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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 July 2010 (08.07.2010)

PCT

(10) International Publication Number
WO 2010/077163 A1

(51) International Patent Classification:
B01J 31/16 (2006.01) *C08F 4/76* (2006.01)
C07F 17/00 (2006.01) *C08F 10/00* (2006.01)

(21) International Application Number:
PCT/RU2008/000814

(22) International Filing Date:
30 December 2008 (30.12.2008)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for RU only)*: **GOSUDARSTVENNOE UCHEBNO-NAUCHNOE UCHREZHDENIE KHIMICHESKY FAKULTET MOSKOVSKOGO GOSUDARSTVENNOGO UNIVERSITETA IM. M.V.LOMONOSOVA** [RU/RU]; GSP-2, Leninskie Gory, dom 1, stroenie 3, MGU im. M.V. Lomonosova, Khimichesky Fakultet, Moscow, 119992 (RU).

(72) Inventor; and
(71) Applicant *(for all designated States except RU, US)*: **TOTAL PETROCHEMICALS RESEARCH FELUY** [BE/BE]; Zone Industrielle C, B-7181 Seneffe (Feluy) (BE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **RAZAVI, Abbas** [IR/BE]; 35, Domaine de la Brisée, B-7000 Mons (BE). **VOSKOBOYNIKOV, Alexander Zelmanovich** [RU/RU]; ul. Akademika Koroleva, 5-93, Moscow, 129515 (RU). **IZMER, Vyatcheslav Valeryevich** [RU/RU]; Remizova street, 2-248, Moscow, 117186 (RU). **KONONOVICH, Dmitry Sergeevich** [RU/RU]; Leninskiye Gory, 1, room V-1152 (right), Moscow, 119234 (RU).

(74) Agent: **POLIKARPOV Alexandr Viktorovich**; NEVIN-PAT, Box 24, St. Petersburg, 191036 (RU).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

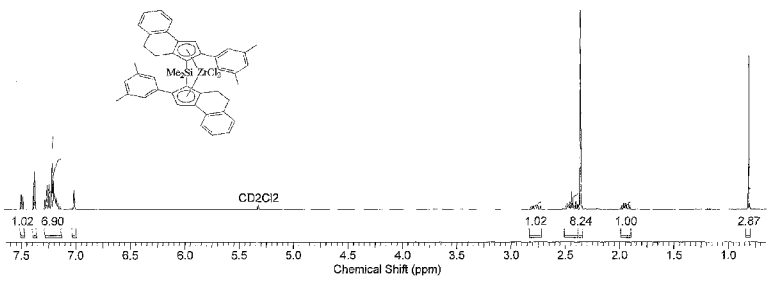
— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: SYNTHESIS OF SUBSTITUTED TETRAHYDROINDENYL COMPLEXES, METALLOCENES PRODUCED THEREFROM AND USE OF THE METALLOCENES IN POLYMERISATION PROCESSES

FIGURE 1



(57) **Abstract**: This invention relates to the synthesis of substituted tetrahydroindenyls and the use of the synthesised complexes in the homo- and co-polymerisation of ethylene and alpha-olefins.

WO 2010/077163 A1

SYNTHESIS OF SUBSTITUTED TETRAHYDROINDENYL COMPLEXES, METALLOCENES PRODUCED THEREFROM AND USE OF THE METALLOCENES IN POLYMERISATION PROCESSES

This invention relates to the synthesis of substituted tetrahydroindenyls.

A C2-symmetric metallocene catalyst component can appear in two stereo-isomeric forms: a racemic form and a meso form. A stereospecific catalyst is used to prepare stereoregular polyolefins. It is generally known that the racemic form induces a reproducible orientation of incoming monomers when the catalyst component is used in an olefin polymerisation reaction. This is desirable for producing an isotactic polyolefin.

Attempts have been made either to avoid the production of the meso isomer or to separate the desirable racemic isomer from the meso isomer, but the separation step is costly and it has been observed that after purification the meso isomer is reintroduced in the system under the effect of light or heat. Hydrogenation of the catalyst component avoids the formation of the meso isomer and/or its "re-formation" under the effect of light or heat. As such, a hydrogenated metallocene catalyst component is known to be useful in olefin polymerisation.

In the specific context of bridged bis-indenyl-based metallocenes, it is known in the art that these give rise to the formation of two isomeric metallocenes (racemic and meso) with different catalytic properties. The non-stereo specific meso component contributes to the formation of an undesirable low molecular weight atactic polymer fraction whereas the racemic component produces a highly stereoregular polymer fraction. In addition, starting from pure racemic ingredients, heat and light induce the transformation of part of the racemic precatalyst into the meso isomer, thereby leading to the formation of lower molecular weight "solubles" after activation and during the polymerisation. This is particularly detrimental in the production of ethylene/propylene copolymers.

It has been observed that hydrogenation of the indenyl rings reduces the production of the meso isomer during the final steps of the metallocene synthesis, but so far

hydrogenation has been carried out only on the final catalyst and has been successful for unsubstituted bis-indenyl components and with somewhat success on mono-substituted bis-indenyl components.

J. Organomet. Chem. (1982), 232, 233-247 describes the synthesis of ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)-titanium dichloride. This is made by hydrogenation of ethylene-bis(indenyl)titanium dichloride using either a palladium-on-charcoal hydrogenation catalyst or a PtO_2 hydrogenation catalyst. This hydrogenation reaction is said, in principle to give the chiral compound in sufficiently pure form. However, in practice, chromatographic separation is needed in order to eliminate the achiral meso-isomer, which represent a major portion of the product.

EP-A-344887 is concerned with a chiral silicon-bridged metallocene catalyst that polymerises α-olefins with high isotacticity, with a minimum number of inversions and at high rates of catalyst activity. In Example 1, the compound 1,1'-dimethylsilanylene bridged bis(indenyl) zirconium dichloride was prepared. Further, the tetrahydroindenyl derivative of this compound was prepared by adding methylene chloride and platinum black or platinum (IV) oxide. Following hydrogenation, the insoluble racemic isomer was filtered off and crystallised. Similarly in Example 7, tetramethyldisiloxane bridged bis(tetrahydroindenyl) zirconium dichloride was prepared.

Summarising the state of the art as outlined above, US-5,883,275 acknowledges that the synthesis of hydrogenated or partially hydrogenated metallocenes generally starts from the corresponding metallocenes having aromatic ligands. It further is stated that the known synthetic procedures for hydrogenating the aromatic ligand skeleton of metallocenes in principle all follow the same route. The metallocene is dissolved or suspended in dichloromethane and hydrogenated in the presence of platinum back or platinum dioxide under a high pressure of hydrogen. However, US-5,883,275 alleges some disadvantages of these known procedures. It however discloses an alternative method for synthesising hydrogenated metallocene. As in previously known methods, their procedure also starts from the corresponding metallocene having aromatic ligands. However, a new method for hydrogenation is

disclosed wherein the metallocene to be treated with hydrogen in the presence of a hydrogenation catalyst is in a non-halogenated solvent. This non-halogenated solvent is essential for making it possible to employ very active hydrogenation catalysts, to carry out the hydrogenation reaction at relatively low hydrogen pressure and to work at temperatures above 0°C.

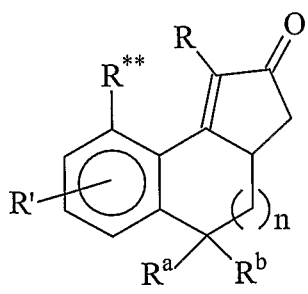
J. Organomet. Chem., 604 (2000), 12-19, also reports the hydrogenation of bis(indenyl) zirconium dichloride into the corresponding bis(tetrahydroindenyl) zirconium dichloride. It is however further acknowledged that the ability to hydrogenate the six-membered ring in indenyl metal complexes is not general. This document reports a different approach for synthesising bis(tetrahydroindenyl) lanthanum chlorides directly from "pre-reduced" bis(tetrahydroindenyl) ligands. The synthesis of 2-methyl-4, 5,6,7-tetrahydroindenyl lithium is shown in scheme 1 of this document. The synthesis of silyl-bridged bis(tetrahydroindene) is shown in Scheme 2.

In view of the above, it will be understood that there is a need for further, and preferably improved, methods for making a hydrogenated metallocene catalyst component, which catalyst component preferably polymerises α-olefins to high isotacticity.

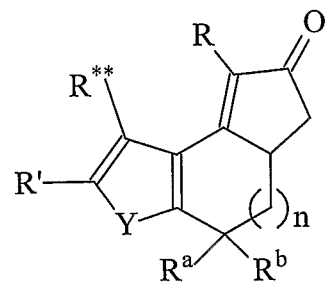
It is an aim of the present invention to provide a method for preparing bridged substituted bis-tetrahydroindenyl catalyst components.

Accordingly, the present invention discloses a method for preparing substituted bis-tetrahydroindenyl ligands that comprises the steps of:

a) preparing a complex of general formula I or formula I'

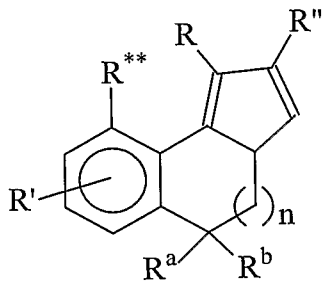


(I)

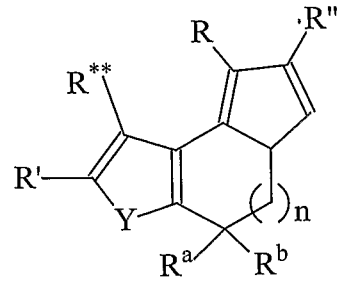


(I')

b) reacting complex I or I' with R"Li, followed by acidification with diluted acid, in order to prepare respectively complex II or complex II'

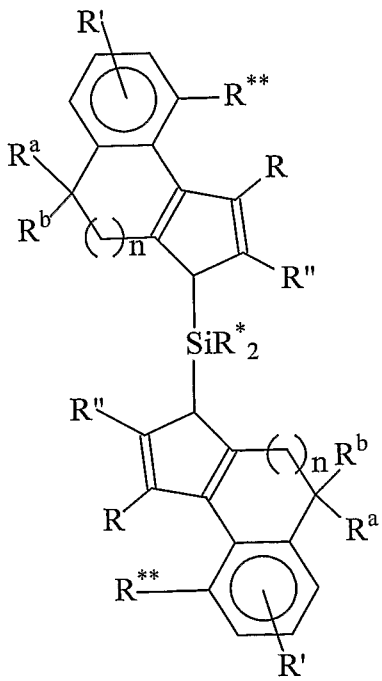


(II)

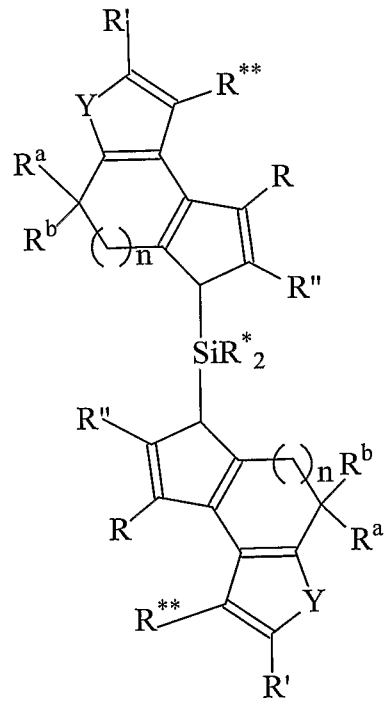


(II')

c) optionally reacting complex II or complex II' with $R^*_2SiX_2$ in the presence of ^{n}BuLi in order to prepare ligand III or ligand III'



(III)



(III')

wherein R, R', R", R^a and R^b are each independently selected from hydrogen, or hydrocarbyl having up to 10 carbon atoms,

wherein R* and R** are each independently selected from unsubstituted or substituted alkyl or aryl having up to 8 carbon atoms, including polynuclear fused aromatic rings,

wherein Y is a metal Group 13, 14, 15 or 16 of the Periodic Table,

wherein X is halogen or alkyl having up to 6 carbon atoms, and

wherein n is 0, 1 or 2.

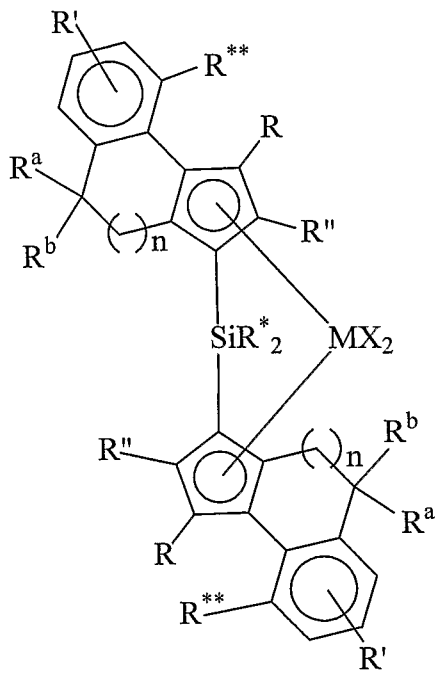
Preferably, step c) is not omitted and the silyl bridge is present.

Preferably R^a and R^b are the same and are hydrogen.

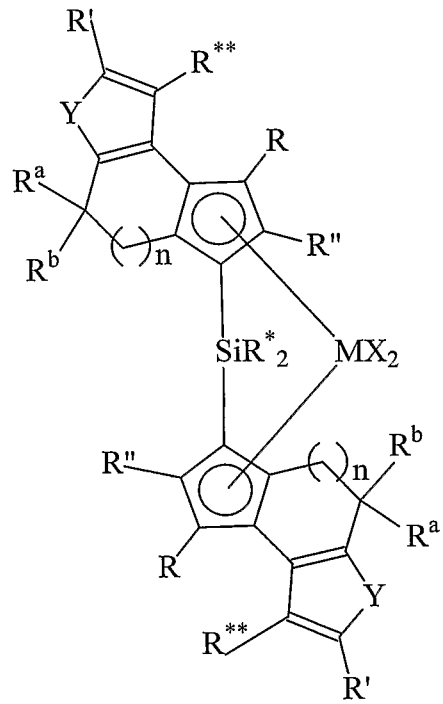
Preferably, n is equal to 0.

Preferably, at least one of R, R* or R** is at least as bulky as ^{t}Bu.

A second aspect of the present invention provides a hydrogenated metallocene catalyst component of formula IV or IV'



(IV)



(IV')

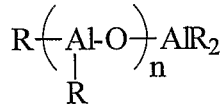
Metallocene catalyst component of formula IV or IV' is prepared by metallation reaction of the ligand of formula III or III' by a metallic salt of formula MX'_4 wherein M is a metal group 4 of the Periodic Table and X' is halogen or alkyl having up to 6 carbon atoms.

This invention is particularly concerned with the preparation of ansa-metallocenes involving indenyls bearing bulky substituents on the cyclopentadienyl and/or on the phenyl fragments. This is believed to result in a very high stability of the racemic complexes toward epimerisation in solution.

A third aspect of the present invention provides a catalyst system comprising the catalyst component of formula IV or IV' and an aluminium- or boron-containing activating agent having an ionising action.

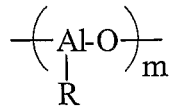
Suitable aluminium-containing activating agents comprise an alumoxane, an alkyl aluminium compound and/or a Lewis acid.

The alumoxanes that can be used in the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula (A):



(A)

for oligomeric linear alumoxanes; and formula (B)



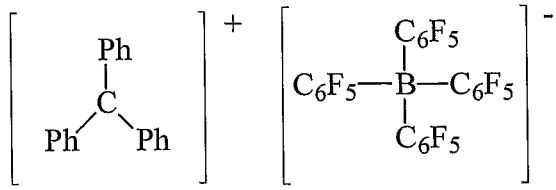
(B)

for oligomeric cyclic alumoxanes,

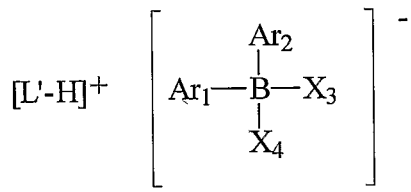
wherein n is 1-40, preferably 10-20; m is 3-40, preferably 3-20; and R is a C_1-C_8 alkyl group, preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

The amount of alumoxane and metallocene usefully employed in the preparation of a solid support catalyst can vary over a wide range. Generally the aluminium to transition metal mole ratio is in the range between 200:1 and 2000:1, preferably in the range 500:1 and 1000:1.

Suitable boron-containing activating agents may comprise a triphenylcarbenium boronate, such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696:



or those of the general formula below, as described in EP-A-0277004 (page 6, line 30 to page 7, line 7):



The present invention also provides a method for homo- or co-polymerising ethylene and alpha-olefins that comprises the steps of:

a) injecting into the reactor the active catalyst system of the present invention;
b) injecting into the reactor the monomer and optional comonomer;
c) maintaining under polymerisation condition;
d) retrieving a polymer.

The preferred monomers are ethylene and propylene and the preferred comonomers are propylene, 1-butene and 1-hexene.

The present invention also provides polyolefins, obtainable by the method described hereabove.

The catalyst system of the present invention may be employed in any polymerisation method such as a slurry polymerisation, a solution polymerisation, or a gas phase polymerisation, provided that the required catalytic activity is not impaired. In a preferred embodiment of the present invention, the catalyst system is employed in a solution polymerisation process, which is homogeneous, or a slurry process, which is heterogeneous. In a solution process, typical solvents include hydrocarbons having 4-7 carbon atoms such as heptane, toluene or cyclohexane. In a slurry process it is necessary to immobilise the catalyst system on an inert support.

The polyolefins prepared with the hydrogenated catalyst system of the present invention have less regio-defects and are more stereo-regular than those obtained with their non-hydrogenated counterpart.

List of figures

Figure 1 represents the ^1H NMR spectrum in CD_2Cl_2 of dichloro[3,3'-bis(dimethylsilanediyl) di(η^5-[2-(3,5-dimethylphenyl)-4,5-dihydro-3H-cyclopenta[a]naphthalen-3-yl]] zirconium.

Figure 2 is the ORTEP representation of the molecular structure of dichloro[3,3'-bis(dimethylsilanediyl) di(η^5-[2-(3,5-dimethylphenyl)-4,5-dihydro-3H-cyclopenta[a]naphthalen-3-yl]] zirconium wherein thermal ellipsoids are drawn at the 50% probability level.

Figure 3 represents the ^1H NMR spectrum of dichloro[3,3'-bis(dimethylsilanediyl) di(η^5-[2-(4-tert-butylphenyl)-4,5-dihydro-3H-cyclopenta[a]naphthalen-3-yl]]zirconium in CD_2Cl_2.

Figure 4 is the ORTEP representation of the molecular structure of dichloro[3,3'-bis(dimethylsilanediyl) di(η^5-[2-(4-tert-butylphenyl)-4,5-dihydro-3H-

cyclopenta[a]naphthalen-3-yl]]zirconium wherein thermal ellipsoids are drawn at the 50% probability level.

Figure 5 represents the ^{1}H NMR spectrum in CD_2Cl_2 of dichloro[3,3'-bis(dimethylsilanediyl) di(η^5-(8-*tert*-butyl-2-phenyl-4,5-dihydro-3*H*-cyclopenta[*a*]naphthalen-3-yl)]zirconium.

Figure 6 is the ORTEP representation of the molecular structure of dichloro[3,3'-bis(dimethylsilanediyl) di(η^5-(8-*tert*-butyl-2-phenyl-4,5-dihydro-3*H*-cyclopenta[*a*]naphthalen-3-yl)]zirconium.

Figure 7 represents the ^{1}H NMR spectrum in CD_2Cl_2 of bis[η^5-(2-phenyl-4,5-dihydro-3H-cyclopenta[*c*]phenanthren-3-yl)zirconium dichloride.

Figure 8 is the ORTEP representation of the molecular structure of bis[η^5-(2-phenyl-4,5-dihydro-3H-cyclopenta[*c*]phenanthren-3-yl)zirconium dichloride.

Figure 9 represents the ^{1}H NMR spectrum in CD_2Cl_2 of dichloro[6,6'-bis(dimethylsilanediyl)di(η^5-(7-phenyl-5,6-dihydro-4*H*-indeno[5,4-*b*]thiophene-6-yl)]zirconium.

Figure 10 is the ORTEP representation of the molecular structure of dichloro[6,6'-bis(dimethylsilanediyl)di(η^5-(7-phenyl-5,6-dihydro-4*H*-indeno[5,4-*b*]thiophene-6-yl)]zirconium.

Examples

Example 1

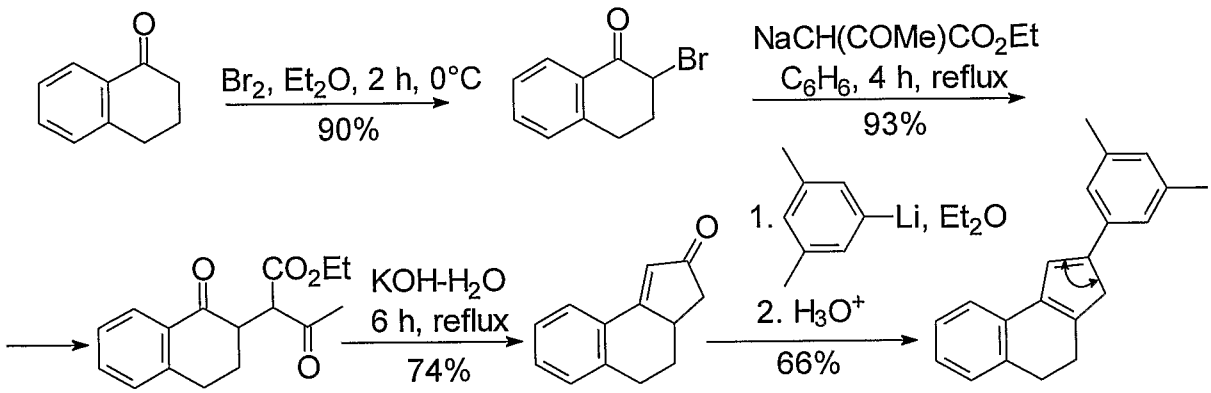
Preparation of

2-(3,5-dimethylphenyl)-4,5-dihydro-1*H*-cyclopenta[*a*]-naphthalene and 2-(3,5-dimethylphenyl)-4,5-dihydro-3*H*-cyclopenta[*a*]-naphthalene.

and of

Dichloro[3,3'-bis(dimethylsilanediyl)di(η^5-[2-(3,5-dimethylphenyl)-4,5-dihydro-3H-cyclopenta[a]naphthalen-3-yl]]zirconium.

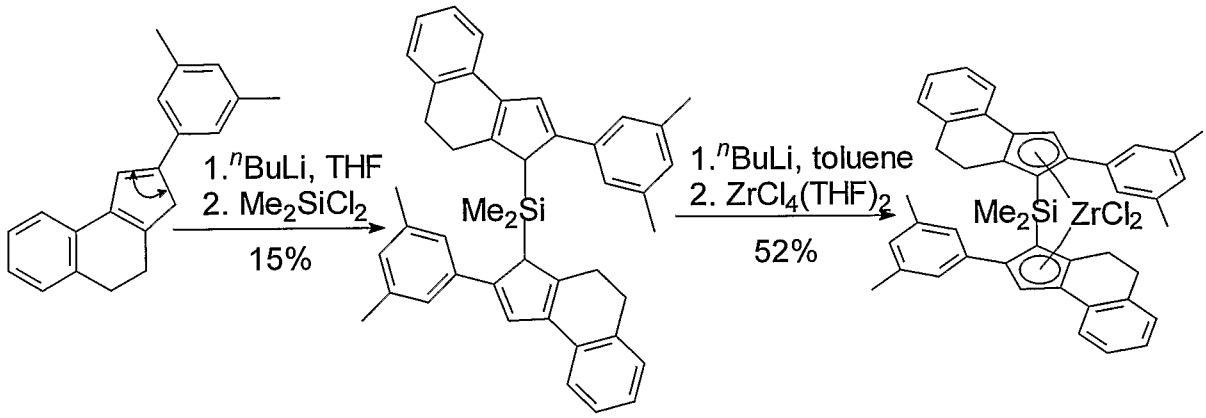
The preparation is represented by the following scheme:



α-tetralone was brominated in the presence of diethylether (Et_2O) at a temperature of 0°C for a period of time of 2 hours. It was followed by treatment with sodium salt of ethyl acetoacetate at reflux and for a period of time of 4 hours and then by cyclisation of ethyl 3-oxo-2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)butanoate in the presence of base KOH-H_2O at reflux and for a period of time of 6 hours to give the desired cyclopentenone with a yield of 62% . The cyclopentenone was treated with MeLi and the formed alcohol was dehydrated in order to form 2-methyl-4,5-dihydro-3a*H*-cyclopenta[*a*]naphthalene with a yield of 43%. 3,3a,4,5-Tetrahydro-2*H*-cyclopenta[*a*]-naphthalen-2-one was then reacted with 3,5-dimethylphenyllithium in ether. The acidification of the reaction mixture gave a mixture of ligands 2-(3,5-dimethylphenyl)-4,5-dihydro-3*H*-cyclopenta[*a*]-naphthalene and 2-(3,5-dimethylphenyl)-4,5-dihydro-1*H*-cyclopenta[*a*]naphthalene with a yield of 66%.

A lithium salt of this ligand was treated with 0.5 eqv of dichlorodimethylsilane in tetrahydrofuran (THF) to form the respective *bis*(cyclopentadienyl)dimethylsilane. This *bis*-cyclopentadienyl ligand was isolated from the crude product in low yield by a flash chromatography on Silica Gel 60. These low yield of formation of the ligands was the major difficulty encountered in synthesising the ansa-metallocenes. The chelating ligand was metallated with 2 eqv of ^{n}BuLi in toluene-hexanes and metallic

salt $ZrCl_4(THF)_2$ to synthesize the desired *ansa*-zirconocene. This mixture was stirred overnight at room temperature and then filtered through glass frit. Crystals precipitated from the filtrate at a temperature of -30°C were collected and dried in vacuum. NMR spectroscopy of the crystalline precipitate revealed pure *racemic* *ansa*-metallocene. ^1H NMR spectrum of this compound (in CD_2Cl_2) is shown in the figure 1. This *rac*-complex was isolated with a yield of 52% resulting from the high stability of this isomer as compared with its *meso*-counterpart.



This *ansa*-zirconocene was successfully characterised by X-ray crystal structure analysis. Figure 2 is the ORTEP representation of the molecular structure of this complex involving 2-(3,5-dimethylphenyl)-4,5-dihydrocyclopenta[*a*]naphthyl fragment wherein thermal ellipsoids are drawn at the 50% probability level.

The key geometric parameters of the first independent molecule are as follows:

- bond length Zr-Cp(c) = 2.234(1) Angströms;
- angle between two cyclopentadienyl planes = 61.0°.

The key geometric paramerers of the second independent molecule are as follows:

- bond length Zr-Cp(c) = 2.238(1) Angströms;
- angle between two cyclopentadienyl planes = 59.6°.

Both independent molecules represent the respective racemic complexes.

Example 2

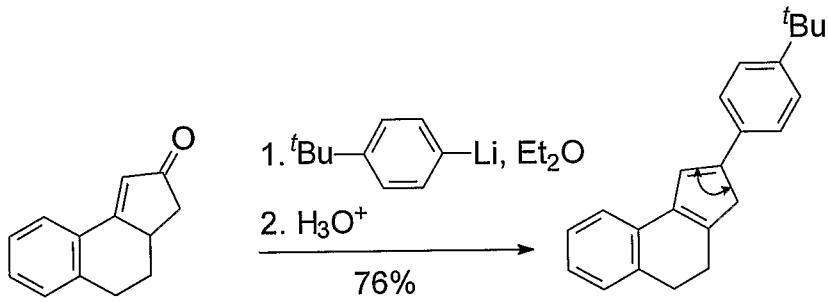
Preparation of

2-(4-*tert*-butylphenyl)-4,5-dihydro-1*H*-cyclopenta[*a*]naphthalene and 2-(4-*tert*-butylphenyl)-4,5-dihydro-3*H*-cyclopenta[*a*]naphthalene.

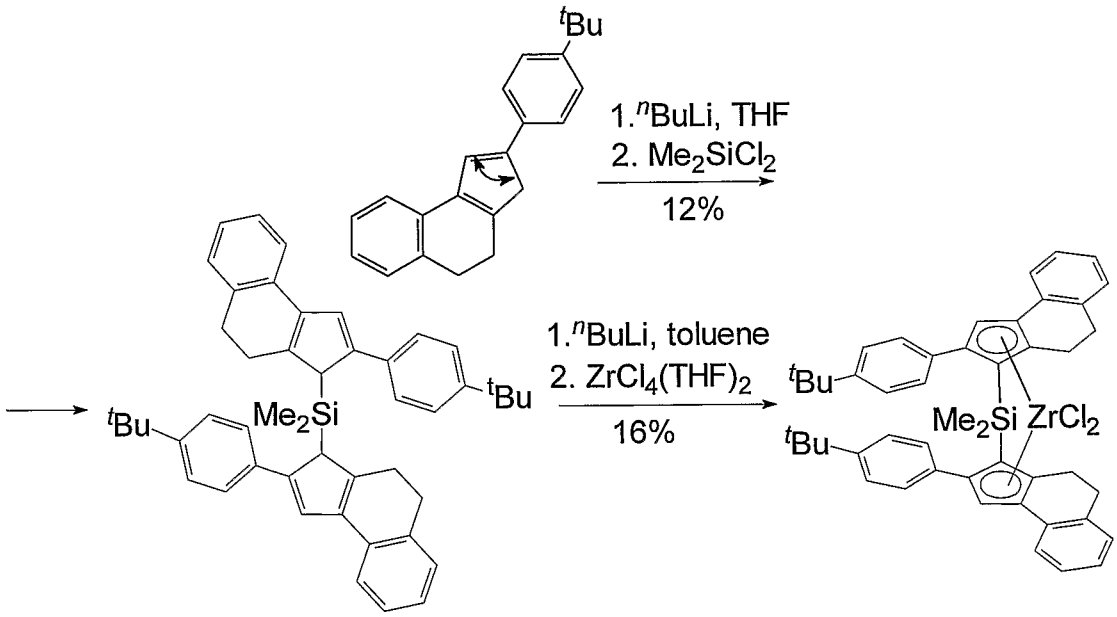
and of

Dichloro[3,3'-bis(dimethylsilanediyl)di(η^5-[2-(4-tert-butylphenyl)-4,5-dihydro-3H-cyclopenta[a]naphthalen-3-yl]]zirconium.

The preparation proceeds as in example 1 except that in the final step for preparing the ligand one equivalent of 4-*tert*-butylphenyllithium in ether is added to 3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalen-2-one, followed by acidification of the reaction mixture. The final ligand is a mixture of 2-(4-*tert*-butylphenyl)-4,5-dihydro-3*H*-cyclopenta[*a*]naphthalene and 2-(4-*tert*-butylphenyl)-4,5-dihydro-1*H*-cyclopenta[*a*]naphthalene obtained with a yield of 76%, as represented in the scheme herebelow.



Lithium salts of these ligands were treated with 0.5 eqv of dichlorodimethylsilane in THF to form the respective *bis*(cyclopentadienyl)dimethylsilanes. This mixture of *bis*-cyclopentadienyl ligands was isolated from the crude product in low yield by a flash chromatography on Silica Gel 60. Next, this chelating ligand was metallated with 2 equivalents of ^{n}BuLi in toluene-hexanes, and metallic salt $ZrCl_4(THF)_2$. This mixture was stirred overnight at room temperature and then filtered through glass frit. Crystals precipitated from the filtrate at -30°C were collected and dried in vacuum. On the evidence of NMR spectroscopy, this crystalline precipitate is pure *meso ansa*-metallocene. ^{1}H NMR spectrum of this compound (in CD_2Cl_2) is shown in figure 3. This *meso*-complex was isolated with a yield of 16%.



The *meso*-complex was characterised by X-ray crystal structure analysis. The ORTEP representation of its molecular structure can be seen in figure 4. The key geometric parameters of this structure are the following:

- bond lengths Zr-Cp(c) and Zr-Cp(c)' are respectively 2.234(1) and 2.237(1) Angströms;
- bond angle Cp(c)-Zr-Cp(c)' is 127.6°.

Example 3

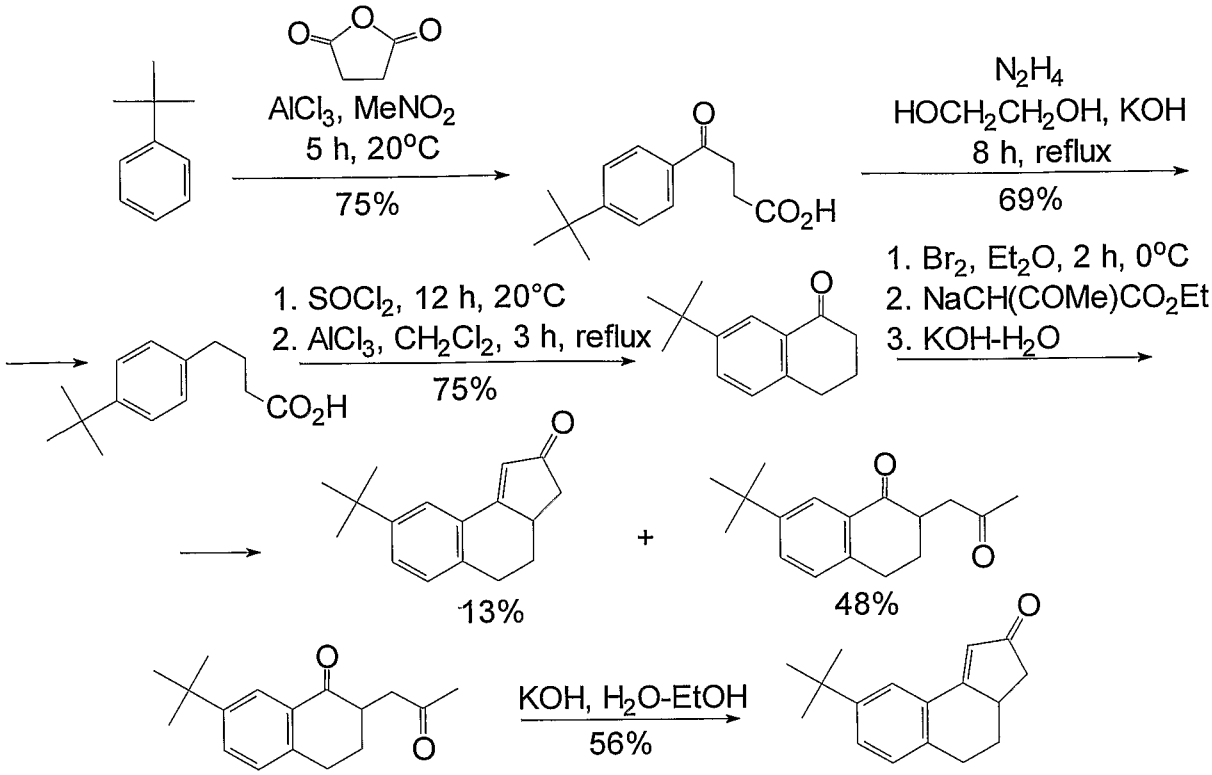
Preparation of

2-phenyl-8-*tert*-butyl-4,5-dihydro-1*H*-cyclopenta[*a*]naphthalene and 2-phenyl-8-*tert*-butyl-4,5-dihydro-3*H*-cyclopenta[*a*]naphthalene.

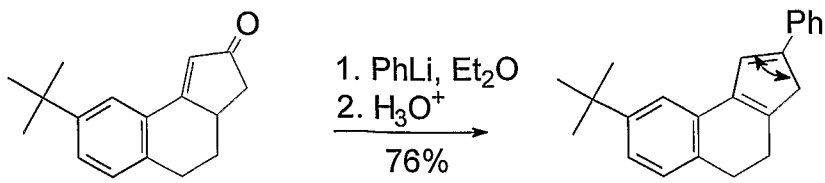
and of

Dichloro[3,3'-bis(dimethylsilanediyl)di(η^5-(8-*tert*-butyl-2-phenyl-4,5-dihydro-3*H*-cyclopenta[*a*]naphthalen-3-yl)]zirconium.

The preparation is described in the following scheme.



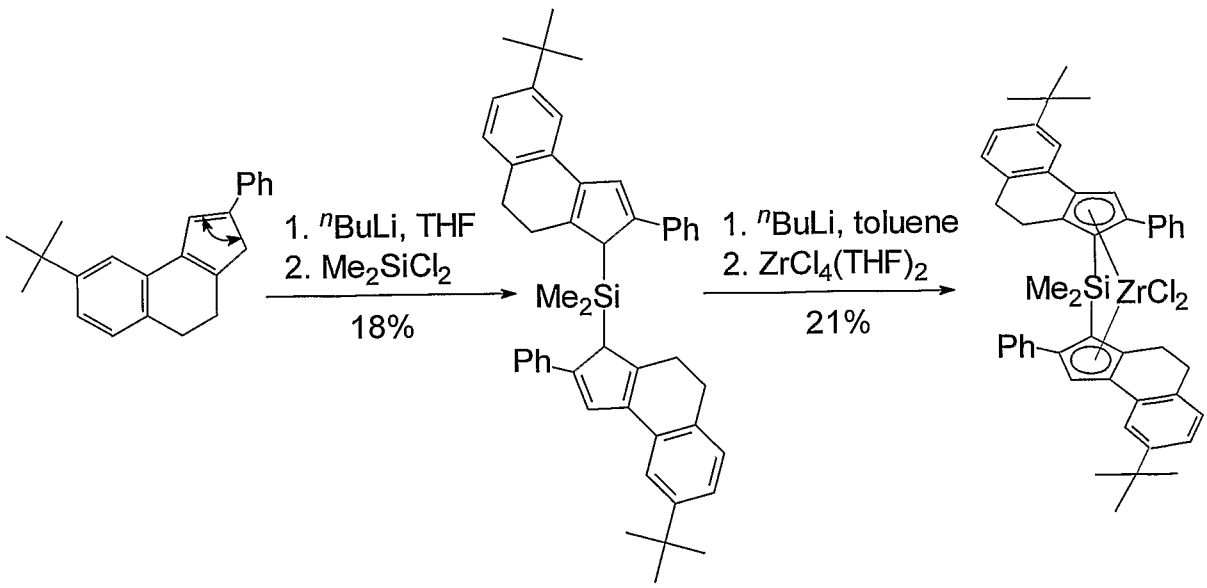
Starting material tert-butyl benzene was acylated to form a keto-acid that was subsequently reduced. Cyclisation of the resulting product was then carried out in the presence of $AlCl_3$ to give 7-*tert*-butyl-3,4-dihydronaphthalen-1(2*H*)-one and with an overall yield of 39%. Bromination of this product, followed by alkylation and cyclisation in aqueous KOH gave a mixture of 8-*tert*-butyl-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalen-2-one and 7-*tert*-butyl-2-(2-oxopropyl)-3,4-dihydronaphthalen-1(2*H*)-one in a 1/3.5 ratio. The undesired 7-*tert*-butyl-2-(2-oxopropyl)-3,4-dihydronaphthalen-1(2*H*)-one was isolated and treated in alcoholic KOH to give the desired 8-*tert*-butyl-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalen-2-one in moderate yield. The latter product was further reacted with one equivalent of PhLi in ether followed by acidification of the reaction medium to give a mixture of 2-phenyl-8-*tert*-butyl-4,5-dihydro-1*H*-cyclopenta[*a*]naphthalene and 2-phenyl-8-*tert*-butyl-4,5-dihydro-3*H*-cyclopenta[*a*]naphthalene as shown in the scheme below



The lithium salt of this ligand was treated with 0.5 eqv of Me_2SiCl_2 in THF to form the respective *bis*(cyclopentadienyl)dimethylsilane. This *bis*-cyclopentadienyl ligand was isolated from the crude product with a yield of 18% repeating flash chromatography on Silica Gel 60. It was metallated with 2 eqv of ^{n}BuLi in toluene-hexanes, and then with metallic salt $ZrCl_4(THF)_2$. This mixture was stirred overnight at room temperature and then filtered through glass frit. Crystals precipitated from the filtrate at a temperature of -30°C were collected and dried in vacuum. On the evidence of ^{1}H NMR spectroscopy, this product isolated with a yield of 21% is a mixture of *rac*- and *meso*-complexes in a ratio of 1 to 4. This ^{1}H NMR spectrum is shown in figure 5. The *meso*-isomer was characterised by X-ray crystal structure analysis. Figure 6 is the ORTEP representation of the molecular structure of this meso-complex with thermal ellipsoids drawn at the 50% probability level.

The key geometric paramerers of this structure are:

- bond lengths Zr-Cp(c) and Zr-Cp(c)' are respectively 2.222(1) and 2.221(1) Angströms;
- angle between two cyclopentadienyl planes is 56.4°.



Example 4

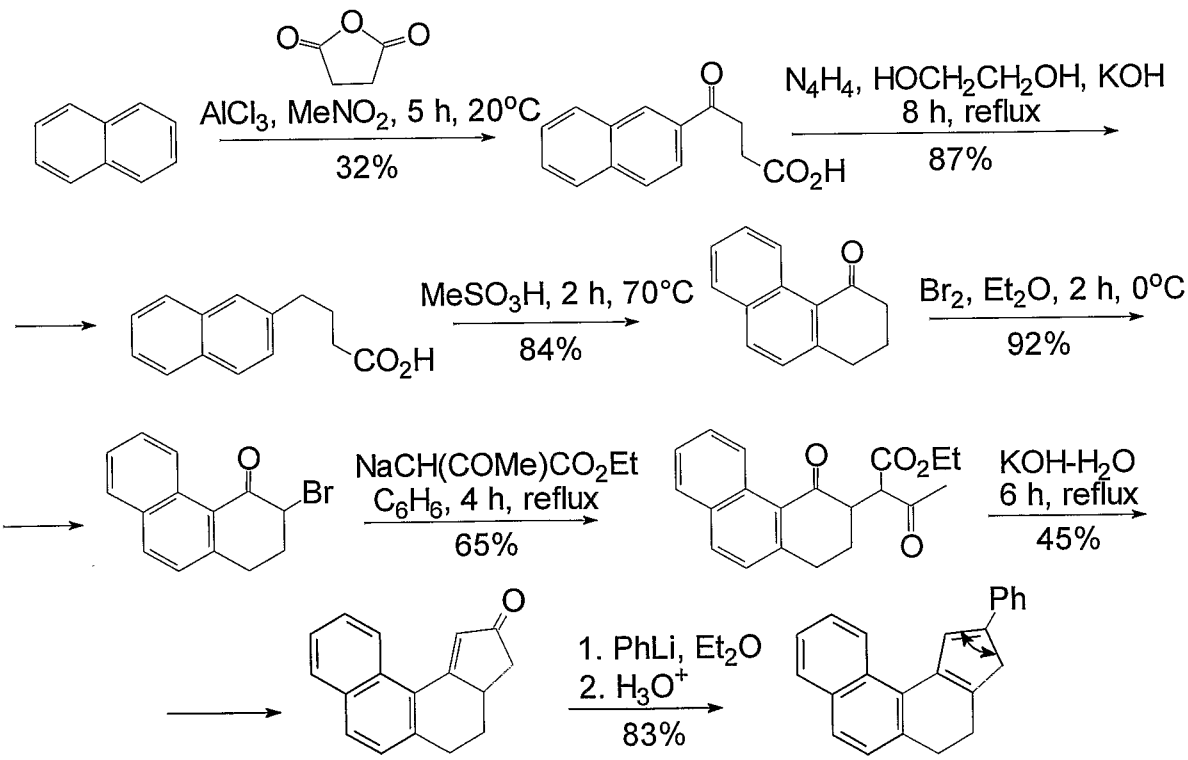
Preparation of

3,3a,4,5-tetrahydro-2*H*-cyclopenta[*c*]-phenanthren-2-one

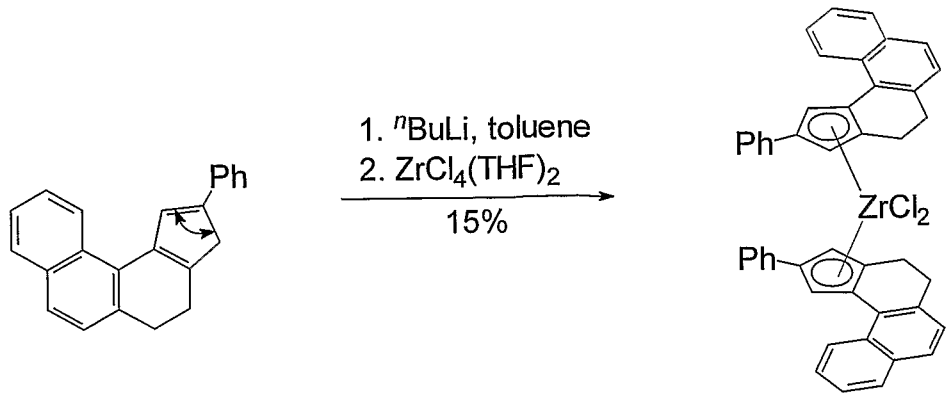
and of

Bis[η^5-(2-phenyl-4,5-dihydro-3H-cyclopenta[*c*]phenanthren-3-yl)zirconium dichloride.

This complex was prepared starting from naphthalene and following a scheme similar to that of example 3 as seen herebelow.



The chelating ligand was metallated with 2 equivalents of ^{n}BuLi in toluene-hexanes followed by addition of metallic salt $ZrCl_4(THF)_2$ to form the unbridged metallic complex.



The rac-complex was unambiguously characterised by NMR spectroscopy as seen in Figure 7 and by X-ray crystal structure analysis.

Figure 8 is the ORTEP representation of the molecular structure of the racemic complex with thermal ellipsoids drawn at the 50% probability level. The key geometric paramerers of this structure are:

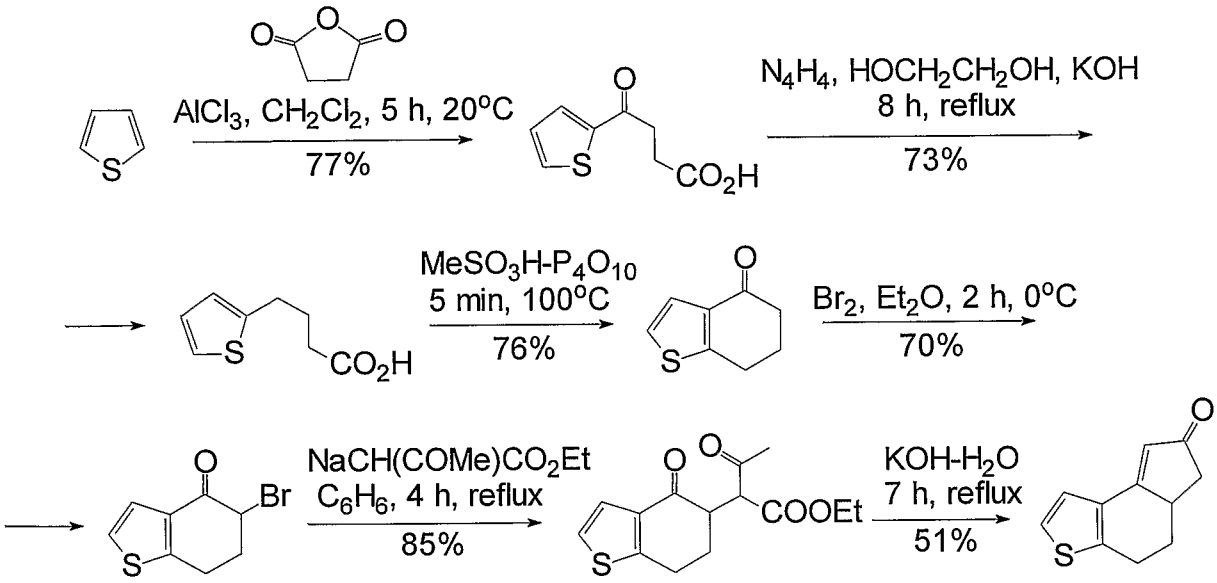
- bond lengths of Zr-Cp(c) and Zr-Cp(c)' arerespectively 2.229(2) and 2.244(2) Angströms;
- angle between Zr-Cp(A) and Zr-Cp'(A) axis is 132.70(6)°,
- angle between Cp and Cp' planes is 50.91(6)°.

It was observed that rotation in this unbridged metallic complex was hindered by the presence of the very bulky substituents.

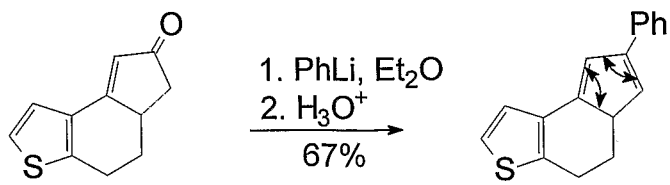
Example 5

Preparation of dichloro[6,6'-bis(dimethylsilanediyl)di(η^5-(7-phenyl-5,6-dihydro-4*H*-indeno[5,4-*b*]thiophene-6-yl)]zirconium.

The preparation is described in the following scheme.



6,7-dihydro-1-benzothiophen-4(5*H*)-one was obtained with an overall yield of 43% via the acylation of thiophene by succinic anhydride followed by reduction of the ketone formed and by the cyclisation of 4-(2-thienyl)butanoic acid in the presence of the laton`s reagent. Next, 4,5,5a,6-tetrahydro-7*H*-indeno[5,4-*b*]thiophen-7-one was synthesised from 6,7-dihydro-1-benzothiophen-4(5*H*)-one with an overall yield of 30%. The latter product was further reacted with one equivalent of PhLi in ether followed by acidification of the reaction medium to give a mixture of 7-phenyl-5,5a-dihydro-4*H*-indeno[5,4-*b*]thiophene and 7-phenyl-5,8-dihydro-4*H*-indeno[5,4-*b*]thiophene as shown in the scheme below

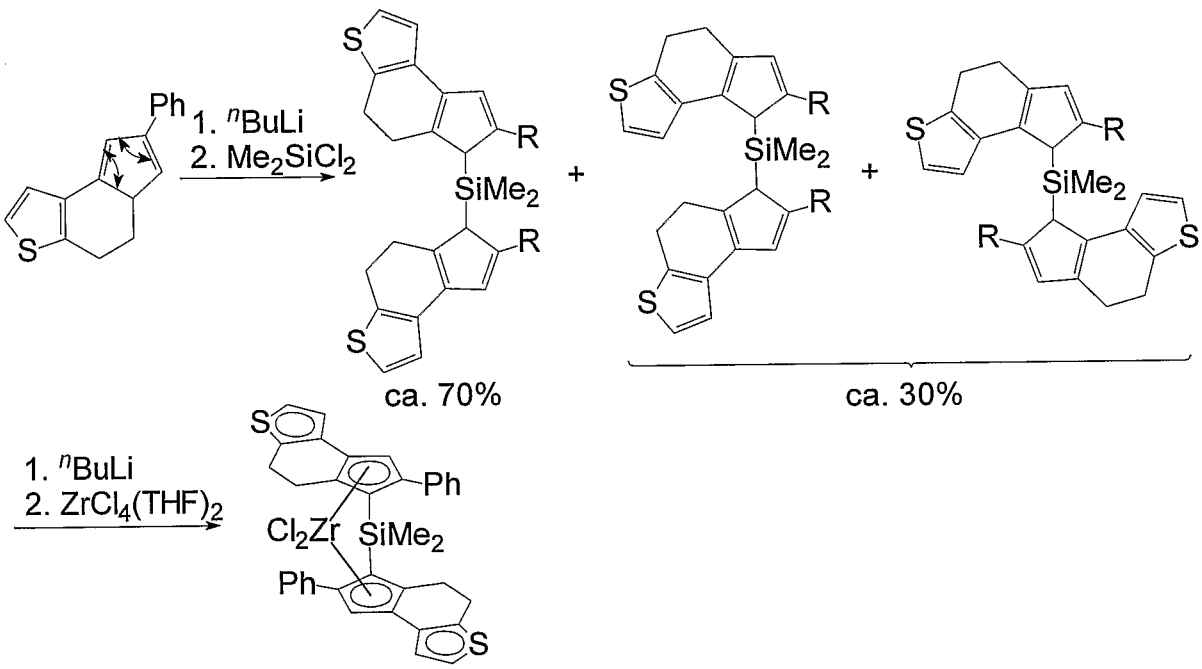


The lithium salt of this ligand was treated with 0.5 eqv of Me_2SiCl_2 in THF to form the respective *bis*(cyclopentadienyl)dimethylsilane. This *bis*-cyclopentadienyl ligand was isolated as a mixture of the Me_2Si-bridging ligands involving ca. 70% of the desired isomers with a yield of 17% by repeating flash chromatography on Silica Gel 60. It was metallated with 2 eqv of ^{n}BuLi in toluene-hexanes, and then with metallic salt $ZrCl_4(THF)_2$. This mixture was stirred overnight at room temperature and then filtered

through glass frit. Crystals precipitated from the filtrate at a temperature of -30°C were collected and dried in vacuum. On the evidence of ^{1}H NMR spectroscopy, this product isolated with a yield of 13% is a mixture of *rac*- and *meso*-complexes in a ratio of 1 to 5. This ^{1}H NMR spectrum is shown in figure 9. The *meso*-isomer was characterised by X-ray crystal structure analysis. Figure 10 is the ORTEP representation of the molecular structure of this meso-complex with thermal ellipsoids drawn at the 50% probability level.

The key geometric paramerers of this structure are:

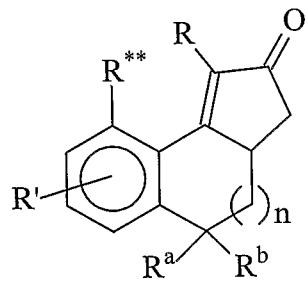
- bond lengths Zr-Cp(c) and Zr-Cp(c)' are 2.239(1) Angströms;
- angle between two cyclopentadienyl planes is 59.2°.



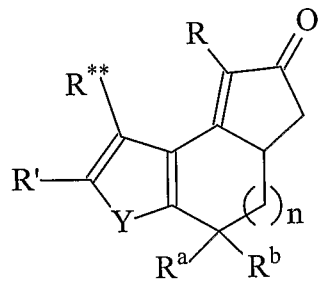
CLAIMS

1. A method for preparing substituted bis-tetrahydroindenyl ligands that comprises

a) preparing a complex of general formula I or I'

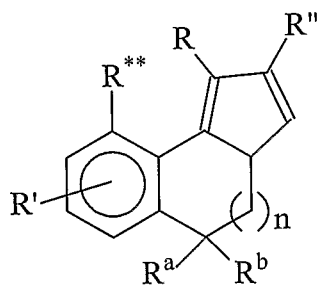


(I)

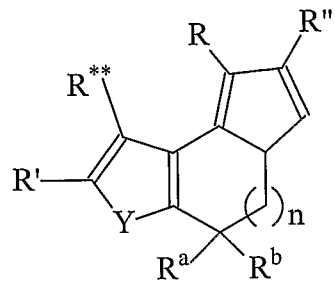


(I')

b) reacting complex I or complex I' with R"Li followed by acidification with a diluted acid in order to prepare complex II or complex II'

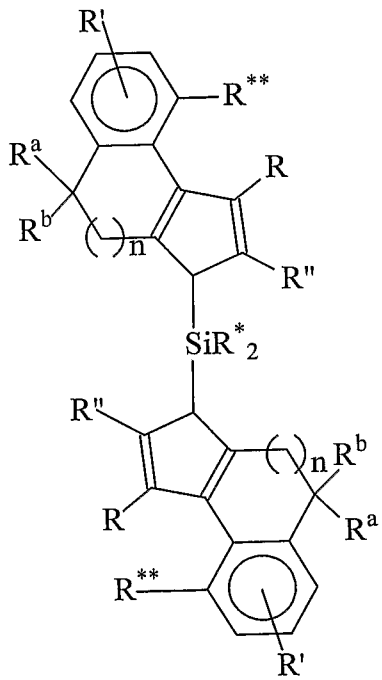


(II)

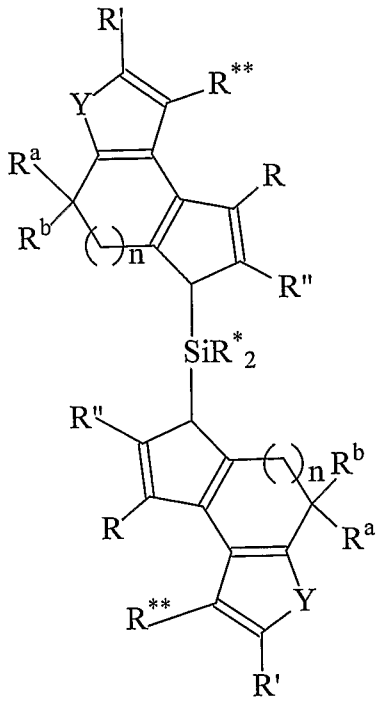


(II')

c) optionally reacting complex II or complex II' with $R^*_2SiX_2$ in the presence of nBuLi in order to prepare ligand III or ligand III'



(III)



(III')

wherein R, R', R", R^a and R^b are each independently selected from hydrogen, or hydrocarbyl having up to 10 carbon atoms,

wherein R* and R** are each independently selected from unsubstituted or substituted alkyl or aryl having up to 8 carbon atoms, including polynuclear fused aromatic rings,

wherein Y is a metal Group 13, 14, 15 or 16 of the Periodic Table,

wherein X is halogen or alkyl having up to 6 carbon atoms, and

wherein n is 0, 1 or 2.

2. The method of claim 1 wherein step c) is present.

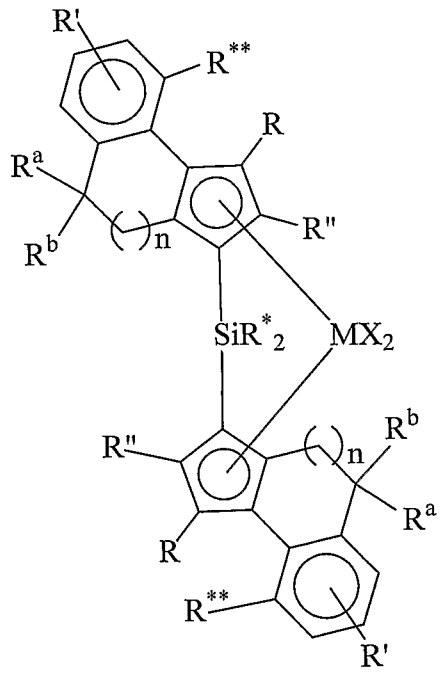
3. The method of claim 1 or claim 2 wherein R^a and R^b are the same and are hydrogen.

4. The method of any one of the preceding claims wherein at least one of R, R* or R** is at least as bulky as tert-butyl.

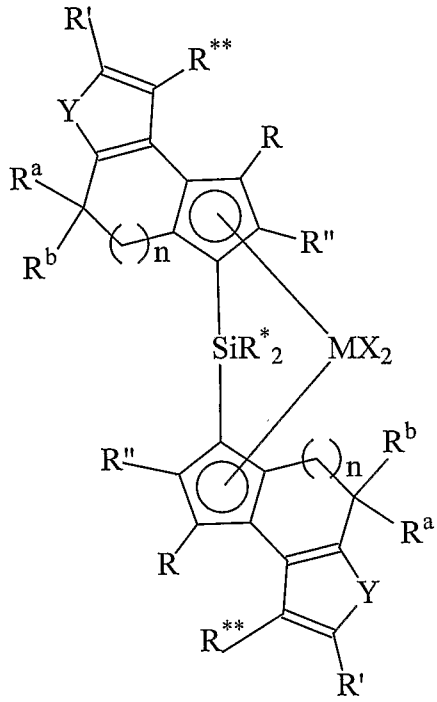
5. The method of any one of the preceding claims wherein n is zero.

6. Ligand of formula III or formula III' obtainable by the method of any one of claims 1 to5.

7. Metallocene catalyst component of formula IV or of formula IV' obtainable by metallation reaction of the ligand of claim 6 with a metallic salt of formula MX_n wherein M is a metal Group 4 of the Periodic Table and X is halogen or alkyl group having up to 6 carbon atoms.



(IV)



(IV')

8. Active catalyst system comprising the metallocene catalyst component of claim 7 and an activating agent having an ionising action selected from the group of alumoxane, alkyl aluminium compound, Lewis acid or combination thereof.

9. A method for homo- or co-polymerising ethylene and alpha-olefins that comprises the steps of:

a) injecting into the reactor the active catalyst system of claim 8;

b) injecting into the reactor the monomer and optional comonomers;

c) maintaining under polymerisation condition;

d) retrieving a polymer.

10. The method of claim 9 wherein the monomer ethylene or propylene and the comonomers are propylene, 1-butene and 1-hexene.

FIGURE 1

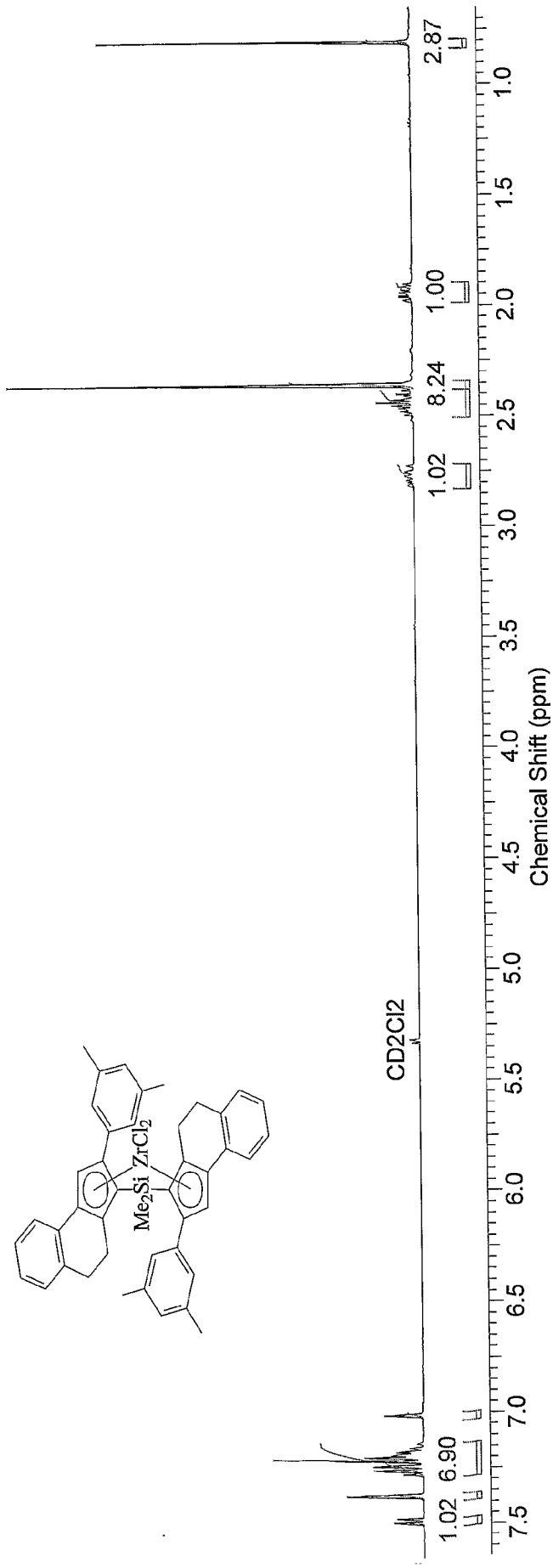

2.87
1.00
8.24
1.02
1.02 6.90
CD2Cl2
Me2Si ZrCl2
Chemical Shift (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

FIGURE 2

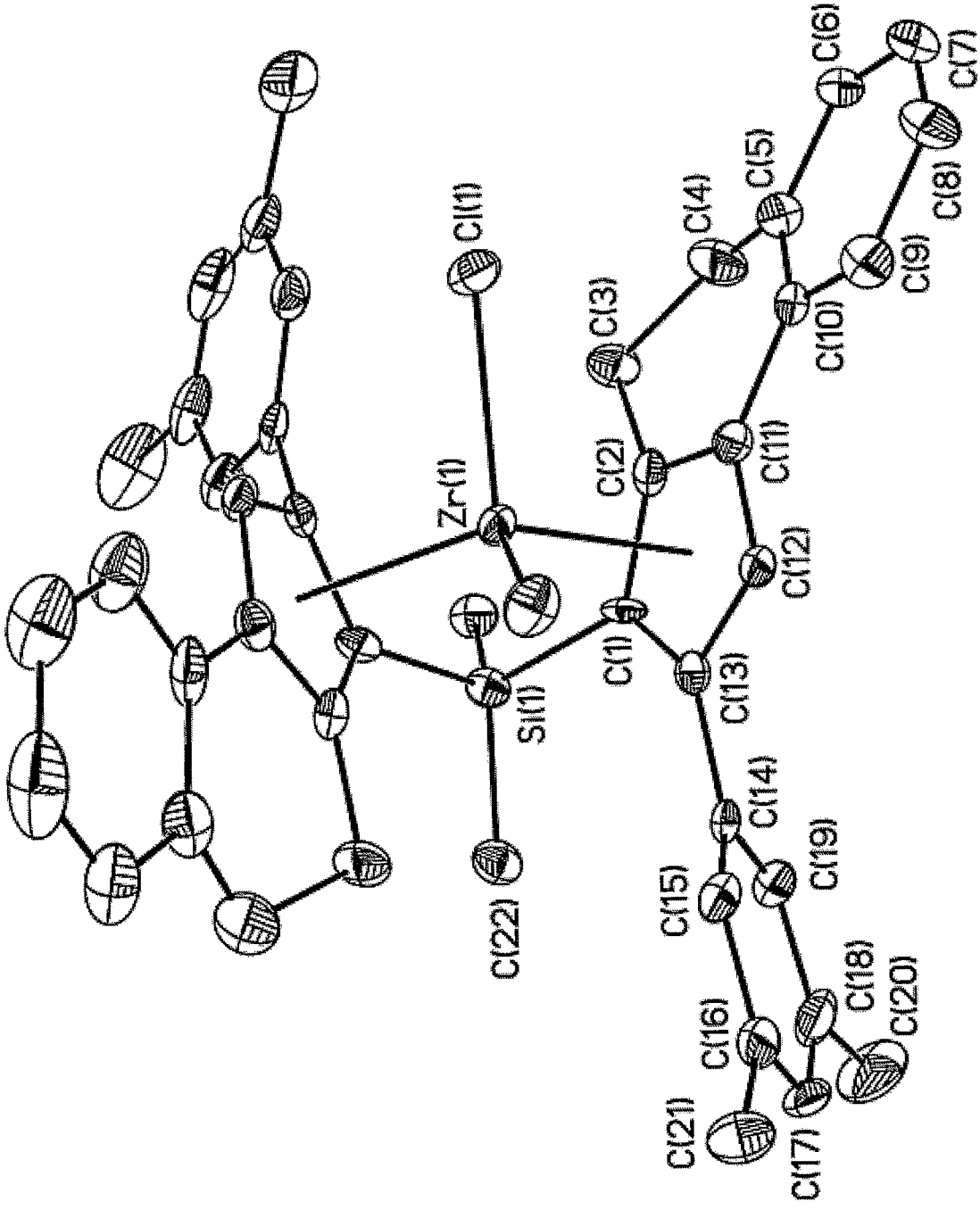

C(6)
C(7)
C(5)
C(8)
C(4)
C(9)
Cl(1)
C(3)
C(10)
C(2)
C(11)
Zr(1)
C(12)
C(1)
C(13)
Si(1)
C(14)
C(19)
C(15)
C(22)
C(18)
C(16)
C(20)
C(21)
C(17)

FIGURE 3

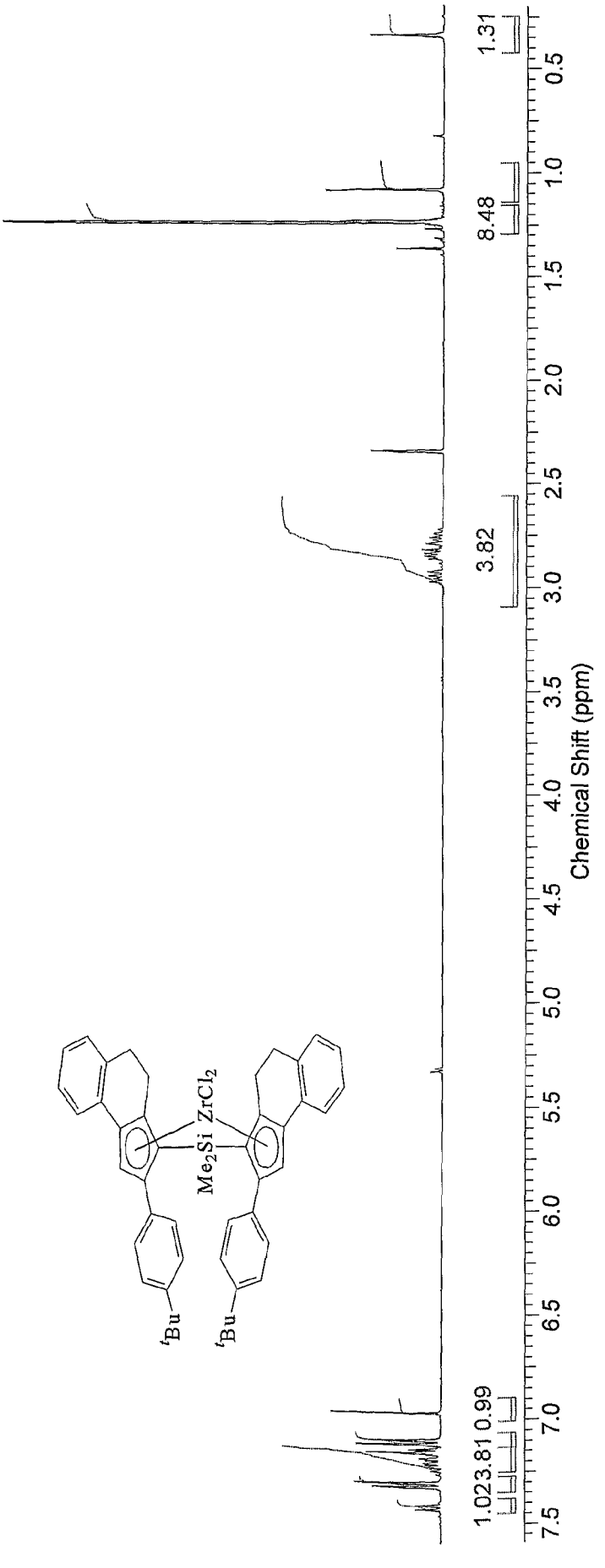

1.31
8.48
3.82
1.02 3.81 0.99
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)
Me2Si ZrCl2
tBu
tBu

FIGURE 4

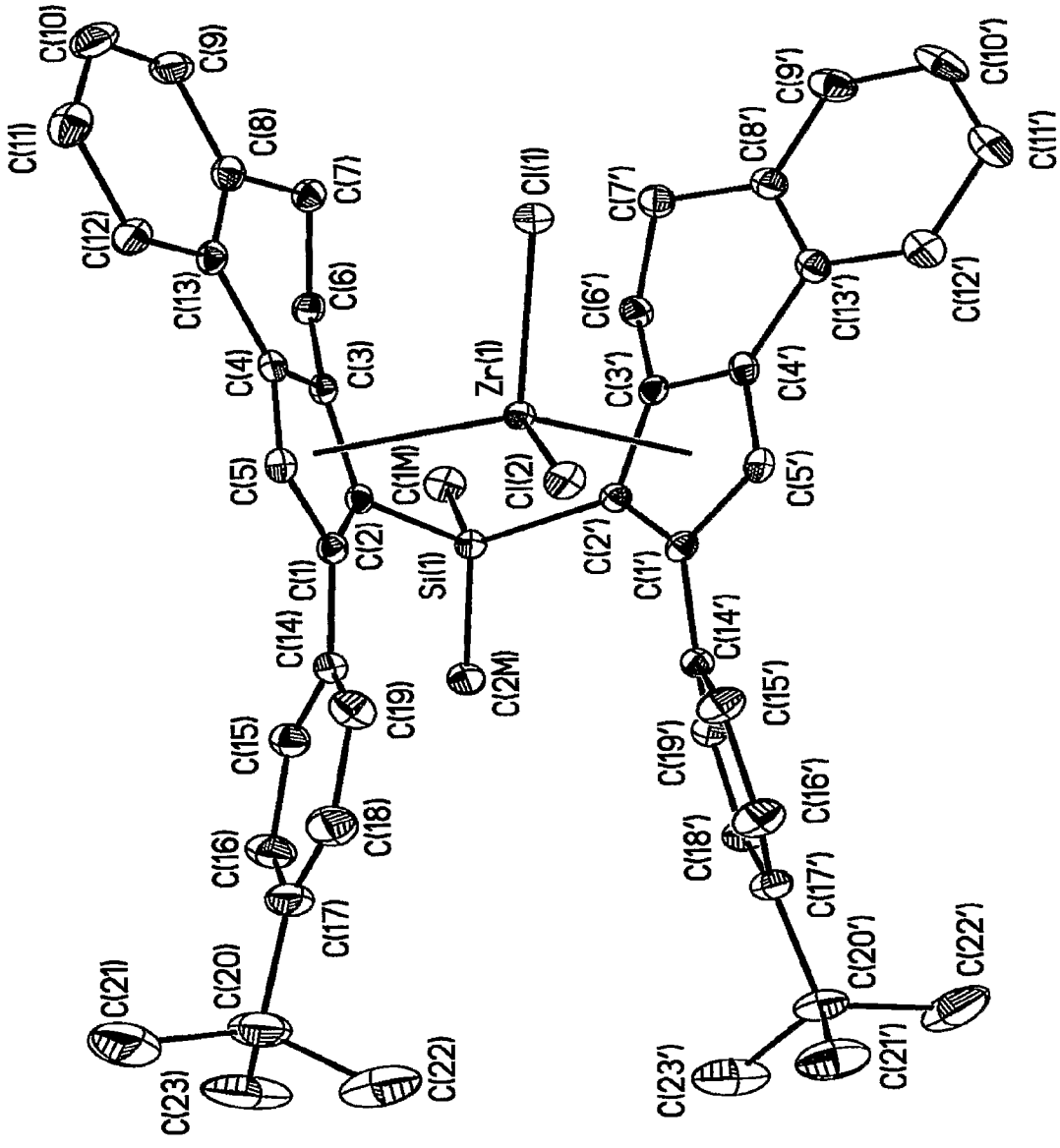

C(10)
C(9)
C(11)
C(8)
C(12)
C(7)
C(13)
C(6)
C(4)
C(3)
C(5)
C(2)
C(1)
C(14)
C(19)
C(15)
C(18)
C(16)
C(17)
C(20)
C(21)
C(23)
C(22)
C(1M)
Si(1)
C(2M)
Zr(1)
Cl(1)
Cl(2)
C(1')
C(2')
C(3')
C(4')
C(5')
C(6')
C(7')
C(8')
C(9')
C(10')
C(11')
C(12')
C(13')
C(14')
C(15')
C(16')
C(17')
C(18')
C(19')
C(20')
C(21')
C(22')
C(23')

FIGURE 5

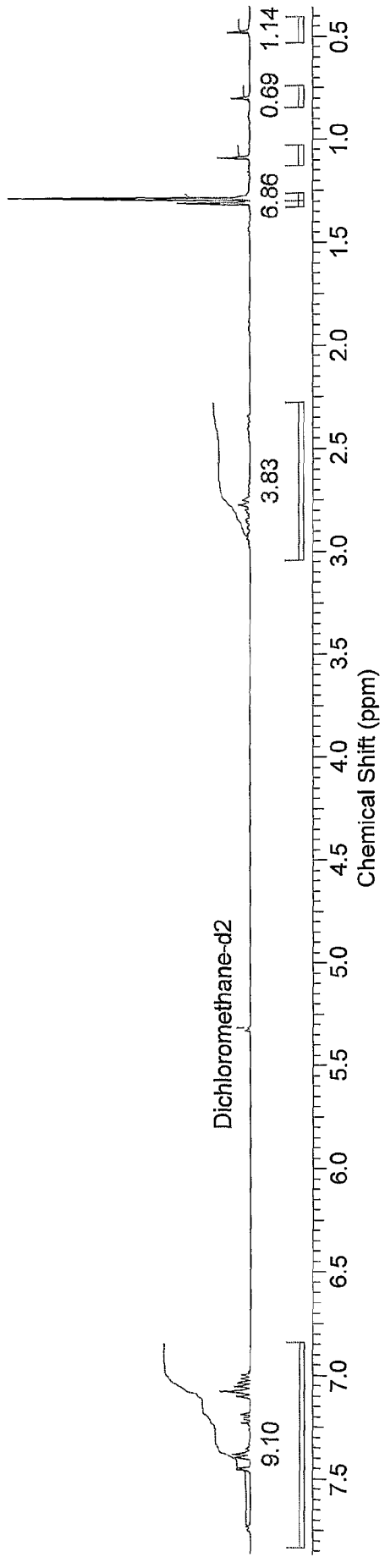

9.10
3.83
6.86
0.69
1.14
Dichloromethane-d2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

FIGURE 6

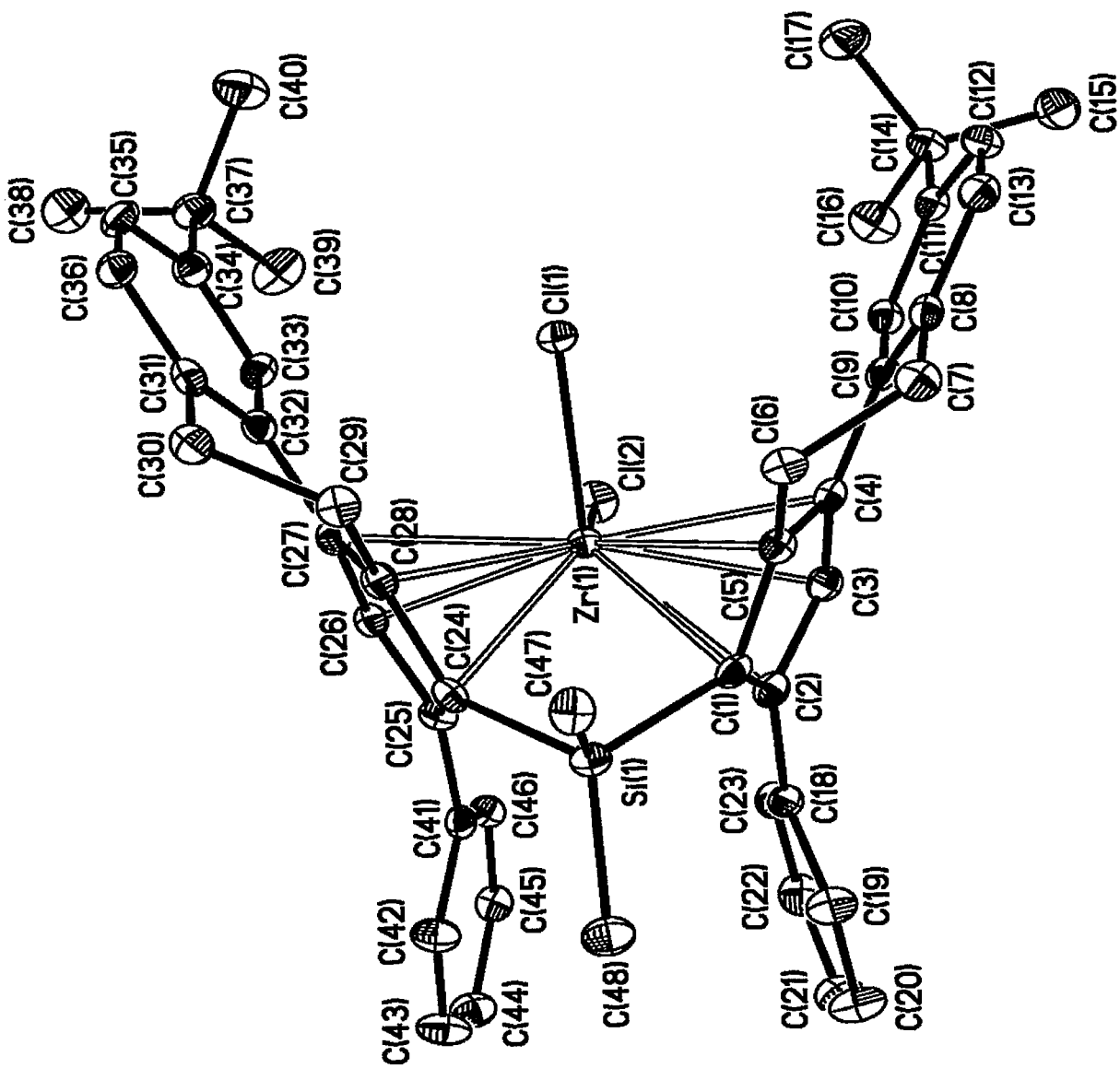

C(17)
C(12)
C(15)
C(14)
C(16)
C(13)
C(11)
C(10)
C(8)
C(9)
C(7)
C(6)
C(4)
C(3)
C(5)
C(2)
C(1)
C(18)
C(23)
C(22)
C(19)
C(21)
C(20)
Si(1)
C(48)
C(47)
Zr(1)
Cl(1)
Cl(2)
C(40)
C(35)
C(38)
C(37)
C(36)
C(34)
C(39)
C(31)
C(33)
C(30)
C(32)
C(29)
C(27)
C(28)
C(26)
C(24)
C(25)
C(41)
C(46)
C(42)
C(45)
C(43)
C(44)

FIGURE 7

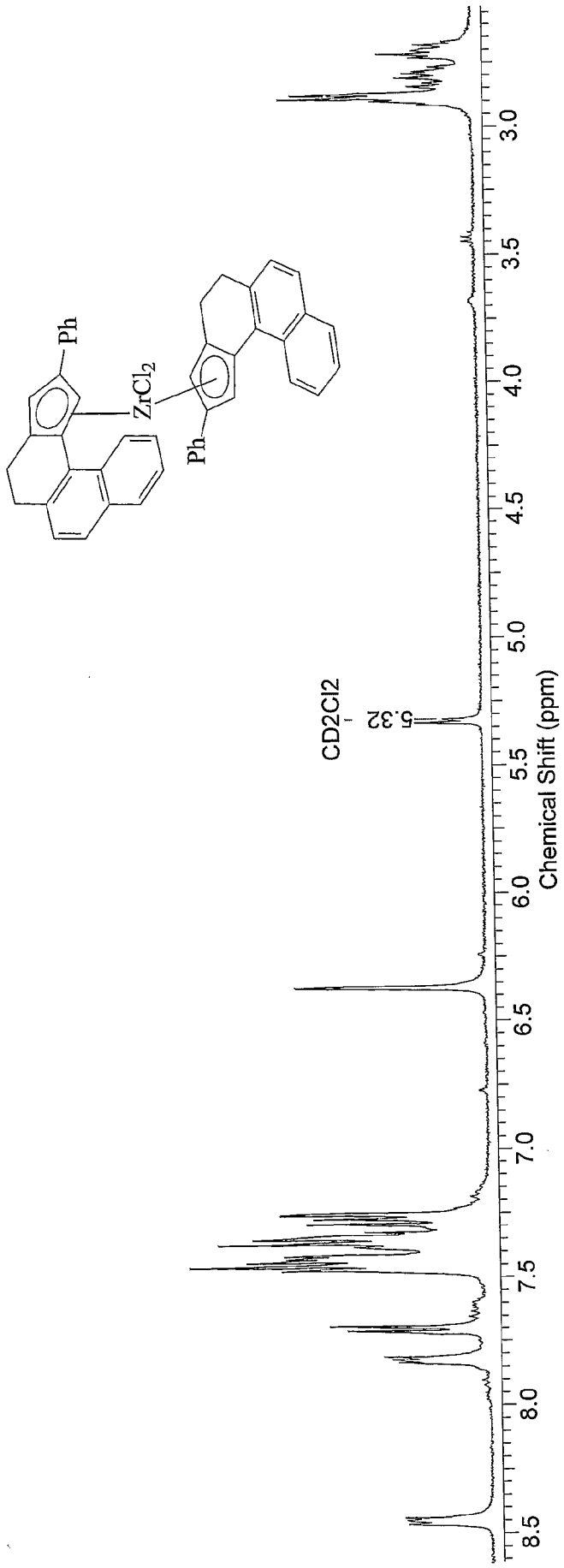

Ph
ZrCl2
Ph
CD2Cl2
5.32
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
Chemical Shift (ppm)

FIGURE 8

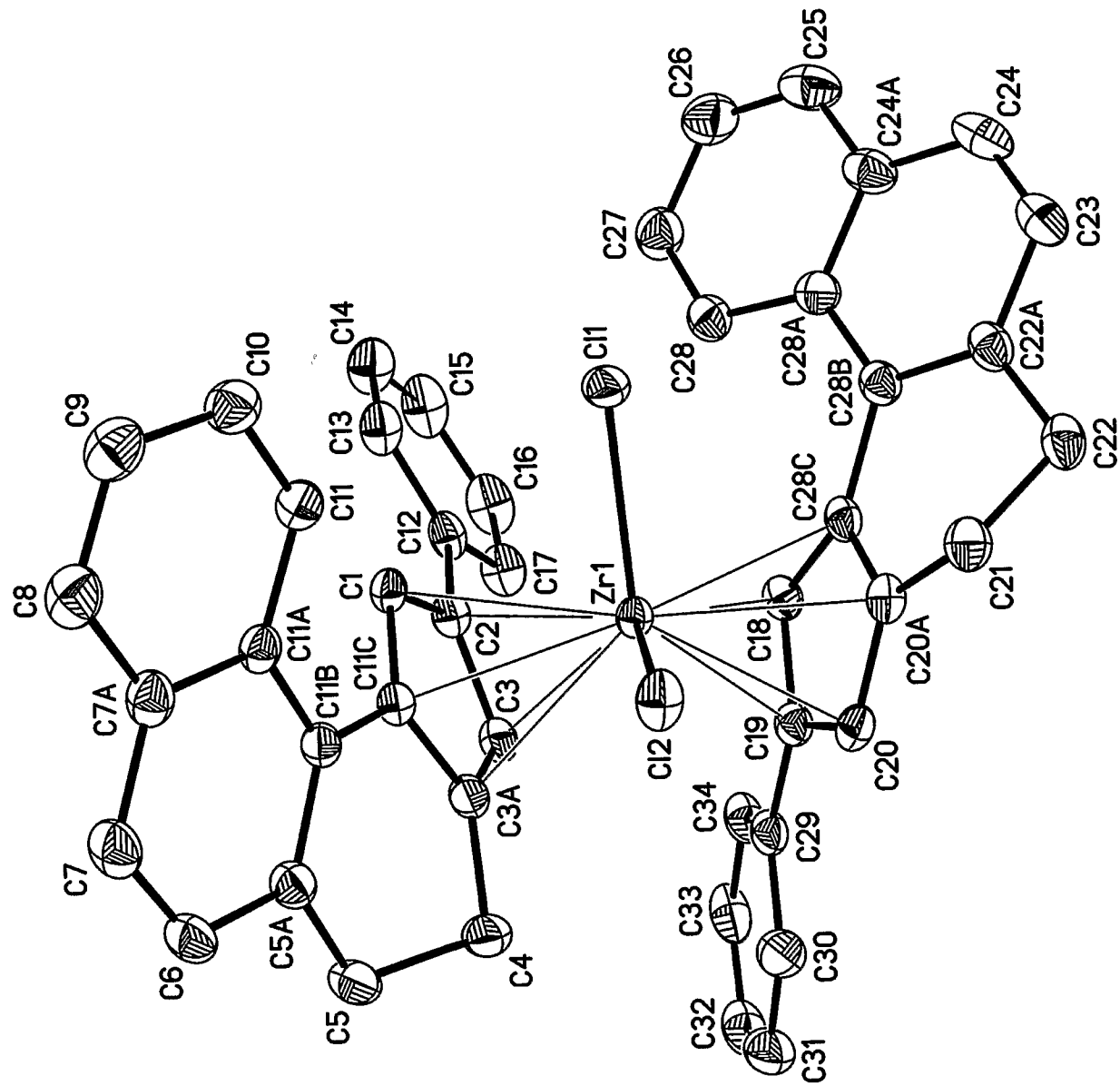

C26
C25
C24A
C24
C27
C23
C28
C28A
C22A
C28B
C22
C28C
C21
C20A
C18
C20
C19
C34
C29
C33
C30
C32
C31
Cl1
Cl2
Zr1
C14
C15
C13
C16
C12
C17
C1
C2
C3
C3A
C10
C9
C11
C8
C11A
C11C
C11B
C7A
C7
C6
C5A
C5
C4

FIGURE 9

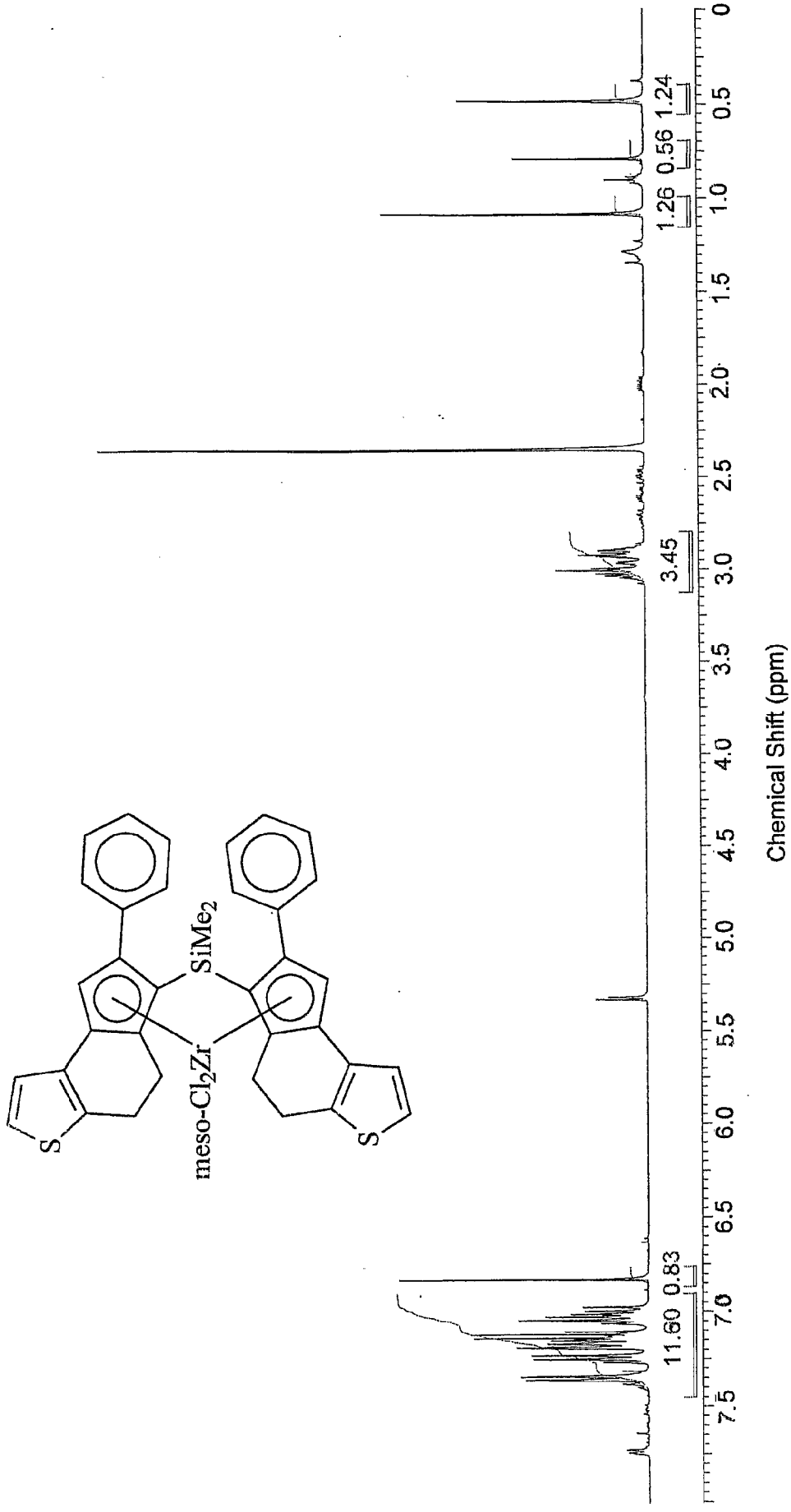
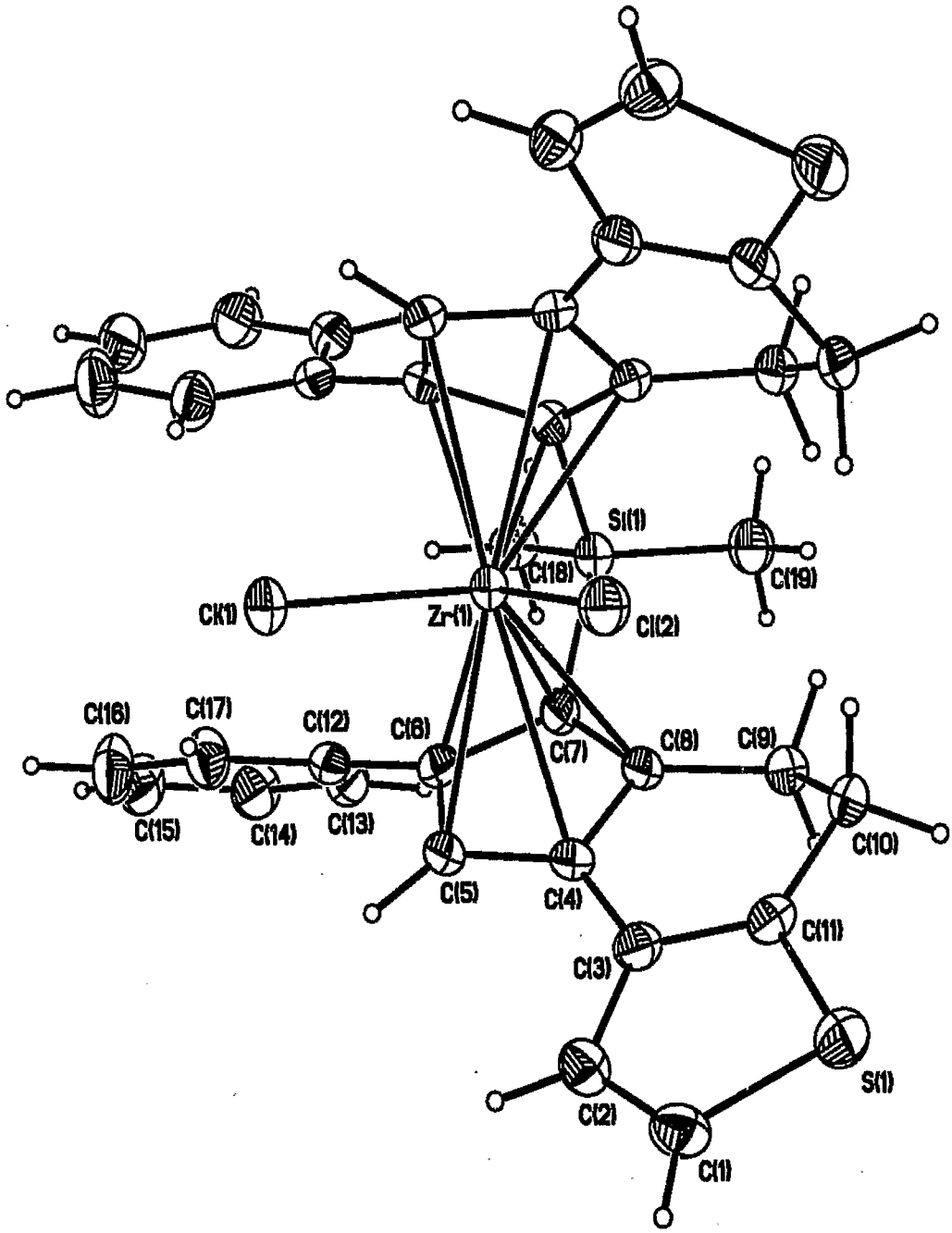

meso-Cl2Zr
SiMe2
S
S
11.60
0.83
3.45
1.26
0.56
1.24
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

FIGURE 10


Si(1)
C(18)
C(19)
Cl(1)
Zr(1)
Cl(2)
C(16)
C(17)
C(12)
C(6)
C(7)
C(8)
C(9)
C(15)
C(14)
C(13)
C(10)
C(5)
C(4)
C(11)
C(3)
S(1)
C(2)
C(1)

INTERNATIONAL SEARCH REPORT

International application No
PCT/RU2008/000814

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J31/16 C07F17/00 C08F4/76 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/037838 A1 (BASELL POLYOLEFINE GMBH) 6 May 2004 (2004-05-06) page 18, lines 6, 7, 14, 26 & 27	6-7
Y	WO 01/74745 A1 (ENICHEM SPA) 11 October 2001 (2001-10-11) the whole document	1-10

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 October 2009	08/10/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Elliott, Adrian

INTERNATIONAL SEARCH REPORT

International application No
PCT/RU2008/000814

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WILD F R W P ET AL: "ansa-Metallocene derivatives. IV. Synthesis and molecular structure of chiral ansa-titanocene derivatives with bridged tetrahydroindenyl ligands" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 232, no. 3, 22 June 1982 (1982-06-22) , pages 233-247, XP002089631 ISSN: 0022-328X DOI: 10.1016/S0022-328X(00)89067-1 cited in the application the whole document	1-10
Y	EP 0 344 887 A2 (EXXON CHEMICAL PATENTS INC) 6 December 1989 (1989-12-06) cited in the application the whole document	1-10
Y	HALTERMAN R L ET AL: "Synthesis and structure of ansa-metallocene complexes (M=ZrCl2, TiCl2, YCl, and LuCl) containing the bis(2-methyl-4,5,6,7-tetrahydroinden-yl) dimethylsilane ligand" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 604, no. 1, 5 June 2000 (2000-06-05), pages 12-19, XP004215344 ISSN: 0022-328X DOI: 10.1016/S0022-328X(00)00177-7 cited in the application the whole document	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/RU2008/000814

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 2004037838 A1	06-05-2004	AT	399789 T	15-07-2008
		AU	2003274058 A1	13-05-2004
		BR	0315584 A	30-08-2005
		CN	1694892 A	09-11-2005
		DE	10250025 A1	06-05-2004
		EP	1554295 A1	20-07-2005
		ES	2307973 T3	01-12-2008
		JP	2006503910 T	02-02-2006
		MX	PA05002338 A	23-05-2005
		RU	2333215 C2	10-09-2008
		US	2008200708 A1	21-08-2008
WO 0174745 A1	11-10-2001	AR	029503 A1	02-07-2003
		AT	286496 T	15-01-2005
		AU	3930801 A	15-10-2001
		CA	2404549 A1	11-10-2001
		DE	60108231 D1	10-02-2005
		DE	60108231 T2	15-12-2005
		EP	1268375 A1	02-01-2003
		ES	2234819 T3	01-07-2005
		IT	MI20000680 A1	01-10-2001
		JP	2003529572 T	07-10-2003
		MX	PA02009374 A	14-05-2004
		TW	222964 B	01-11-2004
		US	2003166800 A1	04-09-2003
EP 0344887 A2	06-12-1989	AU	629818 B2	15-10-1992
		AU	3147889 A	21-09-1989
		BR	8901277 A	07-11-1989
		CA	1341404 C	03-12-2002
		CS	8901726 A3	18-03-1992
		DK	137989 A	22-09-1989
		FI	891310 A	22-09-1989
		HU	53114 A2	28-09-1990
		JP	2131488 A	21-05-1990
		JP	2775058 B2	09-07-1998
		JP	3117078 B2	11-12-2000
		JP	10218889 A	18-08-1998
		NO	891209 A	22-09-1989
		PL	278381 A1	27-11-1989
		PT	90048 A	10-11-1989
		YU	57689 A1	31-10-1991