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"Bidentate" and "tridentate" sulfonamide ligands for titanium complexes: crystal structures and solution dynamics elucidating an η^2 or η^3-coordination mode †

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Highly air- and moisture-sensitive complexes having sulfonamide ligands, $(TsNR)_2Ti(NMe_2)_2$ (Ts = *p*-$MeC_6H_4SO_2$), were prepared by treatment of two equivalents of TsNHR with $Ti(NMe_2)_4$ at room temperature. One of the compounds, where R = *i*-Pr (**1**), was studied in detail; the crystal structure of **1** revealed that both of the TsN*i*-Pr ligands were bound to the metal in an η^2-coordination mode. Solution dynamics of **1** showed that an η^1/η^2 interconversion occurred above 60 °C with an activation energy of 15.8 kcal mol^{-1}. Treatment of $Ti(NMe_2)_4$ with the sulfonamide $TsHN(CH_2)_2O(CH_2)_2NHTs$ (**3**), led to the formation of $[TsN(CH_2)_2O(CH_2)_2NTs]Ti(NMe_2)_2$ (**2**) in high yield, in which the sulfonamide moiety was coordinated to the titanium center in an η^3 (NON) mode. No sign of η^1/η^2 interconversion of the sulfonamide ligands was seen in solution. Treatment of **2** with Me_3SiCl resulted in the formation of $[\{TsN(CH_2)_2O(CH_2)_2NTs\}Ti(NMe_2)Cl]_2$ (**4**) and $[\{TsN(CH_2)_2O(CH_2)_2NTs\}TiCl_2]_2$ (**5**). An X-ray structure determination of **4** revealed that sulfonyl oxygen bridging resulted in the formation of an eight membered ring.

Introduction

Hapticity changes in conjugated π-ligands are thoroughly investigated phenomena in organometallic chemistry;[1] in particular, the η^1/η^3 interconversion of allyl[2] and pseudo-allyl ligands[3] is often seen in a wide variety of organotransition metal compounds. As novel types of pseudo-allyl ligands, the coordination behavior of sulfonamides in certain titanium complexes has attracted the attention of organic and organometallic chemists in relation to their catalytic activity towards enantioselective addition of organometallic reagents to aldehydes.[4] Walsh[5–7] and Gagné[8] have reported the isolation and structure determination of several titanium compounds bearing sulfonamides derived from 1,2-cyclohexanediamine or 1,2-diphenylethylenediamine (see Fig. 1), in which one of the tosylamide groups is bonded to the titanium center *via* N and O (referred to as η^2), and the other *via* N (referred to as η^1).[5,7,8] However, this bonding mode was not seen in solution due to the fact that either rapid η^1/η^2 interconversion within the NMR time scale occurs, or a symmetric η^2:η^2-coordination mode of the ligand is lower in energy.[6,7]

We were interested in investigating the possibility of whether substantial strain in titanacyclopentane structures derived from tosylamide ligands could be the reason why such ligands are bound to the metal in coordination mode **B**. Reaction of these sulfonamide ligands with titanium precursors resulted in the formation of three possible titanacyclopentane structures, **A**–**C**, as shown in Fig. 1. The coordination modes in **A**, **B**, and **C** are η^2 (NN), η^3 (NNO) and η^4 (NONO), respectively. If one considers coordination types **B** or **C**, the Ti–O bonds should provide additional strain on the titanacyclic structure. We suspected that coordination mode **B** might be attributed to the fact that the electronically favorable mode **C** cannot be adopted due to special structural circumstances from tosylamide ligands producing the titanacyclopentane structures; this prompted us to synthesize titanium compounds of type **D** and **E**, bearing other sulfonamide ligands as shown in Fig. 1. In compound type **D**, titanium and the sulfonamide ligands do not form a titanacyclopentane structure, in which the η^4 (NONO) mode is less favorable than the η^3 (NNO) or η^2 (NN) modes. In contrast, it is known that the titanium in compounds of type **E** bond strongly to the central oxygen of the $TsN(CH_2)_2O(CH_2)_2$-

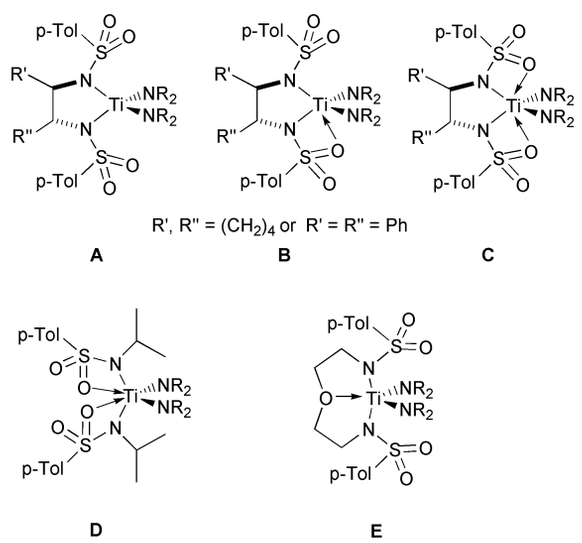


Fig. 1 Sulfonamide complexes of titanium containing sulfonamide ligands with various coordination modes.

† Electronic supplementary information (ESI) available: the ^1H NMR charts of a reaction mixture of $Ti(NMe_2)_4$ and 1.1, 1.6, and 3.0 equiv. of *i*-PrNHTs. See http://www.rsc.org/suppdata/dt/b1/b110481k/

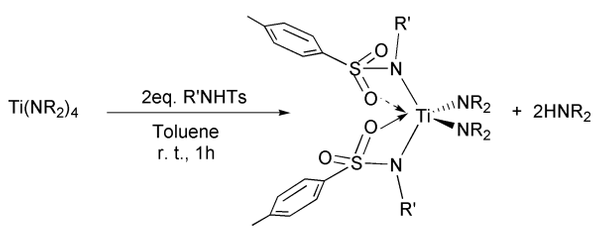
NTs (Ts = p-$MeC_6H_4SO_2$) ligand (a "tridentate" sulfonamide ligand), providing a pentacoordinate structure.[9–12] Molecular modeling studies on compounds of type **E** indicate that neither the coordination mode **C** nor **B** is favorable for the sulfonamide moiety.

In this paper we describe the crystal structures and solution dynamics of a series of compounds of type **D** and **E**. As we had expected, sulfonamide ligands of type **D** gave titanium complexes bearing both of the sulfonamides bonding in an η^2-fashion. In contrast, the coordination mode of sulfonamide moieties in the pentacoordinate complexes is η^3 (NON). In the cases where at least one of the NR_2 groups of compounds of type **E** is replaced by Cl, interaction of one titanium with the oxygen in the sulfonamide moiety bonding to another titanium produces dimeric structures.

Results and discussion

Preparation and characterization of $(i\text{-PrNTs})_2Ti(NMe_2)_2$ (1)

Titanium amide compounds bearing tosylamide ligands $(RNTs)_2Ti(NMe_2)_2$ and $(RNTs)_2Ti(NEt_2)_2$ can generally be synthesized by the reaction of RNHTs (2 equiv.) with either $Ti(NMe_2)_4$ or $Ti(NEt_2)_4$ in benzene or toluene as shown in Scheme 1. Although the characterization of the product



Scheme 1 Preparation of $(R'NTs)_2Ti(NR_2)_2$ (**1**; R = Me, R′ = *i*-Pr).

could be carried out unequivocally on the basis of ^1H and ^{13}C NMR analyses, it was difficult to obtain a complete elemental analysis of these products because of their high moisture sensitivity. Complete characterization of one of the compounds, $(i\text{-PrNTs})_2Ti(NMe_2)_2$ (**1**), which gave relatively large crystals, was successfully performed, and thus we carried out more detailed studies with **1** including its crystal structure and its solution dynamics.

The reaction of HNTs(*i*-Pr) (2 equiv.) with $Ti(NMe_2)_4$ took place instantly at room temperature, giving **1** as dark red crystals in up to 76% isolated yield. ^1H NMR and ^{13}C NMR spectra of **1** at −20 °C showed the two NMe_2 groups to be magnetically equivalent with the methyl signals appearing as one sharp singlet. Similarly, the two *i*-PrNTs groups in **1** are also magnetically equivalent, and two methyl signals due to the *i*-Pr groups are diastereotopic appearing as two doublets in the ^1H NMR and as two independent peaks in the ^{13}C NMR. These spectroscopic data are consistent with those expected for **1**, in which four nitrogen ligands are arranged tetrahedrally and both tosylamides are bonded to the titanium center in coordination mode **D** as shown in Scheme 1. Replacement of the NMe_2 ligands in $Ti(NMe_2)_4$ by the tosylamide is stepwise, and the formation of $[(i\text{-Pr})NTs]Ti(NMe_2)_3$ was detectable in the ^1H NMR by addition of 1.1 equiv. of HNTs(*i*-Pr) to $Ti(NMe_2)_4$. Peaks due to $[(i\text{-Pr})NTs]Ti(NMe_2)_3$ [δ 0.97 and 1.18 (br d each, J = 0.07 Hz, Me of *i*-Pr), 3.60 (m, CH of *i*-Pr), 3.27 (s, NMe_2)], **1**, and unreacted $Ti(NMe_2)_4$ were visible in a ratio of 5 : 1 : 0.6. The ratio was changed to 1 : 2 : 0, when 1.6 equiv. of the ligand was added to $Ti(NMe_2)_4$. In the presence of an excess amount (3 equiv.) of HNTs(*i*-Pr), only **1** and unreacted ligand were visible (1 : 1), and neither $[(i\text{-Pr})NTs]_3Ti(NMe_2)$ nor $[(i\text{-Pr})NTs]_4Ti$ could be detected.

The structure of **1** was confirmed by X-ray structure determination as illustrated in Fig. 2. The dimethylamino

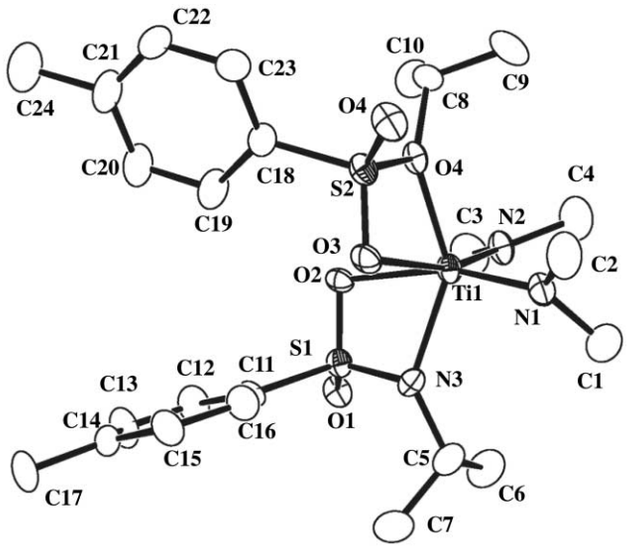


Fig. 2 The ORTEP[24] drawing of **1** with 50% probability thermal ellipsoids.

Table 1 Selected bond lengths (Å) and angles (°) for **1**

Ti(1)–N(1)	1.901(5)	S(1)–O(1)	1.442(4)
Ti(1)–N(2)	1.885(4)	S(1)–O(2)	1.479(3)
Ti(1)–N(3)	2.103(4)	S(2)–O(3)	1.470(3)
Ti(1)–N(4)	2.045(4)	S(2)–O(4)	1.432(4)
Ti(1)–O(2)	2.226(4)	S(1)–N(3)	1.568(4)
Ti(1)–O(3)	2.338(4)	S(2)–N(4)	1.576(4)
N(1)–Ti(1)–N(2)	96.5(2)	N(3)–Ti(1)–O(3)	89.45(15)
N(1)–Ti(1)–N(3)	99.01(19)	N(4)–Ti(1)–O(2)	87.75(15)
N(1)–Ti(1)–N(4)	104.52(19)	N(4)–Ti(1)–O(3)	63.84(14)
N(2)–Ti(1)–N(3)	103.26(18)	O(2)–Ti(1)–O(3)	83.20(13)
N(2)–Ti(1)–N(4)	100.21(18)	Ti(1)–N(3)–S(1)	98.9(2)
N(3)–Ti(1)–N(4)	144.41(17)	Ti(1)–N(4)–S(2)	102.6(2)
N(1)–Ti(1)–O(2)	163.02(17)	N(3)–S(1)–O(1)	117.3(2)
N(1)–Ti(1)–O(3)	91.64(18)	N(3)–S(1)–O(2)	99.4(2)
N(2)–Ti(1)–O(2)	92.76(17)	N(4)–S(2)–O(3)	99.8(2)
N(2)–Ti(1)–O(3)	163.60(16)	N(4)–S(2)–O(4)	115.4(2)
N(3)–Ti(1)–O(2)	64.89(14)		

groups are planar, suggesting electron donation from the Me_2N group to the titanium atom. Although the planar dimethylamino moiety is indicative of the existence of Ti–N multiple bonds, facile rotation of the Me_2N group around the Ti–N bond in solution was evidenced by the appearance of a single ^1H or ^{13}C resonance due to the NMe_2 group. This rotation could not be stopped at −60 °C. The Ti–N bond distances (Table 1) are similar to those reported in other titanium amide complexes bearing a tosylamide ligand derived from *trans*-1,2-cyclohexanediamine (Ti–NR_2, 1.86–1.89 Å; Ti–N(R)Ts, 2.05–2.10 Å).[7] In contrast, the following results are significantly different. First, both of the oxygen atoms in the tosylamide moieties are bonded to the Ti center (in coordination mode **D**). In sharp contrast to the type **A**–**C** tosylamide ligands producing the titanacyclopentane structure, the type **D** tosylamide ligands do not provide a steric bias to the complex by their η^2:η^2-coordination mode; this suggests that such a coordination mode is electronically preferable to the others.[7] Secondly, the arrangement of four N and two O atoms is pseudo-octahedral, and the two O atoms are in a *cis* orientation. In contrast, two N(Ts) moieties are *trans* oriented. This arrangement could minimize the steric repulsion between two bulky isopropyl groups. Electronically negative oxygen atoms may be favorably located at positions *trans* to electron-donating NMe_2 groups. In the cyclohexanediamide complexes, the structure of the ligand forced two N(Ts) atoms to be located at *cis* positions. The Ti–O and Ti–N distances of **1** are similar to those seen in the Ti(η^2-tosylamide) moiety in the sulfonamide complexes of Walsh

and Gagné (Ti–O, 2.167–2.264 Å; Ti–N, 2.048–2.103 Å).[5,7,8] The small Ti–N–S bond angles are another indication of η^2-coordination of the sulfonamide ligands in **1**; in Gagné's complex, those of the bound and unbound sulfonamides are 99.1 and 107.5°, respectively.[8] Shorter N–S bonds and longer O–S bonds than those of uncoordinated sulfonamides are indicative of contribution of the sulfonate type coordination suggested by Anwander and coworkers.[13]

As described above, the crystal structure of **1** revealed the η^2:η^2-coordination mode of the *i*-PrNTs ligands. Of interest is the possibility of η^1/η^2 interconversion in solution. As shown in Fig. 3, two of the methyl groups in the isopropyl group appear

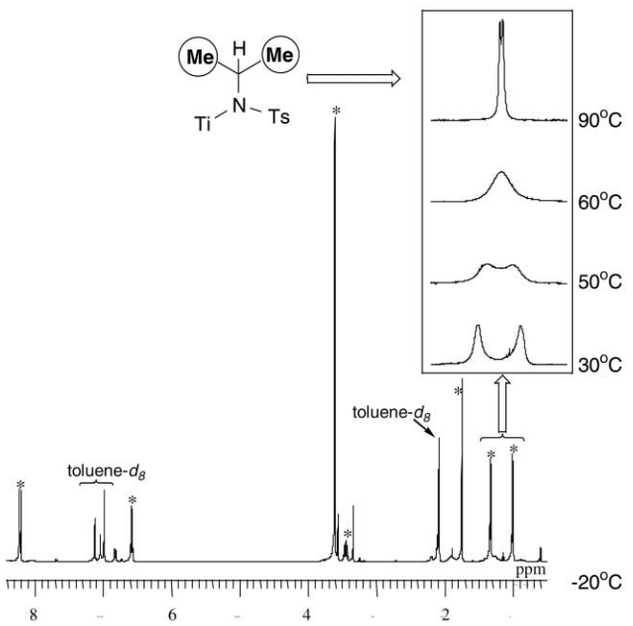
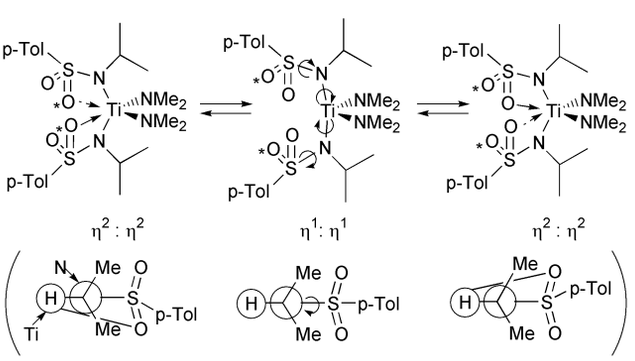


Fig. 3 ^{1}H NMR spectra of **1** (*) at −20, 30, 50, 60, and 90 °C in toluene-d_8.

as two independent signals, because the η^2-bonding mode makes a cyclic structure involving Ti, O, S, and N leading to these methyl groups becoming diastereotopic. In contrast, the η^1-bonding mode allows free rotation of the sulfonamide ligand around the Ti–N or N–S bonds, which makes the two methyl ^{1}H resonances equivalent. The η^1/η^2 exchange process was clearly visible in the variable temperature NMR studies as shown in Fig. 3. The diastereotopic methyl groups appear as two independent doublets at −20 °C, which become broadened at 30 °C, coalesced at 60 °C, and became a sharp single doublet at 90 °C. One reasonable interpretation of these results is conversion of one η^2:η^2-coordination mode to the other η^2:η^2-mode *via* an η^1:η^1-transition state as shown in Scheme 2; the

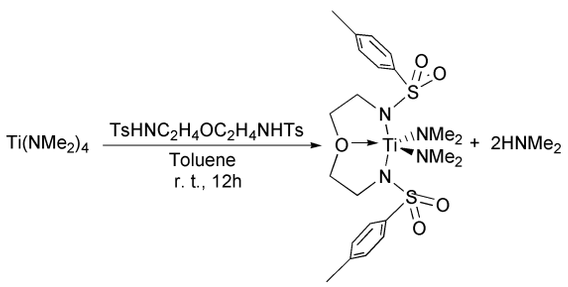


Scheme 2 Reversible η^1/η^2 interconversion of **1**.

two coordination modes are rapidly interconverted on the NMR time scale above 60 °C. Calculated $\Delta G^{\ddagger}$ from the coalescence temperature, which corresponded to the energy of the Ti–O(SON) bond fission, was *ca.* 15.8 kcal mol^{-1}. As a close example, Jordan and coworkers reported a racemization energy for $[(pyAr_2CO)_2Ti(NMe_2)_2]$, in which the reversible dissociation of the pyridine moiety induces the racemization, to be 12–13 kcal mol^{-1}, and the higher dissociation/recombination energy of the sulfonamide ligands in **1** indicates the strong coordinating ability of the oxygen atoms of the sulfonamide ligands.[14]

Preparation and characterization of $[(TsNCH_2CH_2)_2O]Ti(X)_2$ (X = NMe_2 or Cl) 2, 4, 5

Pentacoordinated titanium complexes bearing a trigonal bipyramidal structure have recently been actively investigated by Schrock and coworkers, in which 4-oxaheptanediamine derivatives were used as a tridentate ligand.[9–12] Treatment of $(TsNHCH_2CH_2)_2O$ (**3**) with $Ti(NMe_2)_4$ in toluene afforded the corresponding titanium complex, $[(TsNCH_2CH_2)_2O]Ti(NMe_2)_2$ (**2**), in quantitative yield (Scheme 3). The product was isolable



Scheme 3 Preparation of $(TsNC_2H_4OC_2H_4NTs)Ti(NMe_2)_2$ (**2**).

as orange microcrystals, and was more stable towards air and moisture than **1** and other $(RNTs)_2Ti(NR'_2)_2$ compounds. In the ^{1}H and ^{13}C NMR spectra, peaks due to the two NMe_2 moieties appeared equivalent, while two ^{1}H resonances due to the NCH_2 and OCH_2 moieties or ^{1}H and ^{13}C signals derived from the tosyl groups were also magnetically equivalent. Significant downfield shift of ^{1}H and ^{13}C peaks due to the OCH_2 group indicated coordination of the oxygen atom to the titanium center. A single-crystal X-ray diffraction study of **2** revealed the distorted-trigonal bipyramidal structure shown in Fig. 4, in which two N atoms of the NMe_2 moieties and the

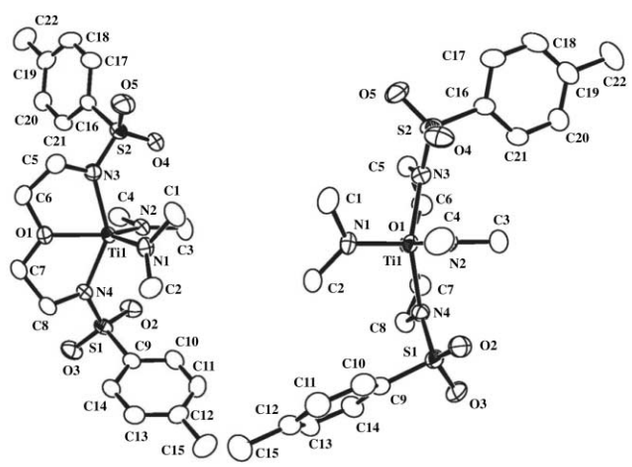


Fig. 4 The ORTEP drawing of **2** with 50% probability thermal ellipsoids. Entire view (left) and front view (right).

oxygen atom in the $TsN(CH_2)_2O(CH_2)_2NTs$ ligand occupy the equatorial positions, and two N atoms of the tosylamide moieties are located at the apical positions. A striking difference between the crystal structure of **2** and **1** and the Walsh complexes[5–7] is that no bonding interaction was seen between the Ti atom and the oxygen atoms in the sulfonamide moieties (Ti–O distances > 3.5 Å). The N–S or S–O bond distances in **2** (Table 2) are similar to those observed in uncoordinated

Table 2 Selected bond lengths (Å) and angles (°) for **2**

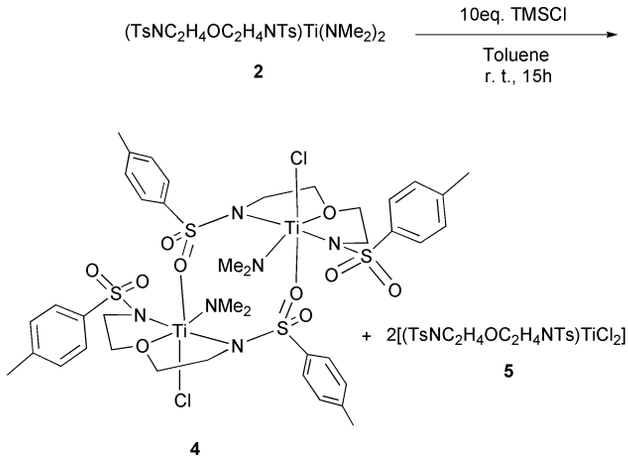
S(1)–O(2)	1.433(2)	Ti(1)–N(1)	1.863(2)
S(1)–O(3)	1.445(2)	Ti(1)–N(2)	1.838(2)
S(2)–O(4)	1.438(2)	Ti(1)–N(3)	2.090(2)
S(2)–O(5)	1.440(2)	Ti(1)–N(4)	2.083(2)
S(2)–N(3)	1.604(2)	Ti(1)–O(1)	2.1651(17)
S(1)–N(4)	1.6112		
N(1)–Ti(1)–N(2)	104.59(9)	N(3)–Ti(1)–O(1)	74.03(8)
N(1)–Ti(1)–N(3)	103.69(9)	N(4)–Ti(1)–O(1)	74.27(7)
N(1)–Ti(1)–N(4)	103.37(9)	Ti(1)–N(3)–S(2)	131.00(12)
N(2)–Ti(1)–N(3)	97.67(9)	Ti(1)–N(4)–S(1)	130.45(12)
N(2)–Ti(1)–N(4)	98.69(9)	N(4)–S(1)–O(2)	109.75(11)
N(3)–Ti(1)–N(4)	143.52(8)	N(4)–S(1)–O(3)	110.26(12)
N(1)–Ti(1)–O(1)	109.11(8)	N(3)–S(2)–O(4)	109.19(11)
N(2)–Ti(1)–O(1)	146.29(8)	N(3)–S(2)–O(5)	110.98(13)

tosylamides. The $TsN(CH_2)_2O(CH_2)_2NTs$ ligand in **2** provides a bicyclic substructure containing one Ti, two N, one O, and four C atoms. This bicyclic structure of **2** gave large Ti–N–S bond angles, which are unfavorable for the η^2-coordination of the sulfonamide moieties in **2**. If the η^2-coordination mode, which provides short Ti–O(sulfonamide) bonds and small Ti–N–S angles, was adopted by **2**, it would give significant ring strain to the bicyclic substructure. We carried out variable temperature NMR studies of **2**, and found no dynamic behavior suggesting η^1/η^2-interconversion in solution. Some of the pentacoordinated titanium amides reported by Schrock and coworkers have a pseudo-square pyramidal structure, and in some cases structural isomerization such as Berry rotation was observed.[10] The spectroscopic data of **2** showed no suggestion of the existence of other structures.

The structures of **1** and **2** suggest that two type **D** sulfonamide ligands are bound to the $Ti(NMe_2)_2$ moiety in an η^2:η^2-coordination mode, whereas the type **E** ligand providing the bicyclic substructure which is unfavorable for the Ti–O(sulfonamide) bonding adopts an NON coordination mode. Since the tosylamide ligand derived from *trans*-1,2-cyclohexanediamine provides a coordination environment for the titanium compounds in which the Ti–O(sulfonamide) bonding is less unfavorable than the type **E** bonding, it seems reasonable to expect to see the **B**-type bonding mode in many of the compounds. However, it is of interest that the type **C** bonding mode is seen in one of the complexes, $\{1,2\text{-}(TsN)_2C_6H_{10}\}Ti\{O(i\text{-}Pr)\}_2$.[6] We suspected that this might be attributable to higher Lewis acidity of the titanium center in $\{1,2\text{-}(TsN)_2C_6H_{10}\}Ti\{O(i\text{-}Pr)\}_2$ than that in $\{1,2\text{-}(TsN)_2C_6H_{10}\}Ti(NMe_2)_2$, which facilitates the coordination of sulfonamide-oxygen atoms to the titanium center. In this context, we were interested in the preparation of $[(TsNCH_2CH_2)_2O]TiCl(NMe_2)$ (**4**) and $[(TsNCH_2CH_2)_2O]TiCl_2$ (**5**) by replacement of one or two NMe_2 ligands in **2** by electron-withdrawing chlorine atoms.

Treatment of **2** with excess Me_3SiCl[12,15] at room temperature for 15 h gave a mixture of **4** and a compound having no Me_2N group, which can be assigned as dichloride **5** from the spectroscopic evidence and elemental analysis, in a ratio of 31 : 69 (determined by ^1H NMR) as shown in Scheme 4. Fractional recrystallization of this mixture from CH_2Cl_2 and hexane afforded **4** and **5** in 18 and 69% yield, respectively. The isolated **4** contained a small amount of **5** as an impurity; however, a single crystal suitable for X-ray structure determination was successfully grown. In contrast, **5** was isolated without contamination of **4** by fractional recrystallization. The selective preparation of **5** was achieved by heating a mixture of **2** and Me_3SiCl at 60 °C for 15 h (83% isolated yield).

As shown in Fig. 5, (see also Table 3) crystallography showed the dimeric structure of **4**, in which one of the sulfonyl oxygen atoms in the $[(TsNCH_2CH_2)_2O]TiCl(NMe_2)$ unit is bonding with the titanium center of a second $[(TsNCH_2CH_2)_2O]TiCl(NMe_2)$ unit. The sulfonyl oxygen bridging results in the formation of eight-membered dimetallacycles,[13,16] which have also been seen in Anwander's yttrium complex.[13] The ligands around the titanium atom are octahedrally arranged, and the chlorine atom is located at a *trans* position to the sulfonyl



Scheme 4 Reaction of $(TsNC_2H_4OC_2H_4NTs)Ti(NMe_2)_2$ (**2**) with Me_3SiCl.

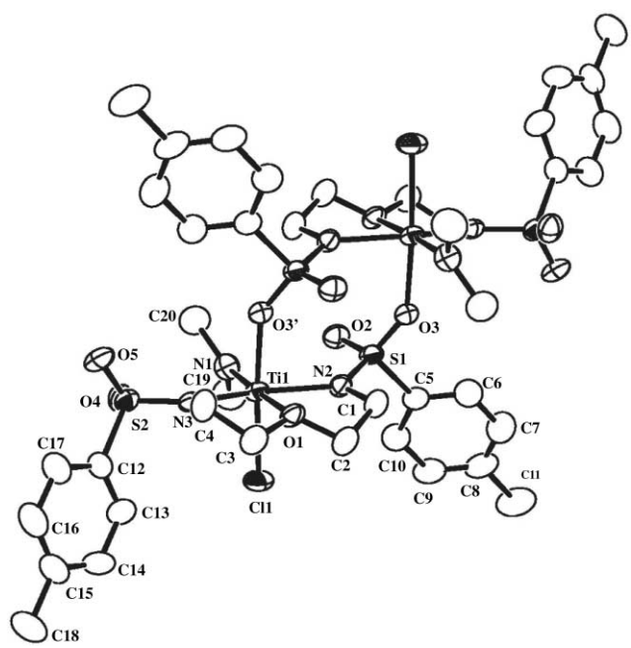


Fig. 5 The ORTEP drawing of **4**. 50% probability of the thermal ellipsoids. Symmetry transformations generate equivalent atoms. The oxygen atom O(3′) is defined as the equivalent atom of O(3). Two CH_2Cl_2 molecules, which are included in the lattice, are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for **4**

Ti(1)–N(1)	1.871(5)	S(1)–O(2)	1.443(4)
Ti(1)–N(2)	2.119(4)	S(1)–O(3)	1.476(3)
Ti(1)–N(3)	2.057(4)	S(2)–O(4)	1.436(4)
Ti(1)–O(1)	2.158(4)	S(2)–O(5)	1.437(4)
Ti(1)–O(3′)	2.116(3)	S(1)–N(2)	1.574(4)
Ti(1)–Cl(1)	2.3332(15)	S(2)–N(3)	1.598(4)
N(1)–Ti(1)–N(2)	106.82(18)	N(2)–Ti(1)–Cl(1)	91.21(12)
N(1)–Ti(1)–N(3)	103.27(19)	N(3)–Ti(1)–Cl(1)	93.42(13)
N(2)–Ti(1)–N(3)	148.92(18)	O(3′)–Ti(1)–Cl(1)	172.07(11)
N(1)–Ti(1)–O(1)	175.85(17)	O(1)–Ti(1)–Cl(1)	88.39(10)
N(2)–Ti(1)–O(1)	73.86(15)	Ti(1)–N(3)–S(2)	131.9(3)
N(3)–Ti(1)–O(1)	75.57(16)	Ti(1)–N(2)–S(1)	129.1(3)
N(1)–Ti(1)–O(3′)	92.26(17)	N(2)–S(1)–O(2)	111.0(2)
N(2)–Ti(1)–O(3′)	86.43(15)	N(2)–S(1)–O(3)	110.5(2)
N(3)–Ti(1)–O(3′)	84.79(15)	N(3)–S(2)–O(4)	109.0(2)
O(1)–Ti(1)–O(3′)	83.68(13)	N(3)–S(2)–O(5)	110.4(2)
N(1)–Ti(1)–Cl(1)	95.67(15)		

oxygen. Interestingly, this dimeric structure was not seen in solution. In CD_2Cl_2 or toluene-d_8, only signals due to the monomeric $[(TsNCH_2CH_2)_2O]TiCl(NMe_2)$ unit were visible at −60 to 60 °C. ^{1}H and ^{13}C NMR spectra of **4** are closely similar to those of **2** except for a significant downfield shift of a peak due to the NMe_2 group ($\Delta\delta_H$ 0.63 ppm, $\Delta\delta_C$ 5.8 ppm). The results indicate that the sulfonyl oxygen bridge is easily cleaved in solution, and **4** exists as a monomer like **2** in solution.

Formation of the dimeric form of **4** can be attributed to the increase in Lewis acidity of the titanium center by replacement of one NMe_2 group in **2** by a more electron negative Cl atom. This indicates that sulfonate oxygen bridging should also exist in the dichloro analogue **5**. Although a single crystal of **5** was unfortunately unavailable, appearance of two sets of seven ^{13}C resonances due to the $TsN(CH_2)_2O(CH_2)_2NTs$ ligand in **5** indicates that **5** exists as a dimer in solution. Since the spectral data are consistent with a dimer of $[(TsNCH_2CH_2)_2O]TiCl_2$, we tentatively concluded that **5** is dimeric in both solution and solid states. We attempted to synthesise $(i\text{-PrNTs})_2TiCl_2$ by treatment of **1** with Me_3SiCl under the same conditions used for the preparation of **5**, which might give us novel titanium complexes having dimeric or polymeric structures *via* sulfonate oxygen bridging. All of **1** was consumed after 12 h, and a mixture of compounds including substantial amounts of *i*-PrNHTs was formed. Two titanium species, which showed no signal due to the NMe_2 moiety in their ^{1}H and ^{13}C NMR, were included in this mixture. ^{1}H and ^{13}C resonances due to the *CH*Me_2 group of these two titanium species showed characteristic downfield shifts compared with those of **1**; this indicates that two isomers of $(i\text{-PrNTs})_2TiCl_2$ may be formed. However, the high sensitivity of the compounds to moisture prevented detailed studies after isolation.

Concluding remarks

In this paper, we describe a novel titanium compound **1** which has two η^2-tosylamide ligands, whereas the two sulfonamide moieties of the $TsN(CH_2)_2O(CH_2)_2NTs$ tosylamide ligand in **2** were bound to the metal center in type **A** coordination mode. Compared with the η^1:η^2-complexes reported by Walsh and Gagné,[5–8] **1** does not include the titanacyclopentane structure, whereas **2** has a bicyclic titanacycle. No ring strain due to the titanacycle in **1** causes adoption of the type **D** coordinated mode, while the special ring strain due to the bicyclic structure in **2** is favorable for the type **A** coordination mode. From the solution dynamics of **1** a reversible dissociation energy of the Ti–O(sulfonamide) bond was first estimated as *ca.* 16 kcal mol^{-1}. Replacement of the dimethylamide ligands in **2** by electronically negative chlorine atoms actually increased the Lewis acidity of the titanium center; this resulted in stabilization of the complex by making dimeric structures *via* sulfonamide oxygen bridging as shown in the crystal structure of **4**. These results show that the sulfonamides are unique ligands having the capability to act as both N and NO ligands; interconversion between both modes is facile. The sulfonamide groups sometimes behave as a unique bridging ligand, when the titanium atom is Lewis acidic enough. These findings are new and interesting in the coordination chemistry of pseudo-allyl ligands.

We expect that these unique properties of sulfonamides as auxiliary ligands could provide new aspects in catalysis. The possibility of tosylamide ligands as a Cp-substitute in Ti, Zr, or lanthanide olefin polymerization catalysts[17] has been pointed out by Walsh[7] and Anwander without details.[13] In this context, ethylene polymerization was examined in the presence of 10 μmol of **1**, **2**, or **5** and 10 mmol of MAO at room temperature under 10 atm of ethylene in a 100 mL stainless steel autoclave to give polyethylene with mp > 135 °C and η > 4.0. Activity of the catalyst (**1**; 0.070, **2**; 0.026, **5**; 0.124 kg per mmol Ti per h) was much smaller than that with Cp_2ZrCl_2 (2.14 kg per mmol Ti per h) under the same conditions. Ethylene polymerization catalyzed by $[(RNC_2H_4)_2O]TiR_2$ in the presence of fluorinated boron compounds was extensively studied by Schrock and coworkers.[10,11] Attempted syntheses of dialkyl derivatives of **5** led to decomposition of the complexes, and exploration of highly active polymerization catalysts bearing tosylamide ligands is at present unsuccessful.

Experimental

General methods

All manipulations were carried out under a dry argon or nitrogen atmosphere using the combination of a nitrogen-filled glove box, high-vacuum line, and Schlenk techniques. All of the solvents were distilled from drying reagents (Na/Ph_2CO for toluene, hexane, THF, Et_2O, C_6D_6, and $C_6D_5CD_3$; CaH_2 for CH_2Cl_2 and CD_2Cl_2; KOH for NEt_3) just before use. $Ti(NMe_2)_4$ was prepared according to the literature.[18] ^{1}H NMR spectra were taken with a JEOL Lambda 400 or 600 spectrometer at room temperature unless otherwise noted. Chemical shifts were recorded in ppm from the solvent signal, of which assignments were made with the aid of H–H COSY, and C–H COSY techniques. Polymer analysis was done at the TOSOH Analysis and Research Center.

Preparation of sulfonamide ligands, *i*-PrNHTs and $TsHN(CH_2)_2O(CH_2)_2NHTs$ (3)

In a typical example, *p*-toluenesulfonyl chloride (2.29 g, 12 mmol) dissolved in Et_2O (30 mL) was treated with isopropylamine (1.12 mL, 13.2 mmol) and NEt_3 (1.84 mL, 13.2 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. After removal of the solvent *in vacuo*, the residue was purified by column chromatography {silica gel (Wakogel FC-60), 2.75 × 9.5 cm, eluent hexane and EtOAc (1 : 1)} to give the desired product (2.53 g, 11.8 mmol, 98%). Using a similar procedure, the $TsHN(CH_2)_2O(CH_2)_2NHTs$ tosylamide ligand was obtained from 2,2′-oxybis(ethylamine)dihydrochloride (1.86 g, 4.51 mmol, 71%).

***i*-PrNHTs.** Colorless solid (mp 50–51 °C). ^{1}H NMR ($CDCl_3$): δ 1.07 (d, J = 6.5Hz, Me of *i*-Pr, 6H), 2.43 (s, Me of Ts, 3H), 3.44 (sept, J = 6.5Hz, CH of *i*-Pr, 1H), 4.62 (d, J = 2.4 Hz, NH, 1H), 7.28 (d, J = 8.2 Hz, *m*-H of Ts, 2H), 7.77 (d, J = 8.2 Hz, *o*-H of Ts, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.5 (Me of Ts), 23.7 (Me of *i*-Pr), 46.0 (CH of *i*-Pr), 126.8 (CH of Ts), 127.0 (CH of Ts) 138.1 (4°), 143.2 (4°). Anal. Calcd. for $C_{10}H_{15}NO_2S$: C; 56.31, H; 7.09, N; 6.57. Found: C; 56.24, H; 7.07, N; 6.54%.

$TsHN(CH_2)_2O(CH_2)_2NHTs$ (3). 71% yield; white solid (mp 105–107 °C). ^{1}H NMR ($CDCl_3$): δ 2.43 (s, Me of Ts, 6H), 3.08 (br q, J = 5.0 Hz, CH_2N, 4H), 3.39 (br t, J = 5.0 Hz, OCH_2, 4H), 4.92 (br s, NH, 2H), 7.31 (d, J = 7.8 Hz, *m*-H of Ts, 4H), 7.74 (d, J = 7.8 Hz, *o*-H of Ts, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.5 (Me of Ts), 42.8 (CH_2N), 69.3 (OCH_2), 127.1 (*o*-C of Ts), 129.8 (*m*-C of Ts), 136.9 (4°) 143.6 (4°). Anal. Calcd. for $C_{18}H_{24}N_2O_5S_2$: C; 52.43, H; 5.83, N; 6.80. Found: C; 52.50, H; 5.90, N; 6.85%.

Preparation of $(i\text{-PrNTs})_2Ti(NMe_2)_2$ (1)

A 50 mL Schlenk tube was charged with $Ti(NMe_2)_4$ (100 mg, 0.45 mmol) and *i*-PrNHTs (178 mg, 0.89 mmol) (weighed in a glove box) and the atmosphere was replaced by argon. Then toluene (20 mL) was added, and the solution was stirred at room temperature for 1 h. After removal of the solvent *in vacuo*, the residue was washed with several portions of Et_2O (0.5 mL each). Recrystallization of the crude product from toluene–hexane (1 : 2) at −30 °C gave dark red crystals of $(i\text{-PrNTs})_2Ti(NMe_2)_2$ (**1**) (189 mg, 0.33 mmol, 76%); mp 170–171 °C. ^{1}H

Table 4 Crystallographic data for **1**, **2** and **4**

	1	**2**	**4**
Empirical formula	$C_{24}H_{40}N_4O_4S_2Ti$	$C_{22}H_{34}N_4O_5S_2Ti$	$C_{40}H_{56}Cl_2N_6O_{10}S_4Ti_2 \cdot 2(CH_2Cl_2)$
M	560.62	546.55	1245.70
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	8.708(3)	14.0471(9)	11.1393(5)
b/Å	16.383(4)	11.8424(6)	17.965(1)
c/Å	19.432(5)	15.7599(9)	13.887(1)
β/°	90.53(4)	100.603(4)	91.168(3)
V/Å^3	2772.1(14)	2576.9(3)	2778.5(3)
Z	4	4	2
D_c/Mg m^{-3}	1.343	1.409	1.489
μ/mm^{-1}	0.495	0.534	0.783
F(000)	1192	1152	1288
Crystal size/mm	0.40 × 0.15 × 0.15	0.45 × 0.30 × 0.10	0.60 × 0.60 × 0.40
Reflections measured	13280	6171	6531
Independent reflections	6351 [R(int) = 0.2618]	5886 [R(int) = 0.04244]	6149 [R(int) = 0.11879]
Reflections observed (>2σ)	2267	4027	2796
GOF	0.950	1.023	0.938
R_1 ($I > 2\sigma(I)$)	0.0568	0.0395	0.0744
wR_2 ($I > 2\sigma(I)$)	0.1103	0.0977	0.1401
R_1 (all data)	0.2625	0.0719	0.1714
wR_2 (all data)	0.1659	0.1155	0.1757
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.484, −0.682	0.331, −0.463	0.458, −0.676

NMR ($C_6D_5CD_3$, −20 °C): δ 1.00 (d, J = 6.6 Hz, Me of *i*-Pr, 6H), 1.33 (d, J = 6.6 Hz, Me of *i*-Pr, 6H), 1.75 (s, Me of Ts, 6H), 3.45 (sept, J = 6.6 Hz, CH of *i*-Pr, 2H), 3.61 (s, Me of NMe_2, 12H), 6.58 (d, J = 8.3 Hz, *m*-H of Ts, 4H), 8.22 (d, J = 8.3 Hz, *o*-H of Ts, 4H). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, −20 °C): δ 20.9 (Me of Ts), 23.7 (Me of *i*-Pr), 25.2 (Me of *i*-Pr), 49.9 (CH of *i*-Pr), 50.2 (Me of NMe_2), 128.2 (*o*-C of Ts), 129.3 (*m*-C of Ts), 138.0 (4°), 142.5 (4°). Anal. Calcd. for $C_{24}H_{40}N_4O_4S_2Ti$: C; 51.42, H; 7.19, N; 9.99. Found: C; 51.40, H; 7.18, N; 9.66%.

Preparation of [TsN(CH$_2$)$_2$O(CH$_2$)$_2$NTs]Ti(NMe$_2$)$_2$ (2)

A 50 mL Schlenk tube was charged with $Ti(NMe_2)_4$ (24 mg, 0.11 mmol) and $TsHN(CH_2)_2O(CH_2)_2NHTs$ (44 mg, 0.11 mmol) (weighed in a globe box) and the atmosphere was replaced by argon. Toluene (30 mL) was added, and the mixture was stirred at room temperature for 12 h. After removal of the solvent *in vacuo*, the residue was purified by recrystallization from dichloromethane–hexane (1 : 2) to give $[TsN(CH_2)_2O(CH_2)_2NTs]Ti(NMe_2)_2$ (**2**) as orange plates (58 mg, 0.10 mmol, 90%); mp 135–136 °C. ^1H NMR (CD_2Cl_2): δ 2.33 (s, Me of Ts, 6H), 3.29 (s, Me of NMe_2, 12H), 3.37 (t, J = 5.4 Hz, NCH_2, 4H), 3.76 (t, J = 5.4 Hz, OCH_2, 4H), 7.20 (d, J = 8.1 Hz, *m*-H of Ts, 4H), 7.60 (d, J = 8.1 Hz, *o*-H of Ts, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.8 (Me of Ts), 45.1 (NMe_2), 48.0 (CH_2N), 74.8 (OCH_2), 126.5 (*o*-C of Ts), 128.9 (*m*-C of Ts), 139.9 (4°), 141.3 (4°). Anal. Calcd. for $C_{22}H_{34}N_4O_5S_2Ti$: C; 48.35, H; 6.27, N; 10.25. Found: C; 47.98, H; 6.17, N; 9.97%.

Preparation of [{TsN(CH$_2$)$_2$O(CH$_2$)$_2$NTs}Ti(NMe$_2$)Cl]$_2$ (4) and [{TsN(CH$_2$)$_2$O(CH$_2$)$_2$NTs}TiCl$_2$]$_2$ (5)

A 50 mL Schlenk tube was charged with $[TsN(CH_2)_2O(CH_2)_2NTs]Ti(NMe_2)_2$ (**2**) (36 mg, 0.06 mmol) and the atmosphere was replaced by argon. Toluene (30 mL) was added, and Me_3SiCl (65 mg, 0.7 mL, 0.60 mmol) was added to the resulting suspension of **2** at room temperature. The reaction mixture was stirred at room temperature for 15 h, and the solvent was removed *in vacuo*. Recrystallization from dichloromethane–hexane (1 : 1) at room temperature gave $[\{TsN(CH_2)_2O(CH_2)_2NTs\}TiCl_2]_2$ (**5**) (13 mg) as yellow plate crystals. Further recrystallization of the residue produced by concentration of the supernatant from dichloromethane–hexane (1 : 2) at room temperature gave a mixture of $[\{TsN(CH_2)_2O(CH_2)_2NTs\}Ti(NMe_2)Cl]_2$ (**4**) as dark red crystals (6 mg) and **5** (9 mg) (detected by ^1H NMR spectroscopy). Total yields of **4** and **5** were 18% (6 mg, 0.01 mmol) and 69% (22 mg, 0.04 mmol), respectively. At 60 °C, only **5** was available in 83% yield after 15 h.

[{(TsNC$_2$H$_4$)$_2$O}Ti(NMe$_2$)Cl]$_2$ (4). mp 137–139 °C. ^1H NMR (CD_2Cl_2): δ 2.44 (Me of Ts, 6H), 3.32 (br s, NCH_2, 4H), 3.74 (br s, OCH_2, 4H), 3.92 (s, Me of NMe_2, 6H), 7.37 (d, J = 8.6 Hz, *m*-H of Ts, 4H), 8.06 (d, J = 8.6 Hz, *o*-H of Ts, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.5 (Me of Ts), 47.6 (br s, CH_2N), 50.9 (Me of NMe_2), 68.9 (br s, OCH_2), 127.5 (*o*-C of Ts), 129.0 (*m*-C of Ts), 134.0 (4°), 144.0 (4°).

[{(TsNC$_2$H$_4$)$_2$O}TiCl$_2$]$_2$ (5). mp 142–144 °C. ^1H NMR (CD_2Cl_2): δ 2.34, 2.41 (s, Me of Ts, 6H), Two pairs of NCH_aH_a'-$CH_bH_b'O$ signals were seen. 3.26–3.34 (m, CH_2 of H_a or H_a', 1H), 3.50–3.65 (m, CH_2 of H_a or H_a', 2H), 3.71–3.79 (m, CH_2 of H_a or H_a', 1H), 3.97–4.12 (m, CH_2 of H_b or H_b', 3H), 4.30–4.41 (m, CH_2 of H_b or H_b', 1H), 7.22, 7.26 (d each, J = 8.6 Hz, *m*-H of Ts, 4H), 7.98, 7.99 (d each, J = 8.6 Hz, *o*-H of Ts, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.9, 21.0 (Me of Ts), 50.1, 51.6 (CH_2N), 74.8, 76.0 (OCH_2), 127.7 (*o*-C of Ts), 128.3 (*o*-C of Ts), 129.0 (*m*-C of Ts), 129.1 (*m*-C of Ts), 134.4 (4°),137.9 (4°), 142.2 (4°), 143.8 (4°). Anal. Calcd. for $C_{36}H_{44}Cl_4N_4O_{10}S_4Ti_2$: C; 40.85, H; 4.19, N; 5.29. Found: C; 40.28, H; 4.48, N; 5.42%.

Typical procedure for ethylene polymerization

In a 100 mL Schlenk tube, $[TsN(CH_2)_2O(CH_2)_2NTs]TiCl_2$ (**4**) (5.29 mg, 10 μmol) was measured in a glove box and the atmosphere was replaced by argon. A toluene solution of 1000 equiv. of MAO (50 mL, 0.2 M, 10 mmol) was added, and the mixture stirred for 1 h. The resulting solution was moved to a 100 mL autoclave fitted with a Teflon inner tube by cannula. Ethylene (10 atm) was then applied. After 30 min, the polymerization was quenched by stopping the ethylene supply, and the mixture was treated with methanol (200 mL) and conc. HCl (6 mL) for 1 h in order to remove any aluminium residue. The white precipitate formed was filtered off and washed with methanol. The resulting powder was dried for 15 h *in vacuo* to give polyethylene (621 mg).

X-Ray diffraction analyses for 1, 2, and 4

A single crystal of **1** was obtained from a toluene-d_8 solution at −30 °C in a sealed NMR tube, whereas those of **2** and **4** were obtained from a mixture of CH_2Cl_2 and hexane at room temperature. X-Ray crystallography was performed on an

Enraf-Nonius CAD4 four cycle axis diffractometer (for **1**) or Rigaku RAXIS RAPID imaging plate diffractometer (for **2** and **4**) with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The diffraction data of **1** were collected at 296(2) K using the ω–2θ technique to a maximum 2θ value of 55.0°, whereas those of **2** and **4** were collected at 223(2) K in the θ ranges $1.79 \leq \theta \leq 27.48°$ and $2.63 \leq \theta \leq 27.48°$, respectively (44 oscillation exposures). Data collection and cell refinement of **1** were carried out using the program system 'CAD4 Express'[19] on a MS VAX computer, whereas those of **2** and **4** were done using "MSC/AFC Diffractometer Control"[20] on a Pentium computer. The structure was solved by direct methods (SIR-97, **1**)[21] or the Patterson method (DIRDIF-94 PATTY, **2** and **4**),[22] and was refined using full-matrix least squares (SHELXL-97)[23] based on F^2 for all independent reflections measured. The H atoms were located at ideal positions except for those of the methyl groups which were allowed to rotate about the CH_3 (adjacent atom) bonds. They were included in the refinement, but were restricted to riding on the carbons to which they were bonded. Isotropic thermal factors for the H atoms were held to 1.2 to 1.5 times (for methyl groups) U_{eq} of the parent atoms. Further details are listed in Table 4.

CCDC reference numbers 160977–160979.

See http://www.rsc.org/suppdata/dt/b1/b110481k/ for crystallographic data in CIF or other electronic format.

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