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Description

[0001] The present invention relates to a process for producing a crosslink-cyclized cyclopentadiene, and a process for producing a dihalobis(η-crosslink-cyclized cyclopentadienyl)metal compound containing the crosslink-cyclized cyclopentadiene.

BACKGROUND OF THE INVENTION

[0002] Cyclopentadienes are widely used not only as monomers for producing various polymers but also in the production of metallocene compounds of transition metals such as titanium, zirconium and hafnium. The metallocene compounds are widely utilized as effective ligand components of olefin polymerization catalysts.

[0003] Regarding the conventional production of a crosslink-cyclized cyclopentadiene, for example, with respect to the process for producing 1,3-dimethylcyclopentadiene, Japanese Patent Laid-open Publication No. 62(1987)-72630 describes a process comprising reacting dicyclopentadiene with methanol in the presence of an alkali metal oxide. However, this process has a drawback in that the desired product cannot be efficiently obtained due to, for example, by-products of position isomers.

[0004] Further, Japanese Patent Laid-open Publication No. 3(1991)-215437 describes a process comprising performing a vapor-phase cyclization dehydration of 5-methyl-5-hexen-2-one in the presence of a catalyst such as alumina. However, this process has drawbacks in that the raw materials are expensive and that the reaction must be performed in a vapor phase at such high temperatures as over 200°C to thereby necessitate special apparatus.

[0005] Still further, Japanese Patent Laid-open Publication No. 8(1996)-208533 describes a process for producing a cyclopentadiene, comprising performing a cyclization dehydration of an unsaturated carbonyl compound in the presence of a solid acid catalyst in a vapor phase. However, this process also has a drawback in that the reaction comprises a cyclization dehydration in a vapor phase and the reaction temperature is as high as 330 to 430°C (as indicated in working example portions) to thereby necessitate special apparatus.

[0006] With respect to a crosslink-cyclized cyclopentadiene of the general formula:

\[
\text{CH}_2\text{n} \quad R^1 \quad (\text{CH}_2\text{n}) \quad R^2
\]

the formula has been shown in, for example, Japanese Patent Laid-open Publication No. 9(1997)-132537 in connection with the use as ligands of metallocene catalysts for olefin polymerization. However, there is no particular teaching having been published as to a crosslink-cyclized cyclopentadiene wherein both R1 and R2 are alkyl groups and as to the process for producing the same. Further, there is no particular synthetic example published for such a compound as far as the inventors’ investigations have been made.


OBJECT OF THE INVENTION

[0008] The present invention has been made with a view toward solving the above problems of the prior art. It is an object of the present invention to provide a process for producing a crosslink-cyclized cyclopentadiene with high yield under mild conditions without the need to install special apparatus. It is another object of the present invention to provide a process for producing a crosslink-cyclized cyclopentadiene comprising a cyclopentadiene substituted with two alkyl groups.

[0009] It is a further object of the present invention to provide a process for producing a dihalobis(η-crosslink-cyclized alkyl-substituted cyclopentadienyl)metal compound wherein the above crosslink-cyclized cyclopentadiene is incorpo-
SUMMARY OF THE INVENTION

[0010] The inventors have made extensive and intensive studies with a view toward solving the above problems. As a result, they have found a process for producing a crosslink-cyclized cyclopentadiene with high yield under mild conditions without the need to install special apparatus, wherein a crosslink-cyclized cyclopentenone is reacted with an alkali metal borohydride to thereby reduce the same and wherein the thus obtained crosslink-cyclized cyclopentenol is reacted with a dehydrating agent to thereby reduce the same.

[0011] Moreover, the inventors have found a process for producing a dihalobis(η-crosslink-cyclized alkyl-substituted cyclopentadienyl)metal compound wherein the above crosslink-cyclized cyclopentadiene is incorporated.

[0012] The present invention has been completed on the basis of these findings.

[0013] According to the invention, there is provided a process for producing a crosslink-cyclized cyclopentadiene, comprising the steps of;

reacting a cyclopentenone of the general formula (I) with 2 to 3 molar equivalents of an alkali metal borohydride compound at 0 to 30°C for 2 to 8 hours;

\[
\text{(I)}
\]

wherein each of R\(^1\) and R\(^2\) independently represents a linear or branched saturated alkyl group having 1 to 6 carbon atoms, and n is an integer of 3 to 10,

to thereby reduce the cyclopentenone (reduction step A) into a cyclopentenol of the general formula (II):

\[
\text{(II)}
\]

wherein R\(^1\), R\(^2\) and n are as defined above with respect to the general formula (I); and

reacting the cyclopentenol with a dehydrating agent to thereby dehydrate the cyclopentenol (dehydration step B) into a crosslink-cyclized cyclopentadiene of the general formula (III):
wherein \( R^1, R^2 \) and \( n \) are as defined above with respect to the general formula (I), and the broken line in the 5-membered ring denotes that the 5-membered ring has two double bonds.

[0014] The alkali metal borohydride compound is preferably sodium borohydride or potassium borohydride. The reduction step A is performed at 0 to 30°C. The dehydrating agent is preferably a strong acid. The dehydration step B is preferably performed at -10 to 100°C.

[0015] There is also provided a process for producing a dihalobis (η-crosslink-cyclized cyclopentadienyl)metal compound of the general formula (V):

\[
\text{(III)}
\]

wherein each of \( R^1 \) and \( R^2 \) independently represents a linear or branched saturated alkyl group having 1 to 6 carbon atoms; \( n \) is an integer of 3 to 10; \( M \) represents Ti, Zr or Hf; and \( X \) represents a halogen atom selected from among a chlorine atom, a bromine atom, an iodine atom and a fluorine atom; comprising producing a crosslink-cyclized cyclopentadiene of general formula III by the method described above, followed by reacting said cyclopentadiene with a metal halide in the presence of a base.

BRIEF DESCRIPTION OF THE DRAWING

[0016]

Fig. 1 is an NMR spectrum chart of 7,9-dimethylbicyclo[4,3,0]nona-1(9)-en-8-ol.
Fig. 2 is an NMR spectrum chart of 7,9-dimethylbicyclo[4,3,0]nonadiene.
Fig. 3 is an NMR spectrum chart of dichlorobis(7,9-dimethylbicyclo[4,3,0]nonadienyl)zirconium.
DETAILED DESCRIPTION OF THE INVENTION

[0017] The processes for producing the crosslink-cyclized cyclopentadiene and the dihalobis(η-crosslink-cyclized cyclopentadienyl)metal comprising crosslink-cyclized cyclopentadiene according to the invention will be described in detail below.

[Process for producing crosslink-cyclized cyclopentadiene]

[0018] In the process for producing a crosslink-cyclized cyclopentadiene according to the invention, first, a cyclopentenone is reacted with an alkali metal borohydride compound to thereby reduce the cyclopentenone (reduction step A) into a cyclopentenol. Thereafter, the cyclopentenol is reacted with a dehydrating agent to thereby dehydrate the cyclopentenol (dehydration step B) into a crosslink-cyclized cyclopentadiene.

Crosslink-cyclized cyclopentenone

[0019] The crosslink-cyclized cyclopentenone as a starting material of the crosslink-cyclized cyclopentadiene of the present invention is represented by the general formula (I):

![Diagram of crosslink-cyclized cyclopentenone]

\[ (\text{CH}_2)_n \]

wherein each of \( R^1 \) and \( R^2 \) independently represents a linear or branched saturated alkyl group having 1 to 6 carbon atoms, and \( n \) is an integer of 3 to 10.

[0020] The linear or branched saturated alkyl group having 1 to 6 carbon atoms, represented by \( R^1 \) and \( R^2 \), can be, for example, any of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, n-hexyl and isohexyl. The above crosslink-cyclized cyclopentenone represented by the general formula (I) can be, for example, any of:

- 6,8-dimethylbicyclo[3,3,0]octa-1(8)-en-7-one,
- 6,8-diethylbicyclo[3,3,0]octa-1(8)-en-7-one,
- 6,8-diisopropylbicyclo[3,3,0]octa-1(8)-en-7-one,
- 6-methyl-8-n-butylbicyclo[3,3,0]octa-1(8)-en-7-one,
- 7,9-dimethylbicyclo[4,3,0]nona-1(9)-en-8-one,
- 7,9-diethylbicyclo[4,3,0]nona-1(9)-en-8-one,
- 7,9-disopropylbicyclo[9,3,0]nona-1(9)-en-8-one,
- 7-methyl-9-n-butylbicyclo[4,3,0]nona-1(9)-en-8-one,
- 8,10-dimethylbicyclo[5,3,0]deca-1(10)-en-9-one,
- 8,10-diethylbicyclo[5,3,0]deca-1(10)-en-9-one,
- 8,10-diisopropylbicyclo[5,3,0]deca-1(10)-en-9-one,
- 8-methyl-10-n-butylbicyclo[5,3,0]deca-1(10)-en-9-one,
- 9,11-dimethylbicyclo[6,3,0]undeca-1(11)-en-10-one,
- 9,11-diethylbicyclo[6,3,0]undeca-1(11)-en-10-one,
- 9,11-disopropylbicyclo[6,3,0]undeca-1(11)-en-10-one,
- 9-methyl-11-n-butylbicyclo[6,3,0]undeca-1(11)-en-10-one,
- 10,12-dimethylbicyclo[7,3,0]dodeca-1(12)-en-11-one,
- 10,12-diethylbicyclo[7,3,0]dodeca-1(12)-en-11-one,
These crosslink-cyclized cyclopentenones can be synthesized by known methods, for example, the method described in J. Am. Chem. Soc., 100, 1799 (1978).

[Reduction step A]

Alkali metal hydride

As the alkali metal borohydride compound for use in the reduction step A of the present invention, sodium borohydride and potassium borohydride are preferred, and sodium borohydride is especially preferred.

The alkali metal borohydride is used in a molar amount of 2 to 3 times that of the above crosslink-cyclized cyclopentenone.

Solvent (reduction step A)

The reduction reaction of the reduction step A of the present invention is preferably performed in the presence of a solvent. As a suitable solvent, there can be mentioned, for example, an alcohol such as methanol or ethanol, an ether such as tetrahydrofuran, 1,3-dioxolane, dimethoxyethane, dioxane, diethyl ether or dibutyl ether, water and DMF.

The above solvents can be used individually or in combination.

It is generally preferred that the solvent be used in an amount of 1 to 20 parts by weight, especially 3 to 8 parts by weight, and still especially 4 to 6 parts by weight, per 100 parts by weight of alkali metal borohydride.

Reaction condition (reduction step A)

In the reaction of crosslink-cyclized cyclopentenone and alkali metal borohydride, the reaction temperature is in the range of about 0 to 30°C. The reaction time is in the range of 2 to 8 hr. This reaction is preferably performed in an atmosphere of inert gas such as nitrogen gas.

The reduction reaction can be selectively advanced by carrying out the reaction of crosslink-cyclized cyclopentenone and alkali metal borohydride under the above conditions to thereby enable obtaining the desired crosslink-cyclized cyclopentenol with high yield.

After the completion of the reaction, the product can be obtained by, for example, sequentially performing acid neutralization of a solution containing the reaction product, isolation and purification. Instead, without isolating the reaction product, the solution containing the reaction product can directly be subjected to the subsequent dehydration reaction (B) of formed crosslink-cyclized cyclopentenol. The product yield is generally in the range of about 70 to 90% based on the cyclopentenol.

The thus obtained product is crosslink-cyclized cyclopentenol of the general formula (II):
wherein R₁, R₂ and n are as defined above with respect to the general formula (I).

[Dehydration step B]

Dehydrating agent

[0031] The dehydrating agent for use in the dehydration reaction of cyclopentenol of the general formula (II) in the dehydration step B of the present invention is preferably an acid dehydrating agent, still preferably a strong acid. As the acid dehydrating agent, there can be mentioned, for example, hydrochloric acid, paratoluenesulfonic acid and sulfuric acid.

[0032] It is preferred that the dehydrating agent be used in a molar amount of 0.01 to 1.0 time, especially 0.05 to 0.5 time, and still especially 0.10 to 0.25 time, that of the above crosslink-cyclized cyclopentenol.

Solvent (dehydration step B)

[0033] The dehydration reaction of the dehydration step B of the present invention is preferably performed in the presence of a solvent. Any solvents can be employed as long as they are inert to the reaction. For example, solvents used in the above reduction step A and hydrocarbon solvents can be employed as the solvent. In particular, in the dehydration step B, there can preferably be employed polar solvents capable of oil/water separation, for example, ether solvents such as tetrahydrofuran, 1,3-dioxolane, dimethoxyethane, dioxane, diethyl ether and dibutyl ether. These solvents can be used individually or in combination.

[0034] It is generally preferred that the solvent be used in an amount of 1 to 20 parts by weight, especially 3 to 10 parts by weight, and still especially 5 to 7 parts by weight, per 100 parts by weight of crosslink-cyclized cyclopentenol.

Reaction condition (dehydration step B)

[0035] In the reaction of crosslink-cyclized cyclopentenol and dehydrating agent, it is generally preferred that the reaction temperature be in the range of about -10 to 60°C, especially 0 to 40°C, and still especially 10 to 30°C. It is generally preferred that the reaction time be in the range of 1 to 48 hr, especially 4 to 12 hr. This reaction is preferably performed in an atmosphere of inert gas such as nitrogen gas.

[0036] The desired crosslink-cyclized cyclopentadiene can be obtained by carrying out the reaction of crosslink-cyclized cyclopentenol and dehydrating agent under the above conditions.

[0037] After the completion of the reaction, the product can be obtained by, for example, sequentially performing neutralization of a solution containing the reaction product, isolation and purification. The product yield is generally in the range of about 70 to 90% based on the cyclopentenone.

[0038] The thus obtained product is crosslink-cyclized cyclopentadiene of the general formula (III):
wherein $R_1$, $R_2$ and $n$ are as defined above with respect to the general formula (I), and the broken line in the 5-membered ring denotes that the 5-membered ring has two double bonds.

The crosslink-cyclized cyclopentadiene of general formula III obtained by the present invention can be, for example, any of:

- 6,8-dimethylbicyclo[3,3,0]octadiene,
- 6,8-diethylbicyclo[3,3,0]octadiene,
- 6,8-diisopropylbicyclo[3,3,0]octadiene,
- 6-methyl-8-n-butylbicyclo[3,3,0]octadiene,
- 7,9-dimethylbicyclo[4,3,0]nonadiene,
- 7,9-diethylbicyclo[4,3,0]nonadiene,
- 7,9-diisopropylbicyclo[4,3,0]nonadiene,
- 7-methyl-9-n-butylbicyclo[4,3,0]nonadiene,
- 8,10-dimethylbicyclo[5,3,0]decadiene,
- 8,10-diethylbicyclo[5,3,0]decadiene,
- 8,10-diisopropylbicyclo[5,3,0]decadiene,
- 8-methyl-10-n-butylbicyclo[5,3,0]decadiene,
- 9,11-dimethylbicyclo[6,3,0]undecadiene,
- 9,11-diethylbicyclo[6,3,0]undecadiene,
- 9,11-diisopropylbicyclo[6,3,0]undecadiene,
- 9-methyl-11-n-butylbicyclo[6,3,0]undecadiene,
- 10,12-dimethylbicyclo[7,3,0]dodecadiene,
- 10,12-diethylbicyclo[7,3,0]dodecadiene,
- 10,12-diisopropylbicyclo[7,3,0]dodecadiene,
- 10-methyl-12-n-butylbicyclo[7,3,0]dodecadiene,
- 11,13-dimethylbicyclo[8,3,0]tridecadiene,
- 11,13-diethylbicyclo[8,3,0]tridecadiene,
- 11,13-diisopropylbicyclo[8,3,0]tridecadiene,
- 11-methyl-13-n-butylbicyclo[8,3,0]tridecadiene,
- 12,14-dimethylbicyclo[9,3,0]tetradecadiene,
- 12,14-diethylbicyclo[9,3,0]tetradecadiene,
- 12,14-diisopropylbicyclo[9,3,0]tetradecadiene,
- 12-methyl-14-n-butylbicyclo[9,3,0]tetradecadiene,
- 13,15-dimethylbicyclo[10,3,0]pentadecadiene,
- 13,15-diethylbicyclo[10,3,0]pentadecadiene,
- 13,15-diisopropylbicyclo[10,3,0]pentadecadiene, and

The double bonds of these diene compounds may contain position isomers as a result of isomerization.
The process for producing the dihalobis(η-crosslink-cyclized cyclopentadienyl)metal compound according to the invention, will now be described.

The dihalobis(η-crosslink-cyclized cyclopentadienyl)metal compound can be synthesized by reacting the above obtained crosslink-cyclized cyclopentadiene of the general formula (III) with a metal halide in the presence of a base.

In the reaction of the cyclopentadiene with a metal halide in the presence of a base for obtaining the dihalobis(η-crosslink-cyclized cyclopentadienyl)metal compound, use can be made of an inert solvent. For example, the process comprising reacting the crosslink-cyclized cyclopentadiene with a base in a solvent in advance and mixing the resultant reaction mixture with a metal halide suspension is preferably employed.

The base for use in the present invention can be, for example, n-butyllithium or sodium hydride.

As the solvent for use to mix the crosslink-cyclized cyclopentadiene and the base in advance, there can be employed solvents inert to the reaction, for example, an ether such as tetrahydrofuran, 1,3-dioxolane, dimethoxyethane, dioxane, diethyl ether or dibutyl ether, a saturated aliphatic or alicyclic solvent such as n-hexane or cyclohexane and an aromatic solvent such as toluene or benzene.

It is generally preferred that the base be used in a molar amount of 0.8 to 1.5 times, especially 0.9 to 1.2 times, and still especially 0.98 to 1.08 times, that of the above crosslink-cyclized cyclopentadiene.

The temperature at which the crosslink-cyclized cyclopentadiene is reacted with the base is generally in the range of -20 to 50°C, preferably 0 to 30°C. The reaction time is generally in the range of 30 to 48 hr, preferably 5 to 30 hr.

The metal halide compound for use in the present invention can be any of a titanium halide, a zirconium halide and a hafnium halide. Of these, a zirconium halide is preferably employed. For example, the metal halide compound can be any of fluorides, chlorides, bromides and iodides of titaniums (II), (III) and (IV); fluorides, chlorides, bromides and iodides of zirconiums (II), (III) and (IV); and fluorides, chlorides, bromides and iodides of hafniums (II), (III) and (IV). Of these, titanium (IV), zirconium (IV) and hafnium (IV) halides are preferred, and titanium tetrachloride, zirconium tetrachloride and hafnium tetrachloride are especially preferred.

As the solvent for suspending the metal halide compound, there can be employed solvents inert to the reaction, for example, hexane, heptane, toluene and ethers such as tetrahydrofuran, 1,3-dioxolane, dimethoxyethane, dioxane, diethyl ether and dibutyl ether.

It is preferred that the metal halide be used in a molar amount of 0.3 to 0.8 time, especially 0.4 to 0.6 time, and still especially 0.45 to 0.55 time, that of the crosslink-cyclized cyclopentadiene.

The dihalobis(η-crosslink-cyclized cyclopentadienyl)metal compound can be obtained by adding the suspension of metal halide to the reaction mixture of crosslink-cyclized cyclopentadiene and base to thereby effect a reaction therebetween. The reaction temperature is generally in the range of -20 to 50°C, preferably 0 to 30°C. The reaction time is generally in the range of 3 to 72 hr, preferably 10 to 48 hr.

The thus obtained dihalobis(η-crosslink-cyclized cyclopentadienyl)metal compound is represented by the following general formula (V), and finds applications as an olefin polymerization catalyst, as a carbometallization agent for acetylene compounds, in the synthesis of a starting material of monohydride homologues and as a vulcanizing agent for silicones and rubbers;
wherein each of \( R_1 \) and \( R_2 \) independently represents a linear or branched saturated alkyl group having 1 to 6 carbon atoms; \( n \) is an integer of 3 to 10; \( M \) represents Ti, Zr or Hf; and \( X \) represents a halogen atom selected from among a chlorine atom, a bromine atom, an iodine atom and a fluorine atom.

As examples thereof, there can be mentioned dihalobis (\( \eta \)-crosslink-cyclized cyclopentadieny1) metal compounds formed by reactions between crosslink-cyclized cyclopentadienes as set forth above as particular compounds of the general formula (III) and titanium, zirconium and hafnium halides. Preferred products are, for example, dichlorobis (\( \eta \)-crosslink-cyclized cyclopentadieny1) titanium, dichlorobis\( \eta \)-crosslink-cyclized cyclopentadieny1)zirconium and dichlorobis\( \eta \)-crosslink-cyclized cyclopentadieny1) hafnium.

**EFFECT OF THE INVENTION**

The process for producing a crosslink-cyclized cyclopentadiene according to the invention enables producing a crosslink-cyclized cyclopentadiene with high yield under mild conditions without the need to install special apparatus. Further, the invention enables providing a dihalobis\( \eta \)-crosslink-cyclized cyclopentadieny1)metal compound containing the above crosslink-cyclized cyclopentadiene as ligands.

**EXAMPLE**

**Example 1**

[Synthesis of 7,9-dimethylbicyclo[4,3,0]nona-1(9)-en-8-ol]

Methanol (4 g) solution containing 1.64 g (10 mmol) of 7,9-dimethylbicyclo[4,3,0]nona-1(9)-en-8-one prepared by the method of J. Am. Chem. Soc., 100, 1799 (1978) was dropped over a period of 10 min into a suspension obtained by suspending 0.76 g (20 mmol) of sodium borohydride in 5 g of tetrahydrofuran (THF). The mixture was agitated at room temperature (25°C) for 4 hr. The thus obtained reaction mixture was cooled to 10°C or below, and 10 g of 2 N hydrochloric acid was dropped thereinto so as to effect neutralization with the pH value adjusted to 7. 10 g of ethyl acetate was added to the reaction mixture. An organic layer was separated, washed with water and dried over sodium sulfate. The sodium sulfate was filtered off, and the solvent was distilled off in vacuum. Thus, 1.94 g of colorless oily compound was obtained (73% purity and 85% yield).

The thus obtained compound was incorporated in CDCl\(_3\) and analyzed by \(^1\)H-NMR (400 MHz). It was found that the compound was 7,9-dimethylbicyclo[4,3,0]nona-1(9)-en-8-ol. Spectrum chart obtained by the \(^1\)H-NMR (400 MHz) analysis is shown in Fig. 1.

**Synthesis of 7,9-dimethylbicyclo[4,3,0]nonadiene**

2 g of 2 N hydrochloric acid was dropped into a solution obtained by dissolving 3.38 g (15 mmol) of the above
obtained 7,9-dimethylbicyclo[4,3,0]nona-1(9)-en-8-ol in 10 g of cyclohexane and 10 g of THF, and agitated at room temperature (25°C) for 9 hr. A saturated aqueous solution of NaHCO₃ (4 mmol) was added to the reaction mixture so as to adjust the pH value to 9. 10 g of cyclohexane was added to the resultant reaction mixture. An organic layer was separated, washed with water and dried over sodium sulfate. The sodium sulfate was filtered off, and the solvent was distilled off in vacuum. Thus, 3.15 g of colorless oily compound was obtained. The purity was 63%, and the yield was 90% based on the 7,9-dimethylbicyclo[4,3,0]nona-1(9)-en-8-ol.

**Example 2**

[Synthesis of dichlorobis(7,9-dimethylbicyclo[4,3,0]nonadienyl)zirconium]

A THF (6g) solution containing 2.35 g (10 mmol) of 7,9-dimethylbicyclo[4,3,0]nonadiene synthesized in the same manner as in Example 1 was cooled to 5°C in a nitrogen atmosphere. 6.5 ml (1.6 mmol) of a hexane solution of n-BuLi (10.4 mmol) was dropped into the solution. After the dropping, the reaction mixture was slowly heated up to room temperature (25°C). At this temperature, the mixture was agitated for 24 hr. Thus, a yellowish-brown suspension was obtained. The obtained yellowish-brown suspension was dropped into a suspension of 1.16 g (5 mmol) of zirconium tetrachloride in 10 g of heptane while maintaining the temperature at 10°C or below by cooling with ice. Thereafter, the reaction mixture was heated up to room temperature (25°C) and agitated for 48 hr. Thus, a blackish-brown suspension was obtained. This blackish-brown suspension was filtered to thereby obtain a yellowish-brown solution, from which the solvent was distilled off. Precipitated crystal was collected by filtration. Thus, 20 mg of desired crystal was obtained. The purity was about 90%, and the yield was 1% based on the 7,9-dimethylbicyclo[4,3,0]nonadiene.

**Claims**

1. A process for producing a crosslink-cyclized cyclopentadiene, comprising the steps of:

   reacting a cyclopentenone of the general formula (I) with 2 to 3 molar equivalents of an alkali metal borohydride compound at 0 to 30°C for 2 to 8 hours;

   \[
   \begin{align*}
   &\text{(CH}_2)_n \\
   &\text{R}^1 \quad \text{R}^2 \\
   &\text{O} \\
   &\text{(I)}
   \end{align*}
   \]

   wherein each of R¹ and R² independently represents a linear or branched saturated alkyl group having 1 to 6 carbon atoms, and n is an integer of 3 to 10,

   to thereby reduce the cyclopentenone (reduction step A) into a cyclopentenol of the general formula (II):
wherein $R_1$, $R_2$ and $n$ are as defined above; and reacting the cyclopentenol with a dehydrating agent to thereby dehydrate the cyclopentenol (dehydration step B) into a crosslink-cyclized cyclopentadiene of the general formula (III):

$$\text{(III)}$$

wherein $R_1$, $R_2$ and $n$ are as defined above, and the broken line in the 5-membered ring denotes that the 5-membered ring has two double bonds.

2. The process as claimed in claim 1, wherein the alkali metal borohydride compound is sodium borohydride or potassium borohydride.

3. The process as claimed in claim 1 or claim 2, wherein the dehydrating agent is a strong acid.

4. The process as claimed in any of claims 1 to 3, wherein the dehydration step B is performed at -10 to 100°C.

5. A process for producing a dihalobis ($\eta$-crosslink-cyclized cyclopentadienyl)metal compound of the general formula (V):
wherein each of $R^1$ and $R^2$ independently represents a linear or branched saturated alkyl group having 1 to 6 carbon atoms; $n$ is an integer of 3 to 10; $M$ represents Ti, Zr or Hf; and $X$ represents a halogen atom selected from among a chlorine atom, a bromine atom, an iodine atom and a fluorine atom;

comprising the process as defined in claim 1, followed by reacting the cyclopentadiene of general formula III with a metal halide in the presence of a base.

**Patentansprüche**

1. Verfahren zur Herstellung eines vernetzt-zyklisierten Cyclopentadiens, **dadurch gekennzeichnet, dass** es folgende Schritte umfasst:

   Herbeiführen einer Reaktion eines Cyclopentenons der allgemeinen Formel (I) mit 2 bis 3 molaren Äquivalenten einer Alkalimetallborhydridverbindung bei 0 bis 30 °C während 2 bis 8 Stunden,

   worin $R^1$ und $R^2$ jeweils unabhängig voneinander eine lineare oder verzweigte gesättigte Alkylgruppe mit 1 bis 6 Kohlenstoffatomen bezeichnen und $n$ eine Ganzzahl von 3 bis 10 ist, um **dadurch** das Cyclopentanon (Reduktionsschritt A) in ein Cyclopentenol der allgemeinen Formel (II):
zu reduzieren,
worin R₁, R₂ und n der obigen Definition entsprechen; und
Herbeiführen einer Reaktion des Cyclopentenols mit einem Dehydratationsmittel, um dadurch das Cyclopentenol (Dehydratisierungsschritt B) zu einem vernetzt-zyklisierten Cyclopentadien der allgemeinen Formel (III):

zu dehydratisieren,
worin R₁, R₂ und R₃ der obigen Definition entsprechen und die gestrichelte Linie in dem 5-gliedrigen Ring bedeutet, dass der 5-gliedrige Ring zwei Doppelbindungen aufweist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Alkalimetallborhydridverbindung Natriumborhydrid oder Kaliumborhydrid ist.

3. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, dass das Dehydratationsmittel eine starke Säure ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass der Dehydratisierungsschritt B bei -10 bis 100 °C ausgeführt wird.

5. Verfahren zur Herstellung einer Dihalobis(ν-vernetzt-zyklisiertes Cyclopentadienyl)Metallverbindung der allgemeinen Formel (V):
ist, 

**dadurch gekennzeichnet, dass** $R_1$ und $R_2$ jeweils unabhängig voneinander eine lineare oder verzweigte gesättigte Alkylgruppe mit 1 bis 6 Kohlenstoffatomen bezeichnen, $n$ eine Ganzzahl von 3 bis 10 ist, $M$ für Ti, Zr oder Hf steht und $X$ ein Halogenatom darstellt, das aus der Gruppe Chloratom, Bromatom, Jodatom und Fluoratom ausgewählt wurde,

umfassend das Verfahren gemäß Anspruch 1, gefolgt von der Herbeiführung einer Reaktion zwischen dem Cyclopentadien der allgemeinen Formel III mit einem Metallhalogenid in Anwesenheit einer Base.

**Revendications**

1. Procédé de production d’un cyclopentadiène cyclisé par réticulation, comprenant les étapes de :

   réaction d’une cyclopenténone de formule générale (I) avec de 2 à 3 équivalents molaires d’un composé borohydure de métal alcalin entre 0 et 30°C pendant de 2 à 8 heures ;

   [Diagramm (I)]

   dans laquelle chacun parmi $R_1$ et $R_2$ représente indépendamment un groupe alkyle saturé, linéaire ou ramifié, ayant de 1 à 6 atomes de carbone, et $n$ est un entier de 3 à 10, pour ainsi réduire la cyclopenténone (étape de réduction A) en un cyclopenténol de formule générale (II) :
dans laquelle \( R_1 \), \( R_2 \) et \( n \) sont tels que définis ci-dessus ; et réaction du cyclopenténol avec un agent de déshydratation pour ainsi déshydrater le cyclopenténol (étape de déshydratation B) en un cyclopentadiène cyclisé par réticulation de formule générale (III) :

\[
\begin{align*}
& \text{(II)} \\
& \text{dans laquelle } R_1, R_2 \text{ et } n \text{ sont tels que définis ci-dessus, et la ligne en pointillés dans le noyau à 5 chaînons indique que le noyau à 5 chaînons renferme deux doubles liaisons.} \\
\end{align*}
\]

2. Procédé selon la revendication 1, dans lequel le composé borohydrure de métal alcalin est le borohydrure de sodium ou le borohydrure de potassium.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel l’agent de déshydratation est un acide fort.

4. Procédé selon l’une quelconque des revendications 1 à 3, dans lequel l’étape de déshydratation B est réalisée entre -10 et 100°C.

5. Procédé de production d’un composé dihalogénobis(cyclopentadiényle cyclisé par réticulation \( \eta \))-métal de formule générale (V) :

\[
\begin{align*}
& \text{(III)} \\
& \text{dans laquelle } R_1, R_2 \text{ et } n \text{ sont tels que définis ci-dessus, et la ligne en pointillés dans le noyau à 5 chaînons renferme deux doubles liaisons.}
\end{align*}
\]
dans laquelle chacun parmi $R^1$ et $R^2$ représente indépendamment un groupe alkyle saturé, linéaire ou ramifié, ayant de 1 à 6 atomes de carbone ; $n$ est un entier de 3 à 10 ; $M$ représente Ti, Zr ou Hf ; et $X$ représente un atome d'halogène choisi parmi un atome de chlore, un atome de brome, un atome d'iode et un atome de fluor ; comprenant le procédé tel que défini dans la revendication 1, suivi de la réaction du cyclopentadiène de formule générale III avec un halogénure métallique en présence d'une base.