# Ancillary Ligand and Olefin Substituent Effects on Olefin Dissociation for Cationic Zirconocene Complexes Bearing a Coordinated Pendant Olefin

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A series of zirconocene complexes bearing 2,2-dimethyl-2-sila-4-pentenyl substituents (and methyl-substituted olefin variants) ($(\eta^5\text{-}C_5H_5)_2Zr(CH_3)(CH_2SiMe_2CH_2CR^1{=}CR^2R^3)$ ($R^1$, $R^2$, $R^3$ = H, $CH_3$, **1**, **5**−**7**), $(\eta^5\text{-}C_5H_4CMe_3)_2Zr(CH_3)(CH_2SiMe_2CH_2CH{=}CH_2)$ (**2**), $\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Zr(CH_3)(CH_2SiMe_2CH_2CH{=}CH_2)$ (**3**), and $\{1,2\text{-}(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2Zr(CH_3)(CH_2SiMe_2CH_2CH{=}CH_2)$ (**4**)) have been prepared. Methide abstraction with $B(C_6F_5)_3$ results in reversible coordination of the tethered olefin to the cationic zirconium center. The kinetics of olefin dissociation have been examined using NMR methods, and the effects of ligand variation for unlinked, singly [$SiMe_2$]-linked, and doubly [$SiMe_2$]-linked bis(cyclopentadienyl) arrangements have been compared ($\Delta G^{\ddagger}$ values for olefin dissociation vary from 11.4 to 15.6 kcal·mol$^{-1}$ measured over the temperature range 223−283 K). For the cation derived from **4** the kinetics for olefin dissociation and site epimerization (inversion at zirconium) can be distinguished. Additionally, with this ligand system competitive binding of the olefin and the $[CH_3B(C_6F_5)_3]$ anion is observed. Methide abstraction from $\{1,2\text{-}(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Zr(CH_3)(CH_2CMe_2CH_2CH{=}CH_2)$ results in rapid $\beta$-allyl elimination with loss of isobutene to cleanly afford the allyl cation $[\{1,2\text{-}(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2\}Zr(\eta^3\text{-}CH_2CH{=}CH_2)]^+$.

## Introduction

Ziegler−Natta polymerization catalysis is practiced on an enormous scale with both heterogeneous and homogeneous catalysts. Metallocene-based catalysts have allowed a more careful study of the mechanism than was possible with heterogeneous catalysts. In this regard, model complexes have been designed to stabilize intermediates that are transient under typical catalytic conditions. For example, several research groups have prepared cationic, $d^0$ metal olefin complexes of such catalyst systems by tethering an olefin to an alkoxy, alkyl, or cyclopentadienyl ligand.[1] We have employed this strategy to examine factors affecting olefin binding in cationic zirconocenes by constructing olefin complexes with the general formula shown in Scheme 1.[2] This series spans a limited range of unlinked, singly linked, and doubly linked bis(cyclopentadienyl) ligands as well as methyl substitution of the coordinated olefin.

## Results and Discussion

**Synthesis of Pentenyl and Hexenyl Iodides and Methyl(4-pentenyl)zirconocenes.** The syntheses of both 4,4-dimethyl-5-iodo-4-sila-1-pentene and 2,4,4-trimethyl-5-iodo-4-sila-1-pentene were accomplished according to literature precedent by the reaction of the respective Grignard reagent with $ClCH_2Si(CH_3)_2Cl$ in ethereal solvent, followed by reaction with NaI.[3] On the other hand, the preparations of the *cis*- and *trans*-5,5-dimethyl-6-iodo-5-sila-2-hexenes were not as straightforward. In both cases the respective 2-butenyltrichlorosilane was prepared according to literature methods.[4] These were treated with 2 equiv of methylmagnesium chloride to yield the respective 2-butenyldimethylchlorosilane, followed by addition of $BrCH_2Li$. $BrCH_2Li$ was prepared in situ from the reaction of $CH_2Br_2$ with *n*-BuLi *in the presence of the silyl chloride at −78 °C*. Much lower yields were obtained if the silyl chloride was added after the preparation of $BrCH_2Li$. We note in passing that this appears to be a novel use of this reagent, which previously has been studied extensively as a $[CH_2]$ homologation reagent with alkylcatechol boranes[5] and represents an improvement over current methods for preparing halomethyl(trialkyl)silanes.[6]

(1) (a)Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867. (b) Casey, C. P.; Hallenbeck, S. L.; Pollock, D. W.; Landis, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 9770. (c) Casey, C. P.; Hallenbeck. S. L.; Wright, J. M.; Landis, C. R. *J. Am. Chem. Soc.* **1997**, *119*, 9681. (d) Casey, C. P.; Fagan, M. A.; Hallenbeck, S. L. *Organometallics* **1998**, *17*, 287. (e) Galakhov, M. V.; Heinz, G.; Royo, P. J. *Chem. Soc., Chem. Commun.* **1998**. (f) Casey, C. P.; Carpenetti, D. W.; Sakuri, H. *J. Am. Chem. Soc.* **1999**, *121*, 9483. (g) Casey, C. P.; Carpenetti, D. W. *Organometallics* **2000**, *19*, 3970. (h) Carpentier, J.-F.; Wu, Z.; Lee, C. W.; Strömberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750. (i) Carpentier, J.-F.; Maryin V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898.

(2) Information on cation **8** is presented in the accompanying article: Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *Organometallics* **2001**, *20*, 4262.

(3) Fleming, I.; Patel, S. K.; Urdi, C. J. *J. Chem. Soc., Perkin Trans 1* **1989**, 115.

(4) Iseki, K.; Kuroki, Y.; Takahashi, M.; Satoshi, K.; Kobayashi, Y. *Tetrahedron* **1997**, 3513.

(5) Michnick, T. J.; Matteson, D. S. *Synlett* **1991**, 631.

(6) Cunico, R. F.; Gill, H. S. *Organometallics* **1982**, *1*, 1.

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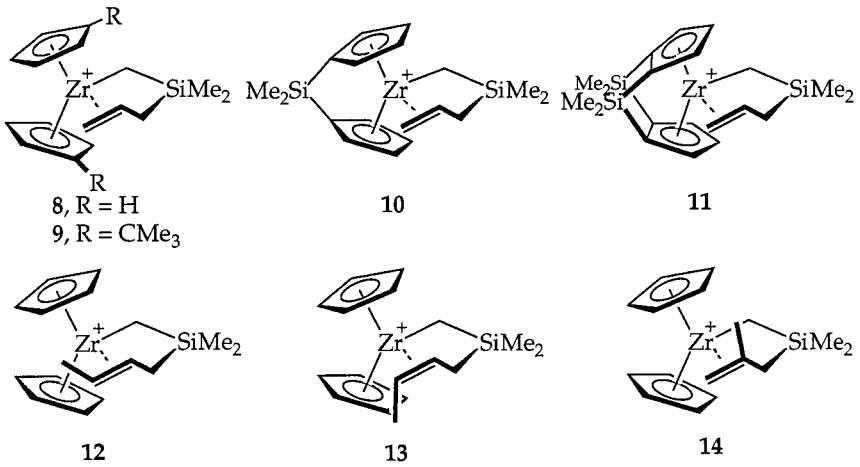
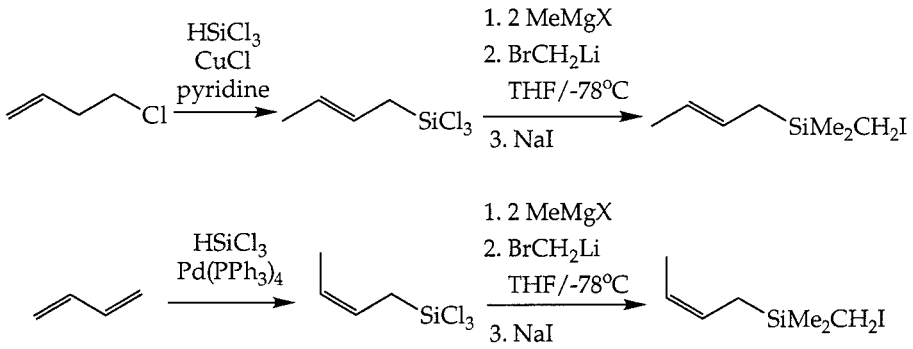
**Scheme 1**



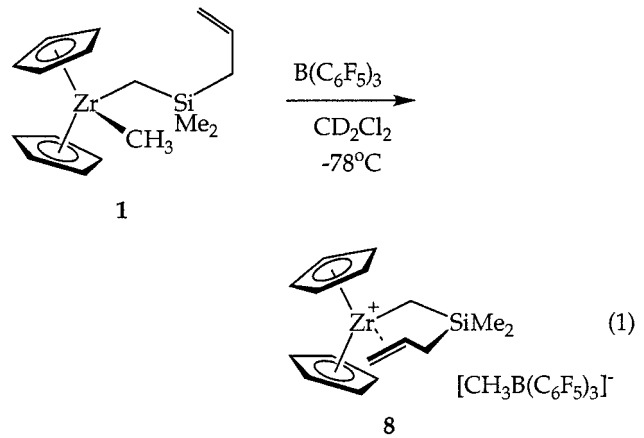

**Scheme 2**




After purification by column separation on silica gel, the hexenyl bromide was treated with NaI to give the hexenyl iodide.

The methyl(4-pentenyl)zirconocenes were generally obtained as oils via treatment of the appropriate 4-pentenyllithium reagent, generated in situ by lithium−halogen exchange, with a methylchlorozirconocene (Scheme 3).

**Preparation and Kinetic Studies of Cationic Pendant Olefin Complexes.** Abstraction of methide from **1** with $B(C_6F_5)_3$ at −78 °C results in the immediate formation of **8** (eq 1).



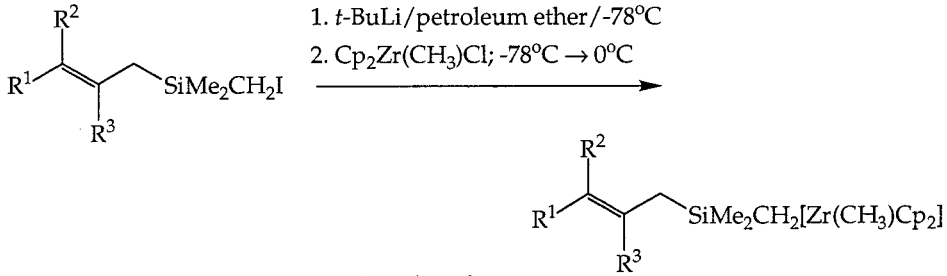

(1)

Several features in the $^1$H NMR spectrum ($CD_2Cl_2$, −78 °C) of static **8** are notable: (1) the two protons on the α-carbon display a chemical shift difference of 2.3 ppm (0.19, 2.55), (2) the protons on the terminal vinyl carbon are separated 3.6 ppm (2.25, 5.87), (3) the proton on the internal olefin carbon is at 8.6 ppm, 2 ppm downfield from its position for **1**. The first two features suggest differing proton positions relative to the magnetic fields resulting from cyclopentadienyl ring currents. The large downfield shift for the proton of the internal vinylic carbon has been suggested to result from resonance structures with a positive charge on this carbon,[1a,f] a suggestion that is certainly supported by the very downfield chemical shift for this proton of **8**. The presence of a $\beta$-silicon would further stabilize such a resonance structure.[7]

When solutions of **8** are warmed, a dynamic process ensues, which we attribute to olefin dissociation followed by fast recoordination. The $\Delta G^{\ddagger}(248\ \mathrm{K}) = 13.1$ kcal·mol$^{-1}$. We have modeled the coalescence using GNMR line shape analysis[8] and determined that the activation parameters for this process are $\Delta H^{\ddagger} = 13.4$ kcal·mol$^{-1}$, $\Delta S^{\ddagger} = 0.7$ eu. The rates measured to determine the activation parameters for most cases were obtained over only 20−25 °C ranges. Thus, while our Eyring plots have an excellent fit to the data, we do not have enough confidence in activation parameters derived from this limited temperature range to draw firm conclusions from them. Hence, we are confident only to compare free energies of activation, which appear to approximate the corresponding enthalpies of activation in most cases, since the activation entropies are near zero.

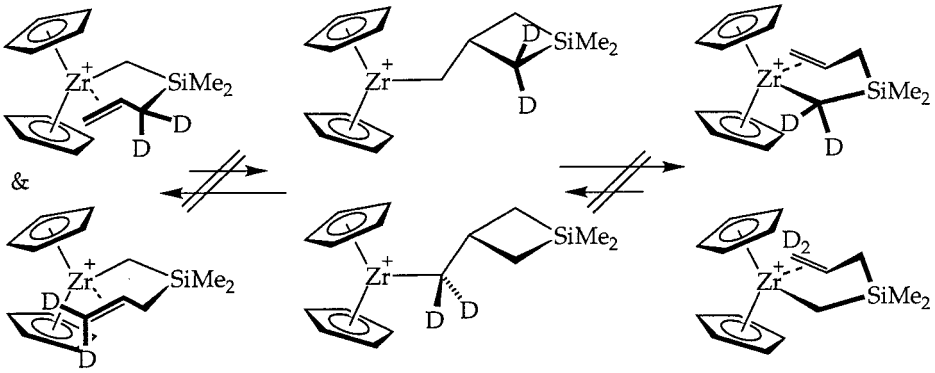
(7) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
(8) *gNMR*, v. 3.6; Cherwell Scientific Publishing: Oxford, 1996.

**Scheme 3**



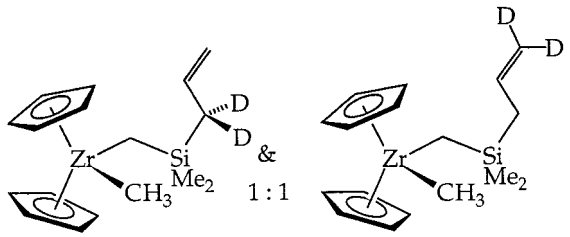

$R^1 = R^2 = R^3 = H$; $[ZrCp_2] = [Zr(C_5H_5)_2]$; **1**
$R^1 = R^2 = R^3 = H$; $[ZrCp_2] = [Zr(C_5H_4CMe_3)_2]$; **2**
$R^1 = R^2 = R^3 = H$; $[ZrCp_2] = [Zr\{(C_5H_4)_2SiMe_2\}]$; **3**
$R^1 = R^2 = R^3 = H$; $[ZrCp_2] = [Zr\{(C_5H_3)_2(1,2\text{-}SiMe_2)_2\}]$; **4**
$R^1 = CH_3$; $R^2 = R^3 = H$; $[ZrCp_2] = [Zr(C_5H_5)_2]$; **5**
$R^1 = R^3 = H$; $R^2 = CH_3$; $[ZrCp_2] = [Zr(C_5H_5)_2]$; **6**
$R^1 = R^2 = H$; $R^3 = CH_3$; $[ZrCp_2] = [Zr(C_5H_5)_2]$; **7**

**Scheme 4**




The possibility of a counteranion effect on the olefin dissociation was considered, and use of an alternative, less coordinating anion was attempted with $[Ph_3C][B(C_6F_5)_4]$ as a methide abstracting reagent. Unfortunately, significant amounts (>80%) of what appears to be the methyl-bridged dimeric cation, $\{[(\eta^5\text{-}C_5H_5)_2Zr(CH_2SiMe_2CH_2CH{=}CH_2)]_2(\mu_2\text{-}CH_3)\}^+$, are formed when stoichiometric amounts of $[Ph_3C][B(C_6F_5)_4]$ are used. Rates were measured for comparison by addition of 3 molar equiv of either $[n\text{-}Bu_4N]^+[CH_3B(C_6F_5)_3]^-$ or $[n\text{-}Bu_4N]^+[B(C_6F_5)_4]^-$ to $CD_2Cl_2$ solutions of **8**, thus holding the ionic strength constant. The resulting variable-temperature $^1H$ NMR spectra for these two samples are indistinguishable from each other. We conclude therefore that excess $[CH_3B(C_6F_5)_3]^-$ does not significantly change the rate of olefin dissociation. Solvent assistance has also been considered. The instability of **8** and its exceedingly high Lewis acidity restrict the choice of solvent. Whereas the rate of olefin dissociation in $CD_2Cl_2$ and $C_6D_5Cl$ are the same within experimental error, the similarity of these two solvents leaves open the issue of solvent assistance in olefin dissociation.

To determine whether reversible olefin insertion was occurring, isotopically labeled complex **1** with deuterium at the $\gamma$-carbon was prepared. Since the synthesis utilizes a 1:1 mixture of $CD_2CHCH_2MgBr$ and $CH_2CHCD_2MgBr$, the incorporation of deuterium was 50% at the $\gamma$-carbon and 50% at the terminal olefin carbon.



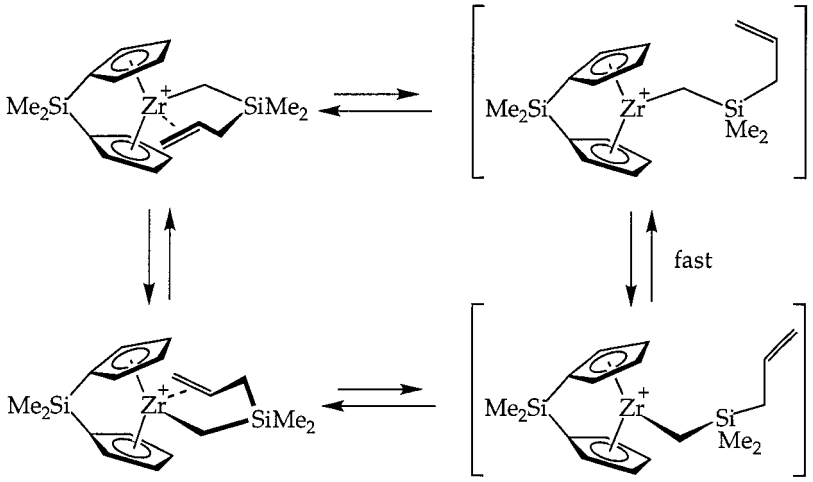

**1**-$d_2$

Upon activation with $B(C_6F_5)_3$ there was no observed change in the peak intensities of the protons at the α-carbon or at the $\gamma$-carbon, which would be expected for reversible insertion and ring opening of the resulting cyclobutylmethylzirconocenium cation (Scheme 4), indicating that no insertion is occurring.

We were surprised by the lack of observed insertion and thus undertook a DFT calculation to estimate the thermodynamics of the process. A comparison of the sila-substituted cyclization to the all-carbon analogue indicated that 1,1,3-trimethyl-1-silacyclobutane is 3 kcal·mol$^{-1}$ higher in energy than 4,4-dimethyl-4-sila-1-pentene, as compared to only 0.2 kcal·mol$^{-1}$ for the 4,4-dimethyl-1-pentene to 1,1,3-trimethylcyclobutane conversion.[9] The calculated difference of only 2.8 kcal·mol$^{-1}$ would not seem to account for the very slow insertion

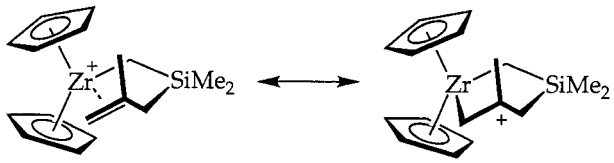
(9) *Jaguar 3.5*; Schrodinger, Inc.: Portland, Oregon, 1998.

**Scheme 5**




**8**-$d_2$, considering the relatively facile insertion ($\Delta G^{\ddagger}$(248 K) = 14.4 kcal·mol$^{-1}$) reported by Casey and co-workers for ($\eta^5$-$C_5Me_5)_2Y(CD_2CMe_2CH_2CH{=}CH_2)$.[1c] Higher temperatures were not examined, because above −30 °C **8** begins to decompose irreversibly.

**Olefin Substituent Effects.** To address the effects of methyl substitution on olefin binding to $d^0$ metals, we sought to prepare olefins with a single methyl group at each vinylic position. The *cis*-hexenyl complex **13** was prepared by methide abstraction from **6** with $B(C_6F_5)_3$ in $CD_2Cl_2$ at −78 °C. However, the major species in solution is the ion pair complex with only a small fraction identified as the complex **13** having coordinated olefin. This assignment is consistent with the proton spectra, although not all of the peaks could be assigned, and the fluorine NMR, which shows [$C_6F_5$] resonances corresponding to both coordinated and free $[CH_3B(C_6F_5)_3]^-$. The barrier for olefin exchange was determined by NMR simulation and was found to be 11.4 kcal·mol$^{-1}$ at 223 K, considerably lower than that of the parent complex **8**. The *trans*-hexenyl complex **5** was similarly activated and did, in fact, yield complex **12** with a coordinated olefin and solvent-separated $[CH_3B(C_6F_5)_3]^-$ as the major species. There also appears to be a small amount of the anion coordinated species. The ratio of these two species does not change over a wide variety of temperatures, and they do not appear to exchange with each other on the NMR time scale at temperatures up to −30 ° C. NMR simulation of the peak coalescence revealed that the free energy of activation was 13.3 kcal·mol$^{-1}$ at 248 K for olefin dissociation, curiously essentially unchanged from the parent pentenyl complex **8**. Examining simple models of the *cis*- and *trans*-hexenyl systems does lead one to predict greater steric repulsion with olefin coordination for **13** vs **12**; complex **13** has the *cis* methyl directed toward a cyclopentadienyl ligand. Perhaps most interesting is the relatively strong olefin binding for **14** that results from methide abstraction from complex **7**. The activation free energy for olefin dissociation is measured to be 14.4 kcal·mol$^{-1}$ at 248 K, 1.3 kcal·mol$^{-1}$ greater than less crowded **8**.[10] On the basis of sterics alone, we would expect the olefin dissociation barrier for **14** to be less than for the parent complex **8**. Clearly this result is consistent with the notion that positive charge builds up at the internal olefin carbon: the electron-donating methyl stabilizes the positive charge in resonance structure **14b**.




**14a** **14b**

**Ancillary Ligand Effects for Complexes Unlinked and Singly Linked Zirconocenium Olefin Cations.** Cations **9** and **10** were prepared in a fashion similar to **8**, and the dynamic behavior was examined by variable-temperature by NMR spectroscopy. The free energies of activation for these complexes were also very similar to that of **8**: $\Delta G^{\ddagger}$(248 K) = 13.2 kcal·mol$^{-1}$ for **9**; $\Delta G^{\ddagger}$(248 K) = 12.8 kcal·mol$^{-1}$ for **10**. Despite the presence of an *ansa* [$SiMe_2$] linker or a sterically rather demanding *tert*-butyl cyclopentadienyl substituent, the olefin dissociation rates among the three metallocenium cations are essentially the same. Significantly, for both complexes **9** and **10**, line shape analysis reveals that site epimerization (inversion at Zr, Scheme 5) occurs simultaneously with olefin dissociation.[11]

**Doubly Bridged *ansa*-Metallocenium Cation Olefin Complex.** Despite the similarity of olefin dissociation barriers for complexes **8**, **9**, and **10**, the fluxional character of the doubly [$SiMe_2$]-bridged complex **11** is distinct. For complex **11**, dynamic NMR behavior due to olefin dissociation in $CD_2Cl_2$ is not apparent until 0 °C, as opposed to −55 °C for **8**. The free energy of activation for **11** (in $C_6D_5Br$, $\Delta G^{\ddagger}$(283 K) = 15.6 kcal·mol$^{-1}$) is more than 2 kcal·mol$^{-1}$ greater than for **8**. Since the barriers for olefin dissociation are not measurably different with $[CH_3B(C_6F_5)_3]^-$ or $[B(C_6F_5)_4]^-$ as counterion, it appears that the anion does not assist in olefin dissociation. Additionally, at this temperature, and even up to 75 °C, olefin dissociation and recoordi-

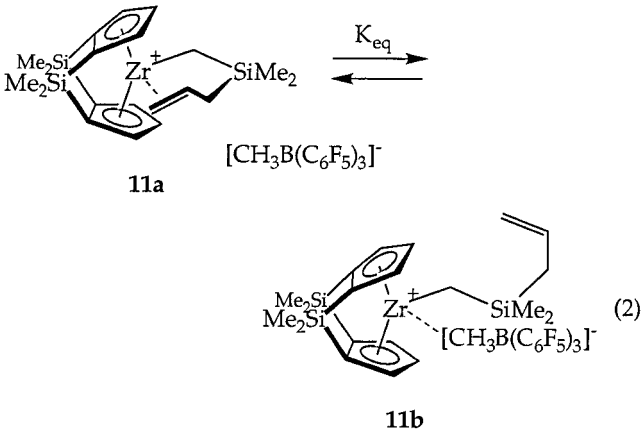
(10) This value for $\Delta G^{\ddagger}$ is extrapolated from activation parameters that were determined from an Eyring plot determined over a 30 °C range; the free energy at 273 K is 14.8 kcal·mol$^{-1}$.

(11) Although the symmetry for **8** does not allow measurement of the site epimerization rate, we assume that inversion at zirconium also accompanies olefin dissociation for this cation.

nation *is not accompanied by site epimerization*. It has been observed for this type of doubly bridged zirconocene complexes that the mechanism for ligand exchange is dissociative, whereas unbridged zirconocenes exchange ligands via an associative mechanism.[12] In light of these differences, it may be argued that olefin dissociation for complexes **8**, **9**, and **10** involves solvent assistance, whereas olefin facial exchange for complex **11** is entirely dissociative. Exactly how these differences influence the relative barriers for site epimerization are not clear (see ref 12b).

Site epimerization for complex **11** cannot be observed by NMR until 85 °C ($\Delta G^{\ddagger}$(358 K) = 21.2 kcal·mol$^{-1}$) and then only when **4** is activated with the $[Ph_3C][B(C_6F_5)_4]$ in $C_6D_5Cl$; all other combinations of solvent and activator that were attempted resulted in decomposition at lower temperatures. This inversion at zirconium for **11** is not complicated by the presence of donor molecules, coordinating anions, or (potentially agostic) $\beta$-hydrogens[13] and allows us to place a lower limit on the barrier for site epimerization of ca. 5.3 kcal·mol$^{-1}$ at 85 °C. The height of this barrier provides some of the strongest evidence to date of an inherent hindrance to site epimerization for cationic zirconocenium alkyls, as predicted by theoretical calculations.[14]

For this ligand system we can observe competitive binding of the $[CH_3B(C_6F_5)_3]^-$ to the metal center in $C_6D_5Cl$ (eq 2).

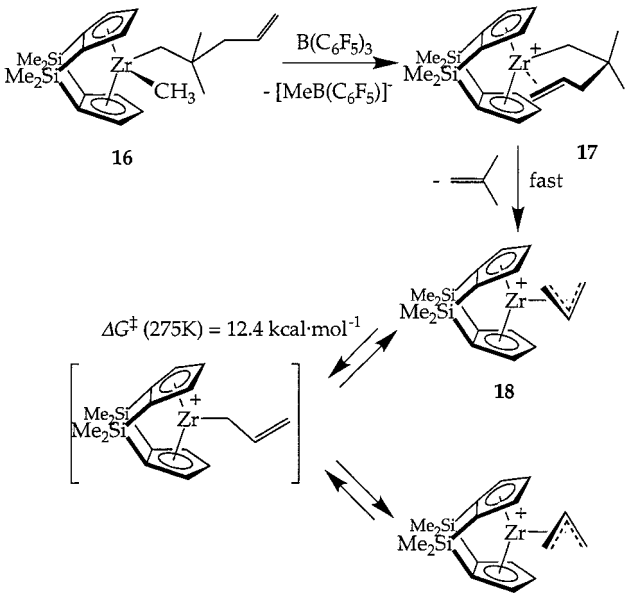



(2)

The equilibrium was examined between 0 and 65 ° C, revealing the following thermodynamic parameters in $C_6D_5Cl$: $\Delta H° = 7.2$ kcal·mol$^{-1}$ and $\Delta S° = 22$ e.u. Since the equilibrium favors the formation of the coordinated olefin complex at higher temperatures, despite two species forming one, the separated ions must organize the solvent significantly. The same species appears in $C_6D_5Br$ and $CD_2Cl_2$, but the equilibrium cannot be measured accurately because it does not appear until higher temperatures, just before decomposition sets in.[15]

**Attempts to Prepare a Doubly Bridged *ansa*-Metallocenium Cation with an All-Carbon Pendant Olefin: $\beta$-Allyl Elimination.** We have also synthesized the neutral zirconocene methyl-2,2-dimethyl-4-pentenyl complexes **16**. In view of the reluctance of the pendant sila-substituted pentenes to undergo reversible olefin insertion, we prepared this complex as a precursor to a cation that could serve as a model for olefin insertion into a zirconium−carbon bond. To our surprise, upon the addition of either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ at −40 °C in $C_6D_5Cl$ or $C_6D_5Br$ only allyl cation **18**, resulting from rapid and clean $\beta$-allyl elimination and loss of isobutene from the presumed intermediate **17**, was observed (Scheme 6).[16] There was no evidence of $\beta$-methyl elimination occurring. So far as we are aware, this process represents the first example of $\beta$-allyl elimination.

**Scheme 6**




The resulting cationic $\eta^3$-allyl complex is fluxional, and its dynamics have been examined by magnetization transfer ($\Delta G^{\ddagger}$(275 K) = 12. 4 kcal·mol$^{-1}$). The fluxional process can be described as an $\eta^3 \rightleftarrows \eta^1$ isomerization, leading to stepwise interconversion of the *syn* and *anti* methylene protons.

## Conclusions

For this series of zirconocene alkyl cations with pendant olefins, coordination of the C=C double bond to zirconium is observed. Dynamic NMR behavior indicates olefin dissociation and fast recoordination. The binding of olefins with methyl substitution on the terminal vinyl carbon appears to be influenced primarily

(12) (a) Wendt O.; Bercaw, J. E. Manuscript in preparation. (b) Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2001**, *123*, 1483.

(13) (a) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128. (b) Casey, C. P.; Fagan, M. A.; Hallenbeck, S. L. *Organometallics* **1998**, *17*, 287.

(14) Bierwagen, E. P.; Bercaw, J. E.; Goddard, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 1481.

(15) Compound **11**, when heated to higher temperatures, decomposes to give a halide-bridged dication dimer. This arises from metal−halogen exchange with the bromobenzene solvent. After sitting overnight in an NMR tube, crystals of this species grew. We determined the structure of this species using X-ray crystallography, revealing it to be a Zr(IV) bromide-bridged dimer $[[\{1,2\text{-}(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2Zr\}_2(\mu_2\text{-}Br)_2][B(C_6F_5)_4]_2$ (**15**) (see Supporting Information). Unfortunately, the amount of **15** that was isolated precluded further study. The precise mechanism of the reaction forming **15** is unknown at this time.

(16) The pentenyl complex, **17**, can only be observed when **16** is activated at −78 °C with $[Ph_3C][B(C_6F_5)_4]$ in $CD_2Cl_2$. Although it is not entirely pure, the diagnostic peaks in the $^1$H NMR spectrum of the olefin complex can be observed: a multiplet at 8.4 ppm and a matching set of doublets at −0.4 and 2.8 ppm. Upon warming to −50 °C, all peaks corresponding to **17** disappear, but the course of the decomposition of the proposed olefin complex is not easily followed.

by steric considerations, whereas methyl substitution of the internal vinyl carbon appears to stabilize a positive charge buildup, stabilizing the olefin complex. Singly cyclopentadienyl-substituted and singly [$SiMe_2$]-linked zirconocenium cations have barriers for pendant olefin dissociation that are essentially unchanged from the parent bis(cyclopentadienyl) system. In the doubly [$SiMe_2$]-linked complex, olefin dissociation is much faster than site epimerization, a process that involves inversion at zirconium by moving the alkyl group. By contrast, site epimerization is more rapid than olefin dissociation for the other cations examined. We interpret this difference as an indication that olefin dissociation in doubly linked metallocenes occurs by a dissociative mechanism, while olefin dissociation from the unlinked and singly linked *ansa*-zirconocenes is solvent assisted. The analogous, all-carbon tethered olefin could not be isolated; isobutene is rapidly eliminated, and the zirconocenium allyl cation is generated by facile $\beta$-allyl elimination.

## Experimental Section

**General Considerations.** All reactions were carried out using standard Schlenk techniques or in an inert atmosphere glovebox. $^1$H, $^{13}$C, and $^{19}$F NMR spectra were obtained using a Varian Inova500 or Varian Inova 300 MHz spectrometer. All NMR solvents were distilled from $CaH_2$. ($\eta^5$-$C_5H_5)_2Zr(CH_3)(Cl)$,[17] {$Me_2Si(\eta^5$-$C_5H_4)_2$}$Zr(CH_3)(Cl)$,[18] $B(C_6F_5)_3$,[19] $[Ph_3C][B(C_6F_5)_4]$,[20] {1,2-$(SiMe_2)_2(\eta^5$-$C_5H_3)_2Zr(CH_3)Cl$,[21] *trans*-$Cl_3SiCH_2CHCHCH_3$,[3] *cis*-$Cl_3SiCH_2CHCHCH_3$,[3] and $CH_2CHCD_2MgBr$[22] were prepared according to literature procedures. All solvents were dried on columns of anhydrous alumina and molecular sieves (4 Å). Reagents were purchased from Aldrich Chemical and were used as received.

**Line Shape Simulation Experiments.** Line shape analyses of dynamic $^1$H spectra were carried out on a Varian Inova 500 MHz spectrometer. Reaction temperatures were determined by measuring the peak separation of an ethylene glycol or methanol standard before or after the experiments. The program gNMR was used to simulate the NMR spectra.[8] To simulate the olefin dissociation and recoordination to the opposite face, the signals from either the diastereotopic cyclopentadienyl protons, α-protons, or $\gamma$-protons were studied. Specifically, the peaks for the diastereotopic protons of the cyclopentadienyl rings were simulated for **8**; the allylic protons were simulated for **9**; the allylic protons were simulated for **10**; the α-protons were simulated for **12**; the α-protons were simulated for complex **13**; and the α-protons were simulated for complex **14**. An example of the line shape analysis is given in the Supporting Information section. The rate of site epimerization for complexes **9**, **10**, and **11** was determined by examining the coalescence of peaks due to diastereotopic protons of the cyclopentadienyl ligands, as well as the peaks corresponding to dimethylsilyl groups that bridge cyclopentadienyl ligands.

**Magnetization Transfer Experiments.** Magnetization transfer experiments were carried out on a Varian Unity$^+$ 500 MHz spectrometer. Reaction temperatures were determined by measuring the peak separation of an ethylene glycol or methanol standard before and after the experiments. Relaxation times ($T_1$) for the resonances of interest were measured at each temperature before the magnetization transfer experiment using the inversion recovery method. Magnetization transfer spectra were obtained by using a DANTE pulse sequence.[23] The data were fitted using the program CIFIT.[24]

**Simplified One-Pot Preparation of $(C_5H_4)_2(SiMe_2)_2$.** A 1 L Schlenk flask was purged with Ar, and 400 mL THF was added via cannula transfer. Cyclopentadiene (20 g, 303 mmol) was added. This mixture was cooled to 0 °C, and *n*-butyllithium (189 mL, 303 mmol) was added by syringe, eventually forming a white precipitate. This mixture was allowed to stir for 1 h at room temperature. $SiCl_2Me_2$ (18.38 mL, 151 mmol) was added dropwise by syringe to the solution at 0 °C over 10 min. This solution was allowed to warm to room temperature and stir for 1 h. The butyllithium and $SiCl_2Me_2$ additions were repeated one time. After the $SiCl_2Me_2$ addition, the solution was allowed to warm to room temperature and stir overnight. The solvent was then removed in vacuo, and 400 mL of petroleum ether was added; the resulting slurry was stirred and filtered at room temperature, then quickly attached to an inert atmosphere filter frit and filtered. The remaining solid was rinsed with an additional 150 mL of petroleum ether. The solution was concentrated to ~100 mL and cooled to 0° C for 1 h. The solid precipitate was filtered and rinsed twice with cold petroleum ether. A colorless powder (15.3 g) was obtained for an overall yield of 42%. The filtrate was collected and placed in a freezer at −30° C, and more pure product was later recovered. $^1$H NMR (benzene-$d_6$, 300 MHz) isomer 1: $\delta$ −0.44 (s, 6H, Si(C$H_3$), 0.37 (s, 6H, Si(C$H_3$), 3.44 (s, 2H, SiC$H$), 6.64 (m, 6H, Cp$H$), 6.94 (m, 2H, Cp$H$); isomer 2: $\delta$ −1.23 (s, 3H, Si(C$H_3$), 0.21 (s, 3H, Si(C$H_3$), 0.32 (s, 3H, Si(C$H_3$), 0.44 (s, 3H, Si(C$H_3$), 3.54 (s, 2H, SiC$H$), 6.64 (m, 6H, Cp$H$), 6.82 (m, 2H, Cp$H$).

**4,4-Dimethyl-5-iodo-4-sila-1-pentene.** Allylmagnesium bromide (67.5 mL, 2 M in THF) was added dropwise to a 500 mL ether solution of chloro(chloromethyl)dimethylsilane (19.2 g, 135 mmol) at 0 °C over 1 h. This mixture was allowed to warm to room temperature and stir overnight. The product was carefully quenched with 100 mL of $H_2O$. The organic layer was rinsed 3 times with 100 mL of $H_2O$ and once with 100 mL of brine. The crude oil was dissolved in 125 mL of dry acetone, NaI (40 g, 266 mmol) was added, and the mixture was stirred for 18 h. This mixture was taken up in 100 mL of pentane and 100 mL of $H_2O$. The organic layer was washed with an additional 100 mL of $H_2O$. The solvent was removed by rotary evaporation, and the oil was distilled at 68−74 °C/10 mmHg. A colorless oil (15.6 g) was collected for a 48% yield. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.16 (s, 6H, Si(C$H_3$)$_2$), 1.66 (d, 2H SiC$H_2$CH, $J_{HH}$ = 7.2 Hz), 2.01 (s, 2H, IC$H_2$Si), 4.9 (m, 2H, $SiCH_2CHCH_2$), 5.78 (m, 1H, $SiCH_2CH$). Anal. Calcd for $C_6H_{11}SiI$: C, 30.01; H, 5.46. Found: C, 30.21; H, 5.45.

**2,4,4-Trimethyl-5-iodo-4-sila-1-pentene.** This compound was prepared analogously to 4,4-dimethyl-5-iodo-4-sila-1-pentene using $CH_2C(CH_3)CH_2MgCl$ in place of allylmagnesium bromide. The final product was distilled at 95 °C/25 mmHg and was isolated in 32% overall yield. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.19(s, 6H, Si(C$H_3$)$_2$), 1.62 (s, 2H, SiC$H_2$CCH$_3$), 1.70 (s, 3H, CC$H_3$), 2.05 (s, 2H, IC$H_2$Si), 4.55 (s, 1H, CH$H$CCH$_3$($CH_2$-Si)), 4.65 (s, 1H, C$H$HCCH$_3$($CH_2$Si)). Anal. Calcd for $C_7H_{13}SiI$:C, 33.08; H, 5.95. Found: C, 33.21; H, 5.91.

**5,5-Dimethyl-6-iodo-5-sila-*cis*-2-hexene.** A solution of *cis*-$Cl_3SiCH_2CHCHCH_3$ (27.15 g, 143.3 mmol), prepared according to literature procedure, in 1 L of diethyl ether was cooled to 0 °C. Methylmagnesium chloride (95.5 mL, 3 M, 286.6 mmol)

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was added over the course of 1 h. The volatiles were removed by distillation under Ar, and three fractions were obtained with varying amounts of methylated products. The first two fractions were collected from 95 to 107 °C. Over the course of 15 min, *n*-butyllithium (26.6 mL, 1.6 M, 42.5 mmol) was added *along the walls of the flask* cooled to −78 °C to a 100 mL THF solution of $CH_2Br_2$ (2.97 mL, 42.5 mmol) and the mixture of *cis*-butenylsilyl chloride. This mixture was allowed to stir at −78 °C for an additional 15 min and then allowed to warm and stir at room temperature for 20 min. A 20 mL portion of pentane was added, the organic solution was rinsed repeatedly with $H_2O$, and the volatiles were dried over $MgSO_4$. The product was purified by column chromatography with a pentane eluant. The oil was distilled at 75−80 °C/18 Torr for further purification. The oil and NaI (3 g, 20 mmol) were added to 25 mL of dry acetone and stirred for 24 h. The mixture was added to 100 mL of pentane, rinsed four times with 50 mL of $H_2O$, and then dried over $MgSO_4$. The volatiles were removed by rotary evaporation, and the resulting oil was obtained in 9.1% yield. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.17 (s, 6H, Si(C$H_3$)$_2$)), 1.58 (d, 3H, CHC$H_3$), 1.63 (d, 2H, C$H_2$CH), 2.02 (s, 2H, IC$H_2$Si), 5.4 (m, 2H, $CH_2CHCHCH_3$). Anal. Calcd for $C_7H_{13}SiI$: C, 33.08; H, 5.95. Found: C, 33.60; H, 6.0.

**5,5-Dimethyl-6-iodo-5-sila-*trans*-2-hexene.** Starting with *trans*-$Cl_3SiCH_2CHCHCH_3$, which is prepared according to literature procedure, the preparation of this compound is identical to that of 5,5-dimethyl-6-iodo-5-sila-*cis*-2-hexene. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.14 (s, 6H, Si(C$H_3$)$_2$), 1.56 (d, 2H, C$H_2$CH), 1.63 (d, 3H, CHC$H_3$), 2.0 (s, 2H, IC$H_2$Si), 5.35 (m, 2H, $CH_2CHCHCH_3$). Anal. Calcd for $C_7H_{13}SiI$: C, 33.08; H, 5.95. Found: C, 34.07; H, 6.09.

**3,3-Dideutero-4,4-dimethyl-5-iodo-4-sila-1-pentene.** This compound was prepared analogously to 4,4-dimethyl-5-iodo-4-sila-1-pentene using $CH_2CHCD_2MgBr$ (and $CD_2CHCH_2$-MgBr), which is prepared according to literature procedure. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 0.19(s, 6H, Si(C$H_3$)$_2$), 1.62 (d, 1H, SiC$H_2$CH), 2.0 (s, 2H, IC$H_2$Si), 4.85 (m, 1H, C$H_2$CH($CH_2$-Si)), 5.7 (m, 1H, $CH_2CH(CH_2Si)$). Anal. Calcd for $C_6H_9D_2SiI$: C, 29.76; H, 5.45. Found: C, 29.82; H 5.51.

**General Procedure for Preparation of Zirconocene Methylpentenyl Complexes (1, 2, 4−7).** A 25 mL Schlenk flask with a rubber septum was purged with $N_2$ for 10 min. A 10 mL portion of a degassed 3:2 mixture of petroleum ether and diethyl ether was added by syringe. To this mixture was added 4,4-dimethyl-5-iodo-4-sila-1-pentene (240 mg, 1.0 mmol) by syringe. This mixture was cooled to −78 °C, and *tert*-butyllithium (1.18 mL, 2.0 mmol) was added dropwise by syringe over 7 min and stirred for 20 min at −78 °C. A toluene solution containing $Cp_2Zr(CH_3)(Cl)$ (300 mg, 1.1 mmol) was added by syringe in <1 min, the mixture was stirred for 5 min at −78 °C, and then allowed to warm slowly to 0 °C over the course of 2 h. The solvent was removed in vacuo. The flask was filled with argon, quickly attached to a swivel frit assembly, and evacuated. A 10 mL sample of petroleum ether was vacuum transferred onto the solid stirred at room temperature and then filtered. The remaining solid was rinsed once, and the petroleum ether was removed in vacuo, leaving behind a yellow oil, which was left under vacuum for 30 min to remove residual solvent.

**($\eta^5$-$C_5H_5$)$_2$Zr($CH_3$)($CH_2SiMe_2CH_2CH{=}CH_2$) (1).** $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.17 (s, 3H, ZrC$H_3$), 0.04 (s, 6H, Si(C$H_3$)$_2$), 0.05 (s, 2H, ZrC$H_2$Si), 1.50 (d of t, 2H, SiC$H_2$-CHCH$_2$, $J_{HH}$ = 8.2, 1.1 Hz), 4.90 (m, 2H, $SiCH_2CHCH_2$), 5.71 (s, 10H, Cp*H*), 5.73 (s, 1H, $SiCH_2CHCH_2$). $^{13}$C (benzene-$d_6$, 125.70 MHz): $\delta$ 1.0, 28.5, 28.6, 44.8, 110.2, 112.1, 136.6.

**($\eta^5$-$C_5H_5$)$_2$Zr($CH_3$)($CH_2SiMe_2CD_2CH{=}CH_2$)/($\eta^5$-$C_5H_5$)$_2$Zr-($CH_3$)($CH_2SiMe_2CH_2CH{=}CD_2$) (1-*d*$_2$).** $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.17 (s, 3H, ZrC$H_3$), 0.04 (s, 6H, Si(C$H_3$)$_2$), 0.05 (s, 2H, ZrC$H_2$Si), 1.50 (d, 1H, SiC$H_2$CHCD$_2$, $J_{HH}$ = 8.2 Hz), 4.90 (m, 1H, $SiCD_2CHCH_2$), 5.71 (s, 10H, Cp*H*), 5.73 (s, 1H, $SiCH_2CHCH_2$). $^{13}$C (benzene-$d_6$, 125.70 MHz): $\delta$ 1.0, 28.5, 28.6, 44.8, 110.2, 112.1, 136.6.

**($\eta^5$-$C_5H_4CMe_3$)$_2$Zr($CH_3$)($CH_2SiMe_2CH_2CH{=}CH_2$) (2).** $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.01 (s, 3H, ZrC$H_3$), 0.13 (s, 6H, $ZrCH_2Si(CH_3)_2$), 0.11 (s, 2H, ZrC$H_2$Si), 1.13 (s, 18H, C(C$H_3$)$_3$), 1.58 (d, 2H, SiC$H_2$CH, $J_{HH}$ = 8.2 Hz), 5.0 (m, 2H, $SiCH_2CHCH_2$), 5.50 (q, 2H, Cp*H*, $J_{HH}$ = 2.4 Hz), 5.60 (q, 2H, Cp*H*, $J_{HH}$ = 2.4 Hz), 5.92 (q, 2H, Cp*H*, $J_{HH}$ = 2.4 Hz), 5.95 (m, 1H, $SiCH_2CH$), 6.16 (q, 2H, Cp*H*, $J_{HH}$ = 2.4 Hz). $^{13}$C (benzene-$d_6$, 125.70 MHz): $\delta$ 0.8, 28.6, 30.9, 31.7, 32.9, 41.1, 106.7, 107.7, 108.2, 109.3, 111.1, 112.0, 138.9.

**{($SiMe_2$)$_2$($\eta^5$-$C_5H_3$)$_2$}Zr($CH_3$)($CH_2SiMe_2CH_2CH{=}CH_2$) (4).** $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.19 (s, 3H, ZrC$H_3$), −0.05 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.07 (s, 5H, $Cp_2Si(CH_3)(CH_3)$, ZrC$H_2$), 0.14 (s, 6H, $ZrCH_2Si(CH_3)_2$), 0.44 (s, 6H, (Si(C$H_3$)-(C$H_3$))$_2$), 1.57 (d, 2H, SiC$H_2$CHCH$_2$, $J_{HH}$ = 8.1 Hz), 5.0 (m, 2H, $SiCH_2CHCH_2$), 5.95 (m, 1H, $SiCH_2CH$), 6.31 (t, 2H, Cp*H*, $J_{HH}$ = 2.7), 6.59 (m, 4H, Cp*H*). $^{13}$C (benzene-$d_6$, 125.70 MHz): $\delta$ −4.8, −3.9, 0.4, 2.4, 2.5, 28.3, 29.9, 33.2, 110.2, 112.1, 113.0, 113.1, 134.2, 136.7.

**($\eta^5$-$C_5H_5$)$_2$Zr($CH_3$)(*trans*-$CH_2SiMe_2CH_2CH{=}CHCH_3$) (5).** $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.17 (s, 3H, ZrC$H_3$), 0.06 (s, 6H, Si(C$H_3$)$_2$), 0.09 (s, 2H, ZrC$H_2$Si), 1.46 (d of qt, 2H, SiC$H_2$CHCH, $J_{HH}$ = 7.8, 1.3 Hz), 1.70 (d of q, 3H, CHCHC$H_3$, $J_{HH}$ = 6.3, 1.4 Hz), 5.36 (m, 1H, CHC*H*CH$_3$), 5.54 (s, 1H, C*H*CHCH$_3$), 5.72 (s, 10H, Cp*H*). $^{13}$C (benzene-$d_6$, 125.70 MHz): $\delta$ 1.2, 18.3, 26.4, 28.4, 45.6, 110.2, 122.6, 128.8.

**($\eta^5$−$C_5H_5$)$_2$Zr($CH_3$)(*cis*-$CH_2SiMe_2CH_2CH{=}CHCH_3$) (6).** $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.19 (s, 3H, ZrC$H_3$), 0.05 (s, 6H, Si(C$H_3$)$_2$), 0.09 (s, 2H, ZrC$H_2$Si), 1.50 (d, 2H, SiC$H_2$-CHCH), 1.62 (d, 3H, CHCHC$H_3$), 5.47 (m, 1H, CHC*H*CH$_3$), 5.63 (s, 1H, C*H*CHCH$_3$), 5.75 (s, 10H, Cp*H*). $^{13}$C ($CD_2Cl_2$, 125.70 MHz): $\delta$ 2.8, 14.6, 23.4, 29.5, 47.9, 112.2, 122.3, 129.8. $^{13}$C NMR spectra was taken in $CD_2Cl_2$ in order to identify a resonance that was obscured in benzene-$d_6$.

**($\eta^5$-$C_5H_5$)$_2$Zr($CH_3$)($CH_2SiMe_2CH_2C(CH_3){=}CH_2$) (7).** $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.11 (s, 3H, ZrC$H_3$), 0.19 (s, 6H, Si(C$H_3$)$_2$), 0.2 (s, 2H, ZrC$H_2$Si), 1.62 (s, 2H, SiC$H_2$-CCH$_3$), 1.80 (s, 3H, CC$H_3$), 4.70 (s, 1H, $SiCH_2C(CH_3)CHH$), 4.80 (s, 1H, $SiCH_2C(CH_3)CHH$), 5.75 (s, 10H, Cp*H*). $^{13}$C (benzene-$d_6$, 125.70 MHz): $\delta$ 1.7, 25.6, 28.6, 32.4, 45.3, 107.9, 110.2, 144.7.

**{($SiMe_2$)$_2$($\eta^5$-$C_5H_3$)$_2$}Zr($CH_3$)($CH_2CMe_2CH_2CH{=}CH_2$) (15).** $^1$H NMR (benzene-$d_6$, 300 MHz): $\delta$ −0.61 (s, 3H, ZrC$H_3$), 0.10 (s, 3H, Si(C$H_3$)), 0.12 (s, 3H, Si(C$H_3$)), 0.45 (s, 6H, (Si(C$H_3$)-(C$H_3$))$_2$), 0.62 (s, 2H, $ZrCH_2Si(CH_3)_2$), 0.97 (s, 6H, $ZrCH_2C$-(C$H_3$)$_2$), 2.00 (d, 2H, C(C$H_3$)$_2$C$H_2$CHCH$_2$, $J_{HH}$ = 7.5 Hz), 5.07 (m, 2H, C(C$H_3$)$_2$CH$_2$CHC$H_2$), 5.90 (m, 1H, C(C$H_3$)$_2$CH$_2$C*H*), 6.32 (t, 2H, Cp*H*, $J_{HH}$ = 2.1), 6.59 (s, 2H, Cp*H*), 6.67 (s, 2H, Cp*H*). $^{13}$C (benzene-$d_6$, 75.4 MHz): $\delta$ −4.5, −3.6, 2.6, 2.8, 28.6, 31.8, 37.5, 52.5, 69.2, 110.2, 112.6, 113.3, 116.1, 137.3.

**{$Me_2Si$($\eta^5$-$C_5H_4$)$_2$}Zr($CH_3$)($CH_2SiMe_2CH_2CH{=}CH_2$) (3).** A solution of 4-sila-1-pentenylmagnesium iodide in THF (3.94 mL, 2.87 mmol) was added against an Ar counterflow to a 120 mL methylene chloride solution of $Me_2SiCp_2ZrCl_2$ (1.0 g, 2.87 mmol) in a 250 mL Schlenk flask at 0 °C. This mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed, and benzene was condensed onto the residue and warmed to room temperature. This solids were filtered away, and the solvent was removed from filtrate to afford a solid, which included 5−10% of the bis(pentenyl) and 5−10% of the dichloro complexes and was rinsed two times with petroleum ether. This solid (0.67 g, 1.56 mmol) was dissolved in diethyl ether at −78 °C, and a diethyl ether solution of methyllithium (1.55 mL, 2.34 mmol) was added dropwise. This mixture was stirred at −78 °C for 1 h and then was warmed to room temperature for 1 h. The volatiles were removed, and petroleum ether was condensed onto the solid. After filtration the solvent was removed in vacuo, leaving a yellow oil behind. $^1$H NMR (benzene-$d_6$, 499.85 MHz): $\delta$ −0.06 (s, 3H, ZrC$H_3$), 0.07 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.10 (s, 6H,

$ZrCH_2Si(CH_3)_2$), 0.11 (s, 2H, $ZrCH_2Si$), 0.13 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 1.55 (d of t, 2H, $SiCH_2CHCH_2$), 5.00 (s, 2H, $SiCH_2CHCH_2$, 5.41 (q, 2H, Cp*H*), 5.53 (q, 2H, Cp*H*), 6.53 (q, 2H, Cp*H*), 6.89 (q, 2H, Cp*H*). $^{13}$C (benzene-$d_6$, 125.70 MHz): $\delta$ −5.9, −5.3, 0.8, 28.5, 29.0, 44.8, 102.4, 110.4, 112.1, 114.0, 120.0, 120.6, 136.65.

**General Procedure for Methide Abstraction from the Methylalkenyl Zirconocenes.** Because the alkenyl complexes are typically an oil, calibrated solutions in either $CD_2Cl_2$ or $C_6D_5Cl$ were prepared. In an inert atmosphere glovebox, $B(C_6F_5)_3$ (20 mg, 39.1 $\mu$mol) was weighed out in a screw-capped NMR tube with a Teflon septum. A 0.7 mL sample of NMR solvent was added, and the septum cap was screwed on. The zirconocene solution (60 $\mu$L, 0.5 M, 30 $\mu$mol) was measured in a syringe. Outside of the glovebox, the walls of the NMR tube were cooled to −78 °C, and then the zirconocene solution was added by syringe to the sealed NMR tube and the contents were carefully shaken, keeping the solution cold. The NMR solution immediately became bright yellow.

**[($\eta^5$-$C_5H_5$)$_2$Zr($CH_2SiMe_2CH_2CH{=}CH_2$][MeB($C_6F_5$)$_3$] (8).** $^1$H NMR ($CD_2Cl_2$, 499.85 MHz, −80 °C): $\delta$ 0.06 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 0.38 (d, 1H, ZrC*H*H, $J_{HH}$ = 12.5 Hz), 0.42 (s, 3H, $BCH_3$), 0.46 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 2.01 (d of d, 1H, SiC*H*HCH, $J_{HH}$ = 11 Hz, 11 Hz), 2.12 (m, 1H, SiCH*H*CH), 2.34 (m, 1H, $SiCH_2CHCHH$), 2.57 (d, 1H, ZrCH*H*, $J_{HH}$ = 12.5 Hz), 5.92 (d, 1H, $SiCH_2CHCHH$, $J_{HH}$ = 17 Hz), 6.62 (s, 5H, Cp*H*), 6.65 (s, 5H, Cp*H*), 8.65 (m, 1H, $SiCH_2CH$). $^{13}$C NMR ($CD_2Cl_2$, 125.70 MHz, −80 °C): $\delta$ 0.4 (q, $Si(CH_3)_2$, $J_{C-H}$ = 119), 1.7 (q, $Si(CH_3)_2$, $J_{C-H}$ = 121), 9.8 (q, B-$CH_3$, $J_{C-H}$ = 124.3 Hz), 32.9 (t, $ZrCH_2$, $J_{C-H}$ = 128.7 Hz), 53.5 (t, $SiCH_2CHCH_2$, $J_{C-H}$ = 113.6 Hz), 99.5 ppm (t, $SiCH_2CHCH_2$, $J_{C-H}$ = 153 Hz), 113.9 (d of qt, $C_5H_5$, $J_{C-H}$ = 167 Hz), 115.3 (d of qt, $C_5H_5$, $J_{C-H}$ = 167 Hz), 128.1 (s, B−C), 136.0 (d, C−F, $J_{CF}$=247 Hz), 137.0 (d, C−F, $J_{CF}$ = 244 Hz), 147.7 (d, C−F, $J_{CF}$ = 246), 175.1 (d, $SiCH_2CHCH_2$, $J_{C-H}$ = 155 Hz). $^{19}$F NMR ($CD_2Cl_2$, 470.25 MHz, −80 °C): $\delta$ −167.0 (s, 6F), −164.3 (s, 3F, $J_{FF}$ = 21 Hz), −134.0 (s, 6F).

**[($\eta^5$-$C_5H_5$)$_2$Zr($CH_2SiMe_2CD_2CH{=}CH_2$][MeB($C_6F_5$)$_3$]/[($\eta^5$-$C_5H_5$)$_2$Zr($CH_2SiMe_2CH_2CH{=}CD_2$][MeB($C_6F_5$)$_3$] (8-$d_2$).** $^1$H NMR ($CD_2Cl_2$, 499.85 MHz, −80 °C): $\delta$ 0.02 (s, 3H, $Si(CH_3)(CH_3)$), 0.25 (d, 1H, ZrC*H*HSi$CH_2$, $J_{HH}$ = 13 Hz), 0.30 (d, 1H, ZrC*H*HSi$CD_2$, $J_{HH}$ = 13 Hz), 0.36 (s, 3H, $BCH_3$), 0.41 (s, 3H, $Si(CH_3)(CH_3)$), 2.01 (d of d, 0.5H, SiC*H*HCH, $J_{HH}$ = 11 Hz, 11 Hz), 2.12 (m, 0.5H, SiCH*H*CH), 2.34 (m, 0.5H, $SiCH_2CHCHH$), 2.51 (d, 1H, ZrCH*H*, $J_{HH}$ = 13 Hz), 5.92 (d, 0.5H, $SiCH_2CHCHH$, $J_{HH}$ = 17 Hz), 6.57 (s, 5H, Cp*H*), 6.59 (s, 5H, Cp*H*), 8.62 (m, 1H, $SiCH_2CH$).

**[($\eta^5$-$C_5H_4CMe_3$)$_2$Zr($CH_2SiMe_2CH_2CH{=}CH_2$][MeB($C_6F_5$)$_3$] (9).** $^1$H NMR ($CD_2Cl_2$, 499.85 MHz, −80 °C): $\delta$ −0.31 (d, 1H, ZrC*H*H, $J_{HH}$ = 12.5 Hz), 0.04 (s, 3H, $Si(CH_3)_2$), 0.42 (s, 3H, $BCH_3$), 0.52 (s, 3H, $Si(CH_3)_2$), 1.09 (s, 18H, $CCH_3$), 2.04 (m, 2H, $SiCH_2CHCH_2$), 2.19 (t, 1H, Si 5.67$CH_2CHCH_2$), 2.60 (d, 1H, ZrCH*H*, $J_{HH}$ = 12.5 Hz), 5.96 (s, 1H, Cp*H*), 6.31 (s, 1H, Cp*H*), 6.55 (s, 2H, Cp*H*), 6.71 (s, 1H, Cp*H*), 6.99 (s, 1H, Cp*H*), 7.11 (s, 2H, Cp*H*), 8.81 (m, 1H, $SiCH_2CHCH_2$). $^{13}$C NMR ($CD_2Cl_2$, 125.70 MHz, −80 °C): $\delta$ 1.0, 3.2, 10.0, 31.3, 31.3, 33.3, 33.8, 34.3, 52.0, 99.0, 108.0, 110.5, 110.6, 111.8, 112.5, 115.9, 118.9, 119.7, 128.61, 135.6 (d, $J_{CF}$ = 242 Hz), 137.5 (d, $J_{CF}$ = 236 Hz), 145.0, 148.6(d, $J_{CF}$ = 234 Hz), 179.7. $^{19}$F NMR ($CD_2Cl_2$, 470.25 MHz, −80 °C): $\delta$ −168.3 (t, 6F, $J_{FF}$ = 21 Hz), −165.6 (t, 3F, $J_{FF}$ = 21 Hz), −135.2 (d, 6F, $J_{FF}$ = 22 Hz).

**[{$Me_2Si(\eta^5$-$C_5H_4)_2$}Zr($CH_2SiMe_2CH_2CH{=}CH_2$][MeB($C_6F_5$)$_3$] (10).** $^1$H NMR ($CD_2Cl_2$, 499.85 MHz, −80 °C): $\delta$ 0.06 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 0.36 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 0.41 (s, 3H, $BCH_3$), 0.66 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.71 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.88 (s, 1H, ZrCH*H*Si, $J_{HH}$ = 13 Hz), 2.01 (d of d, 1H, SiCH*H*CHCH$_2$, $J_{HH}$ = 12.2 Hz), 2.18 (m, 1H, SiC*H*H-CHCH$_2$), 2.34 (d, 1H, ZrC*H*HSi, $J_{HH}$ = 13 Hz), 2.74 (d, 1H, $SiCH_2CHCHH$, $J_{HH}$ = 6.5), 5.78 (s, 2H, Cp*H*), 5.80 (s, 1H, Cp*H*), 5.82 (s, 1H, Cp*H*), 5.99 (d, 1H, $SiCH_2CHCHH$, $J_{HH}$ = 17 Hz), 7.27 (s, 1H, Cp*H*), 7.35 (s, 1H, Cp*H*), 7.44 (s, 1H, Cp*H*), 7.52 (s, 1H, Cp*H*). $^{13}$C NMR ($CD_2Cl_2$, 125.70 MHz, −80 °C): $\delta$ −5.5, −5.4, 1.2, 1.4, 10.0, 32.6, 52.0, 100.1, 104.5, 107.6, 113.4, 114.1, 118.3, 118.8, 121.1, 123.6, 125.0, 128.4, 136.5 (d, $J_{CF}$ = 240 Hz), 137.9 (d, $J_{CF}$ = 242 Hz), 142.3 (d, $J_{CF}$ = 238 Hz), 168.1. $^{19}$F NMR ($CD_2Cl_2$, 470.25 MHz, −80 °C): $\delta$ −168.4 (t, 6F, $J_{FF}$ = 20 Hz), −162.2 (t, 3F, $J_{FF}$ = 21 Hz), −135.1 (d, 6F, $J_{FF}$ = 21 Hz).

**[{$(SiMe_2)_2(\eta^5$-$C_5H_3)_2$}Zr($CH_2SiMe_2CH_2CH{=}CH_2$)][MeB($C_6F_5$)$_3$] (11-MeBArF).** $^1$H NMR ($C_6D_5Cl$, 499.85 MHz, −40 °C): $\delta$ −0.09 (d, 1H, ZrC*H*H, $J_{HH}$ = 13.5 Hz), −0.05 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.02 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 0.05 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.31 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 0.66 (s, 6H, $Cp_2(Si(CH_3)(CH_3))_2$), 1.44 (s, 3H, $BCH_3$), 1.74 (1H, d of d, SiC*H*HCHCH$_2$, $J_{HH}$ = 8.4, 12.3 Hz), 1.88 (m, 1H, SiH*H*-CHCH$_2$), 1.96 (d, 1H, ZrCH*H*, $J_{HH}$ = 13.5 Hz), 1.97 (m, 1H, $SiCH_2CHCHH$), 5.49 (d of d, 1H, $SiCH_2CHCHH$, $J_{HH}$ = 2.9, 17 Hz), 6.10 (s, 1H, Cp*H*), 6.15 (s, 1H, Cp*H*), 6.57 (s, 1H, Cp*H*), 6.64 (s, 1H, Cp*H*), 6.92 (s, 1H, Cp*H*), 6.97 (s, 1H, Cp*H*), 8.08 (m, 1H, $SiCH_2CHCH_2$). $^{13}$C NMR ($C_6D_5Cl$, 125.70 MHz, −40 °C): $\delta$ −5.0, 4.2, 0.1, 1.2, 1.9, 2.1, 33.4, 46.9, 98.9, 115.1, 117.4, 117.5, 117.9, 118.0, 136.0, 137.1 (d, $J_{CF}$ = 233 Hz), 137.8 (d, $J_{CF}$ = 241 Hz), 148.9 (d, $J_{CF}$ = 253 Hz), 170.1. $^{19}$F NMR ($CD_2Cl_2$, 470.25 MHz, −40 °C): $\delta$ −167.7 (t, 6F, $J_{FF}$ = 23 Hz), −165.1 (t, 3F, $J_{FF}$ = 21 Hz), −135.0 (d, 6F, $J_{FF}$ = 21 Hz).

**[{$(SiMe_2)_2(\eta^5$-$C_5H_3)_2$}Zr($CH_2SiMe_2CH_2CH{=}CH_2$)][B($C_6F_5$)$_4$] (11-BArF$_4$).** $^1$H NMR ($C_6D_5Cl$, 499.85 MHz, −40 °C): $\delta$ −0.08 (d, 1H, ZrC*H*H, $J_{HH}$ = 13.5 Hz), −0.04 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.03 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 0.08 (s, 3H, $Cp_2Si(CH_3)(CH_3)$), 0.33 (s, 3H, $ZrCH_2Si(CH_3)(CH_3)$), 0.67 (s, 6H, $Cp_2(Si(CH_3)(CH_3))_2$), 1.75 (1H, d of d, SiC*H*HCHCH$_2$, $J_{HH}$ = 8.4, 12.3 Hz), 1.92 (m, 1H, SiH*H*CHCH$_2$), 1.97 (d, 1H, ZrCH*H*, $J_{HH}$ = 13.5 Hz), 1.99 (m, 1H, $SiCH_2CHCHH$), 2.15 (s, 3H, $Ph_3CCH_3$), 5.49 (d of d, 1H, $SiCH_2CHCHH$, $J_{HH}$ = 2.9, 17 Hz), 6.09 (s, 1H, Cp*H*), 6.16 (s, 1H, Cp*H*), 6.59 (s, 1H, Cp*H*), 6.67 (s, 1H, Cp*H*), 6.92 (s, 1H, Cp*H*), 6.98 (s, 1H, Cp*H*), 8.10 (m, 1H, $SiCH_2CHCH_2$). $^{13}$C NMR ($C_6D_5Cl$, 125.70 MHz, −40 °C): $\delta$ −5.0, 4.3, 0.1, 1.2, 1.9, 2.1, 30.6, 33.4, 46.9, 52.7, 98.8, 115.1, 117.5, 117.7, 117.9, 118.1, 170.2. $^{19}$F NMR ($CD_2Cl_2$, 470.25 MHz, −40 °C): $\delta$ −169.2 (s, 8F), −165.3 (t, 4F, $J_{FF}$ = 21 Hz), −136.0 (s, 8F).

**[($\eta^5$-$C_5H_5$)$_2$Zr(*trans*-$CH_2SiMe_2CH_2CH{=}CHCH_3$][MeB($C_6F_5$)$_3$] (12).** Coordinated olefin complex: $^1$H NMR ($CD_2Cl_2$, 499.85 MHz, −80 °C): −0.32 (d, 1H, ZrC*H*H, $J_{HH}$ = 13.5 Hz), 0.03 (s, 3H, $Si(CH_3)(CH_3)$), 0.25 (d, 3H, $CHCHCH_3$, $J_{HH}$ = 5.5 Hz), 0.42 (s, 3H, $BCH_3$), 0.47 (s, 3H, $Si(CH_3)(CH_3)$), 1.76 (d of d, 1H, SiC*H*HCHCH$_2$, $J_{HH}$ = 12 Hz, $J_{HH}$ = 12 Hz), 1.85 (m, 1H, SiC*H*HCHCH), 2.09 (d, 1H, ZrCH*H*, $J_{HH}$ = 13.5 Hz), 5.68 (m, 1H, $CHCHCH_3$), 7.55 (m, 1H, $SiCH_2CHCH$). $^{13}$C NMR ($CD_2Cl_2$, 125.70 MHz, −80 °C): $\delta$ 0.7, 5.0, 9.5, 9.8 ($BCH_3$), 30.0, 45.9, 99.8, 112.0, 113.7, 128.3, 136.8, 137.7, 148.1, 167.4. $^{19}$F NMR ($CD_2Cl_2$, 470.25 MHz, −80 °C): $\delta$ −135.3 (d, $J_{FF}$ = 20 Hz), −165.5 (t, $J_{FF}$ = 19 Hz), −168.3 (t, $J_{FF}$ = 19 Hz). Ion pair complex: $^{19}$F NMR ($CD_2Cl_2$, 470.25, −80 °C): $\delta$ −166.4 (t, 6F, $J_{FF}$ = 19 Hz), −161.6 (t, 3F, $J_{FF}$ = 20 Hz), −136.2 (d, 6F, $J_{FF}$ = 20 Hz).

**[($\eta^5$-$C_5H_5$)$_2$Zr(*cis*-$CH_2SiMe_2CH_2CH{=}CHCH_3$][MeB($C_6F_5$)$_3$] (13).** $^1$H NMR ($CD_2Cl_2$, 499.85 MHz, 499.85 MHz, −80 °C) coordinated anion: $\delta$ −0.05 (s, 6H, $Si(CH_3)_2$), 0.33 (s, 3H, $BCH_3$), 1.37 (d, 2H, $SiCH_2CHCH$), 1.42 (d, 3H, $CHCHCH_3$), 1.53 (s, 2H, $ZrCH_2$), 5.37 (m, 2H, $SiCH_2CHCHCH_3$), 6.25 (s, 10H, Cp*H*). $^{19}$F NMR ($CD_2Cl_2$, 282.15 MHz, −80 °C): $\delta$ −166.3 (t, $J_{FF}$ = 23 Hz), −161.5 (t, $J_{FF}$ = 23 Hz), −136.2 (d, $J_{FF}$ = 23 Hz); coordinated olefin: $\delta$ −0.04 (s, shoulder on larger peak from coordinated anion, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$), 1.16 (d, 1H, ZrC*H*H, $J_{HH}$ = 12.9 Hz), 1.90 (d, 3H, $CHCH_3$, $J_{HH}$ = 6.3 Hz), 2.93 (d, 1H, ZrCH*H*, $J_{HH}$ = 12.9 Hz), 4.68 (m, 1H, $CHCH_3$), 6.34 (s, 5H, Cp*H*), 6.56 (s, 5H, Cp*H*), 7.10 (m, 1H, $CH_2CH$).

**[($\eta^5$-$C_5H_5$)$_2$Zr($CH_2SiMe_2CH_2C(CH_3){=}CH_2$][MeB($C_6F_5$)$_3$] (14).** $^1$H NMR ($CD_2Cl_2$, 499.85 MHz, −80 °C): 0.11 (s, 3H, $Si(CH_3)(CH_3)$), 0.26 (d, 3H, $CHCHCH_3$, $J_{HH}$ = 5.5 Hz), 0.39 (s, 3H, $BCH_3$), 0.41 (s, 3H, $Si(CH_3)(CH_3)$), 0.64 (d, 1H, ZrC*H*H,

$J_{HH}$ = 13.5 Hz), 2.05 (d, 1H, ZrCH*H*, $J_{HH}$ = 13 Hz), 2.12 (d of d, 1H, SiC*H*HCHCH, $J_{HH}$ = 9 Hz, $J_{HH}$ = 4 Hz), 2.24 (d, 1H, SiC*H*HC($CH_3$)$CH_2$, $J_{HH}$ = 10 Hz), 2.52 (overlapping, 1H, $SiCH_2C(CH_3)CHH$, $J_{HH}$ = 6.5), 2.52 (s, 1H, $SiCH_2C(CH_3)CHH$, $J_{HH}$ = 6.5 Hz), 5.46 (d, 1H, CHC*H*$CH_3$, $J_{HH}$ = 5.5 Hz), 6.49 (s, 5H, Cp*H*), 6.61 (s, 5H, Cp*H*). $^{13}$C NMR ($CD_2Cl_2$, 125.70 MHz, −80 °C): $\delta$ 1.8, 3.0, 10.1, 31.7, 39.2, 52.5, 90.9, 115.6, 116.1, 129.1, 136.3 (d, $J_{CF}$ = 242 Hz), 137.9 (d, $J_{CF}$ = 239 Hz), 148.0 (d, $J_{CF}$ = 236 Hz). $^{19}$F NMR ($CD_2Cl_2$, 470.25 MHz, −80 °C): $\delta$ −168.3 (t, $J_{FF}$ = 19 Hz), −165.5 (t, $J_{FF}$ = 19 Hz), −135.3 (d, $J_{FF}$ = 20 Hz).

**[{(SiMe$_2$)$_2$($\eta^5$-C$_5$H$_3$)$_2$}Zr(CH$_2$CMe$_2$CH$_2$CH=CH$_2$)][B(C$_6$F$_5$)$_4$] (18-MeBArF$_3$).** $^1$H NMR ($C_6D_5Cl$, 499.85 MHz, −50 °C): $\delta$ −0.05 (s, 6H, SiC$H_3$), 0.05 (s, 6H, SiC$H_3$), 1.44 (s, 3H, BC$H_3$), 2.71 (2H, d, C*H*H, $J_{HH}$ = 7.5 Hz), 3.07 (2H, d, CH*H*, $J_{HH}$ = 15.0 Hz), 5.83 (s, 1H, Cp*H*), 5.88 (s, 1H, Cp*H*), 5.97 (m, 1H, $CH_2CHCH_2$ 6.05 (s, 2H, Cp*H*), 6.38 (s, 2H, Cp*H*). $^{13}$C NMR ($CD_2Cl_2$, 125.70 MHz, −80 °C): $\delta$ −4.6, 3.0, 10.9, 24.6, 69.3, 107.2, 107.8, 108.0, 108.2, 111.6, 132.8, 142.4, 135.5, 137.0 (d, $J_{CF}$ = 240 Hz), 138.2 (d, $J_{CF}$ = 241 Hz), 149.1 (d, $J_{FF}$ = 231 Hz).

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**Supporting Information Available:** $^1$H NMR spectra for compounds **1**, **1-*d*$_2$**, **2**, **3**, **4**, **5**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **17**, and **18**, together with those portions of the spectra for **14** that were simultaed with gNMR; details of the X-ray crystal structure determination for [[{1,2-(SiMe$_2$)$_2$($\eta^5$-C$_5$H$_3$)$_2$Zr]$_2$($\mu_2$-Br)$_2$][B(C$_6$F$_5$)$_4$]$_2$ (**15**), including tables of crystal data, atomic coordinates, bond distances and angles, and structure factors. This material is available free of charge via the Internet at http://pubs.acs.org.

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