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Binuclear monoindenyl–titanium(IV) complexes. Synthesis and styrene polymerization catalysis[1]

Juan C. Flores *, Thomas E. Ready, James C.W. Chien, Marvin D. Rausch

Department of Chemistry, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, 01003, USA

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Abstract

The first binuclear monoindenyl–titanium(IV) complexes have been synthesized by the stepwise reaction of [1,2-C_2H_4(1-Ind)$_2$]Li_2 with 2 equiv of ClTi(O-*i*-Pr)$_3$, giving a 1:1 *rac* and *meso* mixture of 1,2-C_2H_4[1-IndTi(O-*i*-Pr)$_3$]$_2$ (**2**), followed by an in situ chlorination reaction with $CH_3C(O)Cl$ in ethyl ether to form 1,2-C_2H_4[1-IndTi(O-*i*-Pr)Cl_2]$_2$ (**3**). Further reaction of **3** with $CH_3C(O)Cl$ in CH_2Cl_2 afforded 1,2-C_2H_4[1-IndTiCl_3] (**4**). Styrene polymerization studies with methylaluminoxane (MAO) as cocatalyst demonstrated **3** and **4** to be highly syndiospecific catalyst precursors, although their activities were one order of magnitude lower than for the reference mononuclear compound IndTiCl_3 (**1**). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Indenyl; Binuclear complexes; Styrene; Polymerization

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1. Introduction

The first syndiospecific polymerization of styrene at room temperature and above, using organotitanium compounds activated with methylaluminoxane (MAO), was first reported by Ishihara and coworkers [1]. They found that (η^5-cyclopentadienyl)trichlorotitanium (CpTiCl_3) and (η^5-pentamethylcyclopentadienyl)trichlorotitanium (Cp*TiCl_3) formed the most active catalysts. Further studies on these and other monocyclopentadienyl–titanium complexes, activated with MAO or other cation-forming cocatalysts, have subsequently been described [2]. We have recently demonstrated that (η^5-indenyl)trichlorotitanium, IndTiCl_3 (**1**)/MAO, is a more active and syndiospecific catalyst system than CpTiCl_3/MAO over a wide range of polymerization conditions [3]. Commercial production of syndiotactic polystyrene (*s*-PS) is scheduled in the near future [4]. At the present time, however, research efforts have been limited to mononuclear half-sandwich organotitanium compounds. As in the case of ethylene and propylene polymerizations, few studies have been reported using binuclear systems [5]. Several binuclear monocyclopentadienyl–titanium(IV) compounds have recently been synthesized by Royo et al. who made use of a metathesis reaction of bifunctionalized ligands comprising two linked cyclopentadienyl rings with 2 equiv of TiCl_4 [6].

One of our interests in this area involves the synthesis of new binuclear monoindenyl–titanium complexes, and a study of the effects on activity (**A**) and syndiospecificity (S.Y.) [7] resulting from possible cooperative chemical behavior between the two metal centers. We report here the synthesis of the binuclear compounds: 1,2-C_2H_4[1-IndTi(O-*i*-Pr)$_3$]$_2$ (**2**), 1,2-C_2H_4[1-IndTi(O-*i*-Pr)Cl_2]$_2$ (**3**), and 1,2-C_2H_4[1-IndTiCl_3]$_2$ (**4**). Compounds **3** and **4** have been employed as catalyst precursors for the syndiospecific polymerization of styrene when activated with MAO.

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* Corresponding author. Present address: Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871-Alcalá de Henares, Madrid, Spain.

[1] Dedicated to Professor R. Bruce King in honor of his long and dedicated service to organometallic chemistry.

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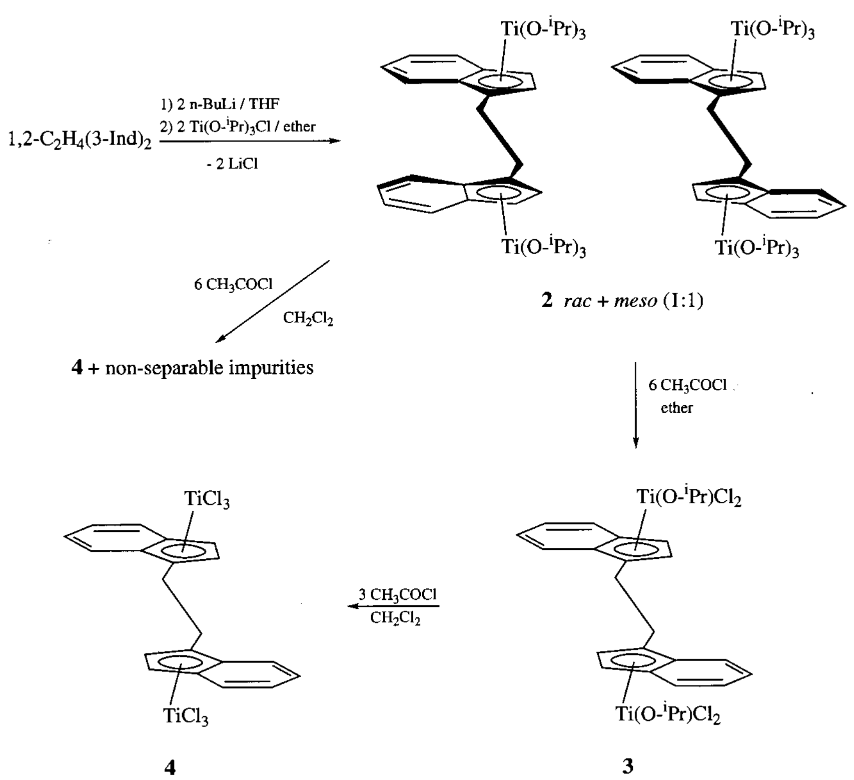

Scheme 1.

2. Results and discussion

2.1. Synthesis

The synthesis of monocyclopentadienyl trichlorotitanium compounds through chlorination of the corresponding trialkoxide derivative with acetyl chloride has been reported by Nesmeyanov et al. [8]. This procedure was adapted in this work. A reaction of $[1,2\text{-}C_2H_4(1\text{-}Ind)_2]Li_2$ in the dark with 2 equiv of $ClTi(O\text{-}i\text{-}Pr)_3$ in ethyl ether, keeping the temperature always below 0°C, produced the binuclear compound **2** as an orange oil in 98% yield (Scheme I).

Distillation, recrystallization, or Bio-beads liquid chromatography ([2]i) all failed to purify **2** because of its air-, light-, and temperature-sensitivity. Nevertheless, a ^{1}H-NMR spectrum of the crude product indicated that compound **2** was sufficiently pure for subsequent chlorination (vide infra). The ^{1}H-NMR spectrum of **2** is consistent with a 1:1 mixture of *racemic* and *meso* diastereomers. It includes widely (δ 6.55 and 6.45, $J_{2,3} = 3.3$ Hz) and narrowly (δ 6.29 and 6.27, $J_{2,3} = 3.1$ Hz) separated pairs of doublets for the indenyl 2,3-protons, one pair for each isomer. The single proton of the *iso*-propoxide groups ($O\text{-}CHMe_2$) also appears as two signals (δ 4.45 and 4.42, 2 hept, $^3J = 6.1$ Hz). The two methyls on each *iso*-propoxy group are diastereotopic which splits the doublet expected for each isomer into two doublets separated by just 1.2 Hz. This small splitting is not resolved in the heptets for the single proton of the $O\text{-}CHMe_2$ groups. The ethylene bridge protons form an AA′BB′ spin system which appears as a singlet for one isomer (δ 3.35) [9–11] and a multiplet for the other one (δ 3.45–3.20). Brief heating of **2** to 50°C causes its decomposition, as demonstrated by changes in its ^{1}H-NMR spectrum (see Section 4).

An in situ reaction of **2** with 6 equiv of $CH_3C(O)Cl$ in ethyl ether produced a red solid and a deep red solution. After work-up, the solid was characterized as compound **3**, whereas the solution contained a complicated mixture of several compounds (Scheme 1). The progressive exchange of alkoxide by chloride substituents lowers the solubilities of the resulting products in ethyl ether. As a result, **3** was precipitated out of the solution and further chlorination did not occur in this solvent. However, when **3** was dissolved in CH_2Cl_2, and then treated with excess of $CH_3C(O)Cl$, complete chlorination occurred to give compound **4** as a microcrystalline purple–black solid (Scheme 1).

Compound **4** could also be detected when **2** was directly chlorinated in CH_2Cl_2, but this single step afforded only impure **4** which could not be further purified. Also, it is worth mentioning that the same result, a mixture of **4** with non-separable impurities, was obtained when the disilylated compound $1,2\text{-}C_2H_4\{3\text{-}[1\text{-}Ind(SiMe_3)]\}_2$ [12] was reacted with 2 equiv of $TiCl_4$ in toluene or CH_2Cl_2 as a solvent.

Table 1
Styrene polymerization catalyzed by **1**, **3** or **4**/MAO[a]

Run no.	[Ti] (μm)	Al/Ti	*T*p (°C)	$IndTiCl_3$ (1)		$\{Et[IndTi(O-{}^iPr)Cl_2]_2\}$ (**3**)			$\{Et[IndTiCl_3]_2\}$ (**4**)		
				$A^b \times 10^{-7}$	S.Y.[c]	Yield (g)	$A^b \times 10^{-6}$	S.Y.[c]	Yield (g)	$A^b \times 10^{-6}$	S.Y.[c]
1	25	2000	25			0.072	1.32	96	0.088	3.24	93
2	25	4000	25	1.70	92	0.079	1.45	94	0.036	1.32	80
3	50	2000	25	0.96	97	0.060	0.55	95	0.070	1.29	96
4	50	4000	25	1.90	97	0.108	1.00	94	0.065	1.20	80
5	50	4000	50	3.70	98	0.174	1.60	95	0.055	1.01	87
6	50	4000	75	1.80	96	0.072	0.66	87	0.033	0.61	70
7	50	4000	100	1.10	90	0.045	0.41		0.010	0.18	

[a] Polymerization conditions: volume, 50 ml toluene + 5 ml styrene; $t_p = 0.5$ h.

[b] Gram of polymer/($mol_{Ti} \times mol_{styrene} \times h$).

[c] S.Y. = (g of 2-butanone insoluble polymer/g of bulk polymer) × 100.

Surprisingly, the ^{1}H-NMR spectra of **3** and **4** show the presence of only one pure isomer (*rac* or *meso*). The indenyl 2,3-protons in the former appear as just one set of two well-separated doublets (δ 6.70 and 6.61, $J_{2,3} =$ 3.4 Hz), the O–C*H*Me_2 proton as one single heptet (δ 4.96, $^3J = 6.2$ Hz), the ethylene bridge as a singlet (δ 3.45), and the methyls of the *iso*-propoxide groups as two doublets (δ 1.37 and 1.36, $^3J = 6.2$ Hz). The separation of these doublets is now 1.8 Hz, and corresponds to the same diastereotopic behavior discussed above for **2**. The spectrum of **4** is even simpler. In $CDCl_3$ for example, in addition to the aromatic protons of the six-membered rings, the protons on 2,3-positions are observed as one set of two doublets (δ 7.16 and 6.94, $J_{2,3} = 3.4$ Hz), and the ethylene bridge as a singlet (δ 3.63).

These results together with the low yield (30%) in the isolation of **3**, suggest that the chlorination reaction of **2** (1:1 *rac* and *meso* mixture) in ethyl ether produces the specific formation of one diastereomer of **3**, whereas the reaction of the latter with $CH_3C(O)Cl$ in CH_2Cl_2 proceeds with no *rac*/*meso* isomerization to give the same diastereomer of **4** in 77% isolated yield.

In the absence of X-ray molecular determinations for **3** or **4** it is not possible to clarify if they are the *rac* or *meso* isomer. However, the characteristic pattern with one widely and one narrowly separated pairs of indenyl 2,3-proton signals, has been previously observed in the ^{1}H-NMR spectrum of such isomers in mononuclear compounds where the ligand chelates the metal center (e.g. *rac*- and *meso*-$[(1,2\text{-}C_2H_4)Ind_2]TiCl_2$); it was found that the wide one corresponds to the *rac*-diastereomer [13]. The same observation has been made for the binuclear complex $\{rac\text{-}Me_2Si[1\text{-}IndZr(NMe_2)_3]_2\}$, very recently reported by Jordan [14]. Besides, the AA′BB′ spin system of the ethylene bridge appears as a singlet in the corresponding spectra of **3** and **4** [9]. Therefore, we tentatively suggest that **3** and **4** are most likely obtained as the *racemic* diastereomer by using the synthetic procedures reported here.

2.2. Styrene polymerization

Previously we reported that the **1**/MAO catalyst system was highly active and syndiospecific for the polymerization of styrene, and was relatively insensitive to polymerization conditions as compared to $CpTiCl_3$/MAO [3]. Selected data for the mononuclear reference compound **1** are summarized in Table 1, together with the results obtained with the binuclear precursors **3** and **4** at the same polymerization conditions. The **A** for **3** and **4** is one order of magnitude lower than that for **1**. However, the syndiospecificities of both dimetallic complexes are comparable to the reference compound. Together with a different yield in the formation of active species starting from **1** or from **3** or **4** (vide infra), these findings can be explained if the two metal centers act independently of one another, and if the proximity of a very bulky substituent on the indenyl ring ($C_2H_4[IndTi(\text{polymer chain})X_{2-n})$ slows the propagation rate of the process.

A comparison of the behavior at **1** with **4** (both compounds are trichlorides) shows that the polymerization conditions affect the performance of the latter much more than they do the former. Thus, **4** is most efficient at low [Ti] and [MAO] (run 1–4), and at lower T_p.

For **1**, **3** and several other catalysts studied in our laboratories the maximum in **A** and S.Y. is achieved at temperatures between 50–75°C ([2]c, d, i, j), whereas for **4** increasing *T*p results in the progressive loss of **A** and S.Y. (run 4–7). At this point, it is worth mentioning that the purple–black compound **4** in THF turned spontaneously and instantaneously to a clear green–blue solution, from which neither compound **4** nor any other Ti(IV) organometallic species were detected by ^{1}H-NMR. This observation is in agreement with the behavior of the binuclear compound $[\mu\text{-}\eta^5{:}\eta^5(C_{10}H_8)(TiCl_3)_2]$ which decomposes to $TiCl_3 \cdot (THF)_3$ in the same solvent ([6]a). Therefore, this tendency to reductive decomposition seems to be an inherent feature of binuclear monocyclopentadienyl trichlorotitanium compounds. Besides, EPR studies have shown MAO to be a very effective reducing reagent for monocyclopentadienyl titanium complexes ([2]d). Thus, the trend of **4** vs [MAO] and vs T_p can be explained as a result of the poor redox stability of **4**.

Both **A** and S.Y. are similar for **3** and **4**, however, **3** behaves more like **1** in the sense that both catalysts are affected in the same way by the polymerization conditions (compare the trend of **A** and S.Y. For 1 and 3 in run 2–6). This result can be attributed to the bulkier and more nucleophilic O-*i*-Pr group, which should stabilize the active cationic species ([2]c, e).

3. Conclusions

Ethylene bridged bis(indenyl) binuclear titanium derivatives are more conveniently prepared by stepwise in situ chlorination of the alkoxide compound **2**. Reaction of **2** with $CH_3C(O)Cl$ in ethyl ether led to the formation of **3** as a pure diastereomer. Subsequent chlorination of **3** in CH_2Cl_2 afforded **4**, and there was no indication of *rac*/*meso* isomerization during this reaction. Compounds **2**, **3** and **4** are the first examples of binuclear monoindenyltitanium(IV) complexes.

Finally, styrene polymerization catalysis using MAO as cocatalyst showed the binuclear compounds **3** and **4** to be less active than the mononuclear (i.e. **1**) by one order of magnitude, but with comparable syndiospecificity.

4. Experimental section

4.1. General

Experimental details concerning the polymerization of styrene have been given elsewhere ([2]i, [3]). All operations were performed under an argon atmosphere using Schlenk or glove box techniques. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and P_2O_5. Solvents and $CH_3C(O)Cl$ were purified as described elsewhere [15]. MAO was purchased from Akzo and other chemicals from Aldrich, unless otherwise stated. 1,2-Bis(3-indenyl)ethane [16] was prepared according to a literature procedure. ^{1}H-NMR spectra were recorded on a Varian XL200 FT spectrometer. Chemical shifts (δ) are reported in ppm referenced to TMS. Elemental analyses were performed by the University of Massachusetts Microanalytical laboratory.

4.2. Synthesis of 1,2-Bis[(1-indenyl)titanium triisopropoxide]ethane (2)

1,2-Bis(3-indenyl)ethane (1.17 g, 4.5 mmol) in THF (30 ml) was treated with 2 equiv of *n*-BuLi (1.6 M in hexanes) at −78°C. The reaction mixture was allowed to warm to room temperature and stirred for an additional hour. The solvent was removed by vacuum distillation and the residue washed with pentane (2 × 50 ml). The resulting off-white dilithium salt was suspended in ethyl ether (60 ml), and treated with a solution of chlorotitanium triisopropoxide (2.4 g, 9.2 mmol) in ethyl ether (30 ml) at −78°C. The mixture was slowly warmed to 0°C, kept out of light, and stirred overnight at 0°C. After filtration of the yellow–orange solution, 0.39 g of LiCl (98%) was collected. The solvent of the filtrate was removed under vacuum in darkness, and at temperatures never above 0°C. This procedure afforded 3.15 g of crude **2** (98%) as an air, light, and temperature sensitive orange oil, which failed to crystallize. ^{1}H-NMR ($CDCl_3$): δ 7.63–7.50 (m, 4H, arom.); 7.18–7.03 (m, 4H, arom.); 6.55, 6.45 (2d, $J_{2,3} = 3.3$ Hz) and 6.29, 6.27 (2d, $J_{2,3} = 3.1$ Hz) [*rac* and *meso* isomers (1:1), 4H, protons on 2- and 3-positions]; 4.45, 4.42 (*rac* and *meso* (1:1), 2 hept, 6H, $CH(Me)_2$, $^3J = 6.1$ Hz); 3.35 (s) and 3.45–3.20 (m) (*rac* and *meso* (1:1), 4H, CH_2CH_2); 1.02, 1.19 (2d) and 1.00, 0.99 (2d) [*rac* and *meso* (1:1), 36H, $CH(Me)_2$, $^3J = 6.1$ Hz].

A sample of **2** in $CDCl_3$, briefly warmed to 50°C and monitored in 30 min intervals for 2 h by ^{1}H-NMR, showed gradual disappearance of the signals for the *rac*- and *meso*-binuclear titanium complex mixture, together with the formation of a decomposition product (δ 4.40, hept, $CH(Me)_2$, $J = 6.0$ Hz; 1.24, d, $CH(Me)_2$, $^3J = 6.0$ Hz). The latter resonances were also observed by ^{1}H-NMR in samples of **2** which had been manipulated in light and at room temperature.

4.3. Synthesis of 1,2-Bis[(1-indenyl)dichlorotitanium monoisopropoxide]-ethane (3)

A mixture of *rac*- and *meso*-**2** was prepared as described above from $[1,2\text{-}C_2H_4(1\text{-Ind})_2]Li_2$ (8.17 mmol) and $ClTi(O\text{-}i\text{-}Pr)_3$ (4.25 g, 16.3 mmol) in ethyl ether (100 ml). After filtration of the LiCl, the filtrate was cooled to −78°C and reacted in situ with 6 equiv of prepurified acetyl chloride (3.85 g, 49.0 mmol). The reaction mixture was slowly warmed to room temperature and stirred for 24 h, forming a red precipitate and a deep red solution. The red solid was separated from the solution, washed with ethyl ether (2 × 20 ml), and recrystallized from a mixture CH_2Cl_2/ethyl ether (3:1), affording **3** as fairly stable, red microcrystalline solid. Yield: 1.51 g (30%). ^{1}H-NMR ($CDCl_3$): δ 7.78–7.71 (m, 2H, arom.); 7.67–7.60 (m, 2H, arom.); 7.49–7.35 (m, 4H, arom.); 6.70, 6.61 (2d, 4H, protons on 2- and

3-positions, $J_{2,3} = 3.4$ Hz); 4.96 (hept, 2H, $CH(Me)_2$, $^3J = 6.2$ Hz); 3.45 (s, 4H, CH_2CH_2); 1.37, 1.36 (2d, 12H, $CH(Me)_2$, $^3J = 6.2$ Hz). Anal. Found: C, 51.23; H, 4.78; Cl, 21.52. $C_{26}H_{30}Cl_4O_2Ti_2$. Calc.: C, 51.02; H, 4.94; Cl, 23.17%.

4.4. Synthesis of 1,2-Bis[1-indenyltrichlorotitanium]ethane (4)

Compound **3** (0.89 g, 1.4 mmol) was treated with $CH_3C(O)Cl$ (0.34 g, 4.3 mmol, 50% excess) in CH_2Cl_2 (100 ml). The red mixture was stirred for 2 days at room temperature, giving a microcrystalline purple–black precipitate and a dark-purple solution. Filtration and concentration of the mother liquor (ca. 20 ml) gave a second crop of microcrystals, which was combined with the first one, washed with ethyl ether/CH_2Cl_2 (3:1) (2 × 50 ml) and recrystallized from CH_2Cl_2/toluene (2:1), precipitating **4** as a fairly stable, microcrystalline purple–black solid. Yield: 0.62 g (77%). ^{1}H-NMR ($CDCl_3$): δ 7.88–7.75 (m, 2H, arom.); 7.66–7.45 (m, 6H, arom.); 7.16, 6.94 (2d, 4H, protons on 2- and 3-positions, $J_{2,3} = 3.4$ Hz); 3.63 (s, 4H, CH_2CH_2). ^{1}H-NMR (C_6D_6): δ 7.18–7.09 (m, 4H, arom.); 6.87–6.75 (m, 4H, arom.); 6.34, 6.06 (2d, 4H, protons on 2- and 3-positions, $J_{2,3} = 3.3$ Hz); 3.12 (s, 4H, CH_2CH_2). ^{1}H-NMR (CD_2Cl_2): δ 7.90–7.79 (m, 2H, arom.); 7.65–7.44 (m, 6H, arom.); 7.18 and 6.96 (2d, 4H, protons on 2- and 3-positions, $J_{2,3} = 3.5$ Hz); 3.63 (s, 4H, CH_2CH_2). Anal. Found: C, 42.83; H, 3.06; Cl, 36.83. $C_{20}H_{16}C_{16}Ti_2$. Calc.: C, 42.53; H, 2.85; Cl, 37.66%.

Compound **4** was also detected by ^{1}H-NMR in the crude products of both the reaction of $\{1,2\text{-}C_2H_4[3\text{-}(1\text{-}IndSiMe_3)_2]\}$ with 2 equiv of $TiCl_4$ in toluene or CH_2Cl_2, and in situ chlorination of **2** with 6 equiv of $CH_3C(O)Cl$ but in CH_2Cl_2 as the solvent instead of ethyl ether. In both cases, it was not possible to remove the by-product impurities by recrystallization.

Acknowledgements

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[12] A 1:1 mixture of *rac*- and *meso*-1,2-bis(1-trimethylsilyl)-3-indenyl]ethane was prepared as follows: 1,2-bis(3-indenyl)ethane (1.30 g, 5.0 mmol) was reacted with 2 equiv of *n*-BuLi at − 78°C in THF (60 ml). After one hour at room temperature, Me_3SiCl (1.09 g, 10 mmol) was added at − 78°C and the mixture stirred at room temperature overnight. The solvent was distilled under vacuum and the residue extracted with pentane (2 × 60 ml). Removal of the pentane afforded the title compound as a yellow solid which was recrystallized from a minimum amount of pentane. Yield: 1.86 g (92%). ^{1}H-NMR ($CDCl_3$): δ 7.53–7.41 (m, 4H, arom.); 7.33–7.14 (m, 4H, arom.); 6.43, 6.39 (2d, *rac* and *meso* isomers (1:1), 2H, sp^2–2 positions, $J_{1,2} = 1.6$ Hz), 3.41 (br s, 8 Hz, 2H, sp^3–1 positions); 3.01 (br s, 6 Hz, 4H, CH_2CH_2); − 0.04, − 0.05 (2s, *rac* and *meso* isomers (1:1), 18 H, $SiMe_3$). Anal. Found: C, 77.76; H, 8.66. $C_{26}H_{34}Si_2$. Calc.: C, 77.54; H, 8.51.

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