Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 457



Linear or cross-shaped di(cyclopentadienyltitanium) compounds with aryl or heteroaryl spacers†

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Received 18th August 2010, Accepted 28th September 2010 DOI: 10.1039/c0dt01060j

The preparation of hexamethylated and hexabenzylated arylene or heteroarylene bridged dinuclear di(cyclopentadienyltitanium) compounds from the reaction of the corresponding hexachlorides with methyllithium or benzylmagnesium chloride is described. The spacers between the cyclopentadienyl rings consist of one, two or three phenylene groups, a dioctyloxyphenylene group or a 2,2'-bithienylene group. The corresponding hexachlorides and hexaisopropoxides have also been prepared.

Introduction

In the past few years, hybrid materials have received particular attention. These new materials, where organic and inorganic networks are linked through weak or strong bonds show interesting properties in optics, electronics, membranes, coatings, etc.¹ Class II hybrid materials where the organic and the inorganic components are connected through covalent bonds have been mainly developed from silicon derivatives. These organometallic compounds show strong metal-carbon bonds that resist acidic, basic or fluoride catalyzed sol-gel conditions. Disilylated compounds where two silicon atoms bearing three alkoxyl groups are linked by a spacer proved to be excellent precursors of various types of microporous or mesoporous silica.² Moreover molecular engineering allowed preparation of functionalized materials that are organized by selfassembly³ or by the use of surfactants.⁴ Besides silicon-based hybrid materials, tin-based hybrids materials with alkyl- and aryltin bonds were recently described.⁵ As in the case of silicon, van der Waals and π -stacking interactions were strong enough to organize these materials. The presence of long alkyl chains grafted on the main metal-metal chain allowed the building of a highly organized monoclinic structure.6

Up to now, hybrid materials with metal–carbon bonds have been limited to silicon and tin as metals. To the best of our knowledge no example has been described with transition metals. In the case of titanium, for instance, the σ -titanium–carbon bonds are not hydrolytically stable enough to allow the successful preparation of materials based on oxygen–titanium–carbon linkages. The titanium-based hybrid materials prepared up to now are based on oxygen–titanium–oxygen–carbon bonding. Two main preparative approaches have been used for their syntheses. The first one

ylene group or a 2,2'-bithienylene also been prepared. consists of linking oxo-titanium clusters obtained by hydrolysis of titanium tetraalkoxides to an organic network of *in situ* polymerized ligands such as unsaturated acids.⁷ In the second approach, preformed oxo-titanium clusters containing eight metal atoms are linked with difunctional phthalic acid.⁸ In the first case, aggregation of clusters takes place leading to larger oxo-titanium

species.^{7c,7d,9} We report here our studies concerning the synthesis of suitable precursors able to allow the preparation of a new type of titaniumbased hybrid materials where both networks are linked through strong titanium–cyclopentadienyl bonds. These compounds are di(polymethylcyclopentadienyltitanium) derivatives where the cyclopentadienyl groups are bounded by different spacers and where the titanium atoms bear hydrolyzable groups. It was very important to get spacers of different lengths in order to enable the study of an eventual ordering in the corresponding materials. The presence of various hydrolyzable groups was also important to change the rates of hydrolysis of the precursors, one of the factors acting upon the kinetics of the formation of the hybrid materials.

Results and discussion

To get precursors with the requisite properties, we focused first on bis(tetramethylcyclopentadienyl) compounds with aromatic spacers. Aromatic spacers were selected because (1) they were expected to lead to ligands more easily prepared than ligands with aliphatic spacers, (2) they are not prone to give disubstitution of titanium compounds, and (3) they would give ligands with high self-assembly capacity by π -stacking interactions. We chose to substitute the cyclopentadienyl groups with methyl substituents to get more stable ligand-metal bonds. The synthesis of such compounds is well documented. It starts with the condensation of a bimetallic species, Grignard or lithium reagents, with tetramethylcyclopentenone, followed by dehydration of the formed diol. Then, to introduce the metal atoms, the

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 $[\]dagger$ Electronic supplementary information (ESI) available: Full synthesis and characterization for 3a-7a and 8-11. See DOI: 10.1039/c0dt01060j

dicyclopentadienyl lithium salts can react either with a trialkoxychlorotitanium or could be transmetallated into a disilylated compound, as was shown for monometallic compounds,¹⁰ that allows a smooth reaction with titanium tetrachloride avoiding a secondary reduction into titanium(III) species. As in some cases the disilvlation of bis(tetramethylcyclopentadienyl) compounds did not lead us to satisfactory yields of disilylated derivatives, we turned to the procedure using a trialkoxychlorotitanium described by Do et al.¹¹ This procedure has also the advantage of avoiding the formation of monosubstitution compound,¹² 4-(tetramethylcyclopentadienyl)biphenyl, a by-product in the preparation of 4,4'-bis(tetramethylcyclopentadienyl)biphenyl. This method was successfully extended to 1c with a phenylene group, to 3c with a triphenylene group and to 4b bearing only two methyl groups on the cyclopentadienyl groups. It was modified by the use of dichlorodimethylsilane instead of chlorotrimethylsilane to get a faster chlorination step (Scheme 1).

The octyloxyl substituted complexes were prepared in the same manner as the unsubstituted ones. The dimetallation of 2,5-dibromo-1,4-dioctyloxybenzene with t-butyllithium in diethylether furnished a dilithiated derivative which was then condensed with 2,3,4,5-tetramethycyclopentenone. In this case, however, the expected diol was not obtained perhaps due to steric hindrance of the long alkyl chains. In order to reduce the steric hindrance and to ease the attack of the dilithiated derivative on the ketone, the 2,3,4,5-tetramethylcyclopentenone was replaced by 3.4-dimethycyclopentenone. The required diol was then obtained in good yield. It was not purified and was subsequently dehydrated at room temperature by treatment with a catalytic amount of ptoluenesulfonic acid. Recrystallization in toluene gave the dicyclopentadienyl ligand in good yield. Its treatment with two equivalents of n-butyllithium led to the corresponding dilithiated derivative as a white powder that was metallated with a stoichiometric amount of chlorotriisopropoxytitanium. The coupling was more difficult than with laterally unsubstituted spacers. The expected product was recovered in satisfactory yield only after refluxing for 4 days. Washing the unreacted chlorotriisopropoxytitanium with pentane led to the sensitive hexaisopropoxydititanium 5b with a cross-shaped spacer. It was chlorinated to give 5c as shining violet crystals.

Precursors with a bithienylene spacer were then prepared as this spacer should potentially increase stacking interactions between the ligands by sulfur–sulfur interactions. A bis(tetramethylcyclopentadienyl) ligand with a thienylene spacer was reported recently and used in germanium, tin¹³ and iron chemistry.¹⁴ It was obtained in low yield (10%) by a two-step procedure involving a monocyclopentadienyl substituted intermediate. The one-step procedure described above that involves in this case the addition of 5,5'-dilithio-2,2'-bithiophene¹⁵ on 2,3,4,5-tetramethylcyclopentenone led to the required new ligand in higher yields (49%). Successive di-titanation and chlorination of the metal atoms were achieved by reaction with chlorotriisopropoxytitanium and dichlorodimethylsilane, respectively, to give **6c** as shining violet crystals.

As was shown for other dinuclear compounds with aromatic spacers¹⁶ not involved in cyclic frameworks,¹⁷ we assume that the two TiX_3 moieties have an anti-orientation with respect to the spacer.



Scheme 1 Synthesis of complexes 1-6.

Subsequent methylation¹⁸ of **1c**, **2c**, **3c**, **5c** and **6c** with a slight excess of methyllithium in diethyl ether at -78 °C for 2 h and then at room temperature for 1 h followed by evaporation of the solvent, extraction with toluene, filtration on dry Celite and evaporation of toluene, afforded the corresponding hexamethylated derivatives **1d**, **2d**, **3d**, **5d** and **6d** as yellow-green microcrystalline powders in satisfactory yields. Evaporation of toluene was conducted at temperature below 35 °C in order to limit an extensive decomposition of the alkylated complexes. They were purified by recrystallization from pentane. They looked to be more oxygen, moisture and heat sensitive than the analogous



Fig. 1 ¹H (top) and ¹³C (bottom) NMR spectra of 6d.

cyclopentadienyltrimethyltitaniums and had to be manipulated while shaded from light at room temperature. Benzylation of **2c** and **3c** was performed analogously with benzylmagnesium chloride instead of methyllithium. Although alkylated compounds were too sensitive to be shipped for microanalysis, fresh solutions in C_6D_6 or CDCl₃ were found quite pure by NMR as it is shown in Fig. 1 for **6d**.

To get reference compounds for spectroscopic studies on the materials derived from the above described precursors, we needed monomeric titanium oxides with a phenyltetramethylcyclopentadienyl ligand. They were obtained by hydrolysis of trimethyl(phenyltetramethylcyclopentadienyl)titanium by an improvement of the procedure which was described for a pentamethylcyclopentadienyl compound (Scheme 2).¹⁹

The trichloride **8** was obtained more rapidly and in better yield than described²⁰ by using the more reactive (phenylte-tramethylcyclopentadienyl)dimethylsilane **7** instead of the corresponding trimethylsilane. At -60 °C in chloroform, the ¹H NMR spectrum of **7** indicates that it is a 78/22 mix-ture of two silanes that isomerize at room temperature by a rapid intramolecular sigmatropic rearrangement.²¹ Then the trichloride was alkylated with methyllithium¹⁸ to give the new trimethyl(phenyltetramethylcyclopentadienyl)titanium. Its partial hydrolysis under water vapour led to the tetramethylated oxide



Scheme 2 Synthesis of complexes 10 and 11.

10 in high yield. When an excess of water was used, the ¹H NMR spectrum of the crude mixture showed that 11 was mainly formed together with some uncharacterized oligomers. However, the isolated yield was about three times higher than

previously reported from the triethylamine-catalyzed hydrolysis of the trichloride 8^{20}

Conclusions

In summary, new hexaalkylditaniums suitable for the preparation of hybrid materials have been obtained from the alkylation of the corresponding hexachlorides. Various spacers with one, two or three benzene rings, or a bithienylene group were used. An improved synthesis of (phenyltetramethylcyclopentadienyl)titanium oxides, dimer or tetramer, has also been presented.

Experimental

General procedures

All reactions were carried out under a nitrogen atmosphere. Pentane, THF, toluene and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Acetonitrile and dichloromethane were distilled over CaH₂. ¹H, and ¹³C NMR spectra were recorded on Bruker DPX 200, AC 250 or DPX 300 spectrometers. Elemental analyses were performed by the "Service d'analyse du CNRS" at Vernaison, France. 1,4-Bis(tetramethylcyclopentadienyl)benzene (**1a**),²² 4,4'-bis-(tetramethylcyclopentadienyl)biphenyl (**2a**),¹¹ 4,4'-biphenylene-bis(2,3,4,5-tetramethylcyclopentadienyl)di(triisopropoxytitanium) (**2b**)¹¹ and 4,4'-biphenylenebis(2,3,4,5-tetramethylcyclopentadienyl)di(titanium trichloride) (**2c**)¹¹ were synthesized *via* a literature procedure.

Syntheses

1,4 - Phenylenebis(2,3,4,5 - tetramethylcyclopentadienyl)di(triisopropoxytitanium) (1b). In a dry Schlenk tube under nitrogen, a solution of n-BuLi (7.19 mL, 17.98 mol L⁻¹) in pentane was added dropwise to a solution of 1,4-bis(2,3,4,5tetramethylcyclopentadienyl)benzene (1a) (2.86 g, 8.99 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight. A solution of chlorotriisopropoxytitanium (4.68 g, 17.99 mmol) in THF (30 mL) was added to the reaction mixture at 0 °C and the resulting mixture was refluxed for 3 days. The solvent was evaporated under vacuum and the residue was extracted with pentane. A yellow solid was obtained after evaporation of the solvent which was then washed 3 times with pentane to give the required product. Yield: 67%. Anal. Calcd. for C42H70Ti2O6: C, 65.79; H, 9.20. Found: C, 65.27; H, 9.69. NMR (CDCl₃) $\delta_{\rm H}$: 1.06 (36H, d, ${}^{3}J_{\rm H-H}$ = 6.1 Hz, Me), 2.06 (12H, s, Me), 2.12 (12H, s, Me), 4.48 (6H, m, ${}^{3}J_{H-H} = 6.1$ Hz, CH), 7.36 (4H, s, CH); δ_c: 11.5, 12.5, 26.5, 75.4, 121.7, 122.1, 124.6, 130.0, 133.4.

4,4" - **Terphenylenebis(2,3,4,5** - **tetramethylcyclopentadienyl)di-**(**triisopropoxytitanium**) (**3b**). The same procedure was followed as for **1b** except that 4,4"-bis(2,3,4,5-tetramethylcyclopentadienyl)terphenyl (**3a**) was used instead of 1,4-bis(2,3,4,5-tetramethylcyclopentadienyl)benzene (**1a**). Yield: 68%. Anal. Calcd. for $C_{54}H_{78}Ti_2O_6$: C, 70.58; H, 8.55. Found: C, 70.94; H, 8.73. NMR (CDCl₃) $\delta_{\rm H}$: 1.00 (36H, d, ${}^3J_{\rm H-H} = 6.1$ Hz, Me), 1.99 (12H, s, Me), 2.06 (12H, s, Me), 4.43 (6H, m, ${}^3J_{\rm H-H} = 6.1$ Hz, CH), 7.40 (4H, d, ${}^3J_{\rm H-H} = 8.3$ Hz, CH), 7.58 (4H, d, ${}^3J_{\rm H-H} =$ 8.3 Hz, CH), 7.67 (4H, s, CH); $\delta_{\rm C}$: 11.5, 12.5, 26.5, 75.6, 121.8, 122.0, 124.0, 126.1, 127.4, 131.3, 135.3, 138.1, 139.9.

4,4"-Terphenylenebis(3,4-dimethylcyclopentadienyl)di(triisopropoxytitanium) (4b). The same procedure was followed as for **1b** except that 4,4"-bis(3,4-dimethylcyclopentadienyl) terphenyl (**4a**) was used instead of 1,4-bis(2,3,4,5-tetramethylcyclopentadienyl)benzene (**1a**). (Yield 42%) NMR (CDCl₃) $\delta_{\rm H}$: 1.02 (36H, d, ${}^{3}J_{\rm H-H}$ = 6.1 Hz, Me), 2.14 (12H, s, Me), 4.46 (6H, m, ${}^{3}J_{\rm H-H}$ = 6.1 Hz, CH), 6.39 (4H, s, CH) 7.61 (8H, s, CH), 7.70 (4H, s, CH); $\delta_{\rm C}$: 13.38, 26.19, 76.98, 109.66, 126.0, 126.9, 127.3, 134.6, 138.3, 139.8.

1,4-Dioctyloxyphenylene-2,5-bis(3,4-dimethylcyclopentadienyl)di(triisopropoxytitanium) (5b). The same procedure was followed as for **1b** except that 2,5-bis(3,4-dimethylcyclopentadienyl)-1,4dioctyloxybenzene (**5a**) was used instead of 1,4-bis(2,3,4,5tetramethylcyclopentadienyl)benzene (**1a**) and the reaction mixture was refluxed for 4 days. Yield: 95%. Anal. Calcd. for $C_{54}H_{94}Ti_2O_8$: C, 67.06; H, 9.80. Found: C, 66.42; H, 9.79. NMR (CDCl₃) $\delta_{\rm H}$: 0.87 (6H, t, ${}^{3}J_{\rm H-H}$ = 6.5 Hz, Me), 1.03 (36H, d, ${}^{3}J_{\rm H-H}$ = 6.1 Hz, Me), 1.21–1.89 (24H, m, CH₂), 2.12 (12H, s, Me), 3.99 (4H, t, ${}^{3}J_{\rm H-H}$ = 6.5 Hz, CH₂O), 4.50 (6H, m, ${}^{3}J_{\rm H-H}$ = 6.1 Hz, CH), 6.56 (4H, s, CH), 7.11 (2H, s, CH); $\delta_{\rm C}$: 13.3, 14.3, 22.9, 26.2, 26.5, 29.5, 29.6, 29.8, 32.0, 69.4, 76.6, 112.7, 113.0, 121.1, 122.8, 125.1, 150.3.

5,5'-Bithienylenebis(2,3,4,5-tetramethylcyclopentadienyl)di(triisopropoxytitanium) (6b). The same procedure was that 5,5'-bis(2,3,4,5-tetrafollowed as for (1b) except methylcyclopentadienyl)bithiophene (6a) was used instead of 1,4-bis(2,3,4,5-tetramethylcyclopentadienyl)benzene (1a) and the reaction mixture was refluxed for 2 days. Yield: 40%. Anal. Calcd. for C₄₄H₇₀S₂Ti₂O₆: C, 61.82; H, 8.25. Found: C, 61.17; H, 7.96. NMR (CDCl₃) $\delta_{\rm H}$: 1.11 (36H, d, ${}^{3}J_{\rm H-H}$ = 6.0 Hz, Me), 2.06 (12H, s, Me), 2.20 (12H, s, Me), 4.58 (6H, m, ${}^{3}J_{H-H} = 6.0$ Hz, CH), 6.91 (2H, d, ${}^{3}J_{H-H} = 3.8$ Hz, CH), 7.11 (2H, d, ${}^{3}J_{H-H} = 3.8$ Hz, CH); δ_c: 11.5, 12.7, 26.5, 75.8, 116.4, 122.2, 122.4, 122.6, 127.9, 136.4, 136.9.

1,4 - Phenylenebis(2,3,4,5 - tetramethylcyclopentadienyl)di(titanium trichloride) (1c). In a dry Schlenk tube under nitrogen, chlorotrimethylsilane (5.09 g, 46.99 mmol) was added slowly to a solution of 1,4-phenylenebis(2,3,4,5tetramethylcyclopentadienyl)di(triisopropoxytitanium) (1b) (2 g, 2.61 mmol) in dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. A slow formation of red precipitates was observed. The precipitates were allowed to settle down and the solvent was decanted off. The red compound was washed several times with acetonitrile and dried in vacuum. The required product was obtained as red crystals. Due to very low solubility of the compound in CDCl₃ and other solvents, it was not possible to obtain a good ¹³C NMR. Yield: 84%. Anal. Calcd. for C₂₄H₂₈Ti₂Cl₆: C, 46.13; H, 4.51. Found: C, 45.59; H, 4.56. NMR (CDCl₃) $\delta_{\rm H}$: 2.45 (12H, s, Me), 2.52 (12H, s, Me), 7.47 (4H, s, CH).

4,4" - Terphenylenebis (2,3,4,5 - tetramethylcyclopentadienyl) di-(titanium trichloride) (3c). The same procedure was followed as for 1c except that 3b was used instead of 1b. Yield: 87%. Anal. Calcd. for $C_{36}H_{36}Ti_2Cl_6$: C, 55.64; H, 4.67. Found: C, 55.32; H, 4.92. NMR (CDCl₃) $\delta_{\rm H}$: 2.46 (12H, s, Me), 2.54 (12H, s, Me), 7.47 (4H, d, ${}^{3}J_{\rm H-H}$ = 8.3 Hz, CH), 7.73 (4H, d, ${}^{3}J_{\rm H-H}$ = 8.3 Hz, CH), 7.75 (4H, s, CH); $\delta_{\rm C}$: 14.9, 15.8, 127.1, 127.8, 131.1, 132.4, 136.4, 139.0, 139.7, 140.9, 142.5.

1,4-Dioctyloxy-2,5-phenylenebis(3,4-dimethylcyclopentadienyl)di(titanium trichloride) (5c). The same procedure was followed as for **1c** except that **5b** was used instead of **1b** and Me₃SiCl was replaced by Me₂SiCl₂. The reaction mixture was stirred for 2 days at room temperature. Yield: 61%. Anal. Calcd. for $C_{36}H_{52}O_2Ti_2Cl_6$: C, 52.39; H, 6.35. Found: C, 53.68; H, 6.87. NMR (CDCl₃) $\delta_{\rm H}$: 0.87 (6H, t, ³*J*_{H-H} = 6.5 Hz, Me), 1.30–1.99 (24H, m, CH₂), 2.49 (12H, s, Me), 4.13 (4H, t, ³*J*_{H-H} = 6.5 Hz, CH₂O), 7.29 (2H, s, CH), 7.40 (4H, s, CH); $\delta_{\rm C}$: 14.3, 16.2, 22.8, 26.5, 29.4, 29.5, 29.6, 32.0, 69.6, 113.0, 122.9, 124.3, 136.9, 139.3, 150.4.

5,5'-Bithienylenebis(2,3,4,5-tetramethylcyclopentadienyl)di(titanium trichloride) (6c). The same procedure was followed as for **1c** except that **6b** was used instead of **1b** and Me₃SiCl was replaced by Me₂SiCl₂. Yield: 44%. Anal. Calcd. for C₂₆H₂₈S₂Ti₂Cl₆: C, 43.79; H, 3.96. Found: C, 43.34; H, 3.67. NMR (CD₂Cl₂) $\delta_{\rm H}$: 2.42 (12H, s, Me), 2.64 (12H, s, Me), 7.22 (2H, d, ${}^{3}J_{\rm H-H}$ = 3.8 Hz, CH), 7.30 (2H, d, ${}^{3}J_{\rm H-H}$ = 3.8 Hz, CH).

1,4 - Phenylenebis(2,3,4,5 - tetramethylcyclopentadienyl)di(trimethyltitanium) (1d). In a dry Schlenk tube under nitrogen, covered with an aluminium foil, a solution of MeLi (8.16 mL, 13.05 mmol) in diethyl ether was added slowly to a solution of 1.4-phenylenebis(2.3.4.5-tetramethylcyclopentadienyl)di(titanium trichloride) (1c) (1.36 g, 2.17 mmol) in diethyl ether (30 mL) at -78 °C. The reaction mixture was stirred at this temperature for 2 h and then at room temperature for 1 h. The solvent was removed under vacuum and the residue was extracted with toluene. The corresponding solution was then filtered on dry Celite. The required product was obtained as a yellowish green powder after the evaporation of the solvent at reduced temperature $(< 35 \ ^{\circ}C)$ to avoid premature decomposition of the complex. It was recrystallised in pentane. Yield: 62%. NMR (CDCl₃) $\delta_{\rm H}$: 0.90 (18H, s, Me), 2.01 (12H, s, Me), 2.07 (12H, s, Me), 7.11 (4H, s, CH); $\delta_{\rm C}$: 12.4, 13.3, 63.4, 120.3, 124.1, 129.7, 130.1, 134.1.

4,4' - Biphenylenebis(2,3,4,5 - tetramethylcyclopentadienyl)di(trimethyltitanium) (2d). The same procedure was followed as for **1d** using **2c** instead of **1c**. Yield: 71%. NMR (CDCl₃) $\delta_{\rm H}$: 0.89 (18H, s, Me), 1.99 (12H, s, Me), 2.06 (12H, s, Me), 7.16 (4H, d, ${}^{3}J_{\rm H-H}$ = 8.1 Hz, CH), 7.55 (4H, d, ${}^{3}J_{\rm H-H}$ = 8.1 Hz, CH); $\delta_{\rm C}$: 12.4, 13.2, 63.4, 120.3, 124.1, 126.5, 129.8, 130.7, 134.9, 138.8.

4,4" - **Terphenylenebis(2,3,4,5** - **tetramethylcyclopentadienyl)di-**(**trimethyltitanium) (3d).** The same procedure was followed as for **1d** using **3c** instead of **1c**. Yield: 50%. NMR (CDCl₃) $\delta_{\rm H}$: 0.94 (18H, s, Me), 2.03 (12H, s, Me), 2.11 (12H, s, Me), 7.22 (4H, d, ³J_{H-H} = 8.3 Hz, CH), 7.63 (4H, d, ³J_{H-H} = 8.3 Hz, CH), 7.71 (4H, s, CH); $\delta_{\rm C}$: 12.4, 13.2, 63.5, 120.4, 124.2, 126.6, 127.5, 129.8, 130.8, 135.0, 138.9, 139.7.

1,4-Dioctyloxy-2,5-phenylenebis(3,4-dimethylcyclopentadienyl)di(trimethyltitanium) (5d). The same procedure was followed as for 1d using 5c instead of 1c. Yield: 87%. NMR (CD₂Cl₂) $\delta_{\rm H}$: 0.89 (6H, t, ${}^{3}J_{\rm H-H}$ = 6.5 Hz, Me), 0.90 (18H, s, Me), 1.31–1.85 (24H, m, CH₂), 2.06 (12H, s, Me), 3.94 (4H, t, ${}^{3}J_{\rm H-H}$ = 6.5 Hz, CH₂O), 6.63 (4H, s, CH), 6.95 (2H, s, CH); $\delta_{\rm C}$: δ 14.1, 14.4, 23.2, 29.9, 30.0, 32.4, 62.3, 68.9, 111.7, 112.0, 122.8, 124.5, 125.1, 149.6.

5,5' - Bithienylenebis(2,3,4,5 - tetramethylcyclopentadienyl)di(trimethyltitanium) (6d). The same procedure was followed as for **1d** using **6c** instead of **1c**. Yield: 81%. NMR (CDCl₃) $\delta_{\rm H}$: 0.94 (18H, s, Me), 2.00 (12H, s, Me), 2.18 (12H, s, Me), 6.78 (4H, d, ${}^{3}J_{\rm H-H} = 3.7$ Hz, CH), 7.07 (4H, d, ${}^{3}J_{\rm H-H} = 3.7$ Hz, CH); $\delta_{\rm C}$: 12.4, 13.5, 64.4, 120.4, 121.7, 123.2, 124.4, 127.8, 129.2, 136.5.

4,4'-Biphenylenebis(2,3,4,5-tetramethylcyclopentadienyl)di(tribenzyltitanium) (2e). The same procedure was followed as for **2d** using benzylmagnesium chloride instead of MeLi. The required product was obtained as a red powder after the evaporation of the solvent. Yield: 95%. NMR (CDCl₃) $\delta_{\rm H}$: 1.96 (12H, s, Me), 2.03 (12H, s, Me), 2.81 (s, 12H, CH₂Ph), 6.62–7.70 (38H, m, CH); $\delta_{\rm C}$: 12.4, 13.3, 96.7, 122.5, 122.7, 125.7, 126.8, 128.4, 128.6, 130.9, 134.2, 139.3, 139.8, 150.1.

4,4" - Terphenylenebis(**2,3,4,5** - tetramethylcyclopentadienyl)di-(tribenzyltitanium) (3e). The same procedure was followed as for **2e** using **3c** instead of **2c**. Yield: 92%. NMR (CDCl₃) $\delta_{\rm H}$: 1.96 (12H, s, Me), 2.03 (12H, s, Me), 2.81 (s, 12H, CH₂Ph), 6.62–7.72 (38H, m, CH), 7.78 (4H, s, CH); $\delta_{\rm C}$: 12.4, 13.4, 96.7, 122.5, 122.7, 125.7, 126.8, 127.6, 128.5, 130.9, 134.2, 139.3, 139.8, 150.1.

Acknowledgements

Acknowledgement is made to the Aquitaine Region and the CNRS (Material Program Grant) for partial financial support of this work.

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