Cationic Zirconium and Hafnium Isobutyl Complexes as Models for Intermediates in Metallocene-Catalyzed Propylene Polymerizations. Detection of an α-Agostic Interaction in $(C_5Me_5)_2Hf(CH_2CHMe_2)(PMe_3)^+$

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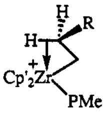
A series of cationic Zr and Hf isobutyl complexes has been prepared to model the $Cp_2M\{CH_2CH(R)(R')\}^+$ and $Cp_2M\{CH_2CH(R)(R')\}(\alpha\text{-olefin})^+$ intermediates in metallocene-catalyzed α-olefin polymerizations (R′ = growing poly(α-olefin) chain). The cationic hydride $[Cp'_2Zr(H)(THF)][BPh_4]$ (**5**, Cp′ = C_5H_4Me) reversibly inserts isobutylene at 23 °C to afford $[Cp'_2Zr(CH_2CHMe_2)(THF)][BPh_4]$ (**6**), in which the isobutyl group adopts a normal structure. The reaction of **6** with PMe_3 yields $[Cp'_2Zr(CH_2CHMe_2)(PMe_3)][BPh_4]$ (**7**) which adopts a β-agostic structure and undergoes β-H elimination above −13 °C. The reaction of the hafnacyclobutane $Cp^*_2Hf(CH_2CHMeCH_2\text{-})$ (**10**) with $[HNBu_3][BPh_4]$ in the presence of PMe_3 yields $[Cp^*_2Hf(CH_2CHMe_2)(PMe_3)][BPh_4]$ (**12**). NMR data, including isotope perturbation of resonance results for deuterium labeled analogues, establish that the isobutyl group of **12** is distorted by an α-agostic interaction. The reaction of **12** with THF, and the reaction of **10** with $[HNBu_3][BPh_4]$ in THF yield $[Cp^*_2Hf(CH_2CHMe_2)(THF)][BPh_4]$ (**14**). Solution NMR data, solid state IR data, and X-ray crystallographic results establish that the isobutyl group of **14** is distorted (Hf–C–C angle 137.5(8)°) but that $Hf\cdots H_\alpha$ agostic interactions are absent. Crystal data for **14**: space group $P2_1/c$, $a = 10.747(3)$ Å, $b = 21.417(3)$ Å, $c = 21.783(8)$ Å, $\beta = 101.83(4)°$, $V = 5365(6)$ Å^3, $Z = 4$, $R = 0.053$, $R_w = 0.086$. **14** undergoes predominant β-Me elimination at 58 °C. The structures of $Cp'_2Hf(^nBu)(L)^+$ (**17**, L = THF, normal butyl group; **19**, L = PMe_3, β-agostic butyl group) are analogous to those of the corresponding $Cp'_2Zr(^nBu)(L)^+$ complexes. The structures and reactivity of **6**, **7**, **12**, and **14** are rationalized in terms of the steric and electronic properties of the $C_5R_5^-$ and L ligands.

We recently reported that cationic zirconocene alkyl complexes $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$ (**1**, Cp′ = C_5H_4Me) and $Cp'_2Zr(CH_2CH_2R)(RCN)^+$ (**2**) adopt β-agostic structures in which the electron deficient metal center is stabilized by $Zr\cdots H_\beta$ interactions.[1-3] Hlatky and Turner had previously observed a β-agostic interaction in the base-free zwitterion $Cp^*_2Zr^+(2\text{-Et-5-}\{B^-(4\text{-EtPh})_3\}\text{-6-}(\mu\text{-H})Ph)$ (**3**).[4] On the basis of these observations, we proposed that the $(C_5R_5)_2Zr(CH_2CH_2R')^+$ and $(C_5R_5)_2Zr(CH_2CH_2R')(ethylene)^+$ intermediates (R′ = growing polyethylene chain) in zirconocene-catalyzed ethylene polymerizations adopt β-agostic structures in the ground state.[5] The structures of these alkyl complexes are sensitive to ligand electronic effects. In particular, $Cp'_2Zr(CH_2CH_2R)(THF)^+$ (**4**) species adopt normal, undistorted alkyl group structures because Zr–O π-bonding utilizes the Zr LUMO required for the $Zr\cdots H_\beta$ interaction.[6,7]



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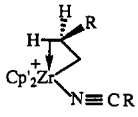

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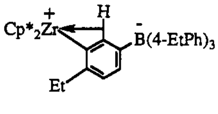

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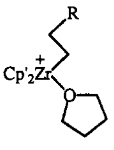

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Little is known about the structures of cationic $Cp_2M\{CH_2CH(R)(R')\}(L)^+$ complexes which contain *two* β-substituents.[8] Species of this type are of interest as models for the $Cp_2Zr\{CH_2CH(R)(R')\}^+$ and $Cp_2Zr\{CH_2CH(R)(R')\}(\alpha\text{-olefin})^+$ intermediates in metallocene-catalyzed α-olefin polymerizations (R′ = growing poly(α-olefin) chain). Analyses of poly- and oligopropylenes prepared by relatively uncrowded metallocene catalysts derived from Cp'_2ZrCl_2, $Me_2Si(C_5H_4)_2ZrCl_2$, $Me_2Si(C_5Me_4)_2ZrCl_2$, and $(indenyl)_2ZrCl_2$, and chiral catalysts derived from $(EBTHI)_2ZrX_2$ (EBTHI = ethylenebis(tetrahydroindenyl)), have shown that the predominant

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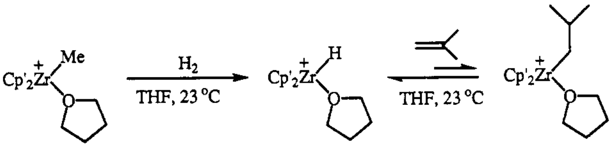
chain transfer process is β-H elimination.[9] This indicates that β-agostic M···H$_\beta$ ground state structures analogous to 1 and 2 are clearly possible for the active $Cp_2Zr\{CH_2CH(Me)(R)\}^+$ and $Cp_2Zr\{CH_2CH(Me)(R)\}(propylene)^+$ cations in these systems. On the other hand, Teuben and Resconi have reported that β-methyl transfer is the predominant chain transfer process in $Cp^*{}_2M(Me)(THT)^+$ (THT = tetrahydrothiophene)-catalyzed propylene oligomerizations and $Cp^*{}_2MCl_2$/MAO-catalyzed propylene polymerizations (M = Zr, Hf).[9a,10] It was proposed that steric interactions between the C_5Me_5 ligands and the M–$CH_2CH(Me)(R)$ chain in the crowded $Cp^*{}_2M\{CH_2CH(Me)(R)\}^+$ species disfavor the M–$CH_2CH(Me)(R)$ conformation leading to β-H elimination. This is consistent with earlier observations that $Cp^*{}_2LuCH_2CHMe_2$ undergoes β-Me elimination[11] and that $Cp^*{}_2Sc(CH_2CH_3)$ adopts a β-agostic structure while the higher $Cp^*{}_2Sc(CH_2CH_2R)$ alkyls do not.[12] These observations suggest that the steric properties of the C_5R_5 ligands strongly influence the structures of $(C_5R_5)_2M\{CH_2CH(R)(R')\}(L)^+$ species and that β-agostic structures are unlikely to be favored when the C_5R_5 ligands are bulky.

Crowded $(C_5R_5)_2M\{(CH_2CH(Me)(R)\}(L)^+$ complexes in which β-agostic structures are disfavored or precluded by steric interactions might be stabilized by agostic M···HC interactions involving α or more remote C–H bonds.[13] Agostic M···H$_\alpha$ interactions have been observed in several crowded M–CH_2SiMe_3, M–CH_2CMe_3, and M–CH_2Ph complexes which, however, lack β-hydrogens.[14–16] On the other hand, while the Zr–CH_2SiMe_3 ligand of $Cp^*{}_2Zr(CH_2SiMe_3)(THF)^+$ is distorted (M–C–C angle = 149.3°, $J_{C_\alpha H}$ = 100.1 Hz), the long Zr–H$_\alpha$ distances appear to rule out significant Zr···H$_\alpha$ interactions.[17] Recent studies by Brintzinger[18] and Bercaw[19] provide strong evidence for the existance of α-agostic interactions in the transition states for α-olefin insertion at metallocene centers.

The isobutyl ligand is the simplest alkyl which reasonably mimics a growing polypropylene chain. Here we describe the synthesis, characterization, and reactivity of a series of cationic isobutyl species of general structure $(C_5R_5)_2M(CH_2CHMe_2)(L)^+$ (M = Zr, Hf). These studies provide insight into how the electronic and steric properties of the C_5R_5 and L ligands influence the structure of $MCH_2CH(R)(R')$ groups in cationic systems of this type.

Results

Synthesis and Characterization of $[(C_5H_4Me)_2Zr(CH_2CHMe_2)(L)][BPh_4]$ (L = THF, PMe$_3$). The cationic hydride complex $[Cp'_2Zr(H)(THF)][BPh_4]$ (5), which is prepared by hydrogenolysis of $[Cp'_2Zr(Me)(THF)][BPh_4]$,[1b,6] reversibly inserts isobutylene at 23 °C to afford $[Cp'_2Zr(CH_2CHMe_2)(THF)][BPh_4]$ (6, eq 1). Complex 6 is stable in the presence of excess isobutylene, but reverts to 5 and isobutylene when the excess olefin is removed, and thus could not be isolated. NMR data for 6 (Table 1) are similar to data for $Cp'_2Zr(CH_2CH_2R)(THF)^+$ complexes 4 and are consistent with a normal, undistorted isobutyl group. Key NMR data for 6 (THF-d_8, 23 °C) include a low field H$_\beta$ resonance (δ 2.50), which is downfield from the H$_\alpha$ resonance (δ 1.15), and normal ^{13}C parameters for C$_\beta$ (δ 36.8, J_{CH} = 126 Hz). The $J_{C_\alpha H}$ value for C$_\alpha$ (δ 87.8, J_{CH} = 112 Hz) is slightly reduced due to the electropositive Zr.[20] Presumably, Zr–O(THF) π-bonding is favored over agostic Zr···H interactions.



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The reaction of 6 with PMe$_3$ in CD_2Cl_2 yields the thermally sensitive PMe$_3$ adduct $[Cp'_2Zr(CH_2CHMe_2)(PMe_3)][BPh_4]$ (7, eq 2), which was characterized by low-temperature NMR spectroscopy. NMR data for 7 are similar to data for 1 and 2 and indicate that the isobutyl group is distorted by a β-agostic interaction. Key NMR data for 7 (CD_2Cl_2, −50 °C) include high field H$_\beta$ (δ −4.03) and C$_\beta$ (δ 11.4) resonances and a reduced $J_{C_\beta H}$ value (90.6 Hz). Additionally, the $J_{C_\alpha H}$ value is large (135 Hz),

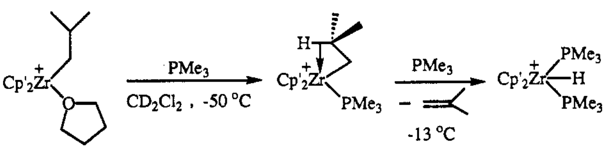

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Table 1. ^{1}H and ^{13}C NMR Data for New Compounds

compd (solvent[a,b]	^{1}H (δ, J values in Hz)	assign	^{13}C (δ, J values in Hz)	assign
$Cp'_2Zr(CH_2CHMe_2)(THF)^+$ (**6**) (THF-d_8)[c]	6.22 (brs, 4H)	C_5H_4Me	126.1 (s)	Cp′
	6.15 (m, 4H)	C_5H_4Me	116.8 (d, J = ca. 180)	Cp′
	2.50 (m, 1H)	β-CH	114.8 (d, J = ca. 180)	Cp′
	2.10 (s, 6H)	C_5H_4Me	87.9 (t, J = 112)	α-CH_2
	1.14 (d, J = 6.6, 2H)	α-CH_2	36.8 (d, J = 126)	β-CH_2
	0.94 (d, J = 6.6, 6H)	γ-CH_3	27.9 (q, J = 125)	γ-CH_3
			14.7 (q, J = 128)	C_5H_4Me
$Cp'_2Zr(CH_2CHMe_2)(PMe_3)^+$ (**7**) (CD_2Cl_2, −50 °C)	5.68 (br s, 2H)	C_5H_4Me	121.0 (s)	Cp′
	5.56 (br s, 6H)	C_5H_4Me	110.4 (d, J = 176)	Cp′
	2.19 (s, 6H)	C_5H_4Me	109.3 (d, J = 173)	Cp′
	1.38 (d, J = 9.0, 9H)	PMe_3	107.7 (d, J = 173)	Cp′
	1.06 (br s, 6H)	γ-CH_3	103.9 (d, J = 173)	Cp′
	0.87 (br s, 2H)	α-CH_2	41.0 (t of d, J_{CH} = 135; J_{CP} = 15)	α-CH
	−4.03 (br s, 1H)	β-CH	27.0 (q, J = 128)	γ-CH
			15.7 (q, J = 126)	C_5H_4Me
			15.2 (q of d, J_{CH} = 129; J_{CP} = 24)	PMe_3
			11.4 (d, J = 90.6)	β-CH
$Cp^*_2Hf(CH_2CHMe_2)(PMe_3)^+$ (**12**)[d] (CD_2Cl_2, −40 °C)	2.89 (m, 1H)	β-CH	121.6 (s)	C_5Me_5
	2.05 (s, 30H)	C_5Me_5	111.4 (t, J = 102)	α-CH_2[e]
	1.39 (d, J = 7.5, 9H)	PMe_3	34.2 (d, J = 126)	β-CH
	0.77 (d, J = 6.4, 6H)	γ-CH_3	28.1 (q, J = 129)	γ-CH_3
	−0.49 (d,d J_{HH} = 6.5; J_{PH} = 2.5, 2H)	α-CH_2	15.4 (q of m, J = 129)	PMe_3
			12.3 (q, J = 128)	C_5Me_5
$Cp^*_2Hf(CH_2CHMe_2)Cl$ (**13**) (CD_2Cl_2)	1.95 (s, 30H)	C_5Me_5	119.5 (s)	C_5Me_5
	0.88 (m, 1H)	β-CH	66.8 (t, J = 113)	α-CH_2
	0.78 (d, J = 6.3, 6H)	γ-CH_3	31.2 (d, J = 130)	β-CH
	0.07 (d, J = 5.9, 2H)	α-CH_2	29.2 (q, J = 125)	γ-CH_3
			14.3 (q, J = 128)	C_5Me_5
$Cp^*_2Hf(CH_2CHMe_2)(THF)^+$ (**14**) (THF-d_8)[c]	2.85 (m, 1H)	β-CH	124.9 (s)	C_5Me_5
	2.03 (s, 30H)	C_5Me_5	90.8 (t, J = 102)	α-CH_2
	1.00 (d, J = 6.5, 6H)	γ-CH	34.8 (t, J = 126)	β-CH
	0.69 (d, J = 7.1, 2H)	α-CH_2	29.0 (q, J = 126)	γ-CH_3
			12.0 (q, J = 127)	C_5Me_5
$Cp'_2Hf(^nBu)(THF)^+$ (**17**) (THF-d_8, −60 °C)	6.47 (br s, 4H)	C_5H_4Me	128 (s)	Cp′
	6.40 (br s, 2H)	C_5H_4Me	115.8 (d, J = 178)	Cp′
	6.37 (br s, 2H)	C_5H_4Me	114.5 (d, J = 178)	Cp′
	2.27 (m, 2H)	C_5H_4Me	112.7 (d, J = 178)	Cp′
	1.60 (m, 2H)	β-CH_2	63.0 (t, J = 113)	α-CH_2
	1.27 (m, 2H)	γ-CH_2	31.8 (t, J = 126)	γ-CH_2
	1.09 (m, 2H)	α-CH_2	35.0 (t, J = 124)	β-CH_2
	0.91 (t, J = 7.1, 3H)	δ-CH_3	14.6 (q, J = 128)	C_5H_4Me, δCH_3
$Cp'_2Hf(^nBu)_2$ (**18**) (THF-d_8)	5.82 (m, 4H)	C_5H_4Me	122.6 (s)	Cp′
	5.79 (m, 4H)	C_5H_4Me	112.0 (d, J = 153)	Cp′
	2.12 (s, 6H)	C_5H_4Me	109.0 (d, J = 164)	Cp′
	1.34 (m, 4H)	β-CH_2	58.0 (t, J = 110)	α-CH_2
	1.12 (m, 4H)	γ-CH_2	35.1 (t, J = 120)	β-CH_2
	0.81 (t, J = 7.2, 6H)	δ-CH_3	31.6 (t, J = 127)	γ-CH_2
	−0.03 (m, 4H)	α-CH_2	14.9 (q, J = 126)	C_5H_4Me
			14.1 (q, J = 123)	δ-CH_3
$Cp'_2Hf(^nBu)(PMe_3)^+$ (**19**) (CD_2Cl_2, −60 °C)[f]	5.73 (s, 4H)	C_5H_4Me	120.8 (s)	Cp′
	5.53 (s, 4H)	C_5H_4Me	108.0 (d, J = 175)	Cp′
	2.06 (s, 6H)	C_5H_4Me	105.2 (d, J = 175)	Cp′
	1.25 (m, obscured)	γ-CH_2	40.5 (t, J = 135)	α-CH_2
	1.15 (br s, 9H)	PMe_3	26.2 (t, J = 128)	γ-CH_2
	0.95 (t, J = 6.8, 3H)	δ-CH_3	15.2 (q, J = 129)	PMe_3
	0.50 (t, J = 7.6, 2H)	α-CH_2	14.6 (q, J = 127)	C_4H_5Me
	−1.50 (t, J = 6.5, 2H)	β-CH_2	14.4 (q, J = 124)	δ-CH_3
			12.6 (t, J = 103)	β-CH_2
$Cp'_2Hf(H)(PMe_3)_2^+$ (**20**) (CD_2Cl_2)	5.38 (m, 8H)	C_5H_4Me	116.6 (s)	Cp′
	3.09 (t, J_{PH} = 95.8, H)	Hf–H	106.8 (d, J = 179)	Cp′
	2.19 (s, 6H)	C_5H_4Me	99.0 (d, J = 174)	Cp′
	1.45 (vir t, J = 0.9, 18H)	PMe_3	19.5 (q of m, J_{CH} = 129)	PMe_3
			15.9 (q, J = 129)	C_5H_4Me

[a] Spectra for **6**, **7**, **12**, and **14** also contain BPh_4^- resonances. Spectra for **17**, **19**, and **20** also contain $B(3,5\text{-}\{CF_3\}_2\text{-}C_6H_3)_4^-$ resonances. [b] Spectra are recorded at 23 °C unless indicated. [c] Exchange of coordinated and free THF and THF-d_8 is rapid on the NMR time scale. [d] Contains ca. 1 equiv of free PMe_3. Exchange of free and coordinated PMe_3 is slow in the NMR time scale. [e] $J_{C_\alpha P}$ = 5 Hz from $\{^1H\}^{13}C$ spectrum. [f] Contains ca. 2 equiv of free PMe_3.

consistent with an acute $Zr–C_\alpha–C_\beta$ angle.[21] Two isomers which differ in the positions of the Zr–C and $Zr\cdots H_\beta$ ligands ("C-inside" and "C outside") are possible for **7**. Low-temperature ^{1}H NMR spectra (to −90 °C) exhibit broadening of the alkyl and $C_5H_4CH_3$ resonances but no splitting, indicating that exchange between the C-inside and C outside isomers is rapid on the NMR time scale (eq 3) or that **7** adopts only one structure in solution.[22] Above −13 °C, **7** undergoes β-H elimination to afford the

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[21] The large J_{CH} value reflects the high s content in the C_α–H bonds which results from the decrease in the $Z–C_\alpha–C_\beta$ angle. For comparison, J_{CH} for cyclobutane is 134 Hz. (a) Aydin, R.; Günther, H. *J. Am. Chem. Soc.* **1981**, *103*, 1301. (b) Yonezawa, T.; Moreshima, I.; Fujii, M.; Fukuii, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1266. (c) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; Chapters 9, 10.

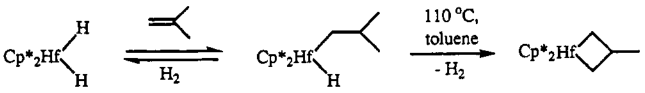
previously characterized hydride complex $Cp'_2Zr(H)(PMe_3)_2^+$ (8) and isobutylene (eq 2).

(3)

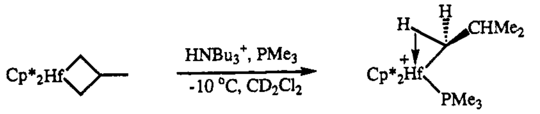
7, C-inside 7, C-outside

Attempted Synthesis of $(C_5Me_5)_2Zr(CH_2CHMe_2)(L)^+$ Species. To probe the influence of C_5R_5 steric properties on the structure of $(C_5R_5)_2Zr(CH_2CHMe_2)(L)^+$ species, the synthesis of Cp* analogues of 7 was explored. We were unable to prepare $Cp^*_2Zr(CH_2CHMe_2)(THF)^+$. For example, $Cp^*_2Zr(H)(THF)^+$, generated in situ by protonolysis of $Cp^*_2ZrH_2$ with $[HNBu_3][BPh_4]$ in THF,[23,24] does not react with isobutylene (>3 equiv) at −60 or 23 °C. Protonolysis of $Cp^*_2Zr(CH_2CHMe_2)(H)$ (9)[25] with $[HNBu_3][BPh_4]$ or $[HNMe_2Ph][BPh_4]$ in THF (<5 min, 23 °C) yields $Cp^*_2Zr(H)(THF)^+$ (100%) and isobutane. Teuben previously reported a similar result for the analogous Hf system.[10] Complex 9 reacts sluggishly with $[Cp'_2Fe][BPh_4]$ in THF (<25%, 24 h, 23 °C) to yield isobutane and unidentified organometallic products.[26]

Synthesis and Characterization of $Cp^*_2Hf(CH_2CHMe_2)(PMe_3)^+$. An alternative possible route to $Cp^*_2M(CH_2CHMe_2)(L)^+$ species is via protonation of $Cp^*_2M(CH_2CHMeCH_2-)$ metallacyclobutanes.[17,24a] Roddick and Bercaw have prepared the hafnacyclobutane $Cp^*_2M(CH_2CHMeCH_2-)$ (10) by thermolysis of $Cp^*_2Hf(CH_2CHMe_2)(H)$ (11) in the presence of excess isobutylene in toluene (eq 4).[27] The reaction of 10 with $[HNBu_3][BPh_4]$ in the presence of PMe_3 (CH_2Cl_2, −10 °C) yields the thermally sensitive cationic PMe_3 adduct $[Cp^*_2Hf(CH_2CHMe_2)(PMe_3)][BPh_4]$ (12, eq 5) which has been characterized spectroscopically. The ^1H and ^{13}C NMR data (CD_2Cl_2, −40 °C) for the $HfCH_2CHMe_2$ group of 12 are normal (H_β, δ 2.90; C_β δ 35.0, $J_{C_\beta H} = 126$ Hz). However, data for the $HfCH_2$ group are unusual: the H_α resonance appears at a higher field (δ −0.48) than the corresponding resonance for 11 (δ −0.21), the C_α resonance appears at a low field (δ 111.1), and the $J_{C_\alpha H}$ value is reduced (102 Hz). At −90 °C, the H_α resonance is shifted upfield (δ −0.61) but is not split. The other ^1H NMR resonances and the ^{31}P resonance also shift slightly but do not split as the temperature is lowered.[28]



11 10 (4)

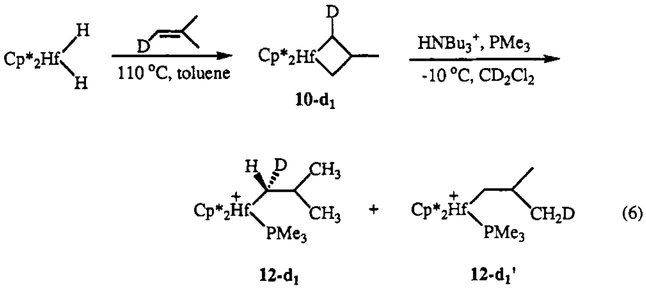


(5)

10 12

One possible explanation for these observations is that the isobutyl group of 12 is distorted by an agostic Hf···H_α interaction, as indicated in eq 5. However, the NMR data alone do not establish that such interactions are present, as steric interactions between the bulky Cp* ligands and the isobutyl group might result in a large Hf–C–C angle and an associated reduced J_{CH} value and unusual ^1H and ^{13}C chemical shifts.[14c,17] To distinguish between these possibilities, isotope perturbation of resonances (IPR) experiments were performed.[29]

The deuterium labeled isobutyl hydride complex $Cp^*_2Hf(CHDCHMe_2)(H)$ (11-d_1) was generated in situ by reaction of $Cp^*_2HfH_2$ and $CHD{=}CMe_2$ and thermolyzed in the presence of excess $CHD{=}CMe_2$ to yield the labeled hafnacyclobutane $Cp^*_2Hf(CHDCHMeCH_2-)$ (10-d_1, eq 6).



10-d_1

(6)

12-d_1 12-d_1'

Protonolysis of 10-d_1 with $[HNBu_3][BPh_4]$ in the presence of PMe_3 in CD_2Cl_2 yielded a solution containing a 1/1 mixture of $Cp^*_2Hf(CHDCHMe_2)(PMe_3)^+$ (12-d_1) and $Cp^*_2Hf\{CH_2CH(CH_2D)(Me)\}(PMe_3)^+$ (12-d_1', eq 6). Variable-temperature ^1H NMR spectra of this solution revealed a substantial IPR effect on the H_α resonance: $\Delta\delta = \delta(\mathbf{12}\text{-}d_1') - \delta(\mathbf{12}\text{-}d_1) = 0.38$ at −10 °C, 0.47 at −50 °C, and 0.58 at −90 °C. The H_α regions of selected ^1H NMR spectra from a representative IPR experiment are shown in Figure 1.[30] For comparison, the $HfCHDCHMe_2$ and $HfCH_2CH(CH_2D)(Me)$ resonances of 12-d_1 and 12-d_1' could not be distinguished.[31] Variable-temperature ^{13}C NMR spectra also revealed an IPR effect on the $J_{C_\alpha H}$ value: at −60 °C, $J_{C_\alpha H} = 91$ Hz for 12-d_1 and 100 Hz for 12-d_1'. These results clearly establish that the two C_α–H bond strengths are different, and thus indicate that a single Hf···H_α agostic interaction is present in the static structure of 12.

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(22) The H_β resonance of 5 shifts slightly upfield to δ −4.46 at −90 °C.

(23) Data for $[Cp^*_2Zr(H)(THF)][BPh_4]$: ^1H NMR (THF-d_8) δ 7.92 (s, 1H, ZrH), 1.98 (s, 30H, Cp*); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 124.5 (C_5Me_5), 12.0 (C_4Me_5). This complex reacts with CH_3CN to yield $[Cp^*_2Zr\{N{=}C(CH_3)(H)\}(CH_3CN)][BPh_4]$: ^1H NMR (CD_3CN) δ 8.56 (q, $J = 4.8$ Hz, 1H=CH), 1.93 (s, 3H, free CH_3CN), 1.84 (s, 30 H, Cp*), 1.81 (d, $J = 4.8$ Hz, 3H, $=CCH_3$).

(24) Synthesis of cationic d^0 metallocene alkyls via protonolysis: (a) Turner, H. W.; Hlatky, G. G. Eur. Pat. Appl. 0 277 003, 1988. (b) Turner, H. W. Eur. Pat. Appl. 0 277 004, 1988. (c) Lin, Z.; LeMarechal, J.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127. (d) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610.

(25) Manriquez, J. M.; McAlister, O. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Soc. Chem.* **1978**, *100*, 2716.

(26) Synthesis of cationic d^0 metallocene alkyls via M–R oxidative cleavage reactions: (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (b) Borkowsky, S. L.; Jordan, R. F.; Hinch; G. D. *Organometallics* **1991**, *10*, 1268.

(27) (a) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97. (b) Roddick, D. M. *Diss. Abstr. Int., B* **1984**, *45*, 1773.

(28) (a) ^1H NMR chemical shifts for 12 at −10 and −90 °C are as follows: Cp* δ 2.07, 2.00; H_α −0.43, −0.61; H_β 2.95, 2.86; H_γ 0.81, 0.72; PMe_3 1.40, 1.47. (b) The ^{31}P resonance of 12 shifts from δ −7.3 at −10 °C to −6.3 at −110 °C.

(29) (a) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558. (b) Calvert, B. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(30) The H_α resonance for 12-d_1 appears as a multiplet with a line width of ca. 12 Hz. This is consistent with the complex splitting pattern expected to result from coupling to $^{31}PMe_3$ ($J_{PH} = 2.5$ Hz), D_α (J_{DH} ca. 2 Hz), and H_β ($J_{HH} = 6.5$ Hz). The H_α resonance for 12-d_1' appears as a slightly broader multiplet (line width ca. 15 Hz) which results from overlap of the (d of d) resonances of the two H_α's, which are slightly diastereotopic due to the neighboring β-CH(Me)(CH_2D) center.

(31) These resonances appear as a multiplet (δ 0.75) with a line width of ca. 14 Hz (0.04 δ). Therefore, the isotope shift is less than this value.

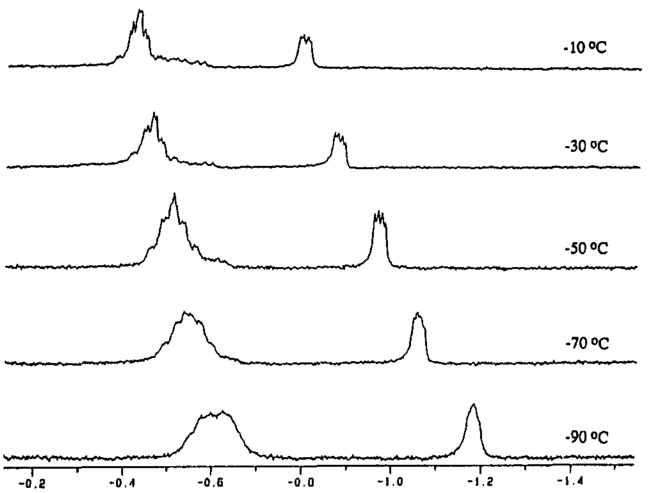
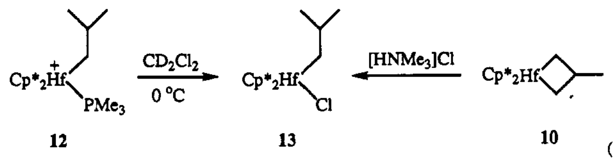


Figure 1. Variable-temperature ^1H NMR spectra (H_α region) of a mixture of $Cp^*_2Hf(CHDCHMe_2)(PMe_3)^+$ (12-d_1) and $Cp^*_2Hf\{CH_2CH(CH_2D)(Me)\}(PMe_3)^+$ (12-d_1'), generated in situ by reaction of 10-d_1 with $[HNBu_3][BPh_4]$. The H_α resonances of 12-d_1 and 12-d_1' appear at ca. δ -1.2 and -0.6, respectively. The Δδ values (in ppm; see text) are as follows: -90 °C, 0.58; -70 °C, 0.52; -50 °C, 0.47; -30 °C, 0.43; -10 °C, 0.38. The multiplet centered at δ -0.51 is due to the β-H of a small amount of unreacted 10-d_1.

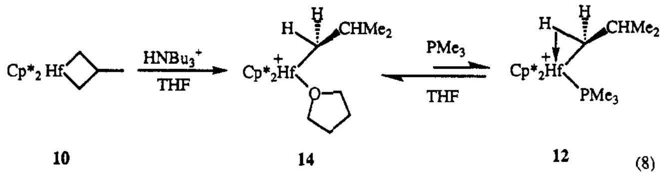
The lack of splitting of the H_α resonance at low temperature indicates that exchange of the agostic and terminal α-hydrogens of 12 is rapid and that the observed δ(H_α) and $J_{C_\alpha H}$ are average values.[32] The origin of the temperature variation of δ(H_α) is unknown. Possible sources include temperature-dependent conformational changes (e.g., C inside vs C-outside, Cp* rotation, etc.), shifts in a (rapid) equilibrium between agostic and nonagostic structures, or an increase in the strength of the Hf···H_α interaction at low temperature.[33]

In CD_2Cl_2 solution at 0 °C, 12 reacts rapidly with the solvent to form $Cp^*_2Hf(CH_2CHMe_2)Cl$ (13, eq 7), the identity of which was confirmed by independent synthesis from 10 and $[HNMe_3]Cl$. NMR data for 13 are consistent with a normal isobutyl group structure. The H_β resonance (δ 0.88) appears downfield from the H_α resonance (δ 0.08), and normal ^{13}C shifts and J_{CH} values are observed for C_β (δ 31.2, J_{CH} = 130 Hz) and C_α (δ 66.8, J_{CH} = 113 Hz).



(7)

Synthesis, Structure, and Reactivity of $[Cp^*_2Hf(CH_2CHMe_2)(THF)][BPh_4]$ (14). To explore the influence of the Lewis base ligand L on the structure of $Cp^*_2M(CH_2CHMe_2)(L)^+$ species, and to prepare more thermally stable species, the synthesis of $Cp^*_2Hf(CH_2CHMe_2)(THF)^+$ was pursued. The reaction of 10 with $[HNBu_3][BPh_4]$ in THF yields $[Cp^*_2Hf(CH_2CHMe_2)(THF)][BPh_4]$ (14) which can be isolated (53%) as a yellow crystalline solid by recrystallization from THF/hexane (eq 8). Complex 14 is also formed by dissolution of 12 in THF. Certain NMR data for 14 are similar to data for 12; in particular, a low field C_α resonance (δ 90.8) and a reduced $J_{C_\alpha H}$ value (102 Hz) are observed. However, the H_α resonance appears further downfield at δ 0.67 and does not shift with temperature. Moreover, no IPR effects are observed in the ^1H or ^{13}C NMR spectra of mixtures of $[Cp^*_2Hf(CHDCHMe_2)(THF)][BPh_4]$ (14-d_1) and $[Cp^*_2Hf\{CH_2CH(CH_2D)Me\}(THF)][BPh_4]$ (14-d_1'), generated by reaction of 10-d_1 with $[HNBu_3][BPh_4]$ in THF-d_8. The chemical shift difference Δδ = δ(14-d_1') - δ(14-d_1) = 0.07 δ is invariant with temperature between +20 and -40 °C and can be ascribed to a normal isotope shift.[34] Thus, while the NMR parameters suggest that the $HfCH_2CHMe_2$ structure of 14 is similar to that of 12, there is no corroborating evidence for the presence of agostic interactions in this case.



(8)

The solid state structure of 14 has been probed by IR spectroscopy and X-ray diffraction. The $\nu_{C_\alpha H}$ IR band for 14 (KBr) cannot be distinguished from the other ν_{CH} bands. The IR spectrum of a 1/1 mixture of 14-d_1 and 14-d_1' is nearly identical to that of 14, but contains two new weak bands at 2065 and 2115 cm^{-1}. These are assigned as the ν_{CD} bands of the Hf*C*DH– group of 14-d_1 and the $HfCH_2CH(Me)(CDH_2)$ group of 14-d_1' respectively. From these data, values for $\nu_{C_\alpha H}$ (2920 cm^{-1}) and $\nu_{C_\gamma H}$ (2991 cm^{-1}) for 14 may be estimated. The normal $\nu_{C_\alpha H}$ value is inconsistent with an α-agostic structure.

Slow crystallization of 14 from THF/hexane at -40 °C yields crystals of 14·2THF which are suitable for single crystal X-ray diffraction. The solid state structure of 14 consists of discrete $Cp^*_2Hf(CH_2CHMe_2)(THF)^+$ and BPh_4^- ions. The structure of the cation of 14 is shown in Figure 2. Crystallographic details, key bond distances and angles, and atomic coordinates are listed in Tables 2–4.

The $Cp^*_2Hf(CH_2CHMe_2)(THF)^+$ cation adopts a normal bent metallocene structure in which the centroid–Hf–centroid angle and Hf–centroid distances are in the range observed for other Cp^*_2Hf complexes.[35,36] The THF ligand lies parallel to the C5–Hf–O "equatorial" plane (C1–O–C4/C5–Hf–O dihedral angle = 5.4°). This orientation precludes Hf–O π-bonding, as the filled O p (b_1) orbital is perpendicular to the Hf LUMO which lies in the equatorial plane.[37] The structures of $Cp^*_2Ti(Me)(THF)^+$ and $Cp^*_2Zr(CH_2SiMe_3)(THF)^+$ are analogous.[17,38] In these

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(32) Exchange of the terminal and agostic β-hydrogens of 1 and 2 is also rapid at low temperture.

(33) Other agostic systems exhibit similar temperature-dependent spectra. For example, see the data for (dmpe)$TiCl_3Et$ in: Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629.

(34) (a) This value is slightly larger than the values usually observed for alkanes (0.02 δ) due to the presence of the electropositive metal. See the discussion of Gibson *et al.* in footnote 18 of ref 14a. (b) The location of the ^2H label of 14-d_1 was confirmed by the ^{13}C spectrum which contained a triplet (J_{CD} = 15.4 Hz) for C_α which is shifted upfield by 0.8 δ from the corresponding signal for 14-d_1'.

(35) For structural data on representative Cp^*_2Hf complexes, see: (a) Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592. (b) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309. (c) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1352.

(36) Contrast with the structure of $[Cp^*_2Hf(CH_3)(tetrahydrothiophene)][BPh_4]$.[10a]

(37) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(38) Bochmann, M.; Jagger, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838.

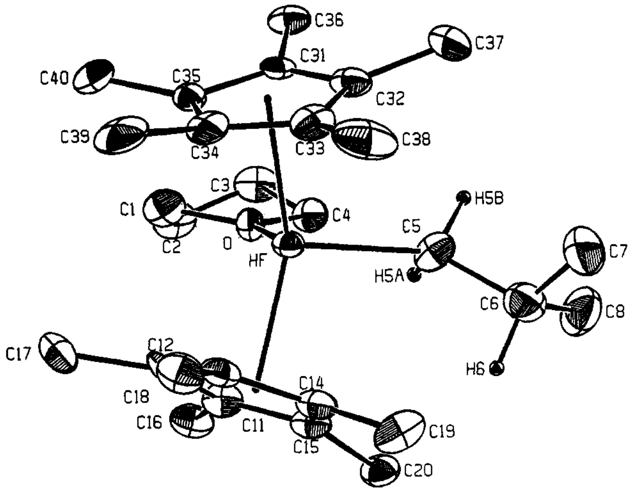

Figure 2. View of the $Cp^*_2Hf(CH_2CHMe_2)(THF)^+$ cation of 14. Only the α- and β-hydrogen atoms are shown for clarity.

Table 2. Crystallographic Data for $[(C_5Me_5)_2Hf(CH_2CHMe_2)(THF)][B(C_6H_5)_4]\cdot 2THF$ (14)

empirical formula	$C_{52}H_{67}BOHf\cdot 2C_4H_8O$
fw	1041.63
cryst size (mm)	0.17 × 0.45 × 0.49
cryst color	pale yellow
T (K)	120
space group	$P2_1/c$
a (Å)	10.747(3)
b (Å)	21.417(3)
c (Å)	21.783(8)
β (deg)	101.83(4)
V (Å^3)	5365(6)
Z	4
d_{calcd} (g/cm^3)	1.27
cell dimen determination	25 reflns; $19 < 2\theta < 24$
λ(Mo Kα radiation, Å)	0.7107
scan ratio (ω/θ)	1
ω scan range (deg)	$0.90 + \tan(\theta)$
scan speed (deg/min)	0.83–5.0
scan limit (deg)	$4 < 2\theta < 50$
data collected h,k,l	–1, 12; –1, 27; –25, 25
no. of total reflns	11 395
no. of unique reflns	9369
no. of reflns used, $I < 3\sigma(I)$	6123
R_{int}	0.045
max decay cor factor	1.247
μ, cm^{-1}	19.66
av empirical abs cor factor	1.11
structure soln method	Patterson/Fourier
refinement	non-H anisotropic; H5A, H5B, H6 isotropic; other H at calculated positions, $B_H = 1.3B_C$
tot. no. of params	588
R	0.053
R_w	0.086
weighting coefficients: P, Q[a]	0.05, 0.0
SDOUW[b]	1.14
max shift/esd	0.16
max resid density (e/Å^3)	2.73

[a] $w = [\sigma_F^2 + (PF)^2 + Q]^{-1}$. [b] *S*tandard *D*eviation of *U*nit *W*eight.

systems the electronically favored perpendicular THF bonding mode (which allows for M–O π-bonding) is strongly disfavored by repulsive steric interactions between the THF and the Cp* ligands.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 14[a]

Hf–O	2.221(6)	av Hf–C_{ring1}	2.54(4)
Hf–C5	2.25(1)	av Hf–C_{ring2}	2.55(2)
Hf–C_o	2.231	av C–C_{ring1}	1.41(1)
Hf–C_{oo}	2.241	av C–C_{ring2}	1.42(2)
Hf–H5A	2.64(8)	av C–C_{Me}	1.50(1)
Hf–H5B	3.04(8)	O–C1	1.46(1)
C5–C6	1.53(2)	O–C4	1.50(1)
C6–C7	1.53(2)	C1–C2	1.53(2)
C6–C8	1.54(2)	C2–C3	1.51(2)
C3–C4	1.50(2)		
O–Hf–C5	89.7(3)	Hf–C5–C6	137.5(8)
O–Hf–C_o	105.4	C1–O–C4	107.1(8)
O–Hf–C_{oo}	105.0	C7–C6–C8	108(1)
C5–Hf–C_o	104.7	C5–C6–C7	112(1)
C5–Hf–C_{oo}	107.0	C5–C6–C8	111(1)
C_o–Hf–C_{oo}	135.7		

[a] C_o = centroid of the C11–C15 Cp* ring (ring 1). C_{oo} = centroid of the C31–C35 Cp* ring (ring 2).

The isobutyl group is directed away from the THF ligand and adopts a conformation in which C_β and the β-CH_3 groups lie near the equatorial plane between the Cp* ligands. Distances between these atoms and the O–Hf–C5 plane are C6, 0.56 Å; C7, 0.37 Å; and C8, 0.73 Å. The Hf–C5 bond distance (2.24 Å) is similar to those of related cationic complexes (e.g., 2.23 Å for $Cp^*_2Hf(CH_3)(THT)^+$);[10a] however, the Hf–C5–C6 angle is considerably larger (137.5(8)°) than the normal tetrahedral value. The isobutyl hydrogen atoms H5A, H5B, and H6 were located and refined isotropically, though their positions are very approximate. H5A is located ca. 0.5 Å from the O–Hf–C5 "equatorial plane" and points somewhat toward Hf (Hf–C5–H5A angle 93.5(6)°). However, the estimated Hf–H5A distance (2.64(8) Å) is far longer than the Zr–H distances in cationic zirconocene species with well characterized Zr···H_β interactions (e.g., $Cp'_2Zr\{CH_2CH_2(\mu\text{-}H)\}(PMe_3)^+$, Zr–$H_{\beta_{bridge}}$ = 2.16 Å; 3, Zr–$H_{\beta_{bridge}}$ = 2.14 Å). Thus the position of H5A is probably an indirect manifestation of the isobutyl–Cp* steric interactions rather than a direct result of Hf–H electronic interactions. The existence of several close (2.0–2.5 Å) contacts between the isobutyl and Cp* hydrogens indicates that the isobutyl group orientation is dictated primarily by steric interactions between these ligands.[39] The estimated Hf–H6A distance is >3.0 Å. The X-ray results confirm the inference from the IR data that Hf···H_α interactions are not present in 14 in the solid state.

The solution NMR data for 14 are consistent with the solid state structure. The reduced $J_{C_\alpha H}$ value can be traced to the large Hf–C_α–C_β angle, which should result in reduced s character in the C–H_α bonds.[40] Furthermore, the lack of an observable IPR effect is consistent with the absence of a significant Hf–H_α interaction.

Complex 14 is stable in the solid state and in THF solution at 23 °C. Surprisingly, the THF ligand is only partially replaced by PMe_3 in CD_2Cl_2 to yield 12 (K_{eq} = 0.07(1), –10 °C, eq 8). This contrasts with $Cp_2M(R)(THF)^+$ and $Cp'_2M(R)(THF)^+$ species which generally undergo complete substitution by PMe_3.[5a] Evidently, the steric bulk of the Cp^*_2Hf framework disfavors coordination of the bulky PMe_3.[41]

β-Hydrogen vs β-Methyl Elimination of $Cp^*_2Hf(CH_2CMe_2)(L)^+$ Complexes. Thermolysis of 14 (THF-d_8, 58 °C, 19 h) yields a 6/1 mixture of propene and isobutylene (eq 9), confirming the observations of Teuben and Resconi that β-Me elimination is favored for

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[39] Close contacts (in Å): H5A–H20B 2.29, H6–H20B 2.24, H6–H20C 2.06, H6–H19A 2.12, H5B–H37A 2.47, H7A–H37C 2.50.

[40] See discussion of Marks *et al.* in ref 14c.

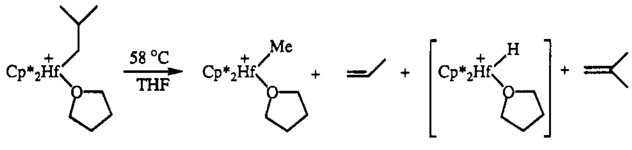
[41] (a) Molecular mechanics studies using Rappé's Universal Force Field indicate the presence of close H–H contacts when the Hf–P distance is <2.7 Å, a reasonable distance based on structures of related complexes. (b) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goodard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.

Table 4. Atomic Coordinates for 14

atom	x	y	z	B^a (Å^2)
Hf	0.42812(3)	0.11670(2)	0.67339(2)	2.101(6)
O	0.3725(6)	0.1383(3)	0.7633(3)	2.3(1)
C1	0.406(1)	0.1057(5)	0.8214(5)	4.1(3)
C2	0.324(1)	0.1296(6)	0.8650(5)	4.5(3)
C3	0.322(1)	0.1923(5)	0.8483(5)	3.9(2)
C4	0.308(1)	0.1918(4)	0.7782(6)	3.5(2)
C5	0.332(1)	0.1969(5)	0.6303(5)	3.4(2)
C6	0.261(1)	0.2168(5)	0.5659(6)	4.3(3)
C7	0.352(2)	0.2367(6)	0.5246(7)	6.0(4)
C8	0.172(2)	0.2669(6)	0.5717(7)	6.0(4)
C11	0.245(1)	0.0482(4)	0.6753(5)	2.9(2)
C12	0.354(1)	0.0154(4)	0.6730(5)	3.3(2)
C13	0.3851(9)	0.0251(4)	0.6144(4)	2.6(2)
C14	0.2977(9)	0.0647(4)	0.5797(5)	2.9(2)
C15	0.2074(9)	0.0777(4)	0.6178(5)	3.0(2)
C16	0.165(1)	0.0449(5)	0.7238(5)	3.8(2)
C17	0.414(1)	−0.0299(4)	0.7205(5)	3.4(2)
C18	0.468(1)	−0.0122(5)	0.5840(5)	3.6(2)
C19	0.292(1)	0.0785(5)	0.5120(5)	3.5(2)
C20	0.0853(9)	0.1094(5)	0.5976(5)	3.3(2)
C31	0.6276(8)	0.1654(4)	0.7319(5)	2.5(2)
C32	0.6176(9)	0.1789(4)	0.6683(5)	2.8(2)
C33	0.6351(9)	0.1287(5)	0.6349(5)	3.2(2)
C34	0.6601(8)	0.0840(5)	0.6795(5)	3.1(2)
C35	0.6508(8)	0.1047(4)	0.7388(5)	2.4(2)
C36	0.6326(9)	0.2084(4)	0.7831(5)	3.0(2)
C37	0.619(1)	0.2388(5)	0.6436(6)	4.3(3)
C38	0.652(1)	0.1235(6)	0.5693(6)	4.9(3)
C39	0.723(1)	0.0268(6)	0.6729(7)	4.8(3)
C40	0.6928(9)	0.0723(5)	0.7994(5)	3.6(2)
C41	0.943(1)	0.1155(5)	0.2280(6)	4.1(2)
C42	0.817(1)	0.1240(6)	0.2042(5)	4.4(3)
C43	0.745(1)	0.0908(7)	0.1552(6)	6.5(3)
C44	0.802(2)	0.0466(8)	0.1298(7)	7.6(4)
C45	0.930(2)	0.0340(7)	0.1537(7)	6.3(4)
C46	0.997(1)	0.0701(6)	0.2016(6)	5.1(3)
C51	0.966(1)	0.1247(5)	0.3481(5)	3.5(2)
C52	1.017(1)	0.0733(4)	0.3763(5)	3.2(2)
C53	0.968(1)	0.0473(4)	0.4240(5)	3.1(2)
C54	0.8632(9)	0.0692(5)	0.4431(5)	3.6(2)
C55	0.809(1)	0.1191(6)	0.4163(6)	4.4(3)
C56	0.859(1)	0.1443(5)	0.3688(6)	3.8(2)
C61	0.9879(9)	0.2220(5)	0.2815(6)	4.0(2)
C62	0.957(1)	0.2487(6)	0.2237(7)	5.9(3)
C63	0.938(1)	0.3080(6)	0.2176(9)	8.4(4)
C64	0.956(1)	0.3423(5)	0.268(1)	10.3(5)
C65	0.983(1)	0.3166(5)	0.3278(9)	7.0(4)
C66	1.001(1)	0.2574(5)	0.3338(7)	4.9(3)
C71	1.174(1)	0.1505(5)	0.2983(5)	3.4(2)
C72	1.254(1)	0.1524(5)	0.3589(5)	3.6(2)
C73	1.387(1)	0.1565(5)	0.3657(6)	3.9(2)
C74	1.442(1)	0.1586(5)	0.3157(6)	4.0(2)
C75	1.369(1)	0.1579(5)	0.2557(6)	4.2(3)
C76	1.236(1)	0.1539(5)	0.2478(5)	3.6(2)
C100	0.640(1)	0.1739(7)	0.9435(6)	10.8(4)
C101	0.686(2)	0.229(1)	0.9556(9)	9.3(6)
C102	0.813(2)	0.227(1)	0.9932(9)	8.8(6)
C103	0.830(2)	0.167(1)	1.015(1)	10.3(7)
C104	0.707(3)	0.138(1)	0.987(1)	17.2(9)
C200	0.320(3)	0.034(1)	−0.003(1)	8.3(6)*
C201	0.420(4)	0.051(2)	0.043(2)	8.1(9)*
C202	0.354(4)	0.069(2)	0.106(2)	7.8(9)*
C203	0.222(3)	0.061(2)	0.075(2)	16(1)*
C204	0.211(4)	0.068(2)	0.012(2)	9(1)*
C300	−1.326(4)	0.492(2)	0.461(2)	15(1)*
C301	−1.406(4)	0.528(2)	0.423(2)	9(1)*
C302	−1.362(5)	0.587(2)	0.430(2)	10.6*
C304	−1.196(5)	0.520(2)	0.466(2)	10(1)*
B	1.018(1)	0.1516(5)	0.2894(5)	3.2(2)
CP1	0.2978	0.0462	0.6320	4*
CP2	0.6381	0.1323	0.6906	4*

[a] Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

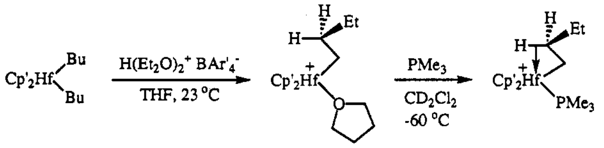
$Cp^*_2M\{CH_2CH(Me)(R)\}^+$ species. The organometallic product of β-Me elimination, $Cp^*_2Hf(CH_3)(THF)^+$ (**15**), was observed by ^{1}H NMR.[42] However, the expected β-H elimination product, $Cp^*_2Hf(H)(THF)^+$ (**16**), was not observed. This may be due to the small amount of **16** formed (ca. 14 %), or to further reaction of this species (e.g., nucleophilic ring-opening of the coordinated THF).[43]



14 **15** 6/1 **16** (9)

The rather severe conditions required to induce β-Me elimination of **14** (58 °C vs −13 °C for β-H elimination of **5** in CD_2Cl_2) suggests that THF dissociation precedes β-Me elimination. It was not possible to investigate the competition between β-H and β-Me elimination for the more labile species **12** due to its rapid reaction with CH_2Cl_2 and THF and its insolubility in hydrocarbon solvents. However, the reaction of **10** with $[HNBu_3][C_2B_9H_{12}]$ in benzene-d_6 (23 °C, <1 h) yields propene and isobutylene in a 5/1 ratio. The expected intermediate $[Cp^*_2Hf(CH_2CHMe_2)][C_2B_9H_{12}]$ was not observed when this reaction was monitored by ^{1}H NMR spectroscopy, indicating that it undergoes rapid β-H/β-Me elimination under these conditions.[44]

Synthesis, Solution Structure, and Reactivity of $[Cp'_2Hf(^nBu)(L)][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$ (L = THF, PMe_3). Complexes **12** and **14** are the first cationic, higher alkyl (i.e. greater than CH_3) hafnocene complexes to be prepared.[45] In order to make structural comparisons between these complexes and related cationic zirconocene alkyls, the influence of the metal (Hf vs Zr) on the alkyl group structure must be considered. Subtle structural differences between neutral Zr and Hf species with identical ligands (e.g., $(\eta^5\text{-}Cp)_3(\eta^1\text{-}Cp)Zr$ vs $(\eta^5\text{-}Cp)_2Hf(\eta^1\text{-}Cp)_2$) have been observed previously.[46] Accordingly, a series of cationic Hf alkyl complexes which are direct analogues of previously characterized Zr alkyls was prepared (eq 10). The cationic Hf n-butyl species $[Cp'_2Hf(^nBu)(THF)][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$ (**17**) was generated in situ in THF by protonolysis of $Cp'_2Hf(^nBu)_2$ (**18**) with



18 **17** **19** (10)

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(42) ^{1}H NM R data for **15** (THF-d_8): δ 3.61 (m, 4H, free THF), 1.92 (s, 30H, Cp*), 1.77 (m, 4H, free THF), 0.16 (s, 3H, Hf–Me). Teuben *et al.* report identical data for $Cp^*_2Hf(Me)(THT)^+$ in THF-d_8, in which ligand substitution occurs.[10]

(43) Guo, Z.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1992**, *11*, 2690.

(44) (a) The organometallic products of this reaction will be discussed elsewhere. Hinch, G. D.; Guo, Z.; Jordan, R. F. Manuscript in preparation. (b) For the use of $C_2B_{11}H_{12}^-$ as a weakly coordinating anion in cationic metallocene systems, see ref 4.

(45) For other cationic Hf complexes see ref 10a and: (a) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501. (b) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1.

(46) (a) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238. (b) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 692.

$[H(Et_2O)_2][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$. The weaker acids $[HN^nBu_3][BPh_4]$, $[HNMe_3][BPh_4]$, and $[HNMe_2Ph][BPh_4]$ and the oxidizing agent $[Cp'_2Fe][BPh_4]$ were found to be unreactive with **18** (THF, 23 °C). NMR data for **17** are similar to data for $Cp'_2Zr(^nBu)(THF)^+$ and indicate that the butyl group adopts a normal, undistorted structure.[1] Complex **17** reacts readily with PMe_3 at −60 °C in CD_2Cl_2 to yield the thermally sensitive phosphine adduct $[Cp'_2Hf(^nBu)(PMe_3)][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$ (**19**). Low-temperature NMR data for **19** are similar to data for $Cp'_2Zr(^nBu)(PMe_3)^+$ and establish that this species adopts a β-agostic structure. Key NMR parameters include high field H_β (δ −1.50) and C_β (δ 12.6) resonances, a large $J_{C_\alpha H}$ value (135 Hz, vs 113 Hz for **17** and 110 Hz for **18**), and a reduced $J_{C_\beta H}$ (103 Hz) value. At 0 °C in the presence of excess PMe_3, **19** undergoes β-H elimination to yield 1-butene and $[Cp'_2Hf(H)(PMe_{32}][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$ (**20**), which was characterized by multinuclear NMR spectroscopy.[47] Several Zr analogues of **20** were characterized previously.[48] As these structural trends and reactivity properties are analogous to those observed for $Cp'_2Zr(^nBu)(L)^+$ complexes, we conclude that the metal (Zr vs Hf) does not strongly influence the alkyl group structure in these systems.

Discussion

The structures and reactivity of the relatively uncrowded $Cp'_2Zr(CH_2CHMe_2)(L)^+$ complexes **6** (L = THF) and **7** (L = PMe_3) parallel those observed previously for $Cp'_2Zr(CH_2CH_2R)(L)^+$ species **1**, **2**, and **4**, which contain only a single alkyl substituent on the β-carbon. Thus, PMe_3 adduct **7** adopts a β-agostic structure in which the electron deficiency at the formally 16-electron Zr center is relieved by the $Zr\cdots H_\beta$ interaction. In contrast, THF adduct **6** exhibits a normal structure, most likely because π-donation from the THF oxygen destabilizes the Zr LUMO required for a $Zr\cdots H$ interaction. The observation that PMe_3 displaces THF suggests that PMe_3 is a stronger net electron donor than THF in these uncrowded species. However, PMe_3 coordinates via σ-donation only, and thus leaves the Zr LUMO unperturbed and available for the $Zr\cdots H_\beta$ interaction. The accessibility of β-agostic structures in these uncrowded systems is reflected in the thermolysis behavior: both **6** and **7** undergo β-elimination under mild conditions.

The structures of $Cp^*_2Hf(CH_2CHMe_2)(L)^+$ complexes **12** (L = PMe_3) and **14** (L = THF) are quite different from those of the Cp'_2Zr analogues. Neither **12** nor **14** adopts a β-agostic structure. NMR data do indicate that the isobutyl groups of both **12** and **14** are distorted by large Hf–C–C angles. However, the lack of IPR effects in the NMR spectra of **14**-d_1 and **14**-d_1', the absence of low frequency IR bands associated with $Zr\cdots HC$ interactions, and the absence of obvious close $Hf\cdots H_\alpha$ contacts in the X-ray structure indicate that $Hf\cdots H_\alpha$ interactions are not present in **14**. The large Hf–C–C angle in this complex can be traced to steric interactions between the isobutyl group and the bulky Cp* ligands.

The THF ligand of **14** adopts an "in plane" orientation which precludes a significant Zr–O π interaction. The absence of agostic interactions in **14** is thus surprising given the general tendency for $Cp'_2M(CH_2CH_2R(L)^+$ (M = Zr, Hf) and $Cp'_2Zr(CH_2CHMe_2)(L)^+$ species to exhibit agostic interactions when L is a not a π-donor ligand.[1,2] Evidently, the strongly electron donating Cp* ligands reduce the electrophilicity of the metal center in **14** to the point where the stabilization which would be provided by an agostic $Hf\cdots H$ interaction does not outweigh the strain (associated with unusual bond angles) and the unfavorable steric interactions which would accompany formation of a $Hf\cdots HC$ agostic bond.

The observation of IPR effects in the NMR spectra of isotopically labeled derivatives **12**-d_1 and **12**-d_1' provides convincing evidence for the presence of a single $Hf\cdots H_\alpha$ interaction in **12**. A reasonable rationale for the presence of an agostic interaction in **12** but not **14** is that, due to unfavorable steric interactions, PMe_3 is a weaker donor toward $Cp^*Hf(CH_2CHMe_2)^+$ than is THF. Thus, the metal center in **12** is more electron deficient than that in **14**, and the $Hf\cdots H_\alpha$ interaction is more favored. The observation that **12** reacts with THF to yield **14** but that the reverse reaction occurs to only a small extent supports this proposal.

As proposed by Teuben and Resconi,[9a,10] steric interactions between the isobutyl methyl groups and the bulky Cp* ligands disfavor $Hf\cdots H_\beta$ interactions in **12** and **14**. These same effects disfavor β-H elimination, and β-Me elimination is the predominant thermolysis pathway.

Experimental Section

All manipulations were performed under a N_2 atmosphere or under vacuum using a Vacuum Atmospheres drybox or a high vacuum line. CH_2Cl_2 was distilled from CaH_2. Hexane, ether, benzene-d_6, toluene-d_8, and THF-d_8 were distilled from Na/benzophenone. CD_2Cl_2 was distilled from P_2O_5. Solvents were stored in evacuated bulbs, and generally vacuum-transferred to reaction flasks or NMR tubes. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc. NMR spectra were obtained on Bruker AC-300 or AMX-360 instruments. ^1H and ^{13}C chemical shifts are reported vs $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^{31}P NMR spectra are referenced to external H_3PO_4. NMR data for the counterions are as follows:

BPh_4^-: ^1H NMR (CD_2Cl_2) δ 7.35 (m, 8H), 7.05 (t, J = 7.4 Hz, 8H), 6.09 (t, J = 7.4 Hz, 4H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 165.4 (q, J = 49.3 Hz), 136.6, 126.0, 122.2.

$B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$: ^1H NMR (CD_2Cl_2) δ 7.75 (s, 8H), 7.65 (s, 4H); ^{13}C NMR (CD_2Cl_2) δ 161.5 (q, J = 49.5 Hz), 134.4 (d, J_{CH} = 159 Hz), 129.1 (q, J_{CF} = 28.9 Hz), 124.2 (q, J_{CF} = 273.3), 117.9 (d, J_{CH} = 165 Hz).

Isobutylene-d_1 ($CHD{=}CMe_2$) was prepared by reaction of $BrMgCH{=}CMe_2$ with D_2O (^1H NMR (C_6D_6, 23 °C) δ 4.73 (br m, 1H, CHD)=), 1.58 (d, J = 1.2 Hz, 6H, $=CMe_2$); ^2H NMR (C_6D_6, 23 °C) δ 4.72 (s, $CHD{=}$)). $Cp^*_2Hf(CH_2CH(CH_3)CH_2-)$ was prepared by thermolysis of $Cp^*_2HfH_2$ in the presence of excess isobutylene, as described by Roddick.[27b] $Cp^*_2Hf(CHDCHMeCH_2-)$ was prepared in an analogous manner using $CHD{=}CMe_2$ (^1H NMR (CD_2Cl_2, 23 °C) δ 1.88 (s, 15 H, *Cp**), 1.77 (s, 15H, *Cp**), 1.15 (d, J = 6.0 Hz, 3H, β-CH_3), 0.90 (m, 1.5 H, α-CH_2 + CDH), 0.44 (m, 1.5 H, α-CH_2 + CDH), −0.48 (m, 1H, β H); ^2H NMR (CD_2Cl_2, 23 °C) δ 0.92, 0.45 (α-CHD)). The following compounds were prepared by literature procedures: $[H(Et_2O)_2][B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]$,[49] $Cp^*_2Zr(CH_2CHMe_2)(H)$,[25] $[Cp'_2Zr(H)(THF)][BPh_4]$,[1b,6] Cp'_2HfCl_2,[50] $[HNBu_3][BPh_4]$.[51] $HfCl_4$ (98%) was obtained from Aldrich.

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[47] A small amount of butane (ca. 13%) is also formed.

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[51] Barker, B. J.; Sears, P. G. *J. Phys. Chem.* 1974, *78*, 2687.

[Cp′$_2$Zr(CH$_2$CHMe$_2$)(THF)][BPh$_4$] (6). An NMR tube containing a THF-d_8 solution (0.5 mL) of [Cp′$_2$Zr(H)(THF)]-[BPh$_4$] (32.3 mg, 0.0457 mmol, generated in situ by reaction of [Cp′$_2$Zr(CH$_3$)(THF)][BPh$_4$] with H$_2$ in THF-d_8) was charged with isobutylene (4.70 mg, 0.0842 mmol) at −196 °C. The tube was warmed to 23 °C and allowed to stand for 30 min with occasional shaking to afford a yellow solution of 4 (98%, NMR). In the absence of isobutylene, 4 rapidly (min) decomposed to [Cp′$_2$Zr(H)(THF)][BPh$_4$].

[Cp′$_2$Zr(CH$_2$CHMe$_2$)(PMe$_3$)][BPh$_4$] (7). An NMR tube containing a solution of **6** (32.3 mg, 0.0457 mmol) in CD$_2$Cl$_2$ (0.5 mL) and isobutylene (1.5 equiv) was charged with PMe$_3$ (7.00 mg, 0.0921 mmol) at −196 °C. The tube was warmed to −78 °C and agitated. The volatiles were removed under vacuum at −78 °C (4 days), giving a deep-yellow oily solid. The solid was dissolved in CD$_2$Cl$_2$ (0.5 mL, added by vacuum-transfer at −78 °C) and the tube was maintained at −78 °C prior to NMR analysis at −50 °C. ^{1}H and ^{13}C NMR spectra revealed the presence of **7** (95%, NMR). ^{31}P NMR (CD$_2$Cl$_2$, −50 °C): δ 0.97.

[Cp*$_2$Hf(CH$_2$CHMe$_2$)(PMe$_3$)][BPh$_4$] (12). To an NMR tube containing Cp*$_2$Hf(CH$_2$CH(Me)CH$_2$–) (**10**, 18.0 mg, 0.0360 mmol) and [HNBu$_3$][BPh$_4$] (18.5 mg, 0.0422 mmol) was added CD$_2$Cl$_2$ (ca. 0.5 mL) and PMe$_3$ (5.5 mg, 0.072 mmol) by vacuum-transfer at −196 °C. The tube was warmed to −78 °C, agitated to effect mixing of the reactants, and then slowly warmed to −10 °C (15 min) to afford a yellow solution. The tube was maintained at −78 °C prior to NMR analysis. ^{1}H and ^{13}C NMR data established the presence of **12** (90%, NMR) and free PMe$_3$. ^{31}P NMR (CD$_2$Cl$_2$, −40 °C): δ −7.3 (**12**), −60.7 (free PMe$_3$).

Solutions of a 1/1 mixture of [Cp*$_2$Hf(CHDCHMe$_2$)(PMe$_3$)]-[BPh$_4$] (**12**-d_1) and [Cp*$_2$Hf(CH$_2$CH(CH$_2$D)Me)(PMe$_3$)][BPh$_4$] (**12**-d_1') in CD$_2$Cl$_2$ for IPR measurements were prepared in a similar manner using **10**-d_1.

Cp*$_2$Hf(CH$_2$CHMe$_2$)Cl (13). To an NMR tube containing Cp*$_2$Hf(CH$_2$CHMeCH$_2$–) (**10**, 25.9 mg, 0.0518 mmol) and [HNMe$_3$]Cl (24.1 mg, 0.390 mmol) was vacuum-transferred CD$_2$Cl$_2$ (0.5 mL) at −78 °C. The tube was warmed to 23 °C and allowed to stand with occasional shaking for 4 h to afford a colorless solution of **13** (100%, NMR).

[Cp*$_2$Hf(CH$_2$CHMe$_2$)(THF)][BPh$_4$] (14). Solid [HNBu$_3$]-[BPh$_4$] (0.245 g, 0.482 mmol) was added to a solution of Cp*$_2$-Hf(CH$_2$CH(Me)CH$_2$–) (0.352 g, 0.481 mmol) in THF (15 mL). The solution was stirred for 24 h at 23 °C. The solution volume was reduced to 10 mL under vacuum and ca. 2 mL of hexane was slowly added to induce precipitation. Filtration yielded a solid which contained **14** and a trace amount of [HNBu$_3$][BPh$_4$]. This crude product was recrystallized from THF/hexane to afford **14** as yellow crystals (0.22 g, 51%). Anal. Calcd for C$_{52}$H$_{67}$BHfO: C, 70.45; H, 7.62. Found: C, 70.21; H, 7.37.

Reaction of 14 with PMe$_3$. A solution of **14** (25 mg, 0.028 mmol) in CD$_2$Cl$_2$ (0.05 mL) was cooled to −196 °C and varying amounts of PMe$_3$ (1.5–3.0 equiv) were added by vacuum-transfer. The tube was maintained at −78 °C prior to NMR analysis at −10 °C. ^{1}H and ^{13}C NMR spectra revealed partial conversion of **14** to **12**. K_{eq} was determined to be 0.07(1) at −10 °C from the ^{1}H NMR integrals.

Cp′$_2$Hf(^{n}Bu)$_2$ (18). To a solution of Cp′$_2$HfCl$_2$ (3.05 g, 7.52 mmol) in Et$_2$O (50 mL) was added BuLi (6.6 mL, 2.5 M hexane solution, 16.5 mmol) by syringe under a N$_2$ counterflow at −78 °C. Vacuum was established immediately. The reaction mixture was stirred at −78 °C for 30 min, allowed to warm to room temperature, and then stirred an additional 12 h. The brown reaction mixture was filtered, and the colorless precipitate was washed with Et$_2$O (2 × 10 mL). The combined filtrate and washes were evaporated under vacuum to afford Cp′$_2$Hf(^{n}Bu)$_2$ as an oily solid (2.0 g, 60%). Anal. Calcd for C$_{20}$H$_{32}$Hf: C, 53.27; H, 7.15. Found: C, 53.14; H, 7.06.

Generation and Fate of [Cp′$_2$Hf(^{n}Bu)(L)][B(3,5-{CF$_3$}$_2$-C$_6$H$_3$)$_4$] (L = THF (17), PMe$_3$ (19)). An NMR tube was charged with Cp′$_2$Hf(^{n}Bu)$_2$ (22.0 mg, 0.0481 mmol) and [H(Et$_2$O)$_2$][B(3,5-{CF$_3$}$_2$C$_6$H$_3$)$_4$] (50.5 mg, 0.0481 mmol), and THF-d_8 (0.05 mL) was added by vacuum-transfer at −78 °C. The tube was warmed to 23 °C for ca. 15 min. A ^{1}H NMR spectrum confirmed the formation of [Cp′$_2$Hf(^{n}Bu)(THF)][B(3,5-{CF$_3$}$_2$C$_6$H$_3$)$_4$] (**17**, >95%). The volatiles were removed under vacuum to afford **17** as a yellow solid. The tube was cooled to −196 °C, and CD$_2$Cl$_2$ (0.5 mL) and PMe$_3$ (8.4 mg, 0.11 mmol) were added by vacuum transfer. The tube was kept at −78 °C prior to NMR analysis at −60 °C. ^{1}H, ^{13}C, and ^{31}P NMR spectra indicated the formation of **19** (>95%) and free PMe$_3$. ^{31}P NMR (CD$_2$Cl$_2$, −60 °C): δ 27.0 (**19**), −59.3 (free PMe$_3$).

At 0 °C, **19** decomposed to [Cp′$_2$Hf(H)(PMe$_3$)$_2$][B(3,5-{CF$_3$}$_2$C$_6$H$_3$)] (**20**) and 1-butene. ^{31}P NMR (CD$_2$Cl$_2$, 23 °C): δ −1.32 (**20**).

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and thermal parameters and figures showing the packing diagram and an alternate view of the cation of 14 (16 pages). Ordering information is given on any current masthead page.

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