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Boron−Silicon Exchange Reactions of Boron Trihalides with Trimethylsilyl-Substituted Metallocenes

Paul A. Deck,* Travis S. Fisher, and J. Sloan Downey

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0121

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The reaction of (η^5-$C_5H_4SiMe_3$)$_2$Fe with excess BCl_3 in CH_2Cl_2 at −78 °C affords a mixture of metathesis product (η^5-$C_5H_4BCl_2$)$_2$Fe and an isomer, [η^5-1,3-$C_5H_3(BCl_2)_2$]Fe(η^5-C_5H_5). In contrast, BCl_3 does not react appreciably with trimethylsilyl-substituted group 4 metallocenes below 80 °C. When (η^5-$C_5H_4SiMe_3$)$_2MCl_2$ (M = Ti, Zr) is treated with excess BBr_3 in CH_2Cl_2 at 80 °C for several days, one methyl group is selectively cleaved from each trimethylsilyl substituent to afford (η^5-$C_5H_4SiMe_2Br$)$_2MBr_2$ (M = Ti, Zr) in useful yields. Exposure of crystalline samples of these bromodimethylsilyl-substituted group 4 metallocene dibromides to ambient atmosphere for several days results in selective, quantitative hydrolysis to afford the disiloxane-linked ansa-metallocene dibromides, [(η^5-$C_5H_4SiMe_2$)$_2$O]MBr_2. Two other bromodimethylsilyl-substituted metallocenes, (η^5-$C_5H_4SiMe_2Br$)(η^5-C_5Me_5)MBr_2 and [η^5-1,3-$C_5H_3(SiMe_2Br)_2$]$_2ZrBr_2$ are also prepared by treatment of the corresponding trimethylsilyl-substituted precursors with boron tribromide. The latter tetrasubstituted complex is hydrolyzed by ambient atmosphere to afford a metallocene with two tetramethyldisiloxane bridges.

Introduction

Metathesis reactions of boron halides and organo-group 14 compounds have found increasing use in recent syntheses of metallocene and other η^5-cyclopentadienyl (Cp) complexes bearing boryl substituents (BX_2, X = alkyl, halo, alkoxy, or dialkylamido).[1] The electrophilicity and synthetic versatility of boryl substituents suggest new approaches to the design of Ziegler−Natta olefin polymerization catalysts having unusual molecular architecture and functionality.[2]

The primary synthetic approach to borylated metallocenes attaches the reactive boryl substituents to neutral cyclopentadienes by B−Si (or B−Sn) metathesis *prior* to metal complexation. Cyclopentadienyl *anions* are, however, functionally incompatible with BX_2 groups having labile X ligands such as Cl or Br. One avoids this incompatibility by incorporating a trimethylsilyl substituent on the cyclopentadiene; subsequent reaction with early transition metal halides then affords the desired borylated Cp complex with elimination of chlorotrimethylsilane.

Alternatively, boryl groups can be attached to the ligands already coordinated to the transition metal. For example, ferrocene undergoes *direct* borylation with boron tribromide at elevated temperatures,[3] while treatment of certain transition metal Cp complexes with tris(pentafluorophenyl)borane affords products in which a Cp ligand is triarylborato-functionalized.[4]

Desilylation of trimethylsilyl-substituted arenes with boron trihalides is remarkably facile.[5] The present contribution reports the variations observed in the reactivity and chemoselectivity of trimethylsilyl-substituted ferrocenes and group 4 metallocene dichlorides toward boron trihalides.

Results and Discussion

Reactions of Ferrocenes. 1,1′-Bis(trimethylsilyl)ferrocene (**1**) reacts readily with an excess of boron trichloride in dichloromethane under mild conditions (Scheme 1) to afford moderate isolated yields (65%) of the corresponding 1,1′-bis(dichloroboryl)ferrocene (**2**) after recrystallization. ^1H NMR analysis of the crude reaction mixture indicates a nearly quantitative conversion to a mixture of two diborylated products in the temperature-dependent ratios shown. The minor regioisomer (**3**, not isolated) exhibits a singlet (δ 3.75, 5 H), a doublet (δ 4.58, *J* = 2.2 Hz, 2 H), and a triplet (δ 4.94, *J* = 2.2 Hz, 1 H) in C_6D_6 solution.[3b] Although the

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(2) (a) Piers, W. E.; Spence, R. E. v. H. *Organometallics* **1995**, *14*, 4617. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (c) Skrzypczak-Jankun, E.; Cheesman, B. V.; Zheng, B.; Lemert, R. M.; Asthana, S.; Srebnik, M. *J. Chem. Soc., Chem. Commun.* **1994**, 127. (d) Zheng, B.; Srebnik, M. *J. Organomet. Chem.* **1994**, *474*, 49. (e) Erker, G. *Tetrahedron* **1995**, *15*, 4277. (f) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226.

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(4) (a) Ruwwe, J.; Erker, G.; Frohlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80. (b) Temme, B.; Karl, J.; Erker, G. *Chem. Eur. J.* **1996**, *2*, 919. (c) Temme, B.; Erker, G.; Karl, J.; Luftmann, H.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755.

(5) (a) Gross, U.; Kaufmann, D. *Chem. Ber.* **1987**, *120*, 991−4. (b) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901−5. (c) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 853−4.

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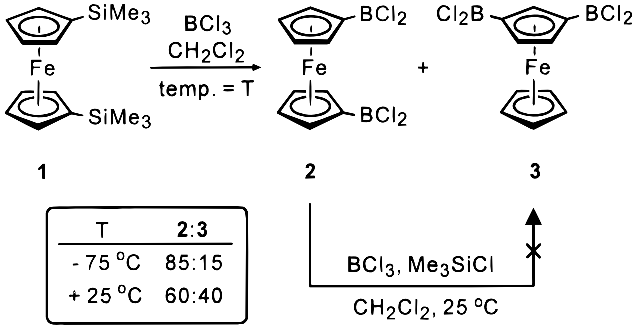
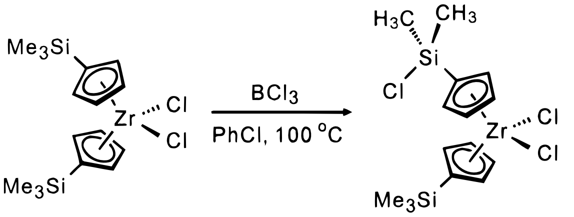
mechanism of formation of **3** remains unclear,[6] a product resubmission experiment shows that **2** does *not* rearrange to **3** when subjected to boron trichloride and chlorotrimethylsilane in dichloromethane at room temperature (Scheme 1).

Scheme 1



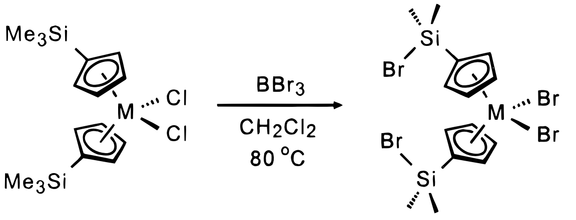
Reactions of Group 4 Metallocenes. Encouraged by the mild conditions for desilaborylation of ferrocene, we next investigated the reactivity of trimethylsilyl-substituted titanocene and zirconocene dichlorides with boron trihalides. These group 4 metallocenes were *inert* with respect to Cp−Si cleavage by boron trichloride (or boron tribromide) even under relatively severe conditions (PhCl solution, 100 °C).[7] Instead, product mixtures were consistent with halodemethylation of the trimethylsilyl groups (eq 1).[8] For example, when the zirconocene dichloride (**4b**) was treated with boron trichloride in chlorobenzene at 100 °C for 2 d, a 30% conversion to **5b** was observed by ^{1}H NMR analysis of the crude product mixture. When **4b** was treated with a 10-fold excess of the more reactive boron tribromide in $CDCl_3$ at 25 °C, examination of the ^{1}H NMR spectrum over a period of 6 days showed stepwise (and ultimately quantitative) conversion to the bis(bromodimethylsilyl)-substituted complex (**6b**).[9]



(1)

4b **5b**

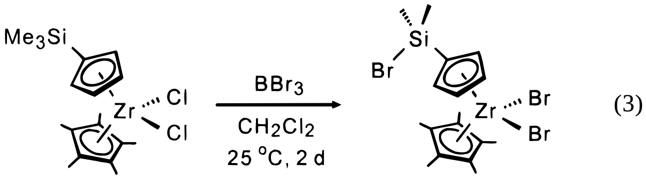
Preparative reactions (eq 2) of the metallocenes (**4**) with boron tribromide in dichloromethane at 80−100 °C efficiently afforded 1,1′-bis(bromodimethylsilyl)metallocene dibromides (**6**) in yields of 50% (M = Ti) and 77% (M = Zr). This highly selective reaction cleaves only one methyl group from each of among one and four trimethylsilyl substituents. As additional examples, the mixed-ligand complex (**7**) was converted to the bromodimethylsilyl-substituted derivative (**8**) in 82% yield (eq 3), while the tetrakis(trimethylsilyl)zirconocene dichloride (**9**) afforded the corresponding tetrakis(bromodimethylsilyl)zirconocene dibromide (**10**) in 80% yield (eq 4).



(2)

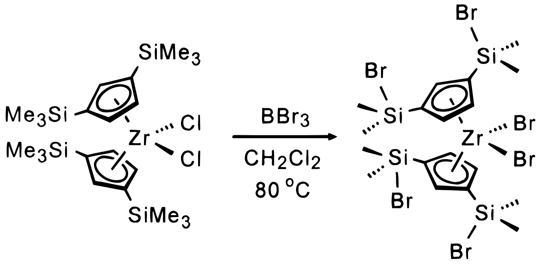
4a: M = Ti
4b: M = Zr

6a: M = Ti
6b: M = Zr



(3)

7 **8**



(4)

9 **10**

The tetrasubstituted product (**10**) exhibited the anticipated pairs of distinct singlets in the ^{1}H and proton-decoupled ^{13}C NMR spectra corresponding to the diastereotopic methyl groups of the four equivalent bromodimethylsilyl substituents.

Previously reported work shows that some of the analogous chlorodimethylsilyl-substituted Cp complexes of titanium and zirconium are prepared by attaching a chlorodimethylsilyl group to a trimethylsilyl-substituted cyclopentadiene followed by chemoselective chlorotrimethylsilane elimination.[10] This approach affords the substituted half-sandwich [(η^5-$C_5H_4SiMe_2Cl$)MCl_3] complexes with either M = Ti or Zr, but the *metallocene*

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(6) For a discussion of rearrangments in electrophilic substitution reactions of ferrocenes, see: (a) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organomet. Chem.* **1982**, *8*, 1016. (b) Silverthorn, W. E. *Adv. Organomet. Chem.* **1973**, *13*, 47. (c) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1972**, *40*, 197. (d) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1973**, *57*, C15. (e) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1977**, *141*, 355.

(7) This finding was not entirely unexpected, as electrophilic substitution reactions of group 4 or other d^0 metallocenes have not to our knowledge been reliably demonstrated.

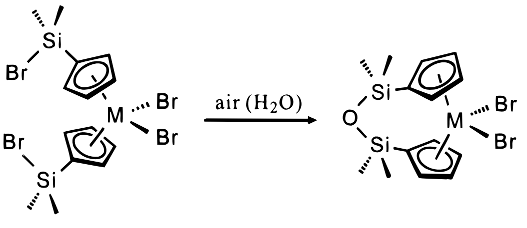
(8) Cleavage of alkyl−Si bonds by boron trihalides was previously shown to occur for selected organosilanes under forcing conditions. See ref 5.

(9) Transhalogenation at the transition metal occurs immediately after addition of the boron halide reagent. The resulting complex, $(Me_3SiCp)_2ZrBr_2$, was assigned to the pair of equally integrating triplets (J = 2.2 Hz) at 6.79 and 6.52 ppm in the ^{1}H NMR spectrum, while the singlet assigned to the trimethylsilyl substituent shifted downfield about 0.04 ppm relative to the starting metallocene dichloride. (a) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R. S.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106. (b) Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592. After 1 day, a set of four equally integrating triplets (J = 2.3 Hz) at 6.88, 6.83, 6.58, and 6.54 ppm was observed in the ^{1}H NMR spectrum, corresponding to an intermediate in which only one trimethylsilyl group was bromodemethylated, while a new signal for the bromodimethylsilyl substituent appeared at 0.96 ppm. Small signals arising from the product (**6b**) were also observed after 1 day.

(10) Ciruelos, S.; Cuenca, T.; Gómez-Sal, P.; Manzanero, A.; Royo, P.*Organometallics* **1995**, *14*, 177.

complex is only obtained with M = Zr.[11] Our complementary method, in which similar functionality is established *after* metal complexation, appears somewhat more suited to the preparation of multiply halodimethylsilylated metallocenes such as **6** and **10**.

Hydrolysis of Bromodimethylsilyl-Substituted Group 4 Metallocene Dichlorides. According to Royo and co-workers, bis(chlorodimethylsilyl)zirconocene dichloride reacts selectively with water in THF solution to afford an *ansa*-metallocene having a disiloxane linkage.[10] We now report that the corresponding bis(bromodimethylsilyl)metallocene dibromides (**6**) also undergo such chemoselective hydrolysis (eq 5). The bromodimethylsilyl substituents in the metallocenes **6** are sufficiently reactive, however, that conversions into the corresponding analytically pure disiloxanes (**11**) are achieved nearly quantitatively (90−95% isolated yields) by exposure of the crystalline starting materials to ambient atmosphere for several days. In the NMR spectra of the disiloxanes, the change in the ^{1}H chemical shifts of the methyl groups from the bis(bromodimethylsilyl)-substituted starting materials (0.6 ppm upfield) supports the disiloxane structural assignments.[10]

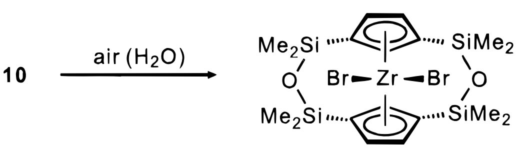


(5)

6a: M = Ti
6b: M = Zr

11a: M = Ti
11b: M = Zr

Metallocenes with two bridging groups are the subject of investigation elsewhere as catalysts for olefin polymerization.[12] Our synthetic approach is readily applied to the construction of such a molecule. Exposure of tetrakis(trimethylsilyl)zirconocene dichloride (**10**) to air for 3 d (eq 6) cleanly afforded the bis(disiloxane) compound (**12**) in 90% yield.



(6)

12

Conclusions

The reactivity of trimethylsilyl-substituted Cp ligands toward boron trihalides depends highly on the transition metal species to which the Cp ligand is coordinated. If the metal species is 1,1′-bis(trimethylsilyl)ferrocene, Cp−Si cleavage affords a mixture of regioisomeric bis(dichloroborylated) ferrocenes. In contrast, zirconocene and titanocene dichlorides retain the Cp−Si bond upon treatment with boron tribromide but undergo selective Si−CH$_3$ cleavage to afford (multiply) bromodimethylsilyl-functionalized metallocene dibromides. The latter complexes undergo chemoselective hydrolysis to disiloxane-bridged *ansa*-metallocenes.

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 trihalides were used as received from Aldrich. 1,1′-Bis(trimethylsilyl)ferrocene (**1**) was prepared from 1,1′-dilithioferrocene[13] and chlorotrimethylsilane following published procedures.[14] The group 4 metallocene dichlorides **4a**, **4b**, **7**, and **9** were prepared by published procedures.[15] NMR spectra were recorded using a Varian U-400 or a Bruker AM-360 instrument. Elemental analyses were performed by Oneida Research Services (Whitesboro, NY).

Reaction of 1,1′-Bis(trimethylsilyl)ferrocene with Boron Trichloride. To a stirred solution of boron trichloride (4.0 mL, 1.0 M in dichloromethane, 5.0 mmol) in dichloromethane (50 mL) maintained at −78 °C was added the starting ferrocene (**1**, 0.33 g, 1.0 mmol) using a pipet. After the solution was stirred at −78 °C for 2 h, the volatile components were removed under vacuum while warming the solution slowly to room temperature to afford 0.34 g (98%) of a red-brown solid. ^{1}H NMR showed the crude product to be an 85:15 mixture of bis(dichloroboryl)ferrocenes **2** and **3**, respectively, along with a dark, intractable impurity, possibly a mixture of ferrocenium species.[3d,e] (When the otherwise identical reaction was carried out at room temperature, a 60:40 mixture of **2** and **3** was similarly obtained. Product ratios did not differ significantly when twice as much BCl$_3$ was used.) Recrystallization of the red-brown residue from pentane afforded 0.493 g (1.42 mmol, 65%) of deep red needles, which were found to be 95% pure **2** from ^{1}H NMR analysis consistent with published data.[3d,e]

Resubmission Experiment. A sample of the ferrocene **2** was recrystallized from hexanes and found to be 98% pure by ^{1}H NMR analysis. Treatment of this sample with 10 equiv of BCl$_3$ and 2 equiv of Me$_3$SiCl in dichloromethane at room temperature for 6 h followed by filtration to remove a small amount of an intractable black solid and evaporation of the filtrate led to the recovery of **2** as determined by ^{1}H NMR analysis.

Synthesis of (η^5-C$_5$H$_4$SiMe$_2$Br)(η^5-C$_5$Me$_5$)ZrBr$_2$ (8). To a solution of **7** (230 mg, 0.53 mmol) in 15 mL of CH$_2$Cl$_2$ was added boron tribromide (5.0 mL, 1.0 M in CH$_2$Cl$_2$, 5.0 mmol). The mixture was stirred at 25 °C for 2 d, during which the clear solution became dark green. The volatile components were then removed under reduced pressure, and the solid green-black residue was recrystallized from hexanes to afford 257 mg (0.44 mmol, 82%) of green crystals. ^{1}H NMR (CDCl$_3$):

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[11] Similar selectivity was demonstrated previously: (a) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210. (b) Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37. (c) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.

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δ 6.70 (t, $J = 2.2$ Hz, 2 H), 6.09 (t, $J = 2.2$ Hz, 2 H), 2.04 (s, 15 H), 1.01 (s, 6 H). ^{13}C NMR (CDCl$_3$): δ 125.9 (CH), 125.3 (CH), 123.9 (C), 114.7 (C), 13.3 (CH$_3$), 4.2 (CH$_3$). Anal. Calcd for $C_{17}H_{25}Br_3SiZr$: C, 34.70; H, 4.28. Found: C 34.76; H, 4.23.

Synthesis of (η^5-$C_5H_4SiMe_2Br$)$_2$TiBr$_2$ (6a). To a solution of **4a** (200 mg, 0.51 mmol) in 50 mL of CH_2Cl_2 was added BBr_3 (5.0 mL, 1.0 M in CH_2Cl_2, 5.0 mmol). The reactor was sealed, and the mixture was stirred at 90 °C for 2 d and then cooled. After removal of the volatile components under vacuum, the dark residue was crystallized from hexane to afford 155 mg (0.25 mmol, 50%) of pale green needles. ^{1}H NMR (CDCl$_3$): δ 7.07 (t, $J = 2.2$ Hz, 4 H); 6.66 (t, $J = 2.3$ Hz, 4 H), 0.98 (s, 12 H). ^{13}C NMR (CDCl$_3$): δ 128.6 (CH), 125.9 (CH), 121.4 (C), 0.7 (CH$_3$). Anal. Calcd for $C_{14}H_{20}Br_4Si_2Ti$: C, 27.48; H, 3.29. Found: C, 27.86; H, 2.93.

Synthesis of (η^5-$C_5H_4SiMe_2Br$)$_2$ZrBr$_2$ (6b). To a solution of **4b** (437 mg, 1.00 mmol) in 30 mL of CH_2Cl_2 was added BBr_3 (5.0 mL, 1.0 M in CH_2Cl_2, 5.0 mmol). The reactor was sealed, and the mixture was stirred at 90 °C for 4 d and then cooled. After removal of the volatile components under vacuum, the dark residue was taken up in 20 mL of toluene and filtered. The dark filtrate was evaporated, and the residue was crystallized from 30 mL of hexane to afford 504 mg (0.77 mmol, 77%) of green needles. ^{1}H NMR (CDCl$_3$): δ 6.92 (t, $J = 2.4$ Hz, 4 H), 6.62 (t, $J = 2.2$ Hz, 4 H), 0.97 (s, 12 H). ^{13}C NMR (CDCl$_3$): δ 126.3 (CH), 121.6 (C), 116.3 (CH), 4.7 (CH$_3$). Anal. Calcd for $C_{14}H_{20}Br_4Si_2Zr$: C, 25.66; H, 3.08. Found: C, 25.85; H, 2.90.

Synthesis of [η^5-1,3-C_5H_3(SiMe$_2$Br)$_2$]$_2$ZrBr$_2$ (10). To a solution of **9** (372 mg, 0.64 mmol) in 25 mL of CH_2Cl_2 was added BBr_3 (5.0 mL, 1.0 M in CH_2Cl_2, 5.0 mmol). The reactor was sealed, and the mixture was stirred at 80 °C for 4 d. Removal of the volatile components under vacuum and crystallization from hexanes afforded 474 mg (0.51 mmol, 80%) of pale green needles in two crops. ^{1}H NMR (CDCl$_3$): δ 7.47 (t, $J = 2.0$ Hz, 2 H), 6.77 (t, $J = 2.0$ Hz, 4 H), 0.93 (s, 12 H), 0.90 (s, 12 H). ^{13}C NMR (CDCl$_3$): δ 143.2 (CH), 126.0 (C), 123.1 (CH), 4.9 (CH$_3$), 3.8 (CH$_3$). Anal. Calcd for $C_{18}H_{30}Br_6Si_4Zr$: C, 23.26; H, 3.25. Found: C, 23.38; H, 3.09.

Synthesis of [(η^5-$C_5H_4SiMe_2$)$_2$O]TiBr$_2$ (11a). Crystalline **6a** (100 mg) was allowed to stand in a beaker with a perforated cover for 1 week under ambient air. The resulting dark green solid was recovered in about 95% yield and found to be pure. ^{1}H NMR (CDCl$_3$): δ 7.12 (dd, $^3J = 2.2$ Hz, $^4J = 2.6$ Hz, 4 H); 6.84 (t, $^3J = 2.2$ Hz, $^4J = 2.6$ Hz, 4 H), 0.38 (s, 12 H). ^{13}C NMR (CDCl$_3$): δ 128.6 (CH), 125.9 (CH), 121.4 (C), 0.7 (CH$_3$). Anal. Calcd for $C_{14}H_{20}Br_2OSi_2Ti$: C, 35.92; H, 4.31. Found: C, 35.66; H, 4.15.

Synthesis of [(η^5-$C_5H_4SiMe_2$)$_2$O]ZrBr$_2$ (11b). Crystalline **6b** (100 mg) was allowed to stand under ambient air for 1 week in a beaker with a perforated cover. The resulting pale green solid was recovered in about 90% yield and found to be pure. ^{1}H NMR (CDCl$_3$): δ 6.92 (t, $J = 2.2$ Hz, 4 H), 6.68 (t, $J = 2.3$ Hz, 4 H), 0.38 (s, 12 H). ^{13}C NMR (CDCl$_3$): δ 125.2 (CH), 121.4 (CH), 117.0 (C), 0.80 (CH$_3$). Anal. Calcd for $C_{14}H_{20}Br_2OSi_2Zr$: C, 32.87; H, 3.94. Found: C, 33.09; H, 3.97.

Synthesis of [(η^5-1,3-C_5H_3)(SiMe$_2$OSiMe$_2$)$_2$(η^5-1,3-C_5H_3)]ZrBr$_2$ (12). Crystalline **10** (100 mg) was allowed to stand under ambient air for 3 days in a beaker with a perforated cover. The resulting colorless solid was recovered in about 90% yield. An analytical sample was obtained by crystallization from hexanes. ^{1}H NMR (CDCl$_3$): δ 7.25 (d, $J = 1.8$ Hz, 4 H), 7.09 (t, 1.8 Hz, 2 H), 0.45 (s, 12 H), 0.36 (s, 12 H). ^{13}C NMR (CDCl$_3$): δ 133.6 (CH), 125.5 (CH), 123.8 (C), 2.0 (CH$_3$), −0.5 (CH$_3$). Anal. Calcd for $C_{18}H_{30}Br_2O_2Si_4Zr$: C, 33.69; H, 4.71. Found: C, 33.57; H, 4.52.

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