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SELECTIVE CATALYTIC HYDROGENATION OF 1,4-DIENES TO *cis*-MONOENES USING (NAPHTHALENE)(TRICARBONYL)CHROMIUM *

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Summary

Methylene interrupted dienes react with (naphthalene)(tricarbonyl)chromium under H_2 to yield a mixture of positionally isomeric *cis*-monoene products. The isomer distribution, reactions with proposed organic intermediates, and kinetic studies suggest a mechanistic pathway that includes (1) loss of the arene from the metal fragment, (2) isomerization of the 1,4 diene to 1,3 conjugated dienes, and (3) subsequent reduction of the conjugated dienes to the isomeric *cis*-monoene products. The active metal fragment appears to be selective in the isomerization of 1,4 to 1,3 dienes and inert toward *cis* to *trans* geometrical isomerization of the monoene products. The results of kinetic studies using methyl *cis,cis*-9,12-octadecadienoate (methyl linoleate) as a substrate for the hydrogenation reactions are discussed.

Introduction

Catalytic hydrogenations of naturally occurring oils are often necessary to remove undesired polyunsaturation [1,2]. The selective hydrogenation of methylene interrupted polyenes to yield only *cis*-olefin products is often an economically desirable step in the processing of such oils as soybean, cottonseed, etc. Typically, such commercial hydrogenations are performed with heterogeneous catalysts that give excellent selectivity for degree of unsaturation, but these same catalysts do give products that contain varying degrees of both *trans*-olefins and positional isomers [2].

In order to develop more selective hydrogenation catalysts for control of the *trans*-isomerization problems, we initiated a study using homogeneous catalysts to promote the hydrogenation of polyunsaturated materials to only *cis*-monoene products. A logical starting point for our studies was the well known (η^6-arene)(tricarbonyl)chromium complexes that have been demonstrated to be selective hydro-

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* Dedicated to Professor Jack Halpern on the occasion of his 60th birthday.

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genation catalysts for conjugated dienes yielding only *cis*-monoene products [4]. While several mechanistic schemes have been suggested for these reactions [4,5], they share the common feature that the active metal fragment, "$Cr(CO)_3$", is generated in situ by thermal [6,7] or photochemical [8] activation of a coordinatively saturated $L_3Cr(CO)_3$ complex (L_3 = arene, $(CH_3CN)_3$ or $(CO)_3$). This fragment then coordinates with the conjugated diene to give an active complex which can add H_2. An intermediate conjugated diene-hydride chromium complex adds hydrogen in a 1,4 fashion to the diene to give the *cis*-monoene.

In previous studies involving methylene interrupted diene substrates [9], investigators have also used benzene or substituted benzene complexes as the source of the "$Cr(CO)_3$" fragment, but these benzenoid chromium complexes have the disadvantage that rigorous reaction conditions are required to achieve reasonable reaction rates (165 °C, 500 p.s.i. H_2) and at such high temperatures, undesirable side reactions occur; e.g., geometrical isomerization of the *cis*-monoene products to *trans*-olefins. Consequently, at least based on the literature, it appeared that the $Cr(CO)_3$ complexes would not be suited to our goal of selective reductions of methylene interrupted dienes.

We describe here studies which show that methylene interrupted dienes can in fact be selectively hydrogenated to yield *cis*-monoenes using $Cr(arene)(CO)_3$ complexes. There are two major factors that make these catalysts function: (1) higher benzenoid rings (such as naphthalene) dissociate more readily allowing lower reaction temperatures [10], and (2) such catalysts not only give selective hydrogenation, but selectively isomerize the methylene interrupted diene to conjugated diene without extensive double bond migration. We report here the use and characterization of these reaction systems, as well as kinetic and mechanistic studies detailing the mode of action of these remarkably selective hydrogenation catalysts for the reduction of the methylene interrupted diene, methyl *cis,cis*-9,12-octadecadienoate (methyl linoleate).

Experimental

Equipment. FT-IR spectra were recorded on a Digilab FTS-15 spectrometer. NMR characterizations and decoupling experiments were performed on a JEOL FX-270 spectrometer. Reaction mixtures were analyzed on a Hewlett–Packard 5880A gas chromatograph equipped with a Level IV terminal, flame ionization detector and a J&W Scientific 30 m × 0.25 mm DB-1 capillary column. GC-mass spectral data were collected on a Hewlett–Packard HP5985B quadrupole mass spectrometer interfaced with a HP5840A g.c. Quartz Griffen–Worden pressure vessels were purchased from Kontes Glass Co. and used in reactions for pressures less than 250 p.s.i. For reactions at pressures of 250 p.s.i. or greater, reactions were run in a glass lined Autoclave Engineers rocking autoclave. Both the autoclave and the Griffen–Worden pressure reactors were modified to allow facile sampling of the reaction mixture [11].

Materials. Methyl linoleate, methyl oleate, methyl elaidate, methyl ricinoleate and methyl ricinelaidate were used as supplied by Nu Check Prep, Inc., Elysian, Minn. Methyl esters of saturated organic acids and terminal diacids with chain lengths C_3 to C_{18} were supplied by Chemical Procurement Laboratories, Inc. and used as GC standards. All chemical manipulations were performed under an inert atmosphere using standard Schlenk techniques. All solvents were distilled under nitrogen from appropriate drying agents before use. Reaction mixtures and apparatus for hydrogenations were assembled and sealed in the inert atmosphere of a Vacuum Atmospheres Drybox. Ultra high purity hydrogen (99.99%) and deuterium were supplied by Matheson.

Synthesis. (Arene)(tricarbonyl)chromium complexes were prepared using the procedure previously described [12]. Dinaphthalenechromium was prepared using metal vapor synthetic methods [13].

cis,trans-9,11-Methyloctadecadienoate. This substrate was prepared in two steps by reaction of methyl ricinoleate (methyl-*cis*-12-hydroxy-9-octadecenoate) (3.53 g, 11.2 mmol) with *p*-toluenesulfonyl chloride (3.13 g, 16.4 mmol) in 15 ml of freshly distilled pyridine. The reaction mixture was stirred for 2 h at room temperature then allowed to react overnight at −40 °C. After filtration of the pyridinium chloride, the filtrate was diluted with 100 ml diethyl ether. The organic layer was extracted with 1*N* HCl, H_2O and dried over Na_2SO_4. Evaporation of the solvent yielded 7.38 g (95%) of the 12-tosylate. This material was further allowed to react with neat 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 55 °C for 48 h. The reaction mixture was diluted with 100 ml hexane and extracted with 1*N* HCl, H_2O and dried over Na_2SO_4. Evaporation of the solvent yielded 3.0 g of crude material which was purified by argentation chromatography [14] to yield 1.8 g (54% overall yield) of the desired compound. Spectroscopic characterization agreed with literature values [15].

trans,trans-9,11-Methyloctadecadienoate. This material was prepared in 57% overall yield by the method described above starting from methyl ricinelaidate (*trans*-12-hydroxy-9-octadecenoate).

Procedures. Reaction mixtures in the concentration range of 0.03 to 0.045 molar in substrate with 1 to 10 mol % catalyst in hexane were placed in either (1) a Griffen-Worden pressure vessel and shaken in a thermostatically controlled oil bath under an atmosphere of hydrogen (pressures < 250 p.s.i.) or an Autoclave Engineers rocking autoclave under an atmosphere of hydrogen (pressures > 250 p.s.i.). Aliquots were taken from the pressure reactors under the reaction conditions and these kinetic samples analyzed directly by gas chromatography. Reduction products were separated using a 30 m × 0.25 mm DB-1 capillary column with a 25 micron film thickness. Helium was used as the carrier and make-up gas. Other chromatographic conditions: sample volume 2 microliters; column flow 1.9 ml/min; split ratio 100/1; injector temperature 280 °C; detector temperature 360 °C; oven temperature program 160 °C for 1 minute, then increased at a rate of 2 °C/min to 185 °C, holding for 20 min, then increase at a rate of 30 °C/min to 315 °C, holding for 5 min.

The degree of unsaturation for the fatty ester products from these reductions was determined by GC-mass spectral analysis and determined to be monoene in all cases. No fully reduced (saturated) esters were detected. The *E* or *Z* geometry of the monoene products were determined in the gross sample by FT-IR [16]. The distribution and position of the unsaturation in the monoene products were determined by ozonolysis/esterification [14] and the analysis of the resulting monoester and diester fragments by gas chromatography was done using a different temperature program: initial temperature 65 °C increased at a rate of 4 °C/min to 225 °C, then holding for 5 min.

Product analysis. In order to accurately follow the reaction kinetics in the reduction of methyl linoleate, complete characterization of the reaction products was necessary. In addition for rate studies, developing a routine analytical method was required for rapid composition analysis of reaction mixture aliquots. Capillary gas chromatography with flame ionization detection allowed separation and quantification of the components in the reaction mixture. This combined with the ability to sample pressure reactions [11] permitted facile kinetic analysis.

Identification of the reaction products was accomplished by utilizing several analytical techniques. GC-mass spectral analysis made it possible to assess the degree of hydrogenation; with all catalysts the product mixtures are uniformly methyl octadecenoates. This was supported by classical methodology [17]; iodine value determinations *IV* 85.8 (theoretical *IV* 86.1).

The geometry about the double bond in the bulk reaction products was determined by an accepted infrared spectroscopy method [16] utilizing the C–H wag of the *trans*-monoolefin at 967 cm^{-1}. FT-IR allowed detailed line shape analysis and gives reproducible compositions. The distributions of positional isomers in the unsaturated eighteen carbon esters were determined by cleaving the olefins via ozonolysis/esterification [18] and subsequent GC analysis of the mono- and di-ester fragments. This methodology makes it possible to determine the position of the various monoene isomer products and provides a quantitative method for determination of the yield of each positional isomer product.

Results

General. In our initial experiments the known selective diene hydrogenation catalysts, (benzene)(tricarbonyl)chromium and (methyl benzoate)(tricarbonyl)chromium were tested for hydrogenation activity with methyl linoleate substrate in glass lined autoclaves. Our results were contrary to those noted in the literature [9,10]. Previous workers consistently used unlined, stirred, stainless steel high pressure reactors. Control experiments in our laboratories demonstrated that stainless steel surfaces under the literature reaction conditions (165 °C, 500 p.s.i. H_2) are not inert toward methyl linoleate but that substantial isomerization of methyl lineoleate occurs to yield conjugated methyl linoleates and *trans*-monoene products as well. We have found that the hydrogenation of methyl linoleate in glass does occur at temperatures near 180 °C using (benzene)(tricarbonyl)chromium; however, the mono-unsaturated fatty ester products contain high concentrations of *trans*-olefins and a broad distribution of positional isomers (Δ^8 to Δ^{13}). At lower temperatures (135 °C) this catalyst is completely inactive.

The corresponding (naphthalene)(tricarbonyl)chromium complex at 180 °C yields a product mixture identical to that obtained with the (benzene)(tricarbonyl)chromium complex. But, at 135 °C the (naphthalene)(tricarbonyl)chromium complex is still very active. Additionally, the composition of the monoene products are also much different than that observed at 180 °C. The number of components is reduced from 10 to 4, and each of the four is a mono-olefin. Further, the concentration of the *trans*-monoene component in the product drops from 30% to less than 1% after complete conversion of the diene to monoene (Fig. 1). The four monoenes are produced in the ratio 1/1/1/1 and have been characterized as the Δ^9-, Δ^{10}-, Δ^{11}-, and Δ^{12}-isomers of methyl *cis*-octadecenoate (methyl iso-oleates).

Control experiments in which both *cis*-methyl oleate and *cis,cis*-methyl linoleate were subjected to identical hydrogenation conditions (180 °C, 500 p.s.i. H_2,) using the (benzene)(tricarbonyl)chromium complex as catalyst, revealed that the rate of *trans*-monoene product formation was identical in each case.

Solvent effects were also observed to play an important role in these hydrogenations. Hydrocarbon solvents (hexane) afforded the greatest rates for the reductions of methyl linoleate at lower temperatures using the (naphthalene)(tricarbonyl)chromium catalyst. In contrast to the reduction of conjugated dienes [8b,10b], the substitution of coordinating solvents such as acetone, acetonitrile, ethyl acetate or THF totally deactivate the naphthalene catalyst toward the reduction of the methylene interrupted dienes such as methyl linoleate.

Mechanistic studies. To aid our mechanistic understanding of the enhanced catalytic chemistry exhibited by (naphthalene)(tricarbonyl)chromium in the hydrogenation of methylene interrupted dienes, several important studies were carried out. A significant observation is that the methyl *cis,cis*-9,12-octadecadienoate (methyl linoleate) substrate always yields an equimolar mixture of Δ^9-, Δ^{10}-, Δ^{11}-, and Δ^{12}-*cis*-monoene (iso-oleate) products. This is true regardless of the substrate/catalyst ratio, the hydrogen pressure, the temperature at which the reaction is run (from 80 up to 165 °C, the temperature at which isomerization begins to occur), and the hydrocarbon solvent. When the methyl *cis,trans*-9,11-octadecadienoate is used as substrate, the reactions are much faster and a different product mixture results. In this case only two *cis*-monoene products are obtained under a variety of conditions (temperatures $< 160\,^\circ C$), namely the methyl *cis*-9- and -10-iso-oleates. When the methyl *trans,trans*-9,11-octadecadienoate substrate is used, the reaction rates are much faster than those observed with methyl linoleate and only the methyl *cis*-10-iso-oleate product is obtained. This latter result is consistent with other reports of hydrogenations of *trans,trans*-conjugated dienes with (arene)(tricarbonyl)chromium catalysts yielding 1,4-hydrogenation products [10].

At temperatures below 160 °C using the (napthalene)(tricarbonyl)chromium

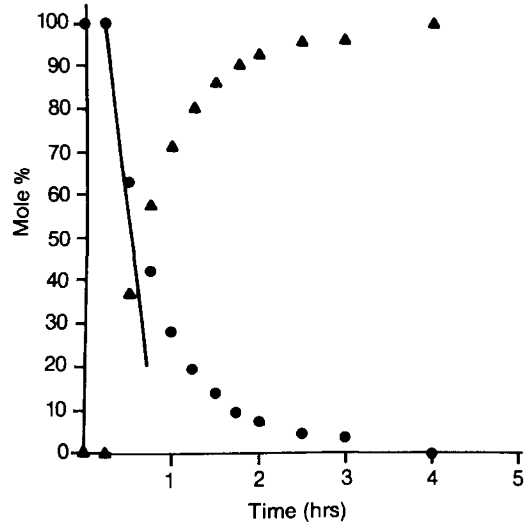

Fig. 1. Reaction profile for the hydrogenation of *cis,cis*-9,12-methyl linoleate (0.045 *M*) under 100 p.s.i. H_2 pressure at 135 °C in hexane: $[Cr(naphthalene)(CO)_3]/[substrate] = 0.1$: (●) methyl linoleate and (▲) reduction products methyl iso-oleates

catalyst, the addition of the product methyl oleate not only has no effect on the reaction (hydrogenation) rate, but also has no effect on the observed isomer ratios of the iso-oleate products. Additional observations include the fact that both the bis(naphthalene)chromium and $Cr(CO)_6$ complexes do not exhibit any catalytic activity in these systems at temperatures below 165 °C. Several reactions were carried out using D_2 gas in place of H_2 under typical reaction conditions (Fig. 1). After an oxidative workup the reaction products were carefully monitored via GC-mass spectral techniques for deuterium containing naphthalene and 1,4-dihydronaphthalene. In none of these studies were any deuterium containing naphthalenes observed. Deuterium incorporation into the substrate was also carefully followed by both direct GC-mass spectral monitoring of the products and by isolating these methyl iso-oleate products and subjecting them to ozonolysis/esterification [18]

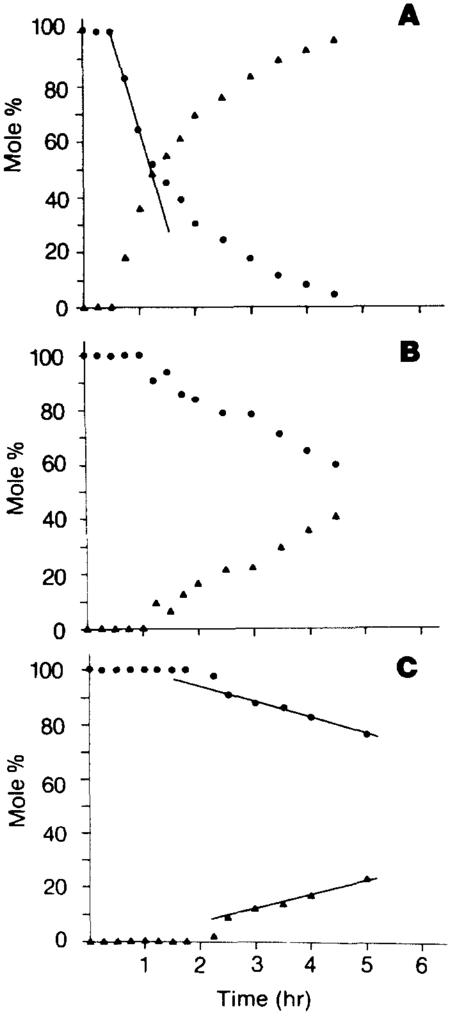

Fig. 2. Reaction profiles for the hydrogenation of methyl linoleate (same conditions as Fig. 1) (a) $[\text{arene}]_{\text{added}}$ 2.5% [substrate]; (b) $[\text{arene}]_{\text{added}}$ 40% [substrate]; (c) $[\text{arene}]_{\text{added}}$ 100% [substrate]. In each plot (●) methyl linoleate and (▲) methyl iso-oleates.

followed by GC-mass spectral analysis of the resultant mono- and di-acid fragments (as their methyl esters). In all cases, the product iso-oleates contained two deuterium atoms. Further, each mono- and di-acid cleavage fragment always contained one deuterium atom.

The effect of added naphthalene on the reaction rate was also studied. In such studies we observed that added arene had a deleterious effect on the rate. As can be seen in the reaction profiles of Fig. 2, the reaction definitely slows down as arene is added. As the added naphthalene concentration increases, the reaction rate not only slows down, but the reaction also appears to approach zero order substrate dependence. As observed for the (benzene)(tricarbonyl)chromium catalysts, the corresponding naphthalene complexes also show an induction period. When additional

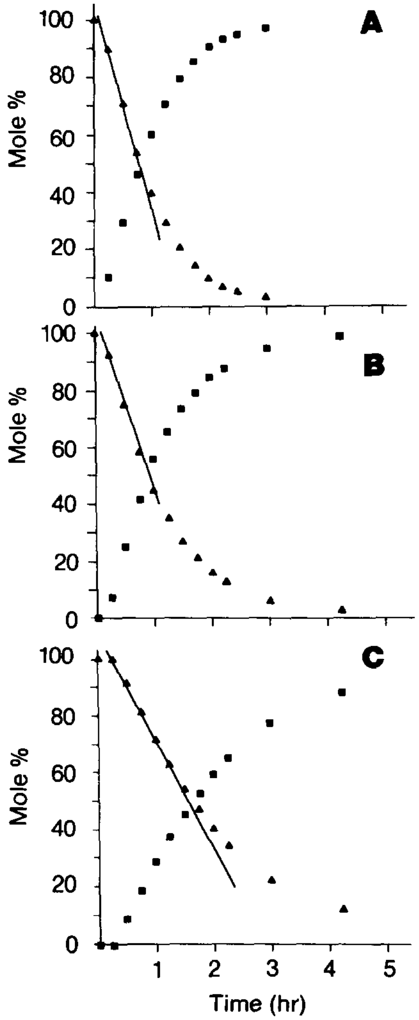

Fig. 3. Reaction profiles for the hydrogenation of methyl linoleate (0.045 *M*) at 120 °C under 100 p.s.i. H_2 pressure in hexane: [Cr(naphthalene)(CO)$_3$] (a) 4.5×10^{-3} *M*, (b) 2.3×10^{-3} *M*, and (c) 4.5×10^{-4} *M*: (▲) methyl linoleate and (■) methyl iso-oleates.

naphthalene is added, this induction period increases. At larger substrate to catalyst ratios the induction period is suppressed.

Kinetic studies. The overall dependence of the reaction rate on the concentration of each reactant was carefully studied. The reaction rates were measured by monitoring the concentration of methyl linoleate and the methyl iso-oleate products by gas chromatography. The rate of appearance of product *cis*-monoenes was found to be equal to the loss of methyl linoleate over 90% of the reaction.

The dependence of the reaction rate on the methylene interrupted diene [substrate] concentration is complex. Neither the plots of ln[methyl iso-oleates] vs. time nor plots of $[\text{methyl iso-oleates}]^{-1}$ versus time at 135 or 120 °C demonstrate linear behavior. At higher substrate/catalyst ratios, the initial reaction profiles demonstrate linear (zero-order) substrate decay, but as the reaction progresses (substrate/catalyst 5–10), the reaction rates slow down and show considerable curvature (Fig. 3). Since the plots of [methyl iso-oleates] vs. time approach linear behavior early in the reaction when there are high substrate to catalyst ratios, approximate rates were determined at 135 and 120 °C using such initial reaction rate data over a range of substrate/catalyst ratios (i.e. 10/1 to 200/1). From these data, the dependence of the reaction velocity on the catalyst concentration was estimated. A plot of ln V_{observed} vs. ln[catalyst] gives a linear relationship with a slope equal to 0.94 (Fig. 4) at 135 °C, but at 120 °C this same plot is not linear.

The rate of reaction was found to be independent of the H_2 pressure over a range from 50 to 2000 p.s.i. Reductions were conveniently run in Griffen–Worden reactors at 100 p.s.i. H_2.

The results from reactions of (naphthalene)(tricarbonyl)chromium and methyl linoleate in hexane in the absence of H_2 (i.e. 100 psi. N_2, 135 °C) are complex. These reactions, not only yield the predicted conjugated dienes, but also other as yet uncharacterized materials that do not appear when H_2 is present. The rates of substrate (methyl linoleate) consumption, however, are similar in the presence and absence of H_2.

Temperature studies. The effect of temperature variation on the reaction rate was studied for the hydrogenation of methyl linoleate in hexane. A linear plot of the ln V_{initial} vs. $1/T_{\text{abs.}}$ was obtained for this reaction (Fig. 5). From this Arrhenius treatment an activation energy, E_a was found to be 16.2 kcal/mol and $\Delta S^{\ddagger}$ equaled −42.4 e.u. at 135 °C.

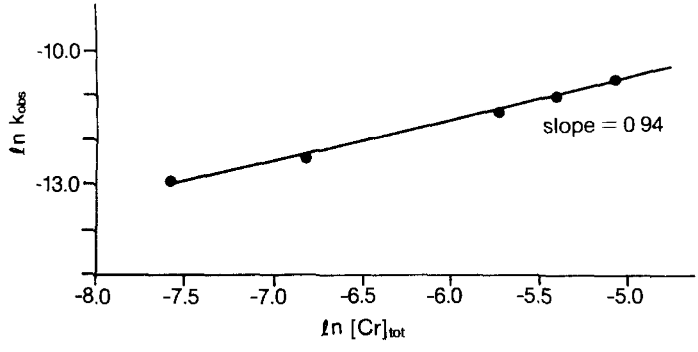

Fig. 4. Plot of the ln $k_{\text{obs.}}$ versus $\ln[\text{Cr}_{\text{tot}}]$ at 135 °C under 100 p.s.i. H_2 pressure in hexane with [methyl linoleate] = 0.045 *M*.

Discussion

The selective hydrogenation chemistry promoted by the (naphthalene)(tricarbonyl)chromium catalyst system is truly remarkable. This catalyst not only affords complete selectivity for diene with no monoene reduction, but also gives only desired *cis*-monoene product. This latter point must mean that the catalyst not only produces *cis*-monoene directly, but does not isomerize the product to the *trans*-olefin under the reaction conditions.

The results with the (naphthalene)(tricarbonyl)chromium are in contrast to and represent a great improvement over earlier work with the analogous (benzene)(tricarbonyl)chromium based catalysts, in which extensive isomerization of the product *cis*-monoenes results [9]. We have shown that this is due to the high temperatures at which the reactions must be run in order to get activity, and also due to the presence of active reactor surfaces. Consequently, isomerization (both geometrical and positional) is not a problem at temperatures below approximately 160 °C; whereas, the corresponding benzene derivative is not active at 160 °C.

The key to the increased reactivity of this naphthalenechromium based catalyst (η^6-naphthalene)(tricarbonyl)chromium likely arises from the increased lability of the naphthalene ligand toward dissociation to liberate an active "$Cr(CO)_3$" fragment as the catalyst (eq. 1):

$$Cr(C_{10}H_8)(CO)_3 \overset{K}{\rightleftarrows} \text{“}Cr(CO)_3\text{”} + C_{10}H_8 \qquad (1)$$

It is not likely that a free "$Cr(CO)_3$" fragment will form, but that a solvated (by an olefinic substrate) complex is a likely intermediate. Nevertheless, the binding of the arene can be seen to play a major role in reactivity with such catalysts. This is further evidenced by the decrease in the reaction rate as additional arene is added. We believe that this reactivity difference between the benzenoid or naphthalene catalysts is due largely to the ability of naphthalene to more easily form an η^4-intermediate without substantial loss of resonance delocalization energy. Such an

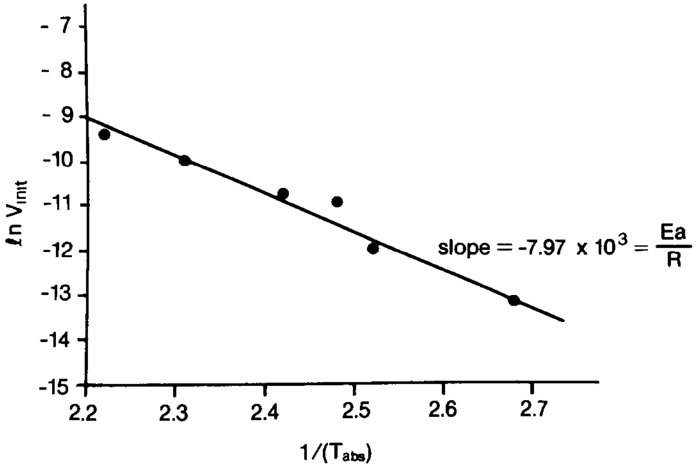

Fig. 5. Plot of ln $V_{initial}$ versus $1/T_{abs}$ for the hydrogenation of methyl linoleate (0.045 *M*) under 100 p.s.i. H_2 pressure in hexane, [substrate]/[catalyst] = 10.

explanation is also consistent with the ability of the $\overline{RuH_2(PPh_3)_2(PPh_2C_6H_4)}^-$ [19] and of $Rh(dppe)(MeOH)_2^+$ [20] complexes to hydrogenate polycyclic aromatics but not benzene. Thus, an intermediate complex could form in which the zerovalent chromium is coordinated to three carbonyls, and η^4-naphthalene, and one of the olefins of the methylene interrupted diene substrate (eq. 2).

$$Cr(\eta^6\text{-}C_{10}H_8)(CO)_3 + \text{diene} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cr(\eta^4\text{-}C_{10}H_8)(CO)_3(\eta^2\text{-diene}) \quad (2)$$

Our experimental observations are consistent with a mechanism in which the methylene interrupted diene must first be isomerized to a conjugated *cis,trans*-diene which then can be reduced to the *cis*-monoene by 1,4 addition of dihydrogen - the accepted mechanism of reduction of conjugated *trans,trans*-dienes with $Cr(CO)_3$ based catalysts [5,8]. A key to understanding the isomerization process resides in the

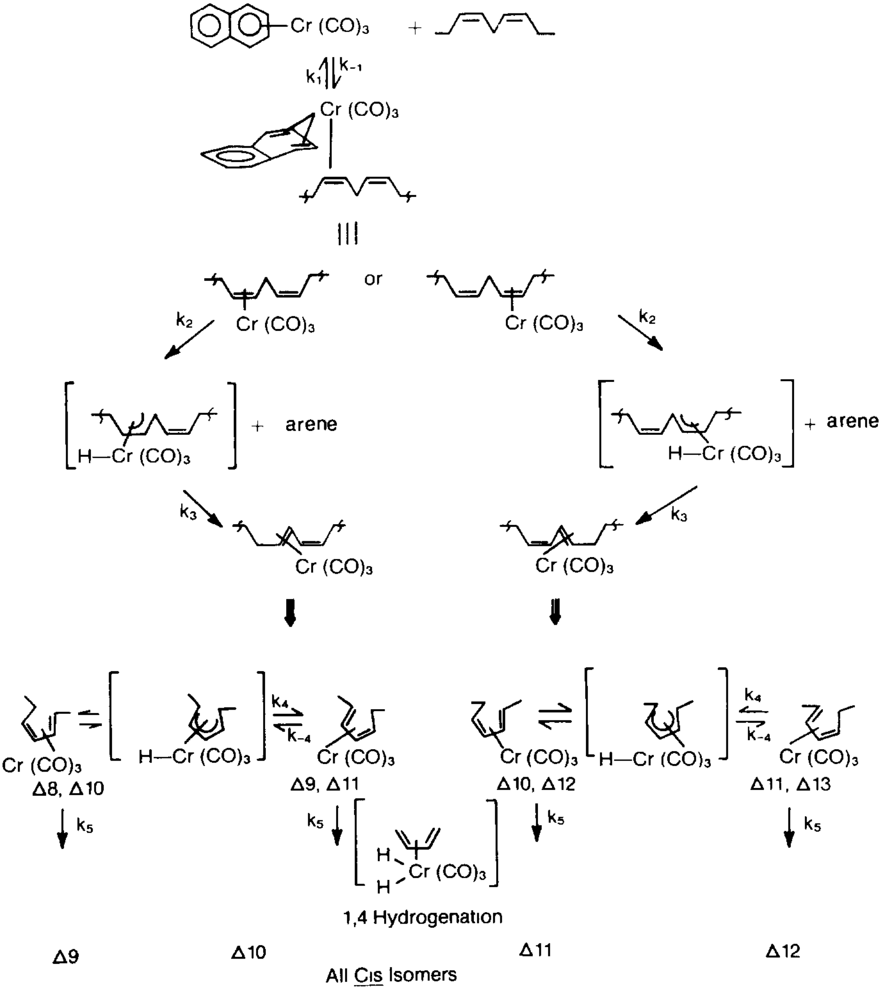

Fig. 6. Representation of the mechanism of the "$Cr(CO)_3$"-based catalysts for the isomerization and reduction of methylene interrupted dienes.

observed experimental products and their relative abundances. Any mechanism must account for the production of but four *cis*-monoenes, the methyl-*cis*-Δ^9-, -Δ^{10}-, -Δ^{11}-, and -Δ^{12}-octadecenoates, in equimolar amounts. A simple direct 1,4 addition of H_2 to a common conjugated diene intermediate will not suffice. The only mechanism that solves this dilemma requires that the isomerization of the methylene interrupted diene proceed through a "π-allyl" hydride intermediate [21] as in (Fig. 6). Assuming this mechanism, initial coordination of the diene must occur either with the Δ^9-double bond or the Δ^{12}-double bond; thus, presenting two different but equally likely and equivalent pathways (eq. 3).

$$\mathrm{Cr}(\eta^4\text{-}\mathrm{C_{10}H_8})(\eta^2\text{-diene})(\mathrm{CO})_3 \xrightarrow{k_2} \mathrm{HCr}(\pi\text{-allyl})(\mathrm{CO})_3 + \mathrm{C_{10}H_8} \tag{3}$$

Such an intermediate would be in equilibrium with the coordinatively unsaturated isomerized product, the *cis,trans*-conjugated diene shown in Fig. 6 (eq. 4):

$$\mathrm{Cr}(\pi\text{-allyl})\mathrm{H}(\mathrm{CO})_3 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{Cr(C.D.)(CO)_3} \tag{4}$$

(C.D. = conjugated diene)

Inspection of models of the *cis,trans*-conjugated diene intermediate reveals that it is uniquely poised to undergo additional isomerization by oxidative addition of one allylic methylene hydrogen; namely, the allylic C–H of the *cis*-olefinic bond. From models, one of the hydrogen atoms of this allylic methylene is observed to point directly at and to be very close to the chromium center in the *cis,trans*-conjugated diene-chromium complex. Assuming this intramolecular oxidative addition of the allylic C–H to yield a hydride pentadienyl [22] intermediate complex (Fig. 6) is fast and that the reverse reaction is fast, especially compared to the intermolecular oxidative addition of dihydrogen to the $\mathrm{Cr(C.D.)(CO)_3}$ complex (eq. 6), then only four products would be produced and in equimolar ratios (in general terms eq. 5).

$$\mathrm{HCr(C_5H_5)(CO)_3} \overset{\substack{k_4 \\ \text{fast}}}{\rightleftarrows} \mathrm{Cr(1,3\text{-}C.D.)(CO)_3} + \mathrm{Cr(2,4\text{-}C.D.)(CO)_3} \tag{5}$$

$$\mathrm{Cr(C.D.)(CO)_3} + \mathrm{H_2} \underset{k_5}{\overset{\text{fast}}{\rightarrow}} \text{“}\mathrm{Cr(CO)_3}\text{”} + cis\text{-monoene} \tag{6}$$

As can be seen in Fig. 6 this mechanism accounts for the equimolar production of only four *cis*-monoene products and it predicts correctly the position of the olefin along the eighteen carbon chain! As noted above, the first step requires the η^2-coordination of the olefin to either the *cis*-Δ^9-olefin on the *cis*-Δ^{12}-olefin of the methyl linoleate. Each mode of coordination is equally likely, but each leads down a different path to different products. If we analyze one of these paths, e.g., the one involving the initial coordination of the Δ^{12}-olefin, the model predicts that two different *cis,trans*-conjugated dienes would form in equimolar amounts: the 8,10-diene and the 9,11-diene. When these add dihydrogen in a 1,4 manner, the result would be the methyl *cis*-9- and *cis*-10-octadecenoates. The other pathway would yield the methyl *cis*-11- and *cis*-12-octadecenoates. Since both paths are equally likely, all four isomers and only those isomers would be predicted to form and in equimolar amounts, as observed.

To test this model the conjugated diene methyl *cis,trans*-9,11-octadecadienoate was independently synthesized and characterized. If the model described is correct, then hydrogenation of this substrate under conditions identical to those used for methyl linoleate should yield two *cis*-isomer products; the 9- and 10-octadecenoates in equimolar amounts. This is precisely the result that was obtained. Further use of the conjugated *trans,trans*-9,11-octadecadiene substrate yields only one isomer, the *cis*-10-monoene. This is as expected based on precedent for *trans,trans*-conjugated diene reductions with $Cr(CO)_3$ based catalysts [5,8], and it also supports our explanation that facile isomerization of the *cis,trans*-conjugated dienes arises from structural factors. Inspection of models of 1,4-disubstituted *trans,trans*-diene-metal complexes reveal that the allylic methylene hydrogen atoms are well removed from the metal and are not well positioned for close interaction with the metal center; thus, oxidative addition of the allylic C–H bond to the chromium is much less likely.

The model is also consistent with all of our other experimental observations. For example in several separate experiments using D_2 gas in place of H_2, we observe that: (1) the arene is not displaced by hydrogenation, (2) that each *cis*-monoene product contains two deuterium atoms, and (3) that the D_2 could not have added in a 1,2 fashion, since the deuterium atoms are positioned 1,4 in relation to the *cis*-monoene in each product.

It is also interesting to note that hydrogenations with (naphthalene)(tricarbonyl)chromium of both the conjugated *trans,trans*-diene and the *cis,trans*-diene are very fast [8] and will proceed even at 40 °C. This is consistent with the notion that the conjugated diene is an excellent ligand for the metal and can compete much more efficiently with the arene than can an isolated olefin for the metal. That this coordination of the olefin is an inherently unfavorable step for the methylene interrupted diene is further supported by the fact that even weakly coordinating solvents suppress the hydrogenation. Apparently this occurs because the solvent effectively competes with the olefin for the coordination sites on the metal.

Kinetic studies. In order to better define the mechanistic possibilities, the effects of different reactants on the observed rates, V, were studied. A most striking result is that the reactions involving hydrogenation of methyl linoleate show no hydrogen dependence. This is consistent with a relatively fast addition of dihydrogen (k_5) to a coordinatively unsaturated conjugated diene-chromium complex, followed by production of the *cis*-monoene product (eq. 6).

Difficulties arise in interpreting our kinetic results when the reaction order in substrate or metal are studied. We have found that the order appears to be very complex for both. A high substrate to catalyst concentration ratio gives an initial zero-order substrate dependence, but as the reaction progresses deviations from this behavior arise tending toward a higher order dependence. The metal dependence, as noted above, is also unusual. At higher temperature (135 °C) and at higher substrate to catalyst ratios (>20), the initial reaction rates obey a first-order $[Cr_{total}]$ dependence, but as the temperature is lowered there is a deviation from this behavior showing less than unity order.

These unusual results can be interpreted in terms of a slow pre-equilibrium (eq. 2). If the first step involving complexation of substrate is an inherently slow process, then an added complexity arised because the actual catalyst concentration wil not reach a steady state rapidly. As a consequence the actual metal dependence will vary early in the reaction. At higher temperatures the equlibrium will be attained more rapidly and this complexity should the be diminished and the metal dependence would approach first-order in the limit as observed.

These complex kinetic results are consistent with the observation of an induction period, which is shortened under conditions that would promote the more rapid formation of the Cr(η^4-arene)(η^2-olefin)(CO)$_3$ complex (eq. 2); i.e., higher temperatures and at higher substrate/catalyst ratios. Thus, the inherently slow reaction of the Cr(η^6-arene)(CO)$_3$ complex with substrate to give a Cr(η^4-arene)(CO)$_3$(olefin) intermediate, is observed as an induction period. Conversely, addition of naphthalene increases this induction period and slows the overall rate of reaction.

The observation of the complex substrate kinetics also needs to be addressed in terms of the mechanism of equations 2–6. As long as the [diene]/[arene] is $\gg 1$ then it is likely that the substrate could intercept the "Cr(CO)$_3$" fragment of eq. 6. to produce the HCr(π-allyl)(CO)$_3$ intermediate of eq. 4 directly. At lower ratios of [diene]/[arene], another pathway will compete; namely, interception of the "Cr(CO)$_3$" fragment with arene to yield the original η^6-complex. This forces the catalyst through the initial pathway of eq. 2. Unfortunately, due to such complexities and to the limitations of our data, we are simply not able to adequately test these details, but the mechanistic interpretation is reasonable and can account for the complexities observed in these reactions.

The true rate-determining step in these reductions, when the [substrate]/[arene] ratio is $\gg 1$ and/or at higher temperatures, would then be the rate of isomerization of an initial η^2-methylene interrupted diene complex (eq. 3) to yield a HCr(π-allyl)(CO)$_3$ complex and free arene. The high activation entropy of this catalytic reaction is not inconsistent with this interpretation, since it is logical that the oxidative addition of an unbound allylic C–H bond to the metal to yield a highly ordered π-allyl hydride would be an entropically unfavorable step [21]. This means that at higher temperatures the initial rates we observe are approximated by k_3, the initial rate of isomerization. Unfortunately, accurate rates of isomerization of the 1,4-diene to 1,3-dienes could not be determined due to side reactions not observed in the presence of H_2.

The observation of the four *cis*-monoene products also indicated that the isomerization via a pentadienyl hydride complex (eq. 5) is very fast relative to the initial complexation and isomerization (k_3) rates. Finally hydrogen addition to a 16-electron Cr(conjugated diene)(CO)$_3$ species (eq. 6, k_5) must be fast relative to k_3 and slow relative to k_4, hence the reactions show no H_2 dependence and equimolar product distributions of the *cis*-monoene positional isomers.

This catalyst system is in marked contrast to other known hydrogenation catalysts since the double bonds do not migrate up or down the carbon chain [23], but are fixed due to the presence of a pentadienyl hydride intermediate. It is also unusual indeed since it can selectively isomerize a 1,4-diene to a 1,3-conjugated diene in the presence of the *cis*-monoene products; i.e., this is a catalytic system that selectively isomerizes bis-allylic C–H positions in the presence of mono-allylic C–H's. Investigations into the possible isolation and structural characterization, as well as, reactions of key organometallic intermediates proposed in Figure 6 are in progress.

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