

# Cp[Tm<sup>Me</sup>]ZrCl<sub>2</sub>, a Tris(2-mercapto-1-methylimidazolyl)hydroborato Complex of Zirconium and a New Type of Precatalyst for Olefin Polymerization

Daniela Buccella, Abraham Shultz, Jonathan G. Melnick, Felicia Konopka, and Gerard Parkin\*

Department of Chemistry, Columbia University, New York, New York 10027

Received June 28, 2006

**Summary:** Cp[Tm<sup>Me</sup>]ZrCl<sub>2</sub>, the first tris(2-mercapto-1-methylimidazolyl)hydroborato complex of zirconium, is obtained by reaction of CpZrCl<sub>3</sub> with [Tm<sup>Me</sup>]K. The molecular structure of Cp[Tm<sup>Me</sup>]ZrCl<sub>2</sub> has been determined by X-ray diffraction, and the geometry closely resembles the bent-metallocene motif of Cp<sub>2</sub>ZrCl<sub>2</sub>. An important distinction, however, is that Cp[Tm<sup>Me</sup>]ZrCl<sub>2</sub> is chiral, with C<sub>1</sub> symmetry. The chirality of Cp[Tm<sup>Me</sup>]ZrCl<sub>2</sub> is a consequence of the fact that the [Tm<sup>Me</sup>] ligand exhibits a propeller-like twist such that it has local C<sub>3</sub> symmetry and is therefore devoid of a mirror plane. Variable-temperature <sup>1</sup>H NMR studies demonstrate that enantiomer interconversion does not occur on the NMR time scale. In combination with methylalumoxane, Cp[Tm<sup>Me</sup>]ZrCl<sub>2</sub> produces an active catalyst for ethylene polymerization.

## Introduction

The tris(2-mercapto-1-R-imidazolyl)hydroborato ligand, [Tm<sup>R</sup>],<sup>1</sup> introduced by Reglinski and Spicer in 1996,<sup>1a</sup> has been shown to be a versatile ligand in coordination chemistry.<sup>2</sup> In view of the fact that the [Tm<sup>R</sup>] ligand belongs to the same L<sub>2</sub>X class as the ubiquitous cyclopentadienyl ligand,<sup>3</sup> it is anticipated that [Tm<sup>R</sup>] will also serve as an ancillary ligand for an extensive and diverse series of organotransition metal compounds. Indeed, several counterparts of well-known cyclopentadienyl complexes are known, as exemplified by mixed-sandwich derivatives, e.g. [Tm<sup>Me</sup>]Ru(Cp),<sup>4</sup> [Tm<sup>Me</sup>]Ru(Cp\*),<sup>5</sup> {[Tm<sup>Me</sup>]Ru(Cp\*)}<sup>+</sup>,<sup>5</sup> {[Tm<sup>Me</sup>]Co(Cp<sup>Me</sup>)}<sup>+</sup>,<sup>6</sup> {[Tm<sup>R</sup>]Ru(*p*-Cym)}<sup>+</sup>,<sup>1g,4</sup> and {[Tm<sup>Me</sup>]Ru(C<sub>6</sub>Me<sub>6</sub>)}<sup>+</sup>,<sup>7</sup> carbonyl derivatives, e.g. {[Tm<sup>Me</sup>]M(CO)<sub>3</sub>}<sup>-</sup> (M = Mo, W),<sup>8</sup> [Tm<sup>Me</sup>]Mo(CO)<sub>3</sub>SnR<sub>3</sub>,<sup>9</sup>

[Tm<sup>Me</sup>]M(CO)<sub>2</sub>(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>) (M = Mo, W),<sup>8</sup> [Tm<sup>Me</sup>]W(CO)<sub>2</sub>(CR),<sup>10</sup> [RTm<sup>R</sup>]Mn(CO)<sub>3</sub>,<sup>1g,4,11</sup> and [RTm<sup>Me</sup>]Re(CO)<sub>3</sub>,<sup>12</sup> and alkyl derivatives, e.g. [Tm<sup>Me</sup>]PtMe<sub>3</sub>.<sup>13–15</sup> To date, however, the majority of studies employing [Tm<sup>R</sup>] ligands have largely focused on the group 6–10 transition metals, with the first examples of group 5 derivatives, namely [Tm<sup>Me</sup>]M(NR)Cl<sub>2</sub> (M = Nb, Ta), having been only recently reported.<sup>16</sup> We are particularly interested in developing the chemistry of [Tm<sup>R</sup>] counterparts of the well-known metallocene systems, Cp<sub>2</sub>MX<sub>2</sub>, and in this paper we describe the synthesis and structural characterization of Cp[Tm<sup>Me</sup>]ZrCl<sub>2</sub>, a relative of Cp<sub>2</sub>ZrCl<sub>2</sub> and the first [Tm<sup>Me</sup>] zirconium derivative.

## Results and Discussion

Tris(2-mercapto-1-R-imidazolyl)hydroborato complexes of the group 4 transition metals are presently unknown, despite efforts to obtain such complexes. For example, attempts to synthesize [Tm<sup>Me</sup>]<sub>x</sub>TiCl<sub>4-x</sub> derivatives via reactions of TiCl<sub>4</sub> or TiCl<sub>4</sub>(THF)<sub>2</sub> with [Tm<sup>Me</sup>]Na were reported to be unsuccessful due to redox/ligand cleavage processes interfering with a simple metathesis reaction.<sup>17,18</sup> Furthermore, the reactions of CpMCl<sub>4</sub> (M = Nb, Ta) with [Tm<sup>Me</sup>]SnPh<sub>3</sub> do not give Cp[Tm<sup>Me</sup>]MCl<sub>3</sub>, but rather give CpM[κ<sup>2</sup>-H(Cl)B(mim<sup>Me</sup>)<sub>2</sub>]Cl<sub>2</sub> derived from

\* To whom correspondence should be addressed. E-mail: parkin@columbia.edu.

(1) See, for example: (a) Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *J. Chem. Soc., Chem. Commun.* **1996**, 1975–1976. (b) Reglinski, J.; Garner, M.; Cassidy, I. D.; Slavin, P. A.; Spicer, M. D.; Armstrong, D. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2119–2126. (c) Santini, C.; Lobbia, G. G.; Pettinari, C.; Pellei, M.; Valle, G.; Calogero, S. *Inorg. Chem.* **1998**, *37*, 890–900. (d) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Chem. Commun.* **1999**, 2301–2302. (e) Tesmer, M.; Shu, M.; Vahrenkamp, H. *Inorg. Chem.* **2001**, *40*, 4022–4029. (f) Bakbak, S.; Bhatia, V. K.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Polyhedron* **2001**, *20*, 3343–3348. (g) Bailey, P. J.; Dawson, A.; McCormack, C.; Moggach, S. A.; Oswald, I. D. H.; Parsons, S.; Rankin, D. W. H.; Turner, A. *Inorg. Chem.* **2005**, *44*, 8884–8898.

(2) For example, we have employed the [Tm<sup>R</sup>] system to mimic aspects of the sulfur-rich active sites in zinc enzymes and proteins. See: (a) Morlok, M. M.; Janak, K. E.; Zhu, G.; Quarless, D. A.; Parkin, G. *J. Am. Chem. Soc.* **2005**, *127*, 14039–14050. (b) Bridgewater, B. M.; Fillebeen, T.; Friesner, R. A.; Parkin, G. *Dalton Trans.* **2000**, 4494–4496. (c) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Chem. Commun.* **1999**, 2301–2302. (d) Bridgewater, B. M.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 7140–7141.

(3) For a discussion of the L<sub>2</sub>X covalent bond classification of ligands, see: Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127–148.

(4) Bailey, P. J.; Llorono-Gonzales, D. J.; McCormack, C.; Parsons, S.; Price, M. *Inorg. Chim. Acta* **2003**, *354*, 61–67.

(5) Kuan, S. L.; Leong, W. K.; Goh, L. Y.; Webster, R. D. *Organometallics* **2005**, *24*, 4639–4648.

(6) Dodds, C. A.; Lehmann, M.-A.; Ojo, J. F.; Reglinski, J.; Spicer, M. D. *Inorg. Chem.* **2004**, *43*, 4927–4934.

(7) Kuan, S. L.; Leong, W. K.; Goh, L. Y.; Webster, R. D. *J. Organomet. Chem.* **2006**, *691*, 907–915.

(8) Garner, M.; Lehmann, M.-A.; Reglinski, J.; Spicer, M. D. *Organometallics* **2001**, *20*, 5233–5236.

(9) Foreman, M. R. St.-J.; Hill, A. F.; Smith, M. K.; Tshabang, N. *Organometallics* **2005**, *24*, 5224–5226.

(10) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 3831–3840.

(11) Graham, L. A.; Fout, A. R.; Kuehne, K. R.; White, J. L.; Mookherji, B.; Marks, F. M.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L.; Rabinovich, D. *Dalton Trans.* **2005**, 171–180.

(12) (a) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **2001**, *632*, 41–48. (b) Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. *Dalton Trans.* **2003**, 2757–2760.

(13) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 4889–4892.

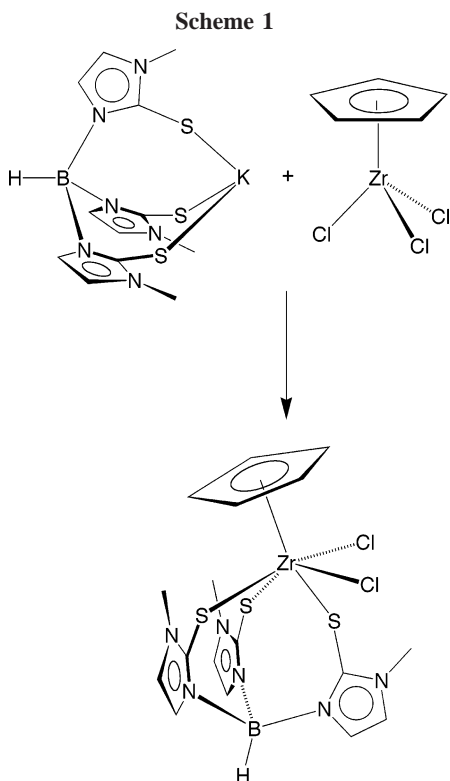
(14) Organometallic compounds of the main-group elements are also known: e.g., [Tm<sup>Bu</sup>]ZnMe and [Tm<sup>Bu</sup>]CdMe. See: (a) Melnick, J. G.; Docrat, A.; Parkin, G. *Chem. Commun.* **2004**, 2870–2871. (b) Melnick, J. G.; Parkin, G. *Dalton Trans.*, in press.

(15) For a variety of {Cp[TP]M} derivatives, see: Bruncker, T. J.; Cowley, A. R.; O'Hare, D. *Organometallics* **2002**, *21*, 3123–3138.

(16) Hill, A. F.; Rae, A. D.; Smith, M. K. *Inorg. Chem.* **2005**, *44*, 7316–7318.

(17) Hill, A. F.; Smith, M. K. *Dalton Trans.* **2006**, 28–30.

(18) Bis(2-mercapto-1-R-imidazolyl)hydroborato complexes of group 4 metals have, nevertheless, been reported. Thus, [Bm<sup>Me</sup>]<sub>2</sub>Ti(=NBu<sup>t</sup>) was obtained via the reaction of [Bm<sup>Me</sup>]Na with Ti(NBu<sup>t</sup>)Cl<sub>2</sub>(py)<sub>2</sub>.<sup>17</sup>



degradation of the ligand.<sup>19</sup> It is, therefore, notable that the zirconium complex  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  may be obtained by treatment of  $\text{CpZrCl}_3$  with  $[\text{Tm}^{\text{Me}}]\text{K}$  in  $\text{CH}_2\text{Cl}_2$  (Scheme 1).<sup>20</sup>

The molecular structure of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  has been determined by X-ray diffraction, as illustrated in Figure 1. The most noteworthy structural feature of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  is that it closely resembles the bent-metallocene geometry of  $\text{Cp}_2\text{ZrCl}_2$ <sup>21</sup> (Figure 2). Thus, as summarized in Table 1, the  $\text{Cp}_{\text{cent}}-\text{Zr}-\text{B}$  angle of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  is similar to the  $\text{Cp}_{\text{cent}}-\text{Zr}-\text{Cp}_{\text{cent}}$  angle of  $\text{Cp}_2\text{ZrCl}_2$ , while the  $\text{Cl}-\text{Zr}-\text{Cl}$  bond angles in the two complexes are also similar. For further comparison, the structure of the tris(pyrazolyl)hydroborato complex  $\text{Cp}[\text{Tp}]\text{Zr}(\text{OAr})_2$  (Ar = 2-Ph-C<sub>6</sub>H<sub>4</sub>),<sup>20c</sup> the only structurally characterized  $\text{Cp}[\text{Tp}^{\text{RR}}]\text{ZrX}_2$  derivative listed in the Cambridge Structural Database,<sup>22</sup> is also shown in Figure 2, with the corresponding metrical data being listed in Table 1. The Zr–S bond lengths for  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  span the range 2.66–2.76 Å, which is within the range for structurally characterized compounds listed in the Cambridge Structural Database (2.46–2.83 Å),<sup>22</sup> as illustrated by  $\text{Cp}^*_2\text{Zr}(\text{SPh})_2$  (2.52 Å)<sup>23</sup> and  $\text{Cp}_2\text{Zr}(\kappa^2\text{-S}_2\text{CNMe}_2)(\text{OPh})$  (2.66 and 2.79 Å).<sup>24</sup> Not surprisingly, in view of the  $\text{L}_2\text{X}$  nature and large dative<sup>25</sup> component of the  $[\text{Tm}^{\text{Me}}]-\text{Zr}$  interaction, the Zr–S bond lengths for  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  are at the long end of the distribution.

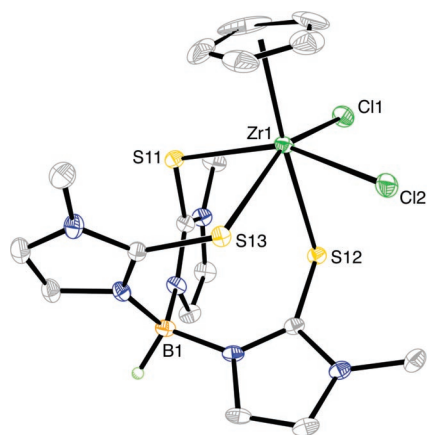
(19) Hill, A. F.; Smith, M. K. *Chem. Commun.* **2005**, 1920–1922.

(20) Tris(pyrazolyl)hydroborato counterparts of the group 4 transition metals include  $\text{Cp}[\text{Tp}]\text{TiCl}_2$ ,<sup>20a</sup>  $\text{Cp}[\text{Tp}]\text{ZrCl}_2$ ,<sup>20b–d</sup>  $\text{Cp}[\text{Tp}]\text{HfCl}_2$ ,<sup>20b,c</sup> and  $\text{Cp}[\text{Tp}^{\text{Me}_2}]\text{ZrCl}_2$ .<sup>20d</sup> (a) Manzer, L. E. *J. Organomet. Chem.* **1975**, *102*, 167–174. (b) Kresinski, R. A.; Jones, C. J.; McCleverty, J. A. *Polyhedron* **1990**, *9*, 2185–2187. (c) Kresinski, R. A.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 603–607. (d) Reger, D. L.; Mahtab, R.; Baxter, J. C.; Lebiada, L. *Inorg. Chem.* **1986**, *25*, 2046–2048.

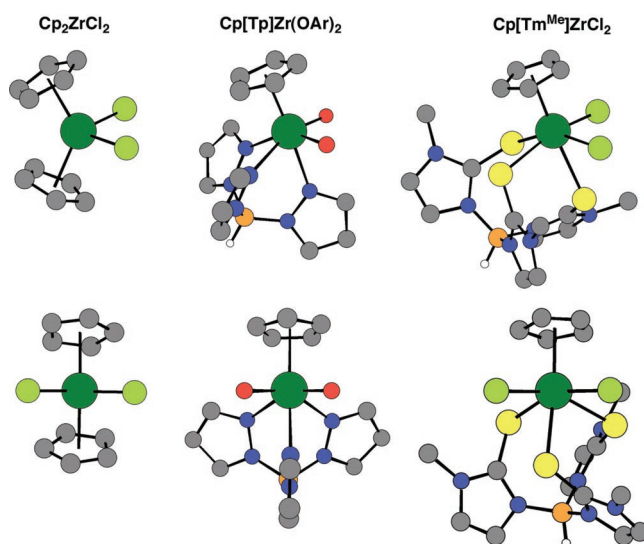
(21) (a) Repo, T.; Klinga, M.; Mutikainen, I.; Su, Y. C.; Leskelä, M.; Polamo, M. *Acta Chem. Scand.* **1996**, *50*, 1116–1120. (b) Corey, J. Y.; Zhu, X.-H.; Brammer, L.; Rath, N. P. *Acta Crystallogr.* **1995**, *C51*, 565–567.

(22) CSD Version 5.27. Allen, F. H.; Kennard, O. 3D Search and Research Using the Cambridge Structural Database. *Chem. Des. Automation News* **1993**, *8*(1), 1, 31–37.

(23) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900–5909.



**Figure 1.** Molecular structure of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  (only one of the two crystallographically independent molecules is shown).



**Figure 2.** Comparison of the molecular structures of  $\text{Cp}_2\text{ZrCl}_2$ ,  $\text{Cp}[\text{Tp}]\text{Zr}(\text{OAr})_2$  (for clarity, the Ar groups are not shown), and  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$ . Note that  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  is devoid of a molecular mirror plane due to the  $\text{C}_3$  nature of the  $[\text{Tm}^{\text{Me}}]$  ligand.

**Table 1.** Comparison of Metrical Data for  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$ ,  $\text{Cp}_2\text{ZrCl}_2$ , and  $\text{Cp}[\text{Tp}]\text{Zr}(\text{OAr})_2^a$

	$\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$	$\text{Cp}_2\text{ZrCl}_2^{b,c}$	$\text{Cp}[\text{Tp}]\text{Zr}(\text{OAr})_2^{d,e}$
Zr–C <sub>range</sub> /Å	2.51–2.57	2.47–2.52	2.54–2.59
Zr–C <sub>av</sub> /Å	2.54	2.50	2.56
Zr–C <sub>pcent</sub> /Å	2.26	2.20	2.27
Zr–Cl/Å	2.52	2.45	—
X–Zr–X/deg	97.9 (X = Cl)	97.0 (X = Cl)	99.3 (X = O)
C <sub>pcent</sub> –Zr–Y/deg	133.5 (Y = B)	129.2 (Y = Cp <sub>pcent</sub> )	131.7 (Y = B)

<sup>a</sup> Average values given where appropriate. <sup>b</sup> Data taken from ref 21a.

<sup>c</sup> Very similar data are obtained from ref 21b. <sup>d</sup> Data taken from 20c. <sup>e</sup> Ar = 2-Ph-C<sub>6</sub>H<sub>4</sub>.

Although the  $\text{Cp}_{\text{cent}}-\text{Zr}-\text{B}$  angles of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  and  $\text{Cp}[\text{Tp}]\text{Zr}(\text{OAr})_2$  are similar, as are the  $\text{Cl}-\text{Zr}-\text{Cl}$  and  $\text{O}-\text{Zr}-\text{O}$  bond angles, an important difference between the structures of the two compounds is concerned with the symmetry of the  $\{\text{Cp}[\text{Tm}^{\text{Me}}]\text{Zr}\}$  and  $\{\text{Cp}[\text{Tp}]\text{Zr}\}$  fragments. Specifically, while the plane defined by  $\text{Cp}_{\text{cent}}-\text{Zr}\cdots\text{B}$  corresponds to an approximate mirror plane for the  $\{\text{Cp}[\text{Tp}]\text{Zr}\}$  moiety, the  $\{\text{Cp}[\text{Tm}^{\text{Me}}]\text{Zr}\}$  unit is devoid of such symmetry. The origin of this difference is that the  $[\text{Tm}^{\text{Me}}]$  ligand exhibits a propeller-like twist such that

(24) Femecc, D. A.; Groy, T. L.; Fay, R. C. *Acta Crystallogr.* **1991**, *C47*, 1811–1814.

(25) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992–1007.

the local coordination symmetry is  $C_3$  rather than  $C_{3v}$ ,<sup>1,10</sup> with the result that the  $[\text{Tm}^{\text{Me}}]$  ligand is chiral; as such, it is impossible for the  $\{\text{Cp}[\text{Tm}^{\text{Me}}]\text{Zr}\}$  fragment to possess mirror symmetry.<sup>26</sup> The different local coordination symmetries of  $[\text{Tp}^{\text{RR}}]$  and  $[\text{Tm}^{\text{R}}]$  ligands derive from the fact that whereas coordination of the  $[\text{Tp}^{\text{RR}}]$  ligand results in a structure comprised of three six-membered rings, the additional atom in the mercaptoimidazolyl fragment results in three eight-membered rings upon coordination of a  $[\text{Tm}^{\text{R}}]$  ligand; as a consequence of the greater size of the linker between boron and the metal, and the constraint imposed by the tripodal nature of the ligand, a twisting results to maintain reasonable bond lengths.

Significantly, the chirality induced by the propeller-like twist of the  $[\text{Tm}^{\text{Me}}]$  ligand is not only relevant to the structure of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  in the solid state, but is also relevant to its structure in solution, as demonstrated by  $^1\text{H}$  NMR spectroscopy. For example, whereas the pyrazolyl groups of the  $[\text{Tp}]$  ligand of  $\text{Cp}[\text{Tp}]\text{ZrCl}_2$  are characterized by a 2:1 set of signals in the  $^1\text{H}$  NMR spectrum,<sup>20d</sup> the mercaptoimidazolyl groups of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  are identified by a 1:1:1 set of signals. Thus, it is evident that the two mercaptoimidazolyl groups trans to the pair of Cl ligands are chemically inequivalent, due to the local  $C_3$  symmetry of the  $[\text{Tm}^{\text{Me}}]$  ligand; variable-temperature  $^1\text{H}$  NMR spectroscopic studies demonstrate that this inequivalence is maintained on the NMR time scale at 70 °C in benzene.<sup>27</sup> In contrast, the  $C_{3v}$  nature of the  $[\text{Tp}]$  ligand causes the two pyrazolyl groups trans to the two Cl ligands of  $\text{Cp}[\text{Tp}]\text{ZrCl}_2$  to be chemically equivalent.

An important reason for pursuing the synthesis of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  relates to the prominent roles that zirconocene compounds have found as catalysts for olefin polymerization<sup>28</sup> and as reagents for organic synthesis.<sup>29,30</sup> With respect to the former topic, considerable effort is being directed towards obtaining polymerization catalysts that incorporate ligands other than cyclopentadienyl.<sup>31–33</sup> For this reason, we have examined the possibility that  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  may serve as a catalyst precursor

(26) Propeller twists of  $[\text{Tp}^{\text{RR}}]$  ligands are known in the solid state when R and R' are bulky substituents. However, the barrier to racemization is not expected to be significant, because the B–(pyrazolyl)–M unit electronically favors a planar geometry and the distortions associated with the propeller twist are solely a consequence of minimizing steric interactions. See, for example: Dowling, C. M.; Leslie, D.; Chisholm, M. H.; Parkin, G. *Main Group Chem.* **1995**, *1*, 29–52.

(27) In this regard, a series of four-coordinate  $[\text{Tm}^{\text{Et}}]\text{MX}$  and  $[\text{Tm}^{\text{Bz}}]\text{MX}$  complexes exhibit coalescence behavior on the NMR time scale, whereas the six-coordinate complexes  $\{[\text{Tm}^{\text{Et}}]\text{Ru}(p\text{-cymene})\}^+$  and  $[\text{Tm}^{\text{Et}}]\text{Mn}(\text{CO})_3$  remain static.<sup>18</sup> On the other hand, the diastereotopic methyl groups of  $[\text{Tm}^{\text{Me}}]\text{W}(\text{CO})_2(\text{CNPri}_2)$  coalesce at 15 °C, while those for  $[\text{Tm}^{\text{Me}}]\text{W}(\text{CO})_2(\text{CC}\equiv\text{CBu}^t)$  coalesce at 90 °C.<sup>10</sup>

(28) (a) Kaminsky, W. *J. Polym. Sci. Part A: Polym. Sci.* **2004**, *42*, 3911–3921. (b) Kaminsky, W. *Adv. Catal.* **2001**, *46*, 89–159. (c) Bochmann, M. *Top. Catal.* **1999**, *7*, 9–22. (d) Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243–296. (e) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413–1418. (f) Busico, V.; Cipullo, R.; Caporaso, L.; Angelini, G.; Segre, A. L. *J. Mol. Catal. A: Chem.* **1998**, *128*, 53–64. (g) Brintzinger, H. H.; Fischer, D.; Mühlaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170. (h) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85–93. (i) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1–29. (j) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143–187. (k) Janiak, C. *Coord. Chem. Rev.* **2006**, *250*, 66–94. (l) Kaminsky, W.; Laban, A. *Appl. Catal. A: Gen.* **2001**, *222*, 47–61. (m) Colacot, T. J.; Hosmane, N. S. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2659–2668.

(29) (a) Fujita, K.; Yorimitsu, H.; Oshima, K. *Chem. Rec.* **2004**, *4*, 110–119. (b) Majoral, J.-P.; Meunier, P.; Igau, A.; Piriou, N.; Zablocka, M.; Skowronska, A.; Bredeau, S. *Coord. Chem. Rev.* **1998**, *178–180*, 145–167. (c) Wipf, P.; Xu, W.; Takahashi, H.; Jahn, H.; Coish, P. D. G. *Pure Appl. Chem.* **1997**, *69*, 639–644. (d) Buchwald, S. L.; Broene, R. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, pp 771–784. (e) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262–1284. (f) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1–19.

**Table 2. Crystal Data and Intensity Collection and Refinement Details for  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2\cdot\text{CHCl}_3$**

lattice	triclinic	Z	4
formula	$\text{C}_{18}\text{H}_{22}\text{BCl}_5\text{N}_6\text{S}_3\text{Zr}$	temp, K	243
formula wt	697.88	radiation ( $\lambda$ ), Å	0.71073
space group	$P\bar{1}$	$\rho$ (calcd), $\text{g cm}^{-3}$	1.622
a, Å	10.881(8)	$\mu$ (Mo K $\alpha$ ), $\text{mm}^{-1}$	1.092
b, Å	14.128(9)	$\theta_{\text{max}}$ , deg	26.02
c, Å	19.276(14)	no. of data	10983
$\alpha$ , deg	76.05(1)	no. of params	622
$\beta$ , deg	85.23(1)	R1	0.0711
$\gamma$ , deg	84.86(1)	wR2	0.1997
V, Å <sup>3</sup>	2858(3)	GOF	1.049

for the polymerization of ethylene. It is, therefore, notable that a combination of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  and methylalumoxane (MAO) produces a catalyst that is capable of polymerizing ethylene with an activity of 209 kg PE  $[\text{mol Zr}]^{-1} [\text{h}]^{-1} [\text{atm C}_2\text{H}_4]^{-1}$  at room temperature, which is modest compared to that obtained from  $\text{Cp}_2\text{ZrCl}_2$  and MAO under comparable conditions (998 kg PE  $[\text{mol Zr}]^{-1} [\text{h}]^{-1} [\text{atm C}_2\text{H}_4]^{-1}$ ).<sup>34,35</sup>

With respect to the polymerization of prochiral  $\alpha$ -olefins, it is well-known that the properties of the polymer depend critically on the symmetry of the catalyst precursor,<sup>28,36</sup> and interesting effects on the tacticity have been observed employing  $C_1$ -symmetric precatalysts.<sup>37,38</sup> For example, the stereoselectivity of  $C_1$ -symmetric zirconocene precatalysts in the polymerization of propylene has been shown to be highly dependent on propylene concentration, varying from isoselective at low concentration to syndiospecific at high concentration.<sup>37</sup> Since the propeller-like twist of the  $[\text{Tm}^{\text{Me}}]$  ligand renders  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  chiral and  $C_1$  symmetric, and since the barrier to enantiomer interconversion is sufficiently large that it does not occur on the NMR time scale, it is possible that catalysts derived from  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  and variants thereof, namely  $\text{Cp}^{\text{R}}[\text{Tm}^{\text{R}}]\text{MX}_2$ , may find applications in the stereocontrol of the polymerization of  $\alpha$ -olefins.

## Conclusions

In summary,  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  may be obtained by the reaction of  $\text{CpZrCl}_3$  with  $[\text{Tm}^{\text{Me}}]\text{K}$ . While the molecular structure of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  closely resembles that of the bent metallocene  $\text{Cp}_2\text{ZrCl}_2$ , an important distinction is that  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  is chiral due to the  $[\text{Tm}^{\text{Me}}]$  ligand possessing a propeller-like twist that destroys a potential mirror plane. Evidence that  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  retains its chirality in solution is provided by the observa-

(30) For a special issue dedicated to zirconocene chemistry, see: *Tetrahedron* **2004**, *60*(6), 1257–1424.

(31) See, for example: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315. (b) Park, S. J.; Han, Y. Y.; Kim, S. K.; Lee, J. S.; Kim, H. K.; Do, Y. K. *J. Organomet. Chem.* **2004**, *689*, 4263–4276.

(32) For example,  $\{[\text{Tp}^{\text{RR}}]\text{M}\}$  (M = Ti, Zr, Hf) complexes have been employed as olefin polymerization precatalysts; see: (a) Lee, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 9384–9385. (b) Murtuza, S.; Casagrande, O. L., Jr.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882–1890. (c) Michiue, K.; Jordan, R. F. *Organometallics* **2004**, *23*, 460–470. (d) Casagrande, A. C. A.; Gil, M. P.; Casagrande, O. L. *J. Braz. Chem. Soc.* **2005**, *16*, 1283–1289. (e) Nakazawa, H.; Ikai, S.; Imaoka, K.; Kai, Y.; Yano, T. *J. Mol. Catal. A: Chem.* **1998**, *132*, 33–41. (f) Michiue, K.; Jordan, R. F. *Macromolecules* **2003**, *36*, 9707–9709. (g) Gil, M. P.; dos Santos, J. H. Z.; Casagrande, O. L., Jr. *J. Mol. Catal. A: Chem.* **2004**, *209*, 163–169. (h) Pires, G. P.; Gil, M. P.; Rohman, J. A.; Stedile, F. C.; Casagrande, O. L., Jr.; dos Santos, J. H. Z.; Sano, T. *J. Appl. Polym. Sci.* **2006**, *99*, 2002–2009. (i) Janiak, C.; Lange, K. C. H.; Scharmann, T. G. *Appl. Organomet. Chem.* **2000**, *14*, 316–324.

(33) For studies using heteroscorpionate ligands, see: Milione, S.; Bertolasi, V.; Cuenca, T.; Grassi, A. *Organometallics* **2005**, *24*, 4915–4925.

(34) Conditions:  $[\text{Zr}] = 2.5 \times 10^{-4}$  M,  $[\text{Al}]:[\text{Zr}] = 6000:1$ , 1 atm of  $\text{C}_2\text{H}_4$ , room temperature.

(35) For the use of  $\text{Cp}[\text{Tp}]\text{ZrCl}_2$  as a precatalyst, see ref 32i.

tion that the two mercaptoimidazolyl groups trans to the pair of Cl ligands are chemically inequivalent on the  $^1\text{H}$  NMR time scale. Finally, in combination with methylalumoxane,  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{-ZrCl}_2$  produces an active catalyst for ethylene polymerization.

### Experimental Section

**General Considerations.** All manipulations were performed using a combination of dry-glovebox, high-vacuum, and Schlenk techniques under a nitrogen atmosphere, unless otherwise specified. Solvents were purified and degassed by standard procedures.  $^1\text{H}$  NMR spectra were measured on Bruker 300 DRX and Bruker 400 DRX spectrometers.  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to  $\text{SiMe}_4$  ( $\delta$  0) and were referenced internally with respect to the protio solvent impurity ( $\delta$  7.16 for  $\text{C}_6\text{D}_5\text{H}$ ;  $\delta$  2.50 for  $\text{Me}_2\text{SO}$ ).<sup>39</sup>  $^{13}\text{C}$  NMR spectra are reported in ppm relative to  $\text{SiMe}_4$  ( $\delta$  0) and were referenced internally with respect to the solvent ( $\delta$  39.52 for  $\text{Me}_2\text{SO}$ ).<sup>39</sup> Coupling constants are given in hertz. Infrared spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer and are reported in  $\text{cm}^{-1}$ .

**Synthesis of  $[\text{Tm}^{\text{Me}}]\text{K}$ .**  $[\text{Tm}^{\text{Me}}]\text{K}$  was obtained by a method analogous to that reported for  $[\text{Tm}^{\text{Me}}]\text{Na}$ .<sup>1b</sup> A mixture of 2-mercapto-1-methylimidazole (3.023 g, 26.7 mmol) and  $\text{KBH}_4$  (0.424 g, 7.86 mmol) were finely ground together and placed in an ampule. The mixture was stirred and heated slowly to 160 °C as the evolution of  $\text{H}_2$  was monitored. The temperature was maintained at 160 °C for 15 min after evolution of  $\text{H}_2$  ceased (ca. 30 min), after which the reaction mixture was cooled to room temperature. The solid obtained was washed sequentially with methanol ( $3 \times 15$  mL), acetone ( $2 \times 10$  mL), and pentane (15 mL) and dried in vacuo to give  $[\text{Tm}^{\text{Me}}]\text{K}$  as a fine white powder (2.137 g, 70%).  $^1\text{H}$  NMR ( $d_6$ -DMSO): 3.38 (s, 9H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 6.40 (d,  $^3J_{\text{HH}} = 2.0$ , 3H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 6.79 (d,  $^3J_{\text{HH}} = 2.0$ , 3H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_6$ -DMSO): 163.3 (3 C of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 120.4 (3 C of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 116.7 (3 C of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 33.7 (3 C of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ).

**Synthesis of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$ .** A suspension of  $\text{CpZrCl}_3$  (134 mg, 0.51 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was added slowly to a suspension of  $[\text{Tm}^{\text{Me}}]\text{K}$  (200 mg, 0.51 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL),

and the mixture was stirred for 1 h at room temperature. After this period, the mixture was filtered and the volatile components were removed from the filtrate in vacuo. The solid obtained was extracted with benzene ( $4 \times 50$  mL). The combined extract was concentrated to ca. 20 mL and then lyophilized to give  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  as a white powder (160 mg, 54%) which may be crystallized from benzene at room temperature. Crystals suitable for X-ray diffraction were obtained from chloroform.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 2.92 (s, 3H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 3.14 (s, 3H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 3.47 (s, 3H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 5.79 (d,  $^3J_{\text{HH}} = 2.0$ , 1H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 5.84 (d,  $^3J_{\text{HH}} = 2.0$ , 1H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 5.90 (d,  $^3J_{\text{HH}} = 2.0$ , 1H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 6.38 (d,  $^3J_{\text{HH}} = 2.0$ , 1H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 6.44 (d,  $^3J_{\text{HH}} = 2.0$ , 1H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 6.47 (d,  $^3J_{\text{HH}} = 2.0$ , 1H of  $\text{HB}\{\text{C}_3\text{N}_2\text{H}_2(\text{CH}_3)\text{S}\}_3$ ), 6.67 (s, 5H, Cp). Anal. Calcd for  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{-ZrCl}_2 \cdot 0.8\text{C}_6\text{H}_6$ : C, 40.9; H, 4.1; N, 13.1. Found: C, 40.9; H, 4.5; N, 13.8. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3155 (w), 3127 (m), 3094 (w), 2946 (w), 2437 (w), 2408 (w), 2322 (w), 2223 (w), 2007 (w), 1894 (w), 1689 (w), 1562 (m), 1463 (s), 1416 (m), 1383 (s), 1324 (w), 1300 (m), 1262 (w), 1208 (s), 1154 (m), 1123 (m), 1088 (m), 1024 (m), 815 (s), 778 (m), 746 (s), 687 (m), 666 (w), 617 (w), 525 (w), 463 (w).

**Ethylene Polymerization by  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2/\text{MAO}$ .** A sample of  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$  (5 mg,  $8.6 \times 10^{-6}$  mol) was treated with MAO (34.5 mL, 10 wt % in toluene,  $5.2 \times 10^{-2}$  mol), corresponding to an Al:Zr ratio of  $\sim 6000$ . Toluene was added such that the total volume of the solution was 35 mL. The mixture was stirred at room temperature for 15 min, after which the solution was degassed and treated with ethylene (1 atm). The reaction vessel was placed in a water bath at room temperature, and the mixture was stirred vigorously for 1 h while the pressure of  $\text{C}_2\text{H}_4$  was maintained at 1 atm during the course of the polymerization. After this period, the reaction was quenched by slow addition of methanol (15 mL) followed by dilute HCl ( $\sim 100$  mL). The polymer was collected by filtration, washed with methanol ( $\sim 10$  mL), water ( $\sim 200$  mL), and methanol ( $\sim 10$  mL), and dried in vacuo to constant weight. Yield of polyethylene: 1.81 g, corresponding to an activity of 209 kg PE [mol Zr] $^{-1}$  [h] $^{-1}$  [atm  $\text{C}_2\text{H}_4$ ] $^{-1}$ . Under identical conditions, a catalyst derived from  $\text{Cp}_2\text{ZrCl}_2$  yielded 8.53 g of polyethylene, corresponding to an activity of 998 kg PE [mol Zr] $^{-1}$  [h] $^{-1}$  [atm  $\text{C}_2\text{H}_4$ ] $^{-1}$ .

**X-ray Structure Determinations.** X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector; crystal data, data collection, and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on  $F^2$  with SHELXTL (version 5.10).<sup>40</sup>

**Acknowledgment.** We thank the U.S. Department of Energy, Office of Basic Energy Sciences (Contract No. DE-FG02-93ER14339), for support of this research.

**Supporting Information Available:** A CIF file giving crystallographic data for  $\text{Cp}[\text{Tm}^{\text{Me}}]\text{ZrCl}_2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM060571L

(40) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.

(36) (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1345. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252. (c) Coates, G. W. *Dalton Trans.* **2002**, 467–475. (d) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res.* **2004**, *37*, 231–241. (e) Schellenberg, J. *Eur. Polym. J.* **2006**, *42*, 487–494. (f) Busico, V.; Cipullo, R.; Talarico, G.; Segre, A. L.; Chadwick, J. C. *Macromolecules* **1997**, *30*, 4786–4790. (g) Razavi, A.; Thewalt, U. *Coord. Chem. Rev.* **2006**, *250*, 155–169. (h) Busico, V.; Cipullo, R. *Polym. Mater.: Sci. Eng.* **2002**, *87*, 47.

(37) (a) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564–573. (b) Miller, S. A.; Bercaw, J. E. *Organometallics* **2002**, *21*, 934–945. (c) Miller, S. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 3576–3592. (d) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988–11989.

(38) (a) Obora, Y.; Stern, C. L.; Marks, T. J.; Nickias, P. N. *Organometallics* **1997**, *16*, 2503–2505. (b) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, *497*, 181–193. (c) Deisenhofer, S.; Feifel, T.; Kukral, J.; Klinga, M.; Leskelä, M.; Rieger, B. *Organometallics* **2003**, *22*, 3495–3501. (d) Leino, R.; Gomez, F. J.; Cole, A. P.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 2072–2082. (e) Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **2000**, *33*, 1546–1552.

(39) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.