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Agostic Zr···Cβ–Si Interactions in $Cp'_2Zr(CH_2CH_2SiMe_3)(L)^+$ Complexes (L = THF, CH_3CN, PMe_3). Evidence for an Organometallic γ-Silicon Effect

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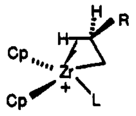
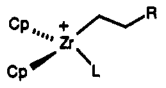
The reaction of $[Cp'_2Zr(H)(THF)][BPh_4]$ ($Cp' = C_5H_4Me$) with vinyltrimethylsilane yields $[Cp'_2Zr(CH_2CH_2SiMe_3)(THF)][BPh_4]$ (**3**), which has been characterized by spectroscopic methods and single-crystal X-ray diffraction. Crystal data for **3**: space group $Pna2_1$, $a = 17.188(4)$ Å, $b = 14.199(4)$ Å, $c = 16.170(10)$ Å, $V = 3930.3(4.5)$ Å^3, $Z = 4$, $R = 0.057$, $R_w = 0.079$. The alkyl group of **3** is highly distorted (Zr–Cα–Cβ (84(1)°), Zr–Cβ 2.57(2) Å); however, the $SiMe_3$ group lies in the O–Zr–Cα–Cβ plane, suggesting that strong agostic Zr···Hβ interactions are absent. The alkyl group distortion of **3** is proposed to result from overlap of the back lobe of the Cβ–Si bond with the Zr LUMO. This direct Zr···Cβ–Si interaction is analogous to the stabilization of silyl-substituted carbocations by the "γ-silicon effect" and appears to be stronger than the Zr···Hβ agostic interactions observed previously for $Cp'_2Zr(CH_2CH_2R)(L)^+$ alkyls. Reaction of **3** with PMe_3 and CH_3CN yields $[Cp'_2Zr(CH_2CH_2SiMe_3)(PMe_3)][BPh_4]$ (**5**) and $[Cp'_2Zr(CH_2CH_2SiMe_3)(CH_3CN)][BPh_4]$ (**6**, two isomers), which, on the basis of spectroscopic parallels with **3**, are assigned analogous Zr···Cβ–Si structures. **3**, **5**, and **6** are resistant to β-H elimination; however, **6** undergoes CH_3CN insertion yielding $Cp'_2Zr\{N{=}C(CH_2CH_2SiMe_3)(CH_3)\}(L)^+$ (**7**, L = CH_3CN; **8**, L = $PMePh_2$, two isomers).

Introduction

Distorted hydrocarbyl ligand structures are a general feature of electrophilic $Cp_2Zr(R)(L)^+$ and $Cp_2Zr(R)^+$ complexes.[1] Simple $Cp_2Zr(CH_2CH_2R)(L)^+$ alkyl complexes (**1**) containing σ-donor L ligands (PR_3, RCN) usually adopt β-agostic structures in which three-center, two-electron Zr···Hβ–C interactions reduce the electron deficiency at Zr.[2,3] Similarly, $Cp_2Zr(CH_2Ph)(CH_3CN)^+$ complexes adopt η^2-benzyl structures in which Zr···Ph interactions stabilize the electron deficient metal center.[4] Replacement of PMe_3 or RCN with a π-donor ligand (THF) or anion (Cl^-) results in normal hydrocarbyl structures (**2**), as the Zr–L or Zr–X π-interaction utilizes the empty Zr orbital required for the agostic interaction. Agostic Zr···Hβ interactions were observed in base-free zwitterions $Cp^*_2Zr^+(m\text{-}C_6H_4B^-Ph_3)$ and were proposed to explain NMR data for $Cp_2Zr(CH_3)(\text{picoline})^+$ species.[5] Agostic Zr···$SiCH_3$ and Zr···Cl–Si interactions have also been observed in related cationic systems.[6] Base-free $Cp_2Zr(R)^+$ ions, which are active species in Cp_2ZrX_2-based olefin polymerization catalysts, likely adopt β-H agostic ground-state structures, and there is evidence for the involvement of α-H agostic interactions in olefin insertion transition states.[7]



1, L = PR_3, RCN



2, L = THF, Cl^-

During studies of β-H agostic $Cp'_2Zr(CH_2CH_2R)(L)^+$ complexes ($Cp' = C_5H_4Me$),[2a] we prepared several $SiMe_3$-substituted alkyls $Cp'_2Zr(CH_2CH_2SiMe_3)(L)^+$.[2a] The spectroscopic and reactivity properties of these cations differ from those of β-H agostic alkyl analogues, suggesting that the $Zr–CH_2CH_2SiMe_3$ ligands might be distorted in a different manner. In this paper we describe more detailed studies which indicate that $Cp'_2Zr(CH_2CH_2SiMe_3)(L)^+$ complexes are stabilized by agostic Zr···Cβ–Si interactions which are reminiscent of the "γ-silicon" effect in carbocation chemistry.[8]

Results and Discussion

Synthesis and Structure of $Cp'_2Zr(CH_2CH_2SiMe_3)(THF)^+$ (3). Hydrogenolysis of $Cp'_2Zr(CH_3)(THF)^+$ or $Cp'_2Zr(CH_2Ph)(THF)^+$ yields the soluble hydride intermediate $Cp'_2Zr(H)(THF)^+$ (eq 1), which provides general

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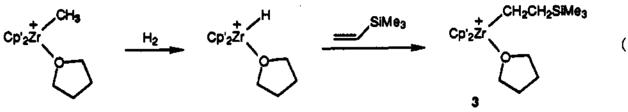
access to cationic alkyls via olefin insertion.[9,10] Reaction of $Cp'_2Zr(H)(THF)^+$ with vinyltrimethylsilane in THF yields $Cp'_2Zr(CH_2CH_2SiMe_3)(THF)^+$ (**3**, 100% NMR), which precipitates as a yellow solid and is isolated in 82% yield (eq 1). The analogous reaction with $Cp'_2Zr(D)(THF)^+$ (prepared from $Cp'_2Zr(R)(THF)^+$ and D_2) yields $Cp'_2Zr(CH_2CHDSiMe_3)(THF)^+$ (**3**-d_1). There is no evidence for the (unknown) 2,1 insertion product $Cp'_2Zr\{CH(SiMe_3)CH_3\}(THF)^+$.[11] Complex **3** decomposes slowly (2 days, 23 °C) in CH_2Cl_2 via chloride abstraction to yield $Cp'_2Zr(CH_2CH_2SiMe_3)Cl$ (**4**), which can also be prepared cleanly via reaction of **3** with $[NMe_4]Cl$.[12]



(1)

NMR data for **3** (Table 1) indicate that the alkyl group is distorted in some fashion. The $ZrCH_2CH_2Si$ ^1H NMR resonance appears at δ −0.99, shifted considerably upfield from the corresponding resonance for neutral chloride analogue **4** (δ −0.06), in which the $CH_2CH_2SiMe_3$ group almost certainly has a normal structure. The $ZrCH_2CH_2Si$ ^{13}C NMR resonance for **3** also appears at relatively high field (δ −3.25, vs 21.7 for **4**). The $Zr–CH_2$ J_{CH} value (141 Hz) is significantly larger than the values for undistorted Zr–alkyl complexes (115–120 Hz; 116 Hz for **4**), suggesting an acute Zr–C–C angle (J_{CH} = ca. 133 Hz for cyclobutanes, ca. 160 Hz for cyclopropanes).[13] The J_{CH} value for the β-CH_2 (111 Hz) is somewhat smaller than the value observed for **4** (116 Hz) or for $Si–CH_2$ groups in organosilicon compounds (117–123 Hz).[14] The ^1H NMR spectrum of **3** at 200 K is very similar to that at ambient temperature, the only significant difference being a slight upfield shift of the $ZrCH_2CH_2$ resonance to δ −1.22. The ^{29}Si resonance for **3** appears at δ 10.8, somewhat downfield of that for $Me_3SiCH_2CH_3$ (δ 1.6).

The NMR data for **3** are similar to data for β-H agostic $Cp'_2Zr(CH_2CH_2R)(L)^+$ (L = PMe_3, RCN) complexes.[2] However, ^1H NMR spectra of solutions containing **3** and **3**-d_1 show no evidence of an isotopic perturbation of resonance (IPR) effect, suggesting that the vibrational frequencies of the two C–H bonds do not differ.[15] IR spectra (KBr) of **3** do not exhibit low-frequency bands attributable to ν_{CH} modes, suggesting that $Zr\cdots H\beta–C$ interactions are not present. In contrast, large IPR effects were observed for suitably labeled $Cp'_2Zr(CH_2CH_2R)(L)^+$ (L = PMe_3, RCN) complexes, and the IR spectrum of $Cp'_2Zr(CH_2CH_3)(PMe_3)^+$ exhibits low-energy ν_{CH} bands for the agostic $Zr\cdots H\beta–C$.[2] While it is well-known that many agostic systems do not exhibit IPR effects or low-frequency IR ν_{CH} bands,[3] the fact that such effects *are* observed for well-characterized β-agostic $Cp'_2Zr(CH_2CHR)(L)^+$ complexes which are very similar to **3** suggests that **3** does not have a β-H agostic structure.

X-ray Structural Analysis of 3. To determine the nature of the alkyl group distortion, **3** was subjected to a single-crystal X-ray diffraction study. X-ray data, positional parameters, and selected bond distances and angles are listed in Tables 2–4. An ORTEP view of the cation of **3** is shown in Figure 1; the BPh_4^- anion is normal. The refinement was complicated by disorder involving one of the Cp′ rings, which was treated successfully using a model with two half-occupied Cp′ orientations (Cp1 and Cp1P in the tables; see Experimental Section for details). For clarity, only one orientation is shown in Figure 1. The $Cp'_2Zr(CH_2CH_2SiMe_3)(THF)^+$ cation adopts a normal bent metallocene structure in which the alkyl and THF ligands lie in the wedge between the Cp′ ligands. The Zr–O81 distance is long (2.320(11) Å), the THF oxygen is somewhat pyramidal (Zr is 0.65 Å out of the C82–O81–C85 plane), and the C82–O81–C85/C31–Zr–O81 dihedral angle is 32.6°, collectively indicating that there is little if any Zr–O π-bonding.[1,16] The most interesting feature of the cation structure is the distortion of the $Zr–CH_2CH_2SiMe_3$ ligand. The Zr–C31–C32 angle is acute (84(1)°), and there is a close Zr–C32 (Zr–Cβ) contact of 2.57(2) Å. Significantly, the $SiMe_3$ group lies almost perfectly *in* the O81–Zr–C31–C32 plane, which implies that the two β-hydrogens (H32A,B) should be above and below this plane. While only H32A was located, and the positions of both H32A and H32B are not known accurately (see Experimental Section), both clearly lie *out* of the O81–Zr–C31 plane. As the LUMO of a 16-electron $Cp_2Zr(R)(L)^+$ fragment is localized in the L–Zr–R plane, these structural data suggest that the Zr center of **3** interacts primarily with the β-carbon rather than with the β-hydrogens of the $CH_2CH_2SiMe_3$ group. The cationic metal center is stabilized by interaction with the back lobe of the Cβ–Si bond ("γ-silicon effect", vide infra), as represented by the resonance structures in Chart 1. Consistent with this interpretation, the Cβ–Si bond is slightly longer (1.92(2) Å) than the Si–Me bonds (1.82(2)–1.85(2) Å) and the Cα–Cβ bond is somewhat short (1.49(5) Å), although the uncertainties in these parameters are large. The Zr–Cβ–Si angle of **3** (174.1°) is nearly linear. For comparison, the bridging H of the β-H agostic complex $Cp'_2Zr(CH_2CH_3)(PMe_3)^+$ lies in the $CH_2–Zr–P$ plane, and NMR experiments establish similar structures for $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$ complexes.[2] The Zr–Cβ contact in $Cp'_2Zr(CH_2CH_3)(PMe_3)^+$ (2.629(9) Å) is slightly longer than that in **3**.

The NMR data for **3** are for the most part consistent with the X-ray diffraction results and the proposed $Zr\cdots C\beta–Si$ interaction. In particular, the large $J_{C\alpha–H}$ value is consistent with the acute Zr–C–C angle, and the lack of an observable IPR effect is consistent with symmetrical placement of the β-hydrogens above and below the O–Zr–C–C plane. The small $J_{C\beta–H}$ value may result from the interaction of the β-carbon with two electropositive

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(10) The counterion is BPh_4^- for all compounds. Throughout this paper Cα refers to the C bonded to Zr, and Cβ refers to the C which is β to Zr and, for **3–6**, bonded to Si.

(11) In contrast, reactions of $Cp_2Zr(\eta^2\text{-pyridyl})^+$ complexes with vinyltrimethylsilane proceed via 2,1 insertion. Guram, A. S.; Jordan, R. F. *Organometallics* **1990**, *9*, 2190.

(12) Several β-silylalkyl Zr compounds are known including $\{Cp^*Zr(Cl)[CH_2CH_2Si(SiMe_3)_3](\mu\text{-}Cl)\}_2$ and $CpCp^*Zr[CH_2CH_2Si(SiMe_3)_3](Cl)$. Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284.

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(14) Selected ^{13}C NMR data for organosilicon compounds are as follows. (a) $Si(CH_2CH_3)_4$: δ 2.86 (q, J_{CH} = 117 Hz, $SiCH_2$), 7.19 (t, J_{CH} = 125 Hz, CH_3). (b) $CH_2{=}CHSiMe_3$: δ 140.9 (d, J_{CH} = 135 Hz, $=CH$), 131.5 (t, J_{CH} = 158.3 Hz, $=CH_2$), −1.08 (q, J_{CH} = 119 Hz, $Si(CH_3)_3$).

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Table 1. ^{1}H and ^{13}C NMR Data[a]

compound (solvent)	^{1}H	assignment	^{13}C	assignment
$\mathrm{Cp'_2Zr(CH_2CH_2SiMe_3)(THF)^+}$ (**3**) ($\mathrm{CD_2Cl_2}$, ^{13}C at 273 K)	5.93 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	123.5 (s)	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	5.83 (m, 4H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	115.1 (d, 172)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	5.73 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	111.5 (d, 172)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	3.59 (m, 4H)	$\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$	109.6 (d, 175)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.05 (s, 6H)	$\mathrm{C_5H_4C}\mathit{H}_3$	105.0 (d, 174)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	1.91 (m, 4H)	$\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$	77.7 (t, 151)	$\mathrm{O(}\mathit{C}\mathrm{H_2CH_2)_2}$
	1.80 (AA′XX′, 2H)	$\mathrm{ZrC}\mathit{H}_2$	46.0 (t, 141)	$\mathrm{Zr}\mathit{C}\mathrm{H_2}$
	0.24 (s, 9H)	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$	26.1 (t, 136)	$\mathrm{O(CH_2}\mathit{C}\mathrm{H_2)_2}$
	−0.99 (AA′XX′, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	15.0 (q, 128)	$\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$
			−1.45 (q, 120)	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$
			−3.25 (t, 111)	$\mathit{C}\mathrm{H_2SiMe_3}$
$\mathrm{Cp'_2Zr(CH_2CH_2SiMe_3)Cl}$ (**4**) ($\mathrm{CD_2Cl_2}$)	6.14 (q, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	126.4	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	6.00 (q, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	116.8	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	5.85 (m, 4H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	112.3	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.19 (s, 6H)	$\mathrm{C_6H_4C}\mathit{H}_3$	111.8	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.92 (AA′XX′, 2H)	$\mathrm{ZrC}\mathit{H}_2$	108.3	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.71 (AA′XX′, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	45.9 (t, 116)	$\mathrm{Zr}\mathit{C}\mathrm{H_2}$
	−0.06 (s, 9H)	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$	21.7 (t, 116)	$\mathit{C}\mathrm{H_2SiMe_3}$
			15.4 (q, 126)	$\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$
			−2.0 (q, 118)	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$
$\mathrm{Cp'_2Zr(CH_2CH_2SiMe_3)(PMe_3)^+}$ (**5**) ($\mathrm{CD_2Cl_2}$, ^{13}C at 233 K)	5.72 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	121.1 (s)	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	5.65 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	110.8 (d, 174)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	5.50 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	107.5 (d, 171)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	5.43 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	104.6 (d, 171)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.03 (s, 6H)	$\mathrm{C_5H_4C}\mathit{H}_3$	101.6 (d, 174)	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	1.37 (d, 9H)	$\mathrm{P(C}\mathit{H}_3\mathrm{)_3}$	33.2 (t, 143)	$\mathrm{Zr}\mathit{C}\mathrm{H_2}$
	1.28 (AA′XX′, 2H)	$\mathrm{ZrC}\mathit{H}_2$	15.1 (q, 130)	$\mathrm{P(}\mathit{C}\mathrm{H_3)_3}$
	0.22 (s, 9H)	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$	14.7 (q, 128)	$\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$
	−2.15 (AA′XX′, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	−0.81 (q, 119)	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$
			−16.9 (t, 110)	$\mathit{C}\mathrm{H_2SiMe_3}$
$\mathrm{Cp'_2Zr(CH_2CH_2SiMe_3)(CH_3CN)^+}$ (**6**-Major) ($\mathrm{CD_2Cl_2}$, 240 K)	5.83 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	135.4	$\mathrm{N}\mathit{C}\mathrm{CH_3}$
	5.78 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	122.2	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	5.75 (br m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	111.8	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	5.66 (br m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	110.1	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.01 (s, 6H)	$\mathrm{C_5H_4C}\mathit{H}_3$	107.0	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	1.64 (AA′XX′, 2H)	$\mathrm{ZrC}\mathit{H}_2$	106.0	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	1.55 (s, 3H)	$\mathrm{NCC}\mathit{H}_3$	42.6 (t, 141)	$\mathrm{Zn}\mathit{C}\mathrm{H_2}$
	0.20 (s, 9H, major)	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$	14.9 (q, 128)	$\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$
	−1.55 (AA′XX′, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	2.40 (q, 138)	$\mathrm{NC}\mathit{C}\mathrm{H_3}$
			−0.70 (q, 119)	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$
			−10.58 (t, 111)	$\mathit{C}\mathrm{H_2SiMe_3}$
$\mathrm{Cp'_2Zr(CH_2CH_2SiMe_3)(CH_3CN)^+}$ (**6**-minor) ($\mathrm{CD_2Cl_2}$, 240 K)	5.52 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	122.1	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	5.49 (m, 4H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	113.1	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	5.34 (m, 2H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	110.2	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	1.92 (s, 6H)	$\mathrm{C_5H_4C}\mathit{H}_3$	109.0	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	1.41 (AA′XX′, 2H)	$\mathrm{ZrC}\mathit{H}_2$	104.3	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.19 (s, 9H)	$\mathrm{Si(C}\mathit{H}_3\mathrm{)_3}$	43.8	$\mathrm{Zr}\mathit{C}\mathrm{H_2}$
	−0.72 (s, 3H)	$\mathrm{NCC}\mathit{H}_3$	14.7	$\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$
	−2.04 (AA′XX′, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	−0.78	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$
			−9.14	$\mathit{C}\mathrm{H_2SiMe_3}$
$\mathrm{Cp'_2Zr\{N{=}C(CH_3)(CH_2CH_2SiMe_3)\}(CH_3CN)^+}$ (**7**)	6.08–6.01 (m, 8H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$		
	2.22–2.17 (m, 2H)	$\mathrm{{=}C(CH_3)C}\mathit{H}_2$	184.5	$\mathrm{{=}}\mathit{C}\mathrm{(CH_3)CH_2}$
	2.05 (s, 6H)	$\mathrm{C_5H_4C}\mathit{H}_3$	125.6	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	1.95 (s, 3H)	$\mathrm{{=}C(C}\mathit{H}_3\mathrm{)CH_2}$	112.9	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.59–0.55 (m, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	109.1	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.01 (s, 9H)	$\mathrm{CH_2Si(C}\mathit{H}_3\mathrm{)_3}$	36.6 (t, 129)	$\mathrm{{=}C(CH_3)}\mathit{C}\mathrm{H_2}$
			28.0 (q, 128)	$\mathrm{{=}C(}\mathit{C}\mathrm{H_3)CH_2}$
			15.1 (q, 127)	$\mathrm{(CH)_4C}\mathit{C}\mathrm{H_3}$
			13.3 (t, 114)	$\mathit{C}\mathrm{H_2SiMe_3}$
			−1.7 (q, 120)	$\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$
$\mathrm{Cp'_2Zr\{N{=}C(CH_3)(CH_2CH_2SiMe_3)\}(PPh_2Me)^+}$ (**8**) (4/5 ratio of isomers, $\mathrm{CD_3CN}$)	7.60–7.35 (m)	$\mathrm{PPh_2Me + BPh_4^-}$	185.9	$\mathrm{{=}}\mathit{C}\mathrm{(CH_3)CH_2}$
	5.88 (m, 4H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	185.3	$\mathrm{{=}}\mathit{C}\mathrm{(CH_3)CH_2}$
	5.80 (m, 4H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	126.6	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	5.72 (m, 4H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	125.8	$\mathrm{(CH)_4}\mathit{C}\mathrm{CH_3}$
	5.65 (m, 4H)	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	112.0	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.30 (AA′XX′, 2H)	$\mathrm{{=}CC}\mathit{H}_2$	111.6	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.27 (AA′XX′, 2H)	$\mathrm{{=}CC}\mathit{H}_2$	108.9	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.15 (s, 3H)	$\mathrm{{=}CC}\mathit{H}_3$	108.5	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.12 (s, 3H)	$\mathrm{{=}CC}\mathit{H}_3$	108.0	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	2.03 (m, 9H)	$\mathrm{CpC}\mathit{H}_3\mathrm{ + PPh_2Me}$	107.9	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.91 (AA′XX′, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	107.8	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.85 (AA′XX′, 2H)	$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$	107.7	$\mathrm{(}\mathit{C}\mathrm{H)_4CCH_3}$
	0.18 (s, 9H)	$\mathrm{CH_2Si(C}\mathit{H}_3\mathrm{)_3}$	40.0	$\mathrm{{=}C(CH_3)}\mathit{C}\mathrm{H_2}$
	0.13 (s, 9H)	$\mathrm{CH_2Si(C}\mathit{H}_3\mathrm{)_3}$	37.6	$\mathrm{{=}C(CH_3)}\mathit{C}\mathrm{H_2}$
			28.7	$\mathrm{{=}C(}\mathit{C}\mathrm{H_3)CH_2}$
			26.0	$\mathrm{{=}C(}\mathit{C}\mathrm{H_3)CH_2}$

Table 1 (Continued)

compound (solvent)	^1H	assignment	^{13}C	assignment
			15.4	PPh_2Me
			15.2	CH_2SiMe_3
			15.0	$(CH)_4CCH_3$
			14.8	$(CH)_4CCH_3$
			14.3	CH_2SiMe_3
			−1.87	$Si(CH_3)_3$

[a] Spectra of cationic complexes contain resonances for free BPh_4^-. Spectra are recorded at 23 °C unless indicated otherwise.

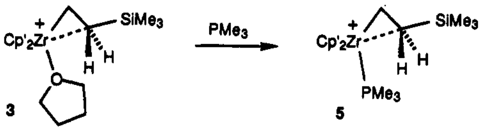
Table 2. Summary of Crystallographic Data for $[(C_5H_4Me)_2Zr(CH_2CH_2SiMe_3)(THF)][BPh_4]$ (3)

empirical formula	$C_{45}H_{55}BOSiZr$
formula wt	742.05
cryst size, mm	0.12 × 0.20 × 0.67 mm
cryst color	pale yellow
space group	$Pna2_1$
a, Å	17.188(4)
b, Å	14.199(4)
c, Å	16.170(10)
V, Å^3	3930.3(4.5)
Z	4
d(calcd), g/cm^3	1.254
cell dimens	20 reflns, 15–26° 2θ
radiation	Mo Kα (λ = 0.710 73 Å)
temp, K	295
scan ratio, $2\theta/\omega$	2.0
scan limit	2–50°
scan speed	0.75–5.5° min^{-1}
scan range	0.7 + 0.35 tan θ
octants sampled	half sphere
no. of reflns collected	11 129
no. of unique reflns	3885
decay (F^2)	<4.5%
agreement between equiv reflns	3.9% on F
no. of reflns with $I > 2\sigma(I)$	1418
μ, cm^{-1}	3.35
abs corr (emp on F)	max 1.00, min 0.918
structure soln	Patterson + DIRDIF
refinement	see text
data/parameter	1418/149
R^a	0.041, 0.057 (see text)
R_w^b	0.051, 0.079 (see text)
wt (Killean and Lawrence)^c	P = 0.04, Q = 0.0
SDOUW^d	1.08
max parameter shifted/esd	0.11
max resid electron density (e/Å^3)	0.6

[a] $R = \sum\Delta F_H/\sum F_{o,H}$ where H = h,k,l and F_o is scaled to F_{calc}. $\Delta F = \|F_o| - |F_c\|$. [b] $[R_w]^2 = \sum w(\Delta F_H)^2/\sum w(F_{o,H})^2$. [c] Killean and Lawrence weights = $1/(S^2 + (PF)^2 + Q)$, where S is the ESD from counting statistics. If several octants are averaged, S is the larger of the two estimates, one based on counting statistics, the other based on the agreement between equivalent reflections. ESD = estimated standard deviation (Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1750). [d] SDOUW = standard deviation in observation of unit weight.

elements,[17] but is also consistent with the presence of weak Zr···Hβ interactions, although as indicated above such interactions were not detected by IR or IPR studies.

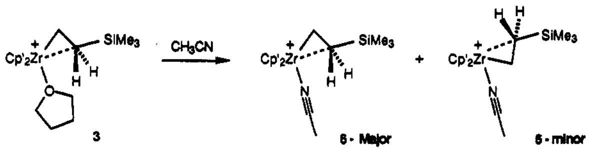
Synthesis and Solution Structure of $Cp'_2Zr(CH_2CH_2SiMe_3)(PMe_3)^+$ (5). To probe the generality of the structural properties of 3, the synthesis of related $Cp'_2Zr(CH_2CH_2SiMe_3)(L)^+$ complexes with L ligands of different electronic and steric properties was investigated. The THF ligand of 3 is readily replaced by PMe_3, yielding $Cp'_2Zr(CH_2CH_2SiMe_3)(PMe_3)^+$ (5) (100% NMR, <1 min, −78 °C, eq 2). Complex 5 is more soluble than 3 and is isolated by recrystallization from THF/hexane in 81% yield. Spectroscopic data for 5 are consistent with a distorted structure analogous to that of 3; key data include high-field β-CH_2 ^1H (δ −2.15) and ^{13}C (δ −16.9) NMR resonances and a large $J_{C\alpha-H}$ value (143 Hz). No IPR effect is observed in the ^1H NMR spectra of solutions containing 5 and $Cp'_2Zr(CH_2CHDSiMe_3)(PMe_3)^+$ (5-d_1). Very low temperature (−125 °C) ^1H NMR spectra of 5 in mixed CD_2Cl_2/THF-d_8 solvent show only one set of signals, consistent with the existence of a single isomer.[18] No low-frequency ν_{CH} bands are observed in the IR spectrum of 5. By analogy to 3, a structure with a Zr···Cβ–Si interaction occupying the central coordination site, as shown in eq 2, is likely.



(2)

Complex 5 is resistant to β-H elimination at ambient temperatures, even in the presence of potential trapping ligands. In contrast, analogous simple $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$ alkyl complexes undergo facile β-H elimination below 23 °C, yielding $Cp'_2Zr(H)(PMe_3)_2^+$ in the presence of excess PMe_3.[2]

Synthesis and Solution Structure of $Cp'_2Zr(CH_2CH_2SiMe_3)(CH_3CN)^+$ (6). Dissolution of 3 in neat CH_3CN, or reaction of 3 with excess CH_3CN in CH_2Cl_2 solution, results in immediate displacement of THF and formation of the mono-CH_3CN complex $Cp'_2Zr(CH_2CH_2SiMe_3)(CH_3CN)^+$ (6, eq 3). Complex 6 decomposes slowly at 23 °C, but can be isolated as described in the Experimental Section. Low-temperature NMR studies (CD_2Cl_2) indicate that 6 exists as a mixture of two isomers (6-Major, 6-minor) which adopt distorted alkyl structures analogous to those of 3 and 5. Key spectroscopic features for 6-Major include (i) high-field β-CH_2 ^1H (δ −1.55) and ^{13}C (δ −10.6) NMR resonances, (ii) a large $J_{C\alpha-H}$ value (141 Hz) and small $J_{C\beta-H}$ value (111 Hz), and (iii) the absence of an observable IPR effect for a solution containing equimolar 6-Major and 6-Major-d_1. NMR data for 6-minor are similar; however, it was not possible to perform IPR studies or to determine accurate J_{CH} values for this minor species.



(3)

The 6-Major/6-minor isomer ratio is a function of the temperature at which 6 is generated from 3. When the solution is maintained at 0 °C during conversion, the 6-Major/6-minor ratio is ca. 1/1. However, when the solution is warmed to 23 °C during the synthesis, the ratio increases to ca. 6/1. Exchange between 6-Major and

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[17] J_{CH} values for μ-CH_2R groups vary considerably depending on the nature of the bridging interaction and the hybridization at C. (a) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Langhauser, F. *Organometallics* **1992**, *11*, 3517. (b) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427.

[18] Very rapid exchange between endo and exo isomers, perhaps catalyzed by free PMe_3, cannot be ruled out.

Table 3. Atomic Coordinates (×10⁴) for $[(C_5H_4Me)_2Zr(CH_2CH_2SiMe_3)(THF)][BPh_4]$ (3)

	x	*y*	*z*	*B*,[a] Å²
Zr	2338.4(0.7)	99.9(0.9)	0 (fixed)	3.91(5)*
Si	4876(2)	494(3)	−599(4)	4.7(2)*
O81	2448(5)	−1182(7)	−882(8)	4.6(5)*
C31	3431(9)	966(13)	178(13)	6(1)*
C32	3794(10)	271(14)	−397(13)	4.9(9)*
C33	5039(11)	1690(15)	−1037(15)	7(1)*
C34	5385(12)	449(15)	394(14)	7(1)*
C35	5326(10)	−452(14)	−1283(13)	6(1)*
C82	3099(11)	−1841(13)	−933(13)	6.2(4)
C83	2808(12)	−2674(15)	−1441(16)	7.9(6)
C84	1972(14)	−2613(16)	−1379(17)	8.7(6)
C85	1759(11)	−1587(14)	−1229(14)	6.5(4)
B	−1306(9)	−88(11)	960(10)	3.5(3)

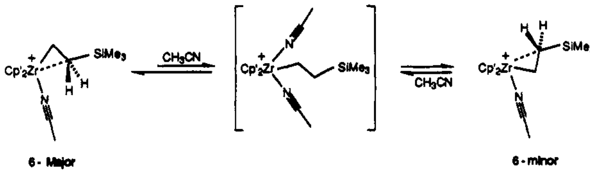
Atomic Coordinates (×10⁴) for Atoms in Rigid Groups[b,c]

	Cp1 *n* = 1	Cp1P *n* = 2	Cp2 *n* = 3	Ph1 *n* = 4	Ph2 *n* = 5	Ph3 *n* = 6	Ph4 *n* = 7
Cn1							
x	2794(24)	2553(31)	1756(16)	−809(17)	−773(18)	−1542(19)	−2134(11)
y	−410(47)	116(35)	1744(22)	−1091(21)	698(33)	342(22)	−296(26)
z	1506(54)	1564(55)	−167(17)	839(45)	1506(29)	19(12)	1478(23)
Cn2							
x	2029(33)	1730(25)	1138(16)	−640(19)	−255(19)	−987(13)	−2572(17)
y	9(43)	182(41)	1071(23)	−1656(43)	392(30)	817(24)	473(14)
z	1544(55)	1392(58)	−46(22)	1526(27)	2120(33)	−460(20)	1759(28)
Cn3							
x	1498(28)	1492(29)	1126(16)	−190(19)	165(19)	−1185(13)	−3305(17)
y	−588(45)	−686(38)	449(23)	−2471(43)	1052(30)	1146(24)	328(14)
z	1142(54)	976(57)	−751(19)	1430(27)	2585(33)	−1249(20)	2122(28)
Cn4							
x	1936(28)	2168(29)	1736(16)	92(17)	69(18)	−1939(19)	−3600(11)
y	−1376(45)	−1284(38)	739(23)	−2722(21)	2016(33)	1002(22)	−587(26)
z	778(54)	935(57)	−1308(19)	648(45)	2436(29)	−1558(12)	2204(23)
Cn5							
x	2737(33)	2824(25)	2126(16)	−77(19)	−449(19)	−2495(13)	−3162(17)
y	−1265(43)	−788(41)	1542(23)	−2157(43)	2321(30)	527(24)	−1356(14)
z	1033(55)	1283(58)	−947(22)	−39(27)	1821(33)	−1079(20)	1923(28)
Cn6							
x	3542(320)	3056(323)	1983(203)	−528(19)	−870(19)	−2296(13)	−2429(17)
y	−12(388)	882(368)	2541(229)	−1342(43)	1662(30)	197(24)	−1210(14)
z	1902(392)	1978(393)	432(227)	57(27)	1356(33)	−291(20)	1560(28)

[a] Starred values denote atoms refined anisotropically; nonstarred atoms were refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] Cp1 and Cp1P are the disordered, half-occupied Cp′ groups. [c] The errors are propagated errors from the rigid group errors and are to be used only in computing errors in distances from an atom in a rigid group to an atom not in the rigid group.

6-minor is slow on the laboratory time scale at 23 °C. However, addition of CH_3CN to a CD_2Cl_2 solution containing both isomers results in rapid and complete conversion to 6-Major. This observation implies that isomer exchange is catalyzed by added nitrile, and that 6-Major is the thermodynamically more stable isomer. By analogy to the X-ray-determined structure of 3, we assign 6-Major the "Cβ-inside" structure in eq 3, in which the Zr⋯Cβ–Si interaction occupies the central coordination site; 6-minor is assigned the "Cβ-outside" structure.[19] The fact that two isomers are observed for 6, while only one isomer is observed for 3 and 5, is attributed to the low steric requirements of the CH_3CN ligand, which permit the η^2-$CH_2CH_2SiMe_3$ ligand to pivot toward the center of the Cp'_2Zr wedge to minimize $Cp'/CH_2CH_2SiMe_3$ steric interactions in the apparently disfavored "Cβ-outside" isomer.

Reaction of simple $Cp'_2Zr(CH_2CH_2R)(CH_3CN)^+$ alkyl complexes with excess CH_3CN results in initial formation of bis-CH_3CN complexes $Cp'_2Zr(CH_2CH_2R)(CH_3CN)_2^+$ which adopt normal alkyl structures. The bis-nitrile complex $Cp'_2Zr(CH_2CH_2SiMe_3)(CH_3CN)_2^+$ is probably an intermediate in the CH_3CN-catalyzed 6-Major/6-minor exchange (eq 4), but is not observed.



(4)

CH_3CN Insertion of 6. In the presence of excess CH_3CN, 6 (generated *in situ* from 3) undergoes CH_3CN insertion yielding $Cp'_2Zr\{N{=}C(CH_2CH_2SiMe_3)(Me)\}(CH_3CN)^+$ (7, 100% NMR, 82% isolated, eq 5). This reaction is 80% complete after 4 h at 20 °C in neat CH_3CN and is somewhat slower in CD_2Cl_2 solution containing 4 equiv of CD_3CN ($t_{1/2}$ = 4.7 h, 20 °C). Characteristic spectroscopic features for 7 include a low-field ^{13}C NMR imino carbon resonance (δ 184.5) and IR $\nu_{C=N}$ and $\nu_{C\equiv N}$ absorbances. Complex 6 reacts similarly with $PMePh_2$ in CD_2Cl_2 solution to yield $Cp'_2Zr\{N{=}C(CH_2CH_2SiMe_3)(Me)\}(PMePh_2)^+$ (8, 100% NMR, <24 h, 23 °C), which was characterized spectroscopically (eq 5). NMR studies show that $PMePh_2$ does not displace the CH_3CN ligand of 6; therefore, a mechanism involving initial insertion of 6, followed by trapping of the intermediate $Cp'_2Zr\{N{=}C(CH_2CH_2SiMe_3)(Me)\}^+$ species, is likely. Complex 8 is also formed by a ligand-exchange reaction of 7 with $PMePh_2$ (eq 5). The ^1H and ^{13}C NMR spectra establish that 8 exists as a mixture of two isomers, as expected for a structure in which the

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[19] Attempts to confirm these assignments by NOE experiments were unsuccessful.

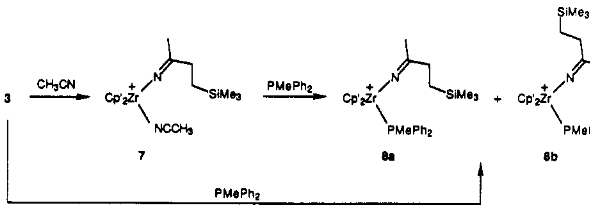
Table 4. Selected Bond Distances (Å) and Angles (deg) for $[(C_5H_4Me)_2Zr(CH_2CH_2SiMe_3)(THF)][BPh_4]$ (3)

Zr–C11	2.66(4)	Zr–C11P	2.56(4)
Zr–C12	2.56(4)	Zr–C12P	2.48(4)
Zr–C13	2.48(4)	Zr–C13P	2.44(4)
Zr–C14	2.54(4)	Zr–C14P	2.50(4)
Zr–C15	2.65(4)	Zr–C15P	2.57(4)
Zr–C21	2.55(4)	Zr–Cp1cen[a,b]	2.27
Zr–C22	2.48(4)	Zr–Cp1Pcen	2.21
Zr–C23	2.46(4)	Zr–Cp2cen	2.20
Zr–C24	2.52(4)		
Zr–C25	2.58(4)		
Zr–C31	2.26(2)	C82–C83	1.52(3)
Zr–C32	2.57(2)	C83–C84	1.44(3)
Zr–O81	2.320(11)	C84–C85	1.52(3)
C31–C32	1.49(5)	C85–O81	1.43(2)
Si–C32	1.92(2)	C–C(Cp')	1.44 fixed
Si–C33	1.85(2`	C11–C16	1.54 fixed
Si–C34	1.82(2)	C11P–C16P	1.54 fixed
Si–C35	1.83(2)	C21–C26	1.54 fixed
O81–C82	1.46(2)		

O81–Zr–C31	115.9(5)
O81–Zr–Cp1cen	97, 106
O81–Zr–Cp2cen	106
C31–Zr–Cp1cen	105, 102
C31–Zr–Cp2cen	101
Cp1cen–Zr–Cp2cen	133, 126
C32–Si–C33	111.3(9)
C32–Si–C34	109(1)
C32–Si–C35	107.4(8)
C33–Si–C34	107(1)
C33–Si–C35	113(1)
C34–Si–C35	109.4(9)
Zr–C31–C32	84(1)
C31–C32–Si	113(1)
C85–O81–C82	111(1)
O81–C82–C83	106(1)
C82–C83–C84	104(2)
C83–C84–C85	108(2)
C84–C85–O81	105(2)
C–C–C(Cp')	108 fixed
C–C–CH$_3$(Cp')	126 fixed

[a] C1n and C1nP are the two disordered, half-occupied Cp' groups. [b] Cpcen is a Cp' ring centroid.

Zr—N=C(CH$_2$CH$_2$SiMe$_3$)(Me) ligand lies in the plane between the Cp' ligands to maximize Zr—N π-bonding.



(5)

There is no evidence for competitive β-H elimination processes in the above reactions. This is in contrast to the behavior of simple Cp'$_2$Zr(CH$_2$CH$_2$R)(CH$_3$CN)$^+$ alkyl complexes which react with CH$_3$CN via β-H elimination and subsequent Zr–H insertion of CH$_3$CN, yielding Cp'$_2$Zr{N=C(H)CH$_3$}(CH$_3$CN)$^+$ and CH$_2$=CHR. For the ethyl derivative Cp'$_2$Zr(CH$_2$CH$_3$)(CH$_3$CN)$_n$$^+$, the insertion and β-H elimination pathways are competitive.[2b]

Bonding Considerations. To elucidate the nature of the Zr–alkyl group bonding in Cp'$_2$Zr(CH$_2$CH$_2$SiMe$_3$)(L)$^+$ complexes **3**, **5**, and **6**, extended Hückel calculations on the model complex Cp$_2$Zr(CH$_2$CH$_2$SiH$_3$)(H$_2$O)$^+$ (**9**), were performed.[20] The structure of model species **9** was based on the X-ray-determined structure of **3**. The O–Zr–C–C–Si framework is identical to that of **3**; however, the Cp ligands were eclipsed, (Zr–centroid = 2.21 Å; Cp–Zr–Cp angle = 130°), the H$_2$O ligand was oriented such that the hydrogens lie in the C–Zr–O plane to preclude Zr–O π bonding (H–O–H angle = 104°, Zr–O = 2.30 Å), and the methylene hydrogens of the CH$_2$CH$_2$SiH$_3$ ligand were placed symmetrically above and below the Zr–C–C–Si plane (H–C–H angles = 110°).

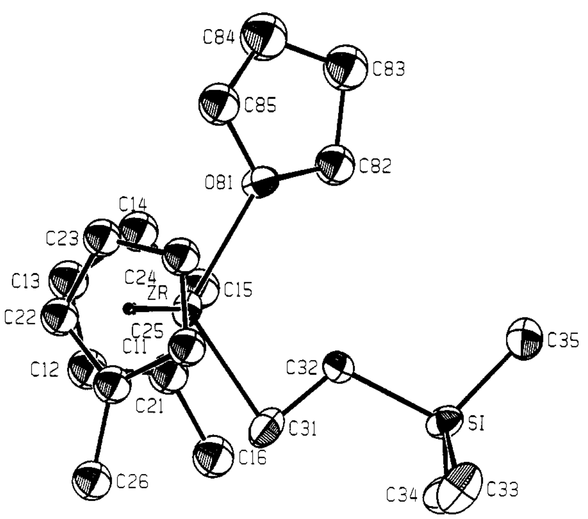
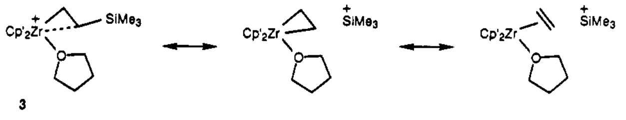


Figure 1. ORTEP view of the (C$_5$H$_4$Me)$_2$Zr(CH$_2$CH$_2$SiMe$_3$)(THF)$^+$ cation (**3**) showing the distorted CH$_2$CH$_2$SiMe$_3$ ligand. The C11–C16 ring is disordered between two orientations; only one is shown for clarity.

Chart 1



The molecular orbitals of **9** are constructed from those of Cp$_2$Zr(H$_2$O)$^{2+}$ and $^-$CH$_2$CH$_2$SiH$_3$ fragments. The important frontier orbitals and the coordinate system chosen for this study are shown in Figure 2. The frontier orbitals of Cp$_2$Zr(H$_2$O)$^{2+}$ are d hybrids which, as expected, are very similar to those of Cp$_2$ZrCl$^+$.[21] The second-lowest unoccupied orbital of this fragment, labeled Zrσ in Figure 2 (xy 35%, $x^2 - y^2$ 20%, z^2 7%), contains a large lobe pointing toward the empty coordination site and is thus a σ acceptor orbital. The LUMO, labeled Zrπ ($x^2 - y^2$ 60%, xy 13%, z^2 11%), is a π acceptor orbital with respect to this site. As for the LUMO of Cp$_2$ZrCl$^+$, the two lobes of Zrπ which point toward the vacant coordination site are unequal in size, with the "outside" lobe larger than the "inside" lobe. A set of three empty orbitals with high Zr d character (xz, z^2, and yz) lies above Zrσ, and a set of four filled Zr–Cp bonding orbitals (including the HOMO) lies below; neither set is important for our analysis. There are two important frontier orbitals of the $^-$CH$_2$CH$_2$SiH$_3$ anion. The HOMO, labeled Cn in Figure 2, is the Cα lone pair orbital (Cα x 42%, Cα y 34%) admixed in an antibonding

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[20] For pertinent calculations on metallocene systems, see: (a) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6432. (b) Lauher, J. U.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (c) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. (d) Zhu, L.; Kostic, N. M. *J. Organomet. Chem.* **1987**, *335*, 395. (e) Sontag, C.; Berke, H.; Sarter, C.; Erker, G. *Helv. Chim. Acta* **1989**, *72*, 1676. (f) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788.

[21] (a) Hyla-Kryspin, I.; Gleiter, R.; Krüger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517. (b) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153. See also: (c) Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R.; Gleiter, R.; Fischbach, U.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4996.

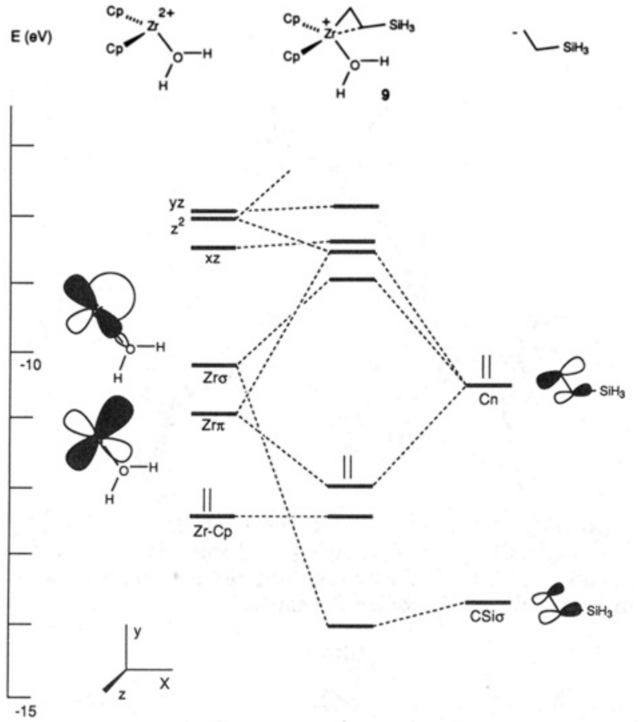


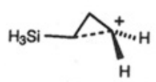
Figure 2. Frontier orbitals of the model species $Cp_2Zr(CH_2CH_2SiH_3)(H_2O)^+$ (**9**) derived by interaction of the frontier orbitals of $Cp_2Zr(H_2O)^{2+}$ and $H_3SiCH_2CH_2^-$ fragments. Results are based on EHMO calculations.

sense with the C–Si bond (total Cβ p 11%, total Si p 7%). This orbital is a π-donor orbital, with the "outside" lobe larger than the "inside" lobe, and has proper symmetry to interact with Zrπ. The second-highest occupied orbital, labeled CSiσ, is a C–Si σ-bonding orbital (Cβ *x* 34%, Cβ *y* 12%, Si *x* 13%, Si *y* 5%) which is mixed (in a bonding sense) with the Cα lone pair orbital (Cα *y* 20%, Cα *x* 3%). CSiσ is a σ-donor orbital with proper symmetry to mix with Zrσ.

Zrπ and Cn mix strongly (overlap population 0.346) producing the HOMO of **9** and an antibonding orbital which mixes further with a higher empty $Cp_2Zr(H_2O)^+$ orbital (Zr z^2). Zrσ and CSiσ also mix (overlap population 0.170), resulting in stabilization of CSiσ and substantial destabilization of Zrσ, which becomes the LUMO of **9**. The interaction of Zrσ with Cn and the interaction of Zrπ with CSiσ are both weak and slightly antibonding due to the symmetry mismatches. Thus a key feature of the electronic structure of **9** is the interaction of the Cβ–Si σ-bond (via its contributions to the Cn and CSi donor orbitals of $^-CH_2CH_2SiH_3$) with the Zr acceptor orbitals. The origin of this interaction can be traced to the difference in electronegativity between C and Si, which results in a large Cβ character in the C–Si σ bond.[22]

Comparison with Other Systems. The stabilization of the Zr^+ center in $Cp_2Zr(CH_2CH_2SiMe_3)(L)^+$ complexes by agostic Zr···Cβ–Si interactions as discussed above is very similar to the stabilization of carbocation (or incipient carbocation) centers by suitably oriented γ-SiR_3 substituents (i.e., by SiR_3 substituents located on the carbon β to the C^+ center). This "γ-silicon effect" has been ascribed to overlap of the back lobe of the Si–C bond with the empty (or reacting) p orbital on the carbocation (or incipient carbocation) as illustrated in **10**. In a classic study, Shiner and co-workers showed that *cis*-3-(trimethylsilyl)cyclohexyl *p*-bromobenzenesulfonate undergoes accelerated solvolysis because the intermediate carbocation is stabilized by such a 1,3 $R_3SiC\cdots C^+$ interaction.[23,24] This effect is absent in the trans isomer, which undergoes normal solvolysis.[25] Theoretical calculations show that $H_3SiCH_2CH_2CH_2^+$ favors a distorted structure (**11**) in which the close $H_3SiC\cdots C^+$ contact (1.75 Å calculated) reflects stabilization of the C^+ center by the electron rich H_3SiCH_2.[26] The structure/bonding properties of **3**, **5**, and **6** and these organosilicon species are very similar.

10



11

Based on the above analysis, it is expected that other M–CH_2CH_2–M′ systems containing electron deficient (M) and electropositive and thus inductively electron donating (M′) metal combinations might exhibit distorted structures in which the C–M′ bond interacts with an empty orbital on M. There are indeed several examples in which distorted alkyl group structures can be rationalized by this bonding model. Some years ago, Kaminsky, Sinn, et al. isolated from Cp_2ZrX_2/AlR_3 systems a remarkable series of compounds in which distorted $-C_2-$ units link Zr and Al centers.[27] One of the most interesting is $[(C_5H_5)_2Zr(CH_2CH(AlEt_2)_2][C_5H_5]$ (**12**), in which the cation and anion are ion-paired via C_5H_5/Al interactions.[28] As illustrated in the drawing of **12**, the Zr–C–C–Al framework of the $(C_5H_5)_2Zr(CH_2CH(AlEt_2)_2^+$ cation is highly distored by a Zr···Cβ–Al interaction. The Zr–C–C angle is highly acute (75.7(3)°), and there is a close Zr–Cβ (2.393(4) Å) contact. The β-carbon is electron rich due to the presence of two electropositive Al substituents, and one $AlEt_2$ group lies within 0.3 Å of the Zr–C–C plane, allowing effective overlap of the back lobe of this Cβ–Al bond with an acceptor orbital on Zr (Al–Cβ–Zr angle 158.6°). The β-H lies far out of the Zr–C–C–Al plane, and the Zr–Hβ distance is long (2.64(6) Å), indicating that there is not a strong Zr–Hβ interaction. Thus the bonding in this cation is similar to that proposed above for the $Cp'_2Zr(CH_2CH_2SiMe_3)(L)^+$ systems. Very similar structures were established for $(C_5H_5)_2Zr\{CH_2CH(AlEt_2)_2\}Cl$ and $(C_5H_5)_2Zr(ClAlEt_3)CH_2CH_2Zr(ClAlEt_3)(C_5H_5)_2$; in these cases agostic Zr···Cβ–Al and Zr···Cβ–Zr interactions stabilize the electron

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[22] Modification of **9** to an undistorted structure (Zr–Cα–Cβ angle = 109°) results in a small increase in the Zr–Cα reduced overlap population (0.459 to 0.562), loss the Zr–Cβ overlap, a slight increase in the Cβ–Si reduced overlap population (0.613 to 0.643), and a small decrease in the total interfragment reduced overlap population (0.393 to 0.366).

[23] (a) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842. (b) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S.; Halley, K. A. *J. Org. Chem.* **1990**, *55*, 653.

[24] The "γ-effect" has also been referred to as a "percaudal interaction" and as "homohyperconjugation". (a) Davis, D. D.; Black, R. H. *J. Organomet. Chem.* **1974**, *82*, C30. (b) Davis, D. D.; Johnson, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7576. (c) Grob, C. A.; Gründel, M.; Sawlewicz, P. *Helv. Chim. Acta* **1988**, *71*, 1502.

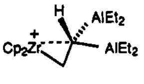
[25] Related examples: (a) Shiner, V. J., Jr.; Ensinger, M. W.; Rutkowske, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 804. (b) Shiner, V. J., Jr.; Ensinger, M. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 7199. (c) Kirmse, W.; Söllenböhmer, F. *J. Am. Chem. Soc.* **1989**, *11*, 4127. (d) Grob, C. A.; Sawlewicz, P. *Tetrahedron Lett.* **1987**, *28*, 951. (e) Lambert, J. B.; Salvador, L. A.; So, J.-H. *Organometallics* **1993**, *12*, 697.

[26] Davidson, E. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 3135.

[27] (a) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (c) Kaminsky, W.; Sinn, H. *Justus Liebigs Ann. Chem.* **1975**, 424. (d) Kaminsky, W.; Vollmer, H.-J. *Justus Liebigs Ann. Chem.* **1975**, 438.

[28] Kopf, J.; Vollmer, H.-J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 271.

deficient Zr centers and Zr–Hβ interactions appear not to be present.[29]



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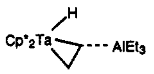
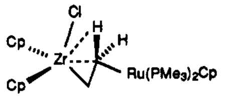


13



14

Somewhat related to the Kaminsky/Sinn complexes are the $Cp^*_2M(H)(CH_2CH_2AlR_3)$ adducts (M = Ta, Nb, R = Me, Et) formed by reaction of $Cp^*_2M(H)(\eta^2\text{-}CH_2CH_2)$ with AlR_3.[30] The X-ray structure of $Cp^*_2Ta(H)(CH_2CH_2AlEt_3)$ (**13**) revealed a near planar H–Ta–C–C–Al framework, an acute Ta–Cα–Cβ angle (76(1)°), a slightly longer Ta–Cβ distance (2.31(2) Å) vs the Ta–Cα distance (2.18(2) Å), and a fairly linear Ta–Cβ–Al arrangement (163.8(9)°). This structure can be represented as a Ta–Cβ–Al agostic zwitterion $Cp^*_2Ta^+(H)CH_2CH_2Al^-Et_3$; however, the long Al–Cβ distance (2.25(2) Å vs Al–Et (1.98 Å)) indicates that the β-carbon interacts more strongly with Ta than with Al.

More recently, Bullock and co-workers have characterized the Zr/Ru dimetalloethane complex $Cp_2Zr(Cl)CH_2CH_2Ru(PMe_3)_2Cp$ (**14**) by X-ray diffraction.[31] The alkyl ligand is highly distorted (Zr–C–C 82.5(6)°; Zr–Cβ 2.549(9) Å), and there is a close Zr···Hβ–C contact (2.19(2) Å), even though the hydrogen lies 0.7 Å out of the Zr–C–C plane. NMR and IR studies confirm the presence of a Zr···Hβ–C agostic interaction. However, the Cl, Zr, Cα, Cβ, and Ru atoms are coplanar to within 0.05 Å, so that the back lobe of the Cβ–Ru bond is positioned for optimal interaction with the Zr LUMO. As there are no apparent steric constraints which would prevent rotation about the Cα–Cβ bond to place a β-H in the Zr–C–C plane where the Zr···Hβ interaction would be optimized, it appears that a Zr···Cβ–Ru interaction is also present. The Zr···Hβ and Zr···Cβ–Ru interactions are apparently closely balanced in this complex.[32]

Relative Strengths of Agostic Interactions and Implications for Reactivity. The studies described above provide strong evidence that $Cp'_2Zr(CH_2CH_2SiMe_3)(L)^+$ complexes are stabilized by direct Zr···Cβ–Si interactions in which the electron rich β-carbon donates electron density to the unsaturated Zr center via overlap of the back lobe of the Cβ–Si bond and the Zr LUMO. Additional weak Zr···Hβ interactions may also be present. The fact that **3** and, presumably **5** and **6** adopt structures which maximize the Zr···Cβ–Si interaction at the expense of the Zr···Hβ agostic interaction implies that Zr···Cβ–Si interactions are stronger than Zr···Hβ interactions in this class of compound. Steric factors (i.e., interaction of the $SiMe_3$ and Cp′ groups) probably do not play a decisive role in determining the structures of **3** and its analogues, as equally crowded $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$ (R = Et, ᵗBu, Ph, etc.) complexes adopt β-H agostic structures in which the R substituent must point toward a Cp′ ligand.[2] Similarly, the isobutyl species $Cp'_2Zr(CH_2CHMe_2)(PMe_3)^+$, which contains two substituents on the β-carbon, also adopts a Zr···Hβ agostic structure.[2c] Several other observations confirm that a Zr···Cβ–Si interaction is stronger than a Zr···Hβ agostic interaction. Zirconocene complexes **2** with simple hydrocarbyl R ligands invariably adopt normal alkyl structures because formation of a Zr–O or Zr–Cl π bond is favored over formation of a three-center, two-electron Zr···Hβ–C bond. In contrast **3** adopts a Zr···Cβ–Si-bridged structure at the expense of a Zr–O π bond. Similarly, $(C_5H_5)_2Zr\{CH_2CH(AlEt_2)_2\}Cl$ and **14** exhibit distorted Zr···Cβ–M structures at the expense of Zr–Cl π-bonding. The Zr···Hβ interactions in $Cp'_2Zr(CH_2CH_2R)(CH_3CN)^+$ species are displaced by coordination of a second CH_3CN ligand and formation of $Cp'_2Zr(CH_2CH_2R)(CH_3CN)_2^+$ complexes with normal alkyl groups; in contrast, as noted above **6** undergoes exchange with free CH_3CN, but does not form an isolable bis-CH_3CN adduct.

The Zr···Cβ–Si interactions in **3**, **5**, and **6** strongly influence the reactivity of these complexes. The β-H agostic $Cp'_2Zr(CH_2CH_2R)(L)^+$ species (L = CH_3CN, PMe_3) undergo rapid β-H elimination in the presence of excess L. In contrast, **5** is resistant to β-H elimination, and in the presence of excess CH_3CN or $PMePh_2$, **6** undergoes only CH_3CN insertion. The absence of β-H elimination from **3**, **5**, and **6** is surprising as the inductive electron donation from the $SiMe_3$ group[33] might have been expected to promote β-H elimination.[34] Evidently, the strong Zr···Cβ–Si interaction, which constrains the β-hydrogen to be out of the O–Zr–C–C plane, inhibits this process.[35]

Experimental Section

All manipulations were performed under N_2 or vacuum using a Vacuum Atmospheres drybox or a high vacuum line as described elsewhere.[36] Solvents were purified by initial distillation from an appropriate drying/deoxygenating agent, stored in evacuated bulbs and vacuum transferred to NMR tubes or reaction vessels.[37] NMR spectra were obtained on Bruker AC-300, WM-360, or AMX-600 instruments; data are listed in Table 1. Spectra of cationic complexes contain resonances for free BPh_4^-. ^1H NMR (CD_2Cl_2): δ 7.37 (m, 8 H), 7.04 (t, J = 7 Hz, 8 H), 6.89 (t, J = 7 Hz, 4 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 164.3 (q), 136.2, 126.0, 122.2. ^{31}P NMR spectra are referenced vs external H_3PO_4, and ^{29}Si spectra are referenced vs external $SiMe_4$. IR spectra (KBr) were recorded on a Matson Cygnus 25 instrument. Elemental analyses were performed by Analytische Laboratorien.

$[Cp'_2Zr(CH_2CH_2SiMe_3)(THF)][BPh_4]$ (3). A solution of $[Cp'_2Zr(H)(THF)][BPh_4]$ in THF, prepared by hydrogenolysis of $[Cp'_2Zr(CH_3)(THF)][BPh_4]$ (0.550 g, 0.751 mmol),[9] was degassed and filtered, and excess vinyltrimethylsilane was added by vacuum transfer at -78 °C. The solution was stirred at 23 °C for 1.5 h, during which time a yellow precipitate formed. The solution volume was reduced to ca. 10 mL. The precipitate was collected by filtration, washed with cold THF, and dried under vacuum, producing 0.457 g (82%) of pale yellow solid. Anal. Calcd for $C_{45}H_{55}BOSiZr$: C, 72.84; H, 7.47; Zr, 12.29. Found: C, 72.67; H, 7.34; Zr, 12.45. Single crystals suitable for X-ray analysis were obtained directly from a nonstirred reaction mixture.

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[29] (a) Kaminsky, W.; Kopf, J.; Thirase, G. *Justus Liebigs. Ann. Chem.* **1974**, 1531. (b) Kopf, J.; Kaminsky, W.; Vollmer, H.-J. *Cryst. Struct. Commun.* **1980**, *9*, 197.

[30] McDade, C.; Gibson, V. C.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1.

[31] (a) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466. (b) Lemke, F. R.; Bullock, R. M. *Organometallics* **1992**, *11*, 4261.

[32] The structure of **14** implies that Zr···Hβ interactions may also be present in **3** even though the β-hydrogens lie out of the Zr–C–C plane; however, as noted in the text, convincing evidence for such interactions was not obtained.

[33] (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; p 17. (b) The $\sigma_I{}^0$ value for $SiMe_3$ is -0.16. See ref 25d and the following: Grob, C. A.; Schaub, B.; Schlageter, M. G. *Helv. Chim. Acta* **1980**, *63*, 57.

[34] Electron donating groups on the β-carbon accelerate β-H elimination. Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

[35] If the thermodynamically preferred isomer **6**-Major is indeed the endo isomer as we have proposed, than isomerization to **6**-minor (the exo isomer) or to an intermediate with a normal $Zr–CH_2CH_2SiMe_3$ structure must precede insertion.

[36] Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992**, *11*, 3098.

[37] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

$[Cp'_2Zr(CH_2CHDSiMe_3)(THF)][BPh_4]$ (3-d_1). 3-d_1 was prepared in the same manner as 3, but D_2 was substituted for H_2. ^{2}H NMR (25 °C, CD_2Cl_2): δ 5.96 (Cp), −0.82 (CHDSi).[38]

Isotopic Perturbation of Resonance for 3. A solution of 3 (0.010 g, 0.013 mmol) and 3-d_1 (0.011 g, 0.015 mmol) in CD_2Cl_2 (0.4 mL) was prepared in a resealable NMR tube, and the ^{1}H NMR spectrum was recorded at 200 and 230 K. $\Delta\delta = (\delta(\beta\text{-C}H_2)$ for 3 − $\delta(\beta\text{-C}H\text{D})$ for 3-d_1) = 0.03 at both temperatures, indicating no IPR effect.

$Cp'_2Zr(CH_2CH_2SiMe_3)Cl$ (4). A slurry of 3 (0.030 g, 0.040 mmol) and $[Me_4N][Cl]$ (0.066 g, 0.62 mmol) in CD_2Cl_2 (0.4 mL) was agitated for 12 h at 23 °C. The ^{1}H NMR spectrum established complete reaction of 3 and clean formation of 5 and free THF. No BPh_4^- resonances were visible as $[Me_4N][BPh_4]$ is insoluble in CD_2Cl_2.

$[Cp'_2Zr(CH_2CH_2SiMe_3)(PMe_3)][BPh_4]$ (5). A slurry of 3 (1.12 g, 1.62 mmol) in 30 mL of THF was prepared and cooled to −196 °C, and PMe_3 (0.41 g, 5.4 mmol) was added via vacuum transfer. The reaction mixture was warmed to 23 °C, and the solid dissolved, yielding a pale lemon yellow solution. The solution was stirred at room temperature for 1 h, concentrated to ca. 15 mL, and transferred to the glovebox. Addition of hexane resulted in precipitation of a pale yellow solid, which was collected and dried under vacuum, yielding 0.98 g (81%) of 4. Anal. Calcd for $C_{44}H_{56}BPSiZr$: C, 70.84; H, 7.57; Zr, 12.23; P, 4.15; Si, 3.76. Found: C, 70.63; H, 7.44; Zr, 12.10; P, 4.07; Si, 3.62. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C): −12.3.

Isotopic Perturbation of Resonance for 5. A solution of 5 and 5-d_1 (labeled in the β position) was prepared by addition of PMe_3 (0.033 mmol) to the solution of 3 and 3-d_1 used for the IPR experiment for 3 (see above). The ^{1}H NMR spectrum was recorded at 190 and 270 K; $\Delta\delta = (\delta(\beta\text{-C}H_2)$ for 5 − $\delta(\beta\text{-C}H\text{D})$ for 5-d_1) = 0.06 and 0.05, respectively, indicating no IPR effect.

$[Cp'_2Zr(CH_2CH_2SiMe_3)(CH_3CN)][BPh_4]$ (6). A slurry of 3 (0.100 g, 0.135 mmol) in CH_3CN (2 mL) was prepared at −78 °C. The mixture was warmed to 23 °C for ca. 1 min and the solid dissolved. The volatiles were removed under vacuum. The process was repeated once more to ensure complete removal of THF. Finally CH_2Cl_2 was added at −78 °C. The solution was warmed to 23 °C for ca. 1 min and all the solid dissolved. The volatiles were removed to ensure the removal of excess CH_3CN. The resulting off-white solid was dried at 23 °C under vacuum for 30 min. The solid was stored at −40 °C as thermal decomposition occurs slowly at 23 °C. ^{1}H NMR analysis of this product (CD_2Cl_2, 235 K) established the 6-Major/6-minor isomer ratio to be 6.1(6). IR (KBr): $\nu_{C\equiv N}$ 2298, 2271 cm^{-1}.

The above procedure was repeated, but the solution was allowed to warm to only 0 °C at each stage, and the final solid was dried at 0 °C. The ^{1}H NMR spectrum (CD_2Cl_2, 235 K) of this product established the 6-Major/6-minor isomer ratio to be 1.2(1).

Isotopic Perturbation of Resonance for 6. A mixture of 3 (0.010 g, 0.0013 mmol) and 3-d_1 (0.010 g, 0.013 mmol) was converted to a mixture of 6-Major and 6-Major-d_1 by the procedure described above. The product was dissolved in CD_2Cl_2 (0.4 mL) at −78 °C and the ^{1}H NMR spectrum recorded at 180, 236, and 270 K. $\Delta\delta = (\delta(\beta\text{-C}H_2)$ for 6-Major − $\delta(\beta\text{-C}H\text{D})$ for 6-Major-d_1) < 0.08 (the width of the multiplet) at all temperatures, indicating no IPR effect.

$[Cp'_2Zr\{N{=}C(CH_3)(CH_2CH_2SiMe_3)\}(NCCH_3)][BPh_4]$ (7). A mixture of 3 (0.900 g, 1.21 mmol) and CH_3CN (50 mL) was prepared at −78 °C and warmed to 23 °C, producing a bright yellow solution. The solution was stirred at 23 °C for 18 h, concentrated to ca. 30 mL, and filtered. The filtrate was evaporated under vacuum, yielding an orange oil. Diethyl ether (ca. 10 mL) was added at −78 °C and the resulting slurry warmed to room temperature. The Et_2O was removed under vacuum, and CH_2Cl_2 (ca. 20 mL) was added at −78 °C. The solution was warmed to room temperature, and the volatiles were removed under vacuum to produce 7 as an amorphous orange solid (0.55 g, 60%). IR (Nujol): $\nu_{C=N}$ 1679; $\nu_{C\equiv N}$ 2310, 2279 cm^{-1}. Anal. Calcd for $C_{45}H_{53}N_2BSiZr$: C, 71.87; H, 7.10; N, 3.72; Zr, 12.13. Found: C, 71.71; H, 6.98; N, 3.62; Zr, 12.40.

$[Cp'_2Zr\{N{=}C(CH_3)(CH_2CH_2SiMe_3)\}(PMePh_2)][BPh_4]$ (8). This species was generated *in situ* (NMR scale) via addition of excess $PMePh_2$ to a solution of 7 in CH_2Cl_2 at −78 °C, warming to 23 °C for 5 min, removal of volatiles under vacuum, and dissolution of the residue in CD_2Cl_2 at −78 °C. Alternatively 8 was generated *in situ* (NMR scale) via reaction of 6 with 1.3 equiv of $PMePh_2$ at 23 °C for 24 h. $^{31}\{^1H\}$ NMR (CD_2Cl_2): δ 10.5 (br s).

X-ray Diffraction Study of 3. The experimental details of the X-ray diffraction data collection using an Enraf-Nonius CAD4 diffractometer are given in Table 2. Special attention was devoted to the location of C32, H32A, and H32B because of the possibility of agostic interactions. Only 29 of 55 hydrogen atoms were initially found from the electron density difference maps, including H31A, H32A, and seven of the $Si(CH_3)_3$ hydrogen atoms. The initial refinement model was as follows: cation, all non-hydrogen atoms anisotropic; anion, all non-hydrogen atoms isotropic; hydrogen atoms, fixed idealized positions; $R = 0.041$, $R_w = 0.051$. Removing H31A,B and H32A,B and refining gave $R = 0.043$ and $R_w = 0.054$. On the electron density difference map at this step, H31A, H31B, and H32A appeared at positions close to their previously calculated positions, but H32B did not appear. The thermal parameters for C16 and the other carbon atoms of the Cp1 group indicated some disorder in the position of this group. At this point we shifted to a rigid group refinement model which treated the apparently disordered Cp1 ring as two half-occupied rigid groups, and the other Cp ring (Cp2) and the four Ph groups of the counterion as rigid groups. Details are given as supplementary material. Refining anisotropically on the non-hydrogen atoms of the cation (except the THF carbon atoms) and isotropically on the remaining non-hydrogen atoms and on H32A and H32B gave $R = 0.057$ and $R_w = 0.079$. Although this model gives higher R values than the initial model, it is believed to be a better representation of the structure. The errors in the H32A and H32B positions are ca. 0.3 Å, so that detailed analysis of these hydrogen atom positions cannot be made. We can conclude, however, that H32A and H32B lie out of the O81–Zr–C31–C32–Si plane. The C31, C32, and Si positions are well determined, and bond distances and bond angles involving these atoms are reliable.

Molecular Orbital Calculations. Calculations were of the extended Hückel type with weighted H_{ij}. Standard orbital exponents and H_{ii} values were used for C, H, O, and Si.[39] Double ζ functions were used for the Zr 4d orbitals; Zr parameters are similar to those used by others: 5s, $H_{ii} = -10.45$ eV, $\zeta = 1.817$; 5p $H_{ii} = -6.684$ eV, $\zeta = 1.776$; 4d $H_{ii} = -11.28$ eV, $\zeta_1 = 3.835$ ($c_1 = 0.6224$), $\zeta_2 = 1.505$ ($c_2 = 0.5782$).[20,21]

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Supplementary Material Available: Additional details of X-ray structure determination for 3 including rigid group model definitions, tables of rigid group coordinates and orientation parameters, anisotropic thermal parameters, H atom coordinates, rigid group H atom coordinates, and BPh_4^- bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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