

POLYMERIZATION OF PROPENE WITH MODIFIED CONSTRAINED GEOMETRY COMPLEXES. DOUBLE-BOND ISOMERIZATION IN PENDANT ALKENYL GROUPS ATTACHED TO CYCLOPENTADIENYL LIGANDS

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Polymerization of propene with dimethylsilylene-bridged (amidocyclopentadienyl)dichlorotitanium(IV) complexes [TiCl₂{η⁵-1-(*t*-BuSiMe₂N-κN)-2,3,4-Me₃-5-R-C₅}], where R = Me (**1**), H (**2**), Ph (**3**), 4-fluorophenyl (**4**), but-2-en-2-yl (**5**), and butyl (**6**), combined with excess methylaluminumoxane revealed a moderate effect of the substituent R on the catalyst activity and the molecular weight of polypropene. The asymmetric substitution in the position adjacent to the bridging carbon atom resulted in polymer yields decreasing in the order **1** > **6** > **3** ≈ **5** > **4** > **2** while polymers with the molecular weights (*M_w*) close to 2.5 × 10⁵ for **1**, **3**, and **4**, 1.5 × 10⁵ for **5** and **6**, and 7.5 × 10⁴ for **2** were obtained. The ¹³C NMR analysis of the polymers has shown that atactic polypropene is slightly enriched with syndiotactic triads for all the catalysts. Investigation of the crystal structure of **5** by X-ray crystallography revealed that the double bond in but-3-en-2-yl had shifted to an internal position to give the isomeric, but-2-en-2-yl-substituted complex. Likewise, the spectroscopic data for complex **7** prepared from the ligand containing but-3-en-1-yl substituent, indicate the absence of terminal double bond.

Keywords: Titanium; CGC catalysts; Propene polymerization; Substituent effects; Double-bond isomerization; X-Ray diffraction; NMR spectroscopy; Half-sandwich complexes.

A new class of single-site, constrained-geometry catalysts (CGC) for polyalkene production¹ emerged with the synthesis of (*tert*-butylamino)di-

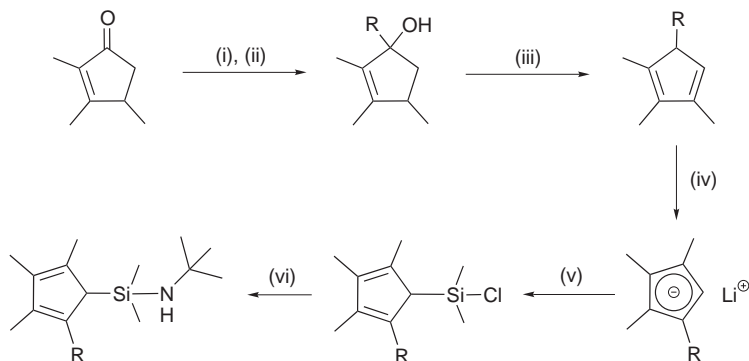
methyl(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silane ligand² and its complex, *ansa*-{(*tert*-butylamido- κ N)dimethyl(η^5 -2,3,4,5-tetramethylcyclopentadienyl)silane}dichlorotitanium(IV) (**1**) (ref.³). Generally, the CGC complexes activated with excess of methylaluminumoxane (MAO) provide more acidic and less sterically encumbered cationic centres⁴ than other single-site metallocene catalysts and, consequently, exhibit very high activities in the polymerization of ethene, propene and in copolymerizations of ethene with terminal alkenes, cycloalkenes and styrene⁵. In attempts to tune polymer properties, the parent CGC complex was modified by replacing the cyclopentadienyl ligand by indenyl or fluorenyl ligands⁶, and their rings⁷ as well as the amide groups were diversely substituted⁸. Recently, an effective route has been developed to CGC complexes substituted on otherwise fully methyl-substituted cyclopentadienyl ring in the vicinal position to the *ansa*-bridge, affording a series of racemic complexes [TiCl₂{ η^5 -1-(*t*-BuSiMe₂N- κ N)-2,3,4-Me₃-5-R-C₅}], where R = H (**2**), Ph (**3**), 4-fluorophenyl (**4**), and but-2-en-2-yl (**5**), the latter compound, however, being incorrectly assigned to possess the but-3-en-2-yl group⁹. The asymmetric auxiliary ligands are expected to moderately modify the activity of CGC catalysts in general, by affecting the selectivity in copolymerizations and by changing the proportion of the syndiotactic form in largely atactic polypropene¹⁰ (PP).

Here, we report the synthesis of CGC complexes with R = Bu (**6**) and but-2-en-1-yl (**7**), the effect of substituent R on activities of **1**–**6**/MAO catalysts in polymerization of propene and the double-bond isomerization occurring in **5** and **7**.

RESULTS AND DISCUSSION

A series of CGC complexes modified by substituent R on the cyclopentadienyl ring in the vicinal position to the carbon atom bearing the dimethylsilylene bridge was extended in order to establish the effect of this substituent in propene polymerization catalyzed by CGC/MAO systems. In addition to recently described compounds⁹ **1**–**5**, new compounds with R = butyl (**6**) and but-2-en-1-yl (**7**) were synthesized. The preparation of new (aminosilyl)cyclopentadiene ligand precursors is described in Scheme 1; the synthesis of **6** and **7** follows the generally used protocol^{5,9}. Whereas the butyl derivative **6** was obtained in so far the highest yield (39%), the yield of **7** was very low, probably due to a high solubility of the crude product mixture. Moreover, NMR spectra of **7** revealed that the terminal double bond in the CGC ligand shifted during the synthesis and isolation, which included a vacuum sublimation, to an internal position. According to NMR spectra,

the isolated complex **7** contained approximately 80% of but-2-en-1-yl and 20% of but-1-en-1-yl derivatives but no but-3-en-1-yl isomer. As these components could be separated neither by crystallization nor by distillation, product **7** remained not fully characterized and was not used as a catalyst component. The occurrence of the double-bond shift in **7** initiated reinvestigation of the structure of **5** where the presence of but-3-en-2-yl group was proposed on the basis of NMR spectra of an impure sample⁹. The NMR spectra of a recrystallized sample unequivocally showed that the product mixture is dominated by the isomer having the double bond shifted to the internal position, and that the resonances of this compound were also present in the spectra of an impure complex but misinterpreted because of the presence of other impurities and broadness of the NMR signals, which may reflect a hindered motion of the unsaturated side chain and the diastereotopic methyl groups at SiMe₂ in racemic **5**.



- (i) BuLi, hexane/THF, R = Bu; ClMgCH₂CH₂CH=CH₂, Et₂O, R = but-3-en-1-yl; (ii) hydrolysis; (iii) -H₂O, catal. I₂; (iv) 1 equiv. BuLi, THF; (v) 1 equiv. Me₂SiCl₂; (vi) 1 equiv. LiNHCMes₃, Et₂O

SCHEME 1

The double-bond isomerization in **5** was further corroborated by single crystal X-ray diffraction analysis (*vide infra*). The double-bond shift in **5** and **7** may occur any time during the reaction affording the CGC complex, or during sublimation of the crude reaction products that requires temperatures up to 170 °C (no pure product could be isolated without sublimation). Since the double-bond shifts to internal positions were not observed during the syntheses of titanocene dichlorides bearing pendant double bonds on the cyclopentadienyl ligands using a similar protocol¹¹, the double-bond shift does not occur in cyclopentadienyl anions. However, a generally higher acidity of titanium in CGC complexes⁴ can be responsible for the double-bond shift, more likely at high temperatures.

Crystal Structure of Compound 5

Compound 5 (Fig. 1, Table I) is planarly chiral but racemic. Hence, the triclinic unit cell accommodates a pair of enantiomeric molecules lying across the crystallographic inversion centre. The molecular framework of 5 is nearly identical with those of 1 and 4 (ref.⁹), as shown in Table II. In asymmetric compounds 4 and 5, likely due to steric demands of the substituent R, the cyclopentadienyl ring is slightly inclined to the titanium atom by the side not bearing the substituent R (*cf.* Ti–C distances for C5 and C4 compared to C2 and C3, respectively, in Table I). The but-2-en-2-yl group is disordered, the ghost position with the double bond directed towards the Ti atom being *ca* 20% abundant. A rough coincidence of the methyl carbon C9 with the sp^2 C7 atom results in a low accuracy of the position determination for C7, C8, and C9 atoms and some averaging of the C–C distances. Even so, the found C6–C7 distance of 1.373(5) Å is distinctly shorter than that of the C7–C8 bond (1.476(5) Å), and justifies the position of the double bond, in agreement with the NMR spectra.

Propene Polymerization with 1-6/MAO Catalysts

All polymerization experiments were carried out under practically identical conditions. The results revealed only moderate effect of the substituent R

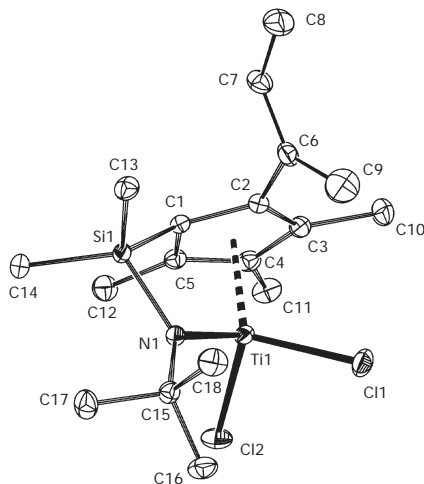


FIG. 1

The molecular structure of compound 5 drawn at 30% probability level showing the atom labeling scheme. All hydrogen atoms are omitted for clarity

both on the catalyst performance and the molecular weight of polypropene, and a negligible effect on stereo- and regioregularity of polypropenes (Table III). The parent system **1**/MAO showed a productivity lower than that recently published for the same Al/Ti ratio 500 and comparable conditions¹²; however, the molecular weight of the polypropene was considerably higher (M_w 244 000 vs 140 000). Since the data for the **1**/MAO systems for different Al/Ti molar ratios show that a lower Al/Ti ratio (289 in ref.¹⁰ vs 500 in ref.¹²) results in a lower catalyst performance (820 kg vs 10 000 kg (PP) mol⁻¹ h⁻¹ in ref.¹²), and in a higher molecular weight (M_w

TABLE I
Bond distances (in Å) and selected bond angles (in °) for complex **5**

Bond distances			
Ti-Cl1	2.2718(5)	Ti-Cl2	2.2859(5)
Ti-N	1.911(1)	Ti-Cg ^a	2.0370(8)
Ti-C1	2.285(2)	Ti-C2	2.355(2)
Ti-C3	2.445(2)	Ti-C4	2.432(2)
Ti-C5	2.336(2)	Si-N	1.763(1)
Si-C1	1.872(2)	N-C15	1.494(2)
C1-C5	1.431(2)	C1-C2	1.440(2)
C2-C3	1.424(2)	C3-C4	1.418(2)
C4-C5	1.423(2)	C2-C6	1.491(2)
C6-C7	1.373(5)	C7-C8	1.476(5)
C6-C9	1.445(8)		
Bond angles			
Cl1-Ti-Cl2	101.49(2)	Cl1-Ti-N	109.69(4)
Cl2-Ti-N	107.29(4)	Cl1-Ti-Cg ^a	115.89(3)
Cl2-Ti-Cg ^a	114.23(3)	N-Ti-Cg ^a	107.86(5)
Si-N-Ti	104.98(7)	N-Si-C1	90.71(6)
C2-C1-C5	106.4(1)	C1-C2-C3	108.7(1)
C2-C3-C4	107.9(1)	C3-C4-C5	108.2(1)
C1-C5-C4	108.9(1)	C2-C6-C9	117.9(3)
C2-C6-C7	115.4(2)	C7-C6-C9	126.7(3)
C6-C7-C8	126.7(4)		

^a Cg denotes the centroid of the cyclopentadienyl ring.

583 000 vs 140 000) a higher M_w of polypropene obtained in the present work (240 000, Table III) under otherwise identical conditions¹² can indicate that an effective Al/Ti ratio is likely lower due to, *e.g.*, ageing of MAO or another reason. In the series of catalysts **1–6**/MAO that were tested under identical conditions, the system containing **1** showed the highest productivity in the order **1** > **6** > **3** \approx **5** > **4** > **2** (see Table III). This order of productivities can be roughly correlated with the electron-donating effect

TABLE II
Comparison of selected bond lengths (in Å) and angles (in °) for complexes **1**, **4**, and **5**

Parameter	1 ^a	4 ^a	5
Ti–Cg ^a	2.033(3)	2.040(4)	2.0370(8)
Ti–Cl1	2.265(1)	2.269(2)	2.2718(5)
Ti–Cl2	2.265(1)	2.274(2)	2.2859(5)
Ti–N	1.910(4)	1.910(3)	1.911(1)
Si–N	1.745(4)	1.744(4)	1.763(1)
N–Ti–Cg ^a	107.8(2)	107.6(2)	107.86(5)
Cl1–Ti–Cl2	103.17(8)	100.68(6)	101.49(2)
Si–N–Ti	105.3(2)	105.6(2)	104.98(7)
N–Si–C1	90.4(2)	90.8(2)	90.71(6)

^a Data from ref.⁹; ^b Cg denotes the centroid of the cyclopentadienyl ring.

TABLE III
Propene polymerization catalyzed by [TiCl₂{η⁵-1-(*t*-BuSiMe₂N-κN)-2,3,4-Me₃-5-R-C₅}]/MAO systems (averages of two runs are given)^a

CGC	R	PP yield, g	A^b	$M_w \times 10^{-2}$	$M_n \times 10^{-2}$	M_w/M_n
1	Me	15.8	5.26	2443	1468	1.67
2	H	3.8	1.26	758	459	1.65
3	Ph	8.25	2.75	2452	1464	1.68
4	4-Fluorophenyl	6.0	2.00	2496	1483	1.68
5	But-2-en-2-yl	7.8	2.60	1616	1004	1.62
6	Bu	11.7	3.90	1555	890	1.69

^a Polymerization conditions: 200 ml toluene, [Ti] = 3×10^5 M, [MAO]/[Ti] = 500, 100 kPa of propene, 50 °C, 30 min. ^b Productivity: 10^3 kg (PP) mol⁻¹ (Ti) h⁻¹.

of the substituent R (Me > Bu > but-2-en-2-yl > Ph > 4-fluorophenyl), which may indicate that the electronic effect (electron density at the Ti atom) controls the reaction rate. The shift of the terminal double bond to internal position in compound **5** explains the absence of any hindrance of the polymerization which could be expected for the pendant terminal double bond. Unfortunately, the polymerization performance of the systems does not correlate (in positive or negative way), with M_w of polypropenes. The CGC complexes bearing aromatic substituents, give high-molecular-weight polymers comparable with M_w of polypropene from **1**/MAO, although their productivities are much lower, while the CGC complexes with aliphatic substituents show higher productivities and much lower molecular weights (Table III). It is apparent that a combination of electronic and steric effects of the substituents controls the productivity and M_w in these cases. This was demonstrated on the **2**/MAO system where the presence of hydrogen at the cyclopentadienyl ring (R = H) results in the by far the lowest productivity and the lowest polymer molecular weight. The polydispersity values $D = M_w/M_n$ close to 1.65 indicate narrow molecular weight distributions and point to the single-site nature of the catalytic species in all the catalytic systems. The dominant performance leading to the formation of high-molecular-weight polymer is not unexpected for the **1**/MAO system because a comparative study of **1**/MAO catalyst (at Al/Ti ratio 289) and a number of CGC catalysts with annelated ring(s) (indenyl, fluorenyl) and with another amido substituent (methylbenzyl, cyclohexyl) also proved its highest productivity and the formation of a high-molecular-weight polymer¹⁰. The ¹³C NMR investigation of the polypropenes showed that a largely atactic polymer is syndiotactically enriched: the ratio of *mm:rr* triads about 14:37 and 1–2% of regioerrors is typical for all the polymers obtained. In fact, larger figures for the syndiotactic enrichment were reported in the above mentioned ref.¹⁰; however, the highest enrichment was observed for the **1**/MAO catalyst, too. Similar results on stereoselectivity of propene polymerization with related CGC catalysts were reported recently¹³. The dominant position of the parent **1**/MAO catalyst is, however, lost when the polymerization of the less sterically demanding ethene is investigated. Recent preliminary results with the same catalytic systems in the polymerization of ethene gave the order of activities **4** > **3** > **5** > **6** > **1** > **2**, the CGC complexes with aromatic substituents showing the highest performance¹⁴.

EXPERIMENTAL

Propene Polymerizations

Solvents and propene (AGA, polymer grade) were purified as reported elsewhere¹⁰. The polymerizations were conducted in a fully pressure- and temperature-controlled 1000-ml stainless steel autoclave, equipped with solvent and catalyst injection systems, at 50 °C. The reactor was pre-dried at 120 °C under vacuum for 1 h. Then, it was charged with toluene (190 ml) and the content stirred at 600 rpm and thermostatted to 50 °C. The reactor was pressurized with propene (2 bar) and the system was allowed to equilibrate for 15 min. Subsequently the MAO/toluene solution was injected, the reactor contents were stirred for 5 min and, finally, the polymerization was initiated by injection of a CGC solution (6 μ mol in 10 ml of toluene). During the run the monomer pressure was kept constant by replenishing flow. After 30 min, the reactor was vented and the reaction mixture quenched by addition of methanol (10 ml). The produced polypropenes were precipitated by pouring the slurry into acidic MeOH (300 ml) and stirring overnight. Finally, the polymer was filtered, washed with methanol and dried in a vacuum rotation evaporation system at 70 °C.

Polymer Characterizations

The GPC measurements were carried out using high-temperature GPC at 135 °C, with 1,2,4-trichlorobenzene as a solvent and narrow MWD polystyrene standard sample as reference. The measurements were performed on a PL-GPC210 instrument (Polymer Laboratories) with four PL-Gel Mixed A Columns, RALLS light-scattering detector (Precision Detector, PD2040 at 800 nm), H502 Viscometer (Viscotek), refractive detector and DM400 data manager (Viscotek). Every value is the average of the two independent measurements. ¹H and ¹³C NMR spectra were run on a Varian VXR-300 and a Unity 500 spectrometer. Chemical shifts are given in ppm (δ -scale), coupling constants (*J*) in Hz. The polypropenes were characterized by ¹³C NMR in C₂D₂Cl₄ solution at 100 °C (ref.¹⁰).

Syntheses of CGC Complexes

Solvents, purification methods, reaction conditions, handling of CGC complexes, and spectral methods were identical with those previously described⁹. Compounds **1–4** used for polymerizations were previously reported⁹; complex **5** was recrystallized from hexane.

NMR data for **5**. ¹H NMR (C₆D₆): 0.39, 0.44 (2 \times s, 3 H, SiMe₂); 1.44 (s, 9 H, CMe₃); 1.49 (dq, ³J_{HH} = 6.8, ⁵J_{HH} = 1.1, 3 H, =CHMe); 1.75 (br s, 3 H, =C(Cp)Me); 2.01, 2.07, 2.08 (3 \times s, 3 H, Me₃C₅); 5.72 (br s, 1 H, =CHMe). ¹³C{¹H} NMR (C₆D₆): 3.9 (br), 5.0 (SiMe₂); 13.1, 13.2 (Me₃C₅); 13.9 (=CHMe); 16.8 (Me₃C₅); 20.0 (br, =C(Cp)Me); 32.4 (CMe₃); 62.8 (CMe₃); 103.5 (Me₃C₅, C-Si); ca 128.6 (=CHMe); 131.4, 136.6, 137.4, 141.6, 152.2 (Me₃C₅, C_{ipso} and =C(Cp)Me).

Synthesis of *rac*-{1-Butyl-2-[(*tert*-butylamido- κ N)dimethylsilyl]-3,4,5-trimethyl- η^5 -cyclopentadienyl}dichlorotitanium(IV) (**6**)

BuLi in hexane (1.6 M, 188 ml, 300 mmol) was reacted with 2,3,4-trimethylcyclopent-2-en-1-one (30 g, 242 mmol; prepared according to ref.¹⁵) in diethyl ether and quenched with an

ice/water slurry. The obtained alcohol in diethyl ether was instantaneously dehydrated by adding a catalytic amount of iodine¹⁶.

1-Butyl-2,3,4-trimethylcyclopentadiene (a mixture of double-bond isomers) was obtained as a colorless liquid. Yield 31.7 g (80%, based on ketone). GC-MS, *m/z* (rel. abundance): 165 (8), 164 ([M]⁺; 58), 149 (11), 136 (9), 135 (72), 122 (42), 121 (100), 120 (12), 119 (20), 117 (9), 116 (21), 108 (30), 107 (80), 106 (16), 105 (65), 103 (13), 93 (74), 92 (12), 91 (88), 79 (45), 78 (12), 77 (50), 65 (18), 55 (13), 53 (16), 51 (12), 43 (12), 41 (34), 39 (28). IR (neat, cm⁻¹): 2958 (vs), 2926 (vs), 2857 (s), 2745 (w), 1652 (m), 1443 (s), 1380 (s), 1183 (w), 1160 (m), 1128 (w), 1110 (w), 952 (w), 850 (w), 739 (w), 689 (vw), 466 (vw).

BuLi in hexane (1.6 M, 32.5 ml, 52 mmol) was added dropwise to a stirred solution of butyltrimethylcyclopentadiene (8.5 g, 52.0 mmol) in diethyl ether (200 ml) and the mixture was stirred for 4 h. Dimethyldichlorosilane (6.7 g, 52 mmol) was introduced slowly under stirring, and the mixture was stirred for another 10 h at room temperature. Diethyl ether and hexane were distilled off and (2-butyl-3,4,5-trimethylcyclopenta-2,4-dien-1-yl)chlorodimethylsilane distilled as a yellowish liquid at 2 kPa from boiling water bath. Yield of C₅HMe₃Bu(SiMe₂Cl) 11.0 g (83%). This silane was reacted with *t*-BuNHLi prepared from *tert*-butylamine (3.2 g, 43.8 mmol) and BuLi (27 ml of 1.6 M solution in hexanes, 43 mmol) to give, after distillation at 125 °C/9 Pa, (*tert*-butylamino)(2-butyl-3,4,5-trimethylcyclopenta-2,4-dienyl)dimethylsilane as a yellow fluorescent oily liquid. Yield 11.0 g (87%). GC-MS, *m/z* (rel. abundance): 293 ([M]⁺; 4), 131 (16), 130 ([Me₂SiNH*t*-Bu]⁺; 100), 121 (12), 119 (10), 114 (13), 105 (21), 91 (15), 74 ([*t*-BuNH₃]⁺; 64), 73 (48), 59 (9), 41 (12). ¹H NMR (C₆D₆): 0.11, 0.13 (2 × s, 3 H, SiMe₂); 0.92 (t, ³J_{HH} = 7.3, 3 H, CH₂Me); 1.11 (s, 9 H, CMe₃); 1.24–1.60 (m, 4 H, 2 × CH₂); 1.84, 1.88, 2.01 (3 × s, 3 H, Me₃C₅); 2.43–2.59 (m, 2 H, CH₂); 2.96 (br s, 1 H, Me₃C₅H). {¹³C}¹H NMR (C₆D₆): 1.3, 1.6 (SiMe₂); 11.4, 14.5 (Me₃C₅); 14.3 (CH₂Me); 15.1 (Me₃C₅); 23.1, 28.5, 33.7 (3 × CH₂); 33.8 (CMe₃); 49.4 (CMe₃); 54.6 (Me₃C₅H, CH); 133.5, 135.1, 135.5, 138.9 (Me₃C₅H, CMe).

In the next step, C₅HMe₃Bu(SiMe₂(NHCMe₃)) (10.5 g, 36.0 mmol) was dissolved in THF (300 ml), BuLi (1.6 M solution in hexanes, 45.0 ml, 72 mmol) was added upon stirring and the resulting yellow solution was stirred for 2 h. A suspension of [TiCl₃(THF)₃] prepared from TiCl₄ (4.0 ml, 36.0 mmol) in 80 ml of THF and BuLi (1.6 M in hexane, 22.5 ml, 36.0 mmol) was added to the solution of the lithium salt, and the mixture was refluxed for 3 h. The solvents were distilled off to reduce the reaction volume to ca 50 ml. After cooling to room temperature, dry PbCl₂ (5.0 g, 18.0 mmol) was added to the reaction mixture and stirring was continued at 40 °C for 2 h. The reaction vessel was then attached to a vacuum-argon line, the remaining volatiles were removed under vacuum, and the reaction products were extracted into hexane (100 ml portions; hexane was added by distillation on the vacuum-argon line). Combined brown extracts were concentrated to ca 40 ml and distributed into 4 ampoules, whose contents were subsequently distilled on a high-vacuum line. The volatiles distilling up to 70 °C were collected in a cooled trap and discarded. Temperature was successively increased to about 210 °C and an orange oil, which partly solidified at room temperature, was collected in a trap cooled with liquid nitrogen at a pressure of 4 Pa. After cooling to room temperature, hexane (20 ml) was distilled into the trap to dissolve the distillate and to separate it from a small amount of a white insoluble solid. The clear hexane solution was cooled to -5 °C overnight. Yellow crystals that separated from a brown-red solution were isolated and recrystallized from hexane. After analogous workup of all the four parts, the combined yield of bright yellow crystalline **6** was 5.7 g (39%); m.p. 112 °C. EI-MS (90 °C, *m/z* (rel. abundance)): 409 ([M]⁺; 0.5), 398 (24), 397 (24), 396 (81), 395 (39), 394

([M - Me]⁺; 100), 393 (16), 392 (11), 338 ([M - *t*-BuN]⁺; 3), 297 (5), 295 ([M - (*t*-BuNSiMe)]⁺; 6), 177 (9), 73 (11), 59 (12), 57 (9), 41 (14), 40 (31). ¹H NMR (C₆D₆): 0.44, 0.51 (2 × s, 3 H, SiMe₂); 0.82 (t, ³J_{HH} = 7.3, 3 H, MeCH₂); 1.16–1.45 (m, 4 H, CH₂CH₂); 1.44 (s, 9 H, Me₃C); 2.02 (s, 6 H, Me₃C₅); 2.07 (s, 3 H, Me₃C₅); 2.46–2.63 (m, 2 H, CH₂). ¹³C{¹H} NMR (C₆D₆): 4.9, 5.8 (SiMe₂); 13.0, 13.1, 14.2, 16.2 (Me₃C₅ and MeCH₂); 22.8, 30.4 (CH₂); 32.7 (Me₃C); 35.4 (CH₂); 62.2 (Me₃C); 103.1, 137.6, 138.1, 141.0, 146.1 (C_{ipso}, C₅Me₃). IR (KBr, cm⁻¹): 2958 (vs), 2929 (s), 2871 (s), 1466 (s), 1450 (m), 1408 (w), 1389 (m), 1375 (m), 1361 (s), 1336 (m), 1298 (vw), 1275 (vw), 1257 (s), 1249 (s), 1229 (m), 1215 (m), 1185 (vs), 1130 (w), 1102 (w), 1067 (vw), 1035 (w), 1023 (w), 987 (s), 919 (w), 845 (vs), 820 (s), 792 (s), 772 (vs), 725 (w), 685 (w), 666 (vw), 646 (w), 619 (vw), 541 (m), 530 (s), 498 (m), 461 (vw), 431 (s), 416 (m).

Synthesis of {1-(But-2-en-1-yl)-2-[(*tert*-butylamido-κN)dimethylsilyl]-3,4,5-trimethyl-η⁵-cyclopentadienyl}dichlorotitanium(IV) (7)

2,3,4-Trimethylcyclopent-2-en-1-one (30 g, 242 mmol; prepared according to ref.¹⁵) in diethyl ether (50 ml) was added dropwise to a Grignard reagent prepared from 4-chlorobut-1-ene (27 g, 300 mmol). After stirring for 2 h and work-up with water, the alcohol formed was instantaneously dehydrated by adding a catalytic amount of iodine¹⁶. Distillation from boiling water bath at 1.4 kPa afforded 1-(but-3-en-1-yl)-2,3,4-trimethylcyclopentadiene (a mixture of double-bond isomers) as a colorless liquid. Yield 33.3 g (85%, based on the ketone). GC-MS, *m/z* (rel. abundance): 162 ([M]⁺; 41), 147 (13), 122 (24), 121 ([C₅Me₄H]⁺; 100), 120 (16), 119 (30), 115 (13), 108 (14), 106 (21), 105 (78), 103 (16), 93 (74), 91 (90), 79 (51), 77 (52), 65 (22), 53 (19), 41 (38), 39 (48). IR (neat, cm⁻¹): 3069 (m), 2950 (s), 2908 (vs), 2851 (s), 2737 (w), 1814 (vw), 1640 (s), 1439 (vs,b), 1380 (s), 1312 (vw), 1156 (vw), 1076 (w), 997 (s), 908 (vs), 850 (w), 687 (vw), 649 (w), 629 (w), 582 (vw), 555 (vw).

In the next step, Li[C₅HMe₃(CH₂CH₂CH=CH₂)] was prepared by adding BuLi (1.6 M in hexane, 34.0 ml) to the above cyclopentadiene (8.8 g, 54.3 mmol), and reacted with neat Me₂SiCl₂ (7.0 g, 54.6 mmol). After refluxing for 1 h, all volatiles were distilled off, and the residue was distilled at 0.8 kPa from boiling water bath. Yield of [2-(but-3-en-1-yl)-3,4,5-trimethylcyclopenta-2,4-dien-1-yl]chlorodimethylsilane was 11.6 g (85%). All the product was reacted with *t*-BuNHLi prepared from *tert*-butylamine (3.27 g, 46.0 mmol) and BuLi (1.6 M solution in hexanes, 28.7 ml, 46 mmol) to give, after distillation at 125 °C/9 Pa, the silane (*tert*-butylamino)[2-(but-3-en-1-yl)-3,4,5-trimethylcyclopenta-2,4-dien-1-yl]dimethylsilane as a yellow fluorescent oily liquid. Yield 11.1 g (83%). GC-MS, *m/z* (rel. abundance): 291 ([M]⁺; 11), 131 (13), 130 ([Me₂SiNH*t*-Bu]⁺; 100), 105 (8), 74 (23), 73 (18). ¹H NMR (C₆D₆): 0.04, 0.09 (2 × s, 3 H, SiMe₂); 1.09 (s, 9 H, CMe₃); 1.80, 1.82, 1.97 (3 × s, 3 H, Me₃C₅); 2.08–2.27 (m, 2 H, CH₂); 2.50–2.67 (m, 2 H, CH₂); 2.91 (s, 1 H, Me₃C₅H); 4.96 (ddt, ³J_{HH} = 10.2, ²J_{HH} = 2.1, ⁴J_{HH} = 1.2, 1 H, =CH₂); 5.05 (ddt, ³J_{HH} = 17.1, ⁴J_{HH} ≈ ²J_{HH} ≈ 2.1, 1 H, =CH₂); 5.84 (ddt, ³J_{HH} = 17.1, 10.2, 6.6, 1 H, =CH). {¹³C} ¹H NMR (C₆D₆): 1.1, 1.7 (SiMe₂); 11.4, 11.5, 15.1 (Me₃C₅); 28.4 (CH₂); 33.9 (CMe₃); 35.7 (CH₂); 49.4 (CMe₃); 54.7 (Me₃C₅H, CH); 114.5 (=CH₂); 133.7, 135.5, 137.9 (Me₃C₅H, CMe); 139.2 (=CH). IR (neat, cm⁻¹): 3380 (w,b), 3073 (m), 2957 (vs), 2927 (s), 2864 (s), 1820 (vw), 1640 (m), 1466 (m), 1447 (s), 1400 (m), 1380 (vs), 1362 (s), 1252 (vs), 1233 (vs), 1115 (w), 1080 (vw), 1020 (vs), 994 (m), 957 (w), 913 (s), 850 (s), 830 (s,b), 800 (w), 781 (m), 766 (m), 724 (w), 680 (w), 636 (m), 557 (vw), 510 (m), 477 (w).

The complex **7** was obtained from $C_5HMe_3(CH_2CH_2CH=CH_2)(SiMe_2NHCMe_3)$ (10.5 g, 36.0 mmol) using the procedure described above. The yield of yellow crystalline product was merely 0.92 g (2.3 mmol, 6.4%). The NMR spectra revealed the presence of the but-2-en-1-yl isomer (ca 80%), likely the presence of but-1-en-1-yl isomer, and the absence of the but-3-en-1-yl isomer. EI-MS (90 °C, m/z (rel. abundance)): 409 (7), 407 ($[M]^+$; 11), 396 (18), 395 (22), 394 (69), 393 (35), 392 ($[M - Me]^+$; 100), 391 (10), 392 (9), 301 (9), 300 (9), 299 (15), 241 (7), 73 (13), 59 (17), 57 (12). 1H NMR (C_6D_6): 0.43, 0.51 (2 \times s, 3 H, $SiMe_2$); 1.43 (s, 9 H, Me_3C); 1.50–1.53 (m, 3 H, =CHMe); 1.99, 2.01, 2.08 (3 \times s, 3 H, Me_3C_5); 3.19–3.26 (m, 1 H, CH_2); 3.52–3.59 (m, 1 H, CH_2); 5.30–5.45 (m, 2 H, CH=CH). $^{13}C\{^1H\}$ NMR (C_6D_6): 5.0, 5.7 ($SiMe_2$); 13.0, 13.1, 13.1 (Me_3C_5); 16.2 ($MeCH=$); 28.6 (CH_2); 32.7 (Me_3C); 62.3 (Me_3C); 103.4 (C_5Me_3 , C_{ipso}); 124.9, 129.3 (CH=CH); 137.8, 138.3, 141.2, 143.9 (C_5Me_3 , C_{ipso}) (resonances of the minor isomer subtracted). IR (KBr, cm^{-1}): 3018 (m), 2971 (s), 2958 (s), 2924 (s), 2868 (m), 1650 (vw), 1641 (w), 1465 (m), 1443 (m), 1399 (m), 1376 (m), 1364 (s), 1334 (m), 1254 (s), 1232 (w), 1217 (m), 1186 (vs), 1128 (w), 1017 (w), 989 (s), 922 (vw), 893 (w), 846 (vs), 819 (s), 795 (s), 772 (vs), 718 (w), 679 (m), 644 (vw), 619 (vw), 552 (m), 540 (w), 513 (m), 499 (m), 429 (s).

Crystal Structure Analysis of Compound **5**

Yellow prisms of **5** were inserted into Lindemann glass capillaries in a glovebox under nitrogen and the capillaries were sealed by flame. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed by HKL program package¹⁷. The structure was solved by direct methods (SIR97¹⁸), followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELX97¹⁹). The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included to calculated positions. A disorder in the position of but-2-en-2-yl group was observed over the C6, C7, C8, and C9 atoms. Apart from the principal position of the group, its ghost rotated by about 170° around the C2–C6 bond could be also located on the difference Fourier map. The two groups were refined with their occupancy factors summing to one while no bond-length restraints were imposed upon the individual moieties.

Crystal data for **5**: $C_{18}H_{31}Cl_2NSiTi$, $M_w = 408.33$, triclinic, $P-1$ (No. 2), $a = 8.3290(2)$ Å, $b = 10.4220(2)$ Å, $c = 13.3790(3)$ Å; $\alpha = 74.944(1)^\circ$, $\beta = 80.144(1)^\circ$, $\gamma = 70.732(1)^\circ$, $V = 1054.01(4)$ Å³, $Z = 2$, $\rho_c = 1.287$ g cm⁻³, $\mu(MoK\alpha) = 0.716$ mm⁻¹, $F(000) = 432$, crystal dimensions $0.38 \times 0.30 \times 0.18$ mm³, θ range 1.0 – 29.1° , 5612 independent diffractions, final $R = 0.0441$, $wR = 0.0876$, GOF = 1.054, largest difference peak and hole on the final difference electron density map 0.562 and -0.466 e Å⁻³.

CCDC 198867 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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