

CONVENTION

AUSTRALIA

Patents Act

APPLICATION FOR A STANDARD PATENT

595896

I/We The Dow Chemical Company

of 2030 Dow Center,  
Abbott Road,  
Midland,  
Michigan 48640,  
UNITED STATES OF AMERICA.

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED

8-2-80

hereby apply for the grant of a standard patent for an invention entitled:

PROCESS FOR PROPYLENE DIMERIZATION

which is described in the accompanying complete specification.

Details of basic application

Number of basic application: 902,740

Convention country in which basic application was filed: UNITED STATES OF AMERICA

Date of basic application : 2 September 1986

Address for Service:

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Dated: 23 June 1987

PHILLIPS ORMONDE & FITZPATRICK  
Attorneys for:  
The Dow Chemical Company,

FEE STAMP TO VALUE OF  
1,170..... ATTACHED  
MAIL OFFICER.....

By:

*David B Fitzpatrick*

Our Ref : 59288  
POF Code: 1037/1037

LODGED AT SUB-OFFICE  
- 2 JUL 1987  
Melbourne



AUSTRALIA

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AUSTRALIA Patent Declaration

DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS

- (a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)
(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

In support of the (a) CONVENTION application made by (b) THE DOW CHEMICAL COMPANY 2030 Dow Center, Abbott Road, Midland, Michigan 48640, United States of America (hereinafter called "applicant(s)" for a patent (c) for an invention entitled (d) PROCESS FOR PROPYLENE DIMERIZATION

- (e) Insert FULL name(s) AND address(es) of declarant(s)
(f) Insert FULL name(s) AND address(es) of actual inventor(s)
(g) Recite how applicant(s) derive(s) title from actual inventor(s)
(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application
(k) Insert PLACE of signing
(l) Insert DATE of signing
(m) Signature(s) of declarant(s)

I/We (e) Richard G. Waterman, General Patent Counsel THE DOW CHEMICAL COMPANY 2030 Dow Center, Abbott Road, Midland, Michigan 48640, United States of America do solemnly and sincerely declare as follows:

- 1. I am/We are the applicant(s) (or, in the case of an application by a body corporate)
2. I am/We are authorized to make this declaration on behalf of the applicant(s)
2. I am/We are the actual inventor(s) of the invention (or, where the applicant(s) is/are not the actual inventor(s))
2. (f) James C. Stevens, 2704 Georgetown, Midland, State of Michigan 48640, United States of America William A. Fordyce, 4103 Washington, Midland, State of Michigan 48640, United States of America
is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:
(g) The applicant Company is the assignee of the said invention from the said actual inventor(s).

(Note: Paragraphs 3 and 4 apply only to Convention applications)

- 3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date, and basic applicant(s) as follows:
(b) U.S. Priority Serial No. 902,740 Filing Date: September 2, 1986 Applicants: James C. Stevens William A. Fordyce United States of America
4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at (k) Midland, Michigan, 48640, Dated (l) June 12 1987 U.S.A. (m) THE DOW CHEMICAL COMPANY

CORP. SEAL

SIGNATURE AS TYPED

Richard G. Waterman signature

RICHARD G. WATERMAN General Patent Counsel

To: The Commissioner of Patents By:

Agent: Phillips, Ormonde & Fitzpatrick

(12) PATENT ABRIDGMENT (11) Document No. AU-B-75033/87  
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 595896

- (54) Title  
PROCESS FOR PROPYLENE DIMERIZATION TO 4-METHYL-1-PENTENE
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- (71) Applicant(s)  
THE DOW CHEMICAL COMPANY
- (72) Inventor(s)  
JAMES C. STEVENS; WILLIAM A. FORDYCE
- (74) Attorney or Agent  
PHILLIPS,ORMONDE & FITZPATRICK
- (56) Prior Art Documents  
EP 268214

(57) The present invention is such a process comprising contacting propylene and a catalyst comprising an element selected from uranium or the rare earth metals under reaction conditions such that 4-methyl-1-pentene is selectively produced. Uranium di(poly-substituted cyclopentadienyl)-hydride complexes are especially selective catalysts. Surprisingly, high selectivity to 4-methyl-1-pentene is obtained using the present invention. The unexpectedly high selectivity advantageously reduces the need for expensive and difficult separation of C<sub>6</sub> by-products.

#### CLAIM

1. A process for the preparation of 4-methyl-1-pentene, comprising contacting propylene and a catalyst comprising at least one <sup>metal or compound of the</sup> element selected from uranium and the rare earth metals under reaction conditions to produce 4-methyl-1-pentene.

AUSTRALIA

Patents Act

COMPLETE SPECIFICATION  
(ORIGINAL)

Application Number:  
Lodged:

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Int. Class

59 5896

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Accepted:  
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This document contains the  
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Section 49 and is correct for  
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Name(s) of Applicant(s):

The Dow Chemical Company

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Complete Specification for the invention entitled:

PROCESS FOR PROPYLENE DIMERIZATION

Our Ref : 59288  
POF Code: 1037/1037

The following statement is a full description of this invention, including  
the best method of performing it known to applicant(s):

6003q/1

### PROCESS FOR PROPYLENE DIMERIZATION

5 The present invention relates to a process for the dimerization of olefins. More specifically, the invention relates to a new method for the preparation of 4-methyl-1-pentene.

10 The compound 4-methyl-1-pentene is useful as a monomer or as a comonomer in the production of polyolefins. Typically, 4-methyl-1-pentene is produced via the catalytic dimerization of propylene. Commonly employed catalysts include those containing alkali metals or nickel. Low-selectivity catalysts include thorium nitrate,  $WCl_6$ , titanium, aluminum alkyls, such as cerium acetylacetonate/aluminum alkyls and certain mixtures of these. Alkali metal catalysts are numerous, but are disadvantageous in that they require high operating temperatures and pressures. Catalysts previously employed for the preparation of 4-methyl-1-pentene via propylene dimerization are all unsatisfactory to the extent that they are not as selective as would be desired. While selectivities to 4-methyl-1-pentene of up to 93 percent have been reported

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(Chemical Abstracts, 100:102722n, using a Na/K-based catalyst), even this is unsatisfactory in view of the difficulty and expense involved in separating 4-methyl-1-pentene from the commonly coproduced C<sub>6</sub> olefin and C<sub>6</sub> alkane by-products.

United States Patent 3,994,945 discloses uranium (IV) tetraallyl compounds and certain halide derivatives thereof. The halide compounds are reported to be useful as catalysts in the stereospecific polymerization of diolefins.

United States Patent 3,816,372 discloses uranium (IV) complexes containing metal carbonium  $\sigma$  bonds. Ligands such as allyl, cyclobutadienyl and cyclopentadienyl are taught to be coordinated to the metal by  $\Pi$  bonds. The compounds are disclosed as being useful in the oligomerization of olefins and diolefins, and in the insertion reaction of neutral molecules such as CO and NO.

United States Patents 3,655,811 and 3,808,150 disclose catalyst compositions consisting essentially of (a) an actinide series metal compound such as thorium nitrate tetrahydrate, (b) a reducing agent, (c) a non-protonic Lewis acid and, as optional preferred ingredients, (d) a trihydrocarbylphosphine and (e) an inert, organic solvent. The catalyst composition is disclosed as being useful for catalyzing the polymerization of olefins or phenyl-substituted olefins to normally liquid polymers or oligomers, such as catalyzing the dimerization of propylene. Table II in each of said patents indicates that the catalyst compositions are not selective to 4-methyl-1-pentene.

In view of the deficiencies of prior art methods, it would be desirable to have a process which would provide improved selectivity to 4-methyl-1-pentene.

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The present invention is such a process comprising contacting propylene and a catalyst comprising an element selected from uranium or the rare earth metals under reaction conditions such that 4-methyl-1-pentene is selectively produced. Uranium di(poly-substituted cyclopentadienyl)-hydride complexes are especially selective catalysts. Surprisingly, high selectivity to 4-methyl-1-pentene is obtained using the present invention. The unexpectedly high selectivity advantageously reduces the need for expensive and difficult separation of C<sub>6</sub> by-products.

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The process of the present invention advantageously employs a catalyst, propylene and, optionally, a solvent.

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Propylene is commercially available, and can be prepared by a number of known methods. In the process of the present invention, propylene can be employed as a gas, a liquid or both.

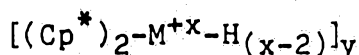
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For the purposes of the present invention, the term "selective" and variations thereof refer to processes which can produce 4-methyl-1-pentene from propylene with a selectivity, as defined hereinafter, of at least 94 mole percent. In the general sense, the term "selectivity" is defined as the moles of 4-methyl-1-pentene in the product stream divided by the total number of moles of reaction products in the reactor effluent stream. Selectivity can also be measured with

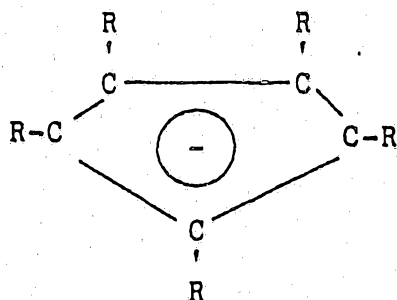
respect to other C<sub>6</sub> olefins or with respect to all C<sub>6</sub> compounds in the product stream. High selectivity with respect to other C<sub>6</sub> olefins is especially important as the separation of other C<sub>6</sub> olefins from 4-methyl-1-pentene is the most difficult separation involved in recovering 4-methyl-1-pentene from the product stream.

The process of the present invention advantageously employs a catalyst comprising at least one element selected from uranium or the rare earth metals. For the purposes of the present invention the rare earth metals include elements having atomic numbers from 57 through 71, i.e., lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Catalysts comprising U, La or Nd are preferred. Mixtures of catalytic metal elements can be employed. Preferred catalysts to be employed in the process of the present invention include uranium or rare earth metal di(poly-substituted cyclopentadienyl)-hydride complexes. The poly-substituted cyclopentadienyl ligands can bear a wide variety of substituents so long as the resulting ligand is substantially inert with respect to propylene, and so long as the substituents are of sufficient size to provide sufficient steric hindrance to make the catalyst composition capable of selectively producing 4-methyl-1-pentene from propylene. More preferred catalysts are represented generally by the formula:



wherein Cp\* is a poly-substituted cyclopentadienyl ligand, M is a metal selected from the group consisting

of uranium and elements having atomic numbers 57 through 71, x can be 3 or 4 and represents the valence of the metal M, and y can be 1 or 2. Preferably, each Cp\* independently is a moiety of the formula:



wherein each R independently is H, alkyl of up to 6 carbon atoms or alkyl substituted silyl such as, for example, trimethylsilyl and triethylsilyl, with the proviso that at least about two R moieties are not H. Preferably, each R is methyl and Y, preferably, is 2. Examples of catalysts which can be employed in the process of the present invention include bis-(pentahaptotetramethylcyclopentadienyl) uranium hydride, bis-(pentahaptobutyltetramethylcyclopentadienyl) uranium hydride, bis-(pentahaptoethyltetramethylcyclopentadienyl) uranium dihydride, bis-(pentahaptopentamethylcyclopentadienyl) uranium hydride, bis-(pentahapto-bis-(trimethylsilyl)cyclopentadienyl) uranium hydride, bis-(pentahaptopentamethylcyclopentadienyl) neodymium hydride, and bis-(pentahaptopentamethylcyclopentadienyl) lanthanum hydride. Bis-(pentahaptopentamethylcyclopentadienyl) uranium hydride is known to exist as a dimer (M = U, y = 2) in which the uranium is present as an equilibrium mixture of the +3 and +4

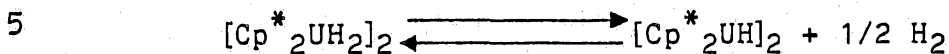
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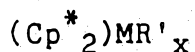
valences. Accordingly, the number of hydride ligands can equal 1 and 2 for this compound:



The most preferred catalyst is bis-(pentahapto-pentamethylcyclopentadienyl) uranium hydride.

10 The preparation of bis-pentamethylcyclopentadienyl uranium alkyls and hydride is reported in J.A.C.S. by Juan M. Manriquez, et al., Vol. 100, pp. 3939-3941 (1978). The preparation of di-  
15 (bis(trimethylsilyl)cyclopentadienyl) uranium dichloride and di-(bis(trimethylsilyl)cyclopentadienyl) uranium dialkyls are reported by Peter B. Hitchcock et al. in J. Chem. Soc., "Chem. Commun.," pp. 561-563 (1983). The preparation of bis-(pentamethylcyclopentadienyl) neodymium hydride and bis-(pentamethylcyclopentadienyl) lanthanum hydride are reported in J.A.C.S., by Gerald Jeske et al., Vol. 107, pp. 8091-8103 (1985).

25 The catalyst can be prepared as described hereinabove or, alternatively, the active catalyst of the present invention can be generated in situ by  
30 subjecting a solution of a uranium di(poly-substituted-cyclopentadienyl) complex to gaseous hydrogen in order to pre-form the hydride catalyst. After removal of the unreacted hydrogen, the catalyst solution is contacted with propylene. Preferred catalyst compositions for  
35 this in situ catalyst generation can be represented by the formula:



5 wherein each R' independently can be a hydrocarbon moiety or a silicon-containing hydrocarbon moiety; and M, x and Cp\* are as described previously. Most preferably, Cp\* is pentahaptopentamethylcyclopentadienyl.

10 The term "hydrocarbon" is well known to those skilled in organic chemistry and refers to a moiety or compound consisting essentially of atoms of carbon and hydrogen. Hydrocarbon moieties can be aromatic or aliphatic; can be saturated or unsaturated; can have carbon chains which are branched, cyclic or straight, and can have mixtures of these attributes. Preferred hydrocarbon moieties have up to 20 carbon atoms and include alkyl, alkenyl, aryl, alkaryl or aralkyl.

15 20 Examples of hydrocarbon moieties include methyl, ethyl, butyl, phenyl, allyl and benzyl. Lower alkyl and lower alkenyl of up to 6 carbon atoms are more preferred.

25 The term "silicon-containing hydrocarbon" refers to hydrocarbons which contain at least one atom of silicon. Examples of silicon-containing hydrocarbon moieties include trimethylsilyl methyl and bis-(trimethylsilyl methyl).

30 It is preferred that the catalyst be employed in a substantially inert environment, i.e., an environment having propylene as essentially the only reactive component of a feed stream. The catalyst of the present invention is, in its purified form,  
35 sensitive to air, water and other materials which provide a source of acidic protons. Accordingly, it is

preferred that the catalyst compositions of the present invention be maintained in an environment which is substantially inert with respect to degradation of the catalyst. This proviso does not apply to the presence  
5 of propylene.

The catalyst is employed in a catalytic amount. Typically, from  $1 \times 10^{-5}$  to  $1 \times 10^{-1}$  weight parts catalyst are employed per weight part propylene.  
10 Preferably, from  $1 \times 10^{-4}$  to  $1 \times 10^{-2}$  weight parts catalyst are employed per weight part propylene.

A solvent is optionally employed in the process of the present invention. The function of the solvent is to assist in the dissolution of the catalyst, or to function as a reaction medium for the in situ formation of the active catalyst by hydrogenation of an alkyl-containing precursor. Examples of typical solvents  
15 include saturated hydrocarbons, such as pentane, hexane, heptane, octane and other normal or branched saturated paraffins; aromatic hydrocarbons, such as benzene, xylene and other alkyl benzenes; cyclic saturated hydrocarbons, such as cyclopentane and cyclohexane, as well as mixtures thereof. Liquid propylene can be employed as a solvent. Toluene is the preferred solvent. The amount of solvent can be varied  
20 widely. Typically, from 5 to 50 weight parts of solvent are employed per weight part of propylene.

The process of the present invention can be operated at any combination of temperature and pressure at which 4-methyl-1-pentene is selectively produced. Typically, the process is conducted at a temperature  
25 ranging from just above the freezing point of the reaction mixture to just below the temperature at which  
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the catalyst decomposes. Preferably, the temperature is from 10°C to 180°C. In general, the reaction proceeds more slowly at lower temperatures. Typically, the process is conducted at a pressure of from 1 to 500 atmospheres (101 to 505 kPa). In general, the reaction proceeds faster as the pressure increases. The reaction rate is a function of temperature, pressure, catalyst concentration, and propylene concentration.

When propylene and a catalyst are contacted under reaction conditions as described hereinabove, 4-methyl-1-pentene is selectively produced. Typically, the selectivity is at least 94 mole percent, preferably at least 96 mole percent, more preferably at least 98 mole percent and most preferably, greater than 99 mole percent. This selectivity can be overall selectivity, i.e., based on all products produced, or it can be selectivity with respect to C<sub>6</sub> alkanes or with respect to C<sub>6</sub> olefins, or all C<sub>6</sub> compounds.

The following examples are given to illustrate the invention and should not be construed as limiting its scope. All parts and percentages are by weight unless otherwise indicated. Cp\* represents the pentamethylcyclopentadienyl moiety in the examples.

#### Example 1

A 100 ml stainless steel bomb was taken into an argon-filled inert atmosphere drybox (<0.2 ppm O<sub>2</sub>) and into the bomb were placed a Teflon®-coated magnetic stir-bar, 15.9 mg of (UCp\*<sub>2</sub>H<sub>2</sub>)<sub>2</sub>, and 25.0 µl each of heptane and 2,2-dimethylbutane (GC internal standards). The bomb was sealed, was removed from the inert atmosphere box and the temperature was maintained at

25°C. Liquid propylene (23 g, 45 ml), which was purified in order to remove oxygen, water and other detrimental species, was added to the bomb. Catalysts which can be employed to remove water, oxygen and other paramagnetic impurities are well known in the art, and include such materials as molecular sieves, alumina, silica and finely divided copper on an alumina matrix, such as Dow Q1<sup>®</sup> catalyst, available from The Dow Chemical Company.

The contents of the bomb were magnetically stirred for 72 hours at 25°C. After 72 hours, the bomb was vented and the contents were analyzed by gas chromatography using a Hewlett-Packard 5880 GC with a 60 meter J & W Narrow Bore Capillary Column bonded with DB-1. The analysis showed 737.2 turnovers (moles of product/moles of uranium) to 4-methyl-1-pentene. The overall selectivity to 4-methyl-1-pentene was 97.84 percent. The major by-products were easily separated C<sub>9</sub>'s (1.774 percent). The selectivity to 4-methyl-1-pentene with respect to other C<sub>6</sub>'s was 99.611 percent.

Example 2

The procedure was identical to that of Example 1 except that the reaction was allowed to proceed at 40°C for 168 hours and 5.9 mg of (UCp\*<sub>2</sub>H<sub>2</sub>)<sub>2</sub> was employed. Analysis by gas chromatography showed a total of 3149.9 turnovers to 4-methyl-1-pentene with an overall selectivity of 95.27 percent and a selectivity to 4-methyl-1-pentene with respect to other C<sub>6</sub>'s of 99.642 percent.

Example 3

5 The procedure was identical to that of  
Example 1 except that the reaction was allowed to  
proceed at 10°C for 72 hours and 9.7 mg of  $(UCp^*_2H_2)_2$   
was employed. Analysis by gas chromatography showed a  
total of 416.9 turnovers to 4-methyl-1-pentene with an  
10 overall selectivity of 98.16 percent and a selectivity  
to 4-methyl-1-pentene with respect to other C<sub>6</sub>'s of  
99.403 percent.

Example 4

15 The procedure was identical to that of  
Example 1 except that the reaction was allowed to  
proceed at 55°C for 72 hours and 10.5 mg of  $(UCp^*_2H_2)_2$   
was employed. Analysis by gas chromatography showed a  
total of 1925.3 turnovers to 4-methyl-1-pentene with an  
20 overall selectivity of 95.24 percent and a selectivity  
to 4-methyl-1-pentene with respect to other C<sub>6</sub>'s of  
99.561 percent.

Example 5

25 The procedure was identical to that of  
Example 1 except that 5.0 ml of toluene was added to  
the bomb in the drybox as a solvent and the reaction  
was allowed to proceed at 60°C for 15 hours, and 12.0 mg  
30 of  $(UCp^*_2H_2)_2$  was employed. Analysis by gas  
chromatography of the reaction products showed a total  
of 404.6 turnovers with an overall selectivity to 4-  
methyl-1-pentene of 97.46 percent and a selectivity to  
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4-methyl-1-pentene with respect to other C<sub>6</sub>'s of 99.440 percent.

Example 6

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The procedure was identical to that of Example 1 except that 11.0 mg of NdCp\*<sub>2</sub>H was employed as the catalyst and the reaction was allowed to proceed at 40°C for 18 hours. After cooling and venting, the contents of the bomb were analyzed using capillary gas chromatography. Analysis by gas chromatography showed a total of 3.7 turnovers with an overall selectivity of 31.88 percent and a selectivity with respect to other C<sub>6</sub>'s of 91.259 percent.

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Example 7

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A 100 ml stainless steel bomb was taken into an argon-filled inert atmosphere drybox (< 0.2 ppm O<sub>2</sub>) and into it was placed a Teflon-coated magnetic stir-bar, 10.4 mg of (UCp\*<sub>2</sub>H<sub>2</sub>)<sub>2</sub>, 5.0 ml of toluene and 25.0 µl of heptane (GC internal standard). The bomb was sealed, removed from the inert atmosphere box and heated to 25°C. The bomb was charged with 125 psig (860 kPa gauge) of propylene gas at 25°C, then sealed and heated to 60°C for a total of 15 hours. The bomb was then cooled, vented, opened and the contents were analyzed by capillary gas chromatography. The analysis revealed the formation of 4-methyl-1-pentene with a catalyst efficiency of 421.2 turnovers and an overall selectivity to 4-methyl-1-pentene of 96.71 percent. The selectivity with respect to other C<sub>6</sub>'s was 99.644 percent.

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Example 8

5 A 300 ml stainless steel bomb was taken into an argon-filled inert atmosphere drybox (<0.2 ppm O<sub>2</sub>) and into it was placed 156.6 mg of UCp\*<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>, 50 ml of toluene, and 500 ml of cyclohexane (GC internal standard). The bomb was sealed, removed from the drybox and charged with 600 psig (4100 kPa gauge) of hydrogen gas to form the catalyst in situ. The 10 solution was stirred at room temperature for 2 hours, after which time the hydrogen was vented. The bomb was then charged with 200 ml of liquid propylene and was heated to 50°C. Samples were taken periodically for capillary GC analysis. The analysis revealed the 15 formation of 4-methyl-1-pentene with an initial rate of 70 turnovers per hour and a total of 2901 turnovers after 136.1 hours. The overall selectivity was 94.3 percent and the selectivity with respect to other 20 C<sub>6</sub>'s was 99.3 percent.

Example 9

25 The procedure was identical to that of Example 8 except that 155.2 mg of UCp\*<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub> was used to form the catalyst in situ and the reaction was allowed to proceed at 25°C. Samples taken for analysis revealed the formation of 4-methyl-1-pentene with an 30 initial rate of 40 turnovers per hour and a total of 1,925 turnovers after 302 hours. The overall selectivity was 96.3 percent and the selectivity with respect to other C<sub>6</sub>'s was 99.2 percent.

Example 10

35 The procedure was identical to that of Example 8 except that 31.2 mg of uranium bis-(1,3-bis-

trimethyl-silylcyclopentadiene)bis-trimethylsilylmethyl  
was used, 500  $\mu$ l of heptane was used for the GC  
internal standard, and the reaction was allowed to  
proceed at 50°C for 22.5 hours. GC analysis showed the  
5 formation of 4-methyl-1-pentene.

Example 11

10 A 100 ml flask was charged with 20 mg of  
 $Cp^*_2La(CH(SiMe_3)_2)$ . Hydrogen gas was admitted to the  
flask at 1 atmosphere pressure, and the solid was  
allowed to stand at room temperature overnight in the  
presence of hydrogen. The hydrogen was then removed  
and 5 ml of toluene was added, followed by propylene  
15 gas in an amount sufficient to bring the pressure in  
the flask to 1 atmosphere, gauge (101 kPa gauge). The  
mixture was allowed to stir for 16 hours. Capillary GC  
analysis of the reaction mixture showed the presence of  
4-methyl-1-pentene.  
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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of 4-methyl-1-pentene, comprising contacting propylene and a catalyst comprising at least one <sup>metal or compound of the</sup> element selected from uranium and the rare earth metals under reaction conditions to produce 4-methyl-1-pentene.

5 2. A process as claimed in Claim 1 wherein the catalyst is a uranium di(poly-substituted cyclopentadienyl)-hydride complex.

10 3. A process as claimed in Claim 1 wherein the catalyst is selected from

(a) a uranium (III)-di(poly-substituted cyclopentadienyl)-hydride complex;

15 (b) a uranium (IV)-di(poly-substituted cyclopentadienyl)-<sup>di</sup>hydrogen complex; and

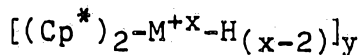
20 (c) a uranium (III) or uranium (IV) di(poly-substituted cyclopentadienyl)-alkyl complex, and the active catalyst is prepared in situ by subjecting the alkyl complex to gaseous hydrogen in order to preform the hydride catalyst.

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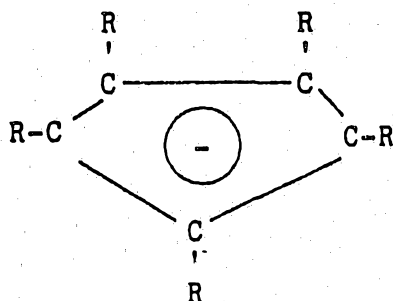


4. A process as claimed in Claim 1 wherein the catalyst is represented by the formula:



5 wherein Cp\* is pentahaptopentamethylcyclopentadienyl, x equals 3 or 4, M is U, and y is 1 or 2, and wherein the contacting is conducted in a substantially inert environment at a temperature of from 10°C to 180°C.

5. A process as claimed in Claim 3 wherein each poly-substituted cyclopentadienyl moiety is represented by the formula:



wherein each R independently is H, alkyl of up to 6 carbon atoms or alkyl-substituted silyl with the proviso that at least 2 R moieties are not H.

6. A process as claimed in Claim 5 wherein each R is methyl or H, with the proviso that at least 2 R moieties are methyl.

7. The process of Claim 4 wherein x is 3 or 4.

8. A process as claimed in any one of the preceding claims wherein the selectivity with respect to other C<sub>6</sub> olefins, with respect to all C<sub>6</sub> compounds



7. A process as claimed in any one of the preceding claims wherein the selectivity with respect to other C<sub>6</sub> olefins, with respect to all C<sub>6</sub> compounds or with respect to all products of the process is at least 94 mole percent.

8. A process as claimed in any one of the preceding claims wherein the selectivity with respect to other C<sub>6</sub> olefins, with respect to all C<sub>6</sub> compounds or with respect to all products of the process is at least 96 mole percent.

9. A process as claimed in any one of the preceding claims wherein the selectivity with respect to other C<sub>6</sub> olefins, with respect to all C<sub>6</sub> compounds or with respect to all products of the process is at least 99 mole percent.

10. A process according to claim 1 substantially as hereinbefore described with reference to any one of the examples.

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