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Synthesis, Structure and Reactivity in Styrene Polymerization by Heterocyclic Alkoxy- and Thiolatotitanium(IV) Complexes

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The reaction of $[Ti(OiPr)_4]$ or $[TiCl_4(THF)_2]$ with two equivalents of pyridyl alcohols or pyridyl or pyrimidinyl thiols has proven to be a good preparative method to obtain a variety of non-metallocene diisopropoxo- or dichlorotitanium(IV) complexes. The complexes $[Ti(X)_2\{2\text{-}(OCH_2)\text{-}6\text{-}R\text{-}(C_5H_3N)\}_2]$ were found to be dynamic at room temperature, with the heterocyclic alkoxy ligand dissociating and recoordinating in a κ^2-N,O chelate fashion, as revealed by a single-crystal X-ray analysis of $[Ti(OiPr)_2\{2\text{-}(OCH_2)(C_5H_4N)\}_2]$ (**1**). The dynamic behavior of some of the resulting thiolato complexes was also studied and the single-crystal X-ray analysis of $[Ti(OiPr)_2\{2\text{-}S\text{-}4,6\text{-}Me_2\text{-}(C_4HN_2)\}_2]$ (**5**) revealed a κ^2-N,S system for these complexes. These complexes show catalytic activity in the polymerization of styrene upon activation with methylaluminoxane.

Introduction

The coordination chemistry of the transition metals has experienced significant developments during the last three decades and at present constitutes an area of great importance due to its theoretical interest and diverse applications in organic synthesis and catalytic processes. The chemistry of the group 4 elements is dominated by complexes that contain cyclopentadienyl ligands or their derivatives. This is due to the fact that in recent years this field has undergone a significant expansion aimed at exploiting applications of these complexes as catalysts in olefin polymerization, hydrogenation, and hydrosilylation reactions. Nevertheless, increasing interest is being shown in the use of alternative ligands, such as alkoxy or amido derivatives, that are capable of stabilizing metal complexes in high oxidation states. In this way, it is possible to design ligands that can stabilize active species in certain catalytic processes so that they can be used instead of Cp ligands.[1]

In this paper we describe the synthesis and characterization of new alkoxy- and thiolatotitanium(IV) complexes bearing heterocyclic rings in the ligands. In addition, the activity of these complexes as styrene polymerization catalysts has been studied.

Results and Discussion

The new complexes $[Ti(X)_2\{2\text{-}(OCH_2)\text{-}6\text{-}R\text{-}(C_5H_3N)\}_2]$ [X = O*i*Pr, R = H (**1**); X = Cl, R = H (**2**); X = Cl, R = Me (**3**)], $[Ti\{2,6\text{-}(OCH_2)_2(C_5H_3N)\}_2]$ (**4**), $[Ti(X)_2(SR)_2]$ [X = O*i*Pr, SR = 2-S-4,6-Me_2-(C_4HN_2) (**5**); X = Cl, SR = 2-S-4,6-Me_2-(C_4HN_2) (**6**); X = O*i*Pr, SR = 2-S-($C_4H_3N_2$) (**7**); X = Cl, SR = 2-S-($C_4H_3N_2$) (**8**); X = O*i*Pr, SR = 2-S-(C_5H_4N) (**9**)], and $[TiCl_2\{2\text{-}S\text{-}(C_5H_4N)\}\{O(CH_2)_4Cl\}]$ (**10**) were prepared by reaction of the corresponding alcohol or thiol with $[Ti(OiPr)_4]$ or $[TiCl_4(THF)_2]$ (Scheme 1).

Complexes **1**–**3** were isolated as white, air-sensitive solids. Complex **1** is very soluble in THF but complexes **2** and **3** are only sparingly soluble in this solvent.

The presence of two isopropoxide or chloride groups and two alkoxypyridine ligands means that several stereochemical configurations are possible, with the possibility of κ^2-O,N coordination of the latter ligands to the metal center. A single-crystal X-ray analysis of compound **1** was carried out in order to provide precise structural details of this compound and the related complexes **2** and **3**. The structure of complex **1** is shown in Figure 1, together with the atom-numbering scheme. The bond lengths and angles for this structure are given in Table 1. Complex **1** crystallizes in the monoclinic space group $P2_1/n$. The Ti atom has a markedly distorted pseudoctahedral geometry, with the alkoxypyridine ligands occupying four sites in a chelate fashion. This arrangement is consistent with the ^{13}C NMR spectra of complexes **1**–**3**, in which the signals assigned to the C2 and C6 atoms of the pyridine moiety are shifted to slightly lower field in comparison with those in the free ligand. In this way, each ligand is bonded to the metal center through both

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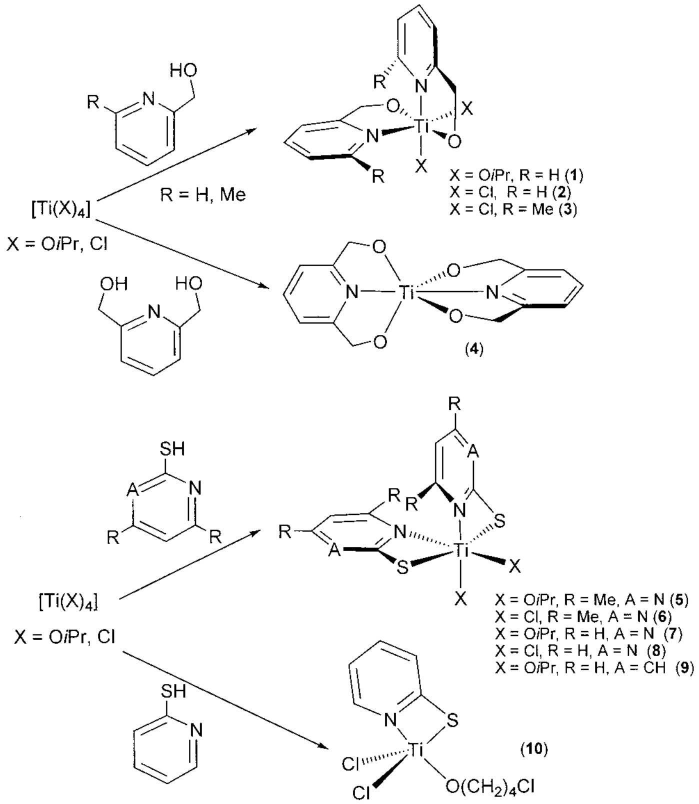


Scheme 1.

the nitrogen and the oxygen atoms. The Ti–O1 and Ti–O2 distances are slightly longer than those found in [Ti(η^5-C_5H_5){2-($OCiPr_2$)-(C_5H_4N)}Cl_2] [1.8267(9) Å],[2] which may indicate low O(pπ)–Ti(dπ) donation to the metal. In contrast, the Ti–N distances are similar in both complexes.

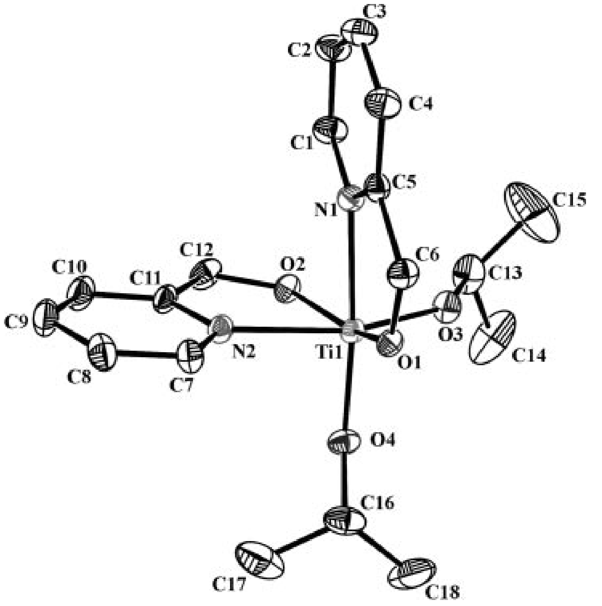
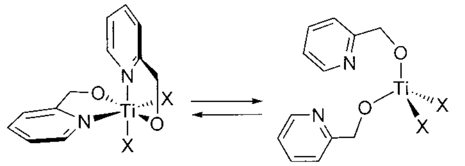


Figure 1. An ORTEP drawing of **1** with the numbering scheme.

It is worth noting that this configuration makes the two hydrogen atoms in the methylene groups inequivalent. In contrast, the ^{1}H NMR spectrum of complex **1** shows one single peak for these hydrogen atoms at room temperature. This behavior can be explained in terms of a dynamic process in solution for this molecule. In this process, the alkoxypyridine ligands probably change their κ^2-N,O coordination to a κ^1-O coordination through a rupture of the metal–nitrogen bonds (Scheme 2). A similar behavior has been observed in zirconium complexes with oxypyridine and oxypyrimidine ligands.[3]



Scheme 2.

A variable-temperature ^{1}H NMR study was also carried out on the complexes. When the ^{1}H NMR spectrum of complex **1** was recorded at 213 K, an AB spin system (δ_A = 5.92, δ_B = 5.89 ppm; J_{AB} = 18.55 Hz) was observed for the inequivalent methylene protons, indicating that, at this temperature, the alkoxypyridine ligands are coordinated in a chelate fashion [$\Delta G^{\ddagger}$ = 54.5(6) kJ mol^{-1}], as found in the X-ray structure. In addition, two signals for the methyl groups of the isopropoxide ligands were found, indicating that free rotation does not occur at this temperature [$\Delta G^{\ddagger}$ = 51.2(5) kJ mol^{-1}]. A similar behavior was observed for complex **2**. The low solubility of complex **3** prevented us from

Table 1. Bond lengths [Å] and angles [°] for **1** and **5**.

1			
Ti(1)–O(3)	1.818(2)	O(1)–Ti(1)–O(2)	154.47(6)
Ti(1)–O(4)	1.820(1)	O(4)–Ti(1)–N(1)	165.27(6)
Ti(1)–O(1)	1.902(1)	O(3)–Ti(1)–N(2)	165.21(6)
Ti(1)–O(2)	1.903(1)	C(6)–O(1)–Ti(1)	125.6(1)
Ti(1)–N(1)	2.242(2)	C(12)–O(2)–Ti(1)	125.6(1)
Ti(1)–N(2)	2.244(2)	C(13)–O(3)–Ti(1)	138.5(1)
O(1)–C(6)	1.381(2)	C(16)–O(4)–Ti(1)	141.6(1)
O(2)–C(12)	1.385(2)	C(5)–N(1)–Ti(1)	114.6(1)
O(3)–C(13)	1.396(2)	C(11)–N(2)–Ti(1)	114.3(1)
O(4)–C(16)	1.401(2)	O(1)–C(6)–C(5)	111.5(1)
N(1)–C(5)	1.325(2)	O(2)–C(12)–C(11)	111.5(1)
N(1)–C(1)	1.347(2)		
N(2)–C(7)	1.337(2)		
N(2)–C(11)	1.337(2)		
C(5)–C(6)	1.502(2)		
C(11)–C(12)	1.500(3)		
5			
Ti(1)–O(1)	1.757(3)	O(2)–Ti(1)–N(1)	154.5(1)
Ti(1)–O(2)	1.766(3)	O(1)–Ti(1)–N(3)	155.2(1)
Ti(1)–N(1)	2.231(3)	S(1)–Ti(1)–S(2)	156.75(4)
Ti(1)–N(3)	2.312(3)	C(11)–S(1)–Ti(1)	81.5(1)
Ti(1)–S(1)	2.470(1)	C(17)–S(2)–Ti(1)	82.8(1)
Ti(1)–S(2)	2.472(1)	C(1)–O(1)–Ti(1)	156.6(2)
S(1)–C(11)	1.727(4)	C(4)–O(2)–Ti(1)	147.2(3)
S(2)–C(17)	1.731(3)	C(11)–N(1)–Ti(1)	99.6(2)
O(1)–C(1)	1.423(4)	C(17)–N(3)–C(20)	117.6(3)
O(2)–C(4)	1.427(5)	C(17)–N(3)–Ti(1)	98.0(2)
N(1)–C(14)	1.351(4)		
N(1)–C(11)	1.357(5)		
N(3)–C(17)	1.349(4)		
N(3)–C(20)	1.354(4)		
C(1)–C(2)	1.496(7)		
C(1)–C(3)	1.504(6)		
C(4)–C(5)	1.465(8)		

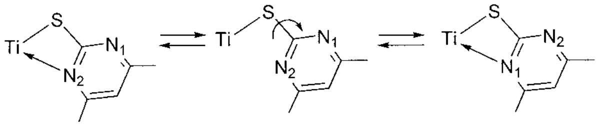
obtaining conclusive results for this complex, although one would expect a similar situation to occur in all three cases.

Attempts to obtain a complex of the type [Ti(X)$_2${2,6-(OCH$_2$)$_2$-(C$_5$H$_3$N)}] were unsuccessful. In all cases, [Ti{2,6-(OCH$_2$)$_2$-(C$_5$H$_3$N)}$_2$] (**4**) was obtained as a very insoluble white solid.

The ^{13}C NMR spectrum of complex **1** is consistent with a disposition in which the dialkoxide ligand shows tridentate coordination and is bonded to the metal atom in a "pincer" fashion.[4]

Similarly, it was not possible to obtain the analogous compound of complex **3** with isopropoxide ligands – a complex mixture of unidentified compounds was obtained in all cases. A possible explanation for this behavior involves the high level of steric hindrance associated with the ligands on the metal center in comparison with the less-crowded chloride complex **3**.

Thiolato complexes **5**–**10** were obtained as yellow (**5**–**9**) or pale-orange (**10**) very air-sensitive solids, with the chloride complexes **6**, **8**, and **10** being only sparingly soluble in THF. The ^{1}H NMR spectrum of **5** shows a broad singlet at $\delta = 2.42$ ppm due to the thiolato methyl groups, indicating that fluxional behavior may be occurring in the molecule. This behavior is probably due to an interchange in the positions of the nitrogen atoms of the pyrimidine groups in the coordination sphere of the titanium atom by rotation around the S–C bonds (see Scheme 3).[3,5] Kempe[6] has described similar complexes with isolobal aminopyridinato ligands. These complexes undergo a dynamic process that implies an interchange between the aminopyridinato ligands. This exchange proceeds via a tetrahedral transition state similar to that we postulate for the exchange in the thiolato complexes



Scheme 3.

A variable-temperature ^{1}H NMR study was carried out on this complex. When the ^{1}H NMR spectrum was recorded at 223 K, two signals corresponding to the methyl groups of the pyrimidine fragments were observed, indicating that rotation around the S–C bond is hindered [$\Delta G^{\ddagger} = 60.5(2)\ \mathrm{kJ\,mol^{-1}}$] for both thiolate ligands, which act as chelate ligands. As the temperature increases, the rotation becomes easier and at temperatures above 293 K only one signal is observed, corresponding to the free rotation of the two equivalent ligands. A similar behavior was observed for complex **7**. The lack of solubility of complexes **6** and **8** prevented us from obtaining results for these compounds, although the ^{13}C NMR spectra indicate that some chelate interaction is present in **6** but not in **8** at room temperature.

A single-crystal X-ray analysis of complex **5** was carried out in order to obtain more precise structural information for this compound and analogous complexes **6**–**10**. The structure of complex **5** is shown in Figure 2, and bond lengths and angles for this structure are given in Table 1.

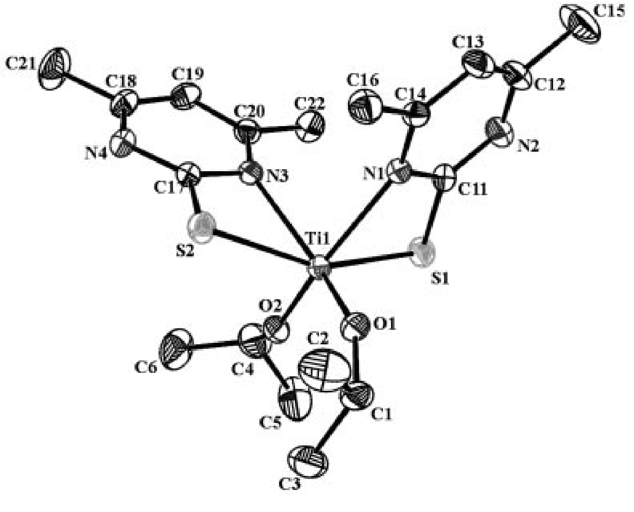
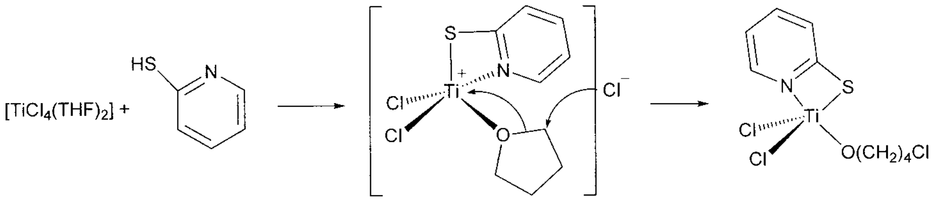


Figure 2. An ORTEP drawing of **5** with the numbering scheme.

To the best of our knowledge, only three structurally characterized titanium thiolatopyridine or -pyrimidine complexes have been described,[7a–7c] and two of these contain cyclopentadienyl ligands. Complex **5** crystallizes in the



Scheme 4.

monoclinic space group $P2_1/n$. The Ti atom shows a highly distorted pseudooctahedral geometry, with two isopropoxide ligands occupying two sites and the other four sites occupied by the thiolatopyrimidine ligands in a chelate fashion. The bonding of the didentate thiolate to the metal center can be considered as being intermediate between the pyridine-2-thiolate form and the canonic amide-thione. The Ti–S distances are longer than those found in cyclopentadienyl and noncyclopentadienyl titanium complexes with thiolato ligands.[7,8] This suggests weaker Ti–S bonds in complex **5**. The Ti–N distances are even longer than those found in the aminopyridinate complexes described above,[6] in accordance with the lability of the Ti–N(pyridine) bonds.

Table 2. Summary of styrene polymerization results. Polymerization conditions: 6 µmol Ti, 2 mL styrene, Al/Ti = 2000:1, *t* = 90 min.

Precatalyst	*T* [K]	Activity [Kg PS/mol Ti/h]
1	273	9
1	298	101
1	333	122
1	363	117
2	273	91
2	298	133
2	333	156
2	363	167
3	273	40
3	298	21
3	333	49
3	363	39
5	273	109
5	298	48
5	333	62
5	363	106
6	273	0
6	298	50
6	333	102
6	363	113
7	273	90
7	298	60
7	333	68
7	363	84
8	273	0
8	298	0
8	333	0
8	363	0
9	273	190
9	298	76
9	333	61
9	363	118
10	273	13
10	298	42
10	333	82
10	363	37

Whereas the reaction of 2-HS-(C_5H_4N) with [Ti(O*i*Pr)$_4$] gives rise to the complex [Ti(O*i*Pr)$_2${2-S-(C_5H_4N)}$_2$] (**9**), the reaction with [$TiCl_4$(THF)$_2$] gives a complex in which the opening of a THF molecule was observed, i.e., [$TiCl_2${2-S-(C_5H_4N)}{O(CH_2)$_4$Cl}] (**10**), as deduced from the ^{1}H NMR spectrum. A similar reactivity has been described previously by some of us[1f,9] in heteroscorpionate complexes of titanium. The formation of this complex can be envisaged as being the result of a nucleophilic THF ring-opening reaction of the intermediate cationic species [$TiCl_2$(THF){2-S-(C_5H_4N)}]Cl, which itself results from the coordination of a thiolate ligand and subsequent loss of a chloride ligand (Scheme 4).

Chelate coordination of the pyridinethiolate ligand can be proposed for both complexes **9** and **10** on the basis of the ^{13}C NMR spectra.

Finally, the catalytic activities of some of the complexes obtained were investigated for styrene polymerization in the range 273–363 K in the presence of 2000 equivalents of methylaluminoxane (MAO) in toluene (Table 2). In all cases, the fraction that was insoluble in 2-butanone contained the majority of the resulting polymer (>98%). In addition, the ^{13}C NMR spectrum in $CDCl_2CDCl_2$ at 393 K contains the characteristic peaks of syndiotactic polystyrene.[10] As can be seen from Table 2, for the alkoxypyridine complexes the activity increases with reaction temperature. In contrast, thiolato complexes show higher activities at low temperature, where they are probably more stable. In any case, the activities are similar to that found for the complex [Ti(O*i*Pr)$_4$] (140 Kg PS/mol Ti/h at 293 K).

Conclusions

The results reported here show that a range of diisopropoxy- or dichlorotitanium(IV) complexes bearing alkoxy or thiolato heterocyclic ligands can be easily prepared by reaction of the simple precursors [Ti(O*i*Pr)$_4$] and [$TiCl_4$(THF)$_2$] with the corresponding alcohols or thiols. The molecular structures of **1** and **5**, as determined by X-ray diffraction, show hexacoordination around the titanium atom, with two chelate heterocyclic substituents. These compounds, as well as some of their analogs, have a dynamic bonding process in solution. Finally, these new complexes, which do not contain cyclopentadienyl units, exhibit moderate activities in styrene polymerization in conjunction with MAO.

Experimental Section

General Remarks: All operations were performed under an inert atmosphere using standard vacuum-line (Schlenk) techniques or an MBRAUN glove-box. Solvents were purified by distillation from the appropriate drying agents before use. Titanium precursors and different alcohols and thiols were purchased from Aldrich, stored under an inert atmosphere, and deoxygenated before use. NMR spectra were obtained with a Varian Inova FT-500 instrument.

Preparation of [Ti(O*i*Pr)$_2${2-(OCH$_2$)(C$_5$H$_4$N)}$_2$] (1): [Ti(O*i*Pr)$_4$] (1 mL, 3.26 mmol) was added to a solution of 2-(hydroxymethyl)pyridine (0.65 mL, 6.52 mmol) in CH$_2$Cl$_2$ (50 mL) and the reaction mixture was stirred for 2 h at room temperature. The resulting colorless solution was evaporated to dryness to give complex **1** as a white solid, which was purified by washing with hexane (yield: 1.22 g, 98%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.01 (d, J = 6.1 Hz, 12 H, CH_3 isopropoxide), 4.61 (sept, J = 6.1 Hz, 2 H, CHO isopropoxide), 5.55 (s, 4 H, CH_2 pyridine), 7.13 (dd, $J_{5,6}$ = 4.6 Hz, $J_{5,4}$ = 8 Hz, 2 H, 5-H pyridine), 7.15 (d, J = 8 Hz, 2 H, 3-H pyridine), 7.61 (dd, $J_{4,5}$ = 8 Hz, $J_{4,3}$ = 8 Hz, 2 H, 4-H pyridine), 8.61 (d, J = 4.6 Hz, 2 H, 6-H pyridine) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 25.66 (*C*H$_3$ isopropoxide), 74.30 (*C*H$_2$ pyridine), 75.30 (*C*HO isopropoxide), 118.91 (C-5 pyridine), 121.78 (C-3 pyridine), 137.45 (C-4 pyridine), 147.19 (C-6 pyridine), 166.06 (C-2 pyridine) ppm. $C_{24}H_{26}N_2O_4Ti$ (453.86): calcd. C 56.55, H 6.86, N 7.33; found C 56.31, H 6.56, N 7.95.

Preparation of [Ti(Cl)$_2${2-(OCH$_2$)(C$_5$H$_4$N)}$_2$] (2): 2-(Hydroxymethyl)pyridine (0.30 mL, 3.01 mmol) was added to a solution of [TiCl$_4$(THF)$_2$] (0.50 g, 1.50 mmol) in THF (25 mL) and the resulting white suspension was stirred for 16 h at room temperature. A white precipitate formed and when the sedimentation was complete the solution was filtered and the white precipitate washed with THF (50 mL) at 60 °C and filtered again. The two solutions were combined and the solvent was evaporated to give complex **2** as a pale-brown solid (yield: 0.20 g, 41%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.86 (s, 4 H, CH_2 pyridine), 7.85 (dd, $J_{5,4}$ = 8 Hz, $J_{5,6}$ = 6 Hz, 2 H, 5-H pyridine), 7.96 (d, J = 8.5 Hz, 2 H, 3-H pyridine), 8.47 (dd, $J_{4,5}$ = 8 Hz, $J_{4,3}$ = 8.5 Hz, 2 H, 4-H pyridine), 8.75 (d, J = 6 Hz, 2 H, 6-H pyridine) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 59.96 (*C*H$_2$ pyridine), 123.93 (C-3 pyridine), 124.95 (C-5 pyridine), 141.76 (C-6 pyridine), 144.96 (C-4 pyridine), 157.27 (C-2 pyridine) ppm. $C_{12}H_{12}Cl_2N_2O_2Ti$ (334.86): calcd. C 43.02, H 3.61, N 8.36; found C 42.81, H 3.56, N 8.95.

Preparation of [Ti(Cl)$_2${2-(OCH$_2$)-6-Me-(C$_5$H$_3$N)}$_2$] (3): 6-Methyl-2-pyridylmethanol (0.18 mL, 1.49 mmol) was added to a solution of [TiCl$_4$(THF)$_2$] (0.25 g, 0.75 mmol) in THF (25 mL) and the resulting white suspension was stirred for 16 h at room temperature. A gray precipitate formed and when sedimentation was complete the solution was filtered to give complex **3** as a gray solid. The solid was washed with hexane (50 mL) and dried under vacuum (yield: 0.27 g, 87%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.72 (s, 6 H, CH_3 pyridine), 4.83 (s, 4 H, CH_2 pyridine), 7.72 (d, J = 7.8 Hz, 2 H, 5-H pyridine), 7.79 (d, J = 7.8 Hz, 2 H, 3-H pyridine), 8.37 (t, J = 7.8 Hz, 2 H, 4-H pyridine) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 20.01 (*C*H$_3$ pyridine), 60.29 (*C*H$_2$ pyridine), 121.98 (C-3 pyridine), 126.14 (C-5 pyridine), 145.75 (C-4 pyridine), 157.49, 154.04 (C-2, C-6 pyridine) ppm. $C_{14}H_{16}Cl_2N_2O_2Ti$ (362.86): calcd. C 58.54, H 7.37, N 6.83; found C 58.15, H 7.52, N 6.91.

Preparation of [Ti{2,6-(OCH$_2$)$_2$(C$_5$H$_3$N)}$_2$] (4): [Ti(O*i*Pr)$_4$] (1 mL, 3.26 mmol) was added to a solution of 2,6-bis(hydroxymethyl)pyridine (0.93 g, 6.52 mmol) in CH$_2$Cl$_2$ (50 mL) and the reaction mixture was stirred for 4 h at room temperature. The resulting colorless solution was evaporated to dryness to give complex **4** as a white solid. The solid was purified by washing with hexane (yield: 1.00 g, 95%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.85 (s, 8 H, CH_2 pyridine), 7.32 (d, J = 7.7 Hz, 4 H, 3-H, 5-H pyridine), 7.88 (t, J = 7.7 Hz, 2 H, 4-H pyridine) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 78.75 (*C*H$_2$ pyridine), 116.60 (C-3, C-5 pyridine), 140.52 (C-4 pyridine), 168.44 (C-2, C-6 pyridine) ppm. $C_{14}H_{14}N_2O_4Ti$ (321.80): calcd. C 52.20, H 4.38, N 8.70; found C 51.64, H 5.01, N 8.37.

Preparation of [Ti(O*i*Pr)$_2${2-S-4,6-Me$_2$-(C$_4$HN$_2$)}$_2$] (5): [Ti(O*i*Pr)$_4$] (1 mL, 3.26 mmol) was added to a solution of 2-mercapto-4,6-dimethylpyrimidine (0.92 g, 6.52 mmol) in CH$_2$Cl$_2$ (50 mL) and the reaction mixture was stirred for 2 h at room temperature. The resulting yellow solution was evaporated to dryness to give complex **5** as a yellow, crystalline solid, which was washed with hexane (yield: 1.17 g, 81%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.26 (d, 12 H, CH_3 isopropoxide), 2.42 (broad signal, 12 H, CH_3 pyrimidine), 4.81 (sept, J = 6.2 Hz, 2 H, CHO isopropoxide), 6.50 (s, 2 H, 5-H pyrimidine) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 23.80, 26.23 (*C*H$_3$ C$_4$, *C*H$_3$, C$_6$ pyrimidine), 25.36 (*C*H$_3$ isopropoxide), 81.64 (*C*HO isopropoxide), 115.17 (C-5 pyrimidine), 168.71 (C-4 pyrimidine), 164.25 (C-6 pyrimidine), 179.20 (C-2 pyrimidine) ppm. $C_{18}H_{28}N_4O_2TiS_2$ (307.52): calcd. C 48.64, H 6.35, N 12.61, S 14.14; found C 49.10, H 5.89, N 12.10, S 13.85.

Preparation of [TiCl$_2${2-S-4,6-Me$_2$-(C$_4$HN$_2$)}$_2$] (6): A solution of 2-mercapto-4,6-dimethylpyrimidine (0.42 mL, 3.00 mmol) in THF (10 mL) was added dropwise to a solution of [TiCl$_4$(THF)$_2$] (0.50 g, 1.50 mmol) in THF (25 mL) and the resulting brown-red suspension was stirred for 16 h at room temperature. Complex **6** was obtained as a pale-yellow solid after sedimentation, subsequent filtration, and drying under vacuum (yield: 0.46 g, 78%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.41 (s, 12 H, CH_3 pyrimidine), 6.95 (s, 2 H, 5-H pyrimidine) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 23.85 (*C*H$_3$ pyrimidine), 118.45 (C-5 pyrimidine), 167.86 (C-4, C-6 pyrimidine), 168.53 (C-2 pyrimidine) ppm. $C_{12}H_{14}ClN_2S_4Ti$ (396.60): calcd. C 36.29, H 3.55, N 14.11, S 16.15; found C 36.46, H 3.22, N 14.45, S 16.52.

Preparation of [Ti(O*i*Pr)$_2${2-S-(C$_4$H$_3$N$_2$)}$_2$] (7): [Ti(O*i*Pr)$_4$] (1 mL, 3.26 mmol) was added to a solution of 2-mercaptopyrimidine (0.75 g, 6.52 mmol) in CH$_2$Cl$_2$ (50 mL) and the reaction mixture was stirred for 2 h at room temperature. The resulting yellow solution was evaporated to dryness and complex **7** was obtained as a yellow, crystalline solid, which was washed with hexane. (yield: 1.24 g, 98%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.24 (d, J = 6 Hz, 12 H, CH_3 isopropoxide), 4.70 (sept, J = 6 Hz, 2 H, CHO isopropoxide), 6.79 (t, J = 5 Hz, 2 H, 5-H pyrimidine), 8.47 (d, J = 5 Hz, 4 H, 4-H, 6-H pyrimidine) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 25.60 (*C*H$_3$ isopropoxide), 81.54 (*C*HO isopropoxide), 114.73 (C-5 pyrimidine), 151.70 (C-4 pyrimidine), 159.92 (C-6 pyrimidine), 179.82 (C-2 pyrimidine) ppm. $C_{14}H_{20}N_4O_2S_2Ti$ (387.86): calcd. C 43.30, H 5.19, N 14.43, S 16.51; found C 43.85, H 5.85, N 14.01, S 16.01.

Preparation of [TiCl$_2${2-S-(C$_4$H$_3$N$_2$)}$_2$] (8): A solution of 2-mercaptopyrimidine (0.27 mL, 2.40 mmol) in THF (10 mL) was added dropwise to a solution of [TiCl$_4$(THF)$_2$] (0.40 g, 1.20 mmol) in THF (50 mL) and the resulting yellow suspension was stirred for 5 h at room temperature. Complex **8** was obtained as a pale-yellow solid after sedimentation, subsequent filtration, and drying under vacuum (yield: 0.37 g, 91%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.89 (t, J = 5.3 Hz, 2 H, 5-H pyrimidine), 8.33 (d, J = 5.3 Hz, 4 H, 4-H, 6-H pyrimidine) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 119.84 (C-5 pyrimidine), 159.26 (C-4, C-6 pyrimidine), 168.51

Table 3. Crystal data and structure refinement for **1** and **5**.

	1	**5**
Empirical formula	$C_{18}H_{26}N_2O_4Ti$	$C_{18}H_{28}N_4O_2S_2Ti$
Formula weight	382.31	444.46
Temperature [K]	200(2)	230(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	11.222(4)	13.156(5)
b [Å]	14.745(5)	12.185(1)
c [Å]	12.124(7)	14.893(8)
β [°]	92.77(3)	105.26(6)
Volume [Å^3]	2004(1)	2303(1)
Z	4	4
Density (calculated) [g cm^{-3}]	1.267	1.282
Absorption coefficient [cm^{-1}]	4.50	5.72
F(000)	808	936
Crystal size [mm]	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.2
Index ranges	$-14 \le h \le 14$	$-17 \le h \le 16$
	$0 \le k \le 19$	$0 \le k \le 16$
	$0 \le l \le 16$	$0 \le l \le 19$
Reflections collected	5021	5731
Independent reflections	4804 [R(int) = 0.0145]	5532 [R(int) = 0.0295]
Data/restraints/parameters	4804/0/230	5532/0/244
Goodness-of-fit on F^2	1.034	1.011
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0382, wR_2 = 0.0974	R_1 = 0.0611, wR_2 = 0.1853
R indices (all data)	R_1 = 0.0556, wR_2 = 0.1052	R_1 = 0.0956, wR_2 = 0.2105
Largest diff. peak and hole [e Å^{-3}]	0.250 and –0.407	0.730 and –0.394

(C-2 pyrimidine) ppm. $C_8H_6Cl_2N_4S_2Ti$ (340.70): calcd. C 28.17, H 1.77, N 16.43, S 18.80; found C 28.40, H 1.54, N 16.68, S 19.23.

Preparation of [Ti(O*i*Pr)$_2${2-S-(C$_5$H$_4$N)}$_2$] (9): [Ti(O*i*Pr)$_4$] (1 mL, 3.26 mmol) was added to a solution of 2-mercaptopyridine (0.73 g, 6.52 mmol) in CH_2Cl_2 (50 mL) and the reaction mixture was stirred for 2 h at room temperature. The resulting yellow solution was evaporated to dryness and complex **9** was obtained as a yellow solid, which was washed with hexane (yield: 1.19 g, 95 %). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.20 (d, J = 5.9 Hz, 12 H, CH_3 isopropoxide), 4.70 (sept, J = 5.9 Hz, 2 H, CHO isopropoxide), 6.72 (dd, $J_{5,6}$ = 6 Hz, $J_{5,4}$ = 7.8 Hz, 2 H, 5-H pyridine), 7.11 (d, J = 8.1 Hz, 2 H, 3-H pyridine), 7.39 (dd, $J_{4,5}$ = 7.8 Hz, $J_{4,3}$ = 8.1 Hz, 2 H, 4-H pyridine), 8.35 (d, J = 8.1 Hz, 2 H, 6-H pyridine) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 25.56 (CH$_3$ isopropoxide), 80.34 (CHO isopropoxide), 116.97 (C-5 pyridine), 126.54 (C-3 pyridine), 137.94 (C-4 pyridine), 144.31 (C-6 pyridine), 170.74 (C-2 pyridine) ppm. $C_{16}H_{22}N_2O_2S_2Ti$ (385.70): calcd. C 49.74, H 5.74, N 7.25, S 16.60; found C 49.21, H 5.25, N 6.87, S 16.21.

Preparation of [TiCl$_2${2-S-(C$_5$H$_4$N)}{O(CH$_2$)$_4$Cl}] (10): A solution of 2-mercaptopyridine (0.33 g, 3.00 mmol) in THF (10 mL) was added dropwise to a solution of [TiCl$_4$(THF)$_2$] (0.50 mL, 1.50 mmol) in THF (25 mL). The resulting orange suspension was stirred for 16 h at room temperature. Complex **10** was obtained as a pale-orange solid after sedimentation, subsequent filtration, and drying under vacuum (yield: 0.38 g, 76 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.78 [m, 4 H, (CH_2)$_2$], 3.22 (m, 2H CH_2Cl), 4.73 (t, J = 5.8 Hz, 2 H, CH_2O), 7.20 (m, 1 H, 5-H pyridine), 7.40 (d, J = 8.4 Hz, 1 H, 3-H pyridine), 7.75 (m, 1 H, 4-H pyridine), 8.46 (d, J = 6.4 Hz, 1 H, 6-H pyridine) ppm. ^{13}C NMR (500 MHz, [D$_6$]-DMSO): δ = 30.19, 32.27 [(CH$_2$)$_2$], 60.78 (CH$_2$Cl), 85.37 (CH$_2$O), 120.09 (C-5 pyridine), 122.33 (C-3 pyridine), 137.96 (C-4 pyridine), 148.20 (C-6 pyridine), 157.89 (C-2 pyridine) ppm. $C_9H_{12}Cl_3NOSTi$ (332.50): calcd. C 32.12, H 3.59, N 4.16, S 9.53; found C 32.41, H 4.00, N 4.32, S 9.14.

Styrene Polymerizations: Polymerizations of styrene using the various catalyst precursors were carried out by adding a suspension of the titanium precursor (6 µmol) in toluene to a 100-mL flask, under an inert atmosphere, containing styrene (2 mL, previously dried with alumina) and a solution of 10 % MAO (12 mmol) in toluene. The final volume of the resulting mixture was 12 mL. Polymerization reactions were run for 90 min at different temperatures and quenched by the addition of 10 % HCl/methanol mixture (50 mL). The resulting polymers were filtered off, washed with methanol, and dried. The bulk polymers were extracted by refluxing in 2-butanone (35 mL) at 80 °C for four hours. The resulting polymers were dried and weighed.

X-ray Crystal-Structure Determinations: Single crystals of a colorless block of **1** and a yellow prism of **5** were placed in a cooled nitrogen gas stream at 200 and 230 K, respectively, on a NONIUS-MACH3 diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å). Table 3 summarizes the crystal data, data collection, and structural solution and refinement parameters for both compounds. Intensity data were collected by using an $\omega/2\theta$ scan technique. Data were corrected for Lorentz and polarization effects and absorption correction was not necessary. The structures were solved by direct methods using the SHELXS computer program,[11] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL97)[12] on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

CCDC-283896 (**1**) and -283897 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] a) V. C. Gibson, S. K. Spitmesser, *Chem. Rev.* **2003**, *103*, 283; b) C. L. Boyd, T. Toupance, B. R. Tyrrell, B. D. Ward, C. R. Wilson, A. R. Cowley, P. Mountford, *Organometallics* **2005**, *24*, 309; c) A. Krajete, G. Steiner, H. Kopacka, K.-H. Ongania, K. Wurst, M. O. Kristen, P. Preishuber-Pflügl, B. Bildstein, *Eur. J. Inorg. Chem.* **2004**, 1740; d) U. G. Joung, T. H. Kim, D. J. Joe, B. Y. Lee, D. M. Shin, Y. K. Cheng, *Polyhedron* **2004**, *23*, 1587; e) Y. Li, A. Turnas, J. T. Ciszewski, A. L. Odom, *Inorg. Chem.* **2002**, *41*, 6298; f) A. Otero, J. Fernández-Baeza, A. Antiñolo, F. Carrillo-Hermosilla, J. Tejeda, E. Díez-Barra, A. Lara-Sánchez, L. Sánchez-Barba, I. López-Solera, *Organometallics* **2001**, *20*, 2428; g) K. K. Kang, S.-P. Hong, Y.-T. Jeong, T. Shiono, T. Ikeda, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3756; h) F. Guérin, D. H. McConville, J. V. Vittal, G. A. P. Yap, *Organometallics* **1998**, *17*, 5172; i) F. Guérin, D. H. McConville, J. J. Vittal, *Organometallics* **1997**, *16*, 1491; j) C. H. Zambrano, A. K. McMullen, L. M. Kobriger, P. E. Fanwick, I. P. Rothwell, *J. Am. Chem. Soc.* **1990**, *112*, 6565.

[2] S. Doherty, R. J. Errington, A. P. Jarvis, S. Collins, W. Clegg, M. R. J. Elsegood, *Organometallics* **1998**, *17*, 3408.

[3] A. Antiñolo, F. Carrillo-Hermosilla, A. E. Corrochano, R. Fandos, J. Fernández-Baeza, A. M. Rodríguez, M. J. Ruiz, A. Otero, *Organometallics* **1999**, *18*, 5219.

[4] R. Fandos, I. López-Solera, A. Otero, A. Rodríguez, M. J. Ruiz, *Organometallics* **2004**, *23*, 5030.

[5] A. Antiñolo, F. Carrillo-Hermosilla, A. E. Corrochano, J. Fernández-Baeza, M. Lanfranchi, A. Otero, M. A. Pellinghelli, *J. Organomet. Chem.* **1999**, *577*, 174.

[6] R. Kempe, P. Arndt, *Inorg. Chem.* **1996**, *35*, 2644.

[7] a) Y. Nakayma, K. Miyamoto, N. Ueyama, A. Nakamura, *Chem. Lett.* **1999**, 391; b) D. R. Corbin, L. C. Francesconi, D. N. Hendrickson, G. D. Stucky, *Inorg. Chem.* **1979**, *18*, 3069; c) D. R. Corbin, L. C. Francesconi, D. N. Hendrickson, G. D. Stucky, *J. Chem. Soc., Chem. Commun.* **1979**, 248; d) R. A. Jones, S. T. Schwab, E. R. Whittlesey, *Polyhedron* **1984**, *3*, 505; e) G. A. Sigel, P. P. Power, *Inorg. Chem.* **1987**, *26*, 2819; f) M. Könemann, W. Stüer, K. Kirschbaum, D. M. Giolando, *Polyhedron* **1994**, *13*, 1415.

[8] a) T. T. Nadasdi, Y. Huang, D. W. Stephan, *Inorg. Chem.* **1993**, *32*, 347; b) A. V. Firth, D. W. Stephan, *Organometallics* **1998**, *17*, 3716; c) T. A. Wark, D. W. Stephan, *Organometallics* **1989**, *8*, 2836.

[9] A. Otero, J. Fernández-Baeza, A. Antiñolo, F. Carrillo-Hermosilla, J. Tejeda, A. Lara-Sánchez, L. Sánchez-Barba, M. Fernández-López, A. M. Rodríguez, I. López-Solera, *Inorg. Chem.* **2002**, *41*, 5193.

[10] a) Y. Inoue, A. Nishioka, R. Chujo, *Makromol. Chem.* **1972**, *156*, 207; b) K. Matsuzaki, T. Uryu, K. Osada, T. Kawamura, *Macromolecules* **1972**, *5*, 816; c) J. C. Randal, *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 889; d) H. Sato, Y. Tanaka, K. Hatada, *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1667.

[11] SHELXS-97, Program for Structure Solution: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[12] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, **1997**.

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