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Selective Tin−Carbon Bond Cleavage Reactions of Trimethylstannylzirconocene Dichloride with Electrophiles

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The reaction of 5,5-bis(trimethylstannyl)cyclopentadiene with $CpZrCl_3$ (Cp = η^5−C_5H_5) affords the monostannylated metallocene complex (η^5−$Me_3SnC_5H_4$)$CpZrCl_2$ (**1**), accompanied by variable amounts of (η^5−$ClMe_2SnC_5H_4$)$CpZrCl_2$ (**2**). The complex (**1**) reacts with BCl_3 or with ICl to afford **2** (Sn−CH_3 cleavage), but with HCl, Cp_2ZrCl_2 is obtained instead (Sn−Cp cleavage). Depending on the reaction conditions, treatment of either **1** or **2** with BBr_3 affords (η^5−$BrMe_2SnC_5H_4$)$CpZrBr_2$ (**3**) or (η^5−$Br_2MeSnC_5H_4$)$CpZrBr_2$ (**4**). The reaction of **1** with excess I_2 affords the iodostannylated complex (η^5−$IMe_2SnC_5H_4$)$CpZrCl_2$ (**5**). Two of the complexes (**2·2$C_6H_5CH_3$** and **4·THF**) are crystallographically characterized. The adduct **4·THF** has a distorted trigonal bipyramidal geometry about tin with a long O−Sn distance of 2.655 Å. We find overall that Me_3Sn substituents undergo electrophilic halodemethylation much more readily than corresponding Me_3Si substituents, whereas the reactivities of the halostannylated complexes toward nucleophiles such as airborne moisture are much lower than those of their halosilylated counterparts.

Introduction

Group 4 metallocenes are an established class of homogeneous catalysts for olefin polymerization.[2] During the past several years, numerous structure−reactivity investigations have yielded a better mechanistic understanding of metallocene-catalyzed processes as well as a wider range of practical applications. The growing availability of general synthetic routes to a wide variety of metallocene structures has facilitated these investigations.

We are exploring synthetic approaches to metallocene complexes bearing highly electrophilic substituents.[3,4] Such species are useful intermediates for the synthesis of *ansa*-metallocenes[3b−d,5,6] and as precursors to surface-immobilized metallocene catalysts.[7] In earlier reports, we showed that Me_3-Si-substituted group 4 metallocene dichlorides undergo selective, efficient conversion to the corresponding $BrMe_2Si$-substituted metallocene dibromides upon treatment with excess BBr_3.[5,6] We now report the results of several reactions of a Me_3Sn-substituted zirconocene dichloride (**1**) with electrophiles (BBr_3, BCl_3, I_2, ICl, and HCl), and we compare the reactivities of the Me_3Sn and Me_3Si substituents toward such electrophiles.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all procedures. Reaction glassware sealed with either Krytox[7] fluorinated lubricant or Kalrez[7] O-rings and flamed out under vacuum was used for reactions involving boron trihalides. BCl_3 (1.0 M solutions in hexanes or dichloromethane), BBr_3, and ICl were used as received from Aldrich. $CpZrCl_3$ was used as received from Strem Chemical Co. $CpZrCl_3C$·DME was prepared according to the procedure of Lund and Livinghouse.[8] 5,5-Bis(trimethylstannyl)cyclopentadiene was prepared by a published procedure,[9] and its purity (>98%) was confirmed by ^{1}H NMR analysis.[10] A JEOL Eclipse instrument (500 MHz for ^{1}H, 125 MHz for ^{13}C) was used for all NMR measurements. NMR-scale

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experiments were carried out in J-Young resealable tubes. Elemental analyses were performed by Desert Analytics (Tucson, AZ).

Synthesis of (η^5-$Me_3SnC_5H_4$)(η^5-C_5H_5)$ZrCl_2$ (1). A suspension of $CpZrCl_3$·DME (1.76 g, 5.0 mmol) and 5,5-$C_5H_4(SnMe_3)_2$ (1.96 g, 5.0 mmol) in 30 mL of toluene was stirred under reflux for 15 h. The resulting yellow solution was evaporated, and the yellow residue was recrystallized from hexane/tetrahydrofuran (THF) to obtain 1.13 g (2.5 mmol, 50%) of light golden plates in two crops. An otherwise identical procedure using $CpZrCl_3$ (1.31 g, 5.0 mmol) as the starting material afforded 1.77 g (3.9 mmol, 78%) of **1**. ^{1}H NMR ($CDCl_3$): δ 6.70 (m, 2 H, C_5H_4), 6.58 (m, 2 H, C_5H_4), 6.44 (s, 5 H, C_5H_5), 0.33 (s, 9 H, $SnMe_3$). ^{13}C NMR ($CDCl_3$): δ 127.1 (CH), 116.9 (CH), 116.1 (C), 115.8 (CH), −7.6 (CH_3). Anal. Calcd for $C_{13}H_{18}Cl_2SnZr$: C, 34.31; H, 3.99. Found: C, 34.52; H, 3.93.

Synthesis of (η^5-$ClMe_2SnC_5H_4$)(η^5-C_5H_5)$ZrCl_2$ (2). A solution of **1** (0.50 g, 1.1 mmol) and BCl_3 (10 mL, 1.0 M in CH_2Cl_2) in 15 mL of CH_2Cl_2 (including 10 mL of solvent from the BCl_3 solution) was stirred at 25 °C for 10 min. The volatile components were then evaporated. Recrystallization of the residue from hexane/toluene afforded 0.43 g (0.90 mmol, 82%) of silver-gray plates in two crops. ^{1}H NMR ($CDCl_3$): δ 6.73 (m, 2 H, C_5H_4), 6.63 (m, 2 H, C_5H_4), 6.49 (s, 5 H, C_5H_5), 0.95 (s, 6 H, $SnMe_2$). ^{13}C NMR ($CDCl_3$): δ 130.6 (C), 124.9 (CH), 116.4 (CH), 115.8 (CH), 0.5 (CH_3). Anal. Calcd for $C_{12}H_{15}Cl_3SnZr$: C, 30.31; H, 3.18. Found: C, 30.65; H, 3.04.

Synthesis of (η^5-$BrMe_2SnC_5H_4$)(η^5-C_5H_5)$ZrBr_2$ (3). A solution of **1** (0.50 g, 1.1 mmol) and BBr_3 (2 mL, 21 mmol) in 10 mL of CH_2Cl_2 was stirred at 25 °C for 10 min, and then the volatile components were evaporated. Recrystallization of the residue from hexane/toluene afforded 0.57 g (0.94 mmol, 85%) of light green-yellow plates in two crops. An otherwise identical procedure using **2** (0.30 g, 0.63 mmol) as the starting material afforded 0.31 g (0.51 mmol, 82%) of **3**. ^{1}H NMR ($CDCl_3$): δ 6.85 (m, 2 H, C_5H_4), 6.60 (m, 2 H, C_5H_4), 6.55 (s, 5 H, C_5H_5), 1.10 (s, 6 H, $SnMe_2$). ^{13}C NMR ($CDCl_3$): δ 129.0 (C), 125.5 (CH), 116.2 (CH), 115.3 (CH), 1.5 (CH_3). Anal. Calcd for $C_{12}H_{15}Br_3SnZr$: C, 23.67; H, 2.48. Found: C, 23.47; H, 2.40.

Synthesis of (η^5-$Br_2MeSnC_5H_4$)(η^5-C_5H_5)$ZrBr_2$ (4). A solution of **1** (0.30 g, 0.66 mmol) and BBr_3 (2 mL) in CH_2Cl_2 (10 mL) was stirred at 25 °C for 15 h. The volatile components were then evaporated. Recrystallization of the brown residue from hexane/toluene afforded 0.29 g (0.43 mmol, 66%) of green-yellow plates. An otherwise identical procedure using **2** (0.23 g, 0.47 mmol) as the starting material afforded 0.22 g (0.32 mmol, 68%) of **4**. ^{1}H NMR ($CDCl_3$): δ 7.01 (m, 2 H, C_5H_4), 6.64 (m, 2 H, C_5H_4), 6.61 (s, 5 H, C_5H_5), 1.70 (s, 3 H, $SnCH_3$). ^{13}C NMR ($CDCl_3$): δ 126.6 (CH), 125.7 (C), 116.5 (CH), 114.3 (CH), 12.0 (CH_3). Anal. Calcd for $C_{11}H_{12}Br_4SnZr$: C, 19.61; H, 1.80. Found: C, 19.80; H, 1.64.

Synthesis of (η^5-$IMe_2SnC_5H_4$)(η^5-C_5H_5)$ZrCl_2$ (5). A solution of **1** (0.30 g, 0.66 mmol) and I_2 (0.84 g, 3.3 mmol) in 10 mL of CH_2Cl_2 was stirred at 25 °C for 15 h. The volatile components were evaporated, including most of the excess iodine. Recrystallization of the residue from hexanes/toluene afforded dark red needles. Washing with hexanes and drying under vacuum afforded 0.18 g (0.32 mmol, 48%) of a pale yellow crystalline solid. ^{1}H NMR ($CDCl_3$): δ 6.72 (m, 2 H, C_5H_4), 6.61 (m, 2 H, C_5H_4), 6.49 (s, 5 H, C_5H_5), 1.17 (s, 6 H, $SnMe_2$). ^{13}C NMR ($CDCl_3$): δ 127.9 (C), 125.4 (CH), 116.3 (CH), 115.5 (CH), 0.8 (CH_3). Anal. Calcd for $C_{12}H_{15}Cl_2ISnZr$: C, 25.42; H, 2.67. Found: C, 25.71; H, 2.65.

NMR-Scale Reaction of 1 with BCl_3. A small amount of BCl_3 was vacuum-transferred from a 1.0 M hexanes solution (Aldrich) to a 10-mg sample of **1** in about 0.7 mL of $CDCl_3$ in a J-Young NMR tube. The NMR tube was then refilled with argon, sealed, and shaken vigorously to mix its contents. The ^{1}H NMR spectrum obtained after 20 min showed a new set of signals assigned to **2** at 7.01 (m, 2 H, C_5H_4), 6.64 (m, 2 H, C_5H_4), 6.61 (s, 5 H, C_5H_5), and 1.70 ppm (s, 6 H, $SnMe_2$). A signal arising from the byproduct $MeBCl_2$ was expected at 1.21 ppm, but instead we observed a broad signal at 1.02 ppm, which we have tentatively assigned to Me_2BCl.[11] Because the initial reaction was limiting in BCl_3, we surmise that the byproduct $MeBCl_2$ reacted further with **1** to afford Me_2BCl. Then, excess BCl_3 was condensed into the tube. After 10 min, all of the remaining substrate (**1**) had reacted to produce the product (**2**). A broad signal at 1.21 ppm (br s, 3 H, CH_3) was tentatively assigned to the byproduct $MeBCl_2$. No significant change was subsequently observed in the ^{1}H NMR spectrum after 1 week at 25 °C.

NMR-Scale Reaction of 1 with BBr_3. Under a nitrogen counterstream, about 0.1 mL of BBr_3 was transferred to a 10-mg sample of **1** dissolved in about 0.7 mL of $CDCl_3$ in a J-Young NMR tube. The tube was sealed and shaken vigorously to mix its contents. The ^{1}H NMR spectrum obtained after 10 min showed that all of the starting complex (**1**) had reacted, and a new complex (**3**) with signals at 6.85 (m, 2 H, C_5H_4), 6.60 (m, 2 H, C_5H_4), 6.55 (s, 5 H, C_5H_5), and 1.10 ppm (s, 6 H, $SnMe_2$) had appeared, along with a byproduct that we assigned to $MeBBr_2$ based on one broad signal at 1.42 ppm.[11] After 8 h, about three-fourths of the intermediate (**3**) was consumed, and new signals at 7.01 (m, 2 H, C_5H_4), 6.64 (m, 2 H, C_5H_4), 6.61 (s, 5 H, C_5H_5), and 1.70 ppm (s, 3 H, CH_3) were assigned to the methyldibromostannylated complex (**4**). Re-examination of the initial spectrum showed that this complex was already present in a small amount after only 10 min. After 15 h (total reaction time), nearly all of the remaining intermediate (**3**) had been replaced by **4**, with a concomitant increase in the intensity of the $MeBBr_2$ signal at 1.42 ppm. After 4 additional days, only **4** was observed.

NMR-Scale Reaction of 1 with I_2. Under a nitrogen counterstream, a small crystal of iodine was added to a 10-mg sample of **1** dissolved in about 0.7 mL of $CDCl_3$ in a J-Young NMR tube. The NMR tube was sealed and shaken vigorously to mix its contents. The ^{1}H NMR spectrum obtained after 10 min showed a partial conversion of **1** to a single product assigned to **5** with signals at 6.72 (m, 2 H, C_5H_4), 6.61 (m, 2 H, C_5H_4), 6.49 (s, 5 H, C_5H_5), and 1.17 ppm (s, 6 H, $SnMe_2$), along with a byproduct that we assigned to CH_3I based on a sharp signal at 2.16 ppm (s, 3 H, CH_3). The spectrum obtained after 1 day showed complete conversion of **1** to **5**, with a concomitant increase in the CH_3I signal.

NMR-Scale Reaction of 1 with ICl. In a nitrogen glovebox, 0.2 mL of a $CDCl_3$ solution containing excess ICl was added to a 10-mg sample of **1** dissolved in about 0.5 mL of $CDCl_3$ in a J-Young NMR tube. The tube was sealed and shaken vigorously to mix its contents. The ^{1}H NMR spectrum obtained after 10 min showed that approximately 80% of **1** had been converted to **2**. A strong signal arising from the byproduct CH_3I was also observed. Neither **5** nor CH_3Cl was detected.

NMR-Scale Reaction of 1 with $CpZrCl_3$. A J-Young NMR tube was charged with 4.6 mg (0.010 mmol) of **1** and 2.6 mg (0.010 mmol) of $CpZrCl_3$. Toluene (about 1 mL) was added, and the tube was sealed and placed into an oil bath maintained at 100 °C. After 15 h, the toluene was evaporated, and about 1 mL of $CDCl_3$ was condensed into the tube. According to ^{1}H NMR analysis, the resulting mixture contained **1**, **2**, and Cp_2ZrCl_2 in a ratio of approximately 3:1:5, respectively.

NMR-Scale Reaction of 1 with $ZrCl_4$. A J-Young NMR tube was charged with 4.6 mg (0.010 mmol) of **1** and 2.3 mg (0.010 mmol) of $ZrCl_4$. Toluene (about 1 mL) was added, and the tube was sealed and placed into an oil bath maintained at 100 °C. After 15 h, the toluene was evaporated, and about 1 mL of $CDCl_3$ was condensed into the tube. The resulting ^{1}H NMR spectrum revealed a complex mixture of unidentified products; however, neither the unreacted starting material (**1**) nor the chlorodemethylated complex (**2**) was observed.

Crystal Structures. Crystals of **2** were obtained by slow evaporation of a 2:1 hexanes/toluene solution under air in a refrigerator at 5 °C.

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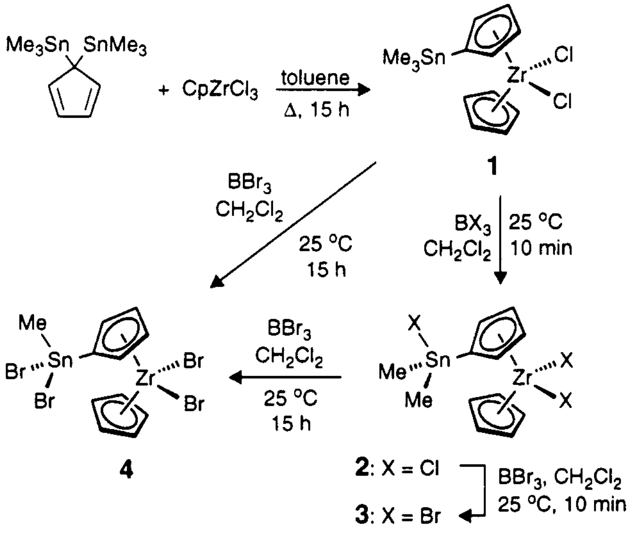
Table 1. Crystallographic Data

	$2 \cdot {}^1/_2$(toluene)	**4·THF**
chemical formula	$C_{12}H_{15}Cl_3SnZr \cdot 2C_7H_8$	$C_{11}H_{12}Br_4SnZr \cdot C_4H_8O$
a (Å)	21.6517(15)	20.6230(2)
b (Å)	12.8720(10)	8.3330(2)
c (Å)	14.1878(9)	11.9970(4)
β (deg)	103.389(5)	102.5120(10)
V (Å)^3	3846.7(5)	2012.74(9)
Z	8	4
formula weight	521.57	745.84
space group	$C2/c$	$P2_1/c$
T (K)	293(5)	100(2)
λ (Mo Kα) (Å)	0.71073	0.71073
ρ_{calc} (mg m^{-3})^a	1.801	2.461
μ (mm^{-1})	2.247	9.698
R^b	0.0384	0.0484
R_w [$I > 2\sigma(I)$]^c	0.0779	0.1189

[a] Experimental crystal densities (ρ_{obsd}) were not obtained. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, observed data ($>2\sigma(I_o)$). [c] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^2$, all data.

Scheme 1

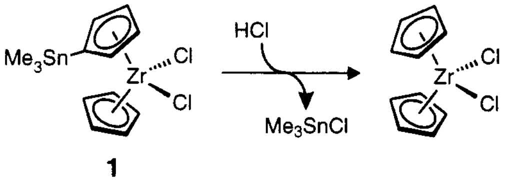


Crystals of **4** were grown from a 1:1 hexanes/THF solution by slow evaporation in a refrigerator at 5 °C under air. Details of the crystallographic experiments, data collection, and refinement are contained in Table 1. Complete tables of crystal data, positional and thermal parameters, bond distances, and bond angles are included in the Supporting Information.

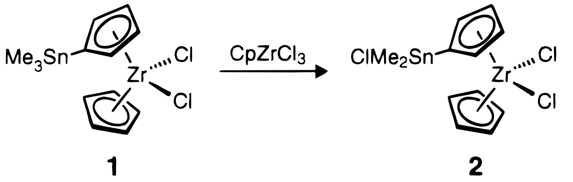
Results

Synthesis of Trimethylstannylzirconocene Dichloride. The usual anionic ligand-substitution routes to metallocene complexes such as **1** are closed, because trimethylstannylcyclopentadiene reacts with bases such as *n*-butyllithium or sodium hydride to afford products in which the Cp–Sn bond is cleaved.[12] Churakov and Kuz'mina prepared $(Me_3SnC_5H_4)TiCl_3$ using an alternative, the chlorotrimethylstannane-elimination reaction of $TiCl_4$ and $(Me_3Sn)_2C_5H_4$ at 25 °C.[13] We adopted this approach to prepare our desired substrate (**1**) from $(SnMe_3)_2C_5H_4$ and $CpZrCl_3$ (Scheme 1). However, neither $CpZrCl_3$ nor $CpZrCl_3 \cdot DME$ reacted with $(Me_3Sn)_2C_5H_4$ at 25 °C, possibly because of the lower reactivity of the zirconium half-metallocene complexes[14] or because neither is soluble in the reaction solvent (toluene). Extended reactions at 110 °C in toluene gave useful yields of **1**. The adduct $CpZrCl_3 \cdot DME$ reacts much more slowly than $CpZrCl_3$ with $(SnMe_3)_2C_5H_4$, probably because the DME ligand decreases the electrophilicity of the zirconium center. The complex (**1**) is ostensibly the first stannylated zirconocene dichloride complex.

Two byproducts, Cp_2ZrCl_2 and **2**, were observed in the reaction of $CpZrCl_3$ and $(SnMe_3)_2C_5H_4$. The amounts of these byproducts varied widely but were usually less than 10%, although in one reaction **2** was the *major* product. We suspected that Cp_2ZrCl_2 might arise from the reaction of $(Me_3SnC_5H_4)CpZrCl_2$ (**1**) with HCl, generated in situ via hydrolysis of $CpZrCl_3$ by adventitious moisture. This hypothesis was tested using an NMR-scale experiment in which purified **1** was treated directly with HCl to afford Cp_2ZrCl_2 and Me_3SnCl (eq 1) according to ^1H NMR analysis. Stannylated aromatic compounds often undergo electrophilic destannylation under similar conditions.[15] We suspected that **1** might undergo a Zr–Cl/Sn–Me metathesis reaction with $ZrCl_4$, a possible impurity in $CpZrCl_3$. A reaction of **1** with $ZrCl_4$ in an NMR tube revealed a complex mixture of several products, from which both the starting material (**1**) and the chlorodemethylated complex (**2**) were absent according to ^1H NMR analysis. We also carried out an NMR-tube reaction of purified **1** with 1 equiv of $CpZrCl_3$ (eq 2) and observed a significant amount of **2**. Thus, the formation of **2** during the reaction of $CpZrCl_3$ and $(SnMe_3)_2C_5H_4$ apparently results from a further reaction of the desired product (**1**) with unreacted $CpZrCl_3$.



(1)



(2)

Electrophilic Halogenation Reactions. As shown in Scheme 1, the stannylated substrate (**1**) underwent rapid chlorodemethylation with boron trichloride at 25 °C to afford the corresponding chlorodimethylstannylated complex (**2**) in 82% yield. When we followed the progress of this reaction in an NMR tube–scale reaction using excess BCl_3, the signals of **1** were absent after 10 min at 25 °C and were replaced by signals assigned to **2**. The product (**2**) complex can withstand exposure to air for several days with negligible decomposition.

We next explored the reactions of **1** and **2** with BBr_3 (Scheme 1). In NMR-scale reactions in $CDCl_3$ at 25 °C, excess BBr_3 converted both **1** and **2** to a common intermediate within 10 min. We assigned the observed spectrum to the tribrominated species (**3**). This interpretation means that both tin and zirconium undergo rapid transhalogenation. The propensity of the tin center toward exchange is consistent with the ease of chlorodemethylation of **1** using BCl_3 discussed above, and transhalogenation

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Scheme 2

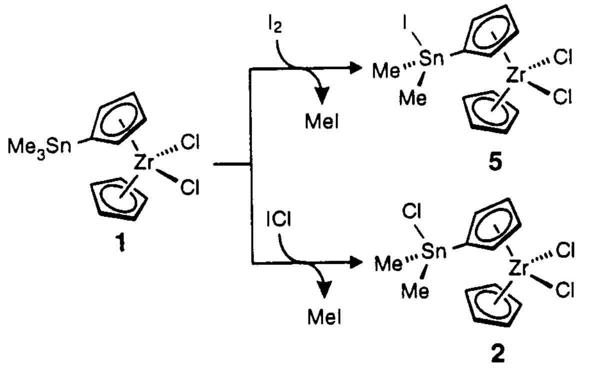

Table 2. $^2J_{SnH}$ and $^1J_{SnC}$ Coupling Constants for Alkylhalostannanes[a]

		^2J (Hz)		^1J (Hz)	
entry	complex	^{119}Sn−^{1}H	^{117}Sn−^{1}H	^{119}Sn−^{13}C	^{117}Sn−^{13}C
1	**1**	57.5	54.8	374	358
2	**2**	67.4	64.6	471	451
3	**3**	66.9	63.7	459	439
4	**4**	84.8	81.1	584	558
5	**5**	65.6	62.8	435	415
6	Me_4Sn	54.3[b]	52.0[b]	338[c,d]	323[c,d]
7	Me_3SnCl	58.5[b]	56.0[b]	379[c]	365[c]
8	Me_3SnBr	58.5[b]	56.0[b]	365[c]	349[c]
9	Me_2SnBr_2	66.0[b]	63.5[b]	460[e]	420[e]
10	$MeSnBr_3$	89.0[b]	85.0[b]	*f*	*f*

[a] Data for **1**−**5** were determined from spectral satellite positions. [b] Data obtained in $CDCl_3$ solution (ref 17). [c] Data obtained in $CDCl_3$ solution (ref 18). [d] Data reported only for ^{119}Sn. Estimated from $J(^{117}Sn-^{13}C) = J(^{119}Sn-^{13}C)\delta(^{117}Sn)/\delta(^{119}Sn)$. [e] Estimated from a single, averaged coupling constant ($J = 440$ Hz) obtained in CH_2Cl_2 (ref 19). [f] No reported values found.

of the $ZrCl_2$ moiety is also already known to be rapid under these conditions.[16] The signals assigned to **3** subsequently disappeared over about 15 h at 25 °C and were replaced by an additional set of signals assigned to the methyldibromostannylated complex (**4**). By control of reaction times, preparative reactions of **1** with BBr_3 afforded either **3** (85% yield) or **4** (68% yield). A reaction of the substrate (**1**) with BBr_3 in chlorobenzene at 140 °C for 15 h failed to produce any of the anticipated Br_3Sn-substituted complex, as determined by ^{1}H NMR analysis. Like the chlorodimethylstannylated complex (**2**), complexes **3** and **4** withstand exposure to air for several days without significant decomposition or hydrolysis.

We next investigated two iodinolysis reactions (Scheme 2). In an NMR-scale reaction of **1** and excess I_2 ($CDCl_3$ solvent), the signals assigned to **1** disappeared over about 1 day, whereas new signals assigned to **5** and to the byproduct CH_3I were observed. When the reaction was carried out on a preparative scale in CH_2Cl_2, a 48% yield of **5** was obtained. The reaction of **1** with ICl was more rapid, proceeding quantitatively to **2** and CH_3I after 10 min, according to ^{1}H NMR analysis of a reaction carried out in an NMR tube in $CDCl_3$ solution. Because this reaction did not afford different metallocene products, we did not investigate it further on a preparative scale.

NMR Studies. The Sn−CH_3 groups of the starting complex (**1**) and the products (**2**, **3**, **4**, and **5**) showed clear tin satellites in both the ^{1}H and ^{13}C NMR spectra. Table 2 compares these data with similar compounds reported elsewhere.[17−19] Comparison of entries 2, 3, and 5 and comparison of entries 7 and 8 suggest that $2J_{SnH}$ is relatively insensitive to the identity of the halide, although a periodic trend toward decreasing $^1J_{SnC}$ with the heavier halides is observed. Pairwise comparisons of entries 1 and 8, 3 and 9, and 4 and 10 suggest that the zirconocene dihalide moiety has an electronic effect similar to that of bromide on the tin atom.

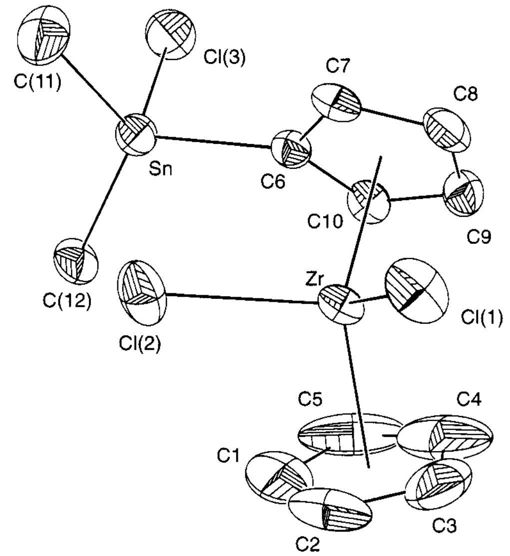

Figure 1. Thermal ellipsoid plot of **2** shown at 50% probability. Hydrogen atoms and disordered toluene solvent molecule omitted. Selected bond distances (Å) and angles (deg): Zr−Cl(1), 2.442(1); Zr−Cl(2), 2.470(1); Zr−Cp(1), 2.193(6); Zr−Cp(2), 2.193(6); Cl(1)−Zr−Cl(2), 95.3(4); Cp(1)−Zr−Cp(2), 129.6(4); Sn−Cl(3), 2.401(2); Sn−C(6), 2.135(4); Sn−C(11), 2.115(5); Sn−C(12), 2.105(4); Cl(3)−Sn−C(6), 97.8(1); Cl(3)−Sn−C(11), 103.8(2); Cl(3)−Sn−C(12), 103.5(2); C(6)−Sn−C(11), 110.5(2); C(6)−Sn−C(12), 116.0(2); C(11)−Sn−C(12), 121.2(2); Cl(3)−Sn−C(6)−C(7), 110.1(3) (torsion). Cp(1) is the centroid of C(1), C(2), C(3), C(4), and C(5). Cp(2) is the centroid of C(6), C(7), C(8), C(9), and C(10).

Crystal Structures of 2 and 4. Crystal data for **2** are presented in Table 1. The unit cell contains a planar region of electron density that presumably resulted from a badly disordered toluene molecule and was modeled accordingly. Relatively precise metric parameters were obtained nevertheless. Although the structure of **2** (Figure 1) is not remarkable, inasmuch as **2** is the first structurally characterized stannylated zirconocene dichloride complex, we wish to comment on the major features of its structure. In an analogous complex, $(Me_3SiC_5H_4)_2ZrCl_2$,[20] the Cp−Zr distances were 2.199 and 2.209 Å, the Cp−Cl distances were 2.476 and 2.505 Å, the Cp−Zr−Cl angle was 129.1°, and the Cl−Zr−Cl angle was 93.7°. Data presented in Figure 1 for the metallocene "core" of **2** are nearly identical. The Cp(ipso carbon)−Sn distance of **2** was 2.135(4) Å, which is somewhat shorter than the corresponding distance of 2.169 Å observed in $(Me_3SnC_5H_4)TiCl_3$.[13] The distorted tetrahedral structure about Sn in **2** is typical of tetrahedral Sn compounds having one chloride and three hydrocarbyl ligands. Of 41 such Sn atoms in the Cambridge Crystallographic Database, the median Cl−Sn−C angle was 101° (range, 91−108°), whereas the median C−Sn−C angle was 116° (range, 104−128°).

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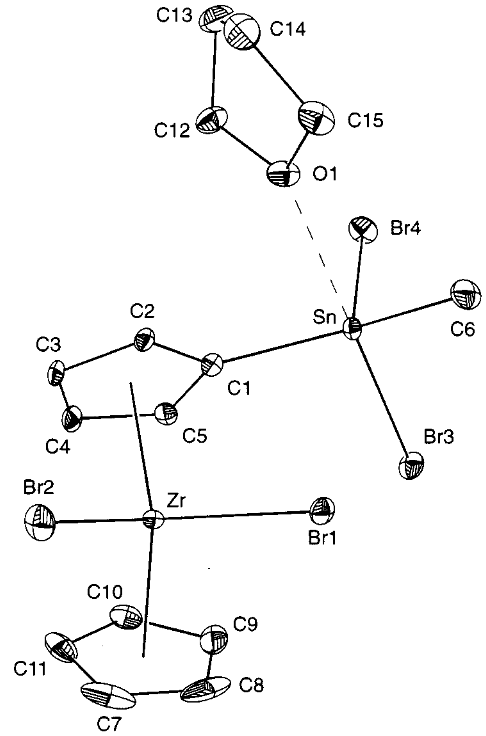

Figure 2. Thermal ellipsoid plot of **4·THF** shown at 50% probability. Hydrogen atoms omitted. Selected bond distances (Å) and angles (deg): Zr−Br(1), 2.6178(5); Zr−Br(2), 2.6001(5); Zr−Cp(1), 2.208(4); Zr−Cp(2), 2.197(4); Br(1)−Zr−Br(2), 95.23(2); Cp(1)−Zr−Cp(2), 128.7(1); Sn−Br(3), 2.5534(5); Sn−Br(4), 2.5139(5); Sn−C(1), 2.113(4); Sn−C(6), 2.111(5); Sn−O(1), 2.655(5); Br(3)−Sn−Br(4), 95.77(2); Br(3)−Sn−C(1), 100.1(1); Br(3)−Sn−C(1), 102.1(2); Br(3)−Sn−O(1), 178.5(2); Br(4)−Sn−C(1), 106.0(1); Br(4)−Sn−C(6), 108.0(1); Br(4)−Sn−O(1), 83.1(2); C(1)−Sn−C(6), 136.9(2); C(1)−Sn−O(1), 79.4(2); C(6)−Sn−O(1), 79.3(2); Br(3)−Sn−C(1)−C(2), −148.0(3) (torsion). Cp(1) is the centroid of C(1), C(2), C(3), C(4), and C(5). Cp(2) is the centroid of C(7), C(8), C(9), C(10), and C(11).

Crystal data for **4·THF** are presented in Table 1. The lattice THF molecule is associated with the tin atom (Figure 2), such that the coordination environment about Sn is pseudo-trigonal-bipyramidal (tbp), with the THF oxygen and one bromide ligand in pseudoaxial positions and the Cp, methyl, and second bromide ligands in the pseudoequatorial plane. The distortion from ideal tbp geometry is evident in the displacement of the Sn from the equatorial plane by 0.37 Å away from the weakly bound, neutral oxygen ligand. The rest of the metallocene "core" exhibits bonding geometries that are completely consistent with other unbridged zirconocene dibromide complexes that have been crystallographically characterized.[20−22]

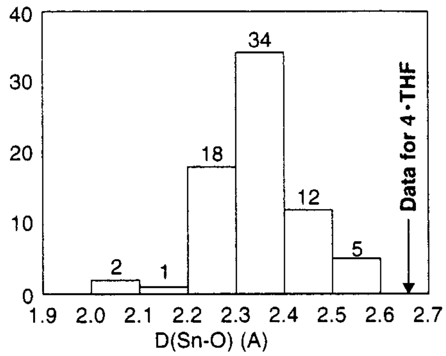

Figure 3. Histogram plot of Sn−O distances (<2.7 Å) for trigonal bipyramidal complexes having the general formula $SnO(CH_3)_nX_{4-n}$, $n = 1-3$, X = Cl, Br, or I. Data obtained from the Cambridge Crystallographic Data Centre.

The Sn−O distance in **4·THF** is rather long in comparison to those observed in analogous structures selected from the Cambridge Structural Database (CSD), such as $ArCl_3Sn{\cdot}THF$ (2.357 Å),[23] $ArCl_2MeSn{\cdot}DMSO$ (2.294 Å),[24] and $Br_3MeSn{\cdot}DMF$ (2.269 Å).[25] We searched the Cambridge Structural Database for tin atoms ligated by 1−3 halogens, 1−3 hydrocarbyl groups, and exactly one oxygen. Compounds in which either the tin or oxygen atoms were bridging or in which the Sn−O bond was part of a ring were excluded. A histogram plot (Figure 3) for the resulting 72 structures shows the typical range of Sn−O distances, and in this context, the Sn−O distance in **4·THF** is indeed long.

Discussion

General Comparisons of Tin and Silicon. Although tin and silicon are formally valence-isoelectronic, many differences are exhibited in the structure and reactivity of their respective compounds. Tin has a larger sp^3 covalent radius (1.40 Å) than silicon (1.18 Å).[26] The radial distributions of the Sn(5s) and Sn(5p) orbitals are more diffuse than those of the Si(3s) and Si(3p) orbitals, as reflected in the following: the lower first ionization energy of Sn (708.2 kJ/mol) versus that of Si (786.3 kJ/mol), the higher polarizability of Sn (7.7 ± 25%) compared to that of Si (5.38 ± 2%),[27] lower homogeneous dissociation energies of Sn−C bonds (69.3 kcal/mol for $(CH_3)_3Sn-CH_3$) compared to those of Si−C bonds (89.8 kcal/mol for $(CH_3)_3Si-CH_3$),[28] and the lower first ionization potential of $Sn(CH_3)_4$ (9.65 eV) versus that of $Si(CH_3)_4$ (10.23 eV).[29]

Reactivity of Si−Me versus Sn−Me Bonds toward Electrophiles. The differences noted above are borne out in the increased susceptibility of $Sn-CH_3$ bonds toward Lewis acidic cleavage relative to $Si-CH_3$ bonds[30] and are demonstrated strikingly in the reactivities of the trimethylstannylated complex (**1**) compared to those of trimethylsilylated analogues. Only about 30% of one $SiMe_3$ group on $(Me_3SiCp)_2ZrCl_2$ was converted into a chlorodimethylsilyl group ($SiMe_2Cl$) upon reaction with BCl_3 at 100 °C for 2 days,[6] whereas the conversion of the single $SnMe_3$ group of **1** to a $SnMe_2Cl$ group was completed in a few minutes at 25 °C upon treatment with BCl_3. Despite the apparently high reactivity of the Me−Sn bonds, the $SnMe_2Cl$ substituent did not undergo further substitution at 25 °C. However, as BBr_3 is a stronger Lewis acid than BCl_3,[31] it was reasonable (in hindsight) to discover that BBr_3 could react

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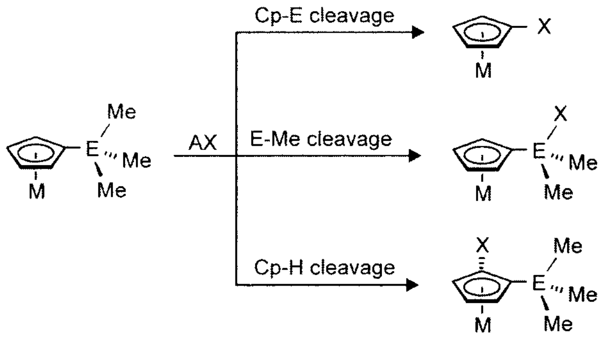
Scheme 3



further to form the $MeBr_2Sn$-substituted zirconocene complex (**4**). In contrast, only one methyl group of the $SiMe_3$ substituent of $(Me_3SiC_5H_4)(Cp)ZrCl_2$ was replaced by bromine upon reaction with BBr_3 at 65 °C for 2 days.[5,6]

Reactivity of Si−X versus Sn−X bonds toward Nucleophiles. An interesting trend in the nucleophilic susceptibility of E−X bonds (E = Si, Sn and X = Cl, Br, I) is also demonstrated here. Whereas **2** is stable to air (ambient moisture) for several days, complexes bearing $BrMe_2Si$ groups undergo rapid hydrolysis in air to afford tetramethyldisiloxane linkages,[3b−d] presumably via hydrolysis of the Si−Br bonds to form an intermediate disilanol, which undergoes subsequent condensation (discharged water is observed).[6] Although tin halides are susceptible to hydrolysis, the complexes reported here (**2**, **3**, **4**, and **5**) appear unusually unreactive in this respect. However, the propensity for tin halides to form adducts with nucleophiles is clearly demonstrated in the observed formation of a crystalline THF adduct of **4**, which retained the coordinated solvent for more than a day in the absence of mother liquors prior to crystallographic analysis.

Reactivity of Cp−E versus E−Me Bonds toward Electrophiles. Periodic trends are emerging in the relative reactivities (Scheme 3) of the Cp−E and E−Me bonds as a function of the coordinated transition metal (M), the group 14 element (E), and the reacting electrophile (AX). We showed earlier that Me_3Si-substituted ferrocenes undergo rapid cleavage of the Cp−Si bond upon treatment with BCl_3 at low temperature,[6] whereas with Me_3Si-substituted zirconocene dichlorides, the Me−Si bonds are cleaved instead.[6] Manners and co-workers showed that Me_3-Sn-substituted ferrocenes are preferentially ortho-borylated by chloroboranes.[32] Corresponding Me_3Si- and Me_3Sn-substituted aromatic hydrocarbons undergo rapid Ar−Si and Ar−Sn cleavage toward electrophiles such as BCl_3.[33] I_2 and ICl also cleave the Sn−Ar bonds of stannylated aromatic complexes to produce iodoarenes.[34] In the present study, only HCl cleaves the Cp−Sn bond, whereas all the other electrophilic reagents (BCl_3, BBr_3, I_2, and ICl) cleave the Sn−Me bond of the stannylated zirconocene dichloride complex. At first glance, it appears that the electron-rich ferrocenes favor ring-substitution processes, possibly by d-electron stabilization of a putative Meisenheimer-type intermediate, whereas the group 4 systems, which have no d-electrons, forbid Cp−E cleavage and allow the slower E−Me cleavage process to be observed by default. However, preliminary observations in a separate, ongoing study have suggested that Me_3Si-substituted cobaltocenium hexafluorophosphates, which are isoelectronic with the ferrocenes, undergo neither Cp−Si nor Si−Me cleavage when treated with BBr_3, even at 80 °C for several hours in $CDCl_3$.

Conclusions

The reactivity of a $SnMe_3$ substituent on zirconocene dichloride toward Lewis acidic halodemethylation using BCl_3 or BBr_3 is much greater than the corresponding reactivity of the $SiMe_3$ substituent. The $SnMe_3$ group also undergoes selective iodinolysis of a single $Sn−CH_3$ bond. The resulting $ClSnMe_2$-, $BrSnMe_2$-, $ISnMe_2$-, and $MeBr_2Sn$-substituted complexes are, in contrast, surprisingly stable toward ambient moisture, considering the facility of hydrolysis demonstrated previously for $BrMe_2Si$-substituted complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $\mathbf{2 \cdot 2C_6H_5CH_3}$ and $\mathbf{4 \cdot THF}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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