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Influence of the Departing Group on the Electrophilic Cleavage of Silicon−Carbon Bonds Adjacent to Zirconocene Dichloride. Preparation of Electrophile-Functionalized Zirconocene Dibromides

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$(EtMe_2SiC_5H_4)CpZrCl_2$ (**5**) reacts with BBr_3 in 1,2-dichloroethane (reflux, 24 h) to afford a 4:1 mixture of $(EtMeBrSiC_5H_4)CpZrBr_2$ (**10**) and $(BrMe_2SiC_5H_4)CpZrBr_2$ (**11**) in a nearly quantitative conversion. Similarly, $({}^tBuMe_2SiC_5H_4)CpZrCl_2$ (**6**) reacts with BBr_3 to afford a 15:1 mixture of $({}^tBuMeBrSiC_5H_4)CpZrBr_2$ (**13**) and **11**. The product **11** is obtained independently by treating $(Me_3SiC_5H_4)CpZrCl_2$ (**12**) with BBr_3. In contrast, Si−Ph bonds are cleaved with complete selectivity in the presence of Si−Me groups. $(PhMe_2SiC_5H_4)_2ZrCl_2$ (**8**) reacts with excess BCl_3 in dichloromethane (reflux, 15 h) to afford $(ClMe_2SiC_5H_4)_2ZrCl_2$ (**14**) in 72% yield. $(Ph_2MeSiC_5H_4)_2ZrCl_2$ (**9**) reacts with excess BBr_3 in 1,2-dichloroethane (reflux, 15 h) to afford $(Br_2MeSiC_5H_4)_2ZrBr_2$ (**15**) in 79% yield. Complexes **9** and **15** were analyzed by single-crystal X-ray diffraction. Crystalline **9** adopts a pseudo-C_2 conformation in which the face of the Ph group of one ligand shows a weak interaction with a C−H bond of the other ligand. Crystalline **15** also adopts a pseudo-C_2 conformation, in which the $SiBr_2$ groups are directed away from the $ZrBr_2$ group.

Introduction

Group 4 metallocene complexes are best known for their applications in olefin polymerization catalysis.[2] Structural variation of the Cp ligands affords control over several technologically important aspects of metallocene-catalyzed olefin polymerization.[3] This control motivates ongoing efforts in several laboratories to conceive new metallocene structures and synthetic methods. Much of this work attempts to define the steric environment of the catalytic site, which influences the stereoselectivity of α-olefin insertion.[4] Fewer investigations have been directed toward the incorporation of reactive functional groups onto the ancillary ligand framework,[5] largely because of the sensitivity of the electrophilic "active species" toward poisoning.[6] However, functional groups are useful for further structural elaboration and for immobilizing precatalytic species on inorganic supports.[7]

We showed earlier that trimethylsilyl substituents on group 4 metallocene dichlorides are susceptible to a *single* electrophilic bromodemethylation upon treatment with boron tribromide.[8] Bromodimethylsilylated metallocenes react with a wide range of nucleophiles such as water,[9] amines,[10] and phenols,[11] while neighboring

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M−Br bonds are comparatively inert. Recently, we also showed that (trimethylstannyl)zirconocene dichloride undergoes cleavage of two Sn−Me bonds upon treatment with BBr_3.[12] Unfortunately, the corresponding Sn−Br bonds are not as reactive as Si−Br bonds toward nucleophiles, diminishing their further synthetic utility. We therefore turned our attention toward understanding the cleavage of Si−R bonds with BBr_3 with the ultimate goal of finding new methods to attach more than one halogen to each silyl substituent, starting from stable, readily prepared metallocene precursors. We now report a study of the reactivity of Si−C bonds adjacent to zirconocene dichloride using BBr_3 as the electrophilic bromodemethylation reagent. In particular, we show that Si−Ph bonds are sufficiently more reactive to enable an efficient synthesis of methyldibromosilyl-functionalized group 4 metallocene complexes.

Experimental Section

General Procedures. Standard inert atmosphere techniques were used for all manipulations. Swivel-frit vessels sealed with Kalrez[7] O-rings and interfaced to a high-vacuum line were used for reactions involving boron trihalides. BCl_3 (1.0 M solution in CH_2Cl_2), BBr_3 (neat), $EtMe_2SiCl$, ${}^tBuMe_2SiCl$, $PhMe_2SiCl$, $Ph_2MeSiCl$, and ${}^tBuSiMe_2OSO_2CF_3$ were used as received from Aldrich. NaCp was prepared from freshly distilled cyclopentadiene and NaH. $ZrCl_4(THF)_2$ was prepared according to Manzer's procedure.[13] (Phenyldimethylsilyl)cyclopentadiene and (methyldiphenylsilyl)cyclopentadiene were prepared according to Kira et al.[14] $CpZrCl_3$ was used as received from Strem Chemicals; $CpZrCl_3(DME)$ was prepared as reported by Lund and Livinghouse.[15] $(Me_3SiC_5H_4)CpZrCl_2$ was prepared according to the method of Siedle et al.[16] NMR spectra were recorded on a JEOL Eclipse-500 instrument. Elemental analyses were performed by Desert Analytics (Tucson, AZ) or Oneida Research Services (Whitesboro, NY).

Synthesis of $EtMe_2SiC_5H_4Li$ (1). A solution of ethyldimethylsilyl chloride (4.91 g, 0.040 mol) and sodium cyclopentadienide (3.50 g, 0.040 mol) in THF (100 mL) was stirred for 3 h at 25 °C and then under reflux for 1 h. After cooling, the solvent was evaporated. Pentane (100 mL) and water (50 mL) were added. The organic layer was separated, washed with saturated aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, and evaporated to afford 5.34 g (0.035 mol, 88%), tentatively assigned to (ethyldimethylsilyl)cyclopentadiene by ${}^1H$ NMR analysis in $CDCl_3$: δ 6.60 (br, 2 H), 6.56 (br, 2 H), 3.42 (br, 1 H), 0.95 (t, 3 H), 0.51 (q, 2 H), −0.06 (s, 6 H). This oil was transferred to a 500 mL Schlenk flask, dissolved in 250 mL of hexanes, and treated with 25 mL of ${}^nBuLi$ solution (1.6 M in hexanes, 0.040 mol). After stirring for 15 h, the white precipitate was collected on a filter and washed with pentane (2 × 50 mL) to afford 5.06 g (0.032 mol, 91%) of **1** as an air-sensitive white solid. ${}^1H$ NMR (THF-d_8): δ 5.79 (m, 2 H), 5.72 (m, 2 H), 0.97 (t, $J = 8.1$ Hz, 3 H), 0.58 (q, $J = 8.1$ Hz, 2 H), 0.09 (s, 6 H). ${}^{13}C$ NMR (THF-d_8): δ 111.8 (CH), 108.7 (C), 106.9 (CH), 10.4 (CH_3), 8.5 (CH_2), −1.1 (CH_3). Satisfactory elemental analysis was not obtained. The ${}^1H$ NMR spectrum is provided in the Supporting Information (Figure S1) as evidence of substantial purity.

Synthesis of ${}^tBuMe_2SiC_5H_4Li$ (2). To a stirred solution of NaCp (1.9 g, 21 mmol) in diethyl ether (50 mL) maintained at 0 °C was added ${}^tBuSiMe_2OSO_2CF_3$ (4.2 g, 16 mmol) in one portion. After stirring for 2 h, the mixture was filtered, and the filtrate was evaporated to afford 1.7 g (10 mmol, 59%) of an orange oil tentatively identified as ${}^tBuMe_2SiC_5H_5$ on the basis of the assignment of 85% of the integratable ${}^1H$ NMR signal intensity in $CDCl_3$: δ 6.9 to 6.5 (m, 4 H), 3.6 to 3.0 (m, 1 H), 1.0 to 0.8 (m, 9 H), 0.2 to −0.2, m, 6 H). The orange oil was dissolved in hexanes (10 mL), filtered through Celite into a 200 mL Schlenk flask, diluted with 100 mL of additional hexanes, and treated with 10 mL of ${}^nBuLi$ solution (1.4 M in hexanes, 14 mmol). After 15 h, no precipitate had formed, so 10 mL of diethyl ether was added to the viscous solution. A white precipitate formed after an additional 5 min of stirring. The precipitate was collected on a filter, washed with 20 mL of pentane, and dried under vacuum to afford 1.3 g (7.0 mmol, 44% based on ${}^tBuMe_2SiOSO_2CF_3$) of **2** as a white solid. ${}^1H$ NMR (THF-d_8): δ 5.96 (m, 2 H), 5.88 (m, 2 H), 0.87 (s, 9 H), 0.12 (s, 6 H). ${}^{13}C$ NMR (THF-d_8): δ 112.8 (CH), 106.6 (CH), missing *ipso* C of C_5H_4 group, 27.5 (CH_3), 18.2 (C), −3.8 (CH_3). Satisfactory elemental analysis was not obtained. The ${}^1H$ NMR spectrum is provided in the Supporting Information (Figure S2) as evidence of substantial purity.

Synthesis of $PhMe_2SiC_5H_4Li$ (3). To a solution of (phenyldimethylsilyl)cyclopentadiene[14] (5.66 g, 28.2 mmol) in hexanes (250 mL) was added 20 mL of ${}^nBuLi$ solution (1.6 M in hexanes, 32 mmol) using a syringe. After stirring for 15 h at 25 °C, the white precipitate was collected by filtration, washed with pentane, and dried under vacuum to afford 5.25 g (25.4 mmol, 90%) of a white powder. ${}^1H$ NMR (THF-d_8): δ 7.58 (m, 2 H), 7.20 (m, 3 H), 5.96 (m, 2 H), 5.87 (m, 2 H), 0.40 (s, 6 H). ${}^{13}C$ NMR (THF-d_8): δ 143.9 (C), 133.8 (CH), 127.3 (CH), 126.9 (CH), 111.69 (CH), 106.1 (CH), −0.9 (CH_3). One (C) signal is missing and may be under a (CH) signal. Satisfactory elemental analysis was not obtained. The ${}^1H$ NMR spectrum is provided in the Supporting Information (Figure S3) as evidence of substantial purity.

Synthesis of $Ph_2MeSiC_5H_4Li$ (4). To a solution of (methyldiphenylsilyl)cyclopentadiene[14] (**4**, 4.77 g, 18.2 mmol) in hexanes (60 mL) was added 15 mL of ${}^nBuLi$ solution (1.6 M in hexanes, 24 mmol) via syringe. After stirring for 15 h at 25 °C, the white precipitate was collected by filtration, washed with pentane, and dried under vacuum to afford 3.95 g (14.7 mmol, 81%) of a white powder. ${}^1H$ NMR (THF-d_8): δ 7.55 (m, 4 H), 7.20 (m, 6 H), 6.08 (m, 2 H), 5.98 (m, 2 H), 0.66 (s, 3 H). ${}^{13}C$ NMR (THF-d_8): δ 141.7 (C), 134.9 (CH), 127.7 (CH), 126.9 (CH), 112.9 (CH), 106.5 (CH), 103.5 (C), −2.5 (CH_3). Satisfactory elemental analysis was not obtained. The ${}^1H$ NMR spectrum is provided in the Supporting Information (Figure S4) as evidence of substantial purity.

Synthesis of $(EtMe_2SiC_5H_4)CpZrCl_2$ (5). A mixture of $EtMe_2SiC_5H_4Li$ (**1**, 0.414 g, 2.60 mmol), $CpZrCl_3(DME)$ (0.881 g, 2.50 mmol), and toluene (50 mL) was stirred at 25 °C for 12 h and then filtered. The filtrate was evaporated, and the residue was recrystallized from hexanes/toluene to obtain 0.710 (1.89 mmol, 76%) of white crystals. ${}^1H$ NMR (CD_2Cl_2): δ 6.71 (m, 2 H), 6.56 (m, 2 H), 6.46 (s, 5 H), 0.92 (t, $J = 7.9$ Hz, 2 H), 0.70 (q, $J = 7.9$ Hz, 3 H), 0.28 (s, 6 H). ${}^{13}C$ NMR (CD_2Cl_2): δ 126.1 (C), 125.7 (CH), 117.6 (CH), 116.3 (CH), 8.7 (CH_3), 7.38 (CH_2), −2.74 (CH_3). Anal. Calcd for $C_{14}H_{20}Cl_2SiZr$: C, 44.42; H, 5.33. Found: C, 44.76; H, 5.58.

Synthesis of $({}^tBuMe_2SiC_5H_4)CpZrCl_2$ (10). A mixture of ${}^tBuMe_2SiCpLi$ (**2**, 651 mg, 3.50 mmol), $CpZrCl_3(DME)$ (1.20 g, 3.40 mmol), and toluene (50 mL) was stirred at 25 °C for 6 h, and then the solvent was evaporated. The residue was

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recrystallized from hexanes/toluene to obtain 1.03 g (2.53 mmol, 74%) of colorless crystals in two crops. ^{1}H NMR ($CDCl_3$): δ 6.70 (m, 2 H), 6.57 (m, 2 H), 6.46 (s, 5 H), 0.79 (s, 9 H), 0.34 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 125.2 (CH), 124.3 (C), 117.2 (CH), 116.0 (CH), 26.3 (CH_3), 17.4 (C), −5.9 (CH_3). Anal. Calcd for $C_{16}H_{24}Cl_2SiZr$: C, 47.27; H, 5.95. Found: C, 46.98; H, 5.85.

Synthesis of (^{t}BuMe$_2$SiC$_5$H$_4$)$_2$ZrCl$_2$ (7). A mixture of ^{t}BuMe$_2$SiCpLi (**2**, 0.781 g, 4.20 mmol) and $ZrCl_4(THF)_2$ (792 mg, 2.1 mmol) in THF (50 mL) was stirred for 12 h at 25 °C. After evaporating the solvent, the residue was recrystallized from hexanes/toluene to afford 0.870 g (1.67 mmol, 80%) of off-white crystals in two crops. ^{1}H NMR ($CDCl_3$): δ 6.61 (m, 4 H), 6.47 (m, 4 H), 0.73 (s, 18 H), 0.29 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 125.8 (CH), 124.1 (C), 116.3 (CH), 26.3 (CH_3), 17.4 (C), −5.9 (CH_3). Anal. Calcd for $C_{22}H_{38}Cl_2Si_2Zr$: C, 50.73; H, 7.35. Found: C, 50.98; H, 7.25.

Synthesis of (PhMe$_2$SiCp)$_2$ZrCl$_2$ (8). A solution of $ZrCl_4(THF)_2$ (3.38 g, 9.0 mmol) and $PhMe_2SiC_5H_4Li$ (**3**, 3.71 g, 18.0 mmol) in THF (200 mL) was stirred at 25 °C for 15 min, and then the solvent was evaporated. The residue was recrystallized from hexane/toluene to afford 3.57 g (6.4 mmol, 71%) of white needles in two crops. ^{1}H NMR ($CDCl_3$): δ 7.48 (m, 4 H), 7.35 (m, 6 H), 6.55 (m, 4 H), 6.25 (m, 4 H), 0.57 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 138.0 (C), 134.0 (CH), 129.4 (CH), 127.9 (CH), 126.1 (CH), 123.8 (C), 117.1 (CH), −1.8 (CH_3). Anal. Calcd for $C_{26}H_{30}Cl_2Si_2Zr$: C, 55.68; H, 5.39. Found: C, 55.71; H, 5.50.

Synthesis of (Ph$_2$MeSiCp)$_2$ZrCl$_2$ (9). A suspension of $ZrCl_4(THF)_2$ (1.13 g, 3.0 mmol) and $Ph_2MeSiC_5H_4Li$ (**4**, 1.70 g, 6.4 mmol) in toluene (60 mL) was stirred under reflux for 3 h. The resulting orange mixture was filtered, and the filtrate was evaporated to afford an orange residue. Recrystallization from toluene afforded 1.22 g (1.8 mmol, 60%) of yellow crystals in three crops. ^{1}H NMR ($CDCl_3$): δ 7.37 (m, 20 H), 6.49 (m, 4 H), 6.05 (m, 4 H), 0.89 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 136.0 (C), 135.2 (CH), 129.8 (CH), 128.0 (CH), 125.8 (CH), 120.7 (C), 119.5 (CH), −3.5 (CH_3). Anal. Calcd for $C_{36}H_{34}Cl_2Si_2Zr$: C, 63.13; H, 5.00. Found: C, 63.45; H, 5.11.

Synthesis of (BrMe$_2$SiC$_5$H$_4$)CpZrBr$_2$ (11). A solution of $(Me_3SiC_5H_4)CpZrCl_2$ (**12**, 540 mg, 1.5 mmol) and BBr_3 (4.0 mL) in 1,2-dichloroethane (50 mL) was stirred under reflux in a sealed glass reaction vessel for 15 h. After cooling the reaction, the volatile components were evaporated, and the product was extracted with hot hexanes. Recrystallization from hexanes afforded 0.580 g (1.1 mmol, 75%) of **11** in two crops of pale green needles. ^{1}H NMR ($CDCl_3$): δ 6.90 (m, 2 H), 6.61 (m, 2 H), 6.57 (s, 5 H), 0.94 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 125.5 (CH), 121.0 (C), 116.8 (CH), 116.3 (CH), 4.3 (CH_3). Anal. Calcd for $C_{12}H_{15}Br_3SiZr$: C, 27.81; H, 2.92. Found: C, 28.03; H, 2.88.

Synthesis of (Me$_3$SiC$_5$H$_4$)CpZrCl$_2$ (12). A solution of $CpZrCl_3$ (1.3 g, 5.0 mmol) and $Me_3SiC_5H_4Li$ (0.73 g, 5.0 mmol) in THF (100 mL) was stirred at 25 °C for 2 h, and then the solvent was evaporated. The residue was extracted with toluene (50 mL), filtered, and evaporated. The crude product was recrystallized from hexanes (120 mL) to obtain 1.0 g (2.7 mmol, 55%) of colorless crystals. ^{1}H NMR ($CDCl_3$): δ 6.70 (m, 2 H), 6.52 (m, 2 H), 6.44 (s, 5 H), 0.23 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 126.4 (C), 125.3 (CH), 117.1 (CH), 115.9 (CH), −0.1 (CH_3). Anal. Calcd for $C_{13}H_{18}Cl_2SiZr$: C, 42.82; H, 4.94. Found: C, 42.45; H, 4.92.

Synthesis of (ClMe$_2$SiCp)$_2$ZrCl$_2$ (14). A solution of $(PhMe_2SiC_5H_4)_2ZrCl_2$ (**8**, 0.70 g, 1.2 mmol) and 50 mL of BCl_3 solution (1.0 M in CH_2Cl_2, 50 mmol) was stirred under reflux for 15 h and then evaporated. Recrystallization of the residue from hexanes afforded 0.43 g (0.90 mmol, 72%) of pink crystals in two crops. ^{1}H NMR ($CDCl_3$): δ 6.81 (m, 4 H), 6.60 (m, 4 H), 0.74 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 126.1 (CH), 122.3 (C), 116.5 (CH), 3.1 (CH_3). These spectra are consistent with those obtained by Royo and co-workers for the same compound prepared by a different method.[9] Anal. Calcd for $C_{14}H_{20}Cl_4Si_2Zr$: C, 35.21; H, 4.22. Found: C, 35.35; H, 4.23.

Synthesis of (Br$_2$MeSiC$_5$H$_4$)$_2$ZrBr$_2$ (15). A solution of $(Ph_2MeSiC_5H_4)_2ZrCl_2$ (**9**, 0.34 g, 0.50 mmol) and BBr_3 (2 mL) in 1,2-dichloroethane (10 mL) was stirred under reflux for 15 h and then evaporated. Recrystallization of the dark solid residue from hexanes/CH_2Cl_2 afforded 0.31 g (0.39 mmol, 79%) of yellow-green needles. ^{1}H NMR ($CDCl_3$): δ 7.07 (m, 4 H), 6.73 (m, 4 H), 1.46 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 126.7 (CH), 118.04 (CH), 118.00 (C), 10.2 (CH_3). Anal. Calcd for $C_{12}H_{14}Br_6Si_2Zr$: C, 18.36; H, 1.80. Found: C, 18.51; H, 1.65.

Reaction of (EtMe$_2$SiC$_5$H$_4$)CpZrCl$_2$ (5) with BBr$_3$. A solution of **5** (0.378 g, 1.00 mmol) and BBr_3 (2 mL) in 1,2-dichloroethane (15 mL) was stirred under reflux for 24 h. After evaporating the volatile components, the dark residue was extracted with 30 mL of hot hexanes, filtered, and evaporated to give 0.460 g (about 85%) of a silver-gray solid. ^{1}H NMR analysis showed two major products assigned to **10** and **11** in a ratio of 4:1. Data for **10**: ^{1}H NMR ($CDCl_3$): δ 6.93 (m, 1 H), 6.91 (m, 1 H), 6.71 (m, 1 H), 6.59 (s, 5 H), 6.54 (m, 1 H), 1.22 (m, 2 H), 1.08 (m, 3 H), 0.88 (s, 3 H). The assignment of **11** was corroborated by spectra obtained for the authentic sample prepared from $(Me_3SiC_5H_4)CpZrCl_2$ and BBr_3 (see above). Recrystallization of crude **10** did not lead to an improvement in its purity, so elemental analysis was not attempted.

Reaction of (^{t}BuMe$_2$SiC$_5$H$_4$)CpZrCl$_2$ (6) with BBr$_3$. A solution of **6** (0.905 g, 2.22 mmol) and BBr_3 (5 mL) in 1,2-dichloroethane (20 mL) was stirred under gentle reflux (about 85 °C) for 24 h. After evaporating the volatile components, the dark residue was extracted with 50 mL of hot hexanes, filtered, and evaporated to give 1.15 g (about 92%) of a gray solid. ^{1}H NMR analysis showed two major products assigned to **13** and **11** in a ratio of about 15:1. Data for **13**: ^{1}H NMR ($CDCl_3$): δ 7.11 (m, 1 H), 7.06 (m, 1 H), 6.86 (m, 1 H), 6.64 (s, 5 H), 6.33 (m, 1 H), 0.92 (s, 9 H), 0.84 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 128.6 (CH), 126.1 (CH), 121.7 (CH), 116.8 (CH), 114.0 (CH), 25.4 (CH_3), 20.5 (C), −1.4 (CH_3); *ipso* C of C_5H_4 group not observed. Recrystallization did not lead to improvement in the purity, so elemental analysis was not attempted.

Crystallographic Studies. Crystals of **9** were grown by preparing a concentrated solution in warm toluene and cooling to 25 °C. Crystals of **15** were obtained by adding dichloromethane in small portions to a warm suspension of **15** in hexanes until the complex dissolved and then allowing the resulting solution to cool to 25 °C. Crystallographic data are presented in Table 1. Complete data collection, solution, and refinement data as well as complete tables of metric parameters are included in the Supporting Information.

Results

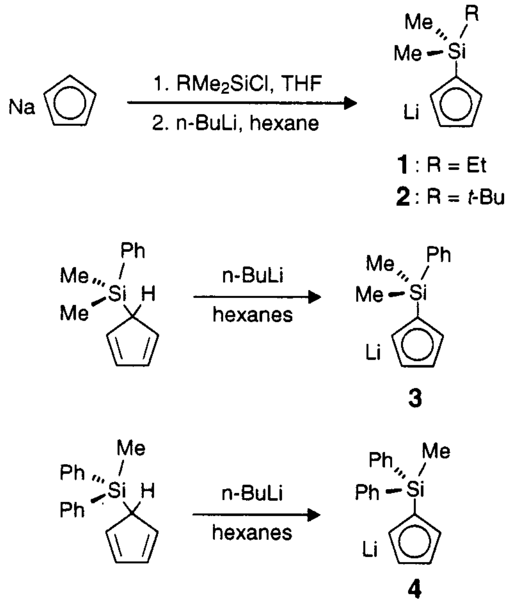
Substrate Syntheses. Ligands **1**−**4** needed for this study were prepared from NaCp and the corresponding chlorosilane reagents (Scheme 1) followed by metalation with ^{n}BuLi. These ligands are not presented here as fully characterized compounds, as satisfactory elemental analyses were not obtained. However, yields obtained in their preparation are presented in the Experimental Section, and NMR spectroscopic evidence for their bulk purity is provided in the Supporting Information to assist those who may wish to prepare these substances by our methods. Further reaction of the lithiated ligands (**1**−**4**) with $CpZrCl_3$, $CpZrCl_3(DME)$, or $ZrCl_4(THF)_2$, (Scheme 2) afforded the desired metallocene dihalide substrates (**5**−**9**) in moderate yields.

Si−R/B−Br Metathesis Selectivity Studies. In the reaction of the $EtMe_2Si$-substituted metallocene (**5**) with BBr_3 in refluxing 1,2-dichloroethane (Scheme 3), the crude product mixture showed a 4:1 mixture of **10** (Si−

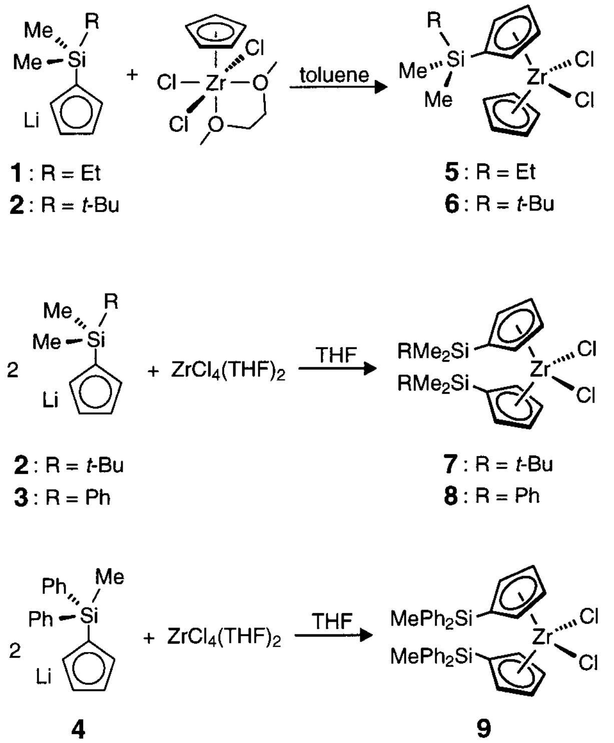
Table 1. Crystallographic Data

	9	15
empirical formula	$C_{36}H_{34}Cl_2Si_2Zr$	$C_{12}H_{14}Br_6Si_2Zr$
fw	684.93	785.03
diffractometer	Siemens P4	Enraf-Nonius Kappa CCD
cryst dimens (mm)	0.35 × 0.35 × 0.35	0.10 × 0.10 × 0.12
cryst syst	triclinic	triclinic
a (Å)	10.1109(14)	6.8170(2)
b (Å)	13.0604(18)	14.6660(4)
c (Å)	13.239(2)	22.1520(7)
α (deg)	80.538(12)	105.3520(15)
β (deg)	103.389(5)	91.5380(18)
γ (deg)	71.456(10)	90.4540(16)
V (Å)^3	1634.4(4)	2134.66(11)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	2	4
D_{calc} (Mg m^{-3})	1.392	2.443
abs coeff (mm^{-1})	0.60	11.8
F_{000}	704	1456
λ (Mo Kα) (Å)	0.71073	0.71073
temp (K)	293(2)	100(2)
θ range for collection	1.60−29.00	1.4−30.00
no. of reflns colld	9883	19 436
no. of indep reflns	8610	12 401
abs corr method	ψ scans	multiscan
no. of data/restrts/params	8610/0/506	12 401/0/383
R [$I > 2\sigma(I)$]	0.0373	0.0400
R_w [$I > 2\sigma(I)$]	0.0785	0.0780
GoF on F^2	0.86	0.85
largest diff peak and hole (e Å^{-3})	0.292, −0.407	1.92, −0.91

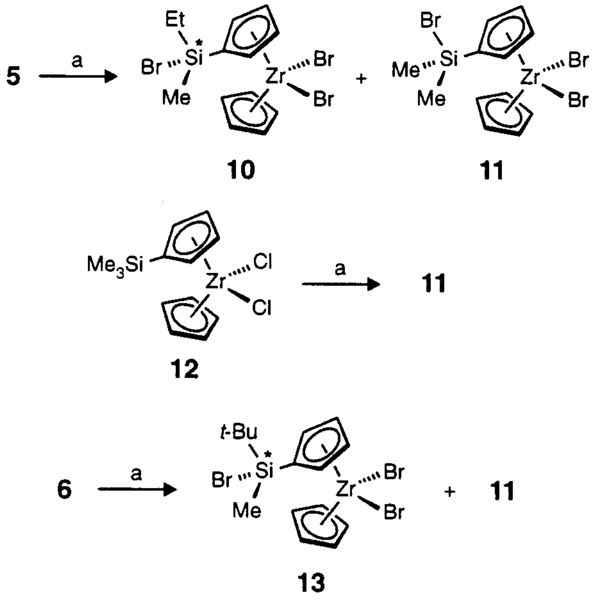
Scheme 1



Scheme 2



Scheme 3



a) BBr_3, $ClCH_2CH_2Cl$, reflux, 12-24 h

Me bond cleavage) and **11** (Si-Et bond cleavage). The product mixture was not significantly enriched in either component upon recrystallization from hexanes/toluene, which prevented us from isolating **10** as a pure substance. Assignment of the products was carried out by ^1H NMR spectroscopic of the product mixtures. The minor product (**11**) retains the C_s symmetry of its precursor (**5**), so only two resonances were observed for $BrMe_2Si$-substituted Cp ligand. The assignment of **11** was confirmed by comparison with an authentic sample prepared from **12** (Scheme 3). The major product (**10**) has C_1 symmetry (stereogenic Si), and all four protons of the EtMeBrSi-substituted Cp ligand are diastereotopic.

The reaction of the ^{t}BuMe_2Si-substituted metallocene (**6**) with BBr_3 in refluxing 1,2-dichloroethane (Scheme 3) was much more selective. The crude product contained a 15:1 mixture of **13** (Si−Me bond cleavage) and **11** (Si−^{t}Bu bond cleavage), according to ^1H NMR spectroscopic analysis. Despite the small amount of **11** present, recrystallization of the crude product did not lead to significantly higher purity of **13**. The ^1H NMR spectrum of **13** showed the expected four signals for the diastereotopic protons of the substituted Cp ligand. With either the $EtMe_2Si$-substituted or ^{t}BuMe_2Si-substituted metallocenes (**5** and **6**), a second bromodealkylation did *not* occur, even after long reaction times, in accord with our previous studies of Me_3Si-substituted group 4 metallocene complexes.[8]

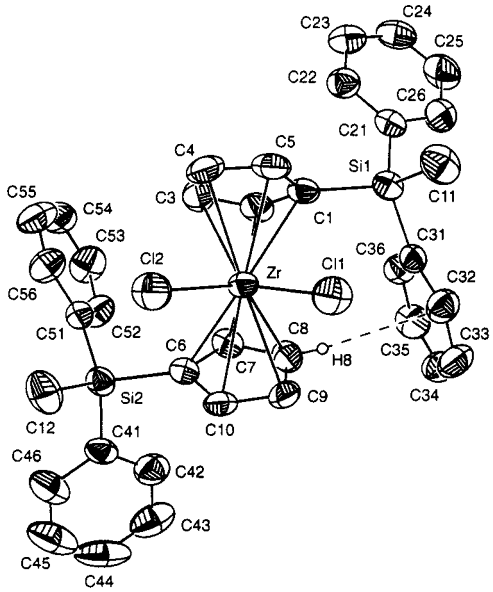
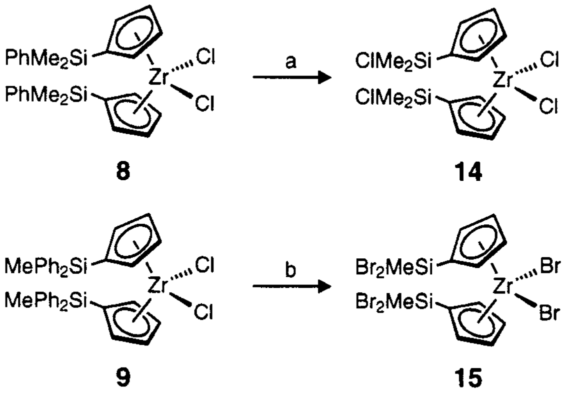


Figure 1. Thermal ellipsoid plot of the molecular structure of **9** shown at 50% probability. Hydrogen atoms (except H8) are omitted for clarity. The dashed line is drawn from H(8) to the C(31)−C(36) ring centroid to indicate a "hydrogen bonding" interaction.

Scheme 4



a) BCl_3, CH_2Cl_2, reflux, 15 h

b) BBr_3, $ClCH_2CH_2Cl$, reflux, 15 h

Si−Ph/B−X Metathesis Studies. When the bis(phenyldimethylsilyl)-substituted zirconocene dichloride (**8**) reacted with excess BCl_3 in refluxing dichloromethane, rapid conversion to bis(chlorodimethylsilyl)zirconocene dichloride (**14**) was observed (Scheme 4). When the corresponding bis(methyldiphenylsilyl)-substituted complex (**9**) was treated with excess BCl_3 under similar conditions, a complex mixture of products was observed, suggesting that some cleavage of a second phenyl group occurred. Treatment of **9** with an excess of the more reactive BBr_3 in refluxing 1,2-dichloroethane afforded the desired 1,1′-bis(methyldibromosilyl)zirconocene dibromide (**15**) in 79% yield.

Structural Results. Crystalline 1,1′-bis(methyldiphenylsilyl)zirconocene dichloride (**9**) was analyzed by X-ray diffraction. A thermal ellipsoid plot of the molecular structure is presented in Figure 1, and selected metric parameters are presented in Table 2. The complex adopts an approximately C_2-symmetric conformation, presumably to avoid intramolecular repulsions of the bulky substituents. Both Ph_2MeSi substituents are oriented so that the methyl groups are directed into the $ZrBr_2$ hemisphere, with C(5)−C(1)−Si(1)−C(11) and C(10)−C(6)−Si(2)−C(12) torsion angles of 17.1° and 42.7°, respectively. Crude semiempirical (PM3) modeling of **9** using Spartan Pro software (Wavefunction, Inc.) suggests that the preferences for particular Cp−Si conformations are relatively weak. Local conformational energy minima with either CH_3 or Ph directed toward the dichloride "wedge" region were found to be within 1 kcal mol^{-1} of one another. A noteworthy feature of the structure of **9** is the presence of an edge-to-face Cp-to-phenyl "hydrogen bonding" contact (presented as a dashed line in Figure 1). The nearly identical H-to-centroid (2.613 Å) and H-to-least-squares-plane (2.602 Å) distances show that the hydrogen atom (H8) is well-centered on the face of the C31−C36 ring.

Table 2. Metric Parameters for Crystalline 9

Bond Distances (Å)			
Cp(1)[a]−Zr	2.210(2)	Si(1)−C(21)	1.881(3)
Cp(2)[b]−Zr	2.224(2)	Si(1)−C(31)	1.872(2)
Zr−Cl(1)	2.4253(9)	Si(2)−C(6)	1.876(2)
Zr−Cl(2)	2.4337(8)	Si(2)−C(12)	1.858(4)
Si(1)−C(1)	1.880(2)	Si(2)−C(41)	1.873(3)
Si(1)−C(11)	1.849(4)	Si(2)−C(51)	1.869(2)
Bond Angles (deg)			
Cp(1)[a]−Zr−Cp(2)[b]	130.2(2)	C(21)−Si(1)−C(31)	109.1(1)
Cl(1)−Zr−Cl(2)	95.90(3)	C(6)−Si(2)−C(12)	113.5(2)
C(1)−Si(1)−C(11)	111.3(1)	C(6)−Si(2)−C(41)	104.1(1)
C(1)−Si(1)−C(21)	104.5(1)	C(6)−Si(2)−C(51)	107.4(1)
C(1)−Si(1)−C(31)	110.0(2)	C(12)−Si(2)−C(41)	109.5(2)
C(11)−Si(1)−C(21)	110.8(2)	C(12)−Si(2)−C(51)	111.5(2)
C(11)−Si(1)−C(31)	110.9(2)	C(41)−Si(2)−C(51)	110.6(1)
Torsional Angles (deg)			
C(2)−C(1)−Si(1)−C(11)	177.5	C(7)−C(6)−Si(2)−C(12)	158.3

[a] Cp(1) is the centroid of C(1), C(2), C(3), C(4), and C(5). [b] Cp(2) is the centroid of C(6), C(7), C(8), C(9), and C(10).

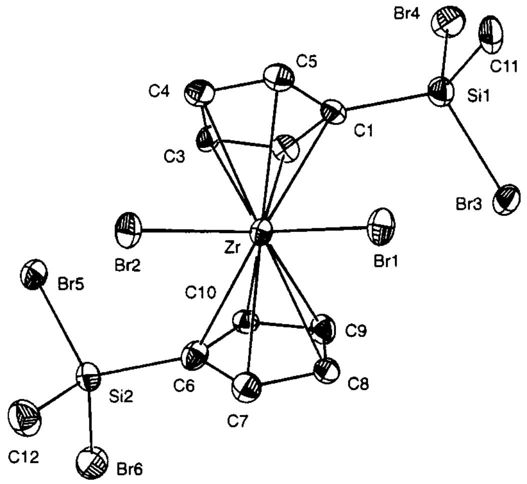


Figure 2. Thermal ellipsoid plot of the molecular structure of **15** (one of two nearly identical molecules in the asymmetric unit) shown at 50% probability. Hydrogen atoms are omitted for clarity.

A thermal ellipsoid plot of the molecular structure of **15** is shown in Figure 2, with accompanying metric data in Table 3. This complex also adopts an approximate C_2-symmetric conformation strikingly similar to that found in its immediate synthetic precursor (**9**), with C(5)−C(1)−Si(1)−C(11) and C(7)−C(6)−Si(2)−C(12) torsion angles of 11.5° and 19.2°, respectively. In the case

Table 3. Metric Parameters for Crystalline 15[a]

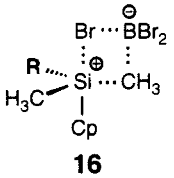
Bond Distances (Å)			
Cp(1)[b]−Zr	2.205(3)	Si(1)−Br(3)	2.218(2)
Cp(2)[c]−Zr	2.206(3)	Si(1)−Br(4)	2.223(2)
Zr−Br(1)	2.6018(8)	Si(2)−C(6)	1.841(6)
Zr−Br(2)	2.6013(8)	Si(2)−C(12)	1.823(6)
Si(1)−C(1)	1.841(6)	Si(2)−Br(5)	2.219(2)
Si(1)−C(11)	1.831(6)	Si(2)−Br(6)	2.231(2)
Bond Angles (deg)			
Cp(1)[b]−Zr−Cp(2)[c]	129.7(2)	Br(3)−Si(1)−Br(4)	105.2(6)
Br(1)−Zr−Br(2)	95.31(2)	C(6)−Si(2)−C(12)	116.4(3)
C(1)−Si(1)−C(11)	114.1(3)	C(6)−Si(2)−Br(5)	110.1(2)
C(1)−Si(1)−Br(3)	112.2(2)	C(6)−Si(2)−Br(6)	104.1(2)
C(1)−Si(1)−Br(4)	105.2(2)	C(12)−Si(2)−Br(5)	111.5(2)
C(11)−Si(1)−Br(3)	110.5(2)	C(12)−Si(2)−Br(6)	108.6(2)
C(11)−Si(1)−Br(4)	109.1(2)	Br(5)−Si(2)−Br(5)	105.2(6)
Torsional Angles (deg)			
C(2)−C(1)−Si(1)−C(11)	1.9(4)	C(7)−C(6)−Si(2)−C(12)	19.2(6)

[a] Data are shown for one of two nearly identical molecules in the asymmetric unit. [b] Cp(1) is the centroid of C(1), C(2), C(3), C(4), and C(5). [c] Cp(2) is the centroid of C(6), C(7), C(8), C(9), and C(10).

of **15**, however, one can rationalize the apparent preference for Cp−Si conformations; the electrostatic dipole of the $ZrBr_2$ group (negative end toward the viewer in Figure 2) opposes the dipoles of the $SiBr_2$ groups (negative end away from the viewer in Figure 2), minimizing the overall polarity of the complex. Examination of several packing diagrams revealed numerous weak Cp−H···Br−Zr and Cp−H···Br−Si contacts ranging in distance from 2.85 to 3.20 Å. These packing forces could also be responsible for the observed Cp−Si conformations. A PM3 modeling study provided no further insight into these Cp−Si conformations.

Discussion

Implications of Observed Exchange Selectivities. The presence of two methyl groups and one ethyl group in **5** favors Si−Me cleavage by a 2-fold statistical factor. The observed ratio of **10**:**11** (4:1) means that intrinsic structural features contribute an additional 2-fold factor to the overall observed selectivity. An electrophilic pathway proceeding via a transition state (or intermediate) in which silicon bears a partial positive charge (**16**) could rationalize this selectivity,[17] and the simplest argument is that the methylene carbon of the ethyl group is sterically more encumbered than the methyl carbons. The drawback of **16** as a proposed transition state is that one would not expect to observe Si−^{t}Bu cleavage products, because Si−^{t}Bu cleavage would require direct approach of the boron atom to the quaternary carbon atom. Yet, Si−^{t}Bu cleavage products account for about 7% of the isolated product mixture. In contrast, the Si−Ph bond was previously known to undergo rapid metathesis with B−X bonds to afford arylboron dihalides in high yields under relatively mild conditions.[18] The relative facility of Si−Ph cleavage in complexes **8** and **9** was expected to be much greater than Si−alkyl cleavage. This difference can be rationalized by using the phenyl substituent to accommodate most of the positive charge as in electrophilic aromatic substitution (**17**).



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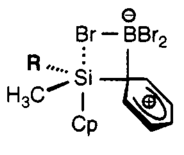
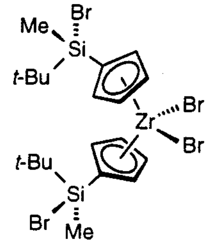


17



***rac*-18**

Context of These Studies. An alternative method has been developed by Royo and co-workers, in which $ClMe_2Si$ and Cl_2MeSi groups were attached to the ligand *prior* to metal complexation.[9,19]

Our Si−R and Si−Ph metathesis approaches introduce the reactive Si−X groups *after* the formation of the metallocene. The availability of these two complementary routes is advantageous to the synthetic chemist designing new metallocene complexes.

Conclusions

Although interesting from a mechanistic point of view, the selectivity observed for Si−Me vs Si−Et cleavage using BBr_3 does not appear to be useful synthetically. The higher selectivity of Si−Me vs Si−^{t}Bu cleavage may enable us to prepare metallocenes such as **18**, which should form both *rac* and *meso* diastereomers. Studies directed toward the preparation of **18** are underway. Phenylated silyl substituents ($PhMe_2Si$ and Ph_2MeSi) are readily introduced into cyclopentadienyl ligands, and these substituents are stable under the conditions required to prepare group 4 metallocenes. After the assembly of the metallocene, the phenyl groups can be easily cleaved using BCl_3 or BBr_3 to afford metallocene complexes having highly electrophilic $ClMe_2Si$ or Br_2MeSi substituents. We are presently exploring the reactivity of methyldibromosilyl-substituted metallocenes (**15**) toward nucleophiles and the immobilization of these functionalized metallocenes on inorganic supports.

Acknowledgment. We thank H.-Y. Kang for the syntheses of **11** and **12**. Funding was provided by the National Science Foundation (CHE-9875446) and Research Corporation (CS0567).

Supporting Information Available: Tables of crystallographic data for complexes **9** (Tables S1−S8) and **15** (Tables S9−S16). ^1H NMR spectra of **1**−**4** (Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Several different permutations of axial and equatorial ligands could be envisioned in the putative metathesis transition state. The permutation selected for diagram **20** was arbitrary, except that we assumed that either the entering halide or leaving hydrocarbyl group would be axial.

(18) 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.

(19) Royo, B.; Royo, P.; Cadenas, L. M. *J. Organomet. Chem.* **1998**, *551*, 293.