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Syntheses of titanium μ-arylimido and μ-pyridylimido complexes bearing (un)substituted cyclopentadienyl ligand

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Abstract

The reactions of $(\eta^5\text{-}C_5H_4CH_2CH_2Br)TiBr_3$, $(\eta^5\text{-}C_5H_4CH_2CH_2OCH_3)TiCl_3$, $(\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}cyclo\text{-}C_4H_7O)TiCl_3$ and $(\eta^5\text{-}C_5H_5)TiCl_3$ with an equivalent of 2-$MeOC_6H_4NHLi$ in the presence of Et_3N afford μ-arylimido complexes, $[(\eta^5\text{-}C_5H_4CH_2CH_2Br)Ti(Br)(\mu\text{-}NC_6H_4OCH_3\text{-}2)]_2$ (**1**), $[(\eta^5\text{-}C_5H_4CH_2CH_2OCH_3)Ti(Cl)(\mu\text{-}NC_6H_4OCH_3\text{-}2)]_2$ (**2**), $[(\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}cyclo\text{-}C_4H_7O)Ti(Cl)(\mu\text{-}NC_6H_4\text{–}OCH_3\text{-}2)]_2$ (**3**), $[(\eta^5\text{-}C_5H_5)Ti(Cl)(\mu\text{-}NC_6H_4OCH_3\text{-}2)]_2$ (**4**), which include intramolecular titanium and oxygen coordination. Complex **4** can also be obtained by reaction of the $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with 2-$MeOC_6H_4NHLi$. Meanwhile refluxing of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with an equivalent of 2-$Me_2NC_6H_4NMg\cdot THF$ in toluene gives another μ-arylimido complex, $[(\eta^5\text{-}C_5H_5)Ti(Cl)(\mu\text{-}NC_6H_4NMe_2\text{-}2)]_2$, which contains intramolecular titanium and nitrogen coordination. In addition, the analogous reactions of the above substituted half-sandwich Cp titanium complexes with PhNHLi in the presence of Et_3N lead to $[(\eta^5\text{-}C_5H_4CH_2CH_2Br)Ti(Br)(\mu\text{-}NPh)]_2$, $[(\eta^5\text{-}C_5H_4CH_2CH_2OCH_3)Ti(Cl)(\mu\text{-}NPh)]_2$. The addition of 2-$MeC_6H_4NHLi$ to $(\eta^5\text{-}C_5H_4CH_2CH_2OCH_3)TiCl_3$ and $(\eta^5\text{-}C_5H_5)TiCl_3$ affords imido derivatives $[(\eta^5\text{-}C_5H_5)Ti(Cl)(\mu\text{-}NC_6H_4CH_3\text{-}2)]_2$ and $[(\eta^5\text{-}C_5H_4CH_2CH_2OCH_3)Ti(Cl)(\mu\text{-}NC_6H_4CH_3\text{-}2)]_2$. $[(\eta^5\text{-}C_5H_5)Ti(Cl)(\mu\text{-}NC_6H_3Me_2\text{-}2,6)]_2$ is prepared by refluxing of $(\eta^5\text{-}C_5H_5)TiCl_3$ and 2,6-$Me_2C_6H_3NMg\cdot THF$ in toluene. The titanium μ-pyridylimido complexes, $[(\eta^5\text{-}C_5H_5)Ti(Cl)(\mu\text{-}NPy\text{-}2)]_2$, $[(\eta^5\text{-}C_5H_4CH_2CH_2OCH_3)Ti(Cl)(\mu\text{-}NPy\text{-}2)]_2$ and $[(\eta^5\text{-}C_5H_4CH_2CH_2Br)Ti(Br)(\mu\text{-}NPy\text{-}2)]_2$, are synthesized by reactions of the above corresponding half sandwich Cp titanium complexes with an equivalent of 2-PyNHLi in the presence of Et_3N, respectively. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with $a = 9.942(2)$, $b = 10.057(3)$, $c = 8.457(2)$ Å, $\alpha = 111.28(2)$, $\beta = 106.71(2)$, $\gamma = 98.12(2)°$, $V = 725.5(4)$ Å^3, $Z = 2$. The catalytic activity and selectivity of compound **4** for the styrene polymerization is also investigated.

Keywords: Titanium; Imido; Pyridyl; Intramolecular coordination; Crystal structure

1. Introduction

Organoimido complexes of the transition metals have attracted considerable interest, particularly those of the electrophilic early transition metals of Group IV. Such complexes have shown potential in both alkane and arene C–H bond activation [1] as well as 2 + 2 cycloadditions [2], catalytic amination of alkynes [3] and adduct chemistry [1c,d,2a,4].

Titanium bridging imido complexes are still comparatively scarce. The first example was reported by Teuben and co-workers [5]. They used $CpTiCl_3$ (Cp=η^5-C_5H_5) in reaction with $Me_3SiN(H)R$ (R = Et, Pr^i, Bu^t, Ph) to yield the amido complexes $CpTi(Cl)_2N(H)R$, which reacted further by HCl abstraction to give the corresponding centrosymmetric binuclear imido complexes $[Cp(Cl)Ti(\mu\text{-}NR)]_2$ (Scheme 1).

Power and co-workers [6] used organomagnesium compound, $(PhNMg\cdot THF)_6$, as a transfer agent for the imido group NPh to a transition-metal center to give the corresponding metal imido complex; particularly they reacted Cp_2TiCl_2 with $(PhNMg\cdot THF)_6$ to afford a asymmetric μ-phenylimido complex $(\eta^5\text{-}C_5H_5)(Cl)Ti(\mu\text{-}NPh)_2Ti(\eta^5\text{-}C_5H_5)_2$ (Scheme 1).

To provide for systematic studies of such compounds, we set out to develop general, high-yield routes to bridging imido species of titanium. In this paper, we report the preparation of bridging imido complexes of

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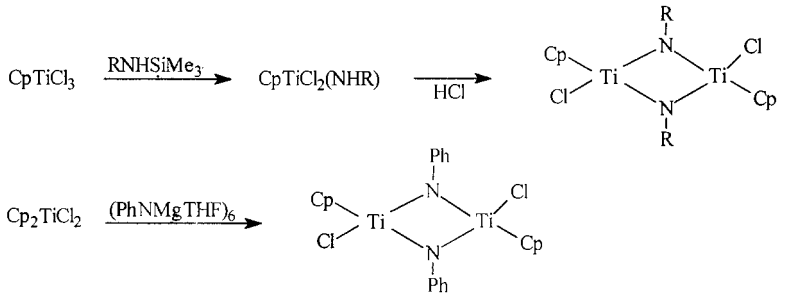


Scheme 1.

titanium bearing (un)substituted cyclopentadienyl. We found that in some of such complexes, there is intramolecular coordination between O and N of substituents and central metal. In this paper, we also report the preparation of titanium μ-pyridylimido complexes as the first example of titanium bridging imido complexes containing a heterocyclic group. As a part of this study, the molecular structure of the bridging imido complex $[(\eta^5\text{-}C_5H_4CH_2CH_2Br)Ti(Br)(\mu\text{-}NC_6H_4OCH_3\text{-}2)]_2$ (**1**) has been determined, and the catalytic behavior of the bridging imido species $[(\eta^5\text{-}C_5H_5)Ti(Cl)(\mu\text{-}NC_6H_4OCH_3\text{-}2)]_2$ (**4**) has been investigated.

2. Results and discussion

2.1. Syntheses of titaniumμ–arylimido complexes with intramolecular coordination

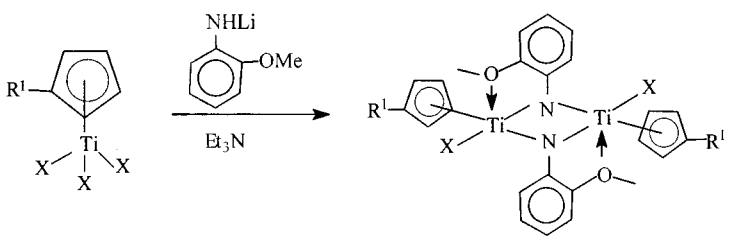
Treatment of $(\eta^5\text{-}C_5H_4CH_2CH_2Br)TiBr_3$, $(\eta^5\text{-}C_5H_4\text{-}CH_2CH_2OCH_3)TiCl_3$, $(\eta^5\text{-}C_5H_4\text{-}CH_2\text{-}cyclo\text{-}C_4H_7O)\text{-}TiCl_3$ and $(\eta^5\text{-}C_5H_5)TiCl_3$ with an equivalent of 2-$MeOC_6H_4NHLi$ at -20°C in the presence of Et_3N, gives the μ-arylimido complexes **1**–**4**, with intramolecular coordination between oxygen and titanium, as dark-red crystals (Scheme 2).

However, by refluxing of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with an equivalent of 2-$MeOC_6H_4NHLi$ in the presence of Et_3N, a dark-red solid is also afforded, which is characterized as **4**, the same product as is produced by treatment of $(\eta^5\text{-}C_5H_5)TiCl_3$ with an equivalent of 2-$MeOC_6H_4NHLi$ in the presence of Et_3N (Scheme 3). This result is quite different from the analogous experiment of Power and co-workers [6], and indicates the abstraction of cyclopentadiene.

Complexes **1**–**4** are very sensitive to air and moisture, and have good solubility in toluene, tetrahydrofuran and chlorinated solvents, but poor solubility in ether and hexane.

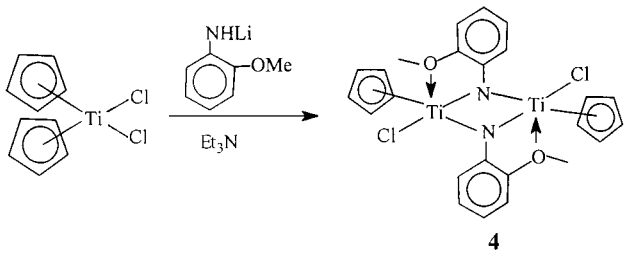
The synthetic process of **1**–**4** may involve formation of an amide precursor followed by an amide abstraction step via deprotonation to give imido species [5].

Complexes **1**–**4** are characterized by spectral and elemental analyses. From the ^{1}H-NMR spectra, significant downfield shifts (ca. 0.4 ppm) are observed for the signals of the methoxyl groups linked to aryl rings compared with the analogous resonance for 2-$MeOC_6H_4NH_2$ in the same deuterated solvent. These indicate the presence of intramolecular coordination between oxygen atoms attached to aryl rings and central metals. Meanwhile the upfield shifts for the signals of methyl and methylene groups linked to cyclopentadienyl in **2** and **3** indicate the absence of coordination



1 $R^1 = BrCH_2CH_2$ X=Br
2 $R^1 = CH_3OCH_2CH_2$ X=Cl
3 R^1 =cyclo-C_4H_7O-CH_2 X=Cl
4 R^1 =H X=Cl

Scheme 2.



Scheme 3.

between oxygen atoms of side chains and central metals, although there is chelation of the oxygen atom to the titanium center in (η^5-$C_5H_4CH_2CH_2OCH_3$)$TiCl_3$ and (η^5-C_5H_4–CH_2-*cyclo*-C_4H_7O)$TiCl_3$ [7].

Complex **1** is also determined by X-ray diffraction; the single-crystal structure is shown in Fig. 1, selected bond lengths and angles are given in Table 1. It is a dimer with the titanium centers linked by bridging arylimido groups giving a central Ti_2N_2 heterocyclic ring. Each titanium atom is bound to an (η^5-$C_5H_4CH_2CH_2Br$) ring and a Br atom. The Ti···Ti distance (2.927(3) Å) is unusually short for a binuclear titanium (IV) complex, and similar distances have been observed in the related species [6,8]. Both Ti–N bond lengths for **1** are in the range reported for other titanium–μ imido compounds; so are the Ti–N–Ti and N–Ti–N angles. However, both Ti–N bond distances differ slightly from each other, indicating the bridging μ-imido ligands may be bound asymmetrically. The Ti–O bond length of 2.348(7) is 1.33 Å shorter than the sum of the van der Waals radii (3.68 Å) [9], indicating a strong interaction between Ti and O.

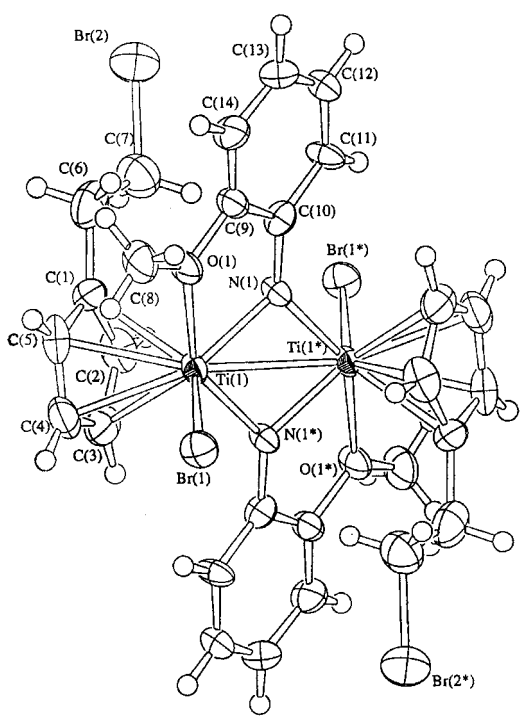


Fig. 1. Molecular structure of compound **1**.

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

Bond lengths			
Ti(1)···Ti(1*)	2.927(3)	Ti(1)–C(1)	2.40(1)
Ti(1)–N(1)	1.969(6)	Ti(1)–C(2)	2.36(1)
Ti(1)–N(1*)	1.908(7)	Ti(1)–C(3)	2.39(1)
Ti(1)–O(1)	2.348(7)	Ti(1)–C(4)	2.385(1)
Ti(1)–Br(1)	2.537(2)	Ti(1)–C(5)	2.398(1)
N(1)–C(10)	1.37(1)		
Bond angles			
Ti(1)–N(1)–Ti(1*)	98.0(3)	Ti(1)–N(1)–C(10)	123.8(6)
N(1)–Ti(1)–N(1*)	82.0(3)	Br(1)–Ti(1)–N(1*)	92.0(2)
Ti(1)–O(1)–C(8)	130.6(5)	Br(1)–Ti(1)–N(1)	120.2(2)
Ti(1)–O(1)–C(9)	112.4(6)		

Having prepared the titanium μ-imido compounds with intramolecular coordination between Ti and O atom, it was decided to synthesize titanium imido complexes with intramolecular coordination between the Ti and N atom. When (η^5-C_5H_5)$TiCl_3$ is treated with an equivalent of 2-$Me_2NC_6H_4NMg$(THF) in refluxing toluene, a dark-red solid is isolated, which is identified spectroscopically as the dimer μ-imido product **5** (Scheme 4).

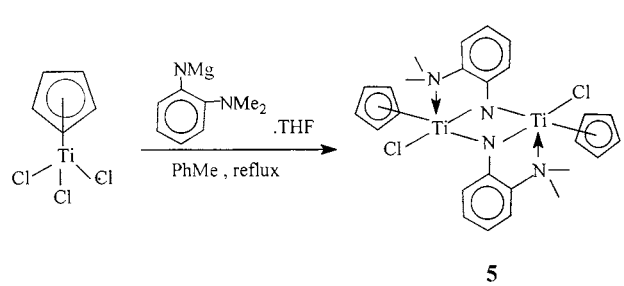
The ^{1}H-NMR spectrum of **5** in $CDCl_3$ shows a significant downfield shift (ca. 0.5 ppm) for the signal of the methyl groups attached to nitrogen (δ 2.89 ppm) in comparison with the analogous resonance for 2-$Me_2NC_6H_4NH_2$ (δ 2.35 ppm). On the basis of this, we propose that there is intramolecular coordination between nitrogen atoms and central metals in compound **5**.

The attempt to prepare similar complexes to **5** containing a substituted cyclopentadienyl was unsuccessful due to steric effects.

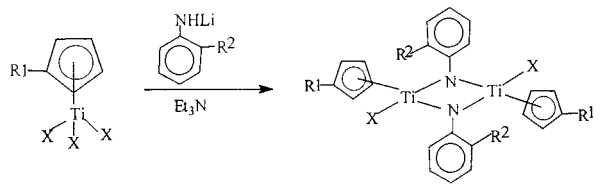
2.2. Syntheses of titanium μ-arylimido complexes containing (un)substituted cyclopentadienyl

Treatment of corresponding substituted Cp titanium trihalides with an equivalent of PhNHLi or 2-MeC_6H_4NHLi at -20°C in the presence of Et_3N gave μ-arylimido complexes **6**–**9** as dark-red crystals (Scheme 5).

Compounds **6**–**9** are more sensitive to air and moisture than compounds **1**–**4**, but have similar solubility in

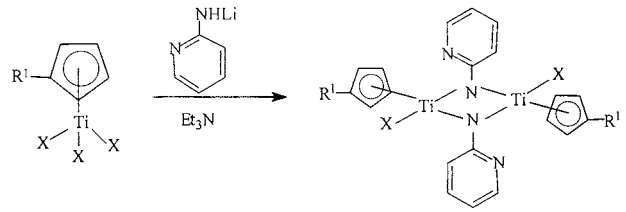


Scheme 4.



6 R1=$BrCH_2CH_2$ R2=H X=Br
7 R1=$CH_3OCH_2CH_2$ R2=H X=Cl
8 R1=H R2=CH_3 X=Cl
9 R1=$CH_3OCH_2CH_2$ R2=CH_3 X=Cl

Scheme 5.



11 R1=H X=Cl
12 R1=$CH_3OCH_2CH_2$ X=Cl
13 R1=$BrCH_2CH_2$ X=Br

Scheme 7.

toluene, tetrahydrofuran and chlorinated solvents. However, **7** and **9** are intermediately soluble in hexane.

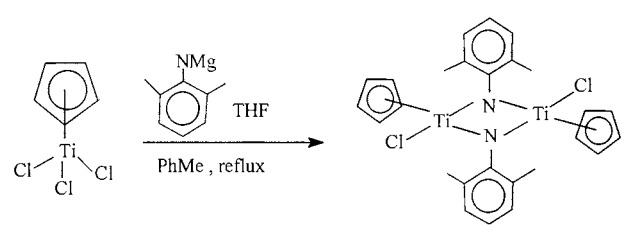
An interesting feature in the ^{1}H-NMR spectra of **7** and **9** in $CDCl_3$ is the upfield shifts (ca. 0.2–0.3 ppm) for the signals of the methyl groups attached to oxygen atoms (δ 3.21, 3.12 ppm) compared with the analogous resonance for (η^5-$C_5H_4CH_2CH_2OCH_3$)$TiCl_3$, (δ 3.43 ppm) in the same deuterated solvent. Even more significant is the shifts to upfield (ca. 0.3–0.5 ppm) of the signals for the methylene groups linked to oxygen atoms (δ 3.39, 3.18 ppm) which are comparable to the value in (η^5-$C_5H_4CH_2CH_2OCH_3$)$TiCl_3$, (δ 3.67 ppm). These differences indicate an important change in the environment of the oxygen atoms. Therefore, we propose that there is no intramolecular coordination between oxygen atoms of side chains and central metals in **7** and **9** although there is chelation of the oxygen atom to the titanium center in the starting material (η^5-$C_5H_4CH_2CH_2OCH_3$)$TiCl_3$ [7].

Refluxing (η^5-C_5H_5)$TiCl_3$ with an equivalent of 2,6-$Me_2C_6H_3NMg$(THF) in a solution of toluene affords titanium imido complex **10** as a dark-red solid in high yield (Scheme 6).

We even tried to synthesize compound **10** by treating (η^5-C_5H_5)$TiCl_3$ with an equivalent of 2,6-$Me_2C_6H_3$-NHLi in the presence of Et_3N, but no pure product was obtained because of separation problems.

2.3. Syntheses of titanium μ-pyridylimido complexes containing (un)substituted cyclopentadienyl

Treatment of the above corresponding substituted Cp titanium trihalides with an equivalent of 2-PyNHLi (Py = pyridyl), which is prepared by the reaction of 2-aminopyridine with *n*-BuLi in THF, at −20°C in the presence of Et_3N, respectively, gives μ-pyridylimido complexes **11**–**13** in good yields as dark-red crystals (Scheme 7).



10

Scheme 6.

Complexes **11**–**13** are more sensitive to air and moisture than μ-arylimido complexes. However, they have similar solubility to **1**–**4**.

Complexes **11**–**13** are characterized by spectral and elemental analyses. Upfield shifts of signals of the methyl and methylene groups attached to oxygen atoms in the ^{1}H-NMR spectra of **12** in $CDCl_3$ are also observed. Therefore, there is no intramolecular coordination between oxygen atoms of side chains and central metals in **12**. In addition, a slightly change of proton signals for the pyridyl in **11**–**13** compared to the 2-aminopyridine is also observed.

2.4. Styrene polymerization study of compound 4

A preliminary styrene polymerization of the typical compound **4** activated by methylaluminoxane (MAO) shows **4**–MAO has catalytic activity of 9.0×10^4 g of PS/(mol of Ti · mol of S · h) (S = styrene, PS = polystyrene) and 64.2% of the PS has syndiotactic structure (s-PS, insoluble in refluxing 2-butanone) under the conditions Al–Ti = 2000 and T_p = 50°C. In comparison, under the same conditions, (η^5-C_5H_5)$TiCl_3$–MAO has activity of 2.1×10^7 g of PS/(mol of Ti·mol of S·h) with 98.3% yield of s-PS.

3. Conclusions

The work described in this paper represents two new approaches to the syntheses of μ-arylimido and μ-pyridylimido complexes via treatment of (un)substituted cyclopentadienyl titanium complexes with ArNHLi–Et_3N, PyNHLi–Et_3N or ArNMg·THF, respectively. Supposing there are coordinatable atoms, such as oxygen and nitrogen, in the *ortho*-position of aryl, μ-arylimido complexes containing intramolecular coordination are given.

4. Experimental

4.1. General considerations

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents (THF, toluene, and *n*-hexane) were dried over the sodium–benzophenone ketyl. Halogenated solvents were distilled from P_2O_5. $C_6H_5NH_2$, 2-$MeOC_6H_4NH_2$, 2-$MeC_6H_4NH_2$, 2,6-$Me_2C_6H_3NH_2$ were distilled from CaH_2 prior to use. 2-$Me_2NC_6H_4NH_2$ was prepared by the reaction of 2-$O_2NC_6H_4NMe_2$ with Fe–HCl. 2-Aminopyridine was available commercially and used as received. *n*-Bu_2Mg was prepared according to the Kamienski method [10]. (η^5-C_5H_5)$TiCl_3$ [11], (η^5-$C_5H_4CH_2CH_2Br$)$TiBr_3$ [12], (η^5-$C_5H_4CH_2CH_2OCH_3$)-$TiCl_3$, (η^5-C_5H_4-CH_2-*cyclo*-C_4H_7O)$TiCl_3$ [7] and (η^5-C_5H_5)$_2TiCl_2$ [13] were prepared according to literature procedures. ^{1}H-NMR spectra were measured on a Gemini-300 NMR Spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. Mass spectra were performed on a Hitachi-80 Mass Spectrometer. IR spectra were recorded on a Magna-IR550 IR Spectrometer.

4.2. Preparation of 2-$MeOC_6H_4NHLi$

To a solution of 4.43 g (36 mmol) of *o*-anisidine in 50 ml of *n*-hexane, 22.5 ml (1.6 M in *n*-hexane, 36 mmol) of *n*-BuLi was added dropwise at 0°C. A white precipitate appeared immediately. Then the reaction mixture was stirred for 2 h at room temperature (r.t.). After filtration of the mixture, the residue was washed with 3×25 ml of *n*-hexane, and 4.3 g of white solid was given in 93% yield.

4.3. Preparation of **1**

To a solution of 0.5 g (1.1 mmol) of (η^5-$C_5H_4CH_2CH_2Br$)$TiBr_3$ in 50 ml of THF, 0.17 g (1.3 mmol) of 2-$MeOC_6H_4NHLi$ in 10 ml of THF was added dropwise at -20°C. A rapid color change from orange to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.13 g (1.3 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Dark-red crystals (0.15 g) were obtained upon slow cooling to -20°C (69% yield based on Ti). M.p. 132°C. Anal. Calc. for $C_{28}H_{30}Br_4N_2O_2Ti_2$: C, 39.94; H, 3.59; N, 3.33. Found: C, 39.95; H, 3.82; N, 3.28. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.87 (m, 4H, CH_2), 3.30 (m, 4H, CH_2), 4.29 (s, 6H, CH_3), 5.89 (m, 2H, C_5H_4), 6.18 (m, 2H, C_5H_4), 6.24 (m, 2H, C_5H_4), 6.35 (m, 2H, C_5H_4), 7.01 (m, 8H, C_6H_4). IR (KBr, cm^{-1}): ν 2939 (s), 2679 (s), 2491 (m), 1603 (m), 1489 (vs), 1456 (m), 1434 (m), 1398 (w), 1262 (s), 1171 (w), 1114 (w), 1036 (m), 804 (vs), 753 (vs), 622 (s), 591 (s). MS: *m*/*z* 668 (M $-$ $C_5H_4CH_2CH_2Br$, 5), 576 (M-$C_5H_4CH_2CH_2Br$ $-$ CH_2Br, 3), 339 (M/2 $-$ Br, 4), 325 (M/2 $-$ CH_2Br, 17), 246 (M/2 $-$ $C_5H_4CH_2CH_2Br$, 9), 91 ($C_5H_4CH_2CH_2$, 100).

4.4. Preparation of **2**

To a solution of 0.45 g (1.62 mmol) of (η^5-$C_5H_4CH_2CH_2OMe$)$TiCl_3$ in 50 ml of THF, 0.25 g (1.94 mmol) of 2-$MeOC_6H_4NHLi$ in 10 ml of THF was added dropwise at -20°C. A rapid color change from orange to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.20 g (1.94 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Dark-red crystals (0.40 g) were obtained upon slow cooling to -20°C (75% yield based on Ti). M.p. 167°C. Anal. Calc. for $C_{30}H_{36}Cl_2N_2O_4Ti_2$: C, 54.99; H, 5.54; N, 4.27. Found: C, 54.90; H, 5.53; N, 4.24. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.67 (m, 4H, CH_2), 3.15 (s, 6H, CH_3), 3.31 (m, 4H, CH_2), 4.22 (s, 6H, CH_3), 5.79 (m, 2H, C_5H_4), 6.00 (m, 2H, C_5H_4), 6.13 (m, 2H, C_5H_4), 6.23 (m, 2H, C_5H_4), 6.85 (m, 2H, C_6H_4), 6.91 (m, 4H, C_6H_4), 7.02 (m, 2H, C_6H_4). IR (KBr, cm^{-1}): ν 3091 (w), 2929 (m), 2868 (s), 1626 (w), 1478 (vs), 1383 (w), 1281 (m), 1256 (vs), 1219 (s), 1180 (m), 1112 (vs), 1038 (m), 1007 (s), 820 (s), 743 (s), 660 (vs). MS: *m*/*z* 619 (M $-$ Cl, 29), 531 (M $-$ $C_5H_4CH_2CH_2OCH_3$, 100), 327 (M/2, 28), 91 ($C_5H_4CH_2CH_2$, 19).

4.5. Preparation of **3**

To a solution of 0.4 g (1.82 mmol) of (η^5-C_5H_4–CH_2-*cyclo*-C_4H_7O)$TiCl_3$ in 20 ml of THF, 0.28 g (2.18 mmol) of 2-$MeOC_6H_4NHLi$ in 10 ml of THF was added dropwise at -20°C. A rapid color change from orange to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.22 g (2.18 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. 0.30 g of dark-red crystals were obtained upon slow cooling to -20°C (61% yield based on Ti). M.p. 182°C. Anal. Calc. for $C_{32}H_{34}Cl_2N_2O_4Ti_2$: C, 57.73; H, 5.70; N, 3.96. Found: C, 57.43; H, 6.23; N, 4.64. ^{1}H-NMR (300 MHz, $CDCl_3$) 6.80 (m, 10H, C_6H_4), 6.21 (m, 2H, C_5H_4), 6.08 (m, 2H, C_5H_4), 5.98 (m, 2H, C_5H_4), 5.80 (m, 2H, C_5H_4), 4.19 (s, 6H), 3.84 (s, 2H), 3.65 (m, 4H), 3.08 (m, 4H),

2.53 (m, 4H), 1.66 (m, 4H). IR (KBr, cm^{-1}): 3431 (m), 3088 (w), 2943 (m), 2863 (m), 1587 (s), 1475 (s), 1397 (m), 1279 (s), 1250 (s), 1217 (s), 1175 (m), 1110 (s), 1035 (s), 1000 (s), 808 (s), 741 (s), 653 (s), 499 (s). MS: *m/z* 657 ($M-CH_3$–Cl, 8), 507 ($M-C_5H_9O$–Cp–CH_3–Cl, 94), 352 ($M/2-1$, 59), 151 (C_5H_9O–Cp + 2, 100), 108 ($C_6H_5OCH_3+1$, 53), 71 (C_4H_8O, 72).

4.6. Preparation of **4**

Method A: to a solution of 0.4 g (1.82 mmol) of (η^5-C_5H_5)$TiCl_3$ in 40 ml of THF, 0.28 g (2.18 mmol) of 2-$MeOC_6H_4NHLi$ in 10 ml of THF was added dropwise at −20°C. A rapid color change from yellow to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.22 g (1.94 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Dark-red crystals (0.30 g) were obtained upon slow cooling to −20°C (61% yield based on Ti). M.p. (dec.) 238°C. Anal. Calc. for $C_{24}H_{24}Cl_2N_2O_2Ti_2$: C, 53.47; H, 4.49; N, 5.20. Found: C, 53.41; H, 4.54; N, 4.83. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.25 (s, 6H, CH_3), 6.21 (s, 10H, C_5H_5), 6.85 (m, 2H, C_6H_4), 6.94 (m, 4H, C_6H_4), 7.05 (m, 2H, C_6H_4). IR (KBr, cm^{-1}): *v* 3099 (w), 2941 (w), 1587 (w), 1475 (s), 1448 (m), 1319 (w), 1279 (m), 1254 (s), 1111 (m), 1008 (s), 899 (w), 813 (vs), 745 (s), 664 (s). MS: *m/z* 538 (M, 46), 503 (M − Cl, 67), 473 ($M-C_5H_5$, 100), 458 ($M-C_5H_5-CH_3$, 39), 148 (C_5H_5TiCl, 20).

Method B: a suspension of 0.8 g (3.2 mmol) of (η^5-C_5H_5)$_2TiCl_2$ and 0.45 g (3.52 mmol) of 2-$MeOC_6H_4NHLi$ in 50 ml of toluene was refluxed for 8 h. Then 0.39 g (3.53 mmol) of Et_3N was added at 90°C. The mixture was refluxed for another 5 h. After removal of precipitate via filtration, the filtrate was concentrated to ca. 30 ml. 0.45 g of dark-red solid was obtained upon slow cooling to −20°C (52% yield based on Ti).

4.7. Preparation of 2-$Me_2NC_6H_4NMg$·THF

A total of 30 ml (18.4 mmol in ether solution) of *n*-Bu_2Mg was added dropwise to 2.5 g (18.4 mmol) of 2-$Me_2NC_6H_4NH_2$ in 20 ml of THF at r.t., and the solution was stirred for 12 h. The resulting white solid was filtered and washed with hexane (3 × 15 ml) to yield 3.5 g of 2-$Me_2NC_6H_4NMg$·THF in 93% yield.

4.8. Preparation of **5**

A suspension of 0.6 g (2.73 mmol) of (η^5-C_5H_5)$TiCl_3$ and 0.63 g (2.73 mmol) of 2-$Me_2NC_6H_4NMg$·THF in 35 ml of toluene was refluxed for 12 h. After removal of precipitate via filtration, the filtrate was concentrated to ca. 20 ml. 0.43 g of dark-red solid was obtained upon slow cooling to −20°C (56% yield). M.p. 260°C. Anal. Calc. for $C_{26}H_{30}Cl_2N_4Ti_2$: C, 55.25; H, 5.35; N, 9.91. Found: C, 54.45; H, 5.12; N, 9.76. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 12H, CH_3), 6.26 (s, 10H, C_5H_5), 6.81 (m, 4H, C_6H_4), 7.16 (m, 4H, C_6H_4). IR (KBr, cm^{-1}): *v* 3055 (w), 2903 (w), 1579 (m), 1469 (s), 1308 (m), 1281 (s), 1261 (m), 1240 (m), 1149 (m), 1097 (m), 1029 (m), 914 (s), 806 (s), 750 (s), 644 (s), 614 (m). MS: *m/z* 499 ($M-C_5H_5$, 1.2), 430 ($M-C_{10}H_8N_2$, 0.7), 91 (C_6H_4-N, 100), 65 (C_5H_5, 15).

4.9. Preparation of PhNHLi

To a solution of 2.70 g (29 mmol) of aniline in 50 ml of *n*-hexane, 20 ml (1.45 M in *n*-hexane, 29 mmol) of *n*-BuLi was added dropwise at 0°C. A white precipitate appeared immediately. Then the reaction mixture was stirred for 2 h at r.t. After filtration of mixture, the residue was washed with 3 × 25 ml of *n*-hexane, and 2.75 g of white solid was given in 96% yield.

4.10. Preparation of **6**

To a solution of 1.29 g (2.8 mmol) of (η^5-$C_5H_4CH_2CH_2Br$)$TiBr_3$ in 50 ml of THF, 0.28 g (1.3 mmol) of PhNHLi in 10 ml of THF was added dropwise at −20°C. A rapid color change from orange to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.31 g (3.4 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Dark-red crystals (0.7 g) were obtained upon slow cooling to −20°C (64% yield based on Ti). M.p. 140°C. Anal. Calc. for $C_{26}H_{26}Br_4N_2Ti_2$: C, 39.94; H, 3.35; N, 3.58. Found: C, 39.94; H, 3.39; N, 3.52. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.92 (t, 4H, ^3J = 6.98 Hz, CH_2), 3.35 (t, 4H, ^3J = 6.98 Hz, CH_2), 6.15 (t, 4H, ^3J = 2.70 Hz, C_5H_4), 6.41 (t, 4H, ^3J = 2.70 Hz, C_5H_4), 6.70 (m, 4H, C_6H_5), 7.04 (m, 2H, C_6H_5), 7.26 (m, 4H, C_6H_5). IR (KBr, cm^{-1}): *v* 2878 (s), 2589 (w), 1564 (m), 1494 (s), 1474 (s), 1235 (s), 862 (s), 805 (vs), 767 (s), 693 (m), 628 (m). MS: *m/z* 782 (M, 46), 703 (M − Br, 75), 620 (M − 2Br, 43), 529 ($M-2Br-C_6H_5N$, 25), 391 (M/2, 23), 91 ($C_5H_4CH_2CH_2$, 100).

4.11. Preparation of **7**

To a solution of 0.63 g (2.27 mmol) of (η^5-$C_5H_4CH_2CH_2OMe$)$TiCl_3$ in 20 ml of THF, 0.27 g (2.72 mmol) of PhNHLi in 10 ml of THF was added dropwise at −20°C. A rapid color change from orange to

red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.28 g (2.72 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Dark-red crystals (0.45 g) were obtained upon slow cooling to −20°C (68% yield based on Ti). M.p. 74°C. Anal. Calc. for $C_{28}H_{32}Cl_2N_2O_2Ti_2$: C, 56.50; H, 5.42; N, 4.71. Found: C, 56.40; H, 5.44; N, 4.86. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.66 (t, 4H, $J=6.46$ Hz, CH_2), 3.21 (s, 6H, CH_3), 3.39 (t, 4H, $J=6.46$ Hz, CH_2), 6.01 (t, 4H, $J=2.65$ Hz, C_5H_4), 6.35 (t, 4H, $J=2.65$ Hz, C_5H_4), 6.67 (m, 4H, C_6H_5), 7.00 (m, 2H, C_6H_5), 7.25 (m, 4H, C_6H_5). IR (KBr, cm^{-1}): ν 2869 (vs), 2588 (s), 2868 (s), 1631 (w), 1600 (m), 1525 (m), 1494 (vs), 1461 (m), 1381 (m), 1197 (w), 1116 (s), 1031 (m), 843 (s), 796 (vs), 743 (s), 617 (s). MS: m/z 559 (M − Cl, 32), 484 (M − Cl − C_6H_5, 15), 471 (M − $C_5H_4CH_2CH_2OCH_3$, 8), 297 (M/2, 100), 91 ($C_5H_4CH_2CH_2$, 8).

4.12. Preparation of 2-MeC_6H_4NHLi

To a solution of 9.7 g (58 mmol) of 2-$MeC_6H_4NH_2$ in 50 ml of *n*-hexane, 40 ml (1.45 M in *n*-hexane, 58 mmol) of *n*-BuLi was added dropwise at 0°C. A white precipitate appeared immediately. Then the reaction mixture was stirred for 2 h at r.t. After filtration of mixture, the residue was washed with 3×25 ml of *n*-hexane, and 9.6 g of white solid was given in 95% yield.

4.13. Preparation of **8**

To a solution of 0.63 g (2.87 mmol) of (η^5-C_5H_5)$TiCl_3$ in 40 ml of THF, 0.32 g (2.87 mmol) of 2-MeC_6H_4NHLi in 10 ml of THF was added dropwise at −20°C. A rapid color change from yellow to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.29 g (2.87 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Dark-red crystals (0.57 g) were obtained upon slow cooling to −20°C (78% yield). M.p. 248°C. Anal. Calc. for $C_{24}H_{24}Cl_2N_2Ti_2$: C, 56.84; H, 4.77; N, 5.52. Found: C, 57.02; H, 4.77; N, 5.29. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 6H, CH_3), 6.32 (s, 5H, C_5H_5), 6.62 (s, 5H, C_5H_5), 6.80 (m, 2H, C_6H_4), 6.95 (m, 2H, C_6H_4), 7.06 (m, 2H, C_6H_4), 7.16 (m, 2H, C_6H_4). IR (KBr, cm^{-1}): ν 2854 (s), 2063 (s), 1978 (m), 1801 (w), 1589 (m), 1498 (s), 1460 (m), 1307 (w), 1144 (w), 1067 (w), 858 (s), 792 (s), 752 (s), 620 (s), 530 (s). MS: m/z 506 (M, 85), 471 (M − Cl, 57), 441 (M − C_5H_5, 17), 404 (M − Cl − C_5H_5, 96), 368 (M − C_5H_5TiCl − Cl, 100), 148 (C_5H_5TiCl, 37).

4.14. Preparation of **9**

To a solution of 0.69 g (2.49 mmol) of (η^5-$C_5H_4CH_2CH_2OMe$)$TiCl_3$ in 20 ml of THF, 0.28 g (2.49 mmol) of 2-MeC_6H_4NHLi in 10 ml of THF was added dropwise at −20°C. A rapid color change from orange to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then 0.25 g (2.72 mmol) of Et_3N in 5 ml of THF was added at r.t. The mixture was stirred for another 4 h. After that, the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Dark-red crystals (0.5 g) were obtained upon slow cooling to −20°C (64% yield). M.p. 96°C. Anal. Calc. for $C_{30}H_{36}Cl_2N_2O_2Ti_2$: C, 57.81; H, 5.82; N, 4.49. Found: C, 57.66; H, 5.71; N, 4.40. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 6H, CH_3), 2.46 (m, 4H, CH_2), 3.12 (s, 6H, CH_3), 3.18 (m, 4H, CH_2), 5.99 (s, 2H, C_5H_4), 6.02 (s, 2H, C_5H_4), 6.39 (d, 2H, C_5H_4), 6.56 (s, 2H, C_5H_4), 6.96 (m, 2H, C_6H_4), 7.14 (m, 2H, C_6H_4), 7.70 (m, 2H, C_6H_4). IR (KBr, cm^{-1}): ν 2916 (s), 2851 (s), 2607 (s), 2015 (w), 1579 (w), 1488 (s), 1459 (m), 1380 (w), 1116 (s), 1036 (m), 843 (s), 793 (s), 752 (s), 618 (m). MS: m/z 589 (M − Cl, 1), 499 (M − $C_5H_4CH_2CH_2OCH_3$, 3), 311 (M/2, 100), 206 (M/2 − C_7H_7N, 34).

4.15. Preparation of 2,6-$Me_2C_6H_3NMg\cdot THF$

A total of 35 ml (0.61 M in ether solution, 21.4 mmol) of *n*-Bu_2Mg was added dropwise to 2.6 g (21.4 mmol) of 2,6-$Me_2C_6H_3NH_2$ in 20 ml of THF at r.t., and the solution was stirred for 12 h. The resulting white solid was filtered and washed with hexane (3×15 ml) to yield 2.0 g of 2,6-$Me_2C_6H_3NMg\cdot THF$ (65% yield).

4.16. Preparation of **10**

A suspension of 0.3 g (1.43 mmol) of (η^5-C_5H_5)$TiCl_3$ and 0.21 g (1.43 mmol) of 2,6-$Me_2C_6H_3NMg\cdot THF$ in 35 ml of toluene was refluxed for 12 h. After removal of precipitate via filtration, the filtrate was concentrated to ca. 20 ml. Dark-red solid (0.25 g) was obtained upon slow cooling to −20°C (65% yield). M.p. 214°C. Anal. Calc. for $C_{26}H_{28}Cl_2N_2Ti_2$: C, 58.35; H, 5.27; N, 5.23. Found: C, 58.40; H, 5.30; N, 5.44. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.70 (s, 12H, CH_3), 6.34 (s, 10H, C_5H_5), 6.97 (m, 6H, C_6H_3). IR (KBr, cm^{-1}): ν 2985 (s), 2851 (s), 2734 (s), 2556 (s), 2237 (m), 1976 (w), 1623 (m), 1585 (m), 1525 (s), 1474 (s), 1441 (m), 1263 (w), 1179 (w), 1093 (w), 1017 (s), 856 (s), 789 (s), 620 (s). MS: m/z 534 (M, 5), 499 (M − Cl, 2), 433 (M − C_5H_5 − Cl, 12), 414 (M − C_8H_9N, 18), 267 (M/2, 8).

4.17. Preparation of 2-PyNHLi

To a solution of 3.29 g (35 mmol) of 2-aminopyridine in 50 ml of THF, 35 ml (1.0 M in *n*-hexane, 35 mmol) of *n*-BuLi was added dropwise at −20°C. Then the reaction mixture was warmed to r.t. and stirred for 2 h. After filtration of mixture, the residue was washed with 3 × 25 ml of *n*-hexane, and 3.3 g of reddish solid was given in 94% yield.

4.18. Preparation of **11**

To a solution of 0.38 g (1.73 mmol) of (η^5-C_5H_5)$TiCl_3$ in 40 ml of THF, 0.17 g (1.73 mmol) of 2-PyNHLi and 0.17 g (1.73 mmol) Et_3N in 10 ml of THF was added dropwise at −20°C. A rapid color change from yellow to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Red crystals (0.21 g) were obtained upon slow cooling to −20°C (51% yield based on Ti). M.p. 162°C. Anal. Calc. for $C_{20}H_{18}Cl_2N_4Ti_2$: C, 49.94; H, 3.77; N, 11.65. Found: C, 49.87; H, 3.67; N, 11.54. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.57 (m, 4H, C_5H_5), 6.66 (m, 6H, C_5H_5), 6.68 (m, 2H, C_5H_4N), 6.90 (m, 2H, C_5H_4N), 7.48 (m, 2H, C_5H_4N), 8.05 (m, 2H, C_5H_4N). IR (KBr, cm^{-1}): *v* 3147 (s), 2970 (s), 1665 (s), 1621 (s), 1546 (w), 1477 (m), 1381 (m), 1325 (w), 1017 (m), 997 (m), 862 (s), 796 (s), 768 (s), 622 (s), 528 (s). MS: *m*/*z* 480 (M, 5), 445 (M − Cl, 10), 415 (M − Cp, 100), 338 (M − Cp − C_5H_4N, 17).

4.19. Preparation of **12**

To a solution of 0.38 g (1.37 mmol) of (η^5-$C_5H_4CH_2CH_2OMe$)$TiCl_3$ in 50 ml of THF, 0.15 g (1.51 mmol) of 2-PyNHLi and 0.15 g (1.51 mmol) Et_3N in 10 ml of THF was added dropwise at −20°C. A rapid color change from yellow to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Red crystals (0.20 g) were obtained upon slow cooling to −20°C (49% yield based on Ti). M.p. 124°C. Anal. Calc. for $C_{26}H_{30}Cl_2N_4O_2Ti_2$: C, 52.29; H, 5.06; N, 9.38. Found: C, 51.97; H, 5.37; N, 9.06. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.59 (t, 4H, $J = 6.45$ Hz, CH_2), 3.21 (s, 6H, CH_3), 3.40 (t, 4H, $J = 6.45$ Hz, CH_2), 6.11 (t, 4H, $J = 2.61$ Hz, C_5H_4), 6.27 (t, 4H, $J = 2.61$ Hz, C_5H_4), 6.62 (m, 2H, C_5H_4N), 6.87 (m, 2H, C_5H_4N), 7.66 (m, 2H, C_5H_4N), 8.05 (m, 2H, C_5H_4N). IR (KBr, cm^{-1}): *v* 3147 (s), 2921 (m), 1665 (s), 1621 (s), 1547 (w), 1476 (w), 1381 (w), 1325 (w), 1165 (w), 1117 (m), 998 (w), 838 (m), 770 (s), 626 (m), 511 (s). MS: *m*/*z* 561 (M − Cl, 17), 473 (M − $C_5H_4CH_2CH_2OCH_3$, 53), 396 (M − $C_5H_4CH_2CH_2OCH_3$ − C_5H_4N, 100), 360 (M − $C_5H_4CH_2CH_2OCH_3$ − C_5H_4N − Cl, 22).

4.20. Preparation of **13**

To a solution of 0.7 g (1.52 mmol) of (η^5-$C_5H_4CH_2CH_2Br$)$TiBr_3$ in 50 ml of THF, 0.15 g (1.52 mmol) of 2-PyNHLi and 0.15 g (1.52 mmol) Et_3N in 10 ml of THF was added dropwise at −20°C. A rapid color change from yellow to red was observed. After addition, the mixture was warmed to r.t. and stirred for 4 h. Then the solvent was removed in reduced pressure, the dark-red residue was extracted with 50 ml of toluene and the resulting extract was concentrated to ca. 30 ml. Red crystals were (0.70 g) obtained upon slow cooling to −20°C (58% yield based on Ti). M.p. 156°C. Anal. Calc. for $C_{24}H_{24}Br_4N_4O_2Ti_2$: C, 36.78; H, 3.09; N, 7.15. Found: C, 36.66; H, 3.20; N, 7.01. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.89 (t, 4H, $^3J = 6.84$ Hz, CH_2), 3.39 (t, 4H, $^3J = 6.84$ Hz, CH_2), 6.16 (t, 4H, $^3J = 2.66$ Hz, C_5H_4), 6.36 (*t*, 4H, $^3J = 2.66$ Hz, C_5H_4), 6.63 (m, 2H, C_5H_4N), 6.75 (m, 2H, C_5H_4N), 7.66 (m, 2H, C_5H_4N), 8.10 (m, 2H, C_5H_4N). IR (KBr, cm^{-1}): *v* 3170 (s), 1666 (vs), 1622 (s), 1477 (w), 1429 (w), 1381 (w), 1325 (w), 1237 (w), 1166 (w), 1053 (w), 998 (w), 832 (m), 791 (s), 626 (m), 535 (s). MS: *m*/*z* 614 (M − $C_5H_4CH_2CH_2Br$, 2), 532 (M − $C_5H_4CH_2CH_2Br$ − Br, 1), 455 (M − $C_5H_4CH_2CH_2Br$ − Br − C_5H_4N, 6), 391 (M/2, 24), 311 (M/2 − Br, 100).

4.21. Styrene polymerization of **4**

To a 20 ml reaction flask equipped with a septum cap, 2 ml of styrene, 5.8 g of MAO, 5 μmol of compound **4** and 10 ml of toluene were added by syringe, and the mixture equilibrated at 50°C using an external temperature bath. After a measured time interval with stirring, the polymerization was quenched by the addition of 10% acidified ethanol. The precipitated polymer was then collected by filtration, washed three times with ethanol and dried on the high-vacuum line overnight. After weighing, the polymer was refluxed in butanone for 2 h, then filtered, dried and weighed to give syndiotactic polystyrene.

4.22. X-ray structure determination of **1**

A suitably sized dark-red crystal of **1** was obtained by crystallization from methylene dichloride–*n*-hexane (1:4). The crystal was mounted in a glass capillary. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å) and a 12 W rotating anode generator. Crystallographic and experimental details

Table 2
Crystal data and structure refinement details for compound **1**

Empirical formula	$TiBr_2NOC_{14}H_{15}$
Temperature (°C)	25
Wavelength (Å)	0.71069
Crystal dimensions (mm)	$0.22 \times 0.23 \times 0.35$
Crystal system	Triclinic
Lattice parameter	
a (Å)	9.9429(2)
b (Å)	10.057(3)
c (Å)	8.457(2)
α (°)	111.28(2)
β (°)	106.71(2)
γ (°)	98.12(2)
V (Å^3)	725.5(4)
Space group	$P\bar{1}$ (no. 2)
Z value	2
$D_{calc.}$ (g cm^{-3})	1.927
$F(000)$	412.00
μ(Mo–K$_\alpha$) (cm^{-1})	61.04
Reflections measured	Total 2028 Unique 1895 ($R_{int} = 0.053$)
Observations ($I > 3.00\sigma(I)$)	1098
Variables	172
Scan width (°)	$(1.68 + 0.35 \tan\theta)$
Residuals: R; R_w	0.036; 0.030
Goodness-of-fit indicator	1.68
Maximum peak in final difference map (e Å^{-3})	0.36
Minimum peak in final difference map (e Å^{-3})	0.51

are summarized in Table 2. The data were collected at a temperature of 25°C using the $\omega - 2\theta$ technique to a maximum 2θ value of 45.0°. The structure was solved by heavy-atom Patterson methods, expanded using Fourier techniques and refined by full-matrix least-squares. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

5. Supplementary material

The X-ray crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC), CCDC no. 135667 for compound **1**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www:http//www.ccdc.cam.ac.uk)

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