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Synthesis, structure and properties of the $Cp_2Zr\{CH(SiMe_3)_2\}^+$ cation

Edward J. Stoebenau III, Richard F. Jordan *

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, IL 60637, United States

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Abstract

The generation and properties of the $Cp_2Zr\{CH(SiMe_3)_2\}^+$ cation are described. An X-ray crystallographic analysis shows that the carborane salt $[Cp_2Zr\{CH(SiMe_3)_2\}][HCB_{11}Me_5Br_6]$ contains an agostic Zr–μ-Me–Si interaction in the solid state. Low temperature NMR spectra of the borate salt $[Cp_2Zr\{CH(SiMe_3)_2\}][B(C_6F_5)_4]$ show that this interaction is retained in solution. Variable temperature NMR spectra establish that the $SiMe_2$(μ-Me) and unbound $SiMe_3$ units of $Cp_2Zr\{CH(SiMe_3)_2\}^+$ exchange by a "pivot" process involving partial rotation around the Zr–$CH(SiMe_3)_2$ bond, with a barrier of $\Delta G^{\ddagger} = 9.2(1)$ kcal/mol at −89 °C. $Cp_2Zr\{CH(SiMe_3)_2\}^+$ does not coordinate alkenes or alkynes.

Keywords: Zirconium; Bis(trimethylsilyl)methyl; Carborane; Dynamic NMR; Crystal structure

1. Introduction

The bis(trimethylsilyl)methyl ligand (–$CH(SiMe_3)_2$) [1] has been used extensively in early transition metal [2] and lanthanide chemistry [3]. Two key features of this ligand are the large cone angle, which facilitates the generation of coordinatively unsaturated species, and the presence of the $SiMe_3$ groups, which stabilize electron-deficient metal centers through α- and β-Si effects [4]. In early work, Lappert exploited these properties to generate neutral zirconium alkyl complexes such as $Cp_2Zr\{CH(SiMe_3)_2\}Me$ (**1**) [5].

Marks synthesized a cationic zirconocene bis(trimethylsilyl)methyl complex, $[Cp''_2Zr\{CH(SiMe_3)_2\}][MeB(C_6F_5)_3]$ (**2**; $Cp'' = 1,2\text{-}Me_2C_5H_3$) [6]. NMR data show that **2** contains a Zr–μ-Me–Si interaction and is only weakly ion-paired in toluene-d_8, CD_2Cl_2, or $CFCl_2D$ solution. The ambient temperature NMR spectra of **2** are consistent with the occurrence of two dynamic processes: a "pivot" of the $CH(SiMe_3)_2$ ligand (i.e. partial rotation around the Zr–$CH(SiMe_3)_2$ bond) which exchanges the agostic and non-agostic $SiMe_3$ groups, and site epimerization at Zr, which exchanges the sides of the Cp″ ligands.

Lanthanide–$CH(SiMe_3)_2$ complexes also often contain agostic interactions. Neutron diffraction studies show that the M–μ-Me–Si interactions in $Cp^*Y\{O(2,6\text{-}{}^tBu_2C_6H_3)\}\{CH(SiMe_3)_2\}$ and $Cp^*La\{CH(SiMe_3)_2\}_2$ involve donation of Si–Me σ-bond electron density to the metal and not $SiCH_2$–H···M interactions [7]. This description has been substantiated by DFT calculations [8]. The fluxional behavior of lanthanide–$CH(SiMe_3)_2$ compounds has been studied in several cases [3c,3d,9].

Here we describe the generation and properties of the $Cp_2Zr\{CH(SiMe_3)_2\}^+$ cation. In order to minimize anion coordination and ion-pairing effects, the weakly coordinating anions $B(C_6F_5)_4^-$ and $HCB_{11}Me_5Br_6^-$ were used [10].

2. Results and discussion

2.1. Synthesis of $Cp_2Zr\{CH(SiMe_3)_2\}^+$ compounds

The reaction of **1** [5b,5c] with $[Ph_3C][B(C_6F_5)_4]$ in benzene yields $[Cp_2Zr\{CH(SiMe_3)_2\}][B(C_6F_5)_4]$ (**3a**) and Ph_3CMe (Eq. (1)). Compound **3a** separates as an oil from

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* Corresponding author. Tel.: +1 773 702 6429; fax: +1 773 702 0805.
E-mail address: rfjordan@uchicago.edu (R.F. Jordan).

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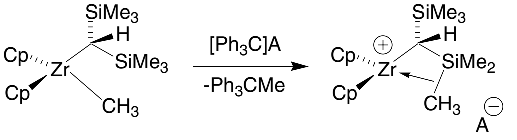
benzene and can be isolated as a red solid by decantation of the supernatant, washing with benzene, and vacuum drying. Some benzene (1–2 equiv) was retained in the isolated samples of **3a**. Compound **3a** can be dissolved in CD_2Cl_2 for low temperature NMR work, and also can be generated in C_6D_5Cl by the reaction shown in Eq. (1). Compound **3a** is moderately stable in both CD_2Cl_2 and C_6D_5Cl at 22 °C, and only ca. 20% decomposition of **3a** occurs in either solvent after 24 h. The carborane salt $[Cp_2Zr\{CH(SiMe_3)_2\}][HCB_{11}Me_5Br_6]$ (**3b**) is formed by the reaction of **1** and $[Ph_3C][HCB_{11}Me_5Br_6]\cdot 2PhMe$ [11] in toluene or C_6D_5Cl and can be isolated as orange crystals by crystallization from toluene/hexanes solution.



(1)

1

3a: A = $B(C_6F_5)_4$
3b: A = $HCB_{11}Me_5Br_6$

2.2. Molecular structure of $[Cp_2Zr\{CH(SiMe_3)_2\}][HCB_{11}Me_5Br_6]$

Compound **3b** crystallizes as discrete cations and anions, with a molecule of toluene in the unit cell [12]. Two views of the cation of **3b** are shown in Fig. 1, selected bond distances and angles are listed in Table 1, and the anion is shown in Fig. 2. The $Cp_2Zr\{CH(SiMe_3)_2\}^+$ cation displays a normal bent metallocene structure [13]. The Zr–$CH(SiMe_3)_2$ bond is displaced from the central coordination site (i.e. from the Cp(centroid)–Zr–Cp(centroid) plane) by 37° and thus occupies a lateral site. The other lateral site is occupied by a Zr–μ-Me–Si interaction. The Si–μ-Me bond (Si(2)–C(15), 1.981(5) Å) is ca. 0.1 Å longer than the two other Si–Me bonds in this $SiMe_3$ group (average 1.873(4) Å) and those in the unbound $SiMe_3$ group (average 1.88(1) Å). There is a close contact between zirconium and the agostic methyl carbon (2.602(4) Å). These data are consistent with donation of Si–Me σ-bond electron density to the metal center, as observed in lanthanide systems [3c,3d,7–9]. The Zr^+–μ-Me–Si interaction is analogous to the C^+–C–Si interactions in β-Si-stabilized carbocations [4]. The *Zr–C*H–*Si*–(μ-*C*H_3) unit is planar (Zr(1)–C(11)–Si(2)–C(15): mean deviation from plane = 0.0496 Å). The Zr–CH–Si angle involving the agostic $SiMe_2$(μ-Me) unit (Zr(1)–C(11)–Si(2), 90.4(2)°) is much smaller than that involving the free $SiMe_3$ group (Zr(1)–C(11)–Si(1), 137.7(2)°). The Zr–$CH(SiMe_3)_2$ bond distance of **3b** (Zr(1)–C(11), 2.244(4) Å) is ca. 0.08 Å shorter than that

Table 1
Selected bond lengths (Å) and angles (deg) for **3b**

C(11)–Zr(1)	2.244(4)	C(15)–Si(2)	1.981(5)
C(11)–Si(1)	1.870(4)	C(16)–Si(2)	1.869(5)
C(11)–Si(2)	1.876(4)	C(17)–Si(2)	1.876(5)
C(12)–Si(1)	1.865(5)	C(15)–Zr(1)	2.602(4)
C(13)–Si(1)	1.894(5)	C(14)–Si(1)	1.876(5)
Si(1)–C(11)–Zr(1)	137.7(2)	C(16)–Si(2)–C(11)	117.0(2)
Si(2)–C(11)–Zr(1)	90.4(2)	C(17)–Si(2)–C(11)	111.4(2)
Si(1)–C(11)–Si(2)	117.2(2)	Si(2)–C(15)–Zr(1)	78.4(2)
C(11)–Si(2)–C(15)	109.9(2)	C(11)–Zr(1)–C(15)	80.9(2)

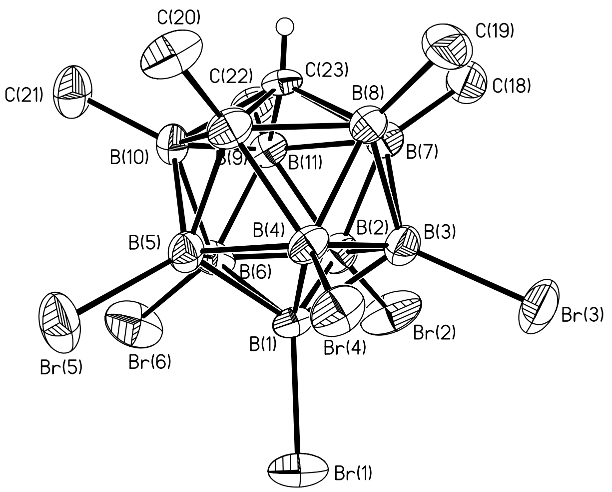


Fig. 2. ORTEP diagram (50% probability ellipsoids) of the $HCB_{11}Me_5Br_6^-$ anion of **3b**. Hydrogen atoms except that on C(23) are omitted.

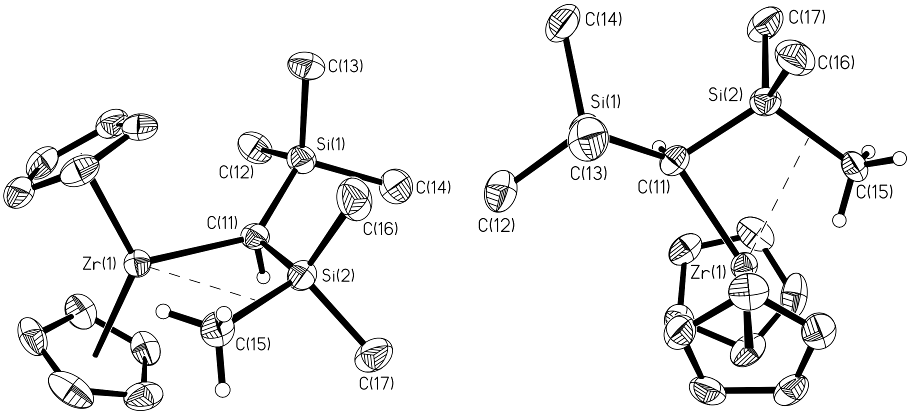


Fig. 1. Two views of the $Cp_2Zr\{CH(SiMe_3)_2\}^+$ cation of **3b**. Hydrogen atoms except those on C(11) and C(15) are omitted.

in $Cp_2Zr\{CH(SiMe_3)_2\}Ph$ (**4**) (2.329(6) Å) [5c], which does not contain an agostic Zr–μ-Me–Si interaction (minimum Zr···Me distance 3.916 Å).

2.3. NMR Properties and solution dynamics of $Cp_2Zr\{CH(SiMe_3)_2\}^+$

The low temperature (−89 °C) ^1H NMR spectrum of **3a** in CD_2Cl_2 contains two sharp Cp resonances in a 1:1 intensity ratio, and four broad $SiMe_3$ signals in a 9:3:3:3 intensity ratio (Fig. 3). The ^{13}C NMR spectrum (CD_2Cl_2, −89 °C) also contains two sharp Cp resonances, along with three broad $Si\mathit{Me}_3$ signals in an approximate 1:3:2 intensity ratio (Fig. 4) [14]. These results are consistent with the retention of the Zr–μ-Me–Si interaction (observed in the solid state for **3b**) in solution for **3a**. The downfield ^{13}C NMR $Si\mathit{Me}_3$ signal (δ 11.3) is assigned to the Zr–μ-$\mathit{C}H_3$–Si carbon, by analogy to the M–μ-Me–Si chemical shifts of $Cp^*_2Y\{CH(SiMe_3)_2\}$ and $Cp^*_2Lu\{CH(SiMe_3)_2\}$, which were assigned by integration of CP/MAS ^{13}C NMR spectra [9a,9b].

As the temperature is raised, the four ^1H NMR $SiMe_3$ signals of **3a** broaden, coalesce between −80 and −70 °C, and sharpen at −39 °C to a sharp singlet near the weighted averaged position of the low temperature $SiMe_3$ resonances, as shown in Fig. 5. However, the two Cp resonances of **3a** remain sharp between −89 and −39 °C. The ambient temperature ^1H and ^{13}C NMR spectra each contain one sharp $SiMe_3$ resonance at the weighted average of the chemical shifts of the low temperature signals, and two sharp Cp resonances. These results show that the μ-Me and terminal SiMe groups of the agostic $SiMe_3$ unit exchange, and that the bound and unbound $SiMe_3$ units exchange, but that the Cp groups do not exchange.

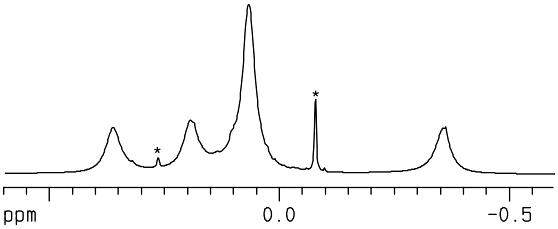


Fig. 3. $SiMe_3$ region of the ^1H NMR spectrum of **3a** (CD_2Cl_2, −89 °C). The resonances labeled with asterisks are from $CH_2(SiMe_3)_2$.

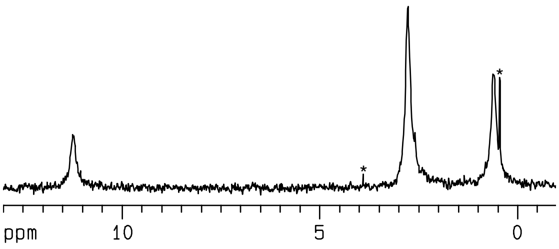


Fig. 4. $SiMe_3$ region of the $^{13}C\{^1H\}$ NMR spectrum of **3a** (CD_2Cl_2, −89 °C). The resonances labeled with asterisks are from $CH_2(SiMe_3)_2$.

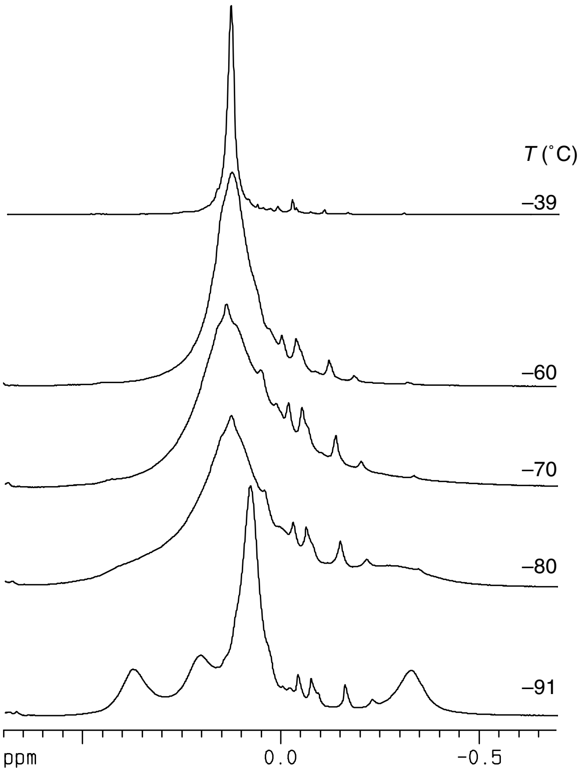
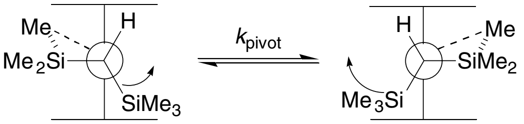


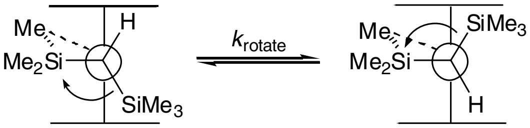
Fig. 5. Variable temperature ^1H NMR spectra of **3a** in CD_2Cl_2. The $SiMe_3$ region is shown.

The simplest dynamic process that explains the variable temperature NMR results for **3a** is a 60° "pivot" around the $Zr–CH(SiMe_3)_2$ bond, with concurrent cleavage and reformation of the Zr–μ-Me–Si interaction, as shown in Eq. (2). This process exchanges all six SiMe groups, but not the two Cp ligands, consistent with the experimental NMR spectra [15].



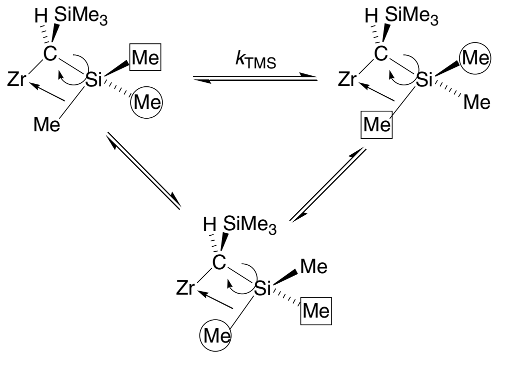
(2)

Full rotation around the $Zr–CH(SiMe_3)_2$ bond, as shown in Eq. (3), can be ruled out, because this process would exchange the two Cp ligands, which is not observed up to 22 °C. In contrast, the neutral compounds **1**, **4**, and $Cp_2Zr\{CH(SiMe_3)_2\}Cl$ (**5**), which do not contain Zr–μ-Me–Si interactions, do undergo full $Zr–CH(SiMe_3)_2$ rotation on the NMR time scale [5c,5e].



(3)

It is also possible that the terminal and bridging methyl groups within the agostic $SiMe_2(\mu\text{-}Me)$ unit are exchanged by CH–$SiMe_3$ bond rotation *independently* of the Zr–CH pivot (Scheme 1). This process would result in greater



Scheme 1.

broadening of the NMR signals for the SiMe$_2$(μ-Me) group compared to that of the free SiMe$_3$ group. In contrast, if independent CH–SiMe$_3$ bond rotation does not occur, then *all* SiMe$_3$ signals will exhibit equal exchange line broadening. The excess line widths due to exchange in **3a** at −89 °C ($\Delta\omega$) are listed in Table 2. These results show that the excess ^{1}H and ^{13}C line widths for the SiMe$_2$(μ-Me) group and the unbound SiMe$_3$ group are equal within experimental uncertainty [16]. Therefore, CH–SiMe$_2$(μ-Me) rotation does not occur at a significant rate independently of the Zr–CH(SiMe$_3$)$_2$ pivot under these conditions [17]. The first-order rate constant for the pivot is $k_{\text{pivot}} = \pi\Delta\omega = 54(6)\ \text{s}^{-1}$ at −89 °C in CD$_2$Cl$_2$, which corresponds to a barrier of $\Delta G^{\ddagger}_{\text{pivot}} = 9.2(1)$ kcal/mol.

The ambient temperature ^{1}H and ^{13}C NMR spectra of **3b** (C$_6$D$_5$Cl, 22 °C) are similar to those of **3a**, except for the anion resonances. The minor chemical shift differences observed for the two cations (maximum $|\Delta\delta_H| = 0.25$; maximum $|\Delta\delta_C| = 3.2$) can be ascribed to ion pairing effects. The B(C$_6$F$_5$)$_4{}^-$ and HCB$_{11}$Me$_5$Br$_6{}^-$ NMR resonances of **3a** and **3b** are not perturbed from those for compounds where anion coordination is expected to be minimal, such as the THF adducts [Cp$'_2$Zr(O^{t}Bu)(THF)][B(C$_6$F$_5$)$_4$] (Cp$'$ = C$_5$H$_4$Me) and [Cp$_2$Zr(C$_6$F$_5$)(THF)][HCB$_{11}$Me$_5$Br$_6$] [18]. The steric bulk of the Cp$_2$Zr{CH(SiMe$_3$)$_2$}$^+$ cation likely prevents site-specific ion pairing with either anion in chlorocarbon solution. It is unknown whether the Cp$_2$Zr{CH(SiMe$_3$)$_2$}$^+$ cation is stabilized by solvent coordination [19].

Table 2
Excess ^{1}H and ^{13}C NMR line widths ($\Delta\omega$) of the SiMe$_3$ resonances of **3a**[a]

Nucleus	δ	$\Delta\omega$ (Hz)[b]
^{1}H	0.4	20.7(1.8)
^{1}H	0.2	18.3(1.5)
^{1}H	**0.1**	**15.4(0.8)**
^{1}H	−0.3	19.8(1.9)
^{13}C	11.3	18.1
^{13}C	**2.8**	**17.7(2.5)**
^{13}C	0.6	18.6(2.3)

[a] At −89 °C in CD$_2$Cl$_2$ solution. The entries for the unbound SiMe$_3$ group are in bold.

[b] $\Delta\omega = \omega - \omega_0$, where ω is the actual line width of the given SiMe$_3$ resonance, and ω_0 is the line width in the absence of exchange, which is assumed to be equal to the line width of the Zr–*C*H(SiMe$_3$)$_2$ resonance. Data are averages of the results from 5 to 8 spectra, except for the ^{13}C resonance at δ 11.3, which could only be accurately determined in one spectrum.

2.4. Reactions of Cp$_2$Zr{CH(SiMe$_3$)$_2$}$^+$ with alkenes and alkynes

One motivation for studying the Cp$_2$Zr{CH(SiMe$_3$)$_2$}$^+$ cation is the possibility that alkene and alkyne insertion reactions may be inhibited by the steric bulk of the CH(SiMe$_3$)$_2{}^-$ ligand [20] and by stabilization of the partial negative charge at the Zr–*C*H(SiMe$_3$)$_2$ carbon by the α-Si effect [4], possibly enabling the observation of Cp$_2$Zr{CH(SiMe$_3$)$_2$}(alkene)$^+$ or Cp$_2$Zr{CH(SiMe$_3$)$_2$}(alkyne)$^+$ species at low temperature. Cp$_2$Zr(R)(alkene)$^+$ and Cp$_2$Zr(R)(alkyne)$^+$ species [21] are of interest as key intermediates in zirconocene-catalyzed alkene polymerization and alkyne oligomerization processes. Non-chelated d^0 metal-alkyl-alkene species are extremely rare, and to date have been detected only by NMR line broadening behavior in mixtures of alkenes and Cp$^*_2$YR species below −140 °C [20c,22].

Low temperature (−89 °C) NMR spectra of CD$_2$Cl$_2$ solutions of **3a** in the presence of ethylene, propylene, 1-hexene, allyltrimethylsilane, or 2-butyne contain only resonances for **3a** and the free alkene or alkyne. No new resonances or line broadening effects indicative of substrate binding are observed. In contrast, Cp$'_2$Zr(O^{t}Bu)$^+$ (Cp$'$ = C$_5$H$_4$Me) readily coordinates these substrates under the same conditions [23]. The steric bulk of the CH(SiMe$_3$)$_2{}^-$ ligand, and the Zr–μ-Me–Si interaction, apparently inhibit substrate coordination to **3a**. There is no consumption of ethylene at −89 °C. However, polyolefin forms when solutions of **3a** and ethylene, propylene, or 1-hexene are warmed to 22 °C for 1 day. It is unknown if the catalytic species is **3a** or a trace impurity.

3. Conclusions

The Cp$_2$Zr{CH(SiMe$_3$)$_2$}$^+$ cation displays a Zr–μ-Me–Si agostic interaction in the solid state and in solution, and undergoes a Zr–CH(SiMe$_3$)$_2$ pivot process that permutes the bound and unbound SiMe$_3$ groups but not the Cp ligands, with a barrier of $\Delta G^{\ddagger}_{\text{pivot}} = 9.2(1)$ kcal/mol at −89 °C. The Cp$_2$Zr{CH(SiMe$_3$)$_2$}$^+$ cation does not coordinate alkenes or alkynes at low temperature in CD$_2$Cl$_2$ solution, under conditions where Cp$'_2$Zr(O^{t}Bu)$^+$ binds these substrates. This difference is ascribed to the steric bulk of the CH(SiMe$_3$)$_2{}^-$ ligand and the Zr–μ-Me–Si agostic interaction.

4. Experimental section

4.1. General procedures

All experiments were performed using glove box or Schlenk techniques under a purified N$_2$ atmosphere, or on a high vacuum line. N_2 was purified by passage through columns of activated molecular sieves and Q-5 oxygen scavenger. CD_2Cl_2 and C_6D_5Cl were distilled from P_2O_5, and C_6H_6 was distilled from Na/benzophenone. $Cp_2Zr\{CH(SiMe_3)_2\}Me$ (**1**) was synthesized by literature procedures [5b,5c,6]. $[Ph_3C][HCB_{11}Me_5Br_6] \cdot 2PhMe$ [11] was provided by Prof. Christopher Reed and Dr. Kee-Chan Kim (University of California, Riverside). Other reagents were received from standard commercial sources. $[Ph_3C][B(C_6F_5)_4]$, ethylene, and propylene were used as received. Allyltrimethylsilane and 1-hexene were dried over CaH_2 prior to use. 2-Butyne was dried over 3 Å molecular sieves before use.

Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). NMR spectra were recorded on Bruker DRX 500 or DRX 400 spectrometers in Teflon-valved NMR tubes at ambient probe temperature unless otherwise noted. ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual solvent signals. ^{19}F NMR spectra are referenced to external neat $CFCl_3$. ^{11}B NMR spectra are referenced to external neat $BF_3 \cdot OEt_2$. NMR probe temperatures were calibrated by a MeOH thermometer [24]. Coupling constants are reported in Hz. NMR spectra of $B(C_6F_5)_4^-$ salts contain resonances at the free anion positions. ^{19}F NMR spectra were obtained for all compounds that contain this anion. NMR spectra of cationic compounds generated *in situ* contain resonances for Ph_3CMe.

4.2. Data for $B(C_6F_5)_4^-$

$^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 148.9 (d, $^1J_{CF} = 242$), 138.8 (d, $^1J_{CF} = 245$), 136.9 (d, $^1J_{CF} = 245$), 124.4 (br). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, −38 °C): δ 148.9 (d, $^1J_{CF} = 240$), 138.8 (d, $^1J_{CF} = 236$), 136.9 (d, $^1J_{CF} = 241$), 124.7 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 147.1 (d, $^1J_{CF} = 244$), 137.4 (d, $^1J_{CF} = 242$), 135.5 (d, $^1J_{CF} = 243$), 122.5 (br). ^{19}F NMR (C_6D_5Cl): δ −131.7 (br s, 8F, *o*-F), −161.8 (t, $J = 21$, 4F, *p*-F), −165.9 (br t, 8F, *m*-F). ^{19}F NMR (C_6D_5Cl, −38 °C): δ −132.0 (br d, 8F, *o*-F), −161.4 (t, $J = 20$, 4F, *p*-F), −165.4 (br t, 8F, *m*-F). ^{19}F NMR (CD_2Cl_2, −89 °C): δ −133.7 (s, 8F, *o*-F), −162.5 (t, $J = 19$, 4F, *p*-F), −166.5 (br t, 8F, *m*-F). ^{11}B NMR (C_6D_5Cl): δ −16.3.

4.3. Data for Ph_3CMe

^1H NMR (C_6D_5Cl): δ 7.14–7.05 (m, 15H, Ph), 2.03 (s, 3H, Me). ^1H NMR (C_6D_5Cl, −38 °C): δ 7.16–7.03 (m, 15H, Ph), 2.01 (s, 3H, Me). ^1H NMR (CD_2Cl_2, −89 °C): δ 7.24 (m, 6H, *m*-Ph), 7.18 (m, 3H, *p*-Ph), 7.03 (d, $J = 7.5$, 6H, *o*-Ph), 2.12 (s, 3H, C*Me*). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 149.4 (*ipso* Ph), 129.0 (Ph), 128.1 (Ph), 126.2 (Ph), 52.8 (*C*Me), 30.6 (Me). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, −38 °C): δ 149.4 (*ipso* Ph), 129.2 (Ph), 128.3 (Ph), 126.4 (Ph), 52.6 (*C*Me), 30.5 (Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 148.4 (*ipso* Ph), 128.1 (Ph), 127.4 (Ph), 125.6 (Ph), 51.6 (*C*Me), 29.5 (C*Me*).

4.4. Generation of $[Cp_2Zr\{CH(SiMe_3)_2\}][B(C_6F_5)_4]$ (3a)

Method I. An NMR tube was charged with **1** (19.9 mg, 0.0503 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (47.9 mg, 0.0519 mmol, 1.03 equiv), and C_6D_5Cl (0.5 mL) was added by vacuum transfer at −196 °C. The tube was warmed to 22 °C and shaken to give a deep yellow solution. NMR spectra were recorded after 15 min and showed that **3a** (95%) and Ph_3CMe had formed. *Method II.* An NMR tube was charged with **1** (23.7 mg, 0.0599 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (55.6 mg, 0.0603 mmol, 1.01 equiv), and C_6H_6 (1.0 mL) was added by vacuum transfer at −196 °C. The tube was warmed to 22 °C and shaken to give a mixture of a dark oil and a yellow supernatant. The tube was maintained at 22 °C and agitated for 2 h. The mixture was concentrated under vacuum to ca. 0.6 mL and washed with benzene (3 × 0.8 mL). The volatiles were removed under vacuum to give a yellow solid. CD_2Cl_2 (0.69 mL) was added by vacuum transfer at −78 °C. The tube was shaken at this temperature, giving a red solution. The tube was placed in a pre-cooled NMR probe, and NMR spectra showed that **3a** was the only metallocene species present. C_6H_6 (1.3 equiv) was also present. Data for **3a**: ^1H NMR (C_6D_5Cl): δ 6.04 (s, 5H, Cp), 5.99 (s, 5H, Cp), 4.41 (s, 1H, Zr–CH), −0.14 (s, 18H, $SiMe_3$). ^1H NMR (CD_2Cl_2, −89 °C): δ 6.502 (s, 5H, Cp), 6.497 (s, 5H, Cp), 4.74 (s, 1H, Zr–CH), 0.38 (br s, 3H, SiMe), 0.21 (br s, 3H, SiMe), 0.08 (br s, 9H, $SiMe_3$), −0.33 (br s, 3H, SiMe). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 116.0 (Cp), 114.6 (Cp), 87.7 (Zr–CH), 3.7 ($SiMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 115.4 (Cp), 113.9 (Cp), 86.7 (Zr–CH), 11.3 (br, SiMe), 2.8 (br, $SiMe_3$), 0.6 (br, $SiMe_2$).

4.5. $[Cp_2Zr(CH(SiMe_3)_2)][HCB_{11}Me_5Br_6]$ (3b)

Compound **1** (36.8 mg, 0.093 mmol), $[Ph_3C][HCB_{11}Me_5Br_6] \cdot 2PhMe$ (106.8 mg, 0.096 mmol, 1.03 equiv), and toluene (30 mL) were added to a glass vial. The mixture was shaken until all the material was dissolved, yielding an orange solution. The solution was layered with hexanes (50 mL) and stored at −35 °C for 4 d, during which time orange microcrystals precipitated from solution. The product was collected by vacuum filtration, washed with hexanes (5 mL), and dried under vacuum for 1 d, to afford an orange powder (45.2 mg, 46%). Data for **3b**: ^1H NMR (C_6D_5Cl): 6.22 (s, 5H, Cp), 6.14 (s, 5H, Cp), 4.16 (s, 1H, Zr–CH), 1.70 (s, 1H, anion CH), 0.49 (s, 15H, anion BMe), −0.10 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 116.6 (Cp), 115.2 (Cp), 84.5 (br, Zr–CH), 54.6 (slightly br, anion CH), 4.3 ($SiMe_3$), −1.3 (br, anion BMe). ^{11}B NMR (C_6D_5Cl): δ −5.8 (1B), −12.7 (5B), −15.4 (5B). Anal. Calc. for $C_{23}H_{45}B_{11}Si_2Br_6Zr$: C, 25.88; H, 4.25%. Found: C, 26.01; H, 4.19%.

Table 3
Summary of X-ray diffraction data for **3b**

Formula	$C_{23}H_{45}B_{11}Si_2Br_6Zr \cdot C_7H_8$
fw	1159.47
Cryst syst	Monoclinic
Space group	$P2_1/c$
a (Å)	9.748(2)
b (Å)	34.401(7)
c (Å)	14.135(3)
β (°)	97.94(3)
V (Å^3)	4695(2)
Z	4
D_{calcd} (g/cm^3)	1.641
T (K)	100
θ Range (deg)	1.57–28.38
Index ranges	$-12 \leqslant h \leqslant 12$; $-44 \leqslant k \leqslant 44$; $-18 \leqslant l \leqslant 18$
Reflections collected	54 733
Independent reflections	11 265
Data/restraints/parameters	11 265/0/467
Cryst color, habit	Orange, brick
GOF on F^2	0.679
R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.0390$ $wR_2 = 0.0733$
R indices (all data)[a]	$R_1 = 0.0824$ $wR_2 = 0.0955$

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$, where $w = q/[\sigma^2(F_0^2) + (aP)^2 + bP]$.

4.6. X-ray diffraction analysis of 3b

Single crystals of **3b** were obtained by slow diffusion of hexanes into a concentrated toluene solution of **3b**. Crystallographic data are summarized in Table 3. Data were collected on a Bruker Smart Apex diffractometer using Mo Kα radiation (0.71073 Å). Following anisotropic refinement of all non-H atoms, ideal H atom positions were calculated. Anisotropic refinement of all non-H atoms and isotropic-riding refinement of H atoms then enabled H(23) to be located and its position refined. Final refinement was anisotropic for all non-H atoms and isotropic-riding for all hydrogens except H(23), whose position was refined. ORTEP diagrams are drawn with 50% probability ellipsoids.

4.7. Reaction of 3a with alkenes or alkynes

A solution of **3a** (0.03–0.06 mmol) in CD_2Cl_2 (ca. 0.6 mL) in an NMR tube was cooled to −196 °C, and substrate (1-hexene, ethylene, propylene, allyltrimethylsilane, or 2-butyne; 0.06–0.2 mmol) was added by vacuum transfer. The tube was warmed to −78 °C and shaken, resulting in a red solution. The tube was placed in an NMR probe that had been pre-cooled to −89 °C. In all cases NMR spectra showed that only **3a** and free substrate were present. No resonances or line broadening effects indicative of formation of $Cp_2Zr\{CH(SiMe_3)_2\}(substrate)^+$ adducts were observed. The tube was warmed to 22 °C for ca. 1 d. NMR spectra showed that $CH_2(SiMe_3)_2$ and unidentified Cp_2Zr species were present. Resonances for polyolefin were observed for 1-hexene and propylene, and solid polymer was observed for ethylene. The fates of 2-butyne and allyltrimethylsilane were not determined.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 291366 for compound **3b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.033.

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[14] The T_1 values of the three $SiMe_3$ ^{13}C resonances are expected to be similar due to the similar environments of the corresponding carbons and the high viscosity of CD_2Cl_2 near its freezing point.

[15] This pivoting process also results in site epimerization at Zr for **3a**, which is not observable with the Cp_2Zr framework [6].

[16] As shown in Fig. 5, the $SiMe_3$ region of the variable temperature spectra of **3a** is quite featureless above −80 °C, and as a result, simulations of these spectra assuming the occurrence of only the pivot process, or of both the pivot and CH–$SiMe_2$(μ-Me) rotation processes at competitive rates, give equally satisfactory fits.

[17] The broadness and close spacing of the $SiMe_3$ resonances precluded ^1H EXSY studies of the dynamics of **3a**.

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