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(54) Title: GROUP IIIB METAL COMPLEXES WITH "CONSTRAINED GEOMETRY" FLUORENYL BASED LIGANDS

(57) Abstract: The present invention discloses a metallocene catalyst component based on a Group IIIB metal of the periodic Table and a bridged heteroatom-fluorenyl ligand. It also discloses its method of preparation and its use in polymerisation.



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5 **Group IIIb metal complexes with « Constrained geometry » fluorenyl based ligands.**

The present invention relates to the field of "constrained geometry catalyst" systems based on Group IIIb metals of the Periodic Table. It also relates to their synthesis and their use in olefin polymerisation.

10

"Constrained geometry catalysts" (CGC) are half-sandwich complexes bearing hetero-bifunctional cyclopentadienyl-amido ligands. They have attracted much attention owing to several reasons:

- replacing of a cyclopentadienyl moiety in linked bis(cyclopentadienyl) ligands
- 15 by a less electron-donating amido group results in the formation of *ansa*-metallocene-like complexes with higher Lewis acidity; and therefore potentially enhanced catalytic activity towards Lewis basic substrates.
- there are many more possibilities to design new catalytic geometries by selecting appropriate substituents on the cyclopentadienyl ring, on the
- 20 bridging atom and on the heteroatom of the side chain.

The synthesis and polymerisation abilities of cyclopentadienyl-amido complexes of group III metals (Sc, Y, Yb, Lu) have been described for example in Shapiro et al. (P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, J. E. Bercaw; in J. Am. Chem. Soc., 1994, 116, 4623.) or in Hultzsich et al. (K. C. Hultzsich, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda; in Organometallics, 2000, 19, 228.), or in Tian et al. (S. Tian, V. M. Arredondo, C. L. Stern, T. J. Marks; in Organometallics, 1999, 18, 2568.), or in Mu et al. (Y. Mu, W. Piers, M.-A. MacDonald, M. J. Zaworotko; in Can. J. Chem., 1995, 73, 2233.) or in Arndt and Okuda (S. Arndt, J. Okuda, in

25 Chem. Rev., 2002, 102, 1953.)

30

All these publications however were limited to lanthanide compounds with combined cyclopentdienyl-amido ligands. None has addressed the field of fluorenyl-amido ligands.

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It is an object of the present invention to prepare in good yield bridged half-sandwich metallocene components based on fluorenyl-heteroatom ligands and based on Group IIIb metals of the Periodic Table.

- 10 It is another aim of the present invention to prepare catalyst components efficient in the controlled polymerisation of styrene.

It is a further aim of the present invention to prepare catalyst components capable of preparing polymethylmethacrylate.

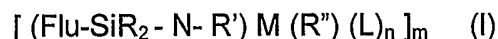
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More generally, the present invention aims at preparing catalyst systems efficient in the controlled polymerisation of polar or non polar monomers.

- Accordingly, the present invention discloses a metallocene catalyst component
20 based on a Group IIIb metal of the Periodic Table and a bridged constrained geometry fluorenyl-based ligand.

In a first embodiment, the present invention discloses a metallocene catalyst component of the general formula

25



wherein Flu is a fluorenyl, substituted or unsubstituted, M is a Group IIIb metal of the Periodic Table, SiR₂ is a structural bridge between N and Flu (9-position) imparting stereorigidity to the component wherein each R is the same or different

and is an alkyl having from 1 to 20 carbon atoms, R' is hydrogen or is of the form $ZR^{\$}_3$ wherein Z is C or Si and R^{\$} is a hydrocarbyl having from 1 to 20 carbon, R'' is hydrogen, or a hydrocarbyl having from 1 to 20 carbon atoms, said hydrocarbyl possibly containing one or more Si atoms, or is a halogen, L is a co-ordinating solvent, n is 0, 1 or 2, and m is 1 or 2.

The substituents on the fluorenyl are not particularly limited, they can be the same or different and are of the form $ZR^{\$}_3$ as defined here-above; they include particularly hydrocarbyls having from 1 to 20 carbon atoms. Preferably, they are located at positions 3 and 6, or at positions 4 and 5, or at positions 2 and 7 and more preferably, they are the same.

M is preferably yttrium, lanthanum or a member of the lanthanide series. Throughout this description, the term "lanthanide series" means the rare earth series of elements having atomic numbers of from 58 to 71. In the lanthanide series M is preferably neodymium, samarium. More preferably, M is yttrium.

Preferably, N is substituted and more preferably, the substituent is tert-butyl.

Preferably, R'' is hydrogen or an alkyl or an aryl or an allyl or a halogen, and m is 1 when R'' is an alkyl or an aryl or an allyl, m is 2 when R'' is hydrogen or a halogen. When R'' is a halogen, it is preferably Cl, I, or Br.

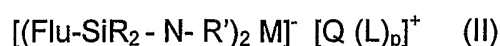
The co-ordinating solvent is typically an ether such as for example tetrahydrofuran (THF), dimethoxyether (DME) or diethyl oxide (Et₂O).

In order to be active in polymerization, compounds of type (I), wherein R'' is a halogen must be alkylated first with an adequate reagent. Typical reagents can be

selected from LiR^* , $\text{R}^* \text{MgX}$, Mg R_2^* , Al R_3^* , $\text{Al R}_n^* \text{X}_{3-n}$, $[\text{Li}]^+[\text{AlR}_n^* \text{X}_{3-n}]^-$ and methylalumoxane (MAO), wherein R^* is an alkyl, aryl or allyl having from 1 to 20 carbon atoms and X is a halogen, preferably Cl. This list should not be considered as limitative.

5

In a second embodiment, the present invention discloses a metallocene catalyst component of the general formula



10 wherein all symbols are as defined in formula (I), Q is an alkali, an earth alkali or a Group IIIa metal of the Periodic Table and p is from 2 to 4.

Q is preferably Li, Na, Mg or Al.

15 When the ion-pair in complex II is fully dissociated, p is 4 and when the ion-pair is partially associated, p is 2 or 3.

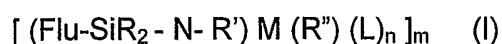
The present invention discloses a first method, based on a salt metathesis reaction method for preparing the catalyst components (I) or (II) that comprises the steps of:

- 20 a) suspending $\text{MX}_3(\text{THF})_n$ in an ether;
- b) suspending a deprotonated dilithium salt $[\text{Flu-SiR}_2 - \text{N} - \text{R}']\text{Li}_2$ in the same or another ether;
- c) carrying out the salt metathesis reaction of suspensions a) and b) at a temperature of from -80°C to 60°C .
- 25 d) recrystallising the crude product obtained in c) after evaporation of volatiles from an ether or a mixture of an ether and an hydrocarbon at a temperature of from -60 to -0°C ;
- e) retrieving a crystalline powder of formula (I) or (II)

In another embodiment of the present invention, complex (I) wherein R" is a halogen, can comprise the additional step of alkylation with an alkylating agent to give complex (I) wherein R" is a hydrocarbonyl as defined above.

- 5 Suitable alkylating agent can be selected from LiR^+ , R^+MgX , MgR^+_2 , AlR^+_3 , $\text{AlR}^+_n\text{X}_{3-n}$, n and $[\text{Li}]^+[\text{AlR}^+_n\text{X}_{3-n}]^-$ wherein R^+ is an alkyl, an aryl or an allyl having from 1 to 20 carbon atoms and X is a halogen, preferably Cl.

The present invention discloses a second method, based on an alkane elimination
10 reaction, for preparing specifically the catalyst component



wherein R" is specifically a hydrocarbonyl having from 1 to 20 carbon atoms, said hydrocarbonyl possibly containing one or more Si atoms, that comprises the steps of reacting the triscarbonyl complex $\text{M}(\text{R}'')_3(\text{L})_n$, either presynthesised or generated in
15 situ, with one equivalent of the diproteo ligand $(\text{FluH-SiR}_2 - \text{NH-R}')$.

The triscarbonyl complex $\text{M}(\text{R}'')_3(\text{L})_n$ is preferably generated in situ as the reaction product of $\text{MCl}_3(\text{THF})_n$ and 3 equivalents of LiR'' . The reaction temperature for the preparation of complex (I) is of from 0 °C up to 75 °C and preferably of from 40 to
20 50 °C. For the second method of preparation described here-above, M is preferably Yttrium and the bridge SiR_2 , is preferably a dialkyl silyl.

These two methods can comprise the additional step of hydrogenolysing carbonyl complex (I) to prepare complex



Suitable hydrogenolysing agents can be selected from dihydrogen or an hydrosilane, e.g. phenylsilane. The reaction is preferably carried out at room temperature at about 25 °C and at atmospheric pressure in a hydrocarbon

solvent, e.g. benzene or toluene. The reaction product is insoluble in both polar (ethers) and non-polar (hydrocarbons) solvents.

The present invention further discloses a catalyst system based upon any one or more of catalyst components of formulas (I) and/or (II) and a suitable activating agent and/or a transfer agent.

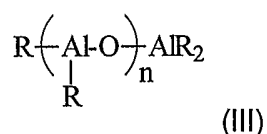
The present invention discloses a process for polymerisation comprising the steps of:

- 10 a) introducing a catalyst system based on any one or more of catalyst components of formulas (I) and/or (II) in the reactor,
- b) optionally introducing an activating agent or a transfer agent in the reactor,
- c) feeding a monomer and an optional comonomer,
- d) maintaining the system under polymerisation conditions,
- 15 e) retrieving the desired polymer.

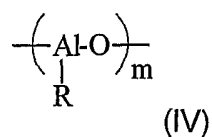
The optional activating agent includes Lewis acids having an ionising action and having a low or no co-ordinating capability. Typically, all the activators used with the metals Group IV of the Periodic Table can be used in the present invention.

- 20 Suitable aluminium-containing activating agents comprise an alumoxane an aluminium alkyl or an alkylaluminate $[\text{Li}]^+[\text{AlR}^*_n\text{X}_{3-n}]^-$

- The alumoxanes that can be used in the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula (III):
- 25



for oligomeric linear alumoxanes; and formula (IV)



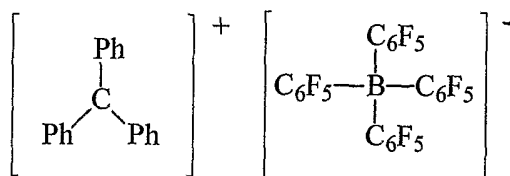
for oligomeric cyclic alumoxanes,

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wherein n is 1-40, preferably 10-20; m is 3-40, preferably 3-20; and R is a C₁-C₈ alkyl group, preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

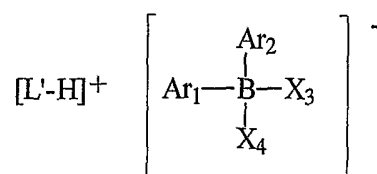
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Suitable boron-containing activating agents may comprise a triphenylcarbenium boronate, such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696:



15

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



20

Other preferred activating agents include hydroxy isobutylaluminium and a metal aluminoxinate.

Alkylating agents of the type $\text{MgR}^{\pm}_2$ can also be used as activating agents, wherein each $\text{R}^{\pm}$ is the same or different and is a hydrocarbyl having from 1 to 20 carbon atoms, and optionally containing one or more Si atoms

- 5 The transfer agents comprise for example H_2 and hydrosilanes of the formula HSiR'''_3 wherein each R''' is the same or different and is either an H atom or a hydrocarbyl having from 1 to 20 carbon atoms. They are selected in accordance with the monomer to be polymerised.
- 10 The monomers that can be used in the present invention include non polar monomers such as for example ethylene, alpha-olefins, styrene and polar monomers such as for example (meth)acrylates or dienes. Preferably, styrene and methyl methacrylate have been used.
- 15 The catalyst system of the present invention may be employed in any type of homo- or co-polymerisation method, provided that the required catalytic activity is not impaired. In a preferred embodiment of the present invention, the catalyst system is employed in a bulk polymerisation process or in a solution polymerisation process, which is homogeneous, or in a slurry process, which is heterogeneous. In a solution
- 20 process, typical solvents include THF or hydrocarbons having from 4 to 7 carbon atoms such as heptane, toluene or cyclohexane. In a slurry process, it is necessary to immobilise the catalyst system on an inert support, particularly a porous solid support such as talc, inorganic oxides and resinous support materials such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided
- 25 form.

Suitable inorganic oxide materials that are desirably employed in accordance with this invention include group IIA, IIIA, IVA, or IVB metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed, either

30 alone or in combination with the silica or alumina, are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for

example, finely divided functionalised polyolefins such as finely divided polyethylene.

Preferably, the support is a silica support having a surface area of from 200-
5 700 m²/g and a pore volume of from 0.5-3 ml/g.

The polymerisation temperatures range from -20 °C up to 100 °C.

The present invention also covers the polymers obtainable by polymerisation in the
10 presence of the catalysts components described hereabove.

LIST OF FIGURES.

Figure 1 represents the crystal structure of the molecule [3,6-di-^tBu-C₁₃H₆-
15 SiMe₂-N^tBu]Y(CH₂SiMe₃)(THF)₂ (1).

Figure 2 represents the ¹H NMR spectrum of complex [3,6-di-^tBu-C₁₃H₆-SiMe₂-
N^tBu]Y(CH₂SiMe₃)(THF)₂ (1) in C₆D₆ at 25 °C.

Figure 3 represents the ¹³C NMR spectrum of complex ([3,6-di-^tBu-C₁₃H₆-SiMe₂-
20 N^tBu]Y(CH₂SiMe₃)(THF)₂ (1) in C₆D₆ at 25 °C.

Figure 4 represents the ¹H NMR spectrum of complex [3,6-di-^tBu-C₁₃H₆-SiMe₂-
N^tBu]Y(CH₂SiMe₃)(THF)₂ (1) in C₆D₆ at -70 °C.

25

Figure 5 represents the ¹H NMR spectrum of complex [(^tBu₂-C₁₃H₆)-SiMe₂-
N^tBu]₂Y][Li(THF)₄]⁺ (2) in THF-d₈ at 25 °C.

Figure 6 represents the ^{13}C NMR spectrum of complex $[\{(\text{tBu}_2\text{-C}_{13}\text{H}_6)\text{-SiMe}_2\text{-N}^t\text{Bu}\}_2\text{Y}][\text{Li}(\text{THF})_4]^+$ (2) in THF- d_8 at 25 °C.

Figure 7 represents the crystal structure of the molecule $[\{3,6\text{-di-}^t\text{Bu-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^t\text{Bu}\}_2\text{La}][\text{Li}(\text{OEt}_2)_2]^+$ (4)

Figure 8 represents the crystal structure of the molecule $[\{3,6\text{-di-}^t\text{Bu-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^t\text{Bu}\}\text{Nd}(\mu\text{-Cl})(\text{THF})_2]_2$ (5).

10

EXAMPLES.

Synthesis of $[3,6\text{-di-}^t\text{Bu-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^t\text{Bu}]\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ (1).

- 15 (a) *NMR scale reaction:* An NMR tube equipped with a teflon valve was charged with $\text{Y}[\text{CH}_2\text{SiMe}_3]_3(\text{THF})_2$ (32.4 mg, 0.065 mmol) and $3,6\text{-di-}^t\text{Bu-C}_{13}\text{H}_6\text{H-SiMe}_2\text{-NH}^t\text{Bu}$ (26.7 mg, 0.065 mmol) and benzene- d_6 (~0.6 mL) was condensed in at –196 °C. The tube was stopped with valve and heated to room temperature. Progress of the reaction was monitored periodically by ^1H NMR spectroscopy.
- 20 (b) *Preparative scale reaction:* Anhydrous YCl_3 (338 mg, 1.73 mmol) was slurried in THF (15 mL) and stirred at 80 °C for 1 h. The solvent was removed in vacuo and the solid residue was suspended in pentane (20 mL). The suspension was cooled to –78 °C, a solution of $\text{LiCH}_2\text{SiMe}_3$ (5.2 mL of a 1M solution in pentane, 5.2 mmol) was added, and the suspension was stirred at 0
- 25 °C for 2 h. The suspension was filtered and the white solid was extracted with pentane (2×10 mL). LiCl was filtered off and a solution of $3,6\text{-di-}^t\text{Bu-C}_{13}\text{H}_6\text{H-SiMe}_2\text{-NH}^t\text{Bu}$ (578 mg, 1.42 mmol) in pentane (30 mL) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 h. The

solution was filtered and concentrated in vacuo. The crude product was $[\text{C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^t\text{Bu}]\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ (1) (0.63 g, 68 %). The ^1H NMR spectrum of complex (1) is represented in Figure 2 and gave the following results: (benzene- d_6 , 200 MHz, 25 °C): δ 8.34 (d, 2H, $^4J_{\text{HH}} = 2.0$ Hz, 4,5 -H), 7.97 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz, 1,8-H), 7.57 (dd, 2H, $J_{\text{HH}} = 2.0, 8.3$ Hz, 2,7-H), 3.0 (m, 8H, $\alpha\text{-CH}_2$, THF) 1.61 (s, 9H, NCCH_3), 1.50 (s, 18H, $\text{CCH}_3(\text{Flu})$), 1.17 (m, 8H, $\beta\text{-CH}_2$, THF), 0.78 (s, 6H, SiCH_3), 0.00 (s, 9H, CH_2SiCH_3), -0.89 (d, $J_{\text{YH}} = 3.3$ Hz, 2H, YCH_2). The ^{13}C NMR of complex (1) is represented in Figure 3 and gave the following results. (benzene- d_6 , 75 MHz, 25 °C): δ 140.7, 139.4, 130.3, 123.9, 117.8, 116.7, 115.5 (C-1,-2, -3, -4, -5, -6, -7, -8), 82.2 (C-9), 69.7 ($\alpha\text{-THF}$), 54.3 (NCCH_3), 36.4 (NCCH_3), 34.7 (Flu-CCH_3), 32.3 (Flu-CCH_3), 30.2 (d, $^1J(\text{Y}, \text{C}) = 45.2$ Hz, YCH_2), 25.1 ($\beta\text{-THF}$), 6.2 (SiCH_3), 4.6 (CH_2SiCH_3). The ^1H NMR spectrum of complex (1) (benzene- d_6 , 200 MHz, -70 °C) is represented in Figure 3. The NMR spectroscopy thus indicates that on the NMR time scale, complex (1) is symmetric in benzene at 25 °C, but appears dissymmetric at a temperature lower than -30 °C.

An X-ray diffraction study of monocrystals of complex (1) revealed that the fluorenyl moiety is bonded via an unusual exocyclic η^3 -fashion, which involves the bridgehead carbon atom of the central ring (C(9A)) and the two adjacent carbon atoms of one six-membered ring (C(9), C(1)), wherein the carbon atoms are numbered as displayed in Figure 1, which represents the structure of molecule (1). There are two THF molecules coordinated per metal atom in molecule (1) as compared with 14-electron mono-solvated $[\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{-SiMe}_2\text{-N}^t\text{Bu}]\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})$ complex described by Hultzsche *et al.* (K. C. Hultzsche, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda; in *Organometallics*, 2000, 19, 228.). Also, molecule (1) can be considered formally as a 14-electron complex and coordination number of the yttrium atom is 6. Both coordinated THF ligands are not

equivalent according to X-ray data; the difference between the two Y-O distances is 0.05 Å, suggesting that one THF molecule could be involved in dissociative processes.

- 5 **Salt Metathesis Reaction between [3,6-di-^tBu-C₁₃H₆-SiMe₂-N^tBu]Li₂ and YCl₃(THF)_n. Preparation of [(^tBu₂-C₁₃H₆)-SiMe₂-N^tBu]₂Y⁻[Li(THF)₄]⁺ (2).** To a solution of ^tBu₂-C₁₃H₆H-SiMe₂-NH^tBu (108 mg, 0.265 mmol) in diethylether (20 mL) at -10 °C was added under vigorous stirring two equiv. of ⁿBuLi (0.33 mL of a 1.6 M solution in hexane, 0.530 mmol). The reaction mixture was allowed to warm to
- 10 ambient temperature and stirred for 8 h. To the resulting orange solution of the dilithium salt in ether cooled to -20 °C was added a suspension of YCl₃ THF-adduct (prepared from 52.0 mg, 0.265 mmol of YCl₃) in ether (30 mL). The mixture was vigorously stirred and warmed to room temperature; the color turned yellow after 30-40 min. The yellow solution was decanted from precipitate, volatiles were
- 15 removed in vacuo and the resulting residue was washed with pentane (2 × 20 mL) to give a yellow powder (101.2 mg). The ¹H NMR spectrum of crude complex (2) shows the existence of two species in solution and gave the following results. (THF-*d*₈, 200 MHz, 25 °C): **1st product:** δ 7.90 (d, 2H, ⁴J_{HH} = 2.1 Hz, 4,5-H), 7.69 (d, 2H, ³J_{HH} = 8.6 Hz, 1,8-H), 6.90 (dd, 2H, J_{HH} = 2.1, 8.6 Hz, 2,7-H), 1.36 (s, 18H, CCH₃(Flu)), 1.20 (s, 9H, NCCH₃), 0.38 (s, 6H, SiCH₃); **2nd product:** δ 7.83 (m, 2H, ⁴J_{HH} = 2.1 Hz, 4,5-H), 7.54 (d, 2H, ³J_{HH} = 8.6 Hz, 1,8-H), 6.84 (dd, 2H, J_{HH} = 2.1, 8.6 Hz, 2,7-H), 1.35 (s, 18H, CCH₃(Flu)), 1.11 (s, 9H, NCCH₃), 0.40 (s, 6H, SiCH₃).
- 20 The crude product was recrystallized from Et₂O:THF:pentane (~ 0.5:1:3) to give yellow crystals (88.2 mg, 55 %). The ¹H NMR of recrystallized complex (2) is
- 25 represented in Figure 5 and gave the following results that show the presence of a sole species. (THF-*d*₈, 300 MHz, 25 °C): δ 7.94 (d, 2H, ⁴J_{HH} = 1.8 Hz, 4,5-H), 7.72 (d, 2H, ³J_{HH} = 8.3 Hz, 1,8-H), 7.13 (dd, 2H, J_{HH} = 1.8, 8.3 Hz, 2,7-H), 1.43 (s, 9H, NCCH₃), 1.36 (s, 18H, CCH₃(Flu)), 0.27 (s, 6H, SiCH₃). The ¹³C NMR spectrum of

complex (2) is represented in Figure 6 and gave the following results. (THF- d_8 , 75 MHz, 25 °C): δ 144.6, 137.8, 133.7, 121.1 (C-1,-8), 120.0 (C-2, -7), 115.5 (C-4,-5), 79.0 (C-9), 54.7 (NCCH₃), 36.9 (NCCH₃), 35.4 (Flu-CCH₃), 33.2 (Flu-CCH₃), 6.2 (SiCH₃).

5

Salt Metathesis Reaction between [3,6-di-^tBu-C₁₃H₆-SiMe₂-N^tBu]Li₂ and LaCl₃(THF)_{*n*}. Preparation of [(^tBu₂-C₁₃H₆)-SiMe₂-N^tBu]₂La⁻[Li(THF)₄]⁺ (3). The same procedure than that described above was carried out from the LaCl₃ THF-adduct (prepared from 186 mg, 0.758 mmol of LaCl₃) and ^tBu₂-C₁₃H₆H-SiMe₂-NH^tBu (310 mg, 0.760 mmol) to yield a yellow microcrystalline solid (440 mg). NMR of the crude complex showed the presence of two species in solution and gave the following results. ¹H NMR (THF- d_8 , 200 MHz, 25 °C): **1st product:** δ 7.93 (d, 2H, ⁴J_{HH} = 2.0 Hz, 4,5-H), 7.73 (dd, 2H, J_{HH} = 0.5, 8.6 Hz, 1,8-H), 6.94 (dd, 2H, J_{HH} = 2.1, 8.6 Hz, 2,7-H), 1.41 (s, 18H, CCH₃(Flu)), 1.25 (s, 9H, NCCH₃), 0.43 (s, 6H, SiCH₃); **2nd product:** δ 7.83 (m, 2H, ⁴J_{HH} = 2.1 Hz, 4,5-H), 7.54 (d, 2H, J_{HH} = 8.6 Hz, 1,8-H), 6.84 (dd, 2H, J_{HH} = 2.1, 8.6 Hz, 2,7-H), 1.35 (s, 18H, CCH₃(Flu)), 1.16 (s, 9H, NCCH₃), 0.45 (s, 6H, SiCH₃). Recrystallization of the crude product from THF-pentane (~1:4) mixture gave pale-orange crystals (0.38 g, 77 %). NMR of the recrystallized complex showed the presence of a sole species in solution and gave the following results. ¹H NMR (Fig. 5.) (THF- d_8 , 300 MHz, 25 °C): δ 7.82 (d, 2H, ⁴J_{HH} = 1.8 Hz, 4,5 -H), 7.53 (d, 2H, ³J_{HH} = 8.2 Hz, 1,8-H), 6.84 (dd, 2H, J_{HH} = 1.8, 8.2 Hz, 2,7-H), 1.35 (s, 18H, CCH₃(Flu)), 1.19 (s, 18H, NCCH₃), 0.39 (s, 6H, SiCH₃). ¹³C NMR (THF- d_8 , 75 MHz, 25 °C): δ 144.4, 131.4, 127.7, 119.5 (C-1,-8), 118.5 (C-2, -7), 114.9 (C-4,-5), 84.4 (C-9), 50.7 (NCCH₃), 35.5 (Flu-CCH₃), 35.4 (NCCH₃), 34.1 (Flu-CCH₃), 6.9 (SiCH₃). Anal. Calcd for C₇₀H₁₁₀N₂O₄LiSi₂La: C, 67.49; H, 8.90; N, 2.25. Found: C, 67.31; H, 8.37; N, 2.40.

Synthesis of $[\{^t\text{Bu}_2\text{-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^t\text{Bu}\}_2\text{La}]^-\text{[Li(Et}_2\text{O)}_2]^+$ (4). To a solution of $^t\text{Bu}_2\text{-C}_{13}\text{H}_6\text{H-SiMe}_2\text{-NH}^t\text{Bu}$ (340 mg, 0.834 mmol) in diethylether (30 mL) at $-10\text{ }^\circ\text{C}$ was added under vigorous stirring two equiv. of $^n\text{BuLi}$ (1.0 mL of a 1.6 M solution in hexane, 1.66 mmol). The reaction mixture was allowed to warm to ambient
5 temperature and stirred for 8 h. To the resulting orange solution of the dilithium salt in ether cooled to $-35\text{ }^\circ\text{C}$ in glovebox was added a powder of $\text{LaCl}_3(\text{THF})_{1.5}$ (295 mg, 0.834 mmol). The mixture was vigorously stirred and warmed to room temperature; the color turned orange-yellow after 20 min. The yellow solution was decanted from precipitate and concentrated in vacuo. Hexane (ca. 2-3 mL) was
10 added to the ether solution and orange-yellow crystals started to grow to get in the next 10 h microcrystals of molecule (4) (0.30 g, 33 %). $^1\text{H NMR}$ ($\text{THF-}d_8$, 200 MHz, $60\text{ }^\circ\text{C}$): δ 7.79 (d, 4H, $^4J_{\text{HH}} = 2.0\text{ Hz}$, 4,5-H), 7.25 (d, 4H, $J_{\text{HH}} = 8.4\text{ Hz}$, 1,8-H), 7.00 (dd, 4H, $J_{\text{HH}} = 2.0, 8.4\text{ Hz}$, 2,7-H), 3.36 (q, 8H, CH_2OCH_3), 1.51 (s, 18H, NCCCH_3), 1.36 (s, 36H, $\text{CCH}_3(\text{Flu})$), 1.08 (t, 12H, CH_2OCH_3), 0.17 (s, 12H, SiCH_3).

15

Synthesis of $[\{^t\text{Bu}_2\text{-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^t\text{Bu}\}\text{Nd}(\mu\text{-Cl})(\text{THF})]_2$ (5). The same procedure as that described above was carried out from the NdCl_3 THF-adduct (prepared from 156 mg, 0.623 mmol of NdCl_3) and $^t\text{Bu}_2\text{-C}_{13}\text{H}_6\text{H-SiMe}_2\text{-NH}^t\text{Bu}$ (255 mg, 0.623 mmol) to yield molecule (5) as a yellow microcrystalline solid (0.45 g, 77%).
20 Crystallization of the reaction mixture from an Et_2O -hexane mixture gave green crystals of molecule (5) suitable for X-ray diffraction (0.15 g, 26%).

Reaction of $[\text{3,6-di-}^t\text{Bu-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^t\text{Bu}]\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2$ (1) with PhSiH_3 or H_2 to produce Y-hydride (6). Method A. To a solution of $[\text{C}_{13}\text{H}_8\text{-SiMe}_2\text{-N}^t\text{Bu}]\text{Y}(\text{CH}_2\text{TMS})(\text{THF})_2$ (0.100 g, 0.137 mmol) in benzene (5 mL) was added
25 phenylsilane (85 μL , 0.688 mmol) at $25\text{ }^\circ\text{C}$. The mixture was stirred for 1 h at this temperature. The yellow precipitate formed was filtrated, washed with benzene (2 mL) and dried in vacuo to give 0.070 g of a pale-yellow microcrystalline product

insoluble in THF and hydrocarbons. **Method B.** A solution of $[\text{C}_{13}\text{H}_8\text{-SiMe}_2\text{-NtBu}]\text{Y}(\text{CH}_2\text{TMS})(\text{THF})_2$ (0.125 g, 0.172 mmol) in benzene (5 mL) was exposed in hydrogen atmosphere (1 atm, 25 °C) for 12 hours to yield after similar workup 30 mg of a pale-yellow insoluble product.

5

Polymerization.

Polymerisation of methyl methacrylate (MMA) and styrene have been carried out with complexes (1), (2) and (6). Complexes (1) and (2) were prepared as disclosed here-above. Complex (6) is an Y-hydride complex. Complex (2) reacts smoothly
10 with bulk MMA at room temperature and 50 °C to give atactic PMMA of narrow molecular weight distribution (MWD). The molecular weight distribution is defined by the polydispersion index D that is the ratio M_w/M_n of the weight average molecular weight M_w over the number average molecular weight M_n . Alkyl complex (1) initiates sluggishly polymerization of MMA and styrene. The
15 polymerization results are displayed in Table I.

TABLE I.

Complex	Condit	Monomer	Temp. °C	Conv. %	M_w 10 ³	MW D	Tacticity		
							<i>rr</i>	<i>mr</i>	<i>mm</i>
2	Bulk	MMA	25	26	250	2.85	26	40	34
2	"	"	50	65	216	3.60	21	40	39
1	"	"	25	Traces	-	-	-	-	-
1	"	"	50	Traces	-	-	-	-	-
1	Toluene	"	25	2	not sol	-	29	29	42
1	"	"	50	2	not sol	-	32	29	40

6	Toluene	"	25	13	19	2.8	33	26	41
1	Bulk	Styrene	25	Traces	-	-	-	-	-
1	"	"	50	3	455	1.81			

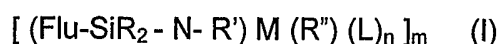
Reaction conditions: MMA/[metal] = 200-500, t = 12 h.

CLAIMS.

1. A metallocene catalyst component based on a Group IIIb metal of the Periodic Table and a bridged constrained geometry fluorenyl-based ligand.

5

2. The metallocene catalyst component according to claim 1 of the general formula



wherein Flu is a fluorenyl, substituted or unsubstituted, M is a Group IIIb metal of the Periodic Table, SiR₂ is a structural bridge between N and Flu (9-position) imparting stereorigidity to the component wherein each R is the same or different and is an alkyl having from 1 to 20 carbon atoms, R' is hydrogen or is of the form ZR[§]₃ wherein Z is C or Si and R[§] is a hydrocarbyl having from 1 to 20 carbon, R'' is hydrogen or is a hydrocarbyl having from 1 to 20 carbon atoms, said hydrocarbyl possibly containing one or more Si atoms, or is a halogen, L is a co-ordinating solvent, n is 0, 1 or 2, and m is 1 or 2.

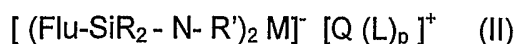
3. The metallocene catalyst component according to claim 2 wherein R'' is selected from hydrogen or an alkyl or an aryl or an allyl.

20

4. The metallocene catalyst component according to claim 2, wherein R'' is a halogen.

5. The metallocene catalyst component according to claim 1 of the general formula

25



wherein Flu is a fluorenyl, substituted or unsubstituted, M is a Group IIIb metal of the Periodic Table, SiR₂ is a structural bridge between N and Flu (9-position)

imparting stereorigidity to the component wherein each R is the same or different and is an alkyl having from 1 to 20 carbon atoms, R' is hydrogen or is of the form $ZR^{\$}_3$ wherein Z is C or Si and $R^{\$}$ is a hydrocarbyl having from 1 to 20 carbon, L is a co-ordinating solvent, Q is an alkali, an earth alkali or a metal Group IIIa of the Periodic Table and p is from 2 to 4.

6. The metallocene catalyst component according to any one of claims 2 to 5, wherein M is yttrium, lanthanum or a member of the lanthanide series (elements having atomic numbers of from 58 to 71).
7. The metallocene catalyst component of claim 6 wherein M is yttrium, lanthanum or neodymium.
8. The metallocene catalyst component according to any one of claims 2 to 7, wherein the substituents on the fluorenyl are the same and are hydrocarbyls having from 1 to 20 carbon atoms.
9. The metallocene catalyst component according to any one of claims 2 to 8, wherein N is substituted and the substituent is tert-butyl.
10. The metallocene catalyst component according to any one of claims 5 to 9 wherein Q is selected from Li, Na, Mg or Al.
11. A process for preparing the metallocene catalyst component of any one of the preceding claims, based on salt metathesis reaction.
12. The process of claim 11 that comprises the steps of:
 - a) suspending $MX_3(THF)_n$ in an ether;

- b) suspending a deprotonated dilithium salt $[\text{Flu-SiR}_2 - \text{N} - \text{R}']\text{Li}_2$ in the same or another ether;
 - c) carrying out the salt metathesis reaction of suspensions a) and b) at a temperature of from $-80\text{ }^\circ\text{C}$ to $60\text{ }^\circ\text{C}$.
 - 5 d) recrystallising the crude product obtained in c) after evaporation of volatiles from an ether or a mixture of an ether and an hydrocarbon at a temperature of from -60 to -0°C ;
 - e) retrieving a crystalline powder of formula (I) or (II)
- 10 13.A process for preparing the metallocene catalyst component of claim 2, based on an alkane elimination reaction.
- 14.A metallocene catalyst system prepared from the metallocene catalyst component of any one of claims 1 to 10 and an activating agent and/or a transfer agent.
- 15
15. A process for polymerisation that comprises the steps of:
- a) introducing a catalyst system based on any one or more of catalyst components of formulas (I) and/or (II) in the reactor,
 - 20 b) optionally introducing an activating agent and/or a transfer agent in the reactor,
 - c) feeding a monomer and an optional comonomer,
 - d) maintaining the system under polymerisation conditions,
 - e) retrieving the desired polymer.
- 25
16. Polymers obtainable from the process of claim 15.

FIGURE 1.

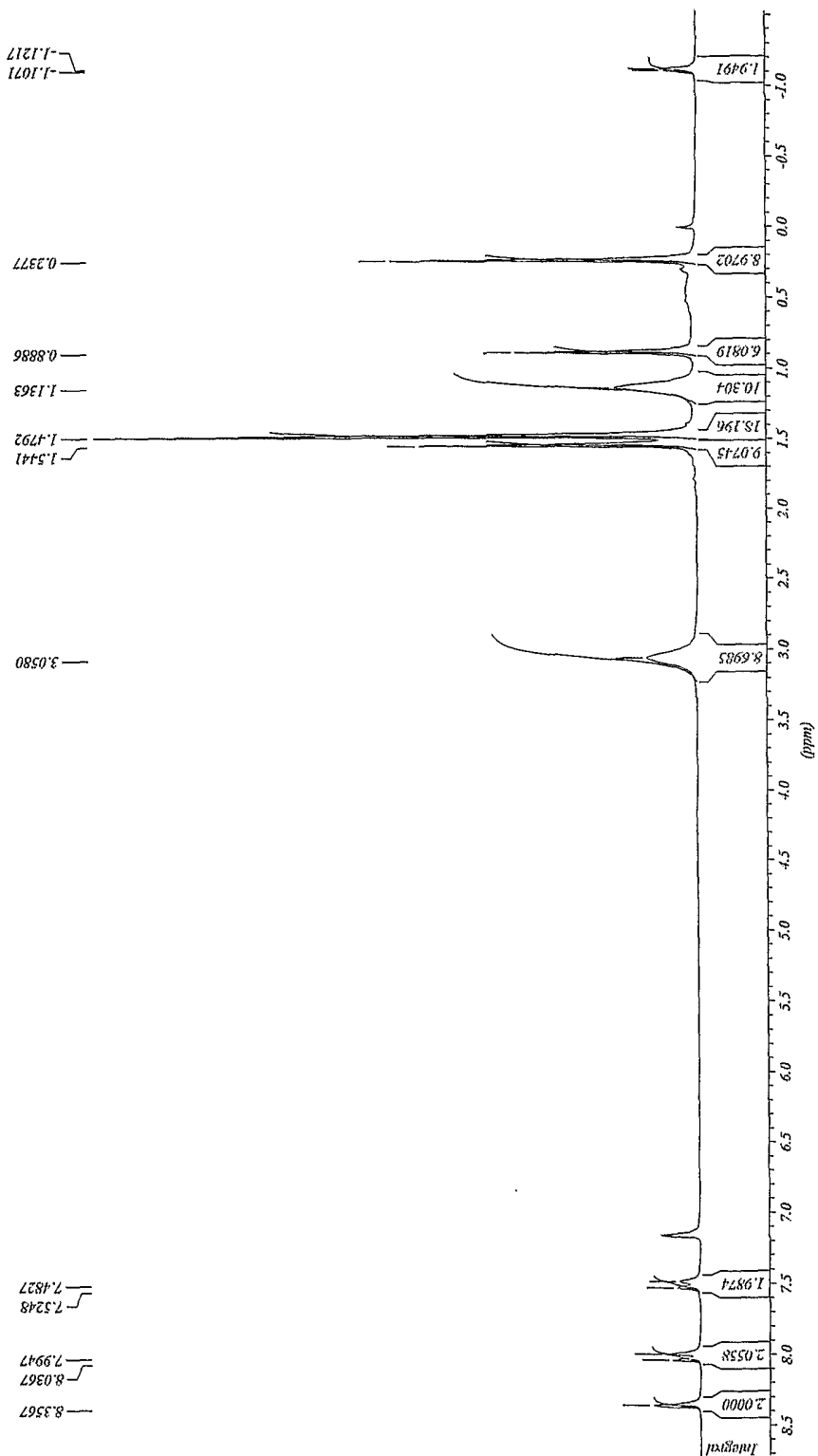


FIGURE 2

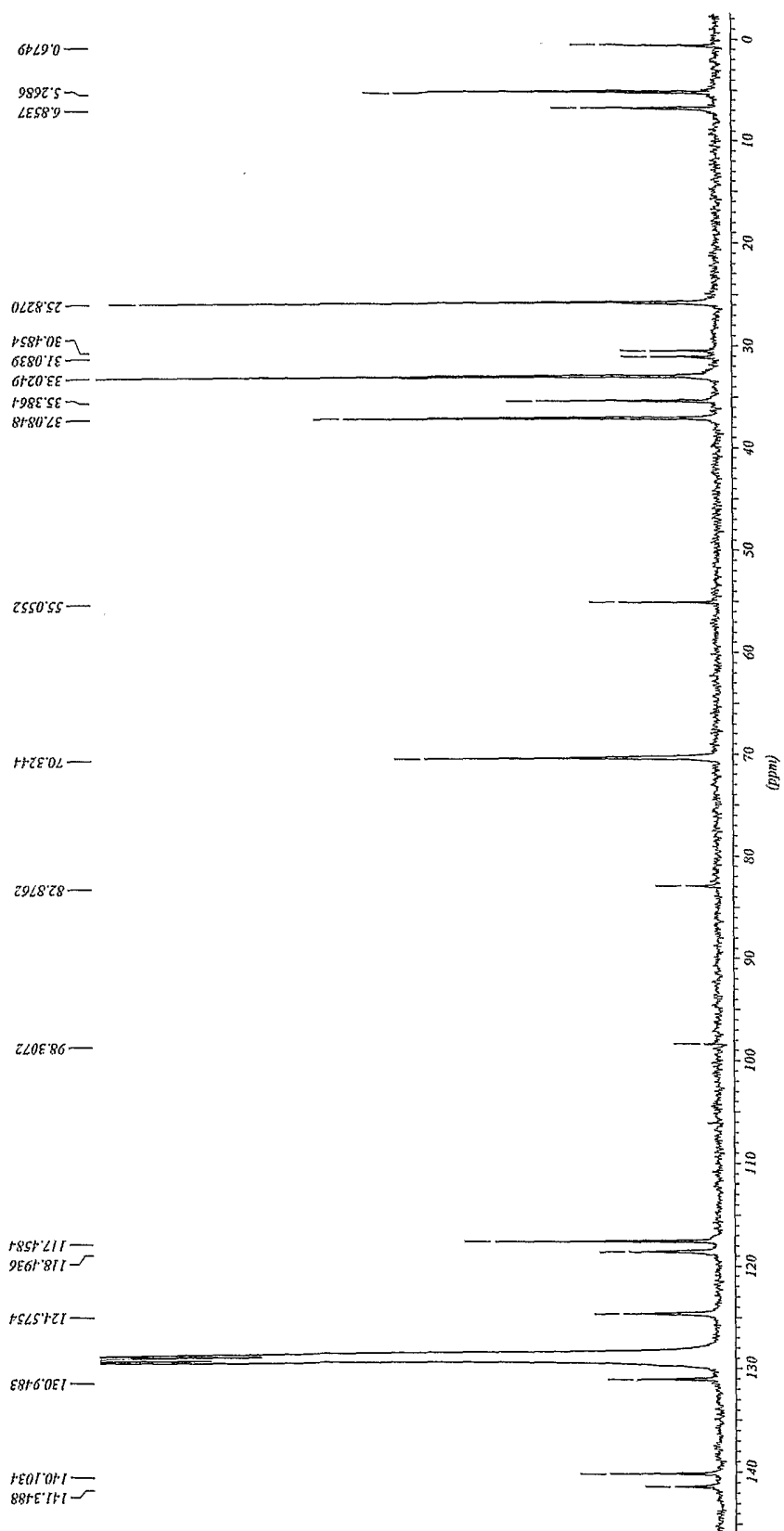


FIGURE 3

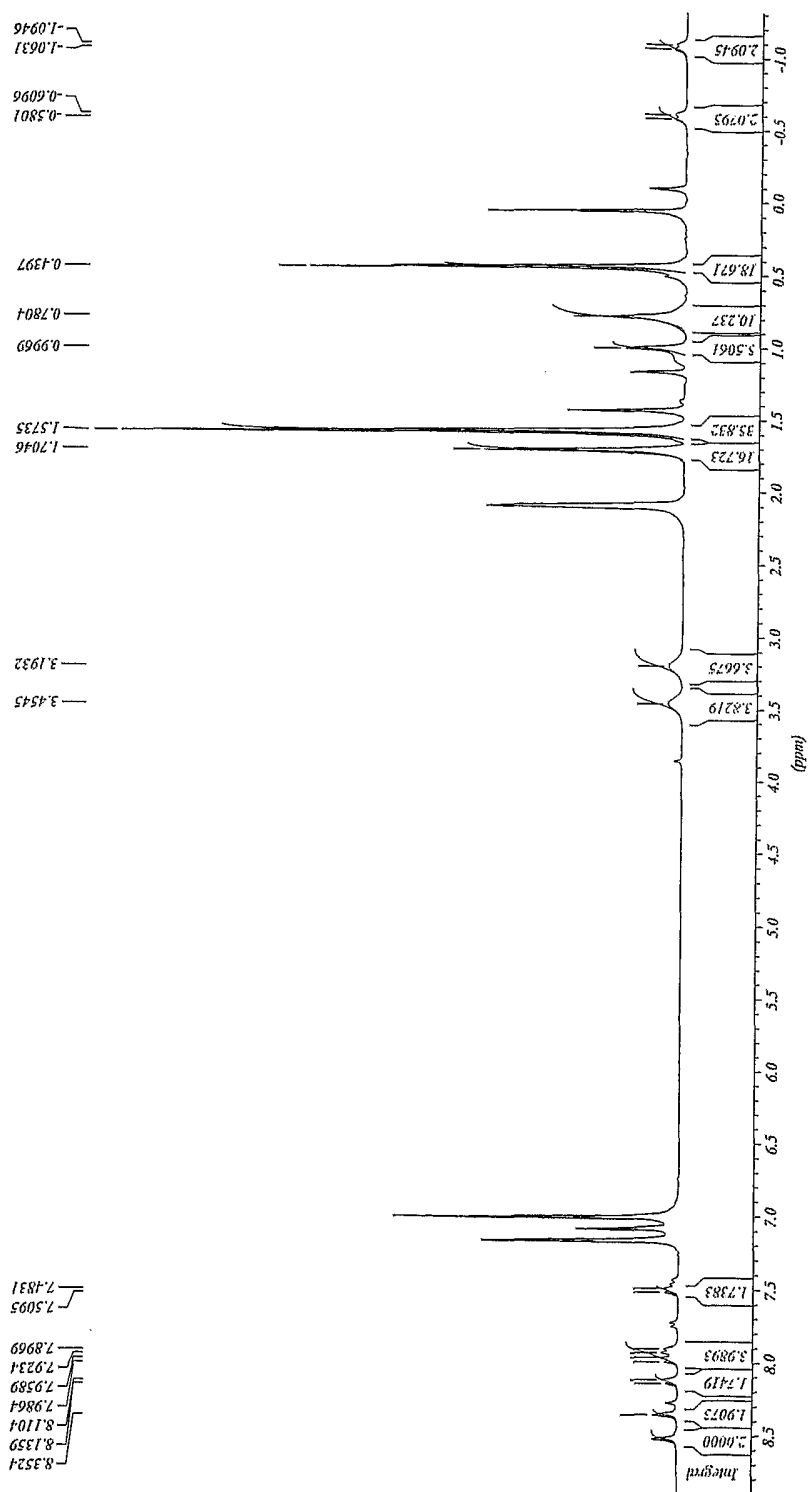


FIGURE 4

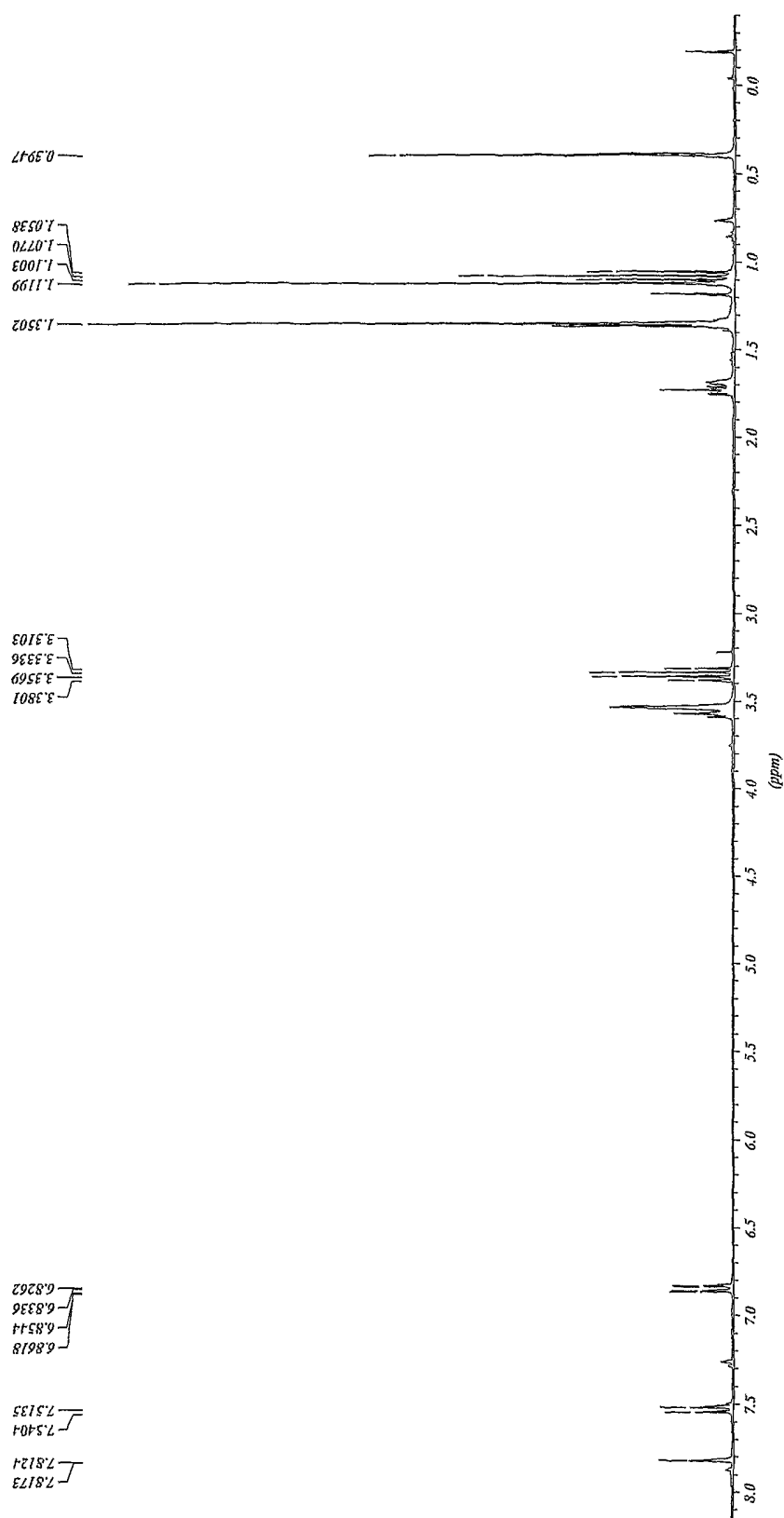


FIGURE 5

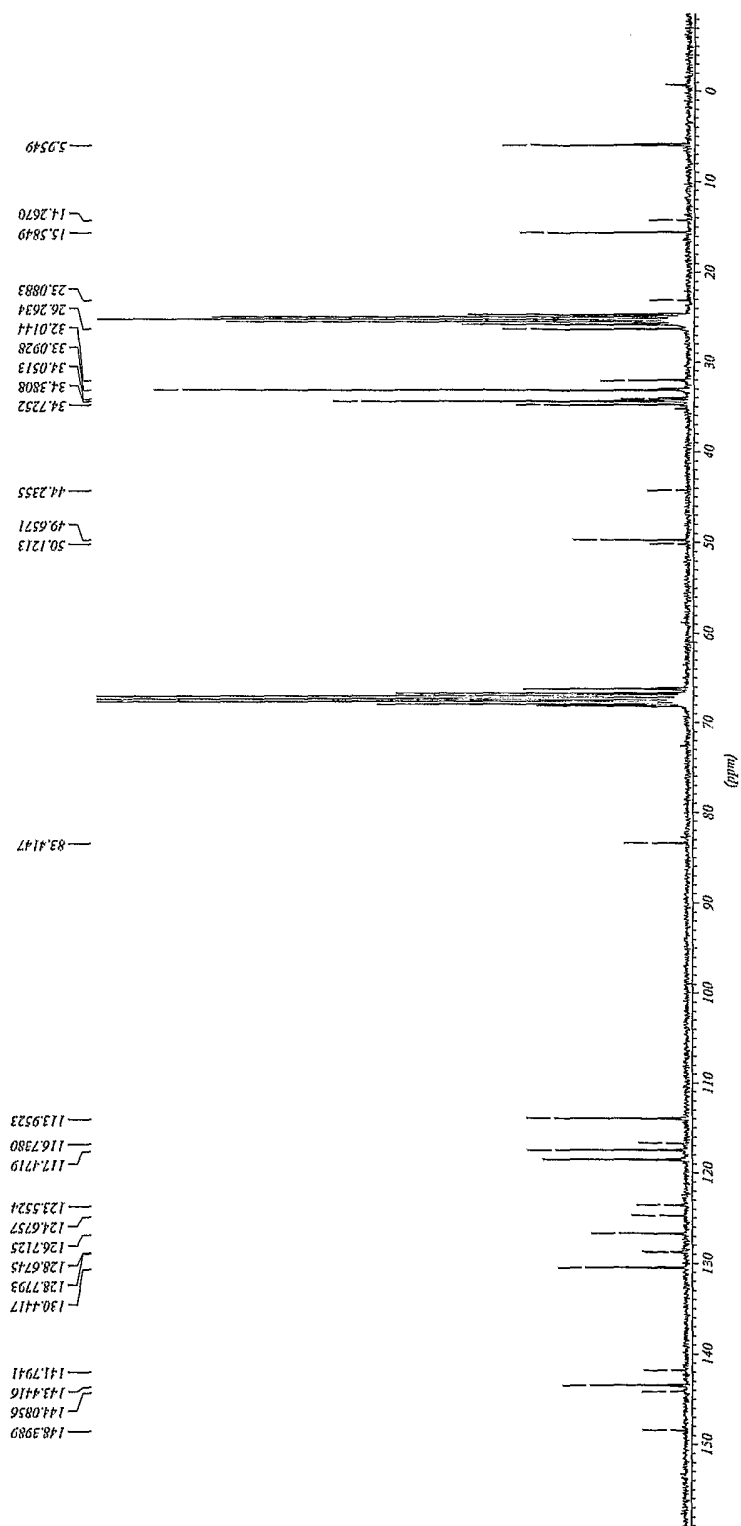


FIGURE 9

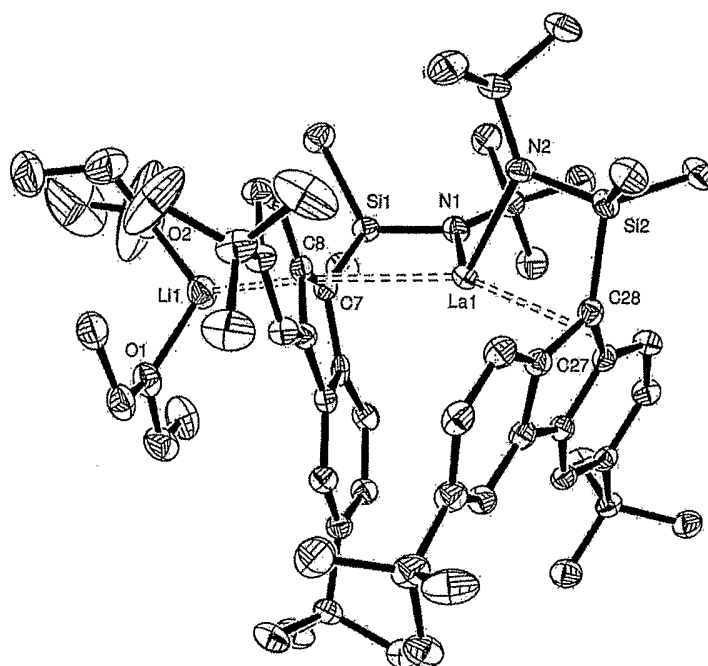


Figure 7.

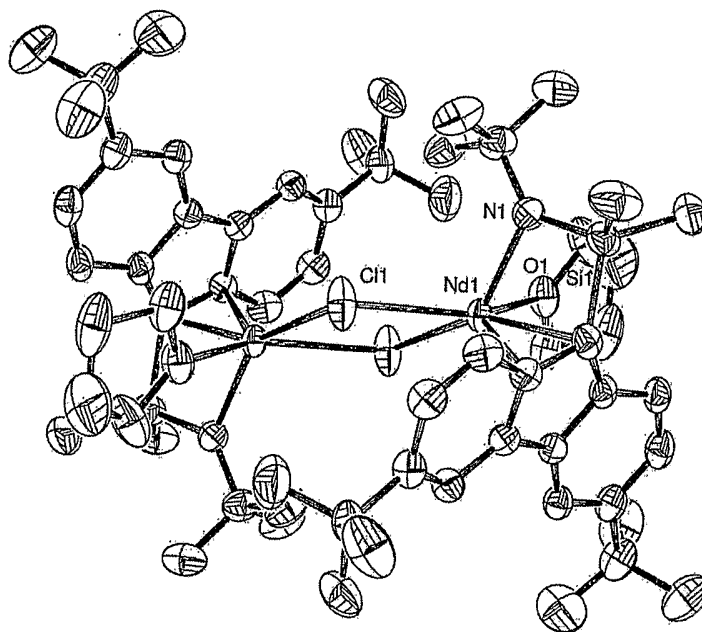


Figure 8.