

DESCRIPTION

TRANSITION METAL COMPLEX, PROCESS FOR PRODUCING THE SAME,
OLEFIN POLYMERIZATION CATALYST CONTAINING THE TRANSITION
METAL COMPLEX AND PROCESS FOR PRODUCING OLEFIN POLYMERS

TECHNICAL FIELD

The present invention relates to a transition metal complex, a process for producing the same, a polymerization catalyst containing the transition metal complex and a process for producing polymers which uses
5 the catalyst.

BACKGROUND ART

A number of reports have already been made on the process for producing olefin polymers using a
10 metallocene complex. For example, JP-A-58-19309 discloses a process for producing olefin polymers which uses a metallocene complex and an aluminoxanone. The process has a problem in that when olefin is polymerized with the disclosed catalyst which uses bis(cyclopenta-
15 dienyl)zirconium dichloride and methylaluminoxane, the molecular weight of the olefin polymer obtained is low. To improve this point, WO87/02370 discloses the use of a reaction product of an organic compound having at least two hydroxyl groups with a transition metal compound.
20 However, the system disclosed in WO87/02370 which uses 2,2'-thiobis(6-tert-butyl-4-methylphenoxy)titanium dichloride and methylaluminoxane, and also a system

disclosed in JP-A-5-230133 which uses 2,2'-thiobis(6-tert-butyl-4-methylphenoxy)titanium dichloride, triisobutylaluminum and triphenylmethyl tetrakis(pentafluorophenyl)borate involve a problem in that the catalytic
5 activity is unsatisfactorily low from the industrial point of view although the molecular weight of the polymer produced is improved.

Moreover, known metallocene complexes, e.g., ethylenebis(indenyl)zirconium dichloride, isopropylidene-
10 (cyclopentadienyl) (fluorenyl)zirconium dichloride and dimethylsilyl(tert-butylamide)-(tetramethylcyclopentadienyl)titanium dichloride, have a problem in that they are insoluble in saturated hydrocarbon solvents although they are soluble in aromatic hydrocarbon
15 solvents and resultantly polymerization catalysts containing such complexes cannot be used for producing polymers using saturated hydrocarbon solvents.

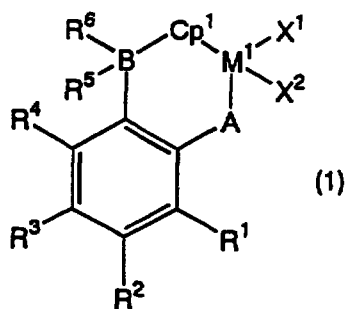
In recognition of the situation, the objects of the present invention are to provide a complex, important
20 from the industrial viewpoint, which has a high activity at reaction temperatures efficient in the industrial process for olefin polymerization and is soluble in saturated hydrocarbon solvents, and to provide a highly active olefin polymerization catalyst containing the
25 complex, and a process for producing olefin polymers which uses the catalyst.

DISCLOSURE OF THE INVENTION

The present inventors have made extensive study on transition metal complexes and olefin polymerization catalysts in order to attain the above-mentioned objects.

5 As the result, the inventors have found a transition metal complex soluble in saturated hydrocarbon solvents which has a ligand comprising an aromatic ring having a hetero atom in the substituent and a cyclopentadienyl ring linked with each other through a covalent bonding
10 group, and have accomplished the present invention on the basis of above finding.

Thus, according to the present invention, there are provided a transition metal complex represented by the formula (1) (hereinafter referred to as compound (1))
15 and a polymerization catalyst containing the complex:



wherein M¹ is a transition metal atom of the group 4 of the periodic table of elements, A is an atom of the group 16 of the periodic table of elements and B is an atom of the group 14 of the periodic table of elements; Cp¹ is a
20 group having a cyclopentadiene type anionic skeleton; and X¹, X², R¹, R², R³, R⁴, R⁵ and R⁶ are each independently a

hydrogen atom, halogen atom, alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon atoms of 2-20; provided that R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally combine with each other to form a ring.

[Transition metal complex]

In the compound [1], the transition metal atom represented by M^1 refers to a transition metal atom of the group 4 of the periodic table of elements (Nomenclature of Inorganic Chemistry, IUPAC, revised ed., 1989) and may be, for example, a titanium atom, zirconium atom and hafnium atom.

The atom of the group 16 of the periodic table of elements represented by A may be, for example, an oxygen atom, sulfur atom and selenium atom, and is

preferably an oxygen atom.

The atom of the group 14 of the periodic table of elements represented by B may be, for example, a carbon atom, silicon atom and germanium atom.

- 5 The group having a cyclopentadiene type anionic skeleton represented as the substituent Cp^1 may be, for example, the η^5 -cyclopentadienyl group, η^5 -methylcyclopentadienyl group, η^5 -dimethylcyclopentadienyl group, η^5 -trimethylcyclopentadienyl group, η^5 -tetramethylcyclopentadienyl group, η^5 -ethylcyclopentadienyl group, η^5 -n-propylcyclopentadienyl group, η^5 -isopropylcyclopentadienyl group, η^5 -n-butylcyclopentadienyl group, η^5 -sec-butylcyclopentadienyl group, η^5 -tert-butylcyclopentadienyl group, η^5 -n-pentylcyclopentadienyl group, η^5 -neopentylcyclopentadienyl group, η^5 -n-hexylcyclopentadienyl group, η^5 -n-octylcyclopentadienyl group, η^5 -phenylcyclopentadienyl group, η^5 -naphthylcyclopentadienyl group, η^5 -trimethylsilylcyclopentadienyl group, η^5 -triethylsilylcyclopentadienyl group, η^5 -tert-butyltrimethylsilylcyclopentadienyl group, η^5 -indenyl group, η^5 -methylindenyl group, η^5 -dimethylindenyl group, η^5 -ethylindenyl group, η^5 -n-propylindenyl group, η^5 -isopropylindenyl group, η^5 -n-butylindenyl group, η^5 -sec-butylindenyl group, η^5 -tert-butylindenyl group, η^5 -n-pentylindenyl
- 10
- 15
- 20

group, η^5 -neopentylindenyl group, η^5 -n-hexylindenyl group, η^5 -n-octylindenyl group, η^5 -n-decylindenyl group, η^5 -phenylindenyl group, η^5 -methylphenylindenyl group, η^5 -naphthylindenyl group, η^5 -trimethylsilylindenyl group,
5 η^5 -triethylsilylindenyl group, η^5 -tert-butyldimethylsilylindenyl group, η^5 -tetrahydroindenyl group, η^5 -fluorenyl group, η^5 -methylfluorenyl group, η^5 -dimethylfluorenyl group, η^5 -ethylfluorenyl group, η^5 -diethylfluorenyl group, η^5 -n-propylfluorenyl group, η^5 -di-n-
10 propylfluorenyl group, η^5 -isopropylfluorenyl group, η^5 -diisopropylfluorenyl group, η^5 -n-butylfluorenyl group, η^5 -sec-butylfluorenyl group, η^5 -tert-butylfluorenyl group, η^5 -di-n-butylfluorenyl group, η^5 -di-sec-butylfluorenyl group, η^5 -di-tert-butylfluorenyl group, η^5 -n-
15 pentylfluorenyl group, η^5 -neopentylfluorenyl group, η^5 -n-hexylfluorenyl group, η^5 -n-octylfluorenyl group, η^5 -n-decylfluorenyl group, η^5 -n-dodecylfluorenyl group, η^5 -phenylfluorenyl group, η^5 -di-phenylfluorenyl group, η^5 -methylphenylfluorenyl group, η^5 -naphthylfluorenyl group,
20 η^5 -trimethylsilylfluorenyl group, η^5 -bis-trimethylsilylfluorenyl group, η^5 -triethylsilylfluorenyl group and η^5 -tert-butyldimethylsilylfluorenyl group, preferred among them being, for example, the η^5 -cyclopentadienyl group, η^5 -methylcyclopentadienyl group, η^5 -tert-butylcyclo-

pentadienyl group, η^5 -tetramethylcyclopentadienyl group, η^5 -indenyl group and η^5 -fluorenyl group.

The halogen atom in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be, for example, a fluorine atom, chlorine atom, bromine atom and iodine atom.

The alkyl group with the number of carbon atoms of 1-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be, for example, the methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, sec-butyl group, tert-butyl group, n-pentyl group, neopentyl group, amyl group, n-hexyl group, n-octyl group, n-decyl group, n-dodecyl group, n-pentadecyl group and n-eicosyl group, preferred among them being, the methyl group, ethyl group, isopropyl group, tert-butyl group and amyl group.

All of these alkyl groups may optionally be substituted with at least one halogen atom, e.g., fluorine atom, chlorine atom, bromine atom and iodine atom. The alkyl group with the number of carbon atoms of 1-20 substituted with at least one halogen atom may be, for example, the fluoromethyl group, difluoromethyl group, trifluoromethyl group, chloromethyl group, dichloromethyl group, trichloromethyl group, bromomethyl group, dibromomethyl group, tribromomethyl group, iodomethyl group, diiodomethyl group, triiodomethyl group, fluoroethyl group, difluoroethyl group, trifluoroethyl group, tetrafluoroethyl group, pentafluoroethyl group, chloroethyl group, dichloroethyl group, trichloro-

ethyl group, tetrachloroethyl group, pentachloroethyl group, bromomethyl group, dibromoethyl group, tribromoethyl group, tetrabromoethyl group, pentabromoethyl group, perfluoropropyl group, perfluorobutyl group, 5 perfluoropentyl group, perfluorohexyl group, perfluorooctyl group, perfluorododecyl group, perfluoropentadecyl group, perfluoroeicosyl group, perchloropropyl group, perchlorobutyl group, perchloropentyl group, perchlorohexyl group, perchlorooctyl group, perchlorododecyl 10 group, perchloropentadecyl group, perchloroeicosyl group, perbromopropyl group, perbromobutyl group, perbromopentyl group, perbromohexyl group, perbromooctyl group, perbromododecyl group, perbromopentadecyl group and perbromoeicosyl group.

15 The aralkyl group with the number of carbon atoms of 7-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be, for example, the benzyl group, (2-methylphenyl)methyl group, (3-methylphenyl)methyl group, (4-methylphenyl)methyl group, (2,3-dimethylphenyl)methyl group, (2,4-dimethylphenyl)methyl group, (2,5-dimethylphenyl)methyl group, (2,6-dimethylphenyl)methyl group, (3,4-dimethylphenyl)methyl group, (4,6-dimethylphenyl)methyl group, (2,3,4-trimethylphenyl)methyl group, (2,3,5-trimethylphenyl)methyl group, (2,3,6-trimethylphenyl)methyl group, (3,4,5-trimethylphenyl)methyl group, 20 (2,4,6-trimethylphenyl)methyl group, (2,3,4,5-tetramethylphenyl)methyl group, (2,3,4,6-tetramethylphenyl)methyl group, (2,3,5,6-tetramethylphenyl)methyl group, 25

(pentamethylphenyl)methyl group, (ethylphenyl)methyl group, (n-propylphenyl)methyl group, (isopropylphenyl)-methyl group, (n-butylphenyl)methyl group, (sec-butylphenyl)methyl group, (tert-butylphenyl)methyl group, (n-pentylphenyl)methyl group, (neopentylphenyl)methyl group, (n-hexylphenyl)methyl group, (n-octylphenyl)methyl group, (n-decylphenyl)methyl group, (n-decylphenyl)methyl group, (n-tetradecylphenyl)methyl group, naphthylmethyl group and anthracenylmethyl group, preferred of these being the benzyl group.

All of these aralkyl groups may optionally be substituted with at least one halogen atom, e.g., fluorine atom, chlorine atom, bromine atom and iodine atom.

The aryl group with the number of carbon atoms of 6-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be, for example, the phenyl group, 2-tolyl group, 3-tolyl group, 4-tolyl group, 2,3-xylyl group, 2,4-xylyl group, 2,5-xylyl group, 2,6-xylyl group, 3,4-xylyl group, 3,5-xylyl group, 2,3,4-trimethylphenyl group, 2,3,5-trimethylphenyl group, 2,3,6-trimethylphenyl group, 2,4,6-trimethylphenyl group, 3,4,5-trimethylphenyl group, 2,3,4,5-tetramethylphenyl group, 2,3,4,6-tetramethylphenyl group, 2,3,5,6-tetramethylphenyl group, penta-methylphenyl group, ethylphenyl group, n-propylphenyl group, isopropylphenyl group, n-butylphenyl group, sec-butylphenyl group, tert-butylphenyl group, n-pentylphenyl group, neopentylphenyl group, n-hexylphenyl group, n-

octylphenyl group, n-decylphenyl group, n-dodecylphenyl group, n-tetradecylphenyl group, naphthyl group and anthracenyl group, preferred of these being the phenyl group.

- 5 All of these aryl groups may optionally be substituted with at least one halogen atom, e.g., fluorine atom, chlorine atom, bromine atom and iodine atom.

- 10 The substituted silyl group with the number of carbon atoms of 1-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 refers to a silyl group substituted with at least one hydrocarbon group. The hydrocarbon group may be, for example, an alkyl group with the number of carbon atoms of 1-10, such as the methyl group, ethyl
- 15 group, n-propyl group, isopropyl group, n-butyl group, sec-butyl group, tert-butyl group, isobutyl group, n-pentyl group, n-hexyl group and cyclohexyl group, and an aryl group, such as phenyl group. Examples of the substituted silyl group with the number of carbon atoms
- 20 of 1-20 include a monosubstituted silyl group with the number of carbon atoms of 1-20, such as the methylsilyl group, ethylsilyl group and phenylsilyl group, di-substituted silyl group with the number of carbon atoms of 2-20, such as the dimethylsilyl group, diethylsilyl
- 25 group and diphenylsilyl group, and tri-substituted silyl groups with the number of carbon atoms of 3-20, such as trimethylsilyl group, triethylsilyl group, tri-n-propylsilyl group, triisopropylsilyl group, tri-n-

butylsilyl group, tri-sec-butylsilyl group, tri-tert-butylsilyl group, tri-isobutylsilyl group, tert-butyl-dimethylsilyl group, tri-n-pentylsilyl group, tri-n-hexylsilyl group, tricyclohexylsilyl group and
5 triphenylsilyl group, preferred of these being the trimethylsilyl group, tert-butyldimethylsilyl group and triphenylsilyl group.

The hydrocarbon groups of each of these substituted silyl groups may optionally be substituted
10 with at least one halogen atom, e.g., fluorine atom, chlorine atom, bromine atom and iodine atom.

The alkoxy group with the number of carbon atoms of 1-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be, for example, the methoxy group, ethoxy
15 group, n-propoxy group, isopropoxy group, n-butoxy group, sec-butoxy group, tert-butoxy group, n-pentoxy group, neopentoxy group, n-hexoxy group, n-octoxy group, n-dodecoxy group, n-pentadecoxy group and n-eicosoxy group, preferred of these being the methoxy group, ethoxy group
20 and tert-butoxy group.

These alkoxy groups may each optionally be substituted with at least one halogen atom, e.g., fluorine atom, chlorine atom, bromine atom and iodine atom.

25 The aralkyloxy group with the number of carbon atoms of 7-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may be, for example, the benzyloxy group, (2-methylphenyl)methoxy group, (3-methylphenyl)methoxy

group, (4-methylphenyl)methoxy group, (2,3-dimethyl-
phenyl)methoxy group, (2,4-dimethylphenyl)methoxy group,
(2,5-dimethylphenyl)methoxy group, (2,6-dimethylphenyl)-
methoxy group, (3,4-dimethylphenyl)methoxy group, (3,5-
5 dimethylphenyl)methoxy group, (2,3,4-trimethylphenyl)-
methoxy group, (2,3,5-trimethylphenyl)methoxy group,
(2,3,6-trimethylphenyl)methoxy group, (2,4,5-
trimethylphenyl)methoxy group, (2,4,6-trimethylphenyl)-
methoxy group, (3,4,5-trimethylphenyl)methoxy group,
10 (2,3,4,5-tetramethylphenyl)methoxy group, (2,3,4,6-
tetramethylphenyl)methoxy group, (2,3,5,6-tetramethyl-
phenyl)methoxy group, (pentamethylphenyl)methoxy group,
(ethylphenyl)methoxy group, (n-propylphenyl)methoxy
group, (isopropylphenyl)methoxy group, (n-butylphenyl)-
15 methoxy group, (sec-butylphenyl)methoxy group, (tert-
butylphenyl)methoxy group, (n-hexylphenyl)methoxy group,
(n-octylphenyl)methoxy group, (n-decylphenyl)methoxy
group, (n-tetradecylphenyl)methoxy group, naphthylmethoxy
group and anthracenylmethoxy group, preferred of these
20 being the benzyloxy group.

These aralkyloxy groups may each optionally be
substituted with at least one halogen atom, e.g.,
fluorine atom, chlorine atom, bromine atom and iodine
atom.

25 The aryloxy group with the number of carbon
atoms of 6-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5
and R^6 may be such an aryloxy group with the number of
carbon atoms of 6-20 as the phenoxy group, 2-methyl-

phenoxy group, 3-methylphenoxy group, 4-methylphenoxy group, 2,3-dimethylphenoxy group, 2,4-dimethylphenoxy group, 2,5-dimethylphenoxy group, 2,6-dimethylphenoxy group, 3,4-dimethylphenoxy group, 3,5-dimethylphenoxy group, 2,3,4-trimethylphenoxy group, 2,3,5-trimethylphenoxy group, 2,3,6-trimethylphenoxy group, 2,4,5-trimethylphenoxy group, 2,4,6-trimethylphenoxy group, 3,4,5-trimethylphenoxy group, 2,3,4,5-tetramethylphenoxy group, 2,3,4,6-tetramethylphenoxy group, pentamethylphenoxy group, ethylphenoxy group, n-propylphenoxy group, isopropylphenoxy group, n-butylphenoxy group, sec-butylphenoxy group, tert-butylphenoxy group, n-hexylphenoxy group, n-octylphenoxy group, n-decylphenoxy group, n-tetradecylphenoxy group, naphthoxy group and anthracenoxy group.

These aryloxy groups may each optionally be substituted with at least one halogen atom, e.g., fluorine atom, chlorine atom, bromine atom and iodine atom.

The di-substituted amino group with the number of carbon atoms of 2-20 in the substituents X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 refers to an amino group substituted with two hydrocarbon groups, the hydrocarbon group being, for example, an alkyl group with the number of carbon atoms of 1-10, such as the methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, sec-butyl group, tert-butyl group, isobutyl group, n-pentyl group, n-hexyl group and cyclohexyl group, and an aryl group such as the

phenyl group. Examples of such di-substituted amino group with the number of carbon atoms of 2-20 include the dimethylamino group, diethylamino group, di-n-propylamino group, diisopropylamino group, di-n-butylamino group, di-
5 sec-butylamino group, di-tert-butylamino group, diisobutylamino group, tert-butylisopropylamino group, di-n-hexylamino group, di-n-octylamino group, di-n-decylamino group, diphenylamino group, bistrimethylsilylamino group and bis-tert-butyl dimethylsilylamino group,
10 preferred of these being the dimethylamino group and diethylamino group.

The substituents R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally combine with each other to form a ring.

X^1 and X^2 are each preferably a halogen atom,
15 alkyl group and aralkyl group, more preferably a halogen atom.

R^1 is preferably an alkyl group with the number of carbon atoms of 1-20, aralkyl group, aryl group, halogenated alkyl group, halogenated aralkyl group,
20 halogenated aryl group or substituted silyl group.

The compounds (1) include transition metal complexes wherein B in the formula (1) is a carbon atom, such as methylene(cyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, methylene(cyclopentadienyl)-
25 (3-tert-butyl-2-phenoxy)titanium dichloride, methylene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride, methylene(cyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride, methylene-

(cyclopentadienyl)(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene(cyclopentadienyl)-(3-trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene(cyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, methylene(cyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3-trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, methylene(methylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride, methylene(tert-butylcyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, methylene(tert-butylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, methylene(tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, methylene(tert-butylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride, methylene(tert-butylcyclopentadienyl)(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene(tert-butylcyclopentadienyl)(3-

- trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride,
methylene(tert-butylcyclopentadienyl)(3-tert-butyl-5-
methoxy-2-phenoxy)titanium dichloride, methylene(tert-
butylcyclopentadienyl)(3-tert-butyl-5-chloro-2-
5 phenoxy)titanium dichloride,
methylene(tetramethylcyclopentadienyl)(3,5-
dimethyl-2-phenoxy)titanium dichloride, methylene(tetra-
methylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium
dichloride, methylene(tetramethylcyclopentadienyl)(3-
10 tert-butyl-5-methyl-2-phenoxy)titanium dichloride,
methylene(tetramethylcyclopentadienyl)(3-phenyl-2-
phenoxy)titanium dichloride, methylene(tetra-
methylcyclopentadienyl)(3-tert-butyl-5-dimethylsilyl-
methyl-2-phenoxy)titanium dichloride, methylene(tetra-
15 methylcyclopentadienyl)(3-trimethylsilyl-5-methyl-2-
phenoxy)titanium dichloride, methylene(tetra-
methylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-
phenoxy)titanium dichloride, methylene(tetra-
methylcyclopentadienyl)(3-tert-butyl-5-chloro-2-
20 phenoxy)titanium dichloride,
methylene(trimethylsilylcyclopentadienyl)(3,5-
dimethyl-2-phenoxy)titanium dichloride, methylene-
(trimethylsilylcyclopentadienyl)(3-tert-butyl-2-phenoxy)-
titanium dichloride, methylene(trimethylsilylcyclo-
25 pentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
dichloride, methylene(trimethylsilylcyclopentadienyl)(3-
phenyl-2-phenoxy)titanium dichloride, methylene-
(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-dimethyl-

- silyl-5-methyl-2-phenoxy)titanium dichloride, methylene-(trimethylsilylcyclopentadienyl)(3-trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene-(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-methoxy-
5 2-phenoxy)titanium dichloride, methylene(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)-titanium dichloride,
methylene(fluorenyl)(3,5-dimethyl-2-phenoxy)-titanium dichloride, methylene(fluorenyl)(3-tert-butyl-2-
10 phenoxy)titanium dichloride, methylene(fluorenyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, methylene(fluorenyl)(3-phenyl-2-phenoxy)titanium dichloride,
methylene(fluorenyl)(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene(fluorenyl)(3-
15 trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, methylene(fluorenyl)(3-tert-butyl-5-methoxy-2-phenoxy)-titanium dichloride, methylene(fluorenyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,
isopropylidene(cyclopentadienyl)(3,5-dimethyl-
20 2-phenoxy)titanium dichloride, isopropylidene(cyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(cyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride,
25 isopropylidene(cyclopentadienyl)(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(cyclopentadienyl)(3-trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, isopro-

pylidene(cyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, isopropylidene(cyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,

- 5 isopropylidene(methylcyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, isopropylidene(methylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, isopropylidene(methylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride,
- 10 isopropylidene(methylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride, isopropylidene(methylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(methylcyclopentadienyl)(3-trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride,
- 15 isopropylidene(methylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, isopropylidene(methylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,
- 20 isopropylidene(tert-butylcyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, isopropylidene(tert-butylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, isopropylidene(tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
- 25 dichloride, isopropylidene(tert-butylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride, isopropylidene(tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene-

(tert-butylcyclopentadienyl)(3-trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(tert-butylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)-titanium dichloride, isopropylidene(tert-butylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,

isopropylidene(tetramethylcyclopentadienyl)-(3,5-dimethyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)-(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)-(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)-(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)-(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, isopropylidene(tetramethylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,

isopropylidene(trimethylsilylcyclopentadienyl)-(3,5-dimethyl-2-phenoxy)titanium dichloride, isopropylidene(trimethylsilylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, isopropylidene(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride, isopropylidene(trimethylsilylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride,

- isopropylidene(trimethylsilylcyclopentadienyl)(3-tert-butyl-
dimethylsilyl-5-methyl-2-phenoxy)titanium
dichloride, isopropylidene(trimethylsilylcyclo-
pentadienyl)(3-trimethylsilyl-5-methyl-2-phenoxy)titanium
5 dichloride, isopropylidene(trimethylsilylcyclo-
pentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium
dichloride, isopropylidene(trimethylsilylcyclopenta-
dienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium
dichloride,
- 10 isopropylidene(fluorenyl)(3,5-dimethyl-2-
phenoxy)titanium dichloride, isopropylidene(fluorenyl)(3-
tert-butyl-2-phenoxy)titanium dichloride, isopropylidene-
(fluorenyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
dichloride, isopropylidene(fluorenyl)(3-phenyl-2-
15 phenoxy)titanium dichloride, isopropylidene(fluorenyl)(3-
tert-butyl-5-methyl-2-phenoxy)titanium
dichloride, isopropylidene(fluorenyl)(3-trimethylsilyl-5-
methyl-2-phenoxy)titanium dichloride, isopropylidene-
(fluorenyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium
20 dichloride, isopropylidene(fluorenyl)(3-tert-butyl-5-
chloro-2-phenoxy)titanium dichloride,
- diphenylmethylenecyclopentadienyl)(3,5-
dimethyl-2-phenoxy)titanium dichloride, diphenyl-
methylenecyclopentadienyl)(3-tert-butyl-2-phenoxy)-
25 titanium dichloride, diphenylmethylenecyclopenta-
dienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
dichloride, diphenylmethylenecyclopentadienyl)(3-phenyl-
2-phenoxy)titanium dichloride, diphenylmethylene-

- (cyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, diphenylmethylenecyclopentadienyl(3-trimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylenecyclopentadienyl(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, diphenylmethylenecyclopentadienyl(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,
- diphenylmethylenemethylcyclopentadienyl(3,5-dimethyl-2-phenoxy)titanium dichloride, diphenylmethylenemethylcyclopentadienyl(3-tert-butyl-2-phenoxy)titanium dichloride, diphenylmethylenemethylcyclopentadienyl(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylenemethylcyclopentadienyl(3-phenyl-2-phenoxy)titanium dichloride,
- diphenylmethylenemethylcyclopentadienyl(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, diphenylmethylenemethylcyclopentadienyl(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylenemethylcyclopentadienyl(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,
- diphenylmethylenetert-butylcyclopentadienyl(3,5-dimethyl-2-phenoxy)titanium dichloride, diphenylmethylenetert-butylcyclopentadienyl(3-tert-butyl-2-phenoxy)titanium dichloride, diphenylmethylenetert-butylcyclopentadienyl(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylenetert-

- butylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium
dichloride, diphenylmethylene(tert-butylcyclopenta-
dienyl)(3-tert-butyltrimethylsilyl-5-methyl-2-
phenoxy)titanium dichloride, diphenylmethylene(tert-
5 butylcyclopentadienyl)(3-trimethylsilyl-5-methyl-2-
phenoxy)titanium dichloride, diphenylmethylene(tert-
butylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-
phenoxy)titanium dichloride, diphenylmethylene(tert-
butylcyclopentadienyl)(3-tert-butyl-5-chloro-2-
10 phenoxy)titanium dichloride,
diphenylmethylene(tetramethylcyclopentadienyl)-
(3,5-dimethyl-2-phenoxy)titanium dichloride, diphenyl-
methylene(tetramethylcyclopentadienyl)(3-tert-butyl-2-
phenoxy)titanium dichloride, diphenylmethylene(tetra-
15 methylcyclopentadienyl)(3-tert-butyl-5-methyl-2-
phenoxy)titanium dichloride, diphenylmethylene(tetra-
methylcyclopentadienyl)(3-phenyl-2-phenoxy)titanium
dichloride, diphenylmethylene(tetramethylcyclopenta-
dienyl)(3-tert-butyltrimethylsilyl-5-methyl-2-phenoxy)-
20 titanium dichloride, diphenylmethylene(tetramethyl-
cyclopentadienyl)(3-trimethylsilyl-5-methyl-2-phenoxy)-
titanium dichloride, diphenylmethylene(tetramethyl-
cyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)-
titanium dichloride, diphenylmethylene(tetramethyl-
25 cyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)-
titanium dichloride,
diphenylmethylene(trimethylsilylcyclopenta-
dienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride,

- diphenylmethylene(trimethylsilylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, diphenylmethylene-(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylene-
- 5 (trimethylsilylcyclopentadienyl)(3-phenyl-2-phenoxy)-titanium dichloride, diphenylmethylene(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylene-(trimethylsilylcyclopentadienyl)(3-tert-trimethylsilyl-5-
- 10 methyl-2-phenoxy)titanium dichloride, diphenylmethylene-(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, diphenylmethylene-(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,
- 15 diphenylmethylene(fluorenyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, diphenylmethylene-(fluorenyl)(3-tert-butyl-2-phenoxy)titanium dichloride, diphenylmethylene(fluorenyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylene-
- 20 (fluorenyl)(3-phenyl-2-phenoxy)titanium dichloride, diphenylmethylene(fluorenyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylene(fluorenyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, diphenylmethylene(fluorenyl)(3-tert-butyl-5-
- 25 methoxy-2-phenoxy)titanium dichloride and diphenylmethylene(fluorenyl)(3-tert-butyl-5-chloro-2-phenoxy)-titanium dichloride; compounds resulting from changing the "titanium" in the above-mentioned compounds to

zirconium or hafnium, compounds resulting from changing the "chloride" in the above-mentioned compounds to bromide, iodide, dimethylamide, diethylamide, n-butoxide or isopropoxide, compounds resulting from changing the
5 "(cyclopentadienyl)" in the above-mentioned compounds to (dimethylcyclopentadienyl), (trimethylcyclopentadienyl), (n-butylcyclopentadienyl), (tert-butyldimethylsilylcyclopentadienyl) or (indenyl); compounds resulting from changing the "3,5-dimethyl-2-phenoxy" in the above-
10 mentioned compounds to 2-phenoxy, 3-methyl-2-phenoxy, 3,5-di-tert-butyl-2-phenoxy, 3-phenyl-5-methyl-2-phenoxy, 3-tert-butyldimethylsilyl-2-phenoxy or 3-trimethylsilyl-2-phenoxy and compounds resulting from changing the "methylene" in the above-mentioned compounds to diethyl-
15 methylene; and transition metal complexes wherein B in the formula (1) is an atom of the group 14 of the periodic table of elements other than carbon atom, such as

dimethylsilyl(cyclopentadienyl)(2-phenoxy)-
20 titanium dichloride, dimethylsilyl(cyclopentadienyl)(3-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(cyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, dimethylsilyl(cyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(cyclo-
25 pentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(cyclopentadienyl)(3,5-di-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(cyclopentadienyl)(5-methyl-3-phenyl-2-phenoxy)titanium

- dichloride, dimethylsilyl(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
- dichloride, dimethylsilyl(cyclopentadienyl)(5-methyl-3-trimethylsilyl-2-phenoxy)titanium dichloride,
- 5 dimethylsilyl(cyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, dimethylsilyl(cyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride, dimethylsilyl(cyclopentadienyl)(3,5-diamyl-2-phenoxy)titanium dichloride,
- 10 dimethylsilyl(methylcyclopentadienyl)(2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(3-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium
- 15 dichloride, dimethylsilyl(methylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(3,5-di-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(5-methyl-3-phenyl-2-phenoxy)titanium
- 20 dichloride, dimethylsilyl(methylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(5-methyl-3-trimethylsilyl-2-phenoxy)titanium dichloride,
- 25 dimethylsilyl(methylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride, dimethylsilyl(methylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,

cyclopentadienyl)(3,5-diamyl-2-phenoxy)titanium
dichloride,

- dimethylsilyl(n-butylcyclopentadienyl)(2-
phenoxy)titanium dichloride, dimethylsilyl(n-butyl-
5 cyclopentadienyl)(3-methyl-2-phenoxy)titanium dichloride,
dimethylsilyl(n-butylcyclopentadienyl)(3,5-dimethyl-2-
phenoxy)titanium dichloride, dimethylsilyl(n-butyl-
cyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium
dichloride, dimethylsilyl(n-butylcyclopentadienyl)(3-
10 tert-butyl-5-methyl-2-phenoxy)titanium dichloride,
dimethylsilyl(n-butylcyclopentadienyl)(3,5-di-tert-butyl-
2-phenoxy)titanium dichloride, dimethylsilyl(n-butyl-
cyclopentadienyl)(5-methyl-3-phenyl-2-phenoxy)titanium
dichloride, dimethylsilyl(n-butylcyclopentadienyl)(3-
15 tert-butyl dimethylsilyl-5-methyl-2-phenoxy)titanium
dichloride, dimethylsilyl(n-butylcyclopentadienyl)(5-
methyl-3-trimethylsilyl-2-phenoxy)titanium dichloride,
dimethylsilyl(n-butylcyclopentadienyl)(3-tert-butyl-5-
methoxy-2-phenoxy)titanium dichloride, dimethylsilyl(n-
20 butylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)-
titanium dichloride, dimethylsilyl(n-butylcyclopenta-
dienyl)(3,5-diamyl-2-phenoxy)titanium dichloride,
dimethylsilyl(tert-butylcyclopentadienyl)(2-
phenoxy)titanium dichloride, dimethylsilyl(tert-
25 butylcyclopentadienyl)(3-methyl-2-phenoxy)titanium
dichloride, dimethylsilyl(tert-butylcyclopentadienyl)-
(3,5-dimethyl-2-phenoxy)titanium dichloride, dimethyl-
silyl(tert-butylcyclopentadienyl)(3-tert-butyl-2-

- phenoxy)titanium dichloride, dimethylsilyl(tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-
titanium dichloride, dimethylsilyl(tert-butylcyclopentadienyl)(3,5-di-tert-butyl-2-phenoxy)titanium
5 dichloride, dimethylsilyl(tert-butylcyclopentadienyl)(5-methyl-3-phenyl-2-phenoxy)titanium dichloride, dimethylsilyl(tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(tert-butylcyclopentadienyl)(5-methyl-3-trimethyl-
10 silyl-2-phenoxy)titanium dichloride, dimethylsilyl(tert-butylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)-titanium dichloride, dimethylsilyl(tert-butylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium
dichloride, dimethylsilyl(tert-butylcyclopentadienyl)-
15 (3,5-diamyl-2-phenoxy)titanium dichloride,
dimethylsilyl(tetramethylcyclopentadienyl)(2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3-methyl-2-phenoxy)titanium
dichloride, dimethylsilyl(tetramethylcyclopentadienyl)-
20 (3,5-dimethyl-2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-
titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3,5-di-tert-butyl-2-phenoxy)titanium
25 dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(5-methyl-3-phenyl-2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-

- silyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(5-methyl-3-trimethylsilyl-2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride, dimethylsilyl(tetramethylcyclopentadienyl)(3,5-diamyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)-(2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)(3-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)-(3,5-dimethyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)(3-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)(3,5-di-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)(5-methyl-3-phenyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)-(3-tert-butyl)dimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)-(5-methyl-3-trimethylsilyl-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium dichloride, dimethylsilyl(trimethylsilylcyclopentadienyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride,

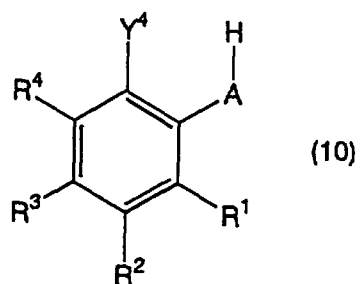
dimethylsilyl(trimethylsilylcyclopentadienyl)(3,5-diamyl-2-phenoxy)titanium dichloride,

- dimethylsilyl(indenyl)(2-phenoxy)titanium dichloride, dimethylsilyl(indenyl)(3-methyl-2-phenoxy)-
- 5 titanium dichloride, dimethylsilyl(indenyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, dimethylsilyl(indenyl)(3-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(indenyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(indenyl)(3,5-di-tert-butyl-2-
- 10 phenoxy)titanium dichloride, dimethylsilyl(indenyl)(5-methyl-3-phenyl-2-phenoxy)titanium dichloride, dimethylsilyl(indenyl)(3-tert-butyl dimethylsilyl-5-methyl-2-phenoxy)titanium dichloride, dimethylsilyl(indenyl)(5-methyl-3-trimethylsilyl-2-phenoxy)titanium dichloride,
- 15 dimethylsilyl(indenyl)(3-tert-butyl-5-methoxy-2-phenoxy)-titanium dichloride, dimethylsilyl(indenyl)(3-tert-butyl-5-chloro-2-phenoxy)titanium dichloride, dimethylsilyl(indenyl)(3,5-diamyl-2-phenoxy)titanium dichloride,
- dimethylsilyl(fluorenyl)(2-phenoxy)titanium
- 20 dichloride, dimethylsilyl(fluorenyl)(3-methyl-2-phenoxy)-titanium dichloride, dimethylsilyl(fluorenyl)(3,5-dimethyl-2-phenoxy)titanium dichloride, dimethylsilyl(fluorenyl)(3-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(fluorenyl)(3-tert-butyl-5-methyl-2-
- 25 phenoxy)titanium dichloride, dimethylsilyl(fluorenyl)-(3,5-di-tert-butyl-2-phenoxy)titanium dichloride, dimethylsilyl(fluorenyl)(5-methyl-3-phenyl-2-phenoxy)-titanium dichloride, dimethylsilyl(fluorenyl)(3-tert-

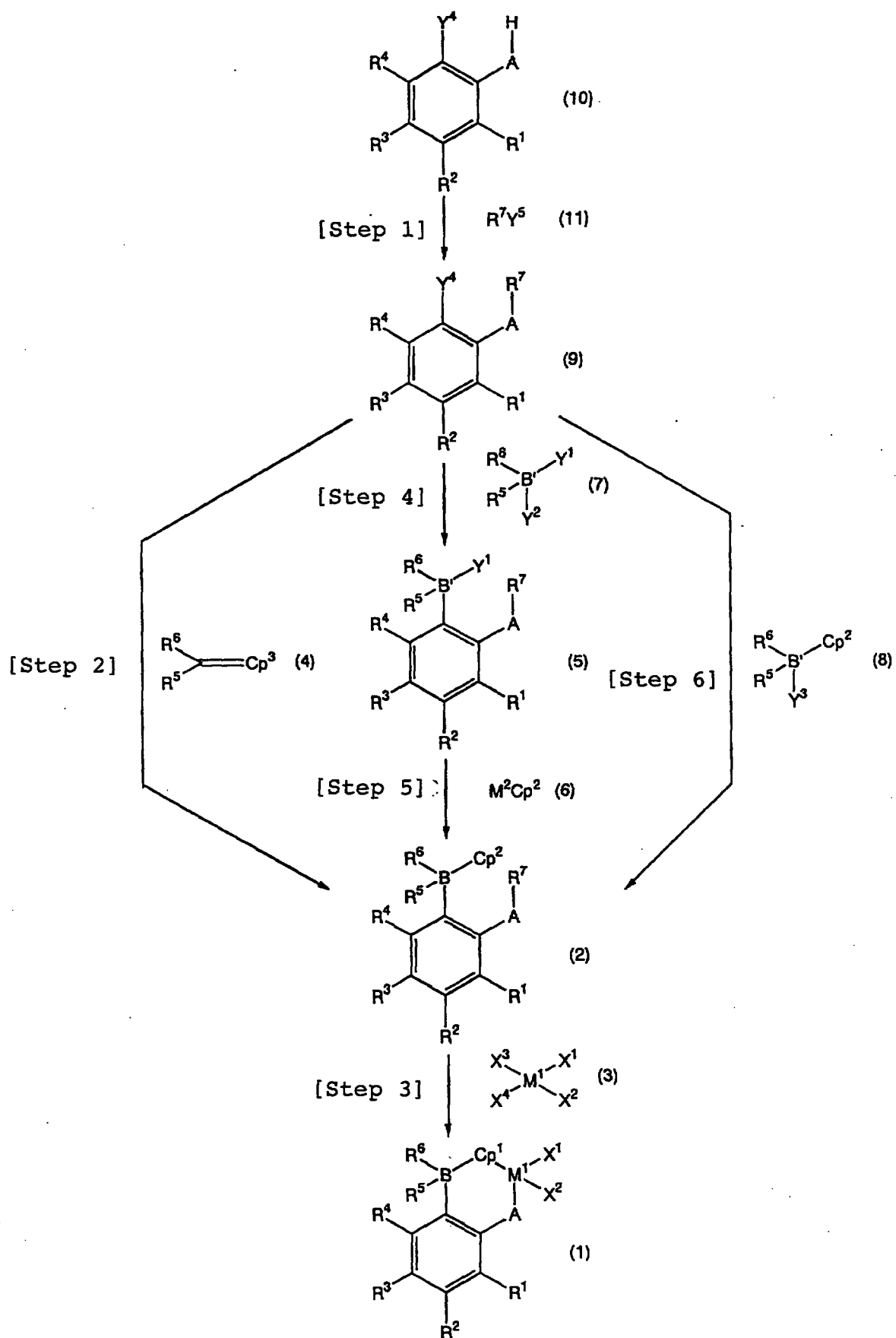
butyldimethylsilyl-5-methyl-2-phenoxy)titanium
dichloride, dimethylsilyl(fluorenyl)(5-methyl-3-tri-
methylsilyl-2-phenoxy)titanium dichloride, dimethylsilyl-
(fluorenyl)(3-tert-butyl-5-methoxy-2-phenoxy)titanium
5 dichloride, dimethylsilyl(fluorenyl)(3-tert-butyl-5-
chloro-2-phenoxy)titanium dichloride, dimethylsilyl-
(fluorenyl)(3,5-diamyl-2-phenoxy)titanium dichloride and
dimethylsilyl(tetramethylcyclopentadienyl)(1-naphthoxy-2-
yl)titanium dichloride; and compounds resulting from
10 changing, in the above-mentioned compounds, "(cyclopenta-
dienyl)" to (dimethylcyclopentadienyl), (trimethylcyclo-
pentadienyl), (ethylcyclopentadienyl), (n-propylcyclo-
pentadienyl), (isopropylcyclopentadienyl), (sec-butyl-
cyclopentadienyl), (isobutylcyclopentadienyl), (tert-
15 butyldimethylsilylcyclopentadienyl), (phenylcyclopenta-
dienyl), (methylindenyl) or (phenylindenyl), compounds
resulting from changing, in the above-mentioned
compounds, "2-phenoxy" to 3-phenyl-2-phenoxy, 3-tri-
methylsilyl-2-phenoxy or 3-tert-butyldimethylsilyl-2-
20 phenoxy, compounds resulting from changing, in the above-
mentioned compounds, "dimethylsilyl" to diethylsilyl,
diphenylsilyl or dimethoxysilyl, compounds resulting from
changing, in the above-mentioned compounds, "titanium" to
zirconium or hafnium, and compounds resulting from
25 changing, in the above-mentioned compounds, "chloride" to
bromide, iodide, dimethylamide, diethylamide, n-butoxide
or isopropoxide.

The compound [1] can be prepared by a process

comprising the following 3 steps or 4 steps using as the starting material a halogenated aryl compound represented by the formula (10) (hereinafter referred to as compound [10]):



- 5 wherein Y⁴ is a halogen atom, and R¹, R², R³ and R⁴ are respectively the same as defined above.



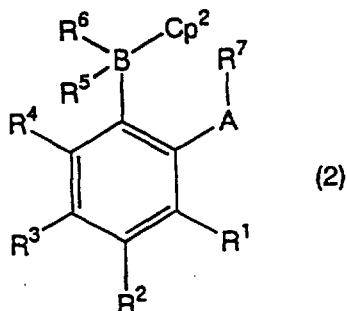
The halogen atom represented as the substituent Y^4 in the compound [10] may be, for example, a chlorine atom, bromine atom and iodine atom.

Examples of the compound [10] include 2-bromo-phenol, 2-bromo-6-methylphenol, 2-bromo-4,6-dimethylphenol, 2-bromo-6-tert-butylphenol, 2-bromo-6-tert-butyl-4-methylphenol, 2-bromo-4,6-di-tert-butylphenol, 2-bromo-6-trimethylsilylphenol, 2-bromo-4-methyl-6-trimethylsilylphenol, 2-bromo-6-tert-butyl-dimethylsilylphenol, 2-bromo-6-tert-butyldimethylsilyl-4-methylphenol, 2-bromo-6-phenylphenol, 2-bromo-4-methyl-6-phenylphenol, 4,6-diamyl-2-bromophenol, 2-bromo-6-tert-butyl-4-methoxyphenol, 2-bromo-6-tert-butyl-4-chlorophenol, and compounds resulting from changing, in the respective compounds described above, "bromo" to chloro or iodo.

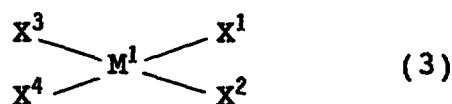
The respective process steps are described in detail below.

[Step 3]

The step of producing the compound [1] by reacting a substituted cyclopentadienyl compound (hereinafter referred to as compound [2]) represented by the formula (2)



wherein Cp^2 is a group having a cyclopentadiene skeleton,
 R^7 is a hydrocarbon group optionally substituted with at
least one halogen atom or a tri-substituted silyl group,
and A, B, R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are respectively the
5 same as defined above, with a base, and then reacting the
resulting reaction product with a transition metal
compound represented by the formula (3) (hereinafter
referred to as compound [3])



wherein X^3 and X^4 are each independently a hydrogen atom,
10 a halogen atom, or a C_1 - C_{20} alkyl group, aralkyl group,
aryl group, substituted silyl group, alkoxy group,
aralkyloxy group or aryloxy group each optionally
substituted with at least one halogen atom, or C_2 - C_{20} di-
substituted amino group; M^1 , X^1 and X^2 are respectively the
15 same as defined above.

The group having a cyclopentadiene skeleton
represented by the substituent Cp^2 in the compound [2] may
be, for example, cyclopentadienyl group, methylcyclo-
pentadienyl group, dimethylcyclopentadienyl group, tri-
20 methylcyclopentadienyl group, tetramethylcyclopentadienyl
group, ethylcyclopentadienyl group, n-propylcyclopenta-
dienyl group, isopropylcyclopentadienyl group, n-butyl-
cyclopentadienyl group, sec-butylcyclopentadienyl group,
tert-butylcyclopentadienyl group, n-pentylcyclopenta-
25 dienyl group, neopentylcyclopentadienyl group, n-hexyl-

cyclopentadienyl group, n-octylcyclopentadienyl group, phenylcyclopentadienyl group, naphthylcyclopentadienyl group, trimethylsilylcyclopentadienyl group, triethylsilylcyclopentadienyl group, tert-butyldimethylsilyl-

5 cyclopentadienyl group, indenyl group, methylindenyl group, dimethylindenyl group, ethylindenyl group, n-propylindenyl group, isopropylindenyl group, n-butylindenyl group, sec-butylindenyl group, tert-butylindenyl group, n-pentylindenyl group, neopentylindenyl group, n-

10 hexylindenyl group, n-octylindenyl group, n-decylindenyl group, phenylindenyl group, methylphenylindenyl group, naphthylindenyl group, trimethylsilylindenyl group, triethylsilylindenyl group, tert-butyldimethylsilylindenyl group, tetrahydroindenyl group, fluorenyl group,

15 methylfluorenyl group, dimethylfluorenyl group, ethylfluorenyl group, diethylfluorenyl group, n-propylfluorenyl group, di-n-propylfluorenyl group, isopropylfluorenyl group, diisopropylfluorenyl group, n-butylfluorenyl group, sec-butylfluorenyl group, tert-

20 butylfluorenyl group, di-n-butylfluorenyl group, di-sec-butylfluorenyl group, di-tert-butylfluorenyl group, n-pentylfluorenyl group, neopentylfluorenyl group, n-hexylfluorenyl group, n-octylfluorenyl group, n-decylfluorenyl group, n-dodecylfluorenyl group, phenyl-

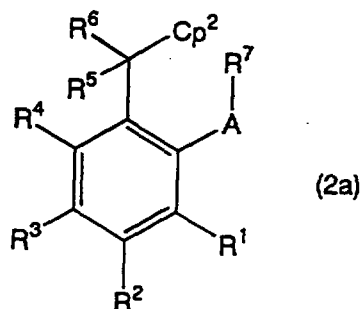
25 fluorenyl group, diphenylfluorenyl group, methylphenylfluorenyl group, naphthylfluorenyl group, tri-methylsilylfluorenyl group, bis-trimethylsilylfluorenyl group, triethylsilylfluorenyl group and tert-butyldimethyl-

silylfluorenyl group, preferred of these being the cyclopentadienyl group, methylcyclopentadienyl group, tert-butylcyclopentadienyl group, tetramethylcyclopentadienyl group, fluorenyl group, indenyl group, etc.

5 The hydrocarbon group denoted as the substituent R^7 may be, for example, an alkyl group with the number of carbon atoms of 1-10, such as the methyl group, ethyl group, propyl group, hexyl group and decyl group, an alkenyl group with the number of carbon atoms of 2-10,
10 such as the vinyl group, allyl group, propenyl group, 2-methyl-2-propenyl group, homoallyl group, hexenyl group and decenyl group, an alkoxyalkyl group, such as the methoxymethyl group and methoxyethoxymethyl group, and an aralkyl group with the number of carbon atoms of 7-12,
15 such as the benzyl group, (4-methylphenyl)methyl group and (2,4,6-trimethylphenyl)methyl group. These hydrocarbon groups may each optionally be substituted with at least one halogen atom. Examples of the hydrocarbon group substituted with a halogen atom include the 2-
20 chloro-2-propenyl group. The trisubstituted silyl group may be, for example, the trimethylsilyl group, triethylsilyl group, tri-n-propylsilyl group, triisopropylsilyl group, tri-n-butylsilyl group, tri-sec-butylsilyl group, tri-tert-butylsilyl group, triisobutylsilyl group, tert-butyl-dimethylsilyl group, tri-n-pentylsilyl group, tri-
25 n-hexylsilyl group, tricyclohexylsilyl group and triphenylsilyl group. Among these substituents R^7 , an alkenyl group, particularly the allyl group, is preferred

because it can give the compound [1] with a good yield.

Such compounds [2] include a substituted cyclopentadienyl compound represented by the formula (2a) (hereinafter referred to as compound [2a]):



- 5 wherein Cp^2 , A, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are respectively the same as defined above, for example, 2-[(cyclopenta-1,4-dienyl)methyl]-1-methoxybenzene, 2-[(cyclopenta-1,4-dienyl)methyl]-1-methoxy-4,6-dimethylbenzene, 2-tert-butyl-6-[(cyclopenta-1,4-dienyl)methyl]-
- 10 1-methoxy-4-methylbenzene, 6-[(cyclopenta-1,4-dienyl)methyl]-1-methoxy-2-phenylbenzene, 1-tert-butyldimethylsilyl-3-[(cyclopenta-1,4-dienyl)methyl]-2-methoxy-5-methylbenzene, 3-[(cyclopenta-1,4-dienyl)methyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 2-tert-butyl-6-[(cyclopenta-1,4-dienyl)methyl]-1-methoxybenzene,
- 15 [(cyclopenta-1,4-dienyl)methyl]-1,4-dimethoxybenzene, 3-tert-butyl-1-chloro-5-[(cyclopenta-1,4-dienyl)methyl]-4-methoxybenzene, 2-tert-butyl-6-[(cyclopenta-1,4-dienyl)methyl]-1-methoxybenzene,
- 20 2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxybenzene, 2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxy-4,6-dimethylbenzene, 6-tert-butyl-2-[1-

- (cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxy-4-methylbenzene, 6-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxy-2-phenylbenzene, 1-tert-butyldimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-2-methoxy-5-methylbenzene, 3-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1,4-dimethoxybenzene, 5-tert-butyl-1-chloro-3-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4-methoxybenzene, 6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxybenzene,
- 1-methoxy-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-methoxy-4,6-dimethyl-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-benzene, 6-tert-butyl-1-methoxy-4-methyl-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-methoxy-6-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-2-phenylbenzene, 1-tert-butyldimethylsilyl-2-methoxy-5-methyl-3-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 2-methoxy-5-methyl-3-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-trimethylsilylbenzene, 6-tert-butyl-1,4-dimethoxy-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 5-tert-butyl-1-chloro-4-methoxy-3-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 6-tert-butyl-1-methoxy-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-benzene, 2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxybenzene, 2-[1-(4-tert-butyl-

- cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxy-4,6-dimethylbenzene, 6-tert-butyl-2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxy-4-methylbenzene, 6-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxy-2-phenylbenzene, 1-tert-butyl-dimethylsilyl-3-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-2-methoxy-5-methylbenzene, 3-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 6-tert-butyl-2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1,4-dimethoxybenzene, 5-tert-butyl-1-chloro-3-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4-methoxybenzene, 6-tert-butyl-2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-methoxybenzene,
- 15 1-methoxy-2-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-methoxy-4,6-dimethyl-2-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 6-tert-butyl-1-methoxy-4-methyl-2-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-methoxy-2-phenyl-6-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-benzene, 1-tert-butyl-dimethylsilyl-2-methoxy-5-methyl-3-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 2-methoxy-5-methyl-3-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-trimethylsilylbenzene, 6-tert-butyl-1,4-dimethoxy-2-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 5-tert-butyl-1-chloro-4-methoxy-3-[1-
- 20
- 25

(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 6-tert-butyl-1-methoxy-2-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-benzene,

- 5 1-methoxy-2-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-methoxy-4,6-dimethyl-2-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 6-tert-butyl-1-methoxy-4-methyl-2-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-methoxy-2-phenyl-6-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-tert-butyl-1,4-dimethoxy-2-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 2-methoxy-5-methyl-1-trimethylsilyl-3-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 6-tert-butyl-1,4-dimethoxy-2-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 5-tert-butyl-1-chloro-4-methoxy-3-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 6-tert-butyl-1-methoxy-2-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene,
- 10
- 15
- 20

- 2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-1-methoxybenzene, 2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-1-methoxy-4,6-dimethylbenzene, 6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-1-methoxy-4-methylbenzene, 6-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-1-methoxy-2-phenylbenzene, 1-tert-butyl-1,4-dimethoxy-2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-2-
- 25

- methoxy-5-methylbenzene, 3-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-1,4-dimethoxybenzene, 5-tert-butyl-1-chloro-3-[1-
- 5 (cyclopenta-1,4-dienyl)-1-ethyl-propyl]-4-methoxybenzene, 6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-1-methoxybenzene,
- 2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenyl-methyl]-1-methoxybenzene, 2-[1-(cyclopenta-1,4-dienyl)-
- 10 1,1-diphenylmethyl]-1-methoxy-4,6-dimethylbenzene, 6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenyl-methyl]-1-methoxy-4-methylbenzene, 2-[1-(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-1-methoxy-6-phenylbenzene, 1-tert-butyl-1-dimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1,1-
- 15 diphenylmethyl]-2-methoxy-5-methylbenzene, 3-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-2-methoxy-5-methyl-1-trimethylsilylbenzene, 6-tert-butyl-2-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-1,4-dimethoxybenzene, 5-tert-butyl-1-chloro-3-[(cyclopenta-1,4-dienyl)-1,1-diphenyl-
- 20 methyl]-4-methoxybenzene, 6-tert-butyl-2-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-1-methoxybenzene,
- 1-allyloxy-2-[(cyclopenta-1,4-dienyl)methyl]-benzene, 1-allyloxy-2-[(cyclopenta-1,4-dienyl)methyl]-4,6-dimethylbenzene, 1-allyloxy-2-tert-butyl-6-
- 25 [(cyclopenta-1,4-dienyl)methyl]-4-methylbenzene, 1-allyloxy-6-[(cyclopenta-1,4-dienyl)methyl]-2-phenylbenzene, 2-allyloxy-1-tert-butyl-1-dimethylsilyl-3-[(cyclopenta-1,4-dienyl)methyl]-5-methylbenzene, 2-

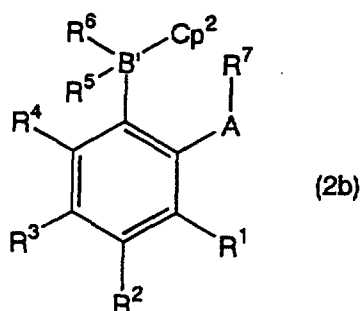
- allyloxy-3-[(cyclopenta-1,4-dienyl)methyl]-5-methyl-1-trimethylsilylbenzene, 1-allyloxy-2-tert-butyl-6-[(cyclopenta-1,4-dienyl)methyl]-4-methoxybenzene, 4-allyloxy-3-tert-butyl-1-chloro-5-[(cyclopenta-1,4-
- 5 dienyl)methyl]benzene, 1-allyloxy-2-tert-butyl-6-[(cyclopenta-1,4-dienyl)methyl]benzene,
- 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4,6-dimethylbenzene, 1-allyloxy-
- 10 6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4-methylbenzene, 1-allyloxy-6-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-2-phenylbenzene, 2-allyloxy-1-tert-butyl-4-dimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-5-methylbenzene, 2-allyloxy-3-[1-
- 15 (cyclopenta-1,4-dienyl)-1-methyl-ethyl]-5-methyl-1-trimethylsilylbenzene, 1-allyloxy-6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4-methoxybenzene,
- 4-allyloxy-5-tert-butyl-1-chloro-3-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-6-tert-butyl-
- 20 2-[1-(cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene,
- 1-allyloxy-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-4,6-dimethyl-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-benzene, 1-allyloxy-6-tert-butyl-4-methyl-2-[1-(4-methyl-
- 25 cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-6-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-2-phenylbenzene, 2-allyloxy-1-tert-butyl-4-dimethylsilyl-5-methyl-3-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-

- methyl-ethyl]benzene, 2-allyloxy-5-methyl-3-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-1-trimethylsilylbenzene, 1-allyloxy-6-tert-butyl-4-methoxy-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 4-
- 5 allyloxy-5-tert-butyl-1-chloro-3-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-6-tert-butyl-2-[1-(4-methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene,
- 1-allyloxy-2-[1-(4-tert-butyl-cyclopenta-1,4-
- 10 dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4,6-dimethylbenzene, 1-allyloxy-6-tert-butyl-2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4-methylbenzene, 1-allyloxy-6-[1-(4-tert-butyl-cyclopenta-1,4-
- 15 dienyl)-1-methyl-ethyl]-2-phenylbenzene, 2-allyloxy-1-tert-butyl-1-dimethylsilyl-3-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-5-methylbenzene, 2-allyloxy-3-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-5-methyl-1-trimethylsilylbenzene, 1-allyloxy-6-
- 20 tert-butyl-2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-4-methoxybenzene, 4-allyloxy-5-tert-butyl-1-chloro-3-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-6-tert-butyl-2-[1-(4-tert-butyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene,
- 25 1-allyloxy-2-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-4,6-dimethyl-2-[1-(2,3,4,5-tetramethyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-

- allyloxy-6-tert-butyl-4-methyl-2-[1-(2,3,4,5-tetramethyl-
cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-
allyloxy-2-phenyl-6-[1-(2,3,4,5-tetramethyl-cyclopenta-
1,4-dienyl)-1-methyl-ethyl]benzene, 2-allyloxy-1-tert-
5 butyldimethylsilyl-5-methyl-3-[1-(2,3,4,5-tetramethyl-
cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 2-
allyloxy-5-methyl-3-[1-(2,3,4,5-tetramethyl-cyclopenta-
1,4-dienyl)-1-methyl-ethyl]-1-trimethylsilylbenzene, 1-
allyloxy-6-tert-butyl-4-methoxy-2-[1-(2,3,4,5-tetra-
10 methyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 4-
allyloxy-5-tert-butyl-1-chloro-3-[1-(2,3,4,5-tetramethyl-
cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 1-
allyloxy-6-tert-butyl-2-[1-(2,3,4,5-tetramethyl-
cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene,
15 1-allyloxy-2-[1-(3-trimethylsilyl-cyclopenta-
1,4-dienyl)-1-methyl-ethyl]benzene, 1-allyloxy-4,6-
dimethyl-2-[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-
methyl-ethyl]benzene, 1-allyloxy-6-tert-butyl-4-methyl-2-
[1-(3-trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-
20 ethyl]benzene, 1-allyloxy-2-phenyl-6-[1-(3-trimethyl-
silyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene, 2-
allyloxy-1-tert-butyldimethylsilyl-5-methyl-3-[1-(3-
trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-
benzene, 2-allyloxy-5-methyl-1-trimethylsilyl-3-[1-(3-
25 trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-
benzene, 1-allyloxy-6-tert-butyl-4-methoxy-2-[1-(3-
trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-
ethyl]benzene, 4-allyloxy-5-tert-butyl-1-chloro-3-[1-(3-

- trimethylsilyl-cyclopenta-1,4-dienyl)-1-methyl-ethyl]-
benzene, 1-allyloxy-6-tert-butyl-2-[1-(3-trimethylsilyl-
cyclopenta-1,4-dienyl)-1-methyl-ethyl]benzene,
1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1-
5 ethyl-propyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-
dienyl)-1-ethyl-propyl]-4,6-dimethylbenzene, 1-allyloxy-
6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-
propyl]-4-methylbenzene, 1-allyloxy-6-[1-(cyclopenta-1,4-
dienyl)-1-ethyl-propyl]-2-phenylbenzene, 2-allyloxy-1-
10 tert-butyldimethylsilyl-3-[1-(cyclopenta-1,4-dienyl)-1-
ethyl-propyl]-5-methylbenzene, 2-allyloxy-3-[1-
(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-5-methyl-1-
trimethylsilylbenzene, 1-allyloxy-6-tert-butyl-2-[1-
(cyclopenta-1,4-dienyl)-1-ethyl-propyl]-4-methoxybenzene,
15 4-allyloxy-5-tert-butyl-1-chloro-3-[1-(cyclopenta-1,4-
dienyl)-1-ethyl-propyl]benzene, 1-allyloxy-6-tert-butyl-
2-[1-(cyclopenta-1,4-dienyl)-1-ethyl-propyl]benzene,
1-allyloxy-2-[1-(cyclopenta-1,4-dienyl)-1,1-
diphenylmethyl]benzene, 1-allyloxy-2-[1-(cyclopenta-1,4-
20 dienyl)-1,1-diphenylmethyl]-4,6-dimethylbenzene, 1-
allyloxy-6-tert-butyl-2-[1-(cyclopenta-1,4-dienyl)-1,1-
diphenylmethyl]-4-methylbenzene, 1-allyloxy-2-[1-
(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-6-phenyl-
benzene, 2-allyloxy-1-tert-butyldimethylsilyl-3-[1-
25 (cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]-5-methyl-
benzene, 2-allyloxy-3-[(cyclopenta-1,4-dienyl)-1,1-
diphenylmethyl]-5-methyl-1-trimethylsilylbenzene, 1-
allyloxy-6-tert-butyl-2-[(cyclopenta-1,4-dienyl)-1,1-

- diphenylmethyl]-4-methoxybenzene, 4-allyloxy-5-tert-butyl-1-chloro-3-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]benzene, 1-allyloxy-6-tert-butyl-2-[(cyclopenta-1,4-dienyl)-1,1-diphenylmethyl]benzene;
- 5 compounds resulting from changing, in the above-mentioned compounds, "methoxy" or "allyloxy" to ethoxy, benzyloxy, trimethylsilyloxy, tert-butyldimethylsilyloxy or methoxymethoxy, compounds resulting from changing "cyclopenta-1,4-dienyl" to dimethylcyclopenta-1,4-dienyl,
- 10 trimethylcyclopenta-1,4-dienyl, n-butylcyclopenta-1,4-dienyl, tert-butyldimethylsilylcyclopenta-1,4-dienyl, indenyl or fluorenyl, compounds resulting from changing "1-methoxybenzene" to 1-methoxy-6-methylbenzene, 1-methoxy-4,6-di-tert-butylbenzene, 1-methoxy-4-methyl-6-
- 15 phenylbenzene, 1-tert-butyldimethylsilyl-2-methoxybenzene, or 2-methoxy-1-trimethylsilylbenzene, and
- a substituted cyclopentadienyl compound represented by the formula (2b) (hereinafter referred to as compound [2b]):



- 20 wherein B' is an element of the group 14 of the periodic table of elements other than carbon atom, and A, Cp², R¹,

R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are respectively the same as defined above, for example, (cyclopenta-1,3-dienyl)(2-methoxyphenyl)dimethylsilane, (cyclopenta-1,3-dienyl)(2-methoxy-3-methylphenyl)dimethylsilane, (cyclopenta-1,3-dienyl)(2-methoxy-3,5-dimethylphenyl)dimethylsilane, (3-tert-butyl-2-methoxyphenyl)(cyclopenta-1,3-dienyl)-dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)-(cyclopenta-1,3-dienyl)dimethylsilane, (3,5-di-tert-butyl-2-methoxyphenyl)(cyclopenta-1,3-dienyl)dimethylsilane, (cyclopenta-1,3-dienyl)(2-methoxy-5-methyl-3-phenylphenyl)dimethylsilane, (cyclopenta-1,3-dienyl)(2-methoxy-5-methyl-3-trimethylsilylphenyl)dimethylsilane, 3-(tert-butyl-dimethylsilyl-2-methoxy-5-methylphenyl)-(cyclopenta-1,3-dienyl)dimethylsilane, (3,5-diamyl-2-methoxyphenyl)(cyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-2,5-dimethoxyphenyl)(cyclopenta-1,3-dienyl)-dimethylsilane, (5-tert-butyl-3-chloro-6-methoxyphenyl)-(cyclopenta-1,3-dienyl)dimethylsilane,
(2-methoxyphenyl)(methylcyclopenta-1,3-dienyl)-dimethylsilane, (2-methoxy-3-methylphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-3,5-dimethylphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-2-methoxyphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (3,5-di-tert-butyl-2-methoxyphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-5-methyl-3-phenylphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (2-

- methoxy-5-methyl-3-trimethylsilylphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (3,5-diamyl-2-methoxyphenyl)-
- 5 (methylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-2,5-dimethoxyphenyl)(methylcyclopenta-1,3-dienyl)-dimethylsilane, (5-tert-butyl-3-chloro-6-methoxyphenyl)-(methylcyclopenta-1,3-dienyl)dimethylsilane,
- (2-methoxyphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-3-methyl-
- 10 phenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)-dimethylsilane, (2-methoxy-3,5-dimethylphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-2-methoxyphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-
- 15 dienyl)dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)-dimethylsilane, (3,5-di-tert-butyl-2-methoxyphenyl)-(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
- (2-methoxy-5-methyl-3-phenylphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-5-
- 20 methyl-3-trimethylsilylphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (3,5-diamyl-2-methoxy-
- 25 phenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)-dimethylsilane, (3-tert-butyl-2,5-dimethoxyphenyl)-(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
- (5-tert-butyl-3-chloro-6-methoxyphenyl)(2,3,4,5-

tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
 (tert-butylcyclopenta-1,3-dienyl)(2-methoxy-
phenyl)dimethylsilane, (tert-butylcyclopenta-1,3-
dienyl)(2-methoxy-3-methylphenyl)dimethylsilane, (tert-
5 butylcyclopenta-1,3-dienyl)(2-methoxy-3,5-dimethyl-
phenyl)dimethylsilane, (tert-butylcyclopenta-1,3-
dienyl)(3-tert-butyl-2-methoxyphenyl)dimethylsilane,
(tert-butylcyclopenta-1,3-dienyl)(3-tert-butyl-2-methoxy-
5-methylphenyl)dimethylsilane, (tert-butylcyclopenta-1,3-
10 dienyl)(3,5-di-tert-butyl-2-methoxyphenyl)dimethylsilane,
(tert-butylcyclopenta-1,3-dienyl)(2-methoxy-5-methyl-3-
phenylphenyl)dimethylsilane, (tert-butylcyclopenta-1,3-
dienyl)(2-methoxy-5-methyl-3-trimethylsilylphenyl)-
dimethylsilane, (tert-butylcyclopenta-1,3-dienyl)(3-tert-
15 butyldimethylsilyl-2-methoxy-5-methylphenyl)dimethyl-
silane, (3,5-diamyl-2-methoxyphenyl)(tert-butylcyclo-
penta-1,3-dienyl)dimethylsilane, (tert-butylcyclopenta-
1,3-dienyl)(3-tert-butyl-2,5-dimethoxyphenyl)dimethyl-
silane, (5-tert-butyl-3-chloro-6-methoxyphenyl)(tert-
20 butylcyclopenta-1,3-dienyl)dimethylsilane,
 (2-methoxyphenyl)(trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (2-methoxy-3-methylphenyl)(tri-
methylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-
methoxy-3,5-dimethylphenyl)(trimethylsilylcyclopenta-1,3-
25 dienyl)dimethylsilane, (3-tert-butyl-2-methoxyphenyl)-
(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (3-
tert-butyl-2-methoxy-5-methylphenyl)(trimethylsilylcyclo-
penta-1,3-dienyl)dimethylsilane,

- (3,5-di-tert-butyl-2-methoxyphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-5-methyl-3-phenylphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-methoxy-5-methyl-3-trimethylsilylphenyl)(trimethylsilylcyclopenta-1,3-dienyl)-
5 dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)(trimethylsilylcyclopenta-1,3-dienyl)-
dimethylsilane, (3,5-diamyl-2-methoxyphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (3-tert-butyl-
10 2,5-dimethoxyphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (5-tert-butyl-3-chloro-6-methoxyphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane,

(inden-1-yl)(2-methoxyphenyl)dimethylsilane,
15 (inden-2-yl)(2-methoxyphenyl)dimethylsilane, (inden-1-yl)(2-methoxy-3-methylphenyl)dimethylsilane, (inden-2-yl)(2-methoxy-3-methylphenyl)dimethylsilane, (inden-1-yl)(2-methoxy-3,5-dimethylphenyl)dimethylsilane, (inden-2-yl)(2-methoxy-3,5-dimethylphenyl)dimethylsilane, (3-
20 tert-butyl-2-methoxyphenyl)(inden-1-yl)dimethylsilane, (3-tert-butyl-2-methoxyphenyl)(inden-2-yl)dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)(inden-1-yl)-
dimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)-
(inden-2-yl)dimethylsilane, (3,5-di-tert-butyl-2-methoxy-
25 phenyl)(inden-1-yl)dimethylsilane, (3,5-di-tert-butyl-2-methoxyphenyl)(inden-2-yl)dimethylsilane, (inden-1-yl)(2-methoxy-5-methyl-3-phenylphenyl)dimethylsilane, (inden-2-yl)(2-methoxy-5-methyl-3-phenylphenyl)dimethylsilane,

- (inden-1-yl)(2-methoxy-5-methyl-3-trimethylsilylphenyl)-
dimethylsilane, (inden-2-yl)(2-methoxy-5-methyl-3-
trimethylsilylphenyl)dimethylsilane, (3-tert-butyl-
dimethylsilyl-2-methoxy-5-methylphenyl)(inden-1-yl)-
5 dimethylsilane, (3-tert-butyl dimethylsilyl-2-methoxy-5-
methylphenyl)(inden-2-yl)dimethylsilane, (3,5-diamyl-2-
methoxyphenyl)(inden-1-yl)dimethylsilane, (3,5-diamyl-2-
methoxyphenyl)(inden-2-yl)dimethylsilane, (3-tert-butyl-
2,5-dimethoxyphenyl)(inden-1-yl)dimethylsilane, (3-tert-
10 butyl-2,5-dimethoxyphenyl)(inden-2-yl)dimethylsilane, (5-
tert-butyl-3-chloro-6-methoxyphenyl)(inden-1-yl)dimethyl-
silane, (5-tert-butyl-3-chloro-6-methoxyphenyl)(inden-2-
yl)dimethylsilane,
(9H-fluoren-9-yl)(2-methoxyphenyl)dimethyl-
15 silane, (9H-fluoren-9-yl)(2-methoxy-3-methylphenyl)-
dimethylsilane, (9H-fluoren-9-yl)(2-methoxy-3,5-
dimethylphenyl)dimethylsilane, (3-tert-butyl-2-
methoxyphenyl)(9H-fluoren-9-yl)dimethylsilane, (3-tert-
butyl-2-methoxy-5-methylphenyl)(9H-fluoren-9-yl)-
20 dimethylsilane, (3,5-di-tert-butyl-2-methoxyphenyl)(9H-
fluoren-9-yl)dimethylsilane, (9H-fluoren-9-yl)(2-methoxy-
5-methyl-3-phenylphenyl)dimethylsilane, (9H-fluoren-9-
yl)(2-methoxy-5-methyl-3-trimethylsilylphenyl)dimethyl-
silane, (3-tert-butyl dimethylsilyl-2-methoxy-5-methyl-
25 phenyl)(9H-fluoren-9-yl)dimethylsilane, (3,5-diamyl-2-
methoxyphenyl)(9H-fluoren-9-yl)dimethylsilane, (3-tert-
butyl-2,5-dimethoxyphenyl)(9H-fluoren-9-yl)dimethyl-
silane, (5-tert-butyl-3-chloro-6-methoxyphenyl)(9H-

fluoren-9-yl)dimethylsilane,

- (2-allyloxyphenyl)(cyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-3-methylphenyl)(cyclopenta-
1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-dimethyl-
5 phenyl)(cyclopenta-1,3-dienyl)dimethylsilane, (2-
allyloxy-3-tert-butylphenyl)(cyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-3-tert-butyl-5-methylphenyl)-
(cyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-
di-tert-butylphenyl)(cyclopenta-1,3-dienyl)dimethyl-
10 silane, (2-allyloxy-5-methyl-3-phenylphenyl)(cyclopenta-
1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-
trimethylsilylphenyl)(cyclopenta-1,3-dienyl)dimethyl-
silane, (2-allyloxy-3-tert-butyltrimethylsilyl-5-methyl-
phenyl)(cyclopenta-1,3-dienyl)dimethylsilane, (2-
15 allyloxy-3,5-diamylphenyl)(cyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-3-tert-butyl-5-methoxy-
phenyl)(cyclopenta-1,3-dienyl)dimethylsilane, (6-
allyloxy-5-tert-butyl-3-chlorophenyl)(cyclopenta-1,3-
dienyl)dimethylsilane,
20 (2-allyloxyphenyl)(methylcyclopenta-1,3-
dienyl)dimethylsilane, (2-allyloxy-3-methylphenyl)-
(methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-
3,5-dimethylphenyl)(methylcyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-3-tert-butylphenyl)(methyl-
25 cyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert-
butyl-5-methylphenyl)(methylcyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-3,5-di-tert-butylphenyl)-
(methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-

- 5-methyl-3-phenylphenyl)(methylcyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilyl-
phenyl)(methylcyclopenta-1,3-dienyl)dimethylsilane, (2-
allyloxy-3-tert-butyltrimethylsilyl-5-methylphenyl)-
5 (methylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-
3,5-diamylphenyl)(methylcyclopenta-1,3-dienyl)dimethyl-
silane, (2-allyloxy-3-tert-butyl-5-methoxyphenyl)(methyl-
cyclopenta-1,3-dienyl)dimethylsilane, (6-allyloxy-5-tert-
butyl-3-chlorophenyl)(methylcyclopenta-1,3-dienyl)-
10 dimethylsilane,
(2-allyloxyphenyl)(2,3,4,5-tetramethylcyclo-
penta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-methyl-
phenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-3,5-dimethylphenyl)(2,3,4,5-
15 tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-
allyloxy-3-tert-butylphenyl)(2,3,4,5-tetramethylcyclo-
penta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert-
butyl-5-methylphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-
dienyl)dimethylsilane, (2-allyloxy-3,5-di-tert-butyl-
20 phenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl)-
(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
(2-allyloxy-5-methyl-3-trimethylsilylphenyl)(2,3,4,5-
tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (2-
25 allyloxy-3-tert-butyltrimethylsilyl-5-methylphenyl)-
(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane,
(2-allyloxy-3,5-diamylphenyl)(2,3,4,5-tetramethylcyclo-
penta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert-

- butyl-5-methoxyphenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)dimethylsilane, (6-allyloxy-5-tert-butyl-3-chlorophenyl)(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)-dimethylsilane, (2-allyloxyphenyl)(tert-butylcyclopenta-
- 5 1,3-dienyl)dimethylsilane, (2-allyloxy-3-methylphenyl)-(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-dimethylphenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert-butylphenyl)-(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-
- 10 allyloxy-3-tert-butyl-5-methylphenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-di-tert-butylphenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-
- 15 methyl-3-trimethylsilylphenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert-butyl)dimethylsilyl-5-methylphenyl)(tert-butylcyclopenta-1,3-dienyl)-dimethylsilane, (2-allyloxy-3,5-diamylphenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-
- 20 tert-butyl-5-methoxyphenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (6-allyloxy-5-tert-butyl-3-chlorophenyl)(tert-butylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxyphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-methylphenyl)-
- 25 (trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3,5-dimethylphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-tert-butylphenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethyl-

silane, (2-allyloxy-3-tert-butyl-5-methylphenyl)-
(trimethylsilylcyclopenta-1,3-dienyl)dimethylsilane, (2-
allyloxy-3,5-di-tert-butylphenyl)(trimethylsilylcyclo-
penta-1,3-dienyl)dimethylsilane, (2-allyloxy-5-methyl-3-
5 phenylphenyl)(trimethylsilylcyclopenta-1,3-dienyl)-
dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilyl-
phenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethyl-
silane, (2-allyloxy-3-tert-butyl-5-dimethylsilyl-5-
methylphenyl)(trimethylsilylcyclopenta-1,3-dienyl)-
10 dimethylsilane, (2-allyloxy-3,5-diamylphenyl)(trimethyl-
silylcyclopenta-1,3-dienyl)dimethylsilane, (2-allyloxy-3-
tert-butyl-5-methoxyphenyl)(trimethylsilylcyclopenta-1,3-
dienyl)dimethylsilane, (6-allyloxy-5-tert-butyl-3-chloro-
phenyl)(trimethylsilylcyclopenta-1,3-dienyl)dimethyl-
15 silane,
(2-allyloxyphenyl)(inden-1-yl)dimethylsilane,
(2-allyloxyphenyl)(inden-2-yl)dimethylsilane, (2-
allyloxy-3-methylphenyl)(inden-1-yl)dimethylsilane, (2-
allyloxy-3-methylphenyl)(inden-2-yl)dimethylsilane, (2-
20 allyloxy-3,5-dimethylphenyl)(inden-1-yl)dimethylsilane,
(2-allyloxy-3,5-dimethylphenyl)(inden-2-yl)dimethyl-
silane, (2-allyloxy-3-tert-butylphenyl)(inden-1-
yl)dimethylsilane, (2-allyloxy-3-tert-butylphenyl)(inden-
2-yl)dimethylsilane, (2-allyloxy-3-tert-butyl-5-methyl-
25 phenyl)(inden-1-yl)dimethylsilane, (2-allyloxy-3-tert-
butyl-5-methylphenyl)(inden-2-yl)dimethylsilane, (2-
allyloxy-3,5-di-tert-butylphenyl)(inden-1-yl)dimethyl-
silane, (2-allyloxy-3,5-di-tert-butylphenyl)(inden-2-

- yl)dimethylsilane, (2-allyloxy-5-methyl-3-phenyl-phenyl)(inden-1-yl)dimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl)(inden-2-yl)dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl)(inden-1-yl)dimethylsilane,
5 (2-allyloxy-5-methyl-3-trimethylsilylphenyl)(inden-2-yl)dimethylsilane, (2-allyloxy-3-tert-butyltrimethylsilyl-5-methylphenyl)(inden-1-yl)dimethylsilane, (2-allyloxy-3-tert-butyltrimethylsilyl-5-methylphenyl)(inden-2-yl)-dimethylsilane, (2-allyloxy-3,5-diamylphenyl)(inden-1-yl)dimethylsilane, (2-allyloxy-3,5-diamylphenyl)(inden-2-yl)dimethylsilane, (2-allyloxy-3-tert-butyl-5-methoxyphenyl)(inden-1-yl)dimethylsilane, (2-allyloxy-3-tert-butyl-5-methoxyphenyl)(inden-2-yl)dimethylsilane, (6-allyloxy-5-tert-butyl-3-chlorophenyl)(inden-1-yl)-
10 dimethylsilane, (6-allyloxy-5-tert-butyl-3-chlorophenyl)(inden-2-yl)dimethylsilane,
15 (2-allyloxyphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-3-methylphenyl)(9H-fluoren-9-yl)-dimethylsilane, (2-allyloxy-3,5-dimethylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-3-tert-butylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-3-tert-butyl-5-methylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-3,5-di-tert-butylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-5-methyl-3-phenyl-phenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-3-tert-butyltrimethylsilyl-5-methylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-3,5-

diamylphenyl)(9H-fluoren-9-yl)dimethylsilane, (2-allyloxy-3-tert-butyl-5-methoxyphenyl)(9H-fluoren-9-yl)-dimethylsilane, (6-allyloxy-5-tert-butyl-3-chlorophenyl)-(9H-fluoren-9-yl)dimethylsilane, and (1-allyloxynaphtha-
5 lene-2-yl)dimethyl(1,2,3,4-tetramethylcyclopentadienyl)-silane; compounds resulting from changing, in the above mentioned compounds, "methoxy" or "allyloxy" to benzyl-oxy, ethoxy, trimethylsilyloxy, tert-butyldimethyl-silyloxy or methoxymethoxy, compounds resulting from
10 changing "dimethylsilane" to diethylsilane, diphenylsilane or dimethoxysilane, compounds resulting from changing "cyclopentadienyl" to dimethylcyclopentadienyl, trimethylcyclopentadienyl, n-propylcyclopentadienyl, isopropylcyclopentadienyl, n-butylcyclopentadienyl,
15 isobutylcyclopentadienyl, sec-butylcyclopentadienyl, tert-butyldimethylsilylcyclopentadienyl, phenylcyclopentadienyl or methylindenyl and compounds resulting from changing "2-methoxyphenyl" to 3-phenyl-2-methoxyphenyl, 3-trimethylsilyl-2-methoxyphenyl or 3-tert-butyldimethyl-
20 silyl-2-methoxyphenyl.

These compounds [2] sometimes have a plural number of isomers originating from difference in the position of a substituent or in the position of a double bond in the cyclopentadiene skeleton of the substituent
25 Cp². The compounds [2] in the present invention include all of these isomers.

In the compound [3], the hydrogen atom, halogen atom, alkyl group with the number of carbon atoms of 1-20

optionally substituted with at least one halogen atom,
aralkyl group with the number of carbon atoms of 7-20
optionally substituted with at least one halogen atom,
aryl group with the number of carbon atoms of 6-20
5 optionally substituted with at least one halogen atom,
substituted silyl group with the number of carbon atoms
of 1-20 optionally substituted with at least one halogen
atom, alkoxy group with the number of carbon atoms of 1-
20 optionally substituted with at least one halogen atom,
10 aralkyloxy group with the number of carbon atoms of 1-20
optionally substituted with at least one halogen atom,
aryloxy group with the number of carbon atoms of 1-20
optionally substituted with at least one halogen atom,
and di-substituted amino group with the number of carbon
15 atoms of 2-20 which are represented as the substituents X^3
and X^4 may respectively be the same as those represented
as the substituents X^1 and X^2 in the compound [1].

Examples of the compound [3] include titanium
halides, e.g., titanium tetrachloride, titanium tetra-
20 bromide and titanium tetraiodide, amidotitanium, e.g.,
tetrakis(dimethylamino)titanium, dichlorobis(dimethyl-
amino)titanium, trichloro(dimethylamino)titanium and
tetrakis(diethylamino)titanium, alkoxytitanium, e.g.,
tetraisopropoxytitanium, tetra-n-butoxytitanium,
25 dichlorodiisopropoxytitanium and trichloroisopropoxy-
titanium, and compounds resulting from changing the
"titanium" of the respective compounds mentioned above to
zirconium or hafnium. The amount of the compound [3] to

be used is in the range of usually 0.5-3 times by mole, preferably 0.7-1.5 times by mole the amount of the compound [2].

The base may be, for example, an organoalkali metal compound, e.g., an organolithium compound, such as methyllithium, ethyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, lithium trimethylsilylacetylide, lithium acetylide, trimethylsilylmethyl-
lithium, vinyl-
lithium, phenyl-
lithium and allyl-
lithium.

10 The amount of the base to be used is in the range of usually 0.5-5 times by mole the amount of the compound [2].

Further, an amine compound may be used together with the base. The amine compound may be, for example, a primary amine compound, such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, tert-butylamine, n-octylamine, n-decylamine, aniline and ethylenediamine, secondary amine compound, such as dimethylamine, diethylamine, di-n-propylamine, di-n-propylamine, di-n-butylamine, di-tert-butylamine, di-n-octylamine, di-n-decylamine, pyrrolidine, hexamethyldisilazane, and diphenylamine, and tertiary amine compound, such as trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, diisopropylethylamine, tri-n-octylamine, tri-n-decylamine, triphenylamine, N,N-dimethylaniline, N,N,N',N'-tetramethylethylenediamine, N-methylpyrrolidine and 4-dimethylaminopyridine. The amount of the amine compound to be used is in the range

of usually 10 times by mole or less, preferably 0.5-10 times by mole, more preferably 1-3 times by mole the amount of the base.

The reaction is usually conducted in a solvent inert to the reaction. Such a solvent is, for example, an aprotic solvent, e.g., aromatic hydrocarbon solvent, such as benzene and toluene, aliphatic hydrocarbon solvent, such as hexane and heptane, ether type solvent, such as diethyl ether, tetrahydrofuran and 1,4-dioxane, amide type solvent, such as hexamethylphosphoric amide and dimethylformamide, polar solvent, such as acetonitrile, propionitrile, acetone, diethyl ketone, methyl isobutyl ketone and cyclohexanone, halogen-containing solvent, such as dichloromethane, dichloroethane, chlorobenzene and dichlorobenzene. These solvents may be used each alone or as a mixture of two or more thereof. The amount of the solvent to be used is in the range of usually 1-200 times by weight, preferably 3-50 times by weight the amount of the compound [2].

The present step may usually be conducted by adding the compound [2] and the base to the solvent and then adding the compound [3] thereto. Sometimes a solid will precipitate out after the addition of the compound (2) and the base. In such a case, the solid taken out from the reaction system may be added to a solvent and then the compound [3] is added thereto. Further, the compound [2], the base and the compound [3] may simultaneously be added to the solvent. The reaction

temperature is in the range of usually from not lower than -100°C to not higher than the boiling point of the solvent, preferably from -80°C to +100°C.

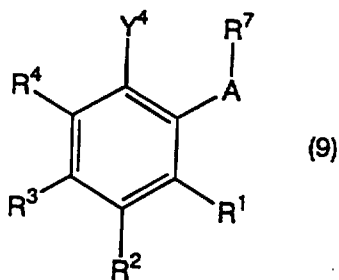
The reaction system is preferably shielded from
5 light to obtain a better yield of the compound [1].

The intended compound [1] can be obtained from the resulting reaction mixture by a conventional method, for example, by filtering off the precipitate formed, concentrating the filtrate to precipitate the compound
10 [1] and then collecting the compound [1] by filtration.

As described above, the compound [2] used in the above [step 1] include the compounds [2a] and the compounds [2b]. The compound [2a] can be prepared through the [step 2] as described below.

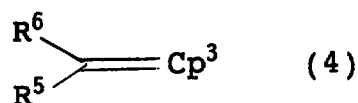
15 [Step 2]

The step of preparing the compound [2a] by reacting a halogenated aryl compound represented by the formula (9) (hereinafter referred to as compound [9]):



wherein A, R¹, R², R³, R⁴, R⁷ and Y⁴ are respectively the
20 same as defined above, with an organoalkali metal salt or metallic magnesium, then reacting the reaction product

with a cyclopentadienyliidene compound represented by the formula (4) (hereinafter referred to as compound [4]):



wherein Cp^3 is a group having a cyclopentadienyliidene skeleton, and R^5 and R^6 are respectively the same as
5 defined above, and then reacting the resulting reaction product with water.

The compound [9] may be, for example, 1-bromo-2-methoxybenzene, 1-bromo-3-methyl-2-methoxybenzene, 1-bromo-3,5-dimethyl-2-methoxybenzene, 1-bromo-3-tert-butyl-2-methoxybenzene, 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene, 1-bromo-3,5-di-tert-butyl-2-methoxybenzene, 1-bromo-2-methoxy-3-phenylbenzene, 1-bromo-2-methoxy-5-methyl-3-phenylbenzene, 1-bromo-2-methoxy-3-trimethylsilylbenzene, 1-bromo-2-methoxy-5-methyl-3-trimethylsilylbenzene, 1-bromo-3-tert-butyl-2-methoxy-5-methyl-3-trimethylsilylbenzene, 1-bromo-3-tert-butyl-2-methoxy-5-methyl-3-phenylbenzene, 1-bromo-3-tert-butyl-2,5-dimethoxybenzene, 1-bromo-3-tert-butyl-5-chloro-2-methoxybenzene, 3,5-diamyl-1-bromo-2-methoxybenzene,
20 2-allyloxy-1-bromobenzene, 2-allyloxy-1-bromo-3-methylbenzene, 2-allyloxy-1-bromo-3,5-dimethylbenzene, 2-allyloxy-1-bromo-3-tert-butylbenzene, 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene, 2-allyloxy-1-bromo-3,5-di-tert-butylbenzene, 2-allyloxy-1-bromo-3-phenylbenzene, 2-allyloxy-1-bromo-5-methyl-3-phenylbenzene, 2-
25 benzene, 2-allyloxy-1-bromo-5-methyl-3-phenylbenzene, 2-

allyloxy-1-bromo-3-trimethylsilylbenzene, 2-allyloxy-1-bromo-5-methyl-3-trimethylsilylbenzene, 2-allyloxy-1-bromo-3-tert-butyltrimethylsilylbenzene, 2-allyloxy-1-bromo-3-tert-butyltrimethylsilyl-5-methylbenzene, 2-allyloxy-1-bromo-3-tert-butyl-5-methoxybenzene, 2-allyloxy-1-bromo-3-tert-butyl-5-chlorobenzene, 2-allyloxy-3,5-dimethyl-1-bromobenzene and 1-allyloxy-2-bromonaphthalene.

Examples of the compound [9] further include compounds resulting from changing the "methoxy" or "allyloxy" of the above-mentioned compounds to benzyloxy, ethoxy, tert-butyltrimethylsilyloxy, trimethylsilyloxy or methoxymethoxy, and compounds resulting from changing the "bromo" to chloro or iodo.

In the compound [4], the group having a cyclopentadienylidene skeleton represented as the substituent Cp^3 may be, for example, the cyclopentadienylidene group, methylcyclopentadienylidene group, dimethylcyclopentadienylidene group, trimethylcyclopentadienylidene group, tetramethylcyclopentadienylidene group, ethylcyclopentadienylidene group, n-propylcyclopentadienylidene group, isopropylcyclopentadienylidene group, n-butylcyclopentadienylidene group, sec-butylcyclopentadienylidene group, tert-butylcyclopentadienylidene group, n-pentylcyclopentadienylidene group, neopentylcyclopentadienylidene group, n-hexylcyclopentadienylidene group, n-octylcyclopentadienylidene group, phenylcyclopentadienylidene group, naphthylcyclopenta-

dienylidene group, trimethylsilylcyclopentadienylidene group, triethylsilylcyclopentadienylidene group, tert-butyl dimethylsilylcyclopentadienylidene group, indenylidene group, methylindenylidene group,

5 dimethylindenylidene group, ethylindenylidene group, n-propylindenylidene group, isopropylindenylidene group, n-butylindenylidene group, sec-butylindenylidene group, tert-butylindenylidene group, n-pentylindenylidene group, neopentylindenylidene group, n-hexylindenylidene group,

10 n-octylindenylidene group, n-decylindenylidene group, phenylindenylidene group, methylphenylindenylidene group, naphthylindenylidene group, trimethylsilylindenylidene group, triethylsilylindenylidene group, tert-butyl dimethylsilylindenylidene group, tetrahydroindenylidene

15 group, fluorenylidene group, methylfluorenylidene group, dimethylfluorenylidene group, ethylfluorenylidene group, diethylfluorenylidene group, n-propylfluorenylidene group, di-n-propylfluorenylidene group, isopropylfluorenylidene group, diisopropylfluorenylidene group, n-

20 butylfluorenylidene group, sec-butylfluorenylidene group, tert-butylfluorenylidene group, di-n-butylfluorenylidene group, di-sec-butylfluorenylidene group, di-tert-butylfluorenylidene group, n-pentylfluorenylidene group, neopentylfluorenylidene group, n-hexylfluorenylidene

25 group, n-octylfluorenylidene group, n-decylfluorenylidene group, n-dodecylfluorenylidene group, phenylfluorenylidene group, diphenylfluorenylidene group, methylphenylfluorenylidene group, naphthylfluorenylidene group,

trimethylsilylfluorenylidene group, bis-trimethylsilylfluorenylidene group, triethylsilylfluorenylidene group and tert-butyldimethylsilylfluorenylidene group, preferred of these being cyclopentadienyli-
5 methylcyclopentadienyli-
dienylidene group, tert-butylcyclopentadienyli-
dienylidene group, tetramethylcyclopentadienyli-
group, indenylidene group, fluorenyli-

Examples of the compound [4] include 5-
methylidene-cyclopenta-1,3-diene, 2-tert-butyl-5-
10 methylidene-cyclopenta-1,3-diene, 2-methyl-5-methylidene-
cyclopenta-1,3-diene, 2-tert-butyldimethylsilyl-5-
methylidene-cyclopenta-1,3-diene, 2-trimethylsilyl-5-
methylidene-cyclopenta-1,3-diene, 5-isopropylidene-
cyclopenta-1,3-diene, 2-tert-butyl-5-isopropylidene-
15 cyclopenta-1,3-diene, 2-methyl-5-isopropylidene-
cyclopenta-1,3-diene, 2-tert-butyldimethylsilyl-5-
isopropylidene-cyclopenta-1,3-diene, 2-trimethylsilyl-5-
isopropylidene-cyclopenta-1,3-diene, 5-(1-ethyl-
propylidene)-cyclopenta-1,3-diene, 2-tert-butyl-5-(1-
20 ethylpropylidene)-cyclopenta-1,3-diene, 2-methyl-5-(1-
ethylpropylidene)-cyclopenta-1,3-diene, 2-tert-butyl-
dimethylsilyl-5-(1-ethylpropylidene)-cyclopenta-1,3-
diene, 2-trimethylsilyl-5-(1-ethylpropylidene)-
cyclopenta-1,3-diene, 5-diphenylmethylidene-cyclopenta-
25 1,3-diene, 2-tert-butyl-5-diphenylmethylidene-cyclopenta-
1,3-diene, 2-methyl-5-diphenylmethylidene-cyclopenta-1,3-
diene, 2-tert-butyldimethylsilyl-5-diphenylmethylidene-
cyclopenta-1,3-diene and 2-trimethylsilyl-5-diphenyl-

methylidene-cyclopenta-1,3-diene.

The amount of the compound [4] to be used is in the range of usually 0.5-3 moles, preferably 0.7-1.5 moles per 1 mole of the compound [9].

5 Examples of the organoalkali metal compound include organolithium compounds, e.g., methyllithium, ethyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, lithium trimethylsilyl acetylide, lithium acetylide, trimethylsilylmethyllithium, vinylithium,
10 phenyllithium and allyllithium.

The amount of the organoalkali metal compound or metallic magnesium to be used per mole of the compound [9] is usually in the range of 0.5-5 moles, the amount of the organoalkali metal compound being preferably in the
15 range of 0.9-2.2 moles and that of metallic magnesium being preferably in the range of 0.9-1.2 moles.

The reaction is usually conducted in a solvent inert to the reaction. Examples of the solvent include aprotic solvents, e.g., aromatic hydrocarbon solvents,
20 such as benzene and toluene, aliphatic hydrocarbon solvents, such as hexane and heptane, ether type solvents, such as diethyl ether, tetrahydrofuran and 1,4-dioxane, amide type solvents, such as hexamethylphosphoric amide and dimethylformamide, polar solvents, such
25 as acetonitrile, propionitrile, acetone, diethyl ketone, methyl isobutyl ketone and cyclohexanone, and halogen-containing solvents, such as dichloromethane, dichloroethane, chlorobenzene and dichlorobenzene. These

solvents may be used each alone or as a mixture of two or more thereof. The amount of the solvent to be used is in the range of usually 1-200 times by weight, preferably 3-50 times by weight the amount of the compound [9].

5 The present step may usually be conducted by adding the compound [9] and the organoalkali metal compound or metallic magnesium to the solvent, then adding the compound [4] thereto, and thereafter adding water or an acidic aqueous solution or the like thereto, 10 but it may also be conducted by adding the compound [9], the compound [4] and the organoalkali metal compound or metallic magnesium simultaneously to the solvent and then adding water or an acidic aqueous solution thereto. The reaction temperature is usually in the range from not 15 lower than -100°C to not higher than the boiling point of the solvent. The temperature is preferably in the range from -80°C to $+40^{\circ}\text{C}$ when the organoalkali metal compound is used, and preferably in the range from 10°C to 100°C when metallic magnesium is used.

20 Examples of the acidic aqueous solution include aqueous ammonium chloride solution and hydrochloric acid. The amount of water or acidic aqueous solution used is in the range of usually 1-200 times by weight, preferably 3-50 times by weight the amount of the compound [9] used.

25 When metallic magnesium is used, the initiation of the reaction can be promoted by using an initiator in combination therewith. Examples of the initiator include molecular halogens, such as bromine and iodine, alkyl

halides, such as methyl iodide, ethyl iodide and ethyl bromide, and alkyl dihalides, such as 1,2-dichloroethane and 1,2-dibromoethane. The amount of the initiator to be used per mole of metallic magnesium is usually in the
5 range of 0.00001-0.1 mole.

The reaction mixture obtained is separated into an organic layer and an aqueous layer, the solution of the compound [2a] being obtained as the organic layer. When a solvent compatible with water was used in the
10 above-mentioned reaction, or when the organic layer and the aqueous layer cannot be easily separated from each other owing to the use of an insufficient amount of the solvent in the above-mentioned reaction, the layer separation is advantageously conducted after adding an
15 organic solvent insoluble in water, such as toluene, ethyl acetate and chlorobenzene, to the reaction mixture.

The compound [2a] may be used in the next [step 3] either as the solution thus obtained as it is or after taken out from the solution.

20 The compound [2a] can be taken out from the solution of the compound [2a], for example, by washing the solution with water, then drying the solution and removing the solvent by distillation. The compound [2a] thus obtained may be further purified by such means as
25 recrystallization, distillation and column chromatography.

When a solid precipitates out after addition of the compound [9] and the organoalkali metal compound or

metallic magnesium to the solvent, followed by addition of the compound [4] thereto, or after addition of the compound [9], the compound [4] and the organoalkali metal compound or metallic magnesium to the solvent, the
5 compound [1] can also be prepared by taking out the solid from the reaction system, adding the solid to a solvent which can be used in the step [3], and then adding the compound [3] thereto.

The compound [9] used in the above-mentioned
10 [step 2] can be prepared through the [step 1] as described below.

[Step 1]

The step of preparing the compound [9] by reacting the compound [10] with a halide represented by
15 the formula (11) (hereinafter referred to as compound [11]):



wherein Y^5 is a halogen atom and R^7 is the same as defined above, in the presence of a base.

20 The halogen atoms represented as the substituent Y^5 in the compound [11] include the chlorine, bromine and iodine atom.

The compound [11] may be, for example, methyl bromide, ethyl bromide, vinyl bromide, allyl bromide, 2-
25 chloro-2-propenyl bromide, 2-bromo-2-propenyl bromide, 2-methyl-2-propenyl bromide, homoallyl bromide, hexenyl bromide and decenyl bromide, and compounds resulting from changing the "bromide" of the above-mentioned compounds

to chloride or iodide. The amount of the compound [11] to be used per mole of the compound [10] is in the range of usually 0.5-5 moles, preferably 0.9-3.3 moles.

The base may be, for example, inorganic bases,
5 such as lithium hydroxide, lithium carbonate, lithium hydrogen carbonate, lithium hydride, lithium methoxide, lithium ethoxide, sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, sodium hydride, sodium methoxide, potassium hydroxide, potassium carbonate,
10 potassium hydrogen carbonate, potassium hydride, potassium methoxide and potassium ethoxide,

amine compounds, e.g., primary amine compounds, such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, tert-butylamine, n-octylamine,
15 n-decylamine, aniline and ethylenediamine, secondary amine compounds, such as dimethylamine, diethylamine, di-n-propylamine, di-n-butylamine, di-tert-butylamine, di-n-octylamine, di-n-decylamine, pyrrolidine, hexamethyldisilazane, and diphenylamine, and
20 tertiary amine compounds, such as trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, diisopropylethylamine, tri-n-octylamine, tri-n-decylamine, triphenylamine, N,N-dimethylaniline, N,N,N',N'-tetramethylethylenediamine, N-methylpyrrolidine, and 4-
25 dimethylaminopyridine, and

such organoalkali metal compounds as organolithium compounds, e.g., methyllithium, ethyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium,

lithium trimethylsilylacetylide, lithium acetylide, trimethylsilylmethylolithium, vinylolithium, phenylolithium and allylolithium. The amount of the base to be used per mole of the compound [10] is in the range of usually 0.5-
5 3 moles, preferably 0.9-1.5 moles.

A catalyst may be used in the reaction. The catalyst may be, for example, quaternary ammonium salts, e.g., benzyltrimethylammonium chloride, benzyltriethylammonium chloride, benzyltri-n-propylammonium chloride,
10 benzyltri-n-butylammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetra-n-propylammonium chloride, and tetra-n-butylammonium chloride, and compounds resulting from changing the "chloride" of the above-mentioned compounds to bromide or
15 iodide. The amount of the catalyst to be used per mole of the compound [10] is in the range of usually 0.00001-0.5 mole, preferably 0.0001-0.1 mole.

The reaction is usually conducted in a solvent inert to the reaction. Examples of the solvent include
20 aprotic solvents, e.g., aromatic hydrocarbon solvents, such as benzene, toluene and xylene, aliphatic hydrocarbon solvents, such as hexane and heptane, ether type solvents, such as diethyl ether, tetrahydrofuran and 1,4-dioxane, amide type solvents such as hexamethylphosphoric
25 amide and dimethylformamide, polar solvents, such as acetonitrile, propionitrile, acetone, diethyl ketone, methyl isobutyl ketone and cyclohexanone, and halogen-containing solvents, such as dichloromethane, dichloro-

ethane, chlorobenzene and dichlorobenzene, and such protic solvents as alcoholic solvents, such as methanol, ethanol, isopropanol and n-butanol. These solvents may be used each alone or as a mixture of two or more
5 thereof. The amount of the solvent to be used is in the range of usually 1-200 times by weight, preferably 5-30 times by weight the amount of the compound [10].

The present step can be conducted, for example, by adding the base to the solvent, then adding the
10 compound [10] thereto and thereafter adding the compound [11] thereto. When the catalyst is used, the reaction is conducted by adding the base and the catalyst to the solvent, then adding the compound [10] thereto and thereafter adding the compound [11] thereto. The
15 reaction temperature is in the range of usually from not lower than -100°C to not higher than the boiling point of the solvent, preferably 0-100°C.

The reaction mixture obtained is mixed with water and then separated into an organic layer and an
20 aqueous layer, the solution of the compound [9] being obtained as the organic layer. When a solvent compatible with water was used in the aforesaid reaction or when the organic layer and aqueous layer cannot be easily separated from each other owing to the use of an
25 insufficient amount of the solvent in the aforesaid reaction, the layer separation is advantageously conducted after adding an organic solvent insoluble in water, such as toluene, ethyl acetate and chlorobenzene,

to the reaction mixture.

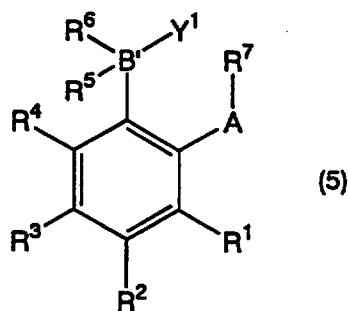
Though the compound [9] may be used in the next step as the solution thus obtained as it is, the compound is usually employed after taken out from the solution.

5 The compound [9] can be taken out from the solution thereof, for example, by washing the solution with water, then drying the solution, and removing the solvent by distillation. The compound [9] thus obtained may be further purified by such means as recrystalliza-
10 tion, distillation and column chromatography.

The compound [2b] can be prepared through the [step 5] as described below.

[Step 5]

The step of preparing the compound [2b] by
15 reacting a halide compound represented by the formula (5) (hereinafter referred to as compound [5]):



wherein Y¹ is a halogen atom, and A, B', R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are respectively the same as defined above, with a cyclopentadienyl metal salt represented by the formula
20 (6) (hereinafter referred to as compound [6]):



wherein M^2 is an alkali metal atom and Cp^2 is the same as defined above.

The halogen atom represented as the substituent Y^1 in the compound [5] is, for example, the chlorine,
5 bromine or iodine atom.

Examples of the compound [5] include chloro(2-methoxyphenyl)dimethylsilane, chloro(2-methoxy-3-methylphenyl)dimethylsilane, chloro(2-methoxy-3,5-dimethylphenyl)dimethylsilane, (3-tert-butyl-2-methoxyphenyl)-
10 chlorodimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)chlorodimethylsilane, (3,5-di-tert-butyl-2-methoxyphenyl)chlorodimethylsilane, chloro(2-methoxy-3-phenylphenyl)dimethylsilane, chloro(2-methoxy-5-methyl-3-phenylphenyl)dimethylsilane, (3-tert-butyl-2-methoxyphenyl)chlorodimethylsilane, (3-tert-butyl-2-methoxy-5-methylphenyl)chlorodimethylsilane, chloro(2-methoxy-3-trimethylsilylphenyl)-
15 dimethylsilane, chloro(2-methoxy-5-methyl-3-trimethylsilylphenyl)dimethylsilane, (3,5-dimethyl-2-methoxyphenyl)-
20 chlorodimethylsilane, (3-tert-butyl-2,5-dimethoxyphenyl)chlorodimethylsilane, (3-tert-butyl-5-chloro-2-methoxyphenyl)chlorodimethylsilane,

(2-allyloxy-phenyl)chlorodimethylsilane, (2-allyloxy-3-methylphenyl)chlorodimethylsilane, (2-
25 allyloxy-3,5-dimethylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert-butylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert-butyl-5-methylphenyl)chlorodimethylsilane, (2-allyloxy-3,5-di-tert-butylphenyl)chlorodi-

methyldimethylsilane, (2-allyloxy-3-phenylphenyl)chlorodimethylsilane, (2-allyloxy-5-methyl-3-phenylphenyl)-chlorodimethylsilane, (2-allyloxy-3-tert-butyl-dimethylsilylphenol)chlorodimethylsilane, (2-allyloxy-3-tert-butyl-dimethylsilyl-4-methylphenyl)chlorodimethylsilane, (2-allyloxy-3-trimethylsilylphenyl)chlorodimethylsilane, (2-allyloxy-5-methyl-3-trimethylsilylphenyl)chlorodimethylsilane, (2-allyloxy-3,5-diamylphenyl)chlorodimethylsilane, (2-allyloxy-3-tert-butyl-5-methoxyphenyl)chlorodimethylsilane, (2-allyloxy-3-tert-butyl-5-chlorophenyl)chlorodimethylsilane and (1-allyloxynaphthalen-2-yl)chlorodimethylsilane.

Examples of the compound [5] further include compounds resulting from changing the "methoxy" or "allyloxy" of the above-mentioned compounds to benzyloxy, ethoxy, trimethylsilyloxy, tert-butyl-dimethylsilyloxy or methoxymethoxy, and compounds resulting from changing the "chlorodimethylsilane" to chlorodiethylsilane, chlorodiphenylsilane, chlorodimethoxysilane, bromodimethylsilane or dimethyliodosilane.

The alkali metal represented as the substituent M^2 in the compound [6] is, for example, lithium, potassium and sodium.

Examples of the compound [6] include cyclopentadienyllithium, methylcyclopentadienyllithium, dimethylcyclopentadienyllithium, trimethylcyclopentadienyllithium, tetramethylcyclopentadienyllithium, ethylcyclopentadienyllithium, n-propylcyclopentadienyl-

- lithium, isopropylcyclopentadienyllithium, tert-butylcyclopentadienyllithium, n-butylcyclopentadienyllithium, sec-butylcyclopentadienyllithium, isobutylcyclopentadienyllithium, di-tert-butylcyclopentadienyllithium, 5 n-hexylcyclopentadienyllithium, phenylcyclopentadienyllithium, trimethylsilylcyclopentadienyllithium, tert-butyltrimethylsilylcyclopentadienyllithium, indenyllithium, methylindenyllithium, phenylindenyllithium, fluorenyllithium,
- 10 cyclopentadienylsodium, methylcyclopentadienylsodium, tetramethylcyclopentadienylsodium, tert-butylcyclopentadienylsodium, n-butylcyclopentadienylsodium, trimethylsilylcyclopentadienylsodium, tert-butyltrimethylsilylcyclopentadienylsodium, indenylsodium, fluorenyl-
- 15 sodium, cyclopentadienylpotassium, methylcyclopentadienylpotassium, tetramethylcyclopentadienylpotassium, tert-butylcyclopentadienylpotassium, n-butylcyclopentadienylpotassium, trimethylsilylcyclopentadienylpotassium, tert-butyltrimethylsilylcyclopentadienylpotassium,
- 20 indenylpotassium and fluorenylpotassium.

The amount of the compound [6] to be used per mole of the compound [5] is in the range of usually 0.5-3 moles, preferably 0.9-1.1 moles.

- The reaction is usually conducted in a solvent 25 inert to the reaction. Examples of the solvent include aprotic solvents, e.g., aromatic hydrocarbon solvents, such as benzene, toluene and xylene, aliphatic hydrocarbon solvents, such as hexane and heptane, ether type

solvents, such as diethyl ether, tetrahydrofuran and 1,4-dioxane, amide type solvents, such as hexamethylphosphoric amide and dimethylformamide, and halogen-containing solvent, such as dichloromethane, dichloroethane, chlorobenzene and dichlorobenzene. These solvents may be used each alone or as a mixture of two or more thereof. The amount of the solvent to be used is in the range of usually 1-200 times by weight, preferably 5-30 times by weight the amount of the compound [5].

10 The present step can be conducted, for example, by mixing the compound [5] and the compound [6] in the solvent. The reaction temperature is in the range of usually from not lower than -100°C to not higher than the boiling point of the solvent, preferably from -80°C to
15 $+35^{\circ}\text{C}$.

 The reaction mixture obtained is mixed with water or an acidic aqueous solution, such as aqueous ammonium chloride solution or hydrochloric acid, and then separated into an organic layer and an aqueous layer, the
20 solution of the compound [2b] being obtained as the organic layer. When a solvent compatible with water was used in the aforesaid reaction or when the organic layer and the aqueous layer cannot be easily separated from each other owing to the use of an insufficient amount of
25 the solvent in the aforesaid reaction, the layer separation is advantageously conducted after adding an organic solvent insoluble in water, such as toluene, ethyl acetate and chlorobenzene, to the reaction mixture.

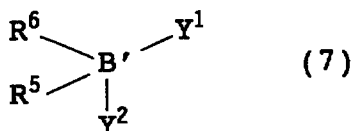
The compound [2b] may be used in the next [step 3] as the solution thus obtained as it is or it may be used after taken out from the solution.

The compound [2b] can be taken out from the solution thereof, for example, by washing the solution with water, then drying the solution and removing the solvent by distillation. The compound [2b] thus obtained may be further purified by such means as recrystallization, distillation and column chromatography.

10 The compound [5] used in the above-mentioned [step 5] can be prepared through the [step 4] as described below.

[Step 4]

15 The step of preparing the compound [5] by reacting the compound [9] with a dihalide compound represented by the formula (7) (hereinafter referred to as compound [7]):



wherein Y^2 is a halogen atom, and B' , R^5 , R^6 and Y^1 are respectively the same as defined above, in the presence of an organoalkali metal compound or metallic magnesium.

20 The compound [9] can be prepared through the [step 1] as described above. In this instance, the compound [9] obtained may be used as the solution obtained as an organic layer by layer separation as it

is, or it may be used after taken out from the solution.

The halogen atom represented as the substituent Y^2 in the compound [7] is, for example, the chlorine, bromine or iodine atom.

- 5 Examples of the compound [7] include dichloro-
dimethylsilane, dichlorodiphenylsilane, dichlorodiethyl-
silane, dichloro-di-n-propylsilane, dichlorodimethoxy-
silane, diallyldichlorosilane, dichlorodivinylsilane,
dichloromethylvinylsilane, dichlorodibenzylsilane,
10 dichlorochloromethylmethylsilane, dibromodimethylsilane
and diiododimethylsilane.

The amount of the compound [7] to be used per mole of the compound [9] is in the range of usually 0.5-50 moles, preferably 0.9-5 moles.

- 15 Examples of the organoalkali metal compounds include organolithium compounds, for example, organolithium compounds, such as methyllithium, ethyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, lithium trimethylsilyl acetylide, lithium acetylide,
20 trimethylsilylmethyllithium, vinylolithium, phenyllithium and allyllithium.

- The amount of the organoalkali metal compound or metallic magnesium to be used per mole of the compound [9] is in the range of usually 0.5-5 moles, preferably
25 0.9-2.2 moles.

The reaction is usually conducted in a solvent inert to the reaction. Examples of the solvent include aprotic solvents, e.g., aromatic hydrocarbon solvents,

such as benzene, toluene and xylene, aliphatic hydrocarbon solvents, such as hexane and heptane, ether type solvents, such as diethyl ether, tetrahydrofuran and 1,4-dioxane, amide type solvents, such as hexamethylphosphoric amide and dimethylformamide, polar solvents, such as acetonitrile, propionitrile, acetone, diethyl ketone, methyl isobutyl ketone and cyclohexanone, and halogen-containing solvents, such as dichloromethane, dichloroethane, chlorobenzene and dichlorobenzene. These solvents may be used each alone or as a mixture of two or more thereof. The amount of the solvent to be used is in the range of usually 1-200 times by weight, preferably 5-30 times by weight the amount of the compound [9].

The present step may be conducted, for example, by adding the compound [9] and the organoalkali metal compound or metallic magnesium to the solvent, and then adding the compound [7] thereto, or it may also be conducted by adding the compound [9], the compound [7] and the organoalkali metal compound or metallic magnesium simultaneously to the solvent. The reaction temperature is not lower than -100°C and not higher than the boiling point of the solvent. The temperature is preferably in the range from -80°C to $+40^{\circ}\text{C}$ when the organoalkali metal compound is used and preferably in the range from 10°C to 100°C when metallic magnesium is used.

When metallic magnesium is used, the initiation of the reaction can be promoted by using an initiator in combination therewith. Examples of the initiator include

molecular halogens, such as bromine and iodine, alkyl halides, such as methyl iodide, ethyl iodide and ethyl bromide and alkyl dihalides, such as 1,2-dichloroethane and 1,2-dibromoethane. The amount of the initiator to be
5 used per mole of metallic magnesium is usually in the range of 0.00001-0.1 mole.

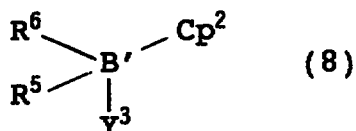
The compound [5] thus obtained may be used in the next [step 5] either as the reaction mixture obtained as it is, or as the residue obtained by concentrating the
10 reaction mixture, or after taken out from the reaction mixture.

The compound [5] can be taken out from the reaction mixture, for example, by concentrating the reaction mixture to obtain a residue, dissolving the
15 residue in a hydrophobic solvent, e.g., an aromatic hydrocarbon solvent, such as toluene, or an aliphatic hydrocarbon solvent, such as hexane or heptane, filtering off the insolubles, and then removing the solvent by distillation. The compound [5] thus obtained may be
20 further purified by such means as recrystallization, distillation and column chromatography.

The compound [2b] can also be prepared through the [step 6] as described below.

[Step 6]

25 The step of preparing the compound [2b] by reacting the compound [9] with a halide compound represented by the formula (8) (hereinafter referred to as compound [8]):



wherein Y^3 is a halogen atom, and B' , Cp^2 , R^5 and R^6 are respectively the same as defined above, in the presence of an organoalkali metal compound or metallic magnesium.

The compound [9] can be prepared through the
5 [step 1] as mentioned above. In this instance, the resulting compound [9] may be used as it is the solution obtained as an organic layer by layer separation, or it may be used after taken out from the solution.

The halogen atom represented as the substituent
10 Y^3 in the compound [8] is, for example, the chlorine, bromine or iodine atom.

Examples of the compound [8] include chloro-
(cyclopentadienyl)dimethylsilane, chlorodimethyl(methyl-
cyclopentadienyl)silane, chlorodimethyl(tetramethylcyclo-
15 pentadienyl)silane, chlorodimethyl(tetramethylcyclopenta-
dienyl)silane, chloro(tert-butylcyclopentadienyl)-
dimethylsilane, chlorodimethyl(trimethylsilylcyclo-
pentadienyl)silane, (inden-1-yl)chlorodimethylsilane,
(inden-2-yl)chlorodimethylsilane and chloro(9H-fluoren-9-
20 yl)dimethylsilane, and further, compounds resulting from
changing the "cyclopentadienyl" of the above-mentioned
compounds to dimethylcyclopentadienyl, n-butylcyclopenta-
dienyl, sec-butylcyclopentadienyl, tert-butyltrimethyl-
silylcyclopentadienyl, trimethylcyclopentadienyl,
25 ethylcyclopentadienyl, n-propylcyclopentadienyl,

isopropylcyclopentadienyl, isobutylcyclopentadienyl, phenylcyclopentadienyl, methyinden-1-yl or methyinden-2-yl, compounds resulting from changing the "dimethyl" to diethyl, diphenyl or dimethoxy, and compounds resulting
5 from changing the "chloro" to bromo or iodo.

The amount of the compound [8] to be used per mole of the compound [9] is in the range of usually 0.5-3 moles, preferably 0.9-1.2 moles.

Examples of the organoalkali metal compound
10 include organolithium compounds, such as methyllithium, ethyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, lithium trimethylsilyl acetylide, lithium acetylide, trimethylsilylmethyllithium, vinylithium, phenyllithium and allyllithium.

15 The amount of the organoalkali metal salt or metallic magnesium to be used per mole of the compound [9] is usually 0.5-5 moles, the amount of the organoalkali metal compound being preferably in the range of 0.9-2.2 moles and that of metallic magnesium being
20 preferably in the range of 0.9-1.2 moles.

The reaction is usually conducted in a solvent inert to the reaction. Examples of the solvent include aprotic solvents, e.g., aromatic hydrocarbon solvents, such as benzene, toluene and xylene, aliphatic hydro-
25 carbon solvents, such as hexane and heptane, ether type solvents, such as diethyl ether, tetrahydrofuran and 1,4-dioxane, amide type solvents, such as hexamethylphosphoric amide and dimethylformamide, polar solvents,

such as acetonitrile, propionitrile, acetone, diethyl ketone, methyl isobutyl ketone and cyclohexanone, and halogen-containing solvents, such as dichloromethane, dichloroethane, chlorobenzene and dichlorobenzene. These
5 solvents may be used each alone or as a mixture of two or more thereof. The amount of the solvent to be used is in the range of usually 1-200 times by weight, preferably 5-30 times by weight the amount of the compound [9].

The present step can be conducted, for example,
10 by adding the compound [9] and the organoalkali metal salt or metallic magnesium to the solvent and then adding the compound [8] thereto or alternatively by adding the compound [9], the compound [8] and the organoalkali metal salt or metallic magnesium simultaneously to the solvent.
15 The reaction temperature is usually not lower than -100°C and not higher than the boiling point of the solvent, the temperature being preferably in the range from -78°C to $+40^{\circ}\text{C}$ when the organoalkali metal compound is used and preferably in the range from 10°C to 100°C when metallic
20 magnesium is used.

When metallic magnesium is used, the initiation of the reaction can be promoted by using an initiator in combination therewith. Examples of the initiator include molecular halogens, such as bromine and iodine, alkyl
25 halides, such as methyl iodide, ethyl iodide and ethyl bromide, and alkyl dihalides, such as 1,2-dichloroethane and 1,2-dibromoethane. The amount of the initiator to be used per mole of metallic magnesium is usually in the

range of 0.00001-0.1 mole.

The reaction mixture obtained is mixed with water or an acidic aqueous solution, such as aqueous ammonium chloride solution or hydrochloric acid, and then
5 separated into an organic layer and an aqueous layer, the solution of the compound [2b] being obtained as the organic layer. When a solvent compatible with water was used in the aforesaid reaction or when the organic layer and the aqueous layer cannot be easily separated from
10 each other owing to the use of an insufficient amount of solvent in the aforesaid reaction, the layer separation is advantageously conducted after adding an organic solvent insoluble in water, such as toluene, ethyl acetate and chlorobenzene, to the reaction mixture.

15 The compound [2b] may be used in the next [step 3] either as the solution thus obtained as it is or after taken out from the solution.

The compound [2b] can be taken out from the solution thereof, for example, by washing the solution
20 with water, then drying the solution, and removing the solvent by distillation. The compound [2b] thus obtained may be further purified by such means as recrystallization, distillation and column chromatography.

[Organoaluminum compound (A)]

25 The compound (A) used in the present invention may be known organoaluminum compounds. Preferred examples thereof include any one compound selected from (A1) an organoaluminum compound represented by the

formula $E^1_aAlZ_{3-a}$, (A2) a cyclic aluminosiloxane having the structure represented by the formula $\{-Al(E^2)-O-\}_b$ and (A3) a linear aluminosiloxane having the structure represented by the formula $E^3\{-Al(E^3)-O-\}_cAlE^3_2$ (wherein E^1 , E^2 and E^3 are each a hydrocarbon group with the number of carbon atoms of 1-8 and all E^1 , all E^2 and all E^3 may be the same with or different from each other; Z is a hydrogen atom or a halogen atom and all Z may be the same with or different from each other; a is the number specified by $0 < a \leq 3$, b is an integer of 2 or greater, and c is an integer of 1 or greater, and mixtures of two or three kinds thereof.

Specific examples of the organoaluminum compound (A1) represented by the formula $E^1_aAlZ_{3-a}$ include trialkylaluminums, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, and trihexylaluminum; dialkylaluminum chlorides, such as dimethylaluminum chloride, diethylaluminum chloride, dipropylaluminum chloride, diisobutylaluminum chloride, and dihexylaluminum chloride; alkylaluminum dichlorides such as methylaluminum dichloride, ethylaluminum dichloride, propylaluminum dichloride, isobutylaluminum dichloride, and hexylaluminum dichloride; and dialkylaluminum hydrides, such as dimethylaluminum hydride, diethylaluminum hydride, dipropylaluminum hydride, diisobutylaluminum hydride and dihexylaluminum hydride.

Preferred of these is a trialkylaluminum, more preferred being triethylaluminum and triisobutylaluminum.

Specific examples of E^2 and E^3 in the cyclic aluminoxane (A2) having the structure represented by the formula $\{-Al(E^2)-O-\}_b$ and in the linear aluminoxane (A3) having the structure represented by the formula

- 5 $E^3\{-Al(E^3)-O-\}_cAlE^3_2$ include alkyl groups, such as the methyl group, ethyl group, normal propyl group, isopropyl group, normal butyl group, isobutyl group, normal pentyl group and neopentyl group; b is an integer of 2 or greater and c is an integer of 1 or greater. Preferably
- 10 E^2 and E^3 are methyl group and isobutyl group, b is 2-40 and c is 1-40.

The above-mentioned aluminoxanes can be prepared by various methods. There is no particular limitation as to the method and known methods may be used

15 for preparation. For example, the aluminoxane is prepared by dissolving a trialkylaluminum (e.g., trimethylaluminum) in a suitable organic solvent (e.g., benzene, or aliphatic hydrocarbon) and then contacting the resulting solution with water; or it may be prepared

20 by contacting a trialkylaluminum (e.g., trimethylaluminum) with a metal salt containing water of crystallization (e.g., copper sulfate hydrate).

[Compound (B)]

In the present invention, any one compound

25 selected from (B1) a boron compound represented by the formula $BQ^1Q^2Q^3$, (B2) a boron compound represented by the formula $Z^+(BQ^1Q^2Q^3Q^4)^-$ and (B3) a boron compound represented by the formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$ is used as the compound

(B).

In the boron compound (B1) represented by the formula $BQ^1Q^2Q^3$, B is a boron atom in the trivalent valence state, Q_1-Q_3 are each a halogen atom, hydrocarbon group
5 containing 1-20 carbon atoms, halogenated hydrocarbon group containing 1-20 carbon atoms, substituted silyl group containing 1-20 carbon atoms, alkoxy group containing 1-20 carbon atoms or di-substituted amino group containing 2-20 carbon atoms, which may be the same
10 with or different from each other. Preferred Q_1-Q_3 each independently a halogen atom, hydrocarbon group containing 1-20 carbon atoms and halogenated hydrocarbon group containing 1-20 carbon atoms.

Specific examples of the Lewis acid (B1)
15 include tris(pentafluorophenyl)borane, tris(2,3,5,6-tetrafluorophenyl)borane, tris(2,3,4,5-tetrafluorophenyl)borane, tris(3,4,5-trifluorophenyl)borane, tris(2,3,4-trifluorophenyl)borane and phenylbis(pentafluorophenyl)borane, most preferred of these being
20 tris(pentafluorophenyl)borane.

In the boron compound (B2) represented by the formula $Z^+(BQ^1Q^2Q^3Q^4)^-$, Z^+ is an inorganic or organic cation, B is a boron atom in the trivalent valence state, and Q^1-Q^4 are the same as defined for Q^1-Q^3 in the above-
25 mentioned compound (B1).

As to specific examples of the compound represented by the formula $Z^+(BQ^1Q^2Q^3Q^4)^-$, Z^+ of the inorganic cation is, for example, a ferrocenium cation,

alkyl-substituted ferrocenium cation and silver cation, and Z^+ of the organic cation is, for example, a triphenylmethyl cation; $(BQ^1Q^2Q^3Q^4)^-$ is, for example, tetrakis(pentafluorophenyl)borate, tetrakis(2,3,5,6-
5 tetrafluorophenyl)borate, tetrakis(2,3,4,5-tetrafluorophenyl)borate, tetrakis(3,4,5-trifluorophenyl)borate, tetrakis(2,2,4-trifluorophenyl)borate, phenylbis(pentafluorophenyl)borate and tetrakis(3,5-bistrifluoromethylphenyl)borate.

10 Examples of the specific combination of these include ferrocenium tetrakis(pentafluorophenyl)borate, 1,1'-dimethylferrocenium tetrakis(pentafluorophenyl)-borate, silver tetrakis(pentafluorophenyl)borate, triphenylmethyl tetrakis(pentafluorophenyl)borate and
15 triphenylmethyl tetrakis(3,5-bistrifluoromethylphenyl)-borate, most preferred of these being triphenylmethyl tetrakis(pentafluorophenyl)borate.

 In the boron compound (B3) represented by the formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$, L is a neutral Lewis base,
20 $(L-H)^-$ is a Brønsted acid, B is a boron atom in the trivalent valence state, and Q_1-Q_4 are the same as defined for Q^1-Q^3 in the above-mentioned compound (B1).

 In the specific example of the compound represented by the formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$, $(L-H)^+$ of the
25 Brønsted acid is, for example, a trialkyl-substituted ammonium, N,N-dialkylanilinium, dialkylammonium and triarylphosphonium, and the $(BQ^1Q^2Q^3Q^4)^-$ may be, for example, the same as those described above.

Examples of the specific combination of these include triethylammonium tetrakis(pentafluorophenyl)-borate, tripropylammonium tetrakis(pentafluorophenyl)-borate, tri(normal butyl)ammonium tetrakis(pentafluoro-
5 phenyl)borate, tri(normal butyl)ammonium tetrakis(3,5-bistrifluoromethylphenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, N,N-diethylanilinium tetrakis(pentafluorophenyl)borate, N,N-2,4,6-pentamethyl-anilinium tetrakis(pentafluorophenyl)borate, N,N-
10 dimethylanilinium tetrakis(3,5-bistrifluoromethylphenyl)-borate, diisopropylammonium tetrakis(pentafluorophenyl)-borate, dicyclohexylammonium tetrakis(pentafluorophenyl)-borate, triphenylphosphonium tetrakis(pentafluorophenyl)-borate, tri(methylphenyl)phosphonium tetrakis(penta-
15 fluorophenyl)borate, and tri(dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate, most preferred of these being tri(normal butyl)ammonium tetrakis(pentafluorophenyl)borate or N,N-dimethylanilinium tetrakis-(pentafluorophenyl)borate.

20 In the present invention, the transition metal complex represented by the formula (1), the compound (A), or further the compound (B) may be charged in any desired order at the time of polymerization. Alternatively, any desired combination of these compounds may be contacted
25 with each other beforehand and the resulting product may be used at the time of polymerization.

As to the amounts of the respective components of the catalyst, the respective components are desirably

used such that the molar ratio of the compound (A) to the transition metal complex may fall within the range of 0.1-10,000, preferably 5-2,000 and the molar ratio of the compound (B) to the transition metal complex may fall
5 within the range of 0.01-100, preferably 0.5-10. With regard to the concentrations of the respective catalyst components when they are used in the form of a solution, the respective components are desirably used such that the concentration of the transition metal complex
10 represented by the formula (1) may fall within the range of 0.0001-5 mmol/l, preferably 0.001-1 mmol/l, the concentration of the compound (A) in terms of Al atom within the range of 0.01-500 mmol/l, preferably 0.1-100 mmol/l and the concentration of the compound (B) within
15 the range of 0.0001-5 mmol/l, preferably 0.001-1 mmol/l.

In the present invention, the monomer used for polymerization may be any of the olefins and diolefins each with the number of carbon atoms of 2-20. Two or more kinds of the monomers may also be used simultaneous-
20 ly. Some examples of the monomer are shown below, but the invention is not limited to these compounds. Specific examples of the olefin include ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, 5-methyl-2-pentene-1 and
25 vinylcyclohexene. The diolefin compounds are, for example, conjugated diene or non-conjugated diene hydrocarbon compounds. Specific examples of the non-conjugated diene compound include 1,5-hexadiene, 1,4-

hexadiene, 1,4-pentadiene, 1,7-octadiene, 1,8-nonadiene,
1,9-decadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-
hexadiene, 7-methyl-1,6-octadiene, 5-ethylidene-2-
norbornene, dicyclopentadiene, 5-vinyl-2-norbornene, 5-
5 methyl-2-norbornene, norbornadiene, 5-methylene-2-
norbornene, 1,5-cyclooctadiene and 5,8-endomethylene-
hexahydronaphthalene. Specific examples of the
conjugated diene compound include 1,3-butadiene,
isoprene, 1,3-hexadiene, 1,3-octadiene, 1,3-
10 cyclooctadiene and 1,3-cyclohexadiene.

Specific examples of the monomers which
constitute copolymers include the combinations of
ethylene and propylene, ethylene and butene-1, ethylene
and hexene-1, and propylene and butene-1, and combina-
15 tions wherein 5-ethylidene-2-norbornene is used in
addition to the above-mentioned combination, but the
invention is not limited thereto.

In the present invention, aromatic vinyl
compounds may also be used as the monomer. Specific
20 examples of the aromatic vinyl compound include styrene,
o-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-
dimethylstyrene, o-ethylstyrene, m-ethylstyrene, p-
ethylstyrene, o-chlorostyrene, p-chlorostyrene, α -
methylstyrene and divinylbenzene.

25 The method of polymerization is not
particularly limited. There may be used, for example,
solution polymerization or slurry polymerization wherein
aliphatic hydrocarbons, such as butane, pentane, hexane,

heptane and octane, aromatic hydrocarbons, such as benzene and toluene, or halogenated hydrocarbons, such as methylene dichloride, are used as the solvent, and gas phase polymerization conducted in gaseous monomers.

- 5 Further, polymerization may be conducted either continuously or batch-wise.

The polymerization temperature may be in the range from -50°C to $+200^{\circ}\text{C}$, but it is particularly preferably in the range from -20°C to $+100^{\circ}\text{C}$. The
10 polymerization pressure is preferably from normal pressure to $60\text{ kg/cm}^2\text{ G}$. The polymerization time, in general, is determined according to the kind of the intended polymer and the reaction apparatus, and may be in the range from 1 minute to 20 hours. In the present
15 invention, chain transfer agents, such as hydrogen, may be added to control the molecular weight of the copolymer.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a flow chart for facilitating the
20 understanding of the present invention. The flow chart merely shows a representative example of one aspect of the present invention, and in no way limits the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

25 The present invention is described below in detail with reference to Examples and Comparative

Examples, but the invention is not limited thereto.

The properties of polymers shown in Examples were determined by the following methods.

- (1) Intrinsic viscosity $[\eta_1]$: A 100 mg sample of
5 the copolymer obtained was dissolved in 50 ml of tetralin at 135°C. The intrinsic viscosity $[\eta_1]$ was determined from the falling velocity of the tetralin solution containing the sample dissolved therein by using an Ubbelohde viscometer set in a water bath kept at 135°C.
- 10 (2) Intrinsic viscosity $[\eta_2]$: A 300 mg sample of the copolymer obtained was dissolved in 100 ml of xylene to give a concentration of about 3 mg/ml. Then the solution was diluted with xylene in dilutions of 1/2, 1/3 and 1/5 to obtain samples of 3 levels of concentration.
15 The intrinsic viscosity $[\eta_2]$ was determined from the falling velocity of the xylene solution containing the sample dissolved therein by using an Ubbelohde viscometer set in an oil bath at 70°C.
- (3) α -Olefin content in copolymer: The α -olefin
20 content in the obtained polymer was determined from the infrared absorption spectra. Determination and calculation were made according to methods described in literature (Takayama, Usami, et al., Characterization of Polyethylene by Infrared Absorption Spectra, or McRae,
25 M.A. and Madams W.F., Die Makromolekulare Chemie, 177, 461 (1976)) by making use of characteristic absorptions originating from α -olefin, e.g., 1375 cm^{-1} (propylene) and

772 cm^{-1} .

Short chain branching (SCB) was expressed in terms of the number of short chain branching per 1,000 carbon atoms.

5 (4) Diolefin content in copolymer: When diolefin units are present in the copolymer, the diolefin content was determined from the infrared absorption spectra in the same manner as (3) above making use of characteristic peaks originating from the diolefin used. For example,
10 when 5-ethylidene-2-norbornene (ENB) was used, the determination was made by using the peak at 1688 cm^{-1} (the peak originating from double bond of ENB).

(5) Melting point of copolymer: The melting point was determined by using Seiko-SSC-5200 under the
15 following conditions.

Temperature increase: from 40°C to 150°C (10°C/min),
kept for 5 minutes

Cooling: from 150°C to 10°C (5°C/min.), kept for
10 minutes

20 Determination: from 10°C to 160°C (5°C/min)

(6) Molecular weight and molecular weight distribution:

These were determined by using a gel permeation chromatography apparatus (mfd. by Waters Corp., 150, C) under the following conditions:

25 Column: TSK gel GMH-HT

Measuring temperature: set at 145°C

Measuring concentration: 10 mg/10 ml o-dichloro-
benzene

(7) Structures of ligand and complex

These were confirmed by ^1H -NMR measurement
(apparatus: AM400, mfd. by Bruker Corp.)

Example 1

5 (1) Synthesis of transition metal complex

(1-1) Synthesis of 1-bromo-3-tert-butyl-5-methyl-2-phenol

In a 4-necked 500-ml flask fitted with a stirrer, under nitrogen atmosphere, 20.1 g (123 mmol) of
10 2-tert-butyl-5-methyl-2-phenol was dissolved in 150 ml of toluene, and successingly 25.9 ml (18.0 g, 246 mmol) of tert-butylamine was added thereto. The resulting solution was cooled to -70°C , and 10.5 ml (32.6 g, 204 mmol) of bromine was slowly added to the solution by
15 means of a syringe. The resulting solution was kept at -70°C and stirred for 2 hours. Thereafter the solution was brought up to room temperature and washed three times, 100 ml of 10% dilute hydrochloric acid being added for each time of washing. The organic layer obtained
20 after washing was dried with anhydrous sodium sulfate. Then, the solvent was removed from the solution by using an evaporator to leave an orange oil. The orange oil was purified by applying the oil to a silica gel column (Wako Gel C100), followed by developing with hexane, and
25 removing the solvent from the obtained fraction. Thus, 18.4 g (75.7 mmol) of a purified colorless oil was obtained. The ^1H -NMR (CD_2Cl_2 solvent) data of the purified oil are shown below.

δ 1.32 (s, 9H), 2.19 (s, 3H), 6.98 (s, 1H),
7.11 (s, 1H)

From the ^1H -NMR data, the colorless oil was identified as 1-bromo-3-tert-butyl-5-methyl-2-phenol.

5 The yield was 62%.

(1-2) Synthesis of 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene

In a 100-ml 4-necked flask fitted with a stirrer, under nitrogen atmosphere, 13.9 g (57.2 mmol) of
10 1-bromo-3-tert-butyl-5-methyl-2-phenol synthesized in (1-1) above was dissolved in 40 ml of acetonitrile, and successingly 3.8 g (67.9 mmol) of potassium hydroxide was added thereto. To the resulting mixture was further added slowly 17.8 ml (40.6 g, 286 mmol) of methyl iodide
15 by means of a syringe, and the reaction mixture was stirred for 12 hours. Thereafter, the solvent was removed with an evaporator to leave a residue. Then 40 ml of hexane was added to the residue to extract hexane solubles. The extraction was repeated three times. The
20 solvent was removed from the extracts to obtain 13.8 g (53.7 mmol) of a pale yellow oil. The ^1H -NMR (CD_2Cl_2 solvent) data of the oil are shown below.

δ 1.31 (s, 9H), 2.20 (s, 3H), 3.81 (s, 3H),
7.02 (s, 1H), 7.18 (s, 1H)

25 From the ^1H -NMR data, the pale yellow oil obtained was identified as 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene. The yield was 94%.

(1-3) Synthesis of 2-cyclopentadienyl-2-(3-tert-

butyl-2-methoxy-5-methylphenyl)propane

In a 100-ml 4-necked flask fitted with a stirrer, under nitrogen atmosphere, 4.61 g(17.9 mmol) of 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene
5 synthesized in (1-2) above was dissolved in 10 ml of dry diethyl ether and the solution was cooled to -70°C . To the solution was slowly added 18.0 mol of n-BuLi (11.1 ml of a n-BuLi solution in hexane of a concentration of 1.62 mol/l) and stirred at -70°C for 2 hours. To the result-
10 ing reaction liquid was further added a solution obtained by dissolving 1.91 g (18.0 mmol) of 6,6-dimethylfulvene in 10 ml of diethyl ether, and then the resulting mixture was slowly brought up to room temperature. Succeedingly, 25 ml of 5 wt% dilute hydrochloric acid was added to the
15 mixture. Then 30 ml of hexane was added to the resulting reaction liquid to extract hexane solubles. The extraction was repeated 3 times. The extract was dried with anhydrous sodium sulfate and the solvent was removed with an evaporator to leave a yellow oil. The yellow oil was
20 purified by applying the oil to a silica gel column (Wako Gel C-100), followed by developing with hexane, and removing the solvent from the fraction obtained. Thus, 3.0 g of purified pale yellow oil was obtained. The $^1\text{H-NMR}$ (CD_2Cl_2 solvent) data of the oil are shown below.
25 δ 1.48 (s, 9H), 1.71 (s, 6H), 2.26 (s, 3H), 3.26 (s, 3H), 6.07-6.62 (m, 5H), 7.22-7.28 (m, 2H)

From the $^1\text{H-NMR}$ data, the yellow oil obtained

was identified as 2-cyclopentadienyl-2-(3-tert-butyl-2-methoxy-5-methylphenyl)propane. The yield was 60%.

(1-4): Synthesis of white solid estimated to be 2-(cyclopentadienyl)(lithium)-2-(3-tert-butyl-2-methoxy-5-methylphenyl)propane

In a 50-ml 4-necked flask fitted with a stirrer, under nitrogen atmosphere, 0.28 g (0.99 mmol) of 2-cyclopentadienyl-2-(3-tert-butyl-2-methoxy-5-methylphenyl)propane synthesized in (1-3) above was dissolved in 20 ml of hexane, and the solution was cooled to -70°C. To the solution was slowly added 1.09 mol of nBuLi (0.67 ml of a solution of nBuLi in hexane of a concentration of 1.62 mol/l). Thereafter, the resulting mixture was slowly brought up to room temperature, whereby a white solid precipitated out. The solid was collected by filtration, washed 3 times using 10 ml of hexane in each washing, and dried under reduced pressure to obtain 0.28 g of a white solid estimated to be 2-(cyclopentadienyl)-(lithium)-2-(3-tert-butyl-2-methoxy-5-methylphenyl)-propane, which is white solid. The yield was 97%.

(1-5) Synthesis of isopropylidene(cyclopentadienyl)-(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride

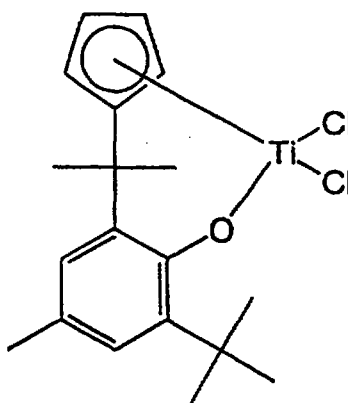
In a 50 ml 4-necked flask fitted with a stirrer, under nitrogen atmosphere, 0.20 g (2.3 mmol) of the white solid estimated to be 2-(cyclopentadienyl)-(lithium)-2-(3-tert-butyl-2-methoxy-5-methylphenyl)-propane synthesized in (1-4) above was added to 10 ml of hexane, and the mixture was cooled to -70°C. To the

mixture was added slowly 0.077 ml (0.13 g, 0.70 mmol) of TiCl_4 with a syringe. The resulting solution was slowly brought up to room temperature. The solution turned liver brown and a dark orange solid deposited.

5 The resulting reaction mixture was filtered to separate into a solid and a solution. The solid was treated 3 times with 10 ml, per one time, of hexane to extract components soluble in hexane, a saturated hydrocarbon solvent. These hexane solutions were
10 combined, concentrated to a volume of 10 ml, and the concentrated liquid was cooled at -20°C and allowed to stand for 12 hours to deposit a yellow solid. The solid was collected by filtration and dried under reduced pressure. The ^1H -NMR (CD_2Cl_2 solvent) data of the yellow
15 solid are shown below.

δ 1.33 (s, 9H), 1.51 (s, 6H), 2.30 (s, 3H),
6.06 (t, 2H), 6.92 (t, 2H), 6.99 (s, 1H), 7.19
(s, 1H)

From the ^1H -NMR data, the yellow solid obtained
20 above was identified as isopropylidene(cyclopentadienyl)-(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride of the following structural formula. The yield was 34%.



(2) Polymerization

An autoclave with an inner volume of 3 l fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then 1 l of toluene as the solvent and 20 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 0.5 mmol of triisobutyl-aluminum, then 2.0 μ mol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in (1) above, and succeedingly 6.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 22.8, $[\eta]$ of 1.13, molecular weight (Mw) of 64,000, molecular weight

distribution (Mw/Mn) of 2.0 and melting point of 96.1°C was produced at a rate of 4.0×10^7 g per mole of titanium per hour.

Example 2

5 (1) Polymerization

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then, 195 ml of toluene as the solvent and 5 ml of hexene-1 as
10 the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of tri-
15 isobutylaluminum, then 1.0 μ mol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1, and succeedingly 3.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymeriza-
20 tion was carried out for 30 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 32.8, $[\eta]$ of 0.98, molecular weight (Mw) of 95,000, molecular weight
25 distribution (Mw/Mn) of 2.8 and melting point of 110.5°C was produced at a rate of 4.0×10^7 g per mole of titanium per hour.

Example 3

(1) Polymerization

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then, 195 ml of toluene as the solvent and 5 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of triethylaluminum, then 1.0 μ mol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1 and succeedingly 3.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 60 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 18.0, $[\eta]$ of 1.20 and melting point of 120.8°C was produced at a rate of 9.9×10^5 g per mol of titanium per hour.

Example 4

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then, 170 ml of toluene as the solvent and 30 ml of hexene-1 as the α -olefin were placed in the autoclave, and the

reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 5.0 mmol, in
5 terms of aluminum atom contained, of methylaluminoxane (mfd. by Tosoh-Akzo K.K., MMAO-3A) and then 1.0 μmol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1 were fed into the reactor. Polymerization was carried out for
10 60 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 28.6 and melting point of 82.3°C was produced at a rate of 7.7×10^5 g per mole of titanium per hour.

15 Example 5

(1) Polymerization

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then,
20 170 ml of toluene as the solvent and 30 ml of hexene-1 as the α-olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside
25 of the system had become stable, 0.5 mmol, in terms of aluminum atom contained, of methylaluminoxane (mfd. by Tosoh-Akzo K.K., MMAO-3A) was fed into the reactor, and then 1.0 μmol of isopropylidene(cyclopentadienyl)(3-tert-

butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1 and 0.5 mmol, in terms of aluminum atom contained, of methylaluminoxane which had been preliminarily contacted with each other were fed into the autoclave. Polymerization was carried out for 60 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 32.4, $[\eta]$ of 1.99 and melting point of 82.0°C was produced at a rate of 5.5×10^5 g per mole of titanium per hour.

Example 6

(1) Synthesis of transition metal complex

(1-1) Synthesis of 1-bromo-2-methoxybenzene

In a 50-ml 4-necked flask fitted with a stirrer, under nitrogen atmosphere, 1.03 g (5.92 mmol) of 1-bromo-2-phenol was dissolved in 20 ml of acetonitrile, and successingly 0.51 g (9.07 mmol) of potassium hydroxide was added thereto. Further, 1.90 ml (4.33 g, 30.5 mmol) of methyl iodide was slowly added thereto with a syringe, and the resulting reaction mixture was stirred for 12 hours. Thereafter, the solvent was removed with an evaporator, and 20 ml of hexane was added to the resulting residue to extract hexane solubles. The extraction was repeated 3 times. The solvent was removed from the extracts obtained to obtain 0.97 g of a pale yellow oil. The yield was 89%. The $^1\text{H-NMR}$ (CD_2Cl_2 solvent) data of the oil are shown below.

δ 3.89 (s, 3H), 6.7-7.7 (m, 4H)

From the ^1H -NMR data, the pale yellow oil obtained was identified as 1-bromo-2-methoxybenzene.

(1-2) Synthesis of 2-(cyclopentadienyl)(lithium)-2-(2-methoxyphenyl)propane

5 In a 100-ml 4-necked flask fitted with a stirrer, under nitrogen atmosphere, 4.50 g (24.1 mmol) of 1-bromo-2-methoxybenzene synthesized in (1-1) above was dissolved in 20 ml of dry diethyl ether, and the solution was cooled to -70°C . Then 24.0 mol of nBuLi (14.8 ml of
10 nBuLi hexane solution of a concentration of 1.62 mol/l) was slowly added thereto, and the resulting liquid was stirred at -70°C for 2 hours. To the reaction liquid was further added 2.64 g (24.9 mmol) of 6,6-dimethylfulvene dissolved in 10 ml of diethyl ether, and thereafter the
15 resulting mixture was slowly brought up to room temperature, whereby a white solid deposited, which was then collected by filtration. The white solid obtained was washed 3 times by using 10 ml of hexane per one time, and then dried under reduced pressure to obtain 4.0 g of
20 white powder.

A small portion of the white powder was hydrolyzed with dilute hydrochloric acid. The ^1H -NMR (C_6D_6 solvent) data of the organic substance thus obtained are as follows.

25 δ 1.66 (s, 3H), 1.75 (s, 3H), 3.26 (s, 3H),
5.9-7.5 (m, 9H)

From the ^1H -NMR data, the organic substance obtained by hydrolysis was identified, as 2-cyclopenta-

dienyl-2-(1-methoxyphenyl)propane, and consequently the white powder was estimated to be 2-(cyclopentadienyl)-(lithium)-2-(2-methoxyphenyl)propane. The yield was 75%.

(1-3) Synthesis of isopropylidene(cyclopentadienyl)-
5 (2-phenoxy)titanium dichloride

In a 50-ml 4-necked flask fitted with a stirrer, under nitrogen atmosphere, 0.20 g (0.92 mmol) of the white powder estimated to be 2-(cyclopentadienyl)-(lithium)-2-(2-methoxyphenyl)propane synthesized in (1-2)
10 above was added to 15 ml of hexane and the mixture was cooled to -70°C. Thereto was slowly added with a syringe a solution of 0.10 ml (0.17 g, 0.91 mmol) of TiCl_4 in 5 ml of hexane. The resulting solution was slowly brought up to room temperature. The solution turned light brown,
15 and a brown solid deposited. The reaction mixture was separated by filtration into a solution and a solid. From the solid were extracted 3 times, with 10 ml of hexane per time, components soluble in hexane, a saturated hydrocarbon solvent. These hexane solutions
20 were combined, concentrated to a volume of 10 ml, and the concentrated liquid was cooled at -20°C and allowed to stand for 12 hours, whereby a yellow solid deposited. The solid was collected by filtration and dried under reduced pressure to obtain 0.10 g of a yellow solid. The
25 ^1H -NMR (CD_2Cl_2 solvent) data of the yellow solid are shown below.

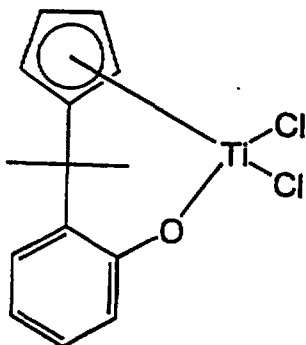
8 1.62 (s, 6H), 6.17 (t, 2H), 6.80 (d, 1H),
7.00 (t, 2H), 7.20 (t, 1H), 7.21 (t, 1H), 7.58

(d, 1H)

Additionally, the ^{13}C -NMR (CD_2Cl_2 solvent) data are shown below.

5 δ 29.8, 37.3, 114.9, 119.8, 122.4, 125.6,
 126.7, 127.8, 136.5, 143.8, 162.7

From the ^1H -NMR data and ^{13}C -NMR data, the yellow solid obtained was identified as isopropylidene(cyclopentadienyl)(2-phenoxy)titanium dichloride of the following structural formula:



10 (2) Polymerization

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then 195 ml of toluene as the solvent and 5 ml of hexene-1 as
15 the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of
20 triisobutylaluminum, then 2.0 μmol of isopropylidene-

(cyclopentadienyl)(2-phenoxy)titanium dichloride synthesized in (1) above and succeedingly 6.0 μmol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization
5 was carried out for 60 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 28.1 and $[\eta]$ of 1.08 was produced at a rate of 1.8×10^6 g per mole of titanium
10 per hour.

Example 7

(1) Polymerization

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure
15 and the inner atmosphere was replaced with argon. Then 195 ml of toluene as the solvent and 5 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the
20 ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.15 mmol of triisobutylaluminum was fed into the reactor, and succeedingly 2.0 μmol of isopropylidene(cyclopentadienyl)(2-phenoxy)titanium dichloride synthesized in
25 Example 6(1) and 0.1 mmol of triisobutylaluminum which had been preliminarily contacted with each other were fed into the autoclave. Polymerization was carried out for 60 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 29.0 was produced at a rate of 3.3×10^6 g per mole of titanium per hour.

Example 8

5 (1) Polymerization

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then 170 ml of toluene as the solvent and 30 ml of hexene-1 as
10 the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 30 kg/cm². After the inside of the system had become stable, 2.0 mmol, in
15 terms of the aluminum atom contained, of methylaluminoxane (mfd. by Tosoh-Akzo K.K., MMAO-3A) and succeedingly 2.0 μ mol of isopropylidene(cyclopentadienyl)(2-phenoxy)titanium dichloride synthesized in
Example 6(1) were fed into the reactor. Polymerization
20 was carried out for 20 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 7.0 and melting point of 123.7°C was produced at a rate of 2.3×10^5 g per mole
25 of titanium per hour.

Comparative Example 1

(1) Polymerization

An autoclave with an inner volume of 400 ml

fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then 170 ml of toluene as the solvent and 30 ml of hexene-1 as the α -olefin were placed in the autoclave, and the
5 reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of triethylaluminum, then 5.0 μ mol of 2,2'-thiobis(6-tert-
10 butyl-4-methylphenoxy)titanium dichloride synthesized according to the method described in WO87/02370 and JP-A-5-230133, and succeedingly 15.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out
15 for 60 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 26.1, $[\eta_1]$ of 3.78 and melting point of 116.8°C was produced at a rate of 2.9×10^4 g per mole of titanium.

20 Example 9

Synthesis of 1,5-dimethyl-3-(1-cyclopentadienyl-1-methyl-ethyl)-2-methoxybenzene

To a solution (100 ml) of 2-bromo-4,6-dimethylanisole (10.32 g) in anhydrous ether was added
25 dropwise at -78°C a 1.69 M hexane solution (56.8 ml) of n-butyllithium, the resulting mixture was brought up to room temperature over 2 hours, and the yellow solution

thus obtained was cooled to -78°C . To the solution was added dropwise 5-isopropylidene-cyclopenta-1,3-diene (5.87 ml), the resulting mixture was brought up to room temperature over 12 hours and further stirred at room
5 temperature for 1 hour.

The reaction mixture was mixed with an aqueous ammonium chloride solution and then separated into an aqueous layer and an organic layer. Toluene solubles were extracted from the aqueous layer by using toluene,
10 and the toluene solution obtained was combined with the above-mentioned organic layer. The resulting organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

15 The organic solution thus treated was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography to obtain yellow oily 1,5-dimethyl-3-(1-cyclopentadienyl-1-methyl-ethyl)-2-methoxybenzene as a mixture of isomers (2.56 g,
20 yield 22%).

^1H NMR (CDCl_3) δ 1.58 (s, 6H), 2.22 (s, 3H),
2.28 (s, 3H), 2.81-2.97 (2H, 2.81:m;2.97:m),
3.26-3.29 (3H, 3.26:m;3.29:m), 6.08-6.48
(m, 3H), 6.86 (d, 1H, $J=1\text{Hz}$), 6.87 (d, 1H,
25 $J=1\text{Hz}$)
mass spectra (EI, m/e) 242, 227, 211, 196, 177,
162, 149, 136, 119, 105, 91, 81, 65

Example 10

Synthesis of isopropylidene(cyclopentadienyl)-
(3,5-dimethyl-2-phenoxy)titanium dichloride

To a hexane solution (10 ml) of 1,5-dimethyl-3-
5 (1-cyclopentadienyl-1-methyl-ethyl)-2-methoxybenzene
(0.727 g) was added dropwise at 0°C a 1.69 M hexane
solution (1.95 ml) of n-butyllithium, the resulting
mixture was brought up to room temperature and stirred
for 12 hours. To the mixture obtained was added at
10 -50°C, while being shielded from light, titanium tetra-
chloride (0.33 ml), the mixture was brought up to room
temperature in 2 hours and further stirred at room
temperature for 12 hours. The slurry thus obtained was
filtered and the filtrate was concentrated to obtain a
15 raw product. The raw product was recrystallized from
hexane to obtain orange crystals of isopropylidene-
(cyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium
dichloride (0.15 g, yield 14%).

¹H NMR (C₆D₆) δ 0.99 (s, 6H), 2.18 (s, 3H), 2.29
20 (s, 3H), 5.46 (t, 2H, J=3Hz), 6.30 (t, 2H,
3Hz), 6.65 (d, 1H, J=2Hz), 6.95 (d, 1H, J=2Hz)

Example 11

Synthesis of 1-phenyl-3-(1-cyclopentadienyl-1-
methyl-ethyl)-2-methoxybenzene

25 To an anhydrous ether solution (100 ml) of 2-
bromo-6-phenylanisole (14.00 g) was added dropwise at
-78°C a 1.69 M hexane solution (63.9 ml) of n-butyl-
lithium, the resulting mixture was brought up to room

temperature over 2 hours, and a yellow solution thus obtained was cooled to -78°C . To the solution was added dropwise 5-isopropylidene-cyclopenta-1,3-diene (6.51 ml), the resulting mixture was brought up to room temperature
5 over 12 hours and further stirred at room temperature for 1 hour.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was
10 treated with toluene to extract toluene solubles therefrom, and the toluene solution obtained was combined with the above-mentioned organic layer to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with
15 anhydrous sodium sulfate.

The organic solution was then stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography to obtain yellow oily 1-phenyl-3-(1-cyclopentadienyl-1-methyl-
20 ethyl)-2-methoxybenzene as a mixture of isomers (6.60 g, yield 43%).

^1H NMR (CDCl_3) δ 1.66 (s, 6H), 2.82-2.96 (m, 5H), 6.07-6.45 (m, 3H), 7.05-7.60 (m, 8H)

Mass spectra (EI, m/e) 290, 275, 260, 210, 183,
25 165, 152, 115, 91, 77

Example 12

Synthesis of isopropylidene(cyclopentadienyl)-
(3-phenyl-2-phenoxy)titanium dichloride

To a hexane solution (20 ml) of 1-phenyl-3-(1-cyclopentadienyl-1-methyl-ethyl)-2-methoxybenzene (1.45 g) was added dropwise at 0°C a 1.69 M hexane solution (3.08 ml) of n-butyllithium, the resulting mixture was brought up to room temperature and stirred for 12 hours. To the mixture obtained was added at -50°C, while being shielded from light, titanium tetrachloride (0.55 ml), the resulting mixture was brought up to room temperature and stirred for 12 hours. The slurry thus obtained was filtered and the filtrate was concentrated to obtain a raw product. The raw product was recrystallized from hexane to obtain orange crystals of isopropylidene-(cyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride (0.46 g, yield 23%).

¹H NMR (C₆D₆) δ 1.20 (s, 6H), 5.39 (t, 2H, J=3Hz), 6.26 (t, 2H, J=3Hz), 7.00-7.20 (m, 5H), 7.26 (dd, 1H, J=2 and 8Hz), 7.40 (t, 1H, J=8Hz), 7.75 (dd, 1H, 2 and 8Hz)

Example 13

Synthesis of 1-tert-butyl-3-[1-(3-tert-butyl-cyclopentadienyl)-1-methyl-ethyl]-2-methoxy-5-methylbenzene

To an anhydrous ether solution (30 ml) of 2-bromo-6-tert-butyl-4-methylanisole (3.86 g) was added dropwise at -78°C a 1.69 M hexane solution (17.8 ml) of n-butyllithium, and then the resulting mixture was brought up to room temperature over 2 hours to obtain a yellow solution. The yellow solution was cooled to

-78°C, then an anhydrous ether solution (10 ml) of 2-tert-butyl-5-isopropylidene-cyclopenta-1,3-diene (2.43 g) was added dropwise to the solution, the resulting mixture was brought up to room temperature over 12 hours, and
5 further stirred for 1 hour at room temperature.

The reaction mixture thus obtained was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with toluene to extract toluene
10 solubles therefrom, and the toluene solution thus obtained was combined with the above-mentioned organic layer to form an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

15 The organic solution was then stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography to obtain yellow oily 1-tert-butyl-3-[1-(3-tert-butyl-cyclopenta-
dienyl)-1-methyl-ethyl]-2-methoxy-5-methylbenzene as a
20 mixture of isomers (1.80 g, yield 35%).

^1H NMR (CDCl_3) δ 1.06-1.19 (m, 15H), 1.37-1.38 (9H; 1.37:s; 1.38:s), 2.31 (s, 3H), 2.76-2.90 (2H; 2.76:m; 2.90:m), 3.24-3.26 (3H; 3.24:s; 3.26:s), 5.72-6.26 (m, 2H), 7.06 (d,
25 1H, $J=1\text{Hz}$), 7.10 (d, 1H, $J=1\text{Hz}$)

Example 14

Synthesis of isopropylidene(3-tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium

dichloride

To a hexane solution (3 ml) of 1-tert-butyl-3-[1-(3-tert-butylcyclopentadienyl)-1-methyl-ethyl]-2-methoxy-5-methylbenzene (0.202 g) was added dropwise at
5 0°C a 1.63 M hexane solution (0.55 ml) of n-butyllithium, the resulting mixture was brought up to room temperature and stirred for 12 hours. To the mixture obtained was added at -50°C, while being shielded from light, titanium tetrachloride (0.066 ml), the resulting mixture was
10 brought up to room temperature over 2 hours and then stirred at room temperature for 12 hours. The slurry thus obtained was filtered and the filtrate was concentrated to obtain a raw product. This was recrystallized from hexane to obtain orange crystals of
15 isopropylidene(3-tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride (0.040 g, yield 15%).

¹H NMR (C₆D₆) δ 1.27 (s, 3H), 1.35 (s, 9H), 1.40 (s, 3H), 1.64 (s, 9H), 2.27 (s, 3H), 5.01 (t, 1H, J=3Hz), 6.41 (t, 1H, J=3Hz), 6.52 (t, 1H, J=3Hz), 7.11 (d, 1H, J=2Hz), 7.14 (d, 1H, J=2Hz)
20

Example 15

Synthesis of 1-tert-butyl-3-[1-(3-methylcyclopentadienyl)-1-methyl-ethyl]-2-methoxy-5-methylbenzene
25

Under nitrogen atmosphere, a 1.69 M hexane solution (100 ml) of n-butyllithium was added dropwise at -78°C to an anhydrous ether solution (300 ml) of 2-bromo-

6-tert-butyl-4-methylanisole (20.97 g), the resulting mixture was brought up to room temperature over 1 hour, and a yellow solution thus obtained was cooled to -78°C. To the solution was added dropwise an anhydrous ether
5 solution (20 ml) of 2-methyl-5-isopropylidene-cyclopenta-1,3-diene (9.78 g), the resulting mixture was brought up to room temperature over 12 hours and then stirred at room temperature for 1 hour.

The reaction mixture thus obtained was mixed
10 with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with toluene to extract toluene solubles therefrom, and the toluene solution thus obtained and the above-mentioned organic layer was
15 combined to obtain an organic solution. The organic layer was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The organic solution was then stripped of the solvent under reduced pressure and the residue was
20 treated by silica gel column chromatography to obtain yellow oily 1-tert-butyl-3-[1-(3-methylcyclopentadienyl)-1-methyl-ethyl]-2-methoxy-5-methylbenzene as a mixture of isomers (3.27 g, yield 13%).

¹H NMR (CDCl₃) δ 1.37-1.39 (9H;1.37:s;1.38:s;
25 1.39:s), 1.59-1.61 (6H;1.56:s;1.60:s;1.61:s),
1.98 (m, 3H), 2.30 (s, 3H), 2.70-2.84 (m, 2H),
3.30-3.35 (3H;3.30:s;3.31:s;3.35:s), 5.75-6.19
(m, 2H), 7.02-7.08 (m, 2H)

Mass spectra (EI, m/e) 298, 283, 267, 241, 227,
219, 189, 179, 161, 147, 121, 105, 91, 57

Example 16

Synthesis of isopropylidene(3-methylcyclo-
5 pentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
dichloride

To a hexane solution (10 ml) of 1-tert-butyl-3-
[1-(3-methylcyclopentadienyl)-1-methyl-ethyl]-2-methoxy-
5-methylbenzene (0.298 g) was added dropwise at 0°C a
10 1.56 M hexane solution (0.96 ml) of n-butyllithium, the
resulting mixture was brought up to room temperature and
stirred for 12 hours. To the resulting mixture was
added, while being shielded from light, at -50°C titanium
tetrachloride (0.11 ml), then the mixture was brought up
15 to room temperature over 3 hours and further stirred at
room temperature for 12 hours. The slurry thus obtained
was filtered and the filtrate was concentrated to obtain
an orange oil of isopropylidene(3-methylcyclopenta-
dienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
20 dichloride (0.10 g, yield 25%).

^1H NMR (C_6D_6) δ 1.38 (s, 3H), 1.41 (s, 3H), 1.68
(s, 9H), 2.24 (s, 3H), 2.27 (s, 3H), 5.34 (t,
1H, J=3Hz), 5.72 (t, 1H, J=3Hz), 6.23 (t, 1H,
J=3Hz), 7.13 (d, 1H, J=1Hz), 7.14 (d, 1H,
25 J=1Hz)

Example 17

Synthesis of 1-tert-butyldimethylsilyl-3-(1-
cyclopentadienyl-1-methyl-ethyl)-2-methoxy-5-

methylbenzene

Under nitrogen atmosphere, a 1.60 M hexane solution (24.0 ml) of n-butyllithium was added dropwise at -78°C to an anhydrous ether solution (80 ml) of 2-bromo-6-tert-butyldimethylsilyl-4-methylanisole (6.00 g), the resulting mixture was brought up to room temperature over 2 hours, and the resulting yellow solution was cooled to -78°C. To the cooled solution was added dropwise an anhydrous ether solution (10 ml) of 5-isopropylidene-cyclopenta-1,3-diene (2.43 g), the resulting mixture was brought up to room temperature over 12 hours and then stirred at room temperature for 1 hour.

The reaction mixture obtained was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with toluene to extract toluene solubles therefrom, and the toluene solution thus obtained was combined with the above-mentioned organic layer to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure and the residue was treated by silica gel column chromatography to obtain yellow oily 1-tert-butyldimethylsilyl-3-(1-cyclopentadienyl-1-methyl-ethyl)-2-methoxy-5-methylbenzene as a mixture of isomers (2.80 g, yield 43%).

^1H NMR (CDCl_3) δ 0.30 (s, 6H), 0.79 (s, 9H),

1.61 (s, 3H), 1.62 (s, 3H), 2.31 (s, 3H), 2.80 (d, 1H, J=2Hz), 2.95 (d, 1H, J=2Hz), 3.19 (s, 3H), 6.10-6.40 (m, 3H), 7.09 (d, 1H, J=2Hz), 7.19 (d, 1H, J=2Hz)

5 Example 18

Synthesis of isopropylidene(cyclopentadienyl)-(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)titanium dichloride

To a hexane solution (30 ml) of 1-tert-butyl-
10 dimethylsilyl-3-(1-cyclopentadienyl-1-methyl-ethyl)-2-methoxy-5-methylbenzene (1.25 g) was added dropwise at 0°C a 1.69 M hexane solution (3.25 ml) of n-butyllithium, the resulting mixture was brought up to room temperature and stirred for 12 hours. To the mixture obtained was
15 added, while being shielded from light, at -50°C titanium tetrachloride (0.41 ml), the resulting mixture was brought up to room temperature over 3 hours and then stirred at room temperature for 12 hours. The resulting slurry was filtered and the filtrate was concentrated to
20 obtain a raw product. This was recrystallized from hexane to obtain orange crystals of isopropylidene-(cyclopentadienyl)(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)titanium dichloride (0.40 g, yield 26%).

¹H NMR (C₆D₆) δ 0.65 (s, 6H), 1.10 (s, 9H), 1.23
25 (s, 6H), 2.25 (s, 3H), 5.56 (t, 2H, J=3Hz), 6.31 (t, 2H, J=3Hz), 7.20 (d, 1H, J=2Hz), 7.28 (d, 1H, J=2Hz)

Example 20

Synthesis of isopropylidene(cyclopentadienyl)-
(3-t-butyl-5-methyl-2-phenoxy)titanium dichloride

To a hexane solution (25 ml) of a white solid
5 (0.51 g, 1.7 mmol) obtained in the same manner as in (1-
4) of Example 1 was added at -70°C titanium tetrachloride
(0.18 ml, 1.6 mmol).

Thereafter, the resulting mixture was brought
up to room temperature over 3 hours and then stirred at
10 room temperature for 12 hours. The solution turned light
brown, and a dark orange solid deposited.

The reaction mixture was filtered to collect
the solid, and hexane solubles were extracted from the
solid by using hexane (120 ml). The hexane solution
15 obtained were combined, then concentrated to a volume of
30 ml, cooled to -20°C, and allowed to stand for 12
hours. The yellow crystals thus deposited were collected
by filtration and dried under reduced pressure to obtain
yellow needle-like crystals of isopropylidene(cyclopenta-
20 dienyl)(3-t-butyl-5-methyl-2-phenoxy)titanium dichloride
(0.40 g, yield 64%).

^1H NMR (CD_2Cl_2) δ 1.33 (s, 9H), 1.51 (s, 6H),
2.30 (s, 3H), 6.06 (t, $J=2.7\text{Hz}$, 2H), 6.92 (t,
 $J=2.7\text{Hz}$, 2H), 6.99 (s, 1H), 7.19 (s, 1H)

25 Mass spectra (CI, m/e) 386

Example 21

Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)chlorodimethylsilane

Into a hexane solution (25 ml) of 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (3.40 g) was added dropwise at -10°C a 1.66 M hexane solution (7.46 ml) of n-butyllithium, and the resulting mixture was stirred at -10°C for 30 minutes.

Into the mixture obtained above was added dropwise dichlorodimethylsilane (1.75 g) over one minute, the resulting mixture was brought up to room temperature, then stirred for 2 hours, and thereafter the solvent and the excess of dichlorodimethylsilane were distilled off. To the residue obtained was added hexane (10 ml), the mixture was filtered, and the filtrate was stripped of the solvent under reduced pressure to obtain (2-allyloxy-3-tert-butyl-5-methylphenyl)chlorodimethylsilane as a pale yellow oil (purity 80%) (3.50 g, yield 78%).

Mass spectra (EI, m/e) 296, 281, 253, 245, 220, 205, 189, 161, 145, 128, 115, 93, 75, 41

Example 22

Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

Into a tetrahydrofuran solution (50 ml) of tetramethylcyclopentadiene (1.55 g) was added dropwise at -10°C a 1.66 M hexane solution (7.87 ml) of n-butyllithium, the resulting mixture was brought up to room

temperature, then stirred for 3 hours and then cooled to -10°C.

Into the mixture obtained above was added dropwise a tetrahydrofuran solution (25 ml), cooled to
5 -10°C, of (2-allyloxy-3-tert-butyl-5-methylphenyl)-chlorodimethylsilane (purity 80%, 3.50 g) over one minute. The resulting mixture was brought up to room temperature and then stirred for 20 hours.

The reaction mixture was mixed with water (50
10 ml) and separated into an aqueous layer and an organic layer. The organic layer was washed with saturated aqueous ammonium chloride solution (50 ml) and then the solvent was distilled off to obtain (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane as a pale yellow oil (purity 58%)
15 (4.52 g, yield 72%).

¹H NMR (CDCl₃) δ 0.13 (s, 6H), 1.42 (s, 9H),
1.69 (s, 6H), 1.79 (s, 6H), 2.28 (s, 3H), 3.42
(s, 1H), 4.40 (dt, 2H, J=2, 2Hz), 5.28 (dq, 1H,
20 J=2, 11Hz), 5.54 (dq, 1H, J=2, 17Hz), 5.99
(ddt, 1H, J=2, 11, 17Hz), 7.03 (d, 1H, J=2Hz),
7.17 (d, 1H, J=2Hz)

Mass spectra (EI, m/e) 382, 341, 261, 162, 121,
41

25 Example 23

Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

To a tetrahydrofuran solution (500 ml) of 2-allyloxy-1-bromo-3-tetra-butyl-5-methylbenzene (33.98 g) was added dropwise at -78°C a 1.56 M hexane solution (76.92 ml) of n-butyllithium and the resulting mixture
5 was stirred for one hour.

The mixture obtained above was added dropwise, while the temperature being maintained at -20°C or below, over 30 minutes into a hexane solution (200 ml) at -78°C of dichlorodimethylsilane (100.0 g). Thereafter the
10 resulting mixture was brought up to room temperature over 2 hours, then stirred for one hour, and the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.

The mixture obtained was dissolved in tetra-
15 hydrofuran (200 ml). Into the solution was added dropwise at -78°C over 30 minutes a solution of tetramethylcyclopentadienyllithium prepared from a tetrahydrofuran solution (400 ml) of tetramethylcyclopentadiene (14.67 g) and a 1.56 M hexane solution (76.92 ml) of n-butyl-
20 lithium. The resulting mixture was brought up to room temperature over 2 hours and then stirred for 12 hours.

Then the reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer
25 was treated with hexane to extract hexane solubles therefrom, and the hexane solution obtained and the above-mentioned organic layer were combined to form an organic solution. The organic solution was washed with

saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent and the residue was treated by silica gel column chromatography (solvent: hexane) to obtain colorless oily (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (24.4 g, yield 53%).

Example 24

Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

Into a mixture of magnesium (0.80 g), iodine (0.05 g) and tetrahydrofuran (200 ml) was added at room temperature 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (0.10 g) and the resulting mixture was stirred at 50°C for one hour.

Into the mixture obtained above was added dropwise at 60°C over 6 hours a toluene solution (20 ml) containing 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (8.10 g) and dichlorodimethylsilane (10.9 g), and the resulting mixture was stirred for one hour.

The solvent and the excess of dichlorodimethylsilane were distilled off from the mixture obtained above under reduced pressure, then tetrahydrofuran (100 ml) was added to the residue, and cooled to -78°C. Into the resulting mixture was added at -78°C a tetrahydrofuran suspension (100 ml) of tetramethylcyclopentadienyllithium (3.71 g) over 5 minutes, the resulting mixture was

brought up to room temperature over 2 hours and then stirred for 15 hours.

The reaction mixture was mixed with water (100 ml) and separated into an aqueous layer and an organic
5 layer. The organic layer was stripped of the solvent to obtain (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl-(tetramethylcyclopentadienyl)silane as a pale yellow oil (purity 45%) (9.70 g, yield 39%).

Example 25

10 Synthesis of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride

To a chlorobenzene solution (10 ml) containing (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-
15 tetramethylcyclopentadienyl)silane (0.96 g) and triethylamine (0.70 ml) was added dropwise at -78°C a 1.56 M hexane solution (1.61 ml) of n-butyllithium, then the resulting mixture was brought up to room temperature over 2 hours and further stirred for 6 hours.

20 The mixture thus obtained was cooled to -78°C and a chlorobenzene solution (3 ml) of titanium tetrachloride (0.276 ml) was added thereto. The resulting mixture was brought up to room temperature over 3 hours while being shielded from light, then stirred for one
25 hour, thereafter brought up to 120°C over one hour and stirred for 35 hours.

The reaction mixture was filtered, and the filtrate was stripped of the solvent to obtain a reddish

brown solid. The solid was recrystallized from a hexane-toluene solvent mixture to obtain red needle-like crystals of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride (0.58 g, yield 50%).

Example 26

Synthesis of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride

10 Into a toluene solution (8 ml) of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (0.28 g) was added dropwise at -78°C a 1.56 M hexane solution (0.70 ml) of n-butyl-lithium, the resulting mixture was brought up to room
15 temperature over 2 hours and then stirred for 12 hours.

 The mixture obtained was cooled to -78°C, and a chlorobenzene solution (2 ml) of titanium tetrachloride (0.080 ml) was added thereto. The resulting mixture was, while being shielded from light, brought up to room
20 temperature over 3 hours, then stirred for one hour, further brought up to 90°C over one hour and stirred for 10 hours.

 The reaction mixture was filtered and the filtrate was stripped of the solvent to obtain a reddish
25 brown solid. The solid was recrystallized from a hexane-toluene solvent mixture to obtain red needle-like crystals of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride (0.14

g, yield 42%).

Example 27

Synthesis of (cyclopentadienyl)(2-methoxy-3,5-dimethylphenyl)dimethylsilane

5 To a tetrahydrofuran solution (100 ml) of 2-bromo-4,6-dimethylanisole (6.45 g) was added dropwise at -78°C a 1.60 M hexane solution (37.5 ml) of n-butyl-lithium, and thereafter the resulting mixture was brought up to room temperature over 2 hours.

10 The mixture obtained above was added dropwise to a hexane solution (200 ml), at -78°C, of dimethyldichlorosilane (19.36 g) over 10 minutes. Then the resulting mixture was brought up to room temperature over 2 hours, then stirred for one hour, and the solvent and
15 the excess of dimethyldichlorosilane were distilled off under reduced pressure.

 The mixture obtained was dissolved in tetrahydrofuran (300 ml). Into the resulting solution was added dropwise at -78°C a 2.0 M tetrahydrofuran solution
20 (15.0 ml) of cyclopentadienylsodium, the resulting mixture was brought up to room temperature over 2 hours and then stirred for 12 hours.

 The reaction mixture was mixed with an aqueous ammonium chloride solution, and separated into an aqueous
25 layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom and the hexane solution obtained was combined with the above-mentioned organic layer to obtain an organic

solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent hexane) to obtain colorless oily (cyclopentadienyl)(2-methoxy-3,5-dimethylphenyl)dimethylsilane (4.30 g, yield 33%).

¹H NMR (CDCl₃) δ 0.17 (s, 6H), 2.05 (s, 3H), 2.31 (s, 3H), 3.65-3.80 (m, 2H), 3.77 (s, 3H), 5.98-6.45 (m, 3H), 7.12 (d, 1H, J=3Hz), 7.22 (d, 1H, J=3Hz)

Example 28

Synthesis of (3-tert-butyl-2-methoxy-5-methylphenyl)cyclopentadienyl)diphenylsilane

To a tetrahydrofuran solution (200 ml) of 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene (7.72 g) was added dropwise at -78°C a 1.60 M hexane solution (37.5 ml) of n-butyllithium, and the resulting mixture was brought up to room temperature over 2 hours.

The mixture obtained above was added dropwise over 15 minutes into a hexane solution (200 ml) at -78°C of diphenyldichlorosilane (7.60 g). Then the resulting mixture was brought up to room temperature over 2 hours, further stirred for one hour, and the solvent was distilled off under reduced pressure.

The mixture thus obtained was dissolved in

tetrahydrofuran (300 ml). Into the resulting solution was added dropwise at -78°C a 2.0 M tetrahydrofuran solution (15.0 ml) of cyclopentadienylsodium, the resulting mixture was brought up to room temperature over
5 2 hours and then stirred for 12 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom,
10 and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

15 The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (3-tert-butyl-2-methoxy-5-methylphenyl)(cyclopentadienyl)diphenylsilane
20 (3.59 g, yield 28%).

^1H NMR (CDCl_3) δ 1.38 (s, 9H), 2.21 (s, 3H),
3.21 (s, 3H), 4.17 (d, 1H, $J=6\text{Hz}$), 4.60 (d, 1H,
 $J=14\text{Hz}$), 6.35-6.78 (m, 3H), 6.98 (d, 1H,
 $J=2\text{Hz}$), 7.01 (d, 1H, $J=2\text{Hz}$), 7.20-7.68 (m, 10H)
25 Mass spectra (EI, m/e) 424, 359, 283, 183, 105

Example 29

Synthesis of (3-tert-butyl-2-methoxy-5-methylphenyl)dimethyl(methylcyclopentadienyl)silane

To a tetrahydrofuran solution (400 ml) of 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene (23.16 g) was added dropwise at -78°C a 1.60 M hexane solution (112.5 ml) of n-butyllithium, and the resulting mixture
5 was brought up to room temperature over 2 hours.

The mixture obtained above was added dropwise over 30 minutes into a hexane solution (200 ml) of dimethyldichlorosilane (58.1 g) of -78°C . Then the resulting mixture was brought up to room temperature over
10 2 hours, further stirred for one hour, and the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.

The mixture thus obtained was dissolved in tetrahydrofuran (200 ml). Into the solution was added
15 dropwise at -78°C a methylcyclopentadienyllithium solution prepared from a tetrahydrofuran solution (400 ml) of methylcyclopentadiene (7.21 g) and a 1.60 M hexane solution (57.69 ml) of n-butyllithium. The resulting mixture was brought up to room temperature over 2 hours
20 and then stirred for 12 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom,
25 and the hexane solution obtained was combined with the above-mentioned organic layer to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with

anhydrous sodium sulfate.

The dried organic solution was stripped of the solvents under reduced pressure, and the residue was treated by silica gel column chromatography (developing
5 solvent: hexane) to obtain colorless oily (3-tert-butyl-2-methoxy-5-methylphenyl)dimethyl(methylcyclopentadienyl)silane (18.05 g) as a mixture of isomers in 64% yield.

¹H NMR (CDCl₃) δ 0.16-0.49 (6H;0.16:s;0.18:s;
10 0.48:s;0.49:s), 1.39-1.42 (9H;1.39:s;1.42:s),
2.04-2.08 (3H;2.04:s;2.08:s), 2.31-2.32
(3H;2.31:s;2.32:s), 2.97-3.05 (m, 1H), 3.61-
3.78 (3H;3.61:s;3.78:s), 5.98-6.73 (m, 3H),
6.82 (d, 1H, J=2Hz), 7.20 (d, 1H, J=2Hz)

15 Example 30

Synthesis of (tert-butylcyclopentadienyl)(3-tert-butyl-2-methoxy-5-methylphenyl)dimethylsilane

To a tetrahydrofuran solution (400 ml) of 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene (23.16 g) was
20 added dropwise at -78°C a 1.60 M hexane solution (112.5 ml) of n-butyllithium and the resulting mixture was brought up to room temperature over 2 hours.

The mixture obtained above was added dropwise into a hexane solution (200 ml) of dimethyldichlorosilane
25 (58.1 g) of -78°C over 30 minutes. Thereafter the resulting mixture was brought up to room temperature over 2 hours, then stirred for one hour, and thereafter the solvent and the excess of dichlorodimethylsilane were

distilled off under reduced pressure.

The mixture obtained was dissolved in tetrahydrofuran (200 ml). Into the resulting solution was added dropwise at -78° over 30 minutes a solution of
5 tert-butylcyclopentadienyllithium prepared from a tetrahydrofuran solution (400 ml) of tert-butylcyclopentadiene (11.00 g) and a 1.60 M hexane solution (57.69 ml) of n-butyllithium. The resulting mixture was brought up to room temperature over 2 hours and then stirred for
10 12 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom,
15 and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

20 The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (3-tert-butyl-2-methoxy-5-methylphenyl)dimethyl(methylcyclopenta-
25 dienyl)silane (18.94 g) as a mixture of isomers in 59% yield.

^1H NMR (CDCl_3) δ 0.08-0.43 (6H;0.08:s;0.13:s;0.42:s;0.43:s), 1.12-1.13 (9H;1.12:s;1.13:s),

1.33-1.36 (9H;1.33:s;1.36:s), 2.22-2.25
(3H;2.22:s;2.25:s), 2.97-3.61 (1H;2.97:s;
3.61:s), 3.71 (3H, s), 5.99-6.70 (m, 3H), 7.05
(d, 1H, J=2Hz), 7.13 (d, 1H, J=2Hz)

5 Example 31

Synthesis of (3-tert-butyl-2-methoxy-5-methylphenyl)(1H-inden-1-yl)dimethylsilane

To a tetrahydrofuran solution (400 ml) of 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene (23.16 g)
10 was added dropwise at -78°C a 1.60 M hexane solution (112.5 ml) of n-butyllithium, and the resulting mixture was brought up to room temperature over 2 hours.

The mixture obtained above was added dropwise into a hexane solution (200 ml) of dimethyldichlorosilane
15 (58.10 g) of -78°C over 30 minutes. Thereafter the resulting mixture was brought up to room temperature over 2 hours, then stirred for one hour and thereafter the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.

20 The mixture thus obtained was dissolved in tetrahydrofuran (200 ml). Into the resulting solution was added dropwise at -78°C over 15 hours an indenyl-lithium solution prepared from a tetrahydrofuran solution (400 ml) of indene (10.45 g) and a 1.60 M hexane solution
25 (57.69 ml) of n-butyllithium, the resulting mixture was brought up to room temperature over 2 hours and then stirred for 12 hours.

The reaction mixture was mixed with an aqueous

ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom, and the hexane solution obtained and the above-mentioned
5 organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the
10 solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (3-tert-butyl-2-methoxy-5-methylphenyl)(1H-inden-1-yl)dimethylsilane (23.63 g) in 75% yield.

15 ^1H NMR (CDCl_3) δ 0.03 (s, 3H), 0.14 (s, 3H), 1.44 (s, 9H), 2.29 (s, 3H), 3.45 (d, 1H, $J=1\text{Hz}$), 3.81 (s, 3H), 6.57 (dd, 1H, $J=2, 5\text{Hz}$), 6.89 (dd, 1H, $J=2, 5\text{Hz}$), 7.03 (d, 1H, $J=2\text{Hz}$), 7.20 (d, 1H, $J=2\text{Hz}$), 7.04-7.50 (m, 4H)

20 Example 32

Synthesis of (3-tert-butyl-2-methoxy-5-methylphenyl)(9H-fluoren-9-yl)dimethylsilane

To a tetrahydrofuran solution (100 ml) of 1-bromo-3-tert-butyl-2-methoxy-5-methylbenzene (7.72 g) was
25 added dropwise at -78°C a 1.60 M hexane solution (37.5 ml) of n-butyllithium, the resulting mixture was brought up to room temperature over 2 hours and then stirred for 3 hours.

The mixture obtained above was added dropwise into a hexane solution (100 ml) of dichlorodimethylsilane (19.36 g) of -78°C over 10 minutes. Thereafter the resulting mixture was brought up to room temperature over 5 2 hours, then stirred for one hour and thereafter the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.

The resulting mixture was dissolved in tetrahydrofuran (150 ml). Into the solution was added dropwise at -78°C a solution of fluorenyllithium prepared from a tetrahydrofuran solution (100 ml) of fluorene (4.99 g) and a 1.60 M hexane solution (18.25 ml) of n-butyllithium, the resulting mixture was brought up to room temperature over 2 hours and then stirred for 12 15 hours.

Then the reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane-solubles 20 therefrom. The hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and dried with anhydrous sodium sulfate.

25 The dried organic solution was stripped of the solvent under reduced pressure, and the residue was recrystallized from a tetrahydrofuran-hexane solvent mixture to obtain colorless crystals of (3-tert-butyl-2-

methoxy-5-methylphenyl)(9H-fluoren-9-yl)dimethylsilane
(6.82 g) in 57% yield.

¹H NMR (CDCl₃) δ 0.21 (s, 6H), 1.50 (s, 9H),
2.33 (s, 3H), 3.82 (s, 3H), 4.40 (s, 1H), 6.99
5 (d, 1H, J=2Hz), 7.29 (d, 1H, J=2Hz), 7.12-7.38
(m, 6H), 7.82 (d, 2H, J=8Hz)

Example 33

Synthesis of (3-tert-butyl-2-methoxy-5-methyl-
phenyl)(9H-fluoren-9-yl)diphenylsilane

10 To a tetrahydrofuran solution (100 ml) of 1-
bromo-3-t-butyl-2-methoxy-5-methylbenzene (5.24 g) was
added dropwise at -78°C a 1.60 M hexane solution (25.0
ml) of n-butyllithium, the resulting mixture was brought
up to room temperature over 2 hours.

15 The mixture obtained above was added dropwise
into a hexane solution (100 ml) of diphenyldichlorosilane
(5.06 g) at -78°C over 10 minutes. Then the resulting
solution was brought up to room temperature over 2 hours,
then stirred for one hour, and the solvent was distilled
20 off under reduced pressure.

The mixture obtained was dissolved in tetra-
hydrofuran (150 ml). To the resulting solution was added
dropwise at -78°C a solution of fluorenyllithium prepared
from a tetrahydrofuran solution (100 ml) of fluorene
25 (3.32 g) and a 1.60 M hexane solution (12.5 ml) of n-
butyllithium, the resulting mixture was brought up to
room temperature over 2 hours, and then stirred for 12
hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom,
5 and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

10 The dried organic solution was stripped of the solvent under reduced pressure, and the residue was recrystallized from pentane to obtain colorless crystals of (3-tert-butyl-2-methoxy-5-methylphenyl)(9H-fluoren-9-yl)diphenylsilane (4.31 g, yield 40%).

15 ^1H NMR (CDCl_3) δ 1.46 (s, 9H), 2.23 (s, 3H), 3.39 (s, 3H), 4.92 (s, 1H), 7.00 (dt, 2H, $J=1$, 7Hz), 7.10 (d, 1H, $J=1\text{Hz}$), 7.14 (d, 4H, $J=8\text{Hz}$), 7.19 (d, 1H, $J=1\text{Hz}$), 7.21-7.30 (m, 10H), 7.52 (d, 2H, $J=8\text{Hz}$)

20 Mass spectra (EI, m/e) 524, 359, 282, 177, 165, 77

Example 34

Synthesis of (3-tert-butyl-2-methoxymethoxy-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopenta-
25 dienyl)silane

To a tetrahydrofuran solution (300 ml) of 1-bromo-3-t-butyl-methoxymethoxy-5-methylbenzene (11.48 g) was added dropwise at -78°C a 1.60 M hexane solution

(25.0 ml) of n-butyllithium, and the resulting mixture was stirred for 1 hour.

The mixture obtained above was added dropwise at a temperature not higher than -20°C over 30 minutes
5 into a hexane solution (200 ml) of dimethyldichlorosilane (5.16 g) of -78°C . Thereafter the resulting mixture was brought up to room temperature over 2 hours, then stirred for one hour, and the solvent was distilled off under reduced pressure.

10 The mixture thus obtained was dissolved in tetrahydrofuran (200 ml). To the resulting solution was added dropwise at -78°C a solution of tetramethylcyclopentadienyllithium prepared from a tetrahydrofuran solution (300 ml) of tetramethylcyclopentadiene (4.88 g)
15 and a 1.60 M hexane solution (25.0 ml) of n-butyllithium. Thereafter the resulting mixture was brought up to room temperature over 2 hours and then stirred for 12 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution, and separated into an aqueous
20 layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom, and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated
25 aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure, and the residue was

treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (3-tert-butyl-2-methoxymethoxy-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (5.60 g) in 36% yield.

- 5 ¹H NMR (CDCl₃) δ 0.13 (s, 6H), 1.39 (s, 9H),
1.69 (s, 6H), 1.78 (s, 6H), 2.29 (s, 3H), 3.43
(s, 1H), 4.40 (dd, 2H, J=2, 2Hz), 5.27 (ddd,
1H, J=2, 2, 9Hz), 5.53 (ddd, 1H, J=2, 2, 17Hz),
6.03 (dddd, 1H, J=2, 2, 2, 9, 17Hz), 7.03 (d,
10 1H, J=2Hz), 7.17 (d, 1H, J=2Hz)

Example 35

Synthesis of (2-benzyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

- 15 To a tetrahydrofuran solution (300 ml) of 2-benzyloxy-1-bromo-3-t-butyl-5-methylbenzene (29.30 g) was added dropwise at -78°C a 1.56 M hexane solution (51.28 ml) of n-butyllithium, and the resulting mixture was stirred for one hour.

- 20 The mixture obtained above was added dropwise at a temperature not higher than -20°C over 30 minutes into a solution of -78°C of dimethyldichlorosilane (100.0 g) dissolved in hexane solution (150 ml). Then the resulting mixture was brought up to room temperature,
25 then stirred for one hour, and the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.

The mixture obtained was dissolved in tetra-

hydrofuran (200 ml). Into the resulting solution was added dropwise at -78°C a solution of tetramethylcyclopentadienyllithium prepared from a tetrahydrofuran solution (500 ml) of tetramethylcyclopentadiene (9.78 g) and a 1.56 M hexane solution (51.28 ml) of n-butyl-
5 lithium. The resulting mixture was brought up to room temperature over 2 hours and then stirred for 12 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution, and separated into an aqueous
10 layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom, and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated
15 aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing
20 solvent: hexane) to obtain colorless oily (2-benzyloxy-3-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (17.6 g, yield 51%).

^1H NMR (CDCl_3) δ 0.01 (s, 6H), 1.33 (s, 9H),
1.52 (s, 6H), 1.67 (s, 6H), 2.24 (s, 3H), 3.32
25 (s, 1H), 4.94 (s, 2H), 6.99 (d, 1H, $J=2\text{Hz}$),
7.13 (d, 1H, $J=2\text{Hz}$), 7.21 (dd, 2H, $J=7, 7\text{Hz}$),
7.29 (dt, 1H, $J=1, 7\text{Hz}$), 7.40 (dd, 2H, $J=1, 7\text{Hz}$)

Mass spectra (EI, m/e) 432, 341, 311, 295, 255,
91, 57

Example 36

Synthesis of (2-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethyl-
5 tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethyl-
cyclopentadienyl)silane

A tetrahydrofuran solution (10 ml) of 3-tert-
butyl-2-tert-butyl-5-methyl-
benzene (0.715 g) was cooled to -78°C, then a hexane
10 solution (1.28 ml) of n-butyllithium was added thereto,
and the resulting mixture was stirred for one hour. To
the mixture obtained was added (2,3,4,5-tetramethyl-
cyclopentadienyl)dimethylsilyl chloride (0.429 g) and the
mixture was stirred at room temperature for 10 hours.

15 The reaction mixture was mixed with an aqueous
ammonium chloride solution (10 ml) and separated into an
aqueous layer and an organic layer. The aqueous layer
was treated with ethyl acetate to extract ethyl acetate
solubles therefrom. The ethyl acetate solution obtained
20 and the above-mentioned organic layer were combined to
obtain an organic solution. The organic solution was
dried with anhydrous sodium sulfate, then stripped of the
solvent, and the residue was treated by silica gel column
chromatography (developing solvent: hexane) to obtain
25 yellow oily (2-tert-butyl-5-methylphenyl)dimethyl(2,3,4,5-tetramethyl-
cyclopentadienyl)silane (0.30 g, yield 34%).

¹H NMR (CDCl₃) δ 0.21 (s, 12H), 0.67 (s, 9H),

1.38 (s, 9H), 1.85 (s, 6H), 2.10 (s, 6H), 2.28
(s, 3H), 3.32 (s, 1H), 6.91 (d, 1H, J=2Hz),
7.05 (d, 1H, J=2Hz)

Mass spectra (EI, m/e) 456, 399, 326, 223, 178,
147, 133, 105, 57

5

Example 37

Synthesis of (2-allyloxy-3-tert-butyl-5-methyl-
phenyl)dimethyl(cyclopentadienyl)silane

To a tetrahydrofuran solution (200 ml) of 2-
10 allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (17.00 g)
was added dropwise at -78°C a 1.66 M hexane solution
(36.2 ml) of n-butyllithium, and the resulting mixture
was stirred for one hour.

The mixture obtained above was added dropwise
15 at a temperature lower than -20°C over 15 minutes into a
solution of -78°C of dimethyldichlorosilane (50.0 g)
dissolved in hexane (100 ml). Then the resulting mixture
was brought up to room temperature over 2 hours, then
stirred for one hour, and the solvent and the excess of
20 dichlorodimethylsilane were distilled off under reduced
pressure.

The mixture obtained was dissolved in tetra-
hydrofuran (75 ml). To the solution was added dropwise
at -78°C a 2 M tetrahydrofuran solution (30 ml) of
25 cyclopentadienylsodium, the resulting mixture was brought
up to room temperature over 2 hours and further stirred
for 12 hours.

The reaction mixture was mixed with an aqueous

ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom, and the hexane solution obtained and the above-mentioned
5 organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the
10 solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(cyclopentadienyl)-silane (7.3 g, yield 37%).

15 ^1H NMR (CDCl_3) δ 0.19 (s, 6H), 1.45 (s, 9H), 2.36 (s, 3H), 3.11 (s, 1H), 4.43 (dt, 2H, $J=2$, 5Hz), 5.31 (dq, 1H, $J=2$, 11Hz), 5.57 (dq, 1H, $J=2$, 17Hz), 6.07 (ddt, 1H, $J=5$, 11, 17Hz), 6.40-6.70 (m, 4H), 7.16 (d, 1H, $J=2\text{Hz}$), 7.22
20 (d, 1H, $J=2\text{Hz}$)

Mass spectra (EI, m/e) 326, 311, 285, 220, 41

Example 38

Synthesis of dimethylsilyl(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride

25 To a toluene solution (15 ml) of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(cyclopentadienyl)-silane (1.62 g) was added dropwise at -78°C a 1.66 M hexane solution (2.99 ml) of n-butyllithium, the

resulting mixture was brought up to room temperature over 2 hours, and then stirred for 12 hours. The mixture obtained was cooled to -78°C , and a toluene solution (5 ml) of titanium tetrachloride (0.545 ml) was added
5 thereto. The resulting mixture, while being shielded from light, was brought up to room temperature over 2 hours and then stirred for 12 hours.

The reaction mixture was filtered, and the filtrate was stripped of the solvent under reduced
10 pressure to obtain a reddish brown solid. The solid was recrystallized from a hexane-toluene solvent mixture to obtain red needle-like crystals of dimethylsilyl(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride (0.72 g, yield 36%).

15 ^1H NMR (C_6D_6) δ 0.27 (s, 6H), 1.63 (s, 9H), 2.21 (s, 3H), 6.09 (t, 2H, $J=2\text{Hz}$), 6.65 (t, 2H, $J=2\text{Hz}$), 7.08 (d, 1H, $J=2\text{Hz}$), 7.21 (d, 1H, $J=2\text{Hz}$)

Example 39

20 Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(tert-butylcyclopentadienyl)silane

To a tetrahydrofuran solution (200 ml) of 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (17.00 g) was added dropwise at -78°C a 1.66 M hexane solution (36.2
25 ml) of n-butyllithium, and the resulting mixture was stirred for one hour.

The mixture obtained above was added dropwise at a temperature not higher than -20°C over 15 minutes

into a solution of -78°C of dimethyldichlorosilane (50.0 g) dissolved in hexane (100 ml). The resulting mixture was then brought up to room temperature over 2 hours, then stirred for one hour, and the solvent and the excess
5 of dimethyldichlorosilane were distilled off under reduced pressure.

The mixture obtained was dissolved in tetrahydrofuran (75 ml). Into the solution was added dropwise at -78°C a solution of tert-butylcyclopentadienyllithium
10 prepared from a tetrahydrofuran solution (250 ml) of 5-isopropylidenecyclopenta-1,3-diene (6.37 g) and a 1.05 M methyllithium-ether solution (57.2 ml), the resulting mixture was brought up to room temperature over 2 hours, and then stirred for 12 hours.

15 The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom. The hexane solution obtained and the above-mentioned
20 organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

The dried organic solution was stripped of the
25 solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(tert-butylcyclopenta-

dienyl)silane (6.58 g, yield 29%) as a mixture of isomers.

¹H NMR (CDCl₃) δ 0.17-0.55 (6H;0.17:s;0.22:s;
0.54:s;0.55:s), 1.22-1.23 (9H;1.22:s;1.23:s),
5 1.43-1.46 (9H;1.43:s;1.46:s), 2.34-2.36
(3H;2.34:s;2.36:s), 3.08-3.76 (1H;3.08:s;
3.76:s), 4.27-4.60 (m, 2H), 5.30-5.62 (m, 2H),
6.08-6.12 (m, 1H), 6.20-6.60 (m, 3H), 7.17 (d,
1H, J=2Hz), 7.23 (d, 1H, J=2Hz)
10 Mass spectra (EI, m/e) 382, 325, 261, 203, 172,
41

Example 40

Synthesis of dimethylsilyl(3-tert-butylcyclo-
pentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
15 dichloride

To a toluene solution (15 ml) of (2-allyloxy-3-
tert-butyl-5-methylphenyl)dimethyl(tert-butylcyclopenta-
dienyl)silane (1.53 g) was added dropwise at -78°C a 1.66
M hexane solution (2.41 ml) of n-butyllithium, the
20 resulting mixture was brought up to room temperature over
2 hours and then stirred for 12 hours. The mixture
obtained was cooled to -78°C, and a toluene solution (5
ml) of titanium tetrachloride (0.440 ml) was added
thereto. The reaction mixture obtained, while being
25 shielded from light, was brought up to room temperature
over 2 hours and then stirred for 12 hours.

The reaction mixture was filtered, and the
filtrate was stripped of the solvent to obtain a reddish

brown solid. The solid was recrystallized from a hexane-toluene solvent mixture to obtain dimethylsilyl(3-tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride (0.09 g, yield 5%) as orange

5 crystals.

^1H NMR (C_6D_6) δ 0.36 (s, 3H), 0.40 (s, 3H), 1.38 (s, 9H), 1.65 (s, 9H), 2.24 (s, 3H), 5.73 (dd, 1H, $J=2$, 3Hz), 6.79 (dd, 1H, $J=2$, 3Hz), 6.82 (dd, 1H, $J=2$, 3Hz), 7.15 (d, 1H, $J=2\text{Hz}$), 7.25 (d, 1H, $J=2\text{Hz}$)

10

Example 41

Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(methylcyclopentadienyl)silane

To a tetrahydrofuran solution (50 ml) of 2-allyloxy-1-bromo-3-tert-5-methylbenzene (5.6 g) was added dropwise at -78°C a 1.65 M hexane solution (12.5 ml) of n-butyllithium, and the resulting mixture was stirred at -78°C for 1.5 hours.

The mixture obtained above was added dropwise into a hexane solution (25 ml) of dichlorodimethylsilane (12.1 g) of -78°C over 3 minutes. The resulting mixture was brought up to room temperature over 2 hours, then stirred for 24 hours, and the solvent and dichlorodimethylsilane were distilled off under reduced pressure.

25 Tetrahydrofuran (50 ml) was added to the mixture obtained above, and further a tetrahydrofuran solution (30 ml) of lithium methylcyclopentadienide (3.0 g) was added thereto at -78°C over one minute, the

resulting mixture was brought up to room temperature over 2 hours and then stirred for 3 hours.

The reaction mixture was mixed with water (40 ml) and separated into an aqueous layer and an organic layer. The organic layer was stripped of the solvent, and the residue obtained was treated with a silica gel column to obtain a pale yellow oil (2.5 g, purity 90%) of an isomer mixture of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(methylcyclopentadienyl)silane. The yield of the intended product was 33%.

^1H NMR (C_6D_6) δ 0.08-0.09 (3H;0.08:s;0.09:s), 0.39-0.41 (3H;0.39:s;0.41:s), 1.32-1.51 (9H;1.32:s;1.36:s;1.39:s;1.51:s), 1.96-2.03 (3H;1.96:s;1.99:s;2.03:s), 2.24-2.27 (3H;2.24:s;2.27:s), 2.90-3.68 (1H;2.90:s;2.98:s;3.68:s), 4.17-4.50 (2H;4.17:m;4.33:s;4.50:d, J=5Hz), 5.22 (d, 1H, J=10Hz), 5.48 (d, 1H, J=17Hz), 5.79-5.98 (m, 1H), 6.14 (d, 1H, J=10Hz), 6.38 (d, 1H), 7.07-7.16 (m, 3H)

Mass spectra (EI, m/e) 340, 325, 298, 283, 245, 221, 205, 189, 159, 145, 120, 91, 75, 61, 41

Example 42

Synthesis of dimethylsilyl(methylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride

To a hexane solution (10 ml) of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(methylcyclopentadienyl)silane (0.75 g) was added dropwise at -78°C a 1.66

M hexane solution (2.1 ml) of n-butyllithium. The resulting mixture was brought up to room temperature over 2 hours and then stirred for 12 hours. To the mixture obtained were added toluene (25 ml) and then, at room
5 temperature, titanium tetrachloride (0.40 g). The resulting mixture was stirred at 75°C for 24 hours while being shielded from light.

The reaction mixture was filtered, and the filtrate was stripped of the solvent to obtain a black
10 tar. The tar was treated with hexane (5 ml) to extract hexane solubles therefrom. The hexane solution thus obtained was stripped of the solvent to obtain a reddish black tar (0.3 g, yield 33%) of dimethylsilyl(methyl-cyclopentadienyl)(3-t-butyl-5-methyl-2-phenoxy)titanium
15 dichloride as an isomer mixture.

^1H NMR (C_6D_6) δ 0.24-0.34 (6H;0.24:s;0.32:s;0.33:s;0.34:s), 1.58-1.64 (9H;1.58:s;1.59:s;1.62:s;1.69:s), 2.15-2.26 (6H;2.15:s;2.19:s;2.21:s;2.24:s;2.26:s), 5.81 (s, 1H), 6.14 (t, 1H, J=2Hz), 6.46 (t, 1H, J=2Hz), 7.12 (d, 1H, J=1Hz), 7.24 (d, 1H, J=1Hz)
20

Example 43

Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)(indenyl)dimethylsilane

25 To a tetrahydrofuran solution (150 ml) of 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (18.9 g) was added dropwise at -78°C a 1.65 M hexane solution (40.4 ml) of n-butyllithium, and the resulting mixture

was stirred at -78°C for 2 hours.

The mixture obtained above was added dropwise to a hexane solution (80 ml) of -78°C of dichloro-
dimethylsilane (12.1 g) over 5 minutes, the resulting
5 mixture was brought up to room temperature over 2 hours,
then stirred for 24 hours, and the solvent and dichloro-
dimethylsilane were distilled off under reduced pressure.

To the mixture obtained was added tetrahydro-
furan (150 ml), the resulting mixture was cooled to
10 -78°C , and a tetrahydrofuran solution (100 ml) of
indenyllithium (8.2 g) was added thereto over 3 minutes.
The resulting mixture was brought up to room temperature
over 2 hours and stirred for 5 hours.

The reaction mixture was mixed with water (100
15 ml) and separated into an aqueous layer and an organic
layer. The organic layer was stripped of the solvent to
obtain an oil. The oil was treated with a silica gel
column to obtain a yellow oil (11.0 g, purity 94%) of an
isomer mixture of (2-allyloxy-3-tert-butyl-5-methyl-
20 phenyl)(indenyl)dimethylsilane. The yield of the
intended product was 43%.

^1H NMR (C_6D_6) δ 0.09 (s, 3H), 0.55 (s, 3H), 1.32-
1.41 (9H; 1.32:s; 1.41:s), 2.28-2.29 (3H; 2.28:s;
2.29:s), 3.40 (s, 1H), 4.03 (s, 1H), 4.15 (t,
25 1H, $J=2\text{Hz}$), 4.39 (dd, 2H, $J=2.2\text{Hz}$), 5.05-5.24
(1H, 5.05:s; 5.08:s; 5.18:s; 5.24:d, $J=9\text{Hz}$), 5.51
(d, 1H, $J=17\text{Hz}$), 5.69-6.08 (m, 1H), 6.54 (dd,
1H, $J=2.6\text{Hz}$), 6.80-7.50 (m, 5H)

Mass spectra (EI, m/e) 340, 325, 298, 283, 245,
221, 205, 189, 159, 145, 120, 91, 75, 61, 41

Example 44

Synthesis of dimethylsilyl(indenyl)(3-tert-
5 butyl-5-methyl-2-phenoxy)titanium dichloride

To a toluene solution (20 ml) of (2-allyloxy-3-
tert-butyl-5-methylphenyl)(indenyl)dimethylsilane (2.2 g)
was added triethylamine (1.50 g) at room temperature.
The resulting mixture was cooled to -30°C, and a 1.66 M
10 hexane solution (4.8 ml) of n-butyllithium was added
dropwise thereto. The resulting mixture was brought up
to room temperature and stirred for 12 hours. To the
mixture obtained was added dropwise titanium tetra-
chloride (1.35 g) at room temperature, and the resulting
15 mixture was stirred at 95°C for 24 hours while being
shielded from light.

The reaction mixture was filtered, the solid
obtained was washed with toluene (15 ml), and the
filtrate was stripped of the solvent to obtain a reddish
20 black oil (2.9 g). Pentane (10 ml) was added to the oil,
and the insoluble portion was dried under reduced
pressure to obtain reddish brown powder of dimethylsilyl-
(indenyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
dichloride (0.25 g, yield 11%).

25 ^1H NMR (C_6D_6) δ 0.45 (s, 3H), 0.50 (s, 3H), 1.44
(s, 9H), 2.27 (s, 3H), 6.69-6.75 (m, 2H), 6.78-
6.80 (1H; 6.79:d, $J=1\text{Hz}$; 6.80:d, $J=1\text{Hz}$), 6.92-
6.98 (m, 1H), 7.15 (s, 1H), 7.23 (dd, 2H,

$J=2.6\text{Hz}$), 7.57 (dt, 1H, $J=9.1\text{Hz}$)

Example 45

Synthesis of (2-allyloxy-3-tert-butyl-5-methylphenyl)dimethyl(9H-fluorene-9-yl)silane

5 To a tetrahydrofuran solution (200 ml) of 2-allyloxy-1-bromo-3-t-butyl-5-methylbenzene (17.00 g) was added dropwise at -78°C a 1.66 M hexane solution (36.2 ml) of n-butyllithium, and the resulting mixture was stirred for 1 hour.

10 The mixture obtained above was added dropwise at a temperature lower than -20°C over 15 minutes to a solution of -78°C of dimethyldichlorosilane (50.0 g) dissolved in hexane (100 ml). The resulting mixture was brought up to room temperature over 2 hours, further
15 stirred for one hour, and the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.

The mixture obtained was dissolved in tetrahydrofuran (75 ml). To the solution was added
20 dropwise at -78°C fluorenyllithium prepared from a tetrahydrofuran solution (250 ml) of fluorene (9.97 g) and a 1.66 M n-butyllithium-hexane solution (36.2 ml). The resulting mixture was then brought up to room temperature over 2 hours and further stirred for 12 hours.

25 The reaction mixture was mixed with aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom,

and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with
5 anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (2-allyloxy-3-
10 tert-butyl-5-methylphenyl)dimethyl(9H-fluoren-9-yl)silane (12.04 g, yield 47%).

^1H NMR (CDCl_3) δ 0.10 (s, 6H), 1.56 (s, 9H), 2.40 (s, 3H), 4.51 (s, 1H), 4.52 (dt, 2H, $J=2$, 4Hz), 5.37 (dq, 1H, $J=2$, 8Hz), 5.63 (dq, 1H, $J=2$, 17Hz), 6.14 (ddt, 1H, $J=4$, 8, 17Hz), 7.08 (d, 1H, $J=2\text{Hz}$), 7.23 (d, 1H, $J=2\text{Hz}$), 7.23 (dd, 2H, $J=7$, 8Hz), 7.39 (dd, 2H, $J=7$, 8Hz), 7.40 (d, 2H, $J=7\text{Hz}$), 7.92 (d, 2H, $J=8\text{Hz}$)
15

Example 46

20 Synthesis of 2-allyloxy-1-bromo-3,5-dimethylbenzene

To a solution of 0°C of 2-bromo-4,6-dimethylphenol (88.02 g) dissolved in acetonitrile (500 ml) was added potassium hydroxide (30.0 g) and the resulting
25 mixture was stirred for 2 hours to obtain a blue solution. Allyl bromide (100 g) was added dropwise at a temperature not higher than 10°C to the blue solution, the mixture was brought up to room temperature and then

stirred for 6 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was
5 treated with hexane to extract hexane solubles therefrom, and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with
10 anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily 2-allyloxy-1-
15 bromo-3,5-dimethylbenzene (85.73 g, yield 81%).

^1H NMR (CDCl_3) δ 2.24 (s, 3H), 2.27 (s, 3H),
4.40 (dt, 2H, $J=1$, 6Hz), 5.27 (dq, 1H, $J=1$,
10Hz), 5.43 (dq, 1H, $J=2$, 17Hz), 6.13 (ddt, 1H,
 $J=6$, 10, 17Hz), 6.91 (dd, 1H, $J=1$, 1Hz), 7.19
20 (dd, 1H, $J=1$, 1Hz)

Example 47

Synthesis of (2-allyloxy-3,5-dimethylphenyl)-
dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

To a tetrahydrofuran solution (200 ml) of 2-
25 allyloxy-1-bromo-3,5-dimethylbenzene (24.10 g) was added dropwise at -78°C a 1.66 M hexane solution (60.24 ml) of n-butyllithium, and the mixture was stirred for 20 minutes.

The mixture obtained above was added dropwise at a temperature lower than -20°C over 30 minutes to a solution at -78°C of dichlorodimethylsilane (100.0 g) dissolved in hexane (100 ml). The resulting mixture was
5 then brought up to room temperature, further stirred for one hour, and the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.

The mixture obtained was dissolved in tetrahydrofuran (200 ml). To the solution was added dropwise
10 at -78°C a solution of tetramethylcyclopentadienyllithium prepared from a tetrahydrofuran solution (400 ml) of tetramethylcyclopentadiene (12.22 g) and a 1.66 M hexane solution (60.24 ml) of n-butyllithium, the resulting mixture was brought up to room temperature over 2 hours
15 and then stirred for 12 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom,
20 and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.

25 The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing solvent: hexane) to obtain colorless oily (2-allyloxy-

3,5-dimethylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (18.8 g, yield 56%).

¹H NMR (CDCl₃) δ 0.10 (s, 6H), 1.70 (s, 6H),
1.80 (s, 6H), 2.27 (s, 3H), 2.28 (s, 3H), 3.40
5 (s, 1H), 4.41 (dt, 2H, J=2, 5Hz), 5.28 (dq, 1H,
J=2, 11Hz), 5.41 (dq, 1H, J=2, 17Hz), 6.12
(ddt, 1H, J=5, 11, 17Hz), 6.94 (d, 1H, J=2Hz),
7.02 (d, 1H, J=2Hz)

Mass spectra (EI, m/e) 340, 299, 219, 178, 41

10 Example 48

Synthesis of 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene

To a solution at 0°C of 2-bromo-4-methyl-6-tert-butylphenol (43.8 g) dissolved in acetonitrile (250
15 ml) was added potassium hydroxide (13.2 g), and the
mixture was stirred for 2 hours to obtain a blue
solution. Allyl bromide (65 g) was added dropwise at a
temperature not higher than 10°C to the blue solution,
the resulting mixture was brought up to room temperature
20 and then stirred for 6 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was
treated with hexane to extract hexane solubles therefrom,
25 and the hexane solution obtained and the above-mentioned
organic layer were combined to obtain an organic
solution. The organic solution was washed with saturated
aqueous sodium chloride solution and then dried with

anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing
5 solvent: hexane) to obtain colorless oily 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (46.07 g, yield 90%).

^1H NMR (CDCl_3) δ 1.38 (s, 9H), 2.27 (s, 3H), 4.57 (dt, 2H, $J=2$, 5Hz), 5.29 (dq, 1H, $J=2$, 11Hz), 5.49 (dq, 1H, $J=2$, 17Hz), 6.13 (ddt, 1H,
10 $J=5$, 11, 17Hz), 7.07 (d, 1H, $J=2\text{Hz}$), 7.25 (d, 1H, $J=2\text{Hz}$)

Example 49

Synthesis of 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene

15 To a mixture of 85% potassium hydroxide (76.61 g) and methyl isobutyl ketone (1000 ml) was added at 10°C over 2 hours 2-bromo-6-tert-butyl-4-methylphenol (230.98 g), and the resulting mixture was then stirred at 25°C for one hour. To the resulting deep blue mixture was
20 added at 10°C allyl bromide (133.07 g), and the mixture obtained was stirred at 25°C for 12 hours.

The reaction mixture was mixed with water (500 ml) and separated into an aqueous layer and an organic layer. The organic layer was washed with saturated
25 aqueous sodium chloride solution and dried with anhydrous sodium sulfate. The solvent was distilled off under reduced pressure from the dried organic layer and the residue was distilled to obtain a colorless oil of 2-

allyloxy-1-bromo-3-tert-butyl-5-methylbenzene (245.25 g, yield 91%).

Boiling point 74-75°C (0.08 mmHg)

¹H NMR (CDCl₃) δ 1.38 (s, 9H), 2.27 (s, 3H),
5 4.57 (dt, 2H, J=2, 5Hz), 5.29 (dq, 1H, J=2, 11Hz), 5.49 (dq, 1H, J=2, 17Hz), 6.13 (ddt, 1H, J=5, 11, 17Hz), 7.07 (d, 1H, J=2Hz), 7.25 (d, 1H, J=2Hz)

Mass spectra (EI, M/e) 282, 269, 241, 226, 203,
10 162, 147, 122, 91, 41

Example 50

Synthesis of 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene

To a mixture (30 ml) of 85% potassium hydroxide
15 (1.82 g), tetra-n-butylammonium bromide (0.040 g) and toluene were added dropwise at 50°C with stirring 2-bromo-6-t-butyl-4-methylphenol (6.08 g) and allyl bromide (3.38 g). Then the resulting mixture was stirred at 50°C for 3 hours.

20 After being cooled to 25°C, the reaction mixture was mixed with water and separated into an aqueous layer and an organic layer. The organic layer was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate.
25 Gas chromatographic analysis using the internal standard method revealed that 2-allyloxy-1-bromo-3-tert-butyl-5-methylbenzene had been formed in 93% yield based on the 2-bromo-6-t-butyl-4-methylphenol used.

Example 51

Synthesis of 2-allyloxy-1-bromo-3-tert-butyl-5-methoxybenzene

To a mixture of 85% potassium hydroxide (4.57 g) and methyl isobutyl ketone (30 ml) was added at 10°C 2-bromo-6-tert-butyl-4-methoxyphenol (16.02 g), and the resulting mixture was stirred at 25°C for 1 hour. To the deep blue solution thus obtained was added at 10°C allyl bromide (8.47 g), and the mixture was then stirred at 25°C for 12 hours.

The reaction mixture was mixed with water and separated into an aqueous layer and an organic layer. The organic layer obtained was washed with saturated aqueous sodium chloride solution and then dried with anhydrous sodium sulfate. The dried organic layer was stripped of the solvent under reduced pressure, and the residue was distilled to obtain pale yellow oily 2-allyloxy-1-bromo-3-tert-butyl-5-methoxybenzene (15.80 g, yield 85%).

B.p. 115-117°C (0.8 mmHg)

¹H NMR (CDCl₃) δ 1.38 (s, 9H), 3.76 (s, 3H), 4.55 (dt, 2H, J=2, 5Hz), 5.29 (dq, 1H, J=2, 11Hz), 5.48 (dq, 1H, J=2, 17Hz), 6.13 (ddt, 1H, J=5, 9, 17Hz), 6.86 (d, 1H, J=3Hz), 6.95 (d, 1H, J=3Hz)

Mass spectra (EI, m/e) 300, 257, 178, 138, 91,

Example 52

Synthesis of (2-allyloxy-3-tert-butyl-5-methoxyphenyl)dimethyl(2,3,4,5-tetramethyl-cyclopentadienyl)silane

- 5 To a hexane solution (90 ml) of 2-allyloxy-1-bromo-3-tert-butyl-5-methoxybenzene (8.98 g) was added dropwise at -78°C a 1.66 M hexane solution (18.07 ml) of n-butyllithium, the resulting mixture was brought up to -30°C and stirred for one hour. The mixture obtained was
- 10 cooled to -78°C , then dichlorodimethylsilane (4.26 g) was added thereto, the resulting mixture was brought up to 25°C over 2 hours, and further stirred for 3 hours. Thereafter, the solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure.
- 15 The mixture thus obtained was dissolved in tetrahydrofuran (50 ml), the resulting solution was added dropwise at -78°C to a tetrahydrofuran solution (100 ml) of tetramethylcyclopentadienyllithium (3.84 g). The resulting mixture was brought up to room temperature over
- 20 2 hours and then stirred for 12 hours.

The reaction mixture was mixed with an aqueous ammonium chloride solution and separated into an aqueous layer and an organic layer. The aqueous layer was treated with hexane to extract hexane solubles therefrom,

25 and the hexane solution obtained and the above-mentioned organic layer were combined to obtain an organic solution. The organic solution was washed with saturated aqueous sodium chloride solution and then dried with

anhydrous sodium sulfate.

The dried organic solution was stripped of the solvent under reduced pressure, and the residue was treated by silica gel column chromatography (developing
5 solvent: hexane) to obtain colorless oily (2-allyloxy-3-tert-butyl-5-methoxyphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (5.00 g, yield 42%).

^1H NMR (CDCl_3) δ 0.14 (s, 6H), 1.39 (s, 9H),
1.70 (s, 6H), 1.78 (s, 6H), 3.42 (s, 1H), 3.80
10 (s, 3H), 4.39 (dt, 2H, $J=2$, 2Hz), 5.27 (dq, 1H,
 $J=2$, 11Hz), 5.53 (dq, 1H, $J=2$, 17Hz), 6.03
(ddt, 1H, $J=2$, 11, 17Hz), 6.75 (d, 1H, $J=3\text{Hz}$),
6.93 (d, 1H, $J=3\text{Hz}$)
Mass spectra (EI, m/e) 399, 261, 236, 221, 162,
15 147, 75

Example 53

Synthesis of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride

20 To a hexane solution (1170 ml) of (3-tert-butyl-2-allyloxy-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (117.5 g, purity 85%) was added dropwise at room temperature a 1.66 M hexane solution (340 ml) of n-butyllithium, and the mixture was
25 stirred for 12 hours. The supernatant of the reaction liquid was removed, and then toluene (1400 ml) and titanium tetrachloride (61 g) were added at room temperature to the remainder of the reaction liquid, and

the resulting mixture was stirred at 95°C for 10 hours while being shielded from light.

The reaction mixture was filtered, and the solid was washed with toluene (500 ml). The filtrate and
5 the washings obtained were combined, and the solvent was distilled off to obtain a reddish black tar. Toluene (250 ml) and hexane (1150 ml) were added to the tar, the resulting mixture was heated to 65°C to form a solution, which was then allowed to stand at -20°C for 24 hours.
10 The precipitate formed was collected by filtration, washed with hexane (80 ml) and dried under reduced pressure to obtain a red solid. The solid was recrystallized from a solvent mixture of toluene (240 ml) and hexane (720 ml) to obtain a red needle-like crystals of
15 dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride (29.1 g, yield 22.6%).

Example 54

Synthesis of (3,5-di-tert-butyl-2-trimethyl-
20 siloxyphenyl)chlorodimethylsilane

To a solution at -70°C of 1-bromo-3,5-di-tert-butyl-2-trimethylsiloxybenzene (39.0 g) dissolved in tetrahydrofuran (100 ml) was added dropwise a 1.68 M hexane solution (71.4 ml) of n-butyllithium, and the
25 mixture was stirred at -70°C for 2 hours.

The mixture obtained above was added dropwise to a solution at -70°C of dichlorodimethylsilane (66.1 ml) dissolved in tetrahydrofuran (70 ml), and the

resulting mixture was brought up to room temperature over 2 hours.

The reaction mixture was stripped of the solvent, and the residue was treated with hexane (70 ml) to extract hexane solubles therefrom. The solvent was distilled off from the hexane solution thus obtained to obtain pale yellow (3,5-di-tert-butyl-2-trimethylsiloxyphenyl)chlorodimethylsilane (40.0 g, yield 99%).

¹H NMR (CDCl₃) δ 0.34 (s, 9H), 0.60 (s, 6H), 1.28 (s, 9H), 1.41 (s, 9H), 7.25 (d, J=2.6Hz, 1H), 7.38 (d, J=2.6Hz, 1H)

Mass spectra (EI, m/e) 370, 355, 313, 247, 167

Example 55

Synthesis of (3,5-di-tert-butyl-2-trimethylsiloxyphenyl)cyclopentadienyldimethylsilane

To a tetrahydrofuran solution (100 ml) at -70°C of cyclopentadienyllithium (2.20 g) was added dropwise a tetrahydrofuran solution (50 ml) of (3,5-di-tert-butyl-2-trimethylsiloxyphenyl)chlorodimethylsilane (9.83 g).

Thereafter the resulting mixture was brought up to room temperature over 2 hours and then stirred at room temperature for 12 hours.

The reaction mixture was stripped of the solvent and the residue was treated with hexane to extract hexane solubles therefrom. The hexane solution obtained was stripped of the solvent to obtain pale yellow (3,5-di-tert-butyl-2-trimethylsiloxyphenyl)-cyclopentadienyldimethylsilane (10.43 g, yield 98%).

^1H NMR (CDCl_3) δ 0.28 (s, 6H), 0.35 (s, 9H),
1.29 (s, 9H), 1.42 (s, 9H), 6.57 (s, 1H), 7.22
(s, 1H), 7.24 (s, 2H), 7.34 (s, 1H), 7.39 (s,
2H)

5 Mass spectra (EI, m/e) 400, 385, 326, 311, 298,
247, 215

Example 56

Synthesis of (3,5-di-tert-butyl-2-trimethyl-
siloxyphe~~n~~yl)dimethyl(trimethylsilylcyclopentadienyl)-
10 silane

To a tetrahydrofuran solution (20 ml) at -70°C
of (trimethylsilylcyclopentadienyl)lithium (0.85 g) was
added dropwise a tetrahydrofuran solution (15 ml) of
(3,5-di-tert-butyl-2-trimethylsiloxyphe~~n~~yl)chlorodi-
15 methylsilane (1.86 g). Thereafter the resulting mixture
was brought up to room temperature over 2 hours and then
stirred at room temperature for 12 hours.

The reaction mixture was stripped of the
solvent and the residue was treated with hexane to
20 extract hexane solubles therefrom. The hexane solution
was stripped of the solvent to obtain pale yellow oily
(3,5-di-tert-butyl-2-trimethylsiloxyphe~~n~~yl)dimethyl-
(trimethylsilylcyclopentadienyl)silane (2.0 g, yield
84%).

25 ^1H NMR (CDCl_3) δ 0.11 (s, 9H), 0.30 (s, 9H),
0.37 (s, 6H), 1.31 (s, 9H), 1.33 (s, 9H), 6.45
(m, 1H), 7.25 (s, 1H), 7.28 (m, 2H), 7.37 (s,
1H), 7.41 (s, 1H)

Mass spectra (EI, m/e) 472, 457, 417, 397, 382,
369, 327, 310, 147, 73

Example 57

Synthesis of (3-tert-butyl-5-methyl-2-
5 trimethylsiloxyphenyl)chlorodimethylsilane

To a mixture at -60°C consisting of 1-bromo-3-
tert-butyl-5-methyl-2-trimethylsiloxybenzene (24.18 g)
and tetrahydrofuran (180 ml) was added dropwise a 1.6 M
hexane solution (54.2 ml) of n-butyllithium over 30
10 minutes, and the resulting mixture was then kept at -40°C
for 3.75 hours.

The mixture obtained above was added dropwise
to a solution at -60°C consisting of dichlorodimethyl-
silane (49.5 g) and tetrahydrofuran (180 ml). The
15 resulting solution was brought up to room temperature
over 2 hours, further stirred for 15 hours, and then the
solvent and the excess of dichlorodimethylsilane were
distilled off under reduced pressure.

The mixture obtained above was treated with
20 hexane to extract hexane solubles therefrom. The hexane
solution obtained was stripped of the solvent under
reduced pressure to obtain white powder of (3-tert-butyl-
5-methyl-2-trimethylsiloxyphenyl)chlorodimethylsilane
(24.7 g, yield 98%).

25 ^1H NMR (CDCl_3) δ 0.35 (s, 9H), 0.62 (s, 6H),
1.42 (s, 9H), 2.28 (s, 3H), 7.06 (s, 1H), 7.19
(s, 1H)

Mass spectra (EI, m/e) 328, 313, 271, 205, 167,

93, 73

Example 58

Synthesis of (3-tert-butyl-5-methyl-2-trimethylsiloxyphenyl)dimethyl(trimethylsilylcyclopentadienyl)silane

To a tetrahydrofuran solution (20 ml) of (trimethylsilylcyclopentadienyl)lithium (1.43 g) was added dropwise at -70°C a solution containing (3-tert-butyl-5-methyl-2-trimethylsiloxyphenyl)chlorodimethylsilane (2.59 g) and tetrahydrofuran (15 ml), then the resulting mixture was brought up to room temperature over 2 hours and further stirred for 12 hours.

The reaction mixture was stripped of the solvent under reduced pressure, and the residue was treated with hexane to extract hexane solubles therefrom. The hexane solution obtained was stripped of the solvent to obtain pale yellow oily (3-tert-butyl-5-methyl-2-trimethylsiloxyphenyl)dimethyl(trimethylsilylcyclopentadienyl)silane (2.9 g, yield 86%).

¹H NMR (CDCl₃) δ 0.14 (s, 9H), 0.25 (s, 9H), 0.34 (s, 6H), 1.28 (s, 9H), 1.42 (s, 3H), 6.45 (s, 1H), 7.23 (s, 1H), 7.25 (s, 2H), 7.34 (s, 1H), 7.39 (s, 1H)

Mass spectra (CI, m/e) 430

Example 59

Synthesis of (3-tert-butyl-2-methoxy-5-methylphenyl)dimethyl(cyclopentadienyl)silane

Into a solution consisting of (3-tert-butyl-2-

methoxy-5-methylphenyl)chlorodimethylsilane (5.0 g),
tetrahydrofuran (35 ml) and hexane (35 ml) was added at
-35°C cyclopentadienyllithium (1.45 g). The resulting
mixture was brought up to room temperature over 2 hours
5 and further stirred at room temperature for 10 hours.

From the resulting white suspension, the
solvent was distilled off under reduced pressure, and the
residue obtained was treated with hexane to extract
hexane solubles therefrom. The hexane solution obtained
10 was stripped of the solvent under reduced pressure to
obtain yellow oily (3-tert-butyl-2-methoxy-5-methyl-
phenyl)dimethyl(cyclopentadienyl)silane (5.07 g, yield
91%).

¹H NMR (CDCl₃) δ 0.22 (s, 6H), 1.35 (s, 9H),
15 2.26 (s, 3H), 3.56 (s, 3H), 5.25 (s, 1H), 5.84
(br, 1H), 5.87 (br, 1H), 6.99 (br, 2H), 7.08
(s, 1H), 7.16 (s, 1H)

Mass spectra (EI, m/e) 300, 255, 205, 179, 161,
89

20 Example 60

Synthesis of (3-tert-butyl-5-methyl-2-
trimethylsiloxyphenyl)dimethyl(cyclopentadienyl)silane

A solution consisting of (3-tert-butyl-5-
methyl-2-trimethylsiloxyphenyl)chlorodimethylsilane (2.5
25 g) and tetrahydrofuran (10 ml) was added dropwise at
-40°C into a solution consisting of cyclopentadienyl-
lithium (0.56 g) and tetrahydrofuran (20 ml). The
resulting mixture was brought up to room temperature over

2 hours and further stirred at room temperature for 10 hours.

The reaction mixture was stripped of the solvent under reduced pressure, and the residue was
5 treated with hexane to extract hexane solubles therefrom. The hexane solution obtained was stripped of the solvent under reduced pressure to obtain pale yellow oily (3-tert-butyl-5-methyl-2-trimethylsiloxyphenyl)dimethyl-(cyclopentadienyl)silane (2.5 g, yield 92%).

10 Mass spectra (EI, m/e) 358, 284, 269, 213, 205, 147, 95, 73

Example 61

Synthesis of (3-tert-butyl-5-methyl-2-trimethylsiloxyphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane
15

Into a solution consisting of 1-bromo-3-tert-butyl-5-methyl-2-trimethylsiloxybenzene (1.54 g) and tetrahydrofuran (15 ml) was added dropwise at -55°C over 10 minutes a 1.6 M hexane solution (3.15 ml) of n-butyl-
20 lithium. The resulting mixture was kept at -45°C for 45 minutes, then a solution consisting of chlorodimethyl-(tetramethylcyclopentadienyl)silane (1.0 g) and tetrahydrofuran (5 ml) was added dropwise thereinto, and the reaction mixture was brought up to room temperature over
25 2 hours. The reaction mixture was stirred at room temperature for 13 days and then stripped of the solvent under reduced pressure.

The mixture thus obtained was treated with

hexane to extract hexane solubles therefrom. The hexane solution obtained was allowed to stand at -40°C overnight and the white solid thus formed was dried to obtain pale yellow oily (3-tert-butyl-5-methyl-2-trimethylsiloxy-phenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)-silane (0.97 g, yield 48%).

¹H NMR (CDCl₃) δ 0.01 (s, 6H), 0.42 (s, 9H), 1.50 (s, 9H), 2.01 (s, 6H), 2.10 (s, 6H), 2.33 (s, 3H), 3.59 (s, 1H), 7.11 (s, 1H), 7.23 (s, 1H)

Example 62

Synthesis of (3-tert-butyl-2-methoxy-5-methyphenyl)chlorodimethylsilane

To a solution consisting of tetrahydrofuran (31.5 ml), hexane (139 ml) and 3-tert-butyl-1-bromo-2-methoxy-5-methylbenzene (45 g) was added dropwise at -40°C over 20 minutes a 1.6 M hexane solution (115 ml) of n-butyllithium. The resulting mixture was kept at -40°C for one hour, and then tetrahydrofuran (31.5 ml) was added dropwise thereto.

The mixture obtained above was added dropwise at -40°C into a solution consisting of dichlorodimethylsilane (131 g) and hexane (306 ml). The resulting mixture was brought up to room temperature over 2 hours and further stirred for 12 hours.

The solvent and the excess of dichlorodimethylsilane were distilled off under reduced pressure from the reaction mixture, and the residue was treated with hexane

to extract hexane solubles therefrom. The hexane solution obtained was stripped of the solvent to obtain pale yellow oily (3-tert-butyl-2-methoxy-5-methylphenyl)-chlorodimethylsilane (41.9 g, yield 84%).

- 5 ¹H NMR (CDCl₃) δ 0.68 (s, 6H), 1.32 (s, 9H),
2.23 (s, 3H), 3.70 (s, 3H), 7.20 (s, 1H), 7.21
(s, 1H)
Mass spectra (EI, m/e) 270, 255, 219, 189, 145,
128, 109, 93

10 Example 63

Synthesis of (3-tert-butyl-2-methoxy-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

- 15 Into a solution consisting of (3-tert-butyl-2-methoxy-5-methylphenyl)chlorodimethylsilane (5.24 g) and tetrahydrofuran (50 ml) was added at -35°C tetramethylcyclopentadienyllithium (2.73 g), the resulting mixture was brought up to room temperature over 2 hours and further stirred at room temperature for 10 hours.

- 20 The reaction mixture obtained was stripped of the solvent under reduced pressure, and the residue was treated with hexane to extract hexane solubles therefrom. The hexane solution obtained was stripped of the solvent under reduced pressure to obtain yellow oily (3-tert-butyl-2-methoxy-5-methylphenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (6.69 g, yield 97%).
- 25

¹H NMR (C₆D₆) δ 0.31 (s, 6H), 1.49 (s, 9H), 1.81 (s, 6H), 1.89 (s, 6H), 2.22 (s, 3H), 3.60 (s,

3H), 5.23 (s, 3H), 7.23 (br, 2H)

Mass spectra (EI, m/e) 356, 299, 235, 205, 179,
161, 89

Example 64

5 Synthesis of dimethylsilyl(tetramethylcyclo-
pentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
dichloride

To a solution consisting of (3-tert-butyl-2-
methoxy-5-methyl-phenyl)dimethyl(2,3,4,5-tetramethyl-
10 cyclopentadienyl)silane (10.04 g), toluene (100 ml) and
triethylamine (6.30 g) was added dropwise at -70°C a 1.63
M hexane solution (19.0 ml) of n-butyllithium, the
resulting mixture was then brought up to room temperature
over 2 hours and further kept at room temperature for 12
15 hours.

Under nitrogen atmosphere at 0°C, the mixture
obtained above was added dropwise to the toluene solution
(50 ml) of titanium tetrachloride (4.82 g), the resulting
mixture was brought up to room temperature over 1 hour
20 and then heated under reflux for 10 hours.

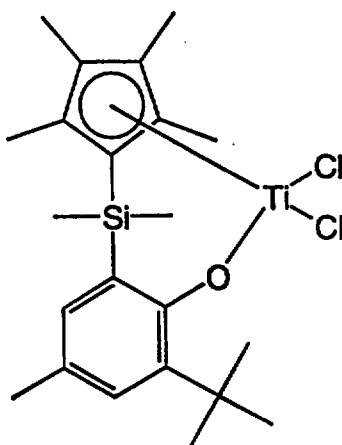
The reaction mixture was filtered, and the
solvent was distilled off from the filtrate. The result-
ing residue was recrystallized from a toluene-hexane
solvent mixture to obtain columnar orange crystals of
25 dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-
5-methyl-2-phenoxy)titanium dichloride having the
following structural formula (3.46 g, yield 27%).

^1H NMR (CDCl_3) δ 0.57 (s, 6H), 1.41 (s, 9H),

2.15 (s, 6H), 2.34 (s, 6H), 2.38 (s, 3H), 7.15 (s, 1H), 7.18 (s, 1H)

^{13}C NMR (CDCl_3) δ 1.25, 14.48, 16.28, 22.47, 31.25, 36.29, 120.23, 130.62, 131.47, 133.86, 135.50, 137.37, 140.82, 142.28, 167.74

Mass spectra (CI, m/e) 458



Example 65

An autoclave with an inner volume of 3 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then 1 ℓ of toluene as the solvent and 20 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutylaluminum, then 2.0 μmol of isopropylidene(cyclopentadienyl)(3-tert-butyldimethylsilyl-5-methyl-2-phenoxy)-titanium dichloride synthesized in Example 18, and succeedingly 6.0 μmol of triphenylmethyl tetrakis-

(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-
5 hexene-1 copolymer having an SCB of 25.0, $[\eta_1]$ of 0.77, molecular weight (M_w) of 35,000, molecular weight distribution (M_w/M_n) of 2.1 and melting point of 94.2°C was produced at a rate of 2.65×10^7 g per mol of titanium per hour.

10 Example 66

An autoclave with an inner volume of 0.4 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 198 ml of toluene as the solvent and 2 ml of hexene-1 as
15 the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of
20 triisobutylaluminum, then 1.0 μ mol of isopropylidene-(cyclopentadienyl)(3,5-dimethyl-2-phenoxy)titanium dichloride synthesized in Example 10, and succeedingly 3.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)-borate were successively charged into the reactor.
25 Polymerization was carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-

hexene-1 copolymer having an SCB of 14.7, $[\eta_1]$ of 1.67, molecular weight (Mw) of 120,000, molecular weight distribution (Mw/Mn) of 11.3 and melting point of 110.6°C was produced at a rate of 2.65×10^7 g per mol of titanium per hour.

Example 67

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then, 198 ml of toluene as the solvent and 2 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of triisobutylaluminum, then 1.0 μ mol of isopropylidene-(cyclopentadienyl)(3-phenyl-2-phenoxy)titanium dichloride synthesized in Example 12, and succeedingly 3.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 18.7, $[\eta_1]$ of 0.62, molecular weight (Mw) of 27,000, molecular weight distribution (Mw/Mn) of 6.7 and melting point of 106.0°C was produced at a rate of 8.82×10^6 g per mol of titanium

per hour.

Example 68

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 198 ml of hexane as the solvent and 2 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of triisobutylaluminum, then 1.0 μ mol of isopropylidene (3-tert-butylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride synthesized in Example 14, and successingly 3.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 32.0, $[\eta_1]$ of 1.34, molecular weight (Mw) of 69,000, molecular weight distribution (Mw/Mn) of 1.9 and melting point of 82.7°C was produced at a rate of 1.75×10^7 g per mol of titanium per hour.

Example 69

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure

and the inner atmosphere was replaced with argon. Then, 185 ml of cyclohexane as the solvent and 15 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 180°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 25 kg/cm². After the inside of the system had become stable, 0.25 mmol of triisobutylaluminum, then 1.0 μ mol of dimethylsilyl-(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 64, and succeedingly 3.0 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate as the toluene solution thereof were successively charged into the reactor. Polymerization was carried out for 2 minutes while controlling the temperature at 180°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 33.6, $[\eta_1]$ of 1.03, molecular weight (Mw) of 51,000, molecular weight distribution (Mw/Mn) of 2.0 and melting point of 87.4°C was produced at a rate of 3.36×10^6 g per mol of titanium per 2 min.

Example 70

An autoclave with an inner volume of 3 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 ℓ of hexane as the solvent and 10 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was

brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutyl-
5 aluminum, then 0.5 μmol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1(1), and succeedingly 3.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate were successively charged into the reactor.
10 Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 27.7, [η₁] of 0.99, molecular weight (M_w) of 46,000, molecular weight
15 distribution (M_w/M_n) of 1.7 and melting point of 93.4°C was produced at a rate of 1.60 × 10⁷ g per mol of titanium per hour.

Example 71

An autoclave with an inner volume of 3 ℓ fitted
20 with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 ℓ of hexane as the solvent and 20 ml of hexene-1 as the α-olefin were placed in the autoclave, and the reactor was brought up to 80°C. After the temperature rise, ethylene
25 was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 0.5 mmol of triethylaluminum,

then 2.0 μmol of isopropylidene (cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1(1), and succeedingly 6.0 μmol of triphenylmethyl tetrakis(pentafluorophenyl)borate were
5 successively charged into the reactor. Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 21.8, $[\eta_1]$ of 1.06,
10 molecular weight (M_w) of 52,000, molecular weight distribution (M_w/M_n) of 1.8 and melting point of 99.5°C was produced at a rate of 1.52×10^7 g per mol of titanium per hour.

Example 72

15 An autoclave with an inner volume of 3 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 ℓ of toluene as the solvent and 20 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was
20 brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 12.0 μmol of triphenylmethyl tetrakis(pentafluorophenyl)borate, then 0.5 mmol of
25 triisobutylaluminum, and thereafter 2.0 μmol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1(1)

which had been precontacted beforehand with 0.5 mmol of triisobutylaluminum for 2 minutes were successively charged into the reactor. Polymerization was carried out for 40 minutes while controlling the temperature at 80°C.

5 As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 25.8, $[\eta_1]$ of 1.18, molecular weight (Mw) of 60,000, molecular weight distribution (Mw/Mn) of 1.9 and melting point of 94.9°C was produced at a rate of 2.27×10^7 g per mol of titanium
10 per hour.

Example 73

 An autoclave with an inner volume of 3 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 ℓ of
15 toluene as the solvent and 20 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the
20 system had become stable, 1.0 mmol of triisobutylaluminum, then 2.0 μ mol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1(1) which had been stored as a hexane solution under nitrogen at room
25 temperature for one month, and succeedingly 6.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization

was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 24.8, $[\eta_1]$ of 1.18, molecular weight (Mw) of 61,000, molecular weight distribution (Mw/Mn) of 1.9 and melting point of 96.3°C was produced at a rate of 3.51×10^7 g per mol of titanium per hour.

Example 74

10 An autoclave with an inner volume of 3 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 l of toluene as the solvent and 20 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was
15 brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutyl-aluminum, then 2.0 μ mol of isopropylidene(cyclopenta-
20 dienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1(1), and succeedingly 1.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)-borate were successively charged into the reactor. Polymerization was carried out for 30 minutes while control-
25 ling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 23.3, $[\eta_1]$ of 1.24,

molecular weight (Mw) of 67,000, molecular weight distribution (Mw/Mn) of 1.7 and melting point of 96.7°C was produced at a rate of 2.00×10^7 g per mol of titanium per hour.

5 Example 75

An autoclave with an inner volume of 3 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 l of toluene as the solvent and 20 ml of hexene-1 as the α -
10 olefin were placed in the autoclave, and the reactor was brought up to 40°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutyl-
15 aluminum, then 2.0 μ mol of isopropylidene(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1(1), and succeedingly 6.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)-
borate were successively charged into the reactor. Poly-
20 merization was carried out for 10 minutes while controlling the temperature at 40°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 14.8, $[\eta_1]$ of 1.93, molecular weight (Mw) of 110,000, molecular weight
25 distribution (Mw/Mn) of 2.1 and melting point of 103.8°C was produced at a rate of 1.27×10^8 g per mol of titanium per hour.

Example 76

An autoclave with an inner volume of 3 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 l of
5 hexane as the solvent and 10 ml of hexene-1 as the α -olefin were placed in the autoclave, hydrogen was added thereinto to a hydrogen pressure of 100 mmHg, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the
10 ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutylaluminum, then 2.0 μ mol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride synthesized in Example 64, and
15 succeedingly 3.0 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-
20 hexene-1 copolymer having an SCB of 27.2, $[\eta_1]$ of 1.69, molecular weight (Mw) of 99,000, molecular weight distribution (Mw/Mn) of 1.9 and melting point of 83.1°C was produced at a rate of 1.50×10^7 g per mol of titanium per hour.

25 Example 77

An autoclave with an inner volume of 3 l fitted with a stirrer was dried under reduced pressure and the

inner atmosphere was replaced with argon. Then, 1 l of hexane as the solvent and 20 ml of hexene-1 as the α -olefin were placed in the autoclave, hydrogen was added thereinto to a hydrogen pressure of 200 mmHg, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 0.75 mmol of triisobutylaluminum, then 0.5 μ mol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 64, and succeedingly 1.5 μ mol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 26.8, $[\eta]$ of 2.22, molecular weight (M_w) of 140,000, molecular weight distribution (M_w/M_n) of 1.6 and melting point of 85.6°C was produced at a rate of 2.00×10^7 g per mol of titanium per hour.

Example 78

An autoclave with an inner volume of 3 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 l of hexane as the solvent and 20 ml of hexene-1 as the α -

olefin were placed in the autoclave, hydrogen was added thereinto to a hydrogen pressure of 100 mmHg, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the
5 ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 0.75 mmol of triisobutylaluminum, then 1.0 μmol of dimethylsilyl-(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 64,
10 and succeedingly 2.0 μmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-
15 hexene-1 copolymer having an SCB of 24.7, $[\eta_1]$ of 2.77, molecular weight (Mw) of 170,000, molecular weight distribution (Mw/Mn) of 1.8 and melting point of 87.4°C was produced at a rate of 3.60×10^7 g per mol of titanium per hour.

20 Example 79

An autoclave with an inner volume of 3 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 ℓ of hexane as the solvent and 10 ml of hexene-1 as the α-
25 olefin were placed in the autoclave, hydrogen was added thereinto to a hydrogen pressure of 100 mmHg, and the reactor was brought up to 80°C. After the temperature

rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutylaluminum, then 0.5 μmol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-
5 titanium dichloride synthesized in Example 64, and succeedingly 3.0 μmol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 30 minutes
10 while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 25.2, $[\eta_1]$ of 1.80, molecular weight (Mw) of 110,000, molecular weight distribution (Mw/Mn) of 1.8 and melting point of 84.8°C
15 was produced at a rate of 4.00×10^7 g per mol of titanium per hour.

Example 80

An autoclave with an inner volume of 3 ℓ fitted with a stirrer was dried under reduced pressure and the
20 inner atmosphere was replaced with argon. Then, 1 ℓ of hexane as the solvent and 20 ml of hexene-1 as the α-olefin were placed in the autoclave, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure
25 being controlled at 12 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutylaluminum, then 2.0 μmol of dimethylsilyl(tetramethyl-

cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-
titanium dichloride synthesized in Example 64, and
succeedingly 6.0 μmol of triphenylmethyl tetrakis-
(pentafluorophenyl)borate were successively charged into
5 the reactor. Polymerization was carried out for 30
minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-
hexene-1 copolymer having an SCB of 24.5, $[\eta_1]$ of 4.06
and melting point of 84.9°C was produced at a rate of
10 3.88×10^7 g per mol of titanium per hour.

Example 81

An autoclave with an inner volume of 3 ℓ fitted
with a stirrer was dried under reduced pressure and the
inner atmosphere was replaced with argon. Then, 1 ℓ of
15 toluene as the solvent and 20 ml of hexene-1 as the α -
olefin were placed in the autoclave, and the reactor was
brought up to 80°C. After the temperature rise, ethylene
was fed into the reactor while the ethylene pressure
being controlled at 12 kg/cm². After the inside of the
20 system had become stable, 1.0 mmol of triethylaluminum,
then 2.0 μmol of dimethylsilyl(tetramethylcyclopenta-
dienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium
dichloride synthesized in Example 64, and succeedingly
6.0 μmol of triphenylmethyl tetrakis(pentafluorophenyl)-
25 borate were successively charged into the reactor.
Polymerization was carried out for 30 minutes while
controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 25.8, $[\eta_1]$ of 2.97 and melting point of 85.9°C was produced at a rate of 1.87×10^7 g per mol of titanium per hour.

5 Example 82

An autoclave with an inner volume of 3 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 1 ℓ of toluene as the solvent and 20 ml of hexene-1 as the α-olefin were placed in the autoclave, and the reactor was brought up to 80°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 12 kg/cm². After the inside of the system had become stable, 1.0 mmol of triisobutyl-
10 aluminum, then 1.0 μmol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride synthesized in Example 64, and
15 succeedingly 6.0 μmol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the
20 reactor. Polymerization was carried out for 30 minutes while controlling the temperature at 80°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 27.2, $[\eta_1]$ of 4.27 and melting point of 84.1°C was produced at a rate of
25 8.70×10^7 g per mol of titanium per hour.

Example 83

An autoclave with an inner volume of 0.4 ℓ

fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 198 ml of toluene as the solvent and 2 ml of hexene-1 as the α -olefin were placed in the autoclave, and the

5 reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 1.0 mmol of methylalumoxane (PMAO, mfd. by Tosoh-Akzo Corp.), then

10 1.0 μ mol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 64, and succeedingly 3.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization

15 was carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 28.3, $[\eta_1]$ of 3.01 and melting point of 80.6°C was produced at a rate of

20 2.76×10^7 g per mol of titanium per hour.

Example 84

An autoclave with an inner volume of 0.4 ℓ fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then,

25 198 ml of toluene as the solvent and 2 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature

rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of triisobutylaluminum, then 1.0 μmol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-
5 titanium dichloride synthesized in Example 64, and succeedingly 3.0 μmol of tris(pentafluorophenyl)borane were successively charged into the reactor. Polymerization was carried out for 10 minutes while controlling the
10 temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 25.4, $[\eta_1]$ of 4.45 and melting point of 85.2°C was produced at a rate of 6.48×10^6 g per mol of titanium per hour.

15 Example 85

An autoclave with an inner volume of 0.4 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 198 ml of hexane as the solvent and 2 ml of hexene-1 as
20 the α-olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 1.0 mmol of
25 methylalumoxane (MMAO type 3A, mfd. by Tosoh-Akzo Corp., toluene solution), then 1.0 μmol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-

titanium dichloride synthesized in Example 64, and
succeedingly 3.0 μmol of triphenylmethyl tetrakis(penta-
fluorophenyl)borate were successively charged into the
reactor. Polymerization was carried out for 10 minutes
5 while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-
hexene=1 copolymer having an SCB of 24.7, $[\eta_1]$ of 1.74,
molecular weight (M_w) of 100,000, molecular weight
distribution (M_w/M_n) of 2.5 and melting point of 93.8°C
10 was produced at a rate of 1.29×10^7 g per mol of titanium
per hour.

Example 86

An autoclave with an inner volume of 0.4 ℓ
fitted with a stirrer was dried under reduced pressure
15 and the inner atmosphere was replaced with argon. Then,
198 ml of hexane as the solvent and 2 ml of hexene-1 as
the α -olefin were placed in the autoclave, and the
reactor was brought up to 60°C. After the temperature
rise, ethylene was fed into the reactor while the
20 ethylene pressure being controlled at 6 kg/cm^2 . After the
inside of the system had become stable, 1.0 mmol of
isobutylalumoxane (PBAO mfd. by Tosoh-Akzo Corp.), then
1.0 μmol of dimethylsilyl(tetramethylcyclopentadienyl)(3-
tert-butyl-5-methyl-2-phenoxy)titanium dichloride
25 synthesized in Example 64, and succeedingly 3.0 μmol of
triphenylmethyl tetrakis(pentafluorophenyl)borate were
successively charged into the reactor. Polymerization

was carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 35.0, $[\eta_1]$ of 3.51 and melting point of 74.1°C was produced at a rate of 3.67×10^7 g per mol of titanium per hour.

Example 87

A toluene solution of methylalumoxane (PMAO, mfd. by Tosoh-Akzo Corp.) was stripped of the solvent and dried under reduced pressure. The dried solid methylalumoxane was again dissolved in toluene.

An autoclave with an inner volume of 0.4 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 198 ml of toluene as the solvent and 2 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 1.0 mmol of the toluene solution of methylalumoxane obtained by treating, drying and redissolving as described above, then 1.0 μ mol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 64, and succeedingly 3.0 μ mol of triphenylmethyl tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was

carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 33.8, $[\eta_1]$ of 3.54, and melting point of 75.6°C was produced at a rate of 3.21×10^7 g per mol of titanium per hour.

Example 88

An autoclave with an inner volume of 0.4 l fitted with a stirrer was dried under reduced pressure and the inner atmosphere was replaced with argon. Then, 198 ml of toluene as the solvent and 2 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the inside of the system had become stable, 0.25 mmol of triisobutylaluminum, then 1.0 μ mol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride synthesized in Example 64, and successingly 3.0 μ mol of N,N-dimethylanilinium tetrakis-(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 31.4, $[\eta_1]$ of 4.17 and melting point of 83.0°C was produced at a rate of 3.56×10^7 g per mol of titanium per hour.

Example 89

An autoclave with an inner volume of 0.4 l fitted with a stirrer was dried under reduced pressure, and the inner atmosphere was replaced with argon. Then, 5 198 ml of hexane as the solvent and 2 ml of hexene-1 as the α -olefin were placed in the autoclave, and the reactor was brought up to 60°C. After the temperature rise, ethylene was fed into the reactor while the ethylene pressure being controlled at 6 kg/cm². After the 10 inside of the system had become stable, 0.25 mmol of triisobutylaluminum, then 1.0 μ mol of dimethylsilyl-(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 64, and succeedingly 3.0 μ mol of N,N-dimethylanilinium 15 tetrakis(pentafluorophenyl)borate were successively charged into the reactor. Polymerization was carried out for 10 minutes while controlling the temperature at 60°C.

As the result of polymerization, an ethylene-hexene-1 copolymer having an SCB of 29.0, $[\eta_1]$ of 3.64 20 and melting point of 80.9°C was produced at a rate of 3.18×10^7 g per mol of titanium per hour.

Example 90

A 2 l glass separable flask fitted with a reflux tube, three dropping funnels, thermometer and 25 monomer blow-in tube was thoroughly flushed with nitrogen, and then 1 l of hexane was placed therein. The feed of ethylene gas and of propylene gas were started

through the blow-in tube at a rate of 8 l/min and 2 l/min, respectively. While the inner temperature being controlled at 30°C with an external water bath jacket and after confirming that the content of the flask had been

5 thoroughly saturated with respective gases, catalyst components were added to the flask from the dropping funnels in the successive order of 0.25 mmol of triisobutylaluminum (1 mmol/ml hexane solution), 0.001 mmol of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-

10 butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1(1) dissolved in hexane, and finally 0.005 mmol of triphenylmethyl tetrakis(pentafluorophenyl)borate dissolved in toluene, to initiate polymerization. After the lapse of 30 minutes, 10 ml of ethanol was added to

15 stop polymerization. After the stop of polymerization, the resulting hexane solution containing polymer was concentrated under reduced pressure and then added into 1 l of ethanol solvent, to precipitate the polymer. The precipitated polymer was dried under reduced pressure at

20 80°C for twenty-four hours. Resultantly 5.6 g of polymer was obtained. The analysis of the polymer showed that the polymer contained 57.8% by weight of propylene units and 42.2% by weight of ethylene units and had an intrinsic viscosity $[\eta_2]$ of 5.64 dl/g.

25 Example 91

Polymerization was carried out in the same manner as in the polymerization of ethylene and propylene

of Example 90 except that 8 mmol of 5-ethylidene-2-norbornene (ENB) was further added. Resultantly, 1.7 g of polymer was obtained. The analysis of the polymer showed that the polymer contained 39.7% by weight of propylene units, 53.5% by weight of ethylene units and 6.75% by weight of ENB units and had an intrinsic viscosity $[\eta_2]$ of 5.64 dl/g.

Example 92

Polymerization was carried out in the same manner as in the polymerization of ethylene and propylene of Example 90 except that butene-1 was fed at a rate of 0.06 l/min in place of propylene, and the amounts of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride and triphenylmethyl tetrakis(pentafluorophenyl)borate used were changed to 0.0002 mmol and 0.001 mmol, respectively. Resultantly, 1.7 g of polymer was obtained. The analysis of the polymer showed that the polymer contained 9.3% by weight of butene-1 units and 90.7% by weight of ethylene units and had an intrinsic viscosity $[\eta_2]$ of 5.99 dl/g.

Example 93

A stainless steel autoclave with an inner volume of 2 l fitted with an electromagnetic stirrer, thermometer and catalyst addition apparatus was thoroughly flushed with nitrogen, and then 800 ml of toluene, 32 g of propylene, 16 mmol of ENB and 50 g of ethylene were charged thereinto. Then the inner temperature was

controlled at 60°C by means of an external warm-water jacket, and after the temperature had become stable, there were added from the catalyst addition apparatus, in the successive order, 0.50 mmol of triisobutylaluminum, 5 0.001 mmol of dimethylsilyl(tetramethylcyclopentadienyl)-(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride synthesized in Example 1 dissolved in hexane, and finally 0.015 mmol of triphenylmethyl tetrakis(pentafluorophenyl)borate, to initiate polymerization. At the point 10 of time when 1 hour had elapsed after the initiation of polymerization, 10 ml of ethanol was added to stop the polymerization. After the stop of polymerization, unreacted monomers were purged and then a toluene solution containing polymer dissolved therein was 15 recovered. The toluene solution was concentrated by heating, and then about 1 l of ethanol was added thereto to precipitate the polymer. The precipitated polymer was dried in a vacuum dryer for twenty-four hours to obtain 53.2 g of polymer. The analysis of the polymer showed 20 that the polymer had a composition of 30.8% by weight of propylene units, 66.7% by weight of ethylene units and 2.5% by weight of ENB units and had an intrinsic viscosity $[\eta_2]$ of 5.98 dl/g.

Example 94

25 The same procedures as in the polymerization of Example 93 were followed except that ENB was not used and the amount of dimethylsilyl(tetramethylcyclopentadienyl)-

(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride was changed to 0.0005 mmol. Resultantly 40.6 g of polymer was obtained. The analysis of the polymer showed that the polymer had a composition of 32.4% by weight of propylene units and 67.6% by weight of ethylene units and had an intrinsic viscosity $[\eta_2]$ of 5.21 dl/g.

Example 95

The same procedures as in the polymerization of Example 94 were followed to polymerize ethylene and butene-1 except that 120.0 g of butene-1 was used in place of propylene, the amount of ethylene was changed to 59.0 g, the amount of triphenylmethyl tetrakis(pentafluorophenyl)borate was changed to 0.002 mmol and polymerization was stopped at the point of time when the amount of ethylene absorbed had reached 3.0 g. As the result, 3.45 g of polymer was obtained. The analysis of the polymer showed that the polymer had a composition of 53.5% by weight of butene-1 units and 46.5% by weight of ethylene units, and had an intrinsic viscosity $[\eta_2]$ of 1.46 dl/g.

Example 96

The same procedures as in the polymerization of Example 95 were followed to polymerize ethylene and butene-1 except that the amounts of butene-1, ethylene and triphenylmethyl tetrakis(pentafluorophenyl)borate used were changed to 15.0 g, 43.0 g and 0.003 mmol, respectively, and the polymerization temperature was

changed to 80°C. Resultantly, 3.47 g of polymer was obtained. The analysis of the polymer showed that the polymer had a composition of 12.0% by weight of butene-1 units and 88.0% by weight of ethylene units and had an
5 intrinsic viscosity $[\eta_2]$ of 3.37 dl/g.

Example 97

The same procedures as in the polymerization of Example 95 were followed except that the amounts of ethylene and butene-1 used were changed to 56 g and 56 g,
10 respectively, 8 mmol of ENB was additionally used, and the amounts of dimethylsilyl(tetramethylcyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)titanium dichloride, triphenylmethyl tetrakis(pentafluorophenyl)-borate and triisobutylaluminum used were changed to 0.002
15 mmol, 0.0025 mmol and 1.00 mmol, respectively. Resultantly, 10.65 g of polymer was obtained. The analysis of the polymer showed that the polymer had a composition of 26.7% by weight of butene-1 units, 71.8% by weight of ethylene units and 1.46% by weight of ENB units and had
20 an intrinsic viscosity $[\eta_2]$ of 2.08 dl/g.

Example 98

A 2 l glass separable flask fitted with a reflux tube, three dropping funnels, thermometer and monomer blow-in tube was thoroughly flushed with
25 nitrogen, and then 1 l of toluene was placed therein. The feed of ethylene gas and of propylene gas were started through the blow-in tube at a rate of 8 l/min and

2 l/min, respectively. While the inner temperature being controlled at 30°C with an external water bath jacket and after confirming that the content of the flask had been thoroughly saturated with respective gases, catalysts
5 were added to the flask from the dropping funnels in the successive order of 0.10 mmol of triisobutylaluminum (1 mmol/ml hexane solution), 0.002 mmol of isopropylidene-(cyclopentadienyl)(3-tert-butyl-5-methyl-2-phenoxy)-titanium dichloride synthesized in Example 1(1) dissolved
10 in hexane, and finally 0.010 mmol of triphenylmethyl tetrakis(pentafluorophenyl)borate dissolved in toluene, to initiate polymerization. After the lapse of 30 minutes, 10 ml of ethanol was added to stop polymerization. After the stop of polymerization, the resulting
15 hexane solution containing polymer was concentrated under reduced pressure and then added into 1 l of ethanol solvent to precipitate the polymer. The precipitated polymer was dried under reduced pressure at 80°C for twenty-four hours. Resultantly, 15.4 g of polymer was
20 obtained. The analysis of the polymer showed that the polymer contained 49.0% by weight of propylene units and 51.0% by weight of ethylene units and had an intrinsic viscosity $[\eta_2]$ of 0.50 dl/g.

Example 99

25 The same procedures as in the polymerization of ethylene and propylene of Example 98 were followed except that the feed rate of ethylene was changed to 7 l/min and

that of propylene to 1 l/min, and 4 mmol of 5-ethylidene-2-norbornene (ENB) was added. Resultantly, 6.6 g of polymer was obtained. The analysis of the polymer showed that the polymer contained 39.0% by weight of propylene
5 units, 59.3% by weight of ethylene units and 1.75% by weight of ENB units and had an intrinsic viscosity $[\eta_2]$ of 1.35 dl/g.

Example 100

The same procedures as in the polymerization of
10 ethylene and propylene of Example 98 were followed except that butene-1 was fed at a rate of 0.11 l/min in place of propylene. Resultantly, 4.2 g of polymer was obtained. The analysis of the polymer showed that the polymer contained 9.2% by weight of butene-1 units and 90.8% by
15 weight of ethylene units and had an intrinsic viscosity $[\eta_2]$ of 1.70 dl/g.

Example 101

The same procedures as in the polymerization of ethylene and butene-1 of Example 100 were followed except
20 that the polymerization temperature was changed to 60°C and the feed rate of butene-1 to 0.13 l/min. Resultantly, 10.6 g of polymer was obtained. The analysis of the polymer showed that the polymer contained 9.2% by weight of butene-1 units and 90.8% by weight of ethylene units
25 and had an intrinsic viscosity $[\eta_2]$ of 1.11 dl/g.

Example 102

The same procedures as in the polymerization of

ethylene and butene-1 of Example 100 were followed except that trimethylaluminum was used in place of triisobutylaluminum. As the result, 4.8 g of polymer was obtained. The analysis of the polymer showed that the polymer
5 contained 11.4% by weight of butene-1 units and 88.6% by weight of ethylene units and had an intrinsic viscosity $[\eta_2]$ of 0.87 dl/g.

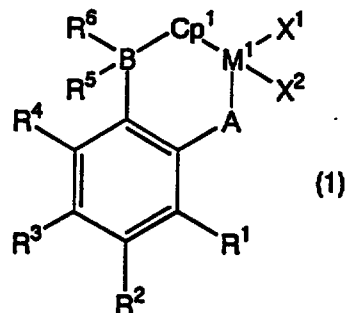
INDUSTRIAL APPLICABILITY

As set forth above, according to the present
10 invention, there are provided a complex soluble in saturated hydrocarbon solvents which has a ligand comprising an aromatic ring having a hetero atom in the substituent and a cyclopentadienyl ring linked with each other through a covalent bonding group, and an olefin
15 polymerization catalyst containing the complex which has a high activity at industrially efficient temperatures. Furthermore, by using the catalyst, olefin polymers, particularly linear low density polyethylene, ethylene- α -olefin copolymer rubber and ethylene- α -olefin-non-
20 conjugated diene copolymer rubber, which have a high molecular weight and narrow composition distribution can be produced with good efficiency.



CLAIMS

1. A transition metal complex represented by the formula (1)



wherein M^1 is a transition metal atom of the group 4 of
5 the periodic table of elements, A is an atom of the group
16 of the periodic table of elements and B is an atom of
the group 14 of the periodic table of elements; Cp^1 is a
group having a cyclopentadiene type anionic skeleton; and
 X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently a
10 hydrogen atom, halogen atom, alkyl group with the number
of carbon atoms of 1-20 optionally substituted with at
least one halogen atom, aralkyl group with the number of
carbon atoms of 7-20 optionally substituted with at least
one halogen atom, aryl group with the number of carbon
15 atoms of 6-20 optionally substituted with at least one
halogen atom, substituted silyl group with the number of
carbon atoms of 1-20 optionally substituted with at least
one halogen atom, alkoxy group with the number of carbon
atoms of 1-20 optionally substituted with at least one
20 halogen atom, aralkyloxy group with the number of carbon



atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the
5 number of carbon atoms of 2-20, provided that R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally combine with each other to form a ring.

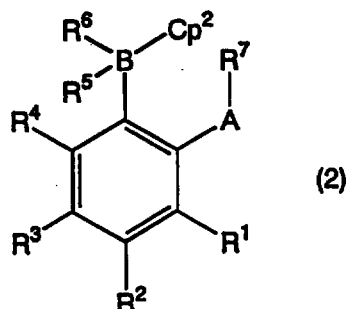
2. The transition metal complex according to claim 1 wherein A in the formula (1) is an oxygen atom.

10 3. The transition metal complex according to claim 1 or 2 wherein R^1 in the formula (1) is an alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally
15 substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom or substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom.

20 4. The transition metal complex according to any of claims 1-3 wherein X^1 and X^2 in the formula (1) is each independently a halogen atom, alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of
25 carbon atoms of 7-20 optionally substituted with at least one halogen atom, or aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom.

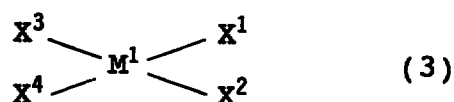


5. A process for producing the transition metal complex according to claim 1 which comprises reacting a substituted cyclopentadienyl compound represented by the formula (2)



5 wherein Cp^2 is a group having a cyclopentadiene skeleton, R^7 is a hydrocarbon group optionally substituted with at least one halogen atom or a tri-substituted silyl group, and A, B, R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are respectively the same as defined above, with a base, and then reacting the

10 resulting reaction product with a transition metal compound represented by the formula (3)



wherein X^3 and X^4 are each independently a hydrogen atom, halogen atom, alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen

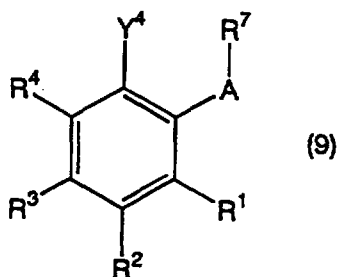
15 atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom,



substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, 5 aralkyloxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon 10 atoms of 2-20, and M^1 , X^1 and X^2 are respectively the same as defined above.

6. The process for producing the transition metal complex according to claim 5 wherein the substituted cyclopentadienyl compound represented by the formula (2) 15 is produced by any of the process [1]-[3] described below:

[I] a process which comprises reacting a halogenated aryl compound represented by the formula (9)

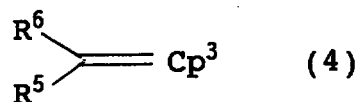


wherein Y^4 is a halogen atom, and A , R^1 , R^2 , R^3 , R^4 , and R^7 20 are respectively the same as defined above, with an



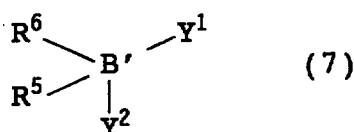


organoalkali metal salt or metallic magnesium, then reacting the reaction product with a cyclopentadienylidene compound represented by the formula (4)

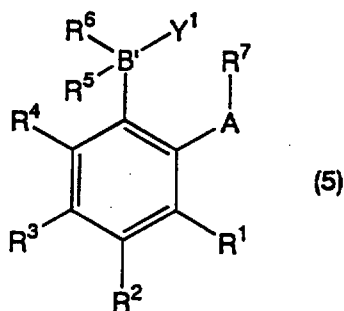


wherein Cp^3 is a group having a cyclopentadienylidene skeleton, and R^5 and R^6 are respectively the same as defined above, and then reacting the resulting reaction product with water;

[II] a process which comprises reacting the halogenated aryl compound represented by the formula (9) with a dihalide compound represented by the formula (7)



wherein Y^1 and Y^2 are each a halogen atom, B' is an atom of group 14 other than carbon atom, and R^5 and R^6 are respectively the same as defined above, in the presence of an organoalkali metal compound or metallic magnesium to obtain a halide compound represented by the formula (5)



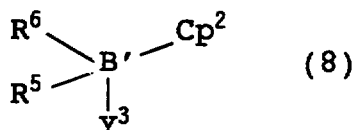


wherein A, B', R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and Y¹ are respectively the same as defined above, and then reacting the halide compound with a cyclopentadienyl metal salt represented by the formula (6)



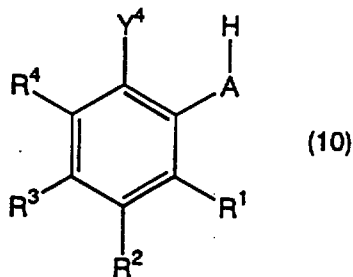
wherein M² is an alkali metal atom, and Cp² is as defined above;

[III] a process which comprises reacting the halogenated aryl compound represented by the formula (9)
10 with a halide compound represented by the formula (8)



wherein Y³ is a halogen atom, and B', Cp², R⁵ and R⁶ are respectively the same as defined above, in the presence of an organoalkali metal compound or metallic magnesium.

7. The process for producing the transition metal
15 complex according to claim 6 wherein the halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound represented by the formula (10)





wherein A, R¹, R², R³, R⁴ and Y⁴ are respectively the same as defined above, with a halide represented by the formula (11)

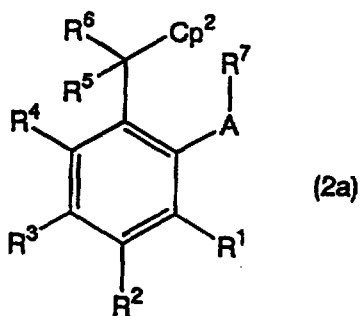


5 wherein Y⁵ is a halogen atom and R⁷ is as defined above, in the presence of a base.

8. A substituted cyclopentadienyl compound represented by the formula (2).

9. A process for producing a substituted cyclo-

10 pentadienyl compound represented by the formula (2a)



wherein A, Cp², R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are respectively the same as defined above, which comprises reacting a halogenated aryl compound represented by the formula (9) with an organoalkali metal salt or metallic
15 magnesium, then reacting the reaction product with a cyclopentadienylidene compound represented by the formula (4), and then reacting the resulting reaction product with water.

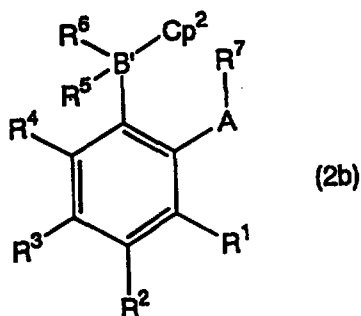
10. The process for producing a substituted cyclo-
20 pentadienyl compound according to claim 9 wherein the





halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound represented by the formula (10) with a halide represented by the formula (11) in the presence of a base.

- 5 11. A process for producing a substituted cyclopentadienyl compound represented by the formula (2b)



(2b)

- wherein A, B', Cp², R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are respectively the same as defined above, which comprises reacting a halide compound represented by the formula (5) with a cyclopentadienyl metal salt represented by the formula (6).

12. The process for producing a substituted cyclopentadienyl compound according to claim 11 wherein the halide compound represented by the formula (5) is produced by reacting a halogenated aryl compound represented by the formula (9) with a dihalide compound represented by the formula (7) in the presence of an organoalkali metal compound or metallic magnesium.

13. The process for producing a substituted cyclopentadienyl compound according to claim 12 wherein



the halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound represented by the formula (10) with a halide represented by the formula (11) in the presence of a base.

- 5 14. A process for producing a substituted cyclopentadienyl compound represented by the formula (2b) which comprises reacting a halogenated aryl compound represented by the formula (9) with a halide compound represented by the formula (8) in the presence of an
10 organoalkali metal compound or metallic magnesium.
15. The process for producing a substituted cyclopentadienyl compound according to claim 14 wherein the halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound
15 represented by the formula (10) with a halide represented by the formula (11) in the presence of a base.
16. A halide compound represented by the formula (5).
17. A process for producing the halide compound
20 according to claim 16 which comprises reacting a halogenated aryl compound represented by the formula (9) with a dihalide compound represented by the formula (7) in the presence of an organoalkali metal compound or metallic magnesium.
- 25 18. The process according to claim 17 wherein the halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound represented by the formula (10) with a halide represented





by the formula (11) in the presence of a base.

19. A halogenated aryl compound represented by the formula (9) wherein R^7 is an alkenyl group.

20. A process for producing the halogenated aryl compound according to claim 19 which comprises reacting a halogenated aryl compound represented by the formula (10) with a halide represented by the formula (11) wherein R^7 is an alkenyl group, in the presence of a base.

21. An olefin polymerization catalyst which comprises the transition metal complex according to any of claims 1-4 and a compound (A) described below:

(A) any one of the following compounds (A1)-(A3) or the mixture of two or three thereof,

(A1) an organoaluminum compound represented by the formula $E^1_a Al Z_{3-a}$

(A2) a cyclic aluminoxane having the structure represented by the formula $\{Al(E^2)-O-\}_b$

(A3) a linear aluminoxane having the structure represented by the formula $E^3\{Al(E^3)-O-\}_c Al E^3_2$

wherein E^1-E^3 are each a hydrocarbon group with the number of carbon atoms of 1-8, and all E^1 , all E^2 and all E^3 may be the same with or different from each other; Z is a hydrogen atom or halogen atom, and all Z may be the same with or different from each other; a is the number specified by $0 < a \leq 3$, b is an integer of 2 or more, and c is an integer of 1 or more.

22. An olefin polymerization catalyst which comprises the transition metal complex according to any





of claims 1-4 and the following compounds (A) and (B):

(A) any one of the following compounds (A1)-(A3) or the mixture of two or three thereof:

(A1) an organoaluminum compound represented by the
5 formula $E^1_a Al Z_{3-a}$

(A2) a cyclic aluminoxane having the structure represented by the formula $\{Al(E^2)-O-\}_b$

(A3) a linear aluminoxane having the structure represented by the formula $E^3\{Al(E^3)-O-\}_c Al E^3_2$

10 wherein E^1-E^3 are each a hydrocarbon group with the number of carbon atoms of 1-8, and all E^1 , all E^2 and all E^3 may be the same with or different from each other; Z is a hydrogen atom or halogen atom and all Z may be the same with or different from each other; a is the number
15 specified by $0 < a \leq 3$, b is an integer of 2 or more and c is an integer of 1 or more,

(B) any of the following compounds (B1)-(B3):

(B1) a boron compound represented by the formula $BQ^1Q^2Q^3$,

20 (B2) a boron compound represented by the formula $Z^+(BQ^1Q^2Q^3Q^4)^-$,

(B3) a boron compound represented by the formula $(L-H)^+(BQ^1Q^2Q^3Q^4)^-$,

wherein B is a boron atom of a tri-valent valence state;
25 Q^1-Q^4 are each a halogen atom, hydrocarbon group with the number of carbon atoms of 1-20, halogenated hydrocarbon group with the number of carbon atoms of 1-20, substituted silyl group with the number of carbon atoms of



1-20, alkoxy group with the number of carbon atoms of 1-20 or di-substituted amino group with the number of carbon atoms of 2-20, and they may be the same with or different from each other.

5 23. The olefin polymerization catalyst according to claim 21 or 22 wherein the compound (A) is triethylaluminum, triisobutylaluminum, or methylaluminoxane.

24. A process for producing olefin polymers which comprises using the olefin polymerization catalyst
10 according to any of the claims 21-23.

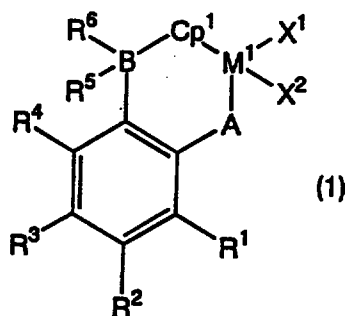
25. The process for producing olefin polymers according to claim 24 wherein the olefin polymer is ethylene- α -olefin copolymer.

26. The process for producing olefin polymer
15 according to claim 24 wherein the olefin polymer is ethylene- α -olefin copolymer rubber.

27. The process for producing olefin polymers according to claim 24 wherein the olefin polymer is ethylene- α -olefin-nonconjugated diene copolymer rubber.

ABSTRACT

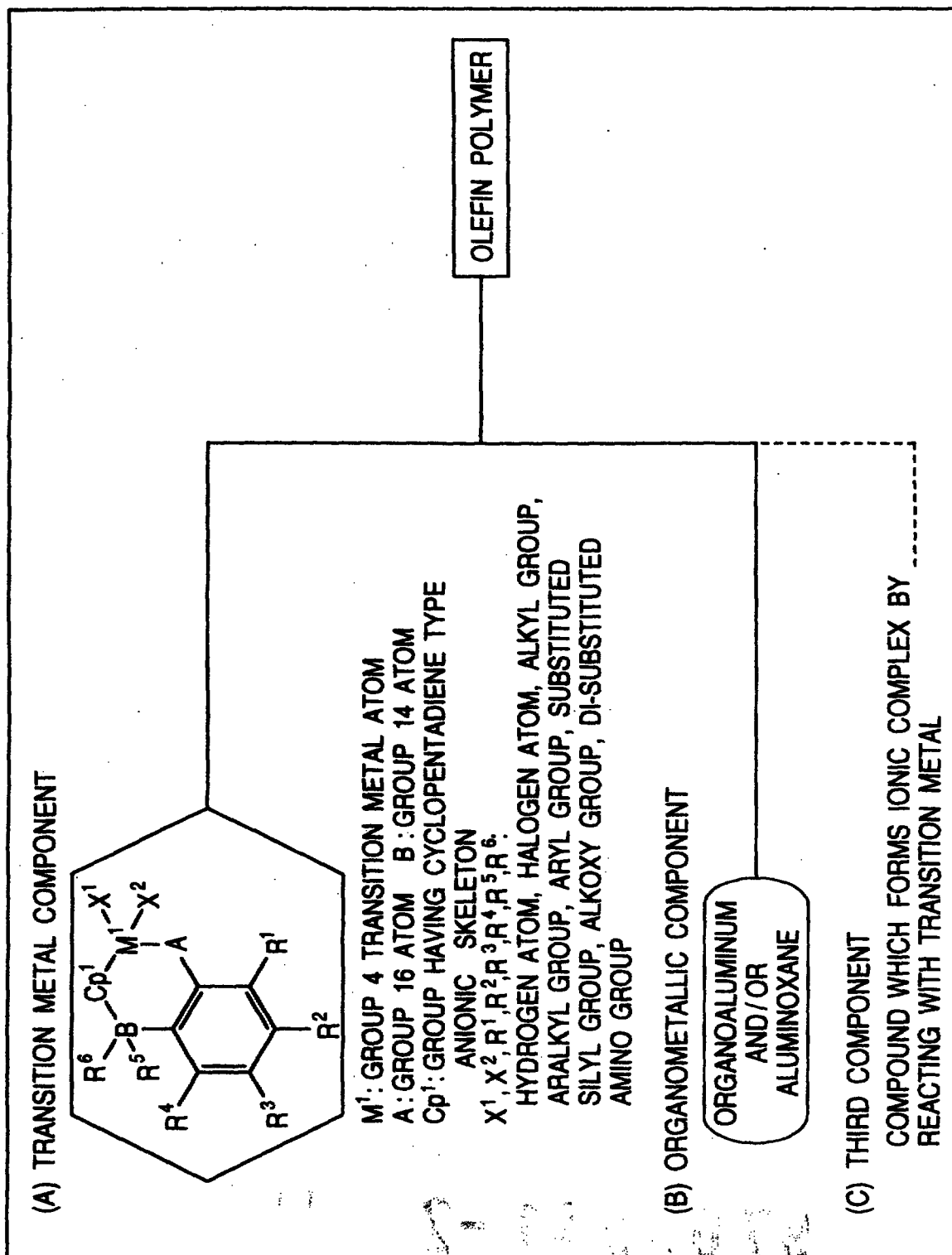
A transition metal complex represented by the formula (1)



wherein M^1 is a transition metal atom of the group 4 of
5 the periodic table of elements, A is an atom of the group
16 of the periodic table of elements, and B is an atom of
the group 14 of the periodic table of elements; Cp^1 is a
group having a cyclopentadiene type anionic skeleton; and
 X^1 , X^2 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently a
10 hydrogen atom, halogen atom, alkyl group with the number
of carbon atoms of 1-20 optionally substituted with at
least one halogen atom, aralkyl group with the number of
carbon atoms of 7-20 optionally substituted with at least
one halogen atom, aryl group with the number of carbon
15 atoms of 6-20 optionally substituted with at least one
halogen atom, substituted silyl group with the number of
carbon atoms of 1-20 optionally substituted with at least
one halogen atom, alkoxy group with the number of carbon
atoms of 1-20 optionally substituted with at least one
20 halogen atom, aralkyloxy group with the number of carbon

atoms of 7-20 optionally substituted with at least one halogen atom or aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the
5 number of carbon atoms of 2-20, provided that R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally combine with each other to form a ring; a process for producing the same; an olefin polymerization catalyst containing the transition metal complex; and a process for producing olefin polymers.

FIG. 1





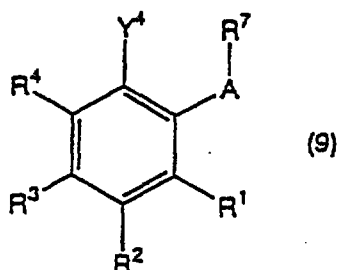
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substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, 5 aralkyloxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon 10 atoms of 2-20, and M^1 , X^1 and X^2 are respectively the same as defined above.

6. The process for producing the transition metal complex according to claim 5 wherein the substituted cyclopentadienyl compound represented by the formula (2) 15 is produced by any of the process [1]-[3] described below:

[I] a process which comprises reacting a halogenated aryl compound represented by the formula (9)



wherein Y^4 is a halogen atom, and

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wherein A is an atom of the group 16 of the periodic table of elements; R^1 is an alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom; R^2 , R^3 , and R^4 are each independently a hydrogen atom, alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of

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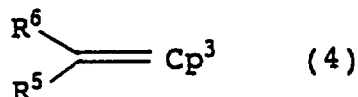
1-20 optionally substituted with at least one halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon atoms of 2-20; and R^7 is a hydrocarbon group optionally substituted with at least one halogen atom or a tri-substituted silyl group" with an

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organoalkali metal salt or metallic magnesium, then reacting the reaction product with a cyclopentadienylidene compound represented by the formula (4)



wherein Cp^3 is a group having a cyclopentadienyliene skeleton, and

wherein R^5 and R^6 are each independently a hydrogen atom, alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with

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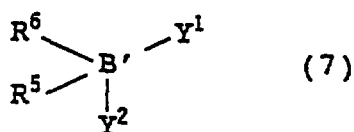
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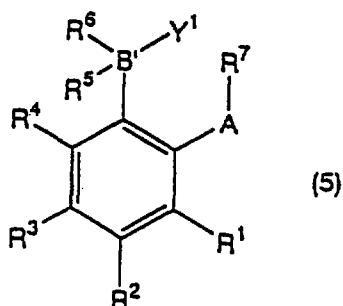
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at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon atoms of 2-20, provided that R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally combine with each other to form a ring, and then reacting the resulting reaction product with water;

[II] a process which comprises reacting the halogenated aryl compound represented by the formula (9) with a dihalide compound represented by the formula (7)

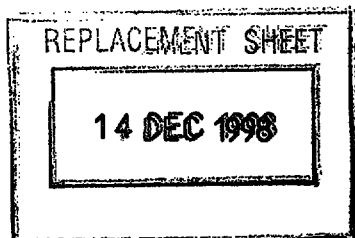


wherein Y^1 and Y^2 are each a halogen atom, B' is an atom of group 14 other than carbon atom, and R^5 and R^6 are respectively the same as defined above, in the presence of an organoalkali metal compound or metallic magnesium to obtain a halide compound represented by the formula (5)



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wherein A is an atom of the group 16 of the periodic table of elements and B is an atom of the group 14 of the periodic table of elements; Y^4 is a halogen atom; R^1 is an alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom; and R^2 , R^3 , and R^4 are each independently a hydrogen atom, alkyl group with the number of carbon atom of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon atoms of 2-20, .



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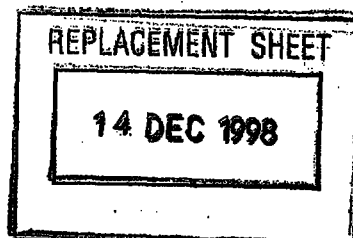
with a halide represented by the
formula (11)



- 5 wherein Y^5 is a halogen atom and R^7 is as defined above,
in the presence of an organoalkali metal compound or amine compound.

8. A substituted cyclopentadienyl compound
represented by the formula (2).

wherein A is an atom of the group 16 of the
periodic table of elements; B is an atom of the group 14
of the periodic table of elements; Cp^2 is a group having
a cyclopentadiene skeleton; R^1 is an alkyl group with
the number of carbon atoms of 1-20 optionally
substituted with at least one halogen atom, aralkyl
group with the number of carbon atoms of 7-20 optionally
substituted with at least one halogen atom, aryl group
with the number of carbon atoms of 6-20 optionally
substituted with at least one halogen atom, or
substituted silyl group with the number of carbon atoms
of 1-20 optionally substituted with at least one halogen
atom; R^2 , R^3 , and R^4 are each independently a hydrogen
atom, alkyl group with the number of carbon atoms of 1-
20 optionally substituted with at least one halogen atom,
aralkyl group with the number of carbon atoms of 7-20
optionally substituted with at least one halogen atom,





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aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon atoms of 2-20; R^5 and R^6 are each independently a hydrogen atom, alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one

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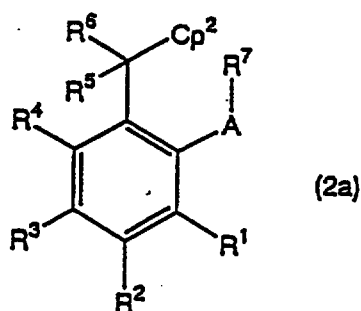
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halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon atoms of 2-20, provided that R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally combine with each other to form a ring; and R^7 is a hydrocarbon group optionally substituted with at least one halogen atom or a tri-substituted silyl group".

9. A process for producing a substituted cyclopentadienyl compound represented by the formula (2a)



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wherein A, Cp^2 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are
defined at the formula (2) in claim 8,
respectively the same as those / which comprises
reacting a halogenated aryl compound represented by the
formula (9) with an organoalkali metal salt or metallic
magnesium, then reacting the reaction product with a
cyclopentadienylidene compound represented by the formula
(4), and then reacting the resulting reaction product
with water.

10. The process for producing a substituted cyclo-
pentadienyl compound according to claim 9 wherein the

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the halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound represented by the formula (10) with a halide represented by the formula (11) in the presence of a base.

- 5 14. A process for producing a substituted cyclopentadienyl compound represented by the formula (2b) which comprises reacting a halogenated aryl compound represented by the formula (9) with a halide compound represented by the formula (8) in the presence of an
10 organoalkali metal compound or metallic magnesium.
15. The process for producing a substituted cyclopentadienyl compound according to claim 14 wherein the halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound
15 represented by the formula (10) with a halide represented by the formula (11) in the presence of a base.
16. A halide compound represented by the formula (5).

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wherein A is an atom of the group 16 of the periodic table of elements; B' is an atom of the group 14 other than carbon atom; R¹ is an alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or substituted silyl group with the number of carbon atoms 1-20 optionally substituted with at least one halogen atom; R², R³, and R⁴ are each independently a hydrogen atom, alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted

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silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon atoms of 2-20; R^5 and R^6 are each independently an alkyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyl group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryl group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, substituted silyl group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, alkoxy group with the number of carbon atoms of 1-20 optionally substituted with at least one halogen atom, aralkyloxy group with the number of carbon atoms of 7-20 optionally substituted with at least one halogen atom, aryloxy group with the number of carbon atoms of 6-20 optionally substituted with at least one halogen atom, or di-substituted amino group with the number of carbon

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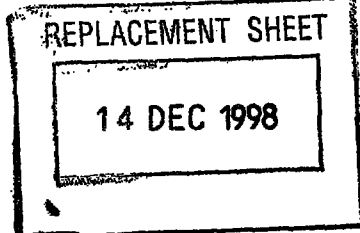
atoms of 2-20, provided that R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may optionally combine with each other to form a ring; R^7 is a hydrocarbon group optionally substituted with at least one halogen atom or a tri-substituted silyl group; and Y^1 is a halogen atom.

17. A process for producing the halide compound according to claim 16 which comprises reacting a halogenated aryl compound represented by the formula (9) with a dihalide compound represented by the formula (7) in the presence of an organoalkali metal compound or metallic magnesium.

18. The process according to claim 17 wherein the halogenated aryl compound represented by the formula (9) is produced by reacting a halogenated aryl compound represented by the formula (10) with a halide represented

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by the formula (11) in the presence of an organoalkali metal compound or amine compound.

19. A halogenated aryl compound represented by the formula (9) wherein R^7 is an alkenyl group.

20. A process for producing the halogenated aryl compound according to claim 19 which comprises reacting a halogenated aryl compound represented by the formula (10) with a halide represented by the formula (11) wherein R^7 is an alkenyl group, in the presence of a base.

21. An olefin polymerization catalyst which comprises the transition metal complex according to any of claims 1-4 and a compound (A) described below:

(A) any one of the following compounds (A1)-(A3) or the mixture of two or three thereof,

(A1) an organoaluminum compound represented by the formula $E^1_a Al Z_{3-a}$

(A2) a cyclic aluminosiloxane having the structure represented by the formula $\{Al(E^2)-O-\}_b$

(A3) a linear aluminosiloxane having the structure represented by the formula $E^3\{Al(E^3)-O-\}_c Al E^3_2$

wherein E^1-E^3 are each a hydrocarbon group with the number of carbon atoms of 1-8, and all E^1 , all E^2 and all E^3 may be the same with or different from each other; Z is a hydrogen atom or halogen atom, and all Z may be the same with or different from each other; a is the number specified by $0 < a \leq 3$, b is an integer of 2 or more, and c is an integer of 1 or more.

22. An olefin polymerization catalyst which comprises the transition metal complex according to any