o-Phenylene-bridged Cp/sulfonamido titanium complexes for ethylene/1-octene copolymerization[†]

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The Suzuki-coupling reaction of 2-(dihydroxyboryl)-3,4-dimethyl-2-cyclopenten-1-one (1) and 2-(dihydroxyboryl)-3-methyl-2-cyclopenten-1-one (2) with 2-bromoaniline derivatives affords cyclopentenone compounds (**3–8**) from which cyclopentadiene compounds, 4,6-R'₂-2-(2,5-Me₂C₅H₃)C₆H₂NH₂ (**9–11**) and 4,6-R'₂-2-(2,3,5-Me₃C₅H₂)C₆H₂NH₂ (**12–14**) are prepared. After sulfonation of the $-NH_2$ group with *p*-TsCl, metallation is carried out by successive addition of Ti(NMe₂)₄ and Me₂SiCl₂ affording *o*-phenylene-bridged Cp/sulfonamido titanium dichloride complexes, [4,6-R'₂-2-(2,5-Me₂C₅H₂)C₆H₂NSO₂C₆H₄CH₃)]TiCl₂ (R' = H, **21**; R' = Me, **22**; R' = F, **23**) and [4,6-R'₂-2-(2,3,5-Me₃C₅H)C₆H₂NSO₂C₆H₄CH₃)]TiCl₂ (R' = H, **24**; R' = Me, **25**; R' = F, **26**). The molecular structures of **24** and [2-(2,5-Me₂C₅H₂)C₆H₄NSO₂C₆H₄CH₃)]TiCl₂ (n⁴ = H, **24**; R' = Me, **25**; R' = F, **26**). The molecular structures of **24** and [2-(2,5-Me₂C₅H₂)C₆H₄NSO₂C₆H₄CH₃)]TiCl₂ (100.90°) than that observed for the CGC (constrained-geometry catalyst), [Me₂Si(η⁵-Me₄Cp)(N'Bu)]TiCl₂ (107.6°) indicating a more "constrained feature" in **24** than in the CGC. Complex **24** shows the highest activity among the newly prepared complexes in ethylene/1-octene copolymerization but it is slightly inferior to the CGC in terms of activity, comonomer-incorporation ability, and molecular weight of the obtained polymers.

Introduction

Among the reported homogeneous Ziegler-Natta catalysts,^{1,2} the most successful one is the silvlene-bridged Cp/amido complex, $[Me_2Si(\eta^5-Me_4C_5)(N'Bu)]TiCl_2$, which is called CGC (constrained-geometry catalyst).³ Advantages of the CGC over the conventional bis(cyclopentadienyl)metallocene catalysts are high α -olefin incorporation, thermal stability, and high molecular weight in the ethylene/ α -olefin copolymerizations, which enable its use in a commercial process. Since Dow and Exxon reported it almost simultaneously in the early 1990s,⁴ various modifications have been carried out either by replacement of the Me₄C₅-unit with other π -donor ligands⁵ or by replacement of the N'Bu-unit with other amides or phosphides.6 In contrast to the large variations in the Me₄C₅- and N'Bu-units, modification of the bridge has not been so abundant and not so successful. Erker reported the preparation of alkylidene (R^1R^2C) or vinylidene ($H_2C=C$)-bridged complexes, but their activities for ethylene polymerization are significantly lower than that of the standard CGC.7 The ethylenebridged complex [(n⁵-Me₄C₅)CH₂CH₂(N'Bu)]TiCl₂ was prepared by Hessen, but it showed much lower α-olefin incorporation.⁸ Recently, we reported o-phenylene-bridged Me₃HC₅/amido titanium complexes and their ethylene/1-hexene copolymerizations.9 We devised a novel synthetic route for the ligand system using the Suzuki-coupling reaction between *N*-alkyl-2-bromoanilines and 2-(dihydroxyboryl)-3,4-dimethyl-2-cyclopenten-1-one (1) (eqn (1)).



Some complexes are superior to the standard CGC in terms of activity and 1-hexene incorporation. Herein, we report the preparation of related *o*-phenylene-bridged Cp/sulfonamido titanium complexes and their ethylene/1-octene copolymerizations. The preparation and structure of a related ethylene bridged Cp/tosylamido titanium dichloride complex were reported without providing any polymerization reactivity.¹⁰

Results and discussion

Synthesis and characterization

Boronic acid **2** is prepared on a 30 g scale in 94% yield from 2-bromo-3-methyl-2-cyclopenten-1-one using almost the same conditions and method as applied for the preparation of $1.^9$ Suzuki-coupling reactions of **1** and **2** with 2-bromoaniline or

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Scheme 1 Legend: (i) 2-BrC₆H₂(R')₂NH₂, Na₂CO₃, Pd(PPh₃)₄ (1 mol%); (ii) MeLi/CeCl₃, then HCl (2 N); (iii) *p*-TsCl/pyridine; (iv) Ti(NMe₂)₄; (v) Me₂SiCl₂.

substituted 2-bromoaniline afford the desired coupled compounds **3–8** in 73–96% yields (Scheme 1). The ¹H NMR, ¹³C NMR, and IR spectra are in agreement with the structures.

Addition of 2 equivalents of MeLi to 3-8 and subsequent acidic work-up does not afford the desired cyclopentadiene compounds, but the same reaction in the presence of anhydrous CeCl₃ furnishes the desired compounds 9-14 in 60-89% yields.¹¹ The 1,5-sigmatropic rearrangement is a facile process in the cyclopentadiene derivatives and it gives rise to a set of isomers for some substituted cyclopentadiene compounds.¹² For compounds 9-14, the isomer, where two hydrogens are attached on the sp³ carbon, is substantially more stable than the other isomers and only a set of signals is observed at room temperature in the ¹H and ¹³C NMR spectra.¹³ Compounds 9–11 are obtained contaminated with an isomer ($\sim 10\%$) which cannot be removed by chromatography on silica gel. Observation of a pair of singlet signals at 4.5-5.0 ppm in the ¹H NMR spectra indicates that the minor isomer has not arisen from the 1,5-sigmatropic rearrangement but from the exocyclic elimination reaction.¹⁴ That kind of undesired isomer is not observed at all in the case of the trimethylcyclopentadiene compounds 12-14.



Sulfonamides 15–20 are obtained from 9–14 by treatment with *p*-toluenesulfonyl chloride (*p*-TsCl) in the presence of pyridine in good yields (80–91% for 15–19, 68% for 20). For compounds 9–14, the Cp-CH₂ proton signals are observed at \sim 3 ppm as singlets or narrow multiplets, but for compounds 15–20 the corresponding signals are observed as AB spin systems, which is explained by the higher rotation barrier around the C(phenylene)–C(cyclopentadiene) bond caused by the attachment of the *p*-toluenesulfonyl group.

Reaction of **15–20** with Ti(NMe₂)₄ in toluene at 60 °C for 12 hours affords the desired chelated bis(dimethylamido)titanium complexes. The Cp-H and the NCH₃ signals are very broad in the case of the complexes derived from **16** and **19**. The broadening is

attributed to a high rotation barrier around the N–S bond caused by the presence of an *ortho*-methyl group on the phenylene-bridge.

Treatment of the bis(dimethylamido)titanium complexes with Me_2SiCl_2 in toluene at room temperature for 1 hour cleanly gives the desired dichlorotitanium complexes.¹⁵ The complexes are soluble in toluene or benzene but insoluble in pentane or hexane. Analytically pure complexes are obtained by layer diffusion of pentane into a benzene solution. Broad single signals are observed for Cp-CH₃ and Cp-H protons, respectively, in the ¹H NMR spectrum of **21**, but for **22** and **23** two Cp-CH₃ signals and two Cp-H signals are observed as singlets and as a pair of doublets (J = 3.2 Hz), respectively. These observations may be explained by the coordination of the oxygen atom to the titanium center (eqn (2)).



Complex 21 is under fluxional motion on the NMR time scale between the two states depicted in eqn (2) and hence broad single Cp-CH₃ and Cp-H signals are observed, respectively. For complex 22, the state change is prohibited (or very slow) at room temperature by the presence of the ortho-methyl group and hence the two methyls and the two hydrogens attached to the cyclopentadienyl are inequivalent, respectively, on the NMR time scale. For complex 23, the fluorine atoms on the phenylene bridge reduce the coordination ability of the nitrogen donor and consequently the oxygen is bound more strongly to the titanium not allowing the state change. A set of broad signals is observed for 24 but, for complexes 25 and 26, two sets of sharp signals are observed in 2 : 1 and 1 : 1 ratios, respectively, which is also explained by the coordination of an oxygen atom to the titanium center. The coordination gives rise to two diastereomers in the case of the unsymmetric trimethylcyclopentadienyl complexes.

X-Ray crystallographic studies

Single crystals of the intermediate bis(dimethylamido)titanium complex $[C_6H_4(Me_2H_2C_5)(NTs)]Ti(NMe_2)_2$ (27) suitable for X-ray crystallography are obtained by layer diffusion of pentane



Fig. 1 Thermal ellipsoid plot (30% probability level) of 27. Selected bond distances (Å) and angles (°): Ti–N(1), 2.1095(15); Ti–N(2), 1.9200(17); Ti–N(3), 1.8935(17); Ti–C(7), 2.3355(19); Ti–C(8), 2.400(2); Ti–C(9), 2.398(2); Ti–C(10), 2.365(2); Ti–C(11), 2.369(2); S–N(1), 1.6249(15); Cp(centroid)–Ti, 2.046; O(1)–Ti, 3.022; S–O(1), 1.4381(16); S–O(2), 1.4396(15); Cp(centroid)–Ti–N(1), 102.95; N(3)–Ti–N(2), 104.12(8); C(2)–N(1)–S, 119.88(12); C(2)–N(1)–Ti, 122.93(12); S–N(1)–Ti, 117.19(8); C(2)–C(1)–C(7), 116.09(17); C(1)–C(2)–N(1), 114.42(16); Cp(centroid)–C(7)–C(1), 172.79; C(7)–Cp(centroid)–Ti, 88.15; Ti–N(1)–S–C(14), 105.5; Ti–N(1)–S–O(1), 7.8.

into a benzene solution. Fig. 1 shows the structure with the selected bond distances and angles. The Cp(centroid)-Ti-N angle has been used as a qualitative measure for the "constrained geometry". The smaller the Cp(centroid)-Ti-N angle is, the more pronounced the "constrained geometry" features should be. The Cp(centroid)-Ti-N angle (102.95°) is smaller than those observed for the standard CGC (107.6°)¹⁶ and for the o-phenylenebridged complex $[2-(\eta^5-2,3,5-Me_3C_5H)C_6H_3NC_6H_{11}]TiCl_2$ (104.6 and 104.8°)⁹ indicating a more "constrained feature" in the ophenylene-bridged Cp/sulfonamido complex. The ipso-carbon on the phenylene bridge does not acutely deviate from the cyclopentadienyl plane (Cp(centroid)–C(bridgehead)–C(Ph) angle, 172.79°) which is in contrast with the observation of acute deviation of the Si atom from the cyclopentadienyl plane for the silvlene-bridged complexes (Cp(centroid)-C(bridgehead)-Si angles for C₅R₄SiMe₂(N-t-Bu) titanium complexes, 150–154°).¹⁷ The Cp(centroid)-Ti vector does not deviate from the normal direction and is situated almost perpendicularly to the cyclopentadienyl plane (Ti-Cp(centroid)-C(bridgehead) angle, 88.15°). The Ti-NTs bond distance (2.1095(15) Å) is substantially longer than those observed for the standard CGC (1.907(4) Å) and $[2-(\eta^{5}-2,3,5-Me_{3}C_{5}H)C_{6}H_{3}NC_{6}H_{11}]TiCl_{2}$ (1.902 Å) indicating a weaker Ti-N bond strength for the sulfonamide complex. The sulfonamide nitrogen atom is perfectly trigonal and the sum of the bond angles around the nitrogen atom amounts to 360.0°. The cyclopentadienyl plane is situated almost perpendicularly to the phenylene plane (angle between the plane, $79.68(8)^{\circ}$) and the titanium atom is situated on the phenylene plane (distance between the Ti and the phenylene plane, 0.194(4) Å). Even though the – $SO_2C_7H_7$ fragment is situated allowing for one oxygen (O(1)) to be close to the titanium atom (dihedral angle of Ti-N(1)-S-O(1),

Layer diffusion of pentane into a C_6D_6 solution of **23** in a NMR cell affords yellow single crystals along with powdery precipitates. An X-ray crystallographic study of the yellow single crystal revealed the structure of an unexpected dinuclear μ -oxo complex **28** (Fig. 2). A similar dinuclear μ -oxo zirconium complex was observed by us when crystal growing was conducted for (Me₂H₂C₅–C(Ph)H–NtBu)ZrCl₂ by the same method.¹⁷ Formation of the water-absorbed complex even in thoroughly dried solvents implies that the complex is highly reactive towards water.



Fig. 2 Thermal ellipsoid plot (30% probability level) of 28.

When crystal growing is conducted with 24 by the same method applied for 23, red single crystals are obtained without formation of any fluffy precipitates. An X-ray crystallographic study revealed the structure of the desired chelated titanium dichloride complex. Two independent molecules are present in the asymmetric unit cell. Fig. 3 shows its structure with the selected bond distances and angles measured for one molecule in the asymmetric unit cell. The metrical parameters measured for the other molecule are almost the same. The Cp(centroid)-Ti-N angle (100.91°) is contracted from that observed for 27 (102.95°). The angle is significantly small when compared with those observed for the standard CGC (107.6°) and the o-phenylene-bridged complex [2- $(\eta^{5}-2,3,5-Me_{3}C_{5}H)-C_{6}H_{3}N-C_{6}H_{11}$ TiCl₂ (104.6 and 104.8°). Even though the "constrained geometry" feature is large in this system, the elements constituting the chlelation are not situated in a severely strained position. That is, the ipso-carbon (C(9)) on the phenylene bridge is situated on the cyclopentadienyl plane $((Cp(centroid)-C(1)-C(9) angle, 174.62^{\circ}))$ and the titanium atom is bonded perpendicularly to the cyclopentadienyl ligand (C(1)-Cp(centroid)-Ti(1), 89.24°) as is observed for 27. The Ti-N distance (2.005(5) Å) is reduced from that observed for 27 (2.1095(15)Å) but still longer than those observed for the CGC (1.907(4) Å)and for [2-(η⁵-2,3,5-Me₃C₅H)C₆H₃NC₆H₁₁]TiCl₂ (1.902 Å). The nitrogen atom is perfectly trigonal (sum of the bond angles around the nitrogen atom, 360.0°). An oxygen atom (O(1)) is situated close to the titanium and the Ti-O distance is 2.414 Å, which is substantially shorter than that observed for 27 (3.022 Å). This short distance along with the ¹H NMR signal pattern described above indicates chemical bonding between these two atoms. An



Fig. 3 Thermal ellipsoid plot (30% probability level) of **24**. Selected bond distances (Å) and angles (°): Ti–N, 2.005(5); Ti–Cl(1), 2.272(2); Ti–Cl(2), 2.274(2); Ti–C(1), 2.356(6); Ti–C(2), 2.401(7), Ti–C(3), 2.403(7); Ti–C(4), 2.364(7); Ti–C(5), 2.344(6); Cp(centroid)–Ti(1), 2.046; S–N, 1.606(5); S–O(1), 1.462(5); S–O(2), 1.426(5); O(1)–Ti(1), 2.416; Cp(centroid)–Ti–N, 100.91; Cl(1)–Ti–Cl(2), 104.98(8); C(10)–N–S, 123.7(4); C(10)–N–Ti, 130.0(4); S–N–Ti, 106.3(3); C(10)–C(9)–C(1), 112.7(5); C(9)–C(10)–N, 112.3(5); Cp(centroid)–C(1)–C(9), 174.62; C(1)–Cp(centroid)–Ti, 89.24; Ti–N–S–C(15), 110.8; Ti–N–S–O(1), 3.1.

oxygen atom is also situated close to the titanium center in case of the related complex [η^5 -CpCH₂CH₂NTs]TiCl₂, which was interpreted as a bonding interaction between these two atoms.¹⁰ By the coordination of the oxygen atom, the S–O(1) distance (1.462(5) Å) is elongated a little (the other S–O distance, 1.426(5) Å; the S–O distances in **27**, 1.4381(16) and 1.4396(15) Å) and the Ti–N–S angle is contracted to 106.3(3)° from the normal angle of 120°. The Ti–N–S angle observed for the oxygen-uncoordinated complex **27** is 117.19(8)°.

Polymerization studies

The prepared complexes were tested for ethylene/1-octene copolymerization after activation with $[Ph_3C][B(C_6F_5)_4]$ in the presence of Al(iBu)₃. The Al(iBu)₃ is added both as a scavenger and as an alkylating agent. The polymerization conditions and the results are summarized in Table 1. The activity is very sensitive not only to the substituents on the phenylene bridge but also to the number of methyl substituents on the cyclopentadienyl ligand. Introduction of dimethyl or diffuoro groups on the phenylene-bridge significantly reduces the activity (entries, 2–3 and 5–6). By placing one more methyl group on the cyclopentadienyl ligand, the activity increases more than two times (entries 1 and 4). The activity of **24** (130 × 10⁶ g mol_{Ti}⁻¹ h⁻¹) nearly reaches that of the CGC (160 × 10⁶ g mol_{Ti}⁻¹ h⁻¹).

The 1-octene content in the copolymer is usually calculated by the analysis of the ¹³C NMR spectrum of the copolymer¹⁸ but, in the case of the copolymers containing significant amounts of α olefin, it can be measured more easily from the ¹H NMR spectrum. In the ¹H NMR spectrum (Fig. 4), the methyl signal (0.93–1.02 ppm) is suitably isolated from the methine and methylene signals (1.30–1.50 ppm) and the 1-octene content can be calculated from the integration values of the two signals. Usually, higher incorporation of α -olefin can be expected for the complex exhibiting the smaller Cp(centroid)–Ti–N angle. Complex **24** has a smaller Cp(centroid)–Ti–N angle than the CGC, but the 1-octene content (15 mol%) of the copolymer obtained with **24** is less than that of the copolymer obtained with the standard CGC (19 mol%). This discrepancy might be due to the additional coordination of the oxygen atom.



Fig. 4 The ¹H NMR spectrum of the ethylene/1-octene copolymer.

Table 1 Ethylene/1-octene copolymerization results ^a	
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Entry	Catalyst ^b	Yield/g	A^c	$T_{\rm m}/^{\circ}{\rm C}$	[Oct]	MI ^d	$M_{ m w}$	$M_{ m w}/M_{ m n}$
1	21	43	51	86.6	14	146	28 000	2.0
2	22	5.3	6.4	104.9		13.1	71 000	6.1
3	23	Trace						
4	24	110	130	92.8	15	26	49 000	3.0
5	25	3.4	4.1	86.0	14	2.7	85 000	3.9
6	26	5.1	6.1	90.7	24	0.23	191 000	6.0
7	CGC	130	160	89.4	19	20	56 000	2.8

^{*a*} Polymerization conditions: 1000 mL toluene solution of 1-octene (0.8 M), 5 μ mol complex, 15 μ mol of [Ph₃C][B(C₆F₅)₄], 0.125 mmol of Al(iBu)₃, 13 bar ethylene, 10 minutes, 90 °C. ^{*b*} Activity in units of 10⁶ g mol_{Ti}⁻¹ h⁻¹. ^{*c*} 1-Octene content in the copolymer measured by ¹H NMR. ^{*d*} Melt index which is the melt flow rate (g per 10 min) at 190 °C and using a load of 2160 g.

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Attachment of one more methyl group to the cyclopentadienyl ligand leads to a significant increase in the molecular weight (entries 1 and 4), but the molecular weight of the polymer obtained with **24** is still slightly smaller than that of the polymer obtained with the CGC (M_w , 49 000 and 56 000 for **24** and the CGC, respectively). The melt flow rate (MI) of the polymer is strongly related to the molecular weight and the MI data are in good accord with the molecular weights measured using GPC.

Conclusion

o-Phenylene-bridged $Me_2H_2C_5$ (or Me_3HC_5)/sulfonamide ligands are prepared. The Suzuki-coupling reaction of 2-(dihydroxyboryl)-3,4-dimethyl-2-cyclopenten-1-one (1) and 2-(dihydroxyboryl)-3-methyl-2-cyclopenten-1-one (2) with 2bromoaniline derivatives is the key step in the preparation. The chelated metal complexes are obtained by successive addition of $Ti(NMe_2)_4$ and Me_2SiCl_2 to the ligands. The ¹H NMR and X-ray crystallographic studies show that both the nitrogen and the oxygen atoms on the sulfonamide coordinate to the titanium for the dichlorotitanium complexes while only the nitrogen atom coordinates for the bis(dimethylamido)titanium complexes. The Cp(centroid)-Ti-N angles measured on the X-ray structures of the o-phenylene-bridged Cp/sulfonamide complexes are substantially smaller than those observed for the CGC and for $[Me_2Si(\eta^5-Me_4C_5)(N'Bu)]TiCl_2$, indicating a more "constrained feature" in the sulfonamide complex, but less 1-octene is incorporated by the sulfonamide complex during ethylene/1-octene copolymerization, which might be attributed to the additional oxygen-coordination. The activity is highly sensitive not only to the substituents on the phenylene bridge but also to the number of methyl substituents on the cyclopentadienyl ligand. The highest activity is observed with the unsubstituted o-phenylene-bridged Me₃HC₅/sulfonamide complex (24) and it nearly reaches that of the CGC.

Experimental

General remarks

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, THF, and C_6D_6 were distilled from sodium benzophenone. NMR spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using Waters Model 150 °C + GPC and the data were analyzed using a polystyrene analyzing curve. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis 3100. Details of synthetic procedures and characterizations of **2–20** are available as ESI.†

Syntheses

Complex 21. Compound **15** (0.500 g, 1.473 mmol), Ti(NMe₂)₄ (0.330 g, 1.473 mmol), and toluene (10 mL) were added to a Schlenk flask. The solution was stirred for 12 hours at 60 °C. Removal of solvent and extraction with pentane gave a red solid. ¹H NMR (C_6D_6): δ 1.66 (s, 6H, CH₃), 1.87 (s, 3H, CH₃), 3.28 (s, 12H,

was added Me₂SiCl₂ (0.570 g, 4.42 mmol). After the solution was stirred for 1 hour at room temperature, all volatiles were removed under vacuum to give a red residue which was triturated in pentane (0.464 g, overall 63%). ¹H NMR (C₆D₆): δ 1.72 (s, 3H, CH₃), 1.79 (s, 6H, CH₃), 6.65 (s, 2H, Cp-H), 6.65 (d, J = 7.6 Hz, 2H, Ts-H), 6.81 $(d, J = 7.2 \text{ Hz}, 1\text{H}, C_6\text{H}_4\text{-}CH), 6.86 (t, J = 7.2 \text{ Hz}, 1\text{H}, C_6\text{H}_4\text{-}CH),$ $6.99 (t, J = 7.2 \text{ Hz}, 1\text{H}, C_6\text{H}_4\text{-}CH), 7.09 (d, J = 7.2 \text{ Hz}, 1\text{H}, C_6\text{H}_4\text{-}$ CH), 8.15 (d, J = 7.6 Hz, 2H, Ts-H) ppm. ¹³C{¹H} NMR (C₆D₆): δ 15.07, 21.44, 114.52, 124.0 (broad), 124.85, 126.23, 128.11, 128.39, 128.88, 129.76, 130.09, 135.30, 143.93, 145.28, 155.01 ppm. Anal. Calc. (C₂₀H₁₉Cl₂NO₂STi): C, 52.65; H, 4.20; N, 3.07%. Found: C, 52.71; H, 4.37; N, 2.93%. **Complex 22.** The compound was synthesized from 16 using the same conditions and procedures as for 21. Overall yield for the dichloride complex from 16 was 68%. The NMR data for the intermediate bis(dimethylamido)titanium complex: ¹H NMR (C₆D₆): δ 1.95 (s, 3H, CH₃), 2.05 (s, 9H, CH₃), 2.17 (s, 3H, CH₃), 3.32 (br s, 12H, NMe₂), 5.94 (s, 2H, Cp-CH), 6.76 (s, 1H, C₆H₂-CH), 6.86 (d, J = 8.0 Hz, 2H, Ts-H), 6.95 (s, 1H, C₆H₂-CH),

8.25 (d, J = 8.0 Hz, 2H, Ts-H) ppm. The analytical data for

the dichlorotitanium complex: ¹H NMR (C_6D_6): δ 1.81 (s, 3H,

CH₃), 1.88 (s, 3H, CH₃), 1.92 (s, 3H, CH₃), 2.08 (s, 3H, CH₃),

2.21 (s, 3H, CH₃), 6.54 (d, J = 3.2 Hz, 1H, Cp–CH), 6.55–6.56

(m, 1H, C_6H_2 -CH), 6.61–6.63 (m, 1H, C_6H_2 -CH), 6.64 (d, J =

8.0 Hz, 2H, Ts-H), 6.68 (d, J = 3.2 Hz, 1H, Cp-CH), 8.10 (d, J =

8.0 Hz, 2H, Ts-H) ppm. ¹³C{¹H} NMR (C₆D₆): δ 14.60, 16.84,

20.76, 20.98, 21.41, 123.35, 125.03, 126.90, 127.77, 128.56, 129.46,

129.93, 133.20, 134.90, 137.12, 137.91, 140.36, 144.63, 145.17,

148.77 ppm. Anal. Calc. (C22H23Cl2NO2STi): C, 54.56; H, 4.79;

N, 2.89%. Found: C, 54.62; H, 4.75; N, 2.93%.

 NMe_2), 5.75 (s, 2H, Cp-H), 6.74 (d, J = 6.8 Hz, 2H, Ts-H), 6.83 (t,

J = 6.8 Hz, 1H, C₆H₄-CH), 6.96 (d, J = 6.8 Hz, 1H, C₆H₄-CH),

7.13 (t, J = 6.8 Hz, 1H, C₆H₄-CH), 7.78 (d, J = 6.8 Hz, 2H, Ts-H),

8.11 (d, J = 6.8 Hz, 1H, C₆H₄-CH) ppm. To a flask containing the

resulting bis(dimethylamido)titanium complex in toluene (10 mL)

Complex 23. The compound was synthesized from 17 using the same conditions and procedures as for 21. Overall yield for the dichloride complex from 17 was 62%. The NMR data for the intermediate bis(dimethylamido)titanium complex: ¹H NMR (C_6D_6) : δ 1.89 (s, 6H, CH₃), 1.93 (s, 3H, CH₃), 3.28 (s, 12H, NMe₂), 5.85 (s, 2H, Cp-CH), 6.46–6.52 (m, 1H, C₆H₂F₂-CH), 6.63-6.66 (m, 1H, C₆H₂F₂-CH), 6.86 (d, J = 8.0 Hz, 2H, Ts-H), 8.24 (d, J = 8.0 Hz, 2H, Ts-H) ppm. The analytical data for the dichlorotitanium complex: ¹H NMR (C₆D₆): δ 1.65 (s, 3H, CH₃), 1.77 (s, 3H, CH₃), 1.83 (s, 3H, CH₃), 6.12 (ddd, ${}^{3}J_{HF} = 7.2$ Hz, ${}^{4}J_{\rm HH} = 2.4$ Hz, ${}^{5}J_{\rm HF} = 1.2$ Hz, 1H, C₆H₂F₂-H), 6.22 (t, ddd, ${}^{3}J_{\rm HF} =$ 14.4 Hz, ${}^{3}J_{\rm HF} = 8.8$ Hz, ${}^{4}J_{\rm HF} = 2.4$ Hz, 1H, C₆H₂F₂-H), 6.53 (d, J = 3.2 Hz, 1H, Cp-CH), 6.64 (d, J = 8.4 Hz, 2H, Ts-H), 6.72 (d, J = 3.2 Hz, 1H, Cp-CH), 8.19 (d, J = 8.4 Hz, 2H, Ts-H), ppm. ¹⁹F NMR (C₆D₆): δ -106.14 (d, J = 6.8 Hz), -114.33 (d, J = 6.8 Hz) ppm. Anal. Calc. (C₂₀H₁₇Cl₂F₂NO₂STi): C, 48.81; H, 3.48; N, 2.85%. Found: C, 48.75; H, 3.52; N, 2.69%.

Complex 24. The compound was synthesized from **18** using the same conditions and procedures as for **21**. Overall yield for the dichloride complex from **18** was 70%. The NMR data for the intermediate bis(dimethylamido)titanium complex: ¹H NMR (C_6D_6): δ 1.64 (s, 3H, CH₃), 1.70 (s, 3H, CH₃), 1.83 (s, 3H, CH₃),

1.89 (s, 3H, CH₃), 3.08 (s, 6H, NMe₂), 3.51 (s, 6H, NMe₂), 5.95 (s, 1H, Cp-CH), 6.76 (d, J = 8.0 Hz, 2H, Ts-H), 6.82 (t, J = 7.2 Hz, 1H, C₆H₄-CH), 6.98 (d, J = 7.2 Hz, 1H, C₆H₄-CH), 7.10 (t, J = 7.2 Hz, 1H, C₆H₄-CH), 7.76 (d, J = 8.0 Hz, 2H, Ts-H), 8.06 (d, J = 7.2 Hz, 1H, C₆H₄-CH) ppm. The analytical data for the dichlorotitanium complex: ¹H NMR (C₆D₆): δ 1.66 (br s, 3H, CH₃), 1.79 (br s, 6H, CH₃), 2.26 (br s, 3H, CH₃), 6.48 (s, 1H, Cp-CH), 6.66 (d, J = 8.0 Hz, 2H, Ts-H), 6.80–6.92 (m, 2H, C₆H₄-CH), 7.01 (br t, J = 7.2 Hz, 1H, C₆H₄-CH), 7.12 (d, J = 7.2 Hz, 1H, C₆H₄-CH), 7.12 (d, J = 7.2 Hz, 1H, C₆H₄-CH), 8.16 (d, J = 8.0 Hz, 2H, Ts-H) ppm. ¹³C{¹H} NMR (C₆D₆): δ 12.80, 15.20, 15.44, 21.41, 114.60, 124.57, 124.62, 125.63, 126.84, 128.41, 128.50, 128.92, 129.27, 129.71, 130.01, 135.61, 135.69, 145.03, 155.27 ppm. Anal. Calc. (C₂₁H₂₁Cl₂NO₂STi): C, 53.64; H, 4.50; N, 2.98%. Found: C, 53.57; H, 4.62; N, 3.09%.

Complex 25. The compound was synthesized from 19 using the same conditions and procedures as for 21. Overall yield for the dichloride complex from 19 was 78%. The NMR data for the intermediate bis(dimethylamido)titanium complex: ¹H NMR (C₆D₆): δ 1.88 (s, 3H, CH₃), 1.95 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 2.14 (s, 6H, CH₃), 2.19 (s, 3H, CH₃), 3.23 (s, 6H, NMe₂), 3.43 (s, 6H, NMe₂), 5.93 (s, 1H, Cp-CH), 6.77 (s, 1H, C₆H₂-CH), 6.85 (d, J =5.6 Hz, 2H, Ts-H), 6.96 (s, 1H, C_6H_2 -CH), 8.23 (d, J = 5.6 Hz, 2H, Ts-H) ppm. The analytical data for the dichlorotitanium complex (2 : 1 mixture): ¹H NMR (C_6D_6): δ 1.80 (s, 3H, CH₃), 1.84 (s, 1H, CH₃), 1.90 (s, 2H, CH₃), 1.92 (s, 2H, CH₃), 1.95 (s, 1H, CH₃), 2.11 (s, 1H, CH₃), 2.13 (s, 2H, CH₃), 2.15 (s, 2H, CH₃), 2.28 (s, 1H, CH₃), 2.29 (s, 1H, CH₃), 2.40 (s, 2H, CH₃), 6.38 (s, 0.33H, Cp-CH), 6.51 (s, 0.67H, Cp-CH), 6.61-6.64 (m, 2H, Ts-H), 6.64 (s, 2H, C₆H₂-CH), 8.08–8.12 (m, 2H, Ts-H) ppm. ¹³C{¹H} NMR(C₆D₆): δ 12.70, 14.42, 14.74, 15.80, 16.32, 17.12, 20.84, 20.86, 21.40, 124.94, 126.01, 126.89, 126.94, 127.77, 128.52, 128.64, 129.07, 129.33, 129.87, 129.91, 130.04, 130.30, 132.99, 133.12, 134.74, 134.83, 135.65, 135.70, 135.82, 137.66, 138.08,

Table 2Crystallographic parameters of 27, 28 and 24^a

139.34, 139.54, 144.49, 144.53, 146.19, 146.27, 148.83 ppm. Anal. Calc. (C $_{23}H_{25}Cl_2NO_2STi$): C, 55.44; H, 5.06; N, 2.81%. Found: C, 55.61; H, 5.10; N, 2.93%.

Complex 26. The compound was synthesized from 20 using the same conditions and procedures as for 21. Overall yield for the dichloride complex from 20 was 69%. The NMR data for the intermediate bis(dimethylamido)titanium complex: ¹H NMR (C₆D₆): δ 1.70 (s, 3H, CH₃), 1.93 (s, 3H, CH₃), 2.00 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 3.12 (s, 6H, NMe₂), 3.44 (s, 6H, NMe₂), 5.88 (s, 1H, Cp-CH), 6.49-6.54 (m, 1H, C₆H₂F₂-CH), 6.65-6.68 (m, 1H, $C_6H_2F_2$ -CH), 6.86 (d, J = 8.0 Hz, 2H, Ts-H), 8.22 (d, J = 8.0 Hz, 2H, Ts-H) ppm. The analytical data for the dichlorotitanium complex (1 : 1 mixture): ¹H NMR (C₆D₆): δ 1.61 (s, 1.5H, CH₃), 1.72 (s, 1.5H, CH₃), 1.81 (s, 1.5H, CH₃), 1.82 (s, 1.5H, CH₃), 1.83 (s, 1.5H, CH₃), 1.90 (s, 1.5H, CH₃), 2.28 (s, 3H, CH₃), 6.26–6.32 (m, 2H, C₆H₂F₂), 6.46 (s, 0.5H, Cp-CH), 6.63 (s, 0.5H, Cp-CH), 6.70 (d, J = 8.0 Hz, 2H, Ts-H), 8.17–8.20 (m, 2H, Ts-H) ppm. ¹⁹F NMR (C₆D₆): δ –107.47 (d, J = 6.8 Hz), –115.56 (d, J = 6.8 Hz) ppm. Anal. Calc. (C₂₁H₁₉Cl₂F₂NO₂STi): C, 49.83; H, 3.78; N, 2.77%. Found: C, 50.02; H, 3.85; N, 2.68%.

Polymerization

To a 2.0 L Büch reactor were added 1.0 L of a toluene solution of 1-octene (0.80 M) and (iBu)₃Al (0.5 mmol). After the solution was heated to 90 °C, it was saturated with ethylene gas (13 bar). An activated catalyst, which was prepared by mixing the complex (5.0 µmol Ti), $[CPh_3]^+[B(C_6F_5)_4]^-$ (15 µmol) and (iBu)₃Al (0.125 mmol) for 2 minutes, was added to the reactor by pressurizing the catalyst-feed tank with N₂. After the ethylene (13 psig) had been fed continuously for 10 minutes, the reaction mixture was drained into a flask containing ethanol to give white precipitates which were collected by filtration and dried under

Formula $C_{24}H_{31}N_3O_2STi$ $C_{40}H_{36}Cl_4F_4N_2O_5S_2Ti_2$ $C_{21}H_{20}Cl_2NO_2STi$	
M 473.48 1002.43 470.25	
Color Red Yellow Red	
Size/mm $0.5 \times 0.1 \times 0.03$ $0.1 \times 0.1 \times 0.06$ $0.2 \times 0.08 \times 0.01$	
a/Å 31.743(3) 8.927(5) 11.194(4)	
b/Å 11.5195(11) 13.917(8) 9.734(3)	
c/Å 13.1968(12) 18.663(10) 19.677(7)	
$a/^{\circ}$ 90 101.172(12) 90	
$\beta/^{\circ}$ 98.297(2) 97.017(13) 90	
$\gamma/^{\circ}$ 90 102.053(13) 90	
$V/Å^3$ 4775.1(8) 2192(2) 2144.2(13)	
Crystal system Monclinic Triclinic Orthorhombic	
Space group $C2/c$ $P\overline{1}$ $P2_12_12_1$	
$D(\text{cale})/\text{g cm}^{-1}$ 1.317 1.519 1.457	
Z 8 2 4	
μ/mm^{-1} 0.471 0.765 0.762	
No. of data collected 24251 30361 21958	
No. of unique data 5993 10937 5347	
No. of variables 288 539 258	
<i>R</i> 0.0376 0.0924 0.0639	
R_w 0.0953 0.1957 0.1429	
Goodness of fit 1.053 0.856 1.050	

^{*a*} Data collected at 293(2) K, $R(F) = \sum ||F_{\circ}|| / \sum |F_{\circ}|| / \sum |F_{\circ}||$ with $F_{\circ} > 2.0\sigma(I)$, $R_{w} = [\sum [w(F_{\circ}^{2} - F_{\circ}^{2})^{2}] / \sum [w(F_{\circ})^{2}]^{2}$ with $F_{\circ} > 2.0\sigma(I)$.

vacuum. The copolymer (10 mg) was dissolved in C_6D_6 in order to record the ¹H NMR spectra at 78 °C.

X-Ray crystallography

Crystals of 24, 27, and 28 were mounted in thin-walled glass capillaries and sealed under argon. The data sets were collected on a Bruker Smart CCD detector single diffractometer. Mo-K α radiation ($\lambda = 0.7107$ Å) was used for all structures. The structures were solved by direct methods using the SHELX-96 program and least-squares refinement using the SHELXL-Plus (5.1) software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. The crystal data and refinement results are summarized in Table 2.

CCDC reference numbers 604506-604508.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605345a

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