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Titanium Complexes Having Chelating Diaryloxo Ligands Bridged by Tellurium and Their Catalytic Behavior in the Polymerization of Ethylene

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A series of titanium complexes having tellurium-bridged chelating bis(aryloxo) ligands, $[TiX_2\{2,2'\text{-}Te(4\text{-}R\text{-}6\text{-}R'\text{-}C_6H_2O)_2\}]_2$ (**5b**, X = Cl, R = Me, R′ = ^{t}Bu; **6a**, X = O^{i}Pr, R = R′ = H; **6b**, X = O^{i}Pr, R = Me, R′ = ^{t}Bu), were prepared. **5b** and **6b** were determined by X-ray crystallography to have chloro- and isopropoxo-bridged dimeric structures. The structural data for these complexes indicated that the Ti−Te coordination bonds were stronger than the similar Ti−S coordination bonds in the corresponding sulfur-bridged complexes. The reaction of $(C_5R_5)TiCl_3$ (R = H, Me) with $2,2'\text{-}Te(4\text{-}R\text{-}6\text{-}R'\text{-}C_6H_2OLi)_2$ gave monocyclopentadienyl derivatives, $(C_5R_5)TiCl\{2,2'\text{-}Te(4\text{-}Me\text{-}6\text{-}^tBu\text{-}C_6H_2O)_2\}$ (**7**, R = H; **8**, R = Me). The monomeric four-legged piano-stool geometry of **8** was revealed by X-ray analysis. Upon addition of methylaluminoxane (MAO), these complexes catalyzed the polymerization of ethylene. The activities of the tellurium-bridged complexes were found to be significantly higher than those of the corresponding methylene-bridged complex.

Introduction

Bulky aryloxide ligands have been of great interest as the ancillary ligands of group 4 transition-metal complexes.[1−17] For example, Miyatake and Kakugo reported that titanium complexes having a sulfur-bridged bis(aryloxo) ligand, $(TBP)TiCl_2$ (**1**, TBP = 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)) and $(TBP)Ti(O^iPr)_2$ (**2**), have shown distinctively high activity for the polymerization of ethylene and propylene upon activation with methylaluminoxane (MAO).[2] The **1**/MAO system is an order of magnitude more active than systems based on the corresponding methylene-bridged

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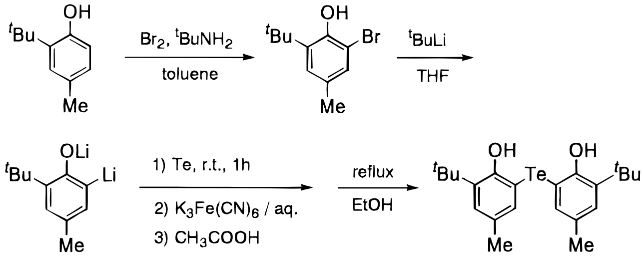
Scheme 1



diaryloxo complex, $\{2,2'\text{-}CH_2(4\text{-Me-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl_2$ (**3**), and the similar 2,2′-diphenolate complexes.[4] Thus, the coordination of sulfur to the metal is the key feature for the high activity of (TBP)TiCl$_2$ (**1**).

The TBP ligand was found to coordinate to the metal in a *fac* fashion.[7,5] A theoretical study reported by Morokuma and co-workers indicated that the coordination of the sulfur atom was essential to reduce the activation energy for olefin insertion into a metal−carbon bond.[10,17] The authors predicted that the insertion barriers for ethylene insertion for the selenium- (5.9 kcal/mol) and tellurium-bridged systems (5.7 kcal/mol) will be lower than that of the corresponding sulfur-bridged system (6.4 kcal/mol), although an oxygen bridge gave a distinctively lower insertion barrier (4.5 kcal/mol).[17] This encouraged us to investigate the study of O−Te−O chelating complexes. To the best of our knowledge, no group 4 metal complexes having an M−Te coordination bond have been reported, although those having M−Te single[18−25] and double bonds[20,26] are known. Thus, complexes having Ti−Te coordination bonds are also interesting in view of the nature of the bonding between transition metals and chalcogen atoms. Here we report the synthesis, structure, and catalytic behavior of novel titanium complexes having a tellurium-bridged chelating diaryloxo ligand.

Results and Discussion

Titanium Complexes. A tellurium-bridged diphenol, 2,2′-tellurodiphenol ((TeBP)H$_2$, **4a**), has been reported.[27] A derivative having bulky alkyl substituents, 2,2′-tellurobis(4-methyl-6-*tert*-butylphenol) ((^{t}Bu$_2$TeBP)H$_2$, **4b**), was synthesized in a similar manner by using 2-*tert*-butyl-4-methylphenol instead of unsubstituted phenol, giving a 35% overall yield (Scheme 1).

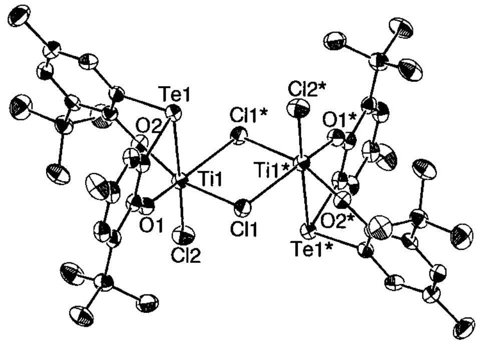
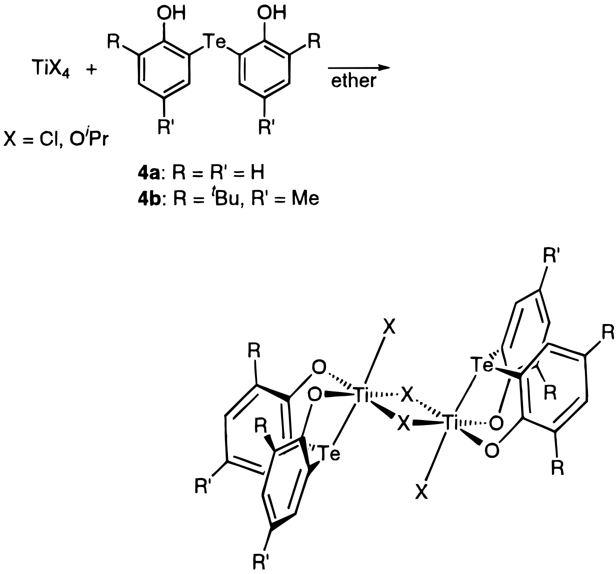


Figure 1. ORTEP drawing of [TiCl$_2$(^{t}Bu$_2$TeBP)]$_2$ (**5b**) with the numbering scheme.

The ligands **4a** and **4b** were mixed with TiX$_4$ (X = Cl, O^{i}Pr) in ether at −78 °C. Slow warming of the mixture to room temperature afforded the titanium complexes **5b**, **6a**, and **6b** as red (**5b**) or colorless (**6a** and **6b**) crystals in more than 70% yield (eq 1). The reaction of TiCl$_4$ with **4a** in toluene gave a dark red precipitate. Atempted purification and identification of the product resulted in failure due to its poor solubility in common organic solvents and low stability in air. The dimeric structures of these complexes were confirmed by X-ray crystallography of **5b** and **6b** (vide infra). These complexes are air- and moisture-sensitive. The complex **6b** is hardly soluble in ether, toluene, and hexane and slightly soluble in THF, while **5b** and **6a** are soluble in ether, THF, and toluene.



4a: R = R' = H
4b: R = ^{t}Bu, R' = Me

(1)

5b: X = Cl, R = ^{t}Bu, R' = Me
6a: X = O^{i}Pr, R = R' = H
6b: X = O^{i}Pr, R = ^{t}Bu, R' = Me

The molecular structures of **5b** and **6b** were revealed by X-ray crystallography, as shown in Figures 1 and 2. Selected bond distances and angles are listed in Table 1. Complex **1** was also structurally characterized for comparison with **5b**, and only selected bond distances and angles are included in Table 1. Complexes **5b** and **6b** are found to be almost isostructural with **1** and **2**, respectively. These four complexes have chloro- or isopropoxo-bridged binuclear structure in which each monomer moiety is related by a crystallographic center of symmetry. Each titanium center in the three complexes has a 6-coordinated distorted-octahedral geometry, as reported for [(TBP)Ti(O^{i}Pr)$_2$]$_2$ (**2**).[7,5] The two bridging groups are located at the position trans to the

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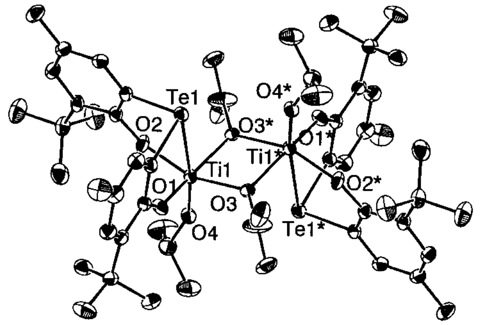


Figure 2. ORTEP drawing of $[Ti(O^iPr)_2(^tBu_2TeBP)]_2$ (**6b**) with the numbering scheme.

Table 1. Selected Bond Distances (Å) and Angles (deg) of $[\{2,2'\text{-}E(4\text{-}Me\text{-}6\text{-}^tBuC_6H_2O)\}TiX_2]_2$ (E = S, Te; X = Cl, O^iPr)

	1 (E = S, X = Cl)	**5b** (E = Te, X = Cl)	**6b** (E = Te, X = O^iPr)
	Bond Distances		
Ti−E	2.664(2) (S)	2.933(1) (Te)	3.021(1) (Te)
Ti−O (phenolate)	1.821(4) (O1) 1.815(4) (O2)	1.805(4) (O1) 1.798(4) (O2)	1.882(4) (O1) 1.876(4) (O2)
Ti−X			
terminal	2.236(2) (Cl2)	2.262(2) (Cl2)	1.775(3) (O4)
bridging	2.461(2) (Cl1) 2.482(2) (Cl1*)	2.520(2) (Cl1) 2.449(2) (Cl1*)	2.017(3) (O3) 2.017(3) (O3*)
	Bond Angles		
O−Ti−O (phenolate)	100.6(2)	97.7(2)	92.5(2)
C−E−C	102.9(3)	96.0(2)	95.1(2)
Ti−E−C	93.2(2) (C2) 93.1(2) (C13)	84.8(2) (C2) 83.3(2) (C13)	84.3(1) (C2) 85.1(1) (C8)
X−Ti−X* (bridging)	78.55(7)	80.43(6)	73.0(1)
Ti−O−C (phenolate)	134.0(4) (O1) 133.7(4) (O2)	142.2(4) (O1) 138.7(4) (O2)	142.9(3) (O1) 141.3(3) (O2)

oxygen atoms of the $^tBu_2TeBP$ ligands, and the tellurium atom occupies a position trans to the terminal chloro and isopropoxo ligands in complexes **5b** and **6b**.

The Ti−Te bond distances in **5b** (2.933(1) Å) and **6b** (3.021(1) Å) are significantly shorter than the sum (3.9 Å) of the van der Waals radii of Ti and Te, indicating that tellurium atoms are coordinating to titanium. To our knowledge, these are the first example of a complex having a Ti−Te coordination bond. In comparison with the Ti−Te single bonds, Ti−Te coordination bonds are longer by 0.1−0.2 Å. The longer Ti−Te distance in **6b**, compared to that in **5b**, can be attributed to the strong trans influence of the isopropoxo ligand. The difference between the observed Ti−Te bond distance and the sum of the van der Waals radii of titanium and tellurium in **5b** (1.0 Å) is larger than that between the observed Ti−S bond distance and the sum of the van der Waals radii of titanium and sulfur in **1** (0.8 Å), indicating that the Ti−Te coordination bonds are stronger than the Ti−S coordination bonds, in accord with the theoretical study.[17] This is also supported by the trans influences; i.e., the Ti−terminal Cl distance trans to tellurium in **5b** (2.262(2) Å) is longer by 0.026 Å than that trans to sulfur in **1** (2.236(2) Å), while it is shorter than that trans to oxygen of THF in $[TiCl_3(O^iPr)(thf)]_2$ (2.283(2) Å).[28] Thus, the strengths of the coordination bonds of neutral group 16 donor ligands are in the order O > Te > S. We speculate that selenium would be located between Te and S in this bond strength order. Such a tendency can also be found in the Ti−O^iPr bond distances trans to sulfur and tellurium in **2** and **6b**, although the difference is smaller than that in the dichloro complexes.

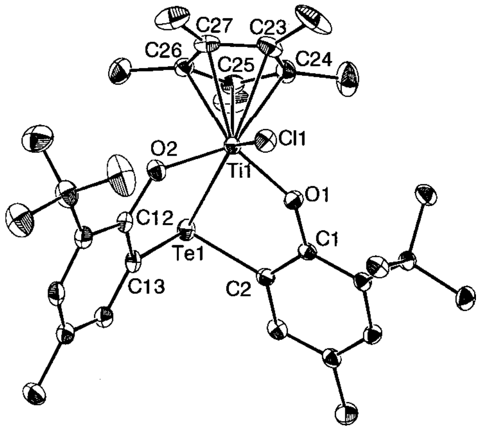
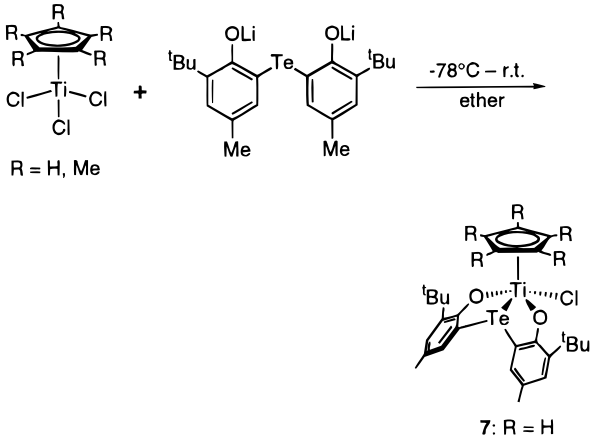


Figure 3. ORTEP drawing of $Cp^*Ti(^tBu_2TeBP)Cl$ (**8**) with the numbering scheme.

The O−Ti−O (phenolate, 97.7(2)°) and C−E−C (96.0(2)°) bond angles in **5b** are significantly narrower than those in **1** (100.6(2) and 102.9(3)°, respectively). In contrast, the Cl−Ti−Cl (bridging) angle in **5b** (80.43(6)°) is wider than that in **1** (78.55(7)°). These indicate that the coordination site available for a catalytic process in the tellurium-bridged complex is larger than that in the sulfur-bridged complex. In the corresponding diisopropoxo complexes, the O−Ti−O angles of **6b** and **2** are equal within the range of standard deviation.

We also prepared monocyclopentadienyl derivatives having these ligands, because some monocyclopentadienyl complexes bearing an aryloxo ligand have recently been found to be highly active catalysts for olefin polymerization.[15] The reaction of $CpTiCl_3$ and Cp^*TiCl_3 (Cp^* = pentamethylcyclopentadienyl) with $(^tBu_2TeBP)\text{-}Li_2$ in diethyl ether afforded $CpTi(^tBu_2TeBP)Cl$ (**7**) and $Cp^*Ti(^tBu_2TeBP)Cl$ (**8**), respectively (eq 2).



(2)

7: R = H
8: R = Me

Complex **8** was structurally characterized by X-ray analysis (Figure 3). Selected bond distances and angles are listed in Table 2. The titanium center in **8** has a four-legged piano-stool geometry in which a chlorine atom is located at the position trans to tellurium. The

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Table 2. Selected Bond Distances (Å) and Angles (deg) of 8

Bond Distances			
Ti−O(1)	1.868(4)	Ti−O(2)	1.877(4)
Ti−Te	3.032(1)	Ti−Cl	2.343(2)
Ti−C(1)	2.396(6)	Ti−C(2)	2.436(6)
Ti−C(3)	2.421(6)	Ti−C(4)	2.390(6)
Ti−C(5)	2.373(6)	Ti−Cp*[a]	2.08
Bond Angles			
O(1)−Ti−O(2)	122.5(2)	O(1)−Ti−Te	73.7(1)
O(1)−Ti−Cl	88.5(1)	O(2)−Ti−Te	73.1(1)
O(2)−Ti−Cl	91.8(1)	Te−Ti−Cl	143.84(6)
Cp*−Ti−O(1)	118.6	Cp*−Ti−O(2)	115.0
Cp*−Ti−Te	106.1	Cp*−Ti−Cl	110.0
Ti−O(1)−C(1)	144.1(3)	Ti−O(2)−C(12)	136.2(3)

[a] Cp* denotes the center of gravity for C(1)−C(5).

Ti−Te bond distance in **8** (3.032(1) Å) is significantly longer than those in **5b** and **6b** due to strong donation from the cyclopentadienyl ligand.

Polymerization of Ethylene. The catalytic activity of these complexes for ethylene polymerization was preliminarily studied upon activation with methylaluminoxane (MAO) in toluene (Table 3). Although complex **6b** was insoluble in toluene, addition of MAO to the suspension of the complexes afforded a homogeneous solution.

The tellurium-bridged complexes **5b** and **6b**, having bulky substituents, showed 20−50 times higher activities than the methylene-bridged bis(aryloxo) complex $\{2,2'\text{-}CH_2(4\text{-}Me\text{-}6\text{-}^tBuC_6H_2O)_2\}TiCl_2$ (**3**). Thus, the coordination of tellurium enhanced the catalytic activity of the catalyst systems. A monodentate bis(aryloxo) complex, $TiCl_2(OC_6H_3Me_2\text{-}2,6)_2(thf)_2$, was almost inactive under the same conditions. In a comparison between **5b** and **1**, the activity of the sulfur-bridged complex **1** is still 3 times higher, which is inconsistent with the prediction from the theoretical study.[17] We speculate that the activity of the Te-bridged system being lower than that of the sulfur-bridged system might come from the instability of active species of the tellurium-bridged system. In our experiments, deactivation of the catalyst was observed (runs 2−4). In fact, the active species seems to be completely deactivated within 1 h under the present conditions. The most probable deactivation process may be some kind of tellurium−aluminum exchange reaction.[29] In a comparison between the dichloro and diisopropoxo complexes **5** and **6**, the dichloro complexes are more active than diisopropoxo complexes, just as was observed for the TBP complexes.[2]

Although the monocyclopentadienyl complexes **7** and **8** have only one chloro ligand, the mono-Cp complex **7** exhibited higher activity than the Cp-free complexes **5** and **6**. If the active species is assumed to be a cationic alkyl complex, one of the two Ti−O bonds should be cleaved to generate the active species. Such mono-Cp mono(aryloxo) complexes have been found to exhibit high activities for olefin polymerization.[15] The bulky Cp* complex seems to be too crowded to catalyze the polymerization (Table 3, run 8).

In conclusion, a series of novel titanium complexes having tellurium-bridged chelating bis(aryloxo) ligands were prepared and their dimeric structures were determined by X-ray crystallography. The structural data for these complexes indicated that the Ti−Te coordination bonds were stronger than the Ti−S coordination bonds. Upon addition of methylaluminoxane, these complexes showed high catalytic activities for the polymerization of ethylene. Both the coordination of the bridging atom and bulky substituents are essential to the observed high activity.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive compounds were carried out by the use of standard Schlenk techniques under an argon atmosphere. $[(TBP)TiCl_2]_2$ (**1**)[2,4] and $Te(C_6H_4OH)_2$ (**4a**)[27] were prepared according to the literature methods. 2-*tert*-Butyl-4-methylphenol was purchased from Tokyo-Kasei Co. Bromine and *tert*-butylamine were purchased from Nacarai Tesque. *tert*-Butyllithium was purchased as a pentane solution from Kanto-Chemical Co. Hexane, THF, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. C_6D_6 was dried over Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. $CDCl_3$ dried over P_2O_5 and pyridine-d_5 dried over CaH_2 were degassed by trap-to-trap distillation. MAO was purchased as a toluene solution from Toso-akzo Co. Ethylene was obtained from Seitetsu-Kagaku Co.

^1H (400 and 270 MHz) spectra were measured on a JEOL JNM-GSX400 or a JEOL JNM-EX270 spectrometer. When $CDCl_3$ and C_6D_6 were used as solvents, the ^1H NMR spectra were referenced to the residual solvent protons at δ 7.26 and 7.20, respectively. When pyridine-d_5 was used, the spectra were referenced to the residual solvent protons at the lowest field at δ 8.70. Elemental analysis was performed at the Elemental Analysis Center, Faculty of Science, Osaka University. All melting points of the compounds were measured in sealed tubes under an argon atmosphere and were not corrected. ESI-MS measurements were performed on a Perkin-Elmer/Sciex API III plus spectrometer.

Preparation of $2,2'\text{-}Te(4\text{-}Me\text{-}6\text{-}^tBuC_6H_2OH)_2$ (4b). A solution of 2-*tert*-butyl-4-methylphenol (7.0 g, 43 mmol) in CH_2Cl_2 (20 mL) was added to a mixture of Br_2 (2.2 mL, 43 mmol) and $^tBuNH_2$ (4.5 mL, 43 mol) in toluene (100 mL) at −78 °C over 2 h. The reaction mixture turned yellow. It was then warmed to room temperature, washed with 3 × 100 mL of water, dried over $MgSO_4$, and concentrated in vacuo. This residue was distilled to give a colorless liquid of 2-bromo-4-methyl-6-*tert*-butylphenol (7.3 g, 70%). *tert*-Butyllithium (20 mL, 1.6 M, 32 mmol) was added at −78 °C to a stirred solution of 2-bromo-4-methyl-6-*tert*-butylphenol (2.6 g, 11 mmol) in THF (20 mL). After 1 h, the cooling bath was removed and the reaction mixture was warmed to ambient temperature. Finely ground elemental tellurium (1.4 g, 11 mmol) was then added to the reaction mixture. The mixture was stirred for 1 h, at which point only trace amounts of unreacted tellurium remained. The solution was poured into water (100 mL) containing $K_3Fe(CN)_6$ (3.5 g, 11 mmol) and acidified with acetic acid. The product was extracted with CH_2Cl_2 (3 × 150 mL), and the separated organic layer was concentrated in vacuo. The residue was dispersed in EtOH (100 mL), and the suspension was refluxed for 2 h. The product was extracted with hexane (40 mL) and evaporated until a precipitate appeared. Cooling the solution to −20 °C afforded **4b** as white crystals (1.20 g, overall yield 35%). Mp: 140−142 °C. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.29 (s, 2H, *Ph 3- or 5-H*), 7.06 (s, 2H, *Ph 3- or 5-H*), 5.91 (s, 2H, *OH*), 2.20 (s, 6H, *Me*), 1.39 (s, 18H, ^{t}*Bu*). Anal. Calcd for $C_{22}H_{30}O_2Te$: C, 58.19; H, 6.66. Found: C, 58.86; H, 6.72.

Preparation of $[\{Te(4\text{-}Me\text{-}6\text{-}^tBuC_6H_2O)_2\}TiCl_2]_2$ (5b). A solution of $Te(4\text{-}Me\text{-}6\text{-}^tBuC_6H_2OH)_2$ (**4b**; 288 mg, 0.63 mmol)

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[29] Terao, J.; Kambe, N.; Sonoda, N. *Synlett* **1996**, 779.

Table 3. Polymerization of Ethylene by Various Catalyst Systems[a]

run	complex	time (h)	activity[b]	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	$[\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl_2]_2$ (**5b**)	0.08	161		
2	$[\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl_2]_2$ (**5b**)	1	70	1.5	3.2
3	$[\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl_2]_2$ (**5b**)	3	21		
4	$[\{Te(C_6H_4O)_2\}Ti(O^iPr)_2]_2$ (**6a**)	6	0.34	1.5	19
5	$[\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Ti(O^iPr)_2]_2$ (**6b**)	1	29	2.5	4.1
6	$[\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl_2]_2$ (**1**)	1	220	0.8	2.2
7	$\{CH_2(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl_2$ (**3**)	1	1.3		
8	$Cp\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl$ (**7**)	1	130	6.7	3.9
9	$Cp^*\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl$ (**8**)	6	2.3	2.4	6.1

[a] Conditions: in toluene, C_2H_4 pressure 1 atm, [metal] = 5×10^{-6} mol, [Al]/[metal] = 1000. [b] In units of kg of PE (mol of Ti)$^{-1}$ atm^{-1} h^{-1}.

in ether (20 mL) was added to a solution of $TiCl_4$ (120 mg, 0.63 mmol) dissolved in ether (2.7 mL) at −78 °C. The reaction mixture immediately turned to a dark red suspension. After the mixture was stirred for 5 min, it was warmed to room temperature and stirred for 1 h. The precipitated dark red microcrystalline solid was separated and dried under vacuum to afford 266 mg of **5b** (74%). Mp: >300 °C. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 7.47 (s, 4H, *Ph 3- or 5-H*), 7.10 (s, 4H, *Ph 3- or 5-H*), 2.26 (s, 12H, *Me*), 1.39 (s, 36H, ^tBu). Anal. Calcd for $C_{44}H_{56}Cl_4O_4Te_2Ti_2\cdot 0.4(ether)$: C, 46.76; H, 5.16. Found: C, 46.76; H, 5.24. ESI-MS (in MeCN): *m/z* 1177 $[(M + Cl)^-]$, 607 $[(M/2 + Cl)^-]$.

Preparation of $[\{Te(C_6H_4O)_2\}Ti(O^iPr)_2]_2$ (6a). A solution of $Te(C_6H_4OH)_2$ (**4a**; 122 mg, 0.39 mmol) in ether (10 mL) was added to a solution of $Ti(O^iPr)_4$ (110 mg, 0.39 mmol) dissolved in ether (5 mL) at −78 °C. The reaction mixture immediately turned to a dark yellow suspension. After the mixture was stirred for 10 min, it was warmed to room temperature to result in the precipitation of a yellow powder. After the mixture was stirred overnight, the yellow powder was separated and dried under vacuum to afford 135 mg of **6a** (73%). Mp: 204 °C. ^1H NMR (270 MHz, pyridine-d_5, 30 °C): δ 7.98 (d, 4H, *3- or 6-H*), 7.20 (t, 4H, *4- or 5-H*), 6.93 (d, 4H, *3- or 6-H*), 6.57 (t, 4H, *4- or 5-H*), 5.02 (br, 4H, $OCH(CH_3)_2$), 1.25 (d, 24H, $OCH(CH_3)_2$). Anal. Calcd for $C_{34}H_{44}O_8Te_2Ti_2$: C, 45.24; H, 4.64. Found: C, 44.92; H, 4.56.

Preparation of $[\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Ti(O^iPr)_2]_2$ (6b). A solution of $Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2OH)_2$ (**4b**; 116 mg, 0.32 mmol) in ether (10 mL) was layered on a solution of $Ti(O^iPr)_4$ (92 mg, 0.32 mmol) dissolved in ether (5 mL) at room temperature. After 2 h, red crystals precipitated. After 15 h, the reaction solution turned almost colorless and red crystals began to completely separate. The crystals were collected and dried under vacuum to afford 146 mg of **6b** (74%). ^1H NMR (400 MHz, THF-d_8, 30 °C): δ 7.48 (s, 4H, *3- or 5-H*), 6.96 (s, 4H, *3- or 5-H*), 3.84 (m, 4H, $OCH(CH_3)_2$), 3.41 (q, 4H, Et_2O), 2.15 (s, 12H, *Me*), 1.7 (br, 24H, $OCH(CH_3)_2$), 1.40 (s, 36H, ^tBu), 1.14 (t, 6H, Et_2O). Anal. Calcd for $C_{56}H_{84}O_8Te_2Ti_2\cdot Et_2O$: C, 55.00; H, 7.23. Found: C, 54.94; H, 7.34.

Preparation of $Cp\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl$ (7). A solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.38 mL, 0.61 mmol) was added to a solution of $Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2OH)_2$ (137 mg, 0.30 mmol) in ether (5 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h to give a solution of $Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2OLi)_2$. To this reaction mixture was added a solution of $CpTiCl_3$ (64 mg, 0.29 mmol) in 5 mL of ether at −78 °C. The reaction mixture was stirred for 6 h at room temperature. Filtration and concentration of the mixture gave **7** as an orange powder (57%). Mp: 185 °C. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 7.88 (s, 2H, *3- or 5-H*), 7.11 (s, 2H, *3- or 5-H*), 6.57 (s, 5H, *Cp*), 2.06 (s, 6H, *Me*), 1.50 (s, 18H, ^tBu). Anal. Calcd for $C_{27}H_{33}ClO_2TeTi$: C, 54.01; H, 5.54. Found: C, 54.62; H, 5.75.

Preparation of $Cp^*\{Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}TiCl$ (8). A solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.44 mL, 0.70 mmol) was added to a solution of $Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2OH)_2$ (159 mg, 0.35 mmol) in ether (5 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h to give a solution of $Te(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2OLi)_2$. To this reaction mixture was added a solution of Cp^*TiCl_3 (104 mg, 0.36 mmol) in 5 mL of ether at −78 °C. The reaction mixture was stirred overnight at room temperature, evaporated to dryness, and extracted with *n*-hexane (40 mL). The extract was concentrated to 1/10 volume to give dark red micocrystals of **8** (131 mg, 56%). Mp: 214 °C dec. ^1H NMR (270 MHz, C_6D_6, 30 °C): δ 7.59 (s, 2H, *3- or 5-H*), 7.15 (s, 2H, *3- or 5-H*), 2.16 (s, 15H, *Cp**), 2.03 (s, 6H, *Me*), 1.56 (s, 18H, ^tBu). Anal. Calcd for $C_{32}H_{43}ClO_2TeTi$: C, 57.31; H, 6.46. Found: C, 56.46; H, 6.34.

Polymerization of Ethylene: Typical Procedure. To a suspension of **5b** (5×10^{-6} mol) in toluene (11 mL) was added a 3.2 M solution of MAO in toluene (1.6 mL, 1000 equiv) via syringe at −78 °C. The reaction mixture was degassed under vacuum and then warmed to room temperature to become a clear solution. After the mixture was stirred at room temperature for 10 min, ethylene (atmospheric pressure) was introduced. The vessel was kept at 25 °C for 1 h, and then the polymerization was quenched by addition of HCl−MeOH. The resulting white polymer was collected by filtation and dried in vacuo (350 mg, 70 kgPE/((mol of Ti) atm h)).

Crystallographic Data Collection and Structure Determination of 1, 5b, 6b, and 8. Crystals of **1**, **5b**, **6b**, and **8** suitable for X-ray diffraction studies were sealed in glass capillaries under an argon atmosphere and mounted on a Rigaku AFC-5R four-circle diffractometer for data collection using Mo Kα radiation. Relevant crystal and data statistics are summarized in Table 4. The unit cell parameters at 23 °C were determined by a least-squares fit to 2θ values of 20 strong higher reflections for all complexes. Three standard reflections were chosen and monitored every 150 reflections. Empirical absorption correction was carried out on the basis of an azimuthal scan. Each sample showed no significant intensity decay during the data collection. The structures of all complexes were solved by direct methods (SHELXS 86)[30] and refined by full-matrix least-squares methods. Measured nonequivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$, where $w^{-1} = \sigma^2(F_o) = \sigma^2(F_o^2)/(4F_o^2)$. The positions of all non-hydrogen atoms for all complexes were found from a difference Fourier electron density map and refined anisotropically. All hydrogen atoms were placed in calculated positions (C−H = 0.95 Å) and constrained to ride on their respective carbon atoms. All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

The pertinent details of data collection and the final cell dimensions for **1**, **5b**, **6b**, and **8** are given in Table 4.

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(30) Sheldrick, G. M. SHELXS86: Program for the Solution of Crystal Structures; Universität Göttingen, Göttingen, Germany, 1986.

(31) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

Table 4. Crystal Data and Collection Parameters

	1	**5b**	**6b**	**8**
formula	$C_{44}H_{56}O_4S_2Ti_2Cl_4$	$C_{58}H_{72}O_4Cl_4Te_2Ti_2$	$C_{60}H_{94}O_9Ti_2Te_2$	$C_{32}H_{43}O_2ClTeTi$
fw	950.66	1326.02	1310.40	670.64
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.636(3)	12.203(2)	11.971(3)	10.580(4)
b, Å	26.464(5)	11.520(2)	14.337(3)	16.657(4)
c, Å	10.333(3)	21.941(2)	11.629(2)	9.582(2)
α, deg			100.20(2)	94.88(2)
β, deg	116.09(2)	95.061(10)	116.51(1)	102.60(2)
γ, deg			66.82(2)	74.15(2)
V, Å^3	2366(1)	3072.3(7)	1641.8(7)	1584.6(7)
Z	2	2	1	2
D_{calcd}, g/cm^3	1.334	1.433	1.325	1.405
$F(000)$	992.00	1336.00	674.00	684.00
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
abs coeff, cm^{-1}	6.90	14.06	11.62	12.82
temp, °C	23.0	23.0	23.0	23.0
scan speed, deg/min	16.0	16.0	16.0	16.0
scan width, deg	$0.94 + 0.35 \tan \theta$	$0.73 + 0.35 \tan \theta$	$1.47 + 0.35 \tan \theta$	$1.63 + 0.35 \tan \theta$
$2\theta_{max}$, deg	55.0	55.0	55.0	55.0
no. of unique data	5573	7048	7520	7238
no. of unique data ($I > 3\sigma(I)$)	2264	4500	4428	5056
no. of variables	253	281	316	334
R	0.055	0.042	0.043	0.049
R_w	0.055	0.054	0.046	0.058
GOF	1.93	1.84	1.65	2.74

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Supporting Information Available: Tables of final positional parameters, final thermal parameters, and bond distances and angles for **1**, **5b**, **6b**, and **8** together with their drawings with all numbering schemes of non-hydrogen atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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