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ALKYLTRANSITION METAL COMPOUNDS
II.* n-ALKYLCHROMIUM SYSTEMS: OLEFIN ISOMERIZATION**

R. P. A. SNEEDEN AND H. H. ZEISS
Monsanto Research S.A., Zürich (Switzerland)

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SUMMARY

A series of experiments with the trimethyl-, triethyl-, tri-n-butyl-, tri-n-decyl- and tri-*p*-tolylchromium systems with various terminal olefins, internal olefins and 1,5-cyclooctadiene under a variety of conditions have been carried out. The results indicate that the activity of the catalyst (probably a hydrido–chromium species) and the rate of isomerization of added olefin are temperature dependent. The consistent isomerization of terminal olefins to *trans*- and *cis*-2-olefins as major product and of 1,5-cyclooctadiene to the 1,4- then the 1,3-diene is in keeping with a mechanism involving the *cis*-addition/elimination of a metal hydride species.

INTRODUCTION

It has already been established that the "decyl–chromium system" furnishes a catalyst capable of isomerizing terminal olefins[1]. Since such a reaction involves essentially the net transfer of hydrogen from one carbon atom to another, and in view of the significance of hydrogen transfer processes to the chemistry of many alkyl–transition metal compounds, the present detailed study of several n-alkyl–chromium systems was undertaken. The main objectives were to determine the influence of various reaction parameters (*e.g.* temperature, nature of olefin, nature of alkyl group attached to chromium etc.) on the overall reaction and to define the products of isomerization. It was anticipated that these studies would simultaneously lead to a better understanding of the nature of the chromium based catalyst and of the isomerization process.

RESULTS AND DISCUSSION

Influence of temperature on the activity of the "decyl–chromium system"

In order to define accurately the best conditions for the preparation of the "alkyl–chromium catalyst", a series of experiments with solvated tridecylchromium and 1-dodecene were carried out. In these, solutions of tridecylchromium were pre-

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* For Part I see ref. 1

** Part of the material in this paper was presented at the Symposium on Allyl and Olefin Complexes of Metals, University of Sheffield, England, April 1967.

pared at various temperatures and allowed to warm to −20, +20 and +65° either alone or in the presence of added 1-decene. 1-Dodecene was used to determine the catalytic activity of the resulting preparations. The results, given in Table 1, indicate that the temperature of preparation of the "decyl–chromium system" is important to the final catalytic activity. Thus when tridecylchromium is prepared at −70° and allowed to warm to 0°, an active catalytic system is obtained. On the other hand, when the same system is heated to +65° (either alone or in the presence of a non-volatile olefin), or when the "decyl–chromium system" is *prepared* at +20°, this catalytic activity is destroyed.

TABLE 1

INFLUENCE OF TEMPERATURE ON ACTIVITY OF "DECYL–CHROMIUM SYSTEM"

Temp. of preparation	Contact temp.[a] and time			Products[b]
	(°C)	(°C)	(h)	
20°	20	20	14	Decane, isomeric decenes (1.94 : 1) Dodecene, little isomerization
−70 to −20° heat to 65° (4 h)	20	20	14	Decane, isomeric decenes (1.71 : 1) Dodecene, little isomerization
−70 to −20° add 1-decene heat to 65° (4 h)	20	20	14	Decane, isomeric decenes (0.49 : 1) Dodecene, little isomerization
−70° to 0°	0	20	14	Decane, isomeric decenes (1.91 : 1) 4-isomeric dodecenes
−70° to −20°	−20	20	14	Decane, isomeric decenes (1.19 : 1) 4-isomeric dodecenes

[a] First figure is the temperature at which the 1-dodecene was added; the second is the temperature of reaction; the third is the overall reaction time. [b] Dodecane was always present in the final reaction products.

Product distribution in, and the influence of temperature on, the isomerization of olefins

The following experiments, at 0 and 20°, with the "ethyl– and decyl–chromium systems", had the combined objectives of defining the influence of temperature on the rate of isomerization of added olefin (1-octene), and of determining the rate of production of the isomeric olefins.

The results presented in Figs. 1 and 2 indicate that:

(*i*) The rate of isomerization is temperature dependent.
(*ii*) Of the two systems studied, the "decyl–chromium" is the more efficient (80% conversion of the terminal olefin as against 60% for the "ethyl–chromium system").
(*iii*) Both systems convert 1-octene rapidly (5 h) to an olefin mixture containing essentially *trans*- and *cis*-2-octene.
(*iv*) Subsequent isomerization to internal olefins (over 20 h) proceeds very slowly.
(*v*) The catalytically active species is some fragmentation product of the original alkylchromium compound.

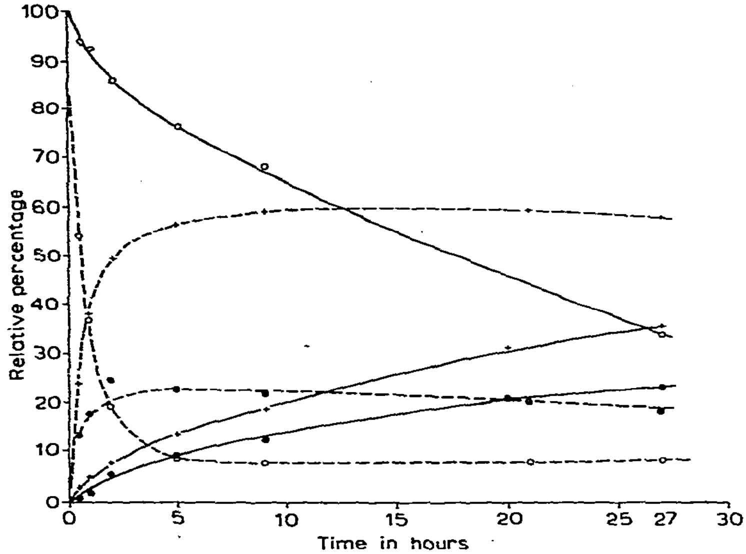

Fig. 1. Isomerization of 1-octene with the "decyl–chromium system": ———, at 0°; – – –, at 20°. ○, 1-octene and *trans*-3-octene; +, *trans*-2-octene; ●, *cis*-2-octene.

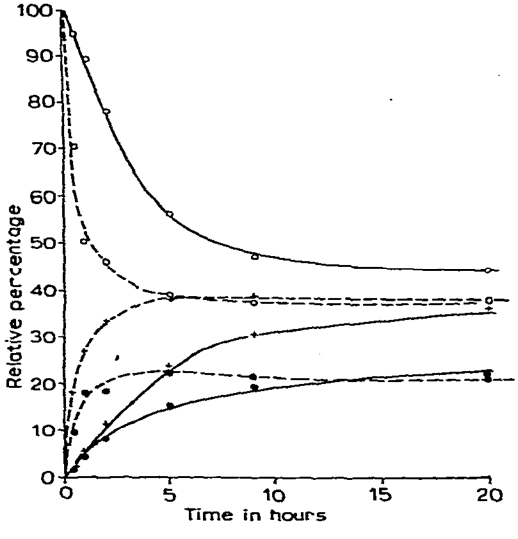

Fig. 2. Isomerization of 1-octene with the "ethyl–chromium system": ———, at 0°, – – – –, at 20°. ○, 1-octene and *trans*-3-octene; +, *trans*-2-octene; ●, *cis*-2-octene.

The alkyl–chromium systems thus resemble the rhodium, ruthenium and iridium complexes[2–4] in their catalytic activity, in that they convert terminal olefins to mixtures of *trans*- and *cis*-2-olefins. This is in contrast to other catalysts (*e.g.* platinum complexes and some metal carbonyls[5]) which rapidly convert terminal olefins to a mixture of all the possible positional and geometric isomers.

Structure of the olefin

In order to determine the influence which the structure of the olefin had upon this isomerization the "alkyl–chromium system" was allowed to react with a variety of straight chained, terminal and internal olefins, and a cyclic diene. The results, summarized in Table 2 indicate that:

(*i*) Straight chain terminal olefins, including 4-phenyl-1-butene are consistently isomerized to a mixture consisting largely of *trans*- and *cis*-2-olefins.

(*ii*) Internal olefins (*e.g. trans*- and *cis*-2-octene) are only slowly isomerized by the present "alkyl–chromium system".

TABLE 2

REACTION OF "ALKYL–CHROMIUM SYSTEM" WITH OLEFINS

Olefinic compound	Alkyl-Cr system	Products
1-Octene	Decyl	Mainly *trans*- + *cis*-2-octene[a]
1-Decene	Ethyl	Mainly *trans*- + *cis*-2-decene[a]
1-Dodecene	Decyl	Mainly *trans*- + *cis*-2-dodecene[a]
trans- + *cis*-2-Octene (37:63)	Decyl	*trans*- + *cis*-2-Octene (47:53)
trans- + *cis*-2-Octene (14:86)	Decyl	*trans*- + *cis*-2-Octene (20:80)
4-Phenyl-1-butene	Ethyl	*trans*- + *cis*-1-Phenyl-2-butene (50% conversion)
Cyclo-1,5-octadiene	Decyl	Cyclo-1,4- + -1,3-octadiene (50% conversion)

[a] The presence of small quantities of alkane and other internal olefins was detected by gas chromatographic analysis.

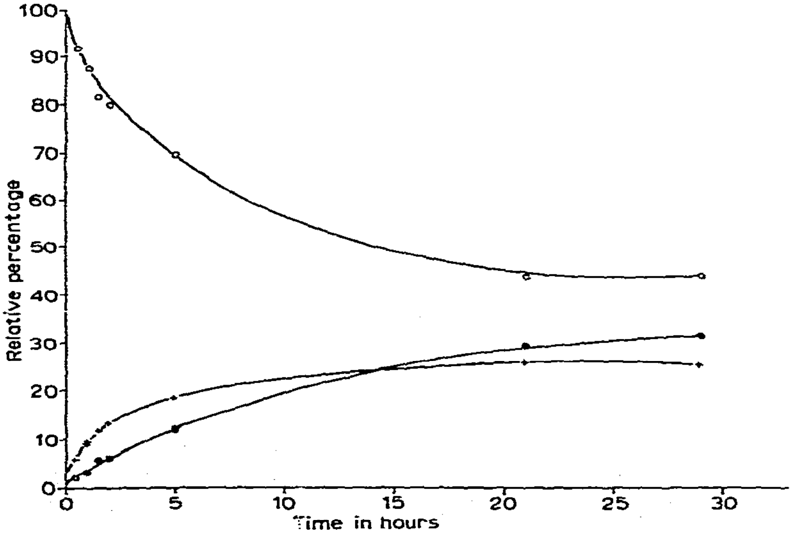

Fig. 3. Isomerization of 1,5-cyclooctadiene with the "decyl–chromium system". ○, 1,5-cyclooctadiene; +, 1,4-cyclooctadiene; ●, 1,3-cyclooctadiene.

(*iii*) 1,5-Cyclooctadiene is converted via the 1,4-isomer to the conjugated 1,3-cyclooctadiene (see Fig. 3). Thus there is again an analogy between the present "alkyl–chromium system" and the rhodium and iridium catalysts[6]. The latter catalysts are however more efficient in this isomerization (100% conversion at much higher temperatures as against 50%).

There is therefore a considerable difference in the rates with which the "alkyl–chromium system" isomerizes terminal olefins and internal olefins. Furthermore the present system will evidently not catalyze appreciably the *cis* to *trans* interconversion. It therefore now appears that steric factors may play a vital role in the present isomerization reaction.

Influence of the nature of the alkyl group attached to chromium

Most of the isomerization experiments, described up to now, were carried out with either the "ethyl– or the decyl–chromium systems". It was therefore of interest to determine whether the structure of the alkyl group attached to the chromium atom had any influence on the formation or activity of the catalyst. Experiments with the "methyl–, ethyl–, n-butyl– and n-decyl–chromium systems", indicated that in every case isomerization of an added terminal olefin occurred. With "neopentylchromium", however, little or no isomerization of added 1-octene was observed at 20° (see *Experimental*).

These limited experiments establish that the structure of the alkyl group attached to chromium influences the final activity of the "alkyl–chromium catalyst". The simplest explanation would be that, in the fragmentation of the triorganochromium compound (to active catalyst), the alkyl group attached to the chromium must be able to supply a hydrogen atom to the metal (by α- or β-elimination).

The interaction of alkylmagnesium halides and transition metal salts has been extensively studied, under a variety of conditions[7–13]. In the early work[7–9] it was reported that the final reaction products consisted of alkane, alkene and colloidal chromium (or other transition metal). It is only relatively recently* that it has been suggested that the final products at 20° are in fact the alkane, isomeric alkenes and a metal hydride (Cr–H[1], Co–H[12], Ni–H[13]).

Mechanism of the isomerization reaction

There have been many mechanisms suggested for the isomerization of terminal olefins[2–5,15,16] and in the absence of isolable intermediates any mechanism must remain speculative. However, the present evidence, together with earlier results[1] suggests that the isomerization of the terminal olefin proceeds with *cis* addition and elimination of a metal hydride. Corroboration of this is found in the fact that whereas solvated tri-*p*-tolylchromium does not isomerize terminal olefins at 20° in tetrahydrofuran, the "black intermediate" leading to π-complex (which is believed to be an arylhydridochromium species[17]) does isomerize added 1-decene (see *Experimental*).

Addition of the metal hydride to the terminal carbon atom of the olefin and subsequent elimination would give back the terminal olefin [eqn. (1)]. Addition to the β-carbon atom would give the secondary alkylchromium compound [eqn. (2), (I)].

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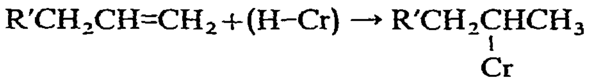
* In 1861 J. A. Wanklyn and L. Carius[14] claimed that diethylzinc reacted with $FeCl_2$ to give an "iron hydride".

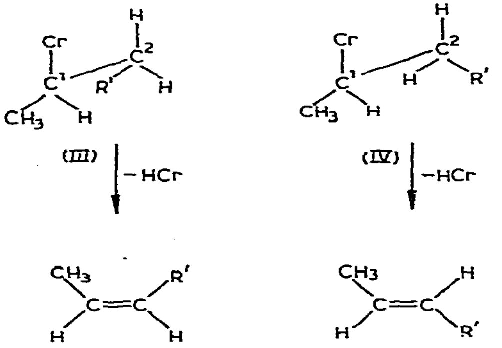
$$RCH{=}CH_2 \underset{-(H-Cr)}{\overset{+(H-Cr)}{\rightleftharpoons}} RCH_2CH_2{-}Cr \qquad (1)$$



$$R'CH_2CH{=}CH_2 + (H{-}Cr) \rightarrow R'CH_2\underset{\underset{Cr}{|}}{C}HCH_3 \qquad (2)$$

(I)

The latter can adopt the conformations (III) or (IV), the repulsion between the bulky groups Cr and CH_3 on C^1, and R′ on C^2, make the latter [(IV)] the more stable for the elimination step.



cis-Elimination of metal hydride from the intermediates (III) and (IV) lead to the *cis*- and *trans*-2-olefin respectively. Since it is probable that the conformer (IV) preponderates, there will be more of the *trans*-olefin formed.

Of the many possible explanations for the observation that the subsequent isomerization to the other internal olefins is slow there are three major ones which are consistent with the present accumulated evidence: (*i*) steric factors influencing the rates of addition of the hydrido-species to *cis*- and *trans*-internal olefins, (*ii*) decomposition or consumption of the catalyst, (*iii*) the possibility that the fragmentation of secondary alkylchromium compounds proceed essentially by a homolytic process to give inactive colloidal metal whereas the n-alkylchromium compounds undergo fragmentation to give amongst other products active metal hydrides.

The present evidence alone, though supporting the metal hydride mechanism does not enable any discrimination between these possibilities and thus further experiments have been undertaken to clarify these points.

EXPERIMENTAL

(with Mr. N. Moser)

The techniques used in the handling of organometallic compounds and the gas chromatographic analyses of alkane/alkene mixtures have already been described[1].

Identification of products

Throughout the present work the hydrocarbons were identified by a direct comparison of their gas chromatographic retention times with those of authentic specimens. The *trans*-5-, -4-, -3-, -2-decenes, 1-decene, *trans*-4-, -3-, -2-octenes, *cis*-2-octene and 1-octene were supplied by Chemical Samples Co., Columbus, Ohio, USA. The phenylbutane, *trans*-4-phenyl-1-butene, *trans*-1-phenyl-1- and -2-butenes were supplied by Fluka AG, Buchs, Switzerland. The 1,4- and 1,3-cyclooctadienes were very kindly supplied by Dr. J. K. Nicholson whilst with MRSA Zürich.

Any other identification procedure is mentioned in the appropriate place in the text.

Influence of temperature on the activity of the decyl–chromium system

In this series of reactions, decylmagnesium chloride in tetrahydrofuran (40 ml, 25.2 mmoles) was allowed to react with a biskly stirred suspension of $CrCl_3(THF)_3$ (3.14 g, 8.4 mmoles), also in tetrahydrofuran (50 ml). The reaction was carried out at various temperatures, (Table 1, column 1), either in the absence or presence of added oxygen-free 1-decene (10 ml, 53 mmoles). The "catalyst" solutions thus prepared were treated with 1-dodecene (10 ml, 45 mmoles), and then allowed to stand at 20° overnight (Table 1, column 2). The reaction mixture was hydrolyzed and the hydrocarbons, isolated with the aid of ether, were subjected to gas chromatographic analysis (Table 1, column 3).

"Decyl– and ethyl–chromium systems" with 1-octene

In two parallel experiments, tetrahydrofuran solutions of tridecylchromium were prepared by the interaction of decylmagnesium chloride (40 ml, 27.2 mmoles) and $CrCl_3 \cdot (THF)_3$ (3.4 g, 9.06 mmoles) in tetrahydrofuran (50 ml) at -70 to $-30°$. In one experiment the resulting solution was warmed to 0°, treated with 1-octene (10 ml) at 0°, and subsequently allowed to stand at 0° for 30 h. In the second experiment, the resulting solution was allowed to warm to 20°, treated with 1-octene at 20°, and subsequently allowed to stand at 20° for 30 h. In both cases, aliquots (5 ml) were withdrawn periodically (see Fig. 1), hydrolyzed, and the resulting hydrocarbon mixture (isolated with the aid of ether) analyzed gas chromatographically* (see Fig. 1).

Two other identical experiments were carried out with the "ethyl–chromium system" [from ethylmagnesium bromide (40 ml, 22 mmoles) and $CrCl_3 \cdot (THF)_3$ (2.73 g, 7.3 mmoles) in tetrahydrofuran (50 ml)] and 1-octene (10 ml). The results are represented by Fig. 2.

At the end of all four experiments the *trans*-2-octene was isolated by preparative scale gas chromatography and identified by a direct comparison of its IR and NMR spectra with those of authentic specimens.

Isomerization of various olefins with "alkyl–chromium systems"

In all the following experiments the "alkyl–chromium systems" were prepared by the interaction of the appropriate alkylmagnesium halide and $CrCl_3 \cdot (THF)_3$, in tetrahydrofuran at $-70°$ to $-30°$. The olefin was added at $-20°$, the reaction mixture allowed to warm to 20° (usually 14 h), hydrolyzed, and the hydrocarbons,

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* In the gas chromatographic analysis of the octenes, on a bis(methoxyethyl) adipate column, the *cis*- and *trans*-2-octene and *trans*-4-octene came as well separated peaks, 1-octene and *trans*-3-octene came together as an asymmetric peak.

isolated with the aid of ether, subjected to gas chromatographic analysis. The results are given in Table 2.

(1) *1-Octene, 1-decene and 1-dodecene.* These reactions with the title olefins were carried out with: the "decyl–chromium system" [decylmagnesium chloride (50 ml, 29 mmoles) and $CrCl_3 \cdot (THF)_3$ (3.6 g, 9.66 mmoles)], the "ethyl–chromium system" [ethylmagnesium bromide (40 ml, 32 mmoles) and $CrCl_3 \cdot (THF)_3$ (3.99 g, 10.6 mmoles) and the "decyl–chromium system" [decylmagnesium chloride (40 ml, 29.2 mmoles) and $CrCl_3 \cdot (THF)_3$ (3.6 g, 9.7 mmoles)], respectively.

(2) *cis- and trans-2-Octene, ratio* 63:37 *and* 86:14. The olefins for these reactions were Fluka "*cis,trans* mixture" and "*cis*": gas chromatographic analysis established the compositions given in the title.

The isomerization experiments were attempted with the "decyl–chromium system" [decylmagnesium chloride (40 ml, 17.2 mmoles) and $CrCl_3 \cdot (THF)_3$ (2.14 g, 5.7 mmoles].

(3) *4-Phenyl-1-butene.* The 4-phenyl-1-butene was obtained by the controlled interaction of allylmagnesium chloride (1 mole) and benzyl chloride (0.5 mole). The crude hydrocarbon was filtered through active alumina, and subsequently distilled over sodium. The 4-phenyl-1-butene obtained in this way had n_D^{20} 1.5058 (lit. 1.5062). ν_{max} 995 and 905 cm^{-1} (no band at 960 cm^{-1}) and was homogeneous on gas chromatographic analysis.

The isomerization experiments were carried out with the "ethyl–chromium system". The products were identified* a direct comparison of their gas chromatographic retention times and IR spectra (for the terminal and *trans*-2-olefin) with authentic specimens.

(4) *Cyclo-1,5-octadiene.* The olefin used in this experiment was purified by filtration through alumina, and subsequent distillation from sodium. The commercial olefin is not isomerized.

The isomerization was carried out with the "decyl–chromium system" [decylmagnesium chloride (50 ml, 21.5 mmoles) and $CrCl_3 \cdot (THF)_3$ (2.65 g, 7.2 mmoles)]. The procedure was similar to that described for the experiments with 1-octene above, aliquots were withdrawn periodically and the hydrocarbons analyzed by gas chromatography, the results are represented in Fig. 3.

Isomerization with the "methyl–chromium system"

Methylmagnesium chloride (60 ml, 56.4 mmoles) and $CrCl_3 \cdot (THF)_3$ (7 g, 18.8 mmoles) were allowed to interact at −70° in tetrahydrofuran (50 ml). The reaction mixture was allowed to warm to −20°, and 1-octene (20 ml) added. The resulting mixture was warmed to 20° (14 h), hydrolyzed, and the hydrocarbons, isolated with the aid of ether were shown, by gas chromatographic analysis to consist of octane (4.25%), 1-octene (40%), *trans*-2-octene (33%), *cis*-2-octene (22%).

Attempted isomerization with neopentylchromium

Neopentylmagnesium bromide (100 ml, 22.5 mmoles) and $CrCl_3 \cdot (THF)_3$ (2.8 g, 7.5 mmoles) were allowed to interact at −70°, in tetrahydrofuran (50 ml). The

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* The presence of 4-phenylbutane (10%) and traces of a substance with the same retention time as tetralin were also detected.

reaction mixture was allowed to warm to 20°, at which temperature a homogeneous blue-violet solution was obtained. 1-Decene (10 ml) was added, and the whole allowed to stand at room temperature for 14 h. The hydrocarbons, isolated with the aid of ether after hydrolysis, were shown by gas chromatographic analysis to consist essentially of 1-decene, together with traces of *cis*- and *trans*-2-decene. The 1-decene fraction was isolated by preparative scale gas chromatography and identified as such by a direct comparison of its IR and NMR spectrum with those of an authentic sample.

Reaction with solvated tri-p-tolylchromium

(1) *At* 20°. A solution of solvated tri-*p*-tolylchromium [from *p*-tolylmagnesium bromide (50 ml, 40.6 mmoles) and $CrCl_3 \cdot (THF)_3$ (5 g, 13.3 mmoles)] in tetrahydrofuran[18] and 1-decene were allowed to stand at 20° for 20 h. The homogeneous red reaction mixture was hydrolyzed and the hydrocarbons, isolated with the aid of ether, were shown by gas chromatographic analysis to consist of toluene and 1-decene.

The 1-decene was isolated by fractional distillation and its identity established by a direct comparison of its IR and NMR spectra with those of authentic material.

(2) *At* 65°. In an analogous experiment, the tetrahydrofuran solution of tri-*p*-tolylchromium and 1-decene was heated under reflux for 3 h, cooled and hydrolyzed. The organometallic compounds consisted of a mixture of bis(arene)–chromium π-complexes, isolated as their tetraphenylborates. Crystallization of the crude material from acetone gave finally pure bis(π-toluene)chromium(I) tetraphenylborate as yellow plates, m.p. 232° (decompn.). The identity of the material was established by a direct comparison of its X-ray powder photograph with that of an authentic specimen[18]. The hydrocarbons were isolated with the aid of ether and were shown by gas chromatographic analysis (Silicone column) to consist of "decenes", toluene and *p,p'*-ditolyl. Gas chromatographic analysis of the hydrocarbon mixture on Carbowax 20 M revealed the presence of 1-decene, *trans*-2-decene and *cis*-2-decene. The *trans*-2-decene was isolated by preparative scale gas chromatography and identified by a direct comparison of its IR and NMR spectra with those of an authentic specimen.

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