Electrophile-Functionalized Metallocene Intermediates. Application in the Diastereoselective Synthesis of a Tetramethyldisiloxane-Bridged C_2-Symmetric *ansa*-Zirconocene Dibromide

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The reactivity of group 4 zirconocene dichlorides incorporating (1-trimethylsilyl)-η^5-indenyl (Me_3SiInd) and η^5-1-(trimethylsilyl)-4,5,6,7-tetrahydroindenyl (Me_3SiTHI) ligands toward boron tribromide was investigated. Whereas the reaction of (Me_3SiInd)$CpZrCl_2$ (**1**) with BBr_3 in CH_2Cl_2 immediately cleaved the indenyl ligand from the metal, (Me_3SiTHI)$CpZrCl_2$ (**3**) reacted with BBr_3 in CH_2Cl_2 at 70 °C for 2 days to obtain [1-($BrSiMe_2$)THI]$CpZrBr_2$ (**6**) in 49% yield. The reaction of (Me_3SiInd)Li (2 equiv) with $ZrCl_4(THF)_2$ afforded pure *rac*-($Me_3SiInd)_2ZrCl_2$ (**2**) in 60% yield. Hydrogenation of (**2**) (50 bar, PtO_2 catalyst) afforded *rac*-($Me_3SiTHI)_2ZrCl_2$ (**4**) in 81% yield. Single-crystal X-ray diffraction analysis of **4** showed that the Zr atom lies on a crystallographic C_2 axis with the C_4H_8 annelated rings projecting into the $ZrCl_2$ hemisphere of the pseudotetrahedral coordination environment. The reaction of **4** with MeLi in toluene afforded *rac*-($Me_3SiTHI)_2ZrMe_2$ (**5**) in 62% yield. ^1H NMR and ^{13}C NMR analysis confirmed the *rac* assignment for **5**. Treatment of **4** with BBr_3 in CH_2Cl_2 at 70 °C for 2 days afforded *rac*-[1-($BrMe_2Si$)THI]$_2ZrBr_2$ (**7**) in 78% yield. The reaction of **7** with moisture in ambient air gave the *ansa*-metallocene *rac*-[μ-O−(1-$Me_2SiTHI)_2$]$ZrBr_2$ (**8**) in 97% yield. In solution, **8** showed time-averaged C_2 symmetry (^1H NMR); however, single-crystal X-ray diffraction analysis showed that **8** adopts an asymmetric conformation in which only one of the C_4H_8 annelated rings projects into the $ZrCl_2$ coordination hemisphere. Neither **4** nor **8** served as a precatalyst for alumoxane-cocatalyzed, homogeneous propylene polymerization.

Introduction

Group 4 metallocene complexes are an important class of single-site catalysts for ethylene and α-olefin polymerization.[2] The ongoing search for wider variations in the properties of metallocene polyolefins and increased control over process parameters stimulates ongoing efforts to design new metallocenes having unusual molecular structures or chemical functionality.[3,4,5] Modification of the steric and electronic environment of a metallocene by introducing unreactive substituents such as alkyl and trimethylsilyl is a persistent theme in the recent literature,[6] especially for the design of rigid, inherently chiral ligand arrays with either C_2 or C_1 symmetry. In principle, C_2 symmetry[7] improves the enantioselectivity of olefin addition processes[8] by decreasing the number of diastereotopic transition states leading to “incorrect” insertion, although useful C_1-symmetric catalysts are known.[9]

Highly nucleophilic or electrophilic functional groups ($-NR_2$, $-OR$, acetyl, etc.) bearing strong donor atoms are usually avoided in metallocene ligand design,[10] because Lewis bases serve as poisons for the highly

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[2] (a) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (b) Montagna, A. A.; Burkhart, R. M.; Dekmezian, A. H. *CHEMTECH* **1997**, *Dec*, 26. (c) Kaminsky, W. *Makromol. Chem. Phys.* **1996**, *197*, 3907. (d) Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds. *Ziegler Catalysis*; Springer: Berlin, 1995. (e) Bochmann, M. *Top. Catal.* **1999**, *7*, 9. (f) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (g) Soga, K.; Shiono, T. *Prog. Polym. Sci.* **1997**, *22*, 1503. (h) Machima, K.; Nakayama, Y.; Nakamura, A. *Adv. Polym. Sci.* **1997**, *133*, 1. (i) Locatelli, P. *Trends Polym. Sci.* **1996**, *4*, 326.

[3] (a) Leino. R.; Luttikhedde, H. J. G.; Lehtonen, A.; Sillanpää, L. A.; Penninkangas, A.; Strandén, J.; Mattinen, J.; Näsman, J. H. *J. Organomet. Chem.* **1998**, *558*, 171. (b) Carter, C. A. G.; McDonald, R.; Stryker, J. M. *Organometallics* **1999**, *18*, 820.

[4] Deck, P. A.; Fisher, T. S.; Downey, J. S. *Organometallics* **1997**, *16*, 1193.

[5] (a) Alcalde, M. I.; Gómez-Sal, M. P.; Royo, P. *Organometallics* **1999**, *18*, 546. (b) De la Mata, F. J.; Giner, P.; Royo, P. *J. Organomet. Chem.* **1999**, *572*, 155. (c) Stelck D. S.; Shapiro P. J.; Basickes N.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4546. (d) Larkin, S. A.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Foo, D. M. J.; Rheingold, A. L. *Organometallics* **1996**, *15*, 2393.

[6] (a) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965. (b) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (c) Hortmann, K.; Brintzinger, H. H. *New J. Chem.* **1992**, *16*, 51. (d) Alt, H. G.; Samuel, E. *Chem. Soc. Rev.* **1998**, *27*, 323. (e) Schneider, M. J.; Suhm, J.; Mülhaupt, R.; Prosenc, M. H.; Brintzinger, H. H. *Macromolecules* **1997**, *30*, 3164. (f) Tagge, C. D.; Kravchenko, R. L.; Lal, T. K.; Waymouth, R. M. *Organometallics*, **1999**, *18*, 380. (g) Grimmond, B. J.; Corey, J. Y.; Rath, N. P. *Organometallics* **1999**, *18*, 404. (h) Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1999**, *18*, 1439.

[7] (a) Gutmann, S.; Burger, P.; Hund, H.-U.; Hofmann, J.; Brintzinger, H.-H. *J. Organomet. Chem.* **1989**, *369*, 343. (b) Schaverien, C. J.; Ernst, R.; Schut, P.; Skiff, W. M.; Resconi, L.; Barbassa, E.; Balboni, D.; Dubitsky, Y. A.; Orpen, A. G.; Mercandelli, P.; Moret, M.; Sironi, A. *J. Am. Chem. Soc.* **1998**, *120*, 9945. (c) Busico, V.; Cipullo, R.; Caporaso, L.; Angelini, G.; Segre, A. L. *J. Mol. Catal. A* **1998**, *128*, 53. (d) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.

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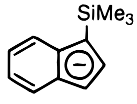
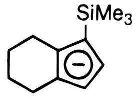
electrophilic species generated upon "activation" of the MX_2 moiety in two-component olefin polymerization catalysts.[11] Nevertheless, metallocene complexes bearing highly reactive functional groups can serve as valuable *intermediates* for further synthetic elaboration of unusual structural motifs and supramolecular frameworks. Examples include tethering a metallocene to an organo-Lewis acid to form a "single-component" catalyst,[12] the synthesis of doubly bridged metallocenophanes,[4] and the immobilization of metallocene complexes on inorganic or polymeric supports.[13]

We recently reported a method for converting "inert" trimethylsilyl (Me_3Si) substituents on group 4 metallocene dichlorides to highly electrophilic bromodimethylsilyl ($BrMe_2Si$) groups by treatment with boron tribromide (BBr_3).[4] The *practical* advantages of this procedure include its selectivity for "activation" of just one methyl group per $SiMe_3$ group, its generality toward Me_3SiCp complexes of all the group 4 metals, and the availability of $SiMe_3$-substituted ligands and complexes by known routes.[14,15] The *fundamental* advantage is the opportunity to introduce one or more highly reactive functional groups *after* establishing the desired metallocene architecture, which is complementary to the approach taken by others.[5] The present contribution demonstrates our approach by extending the scope of our "post-functionalization" method to metallocenes constructed from trimethylsilyl-substituted members of the indenyl/tetrahydroindenyl family of ligands, which serve to define the metallocene molecular symmetry *prior* to the introduction of reactive functional groups.

We first show that although 1-(trimethylsilyl)indenyl ($SiMe_3Ind$) complexes are readily prepared, they undergo rapid ligand dissociation upon reaction with BBr_3. However, hydrogenation of the Zr-coordinated $SiMe_3$-Ind ligand to the corresponding 1-(trimethylsilyl)-4,5,6,7-tetrahydroindenyl ($SiMe_3THI$) ligand stabilizes the complex so that treatment with BBr_3 converts the Me_3-Si group to the corresponding $BrMe_2Si$ group in high yields without any detectable dissociation of the Zr–THI framework. Furthermore, as the complex *rac*-$(1\text{-}SiMe_3Ind)_2ZrCl_2$ is formed from $(SiMe_3Ind)Li$ and $ZrCl_4(THF)_2$ with >98% diastereoselectivity, the hydrogenation/bromodemethylation reaction sequence gives a highly functionalized, C_2-symmetric intermediate, *rac*-$[1\text{-}(BrMe_2Si)THI]_2ZrBr_2$.



Me_3SiInd



Me_3SiTHI

Finally, we show that hydrolysis of this intermediate by ambient air results in *intramolecular* disiloxane formation[4,5a] to afford the tetramethyldisiloxane-linked *ansa*-$(THI)_2ZrBr_2$ complex. This synthetic procedure is complementary to other synthetic methods for the synthesis of disiloxane-linked bis(Ind) and bis(THI) metallocene complexes. In previous approaches, the disiloxane-bridged ligand was assembled *prior* to coordination of the transition metal,[16−19] which gave mixtures of *rac* and *meso* isomers, a common difficulty encountered in the synthesis of bis(Ind) complexes.[8b,20] Instead, we demonstrate that the *ansa* linkage is also established effectively *after* metallocene formation.[4,16d]

Experimental Section

General Procedures. All procedures were carried out using standard inert-atmosphere techniques. Glassware sealed with either Kalrez O-rings or Krytox fluorinated lubricant is recommended for any reaction in which boron trihalides are used. Boron tribromide was used as received from Aldrich. $ZrCl_4(THF)_2$ was prepared from $ZrCl_4$ and a slight excess of THF in dichloromethane at 0 °C. $CpZrCl_3$ was used as received from Strem Chemical Co. $(Me_3SiInd)Li$ was prepared by Merola's procedure.[21] NMR spectra were obtained using a Varian U-400 or a Bruker AM-360 instrument. Elemental analyses were performed by Desert Analytics (Tucson, AZ) or Oneida Research Services (Whitesboro, NY).

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(8) (a) Shaughnessy, K. H.; Waymouth, R. M. *Organometallics* **1998**, *17*, 5728. (b) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Intl. Ed. Engl.* **1996**, *35*, 1262. (c) Broene, R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 12569.

(9) (a) Arndt, M.; Beulich, I. *Macromol. Chem. Phys.* **1998**, *199*, 1221. (b) Obora, Y.; Stern, C. L.; Marks, T. J.; Nickias, P. N. *Organometallics* **1997**, *16*, 2503. (c) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 12114. (d) Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules*, **1992**, *25*, 1242. (e) Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000.

(10) (a) Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J.; Molander, G. A. *Organometallics* **1998**, *17*, 5324. (b) Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 663. (c) Christoffers, J.; Bergman, R. G. *Angew. Chem., Intl. Ed. Engl.* **1995**, *34*, 2266. (d) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics*, **1997**, *16*, 4845. (e) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336.

(11) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(12) (a) van der Heijden, H.; Hessen, B.; Orpen, A. G. *J. Am. Chem. Soc.* **1998**, *120*, 1112. (b) Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081. (c) Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Intl. Ed. Engl.* **1996**, *35*, 80. (d) Sun, Y.; Spence, R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132. (e) Erker, G.; Aul, R. *Chem. Ber.* **1991**, *124*, 1301.

(13) (a) Ciardelli, F.; Altomare, A.; Michelotti, M. *Catal. Today* **1998**, *41*, 149. (b) Peifer, B.; Milius, W.; Alt, H. G. *J. Organomet. Chem.* **1998**, *553*, 205. (c) Lee, D.-H.; Yoon, K.-B.; Lee, H.-B.; Lee, S. W.; Huh, W. S. *J. Polym. Sci. A* **1997**, *35*, 3717. (d) Iiskola, E. I.; Timonen, S.; Pakkanen, T. T.; Härkki, O.; Seppälä, J. V. *Appl. Surf. Sci.* **1997**, *121*, 372.

(14) (a) Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, *3*, 805. (b) Bruce, M. R. M.; Sclafani, A.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 2546. (c) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210. (d) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301. (e) Imori, T.; Tilley, T. D. *Polyhedron* **1994**, *13*, 2231.

(15) (a) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R. S.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106. (b) Antiñolo, A.; Lappert, M. F.; Singh, A.; Winterborn, D. J. W.; Engelhardt, L. M.; Raston, C. L.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans* **1987**, 1463. (c) Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592.

(16) (a) Jung, J.; Noh, S. K.; Lee, H.; Park, S. K.; Lee, D. H.; Kang, K. S. *Polymer (Korea)* **1999**, *23*, 189. (b) Soga, K.; Arai, T.; Ban, H. T.; Uozumi, T. *Macromol. Rapid Commun.* **1995**, *16*, 905. (c) Arai, T.; Ban, H. T.; Uozumi, T.; Soga, K. *Macromol. Chem. Phys.* **1997**, *198*, 229. (d) Ciruelos, S.; Cuenca, T.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1995**, *14*, 177. (e) Curtis, M. D.; D'Errico, J. J.; Duffy, D. N.; Epstein, P. S.; Bell, L. G. *Organometallics* **1983**, *2*, 1808.

(17) (a) Wang, B. Q.; Su, L.; Xu, S.; Feng, R.; Zhou, X.; He, D. *Macromol. Chem. Phys.* **1997**, *198*, 3197. (b) Liang, B.; Li, Y.; Xie, G. *Macromol. Rapid Commun.* **1996**, *17*, 193.

(18) (a) Gräper, J.; Paolucci, G.; Fischer, R. D. *J. Organomet. Chem.* **1995**, *501*, 211. (b) Naderer, H.; Siebel, E.; Fischer, R. D. *J. Organomet. Chem.* **1996**, *518*, 181.

(19) Song. W.; Shackett, K.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1995**, *501*, 375.

(20) (a) Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4038. (b) Kaminsky, W.; Schauwienold, A. M.; Freidanck, F. *J. Mol. Catal. A* **1996**, *112*, 37. (c) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler, R. *Organometallics* **1996**, *15*, 5046. (d) Schmidt, K.; Reinmuth, A.; Rief, U.; Diebold, J.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 1724.

(21) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.

Synthesis of (Me$_3$SiInd)(η^5-C$_5$H$_5$)ZrCl$_2$ (1). A solution of CpZrCl$_3$ (Strem, 2.0 g, 7.6 mmol) and (Me$_3$SiInd)Li (1.7 g, 8.8 mmol) in THF (100 mL) was stirred for 2 h, and then the solvent was evaporated. The resulting yellow residue was extracted with hot toluene (60 mL) and filtered to remove LiCl. Evaporation of the solvent from the filtrate and recrystallization of the residue from hexane/benzene (1:1) afforded 2.3 g (5.6 mmol, 73%) of fine yellow needles in two crops. ^{1}H NMR (CDCl$_3$): δ 7.83 (dd, $^3J = 8.4$ Hz, $^4J = 1.2$ Hz, 1 H), 7.69 (d, $J = 8.4$ Hz, 1 H), 7.36 (s, 1 H), 7.32 (m, 1 H), 7.02 (d, $J = 3.6$ Hz, 1 H), 6.85 (dd, $^3J = 3.6$ Hz, $^4J = 0.4$ Hz, 1 H), 6.07 (s, 5 H), 0.43 (s, 9 H). ^{13}C NMR (CDCl$_3$): δ 132.9 (C), 131.8 (CH), 127.2 (C), 127.0 (CH), 126.1 (CH), 126.0 (CH), 125.6 (CH), 116.7 (CH), 111.5 (C), 110.1 (CH), 0.3 (CH$_3$). Anal. Calcd for C$_{17}$H$_{20}$Cl$_2$SiZr: C, 49.25; H, 4.86. Found: C, 49.05; H, 4.93.

Synthesis of *rac*-(Me$_3$SiInd)$_2$ZrCl$_2$ (2). A solution of ZrCl$_4$(THF)$_2$ (2.3 g, 6.1 mmol) and Li(Me$_3$SiInd) (2.4 g, 12.4 mmol) in THF (200 mL) was stirred at 25 °C for about 15 h. The solution was cooled to -78 °C, and the crude yellow product was collected on a fritted filter and washed with cold CH$_2$Cl$_2$ (3 × 20 mL). A second crop was obtained by concentrating the filtrate. The combined yield was 2.0 g (60%) of a yellow solid, which was found by ^{1}H NMR analysis to consist of a single diastereomeric product. An analytical sample (free of LiCl and other minor organic impurities) was obtained by recrystallization from hot toluene followed by washing the crystalline product with pentane. ^{1}H NMR (CDCl$_3$): δ 7.69 (m, 4 H), 7.25 (m, 4 H), 6.41 (d, $^3J = 3.2$ Hz, 2 H), 6.35 (dd, $^3J = 3.2$ Hz, $J = 0.8$ Hz, 2 H), 0.34 (s, 18 H). ^{13}C NMR (CDCl$_3$): δ 134.6 (C), 127.5 (CH), 127.4 (C), 127.0 (CH), 126.2 (CH), 125.8 (CH), 125.0 (CH), 116.9 (C), 104.7 (CH), 0.03 (CH$_3$). Anal. Calcd for C$_{24}$H$_{30}$Cl$_2$Si$_2$Zr: C, 53.70; H, 5.63. Found: C, 53.69; H, 5.66.

Synthesis of (Me$_3$SiTHI)(η^5-C$_5$H$_5$)ZrCl$_2$ (3). A solution of (Me$_3$SiInd)CpZrCl$_2$ (**1**, 0.78 g, 1.9 mmol) in 150 mL of CH$_2$Cl$_2$ was hydrogenated at 25 °C for 2.5 h in a 300 mL Parr reactor at 50 bar using PtO$_2$ (0.15 g) as the catalyst. The resulting mixture was filtered through Celite to remove PtO$_2$. Evaporation of the filtrate and recrystallization of the crude product from hexanes afforded 0.46 g (1.1 mmol, 58%) of pale green needles. ^{1}H NMR (CDCl$_3$): δ 6.49 (d, $J = 2.8$ Hz, 1 H), 6.43 (s, 5 H), 5.82 (d, $J = 2.8$ Hz, 1 H), 3.00 (m, 2 H), 2.90 (m, 2 H), 1.75 (m, 3 H), 1.60 (m, 1 H), 0.25 (s, 9 H). ^{13}C NMR (CDCl$_3$): δ 141.4 (C), 135.8 (C), 120.5 (C), 118.7 (CH), 114.8 (CH), 112.1 (CH), 25.9 (CH$_2$), 25.0 (CH$_2$), 22.5 (CH$_2$), 22.1 (CH$_2$), 0.1 (CH$_3$). Anal. Calcd for C$_{17}$H$_{24}$Cl$_2$SiZr: C, 48.78; H, 5.78. Found: C, 48.99; H, 6.00.

Synthesis of (Me$_3$SiTHI)$_2$ZrCl$_2$ (4). A solution of (Me$_3$SiInd)$_2$ZrCl$_2$ (**2**, 1.22 g, 2.27 mmol) in 150 mL of CH$_2$Cl$_2$ was hydrogenated at 25 °C for 2.5 h in a 300 mL Parr reactor at 50 bar using PtO$_2$ (80 mg) as the catalyst. The resulting mixture was filtered through a fritted funnel to remove PtO$_2$. Evaporation of the filtrate and recrystallization of the crude product from hexanes afforded 1.00 g (81%) of pale green needles. ^{1}H NMR (CDCl$_3$): δ 6.52 (d, $J = 2.9$ Hz, 2 H), 5.60 (d, $J = 2.9$ Hz, 2 H), 3.01 (m, 4 H), 2.53 (m, 4 H), 1.80 (m, 4 H), 1.65 (m, 4 H), 0.20 (s, 18 H). ^{13}C NMR (CDCl$_3$): δ 140.7 (C), 135.8 (C), 118.5 (C), 116.2 (CH), 112.0 (CH), 25.9 (CH$_2$), 25.1 (CH$_2$), 22.6 (CH$_2$), 22.2 (CH$_2$), 0.02 (CH$_3$). Anal. Calcd for C$_{24}$H$_{38}$Cl$_2$Si$_2$Zr: C, 52.91; H, 7.03. Found: C, 52.71; H, 7.28.

Synthesis of (Me$_3$SiTHI)$_2$Zr(CH$_3$)$_2$ (5). In a swivel-frit apparatus interfaced to a high-vacuum line, a heterogeneous mixture of (Me$_3$SiTHI)$_2$ZrCl$_2$ (**4**, 0.21 g, 0.39 mmol), MeLi (0.50 g, 23 mmol), and toluene (20 mL, vacuum-transferred from NaK$_2$) was stirred for 2 days at 25 °C. After evaporating the solvent, the residue was extracted with hot hexanes and filtered. Evaporation of the solvent afforded 0.12 g (62%) of a white solid. ^{1}H NMR (C$_6$D$_6$): δ 5.53 (d, $J = 2.8$ Hz, 2 H), 5.40 (d, $J = 3.2$ Hz, 2 H), 2.65 (br m, 8 H), 1.65 (br m, 8 H), 0.16 (s, 18 H), -0.29 (s, 6 H). ^{13}C NMR (C$_6$D$_6$): δ 132.5 (C), 128.6 (C), 114.2 (C), 110.4 (CH), 109.2 (CH), 37.4 (CH$_3$), 25.5 (CH$_2$), 24.8 (CH$_2$), 23.3 (CH$_2$), 22.8 (CH$_2$), 0.1 (CH$_3$). Anal. Calcd for C$_{26}$H$_{44}$Si$_2$Zr: C, 61.96; H, 8.80. Found: C, 61.52; H, 8.65.

Synthesis of [1-(BrMe$_2$Si)THI](η^5-C$_5$H$_5$)ZrBr$_2$ (6). In a swivel-frit assembly sealed with Kalrez O-rings, a solution of (Me$_3$SiTHI)CpZrCl$_2$ (**3**, 0.46 g, 1.1 mmol) and BBr$_3$ (0.6 mL, 6.4 mmol) in 25 mL of CH$_2$Cl$_2$ was heated under reflux using a 70 °C bath for 2 days. The mixture was then evaporated, and the residue was extracted with hexanes, filtered, and crystallized from hexanes to afford 0.31 g (49%) of green needles in two crops. ^{1}H NMR (CDCl$_3$): δ 6.54 (d, $J = 3.2$ Hz, 1 H), 6.52 (s, 5 H), 6.01 (d, $J = 2.8$ Hz, 1 H), 3.18 (m, 1H), 2.83 (m, 2 H), 2.64 (m, 1 H), 1.77 (m, 3 H), 1.62 (m, 1 H), 0.85 (s, 3 H), 0.81 (s, 3 H). ^{13}C NMR (CDCl$_3$): δ 141.7 (C), 133.9 (C), 118.9 (CH), 115.9 (C), 115.3 (CH), 113.5 (CH), 26.4 (CH$_2$), 25.5 (CH$_2$), 22.3 (CH$_2$), 22.0 (CH$_2$), 4.9 (CH$_3$), 4.6 (CH$_3$). Anal. Calcd for C$_{16}$H$_{21}$Br$_3$SiZr: C, 33.58; H, 3.70. Found: C, 33.60; H, 3.36.

Synthesis of [1-(Me$_2$BrSi)THI]$_2$ZrBr$_2$ (7). In a swivel-frit assembly sealed with Kalrez O-rings, a solution of (Me$_3$SiTHI)$_2$ZrCl$_2$ (**4**, 0.73 g, 1.3 mmol) and BBr$_3$ (1.5 mL, 16 mmol) in 30 mL of CH$_2$Cl$_2$ was heated under reflux (bath at 70 °C) for 2 days. The volatile components were then removed under vacuum, and the dark residue was extracted with hexanes and filtered. Cooling the filtrate to 0 °C afforded 0.79 g (1.0 mmol, 78%) of dark green crystals in two crops. ^{1}H NMR (CDCl$_3$): δ 6.48 (d, $J = 3.2$ Hz, 2 H), 5.94 (d, $J = 3.2$ Hz, 2 H), 3.24 (m, 2 H), 2.85 (m, 4 H), 2.68 (m, 2 H), 1.0 (m, 6 H), 1.62 (m, 2 H), 0.86 (s, 6 H), 0.80 (s, 6 H). ^{13}C NMR (CDCl$_3$): δ 142.1 (C), 133.0 (C), 117.0 (CH), 115.9 (C), 114.6 (CH), 26.4 (CH$_2$), 25.7 (CH$_2$), 22.2 (CH$_2$), 22.1 (CH$_2$), 4.9 (CH$_3$), 4.3 (CH$_3$). Anal. Calcd for C$_{22}$H$_{32}$Br$_4$Si$_2$Zr: C, 34.61; H, 4.22. Found: C 34.98; H, 4.26.

Synthesis of [μ-O-(Me$_2$SiTHI)$_2$]ZrBr$_2$ (8). In the glovebox, [1-(Me$_2$BrSi)THI]$_2$ZrBr$_2$ (**7**, 0.206 g, 0.26 mmol) was placed in a dry 50 mL beaker and covered with a filter paper. Exposure of the beaker to laboratory air for 3 days and subsequent drying for 15 h in a vacuum desiccator charged with anhydrous CaSO$_4$ (Drierite) afforded 0.163 g (97% yield) of a bright yellow solid. ^{1}H NMR (CDCl$_3$): δ 6.58 (d, $^3J = 3.2$ Hz, 2 H), 6.14 (d, $^3J = 3.2$ Hz, 2 H), 3.04 (m, 4 H), 2.63 (m, 4 H), 1.71 (br m, 8 H), 0.33 (s, 6 H), 0.24 (s, 6 H). ^{13}C NMR (CDCl$_3$): δ 136.7 (C), 135.4 (CH), 124.0 (CH), 116.8 (CH), 115.8 (C), 27.1 (CH$_2$), 25.9 (CH$_2$), 22.9 (CH$_2$), 22.2 (CH$_2$), 2.0 (CH$_3$), 1.7 (CH$_3$). Anal. Calcd for C$_{22}$H$_{32}$Br$_2$OSi$_2$Zr: C, 42.64; H, 5.20. Found: C, 42.43; H, 5.37.

Reaction of (Ind)CpZrCl$_2$ with BBr$_3$. A stirred solution of (Ind)CpZrCl$_2$ (200 mg) in CH$_2$Cl$_2$ (20 mL) was treated with BBr$_3$ (1 mL). The reaction immediately became dark with the formation of a sticky precipitate. The mixture was filtered, and the precipitate was washed with pentane. Analysis of the resulting yellow solid showed primarily a single resonance at 6.87 ppm in the ^{1}H NMR spectrum (CDCl$_3$), which we have tentatively assigned to CpZrBr$_3$. Evaporation of the filtrate afforded a dark residue, which showed a complex cluster of resonances at 7−8 ppm and a doublet at 3.82 ppm ($J = 1.8$ Hz) in the ^{1}H NMR spectrum (CDCl$_3$), which we have tentatively assigned to the 3-position of indene and/or substituted indenes.

Crystallographic Analysis of 4. Colorless needles were grown by slow evaporation of a hexanes solution at 25 °C. A well-formed needle was mounted on a glass fiber with epoxy and fitted to the goniometer of a Siemens (Bruker) P4 diffractometer. Unit cell parameters were determined by least-squares refinement of 25 reflections that had been automatically centered on the diffractometer.[22] Intensity data were collected, processed,[22] and corrected for absorption.[23] The structure was solved by direct methods and refined using the

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[22] *XSCANS* v.2.1; Siemens Analytical X-ray Instruments: Madison, WI, 1994.

Table 1. Crystallographic Data

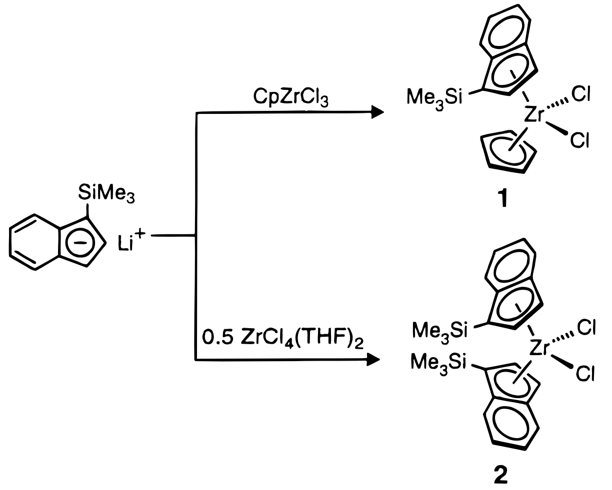
	4	8
empirical formula	$C_{24}H_{38}Cl_2Si_2Zr$	$C_{22}H_{32}Br_2OSi_2Zr$
fw	544.84	619.70
diffractometer	Siemens P4	Siemens P4
cryst dimens (mm)	0.1 × 0.1 × 0.5	0.22 × 0.26 × 0.51
color, habit	colorless, needles	yellow, brick
cryst system	monoclinic	triclinic
a (Å)	11.1550(14)	8.7246(7)
b (Å)	6.8139(8)	9.5242(10)
c (Å)	18.084(2)	14.9618(13)
α (deg)		90.528(8)
β (deg)	103.509(3)	97.120(7)
γ (deg)		90.607(8)
V (Å)^3	1336.5(3)	1233.5(2)
space group	$P2/c$	$P2_1/c$ (No. 14)
Z	2	4
D_{calc} (Mg m^{-3})	1.354	1.668
abs coeff (mm^{-1})	0.710	3.793
F_{000}	568	620
λ (Mo Kα) (Å)	0.71073	0.71073
temp (K)	298(2)	298(2)
θ range for collection	1.88−27.00	2.14−26.00
no. of reflns colld	3942	9656
no. of indep reflns	2928 [R(int) = 0.0471]	4847 [R(int) = 0.0346]
abs corr method	integration	integration
max, min transm	0.9242, 0.8862	0.4022, 0.3056
no. of data/restrts/params	2928/0/159	4847/0/257
final R [$I > 2\sigma(I)$]	R1 = 0.0506, wR2 = 0.0914	R1 = 0.0390, wR2 = 0.0993
R indices (all data)	R1 = 0.0965, wR2 = 0.1073	R1 = 0.0653, wR2 = 0.1045
GoF on F^2	1.030	0.977
largest diff peak, hole (e Å^{-3})	0.562, −0.441	0.841, −0.844

SHELXTL-PC v5.03 program package.[23] The Laue symmetry and systematic absences were consistent with the monoclinic space groups $P2/c$ and Pc. The structure was originally solved in Pc, but refinement was poor. The subroutine ADDSYM of the PLATON program package[24] indicated the molecule has a C_2 axis, consistent with the space group $P2/c$. The final refinement involved an anisotropic model for all non-hydrogen atoms. Aromatic hydrogen atoms were refined independently, whereas a riding model was used for the methyl hydrogens. Crystallographic data for **4** are collected in Table 1. The program package SHELXTL-PC was used for the ensuing molecular graphics generation.[23]

Crystallographic Analysis of 8. Yellow bricks were grown from a hexanes solution containing about 25% benzene. A well-formed crystal was mounted on a glass fiber with epoxy and fitted to the goniometer of a Siemens (Bruker) P4 diffractometer. Unit cell parameters were determined by least-squares refinement of 49 reflections that had been automatically centered on the diffractometer.[22] Intensity data were collected, processed,[22] and corrected for absorption.[23] The structure was solved by direct methods and refined using the SHELXTL-PC v5.03 program package.[23] The Laue symmetry was consistent with the triclinic space group $P\bar{1}$. The final refinement involved an anisotropic model for all non-hydrogen atoms. A riding model was used for all hydrogens. Crystallographic data for **8** are collected in Table 1. The program package SHELXTL-PC was used for the ensuing molecular graphics generation.[23]

Propylene Polymerization Experiments. A 2 L, impeller-stirred autoclave was charged with 600 g of mixed alkanes solvent (Isopar-E from Exxon Chemicals Inc.) and 150 g (nominal) of propylene. Hydrogen was added as a molecular weight control agent by differential pressure expansion from a 75 mL addition tank at 26 psi. When the reactor was heated to 70 °C, catalyst (15 μmol of **4**; 11.5 μmol of **8**) and cocatalyst (MMAO sufficient for Al:Zr = 1000:1) as 0.005 M solutions in toluene were premixed, transferred to a catalyst addition tank, and injected into the reactor. The polymerization conditions were maintained for 30 min. The resulting solution was removed from the reactor and dried in a vacuum oven at 130 °C for 15 h. Reaction using **4** afforded about 500 mg of a white solid, whereas the reaction using **8** afforded about 800 mg of a white solid, which can be accounted for, within experimental error, by alumoxane decomposition byproducts.

Scheme 1



Results and Discussion

Syntheses of Trimethylsilyl-Substituted (η^5-Indenyl)zirconium Complexes. As an extension of our earlier work,[4] we sought to examine the reactivity of Me_3Si-substituted indenyl complexes with boron tribromide. We therefore prepared two simple substrates (Scheme 1). We first prepared the monosubstituted, unsymmetrical complex (**1**) in anticipation of poor diastereoselectivity and difficult purification that is often encountered in the complexation of C_s-symmetric indenyl ligands.[8,20] $CpZrCl_3$ reacted smoothly with (1-Me_3SiInd)Li in tetrahydrofuran to form the unsymmetrical metallocene (**1**) in 73% yield. To our delight, we subsequently discovered that the disubstituted complex (*rac*-**2**) was formed with complete (>98%) diastereoselectivity; that is, the product precipitated from the reaction mixture was found to be a single diastereomer as determined by the absence of an additional set of signals in the ^{1}H NMR spectrum. The stereochemical assignment was inferred from the crystal structure of the hydrogenated bis(THI) analogue (see below). This result stands in contrast to the mixtures of *rac* and *meso* isomers that were previously obtained by installing the disiloxane linkage prior to complexing the $ZrCl_2$ fragment.[17−19]

Reactions of Trimethylsilyl-Substituted (η^5-Indenyl)zirconium Complexes with Boron Tribromide. The reaction of (1-Me_3SiInd)$CpZrCl_2$ (**1**) with BBr_3 in CH_2Cl_2 (eq 1) immediately gave a pale yellow precipitate, which was found to have a single resonance in the ^{1}H NMR spectrum consistent with $CpZrX_3$ (X = Cl, Br, or a combination of these).[25] The soluble component of the reaction yielded a red-brown solid, which had a complex ^{1}H NMR spectrum consistent with a

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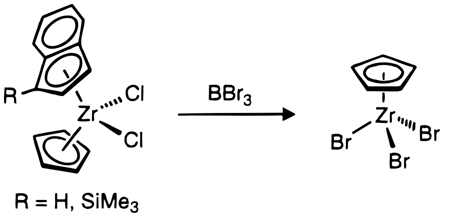
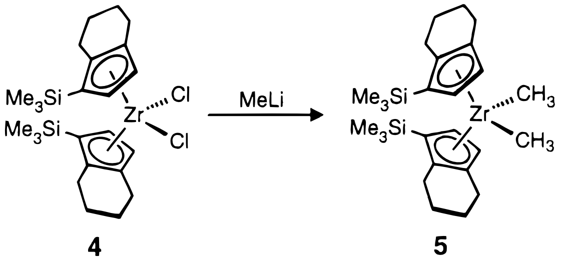
[23] Sheldrick, G. M. *SHELXTL* v5.03 (PC version). *An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; Siemens Analytical X-ray Instruments: Madison, WI, 1995.



(1)

mixture of unidentified substituted indenes. A similar reaction was carried out using the unsubstituted (Ind)-CpZrCl$_2$.[26] Similar results were obtained suggesting that the Ind−Zr bond is simply unstable under conditions required for bromodemethylation of the SiMe$_3$ group. Decomposition was also observed using BCl$_3$ instead of BBr$_3$.

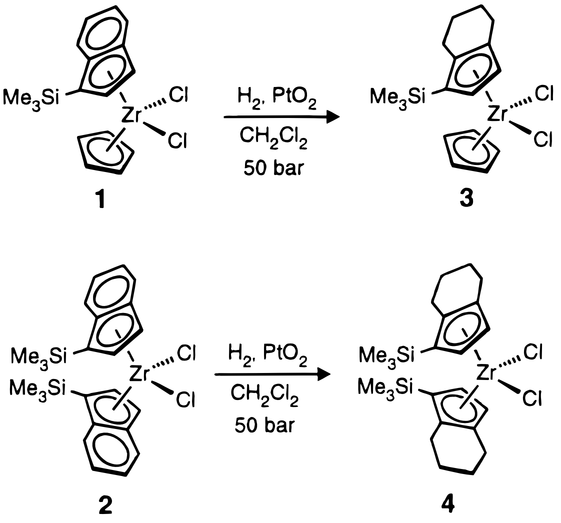
Preparation of Trimethylsilyl-Substituted (η^5-Tetrahydroindenyl)zirconium Complexes. A PtO$_2$-catalyzed hydrogenation[27] of **1** and **2** afforded the THI complexes **3** and **4** in 73% and 81% isolated yields, respectively (Scheme 2). As the use of ^{1}H NMR chemical shifts to assign metallocene diastereoisomers is somewhat controversial,[17a] we desired an alternate test of molecular symmetry. The metallocene dimethyl derivative (**5**) was prepared by treatment of the dichloride **4** with excess methyllithium in toluene suspension (eq 2).



(2)

Both the ^{1}H and ^{13}C NMR spectra showed single resonances (with integration corresponding to 6 H) for the two homotopic Zr−Me ligands, consistent with the C_2-symmetric *rac* diastereomer. In the C_s-symmetric (*meso*) diastereomer (not observed), the two methyl ligands would be diastereotopic and should, in principle, exhibit two distinct resonances. Subsequently, we obtained single crystals of **4** suitable for X-ray diffraction analysis (Table 1, Figure 1). The Zr atom of **4** lies on a crystallographic C_2 axis (space group $P2/c$), such that the two coordination hemispheres adjoined at the ZrCl$_2$ basal plane are rigorously homotopic, with both annellated C$_4$H$_8$ rings projecting in the direction of the ZrCl$_2$ moiety.

Scheme 2



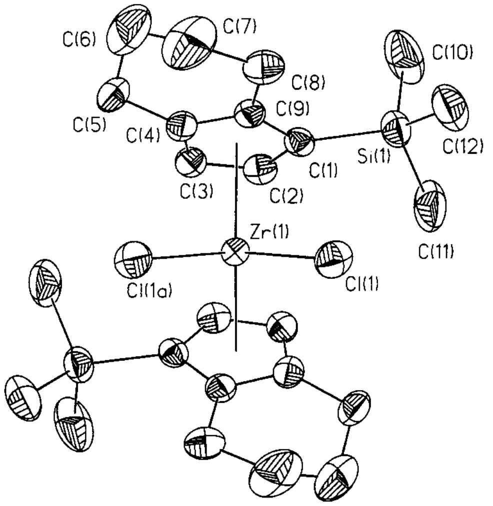


Figure 1. Thermal ellipsoid plot of **4** at 50% probability. Selected bond lengths (Å) and angles (deg): Zr−Cp(centroid), 2.233(4); Zr(1)−Cl(1), 2.444(1); Zr(1)−C(1), 2.531(4); Zr(1)−C(2), 2.462(4); Zr(1)−C(3), 2.492(4); Zr(1)−C(4), 2.608(4); Zr(1)−C(9), 2.597(4); Cl(1)−Zr(1)−Cl(1), 93.70(6); Cp(centroid)−Zr−Cp(centroid) 129.9(2).

Reactions of Trimethylsilyl-Substituted (η^5-Tetrahydroindenyl)zirconium Complexes with Boron Tribromide. As shown in Scheme 3, both Me$_3$Si-substituted tetrahydroindenyl complexes (**3** and **4**) react with excess BBr$_3$ to provide the corresponding BrMe$_2$Si-substituted complexes (**6** and **7**) in 49% and 78% yield, respectively. Both complexes show the characteristic pair of strong singlets in the ^{1}H NMR spectrum for the diastereotopic Si−CH$_3$ groups. As we have previously shown,[4] only *one* methyl group per SiMe$_3$ substituent is substituted with bromide.

Disiloxane-Linked *ansa*-Metallocene Synthesis and Structure. Previous studies showed that bis(halodimethylsilyl)-substituted metallocene dihalides are readily hydrolyzed to form tetramethyldisiloxane-bridged *ansa*-metallocenes.[16] This remarkable selectivity toward intramolecular disiloxane formation also extends to our bis(bromodimethylsilyl)-substituted bis(THI) complex (eq 3, 97% isolated yield of **8**), despite an ostensibly unfavorable conformational “twist” that must take place from a C_2-symmetric structure (**4**, Figure 1) to align the intermediate HOMe$_2$Si groups for

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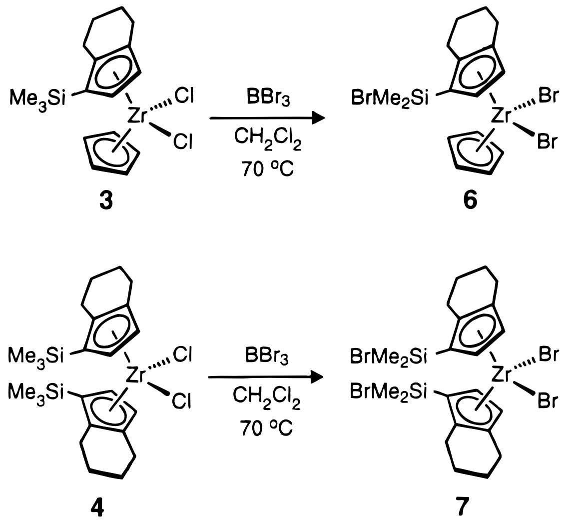
(24) Spek, A. L. *PLATON A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, 1999.

(25) (a) Reid, A. F.; Wailes, P. C. *J. Organomet. Chem.* **1964**, *2*, 329. (b) In a separate experiment, a partially dissolved sample of CpZrCl$_3$ in CDCl$_3$ was treated with excess BBr$_3$ in order to generate CpZrBr$_3$ in situ. The resulting solution showed a single resonance in the ^{1}H NMR spectrum at 6.90, whereas the product isolated from the decomposition reaction showed a single resonance at 6.87. These chemical shifts are within experimental error of one another.

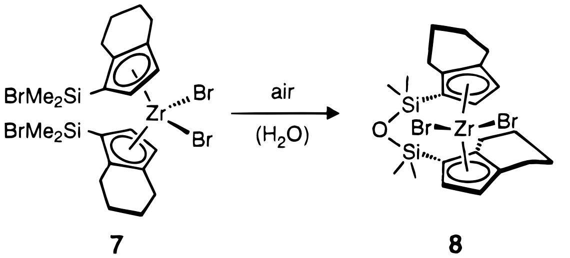
(26) Sodhi, G. S.; Kumar, S.; Kaushik, N. K. *Acta Chim. Hung.* **1983**, *114*, 329.

(27) (a) Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63. (b) Waymouth, R. M.; Bangerter, F.; Pino, P. *Inorg. Chem.* **1988**, *27*, 758.

Scheme 3



a quasi-solid-state condensation process.[28] In crystalline

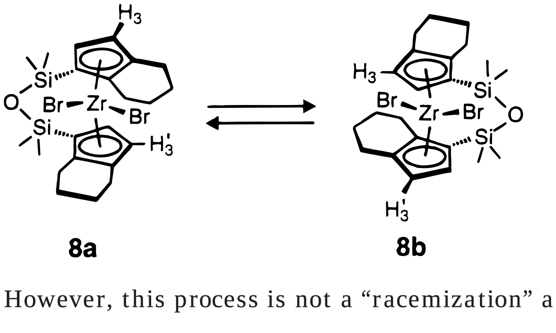


(3)

7 **8**

4, the intramolecular Si(1)···Si(1a) distance is 7.780 Å, whereas smaller intermolecular Si···Si distances (5.564, 6.814, and 6.337 Å) are also present. At first glance, one might not expect the BrMe$_2$Si-substituted complex (**7**) to be isostructural with its Me$_3$Si-substituted precursor (**4**). However, the complexes $[\eta^5\text{-}1,3\text{-}(BrMe_2Si)_2C_5H_3]_2TiBr_2$ and $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2TiF_2$ have similar solid-state molecular geometries.[29] Furthermore, $[\eta^5\text{-}1,3\text{-}(BrMe_2Si)_2C_5H_3]_2TiBr_2$ exhibits a methyl-bromo positional disorder. These findings suggest that the BrMe$_2$Si and Me$_3$Si groups are sufficiently isosteric to effect similar solid-state conformational preferences of M−Cp bonds (M = Ti, Zr).

The *ansa*-metallocene complex (**8**) was characterized by single-crystal X-ray diffraction (Table 1, Figure 2a). Noteworthy is the highly asymmetric coordination environment about Zr, with only one of the C$_4$H$_8$ annelated rings projecting in the direction of the ZrBr$_2$ group. As has already been observed for the corresponding unsaturated bis(indenyl)ZrCl$_2$ complex (**9**, Figure 2b),[18b] the complex **8** exhibits a rapid fluxional process (eq 4) down to at least −80 °C in CD$_2$Cl$_2$ solution.



(4)

8a **8b**

Table 2. Interatomic Distances (Å) and Angles (deg) for 8 and 9

	data for **8**	data for **9**[a]
Zr(1)−Cp(1)[b]	2.247(5)	2.260(4)
Zr(1)−Cp(2)[c]	2.220(5)	2.236(4)
Cp(1)[b]−Zr(1)−Cp(2)[c]	132.2(2)	130.9(3)
Zr(1)−C(1)	2.508(5)	2.519(3)
Zr(1)−C(2)	2.441(4)	2.485(3)
Zr(1)−C(3)	2.508(4)	2.509(3)
Zr(1)−C(4)	2.637(5)	2.653(3)
Zr(1)−C(9)	2.644(5)	2.659(3)
Zr(1)−C(12)	2.488(4)	2.513(3)
Zr(1)−C(13)	2.483(5)	2.505(3)
Zr(1)−C(14)	2.517(5)	2.498(3)
Zr(1)−C(15)	2.558(5)	2.588(3)
Zr(1)−C(20)	2.579(4)	2.618(3)
Si(1)−O(1)	1.632(4)	1.650(2)
Si(2)−O(1)	1.634(4)	1.647(2)
Si(1)−O(1)−Si(2)	142.6(2)	137.9(2)
Zr(1)−X(1)[d]	2.5907(8)	2.441(9)
Zr(1)−X(2)[d]	2.5907(8)	2.422(10)
X(1)[d]−Zr(1)−X(2)[d]	95.33(3)	98.9(4)
Cp(1)[b]···C(1)−Si(1)	8.4(2)	6.0(15)
Cp(2)[c]···C(12)−Si(2)	4.8(2)	5.3(15)
C(1)···C(12)	3.557(5)	3.533[e]
C(2)···C(20)	3.092(5)	3.139[e]
C(3)···C(15)	3.893(5)	3.929[e]
C(4)···C(14)	5.078(5)	5.033[e]
C(9)···C(13)	4.865(5)	4.869[e]
Zr(1)···O(1)	3.953(5)	4.010(15)
O(1)···Zr(1)···X(1)[d]	174.7(3)	172.3[e]

[a] Data with errors for **9** from ref 18b. [b] Cp(1) is defined as the centroid of the C(1)−C(2)−C(3)−C(4)-C(9) ring. [c] Cp(2) is defined as the centroid of the C(12)−C(13)−C(14)−C(15)−C(20) ring. [d] X(1) = Br(1) for **8**, Cl(1) for **9**. X(2) = Br(2) for **8**, Cl(2) for **9**. [e] Ref 31.

However, this process is not a “racemization” as previously suggested,[18b] because the intermolecular rotation process interconverts degenerate (homomeric) species (**8a** and **8b**, eq 4) leading to chemical shift interchange of, for example, H$_3$ and H$_3'$. Racemization would require dissociation of both THI ligands in order to coordinate their opposite (enantiotopic) faces.[30]

The molecular structures of **8** and **9** are remarkably similar, as demonstrated by a comparison of their metric data (Table 2).[31] The labeling scheme presented for **9** in Figure 2b differs from that given in the original report[18b] but will facilitate a direct comparison of corresponding structural features and metric data.

Both **8** and **9** show two slightly different Zr−Cp bond lengths, with the Zr−Cp bond distances and Cp(1)−Zr(1)−Cp(2) angles in **8** equal to the corresponding parameters of **9** within experimental error. Both complexes exhibit exactly the same conformational preference of the disiloxane with respect to the ZrX$_2$ groups, with both O(1)···Zr(1)···X(1) angles 174° within experimental error.

Particularly striking are the variations in Zr−C distances in both complexes.[18] The ring-fusion (“ene”) carbons, C(4), C(9), C(15), and C(20), are considerably further from Zr(1) than the “allyl” Cp carbons, C(1),

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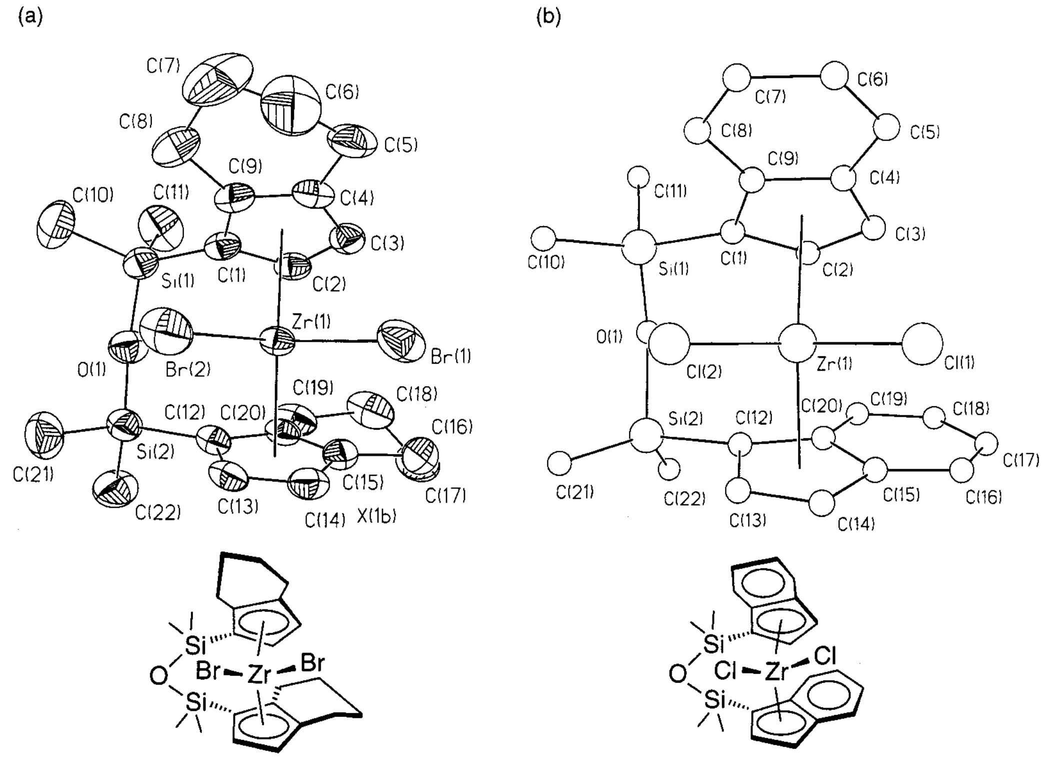
(28) The reaction is a true condensation; liquid water forms in the reaction vessel, presumably from condensation of intermediate HO-SiMe$_2$ substituents to afford the disiloxane and H$_2$O. Furthermore, no solvent is used, but rather the solid precursor is exposed to ambient air.

(29) (a) $[\eta^5\text{-}1,3\text{-}(BrMe_2Si)_2C_5H_3]_2TiBr_2$ has been prepared in our laboratories and was structurally characterized by A. L. Rheingold and co-workers (unpublished results). (b) For the structure of $[\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3]_2TiF_2$, see: Winter, C. H.; Zhou, X.-X.; Heeg, M. J. *Inorg. Chem.* **1992**, *31*, 1808.

(30) Miyake, S.; Henling, L. M.; Bercaw, J. E. *Organometallics* **1998**, *17*, 5528.



8 **9**

Figure 2. Thermal ellipsoid plot of **8** (50% probability) and ball-and-stick plot of **9** (ref 18b).

C(2), C(3), C(12), C(13), and C(14), suggesting that both complexes exhibit significantly "slipped" (η^5–η^3) ligand hapticities. In **9** this feature could be attributed to the "indenyl effect",[32] but in **8** there can be no indenyl effect to rationalize the "partially allyl-like" character[18b] of the ligands. Comparable variations in the distances between Zr and the Cp carbons were also observed in **4** (Figure 1), which has no bridge, as well as in the complex *rac*-[C_2H_4(THI)$_2$]$ZrCl_2$,[33] which has an ethylene bridge. Apparently, then, these variations are an intrinsic feature of the THI–Zr bond and are not the result of any strain peculiar to the ring system of **8**. Zr–O interactions have been proposed to rationalize the temperature dependence of ethylene polymerization activity of methylalumoaxane-activated **9**,[19] but clearly the Zr(1)···O(1) distances in both "unactivated" complexes (**8** and **9**) are far too large to invoke a model wherein decreased electron donation of the ligands upon "ring-slip" is compensated by an oxygen donor.

Propylene Polymerization Experiments. The activities of **4** and **8** for polymerization of propylene were investigated under standard conditions. Partially isobutylated ("modified") methylalumoxane (MMAO) was used as the cocatalyst with an Al:Zr ratio of 1000:1. In both cases, the nominal weight of the "product" obtained could be attributed, within experimental error, to the residual materials from catalyst and cocatalyst degradation/hydrolysis. Thus, neither **4** nor **8** is active for propylene polymerization. This result contributes to an ongoing discussion concerning the activity of complexes similar to **8**. Liang et al. found that *rac*-(**9**) and the $ZrCl_2$ analogue of **8** showed high activity for ethylene but no activity for propylene polymerization under similar conditions.[17b] In contrast, Song et al.[19] observed polymerization activities for both ethylene *and* propylene using *rac*-(**9**).[34]

Conclusions

Boron–silicon exchange is a versatile method for functionalizing metallocene complexes *after* coordination of the ancillary ligands. We have demonstrated the versatility of this method in a highly stereoselective synthesis of a tetramethyldisiloxane-linked bis(THI) *ansa*-metallocene dibromide. Work is underway to investigate the use of complexes such as **8** in the preparation of surface-immobilized C_2-symmetric metallocene dihalide catalysts for olefin polymerization.

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Supporting Information Available: Tables of crystallographic data (excluding structure factor data) for **4** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Structural analysis of **9** (using the PLATON suite of programs, ref 24) and molecular graphics generation of **9** (using SHELXTL v5.03, ref 23) were based on positional parameters and isotropic thermal displacement values published in ref 18a.

(32) (a) Basolo, F. *Pure Appl. Chem.* **1988**, *60*, 1193. (b) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (c) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33. (d) Anderson, S.; Hill, A. F.; Nasir, B. A. *Organometallics* **1995**, *14*, 2987.

(33) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21.

(34) Wang et al. (ref 17a) have contested the results of Song et al., by claiming that the assignment of the *rac* isomer of **9** by Song et al. (by ^{1}H NMR chemical shift correlation, ref 19) was erroneous.