

Synthesis of new oxy and thiolate [hydro-tris(pyrazol-1-yl)borato] titanium and zirconium(IV) complexes. Molecular structure of [Ti(HB(3,5-Me₂pz)₃)Cl₃]

A. Antiñolo^a, F. Carrillo-Hermosilla^a, A.E. Corrochano^a, J. Fernández-Baeza^a,
M. Lanfranchi^b, A. Otero^{a,*}, M.A. Pellinghelli^b

^a *Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Campus Universitario de Ciudad Real, E-13071 Ciudad Real, Spain*

^b *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffattometrica del CNR, viale delle Scienze 78, I-43100 Parma, Italy*

Received 4 August 1998

Abstract

The complexes [M(HB(3,5-Me₂pz)₃)Cl₂(LL)] (pz = pyrazolyl, M = Ti, LL = 2-oxy-6-methylpyridine, 2,4-dimethyl-6-oxypyrimidine; M = Zr, LL = 4,6-dimethyl-2-thiolatepyrimidine) have been prepared by the reaction of the starting materials [M(HB(3,5-Me₂pz)₃)Cl₃] (M = Ti, Zr) and one equivalent of the lithium salt or the protic form of the corresponding hydroxy or thiolato pyridine or pyrimidine. The complexes were characterized by spectroscopic methods. While the titanium complexes are rigid in solution, the zirconium complex is fluxional at room temperature, although limiting static spectra can be obtained at low temperature. The variable temperature ¹H-NMR spectra indicate that a mechanism involving interchange of both nitrogen atoms of pyrimidine, in the coordination sphere of the zirconium atom, can explain this dynamic behavior. In addition, the molecular structure of the starting material [Ti(HB(3,5-Me₂pz)₃)Cl₃] has been determined by X-ray diffraction methods. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Zirconium; Pyrazolylborates; Pyridine; Pyrimidine; Dynamic behavior

1. Introduction

In recent years an extensive chemistry has been developed for Group 4 Cp-derivatives (Cp = cyclopentadienyl ring) in order to explore their potential applications as catalysts in reactions such as olefin polymerization, hydrogenation, and hydrosilylation. However, great interest is currently focused on the preparation of novel complexes with ligands other than Cp, such as hydrido-tris(pyrazol-1-yl)borate, Tp.

Hydrido-tris(pyrazol-1-yl)borato-containing complexes are well documented for practically all transition

metals [1], and several derivatives of titanium and zirconium bearing halide [2], alkoxide [3], alkyl [3b,g], or imido [4] ligands have been described. In the alkyl complexes it has been observed that at least one electron-donating ligand, such as alkoxide, must be present in order to stabilize the corresponding organometallic complex [3b,g]. As an alternative to these stabilizer ligands, hydroxo and mercapto heterocyclic derivatives bearing nitrogen atoms can be used because the nitrogen atom would assist the formation of an additional bond with the metal center in the oxy or thiolate ligand. The first cyclopentadienyl containing early transition metal complexes with these class of ligands were recently described [5] for some of us, but to the best of our knowledge no reports of hydrido-tris(pyrazol-1-

* Corresponding author. Fax: +34-26295318.

E-mail address: aotero@qino-cr-uclm.es (A. Otero)

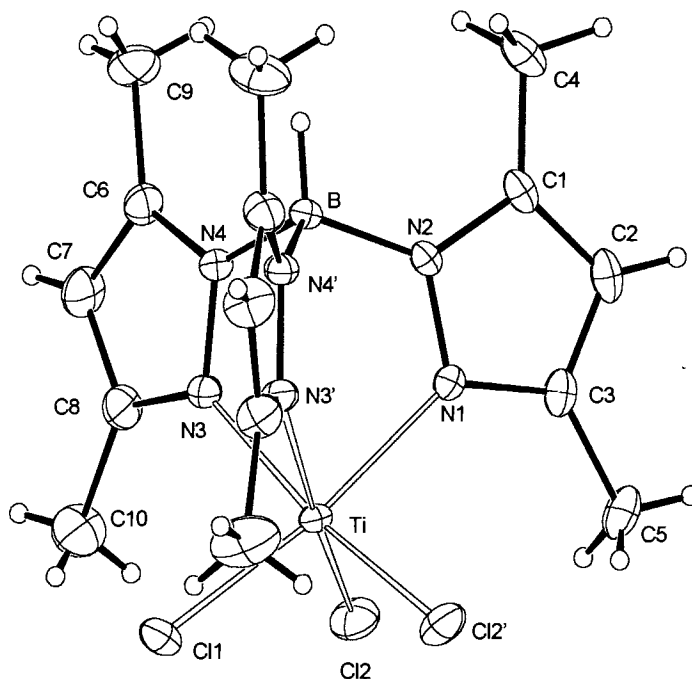


Fig. 1. ORTEP drawing of complex **1** with atom labeling scheme.

yl)borato containing complexes of these metals have been described.

We report here the synthesis and structural characterization of the seven-coordinate $[M(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_2(\text{LL})]$ ($M = \text{Ti}$, $\text{LL} = 2\text{-oxy-6-methylpyridine}$, $2,4\text{-dimethyl-6-oxypyrimidine}$; $M = \text{Zr}$, $\text{LL} = 4,6\text{-dimethyl-2-thiolatepyrimidine}$) complexes, as well as the molecular structure of the starting material $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_3]$ [**2**] which was determined by X-ray diffraction studies.

2. Results and discussion

Suitable crystals for X-ray diffraction studies were obtained from a concentrated dichloromethane solution of $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_3]$ (**1**).

The structure of this complex is shown in Fig. 1 together with the atom numbering scheme. Selected bond lengths and angles are listed in Table 1.

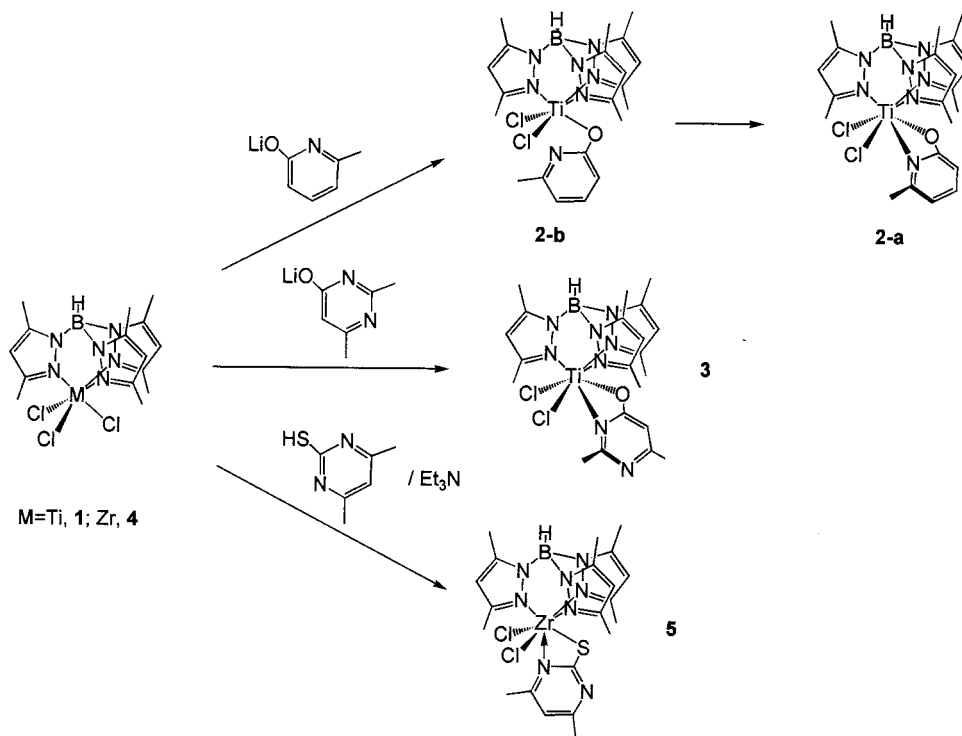
The Ti atom shows a distorted octahedral coordination and the complex presents a pseudo C_{3v} and a crystallographic C_s symmetry with a pz moiety, the B, Ti and Cl1 atoms lying on the mirror plane (Fig. 1). The Ti–Cl (2.271(1), 2.258(1) Å) and Ti–N (2.177(2), 2.164(2) Å) bond distances seem normal if compared with a parent octahedral complex of Ti(IV) $[\text{Tp}^{\text{Menth}^*}\text{TiCl}_3]$ ($\text{Tp}^{\text{Menth}^*} = \text{tris}(7(R)\text{-isopropyl-4}(R)\text{-methyl-4,5,6,7-tetrahydroindazolyl})\text{hydroborate}$) (average 2.26 and 2.15 Å, respectively) [6] while they are significantly shorter if compared with the anionic complex $\text{TpTi}^{\text{III}}\text{Cl}_3^-$ ($\text{Tp} = \text{HB}(\text{pz})_3$) (average 2.40 and 2.18

Å, respectively) [7]. The bond distances and angles in the organic molecule are normal apart some difference in the angle values around C1, C6 and the nitrogen atoms, probably due to steric hindrance. The N–Ti–N angle values are smaller than 90° while the Cl–Ti–Cl are greater. The packing is determined by weak interactions, the most relevant being $\text{C4}\cdots\text{H41}\cdots\text{Cl1}''$ ($\text{H41}\cdots\text{Cl1}'' = 2.80(5)$ Å, $\angle \text{C4}\text{--}\text{H41}\cdots\text{Cl1}'' = 169(5)^\circ$) ($'' = 1 + x, y, 1 + z$) that links the complexes in the mirror plane.

Table 1

Selected bond distances (Å) and angles ($^\circ$) for complex **1** with S.D. in parentheses

Bond distances (Å)	
Ti–Cl1	2.271(1)
Ti–N1	2.177(2)
Ti–Cl2	2.258(1)
Ti–N3	2.164(2)
N1–N2	1.370(3)
N3–N4	1.381(2)
N2–B	1.536(4)
N4–B	1.536(2)
Bond angles ($^\circ$)	
N1–Ti–N3	83.8(0)
N3–Ti–N3'	83.3(1)
Cl2–Ti–N3'	171.3(0)
Cl1–Ti–N1	172.2(1)
Cl2–Ti–N3	90.0(1)
Cl1–Ti–N3	90.4(0)
Cl2–Ti–N1	90.0(0)
Cl1–Ti–Cl2	95.2(0)



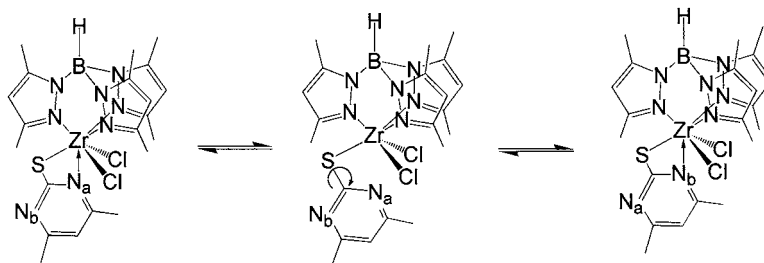
Scheme 1.

The reactions of $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_3]$ (**1**) in THF with one equivalent of lithium 2-oxy-6-methylpyridine (LiOpy') or lithium 2,4-dimethyl-6-oxypyrimidine (LiOpm'), both of which are prepared in situ by reaction of the appropriate 2-hydroxy-6-methylpyridine or 2,4-dimethyl-6-hydroxypyrimidine with *n*-BuLi in THF, afforded the corresponding complexes $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_2(\text{Opy}')] (\mathbf{2})$ and $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_2(\text{Opm}')] (\mathbf{3})$ in high yields (80%), as orange (**2**) or white (**3**), very moisture-sensitive microcrystalline solids (Scheme 1).

Complex **2** was isolated as a mixture of two isomers, **2a** and **2b**, in a 1:1 ratio, but when the reaction mixture in hexane was stirred overnight at 50°C , only one isomer (**2a**) was obtained. Several attempts to isolate the complex **2** as the only isomer **2b** were unsuccessful. These and related complexes were characterized by spectroscopic techniques. The $^1\text{H-NMR}$ spectrum of **2** exhibits three and two distinct sets of H^4 pyrazol-1-yl resonances for the isomers **2a** and **2b**, respectively, indicating the existence of three and two types of pyrazol-1-yl ring in a 1:1:1 and 2:1 ratio, respectively, for these isomers. In addition, the $^1\text{H-NMR}$ spectrum shows six and four sets of methyl resonances for the isomers **2a** and **2b**, respectively (see Section 3). These data are in accordance with their proposed structures, which exhibit C_1 and C_s symmetries, respectively (Scheme 1). For the isomer **2b** a molecular symmetry plane containing one pyrazol-1-yl ring which reflects the other two is considered to be present. A bidentate

and monodentate oxypyridine ligand for isomers **2a** and **2b**, respectively are proposed in their structures, although an additional coordination of the nitrogen atom of the ligand in **2b**, in accordance with their observed C_s symmetry, cannot definitively be ruled out. In order to explain the experimental results, a slow conversion of the six-coordinate monodentate oxypyridine species **2b**, initially resulted in the reaction, to the seven-coordinate bidentate oxypyridine species **2a** in a kinetically controlled step seems reasonable. In addition, an alternative structure for **2a** with an ionic six-coordinate bidentate oxypyridine species $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}(\text{Opy}')] \text{Cl}$ could be considered, and the slow conversion of **2b** to **2a** might well be consistent with an internal nucleophilic attack of the pendant pyridyl nitrogen at titanium center. However, the conductivity measurements indicate that **2a** behaves as a neutral species, and this proposal can be ruled out.

The $^1\text{H-NMR}$ spectrum of **3** also exhibits three and six distinct sets of H^4 pyrazol-1-yl and methyl resonances, respectively, which is in agreement with a C_1 symmetry similar to that proposed for **2a** (see Scheme 1), and an additional coordination of the nitrogen atom of the ligand is also considered. In this case, formation of an analogous complex of **2b** was not detected. Variable temperature $^1\text{H-NMR}$ experiments were carried out for **2a** and **3**, and the results indicate that these complexes exhibit static dispositions even at higher values of temperature. $^{13}\text{C-NMR}$ data for **2a**, **2b** and **3** agree with the aforementioned structural assignments.



Scheme 2.

Thus, the spectra of **2a** and **3** show three and six sets of C⁴ pyrazol-1-yl and methyl resonances, respectively, whereas a more simple spectrum with two and four sets of resonances is present for **2b** (see Section 3). In addition, the ¹H- and ¹³C-NMR spectra exhibit the corresponding resonances for the 2-oxy-6-methylpyridine and 2,4-dimethyl-6-oxypyrimidine groups in the appropriate complexes (see Section 3). In the ¹³C-NMR spectrum of the mixture of **2a** and **2b**, the resonances of the C⁴ pyrazol-1-yl and 2-oxy-6-methylpyridine heterocyclic carbon atoms appear in the same region and the assignment of these was based on a ¹H- ¹³C- HETCOR experiment.

The reaction of complex **1** with one equivalent of lithium 4,6-dimethylpyrimidine-2-thiolate, potassium 4,6-dimethylpyrimidine-2-thiolate or 4,6-dimethyl-2-mercapto-pyrimidine, in the presence or absence of triethylamine, leads to green–blue solutions that contain a complex mixture of paramagnetic titanium species and organic residues. These compounds were not identified.

However, the complex [Zr(HB(3,5-Me₂pz)₃)Cl₃] (**4**) reacts smoothly with one equivalent of 4,6-dimethyl-2-mercapto-pyrimidine (HSpm') in THF, after the addition of triethylamine, to give very moisture sensitive yellow crystals of complex [Zr(HB(3,5-Me₂pz)₃)Cl₂(Spm')] (**5**) in a good yield (85%) (see Scheme 1).

The ¹H-NMR spectrum of **5** at room temperature (r.t.) in toluene-d₈ exhibits two distinct sets of H⁴ pyrazol-1-yl resonances in a 2:1 ratio. This observation is in accordance with their C_s symmetry, as in the case previously described for complex **2b**. In the spectrum of **5**, two broad resonances at 1.95 and 2.95 ppm correspond to the methyl groups attached to the ring in the thiolate ligand. The width of these peaks indicates a fluxional behavior in solution, through which probably both nitrogen atoms interchange their positions in the coordination sphere of the zirconium atom (see Scheme 2). However, this interchange by means of the free rotation around the single S–C bond is not completely favored at r.t. and would make inequivalent the two methyl groups. A very similar situation has been ob-

served in the complex [Zr(η⁵-C₅H₅)₂(η²-C₆H₇N₂S)(Me)] [**5**].

Variable temperature ¹H-NMR spectroscopy showed that these broad peaks become sharp at –10°C. As the temperature is increased the peaks broaden, and at 70°C they coalesce. At higher temperatures, one single resonance appears at 2.48 ppm. The two site exchange equation and the coalescence temperature of 70°C can be used to estimate a value for ΔG[‡] of 15.6 Kcal mol^{–1} for the dynamic process [8].

This means that, although complex **5** is formally a 14e[–] species at low temperature, at relatively mild temperature values a free coordination position at the metal center could be available. It is noteworthy that, even at temperatures as low as –80°C, the molecule retains the symmetry plane with two equivalent pyrazole rings.

Several attempts to prepare zirconium complexes analogous to **2** or **3** were unsuccessful. A complex mixture of products containing the starting ligands along with other, unidentified, compounds was obtained after the reaction of complex **4** with an equivalent of either the lithium salts or the protic forms of HOpy' or HOPm', with or without triethylamine. When these compounds were used in the presence of triethylamine, formation of [Et₃NH]Cl was detected, indicating that the reaction probably occurs in the expected way, and a mixture of very moisture sensitive compounds was obtained. A sample of the bulky product of the reaction between **4** and HOpy'/Et₃N was examined by ¹H-NMR spectroscopy and a major zirconium product containing an Opy' group with a C_s symmetry, similar to that found in complexes **2b** and **5**, together with [Et₃NH]Cl were observed. However, attempts to isolate a pure sample of the proposed zirconium complex were unsuccessful and a mixture of decomposition products was found.

In conclusion, a series of new hydrido-tris(pyrazol-1-yl)borato-containing titanium and zirconium complexes with oxy and thiolate heterocyclic derivatives bearing nitrogen atoms is described. Further investigations are in progress to broaden the scope of this chemistry.

3. Experimental section

3.1. General

All manipulations were performed using either glovebox or Schlenk techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out using a Perkin-Elmer 2400 CHN analyzer. IR spectra were obtained in the region 200–4000 cm^{-1} using a Perkin-Elmer 883 spectrophotometer. ^1H - and ^{13}C -NMR spectra were recorded using Varian-Unity FT-300 and Gemini FT-200 spectrometers, and the chemical shifts were determined by reference to the residual deuterated solvent peaks.

Reagents were purchased from Aldrich: 2-hydroxy-6-methylpyridine, 2,4-dimethyl-6-hydroxypyrimidine and 4,6-dimethyl-2-mercaptopyrimidine were dried under vacuum overnight to remove residual traces of water.

3.2. Preparation of $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_2(\text{OC}_6\text{H}_6\text{N})]$ (**2**)

To a solution of 2-hydroxy-6-methylpyridine (0.08 g, 0.75 mmol) in THF (20 ml), at 0°C , was added a solution of *n*-BuLi in hexane (0.50 ml, 0.80 mmol, 1.6 M). After being stirred at 25°C for 1 h, the resulting solution was added to a suspension of $\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_3$ (**1**) (0.30 g, 0.66 mmol) in THF (40 ml), and the mixture was stirred at r.t. for 16 h. All volatile materials were removed under vacuum and the residue was extracted with CH_2Cl_2 (50 ml). The cloudy orange solution was filtered through celite, and the solvent was evaporated yielding an orange oily material. This oily material was washed with cold hexane (3×15 ml). Complex **2** was obtained, as a mixture of isomers **2a** and **2b** (see text), as a microcrystalline orange solid (0.27 g, 80% yield). The **2a,b** mixture was suspended in hexane (40 ml) and heated at 50°C overnight to give a pale orange precipitate in a quantitative yield, which was identified by ^1H -NMR as the **2a** isomer.

Anal. Calc. for $\text{C}_{21}\text{H}_{27}\text{BCl}_2\text{N}_7\text{OTi}$ (mixture of **2a,b**): C, 48.18; N, 18.71; H, 5.16. Found: C, 48.41; N 18.82; H, 5.40. IR spectrum (cm^{-1} in *nujol*/CsI): $\nu(\text{C}=\text{C}$ and $\text{C}=\text{N}$ of pyridine ring) 1650(m), 1617(m), 1584(m); $\nu(\text{BH})$ 2560 (m).

Spectroscopic data for (**2a**): ^1H -NMR spectrum (ppm, CDCl_3): δ 7.80 [dd, $J_{\text{H4H3}} = 8.8$ Hz, $J_{\text{H4H5}} = 6.9$ Hz, 1H, H^4 (py')], 6.79 [d, $J_{\text{H3H4}} = 8.8$ Hz, 1H, H^3 (py')], 6.66 [d, $J_{\text{H5H4}} = 6.9$ Hz, 1H, H^5 (py')], 5.84, 5.78, 5.62 [s, 1H, s, 1H, s, 1H, H^4 (pz)], 2.89, 2.63, 2.40, 2.39, 2.37, 2.31, 2.30 [s, 3H, s, 3H, s, 3H, s, 3H, s, 3H, s, 3H, s, 3H, s, 3H, s, 3H, s, 3H, s, 3H, Me^3 (pz), Me^6 (py')].

^{13}C -NMR spectrum (ppm, CDCl_3): δ 165.19 [C^2 (py')], [C^6 (py') not observed], 152.10, 150.92, 150.68, 146.62, 143.99, 142.78 [C^3 , C^5 (pz)], 144.88 [CH^4 (py')],

114.69 [CH^3 (py')], 111.72 [CH^5 (py')], 106.21, 105.88, 105.86 [CH^4 (pz)], 19.77 [Me^6 (py')], 15.27, 14.35, 14.13, 12.74, 12.66, 12.34 [Me^3 , Me^5 (pz)].

(**2b**): ^1H -NMR spectrum (ppm, CDCl_3): δ 7.76 [pt, $J_{\text{H4H3}} = 8.2$ Hz, $J_{\text{H4H5}} = 8.1$ Hz, 1H, H^4 (py')], 6.98 [d, $J_{\text{H3H4}} = 8.2$ Hz, 1H, H^3 (py')], 6.93 [d, $J_{\text{H5H4}} = 8.1$ Hz, 1H, H^5 (py')], 5.88 [s, 1H, H^4 (pz)], 5.71 [s, 2H, H^4 (pz)], 2.87, 2.46, 2.43 [s, 3H, 3H, s, 3H, Me^3 , Me^5 (pz), Me^6 (py')], 2.40, 2.37 [s, s, 6H, 6H, Me^3 , Me^5 (pz)].

^{13}C -NMR spectrum (ppm, CDCl_3): δ 169.50 [C^2 (py')], 156.38, 154.01, [C^3 , C^5 (pz)], 152.75, 143.68 [C^3 , C^5 (pz)], 143.19 [C^6 (py')], 139.65 [CH^4 (py')], 119.73 [CH^3 (py')], 114.92 [CH^5 (py')], 107.31, 106.27 [CH^4 (pz)], 24.03, 16.40 [Me^3 , Me^5 (pz)], 19.07, 11.75, 11.05 [Me_3 , Me_5 (pz), Me^6 (py')].

3.3. Preparation of $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_2(\text{OC}_6\text{H}_7\text{N}_2)]$ (**3**)

To a solution of 2,4-dimethyl-6-hydroxypyrimidine (0.15 g, 1.20 mmol) in THF (20 ml) at 0°C , was added a solution of *n*-BuLi in hexane (0.80 ml, 1.20 mmol, 1.6 M). After being stirred at 25°C for 1 h, the resulting yellow solution was added to a suspension of $\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_3$ (**1**) (0.50 g, 1.10 mmol) in THF (40 ml) and the mixture was stirred at r.t. for 16 h. All volatile materials were removed under vacuum and the residue was extracted with CH_2Cl_2 (50 ml). The cloudy, pale yellow solution was filtered through celite, and the solvent was evaporated to give an oily material. The oily material was washed with cold hexane (3×15 ml). Complex **3** was obtained as a microcrystalline white solid (0.47 g, 80% yield).

Anal. Calc. for $\text{C}_{21}\text{H}_{29}\text{BCl}_2\text{N}_8\text{OTi}$: C, 46.78; N, 20.78; H, 5.42. Found: C, 46.30; N, 20.90; H, 5.40. IR spectrum (cm^{-1} in *nujol*/CsI): $\nu(\text{C}=\text{C}$ and $\text{C}=\text{N}$ of pyrimidine ring) 1657(s), 1630(m), 1551(m); $\nu(\text{BH})$ 2510(m).

^1H -NMR spectrum (ppm, CDCl_3): δ 6.55 [s, 1H, H^5 (PM')], 5.85, 5.80, 5.62 (s, 1H, 1H, 1H, H^4 (pz)], 2.85, 2.72, 2.56, 2.40, 2.38, 2.35, 2.28 (s, 3H, s, 3H, s, 3H, s, 6H, s, 3H, s, 3H, s, 3H, Me^3 , Me^5 (pz), Me^2 , Me^4 (PM')].

^{13}C -NMR spectrum (ppm, CDCl_3): δ 161.30 [C^6 (PM')], 158.13 [C^2 (PM')], 152.15, 150.96, 150.68, 144.40, 144.25, 144.10, 142.94 [C^3 , C^5 (pz), C^4 (PM')], 108.79, 106.32, 105.93, 105.37 [CH^4 (pz), CH^5 (PM')], 15.22, 14.34, 14.15, 12.73, 12.67, 12.50, 12.35, 11.40 [Me^3 , Me^5 (pz), Me^2 , Me^4 (PM')].

3.4. Preparation of $[\text{Zr}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_2(\text{SC}_6\text{H}_7\text{N}_2)]$ (**5**)

To a suspension of $\text{Zr}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_3$ (**4**) (1 g, 2.02 mmol) in CH_2Cl_2 (25 ml), was added a solution of 4,6-dimethyl-2-mercaptopyrimidine (0.26 g, 1.82 mmol)

and triethylamine (1.41 ml, 10 mmol) in CH_2Cl_2 (15 ml) at r.t. The reaction was allowed to stir for 6 h. The volatile materials were removed under vacuum and the yellow residue was extracted with toluene (2×15 ml). The resulting yellow solution was concentrated and refrigerated at -30°C for 24 h, to yield complex **5** as a yellow microcrystalline solid (0.92 g, 85% yield).

Anal. Calc. for $\text{C}_{21}\text{H}_{29}\text{BCl}_2\text{N}_8\text{SZr}$: C, 42.14; N, 18.72; H, 4.89. Found: C, 42.30; N, 18.80; H, 4.90. IR spectrum (cm^{-1} in nujol/CsI): $\nu(\text{C}=\text{C}$ and $\text{C}=\text{N}$ of pyrimidine ring) 1620(w), 1585(s), 1551(m); $\nu(\text{BH})$ 2559(m); $\nu(\text{C}-\text{S})$ 640(m).

$^1\text{H-NMR}$ spectrum (ppm, toluene- d_8 , 283 K): δ 5.92 [s, 1H, H^5 (PM')], 5.48, 5.40, [s, 1H, s, 2H, H^4 (pz)], 2.80, 2.07 [s, 3H, s, 3H, Me^3 , Me^5 (pz)], 2.95, 1.95 [s, 3H, s, 3H, Me^4 , Me^6 (PM')], 2.02, 2.68 [s, 6H, s, 6H, Me^3 , Me^5 (pz)].

$^{13}\text{C-NMR}$ spectrum (ppm, toluene- d_8 , 283 K): δ 174.32 [C^2 (PM')], 170.38, 164.34 [C^4 , C^6 (PM')], 153.25, 152.75, 144.10, 144.06 [C^3 , C^5 (pz)], 118.37 [CH^5 (PM')], 107.58, 107.48 [CH^4 (pz)], 24.51, 22.18 [Me^4 , Me^6 (PM')], 17.06, 16.47, 12.84, 12.73 [Me^3 , Me^5 (pz)].

3.5. Crystal structure determination of $[\text{Ti}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)\text{Cl}_3]$

A suitable red crystal was sealed in Lindemann capillary under dry nitrogen and used for data collection. A detailed summary of the experimental and refinement data is presented in Table 2.

Accurate unit-cell parameters were determined by least-squares refinement of the setting angles of 30 randomly distributed and carefully centered reflections with q in the range $11\text{--}20^\circ$. The data collection was performed on a Philips PW 1100 diffractometer by the $q/2q$ scan mode, at 293 K, with a variable scan speed of $3\text{--}9.6^\circ \text{min}^{-1}$ and a scan width of $1.20 + 0.34 \tan q$. All reflections with q in the range $3\text{--}30^\circ$ were measured; of 3113 independent reflections, 2057, having $I > 2s(I)$, were considered observed and used in the analysis. One standard reflection was monitored every 100 measurements, no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following the method of Lehmann and Larsen [9]. Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR92 [10]) and refined first isotropically by full-matrix least-squares using SHELX-76 program [11], then anisotropically by blocked full-matrix least-squares for all the non-hydrogen atoms. All the hydrogen atoms were clearly localized in the final DF map and refined isotropically. The final cycles of refinement were carried out on the basis of 181 variables; after the last cycles, no parameters shifted by more than 0.6 S.D. The highest remaining peak in the final difference map was equivalent to about $0.31 \text{ e } \text{\AA}^{-3}$. In the final

Table 2

Crystal data, data collection and refinements parameters for **1**

Empirical formula	$\text{C}_{15}\text{H}_{22}\text{BCl}_3\text{N}_6\text{Ti}$
Formula weight	451.45
Temperature (K)	293
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	
a (\AA)	8.113(2)
b (\AA)	14.156(4)
c (\AA)	9.099(3)
β ($^\circ$)	100.11(2)
V (\AA^3)	1028.8(5)
Z	2
$D_{\text{calc.}}$ (Mg m^{-3})	1.457
μ (cm^{-1})	8.17
$F(000)$	464
Crystal size (mm)	$0.17 \times 0.26 \times 0.38$
θ range for data collection	$3\text{--}30$
Diffractometer	Philips PW 1100
No. reflections for latt. par.	30
θ range for latt. Par.	$11 \leq \theta \leq 20$
Scan speed (deg min^{-1})	$3\text{--}9.6$
Scan width	$1.20 + 0.34 \tan \theta$
Index ranges	$-11 \leq h \leq 11, 0 \leq k \leq 19, 0 \leq l \leq 12$
Independent reflections	3113
Observed reflections $I > 2\sigma(I)$	2057
Refinement method	Full-matrix least-squares on F
G-O-F	1.23
NP	181
R^a	0.0323
R_w^a	0.0380
Weighting scheme	$k = 0.6987, g = 0.0005$
$w = k[\sigma^2(F_o) + gF_o^2]^{-1}$	
Largest difference peak and hole ($\text{e } \text{\AA}^{-3}$)	0.31 and -0.29

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}.$$

cycles of refinement a weighting scheme $w = k[s^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the k and g values were 0.699 and 0.0005. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from Ref. [12]. All calculations were carried out on the ENCORE 91 of the 'Centro di Studio per la Strutturistica Diffraattometrica' del CNR, Parma. The programs Parst [13] and ORTEP [14] were also used. The crystallographic data and the final atomic coordinates are provided in the supporting information material.

Acknowledgements

A. Antiñolo, F. Carrillo-Hermosilla, A. Corrochano, J. Fernández-Baeza, and A. Otero gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica (DGES) (grant no. PB 95-0023-CO1) of Spain. M.A. Pellinghelli

and M. Lanfranchi gratefully acknowledge financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and Consiglio Nazionale delle Ricerche (CNR) (Rome, Italy).

References

- [1] (a) S. Trofimenko, *Acc. Chem. Res.* 4 (1971) 17. (b) S. Trofimenko, *Chem. Rev.* 72 (1972) 497. (c) S. Trofimenko, *Chem. Rev.* 93 (1993) 943.
- [2] (a) J.K. Kouba, S.S. Wreford, *Inorg. Chem.* 15 (1976) 2313. (b) D.L. Reger, M.E. Tarquini, *Inorg. Chem.* 21 (1982) 840.
- [3] (a) D.L. Reger, M.E. Tarquini, *Inorg. Chem.* 22 (1983) 1064. (b) D.L. Reger, M.E. Tarquini, L. Lebloda, *Organometallics* 2 (1983) 1763. (c) R.A. Kresinski, T.A. Hamor, L. Isam, C.J. Jones, J.A. McCleverty, *Polyhedron* 8 (1989) 845. (d) R.A. Kresinski, C.J. Jones, J.A. McCleverty, *Polyhedron* 9 (1990) 2185. (e) R.A. Kresinski, T.A. Hamor, C.J. Jones, J.A. McCleverty, *J. Chem. Soc. Dalton Trans.* (1991) 603. (f) R.A. Kresinski, T.A. Hamor, C.J. Jones, J.A. McCleverty, *J. Chem. Soc. Dalton Trans.* (1991) 1835. (g) J. Ipaktschi, W. Sulzbach, *J. Organomet. Chem.* 426 (1992) 59.
- [4] S.C. Dunn, P. Mountford, O.V. Shishkin, *Inorg. Chem.* 35 (1996) 1006.
- [5] R. Fandos, M. Lanfranchi, A. Otero, M.A. Pellinghelli, M.J. Ruiz, P. Terreros, *Organometallics* 15 (1996) 4725.
- [6] D.D. LeCloux, M.C. Keyes, M. Osawa, V. Reynolds, W.B. Tolman, *Inorg. Chem.* 33 (1994) 6361.
- [7] D.L. Hughes, G.J. Leigh, D.G. Walker, *J. Chem. Soc. Dalton Trans.* (1988) 1153.
- [8] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.
- [9] M.S. Lehmann, F.K. Larsen, *Acta Crystallogr. Sect. A* 30 (1974) 580.
- [10] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* 27 (1994) 435.
- [11] G.M. Sheldrick, *SHELX-76 program for crystal structure determination*, University of Cambridge, England, 1976.
- [12] *International Tables for X-ray Crystallography*, vol. IV, Kynoch Press, Birmingham, England, 1974.
- [13] M. Nardelli, *Comput. Chem.* 7 (1983) 95.
- [14] C.K. Johnson ORTEP. Report ORNL-3794, revised, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.