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CA 2466308 C 2013/03/19

(11)(21) 2 466 308

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2002/11/07
(87) Date publication PCT/PCT Publication Date: 2003/05/22
(45) Date de délivrance/Issue Date: 2013/03/19
(85) Entrée phase nationale/National Entry: 2004/05/06
(86) N° demande PCT/PCT Application No.: US 2002/035773
(87) N° publication PCT/PCT Publication No.: 2003/042220
(30) Priorité/Priority: 2001/11/09 (US10/045,209)

(51) Cl.Int./Int.Cl. *C07F 7/00* (2006.01), *B01J 31/00* (2006.01), *B01J 31/22* (2006.01), *C07F 17/00* (2006.01), *C08F 10/00* (2006.01), *C08F 4/64* (2006.01), *B01J 31/16* (2006.01), *B01J 31/38* (2006.01)

(72) Inventeurs/Inventors:
GATELY, DANIEL A., US;
SULLIVAN, JEFFREY M., US;
VOLL BARCLAY, KARIN A., US;
ARKIN, DAWN A., US

(73) Propriétaire/Owner:
BOULDER SCIENTIFIC COMPANY, US

(74) Agent: SIM & MCBURNEY

(54) Titre : CONVERSION DE CYCLOPENTADIENYL-SILYLAMINES EN COMPLEXES ORGANOMETALLIQUES COMPRENANT UN FRAGMENT BISALCOXY DE TITANE OU UN FRAGMENT DICHLORURE DE TITANE

(54) Title: CONVERSION OF CYCLOPENTADIENYL SILYL AMINES TO ORGANOMETALLIC COMPLEXES COMPRISING TITANIUM BISALKOXY MOIETY OR TITANIUM DICHLORIDE MOIETY

(57) Abrégé/Abstract:
Conversion of cyclopentadienyl or indenyl compounds to titanium organometallic complexes by treatment with titanium tetraalkoxides is described.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 May 2003 (22.05.2003)

PCT

(10) International Publication Number
WO 03/042220 A3

(51) International Patent Classification[7]: C07F 7/00, 17/00, B01J 31/00, C08F 4/64

(21) International Application Number: PCT/US02/35773

(22) International Filing Date:
7 November 2002 (07.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/045,209 9 November 2001 (09.11.2001) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:
US 10/045,209 (CON)
Filed on 9 November 2001 (09.11.2001)

(71) Applicant *(for all designated States except US)*: **BOULDER SCIENTIFIC COMPANY** [US/US]; 598 Third Street, P.O. Box 548, Mead, CO 80542 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **GATELY, Daniel, A.** [US/US]; 318 East Iowa Avenue, Berthoud, CO 80513 (US). **SULLIVAN, Jeffrey, M.** [US/US]; 3125 Morey Court, Loveland, CO 80537 (US). **VOLL BARCLAY, Karin, A.** [US/US]; 4660 MacArthur Lane, Boulder, CO 80503 (US). **ARKIN, Dawn, A.** [US/US]; 2026 Lincon Street, Longmont, CO 80501 (US).

(74) Agent: **IRONS, Edward, S.**; 3945 - 52nd Street, N. W., Washington, DC 20016 (US).

(81) Designated States *(national)*: AU, CA, JP, NZ, US.

(84) Designated States *(regional)*: European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR).

Published:
— *with international search report*

(88) Date of publication of the international search report:
14 August 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/042220 A3

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(57) Abstract: Conversion of cyclopentadienyl or indenyl compounds to titanium organometallic complexes by treatment with titanium tetraalkoxides is described.

CONVERSION OF CYCLOPENTADIENYL SILYL AMINES TO ORGANOMETALLIC COMPLEXES COMPRISING TITANIUM BISALKOXY MOIETY OR TITANIUM DICHLORIDE MOIETY

FIELD OF THE INVENTION

This invention relates to titanium organometallic complexes which comprise a titanium bisalkoxy moiety or a titanium dichloride moiety.

BACKGROUND OF THE INVENTION

United States patents 5,491,246 and 5,504,223 describe the treatment of $Me_4C_5SiMe_2N^t$-bu$[MgCl]_2(DME)_n$ with titanium tetraisopropoxide to provide $Me_4C_5SiMe_2N^t$-$BuTi(OiPr)_2$ which may be treated with $SiCl_4$ to yield the corresponding dichloride.

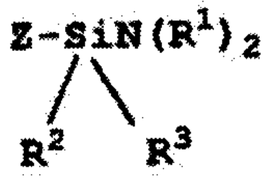
DEFINITIONS

In this specification, the following expressions have the meanings set forth hereinafter:

(1) Cyclopentadienyl means any substituted or unsubstituted cyclopentadienyl compound, group or moiety, including but not limited to any alkylcyclopentadienyl, any indenyl, or any alkyl indenyl compound, group or moiety having one or more C_1 to C_{10} alkyl ring substituents.

(2) Alkoxide means any radical or group having the formula -OR, wherein R is an alkyl group.

(3) Cyclopentadienyl silyl amine means a compound of Formula



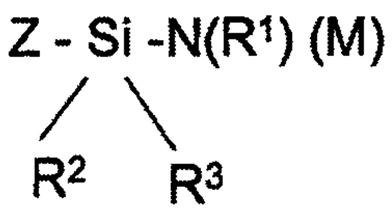
in which Z is a cyclopentadienyl group or moiety and each of R', R2 and R3 is independently, the same or a different alkyl group, preferably a C1 to C10 alkyl group.

SUMMARY OF THE INVENTION

Pursuant to this invention, an alkali metallide of a cyclopentadienyl silyl amine is reacted with a titanium tetraalkoxide $Ti(OR)_4$ in which R is a C_1 to C_{10} alkyl group, preferably an isopropyl group. The reaction mixture contains the desired bisalkoxide and, as a by-product, an alkali metal alkoxide which may be isolated or converted *in situ* to an insoluble alkali metal halide to facilitate removal by filtration. The filtrate contains the desired bisalkoxide which may be converted to the corresponding dichloride by treatment with a halogenating agent, e.g., $SiCl_4$.

According to one aspect of the present invention, there is provided a method for producing a first reaction mixture comprising a solution of a titanium bisalkoxide complex and an alkali metal alkoxide, comprising: (i) treating a cyclopentadienyl silyl amine alkali metallide with a titanium tetraalkoxide in a non-interfering medium in which said titanium bisalkoxide complex and said alkali metal alkoxide are soluble, wherein a mother liquor containing a solution of said titanium bisalkoxide complex in said non-interfering medium is produced.

According to another aspect of the present invention, there is provided the method as described above, wherein said step (i) cyclopentadiene silyl amine alkali metallide has the formula:



and wherein Z is a cyclopentadienyl group, each of R^1, R^2 and R^3 is the same or a different C_1 to C_{10} alkyl group, and M is an alkali metal.

According to another aspect of the present invention, there is provided the method as described above, wherein said alkali metal alkoxide is a lithium alkoxide.

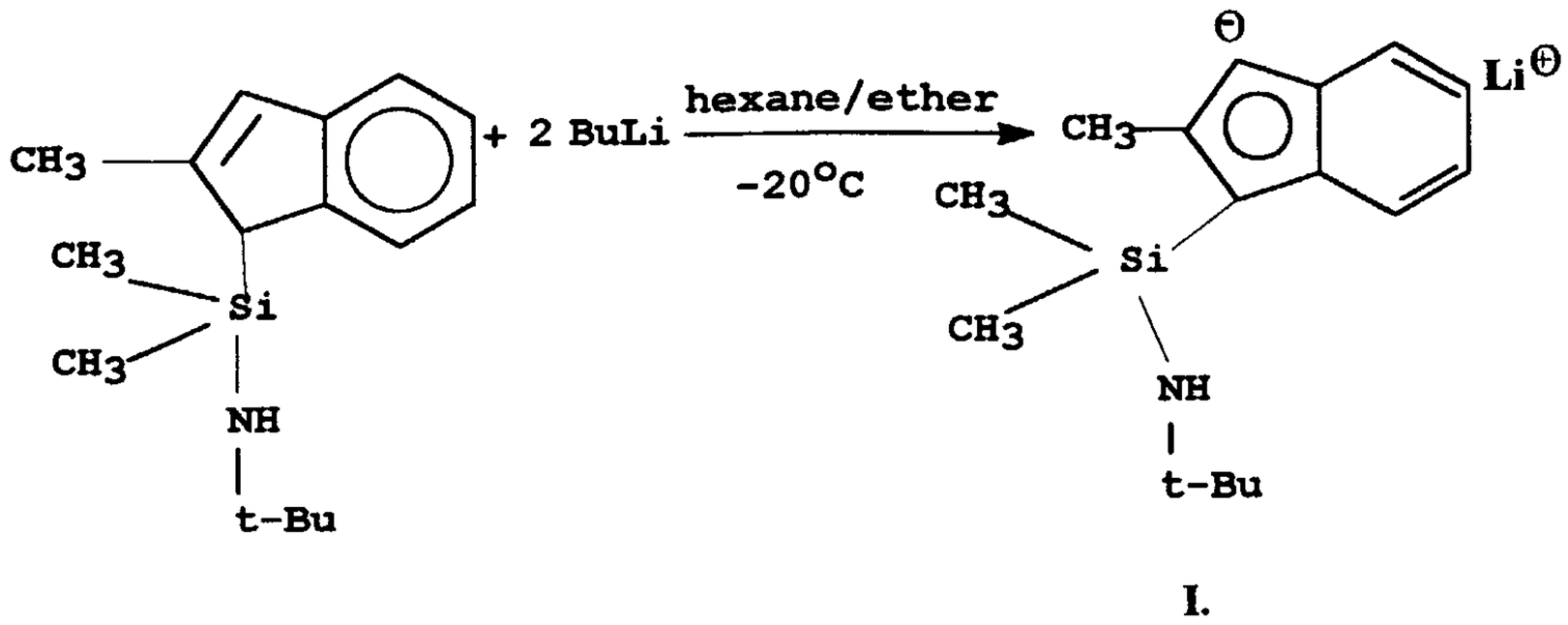
DESCRIPTION OF THE INVENTION

The treatment of a silyl amine with $Ti(OR)_4$ may be accomplished in any solvent or medium in which the desired titanium bisalkoxide is soluble. Preferred solvents or media are about 10% to 25% by weight

mixtures of ethyl ether and a C_6 to C_8 hydrocarbon. The treatment may be accomplished at a temperature of from about -20° to -10°C. The conversion of the alkali metal alkoxide by-product to an alkali metal halide insoluble in the solvent contained in the titanium bisalkoxide synthesis reaction mixture is appropriately conducted at a temperature of from about -35° to -20°C. Conversion of the bisalkoxide to the corresponding dichloride may be accomplished in situ in the synthesis reaction mixture at a temperature of -20°C to room temperature or refluxing temperature. Useful halogenating agents include $SiCl_4$, BCl_3, and $AlCl_3$.

EXAMPLE 1

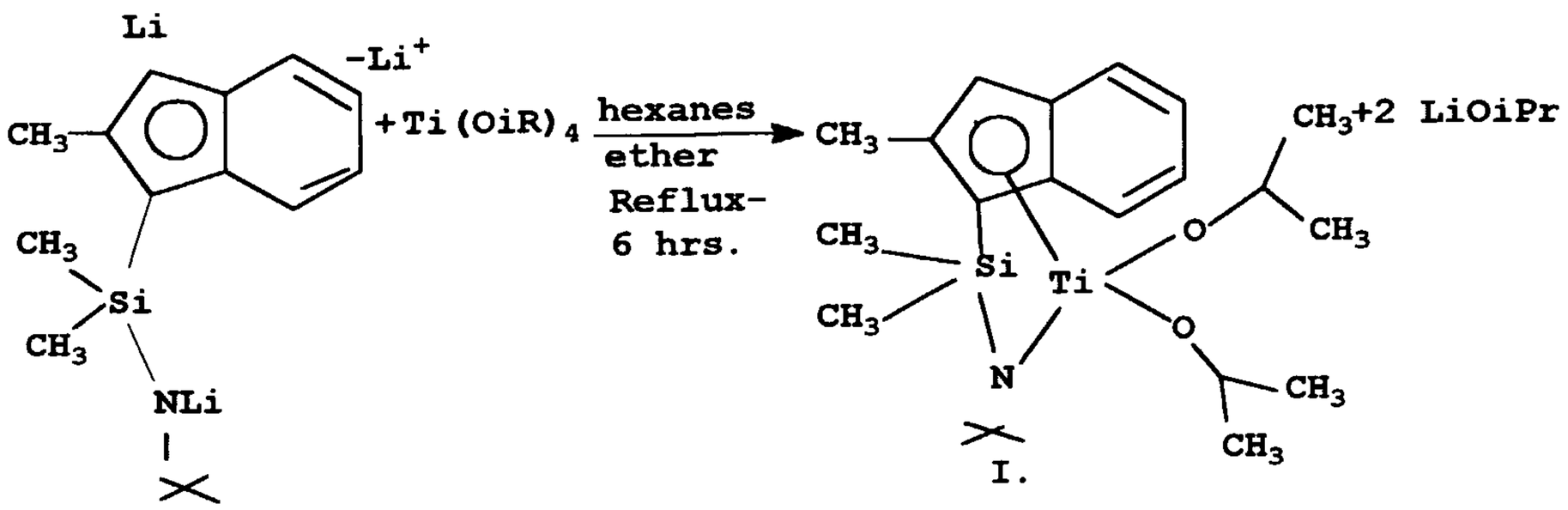
2-Me-indenyl $SiMe_2NH^tBu$ is dilithiated by treatment with butyllithium, e.g., in a 50 weight percent hexane/ether medium at -20°C. See Equation 1:



I.

Equation 1

The dilithiated silyl amine is treated with titanium tetraisopropoxide at a temperature of -35°C, wherein a reaction mixture comprising indenyl $SiMe_2NH^tBu$ titanium isopropoxide and lithium isopropoxide is produced. See Equation 2:



X=alkyl (preferably t-butyl)

Equation 2

The reaction mixture is treated with $SiCl_4$ in an amount, e.g., 0.6 equiv, sufficient to convert LiOiPR in situ to LiCl which is removed by filtration. A hexane wash of the cake may be combined with the mother liquor which is a solution of the desired titanium bisisopropoxide complex in hexanes/ether.

1.5 equivalents of $SiCl_4$ are added to the LiCl-free mother liquor which contains the titanium bis(isopropoxide) complex to provide a second reaction mixture which is refluxed for six hours, and cooled to precipitate the desired titanium dichloride complex for removal by filtration. The cake is washed with hexanes. Titanium dichloride complex yield=70% to 80% (based on the silyl amine).

The embodiments of the present invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for producing a first reaction mixture comprising a solution of a titanium bisalkoxide complex and an alkali metal alkoxide, comprising:

(i) treating a cyclopentadienyl silyl amine alkali metallide with a titanium tetraalkoxide in a non-interfering medium in which said titanium bisalkoxide complex and said alkali metal alkoxide are soluble, wherein a mother liquor containing a solution of said titanium bisalkoxide complex in said non-interfering medium is produced.

2. The method as defined in claim 1, wherein the method further comprises separating said alkali metal alkoxide from said first reaction mixture.

3. The method as defined in claim 1, wherein the method further comprises converting said alkali metal alkoxide in said non-interfering medium to an alkali metal halide.

4. The method as defined in claim 3, wherein said cyclopentadienyl compound is an alkyl cyclopentadienyl compound having at least one C_1 to C_{10} alkyl ring substituent.

5. The method as defined in claim 1, wherein the method further comprises:

(ii) treating said alkali metal alkoxide in said first reaction mixture with a halogenating agent to produce a second reaction mixture wherein said alkali metal alkoxide is converted to an alkali metal halide insoluble in said step (i) non-interfering medium contained in said first reaction mixture, and

(iii) removing said insoluble alkali metal halide from said second reaction mixture wherein a mother liquor containing a

solution of said titanium bisalkoxide complex in said step (i) non-interfering medium is produced.

6. The method as defined in claim 5, wherein the method further comprises: (iv) treating said step (iii) solution of said titanium bisalkoxide complex with a halogenating agent wherein a third reaction mixture comprising an organometallic complex including a titanium dihalide moiety is produced.

7. The method as defined in claim 5, wherein said step (i) cyclopentadienyl silyl amine alkali metallide is lithiated 2-methyl indenyl $SiMe_2NH^tbu$.

8. The method as defined in claim 5, wherein said titanium tetraalkoxide has the formula $Ti(OR)_4$ in which R is a C_1 to C_{10} alkyl group.

9. The method as defined in claim 5, wherein said step (i) treating is accomplished at a temperature of -35° to -20°C.

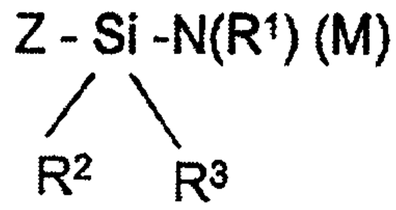
10. The method as defined in claim 5, wherein in step (ii) said alkali metal alkoxide is converted to an alkali metal halide insoluble in situ in said step (i) non-interfering medium contained in said first reaction mixture.

11. The method as defined in claim 5, wherein said step (ii) halogenating agent is $SiCl_4$.

12. The method as defined in claim 5, wherein said non-interfering medium is a mixture of ethyl ether and a C_6 to C_8 hydrocarbon.

13. The method as defined in claim 12, wherein said mixture contains 10% to 25% by weight of said C_6 to C_8 hydrocarbon.

14. The method as defined in claim 5, wherein said step (i) cyclopentadiene silyl amine alkali metallide has the formula:



and wherein Z is a cyclopentadienyl group, each of R^1, R^2 and R^3 is the same or a different C_1 to C_{10} alkyl group, and M is an alkali metal.

15. The method as defined in claim 5, wherein said alkali metal alkoxide is a lithium alkoxide.