* isomers were hydrogenated, leaving some of the *cis,trans* and all of the *cis,cis* isomers unreacted. The small increase in nonconjugated diene can be attributed to hydrogenation of conjugated triene intermediate. Decomposed catalyst was evidenced by the dark green color of the hydrogenated products. One experiment was carried out to determine if the catalyst might be activated by removing any CO formed after heating the catalyst-substrate mixture. This solution was first heated to 170 C under N_2, then cooled to room temperature, flushed, pressurized with H_2 and reheated to 170 C. However, this treatment caused too much catalyst decomposition as evidenced by a conversion of only 18% (Table III, run 15). In hexane, higher hydrogenation temperatures could be used with less catalyst decomposition. Almost complete hydrogenation of the conjugated dienes was achieved by reacting 7 hr at 175 C followed by 1 hr at 200 C (Table III, run 16). Similarly, conjugated soybean esters were almost completely hydrogenated in hexane at 170 and 175 C (Table III, runs 18 and 19). Under these conditions, the less reactive *cis,trans* and *cis,cis* isomers are apparently converted to the *trans,trans* isomers, which is necessary for hydrogenation.

Hydrogenation of Soybean Oil

It was previously found that under temperatures sufficiently high to conjugate polyunsaturated fatty esters (175 C), the more active and thermally stable $Cr(CO)_3$ complexes could also catalyze the hydrogenation of unconjugated fatty esters (9). Effective conjugation of methyl linoleate was also achieved by heating with $Cr(CO)_6$ in hexane at 185 and 195 C in He or N_2 (6). Therefore, in our attempts to hydrogenate soybean oil, conditions were chosen that were known to conjugate the polyunsaturated fatty ester components. Our goal was to hydrogenate the linolenate constituent of soybean oil below 3%, a level generally used commercially to achieve acceptable flavor and oxidative stability (11), with a minimum of *trans* unsaturation.

The first approach investigated consisted of conjugating the polyunsaturated fatty esters by heating under N_2 at 185 C, followed by cooling to room temperature, repressurizing with H_2 and hydrogenating at 175 and 185 C (Table IV, runs 20–21). A better approach consisted of one step hydrogenation at 190–210 C. At 200 C, linolenate in soybean oil was reduced from 7.1 to 0.9% in 6 hr and the hydrogenated product contained only 3.3% *trans* (Table IV, run 23).

Among different solvents investigated, soybean oil was effectively hydrogenated in cyclohexane and THF. Little hydrogenation occurred in methylene chloride, acetone or in absence of solvent (Table IV, runs 25–29). With THF, the product showed a significant increase in *trans* unsaturation. As observed earlier, visible catalyst decomposition occurred when acetone was used at elevated temperatures.

Recycling experiments were carried out by subliming the $Cr(CO)_6$ catalyst from hydrogenated soybean oil using an apparatus with dry ice trap (12). The solvent was first stripped at 2–3 mm Hg pressure and room temperature. The catalyst was then collected by heating the oil to 60–80 C at 0.1 mm Hg. The recovered catalyst was resuspended in hexane solvent and reused twice. Recycling of the catalyst was demonstrated through three hydrogenations. No dimunition of activity was observed throughout the three cycles, and the final product contained only 1.7% *trans* unsaturation (Table IV, run 30). However, atomic absorption analyses indicated that the sublimed hydrogenated products contained 0.09 to 0.1% Cr, representing 9.5 to 10.5% loss of Cr in each cycle. Apparently, a certain amount of catalyst is lost by conversion to a green Cr compound, the identity of which has not been established.

Another series of soybean oil runs were further analyzed statistically to optimize the hydrogenation parameters. Table V shows the means for different factors and levels computed on the basis of 20 runs and 40 samples. The higher temperatures had a significant effect on total conversion as measured by decrease in iodine value (ΔIV), decrease in linolenate (ΔLn), and increase in percent *trans* unsaturation. Increasing catalyst concentration from 1 to 2% significantly affected ΔIV and *trans* content, but no significant effects occurred in going from 2 to 4% catalyst. Neither the temperature nor the catalyst concentration had a significant effect on Ln selectivity. Surprisingly, higher H_2 pressures had a significant effect in decreasing ΔIV and *trans* content, on one hand, and increasing ΔLn and Ln selectivity, on the other hand. No significant interactions were observed with soybean oil. From Table V, it is concluded that to achieve our goal of hydrogenating soybean oil to less than 3% linolenate and a minimum of *trans* unsaturation, optimal conditions include: 200 C, 1% $Cr(CO)_6$, and 500 psi H_2.

DISCUSSION

The same order of selectivity was obtained with $Cr(CO)_6$ as with the arene-$Cr(CO)_3$ complexes in hydrogenating methyl sorbate to *cis*-3-hexenoate. With conjugated fatty esters, the stereoselectivity toward *trans,trans* dienes was particularly high in acetone solvent. Commercially conjugated linoleate containing predominantly *cis,trans* dienes required elevated temperatures necessary to convert them to the *trans,trans* configuration. To achieve this conversion and maximum hydrogenation, it was necessary to use hexane as solvent because $Cr(CO)_6$ decomposed too much in acetone at temperatures exceeding 150 C. With soybean oil, temperatures above 190 C are necessary to conjugate linoleate and linolenate before hydrogenation can occur

TABLE II

Hydrogenation of Methyl Sorbate with $Cr(CO)_6$.
Three Way Analysis of Variance-Mean Values for Various Levels

	Me 3-hexenoate		
Factor	2 hr	4 hr	6 hr
Temperature (T)			
150 C (T_0)	40.48	53.03	60.63
160 C (T_1)	79.68	91.60	95.15
Catalyst Conc. (C)			
1% (C_0)	44.30	59.15	67.28
2% (C_1)	75.85	85.48	88.50
Solvents (S)			
Hexane (H)	48.85	63.65	69.48
Acetone (A)	71.30	80.98	86.30
LSD[a]		8.90	
Standard deviation		5.87	

Interactions

	2 hr		4 hr		6 hr	
C T	T_0	T_1	T_0	T_1	T_0	T_1
C_0	17.95	70.65	31.05	87.25	39.90	94.65
C_1	63.00	88.70	75.00	95.95	81.35	95.65
S T	T_0	T_1	T_0	T_1	T_0	T_1
H	20.75	76.95	34.65	92.65	44.00	94.95
A	60.20	82.40	71.40	90.55	77.25	95.35
S C	C_0	C_1	C_0	C_1	C_0	C_1
H	40.60	57.10	53.90	73.40	59.95	79.00
A	48.00	94.60	64.40	97.55	74.60	98.00

[a] LSD = least significant difference (95% level).

TABLE III

Hydrogenation of Conjugated Fatty Esters with $Cr(CO)_6$[a]

Run no.	Starting materials, conditions	GC Analysis, %			Conversion, %
		Monoene	Diene	Conj. diene	
	Methyl *trans*-9,*trans*-11-octadecadienoate[b]	---	---	100[c]	
12	Acetone, 1% catalyst 150 C, 1.5 hr	95.0	---	5[d]	95
	Conjugated linoleate[e]	26.6	10.4	63.0	
13	Acetone, 1% catalyst 150 C, 4 hr	46.5	18.4	35.0	44
14	Acetone, 2% catalyst 160 C, 6 hr	47.8	16.1	36.1	43
15	Acetone, 4% catalyst 170 C, 4 hr[f]	34.9	13.5	51.6	18
16	Hexane, 1% catalyst				
	175 C, 7 hr	72.3	18.5	9.2	85
	200 C, 1 hr[g]	79.8	19.2	1.0	98
	Conjugated soybean esters[h]	30.0	2.5	49.5[i]	
17	Hexane, 4% catalyst 160 C, 6 hr	36.6	3.7	41.7	28
18	170 C, 6 hr	70.4	8.6	3.0	94
19	175 C, 4 hr	75.3	6.4	0.3	99

[a] All runs were made, unless otherwise noted, with a 150 ml Magne Dash autoclave, at 500 psi H_2, 25 g substrate, and 25 ml solvent.

[b] Used 1.3 g substrate and 50 ml solvent.

[c] 95% *trans,trans* + 5% *cis,trans*.

[d] *cis,trans*.

[e] Commercial Pamolyn 380, Hercules, Inc., Wilmington, DE, esterified and distilled.

[f] Mixture was first heated under N_2 to reaction temp. and held until pressure leveled, then cooled to room temp., the reactor flushed, repressurized with H_2 and hydrogenation carried out at 350 psi.

[g] Same run, continued 1 hr at 200 C.

[h] Contains 18% saturated fatty esters.

[i] Includes ca. 3.5% trienes with two conjugated double bonds.

TABLE IV

Hydrogenation of Soybean Oil[a] with $Cr(CO)_6$

Run no.	Conditions	GC Analysis, %			*Trans*, %
		Monoene	Diene	Triene and (conj. diene)	
20	Hexane, 4% $Cr(CO)_6$[b]				
	(a) 50 psi N_2, 185 C, 6 hr	33.5	19.4	(32.4)	---
	(b) 500 psi H_2, 175 C, 4 hr	51.1	20.1	(14.0)	---
	500 psi H_2, 175 C, 6 hr	60.1	19.5	5.7	---
21	Hexane, 4% $Cr(CO)_6$[b]				
	(a) 50 psi N_2, 185 C, 6 hr	36.0	22.5	(26.8)	---
	(b) 500 psi H_2, 185 C, 6 hr	58.3	23.6	3.4	---
	Hexane, 4% $Cr(CO)_6$, 500 psi H_2, 6 hr				
22	190 C	43.0	38.9	3.3	3.2(GC)
23	200 C	57.0	28.3	0.9	3.3(GC)
24	210 C	63.0	21.4	0.6	6.2(GC)
	4% $Cr(CO)_6$, 200 C, 500 psi H_2, 6 hr				
25	Cyclohexane	47.0	35.8	2.5	1.7(IR)
26	CH_2Cl_2	31.1	47.6	6.7	5.9(IR)
27	THF	54.0	28.6	2.2	22.9(IR)
28	Acetone	34.4	45.5	5.5	5.6(IR)
29	No solvent	30.7	48.8	5.8	2.4(IR)
30	Recycling,[c] 4% $Cr(CO)_6$, 500 psi H_2, 6 hr				
	Cycle 1	40.7	41.3	3.3	---
	Cycle 2	42.4	40.0	2.9	---
	Cycle 3	53.8	29.6	1.8	1.7(GC)

[a] Composition: 11.0% palmitate, 3.8% stearate, 26.3% monoene, 51.8% diene, 7.1% triene.

[b] Two-step: heat in N_2, cool to room temp., reheat in H_2.

[c] Catalyst recovered by sublimation between each cycle and transferred with hexane.

TABLE V

Hydrogenation of Soybean Oil with $Cr(CO)_6$. Three-Way Analysis of Variance-Mean Values for Various Levels[a]

Factors	ΔLn		ΔIV		% Trans		S_{Ln}	
	6 hr	6 hr	4 hr	6 hr	4 hr	6 hr	4 hr	6 hr
Temperature								
200 C	4.02	4.41	23.63	25.39	3.69	3.66	1.69	1.80
210 C	5.22*	5.49*	32.86*	32.79*	5.69*	5.60*	1.70	1.80
LSD	0.97	1.02	3.22	2.84	1.14	1.15	0.54	0.59
Catalyst conc.								
1%	4.24	4.67	22.29	23.66	3.03	3.10	1.88	2.09
2%	4.72	4.78	28.68*	28.95*	5.24*	5.10*	1.70	1.68
4%	4.81	5.36	31.81	32.79	5.14	5.02	1.58	1.77
LSD	1.26	1.33	4.18	3.67	1.47	1.49	0.71	0.76
Pressure, psi								
250	3.41	4.51	31.61	33.77	7.38	8.18	0.72	1.07
500	4.93*	5.13*	29.02	28.79*	4.65*	3.70*	1.76*	1.95*
1000	5.03	5.03	26.45	26.90	3.31	3.55	2.13	2.06
LSD	1.26	1.33	4.18	3.69	1.47	1.49	0.71	0.76
Standard deviation	0.92	0.96	3.07	2.67	1.08	1.08	0.52	0.55

[a] Abbreviations: ΔLn = decrease in % linolenate; ΔIV = decrease in iodine value (calculated by GC); S_{Ln} = linolenate selectivity calculated by a computer method (13); LSD = least significant difference (95% level); * = differences significant at 5% level.

with $Cr(CO)_6$. Remarkably, at these elevated temperatures, it was possible to reduce the linolenate content of soybean oil from 7% to less than 3% without increasing *trans* unsaturation of the products above 3–4%.

The following are some critical mechanistic questions. Are the same intermediates species formed from $Cr(CO)_6$ as from $Cr(CO)_3$ complexes? Why is $Cr(CO)_6$ activated in acetone below 150 C and decomposed in this solvent above 150 C? Why are more *trans* isomers formed with THF solvent and at lower H_2 pressures? What is the green-colored Cr compound formed during hydrogenation of unconjugated fatty esters? Answers to these questions are obviously fundamental to developing a catalytic process of practical importance with $Cr(CO)_6$.

In the conjugation of methyl linoleate with Cr carbonyls, a mechanism was postulated involving formation of $Cr(CO)_3$ by dissociation and allyl $H\text{-}Cr(CO)_3$ intermediates (6). Conjugation results by 1,3-hydrogen shifts yielding *trans*-10,*cis*-12-, and *cis*-9-*trans*-11-dienes, which rearrange into other *cis,trans* isomers by 1,5-shift.

Although no mechanistic studies have been reported on the thermally catalyzed hydrogenation by $Cr(CO)_6$, the loss of CO would be expected to play a key part. Higher temperatures are required for hydrogenation with $Cr(CO)_6$ than with arene-$Cr(CO)_3$ complexes because the former catalysts would be more difficult to dissociate thermally than the latter. In the absence of an arene ligand (or coordinating solvent), $Cr(CO)_6$ would be expected to produce coordinatively unsaturated species reacting either with H_2 or dienes (1,3- or 1,4-) to form the 1,3-diene-$H_2Cr(CO)_3$ complex 4 (Scheme 1).

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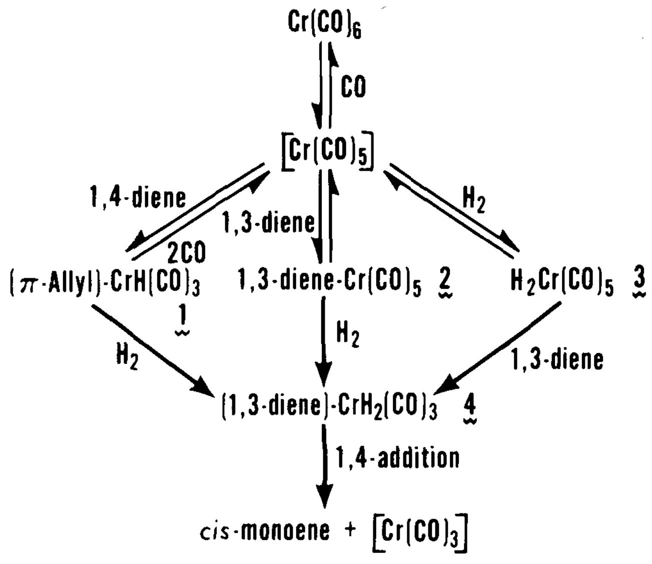

SCHEME 1

Although the various paths leading to 4 may not be distinguished kinetically, there is evidence for both intermediates 2 and 3. Evidence for a diene complex of type 2 was reported by IR studies during photoinduced hydrogenation of 2,4-hexadiene with $Cr(CO)_6$ (14). A chromium carbonyl hydride was reported from the reaction of $Cr(CO)_6$ with alcoholic KOH, and the species suggested was $Cr(CO)_5H_2$ (15). Disproportionation of this hydride produced $Cr(CO)_6$. Small amounts of $Cr(CO)_6$ have been detected during homogeneous hydrogenation with arene-$Cr(CO)_3$ complexes (7,16), and some disproportionation of hydride intermediates may be indicated.

Acetone was shown to accelerate the photo-induced hydrogenation of *trans,trans*-2,4-hexadiene and to form a weakly coordinated complex acetone-$Cr(CO)_5$ (17). Similarly, THF was shown to form an active Cr carbonyl complex catalyst by ligand displacement during homogeneous hydrogenation with naphthalene-$Cr(CO)_3$ (18). In our $Cr(CO)_6$ system, acetone and THF would also be expected to form labile $Cr(CO)_5$ complexes in which the solvent would be more readily displaced by 1,3-diene or H_2 to form intermediate species 2 or 3 respectively (Scheme 1). The same acetone-$Cr(CO)_5$ complex may facilitate thermal degradation of $Cr(CO)_6$ at elevated temperatures. With the cooresponding THF complex, diene displacement may promote the *trans* isomerization observed in our products. Conversely, preferential formation of the hydride intermediate 3 may explain the lower *trans* isomerization observed at higher H_2 pressures.

The loss of catalyst during hydrogenation by formation of a soluble noncarbonyl Cr compound may arise by oxidation due to either traces of O_2 or oxygenated impurities in the fatty ester substrates. Small amounts of free fatty acids or peroxide impurities in the substrates are known to inhibit homogeneous hydrogenation with arene-$Cr(CO)_3$ complexes. Further research is, of course, needed to identify the green Cr compound to provide a clue as to its origin and the basis to minimize catalyst loss on recycling. Since both $Cr(CO)_6$ and arene-$Cr(CO)_3$ complexes show the same hydrogenation selectivity, studies with $Cr(CO)_6$ may further elucidate the mechanism of catalysis by $Cr(CO)_3$ complexes.

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