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Syntheses of group 4 transition metal complexes bearing 2-pyridinethiolate ligands and their catalytic activities for ethylene polymerization

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Abstract

Titanium bis(2-pyridinethiolate) complexes, $Ti(6\text{-R-SPy})_2(NMe_2)_2$ (6-R-SPy = 6-R-2-pyridinethiolate, **3a**: R = H; **3b**: R = Me; **3c**: R = Ph; **3d**: R = C_6H_4-4-Me; **3e**: R = C_6H_4-4-*t*-Bu; **3f**: R = C_6H_3-3,5-Me_2), and the titanium bis(2-pyridinolate) complexes, $Ti(6\text{-Ph-OPy})_2(NMe_2)_2$ (6-Ph-OPy = 6-phenyl-2-pyridinolate, **8**) were prepared by treating $Ti(NMe_2)_4$ with 2 equiv. of 6-R-2-pyridinethiol or 6-Ph-2-pyridinol. The *cis*-configuration of the diamido moieties in the pseudo octahedral geometry was elucidated by X-ray crystallography for **3a**. Reaction of $M(NMe_2)_4$ (M = Ti, Zr) with 4 equiv. of 2-pyridinethiol cleanly gave tetrakis(pyridinethiolate) complexes, $M(6\text{-H-SPy})_4\cdot THF$ (**6**: M = Ti; **7**: M = Zr). The triangular dodecahedral geometries of **6** and **7** were also revealed by X-ray crystallography. These complexes catalyzed ethylene polymerization upon activation with MAO (methylaluminoxane) or MMAO (modified MAO). The catalytic activities of titanium bis(6-aryl-pyridinethiolate) systems were found to be remarkably higher than that of titanium bis(6-methyl-pyridinethiolate) system. Among the complexes synthesized in this study, $Ti[6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-SPy}]_2(NMe_2)_2$ (**3f**)/MMAO showed the highest activity (1200 kg/Ti-mol h atm) for ethylene polymerization at 60 °C under atmospheric pressure. In contrast, the activity of the corresponding 6-aryl-pyridinolate system **8**/MMAO was rather low (9.3 kg/Ti-mol h atm). Both the N–S chelating structure and the bulky aryl substituents are essential for the high activities of the 6-aryl-pyridinethiolate complexes.

Keywords: Group 4 metal complexes; Pyridinethiolate ligand; Ethylene polymerization

1. Introduction

Non-metallocene type group 4 metal complexes are of current interests in the field of olefin polymerization catalysts [1]. The vast majority of the non-metallocene type catalysts contains ''hard'' donating ligands such as a bis(alkoxide) [2–4], bis(amido) [5–11] and N–O chelating ligands [12–17]. Especially, group 4 transition metal complexes bearing phenoxy-imine chelating ligands were reported to show exceptionally high activities for ethylene polymerizations in the presence of methylaluminoxane (MAO) [18,19]. In contrast, the use of the ligands containing ''soft'' donor atoms such as sulfur has still been remained rather unexplored. Most of such sulfur-containing catalysts of group 4 metals include metal to neutral thioether bonds [2,20–22], and any group 4 metal complex with anionic sulfur-donor ligands such as thiolate has never been utilized for olefin polymerization catalysts. This could be attributed to the poor stability of the covalent bonds between hard early transition metals and soft sulfur atom. Most of the reported group 4 metal thiolate complexes are stabilized

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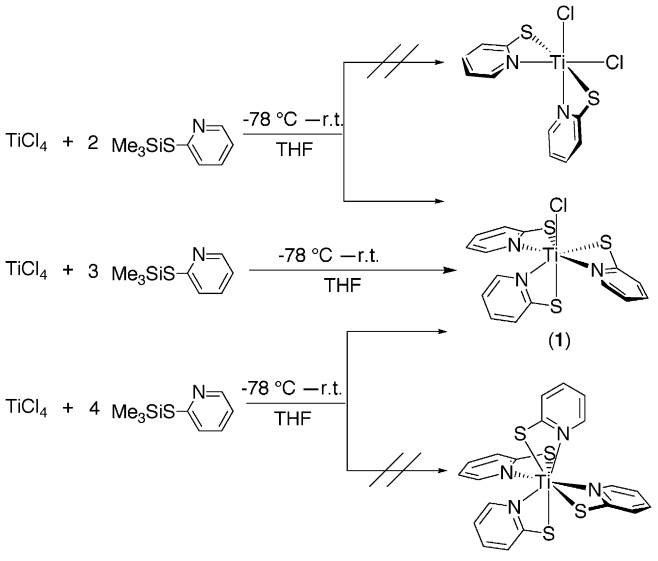
with cyclopentadienyl (Cp) type ligand, and the Cp-free complexes are relatively rare. To our knowledge, only three structurally characterized Cp-free titanium thiolate complexes have been reported, $TiCl_2$(S-*t*-Bu)$_2$(diars) (diars = *o*-phenylene bis(dimethylarsine)) [23], $[Li(OEt_2)_3][Ti^{III}(SAr)_4]$ (Ar = 2,4,6-triisopropylphenyl) [24] and $[NH_2Me_2]_2[Ti(S_2C_6H_4)_3]$ [25]. We expected that chelating coordination could stabilize metal–sulfur covalent bond, and synthesized a titanium tris(2-pyridinethiolate) complex, Ti(6-H-SPy)$_3$Cl·THF (**1**) (6-H-SPy = 2-pyridinethiolate) [26], as well as lanthanoid complexes, [Ln(6-H-SPy)$_2$(hmpa)$_3$]I (Ln = Pr, Nd, Sm, Eu, Er, Yb) [27] and Sm(η^8-C_8H_8)(6-H-SPy)(hmpa)$_2$ [28]. Although sulfur-containing compounds often act as catalyst poison, the titanium tris(pyridinethiolate) complex **1** showed moderate activities for the polymerization of ethylene and styrene upon activation with MAO [26]. In that study, we chose 2-pyridyl trimethylsilyl thioether (Me_3Si(6-H-SPy)) as a reactant instead of thiol or alkali metal thiolate for the synthesis of **1** to avoid difficulties in contamination of salts such as pyridinium chloride and alkali metal chloride. The complex **1** was prepared by the treatment of $TiCl_4$ with 3 equiv. of Me_3Si(6-H-SPy) in good yield, while 1:2 and 1:4 reactions of $TiCl_4$ and Me_3Si(6-H-SPy) did not allow isolation of bis- and tetrakis(2-pyridinethiolate) complexes but only gave **1** in low yield (Scheme 1). In order to prepare bis- and tetrakis(2-pyridinethiolate) complexes of titanium, we used $Ti(NMe_2)_4$ and 2-pyridinethiol as reactants instead of $TiCl_4$ and Me_3Si(6-H-SPy). For the purpose of evaluating the effect of the chalcogen atom and the substituents of the chelating pyridinethiolate ligands on ethylene polymerization catalysis, here we studied the synthesis of dimethylamido complexes of group 4 metals having various substituted 2-pyridinethiolate, pyridinolate, and pyrimidinethiolate ligands, and their catalytic behaviors for ethylene polymerization focusing on their catalytic activities.

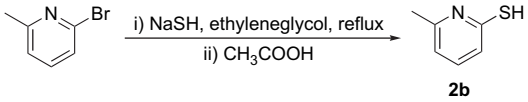


Scheme 1.

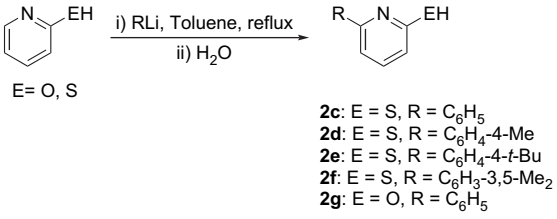
2. Results and discussion

2.1. Ligand design and synthesis

In order to elucidate the effects of substituents and chalcogen atoms of the ligands on ethylene polymerization catalysis, we synthesized a series of pyridinethiol and pyridinol derivatives. 6-Methyl-2-pyridinethiol (6-Me-HSPy: **2b**) was synthesized by treatment of 6-bromo-2-methylpyridine with 2 equiv. of NaSH in ethylene glycol at 150 °C (Eq. (1)). Other 6-substituted 2-pyridinethiols (6-R-HSPy, **2c**: R = Ph; **2d**: R = C_6H_4-4-Me; **2e**: R = C_6H_4-4-*t*-Bu; **2f**: R = C_6H_3-3,5-Me_2), and 6-phenyl-2-pyridinol (6-Ph-HOPy, **2g**) were synthesized by treatment of 2-pyridinethiol (6-H-HSPy, **2a**) or 2-pyridinol with 2 equiv. of aryllithium in toluene (Eq. (2)), and were isolated as yellow or red solids by recrystallization from CH_2Cl_2 and *n*-pentane. The crystal structure of **2d** was determined by X-ray crystallography as shown in Fig. 1, and the selected bond distances and angles are summarized in Table 1. The compound **2c** was also structurally characterized and only the selected bond distances and angles are included in Table 1. 2-Pyridinethiol and 2(1*H*)-pyridinethione are in tautomeric equilibrium [29], and both **2c** and **2d** were crystallized in 2(1*H*)-pyridinethione form. The C12–C13 and C14–C15 bond distances are apparently shorter than C11–C12 and C13–C14 distances due to the localized double bonds.



(1)



(2)

2.2. Syntheses of pyridinethiolate complexes and their derivatives

A series of titanium bis(2-pyridinethiolate) complexes, Ti(6-R-SPy)$_2$(NMe_2)$_2$ (6-R-SPy = 6-R-2-pyridinethiolate, **3a**: R = H; **3b**: R = Me; **3c**: R = Ph; **3d**: R = C_6H_4-4-Me; **3e**: R = C_6H_4-4-*t*-Bu; **3f**: R = C_6H_3-3,5-Me_2) were prepared by the reaction of $Ti(NMe_2)_4$ with 2 equiv. of 6-R-HSPy (**2a–2f**) in THF in 18–57% yield (Eq. (3)). Zirconium bis(2-pyridinethiolate) complexes, Zr(6-R-SPy)$_2$(NMe_2)$_2$ (**4a**: R = H; **4b**: R = C_6H_3-3,5-Me_2) were obtained by using toluene as a reaction solvent in 98% and 24% yield, respectively. A 2-quinolinethiolate derivative, Ti(SQu)$_2$(NMe_2)$_2$ (**5**) (SQu = 2-quinolinethiolate), was also synthesized by the same procedure in 42% yield (Eq. (4)). ^{1}H NMR spectra of **3a–3f**,

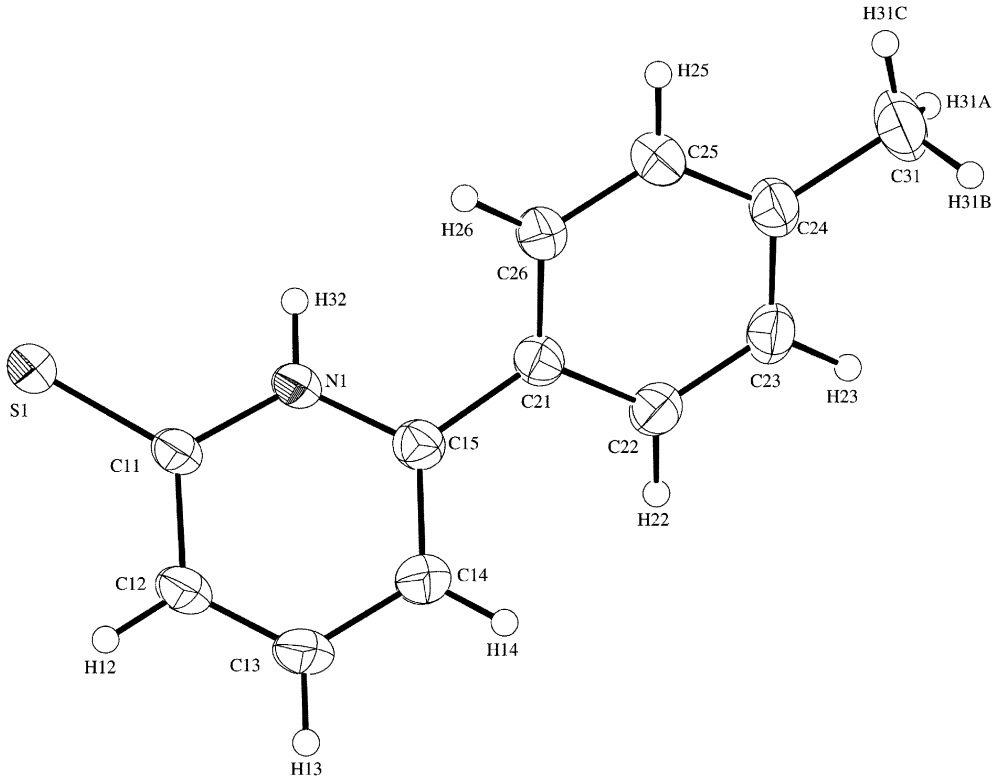
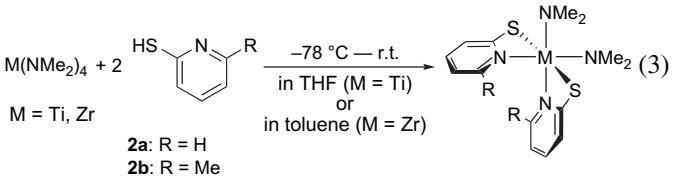


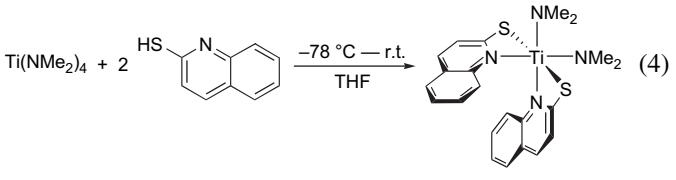
Fig. 1. ORTEP drawing of 6-(4-methylphenyl)-2(1*H*)pyridinethione (**2d**) with a numbering scheme.

4a–**4b** and **5** indicated that the two pyridinethiolate ligands were equivalent in solution. The variable temperature ^{1}H NMR spectra ($CDCl_3$) of these pyridinethiolate complexes did not show significant peak shift in the temperature range from −60 to +60 °C.



2a: R = H
2b: R = Me
2c: R = C_6H_5
2d: R = C_6H_4-4-Me
2e: R = C_6H_4-4-*t*-Bu
2f: R = C_6H_3-3,5-Me_2

3a: M = Ti, R = H
3b: M = Ti, R = Me
3c: M = Ti, R = C_6H_5
3d: M = Ti, R = C_6H_4-4-Me
3e: M = Ti, R = C_6H_4-4-*t*-Bu
3f: M = Ti, R = C_6H_3-3,5-Me_2
4a: M = Zr, R = H
4b: M = Zr, R = C_6H_3-3,5-Me_2

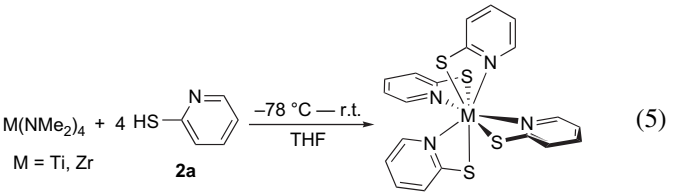


5

Tetrakis(2-pyridinethiolate) complexes, Ti(6-H-SPy)$_4$·THF (**6**) and Zr(6-H-SPy)$_4$·THF (**7**) were prepared by treatment of $M(NMe_2)_4$ (M = Ti, Zr) with 4 equiv. of 6-H-PySH (**2a**) in THF under the same conditions as described for the synthesis of the bis(pyridinethiolate) complexes, and obtained in 72% and 68% yield, respectively (Eq. (5)). ^{1}H NMR spectra of **6** and **7** indicated that the four pyridinethiolate ligands were equivalent in solution.

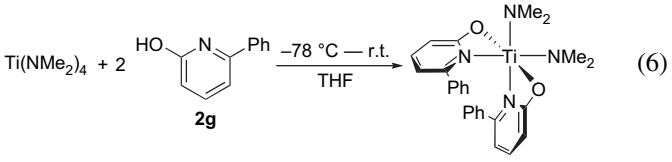
Table 1
Selected bond distances (Å) and angles (°) for **2c** and **2d**

2c		**2d**	
Bond distances			
S1–C11	1.695(3)	S1–C11	1.688(2)
N1–C11	1.366(3)	N1–C11	1.371(3)
N1–C15	1.363(4)	N1–C15	1.369(3)
C11–C12	1.410(4)	C11–C12	1.414(3)
C12–C13	1.363(5)	C12–C13	1.354(3)
C13–C14	1.391(5)	C13–C14	1.405(3)
C14–C15	1.375(4)	C14–C15	1.368(3)
Bond angles			
C11–N1–C15	125.3(2)	C11–N1–C15	124.95(17)
S1–C11–C12	124.0(2)	S1–C11–C12	123.46(16)
N1–C15–C14	118.2(3)	N1–C15–C14	118.05(18)
S1–C11–N1	120.5(2)	S1–C11–N1	120.74(15)
N1–C11–C12	115.5(3)	N1–C11–C12	115.79(19)
N1–C15–C21	117.8(2)	N1–C15–C21	118.84(17)

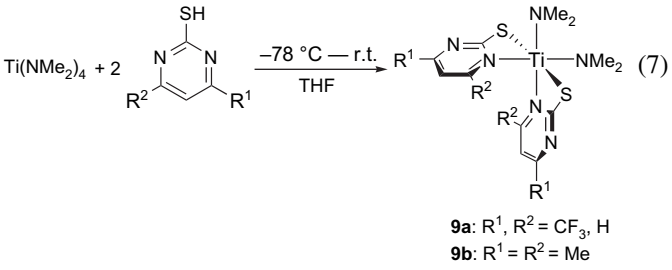


6: M = Ti
7: M = Zr

We also prepared pyridinolate and pyrimidinethiolate complexes for comparison with the pyridinethiolate complexes. A titanium bis(6-phenyl-2-pyridinolate) complex, Ti(6-Ph-OPy)$_2$(NMe$_2$)$_2$ (6-Ph-OPy = 6-Ph-2-pyridinolate, **8**) (Eq. (6)), and bis(pyrimidinethiolate) complexes, Ti(4-R^1-6-R^2-SPm)$_2$(NMe$_2$)$_2$ (4-R^1-6-R^2-SPm = 4-R^1-6-R^2-2-pyrimidinethiolate, **9a**: R^1, R^2 = CF$_3$, H; **9b**: R^1 = R^2 = Me) (Eq. (7)) were synthesized by the same procedure with **3** in 42–62% yield.



(6)



(7)

Figs. 2 and 3 display the ORTEP drawings of **3a** and **6**, respectively. The selected bond distances and angles of **3a** and **6** are summarized in Table 2. The structure of **7** was similar to that of **6**, and the selected bond distances and angles are included in Table 2 as well as those of **1** [26] for comparison. The complex **3a** has a mononuclear six-coordinated distorted octahedral structure with pseudo C_2 symmetry. The two sulfur atoms have *trans* geometry, and the two amido groups are located in *cis* configuration. The complexes **6** and **7** have a mononuclear triangular dodecahedral structure [30–33]. The Ti–S distances of the pyridinethiolate complexes (av. 2.491 Å (**6**), av. 2.434 Å (**1**), and av. 2.484 Å (**3a**)) were significantly longer than those of monodentate thiolate complexes [23–25,34–38]. The C–C distances of the pyridine ring in the pyridnethiolate complexes **1**, **3a**, **6** and **7** are nearly equivalent, indicating delocalized π electrons.

2.3. Ethylene polymerization studies

These complexes catalyzed ethylene polymerization upon activation with 1000 equiv. of methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) in the tested temperature range from −40 to 80 °C. The results for bis- and tetrakis(pyridinethiolate) complexes **3a** and **6** are summarized in Table 3. The activity of the tris(pyridinethiolate) complex **1** is also included in Table 3 for comparison. The catalytic activity of the bis(2-pyridinethiolate) complex **3a**/MAO system strongly depended on polymerization temperature, the highest activity of 17 kg/Ti-mol h atm was observed at lower temperature (−40 °C). The **3a**/MMAO system showed higher catalytic activity (27 kg/Ti-mol h atm at −20 °C) than the **3a**/MAO system. The activity of the titanium tetrakis(pyridinethiolate) complex **6**/MAO (34 kg/Ti-mol h atm at 0 °C) was slightly higher than that of **3a**/MAO and comparable to that of the tris(pyridinethiolate) complex **1**/MAO at −20 °C (38 kg/Ti-mol h atm) [26]. We speculate that **6** might lose at least two of the four pyridinethiolate ligands upon activation with MAO to generate similar active species with that in the **3a**/MAO system. The higher activity of **6** than **3a** would come from higher stability of **6**.

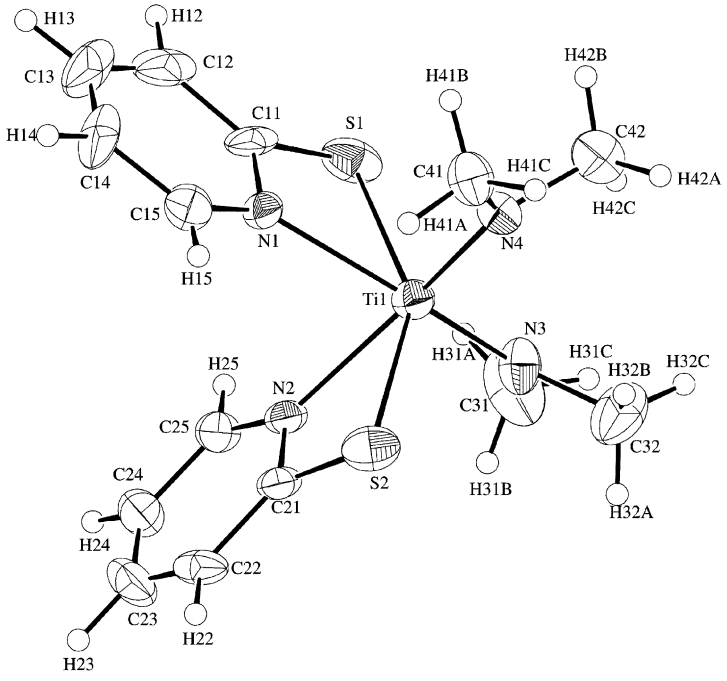


Fig. 2. ORTEP drawing of Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**) with a numbering scheme.

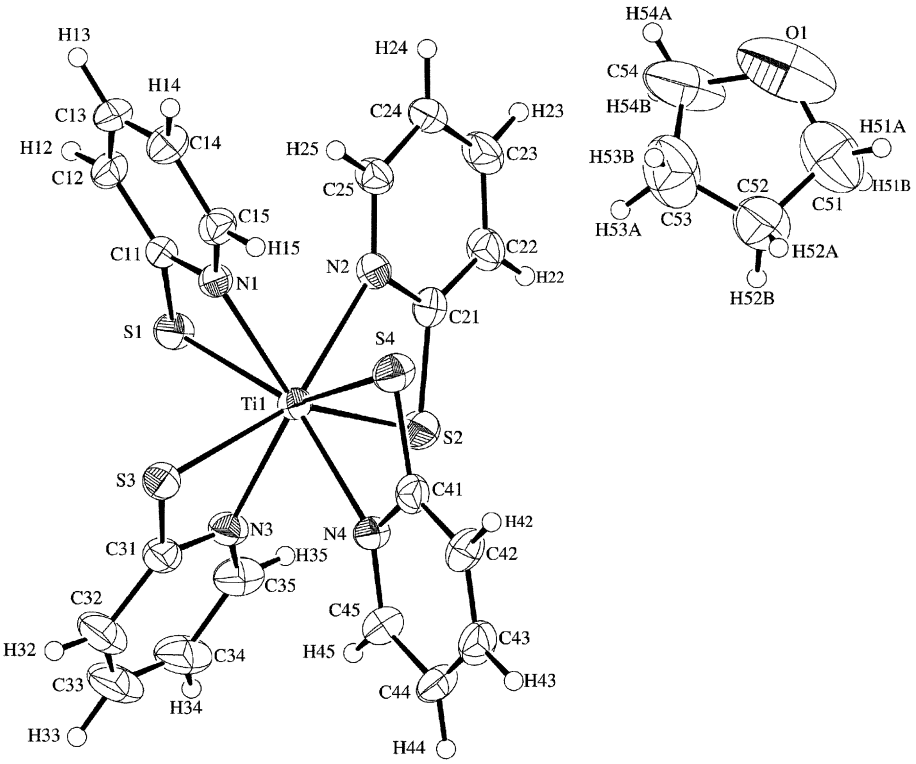


Fig. 3. ORTEP drawing of Ti(6-H-SPy)$_4$ (**6**) with a numbering scheme.

Table 4 summarizes the results of the ethylene polymerizations by using the substituted 2-pyridinethiolate complexes **3b**–**3f** and the quinolinethiolate complex **5**. The activities of the titanium complexes having two 6-substituted pyridinethiolate ligands **3b**–**3f**/MMAO systems were found to increase as the polymerization temperature rose. This is in sharp contrast to the fact that the corresponding unsubstituted 2-pyridinethiolate complex **3a**/MMAO system showed higher activity at lower temperature (−20 °C). Thus, the 6-substituents in these titanium bis(pyridinethiolate) complexes effectively improve the thermal stability of the active species. The methyl substituted complex **3b**/MMAO showed two times higher activities (53 kg/Ti-mol h atm) than that of **3a**/MMAO. We found that aryl-substituted complexes, **3c**–**3f**, were more active by one or two orders of magnitude than the unsubstituted or methyl-substituted complexes. Among those complexes, the 6-(4-methylphenyl)pyridinethiolate complex **3d** and the 6-(3,5-dimethylphenyl)pyridinethiolate complex **3f** showed particularly high activities. The highest activity of the **3f**/MMAO system (1200 kg/Ti-mol h atm) observed at 60 °C was 50 times higher than that of the **3a**/MMAO system and comparable to those of metallocene catalysts. Thus, the bulky aryl substituents are quite effective to enhance the catalytic activity of titanium pyridinethiolate complexes for ethylene polymerization. The catalytic activity of bis(quinolinethiolate) complex **5** (2.9 kg/Ti-mol h atm at 0 °C) was lower than that of the 2-pyridinethiolate complexes.

Table 2
Selected bond distances (Å) and angles (°) for **1**, **3a**, **6** and **7**

Complex	**1**[a]	**3a**	**6**	**7**
Bond distances				
M–S	2.435(2)	2.480(2)	2.5050(16)	2.6306(13)
	2.431(2)	2.487(2)	2.4898(16)	2.5684(13)
			2.5018(16)	2.6127(12)
			2.4699(16)	2.5930(13)
M–N(Py)	2.228(3)	2.188(5)	2.224(4)	2.325(3)
	2.190(5)	2.200(5)	2.296(4)	2.342(4)
			2.233(4)	2.297(4)
			2.284(4)	2.361(3)
M–N(amido)		1.878(4)		
		1.874(4)		
Bond angles				
M–S1–C11	83.6(2)	80.8(3)	82.09(17)	81.78(17)
M–S2–C21	81.0(2)	80.1(2)	83.79(17)	83.18(17)
M–S3–C31			81.88(19)	81.51(15)
M–S4–C41			83.57(19)	82.41(16)

[a] See Ref. [26].

We speculate that the active species in the **3a**/MMAO system is susceptible to deactivation through the reaction of Ti–S bond with MAO at high temperature. The Ti–S bonds in **3b**–**3f**/MMAO systems could be more stable than that of **3a** due to the bulky 6-substituents. The catalytic activity of **3f**/MMAO was only slightly decreased within 30 min at 60 °C, indicating that the active species in this system was significantly thermally robust.

The zirconium bis(2-pyridinethiolate) complexes, **4a** and **4b**, showed much lower activities than the corresponding titanium complexes, **3a** and **3f** (Table 5). A similar tendency was observed in the systems based on aryloxide complexes [2].

Table 3
Polymerization of ethylene catalyzed by the titanium pyridinethiolate complexes (**1**, **3a** and **6**) activated with MAO or MMAO

Run	Complex	Cocatalyst	Temperature (°C)	Activity (kg/M-mol h atm)	$M_n/10^4$[a]	M_w/M_n[a]
1[b]	Ti(6-H-SPy)$_3$Cl (**1**)	MAO	60	1.6	n.d.	n.d.
2[b]	Ti(6-H-SPy)$_3$Cl (**1**)	MAO	40	1.7	n.d.	n.d.
3[b]	Ti(6-H-SPy)$_3$Cl (**1**)	MAO	20	2.2	n.d.	n.d.
4[b]	Ti(6-H-SPy)$_3$Cl (**1**)	MAO	0	11	n.d.	n.d.
5[b]	Ti(6-H-SPy)$_3$Cl (**1**)	MAO	−20	38	n.d.	n.d.
6	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MAO	30	0.56	0.36	192
7	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MAO	0	6.4	0.88	80
8	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MAO	−20	15	2.9	59
9	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MAO	−40	17	18	8.6
10	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MMAO	30	0.97	0.21	186
11	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MMAO	0	10	1.4	71
12	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MMAO	−20	27	7.6	21
13	Ti(6-H-SPy)$_2$(NMe$_2$)$_2$ (**3a**)	MMAO	−40	4.2	33.3	5.7
14	Ti(6-H-SPy)$_4$ (**6**)	MAO	30	1.4	0.11	190
15	Ti(6-H-SPy)$_4$ (**6**)	MAO	0	34	1.5	63
16	Ti(6-H-SPy)$_4$ (**6**)	MAO	−20	20	8.3	16
17	Ti(6-H-SPy)$_4$ (**6**)	MAO	−40	13	8.2	20

Conditions: in toluene, ethylene pressure: 1 atm, time: 1 h, [Al]/[Ti] = 1000.
[a] Determined by GPC analysis in 1,2,4-trichlorobenzene at 140 °C calibrated with standard poly(styrene)s.
[b] See Ref. [26].

Bulky aryl substituents were also effective in the zirconium derivatives; the catalytic activity of **4b** was higher by two orders of magnitude than that of **4a**, although it was still lower by two orders of magnitude than that of **3f**. The zirconium tetrakis(2-pyridinethiolate) complex **7** was also much less active than the corresponding titanium complex **6**.

In order to elucidate the effect of the sulfur atom in the pyridinethiolate complexes, we also studied the catalytic behaviors of the titanium pyridinolate complexes for ethylene polymerization. The catalytic activities of the bis(2-pyridinolate) complex **8** also tended to increase at higher polymerization temperature (Table 6). The bis(2-pyridinolate) complex showed two orders of magnitude lower activities (9.3 kg/Ti-mol h atm at 60 °C) than the corresponding bis(pyridinethiolate) complex **3c**. The cationic species having pyridinolate ligands could be too stabilized to show high activity for the

Table 4
Polymerization of ethylene catalyzed by the substituted pyridinethiolate complexes (**3b**–**3f**) and quinolinethiolate complex (**5**) with MMAO

Run	Complex	Temperature (°C)	Activity (kg/M-mol h atm)	$M_n/10^4$[a]	M_w/M_n[a]
1	Ti(6-Me-SPy)$_2$(NMe$_2$)$_2$ (**3b**)	60	53	2.9	13
2	Ti(6-Me-SPy)$_2$(NMe$_2$)$_2$ (**3b**)	30	39	2.4	26
3	Ti(6-Me-SPy)$_2$(NMe$_2$)$_2$ (**3b**)	0	5.0	2.4	19
4	Ti(6-Me-SPy)$_2$(NMe$_2$)$_2$ (**3b**)	−20	4.6	15	14
5	Ti(6-Ph-SPy)$_2$(NMe$_2$)$_2$ (**3c**)	80	500	3.0	57
6	Ti(6-Ph-SPy)$_2$(NMe$_2$)$_2$ (**3c**)	60	980	×[b]	×[b]
7	Ti(6-Ph-SPy)$_2$(NMe$_2$)$_2$ (**3c**)	30	760	×[b]	×[b]
8	Ti(6-Ph-SPy)$_2$(NMe$_2$)$_2$ (**3c**)	0	500	3.4	16
9	Ti{6-(C$_6$H$_4$-4-Me)-SPy}$_2$(NMe$_2$)$_2$ (**3d**)	80	290	4.1	64
10	Ti{6-(C$_6$H$_4$-4-Me)-SPy}$_2$(NMe$_2$)$_2$ (**3d**)	60	1100	6.2	30
11	Ti{6-(C$_6$H$_4$-4-Me)-SPy}$_2$(NMe$_2$)$_2$ (**3d**)	30	690	1.9	71
12	Ti{6-(C$_6$H$_4$-4-Me)-SPy}$_2$(NMe$_2$)$_2$ (**3d**)	0	330	4.6	21
13	Ti{6-(C$_6$H$_4$-4-*t*-Bu)-SPy}$_2$(NMe$_2$)$_2$ (**3e**)	80	150	2.1	96
14	Ti{6-(C$_6$H$_4$-4-*t*-Bu)-SPy}$_2$(NMe$_2$)$_2$ (**3e**)	60	40	1.9	36
15	Ti{6-(C$_6$H$_4$-4-*t*-Bu)-SPy}$_2$(NMe$_2$)$_2$ (**3e**)	30	40	15	11
16	Ti{6-(C$_6$H$_4$-4-*t*-Bu)-SPy}$_2$(NMe$_2$)$_2$ (**3e**)	0	<0.01	n.d.	n.d.
17	Ti{6-(C$_6$H$_3$-3,5-Me$_2$)-SPy}$_2$(NMe$_2$)$_2$ (**3f**)	80	200	0.97	70
18	Ti{6-(C$_6$H$_3$-3,5-Me$_2$)-SPy}$_2$(NMe$_2$)$_2$ (**3f**)	60	1200	3.5	44
19	Ti{6-(C$_6$H$_3$-3,5-Me$_2$)-SPy}$_2$(NMe$_2$)$_2$ (**3f**)	30	640	4.1	43
20	Ti{6-(C$_6$H$_3$-3,5-Me$_2$)-SPy}$_2$(NMe$_2$)$_2$ (**3f**)	0	610	3.9	44
21[c]	Ti(SQu)$_2$(NMe$_2$)$_2$ (**5**)	30	2.3	0.89	63
22[c]	Ti(SQu)$_2$(NMe$_2$)$_2$ (**5**)	0	1.3	1.5	72
23[c]	Ti(SQu)$_2$(NMe$_2$)$_2$ (**5**)	−20	0.73	5.0	24
24[c]	Ti(SQu)$_2$(NMe$_2$)$_2$ (**5**)	−40	0.55	2.7	40

Conditions: in toluene, ethylene pressure: 1 atm, time: 1 h, [Al]/[Ti] = 1000.
[a] Determined by GPC analysis in 1,2,4-trichlorobenzene at 140 °C calibrated with standard poly(styrene)s.
[b] Hardly soluble in 1,2,4-trichlorobenzene.
[c] Cocatalyst: MAO.

Table 5
Polymerization of ethylene catalyzed by the zirconium substituted pyridinethiolate complexes (**4** and **7**) with MMAO

Run	Complex	Temperature (°C)	Activity (kg/M-mol h atm)	$M_n/10^4$[a]	M_w/M_n[a]
1	$Zr(6\text{-H-SPy})_2(NMe_2)_2$ (**4a**)	30	0.21	n.d.	n.d.
2	$Zr(6\text{-H-SPy})_2(NMe_2)_2$ (**4a**)	0	0.11	n.d.	n.d.
3	$Zr(6\text{-H-SPy})_2(NMe_2)_2$ (**4a**)	−20	0.05	n.d.	n.d.
4	$Zr(6\text{-H-SPy})_2(NMe_2)_2$ (**4a**)	−40	<0.01	n.d.	n.d.
5	$Zr\{6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-SPy}\}_2(NMe_2)_2$ (**4b**)	60	6.7	0.51	180
6	$Zr\{6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-SPy}\}_2(NMe_2)_2$ (**4b**)	30	12	0.53	330
7	$Zr\{6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-SPy}\}_2(NMe_2)_2$ (**4b**)	0	16	5.0	36
8	$Zr\{6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-SPy}\}_2(NMe_2)_2$ (**4b**)	−20	8.2	2.0	100
9[b]	$Zr(6\text{-H-SPy})_4$ (**7**)	30	0.51	n.d.	n.d.
10[b]	$Zr(6\text{-H-SPy})_4$ (**7**)	0	0.34	n.d.	n.d.
11[b]	$Zr(6\text{-H-SPy})_4$ (**7**)	−20	0.18	n.d.	n.d.
12[b]	$Zr(6\text{-H-SPy})_4$ (**7**)	−40	0.093	n.d.	n.d.

Conditions: in toluene, ethylene pressure: 1 atm, time: 1 h, [Al]/[Zr] = 1000.
[a] Determined by GPC analysis in 1,2,4-trichlorobenzene at 140 °C calibrated with standard poly(styrene)s.
[b] Cocatalyst: MAO.

Table 6
Polymerization of ethylene catalyzed by the 6-phenyl-2-pyridinolate complex (**8**) activated with MMAO

Run	Complex	Temperature (°C)	Activity (kg/M-mol h atm)	$M_n/10^4$[a]	M_w/M_n[a]
1	$Ti(6\text{-Ph-OPy})_2(NMe_2)_2$ (**8**)	60	9.3	0.61	40
2	$Ti(6\text{-Ph-OPy})_2(NMe_2)_2$ (**8**)	30	3.8	1.3	75
3	$Ti(6\text{-Ph-OPy})_2(NMe_2)_2$ (**8**)	0	1.2	3.4	49
4	$Ti(6\text{-Ph-OPy})_2(NMe_2)_2$ (**8**)	−20	0.50	7.6	29

Conditions: in toluene, ethylene pressure: 1 atm, time: 1 h, [Al]/[Ti] = 1000.
[a] Determined by GPC analysis in 1,2,4-trichlorobenzene at 140 °C calibrated with standard poly(styrene)s.

Table 7
Polymerization of ethylene catalyzed by the substituted pyrimidinethiolate complex (**9**) activated with MMAO

Run	Complex	Temperature (°C)	Activity (kg/M-mol h atm)	$M_n/10^4$[a]	M_w/M_n[a]
1	$Ti(CF_3\text{-SPm})_2(NMe_2)_2$ (**9a**)	50	20	n.d.	n.d.
2	$Ti(CF_3\text{-SPm})_2(NMe_2)_2$ (**9a**)	30	21	1.8	41
3	$Ti(CF_3\text{-SPm})_2(NMe_2)_2$ (**9a**)	0	17	14	17
4	$Ti(CF_3\text{-SPm})_2(NMe_2)_2$ (**9a**)	−20	8.3	23	11
5	$Ti(4,6\text{-}Me_2\text{-SPm})_2(NMe_2)_2$ (**9b**)	60	2.2	0.83	73
6	$Ti(4,6\text{-}Me_2\text{-SPm})_2(NMe_2)_2$ (**9b**)	30	2.9	1.2	43
7	$Ti(4,6\text{-}Me_2\text{-SPm})_2(NMe_2)_2$ (**9b**)	0	4.1	5.0	41
8	$Ti(4,6\text{-}Me_2\text{-SPm})_2(NMe_2)_2$ (**9b**)	−20	3.4	4.8	40

Conditions: in toluene, ethylene pressure: 1 atm, time: 1 h, [Al]/[Ti] = 1000.
[a] Determined by GPC analysis in 1,2,4-trichlorobenzene at 140 °C calibrated with standard poly(styrene)s.

polymerization. Thus, the coordination of the sulfur atom to titanium substantially contributes to the high activities of the pyridinethiolate complexes.

Table 7 shows the results of ethylene polymerization by titanium bis(pyrimidinethiolate) complexes, **9a** and **9b**. The catalytic activity of the bis(pyrimidinethiolate) complexes was lower than that of the corresponding bis(pyridinethiolate) complex **3b**. The pyrimidinethiolate ligands should be more donating to the metal than the pyridinethiolate ligands, and this could make the pyrimidinethiolate complexes less active. This agrees with the observation that the pyrimidinethiolate complex with electron-withdrawing substituent **9a** showed higher activity than that with electron-donating substituent **9b**.

The polyethylenes obtained with these group 4 metal pyridinethiolate, quinolinethiolate, pyrimidinethiolate, and pyridinolate complexes had very broad molecular weight distributions, indicating multiplicity of active species in these systems. Fig. 4 shows GPC profiles of the polyethylenes produced by the $Ti\{6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-SPy}\}_2(NMe_2)_2$ (**3f**)/MMAO system

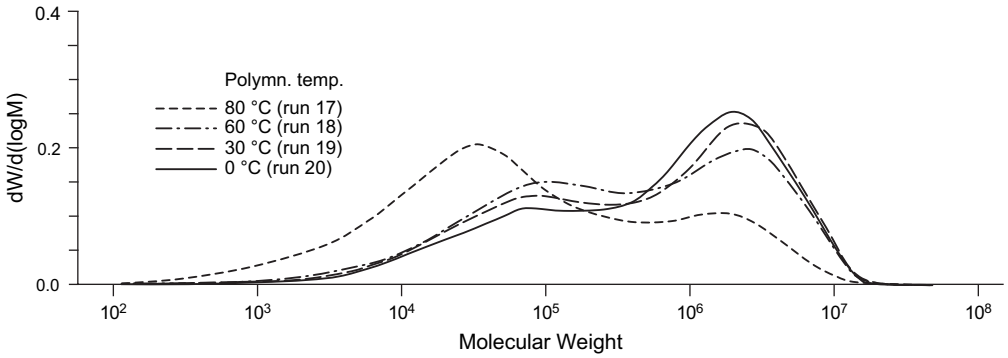


Fig. 4. GPC profiles of the polyethylenes produced by $Ti\{6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-SPy}\}_2(NMe_2)_2$ (**3f**)/MMAO (runs 17–20 in Table 4).

(runs 17–20 in Table 4) for example. Apparent bimodal distribution was observed, and the higher molecular weight fraction decreased at higher polymerization temperature. Taking into account the fact that the tetrakis(pyridinethiolate) complex **6**/MAO showed ethylene polymerization activity, we speculate that the pyridinethiolate ligand could be significantly labile in the presence of cocatalyst, which might result in generation of multiple active species, such as $[Ti(6\text{-}R\text{-}SPy)_2R']^+$ and $[Ti(6\text{-}R\text{-}SPy)R'_2]^+$ ($R' =$ propagating alkyl group).

3. Conclusion

A series of novel dimethylamido complexes of titanium and zirconium having pyridinethiolate, quinolinethiolate, pyridinolate, and pyrimidinethiolate ligands were prepared by the reaction of $M(NMe_2)_4$ (M = Ti, Zr) with the corresponding thiol or alcohol. X-ray analysis of $Ti(6\text{-}H\text{-}SPy)_2(NMe_2)_2$ (**3a**) revealed *cis*-configuration of the diamido moieties in the pseudo octahedral geometry. Molecular structures of $Ti(6\text{-}H\text{-}SPy)_4$ (**6**) and $Zr(6\text{-}H\text{-}SPy)_4$ (**7**) were also determined by X-ray crystallography to have triangular dodecahedral geometry. The catalytic behaviors of these complexes for ethylene polymerization were studied in the presence of MAO or MMAO as a cocatalyst. In the ethylene polymerization with the substituted pyridinethiolate complexes, the 6-aryl substituted pyridinethiolate complexes of titanium were found to exhibit particularly high catalytic activities, and the $Ti\{6\text{-}(C_6H_3\text{-}3,5\text{-}Me_2)\text{-}SPy\}_2(NMe_2)_2$ (**3f**)/MMAO system showed the highest activity (1200 kg/Ti-mol h atm) among these complexes. The pyridinolate complex **8** was much less active than the corresponding pyridinethiolate complex **3c**, indicating that interaction between sulfur and titanium is essential for high activities of the pyridinethiolate complexes. The activities of the bis(quinolinethiolate) complex and bis(pyrimidinethiolate) complexes were lower than those of the bis(6-aryl-2-pyridinethiolate) complexes. Thus, we developed new titanium pyridinethiolate complexes as unprecedented examples of highly active ethylene polymerization catalysts having anionic sulfur-donor ligands.

4. Experimental section

4.1. General considerations

All manipulations involving the treatment of air- and moisture-sensitive organometallic compounds were carried out by the use of standard Schlenk techniques under an argon atmosphere. *n*-Hexane, THF, toluene, and *n*-pentane were dried and deoxygenated by distillation over sodium benzophenone ketyl under an argon atmosphere. Dichloromethane, dichloromethane-d_2, and $CDCl_3$ were distilled under an argon atmosphere after drying over phosphorus pentoxide. Benzene-d_6 was dried over Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. 2-Pyridinethiol (**2a**) was purchased from Tokyo Kasei Co. 2-Bromo-6-methylpyridine and 2-pyridinol were obtained from Nacalai tesque. 2-Quinolinethiol and 4-trifluoromethyl-2-pyrimidinethiol were purchased from Aldrich Chem. Co. 4,6-Dimethyl-2-pyrimidinethiol was purchased from Acros Organics. PhLi was purchased from Kanto Chem. Co. MAO (PMAO-S, 3.15 M) and MMAO (MMAO-3A, 1.89 M) solutions in toluene were obtained from Tosoh Fine Chem. Co. High purity ethylene monomer was supplied by Sumitomo Seika Co.

The ^1H (400 or 270 MHz) and ^{13}C (100 or 67.5 MHz) NMR spectra in benzene-d_6, $CDCl_3$, and CD_2Cl_2 were measured on JEOL JNM-GSX400 or JEOL JNM-EX270 spectrometer. EI-MS and FAB-MS measurements were performed on a JEOL SX-102 spectrometer. All melting points of the complexes were measured in sealed tubes under an argon atmosphere and were not corrected. Gel permeation chromatographic (GPC) analyses were carried out at 140 °C using a Waters 150C liquid chromatograph system, connected to a SHODEX HT806M column, by Japan-Polyolefins Co. Ltd. 1,2,4-Trichlorobenzene was used as an eluent and the GPC columns were calibrated versus poly(styrene) standards.

4.2. Preparation of 6-Me-HSPy (*2b*)

A solution of 2-bromo-6-methylpyridine (5 g, 29.1 mmol) in propylene glycol was slowly added to anhydrous NaSH (8.15 g, 0.145 mol) in propylene glycol under reflux. After 10 h, the reaction mixture cooled to ambient temperature. The sodium bromide was removed by filtration and washed with 100 ml of ethanol. The filtrate, including washings, was evaporated to dryness in vacuo. The residue was dissolved in 200 ml of water and was neutralized with glacial acetic acid. The product was extracted with CH_2Cl_2 and the separated organic layer was concentrated under vacuum. The resulting precipitates were recrystallized from CH_2Cl_2/hexane (1/1) at −20 °C to give yellow crystals of **2b** in 72% yield, m.p. 150 °C. ^1H NMR ($CDCl_3$, 30 °C, 270 MHz): δ 13.11 (br, 1H, SH), 7.37 (d, $^3J_{HH} = 8.6$ Hz, 1H, 5-Py), 7.28 (t, 1H, 4-Py), 6.49 (d, $^3J_{HH} = 7.1$ Hz, 1H, 3-Py), 2.44 (s, 3H, Me). Anal. Calcd. for C_6H_7NS: C, 57.56; H, 5.64; N, 11.19. Found: C, 57.44; H, 5.55; N, 10.83. EI-MS: *m/z* 125.0 (M^+).

4.3. Preparation of 6-Ph-HSPy (*2c*)

To a suspension of 2-pyridinethiol (**2a**) (3.0 g, 26.99 mmol) in toluene (20 ml) was added a solution of PhLi in cyclohexane–diethylether (0.98 M, 60.6 ml, 59.37 mmol) at −78 °C. The reaction mixture immediately turned dark red. After stirring for 1 h, it was allowed to warm to room temperature, and stirred for additional 1 h. All volatiles were removed under reduced pressure. The residue was dispersed in toluene (120 ml), and the suspension was refluxed for 10 h. The solution was slowly poured into water (100 ml) and the separated water layer was neutralized with acetic acid, to precipitate a yellow powder of 6-Ph-HSPy (**2c**). The crude product was recrystallized from CH_2Cl_2/hexane (1/1) at −20 °C to give **2c** as brown microcrystals in 42% yield. ^1H NMR ($CDCl_3$, 30 °C, 400 MHz): δ 12.04 (br, 1H, SH), 7.63–7.24 (m, 7H, Ph, 3,5-Py), 6.84 (d, $^3J_{HH} = 7.1$ Hz, 1H, 4-Py). ^{13}C NMR (CD_2Cl_2, 30 °C, 100 MHz): δ 178.3, 149.2, 137.4, 131.7, 130.8, 129.3, 126.7,

112.0. Anal. Calcd. for $C_{11}H_9NS$: C, 70.55; H, 4.84; N, 7.48. Found: C, 69.82; H, 4.75; N, 7.35. EI-MS: *m/z* 187 (M^+).

4.4. Preparation of 6-(C_6H_4-4-Me)-HSPy (**2d**)

Compound **2d** was prepared from 2-pyridinethiol and Li(C_6H_4-4-Me) by the same procedure as described for **2c** and isolated as yellow microcrystals in 44% yield. ^{1}H NMR ($CDCl_3$, 30 °C, 400 MHz): δ 12.23 (br, 1H, HS), 7.48 (d, 2H, $^3J_{HH} = 8.2$ Hz, *o*-Ph), 7.41 (d, 1H, $^3J_{HH} = 8.6$ Hz, 3-Py), 7.32 (dd, 1H, 4-Py), 7.29 (d, 2H, $^3J_{HH} = 8.1$ Hz, *m*-Ph), 6.85 (d, 1H, $^2J_{HH} = 7.3$ Hz, 5-Py), 2.38 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 30 °C, 100 MHz): δ 177.9, 149.3, 141.2, 137.5, 131.2, 129.7, 129.1, 126.6, 111.7, 21.5. Anal. Calcd. for $C_{12}H_{11}NS$: C, 71.60; H, 5.51; N, 6.96. Found: C, 71.11; H, 5.43; N, 6.73. EI-MS: *m/z* 201 (M^+).

4.5. Preparation of 6-(C_6H_4-4-*t*-Bu)-HSPy (**2e**)

Compound **2e** was prepared from 2-pyridinethiol and Li(C_6H_4-4-*t*-Bu) by the same procedure as described for **2c** and isolated as yellow microcrystals in 42% yield. ^{1}H NMR ($CDCl_3$, 30 °C, 400 MHz): δ 10.77 (br, 1H, SH), 7.53 (s, 4H, *o*,*m*-Ph), 7.47 (d, 1H, $^3J_{HH} = 8.2$ Hz, 3-Py), 7.36 (dd, 1H, 4-Py), 6.85 (d, 1H, $^2J_{HH} = 7.4$ Hz, 5-Py), 1.35 (s, 9H, *t*-Bu). Anal. Calcd. for $C_{15}H_{17}NS$: C, 74.03; H, 7.04; N, 5.76. Found: C, 74.00; H, 7.01; N, 5.78. FAB-MS: *m/z* 243 (M^+).

4.6. Preparation of 6-(C_6H_3-3,5-Me_2)-HSPy (**2f**)

Compound **2f** was prepared from 2-pyridinethiol and Li(C_6H_3-3,5-Me_2) by the same procedure as described for **2c** and isolated as orange crystals in 16% yield. ^{1}H NMR ($CDCl_3$, 30 °C, 400 MHz): δ 11.11 (br, 1H, SH), 7.47 (d, $^3J_{HH} = 8.5$ Hz, 1H, 3-Py), 7.37 (t, 1H, 4-Py), 7.19 (s, 2H, *o*-Ph), 7.15 (s, 1H, *p*-Ph), 6.84 (d, $^3J_{HH} = 7.0$ Hz, 1H, 5-Py), 2.39 (s, 6H, 3,5-Me_2). ^{13}C NMR ($CDCl_3$, 30 °C, 100 MHz): δ 178.7, 149.1, 139.4, 137.5, 132.6, 132.1, 131.5, 124.1, 111.3, 67.9, 25.7, 21.4. Anal. Calcd. for $C_{13}H_{13}NS$: C, 72.52; H, 6.09; N, 6.51. Found: C, 72.33; H, 6.17; N, 6.35. EI-MS: *m/z* 215 (M^+).

4.7. Preparation of 6-Ph-HOPy (**2g**)

Compound **2g** was prepared from 2-pyridinol and PhLi by the same procedure as described for **2c** and isolated as yellow crystals in 37% yield. ^{1}H NMR ($CDCl_3$, 30 °C, 400 MHz): δ 12.24 (br, 1H, OH), 7.71 (d, $^3J_{HH} = 8.1$ Hz, 1H, 3-Py), 7.48 (m, 4H, 3-Py, *o*,*m*-Ph and 5-Py), 6.52 (d, $^3J_{HH} = 8.9$ Hz, 1H, *p*-Ph), 6.46 (d, $^3J_{HH} = 7.1$ Hz, 1H, 4-Py). Anal. Calcd. for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18; O. Found: C, 76.98; H, 5.45; N, 8.02. FAB-MS: *m/z* 171.6 $(M+H)^+$.

4.8. Preparation of Ti(6-H-SPy)$_2$(NMe_2)$_2$ (**3a**)

A solution of 2-pyridinethiol (**2a**) (188 mg, 1.69 mmol) in THF (20 ml) was added to a solution of Ti(NMe_2)$_4$ (189 mg, 0.845 mmol) dissolved in THF (20 ml) at −78 °C. The reaction mixture immediately turned into an orange solution. After stirring for 1 h, it was allowed to warm to room temperature, and stirred for additional 2 h. All volatiles were removed under reduced pressure. The residue was washed with hexane (5.0 ml × 2) and recrystallized from THF/ether (1/2) to give prismatic crystals suitable for X-ray diffraction (152 mg, 51%). ^{1}H NMR (C_6D_6, 30 °C, 400 MHz): δ 8.40 (d, $^3J_{HH} = 5.4$ Hz, 2H, 3-Py), 6.94 (d, $^3J_{HH} = 8.1$ Hz, 2H, 6-Py), 6.61 (t, 2H, 5-Py), 6.07 (t, 2H, 4-Py), 3.53 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6, 30 °C, 100 MHz): δ 172.3, 144.7, 136.9, 126.8, 116.5, 47.4. Anal. Calcd. for $C_{14}H_{20}N_4S_2Ti$: C, 47.19; H, 5.66; N, 15.72. Found: C, 47.67; H, 5.97; N, 15.31. EI-MS: *m/z* 356 (M^+).

4.9. Preparation of Ti(6-Me-SPy)$_2$(NMe_2)$_2$ (**3b**)

Complex **3b** was prepared from 6-Me-HSPy (**2b**) and Ti(NMe_2)$_4$ by the same procedure as described for **3a** and isolated as red crystals in 57% yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 7.22 (t, 2H, 4-Py), 6.85 (d, $^3J_{HH} = 8.5$ Hz, 2H, 5-Py), 6.55 (d, $^3J_{HH} = 7.5$ Hz, 2H, 3-Py), 3.48 (s, 12H, NMe_2), 2.45 (s, 6H, Me). ^{13}C NMR (CD_2Cl_2, 30 °C, 100 MHz): δ 171.4, 156.1, 136.4, 123.1, 117.0, 48.1, 22.0. Anal. Calcd. for $C_{16}H_{24}N_4S_2Ti$: C, 49.99; H, 6.29; N, 14.57. Found: C, 50.58; H, 6.55; N, 13.90. EI-MS: *m/z* 384 (M^+).

4.10. Preparation of Ti(6-Ph-SPy)$_2$(NMe_2)$_2$ (**3c**)

Complex **3c** was prepared from 6-Ph-HSPy (**2c**) and Ti(NMe_2)$_4$ by the same procedure as described for **3a** and isolated as red crystals in 55% yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 7.35 (t, 2H, 4-Py), 7.28 (t, 2H, *p*-Ph), 7.20 (d, $^3J_{HH} = 6.9$ Hz, 4H, *o*-Ph), 7.14 (t, 4H, *m*-Ph), 6.86 (d, $^3J_{HH} = 8.0$ Hz, 2H, 5-Py), 6.76 (d, $^3J_{HH} = 7.7$ Hz, 2H, 3-Py), 3.06 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6, 30 °C, 100 MHz): δ 172.8, 158.1, 138.9, 136.3, 128.1, 127.8, 127.2, 125.1, 117.3, 47.9. Anal. Calcd. for $C_{26}H_{28}N_4S_2Ti$: C, 61.41; H, 5.55; N, 11.02. Found: C, 61.71; H, 5.95; N, 10.77. EI-MS: *m/z* 508 (M^+).

4.11. Preparation of Ti{6-(C_6H_4-4-Me)-SPy}$_2$(NMe_2)$_2$ (**3d**)

Complex **3d** was prepared from 6-(C_6H_4-4-Me)-HSPy (**2d**) and Ti(NMe_2)$_4$ by the same procedure as described for **3a** and isolated as red crystals in 19% yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 7.40 (d, $^3J_{HH} = 8.0$ Hz, 4H, *o*-Ph), 7.37 (t, 2H, 4-Py), 7.11 (d, $^3J_{HH} = 7.8$ Hz, 4H, *m*-Ph), 6.93 (d, $^3J_{HH} = 7.6$ Hz, 2H, 5-Py), 6.81 (d, $^3J_{HH} = 7.8$ Hz, 2H, 3-Py), 3.50 (s, 12H, NMe_2), 2.33 (s, 6H, 4-Me). Anal. Calcd. for $C_{28}H_{32}N_4S_2Ti$: C, 62.67; H, 6.01; N, 10.44. Found: C, 62.83; H, 6.21; N, 10.15. EI-MS: *m/z* 536 (M^+).

4.12. Preparation of Ti{6-(C_6H_4-4-*t*-Bu)-SPy}$_2$(NMe_2)$_2$ (**3e**)

Complex **3e** was prepared from 6-(C_6H_4-4-*t*-Bu)-HSPy (**2e**) and Ti(NMe_2)$_4$ by the same procedure as described for **3a** and isolated as red crystals in 27% yield. ^{1}H NMR (CD_2Cl_2, 30 °C,

400 MHz): δ 7.34 (t, 2H, 4-Py), 7.14 (d, $^3J_{HH} = 7.8$ Hz, 4H, *o*- or *m*-Ph), 7.10 (d, $^3J_{HH} = 7.8$ Hz, 4H, *o*- or *m*-Ph), 6.94 (d, $^3J_{HH} = 8.1$ Hz, 2H, 5-Py), 6.74 (d, $^3J_{HH} = 7.6$ Hz, 2H, 3-Py), 2.96 (s, 12H, NMe_2), 1.25 (s, 18H, 4-*t*-Bu). Anal. Calcd. for $C_{34}H_{44}N_4S_2Ti$: C, 65.79; H, 7.14; N, 9.03. Found: C, 65.82; H, 7.30; N, 8.72. EI-MS: *m/z* 620 (M^+).

4.13. Preparation of Ti{6-(C_6H_3-3,5-Me_2)-SPy}$_2$(NMe_2)$_2$ (3f)

Complex **3f** was prepared from 6-(C_6H_3-3,5-Me_2)-HSPy (**2f**) and $Ti(NMe_2)_4$ by the same procedure as described for **3a** and isolated as red crystals in 31% yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 7.30 (t, 2H, 4-Py), 6.95 (s, 4H, *o*-Ph), 6.89 (s, 2H, *p*-Ph), 6.79 (d, $^3J_{HH} = 8.0$ Hz, 2H, 5-Py), 6.76 (d, $^3J_{HH} = 7.4$ Hz, 2H, 3-Py), 3.56 (s, 12H, NMe_2), 2.11 (s, 12H, 3,5-Me_2). Anal. Calcd. for $C_{30}H_{36}N_4S_2Ti$: C, 63.81; H, 6.43; N, 9.92. Found: C, 63.99; H, 6.70; N, 9.43. EI-MS: *m/z* 564 (M^+).

4.14. Preparation of Zr(6-H-SPy)$_2$(NMe_2)$_2$ (4a)

A solution of 2-pyridinethiol (**2a**) (205.7 mg, 1.85 mmol) in toluene (20 ml) was added to a solution of $Zr(NMe_2)_4$ (247.5 mg, 0.925 mmol) dissolved in toluene (20 ml) at −78 °C. The reaction mixture immediately turned into an orange solution. After stirring for 1 h, it was allowed to warm to room temperature, and stirred for additional 2 h. All volatiles were removed under reduced pressure. The residue was washed with hexane (5.0 ml × 2) and recrystallized from CH_2Cl_2/toluene (1/2) to give orange crystals of **4a** in 98% yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 8.09 (d, $^3J_{HH} = 4.4$ Hz, 2H, 3-Py), 7.31 (t, 2H, 5-Py), 7.05 (d, $^3J_{HH} = 8.3$ Hz, 2H, 6-Py), 6.66 (t, 2H, 4-Py), 3.07 (s, 12H, NMe_2). ^{13}C NMR (CD_2Cl_2, 30 °C, 100 MHz): δ 171.2, 145.3, 138.3, 127.9, 117.5, 42.0. Anal. Calcd. for $C_{14}H_{20}N_4S_2Zr$: C, 42.07; H, 5.04; N, 14.02. Found: C, 42.75; H, 5.53; N, 13.46. EI-MS: *m/z* 398 (M^+).

4.15. Preparation of Zr{6-(C_6H_3-3,5-Me_2)-SPy}$_2$(NMe_2)$_2$ (4b)

Complex **4b** was prepared from 6-(C_6H_3-3,5-Me_2)-HSPy (**2f**) and $Zr(NMe_2)_4$ by the same procedure as described for **4a** and isolated as orange crystals in 24% yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 7.21 (t, 2H, 4-Py), 6.93 (s, 4H, *o*-Ph), 6.79 (s, 2H, *p*-Ph), 6.69 (d, $^3J_{HH} = 8.0$ Hz, 2H, 5-Py), 6.67 (d, $^3J_{HH} = 7.6$ Hz, 2H, 3-Py), 2.95 (s, 12H, NMe_2), 2.16 (s, 12H, 3,5-Me_2). Anal. Calcd. for $C_{30}H_{36}N_4S_2Zr$: C, 59.26; H, 5.97; N, 9.21. Found: C, 59.66; H, 6.25; N, 8.79. EI-MS: *m/z* 606 (M^+).

4.16. Preparation of Ti(SQu)$_2$(NMe_2)$_2$ (5)

Complex **5** was prepared from 2-quinolinethiol and $Ti(NMe_2)_4$ by the same procedure as described for **3a** and isolated as red crystals in 42% yield. ^{1}H NMR (C_6D_6, 30 °C, 400 MHz): δ 9.46 (br, 2H, Qu), 7.33 (t, 2H, Qu), 7.16 (d, $^3J_{HH} = 8.7$ Hz, 2H, Qu), 6.95 (d, $^3J_{HH} = 8.3$ Hz, 4H, Qu), 6.81 (t, 2H, Qu), 3.60 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6, 30 °C, 100 MHz): δ 175.4, 145.9, 136.2, 130.2, 128.6, 126.8, 125.2, 124.6, 124.2, 48.4. Anal. Calcd. for $C_{22}H_{24}N_4S_2Ti$: C, 57.89; H, 5.30; N, 12.27. Found: C, 58.27; H, 5.57; N, 11.82. EI-MS: *m/z* 456 (M^+).

4.17. Preparation of Ti(6-H-SPy)$_4$·THF (6)

A solution of 2-pyridinethiol (**2a**) (159.4 mg, 1.43 mmol) in THF (20 ml) was added to a solution of $Ti(NMe_2)_4$ (120 mg, 0.36 mmol) dissolved in THF (20 ml) at −78 °C. The reaction mixture immediately turned into an orange solution. After stirring for 12 h, it was allowed to warm to room temperature, and stirred for additional 2 h. All volatiles were removed under reduced pressure. The residue was recrystallized from THF to give rectangular crystals suitable for X-ray diffraction (125 mg, 72%). ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 8.09 (d, $^3J_{HH} = 4.7$ Hz, 4H, 6-Py), 7.38 (t, 4H, 4-Py), 6.86 (m, 8H, 3, 5-Py), 3.59 (t, 4H, THF), 1.73 (t, 4H, THF). ^{13}C NMR (C_6D_6, 30 °C, 100 MHz): δ 173.5, 144.2, 138.5, 128.3, 118.3, 68.2 (THF), 26.1 (THF). Anal. Calcd for $C_{20}H_{16}N_4S_4Ti$·THF: C, 51.42; H, 4.31; N, 9.99. Found: C, 51.25; H, 4.27; N, 9.91.

4.18. Preparation of Zr(6-H-SPy)$_4$·THF (7)

Complex **7** was synthesized and isolated as orange crystals in 68% yield in a similar manner to **6**. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 7.93 (d, $^3J_{HH} = 4.6$ Hz, 4H, 6-Py), 7.83 (t, 4H, 4-Py), 7.00 (d, $^3J_{HH} = 8.1$ Hz, 4H, 3-Py), 6.81 (t, 4H, 5-Py) 3.59 (t, 4H, THF), 1.73 (t, 4H, THF). ^{13}C NMR (CD_2Cl_2, 30 °C, 100 MHz): δ 172.8, 143.4, 137.7, 127.5, 117.6, 68.2 (THF), 26.1 (THF). Anal. Calcd. for $C_{20}H_{16}N_4S_4Zr$·THF: C, 47.73; H, 4.01; N, 9.28. Found: C, 47.58; H, 3.91; N, 9.37. EI-MS: *m/z* 530 (M^+).

4.19. Preparation of Ti(6-Ph-OPy)$_2$(NMe_2)$_2$ (8)

Complex **8** was prepared from 6-Ph-HOPy (**2g**) and $Ti(NMe_2)_4$ by the same procedure as described for **3a** and isolated as red crystals in 62% (162.4 mg) yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 7.43 (m, 4H, *o*-Ph), 7.40 (t, 2H, 4-Py), 7.26 (t, 4H, *m*-Ph), 7.24 (t, 2H, *p*-Ph), 6.70 (d, $^3J_{HH} = 7.5$ Hz, 2H, 5-Py), 6.16 (d, $^3J_{HH} = 8.3$ Hz, 2H, 3-Py), 3.20 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6, 30 °C, 100 MHz): δ 171.1, 154.5, 140.1, 137.6, 128.1, 127.5, 127.2, 111.0, 107.6, 46.2. Anal. Calcd. for $C_{26}H_{28}N_4O_2Ti$: C, 65.55; H, 5.92; N, 11.76. Found: C, 65.67; H, 6.19; N, 11.08. EI-MS: *m/z* 476 (M^+).

4.20. Preparation of Ti(CF_3-SPm)$_2$(NMe_2)$_2$ (9a)

Complex **9a** was prepared from 4-trifluoromethyl-2-pyrimidinethiol and $Ti(NMe_2)_4$ by the same procedure as described for **3a** and isolated as red crystals in 44% yield. ^{1}H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 8.62 (d, $^3J_{HH} = 5.1$ Hz, 2H,

4-Pm), 7.00 (d, $^3J_{HH} = 5.4$ Hz, 2H, 5-Pm), 3.46 (s, 12H, NMe_2). ^{13}C NMR (CD_2Cl_2, 30 °C, 100 MHz): δ 180.8, 157.4, 154.9, 118.9, 128.6, 110.6, 47.5. Anal. Calcd. for $C_{14}H_{16}F_6N_6S_2Ti$: C, 34.02; H, 3.26; N, 17.00. Found: C, 34.72; H, 3.59; N, 16.53. EI-MS: *m/z* 494 (M^+).

4.21. Preparation of Ti(4,6-Me$_2$-SPm)$_2$(NMe$_2$)$_2$ (**9b**)

Complex **9b** was prepared from 4,6-dimethyl-2-pyrimidinethiol and $Ti(NMe_2)_4$ by the same procedure as described for **3a** and isolated as red crystals in 42% yield. ^1H NMR (CD_2Cl_2, 30 °C, 400 MHz): δ 6.40 (s, 2H, 5-Pm), 3.42 (s, 12H, NMe_2), 2.27 (s, 12H, 4,6-Me_2). ^{13}C NMR (CD_2Cl_2, 30 °C, 100 MHz): δ 179.2, 126.8, 116.4, 115.1, 68.1, 48.6, 32.0, 26.0, 23.9, 23.1, 14.3. Anal. Calcd. for $C_{16}H_{26}N_6S_2Ti$: C, 46.37; H, 6.32; N, 20.28. Found: C, 46.90; H, 6.55; N, 19.77. EI-MS: *m/z* 414 (M^+).

4.22. Polymerization of ethylene

A typical procedure: To a suspension of **3a** (5 μmol) in toluene (11 ml) was added 3.15 M solution of MAO in toluene (1.59 ml, 1000 equiv.) via syringe at −78 °C. The reaction mixture was degassed under vacuum and then allowed to warm to room temperature to become a clear solution. After the mixture was stirred at room temperature for 10 min, ethylene (atmospheric pressure) was introduced at the prescribed temperature. The vessel was kept at that temperature for 1 h and then the polymerization was quenched by addition of HCl–MeOH. The resulting white polymer was collected by filtration and dried in vacuum.

4.23. Crystallographic data collections and structure determinations of **2c**, **2d**, **3a**, **6** and **7**

Crystals of **2c** and **2d** suitable for X-ray diffraction studies were mounted on a glass fiber. The measurements of **2c** and **2d** were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$). Relevant crystal and data statistics are summarized in Table 8. The unit cell parameters and the orientation matrix at 25 °C were determined by a least-squares fit to 2θ values of 25 strong higher reflections for these compounds. Three standard reflections were chosen and monitored every 150 reflections. Empirical absorption correction was carried out on the basis of an azimuthal scan. Both **2c** and **2d** showed no significant intensity decay during the data collection. The structures of **2c** and **2d** were solved by direct methods (SHELXS-97) [39] and refined by full-matrix least squares refinement (SHELXL-97) [39]. The positions of all non-hydrogen atoms were found from difference Fourier electron density maps and refined anisotoropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and kept fixed. These calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

Crystals of **3a**, **6** and **7** suitable for X-ray diffraction studies were mounted on a cryoloop. The measurements of **3a**, **6** and **7** were made on a Rigaku R-AXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$) at 193 K. Relevant crystal and data statistics are summarized in Table 9. Indexing was performed from one oscillation, which was exposed for 5.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A symmetry-related absorption correction using the program ABSCOR [40] was applied. The

Table 8
Crystal data and collection parameters for **2c** and **2d**

	2c	**2d**
Formula	$C_{11}H_9NS$	$C_{12}H_{11}NS$
Formula weight	187.25	201.28
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$ (#14)	$C2/c$ (#15)
a, Å	10.129(2)	14.2237(17)
b, Å	14.1276(15)	11.3747(19)
c, Å	6.8050(12)	13.623(4)
β, deg	103.907(16)	108.983(18)
V, Å^3	945.2(3)	2084.2(7)
Z	4	8
D_{calcd}, g/cm^3	1.316	1.283
$F(000)$	392	848
μ [Mo Kα], cm^{-1}	2.89	2.67
Temp, K	298(2)	298(2)
Scan speed, deg/min	16.0	16.0
Scan width, deg	$1.63 + 0.30 \tan\theta$	$1.68 + 0.30 \tan\theta$
$2\theta_{max}$, deg	55.0	55.0
Unique data (R_{int})	2671 (0.2936)	2874 (0.0361)
No. of refl. (total)	2181	2396
No. of refl. (unique)	1372	1574
No. of variables	119	128
w$R2$	0.1771	0.1826
R ($I > 2.0\sigma(I)$)	0.0616	0.0555
GOF	1.048	1.053

Table 9
Crystal data and collection parameters for **3a**, **6** and **7**

	3a	**6**	**7**
Formula	$C_{14}H_{20}N_4S_2Ti$	$C_{24}H_{24}N_4OS_4Ti$	$C_{24}H_{24}N_4OS_4Zr$
Formula weight	356.36	560.61	603.93
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$ (#14)	$Pna2_1$ (#33)	$Pna2_1$ (#33)
a, Å	9.3779(12)	22.453(2)	22.3074(6)
b, Å	12.8808(15)	13.1997(9)	13.2458(3)
c, Å	14.7690(14)	8.6460(7)	8.5907(3)
β, deg	101.181(3)	–	–
V, Å^3	1750.2(3)	2562.4(4)	2538.37(13)
Z	4	4	4
D_{calcd}, g/cm^3	1.352	1.453	1.580
$F(000)$	744	1160	1232
μ [Mo Kα], cm^{-1}	7.26	6.85	7.88
Temperature, K	193(2)	193(2)	193(2)
No. of images	56	74	44
Exposure time (min/deg)	5.0	5.0	6.7
$2\theta_{min}$, $2\theta_{max}$, deg	4.8, 54.9	4.8, 54.9	4.8, 55.0
Unique data (R_{int})	7338 (0.1237)	17160 (0.1085)	22264 (0.1450)
No. of refl. (total)	4021	5822	5634
No. of refl. (unique)	1046	3480	3497
No. of variables	194	306	308
w$R2$	0.0943	0.1177	0.0539
R ($I > 2.0\sigma(I)$)	0.0634	0.0583	0.0377
GOF	0.725	0.956	0.708

data were corrected for Lorentz and polarization effects. The structures of these complexes were solved by direct methods (SHELXS-86 [41] for **3a**, SIR-92 [42] for **6**, and SHELXS-97 [39] for **7**), expanded using Fourier techniques (DIRDIF 94) [43], and refined by full-matrix least squares refinement (SHELXL-97) [39]. The positions of all non-hydrogen atoms for the complex were found from difference Fourier electron density maps and refined anisotoropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and kept fixed. These calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

Crystallographic data for the structural analysis of **2c**, **2d**, **3a**, **6** and **7** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. are 606075, 606076, 606077, 606078, and 606079, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: (int code) +44 1223 336 033 or email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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