Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 691 (2006) 4172–4180
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structural characterization of sterically crowded hydridotris(pyrazolyl)borato complexes: Unusual double 1,2-borotropic shift at a titanium centre

Paolo Biagini [a,*], Fausto Calderazzo [b], Fabio Marchetti [b], Anna Maria Romano [a], Silvia Spera [a]

[a] *EniTecnologie S.p.A – Centro Ricerche di Novara "Istituto Guido Donegani", via G. Fauser 4, I-28100 Novara, Italy*
[b] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126 Pisa, Italy*

Received 10 May 2006; received in revised form 8 June 2006; accepted 8 June 2006
Available online 30 June 2006

This paper is dedicated to the memory of Roberto Santi, a highly respected scientist and a friend, deceased on December the 26th 2003.

Abstract

The potassium and thallium(I) derivatives of the hydrido-tris(3-Me_2Bz,5-Me-pyrazol-1-yl)borato ligand, K[$Tp^{Me}2^{Bz,Me}$] (**1**) and Tl[$Tp^{Me}2^{Bz,Me}$] (**2**), are reported. Their reactions with $TiCl_4$ under mild conditions afforded, after rearrangement of the ligand, recognized as a double 1,2-borotropic shift, the related Ti(IV) complex {hydrido-[bis(3-Me,5-Me_2Bz)(3-Me_2Bz,5-Me)-pyrazol-1-yl]borato}trichlorotitanium(IV), [$Tp^{Me}2^{Bz,Me**}$] $TiCl_3$ (**3**). The ^{1}H- and ^{13}C NMR spectra of the new compounds are discussed, the molecular structure of **3** has been determined by X-ray diffraction methods, the titanium centre has a pseudo-octahedral coordination, with the nitrogen and chloride ligands in a *fac* geometry. A possible mechanism of formation of **3** is proposed.

Keywords: Tris(pyrazolyl)borate ligands; Titanium; 1,2-borotropic shift

1. Introduction

Since the first report by Trofimenko [1], hydridotris(pyrazol-1-yl)borato (Tp′) ligands have been extensively used in coordination- and organometallic chemistry [2]. Tp′ ligands offer the possibility of an efficient three-dimensional control around the metal centre and the modulation of electronic effects, because as many as three positions are available for substitution in each pyrazole ring. These features have been applied in several fields of chemistry, from modelling in metallo-enzymes, to catalysis and materials science, through analytical chemistry and organic synthesis [3]. It has recently been observed that Tp′ ligands, bearing bulky substituents in position 3 or 5, generate efficient olefin polymerization catalysts, in the presence of several transition elements such as Group 4 metals [4], vanadium [5] and nickel [6]. In some cases the presence of three bulky groups in position 3 of the pyrazolyl ring produces high steric crowding around the metal centre, so that the formation of isomeric complexes, through a 1,2-borotropic shift which exchanges the positions 3 and 5 of the pyrazolyl ring, can occur under particular conditions [4d,4f,6a]. These isomerizations are well documented in the literature for several transition metals [7] and for aluminium [8]. The 1,2-borotropic shift represents a simple way to obtain new complexes of C_s symmetry, of interest for catalysis [4] and for bio-inorganic chemistry [2c,9].

These observations prompted us to investigate the reactions of sterically hindered Tp′ ligands and here we report the potassium and thallium(I) derivatives of the new hydrido-tris(3-Me_2Bz,5-Me-pyrazol-1-yl)borato ligand,

* Corresponding author. Tel.: +39 0 321 447817; fax: +39 0 321 447241.
E-mail address: paolo.biagini@PolimeriEuropa.com (P. Biagini).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.06.026

K[$Tp^{Me}2^{Bz,Me}$] (**1**) and Tl[$Tp^{Me}2^{Bz,Me}$] (**2**), which are compared in their chemical and spectroscopic features. The reaction of **1** or **2** with $TiCl_4$ affords, after a double isomerization of the ligand, the related Ti(IV) complex {hydrido-[bis(3-Me,5-Me_2Bz)(3-Me_2Bz,5Me)-pyrazol-1-yl]borato}-trichlorotitanium(IV), [$Tp^{Me}2^{Bz,Me**}$]$TiCl_3$ (**3**) [10]. All compounds were spectroscopically characterized and the molecular structure of **3** is described.

2. Results and discussion

The preparation of 5-phenyl-5-methyl-2,4-hexanedione has been carried out by condensation of acetone with the corresponding aromatic α-bromoketone, according to the general method [11] for 1-aryl-2,4-diones. The related 3-(1′,1′-dimethylbenzyl)-5-methyl-pyrazole has been prepared by a conventional method [2c], namely the reaction of the β-diketone with hydrazine, and converted to the corresponding K[$Tp^{Me}2^{Bz,Me}$] (**1**) with the stoichiometric amount of KBH_4 at 240 °C, without solvent. The potassium derivative **1** has been further converted to the corresponding thallium derivative **2**, according to the literature method [2], see Scheme 1.

Both **1** and **2** show an unusual solubility in aliphatic hydrocarbons, probably due to multiple interaction of the metal centre with the nitrogen atoms of the anion. Accordingly, **1** and **2** were recrystallized from hexane.

The NMR spectra of **1** and **2** are in agreement with an idealized C_{3v} symmetry, showing all pyrazolyl groups to be equivalent. The NMR characterization of **1** is straightforward, see Section 3. The thallium complex **2** and its NMR characterization show some interesting aspects. In the ^{1}H NMR spectrum of **2**, only the proton at position 4 of the pyrazolyl ring clearly shows ^{205}Tl–H coupling ($J_{Tl-H} = 6.4$ Hz), while the methyl groups and the aromatic H_{ortho} protons of the dimethylbenzyl groups show just a broadening. As already reported [12], ^{205}Tl–H and ^{205}Tl–^{13}C coupling constants are solvent – and temperature dependent: in this case they were measured in CD_2Cl_2 at room temperature. In the ^{13}C NMR spectrum, ^{205}Tl–^{13}C couplings were observed for the pyrazolyl CH resonance ($J_{Tl-C4} = 25.6$ Hz), for the aromatic carbons ($J_{Tl-C\,ortho} = 81.7$ Hz; $J_{Tl-C\,meta} = 37.6$ Hz; $J_{Tl-C\,para} = 16.7$ Hz; $J_{Tl-Cq} = 55.6$ Hz), for the quaternary carbons on the pyrazolyl ring ($J_{Tl-C5} = 42.6$ Hz) and for the methyl of the dimethylbenzyl groups ($J_{Tl-C} = 96.8$ Hz). These data are in agreement with those already reported for similar compounds [12]. The quite large ^{13}C–^{205}Tl couplings for almost all the carbons of the dimethylbenzyl group suggest that this substituent is close to the thallium centre, therefore in position 3, for the three pyrazole groups, while the methyl groups are in position 5.

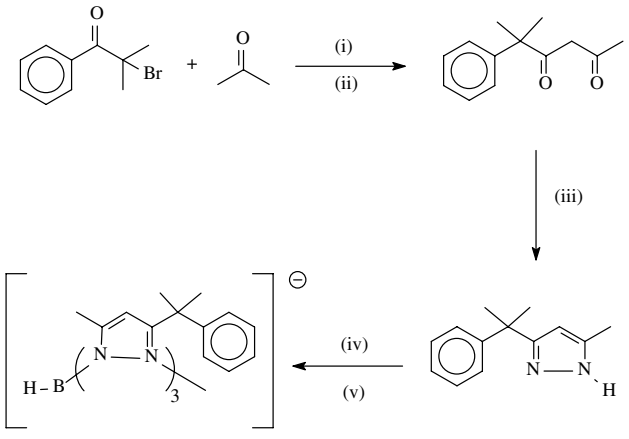
The B-H stretch is quite similar: 2505 cm^{-1} for **1** and 2511 cm^{-1} for **2**. In some cases, depending on the recrystallization conditions, **1** shows two distinct bands (2519, 2461 cm^{-1}) in the B-H stretching region. This behaviour could be ascribed to a solid-state effect, as these materials have the same ^{1}H NMR spectrum in CD_2Cl_2 solution.

Compounds **1** and **2** form with high regioselectivity, no other isomers in solution being detected spectroscopically. These observations could be interpreted by taking into account the steric bulk of the dimethylbenzyl groups, which probably prevents their location in positions 5 of the pyrazole ring, at variance with reports [13] on the synthesis of similar dialkyl-hindered $Tp^{R3,R5}$ ligands (R3 ≠ R5).

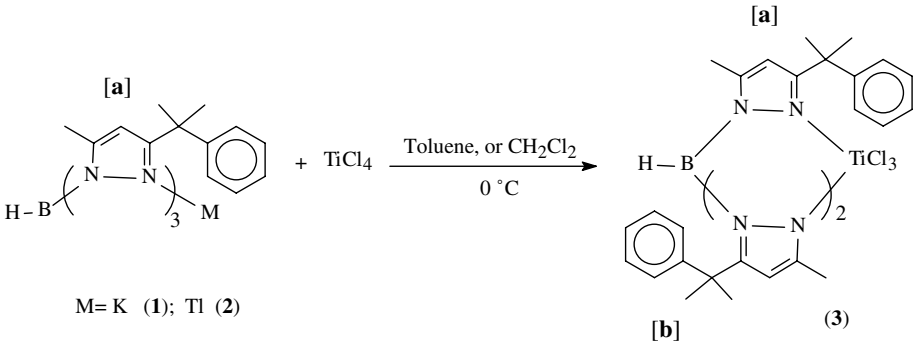
The reaction of K[$Tp^{Me}2^{Bz,Me}$] (**1**) or Tl[$Tp^{Me}2^{Bz,Me}$] (**2**) with one equivalent of $TiCl_4$ in CH_2Cl_2 or toluene at 0 °C, see Scheme 2, affords the Ti(IV) trichloride complex [$Tp^{Me}2^{Bz,Me**}$]$TiCl_3$ (**3**) which was obtained as a red–orange solid in yields as high as 79%, after precipitation with hexane at −18 °C. Compound **3** is well soluble in polar and aromatic solvents, has a poor solubility in aliphatic hydrocarbons, is moderately stable in air in the solid state, while its solutions rapidly decompose on exposure to air.

The structure of **3** has been assigned on the basis of NMR analysis and confirmed in the solid state by an X-ray diffraction experiment. The molecular structure of **3** is shown in Fig. 1, while Table 1 lists the geometrical parameters. The metal has a pseudo-octahedral coordination. Moreover, as it is normally found in titanium–trichloro–pyrazolylborato complexes [4h,7c,14], the three chloride ligands are in a *fac* geometry. The pyrazolylborato ligand shows a configuration of the N(1)–N(2) and N(5)–N(6) rings resulting from a 1,2-borotropic shift and the N(3)–N(4) ring only shows the bulky dimethylbenzyl group in position 3. As a result of this encumbering presence, the Ti–N(3) bond is 0.074 Å longer than the average of the other two Ti–N bonds.

The molecules are held together by van der Waals interactions. The unit cell contains, in addition to four [$Tp^{Me}2^{Bz,Me**}$]$TiCl_3$ molecules, two toluene molecules, which, being placed on inversion centres, are disordered and convey some disorder also to the nearby portions of the titanium-containing complex.



Scheme 1. Synthesis of [$Tp^{Me}2^{Bz,Me}$]$^-$ as its potassium (**1**) or thallium derivatives (**2**). (i): EtMgCl, *t*-BuOH, 0 °C; (ii): refluxing toluene, 4 h; (iii): NH_2–$NH_2 \cdot H_2O$ in refluxing EtOH for 1.5 h; (iv): KBH_4, 240 °C, 4 h; (v): (iv) + $TlNO_3$ in H_2O/organic solvents.



Scheme 2. Preparation of **3**, with the labeling scheme of the pyrazole groups adopted in the NMR characterization.

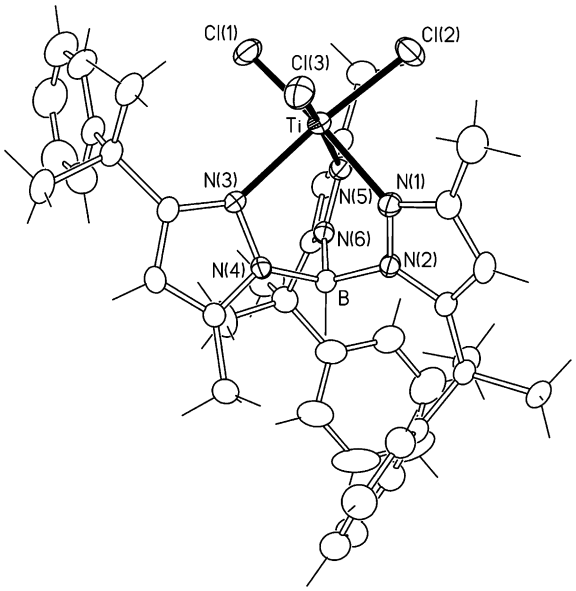


Fig. 1. View of the molecular structure of compound $[Tp^{Me}2^{Bz,Me**}]TiCl_3$ in $\{[Tp^{Me}2^{Bz,Me**}]TiCl_3 \cdot 0.5$ toluene$\}$ (**3** · 0.5 toluene). Thermal ellipsoids are at 30% probability.

Table 1
Bond lengths (Å) and angles (°) around the Ti atom in $\{[Tp^{Me}2^{Bz,Me**}]TiCl_3 \cdot 0.5$toluene$\}$ (**3** · 0.5 toluene)

Ti–Cl(1)	2.242(1)	Ti–N(1)	2.177(3)
Ti–Cl(2)	2.255(1)	Ti–N(3)	2.241(3)
Ti–Cl(3)	2.254(1)	Ti–N(5)	2.158(3)
N(1)–N(2)	1.376(4)	N(2)–B	1.548(5)
N(3)–N(4)	1.387(4)	N(4)–B	1.544(5)
N(5)–N(6)	1.371(4)	N(6)–B	1.561(5)
Cl(1)–Ti–Cl(2)	93.79(6)	Cl(1)–Ti–Cl(3)	99.96(5)
Cl(2)–Ti–Cl(3)	93.94(6)	Cl(1)–Ti–N(1)	171.2(1)
Cl(1)–Ti–N(3)	89.22(9)	Cl(1)–Ti–N(5)	89.99(9)
Cl(2)–Ti–N(1)	89.2(1)	Cl(2)–Ti–N(3)	174.3(1)
Cl(2)–Ti–N(5)	91.0(1)	Cl(3)–Ti–N(1)	88.1(1)
Cl(3)–Ti–N(3)	90.30(9)	Cl(3)–Ti–N(5)	168.6(1)
N(1)–Ti–N(3)	87.2(1)	N(1)–Ti–N(5)	81.6(1)
N(3)–Ti–N(5)	84.2(1)		

The ^{1}H- and ^{13}C NMR spectra of **3** are consistent with the C_s-symmetry of the anion, as for comparison between the ^{1}H NMR spectrum of **1** (Fig. 2a) and that of **3** (Fig. 2b).

The latter shows: (a) two signals of relative intensity 2:1 assigned to pyrazolyl protons at 6.12 and 5.75 ppm, (b) three signals for the methyl benzyl groups at 1.86, 1.42 and 1.25 ppm with relative intensities 6:6:6 and (c) two signals for the methyl group on the pyrazolyl ring, one at 2.69 and the other at very low-frequency, 0.92 ppm, with relative intensity 2:1.

The signals can be grouped as in Table 2, where are also reported (for comparison) the chemical shifts of **1** and **2**. Besides, the *H*-B chemical shifts have also been reported, obtained from boron-decoupled broad-band ^{1}H NMR spectra.

On the basis of the data in Table 2, it can be inferred that there are two sets of pyrazolyl resonances for **3**, one having intensities corresponding to only one pyrazolyl ring [**a**], and the other having intensities pertaining to two pyrazolyl rings [**b**] (see Scheme 2). The benzylic methyl groups in set [**b**], being diastereotopic, give rise to two different signals at 1.42 and 1.25 ppm.

The assignment of the unusual low-frequency chemical shift at 0.92 ppm to the methyl group on the pyrazole, set [**a**], was confirmed by the COSY ^{1}H–^{1}H spectrum reported in Fig. 3, where are clearly evident the cross-peak connecting the *H*-4 protons at 6.12 ppm (set [**b**]) with the pyrazole methyl group at 2.69 ppm and the cross-peak connecting the *H*-4 proton at 5.75 ppm (set [**a**]) with the methyl group at 0.92 ppm.

However, the intensities are reversed with respect to the assignments in the literature [4d,4f], *i.e.* 6.12 ppm (two protons) and 5.75 ppm (one proton). Moreover, in our case the unique pyrazolyl ring is characterized by resonances shifted towards lower frequencies with respect to the literature data. Thus, in our case two pyrazolyl rings undergo a 1,2 borotropic shift to high-frequency while the low-frequency signal maintains the original position. This hypothesis is confirmed by the X-ray crystal structure (see above). A peculiar feature of **3**, disclosed by the X-ray structure is the distance of 3.44 Å between C(14) and the centre of the aromatic ring [C(8)–C(13)], see Fig. 4. Thus, the consistent low-frequency shift (0.92 ppm) of the methyl in position 5 (set [**a**]) (for comparison see the chemical shift of methyl groups in the same position in other Tp′ titanium complexes [14,15]) can reasonably be attributed to the

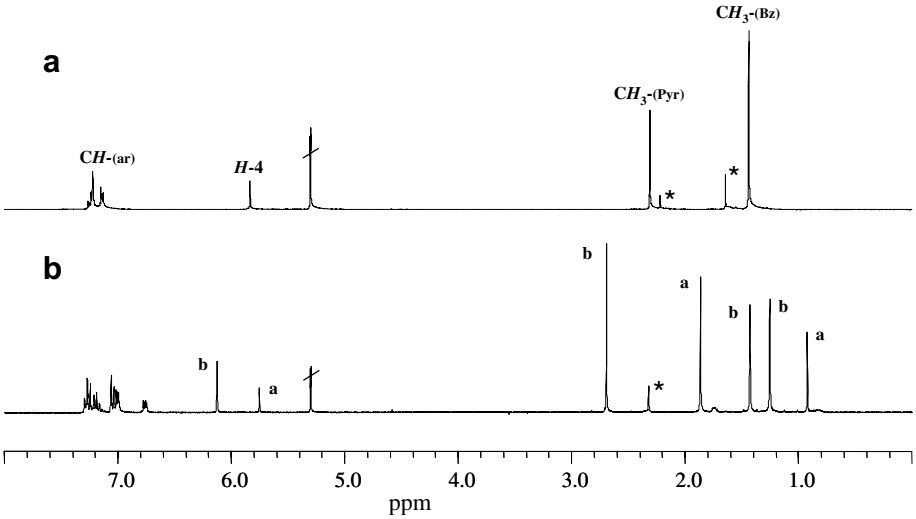


Fig. 2. ^{1}H NMR spectra of K[Tp^{Me}2^{Bz,Me}] (**1**) (a) and [Tp^{Me}2^{Bz,Me**}]TiCl$_3$ (**3**) (b) in CD_2Cl_2 at room temperature. For the labelling scheme, see Table 2 and Scheme 2. The signals marked with an asterisk are due to impurities. The signal at 5.30 ppm is due to CH_2Cl_2.

Table 2
Selected ^{1}H NMR data for compounds **1**, **2** and **3**; in CD_2Cl_2 at room temperature

	H-4		C*H*$_3$-(Pyr)		C*H*$_3$-(Bz)			*H*-B
K[Tp^{Me}2^{Bz,Me}] (**1**)		5.83		2.31	1.44			4.80
(Relative intensity)		*3*		*9*	*18*			*1*
Tl[Tp^{Me}2^{Bz,Me}] (**2**)		5.93 d		2.38	1.42 br			4.70
(Relative intensity)		*3*		*9*	*18*			*1*
[Tp^{Me}2^{Bz,Me**}]TiCl$_3$ (**3**)	6.12	5.75	2.69	0.92	1.86	1.42	1.25	4.05[a]
(Relative intensity)	*2*	*1*	*6*	*3*	*6*	*6*	*6*	*1*
	[**b**]	[**a**]	[**b**]	[**a**]	[**a**]	[**b**]	[**b**]	

[a] In C_7D_8 solution.

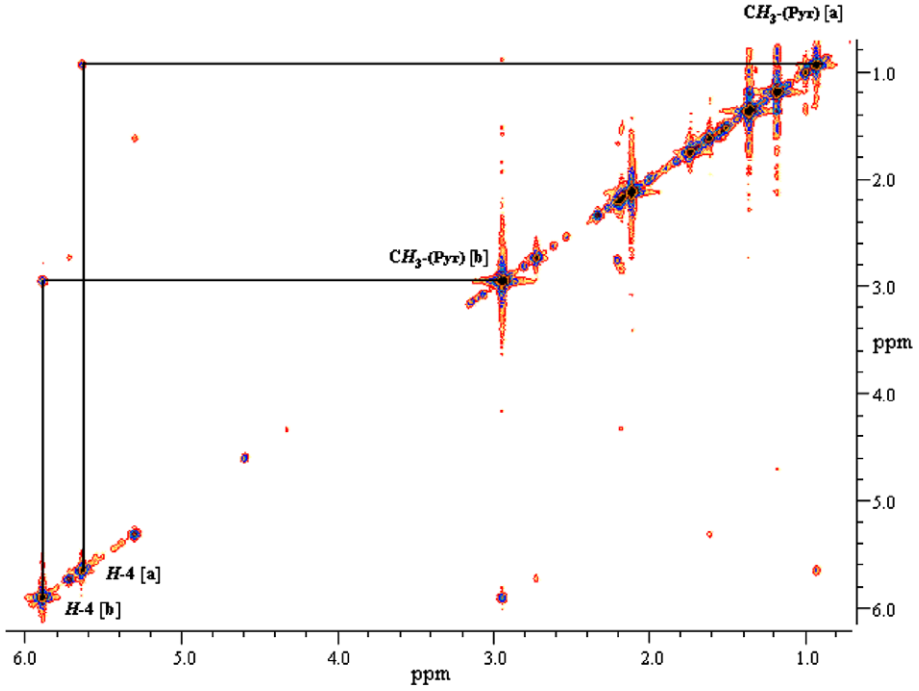


Fig. 3. COSY ^{1}H–^{1}H of [Tp^{Me}2^{Bz,Me**}]TiCl$_3$ (**3**), in CD_2Cl_2 at room temperature.

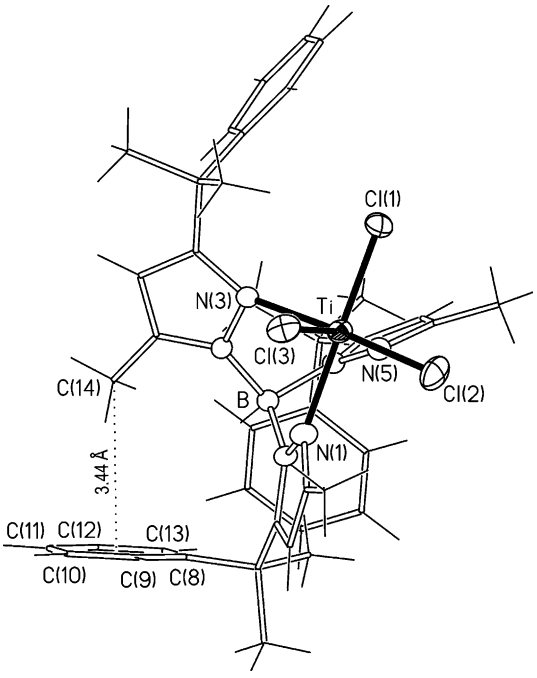


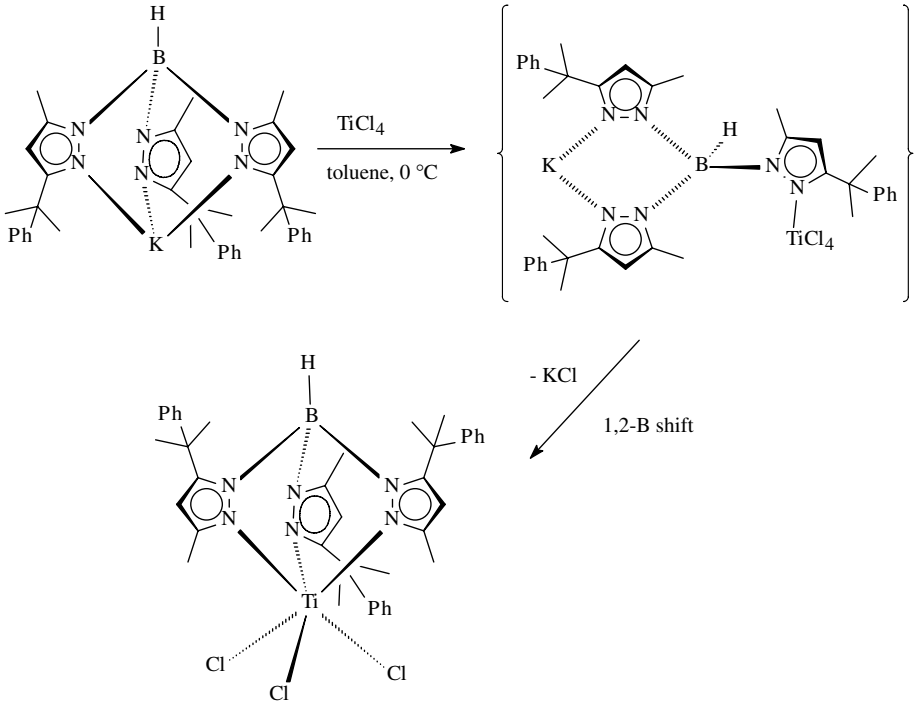
Fig. 4. Projection of the molecular structure of compound [$Tp^{Me}2^{Bz,Me**}$]$TiCl_3$ in {[$Tp^{Me}2^{Bz,Me**}$]$TiCl_3 \cdot 0.5$ toluene} (**3** $\cdot 0.5$ toluene), displaying the short distance between the methyl C(14) and the centre of the aromatic ring [C(8)–C(13)].

shielding effect of the aromatic ring current [16] which can influence the magnetic field around the methyl group.

Obviously, this interpretation stands on the assumption that the solid-state geometrical arrangement is maintained in solution, *i.e.* that the intramolecular interactions are stronger than solid-state effects. In the $^1H\{B^{11}\}$ NMR spectrum the *H*-B resonance at 4.05 ppm (see Table 2) is quite different from the chemical shift observed for complexes **1** and **2**, thus suggesting, also for this proton, a different chemical environment.

The observed B-H stretch at 2564 cm^{-1} for **3** is in agreement with the reported values for other similar dialkyl-$Tp^{R3,R5}$ complexes of titanium(IV) [14,15].

The synthesis of **3** has some unusual features within the chemistry of Tp′ complexes. To the best of our knowledge, **3** is the first compound which is directly obtained through a double 1,2-borotropic shift, starting from the corresponding symmetrical ligand. In fact in the other cases already reported [4f,6a,17] such an isomerization always occurs starting from a Tp^{R*} [Tp^{R*} = HB(3-alkylpyrazolyl)$_2$(5-alkylpyrazolyl)$^-$] transition metal compound and generally it is determined by the formation of the more sterically demanding dinuclear pentacoordinated nickel(II) [6a] or hexacoordinated zirconium(IV) [4f] complexes. Generally a 1,2-borotropic shift is supposed to occur through intermediate species in which the coordination mode of the Tp′ ligand changes from the initial k^3N,N',N'' to k^2 N,N', the transformation being favoured by increasing the temperature and/or in the presence of polar coordinating solvents, such as THF [4d,4f,6a–8]. In the present case, the isomerization of the two pyrazole rings occurs at low temperature and in the absence of oxygenated solvents [18]. A plausible mechanism is shown in Scheme 3. The first interaction with the titanium centre may be realized through the coordination of only one pyrazole ring, while the other



Scheme 3. Possible mechanism of formation of **3**.

two, which eventually still interact with the alkali metal, undergo the 1,2-borotropic shift, which enables the bulky dimethylbenzyl groups to shift to position 5. Finally, also the isomerized pyrazole rings bind to titanium and promote the elimination of the chloride anion.

Support to this hypothesis comes from an experiment in which the reaction between $K[Tp^{Me}2^{Bz,Me}]$ and $TiCl_4$ has been performed directly in a NMR tube, in d^8-toluene at 0 °C at different intervals of time in an attempt to follow the transformation of the system. However, the resonances of **3** were immediately detected, thus suggesting that **3** is already present as such and does not arise from an isomerization of a more symmetric titanium complex. A substantial contribution to the stabilization of the coordinatively unsaturated intermediate species of titanium, described in Scheme 3, could derive from an interaction with the aromatic ring of the dimethylbenzyl group, or from the formation of chloride-bridged dimers, as already reported for Group 4 metals in their reactions with Lewis bases [19]. The observations that some sterically hindered Tp′ ligands can rearrange under mild conditions and that the isomerization could be mediated by electropositive metals (Scheme 3) greatly support the hypothesis that similar processes may generate active species under polymerization conditions, when an excess of aluminium compounds is normally present, which might compete with the transition metal for the coordination of the Tp′ ligand.

3. Experimental

3.1. General procedures

All operations were carried out using standard Schlenk-tube techniques, under an atmosphere of prepurified nitrogen. The reaction vessels were oven-dried prior to use. Solvents were dried by conventional methods.

IR spectra were recorded at 2 cm^{-1} resolution on a Nicolet Nexus FT-IR spectrophotometer; the complexes were analysed in transmission as nujol mulls prepared under exclusion of moisture and air. NMR spectra were recorded with a Varian VXR 300 NMR spectrometer in CD_2Cl_2 [reference peaks: $\delta(^1H) = 5.30$ ppm and $\delta(^{13}C) = 53.7$ ppm] or in $CDCl_3$ solutions [reference peaks: $\delta(^1H) = 7.26$ ppm and $\delta(^{13}C) = 77.0$ ppm] with a pulse width of 7 μs (40°) and a relaxation delay of 1.5 s. $^1H\{^{11}B\}$ broad-band decoupled NMR spectra were obtained with a Bruker Avance 400 MHz instrument. The ^1H–^1H COSY experiment was performed by using the conventional Bruker pulse sequence. Mass spectra were recorded on a Finningan MAT 8400 scan instrument using the DCI technique and *iso*-butane as matrix.

Acetone and *t*-BuOH were distilled over CaH_2. EtMgBr (3 M solution in THF, Acros), 2-bromo-*iso*-butyrophenone (Aldrich), $NH_2NH_2 \cdot H_2O$ (Fluka), KBH_4 (Aldrich), $Tl(NO_3)$ (Aldrich) and $TiCl_4$ (Strem) were used without further purification.

3.2. 5-Phenyl-5-methyl-2,4-hexanedione

To a 3 M THF solution (200 ml) of EtMgBr (0.6 mol), 300 ml of toluene were added, followed by the dropwise addition, in 3 h at 0 °C, of *t*-BuOH (57.5 ml, 0.6 mol) dissolved in 50 ml of toluene. At the end of the addition, the reaction mixture was allowed to warm up to room temperature and stirred overnight. Acetone (22.3 ml, 0.3 mol), diluted with 30 ml of toluene, was slowly added in about 30 min. The resulting solution was treated with 36 ml (0.21 mol) of 2-bromo-*iso*-butyrophenone and refluxed for 4 h, the completion of the reaction being verified by thin layer chromatography (disappearance of the bromo-derivative). The reaction mixture was then hydrolysed, at 0 °C, with 400 ml of H_2SO_4 (5%) and stirred for 3 h. The organic layer was separated and the aqueous phase was extracted with Et_2O (4×100 ml). The resulting organic solution was washed with $NaHCO_3$ (5%) and water to neutrality and finally dried over Na_2SO_4. After evaporation of the volatiles under reduced pressure, a yellow–orange liquid was obtained (43 g), which was distilled affording 32 g [fraction bp (1 mmHg) 69–73 °C] of the yellow 5-phenyl-5-methyl-2,4-hexanedione (75% yield, based on 2-bromo-*iso*-butyrophenone). ^1H NMR ($CDCl_3$): 15.4 (s, 1H, O*H* *en.*); 7.4–7.0 (m, 5H *en.* + 5H *ket.*, $H_{arom.}$); 5.31 (s, 1H, C*H* *en.*); 3.31 (s, 2H, CH_2 *ket.*); 2.00 (s, 3H, CH_3 *ket.*); 1.88 (s, 3H, CH_3 *en.*); 1.50 (s, 6H, CH_3-(Bz) *en.*); 1.47 (s, 6H, CH_3-(Bz) *ket.*) (*en.* = 85 %; *ket.* = 15 %, at room temperature). ^{13}C NMR ($CDCl_3$): 205.5 (*C*O, *ket.*); 201.8 (*C*O, *en.*); 201.5 (*C*O, *ket.*); 187.0 (*C*–OH *en.*); 145.1 (*C*q arom. *en.*); 142.4 (*C*q arom. *ket.*); 128.8, 127.1, 125.9 (*C*H arom. *ket.*); 128.2; 126.4, 126.0 (*C*H arom. *en.*); 97.6 (*C*H *en.*); 52.7; 47.8; 30.0; 26.0; 24.3; 23.5. IR (neat) $\tilde{\nu}/cm^{-1}$: 3409br,w (ν_{OH}), 3088vw, 3060w, 3025w, 2976m, 2931m, 2876vw, 1724w, 1703w, 1626vs ($\nu_{C=O}$), 1599vs ($\nu_{C=O}$), 1496m, 1462w, 1447m, 1418m, 1385w, 1364m, 1303w, 1252s, 1188m, 1156vw, 1118m, 1097s, 1076w, 1054vw, 1031m, 937m, 864s, 793m, 766s, 741w, 700vs, 646w, 555w.

3.3. 3-(1′,1′-Dimethylbenzyl)-5-methyl-pyrazole

To a solution of 19.97 g of 5-phenyl-5-methyl-2,4-hexanedione (97.9 mmol) in 80 ml of EtOH, 25 ml of $NH_2NH_2 \cdot H_2O$ (0.51 mol) dissolved in 50 ml of EtOH, were added dropwise and the reaction mixture was refluxed for 2 h. After addition of 100 ml of Et_2O, the resulting solution was washed with water (3×50 ml) to remove the excess hydrazine, and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, a pale yellow solid was obtained (16.92 g), which was recrystallized from hexane at −18 °C affording 13.04 g (67% yield) of colourless large crystals of 3-(1′,1′-dimethylbenzyl)-5-methyl-pyrazole. Found: C, 77.5; H, 7.9; N, 14.0%. $C_{13}H_{16}N_2$ requires: C, 77.6; H, 8.5; N, 13.9%. Mass spectrum (DCI) m/z: $[M + H^+]$ 201 (100%). ^1H NMR (CD_2Cl_2): 10.12 (s, broad, 1H, N-*H*); 7.27–7.17 (m, 5H, $H_{arom.}$); 5.86 (s, 1H,

H-4); 2.21 (s, 3H, CH_3-5); 1.65 (s, 6H, CH_3-(Bz)). ^{13}C NMR (CD_2Cl_2): 157.5 (1C, *C*q); 149.4 (1C, *C*q); 144.1 (1C, *C*q); 128.5 (2C, *C*H arom.); 126.5 (2C, *C*H arom.); 126.3 (1C, *C*H arom.); 102.6 (1C, *C*H-4); 39.4 (1C, *C*q-(Bz)); 29.9 (2C, *C*H_3-(Bz)); 12.3 (1C, *C*H_3-5). IR (nujol mull) $\tilde{\nu}$/cm^{-1}: 3161w, 3126vw, 3085m, 2727vw, 1599vw, 1570m, 1365w, 1298s, 1238w, 1202w, 1189vw, 1157m, 1115w, 1075m, 1031w, 1017s, 1000w, 944vw, 921vw, 903vw, 860br,m, 788m, 777w, 764m, 759s, 722m, 697vs, 566w, 555w, 507vw.

3.4. Potassium hydrido-tris[3-(1′,1′-dimethylbenzyl)-5-methyl-pyrazol-1-yl]borato, K[Tp^{Me}2^{Bz,Me2}] (**1**)

A mixture of 0.98 g of KBH_4 (18.1 mmol) and 10.97 g of 3-(1′,1′-dimethylbenzyl)-5-methyl-pyrazole (54.6 mmol), maintained under a dinitrogen atmosphere, was heated gradually with stirring up to 240 °C in about 2 h and kept at this temperature until the di-hydrogen evolution was over (3–5 h). The melt was cooled down to room temperature in a nitrogen atmosphere and 70 ml of hexane were added. The resulting slurry was stirred for 1 h and the colourless solid was then recovered by filtration and dried *in vacuo* giving 5.2 g of **1**. An additional crop of product (1.9 g) was recovered by cooling the mother liquor at −18 °C (61% total yield). Found: C, 71.0; H, 7.2; N, 12.8%. $C_{39}H_{46}BKN_6$ requires: C, 72.2; H, 7.1; N, 12.9%. Mass spectrum (DCI) m/z: [M + H$^+$] 650 (100%). ^{1}H NMR (CD_2Cl_2): 7.30–7.10 (m, 15H, $H_{arom.}$); 5.83 (s, 3H, *H*-4); 4.80 (s, broad, 1H, *H*-B); 2.31 (s, 9H, CH_3-5); 1.44 (s, 18H, CH_3-(Bz)). ^{13}C NMR (CD_2Cl_2): 161.3 (1C, *C*-3); 152.0 (1C, *C*q arom.); 144.2 (1C, *C*-5); 128.8 (2C, *C*H arom.); 127.5 (2C, *C*H arom.);126.5 (1C, *C*H arom.); 102.0 (1C, *C*H-4); 40.3 (1C, *C*q-(Bz)); 31.3 (2C, *C*H_3-(Bz)) 14.0 (1C, *C*H_3-5). IR (nujol mull) $\tilde{\nu}$/cm^{-1}: 3085vw, 3057w, 2726vw, 2519w (ν_{BH}), 2461w (ν_{BH}), 1598m, 1578w, 1533s, 1494s, 1446m, 1422w, 1365m, 1360m, 1346s, 1239w, 1202m, 1180m, 1096w, 1072s, 1030w, 1008m, 980w, 926vw, 905vw, 821w, 805m, 779m, 769s, 751w, 728vw, 701vs, 679vw, 654m, 649m, 624w, 571m 515w.

3.5. Thallium hydrido-tris[3-(1′,1′-dimethylbenzyl)-5-methyl- pyrazol-1-yl]borato, Tl[Tp^{Me}2^{Bz,Me2}] (**2**)

In a round-bottomed flask were introduced 0.78 g of KBH_4 (14.4 mmol) and 8.89 g of 3-(1′,1′-dimethylbenzyl)-5-methyl-pyrazole (44.2 mmol). By operating under a nitrogen atmosphere, the solid mixture was gradually heated up to 240 °C and kept at this temperature for about 5 h, up to the end of di-hydrogen evolution. The melt was finally cooled down to room temperature in a di-nitrogen atmosphere and the resulting solid was dissolved in 40 ml of THF. The tetrahydrofuran solution was then added to a mixture of 5 g (18.8 mmol) of $TlNO_3$, in 80 ml of H_2O and 80 ml of CH_2Cl_2. After stirring at room temperature for 1 h, the product was extracted with Et_2O (6 × 20 ml) and the resulting solution was dried over Na_2SO_4. A pale yellow sticky solid was obtained on evaporation of the solvent *in vacuo*: hexane (50 ml) was added and the resulting slurry was stirred for 1 h. The colourless solid was recovered by filtration and dried *in vacuo* giving 4.9 g of **2**. An additional crop of product (1.8 g) was recovered by cooling the mother liquor at −18 °C (57% total yield). Found: C, 56.9; H, 5.8; N, 10.2%. $C_{39}H_{46}BN_6Tl$ requires: C, 57.5; H, 5.7; N, 10.3%. Mass spectrum (DCI) m/z: [M + H$^+$] 815 (100%). ^{1}H NMR (CD_2Cl_2): 7.15 (m, 9H, $H_{meta+para}$); 7.01 (m broad, 6H, H_{ortho}); 5.93 (d, 3H, *H*-4, J_{Tl-H} = 6.4 Hz); 4.70 (s, broad, 1H, *H*-B); 2.38 (s broad, 9H, CH_3-5); 1.42 (s, 18H, CH_3-(Bz)). ^{13}C NMR (CD_2Cl_2): 163.3 (d, 1C, *C*-3, J_{Tl-C} = 42.6 Hz); 152.1 (d, 1C, *C*q arom., J_{Tl-C} = 55.6 Hz); 145.4 (s, 1C, *C*-5); 130.2 (d, 2C, *C*H-*meta*, J_{Tl-C} = 37.6 Hz); 128.6 (d, 2C, *C*H-*ortho*, J_{Tl-C} = 81.7 Hz); 127.6 (d, 1C, *C*H-*para*, J_{Tl-C} = 16.7 Hz); 105.0 (d, 1C, *C*H-4, J_{Tl-C} = 25.6 Hz); 41.3 (s, 1C, *C*q-(Bz)); 33.1 (d, 2C, *C*H_3-(Bz), J_{Tl-C} = 96.8 Hz); 14.9 (s, 1C, *C*H_3-5). IR (nujol mull) $\tilde{\nu}$/cm^{-1}: 3080vw, 3055w, 2723vw, 2511w (ν_{BH}), 1531m, 1494s, 1422m, 1360s, 1340m, 1235w, 1184s, 1157vw, 1067s, 1029w, 1011m, 984w, 831w, 806w, 791m, 764vs, 752m, 722w, 703s, 698s, 653m, 623w, 562m.

3.6. {Hydrido-[(3-Me,5-Me$_2$Bz)$_2$(3-Me$_2$Bz,5Me)-pyrazol-1-yl]borato}trichloro-titanium(IV), [Tp^{Me}2^{Bz,Me2**}]TiCl$_3$ (**3**)

3.6.1. From **1**, in toluene as solvent

In a 250 ml round-bottomed flask were introduced 1.56 g (2.4 mmol) of K[Tp^{Me}2^{Bz,Me2}] (**1**), dissolved in 50 ml of toluene. The colourless solution was cooled with an ice bath and 0.3 ml of $TiCl_4$ (2.7 mmol) in 20 ml of toluene were added dropwise in about 30 min. The resulting orange–brown solution was stirred at 0 °C for 24 h. After removal of KCl by filtration, the volume of the solution was reduced to 30 ml *in vacuo* and 30 ml of hexane were finally added. After cooling at −18 °C, the red–orange crystals which separated out were recovered by filtration and dried *in vacuo* affording 1.09 g of **3** (59% yield). Found: C, 62.0; H, 6.0; N, 9.8; Cl, 12.9%. $C_{39}H_{46}BCl_3N_6Ti$ requires: C, 61.3; H, 6.1; N, 11.0; Cl, 13.9%. Mass spectrum (DCI, negative ion) m/z: [M$^-$] 764 (80%); [M$^-$ − Cl] 727 (20%); [2 pz + Cl] 435 (40%); [pz + Cl] 235 (100%). ^{1}H NMR (CD_2Cl_2): 7.3–6.9 (m, 13H, $H_{arom.}$ [**a** + **b**]); 6.7–6.8 (m, 2H, H_{ortho}[**a**]); 6.12 (s, 2H, *H*-4 [**b**]); 5.75 (s, 1H, *H*-4 [**a**]); 2.69 (s, 6H, CH_3-(Pyr) [**b**]); 1.86 (s, 6H, CH_3-(Bz) [**a**]); 1.42 (s, 6H, CH_3-(Bz) [**b**]); 1.25 (s, 6H, CH_3–(Bz) [**b**]); 0.92 (s, 3H, CH_3-(Pyr) [**a**]). ^{13}C NMR (CD_2Cl_2): 166.9 (1C, *C*-3 [**a**]), 158.3 (2C, *C*-3 [**b**]), 156.5 (2C, *C*q arom. [**b**]), 152.0 (1C, *C*q arom. [**a**]), 150.0 (2C, *C*-5 [**b**]), 147.9 (1C, *C*-5 [**a**]), 130.6–127.1 (*C*H arom.); 110.2 (1C, *C*-4 [**a**]); 109.6 (2C, *C*-4 [**b**]); 44.0 (1C, *C*q-(Bz) [**a**]); 41.3 (2C, *C*q-(Bz) [**b**]); 34.6 (2C, *C*H_3-(Bz) [**b**]); 33.9 (2C, *C*H_3-(Bz) [**b**]); 32.2 (2C, *C*H_3-(Bz) [**a**]); 19.5 (2C, *C*H_3-(Pyr) [**b**]); 12.8 (1C, *C*H_3-(Pyr) [**a**]). IR (nujol mull) $\tilde{\nu}$/cm^{-1}: 3141vw, 3086vw, 3051w, 3021w, 2726vw, 2564m (ν_{BH}), 1600m, 1581w, 1541s, 1530s, 1495s, 1413s, 1365m, 1338m, 1275vw,

1238w, 1208m, 1177s, 1135m, 1100vw, 1085w, 1074w, 1064w, 1052s, 1030w, 1007m, 949vw, 925vw, 905w, 852w, 836m, 815w, 806m, 793w, 769s, 746m, 729m, 717s, 700vs, 672w, 651w, 640m, 626w, 561w.

*3.6.2. From **1**, in dichloromethane*

In a 100 ml round-bottomed flask were introduced 0.97 g (1.5 mmol) of $K[Tp^{Me}2^{Bz,Me2}]$ (**1**) dissolved in 25 ml of CH_2Cl_2; a solution of 0.2 ml (1.8 mmol) of $TiCl_4$ in 25 ml of CH_2Cl_2 was then added dropwise in about 30 min at room temperature. By operating as above described, 0.59 g (52% yield) of **3** were recovered. Analytical and spectroscopic data were in accord with those reported above.

*3.6.3. From **2**, in dichloromethane*

In a 250 ml round-bottomed flask were introduced 0.97 g (1.2 mmol) of $Tl[Tp^{Me}2^{Bz,Me2}]$ (**2**), dissolved in 50 ml of CH_2Cl_2. The colourless solution was cooled with an ice bath and 0.16 ml of $TiCl_4$ (1.4 mmol) in 20 ml of CH_2Cl_2 were added dropwise in about 30 min. The solution, which turned to orange–brown within a few minutes, was stirred at 0 °C for 2 h. Then the solvent was removed *in vacuo* and the residue was treated with 50 ml of toluene, the pale yellow residue of TlCl was separated by decantation, and the resulting red–orange solution was treated with 80 ml of hexane and cooled at −18 °C. The red–orange crystals which separated out were recovered by filtration and dried *in vacuo* affording 0.72 g of **3** (79% yield). ^{1}H NMR (C_7D_8): 7.20–6.80 (m, 15H, *H*arom. [**a** + **b**]); 5.77 (s, 2H, *H*-4 [**b**]); 5.51 (s, 1H, *H*-4 [**a**]); 4.05 (s, broad, 1H, *H*-B); 2.82 (s, 6H, C*H*$_3$-(Pyr) [**b**]); 1.99 (s, 6H, C*H*$_3$–(Bz) [**a**]); 1.23 (s, 6H, C*H*$_3$-(Bz) [**b**]); 1.06(s, 6H, C*H*$_3$-(Bz) [**b**]); 0.80 (s, 3H, C*H*$_3$-(Pyr) [**a**]).

*3.7. Crystal structure determination of compound **3***

Single crystals of (**3** · 0.5 toluene), empirical composition $C_{42.5}H_{50}BCl_3N_6Ti$, FW 809.95 a.m.u., suitable for the X-ray diffraction analysis, were obtained at room temperature by slow diffusion of hexane into a toluene solution. The diffractometric experiment was carried out by using a Bruker AXS P4 instrument equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were collected in the $\omega/2\theta$ scan mode, and three standard reflections were monitored every 97 measurements for checking crystal decay and equipment stability. For data reduction the XSCANS program was used [20]. A suitable crystal was glued at the end of a glass fibre and the unit cell parameters, $a = 13.880(2)$, $b = 16.260(2)$, $c = 18.542(2)$ Å, $\alpha = \gamma = 90$, $\beta = 93.97(1)°$, were calculated from the setting angles of 35 strong reflections. A set of 9287 intensity data were collected between $1.7° \leqslant \theta \leqslant 25.5°$ and corrected for Lorentz polarization and absorption effects (ψ-scan method, $\mu = 0.435$ mm^{-1}). After merging of equivalent reflections $\{R_{int} = [\sum |F_o^2 - F_o^2(\text{mean})| / \sum (F_o^2)] = 0.0371\}$, 7655 independent reflections were obtained. The structure was solved by the standard direct methods in the $P2_1/n$ (No. 14) space group. After completion of the main molecule, a sequence of broad maxima was found in the difference Fourier map around the inversion centre at 0, 0, 1/2, Wyckoff position *b*, due to the presence of a disordered toluene molecule. An idealized toluene molecule was then found to fit the sequence of maxima and introduced in the calculations with an occupancy factor of 1/2. The action of the $\bar{1}$ operator brought the occupancy factor of the site up to 1 and gave account of the disorder. The multiplicity of the site *b* gave a **3**/toluene ratio of 0.5. The following refinement cycles brought some thermal parameters of the phenyl groups in **3** to abnormally high values, possibly due to some degree of disorder induced by the toluene molecule. The refinement was, however, continued without introducing the disorder in those groups.

The calculations were done by using the SHELXTL program [21] and some routines contained in the WINGX suite [22].The final refinement cycle including 511 parameters gave for the 7655 intensity data with $I > 2\sigma(I)$ a R_1 factor of 0.0584, a wR_2 factor of 0.1427 and a *S* factor of 1.010 calculated on F^2.

Acknowledgements

The authors of the University of Pisa wish to thank the Ministero dell'Università e dell'Istruzione, dell'Università e della Ricerca, Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale 2004-5, for financial support.

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 298918 for compound **3**. 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 e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.026).

References

[1] S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842.
[2] (a) S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999;
(b) G. Parkin, Adv. Inorg. Chem. 42 (1995) 291;
(c) N. Kitajima, W.B. Tolman, Progr. Inorg. Chem. 43 (1995) 419;
(d) S. Trofimenko, Chem. Rev. 93 (1993) 943;
(e) S. Trofimenko, Chem. Rev. 72 (1972) 497.
[3] C. Pettinari, C. Santini, Polypyrazolylborate and scorpionate ligands, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, in: A.B. P. Lever (Ed.) Elsevier Pergamon, Oxford, 1, 2004, 159 and ff.
[4] (a) F.A. Kunrath, R.F. de Souza, O.L. Casagrande, Macromol. Rapid Commun. 21 (2000) 277;
(b) L.G. Furlan, M.P. Gil, O.L. Casagrande, Macromol. Rapid Commun. 21 (2000) 1054;

(c) M.P. Gil, J.H.Z. dos Santos, O.L. Casagrande, Macromol. Chem. Phys. 202 (2001) 319;
(d) S. Murtuza, O.L. Casagrande, R.F. Jordan, Organometallics 21 (2002) 1882;
(e) K. Michiue, R.F. Jordan, Macromolecules 36 (2003) 9707;
(f) K. Michiue, R.F. Jordan, Organometallics 23 (2004) 460;
(g) M.P. Gil, J.H.Z. dos Santos, O.L. Casagrande, J. Mol. Catal. A: Chem. 209 (2004) 163;
(h) M.P. Gil, O.L. Casagrande, J. Organomet. Chem. 689 (2004) 286;
(i) G. Parkin, Adv. Inorg. Chem. 42 (1995) 291;
(j) A.H. Cowley, L. Geerts, C.M. Nunn, S. Trofimenko, J. Organomet. Chem. 365 (1989) 19;
(k) K. Yoon, G. Parkin, Polyhedron 14 (1995) 811;
(l) D.D. LeCloux, C.J. Tokar, M. Osawa, R.P. Houser, M.C. Keyes, W.B. Tolman, Organometallics 13 (1994) 2855;
(m) G. Ferguson, M.C. Jennings, F.J. Lalor, C. Shanahan, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 47 (1991) 2079;
(n) A. Rheingold, R.L. Ostrander, B.S. Haggerty, S. Trofimenko, Inorg. Chem. 33 (1994) 3666;
(o) E. Libertini, K. Yoon, G. Parkin, Polyhedron 12 (1993) 2539;
(p) R. Han, G. Parkin, S. Trofimenko, Polyhedron 14 (1995) 387.

[5] O.L. Casagrande, A.C.A. Casagrande, M.P. Gil, J.J. Zacca, R. F. Jordan, Br. 9904045-0 (1999) to OPP Petrochemicals.

[6] (a) F.A. Kunrath, R.F. de Souza, O.L. Casagrande, N.R. Brooks, V.G. Young, Organometallics 22 (2003) 4739;
(b) L.G. Furlan, F.A. Kunrath, R.S. Mauler, R.F. de Souza, O.L. Casagrande, J. Mol. Catal. A: Chem. 214 (2004) 207;
(c) R. Santi, A.M. Romano, A. Sommazzi, M. Grande, C. Bianchini, G. Mantovani, J. Mol. Catal. A: Chem. 229 (2005) 191.

[7] (a) S. Trofimenko, J.C. Calabrese, P.J. Domaille, J.S. Thompson, Inorg. Chem. 28 (1989) 1091;
(b) J.C. Calabrese, S. Trofimenko, Inorg. Chem. 31 (1992) 4810;
(c) D.D. LeCloux, M.C. Keyes, M. Osawa, V. Reynolds, W.B. Tolman, Inorg. Chem. 33 (1994) 6361.

[8] (a) A. Looney, G. Parkin, Polyhedron 9 (1990) 265;
(b) M.H. Chisholm, N.W. Eilerts, J.C. Huffman, Inorg. Chem. 35 (1996) 445.

[9] M. Lukasiewicz, Z. Ciunik, S. Wolowiec, Polyhedron 19 (2000) 2119.

[10] The abbreviation $Tp^{Me}2^{Bz,Me2**}$ is based on Trofimenko's rules [2] and denotes the presence of two dimethylbenzyl groups in position 5 – of the pyrazolyl ring.

[11] (a) A.V. Kel'in, Y. Yu. Kozyrkov, Synthesis (1998) 729;
(b) E.P. Kohler, M. Tishler, J. Am. Chem. Soc. 57 (1935) 217.

[12] C. Lopez, D. Sanz, R.M. Claramunt, S. Trofimenko, J. Elguero, J. Organometal. Chem. 503 (1995) 265.

[13] (a) M. Cano, J.V. Eras, C.J. Jones, J.A. McCleverty, S. Trofimenko, Polyhedron 9 (1990) 619;
(b) O.M. Reinaud, A.L. Rheingold, K.H. Theopold, Inorg. Chem. 33 (1994) 2306.

[14] (a) D.L. Hughes, G.J. Leigh, D.G. Walker, J. Chem. Soc., Dalton Trans. (1988) 1153;
(b) A. Antinolo, F. Carrillo-Hermosilla, A.E. Corrochano, J. Fernandez-Baeza, M. Lanfranchi, A. Otero, M.A. Pellinghelli, J. Organomet. Chem. 577 (1999) 174.

[15] (a) H. Cai, W.H. Lam, X. Yu, X. Liu, Z.Z. Wu, T. Chen, Z. Lin, X.T. Chen, X.Z. You, Z. Xue, Inorg. Chem. 42 (2003) 3008;
(b) J.K. Kouba, S.S. Wreford, Inorg. Chem. 15 (1976) 2313;
(c) J. Ipaktschi, W. Sulzbach, J. Organomet. Chem. 426 (1992) 59.

[16] F.A. Bovey, Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1969.

[17] A. Albinati, M. Bovens, H. Ruegger, L.M. Venanzi, Inorg. Chem. 36 (1997) 5991.

[18] The reaction between $TlTp^{Mes}$ and $ZrCl_4$ or $HfCl_4$, in toluene as solvent has been recently reported to produce mixtures of $Tp^{Mes}ZrCl_3/Tp^{Mes*}ZrCl_3$ and $Tp^{Mes}HfCl_3/Tp^{Mes*}HfCl_3$, respectively [4f].

[19] (a) C.I. Brändén, I. Lindqvist, Acta Chem. Scand. 14 (1960) 726;
(b) L. Burn, Acta Crystallogr. 20 (1966) 739;
(c) I.W. Bassi, M. Calcaterra, R. Intrito, J. Organometal. Chem. 127 (1977) 305;
(d) D.A. Young, J. Mol. Catal. 53 (1989) 433;
(e) E. Solari, C. Floriani, K. Schenk, J. Chem. Soc., Chem. Commun. (1990) 963;
(f) T. Lis, J. Utko, P. Sobota, Acta Crystallogr., Sect. C 49 (1993) 2089;
(g) F. Calderazzo, M. D'Attoma, F. Marchetti, G. Pampaloni, S.I. Troyanov, J. Chem. Soc., Dalton Trans. (1999) 2275.

[20] XSCANS, X-ray Single Crystal Analysis System, Rel. 2.1 Bruker AXS Inc., Madison, Wisconsin, USA, 1994.

[21] G.M. Sheldrick, SHELXTL-Plus, Rel. 5.03, Bruker AXS Inc., Madison, Wisconsin, USA, 1995.

[22] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.